Chocolate Science and Technology

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York
UK
Chocolate Science and Technology
Dedication

This book is dedicated to my dear wife Ellen and our three lovely children, Nana Afra, Maame Agyeiwaa and Kwabena Ohene-Afoakwa (Jnr), whose wisdom, prayers and support have helped me achieve great success in my life.
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The colour plate section (‘Photographs showing chocolate manufacture from cocoa seedling to final product’) follows page 16
Preface

The character of chocolate not only originates in flavour precursors present in cocoa beans but are generated during post-harvest treatments and transformed into desirable odour notes in the manufacturing processes. Complex biochemical modifications of cocoa bean constituents are further altered by thermal reactions in roasting and conching, and in alkalisation. However, less well understood is the extent to which the inherent bean constituents from the cocoa genotype, environmental factors, and post-harvest treatments and processing technologies affect flavour formation and the final flavour quality. This book provides scientific and technological accounts of all these issues as well as for the various biological and genetic factors that modulate variations in flavour formation in cocoa and chocolate. It explains the chemistry of Maillard reactions that leads to flavour development during cocoa processing and chocolate manufacture, using chemical equations and specific technical examples. With the increase of speciality niche products in the modern chocolate confectionery industry, a better understanding of these factors could have significant commercial implications.

Chocolate as a complex emulsion is a luxury food that during consumption evokes a range of stimuli that activate pleasure centres of the human brain. Central to chocolate quality is an appropriate melting behaviour that ensures products are solid at ambient temperature but melt on ingestion to undergo dissolution in oral saliva, with a final assessment of texture after phase inversion. During manufacture, several factors play important roles in shaping chocolate’s rheological behaviour, textural properties, melting characteristics and sensory perception, but the science and technologies involved are poorly understood. With opportunities for improvements in quality possible through improved and more transparent supply chain management, plant breeding strategies and new product development associated with Fairtrade and the development of niche/premium quality products, there is a need for greater understanding of the variables as well as the science and technologies employed.

This book provides detailed, reviewed explanation of the scientific and technological basis of the various chocolate manufacturing processes used in the modern confectionery industry. Using the latest research, it also provides scientific answers to many of the frequently asked questions on process improvements, quality control, quality assurance, and the production of low-fat chocolates and niche/premium products. The ideas and explanations provided in this book evolved from my doctorate research on chocolate technology, and contain findings that impact on quality assurance processes and new product development techniques with significance for cost reduction and improved product quality. The chapters cover the entirety of the science and technology of chocolate manufacture – from cocoa production through manufacturing processes to nutrition and health benefits of chocolate consumption.

It is hoped that this book will be a valuable resource for academic and research institutions around the world, and as a training manual on cocoa processing, chocolate technology and the science of chocolate manufacture. It is aimed at confectionery and chocolate scientists.
in industry and academia, general practicing food scientists and technologists, and food engineers. The chapters on research developments are intended to help generate ideas for new research activities relating to process improvements, product quality control and assurance, as well as development of new niche/premium chocolate products.

It is my vision that this book will inspire African food industries in their quest for adding value to the many raw materials that are produced within the continent, especially cocoa.
I wish to express my sincere gratitude and thanks to my parents – late Mr Joseph Ohene Afoakwa (Esq.) and Mrs Margaret Afoakwa – for ensuring I obtained the best education in spite of the numerous challenges they faced in some periods of their lives. Their profound love, prayers, support and advice strengthened me from my childhood, giving birth to the many dreams and aspirations which have all become realities in my life today. I am also grateful to the government of Ghana and to all cocoa farmers in Ghana whose toil and sweat funded my education through the Ghana Cocoa Board Scholarship Scheme, which I earned all throughout my secondary education, and without which I could not have remained in school and secured a place at university. I am indeed indebted to you all.

My gratitude and appreciation also goes to the Management of Nestlé Product Technology Centre (York, UK) for providing the funding and support for my training in chocolate technology at the Nestlé Product Technology Centre, York, and also to Dr Alistair Paterson, Centre for Food Quality, University of Strathclyde, Glasgow, UK, Mr Mark Fowler, Head of Applied Science Department of Nestlé Product Technology Centre (York, UK) and Dr Steve Beckett (retired confectionery expert) for their support, encouragement, patience and friendliness during the period of my doctoral training in York. Many thanks also go to Joselio Vieira, Angela Ryan, John Rasburn, Peter Cooke, Philip Gunus, Angel Manéz, Jan Kuendiggar, Ramana Sundara and Sylvia Coquerel of Nestlé Product Technology Centre, York, and to Dr Jeremy Hargreaves (Nestlé Head Office, Vevey, Switzerland) whose advice, guidance and support enhanced my understanding into the science and technology of chocolates.

My sincere thanks also go to the many friends and colleagues around the world who have mentored, encouraged and inspired me in various ways throughout my career including Professor Samuel Sefa-Dedeh, Professor George Sodah Ayernor, Professor Ebenezer Asibey-Berko, Professor Anna Larrey, Dr Esther Sakyi-Dawson, Dr Kwaku Tano-Debrah, Dr Agnes Simpson Budu, Dr William Bruce Owusu and Dr George Annor, all of the Department of Nutrition and Food Science, University of Ghana, Legon – Accra, Ghana; Professor Demetre Labadarios (formerly of Stellenbosch University) and Executive Director of Knowledge Systems, Human Sciences Research Council in Cape Town, South Africa; Professor Ruth Oniang’o, Founder and Editor-in-Chief of the African Journal of Food, Agriculture, Nutrition and Development (AJFAND), Nairobi, Kenya; Dr Linley Chiwona-Karlton of the Swedish University of Agricultural Sciences, Uppsala, Sweden; Mr George Ekow Hayford, Quality Assurance and Regulatory Affairs Manager for Nestlé Central West African Region; Dr Gene White, Dr Janey Thornton, Mrs Barbara Belmont, Ms Penny McConnell, Mr Paul Alberghine and Mrs Mary Owens of the Global Child Nutrition Foundation, Washington, DC, USA.

Finally, my profound appreciation and love goes to my siblings Sammy, Juliana, and Regina for their prayers and support throughout my education, and again to my dear wife
Ellen and our lovely children Cita, Nana Afra, Maame Agyeiwaa and Kwabena Ohene-Afoakwa (Jnr) for supporting me and most importantly providing the much needed love, encouragement and affection that strengthened me throughout my career. We all have very good memories of the beautiful cities of London, York and Glasgow, the Nestlé Rowntree Factory and the Nestlé Product Technology Centre in York, UK.
About the author

Emmanuel Ohene Afoakwa, BSc (Hons), MPhil (Ghana), PhD (Strathclyde, UK) in Food Technology, holds Postgraduate Certificates in International Food Laws and Regulations from the Michigan State University, East Lansing, Michigan, USA, and Food Quality Management Systems from the Wageningen University, Wageningen, the Netherlands. He is a member of several professional bodies and has authored and co-authored 112 publications (including 52 peer-reviewed journal publications, 4 books and 56 conference presentations with published abstracts) in food science and technology. As a technical consultant to many multinational food industries in sub-Saharan Africa, he has vast experience in food technology and translates his research findings through process and product development into industrial productions. He spent 3 years training and conducting active research into chocolate manufacture at the Nestlé Product Technology Centre in York, UK, where he acquired various skills and knowledge into the science and technology of chocolate. He has several research and review publications on chocolate science and technology in peer-reviewed journals and has presented several papers on chocolate technology at international conferences around the world including the Annual Meeting of Food Technologists (IFT) in USA, World Congress of Food Science and Technology (IUFoST Bi-annual Congresses) in France and China, and the ZDS Chocolate Technology International Congress by ZDS Solingen in Cologne, Germany. Presently, he is a Senior Lecturer at the Department of Nutrition and Food Science, University of Ghana, Legon – Accra, Ghana, where he has worked for over 12 years, teaching and conducting research into the areas of beverage (chocolate and sugar) science and technology, food chemistry and thermal processing of foods.
1 Chocolate production and consumption patterns

1.1 HISTORY OF COCOA AND CHOCOLATE

The term ‘cocoa’ is a corruption of the word ‘cacao’ that is taken directly from Mayan and Aztec languages. Chocolate is derived from cocoa beans, central to the fruit of cocoa tree, *Theobroma cacao*, which is indigenous to South America and believed to have originated from the Amazon and Orinoco valleys. *Theobroma* (food of the gods) are of the family Sterculiaceae with four principal types: *Criollo*, about 5% of world cocoa production; and the more common *Forastero*, with smaller, flatter and purple beans; *Nacional* with fine flavour, grown in Ecuador. The fourth variety, *Trinitario*, a more disease-resistant hybrid of *Criollo* and *Forastero* is regarded as a flavour bean (Fowler, 1999). *Theobroma cacao* grows between tropics of Cancer and Capricorn, with varieties originating in forest areas of South America. *Forastero* – basic cocoa, grows mainly in Brazil and West Africa, whilst flavour cocoas are largely hybrids and are cultivated in Central and South America. Aztecs in Mexico cultivated cocoa from South America, via Caribbean islands, and Hernandos Cortés, a Spanish, took cocoa to Spain as a beverage and to Spanish Guinea as a crop. The Spanish not only took cocoa to Europe but also introduced the crop into Fernando Po in the seventeenth century, and thus laid the foundation of the future economies of many West African countries. Currently, West Africa produces more than 70% of world cocoa (Awua, 2002; Amoye, 2006; International Cocoa Organisation, ICCO, 2008).

The use of cocoa beans dates back at least 1400 years (Rössner, 1997), when Aztecs and Incas used the beans as currency for trading or to produce the so-called *chocolatl*, a drink made by roasting and grinding cocoa nibs, mashing with water, often adding other ingredients such as vanilla, spices or honey. In the 1520s, the drink was introduced into Spain (Minifie, 1989) although Coe and Coe (1996) emphasised that the European arrivals in the new world, including Christopher Columbus and Herman Cortes, were unimpressed with the Mayan beverage, sweetening it with honey. Nevertheless, the conquistadors familiarised the chocolate beverage throughout Europe, and being expensive, it was initially reserved for consumption by the highest social classes, and only in the seventeenth century that the consumption of chocolate spread through Europe.

As the consumption of chocolate became more and more widespread during the eighteenth century, the Spanish monopoly on the production of cocoa soon became untenable and plantations were soon established by the Italians, Dutch and Portuguese. At this point, chocolate was still consumed in liquid form and was mainly sold as pressed blocks of a grainy mass to be dissolved in water or milk to form a foamy chocolate drink. The mass production of these chocolate blocks also began in the eighteenth century when the British Fry family founded the first chocolate factory in 1728, using hydraulic equipment to grind
the cocoa beans. The first US factory was built by Dr James Baker outside Boston a few decades later, and in 1778 the Frenchman Doret built the first automated machine for grinding cocoa beans. The production of cocoa and chocolate was truly revolutionised by Coenraad Van Houten in 1828 by the invention of a cocoa press, which succeeded in separating cocoa solids from cocoa butter. The resulting defatted cocoa powder was much easier to dissolve in water and other liquids and paved the way, in 1848, for the invention of the first real ‘eating chocolate’, produced from the addition of cocoa butter and sugar to cocoa liquor (Dhoedt, 2008).

In the UK in 1847, Joseph Fry was the first to produce a plain eating chocolate bar, made possible by introduction of cocoa butter as an ingredient (Beckett, 2000). Demand for cocoa then sharply increased, and chocolate processing became mechanised with development of cocoa presses for production of cocoa butter and cocoa powder by Van Houten in 1828, and milk chocolate in 1876 by Daniel Peters, who had the idea of adding milk powder – an invention of Henri Nestlé, a decade earlier. This was followed by the invention of the conching machine in 1880 by Rudolphe Lindt, from where chocolate came to take on the fine taste and creamy texture we now associate with good-quality chocolate. It was still very much an exclusive product, however, and it was not until 1900 when the price of chocolate’s two main ingredients, cocoa and sugar, dropped considerably that chocolate became accessible to the middle class. By the 1930s and 1940s, new and cheaper supplies of raw materials and more efficient production processes had emerged at the cutting-edge of innovation with fast-manufacturing technologies and new marketing techniques through research and development by many companies in Europe and the United States, making chocolate affordable for the wider populace. Chocolate confectionery is now ubiquitous with consumption averaging 8.0 kg/person per annum in many European countries (Nuttall & Hart, 1999; Whitefield, 2005; ICCO, 2008).

1.2 WORLD PRODUCTION AND CONSUMPTION OF COCOA AND CHOCOLATE PRODUCTS

1.2.1 World production and consumption of cocoa

*Theobroma cacao* originated in the Amazon Basin and optimal conditions for growth are 20–30°C (68–86°F), 1500–2500 mm of annual rainfall and 2000 hours of sunshine per year. Table 1.1 shows that density of production is centred within West Africa, accounting for approximately 71% of world cocoa production in 2005–2006 growing season. West African countries are ideal in climatic terms for growing cocoa as a cash crop. However, as a consequence, natural or man-made problems have potentially a disproportionately large impact on cocoa trade. Small holders of West Africa have dominated world production since the 1930s. In 1980s, emergence of Malaysia and Indonesia gave more balanced geographical spread of production.

However, a period of low prices wiped out Malaysia as a major producer and Brazil as a major exporter, increasing share of production of West Africa. In 2005–2006, 71% of world cocoa came from Africa: Côte d’Ivoire, 37.8%; Ghana, 19.9% (ICCO, 2008).

In 2006–2007, world production of cocoa beans dropped by almost 9% from the previous season to 3.4 million tonnes, mainly as a consequence of unfavourable weather conditions in many cocoa-producing areas. West Africa, the main cocoa-producing region, was hit by a severe harmattan and its inherent dry weather, which lasted from the end of 2006 to
Chocolate production and consumption patterns

Table 1.1 World cocoa production between 2004 and 2008

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<td>World total</td>
<td>3379 (100%)</td>
<td>3724 (100%)</td>
<td>3400 (100%)</td>
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<tr>
<td>Africa</td>
<td>2375 (70.3%)</td>
<td>2642 (71.0%)</td>
<td>2392 (70.4%)</td>
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<tr>
<td>Americas</td>
<td>445 (13.2%)</td>
<td>446 (12.0%)</td>
<td>411 (12.1%)</td>
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<tr>
<td>Asia and Oceania</td>
<td>559 (16.5%)</td>
<td>636 (17.1%)</td>
<td>597 (17.5%)</td>
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<tr>
<td>Côte d’Ivoire</td>
<td>1286 (38.1%)</td>
<td>1408 (37.8%)</td>
<td>1292 (38.0%)</td>
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<tr>
<td>Ghana</td>
<td>599 (17.8%)</td>
<td>740 (19.9%)</td>
<td>614 (18.1%)</td>
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<tr>
<td>Indonesia</td>
<td>460</td>
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<td>Cameroon</td>
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<td>166</td>
<td>129</td>
</tr>
<tr>
<td>Brazil</td>
<td>171</td>
<td>162</td>
<td>126</td>
</tr>
<tr>
<td>Ecuador</td>
<td>116</td>
<td>114</td>
<td>114</td>
</tr>
<tr>
<td>Papua New Guinea</td>
<td>48</td>
<td>51</td>
<td>50</td>
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<tr>
<td>Dominican Republic</td>
<td>31</td>
<td>42</td>
<td>47</td>
</tr>
</tbody>
</table>

Note: Figures in parentheses represent percentage (%) of annual production. Totals and differences may differ due to rounding. Source: ICCO (2008).

February 2007, had a strong negative impact on production. In Asia and South America, El Niño-related weather conditions developed in September 2006 and continued until the beginning of 2007. Cocoa production in the two major producing countries was severely hit in 2006–2007.

Production in Ghana declined by 17% from the previous season to 614 000 tonnes, resulting mainly from a very poor mid-crop. In Côte d’Ivoire, cocoa output reached 1 292 000 tonnes, down by 116 000 tonnes from the 2005–2006 season. As in Ghana, the second harvest of the season proved very disappointing, as the trees did not recover from the poor level of soil moisture and lack of rainfall, which lasted until February 2007, causing many developing pods to shrivel. The statistical picture for the mid-crop in Côte d’Ivoire could have been worse. Indeed, the 2007–2008 main crop experienced an early and strong start at the end of August – almost 100 000 tonnes of cocoa beans reached Ivorian ports in September 2007. These cocoa beans were statistically counted as part of the 2006–2007 mid-crop and, consequently, enhanced the production figures of the 2006–2007 cocoa season, while in fact, they were part of the 2007–2008 main crop (ICCO, 2008).

Cocoa consumption, as measured by grindings, increased by 2.5% from the 2005–2006 season to 3 608 000 tonnes in 2006–2007 (Table 1.2). Despite a relative slowdown during that season, the cocoa market was characterised over the last 5 years by a sustained demand for cocoa, rising by 3.8% per annum (based on a 3-year moving average) (ICCO, 2008). It was supported by a strong demand for cocoa butter to rebuild stocks, as well as by rising chocolate consumption in emerging and newly industrialised markets, and changes in chocolate consumption behaviour in mature markets towards higher cocoa content chocolate products.

At the regional level, developments were heterogeneous in 2006–2007, with grindings rising by around 6% in Europe to 1 540 000 tonnes and to 514 000 tonnes in Africa (Table 1.2). Meanwhile, they remained at almost the same level, at 699 000 tonnes in Asia and Oceania and declined by 3% in the Americas to 853 000 tonnes. Processors located in Germany and Ghana contributed to almost half of the increase in world grindings, reflecting
Table 1.2  World consumption/grinding of cocoa beans between 2004 and 2007

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>European</td>
<td>1379 (41.4%)</td>
<td>1456 (41.4%)</td>
<td>1540 (42.7%)</td>
</tr>
<tr>
<td>Germany</td>
<td>235</td>
<td>306</td>
<td>357</td>
</tr>
<tr>
<td>The Netherlands</td>
<td>460</td>
<td>455</td>
<td>465</td>
</tr>
<tr>
<td>Others</td>
<td>684</td>
<td>695</td>
<td>719</td>
</tr>
<tr>
<td>Africa</td>
<td>501 (14.9%)</td>
<td>485 (13.8%)</td>
<td>514 (14.3%)</td>
</tr>
<tr>
<td>Côte d’Ivoire</td>
<td>364</td>
<td>336</td>
<td>336</td>
</tr>
<tr>
<td>Others</td>
<td>137</td>
<td>149</td>
<td>179</td>
</tr>
<tr>
<td>Americas</td>
<td>853 (25.4%)</td>
<td>881 (25.0%)</td>
<td>853 (23.7%)</td>
</tr>
<tr>
<td>The United States</td>
<td>419</td>
<td>432</td>
<td>418</td>
</tr>
<tr>
<td>Brazil</td>
<td>209</td>
<td>223</td>
<td>224</td>
</tr>
<tr>
<td>Others</td>
<td>225</td>
<td>226</td>
<td>212</td>
</tr>
<tr>
<td>Asia and Oceania</td>
<td>622 (18.5%)</td>
<td>698 (19.8%)</td>
<td>699 (19.4%)</td>
</tr>
<tr>
<td>Indonesia</td>
<td>115</td>
<td>140</td>
<td>140</td>
</tr>
<tr>
<td>Malaysia</td>
<td>249</td>
<td>267</td>
<td>270</td>
</tr>
<tr>
<td>Others</td>
<td>258</td>
<td>291</td>
<td>289</td>
</tr>
<tr>
<td>World total</td>
<td>3354</td>
<td>3520</td>
<td>3608</td>
</tr>
<tr>
<td>Origin</td>
<td>1262</td>
<td>1293</td>
<td>1325</td>
</tr>
</tbody>
</table>

Note: Figures in parentheses represent percentage (%) of annual consumption/grinding. Total and difference may differ due to rounding. Source: ICCO (2008).

The installation of additional capacities in these countries. The Netherlands and the United States remained the major cocoa processing countries, each with grindings of more than 400 000 tonnes during the year.

The ICCO (2008) reported that the average consumption of cocoa beans in the world is 0.55 kg/person. Europeans consume most at 1.81 kg/person, followed by Americans (1.38 kg/person), with people of Africa and Asia/Oceania consuming only 0.14 and 0.11 kg/person, respectively. Belgium/Luxembourg had the highest per capita consumption of cocoa beans with 5.97 kg/person, followed by Switzerland (5.28 kg/person), France (3.90 kg/person), Germany (3.76 kg/person) and the UK (3.72 kg/person). Others include United States (2.72 kg/person), Slovenia (2.66 kg/person), Australia (2.65 kg/person), Croatia (2.14 kg/person), Japan (1.29 kg/person), Russia (1.24 kg/person), Brazil (0.53 kg/person), Côte d’Ivoire (0.49 kg/person), Ghana (0.47 kg/person) and China (0.03 kg/person).

1.2.2  World cocoa prices

World cocoa prices have been increasingly fluctuating since the fallout period between 1999 and 2000 when it reached a lowest of about US$940 per tonne. Prices of the beans increased drastically to about US$1850 in 2002, after which regular fluctuations of US$1550 and 1850 were recorded between 2002 and 2007. Average international cocoa prices, as measured by the ICCO daily price, increased in 2006–2007 from the previous cocoa year by 19% to US$1854 per tonne. The large production deficit in the 2006–2007 cocoa season had been the main factor leading to this development in the market (ICCO, 2008). Other bullish factors included the position in the futures markets of cocoa processors and chocolate manufacturers,
having below average forward fixed price coverage, and the weakening US dollar against other major currencies.

The highest price level of the season was reached on 6 July 2007, when prices climbed to £1140 on the London terminal market and US$2144 in New York, their highest levels since 2003. However, the strong increase in recorded prices induced some nervousness among market participants and, at such relatively high prices, the markets were rendered vulnerable to profit-taking. In the second week of July, the cocoa futures markets witnessed a strong adjustment, and after a short-lived recovery, the markets again retreated until the fourth week of August.

Notably, within the first quarter of 2009, cocoa prices were stabilised both in the London and New York markets, and the beans were sold around US$2300–2400 per tonne. However, in May–June 2009, prices were averaging between US$2500 and 2600 per tonne in the international market. Surprisingly, between July and December 2009, prices of cocoa increased sharply from US$2600 in July to US$3500 per tonne in December on both London and New York terminal markets, and this trend in prices apparently will continue to rise in the ensuing year. It is noteworthy that cocoa production continues to be the major agricultural mainstay of the economies of Ghana and La Côte d’Ivoire, representing over 60% of their revenue generation from the agricultural sector; therefore, any price fluctuations would affect the stabilities of these economies.

1.2.3 World consumption of chocolate products

The international global sale of chocolate was estimated at US$74 billion in 2006, an increase of 5% since 2005, and the Western European region accounts for an estimated 45% of global chocolate sales in volume sales. Figures for consumption of chocolate products in 2006 (Fig. 1.1) revealed Switzerland as the leader in chocolate consumption at 9.9 kg/person with Austria at 9.3 kg/person, Norway (8.5 kg/person), Ireland (8.4 kg/person), Germany (8.2 kg/person) and the UK (7.9 kg/person). No African country comes close (International Confectionery Association, 2007). Consumption of chocolate is highest within Western Europe in per capita terms, where household penetration is high and whose consumers eat chocolate several times during an average week. Per capita consumption levels tend to be highest in the more northerly European countries or those with a strong chocolate heritage – major examples include Switzerland, the UK, Belgium, Germany and Ireland.

In recent years, the consumer base has also become more sophisticated, with more people in regions such as the United States and Europe coming to regard themselves as connoisseurs of chocolate. This has led to rising demand for a wide variety of more upmarket ingredients, as well as products made from beans sourced from countries such as Ghana, Ecuador and Venezuela. On a geographical basis, sales are heavily skewed towards Europe and North America, which is to be expected since consumers in these regions are generally more affluent compared with other parts of the world. However, evidence exists that consumers are turning to premium varieties of chocolate with greater frequency elsewhere, notably in parts of the Far East such as Japan, South Korea and Thailand, as well as in Australasia. Some leading chocolate suppliers are now believed to be targeting developing economies such as China and Russia, which suggests a potential market for premium chocolate in these parts of the world.

Much of the recent growth in the market has resulted from the entrance of many of the world’s leading chocolate suppliers, as a result of which levels of new product development have been high. For example, up to 1500 new products have now been launched in the sector since 2002, with more manufacturers striving to develop a strong portfolio of premium
chocolate ranges. Many are now collaborating more heavily with artisanal chocolate producers to develop premium lines.

Demand for dark chocolate is increasing and currently accounts for 8–10% of global chocolate tablet sales. In 2006 it was reported that 33% of chocolate products launched were dark chocolate confectionery and US dark chocolate consumption increased at about 9% per annum over the period 2001–2005. Popularity of dark chocolate relates to research findings on positive impact of cocoa and chocolate on cardiovascular health.

### 1.2.4 World consumption of premium chocolate products

Premium chocolate represents a fast-growing and dynamic market in many parts of the world, with global sales having risen by over 18% within the last year. Sales and consumer
awareness are both growing for a variety of reasons – these include wider availability of premium chocolate at the retail level and high levels of new product activity. Additionally, more consumers are becoming attracted to dark chocolate on account of its health benefits, while ethical concerns have increased demand for organic and Fairtrade chocolate, all of which tend to be positioned at the premium end of the market. At present, sales of premium chocolate are heavily skewed towards the European and North American regions, which together accounted for almost 98% of global value in 2007. This is mainly because consumers are generally more affluent in these parts of the world and purchasing power is therefore higher, as well as many leading suppliers of premium chocolate are headquartered either in the United States or in Europe, the latter of which boasts of a long-standing chocolate manufacturing heritage. However, sales of premium chocolate are now developing in other parts of the world, with a more affluent urban consumer base emerging in countries such as Russia and China.

In spite of recent growth, premium varieties still account for less than 10% of the global chocolate market. This figure rises to around 12% for Europe, and at 32%, it is especially high in Switzerland. The premium sector accounted for almost 18% of the US retail chocolate market in 2007, although this figure is forecast to increase to around a quarter by 2011. From a consumer’s standpoint, purchasers of premium chocolate are increasingly no longer confined to the higher income groups, as a result of which the sector is encroaching on the mainstream chocolate market. With the consumer base continuing to widen, the premium chocolate sector is increasingly coming to mirror trends observed recently in markets such as wine and coffee. More people are now becoming more knowledgeable about specific cocoa varieties and their origins. As the premium chocolate market has grown, more of the leading multinational confectionery suppliers have been developing their products ranges in this area. This has mainly been done via acquisition or collaboration with specialist suppliers. Many companies have also increased levels of new product activity, launching new lines in sectors such as dark, single-origin, organic and Fairtrade chocolate.

1.3 FAIRTRADE COCOA AND CHOCOLATE IN MODERN CONFECTIONERY INDUSTRY

Fairtrade is a trading partnership that aims for sustainable development of excluded and disadvantaged producers, seeking greater equity in international trade by offering better trading conditions, and securing the rights of marginalised producers and workers – especially in the South. Fairtrade Labelling Organizations (FLO) backed by consumers are actively engaged in supporting producers, raising awareness and campaigning for changes in rules and practices of conventional international trade, with regulated terms of trade that ensure that farmers and workers in the poorest countries in the world are adequately protected and can build a more sustainable future (Fairtrade Federation, 1999; EFTA, 2005; FLO, 2006).

The concept of ‘Fairtrade’ has existed since the early 1960s, founded by a group of importers and non-profit retailers in the wealthy, northern European countries and small-scale producers in developing countries. The aim was fighting against low market prices and high dependence on brokers, a more direct type of trade with the European market. Conventional trading relations between the South and the North were believed unfair and unsustainable. Its goal is to tackle poverty in developing countries through trade, and its pragmatic approach is central to its success. However, diversity in the movement, its lack
of structure and economies of production scale were impediments to sustainability. Thus, since the early 1990s, the Fairtrade movement has become more organised and is now growing rapidly with about US$200 million annually in sales (Brown, 1993; Kilian et al., 2006). Fairtrade models that use a broad definition of farmer benefits have been widely studied (Dankers, 2003; Parrish et al., 2005; Shreck, 2005; Jaffee, 2007), and find Fairtrade approaches beneficial to smallholder development. Other studies, which focus on the income effects of higher prices to farmers (LeClair, 2002; Maseland & de Vaal, 2002; Lindsey, 2003; Zehner, 2003), tend to conclude in favour of free trade approaches. Harmonisation of definitions, increased professionalism and emphasis on quality assurance, direct marketing through multiple retailers and establishment of working relations with mainstream businesses to enable economies of scale, have secured steady growth of Fairtrade, coupled with consumer demand for ethical products.

Viewed positively, globalisation of world trade, currently totalling £3.5 trillion per annum, has helped lift 400 million people out of poverty in tiger economies of East Asia and elsewhere (Geographical, 2004). However, although international trade is a powerful redistributor of global wealth, it brings problems such as imbalance of economic power between producers, with wages at subsistence and below in developing countries, compared with retailers and distributors making profits in the supply chain in the developed world (Denny & Elliott, 2003). Fairtrade means better livelihoods for cocoa farmers by modernising farming with productivity improvements, introduction of systems of good practices and improvements in living and working conditions, guaranteeing a minimum price, perhaps more significantly often shortening the value chain in order to return greater revenue. Codes of good practices, containing guidelines for sustainable production, mean farmers benefit from better access for Fairtrade cocoa and chocolate products. This meets new requirements from consumers as demand for Fairtrade cocoa and chocolate products increases. Consumers of Fairtrade cocoa and chocolate products have now value systems that demand products which provide a decent living for farmers, are produced in a socially acceptable way, minimise harm to the environment and which are safe and healthy to enjoy (FLO, 2005). Delivering such products is in the interest of farmers, cocoa processors, traders/exporters and chocolate manufacturers. Benefits resulting to farmers and other stakeholders in the chain delivering ‘Fairtrade cocoa’ are enhanced livelihoods for farmers, improved market access and sustainable increases in production and consumption.

Currently in 2009, over 1.5 million people in developing countries benefit from sales of Fairtrade cocoa in 20 national markets across Europe, North America, Japan and Mexico. The Fairtrade mark appears on a range of cocoa and chocolate products including confectionery, sauces, hot drinks, snack bars and biscuits. This product range grows progressively and standards for new categories are introduced on a regular basis. Since 1997, UK retail sales of Fairtrade cocoa-certified products have grown on average at 50% per annum and currently worth about €300 million. The current dilemmas of marketing Fairtrade goods in mainstream distribution channels can perhaps be best understood in the context of the ‘ethical consumer’ movement (Carrigan & Attalla, 2001; Harrison et al., 2005). ‘Ethical consumerism’ is a seductive concept because it suggests the transformative power of individual choice and action. It is also a message of inclusion – all consumers can, through the simple act of choosing one good in preference to another, create positive social and/or environmental change. A rise of ‘ethical consumerism’ has been documented, with systematic influences on global chocolate trade. Consumer values have shifted from pragmatic, price and value-driven imperatives to a new focus on ethical values and stories behind products (Low & Davenport, 2007; Poelman et al., 2007).
1.3.1 Future of Fairtrade cocoa and confectionery industry

Despite the unprecedented ‘mainstream’ respectability achieved by the Fairtrade cocoa market over the past decade, it is considered as counterhegemonic act of resistance (Shreck, 2005), which seems to be struggling with its relationship to the larger global market. Although the Fairtrade concept is successfully moving from a marginal niche to the mainstream market, there are several factors that present limitations to the potential of this strategy for bringing about lasting social change. First, the structure of international trade (as governed by the World Trade Organization, WTO, and free trade agreements), within which Fairtrade initiatives operate, is not necessarily favourable to the continuous growth of the Fairtrade market. For instance, differentiation of commodities according to how they are produced is contradictory to the WTO’s mission of eliminating barriers to trade. Therefore, explicit commitments to supporting Fairtrade efforts are likely to be found unacceptable by the WTO. Another barrier to market-based resistance stems from the very same enthusiasm that contributes to the growth of alternative trade in the first place. Research suggests that consumers and retailers are beginning to suffer from ‘label fatigue’ as the multiplication of competing certification schemes becomes overwhelming and the differentiation between labels becomes confusing and even questionable (Watkins, 1998; Jaffee et al., 2004). A final limitation of this form of resistance for fostering any transformative change is the producers’ weak understanding of the Fairtrade market, the initiative more generally, and their role as Fairtrade ‘partners’ (Shreck, 2005).

Most multinational ‘specialty’ chocolate processing companies produce premium brands to provide increased incomes and opportunities for farmers, given the premium prices they pay for the special qualities of cocoa they buy. However, this makes the assumption that the value chain used by the multinationals to source their products returns the value to the producers. As shareholder-driven organisations, it is questionable whether it would be in their interest to adopt models that may lead to a perceived reduction in the free market efficiency of their value chains. Despite the concerns expressed that paying premium prices encourages more supply, they complain that the Fairtrade system is too small to supply their needs for high-quality beans. For instance, Nestlé, ADM and Cargill alone directly process over 500 000 tonnes of cocoa beans annually, many times over the quantity accounted for by FLO-registered production. Therefore, even a significant increase in production by Fairtrade growers would have little impact on the conventional cocoa markets, especially since Fairtrade cocoa does not attach any ‘improved quality’ criteria to its production. What would attract these multinational ‘specialty’ chocolate manufacturing companies to Fairtrade cocoa would be the adoption of ‘total quality’ practices, using improved harvesting, fermentation and drying methods to enhance both the physical and flavour quality characteristics, to cater for their special or premium brands. Post-harvest processes such as fermentation and drying have been reported to have strong influence on final cocoa and chocolate flavour qualities (Kattenberg & Kemming, 1993; Clapperton et al., 1994; Afoakwa et al., 2007a; Beckett, 2009).

Sustainability of the rapid growth of Fairtrade cocoa industry could be seen from a broader perspective than ‘fairness’ alone; indeed, it could be assumed to encompass both ‘fairness’ and ‘total quality’. The adoption of sustainable Fairtrade cocoa supply chain would be to provide a mechanism for traceability and efficiency in producing ‘total quality’ produce that conforms to principles of sustainable development, delivered with emphasis on social, environmental, yield and quality factors, which would therefore continue to command premium prices.
1.4 THE CONCEPT OF THIS BOOK

The cocoa and chocolate industry is undergoing dynamic change in the nature of the demand for chocolate. The trends towards niche or premium chocolate products have engendered not only new challenges but also opportunities for all participants in the sector. Until recently, the general perception was that consumption of chocolate in Europe and the United States would begin to stagnate, as these major chocolate markets were reaching saturation. However, consumption behaviour across these mature markets has recently experienced major change, with the increasing appeal of premium chocolate, including organic, Fairtrade, single-origin, reduced sugar and dark and high cocoa content chocolate. Indeed, the confectionery market has increasingly been characterised by consumer demand for taste, convenience and health, and products addressing ethical and environmental concerns.

New product developments and ‘functional foods’ with wholesome ingredients (foods that provide health benefits beyond basic nutrition) have played an important role in the upward trend of the confectionery market. In recent times, many research activities have increasingly been conducted on the health and nutritional benefits of cocoa and chocolate. The findings indicate that flavanoids in cocoa may decrease low-density lipoprotein (‘bad’ cholesterol) oxidation, helping to prevent cardiovascular diseases. In addition, cocoa’s high content in antioxidants has been proved to reduce the risk of cancer. The demand for dark and high cocoa content chocolate, in particular, has surged in response to these positive findings.

The chocolate industry has demonstrated a strong ability to meet these challenges and to benefit from the new opportunities brought about through changing consumer demand. Companies traditionally known for milk chocolate products have been introducing new dark and high cocoa content chocolate products. The global dark chocolate market is now estimated to represent between 5 and 10% of the total market for chocolate tablets (the others being plain milk, plain white and filled chocolate tablets), with a higher share in continental Europe than in the United States and the UK. Similarly, the certified organic and Fairtrade chocolate markets have been booming, increasing at double-digit rates.

The advent of increased demand for chocolate has impacted significantly on the demand for cocoa beans in terms of both quantity and quality. While the chocolate industry has responded proactively to this development, the need for cocoa producers to have further information on this issue was brought to the fore. Such information would provide cocoa-producing countries with a better basis for formulating and implementing policies and programmes regarding cocoa production. One of the main challenges facing producing countries, to enhance their revenues from cocoa, is to meet the changing face of consumer demand. As a result of these increasing chocolate consumption trends, the cocoa processing and chocolate manufacturing industry faces an enormous challenge of meeting the demand and quality criteria expected by the consuming populations. This has to be marched vigorously by increasing production capacities of chocolate manufacturing industries, which also require a great deal of understanding of the science and technology of chocolate.

As chocolate manufacturing is complex and requires numerous technological operations and the addition of a range of ingredients to achieve products of suitable physical and chemical attributes, appearance and taste parameters with prespecified ranges, understanding the science of its manufacturing and the technological processes that can result in the expected product quality is paramount. Additionally, chocolate processing differs due to historical development within a producing company and geographical locations in which products are sold and therefore requires the necessary expertise to achieve the required quality attributes,
rheological characteristics, flavour development and thus sensory perception that are needed to satisfy a specified consuming population.

This book is therefore a mediator in bringing modern scientific and technological knowledge and understanding of the processes involved in cocoa processing and chocolate manufacturing to all who are engaged in the business of learning, making, consuming and using cocoa and chocolate products.
2 Cocoa cultivation, bean composition and chocolate flavour precursor formation and character

2.1 INTRODUCTION

The principal varieties of the cocoa tree *Theobroma cacao* (family Sterculiaceae) are *Criollo*, rarely grown because of disease susceptibility; *Nacional* with fine flavour, grown in Ecuador; *Forastero* from the Amazonas region; and *Trinitario*, a hybrid of *Forastero* and *Criollo*. *Forastero* varieties form most of the ‘bulk’ or ‘basic’ cocoa market. World annual cocoa bean production is approximately 3.5 million metric tonnes and major producers are the Ivory Coast, Ghana, Indonesia, Brazil, Nigeria, Cameroon and Ecuador. There are also a number of smaller producers, particularly of ‘fine’ cocoa, which forms less than 5% of world trade (Coe & Coe, 1996; Awua, 2002; Schwan & Wheals, 2004; Amoye, 2006).

Cocoa consumption has possible health benefits with specific claims recently identified and studied (Erdman et al., 2000; Wollgast & Anklim, 2000b; Weisburger, 2001; Tapiero et al., 2002; Steinburg et al., 2003; Gu et al., 2006; Miller et al., 2006). Cocoa beans and derived products are rich in antioxidants – including catechins, epicatechin and procyanidins – polyphenols similar to those found in wine, vegetables and tea (Kim & Keeney, 1984; Yamagishi et al., 2001; Carnesecchia et al., 2002; Hatano et al., 2002; Kris-Etherton & Keen, 2002; Tapiero et al., 2002; Engler et al., 2004; Grassi et al., 2005; Lamuela-Raventos et al., 2005; Buijsse et al., 2006; Gu et al., 2006; Hermann et al., 2006; Afoakwa et al., 2007a). These contribute as precursors to flavour formation in cocoa and chocolate (Misnawi et al., 2003; Counet et al., 2004; Kiy et al., 2005).

Chocolate has a distinctive flavour character, with specific notes related to bean genotype, growing conditions and processing factors (Clapperton, 1994; Beckett, 2003; Whitefield, 2005). Fermentation is a key processing stage that causes the death of the bean and facilitates removal of the pulp and subsequent drying. During this stage, there is initiation of flavour precursor formation and colour development, and a significant reduction in bitterness.

The chemistry of cocoa beans in fermentations is still under study (Buyukpamukcu et al., 2001; Luna et al., 2002; Misnawi et al., 2003; Schwan & Wheals, 2004; Kiy et al., 2005) as are contributions from roasting and alkalisation (Gill et al., 1984; Jinap & Dimick, 1991; Oberparlaiter & Ziegleder, 1997; Dimick & Hoskin, 1999; Stark et al., 2005; Granvogl et al., 2006; Ramli et al., 2006; Reineccius, 2006; Stark et al., 2006a) and conching (Pontillon, 1995; Plumas et al., 1996; Beckett, 2000; Awua, 2002; Reineccius, 2006). Key flavour compounds in chocolate have been identified (Cerny & Grosch, 1994; Cerny & Fay, 1995; Schnermann & Schieberle, 1997; Schieberle & Pfanner, 1999; Counet et al., 2002; Taylor, 2002; Taylor & Roberts, 2004; Reineccius, 2006; Afoakwa et al., 2008a). However, the biochemical and chemical processes leading to chocolate flavour formation and development, and their relationships to the final character and perceptions of quality are not fully understood.
This chapter discusses cocoa cultivation practices, bean composition and the biochemistry of flavour precursor formation and character in cocoa resulting from the inherent chemical composition of the bean, genotypic variation in bean origin and fermentation processes, and suggests the types of flavour precursors formed and their overall achieved characters.

2.2 COCOA CULTIVATION AND PRACTICES

2.2.1 Cultivation of cocoa

Cocoa cultivation requires an appropriate climate that is mostly found within the area bounded by the Tropics of Cancer and Capricorn. The majority of the world’s cocoa is grown as small or large plantations within 10° North and South of the equator, and best suited for sea level up to a maximum of about 1000 m, although most of the world’s cocoa grows at an altitude of less than 300 m. Cultivation requires temperatures generally within 18–32°C (65–90°F) and rainfall well distributed across the year, with a range between 1000 and 4000 mm (40–160 in.) per year, but preferably between 1500 and 2500 mm (60 and 100 in.).

During cultivation, cocoa prefers high humidity, typically ranging between 70–80% during the day and 90–100% at night. Cocoa trees are usually planted to achieve a final density of 600–1200 trees/ha (1500–3000 trees/acre) and intercropped with food crops (Fig. 2.1). Due to the fragility of the cocoa trees during the early stages of growth, they are mostly protected from strong winds using food crops; for instance, plantain trees are used as wind shield on plantations in Ghana. The trees grow well on most soil but preferably well-aerated soils with good drainage and a pH of neutral to slightly acidic (5.0–7.5), and pest and diseases carefully controlled (Fowler, 1999). Cocoa trees used to grow to a height of approximately 10 m tall at maturity, preferably under the shades of other trees. However, modern breeding methods have led to the development of trees to a standard of approximately 3 m tall to allow for easy harvesting.

Fig. 2.1 Cocoa plantation showing young trees intercropped with food crops (plantain). See Colour Plate No. 2.
2.2.2 Flowering and pod development

The emergence of the bud through the bark of the tree marks the beginning of the cocoa bean development. This takes about 30 days from its histological beginnings to its culmination on the bark surface, and within hours of its emergence, the bud matures, sepals split and the flower continues to mature during the first night following the budding. On the next morning after budding, the flower is fully opened (Fig. 2.2) and the anthers release their pollens.

If not pollinated and fertilised on this day by insects, the flowers continue to abscission on the following day. It is interesting to note that a single healthy cocoa tree produces about 20 000–100 000 flowers yearly but only 1–5% of these get pollinated and develop into pods.

Once successfully pollinated and fertilised, the various stages of embryo and ovule growth continue, the pods reaching maximum size after about 75 days following pollination. The pods then mature for another 65 days, making a total of about 140 days after pollination (Fig. 2.3). The fruits are then allowed to ripen for about 10 days and the pods are harvested. The matured cocoa fruits measure between 100 and 350 mm (4 and 14 in.) long and have a wet weight of approximately 200 g to approximately 1 kg (Mossu, 1992).

A key determinant of properly ripened cocoa fruit is the external appearance. There are considerable variations in the shape, colour and surface texture of the pods depending on genotype (Figs 2.4–2.6). The ripening is visible as changes in the colours of the external pod walls occur and the nature of colour changes is dictated by the genotype of cocoa involved. However, cocoa fruit ripening is generally thought of to be from green or purple to varied shades of red, orange or yellow depending on genotype. The composition of the internal content, comprising the bean and pulp, is extensively discussed in the next section, with emphasis on the bean composition and its influence on chocolate flavour precursor formation and development.

Fig. 2.2 Flowering of cocoa tree during growth. See Colour Plate No. 3.
Fig. 2.3  Mature Amelonado-type cocoa trees bearing unripe pods.

Fig. 2.4  Unharvested West African Forastero (Amelanodo) cocoa fruits.
2.2.3 Harvesting and pod opening

Harvesting of cocoa fruits involves the removal of pods from the trees and the extraction of the beans and pulp from the interior of the pod. While the ripening process occurs in a 7- to 10-day period, the pods can safely be left on the trees for up to 2 weeks before harvesting. Thus, a 3-week window exists during which the cocoa may be considered fit to harvest. There are two concerns that dictate how quickly the harvest is completed – potential for pod diseases and the possibility of bean germination in the pod, if delayed for too long.
During harvesting, a knife or cutlass is normally used to remove the pod from the tree, but there exists a special long-handled tool for removing pods which are higher up the tree (Fig. 2.7).

After removing the pods from the trees, they may be gathered into heaps (Fig. 2.8) and opened immediately or allowed to sit for a few days before opening, a technique known as pod storage, which has been reported to have significant beneficial effects on the flavour quality of the bean during subsequent fermentation and processing. Much of this depends on
the geographic and historical practices encountered in the various growing regions. Details of its significance are discussed in the subsequent sections.

The actual splitting of the pods is done by a variety of means depending on location, including the use of cutlasses or machetes, or cracking with a wooden billet or club. The practice of cutting with cutlass or machetes requires considerable skill as the beans can easily be damaged during the process and subsequent penetration by mould and stored product pests, rendering them as defects. Figures 2.9 and 2.10 show ripe and opened cocoa pods with their constituent cross-sectional and longitudinal bean arrangements, respectively.

There are 30–40 beans or seeds inside the pod attached to a central placenta (Fig. 2.10). The beans are oval and enveloped in a sweet, white mucilaginous pulp. After breaking the pod, the beans are then separated by hand and the placenta is removed. A seed coat or testa separates the seed cotyledons from the pulp. Beans taken directly from the pod to controlled drying conditions develop virtually no chocolate flavour after processing, and fresh beans are free from compounds necessary for the development of chocolate flavour. The process of fermentation is therefore necessary for the formation of constituents or flavour precursors that undergo further development during the roasting process. Thus, the mature in-pod cocoa bean is made up of three components – pulp, testa and cotyledons.

### 2.2.4 Cocoa diseases and pests and their influence on chocolate quality

The cocoa tree is susceptible to a number of diseases and pests that affect the yield of pods from the trees. Due to their versatility in infesting other pods, it is recommended that all diseased pods be harvested with the healthy ones and then separated for destruction. The cocoa pod diseases and pests are as described.
2.2.4.1 Swollen shoot disease

This is a viral disease affecting cocoa and is spread by small whitish insects known as mealy bugs. The pods assume a roundish shape and also diminish in size, causing a drastic reduction in yield from infested trees. Control measures involve cutting down infected trees and adjoining trees and burning them completely. There is, however, no evidence that this disease has any adverse effect on the quality of fruits of the cocoa tree or on the quality of the products after fermentation. This is because a full investigation on these has not been conducted and would be dangerous to assume that no evidence exists.

2.2.4.2 Black pod disease

This disease is characterised by browning, blackening and rotting of cocoa pods and beans. It is caused by the fungi *Phytophthora palmivora* and *Phytophthora megakarya*, the latter being more aggressive and destructive. These fungi attack every portion of the cocoa tree and are controlled by good cultural practices by the removal of infected pods and by spraying with approved fungicides. Their rate of infestation could be reduced by reducing the humidity and by increased aeration on the cocoa farm.

The pods harvested from infected trees may be used with the healthy pods, if the fungal attack has not penetrated the pod walls, hence the beans would be unaffected. If, however, harvesting is delayed and attack is severe, there is some evidence (Awua, 2002) that the free sugars of the pulp are utilised by the fungus, giving rise to a dry pulp similar to that of an unripe pod. If such pods occur in quantity, fermentation is impaired and a product of poor quality results.
2.2.4.3 Witches broom disease

This disease is caused by the fungus *Marasmius perniciosus* and is indigenous to South America. It has, however, spread to surrounding cocoa-growing countries and has caused considerable damage to cocoa trees in Brazil and Trinidad and Tobago. It is characterised by abnormal tufted vegetative growth on the trees at the expense of pod formation. Unless the cocoa pod is almost ripened when attacked, the infection destroys the diseased pods and renders them useless. The infected trees are controlled by spraying with fungicides. However, this disease is absent in the West African cocoa-growing region.

2.2.4.4 Pod borers (capsids, cocoa thrips and mealybugs)

Several insect pests such the capsids and moths feed on young shoots and pods of the cocoa tree. They damage the young soft tissues of the trees by piercing the young shoots with their mouth parts, injecting poisonous saliva and then sucking out the fluid food from the wound, causing the death of the young trees. These infections could be controlled by the application of the recommended insecticides and by leaving a reasonable amount of shade between the young trees. None of these insect pests have been reported to have any direct influence on the quality of manufactured chocolate products. However, it is feared that large-scale insecticide-spraying exercises used in their control may have result in taints in the prepared products. These control techniques may also increase the pesticide levels in the fermented and dried cocoa beans, and may pose problems of high, unacceptable pesticide doses on the international markets. It is therefore recommended that cocoa with these infections is controlled under supervision by agricultural extension officers.

2.3 BEAN COMPOSITION AND FLAVOUR PRECURSOR FORMATION

2.3.1 Chemical composition of the bean

The shell (testa) represents 10–14% dry weight of the cocoa bean, while the kernel or cotyledon is made up of most of the remaining 86–90% (Table 2.1). The cotyledon confers characteristic flavours and aromas of chocolate (Rohan & Stewart, 1967; Osman *et al.*, 2004) and is composed of two types of parenchyma storage cells. Polyphenolic cells (14–20% dry bean weight) contain a single large vacuole filled with polyphenols and alkaloids including caffeine, theobromine and theophylline (Osman *et al.*, 2004). The pigmented polyphenols, when undisturbed, confer deep purple colour to fresh Forastero cotyledons. Lipid–protein cells, on the other hand, have cytoplasm tightly packed with multiple small protein and lipid vacuoles and other components such as starch granules – all of which play roles in defining cocoa flavour and aroma characters (Kim & Keeney, 1984; Nazaruddin *et al.*, 2001).

Reineccius *et al.* (1972) reported that fresh unfermented cocoa beans contained 15.8 mg/g sucrose and trace amounts of fructose, sorbose, mannitol and inositol. Berbert (1979) suggested that sucrose content at 24.8 mg/g unfermented beans formed about 90% of total sugars (27.1 mg/g). The reducing sugars, fructose and glucose form about 6% (0.9 and 0.7 mg/g, respectively) and others (including mannitol and inositol) at less than 0.50 mg/g. Differences have been attributed to method and time of harvesting, type and origin of cocoa beans (Reineccius *et al.*, 1972). Tissue components remain compartmentalised, separating
Table 2.1  Bean composition of unfermented West African (Forastero) cocoa

<table>
<thead>
<tr>
<th>Constituents</th>
<th>Dried beans (%)</th>
<th>Fat-free materials (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cotyledons</td>
<td>89.60</td>
<td>—</td>
</tr>
<tr>
<td>Shell</td>
<td>9.63</td>
<td>—</td>
</tr>
<tr>
<td>Germ</td>
<td>0.77</td>
<td>—</td>
</tr>
<tr>
<td>Fat</td>
<td>53.05</td>
<td>—</td>
</tr>
<tr>
<td>Water</td>
<td>3.65</td>
<td>—</td>
</tr>
<tr>
<td>Ash (total)</td>
<td>2.63</td>
<td>6.07</td>
</tr>
<tr>
<td>Nitrogen</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total nitrogen</td>
<td>2.28</td>
<td>5.27</td>
</tr>
<tr>
<td>Protein nitrogen</td>
<td>1.50</td>
<td>3.46</td>
</tr>
<tr>
<td>Theobromine</td>
<td>1.71</td>
<td>3.95</td>
</tr>
<tr>
<td>Caffeine</td>
<td>0.085</td>
<td>0.196</td>
</tr>
<tr>
<td>Carbohydrates</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glucose</td>
<td>0.30</td>
<td>0.69</td>
</tr>
<tr>
<td>Sucrose</td>
<td>1.58</td>
<td>3.86</td>
</tr>
<tr>
<td>Starch</td>
<td>6.10</td>
<td>14.09</td>
</tr>
<tr>
<td>Pectins</td>
<td>2.25</td>
<td>5.20</td>
</tr>
<tr>
<td>Fibre</td>
<td>2.09</td>
<td>4.83</td>
</tr>
<tr>
<td>Pentosans</td>
<td>1.27</td>
<td>2.93</td>
</tr>
<tr>
<td>Mucilage and gums</td>
<td>0.38</td>
<td>0.88</td>
</tr>
<tr>
<td>Polyphenols</td>
<td>7.54</td>
<td>17.43</td>
</tr>
<tr>
<td>Acids</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetic (free)</td>
<td>0.014</td>
<td>0.032</td>
</tr>
<tr>
<td>Oxalic</td>
<td>0.29</td>
<td>0.67</td>
</tr>
</tbody>
</table>

Sources: Rohan (1963) and Reineccius et al. (1972).

flavour constituents that may interact with cell membrane and wall breakdown during the subsequent fermentation.

2.3.2 Polyphenols and chocolate flavour quality

Cocoa is rich in polyphenols, specifically catechins (flavan-3-ols) and proanthocyanidins, stored in cotyledon pigment cells and cocoa leaves (Osman et al., 2004). Depending on anthocyanin content, pigmentation in polyphenol-storage cells ranges from white to deep purple. Polyphenol and alkaloids, approximately 14–20% bean weight, are central to bean flavour character (Kim & Keeney, 1983). Three groups of polyphenols can be differentiated: catechins or flavan-3-ols (~37%), anthocyanins (~4%) and proanthocyanidins (~58%). The primary catechin is (−)-epicatechin, up to 35% of total polyphenols and from 34.65 to 43.27 mg/g of defatted freshly harvested Criollo and Forastero beans (Kim & Keeney, 1984). Less abundant is (+)-catechin with only traces of (+)-gallocatechin and (−)-epigallocatechin. Nazaruddin et al. (2001) reported total polyphenols ranged from 45 to 52 mg/g in cocoa liquor, 34 to 60 in beans and 20 to 62 in powder: (−)-epicatechin contents were 2.53, 4.61 and 3.81 mg/g, respectively.

The anthocyanin fraction is dominated by cyanidin-3-α-L-arabinoside and cyanidin-3-β-D-galactoside. Procyanidins are mostly flavan-3,4-diols and are four to eight or four to six bound to form dimers, trimers or oligomers with epicatechin as main extension subunit (Romanczyk et al., 1997). Fat-soluble polyphenols in dried fat-free fresh Forastero cocoa form 15–20%, which falls to approximately 5% after fermentation. Contents of 10% or
greater are considered a sign of poor fermentation. Higher concentrations of polyphenols lead to very astringent-tasting chocolate. **Criollo** cocoa beans have approximately two-thirds of this content of polyphenols, and anthocyanins have not been found (Lange & Fincke, 1970; Hansen et al., 2000). Polyphenol reactions with sugar and amino acids contribute flavour and colour to cocoa beans and alkaloids to the bitterness (Lehrian & Patterson, 1983). During fermentation, protein breakdown occurs partly by hydrolysis to peptides and amino acids and partly by conversion to insoluble forms by the actions of polyphenols. Polyphenol oxidase promotes oxidative browning to give the characteristic chocolate brown colour of well-fermented Forastero beans.

### 2.3.3 Effects of proteins and sugars on flavour precursor formation

Cocoa cotyledons contain as storage proteins single albumin and globulin species (Biehl et al., 1982a). The globulin, with two polypeptides of 47 and 31 kDa (Petipher, 1990; Spencer & Hodge, 1992; Voigt et al., 1993), is degraded in fermentation, the albumin (21 kDa) is not. Cocoa-specific aroma precursors can be generated in vitro from globulin in partially purified bean fractions by aspartic endoprotease and carboxypeptidase activities (Voigt et al., 1994a). Cotyledon protein degradation into peptides and free amino acids appears central to flavour formation. The consensus is that the combined action of two proteases, namely aspartic endopeptidase and serine carboxy-(exo)peptidase, on vicilin (7S)-class globulin (VCG) storage polypeptide yields cocoa-specific precursors. The aspartic endopeptidase (EC 3.4.23) hydrolyses peptide bonds in VCG at hydrophobic amino acid residues, forming hydrophobic oligopeptides – substrates for the serine exopeptidase (EC 3.4.16.1) that remove carboxyl terminal hydrophobic amino acid residues (Biehl et al., 1993; Voigt et al., 1994b; Biehl et al., 1996; Biehl & Voigt, 1999). Kirchhoff et al. (1989) observed a correlation between free amino acid accumulation and generation of specific aroma precursors, with pH-dependent proteolytic processes. Activities in both key enzymes are pH dependent, near to pH 3.8 – optimum for aspartic endopeptidase – more hydrophobic oligopeptides and less free amino acids are produced. Whereas close to 5.8 – the optimum for serine exopeptidase – there are increases in hydrophilic oligopeptides and hydrophobic amino acids. Related storage proteins or alternative peptidases both failed to produce appropriate flavour precursors. With a rapid fall to low pH (<4.5), reduction in flavour precursors is observed and slow diffusion of organic acids through cotyledons, timing of initial entry, duration of optimum pH and final pH are crucial for final flavour (Biehl & Voigt, 1999). Thus, bean composition interacts with fermentation in formation of cocoa flavour quality. Analysis of VCG proteins and proteolytic degradation products in five popular genotypes (Forastero, Criollo, Trinitario, SCA 12 and UIT1) concluded that character in chocolate may vary, but all genotypes had potential for abundant aroma content in raw cocoa (Amin et al., 2002).

Electrophoretic (SDS-PAGE) analyses showed polypeptide species at 47, 31 and approximately 14.5 kDa, all derived from post-translational modification of a vicilin (7S) storage protein precursor observed in vivo as a 139-kDa trimer (Biehl et al., 1982b; MacDonald et al., 1994). Polypeptide and cDNA sequence data showed considerable homology to other 7S class storage proteins, and specifically α-globulin in cotton seeds (McHenry & Fritz, 1992; Spencer & Hodge, 1992). Specific cocoa aroma was obtained in vitro when this vicilin globulin was successively degraded by an aspartic endoprotease and a carboxypeptidase and
products were roasted in the presence of reducing sugars (Voigt et al., 1994a, b). Acidification during fermentation is critical for final cocoa quality since the different pH optima of endo-protease and carboxypeptidase activities determine efficiency and products of proteolysis. The outcome is mixtures of hydrophobic and hydrophilic peptides, the latter more important for formation of typical aroma notes. In summary, it can be concluded that proteolysis of globulin is central to cocoa flavour formation.

Low-molecular-weight protein breakdown products and reducing sugars all contribute to Maillard reactions that produce cocoa flavour in roasting (Rohan & Stewart, 1967). Peptides and hydrophobic free amino acids, specifically leucine, alanine, phenylalanine and tyrosine, released during fermentation by aspartic proteinase and carboxypeptidase activities (Voigt et al., 1993, 1994a) contribute to flavour (Mohr et al., 1976) by reacting with fructose and glucose (Lopez et al., 1978). Cocoa fermentation protein breakdown has been characterised by Rohan and Stewart (1967), Lopez et al. (1978), Biehl and Passern (1982) and Biehl et al. (1985) and studied changes in sugars.

2.3.4 Microbial succession and enzymatic activities during flavour precursor generation in cocoa fermentation

During fermentation, microbial activity on the cocoa pulp generates heat and produces ethanol, acetic and lactic acids that kill the bean. Until the pods are split, the beans are microbiologically sterile. Once the pod is split, the beans and pulp are exposed to numerous sources of micro-organisms, including the farmer’s hands and implements, the pods exterior and largely insect activity on the farms. The immediate effect of this exposure is the initiation of the microbiological attack of the sugar-rich acidic pulp. At the initial stages of fermentation process, also known as the anaerobic hydrolytic phase, the pulp condition is anaerobic and anaerobic yeasts flourish.

The yeasts quickly generate an alcoholic fermentation, and the sugars in the pulp are converted to alcohol and carbon dioxide. The citric acid is used in the metabolism of the yeasts. This initiates a slow rise in the pH of the pulp material. The yeasts dominate the first 24–36 hours of the fermentation process, after which the rising pH creates a self-limiting factor on further proliferation. In addition, enzymes released by the yeasts attack the pectin constituents of the cell walls of the pulp mass. The subsequent release of the fluid cell contents runs off the fermenting pulp as what is referred to as ‘sweatings’. Examples of yeasts isolated during cocoa fermentation include Saccharomyces cerevisiae, Kluyveromyces marxianus, Saccharomyces exiguus, Candida castelli, Candida saitoana, Candida guilliermondii, Schizosaccharomyces pombe, Pichia farinosa and Torulopsis spp. (Schwan & Wheals, 2004).

The continuous breakdown of the pulp and its liquefaction result in the formation of voids between the cells in the pulp. The loss of fluids through the sweating process increases the rate of acid depletion as it is carried away in the run-off. These voids increase in size and allow air to percolate through the pulpy mass. The combination of this change from anaerobic to aerobic conditions in the substrate, the rise in pH as the citric acid is consumed and loss through sweating and increasing alcohol content being generated by the fermentation of the sugars leads to the eventual inhibition of yeast activity. This signals the end of the anaerobic phase of the process.

The second phase known as the oxidative condensation phase occurs under aerobic conditions and is initially dominated by lactic acid bacteria. Lactic acid bacteria increase
in numbers when part of the pulp and ‘sweatings’ had largely drained away, and the yeast population is declining. Yeast metabolism favours the growth of acidoduric lactic acid bacteria. Of the lactic acid bacteria isolated from cocoa fermentations Acetobacter lovaniensis, Acetobacter rancens, Acetobacter xylinum, Gluconobacter oxydans, Lactobacillus fermentum, Lactobacillus plantarum, Leuconostoc mesenteroides and Lactococcus (Streptococcus) lactis were the most abundant species in the first 24 hours of fermentation (Schwan & Wheals, 2004). As the microbial activity increases, the temperature of the bean mass also begins to increase until it reaches about 45°C (113°F). The conditions at this temperature are more favourable for the promotion of the growth of acetic acid-forming bacteria, replacing lactic acid formers as the dominant microflora.

After the decline in the populations of yeasts and lactic acid bacteria, the fermenting mass becomes more aerated. This creates conditions suitable for the development of acetic acid bacteria. These bacteria are responsible for the oxidation of ethanol to acetic acid and further oxidation of the latter to carbon dioxide and water. The acidulation of cocoa beans and the high temperature in the fermenting mass, which causes diffusion and hydrolysis of proteins in the cotyledons, have been attributed to the metabolism of these organisms. Thus, the acetic acid bacteria play a key role in the formation of the precursors of chocolate flavour. In general, the members of genus Acetobacter have been found to be more frequent than those of Gluconobacter. Species of Acetobacter aceti and Acetobacter pasteurianus have been isolated in most cocoa beans (Schwan & Wheals, 2004). The acetic acid formers go on to become about 80–90% of the microbial population, and their activities (heat and the acidity) eventually lead to the death of the seeds. This results in the breakdown of cellular components and a variety of reactions are initiated.

The increased aeration, increased pH value (3.5–5.0) of cocoa pulp and a rise in temperature to about 45°C in the cocoa mass in the later stages of fermentation are associated with the development of aerobic spore-forming bacteria of the genus Bacillus. Many Bacillus spp. are thermotolerant and others grow well at elevated temperatures. Bacillus steaethermophilus, Bacillus coagulans and Bacillus circulans were isolated from cocoa beans that had been subjected to drying and roasting (150°C) temperatures. Aerobic spore-forming bacteria produce a variety of chemical compounds under fermentative conditions. These contribute to the acidity and perhaps at times to the off-flavours of fermented cocoa beans. Indeed, it has been suggested that C3–C5 free fatty acids found during the aerobic phase of fermentation and considered to be responsible for off-flavours of chocolate are produced by Bacillus subtilis, Bacillus cereus and Bacillus megaterium. Other substances such as acetic and lactic acids, and 2,3-butanediol, all of which are deleterious to the flavour of chocolate, are also produced by Bacillus spp. (Schwan & Wheals, 2004). Pulp fermentation products penetrate slowly into beans causing swelling and stimulating enzymic reactions that yield flavour precursors, and on roasting characteristic flavour and aroma notes. Fresh beans with low contents of flavour precursors will have limited commercial usage and activities in fermentation will be unable to rectify this shortfall (Rohan & Stewart, 1967; Mohr et al., 1976; Voigt et al., 1994a). Appropriate amounts and ratio of precursors are essential for optimal flavour volatiles production in roasting.

Subcellular changes in the cotyledons release key enzymes affecting reactions between substrates pre-existing in unfermented beans (Hansen et al., 1998). Enzymes exhibit different stabilities during fermentation and may be inactivated by heat, acids, polyphenols and proteases. Aminopeptidase, cotyledon invertase, pulp invertase and polyphenol oxidase are significantly inactivated, carboxypeptidase is partly inactivated, whereas endoprotease and glycosidases remain active during fermentation (Hansen et al., 1998). During the anaerobic
phase, the complex pigment components are attacked by glycosidases and are converted by hydrolysis to sugars and cyanidins. As well, sucrose is converted to glucose and fructose by invertase, the conversion of proteins to peptides and amino acids by proteinase and the conversion of polyphenols to quinines by polyphenols oxidase. During these processes, the colour of the cotyledons slowly changes, and in the case of Forastero varieties, the deep purple tissue is converted to a red-brown colour. As the anaerobic phase nears its termination, the products of the enzymatic actions remain to be further converted in subsequent reactions.

In the aerobic phase, cyanidin and protein–phenolic complexes undergo oxidative reactions, which are eventually expressed as the final spread of brown colour across the cotyledon surfaces as the repurple pigments react. Quinone, generated by the actions of the polyphenols oxidase, now reacts with hydrogen-bearing compounds. These in turn, form complexes with amines, amino acids and sulphur-bearing compounds, leading to the lessening of astringency and bitterness during subsequent roasting of the nibs. Clearly, the changes that occur within the bean during fermentation are very complicated and that the hydrolytic and subsequent oxidative reactions generate numerous biochemical complexes that serve as flavour precursors during the roasting process. The genetic make-up of the bean is also certainly crucial to this process. Hansen et al. (2000) noted that differences in enzyme activities can be partly explained by pod variation and genotype, but in general, activities present in unfermented beans seem not a limiting factor for optimal flavour precursor formation in fermentation. Significant fermentation effects may relate to factors such as storage protein sequence and accessibility, destruction of cell compartmentalisation, enzyme mobilisation and pulp and testa changes.

Proteases affect multiple cellular processes in plants, such as protein maturation and degradations associated with tissue restructuring and cell maintenance (Callis, 1995). Key aspartic proteinases (EC 3.4.23) have been characterised in a number of T. cacao gymnosperms (Mutlu & Gal, 1999), and activity in seeds of T. cacao has been extensively studied by Biehl et al. (1993). Partially purified aspartic proteinase had activity optima at 55°C and pH 3.5. Subsequently, Voigt et al. (1995) purified T. cacao seed aspartic proteinase into a heterodimer of 29 and 13 kDa polypeptides that efficiently hydrolysed T. cacao seed vicilin and (less effectively) trypsin inhibitor into peptides (Voigt et al., 1994a).

Two cDNA species, TcAP1 and TcAP2, respectively, encoding different polypeptides of the plant aspartic proteinase gene family, have been cloned and characterised (Laloi et al., 2002). Both genes are induced early in seed development and show significantly decreased expression as the seeds reach maturity. However, TcAP2 expression is induced to higher levels, suggesting the gene encodes the primary aspartic proteinase in the mature seed. It should also be noted that T. cacao seeds have unusually high levels of such aspartic proteinase activity (Voigt et al., 1994a). Guilloteau et al. (2005) noted that physical and biochemical properties of the active T. cacao seed TcAP2 aspartic proteinase complex are novel, suggesting the highly expressed gene product may represent a previously uncharacterised activity. Purified TcAP2 gene product efficiently degrades cocoa seed vicilin into low molecular products including di- and tripeptides, implying that this gene product may play an important role during fermentation.

A processing sequence is required to produce cocoa beans with good flavour. Pulp sugar fermentation should yield high levels of acids, particularly acetic acid (Voigt et al., 1994a). As seed pH decreases, cell structure is disrupted, which triggers mobilisation and/or activation of the primary aspartic proteinase activity with massive degradation of cellular protein (Biehl et al., 1982b, 1985). Fermentation proteinase and peptidase activities seem critical for good flavour quality (Voigt & Biehl, 1995; Laloi et al., 2002).
Significant differences in enzyme activities exist between cocoa genotypes, but simple and general relationships have not been established between genotype flavour potential and key enzyme activities in unfermented beans. Therefore, how enzymatic processes are regulated, and substrates and products that relate to desirable flavours, and limiting factors for the enzymatic contribution to fermentation processes remain unclear.

### 2.4 EFFECT OF GENOTYPE ON COCOA BEAN FLAVOURS

Genotype influences both flavour quality and intensity in chocolate (Luna et al., 2002; Taylor, 2002; Counet et al., 2004; Taylor & Roberts, 2004), likely determining quantities of precursors and activity of enzymes, and thus contributions to flavour formation. Reineccius (2006) concluded that varietal differences were primarily due to quantitative (as opposed to qualitative) differences in flavour precursor and polyphenol contents. Contents of sugars and enzymic breakdown of polysaccharides form an important source of precursors. However, post-harvest processes (fermentation and drying) and roasting have a strong influence on final flavours (Kattenberg & Kemming, 1993; Clapperton et al., 1994; Luna et al., 2002; Counet & Collin, 2003). Three primary cocoa types, Forastero (bulk grade), Criollo (fine grade) and hybrid, Trinitario (fine grade), show wide variations in final flavour (Beckett, 2000; Awua, 2002; Amoye, 2006). Nacional cocoa is viewed as a third fine variety, producing the well-known Arriba beans with distinctive floral and spicy flavour notes (Despreaux, 1998; Luna et al., 2002; Counet et al., 2004). These differences in flavour can be ascribed to bean composition variation from botanical origin, location of growth and farming conditions. Bulk varieties dominate blends, while fine grades, used in lesser quantities, are selected to make specific contributions to overall flavour profile.

Each bean variety has a unique potential flavour character. But growing conditions such as climate, amount and time of sunshine and rainfall, soil conditions, ripening, time of harvesting, and time between harvesting and bean fermentation – all contribute to variations in final flavour formation. Table 2.2 summarises how differences in genetic origin, cocoa variety and duration of fermentation influence flavour profile but different conditions may lead to significant differences in flavour from a single cocoa variety. A good example is

<table>
<thead>
<tr>
<th>Origin</th>
<th>Cocoa type</th>
<th>Duration (days)</th>
<th>Special flavour character</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ecuador</td>
<td>Nacional (Arriba)</td>
<td>Short 2</td>
<td>Aromatic, floral, spicy, green</td>
</tr>
<tr>
<td>Ecuador</td>
<td>Criollo (CCN51)</td>
<td>2</td>
<td>Acidic, harsh, low cocoa</td>
</tr>
<tr>
<td>Sri Lanka</td>
<td>Trinitario</td>
<td>1.5</td>
<td>Floral, fruity, acidic</td>
</tr>
<tr>
<td>Venezuela</td>
<td>Trinitario</td>
<td>2</td>
<td>Low cocoa, acidic</td>
</tr>
<tr>
<td>Venezuela</td>
<td>Criollo</td>
<td>2</td>
<td>Fruity, nutty</td>
</tr>
<tr>
<td>Zanzibar</td>
<td>Criollo</td>
<td>Medium 6</td>
<td>Floral, fruity</td>
</tr>
<tr>
<td>Venezuela</td>
<td>Forastero</td>
<td>5</td>
<td>Fruity, raisin, caramel</td>
</tr>
<tr>
<td>Ghana</td>
<td>Forastero</td>
<td>5</td>
<td>Strong basic cocoa, fruity notes</td>
</tr>
<tr>
<td>Malaysia</td>
<td>Forastero/Trinitario</td>
<td>6</td>
<td>Acidic, phenolic</td>
</tr>
<tr>
<td>Trinidad</td>
<td>Trinitario</td>
<td>Long 7–8</td>
<td>Winy, raisin, molasses</td>
</tr>
<tr>
<td>Grenada</td>
<td>Trinitario</td>
<td>8–10</td>
<td>Acidic, fruity, molasses</td>
</tr>
<tr>
<td>Congo</td>
<td>Criollo/Forastero</td>
<td>7–10</td>
<td>Acidic, strong cocoa</td>
</tr>
<tr>
<td>Papua New Guinea</td>
<td>Trinitario</td>
<td>7–8</td>
<td>Fruity, acidic</td>
</tr>
</tbody>
</table>

Source: Afoakwa et al. (2008a).
the difference in flavour profile between a single Forastero variety produced originally in Ghana and now grown in Malaysia (Clapperton, 1994), arising possibly through geographic, climatic conditions and duration and/or method of fermentation.

Bulk cocoas typically show strong flavour characters, and fine cocoas are perceived as aromatic or smoother (Kattenberg & Kemming, 1993; Jinap et al., 1995; Luna et al., 2002). Clapperton et al. (1994) noted consistent differences in flavour attribute, specifically overall cocoa flavour intensity, acidity, sourness, bitterness and astringency. Bean origins include the West African Amelonado variety (AML), four Upper Amazon clones – Iquitos Mixed Calabacillo 67 (IMC67), Nanay 33 (NA33), Parinari 7 (PA7) and Scavina 12 (SCA12) – and Unidentified Trinatario (UIT1) grown in Sabah, Malaysia. Flavour characters in UIT1 differed from West African Amelonado, characterised by intense bitterness and astringency associated with caffeine and polyphenol contents. Fermented beans from Southeast Asia and the South Pacific are characterised by a higher acidity (more lactic and acetic acids) than West African beans (Clapperton et al., 1994) due to varietal differences, box fermentation and rapid artificial drying.

Cocoa liquors differ in sensory character. The West African groups (Ghana, Ivory Coast and Nigeria) are generally considered sources of standard (benchmark) cocoa flavour with a balanced but pronounced cocoa character, with subtle to moderate nutty undertones. Cameroonian liquors are renowned for bitterness and those from Ecuador for floral-spicy notes. American and West Indian varieties range from aromatic and winy notes from Trinidad cocoa to the floral or raisin-fruity notes of Ecuadorian stocks, making unique contributions to blends. Asian and Oceanian beans exhibit a range of flavour profiles ranging from subtle cocoa and nutty/sweet notes in Java beans to the intense acid and phenolic notes of Malaysian (De La Cruz et al., 1995). Counet et al. (2004) reported that fine varieties with short fermentation processes had high contents of procyanidins, while Trinitario from New Guinea and Forastero beans were specifically higher in total aroma. Aroma compounds formed during roasting were found to vary quantitatively directly with fermentation time and inversely with procyanidin content of cocoa liquors.

High concentrations of phenol, guaiacol, 2-phenylbutenal and \( \gamma \)-butyrolactone characterise Bahia beans known for typical smoked notes. Also reported are higher contents of 2-methylpropanal and 3-methylbutanal in Caracas (Venezuela) and dried, fermented Trinidad beans (Dimick & Hoskin, 1999). Of Maillard products, Reineccius (2006) reported that roasting yields higher levels of pyrazines in well-fermented beans (Ghana, Bahia) than in less-fermented (Arriba) or unfermented from Sanchez (Dominican Republic) or Tabasco (Mexico). Lower in astringency and bitterness imparted by polyphenols, Criollo beans, in which anthocyanins are absent, is often less fermented than Forastero (Carr et al., 1979; Clapperton, 1994; Clapperton et al., 1994; Luna et al., 2002).
in Figures 2.11 and 2.12. On the first day, the adhering pulp liquefies and drains off, with steady rises in temperature. Under anaerobic conditions, micro-organisms produce acetic acid and ethanol that inhibit germination and contribute to structural changes such as removal of the compartmentalisation of enzymes and substrates, with movements of cytoplasmic components through the cocoa cotyledon generally between 24 and 48 hours of bean fermentation. By the third day, the bean mass will have heated typically around 45°C, remaining at 45–50°C until fermentation is complete (Lehrian & Patterson, 1983; Schwan et al., 1995; Fowler, 1999; Kealey et al., 2001).

Mucilaginous pulp of beans undergoes ethanoic, acetic and lactic fermentations with consequent acid and heat stopping germination, with notable swelling and key changes in cell membranes facilitating enzyme and substrate movements. Differences in pH, titratable
acidity, acetic and lactic acid concentrations, fermentation index and cut test scores for cocoa beans from different origins are reported (Jinap & Dimick, 1990; Luna et al., 2002; Misnawi et al., 2003). Chemistry of cocoa beans fermentation has been reviewed (Ziegleder, 1990; Lopez & Dimick, 1991; Buyukpamukcu et al., 2001; Luna et al., 2002; Misnawi et al., 2003; Schwan & Wheals, 2004; Kyi et al., 2005).

During fermentation, the rate of diffusion of organic acids into the cotyledons, timing of initial entry, duration of the optimum pH and final pH are crucial for optimum flavour formation (Biehl & Voigt, 1999). Beans of higher pH (5.5–5.8) are considered unfermented – with low fermentation index and cut test score – and those of lower pH (4.75–5.19), well fermented. Fermentation techniques can reduce acid notes and maximise chocolate flavours (Lopez, 1979; Holm et al., 1993; Beckett, 1999; Whitefield, 2005). Ziegleder (1991) compared natural acid (pH 5.5–6.5) and alkaline (pH 8.0) cocoa extracts obtained by direct extraction – the former possessed a more intense and chocolate aroma than the latter, attributed to high contents of aromatic acids and sugar degradation products with persistent sweet aromatic and caramel notes. Cocoa beans of lower (4.75–5.19) and higher pH (5.50–5.80) were scored lower for chocolate flavour and higher for off-flavour notes, respectively, and chocolate from intermediate pH (5.20–5.49) beans was scored more highly for chocolate flavour (Jinap et al., 1995).

Sucrose and proteinaceous constituents are partially hydrolysed, phenolic compounds are oxidised and glucose is converted into alcohols, oxidised to acetic and lactic acids during fermentation. Beans subsequently undergo an anaerobic hydrolytic phase, followed by aerobic condensation. Timing, sequence of events and degree of hydrolysis and oxidation vary between fermentations. Concentration of flavour precursors is dependent on enzymatic mechanisms. Colour changes also occur with hydrolysis of phenolic components by glycosidases accompanied by bleaching, influencing final flavour character (Lopez & Quesnel, 1973; Biehl et al., 1990; Lopez & Dimick, 1991, 1995).

Nitrogenous flavour precursors formed during anaerobic phases are dominated by the amino acids and peptides available for non-oxidative carbonyl–amino condensation reactions promoted in elevated temperature phases such as fermentation, drying, roasting and grinding. Although degraded to flavour precursors, residual protein is also diminished by phenol–protein interactions. During aerobic phases, oxygen-mediated reactions occur, such as oxidation of protein–polyphenol complexes formed anaerobically. Such processes reduce astringency and bitterness: oxidised polyphenols influence subsequent degradation reactions (Rohan, 1964; Dimick & Hoskin, 1999; Counet et al., 2004; Kyi et al., 2005).

Fermentation method determines the final quality of products produced, especially flavour. Previous studies on post-harvest pod storage and bean spreading had shown marked improvement in chocolate flavour and reductions in sourness, bitterness and astringency (Meyer et al., 1989; Biehl et al., 1990). In commercial production, similar effects were obtained through combinations of pod storage, pressing and air blasting (Said et al., 1990). Variations in such factors as pod storage and duration affect the pH, titratable acidity and temperature achieved during fermentation, influencing enzyme activities and flavour development (Biehl et al., 1990).

Important flavour-active components produced during fermentation include ethyl-2-methylbutanoate, tetramethylpyrazine and certain pyrazines. Bitter notes are evoked by theobromine and caffeine, together with diketopiperazines formed from roasting through thermal decompositions of proteins. Other flavour precursor compounds derived from amino acids released during fermentations include 3-methylbutanal, phenylacetaldehyde, 2-methyl-3-(methyldithio)furan, 2-ethyl-3,5-dimethyl- and 2,3-diethyl-5-methylpyrazine (Taylor, 2002).
Immature and unfermented beans develop little *chocolate* flavour when roasted, and excessive fermentation yields unwanted *hammy* and *putrid* flavours (Fowler, 1999; Beckett, 2000; Zaibunnisa *et al.*., 2000; Reineccius, 2006).

### 2.5.2 Drying

Flavour development from cocoa beans precursors continues during drying with development of characteristic brown colour. After fermentation, the beans are removed from the heaps or boxes and dried in the sun on raised platforms covered with mats (Figs 2.13 and 2.14) or on the ground (Fig. 2.15) until fully dried within 7–8 sunny days. During the process, major polyphenol oxidising reactions are catalysed by polyphenol oxidases, giving rise to new flavour components, and loss of membrane integrity, inducing brown colour formation. Use of artificial drying can increase cotyledon temperatures, causing case hardening. Dimick and

![Fig. 2.13](image1.jpg) **Fig. 2.13**  Farmers drying cocoa on raised platforms.

![Fig. 2.14](image2.jpg) **Fig. 2.14**  Drying of cocoa beans on raised platforms.
Hoskin (1999) reported that case hardening restricts loss of volatile acids, with detrimental effects on final chocolate flavour.

After fermentation and drying, the target for cocoa beans is approximately 6–8% moisture contents. For storage and transport, moisture contents should be less than 8% or mould growth is possible (Carr et al., 1979; Fowler et al., 1998; Kealey et al., 2001; Awua, 2002). Indicators of well-dried, quality beans are good brown colour and low astringency and bitterness and an absence of off-flavours such as smoky notes and excessive acidity. Sensory assessment of cocoa beans dried using different strategies, i.e. sun drying, air blowing, shade drying and oven drying, suggested sun-dried beans (Figs 2.16 and 2.17) were rated higher in chocolate development with fewer off-notes (Dias & Avila, 1993; Buyukpamukcu et al., 2001; Amoye, 2006; Granvogl et al., 2006). Table 2.3 summarises key odourants in cocoa mass following fermentation and drying stages.
Fig. 2.17  Dried cocoa beans.

Table 2.3  Dominant odour-active volatiles in cocoa mass

<table>
<thead>
<tr>
<th>Compound</th>
<th>Odour quality</th>
<th>Flavour dilution factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>2- and 3-methylbutanoic acid(^b)</td>
<td>Sweaty</td>
<td>2048</td>
</tr>
<tr>
<td>3-Methylbutanal(^{a,b})</td>
<td>Malty</td>
<td>1024</td>
</tr>
<tr>
<td>Ethyl 2-methylbutanoate(^{a,b})</td>
<td>Fruity</td>
<td>1024</td>
</tr>
<tr>
<td>Hexan(^{a,b})</td>
<td>Green</td>
<td>512</td>
</tr>
<tr>
<td>Unknown(^a)</td>
<td>Fruity, waxy</td>
<td>512</td>
</tr>
<tr>
<td>2-Methoxy-3-isopropanoylamine(^{a,b})</td>
<td>Peasy, earthy</td>
<td>512</td>
</tr>
<tr>
<td>(E)-2-octanal(^{a,b})</td>
<td>Fatty, waxy</td>
<td>512</td>
</tr>
<tr>
<td>Unknown(^a)</td>
<td>Tallowy</td>
<td>512</td>
</tr>
<tr>
<td>2-Methyl-3-(methylthio)furan(^{a,b})</td>
<td>Cooked meat-like</td>
<td>512</td>
</tr>
<tr>
<td>2-Ethyl-3,5-dimethylpyrazine(^{a,b})</td>
<td>Earthy, roasty</td>
<td>256</td>
</tr>
<tr>
<td>2,3-Diethyl-5-methylpyrazine(^a)</td>
<td>Earthy, roasty</td>
<td>256</td>
</tr>
<tr>
<td>(E)-2-nonenal(^{a,b})</td>
<td>Tallowy, green</td>
<td>256</td>
</tr>
<tr>
<td>Unknown(^{a,b})</td>
<td>Pungent, grassy</td>
<td>128</td>
</tr>
<tr>
<td>Unknown(^{a,b})</td>
<td>Sweet, waxy</td>
<td>128</td>
</tr>
<tr>
<td>Phenylacetaldehyde(^{a,b})</td>
<td>Honey-like</td>
<td>64</td>
</tr>
<tr>
<td>(Z)-4-heptenal(^{a,b})</td>
<td>Biscuit-like</td>
<td>64</td>
</tr>
<tr>
<td>β-Octenolactone(^{a,b})</td>
<td>Sweet, coconut-like</td>
<td>64</td>
</tr>
<tr>
<td>γ-Decalactone(^b)</td>
<td>Sweet, peach-like</td>
<td>64</td>
</tr>
</tbody>
</table>

Sources: \(^a\)Belitz and Grosch (1999); \(^b\)Schuermmann and Schieberle (1997).
Frauendorfer and Schieberle (2006) identified similar flavour compounds in cocoa powder using molecular sensory correlations. Off-notes from incomplete drying or rain soaking may result in high levels of water activity and mould contamination, producing high concentrations of strongly flavoured carbonyls, leading to alterations in bean flavour, producing hammy off-flavours, which is also correlated with overfermentation (Dimick & Hoskin, 1999; Misnawi et al., 2003).

### 2.6 CONCLUSION

Chocolate flavour resides not only in a volatile aromatic fraction of flavour-active components but also in non-volatile compounds influencing taste perception. Its complex composition depends on the cocoa bean genotype, specifically on contents of bean storage proteins, polysaccharides and polyphenols. The inheritance and regulation of such flavour origins remain an area for advanced research. Enzymic and microbial fermentations after harvest induce physical and chemical changes in beans over 5–7 days with key browning reactions of polyphenol with proteins (∼12–15% total) and peptides, giving colours characteristic of cocoa. Drying limits mould growth during transportation and storage, reducing bean...
moisture content from 60 to 8%. Sun drying is favoured for flavour development and can be carried out above or on hard surfaces, with differences in airflow and final moisture content. Beans are transported under controlled storage conditions to chocolate manufacturing sites, or processed in the origin country to add value with requirements for traceability in quality assurance. Following critical review of the entire process, a summary of the parameters important for chocolate flavour generation has been developed (Fig. 2.18). An appropriate starting composition can be converted through controlled post-harvest treatments and subsequent processing technologies to a high-quality flavour character. Cocoa bean fermentation is crucial to not only the formation of key volatile fractions (alcohols, esters and fatty acids) but also provision of flavour precursors (amino acids and reducing sugars) for important notes contributing to chocolate characters. Drying reduces levels of acidity and astringency in cocoa nibs by decreasing the volatile acids and total polyphenols.
3 Industrial chocolate manufacture – processes and factors influencing quality

3.1 INTRODUCTION

Chocolates are semisolid suspensions of fine solid particles from sugar and cocoa (and milk, depending on type), making about 70% in total, in a continuous fat phase. Cocoa solids are derived from beans obtained from the fruit of *Theobroma cacao*, with world production dominated by Forastero types, made up of small, flattish and purple beans. Another type, Criollo, is presently rare in production; Trinitario, a disease-resistant hybrid of Criollo and Forastero, regarded as a flavour bean (Awua, 2002), is about 5% of world production. Growth of Forastero, in the trade name basic or bulk cocoa, occurs mainly in West Africa and Brazil. Criollo (flavour cocoa) is largely grown in Central and South America. West Africa now produces approximately 70% of world cocoa (ICCO, 2008). New demand for Fairtrade and premium products has stimulated improvements in quality assurance that make possible single variety and origin chocolates.

Primary chocolate categories are dark, milk and white that differ in content of cocoa solid, milk fat and cocoa butter. The outcome is varying proportions of carbohydrate, fat and protein (Table 3.1). Chocolate manufacturing processes (Beckett, 2000; Awua, 2002; Whitefield, 2005) differ due to variation in national consumer preferences and company practices.

Central to chocolate character is continuous phase lipid composition, which influences mouthfeel and melting properties. Chocolate triglycerides are dominated by saturated stearic (34%) and palmitic (27%) fatty acids and monounsaturated oleic acid (34%). Chocolates are solid at ambient (20–25°C) and melt at oral temperature (37°C) during consumption, giving a smooth suspension of particulate solids in cocoa butter and milk fat (Beckett, 1999; Whitefield, 2005). This constrains lipid composition. The oral epithelia are also sensitive to gradations of smoothness, which selects for desirable lipid crystal forms.

Despite high lipid and sugar contents, chocolate consumption makes a positive contribution to human nutrition through provision of antioxidants, principally polyphenols including flavonoids such as epicatechin, catechin and notably the procyanidins. White chocolates differ from milk and dark through the absence of cocoa nibs containing antioxidants, reducing the product’s shelf-life (Beckett, 2000; Whitefield, 2005). Chocolates also contain minerals, specifically potassium, magnesium, copper and iron (Holland et al., 1991). Differences in the sensory characters of chocolate can be attributed to use of different cocoa types, variations in ingredient proportions, use of milk crumb instead of milk powder, blending techniques and processing methods. Specifications depend on type of chocolate and its intended use (Jackson, 1999).

As chocolates melt in the mouth, the continuous fat phase inverts into the oral continuous aqueous phase mixing with saliva that dissolves the sugar particles. Lipids and cocoa solids coat oral epithelial surfaces. Oral particle dissolution influences perception of coarseness
Table 3.1 Dark, milk and white chocolate: major constituents

<table>
<thead>
<tr>
<th>Product</th>
<th>Carbohydrate (%)</th>
<th>Fat (%)</th>
<th>Protein (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dark chocolate</td>
<td>63.5</td>
<td>28.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Milk chocolate</td>
<td>56.9</td>
<td>30.7</td>
<td>7.7</td>
</tr>
<tr>
<td>White chocolate</td>
<td>58.3</td>
<td>30.9</td>
<td>8.0</td>
</tr>
</tbody>
</table>

Source: Afoakwa et al. (2007a).

and solvation at rates corresponding to size and work input such as mastication, tongue compression and swallowing (Lee & Pangborn, 1986). Particle size distribution and ingredient composition therefore influence perception of primary taste (gustation) and oral volatiles release with retronasal flavour characters in magnitude and temporal profile.

Rheological properties of chocolate are important in manufacturing process for obtaining high-quality products with well-defined texture (Servais et al., 2004). Chocolates with high viscosity have a pasty mouthfeel, persisting in the mouth (Beckett, 2000). Viscosity relates to composition, processing strategy and particle size distribution. Apparent viscosity in aqueous solutions influences flavour ‘by mouth’ and taste intensity during consumption (Denker et al., 2006), thus rheological measurements often give information related to sensory character of chocolate.

This chapter assesses current information relating to cocoa processing technology and techniques, bean roasting strategies and their effects on chocolate quality and chocolate manufacturing operations. Factors influencing finished product quality such as particle size distribution and ingredient composition have also been discussed in relation to their effects on the rheological, textural and sensory qualities in chocolates.

### 3.2 COCOA PROCESSING AND TECHNOLOGY

#### 3.2.1 Bean selection and quality criteria

Chocolate manufacturers must follow a set of guidelines and quality criteria if they are to produce products that maintain the consumers’ loyalty to their products. Before processing, the quality of beans is evaluated using two different methods. With the first technique, the beans are assessed for the following indicators:

1. Degree of fermentation
2. Moisture content (maximum 6%)
3. Number of defects
4. Number of broken beans
5. Bean count (number per 100 g)
6. Degree of mouldiness
7. Flavour profile
8. Colour
9. Fat content (minimum 52%)
10. Fat quality relating to percentage of free fatty acids (as oleic acid)
11. Shell content (10–12%)
12. Uniformity of bean size
13. Insect and rodent infestation
The second technique is evaluated based on the size of the beans using either bean count (number of beans per 100 g) or the weight in grams of 100 beans. On the international cocoa market, different bean sizes attract different prices. Beans with smaller sizes usually contain proportionately lower amount of nibs, higher shell content, lower fat content and attract lesser prices. Typically, beans from Asian origin have higher shell content than beans from West Africa.

The bean cut test is used to assess defects and the degree of fermentation. In this process, a sample of 300 beans are randomly selected and split open longitudinally. The cut surfaces are then examined and assessed based on the following criteria:

1. Flat and shrunken beans
2. Mouldy beans
3. Slaty beans
4. Germinated beans
5. Degree of insect and rodent infestation

All these factors affect the flavour and taste of the finished products, for which the beans would be used. Good cocoa beans should be well fermented, dry and free from insect and rodent infestation, abnormal odours and contaminations/adulterations.

Another key criterion is the flavour quality. In this regard, considerations must be given to the desired quality of the finished chocolate and/or products upon which or in which the chocolate would be used. For instance, harsh cocoa and bitter notes are required to contrast a very sweet or heavily flavoured centre, using delicately flavoured beans such as Java beans (Urbanski, 1992). It is important to note that just because a bean comes from a flavour grade stock does not mean it will automatically improve a product’s profile. The overall impact a particular stock has on its inclusion upon the blend has to be carefully assessed. Also noteworthy is the fact that while beans are characteristically typed, flavour quality may vary from year to year, crop to crop, etc., and therefore requires a continuous assessment of availability of the beans before using them in recipe formulations (Urbanski, 1992; Fowler, 1999).

The following are five examples of the varied selection of bean blends in assorted products types and explanations of the reasoning involved in their selections. For the industrial production of:

1. Milk chocolate: The use of predominantly medium roast West African beans with Ecuadorian beans is advised. This blend would deliver a good clean cocoa note with nutty and slightly fruity undertones. It is important to note that the addition of the highly acidic Brazilian and Malaysian beans would negatively contrast with the milky notes desired.
2. Light milk chocolate: This product could be made from lightly roasted Java beans that are known for their light colour and very mild overall flavour with distinctive nutty overtones. This would help attain a good standard of identity for milk chocolate, as the coating would be several shades lighter than a 100% West African bean. It could be best used to complement very delicately flavoured centres.
3. High-quality semisweet chocolate: The use of predominantly West African stock is advised for its cocoa character and slightly nutty undertones (light to medium roast) to heighten desirable notes and limit burnt/bitter notes. This blend when complemented by Caracas and Trinidad beans would contribute floral and slightly spicy notes to create a balanced yet unique profile.
4. **Harsh bittersweet chocolate:** This product is mainly designed for use on very sweet and highly flavoured cream centres as it produces very harsh and bitter coatings. If eaten alone, this coating may be harsh enough to be objectionable to many consumers. However, in a finished piece as described, it complements and balances the product’s flavour. Delicate flavour grades would be wasted in such a product as they would be overridden fully by the bitterness, astringency and acidity of the blend.

5. **Semisweet cookie drop:** The use of the dominant West African beans is advised in this product to provide a good cocoa impact. The strong profiles of the Brazilian and Sanchez components complement and contrast the West African component. In this application, a robust flavour is desirable for contrast in the baked cookies (Minifie, 1989; Urbanski, 1992).

### 3.2.2 Cleaning, breaking and winnowing

Before processing, cocoa beans are passed through the processes of cleaning, breaking and winnowing to obtain nibs of consistent quality. These processes also ensure that the nibs are cleaned (free from dirt and infestation), well broken and properly deshelled. The kernels (nibs) obtained after the process must be of uniform size to achieve constant quality. The process involves, first, sieving the beans and removing all extraneous materials such as stones, strings, coins, wood pieces, soil particles and nails. The cleaned beans are then broken to loosen the shells from the nibs using multiple steps to avoid an excess of fine particles. The products obtained are then sieved into smaller number of fractions to obtain optimal separation during subsequent winnowing. The fractions are then transported to the winnowing cabinet where the lighter broken shells are removed by a stream of air. The breaking and winnowing steps are vital in separating the essential components of the bean, the nibs from the shells, and the shells are then discarded and sold for use as agricultural mulch or as fertilisers. Strong magnets are then used to remove magnetic foreign materials from the nibs, which are then stored, awaiting further processing.

### 3.2.3 Sterilisation

Sterilisation is the technique of exposing the cocoa beans or nibs to sufficiently higher temperatures for a sufficiently long times to destroy all micro-organisms in the beans. Depending on the factory and equipment used, this process can either be done before or after the roasting process. The treatment can be done in a batch or continuous process by wetting or heating with steam, all micro-organisms that might have contaminated the nibs during the post-harvest processes of fermentation, drying, bagging and transportation. The process ensures that the Total Plate Count (TPC) is reduced to less than 500 per gram, and all pathogenic bacteria are destroyed. After sterilisation, the nibs can then be roasted directly (natural process) or can be alkalised first by the Dutch process before roasting. In situations where sterilisation is done after roasting, the heat treatment is used to ensure total destruction of heat-resistant bacteria and spores that might have survived the high temperatures of the roasting process. The procedure is to inject, over a period of about 20 seconds, a fine water spray of steam into the roasting drum at the end of the roasting period (Awua, 2002). This guarantees a considerable reduction in microbial count in the roasted nibs.
3.2.4 Alkalisation

The technique of alkalisation was first introduced by a Dutchman known as van Houten in 1928 and therefore named it as the Dutch process. All cocoa, beans, nibs or liquor that is so treated is described as ‘alkalised’ or ‘Dutched’ (ADM Cocoa, 2006). This consists of treating the cocoa nibs with an alkali solution such as potassium or sodium carbonate. The alkali is used to raise the pH of the beans or nibs from 5.2 to 5.6 to near neutrality at 6.8–7.5, depending on the alkali used, and the purposes are primarily to modify the colour and flavour of cocoa powder or cocoa liquor, and also improve dispersibility or suspension of the cocoa solids in water. During the process, the alkali solution is sprayed into the drum after it has been charged with the nibs, which is then slowly dried at a temperature below 100°C (212°F) (Awua, 2002). The chemistry on effects of alkalisation on colour and flavour formation of cocoa and chocolates have been described in Chapter 4.

3.2.5 Roasting

Cocoa beans are roasted to develop further the original cocoa flavour that exists in the form of precursors generated during the processes of fermentation and drying of the beans. During roasting of the dried fermented beans, several physical and chemical changes take place, which include the following:

1. Loosening of the shells.
2. Moisture loss from the beans to about 2% final content.
3. The nibs (cotyledons) become more friable and generally darken in colour.
4. Additional reduction in the number of micro-organisms present in the beans. This helps attain food-grade products, such as cocoa butter, cocoa powder and cocoa liquor, which have stringent microbiological specifications.
5. Degradation of amino acids takes place and proteins are partly denatured. The natural reducing sugars are almost destroyed during degradation of amino acids.
6. Losses of volatile acids and other substances that contribute to acidity and bitterness. A large number of compounds have been detected in the volatile compounds including aldehydes, ketones, pyrazines, alcohols and esters. The substances that undergo only minimal changes are the fats, polyphenols and alkaloids (Minifie, 1989).

Awua (2002) explained that the degree of changes is related to the time and temperature of roasting and the rate of moisture loss during the process. The roasting temperature varies between 90 and 170°C depending on the type of roasting adopted, being dry or moist roasting.

Three main methods of roasting are employed within the cocoa processing industry and these include the following:

1. Whole bean roasting
2. Nib roasting
3. Liquor roasting

Whole bean roasting is usually the traditional way of producing cocoa liquor. By this process, the beans are roasted first before winnowing to facilitate removal of the shells which are broken by high-speed impact against metal plates. During the process, the heat causes some of the fat to migrate into the shells, thus resulting in a loss of some cocoa butter. This is
particularly important in the case of broken or crushed beans. Nib roasting is done by first removing the shells before roasting, and by this many of the limitations of whole bean roasting are overcome. This also makes it possible to treat the nibs with alkaline or sugar solution during roasting to help improve flavour development in certain types of cocoa. In liquor roasting, thermal pre-treatment is often used before winnowing for liquor roasting. The nib is then ground to liquor before roasting. The major disadvantage of both nib and liquor roasting is that the shell must be removed before it has been loosened from the nib by heating, and this may result in poor separation, especially with some type of cocoa. As a result, a variety of machines have been developed to thermally pre-treat the beans. These develop a high surface temperature and evaporate the internal moisture, which in turn builds up a pressure within the bean, causing the shell to come away from the nib.

3.2.6 Nib grinding and liquor treatment

Nib grinding involves milling of cocoa nibs to form cocoa liquor. The purpose is to produce as low a viscosity as possible to obtain smooth cocoa powder and chocolate taste during subsequent use of the liquor. The nib has a cellular structure containing about 55% cocoa butter in solid form locked within the cells. Grinding of nib cells releases the cocoa butter into liquor with particle size up to 30 μm, and for production of cocoa powder, fine grinding is particularly important. The viscosity of the liquor is related to the degree of roasting preceding the grinding and to moisture content of the nib.

Many machines are used for reducing the nibs into liquor, and these include stone mills, disc mills, pin or hammer mills and bead or ball mills. The grinding is done in a multistage process, and the heat treatment generated during the grinding process causes the cocoa butter in the nib to melt, forming the cocoa liquor. The refined cocoa liquor is heated in storage tanks at a temperature of about 90–100°C for aging and microbial destruction, after which the liquor is packaged for sale (Awua, 2002). Typically approximately 78–90% of cocoa butter is collected by pressing; residual lipids may be removed by supercritical fluid extraction (Beckett, 2000).

3.2.7 Liquor pressing

Cocoa butter constitutes about half the weight of the cocoa nib. This fat is partially removed from the cocoa liquor by means of hydraulic presses applying pressures as high as 520 kg/cm², and the larger presses take a charge of up to 113.4 kg per pressing cycle. Depending on the pressing time and the settings of the press, the resulting cake may have a fat content of between 10 and 24%. Two kinds of cocoa cake can be obtained by the process:

1. High-fat cake containing between 22 and 24% residual fat in the pressed cake
2. Low-fat cake containing between 10 and 12% residual fat in the pressed cake

The cocoa butter extracted is discharged into receptacles from which it is pumped into an intermediate tank for further processing.

3.2.8 Cake grinding (kibbling)

After pressing, the cakes released are quite big to handle and are therefore passed through kibbling machines to be broken down into smaller pieces, known as kibbled cake. The kibbled
cake obtained is stored by fat content and degree of alkalisation, and may be blended before
pulverisation to obtain the desired type of cocoa powder.

3.2.9 Cocoa powder production

The powder grinding lines usually comprise hammer-and-disc or pin mills, which pulverise
cocoa cake particles into the defined level of fineness of cocoa powder. The powder is then
cooled after pulverisation so that the fat of the cocoa powder crystallises into its stable form.
This prevents any discolouration (fat bloom) and the formation of lumps in the bags after
packing, a phenomenon that is caused by insufficient crystallisation of the fat at the moment
of filling (ADM Cocoa, 2006). The free flowing powder is then passed through sieves and
over magnets prior to packing in bulk containers or four-ply multiwall paper bags lined with
polyethylene.

3.3 CHOCOLATE MANUFACTURING PROCESSES

Chocolate manufacturing processes generally share common features (Fig. 3.1) such as:

1. Mixing
2. Refining
3. Conching of chocolate paste
4. Tempering and depositing
5. Moulding and demoulding

The outcome sought is smooth textures of products considered desirable in modern confectionery and elimination of oral perceptions of grittiness.

3.3.1 Mixing

Mixing of ingredients during chocolate manufacture is a fundamental operation employed
using time–temperature combinations in a continuous or batch mixers to obtain constant
formulation consistency. In batch mixing, chocolate containing cocoa liquor, sugar, cocoa
butter, milk fat and milk powder (depending on product category) is thoroughly mixed
normally for 12–15 minutes at 40–50°C. Continuous mixing is usually used by large chocolate
manufacturers such as Nestlé and Cadbury using well-known automated kneaders, producing
somewhat tough texture and plastic consistency (Minifie, 1989; Beckett, 2000; Awua, 2002).

3.3.2 Refining

Refining of chocolate is important to the production of smooth texture that is desirable in modern chocolate confectionery. Mixtures of sugar and cocoa liquor (and milk solids depending on the type of chocolate) at an overall fat content of 8–24% are refined to
particle size of less than 30 µm normally using a combination of two- and five-roll refiners
(Beckett, 1999, 2000). Final particle size critically influences the rheological and sensory
properties. A five-roll refiner (Fig. 3.2) consists of a vertical array of four hollow cylinders,
temperature controlled by internal water flow, held together by hydraulic pressure. A thin film of chocolate is attracted to increasingly faster rollers, travelling up the refiner until removed by a knife blade. Roller shearing fragments solid particles, coating new surfaces with lipid so that these become active, absorbing volatile flavour compounds from cocoa components.

Texture in milk chocolate appears improved by a bimodal distribution of particles with a small proportion having sizes up to 65 µm. Optimum particle size for dark chocolate is lower at less than 35 µm although values are influenced by the product and composition (Awua, 2002). Refiners, in summary, not only affect particle size reduction and agglomerate breakdown, but distribute particles through the continuous phase coating each with lipid.
Fig. 3.2 A typical five-roll refiner.

3.3.3 Conching

Conching is regarded as the endpoint or final operation in the manufacture of bulk chocolate, whether milk or dark. It is an essential process that contributes to development of viscosity, final texture and flavour. Conching is normally carried out by agitating chocolate at more than 50°C for few hours (Beckett, 2000). In the early stages, moisture is reduced with removal of certain undesirable flavour-active volatiles such as acetic acid, and subsequently interactions between disperse and continuous phase are promoted.

In addition to moisture and volatile acid removal, the conching processing promotes flavour development due to the prolonged mixing at elevated temperatures, giving a partly caramelised flavour in non-milk crumb chocolate. The process also aids reduction in viscosity of refiner pastes throughout the process, and reduction in particle size and removal of particle edges (Minifie, 1989; Beckett, 2000; Awua, 2002).

The name of the equipment, the conche, is derived from the Latin word ‘shell’, as the traditional conche used in chocolate manufacture resembled the shape of a shell. Figure 3.3 is an illustration of a Frisse conche. The Frisse conche is a typical example of an overhead conche used in modern chocolate industry. It consists of a large tank with three powerful intermeshing mixer blades, providing shearing and mixing action. The internal mechanics of Frisse conche is as shown in Figure 3.3. Conching times and temperatures vary (Awua, 2002) typically: for milk crumb 10–16 hours at 49–52°C, with milk powder products 16–24 hours at up to 60°C, and with dark chocolates at 70°C and continue up to 82°C. Replacing full-fat milk powder with skimmed milk powder and butter fat, temperatures up to 70°C may be used (Awua, 2002). To give chocolate a suitable viscosity, additional cocoa butter and lecithin can be added towards the end of conching to thin or liquefy the chocolate prior to tempering (Beckett, 2000; Whitefield, 2005).
Fig. 3.3 Illustration of internal mechanics of the Frisse conche.

Table 3.2 Melting point and chain packing of the polymorphic forms of cocoa butter

<table>
<thead>
<tr>
<th>Polymorphic forms of cocoa butter</th>
<th>Melting point (°C)</th>
<th>Chain packing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Form I ( \beta' )</td>
<td>16–18</td>
<td>Double</td>
</tr>
<tr>
<td>Form II ( \alpha )</td>
<td>21–22</td>
<td>Double</td>
</tr>
<tr>
<td>Form III Mixed</td>
<td>25.5</td>
<td>Double</td>
</tr>
<tr>
<td>Form IV ( \beta_1 )</td>
<td>27–29</td>
<td>Double</td>
</tr>
<tr>
<td>Form V ( \beta_2 )</td>
<td>32–34</td>
<td>Triple</td>
</tr>
<tr>
<td>Form VI ( \beta'_1 )</td>
<td>34–36</td>
<td>Triple</td>
</tr>
</tbody>
</table>

Sources: Talbot (1999) and Afoakwa et al. (2007a).

### 3.4 TEMPERING, LIPID CRYSTALLISATION AND CONTINUOUS PHASE CHARACTER DURING CHOCOLATE MANUFACTURE

Cocoa butter can crystallise in a number of polymorphic forms as a function of triglyceride composition, with fatty acid composition influencing how liquid fat solidifies (Awua, 2002). Cocoa butter has six polymorphic forms (I–VI), the principals being \( \alpha \), \( \beta \) and \( \beta' \) (Table 3.2). Form V, a \( \beta \) polymorph, is the most desirable form (in general) in well-tempered chocolate, giving a glossy appearance, good snap, contraction and resistance to bloom (Beckett, 2000).

If chocolate is poorly tempered, the outcome is the \( \beta \) Form IV, which rapidly transforms into Form V. This influences colour as reflected light is disoriented by unstable, disorganised crystal growth (Hartel, 2001). Untempered chocolate is soft and not effectively demoulded. In cocoa butter Forms V and VI are the most stable forms. Form VI is difficult to generate although formed on lengthy storage of tempered chocolate accompanied by fat bloom. In addition, Form VI has a high melting temperature (36°C) and crystals that are large and gritty on the tongue. The unstable Form I has a melting point of 17°C and is rapidly converted into Form II that transforms more slowly into III and IV (Fig. 3.4). Polymorphic triglyceride forms differ in distance between fatty acid chains, angle of tilt relative to plane of chain-end methyl group and manner in which triglycerides pack in crystallisation (Talbot, 1999).

Polymorphic form is determined by processing conditions. Fatty acids crystallise in a double- or triple-chain form depending on triglyceride composition and positional
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Loose compacting

Dense compacting

Stable form

Unstable form

Fig. 3.4 Temperature regimes and degree of stability in six polymorphic forms of cocoa butter (Beckett, 2008).

distribution. Form IV crystallises in a double-chain form, Form V in a triple-chain system that enables closer packing and greater thermodynamic stability. Unstable lower polymorphic forms (II and III) transform into higher melting, more stable forms, with closer packing and lower volume. These changes can be observed in terms of overall contraction of the chocolate, appearance or undesirable fat bloom formation at rates dependent on relative stabilities of the polymorphic forms and temperature (Talbot, 1999). For chocolate to be in an appropriate polymorphic form, tempering is crucial, influencing final quality characteristics such as colour, hardness, handling, finish and shelf-life characteristics.

Tempering involves pre-crystallisation of a small proportion of triglycerides, with crystals forming nuclei (1–3% total) for remaining lipid to set in the correct form. Tempering has four key steps: melting to completion (at 50°C), cooling to point of crystallisation (at 32°C), crystallisation (at 27°C) and conversion of any unstable crystals (at 29–31°C) (Talbot, 1999) (Fig. 3.5). Tempering sequence is a function of recipe, equipment and the final purpose. Before the use of tempering machines, chocolate used to be hand-tempered, and this method is still occasionally used by chocolatiers, who produce relatively small quantities of handmade confections. Current tempering machines (Fig. 3.6) consist of multistage heat exchangers through which chocolate passes at widely differing rates, making it difficult to identify optimum conditions.

Time–temperature combinations are of paramount importance in process design, and in continuous tempering, molten chocolate is usually held at 45°C and then gently cooled to initiate crystal growth. Working with the Buhler ‘MasterSeeder’, Windhab (ETH Zurich, Switzerland) and Mehrle (Buhler AG, Uzwil, Switzerland) found that high shear seed tempering can be beneficial as the kinetics of fat crystal nucleation and polymorphic transformations ($\alpha \rightarrow \beta_2 \rightarrow \beta'_1$) are strongly accelerated by shear forces acting in high-shear flow fields: overall quality of products was better, as fat bloom was reduced (Windhab et al., 2002). During tempering, the temperatures are precisely controlled and the agitation provided enhances nucleation rates. As the viscosity increases, the chocolate is reheated again in the third stage to prevent runway solidification. In the fourth stage, crystals are matured.

Chocolate can also be tempered by the use of high pressure (Yaseda & Mochizuki, 1992) with molten chocolate compressed to 150 bars. This increases chocolate melting point and...
causes it to solidify into solid crystals of all polymorphic forms. When pressure is released, lower polymorphic forms melt leaving behind tempered chocolate. Subsequent batches can be seeded with stable fat crystals.

A well-tempered chocolate will have the following properties: good shape, colour, gloss, contraction from the mould, better weight control, stable product – harder and more heat resistant (fewer finger marks during packaging) and longer shelf-life (Fig. 3.7). The tempering
regime for milk chocolate slightly differs from that for dark due to the influence of milk fat molecules on crystal lattice formation (Haylock & Dodds, 1999). Milk chocolate contains a proportion of butter fat that causes a eutectic effect, which prevents bloom formation, results in a lower melting point, softening of texture and lowering of temperature to obtain crystal seed for the tempering process (around 29.4°C compared to 34.5°C for plain chocolate). Cocoa butter equivalents (CBEs) and replacers (CBRs) may also find application in the chocolate industry. While cocoa butter equivalents are compatible with cocoa butter, CBRs, which do not require tempering, can only be used if almost all the cocoa butter is replaced. These CBRs melt in the same temperature range as cocoa butter, but crystallise only in the $\beta'$ form (Talbot, 1999; Whitefield, 2005).

More recently, the effect of shear on chocolate or cocoa butter tempering has been studied in a number of different flow geometries, for example, scraped surface heat exchanger with cocoa butter and chocolate (Bolliger et al., 1999), Couette geometry with milk chocolate (Stapley et al., 1999) and cocoa butter (Mazzanti et al., 2003), cone and plate system with cocoa butter (MacMillan et al., 2002; Dhonsi & Stapley, 2006), parallel plate viscometer with milk chocolate (Briggs & Wang, 2004) and a helical ribbon device with cocoa butter (Toro-Vazquez et al., 2004).

### 3.5 PARTICLE SIZE DISTRIBUTION IN CHOCOLATE

Particle size distribution is a key determinant of the flow (rheological) properties in chocolates with a direct influence on sensory perception. Beckett (2000) concluded that the largest particles are important for mouthfeel with respect to grittiness, but the smaller ones are more...
important with respect to chocolate flow properties. Traditionally, continental European chocolate has been described as having a fineness of 15–22 µm particle diameter, and that in North America 20–30 µm (Jackson, 1999). However, with increased globalisation of the industry, traditional differences have begun to blur with specifications becoming much more product specific.

Particle size distribution has been used as a tool to control consistency of solid–liquid mixtures to aid pumping and mixing of molten milk chocolate (Mongia & Ziegler, 2000), transportation, atomisation and grinding of foods of high solid content in milk suspensions (Saeseaw et al., 2005), and d-limonene (Soottitantawat et al., 2005). Malvern Instruments identified applicability of their laser diffraction instrument for nearline chocolate process control, indicating the importance of particle size distribution for fluidity control. Understanding and control of factors influencing fluid performance during high solid content processing are necessary, with increasing competitiveness in modern chocolate manufacturing processing (Servais et al., 2002).

Measurement of particle size distribution in chocolate products done by using the laser diffraction technique, also known as low-angle laser light scattering, is fast becoming the preferred standard of analysis in many industries around the world for ranges between 0.1 and 2000 µm for characterisation and quality control. The instrument used, Malvern Mastersizer (Fig. 3.8) produced by Malvern Instruments, offers greater flexibility in the measurement of particle sizes of various confectionery and many industrial materials. The technique relies on the principle that diffraction angle is proportional to particle size. It uses laser as a source of coherent intense light of fixed wavelength, a suitable detector being a slice of photosensitive silicon with a number of discrete detectors and some means of passing the sample through the laser beam. The set-up used is as shown in Figure 3.9. The method used is non-destructive and non-intrusive, hence samples can be recovered if they are valuable, and the result provided is highly reproducible.

Optimisation of particle size distribution in chocolate requires consideration of palate sensitivity. For example, there is a maximum particle size of 30 µm, or a product is perceived as 'gritty or coarse' in the mouth. Particle size affects viscosity as well as texture, and a

![Fig. 3.8](image.png) The Malvern particle size analyser (Malvern MasterSizer).
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Detector measures integral scattering of all particles simultaneously

Fig. 3.9 Illustration of the principle behind particle size distribution measurement by laser diffraction technique.

chocolate milled to a maximum particle size of 20 μm will have a creamier taste and texture than that with 30 μm. Particle size distribution plays clear roles in process fluidity, but is generally restricted to experience-based empirical knowledge (Beckett, 2000). Several clear examples of particle size distribution optimisation show improvement in process efficiency and/or yield in food manufacture. In apple sauces (Missaire et al., 1990) and in mustard (Aguilar et al., 1991), bimodal particle size distribution promoted viscosity reduction and better mixing, yielding improvements in final product shear, time and temperature stability. Villagran et al. (1996) patented a process for reduced fat nut spreads. The process results in bimodal particle size distribution and reduction of spread viscosity, allowing the low-fat spread to display the ‘desirable fluidity, texture and flavour’.

A widely appreciated example of a solid suspension is chocolate, a polydisperse suspension of sugar, cocoa and/or milk solids in a Newtonian fluid (fat phase), hence the applicability of Casson’s equation can model chocolate flow behaviour (Beckett, 2000; Afoakwa et al., 2008b) where solid content varies from 65 to 75%. Many chocolate products have bimodal and trimodal particle size distributions. A typical particle size distribution of commercial enrobing mass is given in Figure 3.10. In bimodal distributions, minima are generally located around 15–25 μm.

Particle size distribution influences chocolate rheology (Chevalley, 1999), with specific surface area and mean particle size influencing yield stress (Beckett, 2000). Bouzas and Brown (1995) noted that ‘a chocolate with particles sized according to the infinite modal distribution may give the lowest plastic viscosity’. Aguilar and Ziegler (1995) employed a bimodal particle size distribution for a controlled reduction in viscosity. Servais et al. (2002) reported that in blends of chocolates of fine (d_{4,3} = 8.5 μm) and coarse (d_{4,3} = 17.0 μm) particles, varying the blend ratio, influenced relationship between packing fraction and the shear viscosity with yield value closely related to mean particle diameter and particlespecific surface area but not packing fraction. A ratio of 60% coarse particles to 40% fine particles gave the lowest viscosity. Generally, chocolate viscosity is controlled by addition of cocoa butter and expensive viscosity modifiers (surface-active ingredients, such as soybean lecithin). Smaller particle sizes in chocolate are known to improve sensory properties (Ziegler et al., 2001), but plastic viscosity and yield stress increase due to increased surface area of...
particles in contact with cocoa butter (Mongia & Ziegler, 2000). Clear benefits of particle size distribution optimisation are reductions in viscosity modifiers and predictive process control.

Despite the application of particle size distribution in determining suspension flow properties, Awua (2002) and Whitefield (2005) explained that it is not the only factor influencing rheological characteristics. Thus, the general principles of modification of suspension viscosity by changing the particle size require review of a system’s properties and compositional factors that contribute to the changes in physical properties, flow behaviour and sensory character of chocolate.

### 3.6 COMPOSITIONAL EFFECTS ON RHEOLOGICAL AND TEXTURAL QUALITIES IN CHOCOLATE

#### 3.6.1 The role of fats

Cocoa nibs consist of about 55% butter, which constitutes around 30% of the final chocolate. Cocoa butter triglycerides have saturated fatty acids at the 1,3-positions and oleic acid at the 2-position. Fatty acid contents are around oleic (35%), stearic (34%) and palmitic acid (26%) with in addition polar lipids, sterols and tocopherols (Talbot, 1999), each depending on factors such as growing conditions and origin. The simple glyceride composition makes chocolate melt over the temperature range of 23–37°C. The lipid crystal Form V ($\beta_2$) is the desirable form in chocolate production and dominant in well-tempered chocolate (Beckett, 2000; Whitefield, 2005).

Some vegetable fats are similar to cocoa butter in triglyceride composition, and such CBEs can be added in any proportion to chocolate, without causing a significant effect on texture. Legally, such vegetable fats are permitted up to 5% in the EU for a product to be sold as...
chocolate (Cocoa and Chocolate Products Regulations, 2003). CBRs, such as the lauric fats, palm kernel or coconut oils, crystallise only in one crystal form, \( \beta' \), in a very different way and are used to totally replace cocoa butter (Talbot, 1999). Low-calorie fats such as Caprenin, which contain fatty acids different from cocoa butter, and are poorly absorbed by the gut, also find application as CBRs. With non-lauric fats, some cocoa butter can be used (Babin, 2005) and the mix can be tempered normally.

Most chocolates contain between 25 and 35% fat, although ice cream coatings are much higher and some special products such as cooking chocolate and vermicelli pieces are lower in fat. The actual level present will depend on the process being used and this affects the texture of the finished chocolate, so a high-quality tablet of chocolate is likely to have a higher fat content and a lower particle size than a chocolate that is used to coat biscuit (Beckett, 2000). The effect of an extra 1% of fat upon the viscosity depends on the amount already present and the viscosity parameters being considered. Above fat content of 32% there is very little change in viscosity with any further additions. A 1% increase to a 28% fat content has a really dramatic effect especially on the plastic viscosity, which is almost halved. The change becomes more dramatic at even lower fat contents as ‘chocolates’ below 23% fat are normally a paste rather than liquid (Beckett, 2000).

The effect of fat is proportionately much higher for the plastic viscosity than the yield value. Beckett (2000) explained that this phenomenon is not surprising as the extra fat only adds to the free moving fat that aids particles when they flow past each other. The majority of the fat is ‘wetting’ fat, which is partially tied to the particle surfaces. This free fat has a large effect on lubricating the flow when it takes place, and so the plastic viscosity decreases dramatically. The yield value is more pronounced with the forces between the solid particles, which in turn are connected with the absolute distance between them, hence their less effect with fat additions.

### 3.6.2 The role of sugar

Sugar is considered an inert ingredient in chocolate with regard to subtleties of flavour, contributing ‘only’ to sweetness. A change of 1–2% in sugar content has a great effect on costs and other economic factors, and at 5% change large flavour changes become apparent (Beckett, 1999). Fine crystalline sucrose is utilised at up to 50% in chocolate confectionery (Krüger, 1999). Lactose, in milk solids, is present at lower levels in an amorphous form and in its glassy state holds a proportion of milk fat (Beckett, 2000), influencing chocolate flavour and flow properties. Lactose enhances the browning by participating in Maillard reactions (Krüger, 1999; Bolenz et al., 2006). Monosaccharides, glucose and fructose are rarely used in chocolate as they are difficult to dry. Consequently, the additional moisture present in chocolate would increase interactions between sugar particles, and increase viscosity. Dextrose and lactose can successfully replace sucrose in milk chocolate (Müller, 2003; Bolenz et al., 2006).

In recent years, sucrose-free chocolates have become popular among consumers and manufacturers because of reduced calorific values, and the fact that these are both non-cariogenic and suitable for diabetics (Zumbe & Grosso, 1993; Olinger, 1994; Olinger & Pepper, 2001; Sokmen & Gunes, 2006). Sugar alcohols, including xylitol, sorbitol, mannitol, erythritol, maltitol, maltitol syrup, isomalt and lactitol, are used for the manufacture of lower calorie or sugar-free products. Replacement of sucrose with sugar alcohols however affects rheological properties and thus the processing conditions and quality of chocolates.
(Zumbe & Grosso, 1993; Wijers, & Sträter, 2001; Sokmen & Gunes, 2006; Krüger, 1999). Sokmen and Gunes (2006) noted that maltitol results in similar rheological properties of chocolate to sucrrose, and thus may be recommended as a good alternative to sucrrose in chocolate formulations. These authors also observed that chocolate with isomalt results in higher plastic viscosity while xylitol causes higher flow behaviour index. Polydextrose may be added as an edible carbohydrate and intense sweeteners used. The EU limits consumption of sugar alcohols to 20 g per day due to laxative effects (Krüger, 1999).

### 3.6.3 The role of milk and other dairy components

As water binds sugar particles, milk solids rather than liquid milk is added to chocolate contributing about 12–25%. Milk contains about 5% lactose, 5% milk fat, 3.5% protein and 0.7% minerals. Milk fat triglycerides, dominated by saturated fatty acids, exhibit a different crystalline structure although adequate amounts of palmitic, stearic and oleic acid are present, the main fatty acids found in cocoa butter (Haylock & Dodds, 1999). Milk fat is mainly liquid (15–20% solid) at ambient, and softens chocolate texture, slows setting, and is used at up to 30% of the total fat content (German & Dillard, 1998), inhibiting fat bloom. Milk fat is prone to oxidation and influences shelf-life (Haylock & Dodds, 1999).

Milk proteins add to the perceived creaminess of milk chocolate, and at 80% caseins and 20% whey proteins, the casein fraction acts as surfactants and reduces viscosity of chocolate; whey proteins, in contrast, increase viscosity (Haylock & Dodds, 1999). Milk solids added as spray-dried skimmed milk powder or full cream milk powder contribute to flavour, texture and liquid flow properties dependent on heat treatment and drying conditions. Milk fat is free to react with the cocoa butter when mixed with skimmed milk powder but strongly bound in full cream milk powder. Skimmed milk powder softens cocoa butter to an extent (Haylock & Dodds, 1999), and addition of milk solids in the form of chocolate crumb is preferred in certain European countries. Chocolate crumb, developed when cocoa liquor is mixed with sugar, milk mass and vacuum dried, is characterised by a brown colour and slightly cooked flavour. Crumb has a longer shelf-life than milk powder as the chocolate liquor provides natural antioxidants – flavonoids (Holland et al., 1991), stabilising it against rancidity (Haylock & Dodds, 1999; Beckett, 2000). Chocolate flavours vary depending on the crumb processing conditions. Whey and lactose powders can be used to reduce sweetness in some chocolate confectionery. Demineralised whey powder is preferred to avoid off-flavour generation (Haylock & Dodds, 1999).

### 3.6.4 The role of surfactants in modern chocolate confectionery

Chocolate has a continuous fat phase in which sugar, being hydrophilic and lipophobic, will not dissolve, so surfaces have to be coated with fat. This does not occur readily and a surface-active agent is beneficial and allows the fat content of the chocolate to be reduced while maintaining desirable flow properties. Choice of natural surfactant – gums, lecithin, soluble polysaccharides or synthetic (carboxymethyl cellulose) – depends on the function in the end product (Schantz & Rohm, 2005).

Lecithin, a byproduct of soya oil production is a mixture of natural phosphoglycerides (Minifie, 1989). In chocolate the most surface-active component of crude lecithin (mainly oleic C18:1 and palmitic acid C16:0) is believed to be phosphatidylcholine (Vernier, 1998).
Lecithin addition dramatically changes yield value and plastic viscosity, and when added at between 0.1 and 0.3% it reduces chocolate viscosity and enhances toleration of higher moisture levels. At more than 0.5%, yield value increases while plastic viscosity continues to fall (Chevalley, 1999; Rector, 2000; Schantz & Rohm, 2005). Increase in yield value is linked to micelle formation in the continuous phase possibly as multilayers around sugar, which hinders flow. Alternatively, reverse micelles may form in the continuous phase and interact with fully covered sugar particles, consequently increasing yield value (Vernier, 1998). Thickening depends on the particle size distribution as smaller particles require more lecithin to coat sugar surfaces. Lecithin can only be added up to 1%, but will always be present in chocolate as traces from both cocoa and milk.

Polyglycerol polyricinoleate (PGPR), obtained by polycondensation of castor oil and glycerol, is a complex mixture with polyglycerol component dominated by di-, tri- and tetraglycerols (Vernier, 1998). Legally approved within the EU, PGPR can be used in cocoa-based confectionery at up to 0.5% (Rector, 2000). It does not have large effects on plastic viscosity but can reduce yield value by 50% at 0.2% or remove it at about 0.8% (Rector, 2000; Schantz & Rohm, 2005), turning chocolate into a Newtonian liquid, so that it flows more readily and settles rapidly. A similar outcome can be achieved by adding more cocoa butter at greater cost as PGPR coats solid particles, displacing cocoa butter to the continuous phase, decreasing yield value. Rector (2000) reported that chocolate with 35% cocoa butter content has a similar yield value to that containing 32% cocoa butter and 0.1% PGPR. PGPR coats solid particles and, with higher molecular weight, extends further into the lipid continuous phase, producing a better steric stabilisation (Vernier, 1998). In contrast to lecithin, PGPR in chocolate does not structure within the suspension, but increases the continuous phase volume fraction and binds residual water in chocolate, making it unavailable to hydrate and swell the solid particles (Rector, 2000; Schantz & Rohm, 2005).

In recent developments, many chocolate manufacturers use PGPR and lecithin in combination for a desirable yield value and plastic viscosity – balancing out viscosity-reducing effects (Vernier, 1998; Schantz & Rohm, 2005). Adding PGPR to chocolate, containing 0.5% of lecithin, gives a further decrease in yield value and only slight increase in plastic viscosity (Rector, 2000). Increases in plastic viscosity at lecithin concentrations above 0.5% are uncontrolled, and effects on yield value reduction by adding PGPR have greater influence on the flow properties of chocolate (Rector, 2000). PGPR seems less effective in inhibiting bloom formation (Walter & Cornillon, 2001).

Glycerol monostearates (GMS), widely used in confectionery industries, are formed by the incomplete esterification of hydroxyl groups of glycerol using a single fatty acid (Heath, 1982). Vernier (1998) reported that glycerol fatty acid esters were inefficient at reducing yield value and increased plastic viscosity through less efficient coverage of sugar particles, thus leading to greater friction. A mixture of sorbitan and glycerol esters of fatty acids gives yield values similar to lecithin but higher plastic viscosity (Vernier, 1998; Rousset et al., 2002).

### 3.7 MOISTURE AND CHOCOLATE FLOW

Molten chocolate typically has moisture contents of 0.5–1.5%, mainly in the cocoa solids, which does not affect chocolate flow. Greater moisture aggregates sugar particles to form gritty lumps, and moisture at sugar particle surfaces increases friction and apparent viscosity.
Beckett (2000) stated that for every 0.3% of extra moisture left within the chocolate at the end of conching, the manufacturer must add an extra 1% fat, and because fat is by far the most expensive major component in chocolate, it is important that as much ‘free’ water is removed as possible. Water at 3–4% increases viscosity and yield value of chocolate markedly (Chevalley, 1999), and viscosity increases up to 20% moisture, after which an aqueous phase is formed (Beckett, 2000).

3.8 CHOCOLATE QUALITY AND DEFECTS

3.8.1 Chocolate quality

The International Organization for Standardization defines quality as ‘the totality of features and characteristics of a product that bear on its ability to satisfy stated or implied needs’. Quality may be judged as good or bad depending on the level of adherence to specifications or standards for the products – with regards to raw material input and finished products – and how well it matches consumer preferences. Chocolate quality is often determined by rheological measurements and sensory evaluation for solid or more viscous food products.

3.8.1.1 Rheological measurements of chocolate quality

Chocolate behaves as a non-Newtonian liquid exhibiting non-ideal plastic behaviour, where shear-thinning occurs once a yield value has been overcome. This is caused by the three-dimensional structure of the material collapsing and asymmetric particles, which align in the stream lines as the shear rate increases, causing a decrease in viscosity until it becomes independent of shear rate at high shear rates. The Herschel–Bulkley model and the Casson model are both used as popular models to fit non-ideal plastic behaviour. The Casson model was adopted in 1973 as the standard rheological equation for chocolate by the International Office of Cocoa, Chocolate and Sugar Confectionery (IOCCC, 1973). The equation denoting the Casson’s model has been outlined and explained in Chapter 7, in addition to various experiments on chocolate rheology and their influences on finished chocolate quality.

In 2000, another study by the International Confectionery Association, IOCCC (2000) showed that the mathematical models used to express the whole flow curve by a single equation using only a small set of parameters are limited in accuracy as chocolate flow properties do not exactly fit the Casson equation. It was therefore suggested that yield values be measured at low shear rates and viscosities at high shear rates if measurements are to be compared between different laboratories. As a result, the IOCCC (2000) now recommends the measurement of stress and viscosity at shear rates between 2 and 50 s$^{-1}$ in 7 minutes using both up and down curves in shear rate, this being preceded by a pre-shear at 5 s$^{-1}$ lasting for 5 minutes. Unfortunately, most factory grade viscometers are however not accurate at a shear rate of 2 s$^{-1}$, hence the yield stress at a shear rate of 5 s$^{-1}$ is taken to relate to the yield value of chocolate. As the stress at 5 s$^{-1}$ is however a completely different order of magnitude to the shear stress calculated by the Casson model, a relationship can be established by dividing the shear stress at 5 s$^{-1}$ by 10. Further, shearing at 50 s$^{-1}$ does not present results that are representative of the actual chocolate structure and is not always achievable when testing very viscous chocolate, using factory grade viscometers, hence a speed of 40 s$^{-1}$ is chosen. In a paper by Servais et al. (2004), it was shown that the viscosity at 40 s$^{-1}$ can be considered as an accurate reference value for the plastic viscosity of chocolate. To relate this plastic
viscosity to the Casson plastic viscosity, it should be multiplied by a factor of 0.74. This calculation does not mean that one could obtain the same values as using the Casson model, but that one could keep the same order of magnitude as before. Furthermore, chocolate exhibits time-dependent behaviour; in other words, a change of shear stress and viscosity at a given shear rate occurs with time, which can be related to the change in the structure of the material. This decrease of viscosity under shear stress with time of shearing, followed by recovery of the structure when the stress is removed, is called thixotropy. A well-conched chocolate should however not be thixotropic (Servais et al., 2004; Afoakwa et al., 2008b).

3.8.1.2 Sensory evaluation of chocolate quality

Chocolate quality may also be defined by consumer tasting which evaluates the eating quality in terms of characteristics such as appearance, taste, mouthfeel, flavour and aftertaste. This may be done either subjectively or objectively. Subjective opinions may be based on likes and dislikes. Objective measures are scoring systems, which are independent of likes or dislikes and need to be determined by a trained panel. Objective measures can also be obtained by instrumental analysis, such as shear measurements, rheology or textural studies. In all cases, the challenge is to relate the data of the instruments to the data obtained by the assessor or achieve a method by which the sensory attributes can be tested rheologically and be meaningful.

Sensory analysis can be of two kinds, analytical and affective. Analytical involves the evaluation for differences or similarities between products and quality or quantity of sensory attributes of products. It is based on an analytical tool and usually carried out by a trained panel of 10–20 assessors. The panel is used to provide objective evaluation, and should not be used to evaluate preference. The affective analysis targets preference or acceptance evaluation or getting opinions, to a product. It uses a large number of panellists, which should be representative of the target population. To study the global perception of a food product, descriptive analytical methods in association with scaling may be used.

In descriptive analysis, various techniques can be used to describe the perceived sensory characteristics of a product, such as Flavour Profile®, Quantitative Descriptive Analysis®, Texture Profile Analysis® and Sensory Spectrum® (Lawless and Heymann, 1998). Descriptive analysis provides a complete description of a product’s sensory characteristics in the form of words (descriptors). The application of multisample tests is very efficient, rather than evaluating single samples, first, by providing a much more complete picture of how products differ one from the other, and, second, by providing information on more than a single product. Human beings achieve a high degree of accuracy and reliability when making relative judgements, but are very poor at making absolute judgements. Therefore, the comparison of multiple samples is more precise. Detailed vocabulary used to evaluate the complete sensory profile of chocolate products and their descriptions have been provided in Chapter 5.

3.8.2 Chocolate defects

When a product has defect(s) in quality, it may either be rendered unwholesome due to food safety concerns or unacceptable in sensory character. In the case of the latter, it may be subjected to rework to meet expected or aspired sensory perceptions. Typically, two main types of defects occur in chocolates during post-processing handling, storage, warehousing and distribution. These include fat and sugar blooms.
3.8.2.1 Fat bloom

Fat bloom occurs when fat crystals protruding chocolate, or chocolate-flavoured coating surface, disturb the reflection of light and appears visible as a whitish film of fat, usually covering the entire surface (Fig. 3.11), making the products unacceptable for marketing and consumption. Figure 3.11(a) and (b) denotes the appearances of fat bloom in milk and dark chocolates, respectively. Although fat-bloomed chocolate does not pose any public health or safety hazards to consumer, the process renders the product unappealing, and therefore renders it inedible. Fat bloom can be caused by the following:

1. Insufficient crystallisation during tempering
2. Recrystallisation without appropriate tempering
3. Inhomogeneity of the chocolate or chocolate-flavoured coatings
4. Differences in temperature between the chocolate and the centre
5. Incorrect cooling conditions
6. Fat migration
7. Touch, also known as touch bloom
8. Inappropriate storage conditions, i.e. humidity and temperature

When chocolate is poorly tempered, there is formation of the soft Form IV that transforms over a period to the denser and stable Form V, influenced by temperature (Afoakwa et al., 2008c, 2009a). During this transformation, some cocoa butter remains in liquid state as the stable form (V) solidifies and contracts. This coupled with the release of thermal energy as a more stable form (V) forms, the liquid fat forces between solid particles and onto the surface where large crystals impart a white appearance to the surface and recognised as fat bloom (Beckett, 2008). Naturally, Form V transforms to the more stable Form VI, slowly over an extended period, again influenced by temperature. This process also results in formation of fat bloom (Afoakwa et al., 2009a). When optimally tempered products are stored under high temperatures such as exposure to sunlight, chocolate melts, and during re-crystallisation, in the absence of seeding to ensure the direct formation of the stable form (V), a gradual transition from unstable to stable forms results in fat bloom. A fourth mechanism of fat blooming occurs with chocolates that have centres. Usually, liquid fat from the centres migrates and

![Fig. 3.11](image)

Typical photographic images of fat-bloomed (a) milk and (b) dark chocolates.
consequently reaches surfaces along with some cocoa butter. Recrystallisation of this cocoa butter results in fat bloom. Chocolate with nut centres is mostly predisposed to this type of bloom.

3.8.2.2 Sugar bloom

Sugar bloom occurs through either poor storage conditions (high humidity) or rapid transition of products from an area of low to high temperature. Both conditions result in sweating of the chocolate, which consequently dissolves sugar. As the surface water evaporates, sugar crystals remain on the surfaces, producing a white appearance.

This phenomenon is often confused with fat bloom but is completely different. The difference can be established microscopically or whichever is simpler by heating the chocolate to 38°C. Fat bloom disappears at this temperature, whereas sugar bloom remains visible.

3.9 CONCLUSION

Chocolate manufacturing is complex and requires several technological operations and processes to achieve the desired product quality. During processing, the physical properties, rheological behaviour and sensory perception of chocolate are influenced largely by its processing techniques, particle size distribution and ingredient composition. To enhance chocolate quality in terms of appearance, texture, taste and flavour, solid particle size distribution and ingredient composition can be manipulated to modify the physical properties, rheological behaviour and sensorial attributes. Several improvements have been made in recent years on chocolate quality using varying processing strategies and ingredient composition. However, the use of particle size distribution and ingredient composition as tools to modify the rheological behaviour and sensory properties of chocolate still requires a greater understanding of underlying principles and factors affecting changes in flow behaviour and other physical quality characteristics. These principles and their underlying processes and quality effects have been extensively studied and reported in Chapter 7.
4 The chemistry of flavour development during cocoa processing and chocolate manufacture

4.1 INTRODUCTION

Chocolate characters not only originate in flavour precursors present in cocoa beans, but are generated during post-harvest treatments and transformed into desirable odour notes in the manufacturing processes. Complex biochemical modifications of bean constituents are further altered by thermal reactions in roasting and conching and in alkaliisation. However, the chemistry of flavour generation and development during the roasting and conching processes, and their relationships with final flavour quality, has not been clear. With increasing speciality niche products in chocolate confectionery, greater understanding of factors contributing to variations in flavour character would have significant commercial implications.

This chapter describes the nature of chocolate flavour characters in cocoa from different origins and the chemistry of their transformations and development through the processes of roasting and alkaliisation during cocoa processing, and conching during industrial chocolate manufacture. It also provides detailed descriptions of the different flavour compounds in dark and milk chocolates and their contributions to the overall flavour/odour characteristics in finished chocolates.

4.2 INFLUENCE OF BEAN SELECTION ON CHOCOLATE FLAVOUR QUALITY

The source of bean used during processing is widely known to have dramatic impact on the flavour of finished chocolate. The African varieties are thought to possess the best ‘cocoa character’ that manufacturers seek for their products. However, apart from the ‘cocoa character’, beans are known to contribute other major attributes to the overall profile of the product. Some of the characteristics considered positive contributions include bitterness, astringency, acidity, burnt and caramelised flavours. The skilled manufacturers therefore design their chocolate recipe using bean blends to complement or to contrast these flavour properties. Minor, but yet important, contributions made by varied bean types include some traits as woody, fruity, spicy, floral, winy, earthy and perfumery characters. Defects usually associated with farm-level influences can include notes such as smoky, hummy, musty, metallic and other negative contributions (Urbanski, 1992).

Cocoa beans from West African origins – Ghana, Côte d’Ivoire and Nigeria – are generally thought of as the ideal or standard cocoa flavour. While there are distinguishable differences between the origins, the group is thought to yield a balanced and pronounced cocoa character with subtle to moderate nutty undertones. Even though the Ivorian and Nigerian stocks
are believed to show more variability from that of Ghana stock, which is known to be of high cocoa quality and attracts a premium price on the international market, the degree of variability in Ghana stock is relatively insignificant when compared to the degree of variabilities found in other origins. Typically, differences in flavour profiles of beans from different origins could be compared by roasting them under standardised conditions. From numerous observations, beans from Côte d’Ivoire (Ivory Coast) yields a good cocoa impact with low levels of acidity and bitterness. Other fair nutty characters could be noted. Brazilian beans also deliver very little cocoa impact but can sometimes be quite acidic, bitter and astringent (Urbanski, 1992; Fowler, 1999). Desirable side notes such as nutty and fruity are absent. There have been reports that there is little, if any, yeast activity in the early stages of fermentation in Bahia beans. Instead, the initial phase of fermentation is dominated by lactic acid bacteria. The dominant role played by the lactic acid producers might be the reason for the acidic properties in Brazilian cocoa. Ecuadorian beans deliver a more balanced flavour profile but lacks the distinct chocolate note found in the Ghanaian beans, roasted under the same conditions (140°C for 30 minutes).

4.3 EFFECT OF ROASTING

Roasting of cocoa is an essential step to further develop chocolate flavour from the precursors formed during fermentation and drying. Whole bean roasting loosens the shell, which is then readily removed in winnowing. Prior to roasting, cocoa beans have bitter, acidic, astringent and nutty flavours. Roasting further diminishes acidity-reducing concentrations of volatile acids such as acetic acid (Beckett, 2000; Granvogl et al., 2006; Ramli et al., 2006) but not non-volatiles such as oxalic, citric, tartaric, succinic and lactic acids (Jinap et al., 1998; Awua, 2002). Degree of cocoa roast shows a time–temperature-dependent relationship over periods of 5–120 minutes and in the range 120–150°C. Low-temperature roasts are employed for milk and certain dark chocolates. An alternative practice is nib roasting where whole beans are pre-heated, at just below 100°C, to loosen the shells, which are then removed. The thermal operations to loosen the shell include hot air shock, steam or infrared heating (Kim & Keeney, 1984; Kealey et al., 2001; Awua, 2002). The nibs are then treated (e.g. alkali and roasted).

Maillard reactions, central to cocoa flavour development, are important in roasting, and free amino acids, peptides and reducing sugars all participate (Rohan & Stewart, 1967). Voigt et al. (1993, 1994a) noted the hydrophobic amino acids – leucine, alanine, phenylalanine and tyrosine – released by proteinase activities in fermentation are important contributors (Mohr et al., 1976; Voigt et al., 1993, 1994a), as are reducing sugars, fructose and glucose, derived from sucrose hydrolysis (Lopez et al., 1978).

Maillard reactions (Fig. 4.1) require heating at pH values above 3, in the presence of water, a reducing sugar such as glucose, and an amino group, generally from protein. Reactions to the left of Figure 4.1 yield flavours, and to the right, colour formation. The 1-DH, 3-DH and 4-DH intermediates are 1-, 3- and 4-deoxyhexosuloses, respectively, all dicarbonyl compounds. Initial amine-assisted degradation of a reducing sugar proceeds by a sugar–amine condensation forming a Schiff base (Fig. 4.2), tautomerising to a 1,2-enaminol (Fig. 4.3). The link between glucose C-1 and fructose C-2 in sucrose prevents ring opening and Schiff base formation, blocking participation in Maillard reactions. Reaction intermediates can act as catalysts or inhibitors for other reactions contributing to flavour (Beckett, 2000; Granvogl et al., 2006; Ramli et al., 2006).
Strecker
Aldehydes

Polymers

Aldehydes

Pyrroles

Glucose + RNH₂

C₃ + C₃

C₂ + C₄

C₁ + C₅

C₃ + C₃

C₂ + C₄

C₁ + C₅

Retro-aldol

3DH enol

1,2-Enaminol

3DH

Fructoseamine

1DH

2,3-Enediol

4DH

pH < 5

pH > 7

Fig. 4.1 Model of Maillard reaction.

Fig. 4.2 Mechanism of sugar–amine condensation to form a Schiff base.
Reducing sugars and amino acids form addition compounds, such as glucosylamines or fructosylamines, with rearrangement of glucosylamines into isomerisation products. At this point, the reaction pH influences the intermediates formed: acidic conditions favour 3-deoxyhexuloses (3-DH), basic or neutral pH favour formation of dehydroreductone intermediates (1-DH). Central to flavour formation are intermediates that have lost amino groups (1-DH compounds); the nature of the amine does not influence ultimate aroma character but may be important for overall reaction rate (Williams, 2000; Granvogl et al., 2006; Stark et al., 2006a). Transformed compounds are not detectable by colour or flavour changes that may be reversible at this stage, but isomerised products are key substrates for subsequent reactions. The 1-DH compounds are dehydrated, fragmented and transaminated, yielding smaller dicarbonyl molecules, or contributing to Strecker degradation reactions, depending on temperature and pH (Dimick & Hoskin, 1999; Williams, 2000; Granvogl et al., 2006; Ramli et al., 2006). Strecker degradation reactions, central to the appropriate flavours for chocolate, involve interactions of numerous compounds, leading to the structure derived from amino acids being split into three parts (Fig. 4.4).

The nature of the amine component is crucial to chocolate flavour formation as not only are these aldehydes themselves flavour active but further reactions yield heterocyclic compounds important to final character. Leucine and glucose yield aroma notes described as ‘sweet chocolate’; threonine and glutamine and glucose give ‘chocolate’ notes when heated to 100°C, and valine and glucose heated to 180°C a note described as ‘penetrating chocolate’ (Dimick & Hoskin, 1999). Such aroma notes indicate reactions have proceeded past the initial stage. Strecker degradation reactions and subsequent formation of a model pyrazine are summarised in Figures 4.5 and 4.6.

In an acidic environment, generally hydroxymethylfurfurals and other furfural products are formed, and at neutral pH, the results of the reaction are reductones. The intermediates are complex and little is known about their structure and the exact nature of their formation.
Fig. 4.4 Formation of amino acid-specific aldehydes through Strecker degradation reaction.

Fig. 4.5 Mechanism of a Strecker degradation reaction.
Fig. 4.6 Formation of pyrazines through the reaction of deoxy intermediates with amino acids.

in food systems. However, the population of intermediate compounds, quantitatively individually dependent on reaction substrate and pH, polymerises and determines final chocolate flavour. Important compounds include pyrazines, pyrroles, pyridines, imidazoles, thiazoles and oxazoles (Dimick & Hoskin, 1999; Counet et al., 2002; Granvogl et al., 2006; Ramli et al., 2006).

4.3.1 Maillard reactions – aldol condensation, polymerisation and cyclisation

These final stages of Maillard reactions are probably least understood, but it is generally accepted that aldol condensation and cyclisation lead to formation of heterocyclic aroma volatiles such as pyrazines (Fig. 4.6), whilst polymerisation produces melanoidin pigments.
### Table 4.1 Degradation products of amino acids found in cocoa products

<table>
<thead>
<tr>
<th>Amino acids</th>
<th>Amine</th>
<th>Aldehyde</th>
<th>Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alanine</td>
<td>Ethylamine</td>
<td>Acetaldehyde</td>
<td>Acetic acid</td>
</tr>
<tr>
<td>Glycine</td>
<td>Methylamine</td>
<td>2-Methylpropanal</td>
<td>Formic acid</td>
</tr>
<tr>
<td>Valine</td>
<td>Isobutylamine</td>
<td>3-Methylbutanal</td>
<td>2-Methylpropanoic acid</td>
</tr>
<tr>
<td>Leucine</td>
<td>Isoamylamine</td>
<td>2-Methylbutanal</td>
<td>3-Methylbutanoic acid</td>
</tr>
<tr>
<td>Isoleucine</td>
<td>2-Phenethylamine</td>
<td>2-Phenylacetaldehyde</td>
<td>2-Methylbutanoic acid</td>
</tr>
<tr>
<td>Threonine</td>
<td>Methional</td>
<td>Methional</td>
<td>2-Hydroxypropanoic acid</td>
</tr>
<tr>
<td>Phenylalanine</td>
<td>2-Phenylacetic acid</td>
<td>2-Phenylacetic acid</td>
<td>2-(4-Hydroxyphenol)</td>
</tr>
<tr>
<td>Tyrosine</td>
<td>2-(4-Hydroxyphenol)</td>
<td>2-(4-Hydroxyphenol)</td>
<td>acetic acid</td>
</tr>
</tbody>
</table>

Sources: Hoskin and Dimick (1984), Dimick and Hoskin (1999) and Afoakwa et al. (2008a).

Dimick and Hoskin (1999) concluded that specific pyrazine structure is dictated by side groups on dioxo compounds. Pyruvaldehyde and valine, for example, yield end products of 2-methyl-propanal and 2,5-dimethyl pyrazine, contributing nutty flavours. Precursors make chocolates rich in pyrazines, with at least 80 contributing significantly to overall flavour (Counet et al., 2002; Stark & Hofmann, 2005), but total concentrations in roasted beans vary: Ghanaian cocoas typically have 698 µg/100 g, Mexican beans as low as 142 µg (Reineccius, 2006). Nitrogenous component contents are a source of flavour differentiations.

Simple degradation products of amino acids in cocoa products are summarised in Table 4.1. However, there are more than 500 compounds identified from volatile and non-volatile chocolate fractions – hydrocarbons, alcohols, aldehydes, ketones, esters, amines, oxazoles, sulphur compounds (Heinzler & Eichner, 1991; Dimick & Hoskin, 1999; Taylor, 2002; Taylor & Roberts, 2004; Reineccius, 2006; Stark et al., 2006b). Aldehydes from amino acids play important roles in chocolate flavour balance. Aldehydes from Strecker degradation of amino acids also produce pyrazines. The amino acid structure dictates the resulting aldehyde and also the amine and acid that can be produced from the amino acid degradation (Table 4.1).

#### 4.3.2 Effects of alkalisation

Alkalisation (treatment of cocoa nibs or liquor with solutions of alkali) is carried out primarily to change colour but also influence flavour of cocoa powder. Alkalising is common for cocoa products such as drinks to enhance dispersibility, solubility or suspension in water, in baking or coatings. The process consists of treating cocoa beans, nibs, liquor, cake or powder with solutions or suspensions of alkali, usually potassium or sodium carbonate. Other alkalis may also be used. The alkalisation process raises the pH from 5.2 to 5.6 to near neutrality at 6.8–7.5, depending on the quantity of alkali used (Minifie, 1989; Awua, 2002; Whitefield, 2005). Figure 4.7 shows natural cocoa powders that have been alkalised to different levels, showing distinct variations in colour of the final product. Dimick and Hoskin (1999) suggested that cocoa nibs from Malaysia and Brazil are characterised by high acidity and low chocolate flavour, limiting possible character developments in processing, and Sharif (1997) showed that improvements in quality of cocoa nibs and liquors from these origins could be achieved by alkali treatments, reducing acidity before nib roasting or thin film processing.
Sharif (1997) noted that alkalising Malaysian cocoa nibs to pH 6.0 did not significantly ($p \leq 0.05$) change flavour relative to a control but chocolates from nibs alkalised to pH of 7.2 and 8.1 were significantly different, and dark chocolate prepared from Ivory Coast, Malaysian and Brazilian cocoa had their sour, bitter, fruit and mouldy notes significantly changed by alkali treatment. The conclusion was that chocolates from alkalised and thin film processed cocoa liquor had better flavours than non-alkalised nib-roasted chocolate (Sharif, 1997). Alkalisation reduces acidity as well as astringency with aspects like typical cocoa and bouquet enhanced and intensified. Reductions in astringency are affected by further polymerisations of flavonoids during alkali treatments (ADM Cocoa Manual, 2006).

### 4.4 FLAVOUR DEVELOPMENT DURING CHOCOLATE MANUFACTURE

#### 4.4.1 Conching

Conching is regarded as essential for final flavour development and appropriate texture. This is the final stage in chocolate manufacture, whether dark or milk. Residual volatile acids and moisture are removed; angular sugar crystals and viscosity are modified and the colour changed due to emulsification and oxidation of tannins (Awua, 2002; Beckett, 2003; Reineccius, 2006; Afoakwa et al., 2007a). Generally a two-stage process, the first stage converts flake or powder into a paste by mechanical or heat energy, driving off moisture and undesirable volatiles, affects oxidations and distributes lipids through a continuous fat phase. Beckett (2000) suggested that oxidations modify precursors developed in fermentation and roasting processes to achieve final cooked flavour and eliminate undesirable astringent and acidic notes. The second stage converts the thick paste into a free-flowing liquid through addition of cocoa butter and lecithin.

Conching conditions show interactions between time and temperature so that higher temperatures reduce processing time. Conching conditions for crumb milk chocolate are 10–16 hours at 49–52°C but 16–24 hours at 60°C for milk powder chocolates; temperatures above...
70°C lead to changes in cooked flavours (Beckett, 2000; Awua, 2002; Beckett, 2003; Whitefield, 2005). Dark chocolates are typically conched at higher temperatures, 70°C or up to 82°C (Minifie, 1989; Awua, 2002). Conditions may be modified (generally shortened) by pre-treatment of chocolate liquors as thin films at temperatures more than 100°C (Minifie, 1989; Afoakwa et al., 2007a).

The air spaces surrounding a conche in operation have an odour of acetic acid, suggesting an initial loss of short-chained volatile fatty acids, such as acetic acid, the end products of fermentation. This was confirmed by quantitative studies (Dimick & Hoskin, 1999; Beckett, 2000). Volatile phenols show 80% reductions in headspace concentrations within a few hours of conching (Beckett, 2000). Hoskin and Dimick (1984) reported that phenols decreased from 21.3 µg/100 g to 10.9 µg/100 g after 44 hours in low roast chocolate, and 10.3 µg/100 g to 6.0 µg/100 g after 24 hours in high roast in conching. In a later paper, Dimick and Hoskin (1999) concluded that polyphenols, through oxidation and enzymatic mechanisms, form complexes with amino acids, peptides and proteins. The outcome is withdrawal of flavour-active volatiles from headspaces and reductions in perceptions of astringency through irreversible phenol interactions, and more ‘mellow’ final flavours.

Hoskin and Dimick (1983) suggested that in conching of dark chocolate, amino acid concentrations do not fall as temperature and/or the concentrations of amino acids and sugars are below thermal thresholds for Maillard reactions. Heinzlzer and Eichner (1991), however, reported that Amadori compounds formed in drying and roasting decrease during conching, and Pontillon (1995) proposed caramelisations of lactose and Maillard reactions with milk proteins (in milk chocolate). A consensus is that chocolates show marked decreases in overall off-flavours after conching (Hoskin & Dimick, 1983; Pontillon, 1995; Plumas et al., 1996; Counet et al., 2002; Beckett, 2003).

Counet and his co-workers (Counet et al., 2002) concluded that key dark chocolate odourants were present prior to conching, during which Strecker aldehydes were partially lost through evaporation and/or chemical reactions. On the other hand, 2-phenyl-5-methyl-2-hexenal content was increased through aldol condensation of phenylacetaldehyde and 3-methylbutanal followed by dehydration (Counet et al., 2002). Schnermann and Schieberle (1997) noted Furaneol and maltol (Table 4.2) were also generated during conching. Of heterocycles, only concentrations of the least volatile compounds were increased, notably polysubstituted ethyl-, isobutyl- and isopentylpyrazines, tri- or tetramethylpyrazine, furans and acetylpyrrole (Table 4.2).

### 4.5 KEY FLAVOUR COMPOUNDS IN MILK CHOCOLATE

Analytical studies have identified more than 600 volatile compounds in cocoa and chocolate products (Schieberle & Pfner, 1999; Taylor, 2002; Taylor & Roberts, 2004; Reineccius, 2006), primarily pyrazines, esters, amines and amides, acids and hydrocarbons. Schnermann and Schieberle (1997) identified as key neutral/basic flavour-active components of milk chocolate: 3-methylbutanal, 2-ethyl-3,5-dimethylpyrazine, 1-octen-3-one, 2-ethyl-3,6-dimethyl pyrazine, 2,3-diethyl-5-methylpyrazine, (Z)-2-nonenal, 2-methyl-3-(methylthio)furan, (E,E)-2,4-nonanadienal, (E,E)-2,4-decadienal and R-δ-decalactone (Table 4.2).

In acidic volatiles, 14 components were identified as contributing to flavour (Table 4.2) with vanillin (vanilla), added also in manufacture, followed by 2- and 3-methylbutanoic acid.
Table 4.2  Flavour compounds identified in milk chocolates

<table>
<thead>
<tr>
<th>No.</th>
<th>Compound</th>
<th>RI</th>
<th>Odour description</th>
<th>FFAP</th>
<th>SE-54</th>
</tr>
</thead>
<tbody>
<tr>
<td>A.</td>
<td><strong>Neutral/basic fractions</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>3-Methylbutanal&lt;sup&gt;α,β&lt;/sup&gt;</td>
<td>920</td>
<td>Malty</td>
<td>651</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2,3-Butandione (diacetyl)&lt;sup&gt;β,γ&lt;/sup&gt;</td>
<td>984</td>
<td>Buttery</td>
<td>592</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Hexanal&lt;sup&gt;β&lt;/sup&gt;</td>
<td>1083</td>
<td>Green</td>
<td>801</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1-Hexen-3-one&lt;sup&gt;β&lt;/sup&gt;</td>
<td>1101</td>
<td>Linseed oil-like</td>
<td>775</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Unknown&lt;sup&gt;β&lt;/sup&gt;</td>
<td>1195</td>
<td>Geranium-like</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>(Z)-4-heptenal&lt;sup&gt;β&lt;/sup&gt;</td>
<td>1246</td>
<td>Sweet, biscuit-like</td>
<td>899</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>5-Methyl-(E)-2-hepten-4-one&lt;sup&gt;β&lt;/sup&gt;</td>
<td>1287</td>
<td>Hazelnut-like</td>
<td>972</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>1-Octen-3-one&lt;sup&gt;β&lt;/sup&gt;</td>
<td>1304</td>
<td>Mushroom-like</td>
<td>980</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Dimethyl trisulphide&lt;sup&gt;δ&lt;/sup&gt;</td>
<td>1384</td>
<td>Sulphurous</td>
<td>968</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>2-Methoxy-3-isopropyldimethylpyrazine&lt;sup&gt;δ,β&lt;/sup&gt;</td>
<td>1400</td>
<td>Earthy</td>
<td>1093</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Trimethylpyrazine&lt;sup&gt;γ&lt;/sup&gt;</td>
<td>1406</td>
<td>Earthy</td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Unknown&lt;sup&gt;β&lt;/sup&gt;</td>
<td>1422</td>
<td>Fruity, waxy</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>2-Methoxy-3-isopropyldimethylpyrazine&lt;sup&gt;β&lt;/sup&gt;</td>
<td>1428</td>
<td>Earthy, beany</td>
<td>1097</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>(E)-2-octenal&lt;sup&gt;β&lt;/sup&gt;</td>
<td>1433</td>
<td>Fatty</td>
<td>1060</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>2-Ethyl-3,6-dimethylpyrazine&lt;sup&gt;δ&lt;/sup&gt;</td>
<td>1445</td>
<td>Nutty</td>
<td>1079</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>Unknown&lt;sup&gt;β&lt;/sup&gt;</td>
<td>1454</td>
<td>Tallowy</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>2-Ethyl-3,5-dimethylpyrazine&lt;sup&gt;δ&lt;/sup&gt;</td>
<td>1461</td>
<td>Potato chip-like</td>
<td>1083</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>2,3-Diethyl-5-methylpyrazine&lt;sup&gt;δ&lt;/sup&gt;</td>
<td>1490</td>
<td>Potato chip-like</td>
<td>1158</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>(Z)-2-nonenal&lt;sup&gt;β&lt;/sup&gt;</td>
<td>1513</td>
<td>Green</td>
<td>1148</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>(E)-2-nonenal&lt;sup&gt;β&lt;/sup&gt;</td>
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<td>1161</td>
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<td>(E,Z)-2,6-nonadienal&lt;sup&gt;β&lt;/sup&gt;</td>
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<td>2-Methyl-3-(methylene) furan&lt;sup&gt;β&lt;/sup&gt;</td>
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<td>Ethyl phenylacetate&lt;sup&gt;β&lt;/sup&gt;</td>
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<td>R-γ-octenolactone (99%)&lt;sup&gt;β&lt;/sup&gt;</td>
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<td>3-Methylindol (skatole)&lt;sup&gt;β&lt;/sup&gt;</td>
<td>2494</td>
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B. **Acidic fractions**

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<td>Butanoic acid&lt;sup&gt;β&lt;/sup&gt;</td>
<td>1610</td>
<td>Buttery, rancid</td>
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<td>2- and 3-methylbutanoic acid&lt;sup&gt;β&lt;/sup&gt;</td>
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<td>Sweaty</td>
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<td>Pentanoic acid&lt;sup&gt;β&lt;/sup&gt;</td>
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<td>39</td>
<td>3-Hydroxy-2-methylpyran-4-one (maltol)</td>
<td>1961</td>
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<td>4-Hydroxy-2,5-dimethyl-3(2H)-furanone (Furaneol)</td>
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<td>3-Hydroxy-4,5-dimethyl-2(5H)-furanone (sotolon)</td>
<td>2182</td>
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<td>48</td>
<td>3-Hydroxy-5-ethyl-4-methyl-2-(5H)-furanone (Abhexon)</td>
<td>2250</td>
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<td>50</td>
<td>Phenylacetic acid</td>
<td>2254</td>
<td>1262</td>
<td>Sweet, flowery</td>
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<td>51</td>
<td>3-Methoxy-4-hydroxybenzaldehyde (vanillin)</td>
<td>2577</td>
<td>1406</td>
<td>Vanilla-like</td>
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</table>

Compound identified in milk chocolates: aBailey et al. (1962); bMohr (1958); cRohan (1969); dVan Praag et al. (1968); eMarion et al. (1967); fRizzi (1967); gVitzthum et al. (1975); hDietrich et al. (1964); iFlament et al. (1967); jZiegleder and Stojacic (1988); kBainbridge and Davies (1912); lDietrich et al. (1964); mZiegleder (1991); nQuesnel and Roberts (1963); oZiegleder and Stojacic (1988); pSchnermann and Schieberle (1997).

FFAP and SE-54 are names of specific capillary columns used by gas chromatograms.

RI, retention index.

(buttery, rancid) and sotolon (fenugreek/maple syrup/caramel) showing the highest odour intensity values. Although 1-octen-3-one and (E,E)-2,4-decadienal have been reported as primary odourants of milk products (Widder et al., 1991; Schieberle et al., 1993), these and, in addition, dimethyl trisulphide and 4-hydroxy-2,5-dimethyl-3(2H)-furanone may also be generated in conching although this is experimentally unproved. In essence, key flavour components of milk chocolate appear to primarily originate in the roasted cocoa mass.

### 4.6 KEY FLAVOUR COMPOUNDS IN DARK CHOCOLATE

In an analytical study of dark chocolate (Counet et al., 2002), a similar aroma extract dilution analysis (AEDA) approach to that of Schieberle and his colleagues was used to identify key flavour-active components and effects of conching on flavour. Of 60 compounds – nitrogen and oxygen heterocycles, aldehydes and ketones, esters, alcohols, hydrocarbons, nitriles and sulphides (Table 4.3) – 10 had not previously been identified as chocolate constituents: 1-pentanol (1), 3-(methylthiol)-propionaldehyde, methylbenzene, pyrazine, ethenylpyrazine, pyridine, 2-methylpyridine, 1-(2-furanylmethyl)-1H-pyrrole, 1H-indole and dimethyl disulphide (Table 4.3). Two others, benzyl alcohol and dihydro-2-methyl-3(2H)-furanone, had only been reported in milk chocolates. Specific nitrogen heterocycles, from Maillard reactions, were concluded as important: 3(or 2),5-dimethyl-2-(or 3)-ethylpyrazine, 3,5-(or 6)-diethyl-2-methylpyrazine, acetylpyrrole and furfurylpyrrole (Table 4.3) all with praline and chocolate notes. The ethyl group in two pyrazine compounds suggests key roles for alanine and/or its Strecker aldehyde, acetaldehyde, in chocolate flavour synthesis (Cerny & Grosch, 1994; Cerny & Fay, 1995).

Four other heterocycles – 2,3-dimethylpyrazine, trimethylpyrazine, tetramethylpyrazine and 2-isopropyl-3-methoxy pyrazine – were identified (Table 4.3). Tetramethylpyrazine, the
<table>
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<td>1-Pentanol&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>2-Heptanol&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>3</td>
<td>Benzyl alcohol&lt;sup&gt;b&lt;/sup&gt;</td>
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<td>4</td>
<td>3,7-Dimethyl-1,6-octadien-3-ol (linalool)&lt;sup&gt;b&lt;/sup&gt;&lt;sup&gt;e&lt;/sup&gt;&lt;sup&gt;f&lt;/sup&gt;&lt;sup&gt;g&lt;/sup&gt;</td>
<td>1086</td>
<td>Flowery</td>
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<td>Chocolate</td>
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<td>3-Methylbutanal&lt;sup&gt;b&lt;/sup&gt;&lt;sup&gt;e&lt;/sup&gt;&lt;sup&gt;–&lt;/sup&gt;&lt;sup&gt;g&lt;/sup&gt;</td>
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<td>Nonanal&lt;sup&gt;b&lt;/sup&gt;&lt;sup&gt;d&lt;/sup&gt;&lt;sup&gt;e&lt;/sup&gt;&lt;sup&gt;–&lt;/sup&gt;&lt;sup&gt;g&lt;/sup&gt;</td>
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<td>Ethynlypyrazine</td>
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<td>2-Ethyl-5(or 6)-methylpyrazine&lt;sup&gt;b,f,g&lt;/sup&gt;</td>
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<td>2-Ethyl-3-methylpyrazine&lt;sup&gt;b,g&lt;/sup&gt;</td>
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<td>Hazelnut, roasted</td>
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<td>2-Ethenyl-6-methylpyrazine</td>
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<td>Roasted, smoky, praline, rum</td>
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<tr>
<td>43</td>
<td>3(or 2),5-Dimethyl-2(or 3)-ethylpyrazine&lt;sup&gt;c,d,g&lt;/sup&gt;</td>
<td>1057</td>
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<td>44</td>
<td>Tetramethylpyrazine&lt;sup&gt;b,f,g&lt;/sup&gt;</td>
<td>1065</td>
<td>Milk coffee, mocha, roasted, green</td>
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<tr>
<td>45</td>
<td>2-Isopropyl-3-methoxypyrazine&lt;sup&gt;c,d,g&lt;/sup&gt;</td>
<td>1081</td>
<td>Garden peas, green, hazelnut</td>
</tr>
<tr>
<td>46</td>
<td>2,3-Diethyl-5-methylpyrazine&lt;sup&gt;c–d,g&lt;/sup&gt;</td>
<td>1135</td>
<td></td>
</tr>
<tr>
<td>47</td>
<td>3,5(or 6)-Diethyl-2-methylpyrazine&lt;sup&gt;f,g&lt;/sup&gt;</td>
<td>1137</td>
<td>Cocoa, chocolate, rum, sweet, roasted</td>
</tr>
<tr>
<td>48</td>
<td>3,5(or 6)-Diethyl-2-methylpyrazine&lt;sup&gt;f,g&lt;/sup&gt;</td>
<td>1139</td>
<td></td>
</tr>
<tr>
<td>49</td>
<td>2,5(or 6)-Dimethyl-3-(2-methylpropyl) pyrazine&lt;sup&gt;g&lt;/sup&gt;</td>
<td>1184</td>
<td>Hazelnut</td>
</tr>
<tr>
<td>50</td>
<td>2,5-Dimethyl-3-(3-methylbutyl)pyrazine&lt;sup&gt;g&lt;/sup&gt;</td>
<td>1296</td>
<td>Roasted, sweet, green</td>
</tr>
<tr>
<td>51</td>
<td>Pyridine&lt;sup&gt;g&lt;/sup&gt;</td>
<td>724</td>
<td></td>
</tr>
<tr>
<td>52</td>
<td>2-Methylpyridine&lt;sup&gt;g&lt;/sup&gt;</td>
<td>800</td>
<td></td>
</tr>
<tr>
<td>53</td>
<td>1-(2-Pyridinyl)-1-propanone&lt;sup&gt;g&lt;/sup&gt;</td>
<td>1114</td>
<td></td>
</tr>
<tr>
<td>54</td>
<td>2-Carboxaldehyde-1H-pyrrole&lt;sup&gt;g&lt;/sup&gt;</td>
<td>986</td>
<td></td>
</tr>
<tr>
<td>55</td>
<td>1-(1H-pyrrol-2-yl)ethanone (acetylpyrrole)&lt;sup&gt;b,f,g&lt;/sup&gt;</td>
<td>1030</td>
<td>Cocoa, chocolate, hazelnut, roasted</td>
</tr>
<tr>
<td>56</td>
<td>3-Ethyl-2,5-dimethyl-1H-pyrrole&lt;sup&gt;g&lt;/sup&gt;</td>
<td>1119</td>
<td>Cocoa, hazelnut, coffee, roasted</td>
</tr>
<tr>
<td>57</td>
<td>1-(2-Furanylmethyl)-1H-pyrrole (furfurylpyrrole)&lt;sup&gt;g&lt;/sup&gt;</td>
<td>1166</td>
<td>Roasted, chocolate, green</td>
</tr>
<tr>
<td>58</td>
<td>1H-indole&lt;sup&gt;g&lt;/sup&gt;</td>
<td>1276</td>
<td></td>
</tr>
<tr>
<td>59</td>
<td>Dimethyl disulphide&lt;sup&gt;g&lt;/sup&gt;</td>
<td>743</td>
<td>Onion, cabbage, sweaty</td>
</tr>
<tr>
<td>60</td>
<td>Dimethyl trisulphide&lt;sup&gt;c,d,g&lt;/sup&gt;</td>
<td>969</td>
<td></td>
</tr>
<tr>
<td>61</td>
<td>2,4-Hexadien-1-ol&lt;sup&gt;g&lt;/sup&gt;</td>
<td>831</td>
<td></td>
</tr>
<tr>
<td>62</td>
<td>Furfuryl alcohol (furfural)&lt;sup&gt;b,e–g&lt;/sup&gt;</td>
<td>827</td>
<td>Caramel-like, sweet</td>
</tr>
<tr>
<td>63</td>
<td>2,5-Dimethyl-4-hydroxy-3(2H)furanone (Furanone)&lt;sup&gt;c,d,g&lt;/sup&gt;</td>
<td>1023</td>
<td></td>
</tr>
<tr>
<td>64</td>
<td>Methylbenzene (toluene)&lt;sup&gt;g&lt;/sup&gt;</td>
<td>772</td>
<td></td>
</tr>
</tbody>
</table>
Table 4.3 (Continued)

<table>
<thead>
<tr>
<th>No.</th>
<th>Compound</th>
<th>RI</th>
<th>Odour description</th>
</tr>
</thead>
<tbody>
<tr>
<td>29</td>
<td>2,3-Butanedione (diacetyl)c–g</td>
<td>578</td>
<td>Buttery (low intensity)</td>
</tr>
<tr>
<td>63</td>
<td>4-Methylcyclohexanoneg</td>
<td>998</td>
<td></td>
</tr>
<tr>
<td>64</td>
<td>3,4,4-Trimethyl-2-cyclopenten-1-oneg</td>
<td>1064</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Ketones</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>65</td>
<td>Phenolf,g</td>
<td>961</td>
<td></td>
</tr>
<tr>
<td>66</td>
<td>4-Methylphenolg</td>
<td>1031</td>
<td></td>
</tr>
<tr>
<td>67</td>
<td>2-Methoxyphenol (guaiaicol)g</td>
<td>1063</td>
<td>Smoked, sweet (low intensity)</td>
</tr>
<tr>
<td>68</td>
<td>4-Hydroxy-3-methoxybenzaldehyde (vanillin)c–g</td>
<td>1366</td>
<td>Vanilla-like</td>
</tr>
<tr>
<td></td>
<td><strong>Phenols</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>51</td>
<td>2,5-Dimethyl-3-{3-methylbutyl}pyrazineg</td>
<td>1289</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Pyrazines</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>69</td>
<td>2-Pyridineamg</td>
<td>803</td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>3-Hydroxy-2-methyl-4-pyrene (maltol)d,g</td>
<td>1086</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Pyridines</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>71</td>
<td>2,3-Dimethyl-1H-pyrroleg</td>
<td>804</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Pyrones</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>72</td>
<td>4,5-Dihydro-2-methylthiazoleg</td>
<td>1151</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Pyroles</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Thiazoles</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*aCompound identified by GC-MS (MS) and/or by retention index on CP-Sil5-CB (RI) and/or by GC-olfactometry (GCO). Sources: bManiere and Dimick (1979); cSchieberle and Pfnuer (1999); dSchnermann and Schieberle (1997); eGhizzoni et al. (1995); fZiegleder and Stojavic (1988); gCounet et al. (2002).*

most abundant pyrazine in dark chocolate at more than 6 ppm, exhibited milk coffee-mocha-roasted notes.

Of 33 particularly flavour-active components in the neutral/basic fraction (Counet et al., 2002), 3 had specifically strong chocolate characters: 2-methylpropanal, 2-methylbutanal and 3-methylbutanal. Others were characterised by Maillard cocoa/praline/nutty/coffee notes: 2,3-dimethylpyrazine, trimethylpyrazine, tetramethylpyrazine, 3(or 2),5-dimethyl-2(or 3)-ethylpyrazine, 3,5(or 6)-diethyl-2-methylpyrazine and furfurylpyrrole. Character in the acidic fraction – phenolic, sweet – was very different from that of the neutral/basic with its essentially chocolate flavour. Only 6 of 18 components (resolved by high-resolution gas chromatography with flame ionisation detector/mass spectrophotometry) were flavour active, and 1, vanillin, was added prior to conching. Furaneol was perceived as sweet and caramel in extracts from both dark chocolates (Counet et al., 2002).

### 4.7 CONCLUSION

Chemical reactions during cocoa processing are complex, contributing to final flavour and textural properties. Differences in flavour characteristics are found in beans of different botanical and geographical origins. During cocoa processing and chocolate manufacture, flavour development is influenced by several factors such as bean selection (origin), roasting, alkalisation and conching (Fig. 4.8). In roasting, Maillard reactions convert flavour precursors
formed during fermentation into two main classes of flavour-active component: pyrazines and aldehydes. Although no new key odourants are synthesised during conching, levels of 2-phenyl-5-methyl-2-hexenal, Furaneol and branched pyrazines significantly increase and form key odourants in both milk and dark chocolates, while Strecker aldehydes are lost by evaporation. These processes suggest an important role of conching in chocolate manufacture in determining final flavour characters. Direct relationships are thus observed between the initial composition and post-harvest treatments (fermentation and drying) of cocoa beans and subsequent processing (roasting and conching) and technological effects on the flavour formation, development and character in chocolate.
5 Sensory character and flavour perception of chocolates

5.1 SUMMARY AND INDUSTRIAL RELEVANCE

The perception of the sensory character of chocolate is related not only to its intrinsic characteristics but also to other parameters such as brand, origin, nutritional facts and price, and to factors connected with the consumer such as perceptive abilities, memory for foods and other psychological and social aspects. The mechanisms of sensory perception are not fully elucidated and instrumental analysis cannot replace sensory for every purpose. Nevertheless, some interesting tools are continuously being developed that could be at least useful for food control and assessment of the specificity of chocolate products.

Chocolate flavour contains many distinct odourous compounds, which have been identified and quantified using orthonasal and retronasal techniques. The release of volatiles from chocolate during consumption is influenced by several factors including mastication, mixing with saliva and changes in temperature and pH. To gain an insight into the kinetics of volatile release, in vivo techniques have been developed, which are capable of monitoring real-time volatile release. The mechanisms of flavour perception and release during mastication have been studied in many solid and semisolid food systems, and are becoming increasingly understood. However, very little is known on the perceptions of sensory character and mechanisms of flavour release in chocolate systems. Furthermore, identification of new techniques to track the release of flavour during chocolate consumption still remains a great challenge. Understanding the mechanisms by which the sensorial properties of chocolate are perceived during manufacture and consumption would help lead to product improvement with enhanced palatability and healthier properties in chocolate confectionery, and will drive consumer acceptance and preference.

5.2 INTRODUCTION

Chocolate has distinct set of sensory characteristics, which dictates its choice and acceptability by consumers. It originates from flavour precursors present in cocoa beans, generated during post-harvest treatments and transformed into chocolate sensorial characters during its manufacture. In addition to the inherent factors as mentioned, others including ingredients used and the processing techniques also influence the sensory quality of finished chocolates such as appearance, taste, texture (hardness and mouthfeel) and flavour. However, flavour is the most important sensory attribute of chocolates, as it is influenced by aroma, taste and texture during consumption. In a more or less conscious way, chocolate consumers’ judgement is based on intrinsic quality attributes of products. Nowadays, chocolate is not a rare or
privileged product. Recognition of its values surely involves previous experience and future expectations carried by promotion or package. However, what makes it so desirable is the perception of its sensory quality.

Chocolate flavour is a complex combination of the olfactory, gustatory and trigeminal sensations perceived during consumption. Taylor and Roberts (2004) and Reineccius (2006) explained that the flavour of foods may be influenced by tactile, thermal, painful and/or kinesthetic effects. However, relating flavour release from foods to flavour release when eating these foods still remains a great challenge. Flavour perception in chocolate is not the simple result of taste and aroma stimuli, but it is essentially a multimodal phenomenon that includes perception of aroma, at the olfactory receptors and perception of taste at the taste buds on the tongue. Other contributing factors include colour, appearance, sound, pain and heat at the inner surface of the mouth and mouthfeel (Taylor & Roberts, 2005). This perceptual dynamism changes as the nature and the intensity of the stimuli change continuously during chocolate consumption. Measurements of these changes with time are essential to the understanding of the relationship between modalities and perception of chocolate flavour.

To elucidate this process, it is necessary to combine quantifications of the release of volatile compounds from the food matrix with sensory evaluation of the food product. As food is eaten, the release of the volatiles from the food is influenced by a number of factors including mastication, mixing with saliva and changes in temperature and pH (Bolan et al., 2006). Therefore, to gain an insight into the kinetics of volatile release, in vivo techniques have been developed, which are capable of monitoring real-time volatile release. Atmospheric pressure chemical ionisation mass spectrometry and proton transfer reaction mass spectrometry are most commonly used for this purpose. With these systems, part of the participant’s breath is continuously sampled, allowing for sensitive and fast monitoring of volatile release. Compounds responsible for flavour perception must be released from the food matrix and then transported to the receptors. Flavour release from various food matrices including cheeses, yoghurts, gums, coffee, custard and cakes, and its subsequent delivery to the olfactory and gustatory receptors has been the extensively researched using orthonasal and retronasal techniques (Delahunty et al., 1996; Buettner & Schieberle, 2000; Linforth et al., 2002; Decourcelle et al., 2004; de Wijk et al., 2006; Denker et al., 2006).

With the increasing advances in chocolate confectionery, many with low fat or lower sugar formulations than the traditional European or Continental recipes, it is becoming increasingly important to understand the factors that affect the perception of sensory character in chocolates, and how the flavour components are released from their matrices during consumption. Most detailed studies on flavour perception and release have been done on simple systems, and relatively very little is known on the perception and release of flavour from complex systems such as chocolate. Hence, the mechanism of chocolate flavour perception and release needs to be further elucidated. This chapter brings greater understanding of knowledge regarding the sensory perception of character and quality in chocolates and explains the mechanism of flavour release during consumption from different chocolate systems.

5.3 SENSORY PERCEPTION OF QUALITY IN CHOCOLATES

Chocolate quality is predominantly defined in terms of sensory characters, which is affected by post-harvest treatment of cocoa (fermentation, drying), and manufacturing processes (roasting, refining, conching and tempering). In most cases, quality of chocolate is defined
by its appearance, texture, taste and flavour. Chocolate consumers are mostly concerned with sensory character, and this forms their basis for quality assessment in attributes of flavour, aroma, texture (mouthfeel) and appearance. To cut costs, some manufacturers use less expensive cocoa butter replacers or equivalents such as shea butter in chocolate production. Although legislation permits a 5% limit, some consumers and manufacturers see this as a decadence of chocolate quality or its adulteration.

Consumers’ perception of chocolate quality depends on geographical location. This is primarily because the entire chocolate world defines quality based on site of manufacture rather than source of raw materials: Switzerland where conching was developed prefers smooth chocolate and the Dutch, noted for the invention of the cocoa powder, produce non-sugary chocolate. A manufacturer’s quality goal is to comply with requisite legislation(s) and meet target consumers’ preferences with niche markets for additional indices such as organics, Fairtrade as well as other ethical considerations (Cidell & Alberts, 2006). Table 5.1 provides detailed information on the vocabulary used to evaluate the sensory character of chocolates and their description.

5.3.1 Appearance

Appearance, flavour and texture are the major determinants of chocolate quality and acceptance, and the guiding trilogy in its manufacture, storage and marketing. On a first sight, what chocolate looks like influences not only our acceptances or choice but also affects the taste and consumers’ likeness or enjoyment for the product. Good-quality chocolate has a continuous light to dark brown colour (depending on the product type) and a glossy appearance. White specks, patches or blotches attributed to migration of fat or sugar to product surfaces are undesirable, known as blooming, and dramatically affect the quality and acceptability of chocolates.

5.3.2 Texture

Chocolate texture is the most complex of all its physical characteristics, and along with flavour, it is the quality that most frequently comes to mind during selection for preference of products. Broadly defined, texture is a subjectively experienced quality parameter that refers to the feel of food in the mouth and the impression one has of its physical characteristics as a result of biting and chewing. A wide variety of words are used to describe chocolate texture depending on whether the emphasis is on structure, consistency or mouthfeel (Table 5.1).

Three textural sensory properties are of great importance in chocolate perception. These are smoothness, meltiness and hardness. With regard to smoothness, some researchers report that it is pointless to refine chocolate below 15 µm as the human buds, and sensory nerve endings cannot distinguish differences below that particle size. If this happens, then peanut butter-like undesirable flavour emerges. Urbanski (1992) states that the optimum lies between 15 and 50 µm, above which products are felt to be gritty. Earlier reports showed that chocolate of 30–35 µm particle size is already perceived as coarse and it has a paramount influence on overall sensory quality.

Texture is also connected with meltiness of cocoa butter. It gives an exceptionally different melt-in-the-mouth characteristic that is unique only to this product. Crystalline structure of cocoa butter not only influences gloss and stability of chocolate but is also responsible for the perception of transition from a hard material to liquid oil at mouth temperature. Hardness
Table 5.1 The sensory vocabulary of chocolates and their descriptions

<table>
<thead>
<tr>
<th>Word</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Appearance</strong></td>
<td></td>
</tr>
<tr>
<td>Colour intensity</td>
<td>This describes the intensity (tint) of typical chocolate colour with the use of descriptions ranging from light brown to dark brown.</td>
</tr>
<tr>
<td>Colour brightness</td>
<td>This is luminescence of colour, with descriptions ranging from dull to shiny.</td>
</tr>
<tr>
<td>Texture on surface</td>
<td>Amount of regular cavities or holes on surface to bottom of chocolate, with descriptions ranging from even to gritty.</td>
</tr>
<tr>
<td>Texture on snap</td>
<td>Amount of irregular cavities or holes on the snap surface of chocolate, with descriptions ranging from even to gritty.</td>
</tr>
<tr>
<td>Melting in hand</td>
<td>The level of chocolate melting after 30 seconds of contact in the hand, with descriptions from melted little to melted very much.</td>
</tr>
<tr>
<td><strong>Flavour/aroma</strong></td>
<td></td>
</tr>
<tr>
<td>Fruity/citrus/berry</td>
<td>This is reminiscent of the odour and taste of fruits. The natural aroma of berries is highly associated with this attribute. The perception of high acidity in some chocolates is correlated with citrus characteristic.</td>
</tr>
<tr>
<td>Floral/fragrant</td>
<td>This is similar to the fragrance of flowers. It describes the flavour of chocolates typical of Ecuadorian Arriba and attract premium prices on the market. It is associated with the slight scent of different types of flowers including honeysuckle, jasmine, dandelion and nettles. It is mainly found when an intense fruity or green aroma is perceived but rarely found having a high intensity by itself in chocolates manufactured from West African Forastero cocoa.</td>
</tr>
<tr>
<td>Cereal/toasty/wheaty</td>
<td>This describes flavour characteristic of cereal, malt and toast. It includes scents such as the aroma and flavour of uncooked or roasted grain (including roasted corn, barley or wheat), malt extract and the aroma and flavour of freshly baked bread and freshly made toast. This descriptor has a common denominator, a grain-type flavour.</td>
</tr>
<tr>
<td>Malty</td>
<td>An aromatic sensation created by a moderately volatile set of aldehydes and ketones that produce sensations, reminiscent of toasted grains. This is sometimes noted in milk chocolates.</td>
</tr>
<tr>
<td>Green/grassy</td>
<td>This flavour descriptor includes three terms, which are associated with odours, reminiscent of a freshly mowed lawn, fresh green grass or herbs, green foliage, green beans or unripe fruit.</td>
</tr>
<tr>
<td>Nutty/peanuts</td>
<td>This flavour is reminiscent of the odour and flavour of fresh nuts (distinct from rancid nuts) and not of bitter almonds. They are predominantly present in chocolates containing nuts (peanuts, almonds, etc.).</td>
</tr>
<tr>
<td>Almonds</td>
<td>This flavour is reminiscent of the odour and flavour of fresh almond nuts with a sweet-scented undertone. It is sometimes noted in chocolates manufactured using almond nuts.</td>
</tr>
<tr>
<td>Caramel</td>
<td>This flavour descriptor is reminiscent of the odour and flavour produced when caramelising sugar without burning it. It is present in most milk chocolates manufactured using the crumb process. Consumers are cautioned not to use this attribute to describe a burning note.</td>
</tr>
<tr>
<td>Chocolate/cocoa</td>
<td>This descriptor is reminiscent of the aroma and flavour of cocoa powder and chocolate (including dark chocolate and milk chocolate). It is an aroma that is sometimes referred to as cocoa-like.</td>
</tr>
<tr>
<td>Sweet/candy</td>
<td>An aromatic sensation created by a highly volatile set of aldehydes and esters that produce sweet fragrance sensations reminiscent of a flower. They are typically present in low-fat chocolates containing high sugar or sweetener levels.</td>
</tr>
<tr>
<td>Word</td>
<td>Description</td>
</tr>
<tr>
<td>--------------------</td>
<td>-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Burnt/smoky</td>
<td>This flavour descriptor is similar to that found in burnt food. The odour is associated with smoke produced when burning wood. This descriptor is frequently used to indicate the degree of roast commonly found by consumers of products from oven-roasted cocoa.</td>
</tr>
<tr>
<td>Roasted/toasted</td>
<td>This descriptor is similar to that found in roasted or toasted grains. The odour is associated with aroma produced when roasting or toasting food. This descriptor is frequently used to indicate the degree of roast commonly found by consumers of products from oven-roasted cocoa.</td>
</tr>
<tr>
<td>Fermented</td>
<td>A taste fault in chocolates producing a highly displeasing sour sensation on the tongue. This is the result of enzyme activity in the cocoa beans, changing the sugars to acids during the fermentation and drying processes.</td>
</tr>
<tr>
<td>Acidic/sour</td>
<td>A basic flavour characterised by the smell of an organic acid solution. In chocolates, this is a non-desirable, sharp and pleasing aroma particularly strong with certain origins (Malaysian and Indonesian) as opposed to fermented or sour smell, arises essentially due to the high acid generations in these cocoas during fermentation.</td>
</tr>
<tr>
<td>Vanilla</td>
<td>This descriptor is reminiscent of the aroma of vanilla and mostly found in vanilla-flavoured chocolates.</td>
</tr>
<tr>
<td>Milky/creamy</td>
<td>This descriptor is reminiscent of chocolates containing moderately high levels of milk solids, the result of pronounced amounts of milk present in the product.</td>
</tr>
<tr>
<td>Walnuts</td>
<td>This is reminiscent of the odour and flavour of fresh walnuts, typically present in chocolates containing walnuts or its artificial flavours.</td>
</tr>
<tr>
<td>Hazelnut</td>
<td>This is reminiscent of the odour and flavour of fresh hazelnuts, typically present in chocolates containing hazelnuts or its artificial flavours.</td>
</tr>
<tr>
<td>Bittersweet</td>
<td>This descriptor is typical of the aroma of dark chocolate giving both sweet and bitter flavour notes. Generally, normal characteristics of chocolates connected with their chemical constitution, influenced by degree of roasting and ingredient formulations.</td>
</tr>
<tr>
<td>Puckery</td>
<td>A secondary chocolate flavour sensation characterised by a predominately puckering, sour sensation along the sides of the tongue. Rarely found in chocolates but when present, they are caused by higher-than-normal percentage of sour acids, almost giving the taste a puckering sensation.</td>
</tr>
<tr>
<td>Taste</td>
<td></td>
</tr>
<tr>
<td>Sweetness</td>
<td>This is a basic taste descriptor characterised by solutions of sucrose or fructose which are commonly associated with sweet aroma descriptors such as fruity, chocolate and caramel. It is generally used for describing chocolates which are free from off-flavours.</td>
</tr>
<tr>
<td>Bitterness</td>
<td>A primary taste characterised by the solution of caffeine, quinine and certain alkaloids. This taste is considered desirable up to a certain level and is affected by the degree of roasting procedures.</td>
</tr>
<tr>
<td>Saltiness</td>
<td>A primary taste characterised by a solution of sodium chloride or other salts.</td>
</tr>
<tr>
<td>Acidic/acidity</td>
<td>A basic taste characterised by the solution of an organic acid. A desirable sharp and pleasing taste particularly strong with certain origins as opposed to an overfermented sour taste.</td>
</tr>
<tr>
<td>Fruity/citrus/berry</td>
<td>This is reminiscent of the taste of fruits. The natural taste of berries is highly associated with this attribute. The perception of high acidity in some chocolate is correlated with the fruity flavour characteristic of Arriba-type cocoas from the Ecuadorian region.</td>
</tr>
<tr>
<td>Word</td>
<td>Description</td>
</tr>
<tr>
<td>-------------------</td>
<td>---------------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td><strong>Mouthfeel</strong></td>
<td></td>
</tr>
<tr>
<td>Smooth</td>
<td>This is the perception of fineness or consistency of chocolate during mastication, and it is detected by rolling the sample between the tongue and the palate. Descriptions used vary from very smooth to very gritty.</td>
</tr>
<tr>
<td>Gritty</td>
<td>This is the perception of roughness of chocolate matrix due to detection of solid particles of sizes $&gt; 35 \mu m$ by the tongue during mastication. Grittiness is normally detected by rolling the sample between the tongue and the palate. Descriptions used vary from very gritty to very smooth.</td>
</tr>
<tr>
<td>Harsh/acrid</td>
<td>Sensation at the same time bitter and astringent, raspy and disagreeable, particularly found in some poor-quality cocoa beans, often due to imperfect fermentation.</td>
</tr>
<tr>
<td>Astringency/acidic</td>
<td>A basic taste characterised by the solution of an organic acid. A desirable sharp and pleasing taste particularly strong with certain origins as opposed to an overfermented sour taste.</td>
</tr>
<tr>
<td><strong>Aftertaste</strong></td>
<td></td>
</tr>
<tr>
<td>Sweet</td>
<td>This is a basic taste descriptor characterised by solutions of sucrose or fructose which are commonly associated with sweet aroma descriptors such as excessive sugary or fruity. Sweetness as aftertaste could often be detected in low-sugar chocolates manufactured with sweeteners.</td>
</tr>
<tr>
<td>Bitter</td>
<td>A primary taste characterised by the solution of caffeine, quinine and certain alkaloids. This taste is considered desirable up to a certain level and is affected by the degree of roasting procedures.</td>
</tr>
<tr>
<td>Acidic/sour</td>
<td>A basic taste characterised by the solution of an organic acid. A desirable sharp and pleasing taste particularly strong with certain cocoa origins as opposed to an overfermented sour taste.</td>
</tr>
<tr>
<td>Acrid</td>
<td>A secondary chocolate taste sensation characterised by a predominantly piercing sour sensation on the posterior sides of the tongue, caused by higher-than-normal percentage of sour acids developed in the cocoa beans during fermentation.</td>
</tr>
<tr>
<td>Burnt/smoky</td>
<td>This taste descriptor is similar to that found in burnt food. It is associated with smoke produced when burning wood. This descriptor is frequently used to indicate the degree of roast commonly found by consumers of overroasted chocolates.</td>
</tr>
<tr>
<td>Nutty</td>
<td>A taste sensation created by a moderately volatile set of aldehydes and ketones that produce sensations, reminiscent of roasted nuts. Characteristic of chocolate products manufactured with additions of some nut to enhance the flavour.</td>
</tr>
<tr>
<td>Puckery</td>
<td>A secondary sensation characterised by predominantly souring along the sides of the tongue, caused by higher-than-normal percentage of sour acids, giving the taste a puckering sensation.</td>
</tr>
<tr>
<td>Astringent</td>
<td>A secondary taste descriptor characterised by predominantly searing, salty sensation on the anterior sides of the tongue. In chocolates, astringency is identified with undesirable acidity generation during cocoa fermentation and drying.</td>
</tr>
<tr>
<td>Bittersweet</td>
<td>This taste descriptor is typical of the flavour of dark chocolate, giving both sweet and bitter flavour notes. Generally, normal characteristics of chocolate connected with their chemical constitution, influenced by degree of roasting and the method of processing.</td>
</tr>
</tbody>
</table>
Table 5.1 (Continued)

<table>
<thead>
<tr>
<th>Word</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Texture</strong></td>
<td></td>
</tr>
<tr>
<td>Hardness at first bite</td>
<td>This is the measure of the amount of force needed to bite through a piece of chocolate by half using the incisors, by use of descriptions ranging from very soft to very hard.</td>
</tr>
<tr>
<td>Smoothness</td>
<td>This is the perception of fineness of chocolate during mastication, and it is detected by rolling the sample between the tongue and the palate. Descriptions used vary from very smooth to very gritty.</td>
</tr>
<tr>
<td>Adhesiveness</td>
<td>This is an impression of force needed for removal of chocolate from gums after five chews, by use of descriptions ranging from no force to high force.</td>
</tr>
<tr>
<td>Thickness</td>
<td>This is the perception of the viscosity of chocolate sample after melting in the mouth.</td>
</tr>
<tr>
<td>Chunky</td>
<td>A perception of the degree of bulkiness of chocolate sample during the first bite.</td>
</tr>
<tr>
<td>Melting in mouth</td>
<td>Amount of melted chocolate sample after 30 seconds, and ranges from little to very much melted.</td>
</tr>
</tbody>
</table>

plays an important role in the sensory assessment of chocolate. Plain chocolate brands show greater bite firmness than milk chocolates, and with respect to fineness, they are judged to be of a superior quality (Markov & Tscheuschner, 1989). Investigations of Markov and Tscheuschner (1989) show that brands of plain chocolate (special dark, dark and semisweet chocolate) melt more slowly than milk chocolates where the type of extender fat used is very important.

Desirable in chocolate is a firm solid product with a good snap at ambient and glossy appearance that melts easily in the mouth with a smooth mouthfeel. Excessively soft or hard, poor snap, sticky surface, not melting readily in the mouth and a gritty mouthfeel are all defects in texture. Mouthfeel of chocolate is subjective to geographical location of consumers (Cidell & Alberts, 2006), so assessment must be made in the context of market for which the product was developed. In dark chocolate, hardness and mouthfeel are influenced by particle size distribution, fat and lecithin content (Tyle, 1993; Afoakwa et al., 2008b); therefore, optimisation of grinding, refining and conching processes as well as composition controls chocolate texture. Tempering is central to gloss, snap, firmness and melting characteristics (Ley, 1988; Afoakwa et al., 2008c; Beckett, 2009).

### 5.3.3 Taste

The taste of chocolate is one of the key determinants of its acceptance or rejection. It is a cumulative experience of what we see with our eyes, taste with our tongue and smell with our noses. Upon seeing a chocolate product, visual cues set an expectation of delight and trepidation, dictating the first impression of acceptance or rejection of the food. Five basic taste receptors on our tongue detect the different taste characters in chocolate: sweet, salt, acid, bitter and umami. However, more complex taste sensations include the effects of heat, cooling and carbonation. These are detected by the trigeminal system, or ‘free nerve endings’ in the mouth and nose. Taste of food is intriguing, emotionally evocative and transportative, as it engages more of our senses. For instance, a delicious piece of chocolate when melting
in the mouth can often be accompanied by exclamations of pleasure. The taste of chocolate products being sweet, bitter, sour or salty (Table 5.1) is used as a critical factor for quality, and also dictates their preference and marketability by consumers. Chocolate taste is influenced to a very large extent by the ingredient composition than processing technology.

### 5.3.4 Flavour and aroma

Flavour is the most important factor that determines the acceptance and preference for chocolate products. Derived from cocoa genotype as well as post-harvest processing, it contributes immensely to final flavour and aroma of finished chocolates. Many researchers try to discover the phenomenon of chocolate taste, but up to now there is no definitive molecular description of this. From the sensory context, it is possible to indicate which flavours are recognised as positive or negative. Basically, the positive notes are those of aromatic character, acid, fruit, bitter and burnt (to some extent of course). Then the auxiliary flavours that are described as somewhat desirable are honey, malt, fudge, toffee, caramel and raisins. Undesirable flavours are beany, pungent, tobacco, herbal, spicy, phenolic, green, bready, earthy, mouldy, medicinal and hammy/smoky notes (Urbanski, 1992; Viaene & Januszewska, 1999). A complete chocolate flavour vocabulary and their descriptions have been given in Table 5.1.

Undesirable flavours are difficult to eliminate during manufacture, notably slaty beans which lack cocoa flavour; smoky or hammy notes to smoke contamination; inadequate drying with subsequent mould growth yields harsh and unpleasant flavours (Coe & Coe, 1996). Mechanical driers can enhance rates for loss of water and reduce those for loss of volatile acids, resulting in acidic cocoa influencing conching, and increase processing costs. Process control during roasting is important to yield the full cocoa flavour and ensuring uniform optimal roasting despite differences in bean sizes. Conching also plays a key role through volatilisation of undesirable compounds, as such failure to optimise this process component can cause diminished chocolate flavour (Beckett, 2008).

### 5.4 SENSORY ASSESSMENT OF CHOCOLATES

The sensory qualities of chocolates are mostly evaluated using descriptive sensory tests. In sensory evaluation, these tests are amongst the most sophisticated tools in the arsenal of the sensory scientist (Lawless & Heymann, 1998) and involve the detection (discrimination) and description of both the qualitative and quantitative sensory components of a consumer product by trained panels of judges (Meilgaard et al., 1991). Sometimes, many different basic procedures, such as the duo–trio test, are frequently used to compare products and determine if one is different from another. The qualitative aspects of a chocolate product include appearance, flavour, texture and taste, which distinguish one product from another. Sensory judges then quantify these product aspects in order to facilitate description of the perceived product attributes.

Recent surveys suggest that the use and application of descriptive sensory testing have increased rapidly, and will continue to do so in the confectionery industry for many years. A major strength of descriptive analysis is its ability to allow relationships between descriptive sensory and instrumental or consumer preference measurements to be determined. Knowledge of ‘desired composition’ allows for product optimisation, and validated models
between descriptive sensory and the relevant instrumental and/or preference measures are highly desirable and are increasingly being utilised within the confectionery industry.

Descriptive sensory analyses are also used for quality control, for the comparison of product prototypes to understand consumer responses in relation to products’ sensory attributes, and for sensory mapping and product matching (Gacula, 1997). It may also be used to track product changes over time with respect to understanding shelf-life and packaging effects, to investigate the effects of ingredients or processing variables on the final sensory quality of a product, and to investigate consumers’ perceptions of products (e.g. free-choice profiling).

There are several different methods of descriptive analysis that could be used to evaluate various sensory qualities of chocolate, including the flavour profile method, texture profile method, descriptive analysis, the spectrum method, quantitative flavour profiling, free-choice profiling and generic descriptive analysis. The specific methods reflect various sensory philosophies and approaches (Lawless & Heymann, 1998); however, generic descriptive analysis, which can combine different approaches from all these methods, is frequently employed during practical applications in order to meet specific project objectives.

Free-choice profiling might be an alternative because it is more rapid (assessors use their own descriptors), but direct comparisons of products are sometimes difficult.

### 5.5 FACTOR INFLUENCING CHOCOLATE FLAVOUR

The flavour of chocolate is made up of many odorous compounds – at least 800 of these have been identified chemically and probably many remain to be discovered (Counet et al., 2004; Taylor, 2004; Reineccius, 2006; Afoakwa et al., 2009b). In sensory terms, there are several qualities which are required in a good chocolate and which can be affected by processing. There is no accepted international list of terms for describing the taste of chocolate, but some of the more common ones, together with the processes which control them, are given in Figure 5.1. The flavour of a chocolate will obviously depend on the ingredients from which it is made.

Plain chocolate containing more of the same cocoa will have a richer cocoa taste; however, by changing the roast and/or the particle size distribution, it is possible to obtain a stronger cocoa flavour with less cocoa present (Voltz & Beckett, 1997). Particle size distribution is suspected to play a large role in determining chocolate flavour release. This hypothesis has been studied and would be discussed in detail in Chapter 11. The changing matrix from varying particle size distribution can be illustrated by grinding the same chocolate to a different fineness and carrying out taste tests. This is probably because the grinding changed the surface area of the different components; for example, initially the cocoa will have a much bigger surface area than the sugar (because the sugar has been pre-ground), but as the chocolate becomes finer the two will become more nearly equal. In addition, the viscosity is affected, which changes the residence time of the particles in the mouth. Both these factors will alter the probability of a particle touching one of the flavour receptors and hence would affect the flavour release.

In most chocolates, there is a balance between the cocoa and milk flavours. A harsh cocoa hides the milky creamy flavours, but once the cocoa intensity is reduced, the creaminess comes to the fore. Thus, milkiness depends strongly on the non-fat milk solids and the form in which they are incorporated into the chocolate. As well as noting the similarity in composition of the chocolate, Jackson (1999) noted the wide diversity of chocolate flavours in the market. Perhaps the most distinctive ‘house’ flavours are those of Hershey and Cadbury. In both cases
these can be produced from chocolate crumb (made by drying a milk–sugar–cocoa liquor mixture to about 1%). Here the heating under moist conditions produces cooked Maillard flavour notes, which are normally quite different from those found when heating the chocolate components in a drier condition in the conche. In addition, it is possible to produce other flavour notes by pre-treating the milk before producing the crumb (Beckett, 2003).

**5.6 FLAVOUR RELEASE AND PERCEPTION OF SWEETNESS IN CHOCOLATE**

Chocolate volatile flavour compounds are inherent in cocoa solids, and are perceived when released into the fat phase, and consequently vaporised and detected as it passes from the
gustatory to the olfactory space during mastication. Its rate of release and concentration is thus modulated by its concentration in cocoa solids and the particle’s surface area. Additionally, the release of chocolate flavour depends on the speed with which the flavour components reach the different receptors in the mouth and nose, which in turn depends on the viscosity of the chocolate and how it melts. This means that the flavour of chocolates with the same composition can vary if they flow differently. The perceived flavour characteristics are due to a combination of the taste, imparted by the non-volatile components, and the smell, imparted by the volatile components during consumption (Beckett, 2003).

The concentration of volatile compounds in the gustatory–olfactory space possibly affects the rapidity of saturation of mucosal fluids (that bathe the olfactory sensors) due to the high concentration gradient between the gaseous and liquid phases at perception, consequently eliciting a strong intensity for the perceived flavour/aroma. Thus, flavour volatiles that are released saturate the gustatory–olfactory space faster, eliciting a response of higher intensity, than volatiles that slowly saturate the space. This concept explains the effect of particle size variations on volatile flavour release and perception (Fig. 5.2).

Similar explanation can be made for non-volatile flavour aspects in cocoa solids such as bitterness, except that they are detected on the surface of the tongue after direct diffusion into saliva during mastication, as opposed to the volatiles that undergo a two-phase transition driven by increasing concentration gradient till it diffuses into fluid surrounding the olfactory receptors where it is detected.

Sweetness relates to solubilisation of the entire sugar crystal unlike bitterness, a component of cocoa solid amongst other volatile and non-volatiles. As such, large sugar crystals with a greater number of sugar molecules (high concentration) will elicit greater intensity of sweetness per unit area of the tongue than smaller crystal with lower number of sugar...
molecules. It is therefore suggested that in the case of sugar crystals, increased surface area affects its solubility rather than intensity (Beckett, 2008) of perception as the molecules that elicit sweetness form a solid crystalline structure that dissolves rather than diffuses. The surface area of particles will influence sweetness if sugar molecules were to be integrated into a solid matrix, in which case its release and perception from the solid matrix would be affected by variation in surface area.

5.7 DYNAMISM OF FLAVOUR PERCEPTION IN CHOCOLATE

Flavour perception is a complex process with sensory input from the tongue (gustation), the nose (olfaction) and the sense of touch (texture of the product) while a food or beverage is sipped, slurped, chewed and swallowed. Most undesirable attributes are perceived on the tongue, which determines the basic taste impression. We can perceive five basic taste directions on the tongue: sour, bitter, salt, sweet and umami (delicious). The different taste receptors on the tongue (ion channels and G-protein-coupled receptors) have all been identified, studied and characterised by flavour scientists (Eckert & Riker, 2007).

In general, flavour is considered as a combination of aroma, taste and trigeminal perceptions from stimulation of the mouth and nasal area. In chocolates, textural properties (hardness, consistency, cohesiveness and mouthfeel), salivation and oral manipulation may affect flavour release together with temperature, surface area and enzymes present. The volatile molecules released lead to aroma perception, which is sensed in the roof of the nose, at the nasal cavity. These volatile components are carried to the nasal cavity with air through the retronasal pathway during mastication. In the nasal cavity there are approximately 1000 types of odour receptor proteins to which the odourants may bind (Laing & Jinks, 1999; Taylor, 2004; Reineccius, 2006). When an odourant binds to a receptor protein, its chemical energy is transformed into electrical energy, which is then transmitted to olfactory structures in the brain. Each odourant produces its own characteristic spatial map in the olfactory bulb and other brain structures. The number of receptor cells involved is odourant and concentration dependent (Laing & Jinks, 1996). It is common view that only five types of taste qualities exist, namely sweet, salty, sour, bitter and umami. Figure 5.3 illustrates the location of flavour receptors in the human head.

Non-volatile molecules of foods may produce taste perceptions. These non-volatile compounds interact with taste-sensitive regions of the oral cavity, i.e. with taste receptor cells. Activation of trigeminal nerve endings in the oral and nasal areas is formed by these volatile and non-volatile substances, giving sensations of chemical burn (e.g. minty and peppermint) and irritation (e.g. carbon dioxide). Since the sensations of odour, taste and the trigeminal sense are difficult to locate and separate analytically when eating, the term ‘flavour’ is used to accommodate these perceptions. Chocolate flavour perception is time-dependent, as its structure changes during eating because of several factors, such as salivation and mastication (Beckett, 2003).

Many methods for the analysis of volatile flavour compounds in chocolate have been developed to give information on the total volatile composition of the food or the volatiles in the air above it (orthonasal perception). Recently, studies have been performed to investigate the flavour perception during consumption. For this reason, many mouth model systems enabling the investigation of the saliva, temperature and mastication on flavour release were
developed (Roberts & Acree, 1995; Deibler et al., 2001; Rabe et al., 2004). They simulate in a more or less simple way the eating and drinking processes, respectively. The complex swallowing process was visualised by video fluoroscopy and real-time magnetic resonance imaging, providing information about the transfer of aroma compounds to the odour receptors in the nasopharynx (Büttner et al., 2001).

5.8 RETRONASAL FLAVOUR RELEASE AND PERCEPTION DURING CHOCOLATE CONSUMPTION

The processes that occur in the mouth during chocolate consumption alter the physical properties of the food and can dramatically affect the perception of flavour and texture. Details of oral processing of a wide variety of food have been gathered using many different techniques, ranging from observations of muscle activity, jaw movement (Heath & Prinz, 1999), particle size distribution (Lucas & Luke, 1983), mixing efficiency (Prinz, 1999), bite mark analysis (Prinz & Lucas, 2000), facial movement, direct observation by videofluorography (Palmer & Hiiemae, 1997; Hiinemae & Palmer, 1999) and ultrasound imaging (Soder & Miller, 2002). Common findings from all these sources are that the following steps are involved in mastication: (i) food is placed onto the anterior one-third of the tongue; (ii) the tongue is elevated, compressing the food against the palate; (iii) the tongue is depressed, transferring solid foods to the post-canine teeth; (iv) communition; (v) swallowing; and (vi) clearance (Prinz & de Wijk, 2004).

Chocolate, solid at room temperature (20–25°C), melts at body temperature (37°C), during consumption giving a smooth suspension of particulate solids (of sugar, cocoa and non-fat solids in case of milk chocolate) in cocoa butter (with milk fat for milk chocolate). The process of eating, from ingestion to swallowing, is modulated by oral sensations that are in turn affected by the process itself (Alfonso et al., 2002). Food begins to be assessed even before it is placed in the mouth, which can result in increased salivation, and a decision is made as to the size of bite to be taken. The first bite is taken and the food is placed on tip of the tongue. At this point, the temperature is assessed, both in absolute terms and in terms of...
its rate of heating or cooling, which in turn allows the fat content of the food to be assessed (Prinz & de Wijk, 2004).

In the interval between the chocolate entering the mouth and being swallowed, its temperature equilibrates to mouth temperature, it is mixed with saliva allowing the various salivary enzymes to exert their effects, and the solids are melted into semiliquids, which may then undergo shear-thinning. As the chocolate melts, the continuous fat phase goes through an inversion to a continuous water phase and mixes with saliva, which acts as solvent for the sugar particles and coats all particle surfaces to facilitate swallowing. Suspended particles, with the exception of cocoa, are dissolved in the mouth at a rate corresponding to their size and work input in the form of mastication, tongue compression and swallowing (Lee & Pangborn, 1986), and the rate of dissolution of particles can influence the perception of flavour (Martin, 1987). Fragmentation of the solid particles during melting increases the surface area that is exposed to the saliva, thus increasing the rate at which taste compounds can dissolve into the saliva and from there be transported to the taste receptors. The increase in surface area and the warming of the particulate components facilitate the release of volatiles, giving rise to enhanced flavour sensations (Engelen et al., 2003). Furthermore, aerosols may form as the tongue is removed from the palate, again intensifying flavour release.

While the tongue is in contact with the palate, the food is subjected to high shear forces, which not only lead to shear-thinning of the stimulus but can also result in coalescence of fat droplets, wetting the mucosal surface with oil, increasing the surface area available for volatilisation and allowing more intimate contact between the oil and the taste receptors (Prinz & de Wijk, 2004). All these effects combine to enhance the flavour perception and release during chocolate consumption. Changes in particle size distribution are therefore expected to affect the rate and magnitude of taste and flavour attributes associated with the particulate components. Prinz and de Wijk (2004) noted that in solid foods, the particle size distribution resulting from fragmentation through chewing and the resulting production of new surface area can be quantified (Liedberg & Owall, 1995; Prinz & Lucas, 1997). In the same way that the oral behaviours described above can increase the intensity of oral sensations, the intensity of orthonasal olfaction can be increased by sniffing. This increases the volume of air passing over the olfactory epithelium and induces turbulence in the airflow, which facilitates mass transfer (Laing, 1983). Holding the head downwards can further enhance retronasal olfaction by allowing the ovula to come forwards, facilitating the flow of aromas from the mouth to the nose (Zafar et al., 2000; Matsubara et al., 2002; Prinz & de Wijk, 2004). The temporal aspects of flavour release and its effect on perception have been studied in chewing gum (Neyraud et al., 2003).

The ease with which chocolate can be melted and manipulated in the mouth depends on the properties of the suspension. Chocolates with high viscosity are known to have a pasty mouthfeel and persist for a longer time in the mouth (Afoakwa et al., 2008d). Viscosity of chocolates can vary for the same composition due to differences in their particle size distribution. The modification of apparent viscosity in aqueous solutions is known to affect the perception of aroma, flavour by mouth and taste intensity during consumption (Denker et al., 2006). Viscosity, in itself, is an important descriptive sensory attribute of fluid and semisolid foods. Procedures for the determination of chocolate viscosity emphasise its inherent nature. The dynamic behaviour of perceived sensory attributes in combination with the effect of melting on taste and flavour in chocolates has been investigated using retronasal flavour release and time–intensity (TI) methods (Daget & Vallis, 1994; Janestad et al., 2000; Ziegler et al., 2001).
5.9 MEASUREMENT OF FLAVOUR RELEASE AND INTENSITY IN CHOCOLATES

Chocolate exhibits the unique property of melting from a solid state at room temperature to a smooth dense suspension in the mouth at body temperature. The melting of chocolate in the mouth is defined by the characteristics of the lipid phase (Beckett, 2003) and facilitates the perception of its characteristic taste, flavour and textural attributes. The intensity of perceived flavour changes dynamically over time as the chocolate is melted, manipulated and mixed with saliva for swallowing (Lee & Pangborn, 1986).

Traditionally, the sensory attributes of milk chocolate have been measured as single-point values using quantitative descriptive methods (Burger, 1992). Attributes that are typical of and contribute to the flavour of milk chocolate have been measured using trained panelists to assess the changes in chocolate quality due to process and composition (Aguilar & Ziegler, 1995). These methods, however, provide only a single facet of information about the sample. Information such as the rate at which an attribute is perceived to its maximum intensity or the duration for which an attribute is perceived can be equally important in forming a basis of differentiation between samples. Such information can be obtained through the use of TI analysis (Noble et al., 1991).

Time–intensity techniques provide a visual relationship between the perceived strength of a single attribute and the duration of its perception (Burger, 1992). In addition to providing information regarding the intensity perception of the attribute, this technique allows for comparison of samples on the basis of rate parameters and it can be used to differentiate between samples that might show similar responses on a descriptive scale (Lundahl, 1992; Guinard et al., 2002; Ovejero-López et al., 2005). Time–intensity measurements allow for establishing a pattern of development and decline of a particular sensory characteristic under study. The methodology offers dynamic, time-related data, which is consistent with the continuous changes in the sensory perception. The dynamic response to the stimulus by the judges results in TI curves. A TI curve is shown in Figure 5.4. Time–intensity curves are interpreted in terms of a number of parameters. These parameters can be representative of the time (e.g. time to maximum intensity), intensity (e.g. maximum intensity of the attribute), rate (e.g. rate of increase to maximum intensity) or the magnitude of perceived stimulation (e.g. area under the curve).

Regarding the analysis of TI data, important progress was made in 1986, when Overbosch and others introduced a method to average curves creating a common intensity range for the TI curves (Overbosch et al., 1986). They focused on three main parameters: the maximum perceived intensity ($I_{\text{max}}$), the time of maximum perceived intensity ($T_{\text{max}}$) and the time after which the flavour is no longer perceived. Later, MacFie and Liu (1992) developed a method based on a different order of averaging variables in two-dimensional curves. They basically normalised in the intensity and time dimensions to yield improvement in the precision of the average curves, using the same set of data (Ovejero-López et al., 2005).

A number of parameters can be extracted from TI curves (Lee & Pangborn, 1986). Applications of computers in sensory science now allow for as many as 13 parameters from one such curve (Noble et al., 1991). The parameters have usually been calculated from a curve obtained by averaging the curves of individual panellists. Simple averaging of the curves, however, does not always represent the data accurately (Dijksterhuis & Eilers, 1997).
The curves obtained for time-intensive analysis are typical of the individual panellists. The unique shape of individual curves presents a challenge for generating a consensus curve and extracting useful information from the data. Averaging of the curves can be influenced by atypical responses and is prone to loss of information (MacFie & Liu, 1992). Construction of a curve to represent the characteristics of individual curves is not straightforward. Several alternative methods have been proposed for the calculation of representative average curves. Some of the suggested alternative methods include normalising of data along the intensity scale (Overbosch et al., 1986), normalising the data along both the time and the intensity scales (MacFie & Liu, 1992), and principal component analysis (van Buuren, 1992; Dijksterhuis et al., 1994; Guinard et al., 2002; Ovejero-López et al., 2005).

The TI methods for scaling sensory attributes pose several challenges with respect to the data collection, training format of the panellists, slower rate of data acquisition and most importantly the data analysis process. In spite of these challenges, TI is the only method available that would allow for assessment of differences between samples of chocolate with varying composition with respect to the perception of basic flavour, taste and texture attributes over the time of consumption. Beckett (2000) explained that finer particles tend to give a claggy or pasty chocolate that is harder to manipulate in the mouth. As a consequence, the perceived intensities and the duration of the perception of flavour and attributes may be affected (Lee et al., 1992). There are conflicting reports about the effect of viscosity on the perception of taste in the literature. While viscosity is known to affect the perception of sweetness in solutions and gel products, it does not affect the perception of chocolate flavour in desserts (Pangborn & Kayasako, 1981), thus requires further investigation especially into chocolate systems.
5.10 **ELECTRONIC NOSES AND TONGUES AS ONLINE SENSORS FOR SENSORY ASSESSMENT OF CHOCOLATES**

Electronic noses and tongues are relatively young and modern technologies that could be employed to assess the flavour/odour quality of chocolates. The processes use chemical array sensor systems for flavour, odour and taste classifications. Electronic noses perform odour assessment on a continuous basis at a low cost based on the concept of mammalian olfactory system. Once the volatile compounds reach the olfactory epithelium, the interactions of odourants with the appropriate chemosensory receptors, olfactory neurons, produce electrical stimuli transmitted to the brain. It was evidenced that a single olfactory neuron responded to several odourants and each odourant was sensed by multiple olfactory neurons.

The e-nose uses ultra-high-speed gas chromatography and a solid-state chemical sensor to quickly analyse the chemistry of flavours, aromas, odours or vapours with parts per trillion sensitivity. It mimics the way the systems of interconnected receptors and neurons in the incomparable and irreplaceable human nose interact and respond to vapour molecules based on analysis of the cross-reactivity of an array of semiselective sensors. The signals are processed via a pattern recognition program. During its operation, an array of sensors, composed of polymers, for example, expands like a sponge when it comes in contact with volatile compounds in the headspace of a sample, increasing the resistance of the composite. The normalised change in resistance is then transmitted to a processor to identify the types, quantity and quality of the odours based on the pattern change in the sensor array (Leake, 2009).

An electronic tongue works with the gas phase of a volatile compound, while an electronic tongue works in the liquid phase of a non-volatile compound. Both instruments can be used to identify flavour varieties and geographical origin, composition, aroma intensity and degree of freshness. Electronic noses are also suitable for measuring release of gases and odours from packaging materials. However, its application requires appropriate sampling steps and the training of electronic noses based on sensory panel classifications to obtain odour-meaningful classifications. Moreover, the biological sensitivity can go down to parts per trillion levels with a response time of milliseconds, whereas instruments barely go under parts per billion levels with a response time of seconds. E-noses could be used for quality control applications in the confectionery industry to detect conformity control of raw materials, processed or end-product quality, batch-to-batch consistency, certification of origin and clean-in-place process monitoring.

On the other hand, electronic tongue (e-tongue) measures dissolved compounds responsible for taste in liquids. It can be used to detect major tastes such as sweet, sour, bitter, salty and umami, which resembles effects of subtaste attributes such as spicy and metallic. This could as well be used in diverse applications in the confectionery industry to do a complete bitterness/sweetness assessment of new products. They could also be used to measure the taste-masking abilities of some confectionery products with new or different ingredients. These capacities could speed up research activities where variations in the sensory qualities of the end products are desired.

5.11 **CONCLUSION**

The sensory character of chocolate plays vital roles in dictating the preference, palatability and acceptability of finished products. During manufacture, several factors combine to
determine the final sensory profile of products, with subsequent impacts on the texture, mouthfeel, taste and flavour/aroma. Factors that determine why and which foods are consumed are numerous, but for chocolate, unique sensory properties are perhaps paramount. Sensory perception of chocolate depends on four factors: wonderful and clear chocolate flavour, sweet taste, smooth texture and luxurious melt-in-the-mouth quality. To remain vibrant in this modern competitive chocolate industry, all these quality attributes must be thoroughly investigated in relation to consumer needs and development of new products.
6 Nutritional and health benefits of cocoa and chocolate consumption

6.1 SUMMARY AND SIGNIFICANCE

Cocoa and chocolate have been acclaimed for several years for their possible medicinal/health benefits, but it is only recently that some of these claims are being more clearly identified and studied. Recent epidemiological and clinical studies have shown that dietary supplementation with flavonoid-rich cocoa and chocolate may exert suppressive effects on low-density lipoprotein (LDL) oxidation and the associated development of atherosclerosis with cardioprotective implications because of their interference in many pathophysiological mechanisms. Some of the identified beneficial effects include antioxidant properties, blood pressure lowering via the induction of nitric oxide (NO)-dependent vasodilation in men, improvement in endothelial function, increased insulin sensitivity, decreased platelet activation and function, as well as modulation of immune function and inflammation. Furthermore, chocolate has been reported to release phenylethylamine and serotonin into the human system, when consumed, producing some aphrodisiac and mood-lifting effects. Since these claims may possibly have implications on consumption levels of cocoa and chocolate products in the global market, understanding the critical factors involved and their potential beneficial effects would be of great importance to consumers.

6.2 INTRODUCTION

Cocoa and chocolate products have recently attracted the attention of many investigators and the general consuming public because of their potential nutritional, medicinal and mystical properties. Chocolate is a very complex food and scientists continue to investigate it in order to unlock its potential benefits and secrets. When consumed, it has been observed to have effects on human behaviour and health. Over the past decade, several studies have reported that their consumption can contribute to the attainment of optimal health and development as well as play an important role in reducing the risk or delaying the development of chronic diseases, such as cardiovascular disease (CVD), cancer and other age-related diseases (Adamson et al., 1999; Hammerstone et al., 2000; Afoakwa, 2008; Cooper et al., 2008).

Recently, chocolate has gained a reputation as being an aphrodisiac in common with lobster, crab legs, pine nuts, walnuts, alcohol and Viagra. In most parts of the world, chocolate is associated with romance, and not without good reason, as it was viewed as an aphrodisiac by the Mayan and Aztec cultures who thought it invigorated men and made women less inhibited (Doughty, 2002). The reputed aphrodisiac qualities of chocolate are most often associated with the simple sensual pleasure of its consumption. Additionally, chocolate’s sweet
and fatty nature is reported to stimulate the hypothalamus, inducing pleasurable sensations as well as affecting the levels of serotonin in the brain, hence enhancing sexual drive (Kenneth, 1996; di Tomaso et al., 1996). Finally, chocolate has been shown to contain unsaturated N-acylethanolamines, which might activate cannabinoid receptors in humans or increase their endocannabinoid levels resulting in heightened sensitivity and euphoria (di Tomaso et al., 1996).

Over the past decade, biochemical and physiological associations among hypertension, diabetes, sexual weakness and CVD have grown steadily, supported by basic, clinical and epidemiological research. As possibilities exist for treating these pathologies through pharmacologic approaches, lifestyle adjustment and diet modification, identification of foods that have aphrodisiac qualities and cardiovascular health benefits and understanding how these food components influence normal human physiology would help improve public health. This chapter discusses current information relating to the acclaimed aphrodisiac and other beneficial health implications of cocoa and chocolate consumption, based on epidemiological, pre-clinical and clinical studies conducted over the past decade.

### 6.3 CHEMISTRY AND COMPOSITION OF COCOA FLAVONOIDS

Cocoa and its derived products – chocolate and cocoa powder – are rich in flavonoids, characterised as flavan-3-ols or flavanols and include the monomeric forms, (−)-epicatechin and (−)-catechin, and the oligomeric form of the monomeric units, the procyanidins (Fig. 6.1) (Wollgast & Anklam, 2000a; Engler & Engler, 2006; Cooper et al., 2008).

These flavonoids are stored in the cotyledon pigment cells of cocoa bean, the fruit of the cocoa tree (Theobroma cacao), and are differentiated in three main groups: catechins or flavan-3-ols (≈37%), anthocyanins (≈4%) and proanthocyanidins (≈58%). Less abundant is (−)-catechin with only traces of (−)-gallocatechin and (−)-epigallocatechin. The anthocyanin fraction is dominated by cyanidin-3-α-L-arabinoside and cyanidin-3-β-D-galactoside. Procyanidins are mostly flavan-3,4-diols, 4–8 or 4–6 bound to form dimers, trimers or oligomers with epicatechin as main extension subunit (Romanczyk et al., 1997; Gu et al., 2006).

The flavonoids represent a ubiquitous and abundant group of polyphenols consumed in the diet, primarily from fruits and vegetables, derived from plants and act as antioxidants due to their free radical scavenging properties, their ability to reduce the formation of free radicals and their ability to stabilise membranes by decreasing membrane fluidity (Arora et al., 2000; Kromhout et al., 2002). These antioxidant properties may contribute to the mounting evidence that a diet rich in fruits and vegetables reduces the risk of CVD. Metabolic and epidemiological studies indicate that regular intake of such products increases the plasma level of antioxidants, a desirable attribute as a defence against reactive oxygen species. As well, the antioxidants in cocoa can prevent the oxidation of LDL cholesterol, related to the mechanism of protection in heart disease. A few studies have shown that reactive oxygen species associated with carcinogenic processes is also inhibited (Krawczyk, 2000; Pietta, 2000; Engler & Engler, 2006). More so, the fats from cocoa (cocoa butter) are mainly stearic triglycerides (C18:0) that are less well absorbed than other fats and tend to be excreted in the faeces. They are thus less bioavailable and have minimal effect on serum cholesterol (Wollgast & Anklam, 2000b; Cooper et al., 2008).
Nutritional and health benefits of cocoa and chocolate consumption

Many investigators have identified the common classes and food sources of flavonoids to include flavanol [quercetin, kaempferol, myricetin (in onions, apples, tea and red wine)], isoflavones [daidzein, genistein (in soy)], flavan-3-ols or flavanols [catechin, epicatechin (in tea, chocolate, red wine)], flavanones [naringenin, hesperitin (in citrus fruits)], flavones [apigenin (in celery), luteolin (in red pepper)] and anthocyanins (in pigments of red fruits such as berries and red grapes) (Engler & Engler, 2006). These different classes of flavonoids are based on their level of oxidation in the basic flavonoid structure (C6–C3–C6), a 15-carbon atom structure arranged in three rings (two aromatic rings on the ends with an oxygenated heterocycle in the middle). Evidence from epidemiological studies suggests that a high intake of dietary flavonoids may reduce the risk of coronary heart disease (Vinson et al., 1999; Wollgast & Anklam, 2000b; Kraus et al., 2001). Flavonoids have also been reported to have a beneficial influence on oxidative stress, vascular function, platelet function and immune response, which may collectively be involved in the process of atherogenesis.

Fig. 6.1 Chemical structure of the major cocoa flavanols: (−)-epicatechin and (+)-catechin and procyanidin.
6.4 CHOCOLATE TYPES AND THEIR MAJOR NUTRITIONAL CONSTITUENTS

Chocolate is a dense suspension of solid particles with an average solid concentration of approximately 60–70% from sugar, cocoa and milk (depending on type), dispersed in a continuous fat phase, which is mostly composed of cocoa butter. After processing, finished chocolates could be moulded into different forms and shapes either manually or mechanically, and packaged for sale. Some of the shapes mostly used include squares, rounded edges, rectangles and ovals as shown in Figure 6.2(a). They may also be presented in the form of round (balls), heart shaped (Fig. 6.2(b)), etc., with specific top designs that are intended to enhance their appeal to consumers. The main chocolate categories are dark, milk and white (Fig. 6.2(c)), differing in content of cocoa solid, milk fat and cocoa butter. The outcome is varying proportions of carbohydrate, fat and protein content (Table 6.1).

Cocoa refers to the non-fat component of cocoa liquor (finely ground cocoa beans), used in chocolate manufacture in the form of cocoa liquor (containing \(\sim\)55% cocoa butter) or cocoa powder (\(\sim\)12% fat), with addition of sugar, cocoa butter and/or milk. Apart from chocolate, other cocoa products include cocoa powder consumed as beverage, which is very popular in most African countries. Despite the varied chemical contents, cocoa and chocolate consumption makes a positive contribution to human nutrition through provision of the major constituents – carbohydrates, fat and protein for energy and other metabolic functions. Chocolates also contain minerals, specifically potassium, magnesium, copper and iron. In addition, cocoa and chocolate fat contain many fatty acids, triglycerides dominated
Table 6.1 Nutritive value of chocolate products

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Cocoa powder</th>
<th>Cocoa liquor</th>
<th>Dark chocolate</th>
<th>Milk chocolate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy (kcal/100 g)</td>
<td>452</td>
<td>580</td>
<td>530</td>
<td>518</td>
</tr>
<tr>
<td>Protein (g/100 g)</td>
<td>20.4</td>
<td>11</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td>Carbohydrate (g/100 g)</td>
<td>35.0</td>
<td>28</td>
<td>55</td>
<td>57</td>
</tr>
<tr>
<td>Fat (g/100 g)</td>
<td>25.6</td>
<td>55</td>
<td>32</td>
<td>33</td>
</tr>
<tr>
<td>Calcium (mg/44 g)</td>
<td>74.4</td>
<td>40.0</td>
<td>14.1</td>
<td>84.0</td>
</tr>
<tr>
<td>Magnesium (mg/44 g)</td>
<td>261.4</td>
<td>138.2</td>
<td>90</td>
<td>26.4</td>
</tr>
<tr>
<td>Iron (mg/44 g)</td>
<td>6.1</td>
<td>5.9</td>
<td>1.4</td>
<td>0.6</td>
</tr>
<tr>
<td>Copper (mg/44 g)</td>
<td>2.0</td>
<td>1.1</td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td>Phosphorus (mg/44 g)</td>
<td>349.8</td>
<td>190.5</td>
<td>58.1</td>
<td>95.0</td>
</tr>
<tr>
<td>Potassium (mg/44 g)</td>
<td>905.5</td>
<td>450.6</td>
<td>160.6</td>
<td>169.4</td>
</tr>
<tr>
<td>Sodium (mg/44 g)</td>
<td>4.0</td>
<td>1.3</td>
<td>4.8</td>
<td>36.1</td>
</tr>
<tr>
<td>Zinc (mg/44 g)</td>
<td>3.5</td>
<td>1.9</td>
<td>0.7</td>
<td>0.6</td>
</tr>
</tbody>
</table>


The antioxidants in cocoa, principally polyphenols, including flavonoids such as epicatechin, catechin and notably the procyanidins are also thought to provide added medicinal/health benefits. However, white chocolates differ from milk and dark through the absence of cocoa solids containing antioxidants, and thus make no potential contribution to the polyphenol-induced improvements in human health. It is also important to note that most dark chocolate contains higher amounts of antioxidant cocoa flavanols than does milk chocolate.

For example, a 40-g serving of milk chocolate provides 394 mg of cocoa flavonoids, whereas dark chocolate contains 951 mg of cocoa flavonoids. Hot cocoa mix, in contrast, contains 45 mg of cocoa flavonoids in a 240-mL serving (Vinson et al., 1999; Engler & Engler, 2006). These numbers represent typical cocoa flavonoid concentrations and are dependent on the chocolate processing methods, which may reduce or retain the amount of flavonoids derived from the cocoa bean. Considering reported research on cocoa and chocolate, respectively, milk chocolate compared to dark (black) chocolate has been less of an object of investigation because the amounts of polyphenols in milk chocolate are smaller than in dark chocolate due to the lower amount of cocoa liquor used in milk chocolate (∼10 ± 15%) compared to dark chocolate (∼30 ± 50%). In addition, milk proteins, especially caseins being relatively proline rich, may impair absorption of procyanidins due to complexation (Wollgast & Anklam, 2000b). Thus, dark chocolate seems a priori to have a higher potential in being the most beneficial to human health.

### 6.5 ANTIOXIDANT PROPERTIES AND THEIR MECHANISM OF ACTION

Cocoa powder and chocolate have been shown to have antioxidant potential and to inhibit LDL oxidation in vitro (Lee et al., 2003). Studies have shown that ingestion of a single bolus of cocoa or chocolate increases the antioxidant capacity of plasma, decreases the formation...
of plasma 2-thiobarbituric acid-reactive substances (TBARS), increases insulin sensitivity, and inhibits LDL oxidation ex vivo (Ou et al., 2001; Lee et al., 2003; Prior et al., 2003; Grassi et al., 2005). Evidence suggests that long-term consumption of cocoa polyphenols also increases the antioxidative capacity of plasma (Wan et al., 2001). However, studies dealing with the effects of long-term consumption of chocolate on lipid peroxidation in vivo are scarce and therefore warrant further investigations.

Several approaches have been used to investigate the mechanism of action of cocoa flavanoids including pre-clinical, clinical and in vitro studies predominantly for their effects on the vascular system, with nitric oxide (NO) concentration being the central target (Fig. 6.3) using their effects on endothelial function, which is thought to be a good biomarker for estimating coronary disease risk (Cooper et al., 2008). In vitro cocoa procyanidins have been shown to be antioxidative as well as chelators of copper and iron and thereby capable of preventing LDL from oxidation. In addition, procyanidins inhibit cyclo-oxygenase 1 and 2 (COX-1 and COX-2), and lipoxygenase. By enhancing levels of NO, having been identified as the endothelial-derived relaxing factor, derived from constitutive endothelial nitric oxide synthase (eNOS), procyanidins could cause vasodilatation (Wollgast & Anklam, 2000b). Romanczyk et al. (1997) suggested that although the polyphenolic compounds inhibit the oxidation of LDL, the more comprehensive effect is their multidimensional effects on atherosclerosis via NO. Beneficial effects of NO modulation include regulation of blood pressure, lowering NO affected hypercholesterolemia and monocyte adhesion, all of which are involved in the progression of atherosclerosis. As well, many clinical trials have shown improved epithelial function after chocolate consumption, with neutral effects on total serum cholesterol (Mathur et al., 2002; Engler et al., 2003; Engler et al., 2004; Engler & Engler, 2006). Other effects related to CVD risk include inhibition of platelet activation and aggregation (Rein et al., 2000a; Steinburg et al., 2003; Lamuela-Raventos et al., 2005). This is probably due to the high content of stearic acid (~30% of fatty acids), which is considered to be neutral with respect to total and LDL cholesterol.

Consumption of cocoa or dark chocolate might also have beneficial effects on serum lipids. In a recent study, the consumption of cocoa with dark chocolate increased the serum concentration of low-density lipoprotein (LDL) cholesterol by 4%, as a result of the antioxidant properties of flavonoids, which might have partially accounted for the protective effect. The oxidative modification of LDL also plays an important role in atherogenesis, and agents that are able to prevent LDL oxidation in the arterial wall have been noted to delay the onset of atherosclerosis in humans (Engler et al., 2003; Steinburg et al., 2003; Cooper et al., 2008).

### 6.6 EFFECTS ON ENDOTHELIAL FUNCTION, BLOOD PRESSURE AND CARDIOVASCULAR SYSTEM

Investigators have recently focused attention on flavan-3-ols as bioactive compounds, particularly with respect to their beneficial effects on endothelial function, blood pressure and cardiovascular function. Many of these studies have reported that cocoa and chocolate consumption are associated with short-term improvements in delayed oxidation of LDL cholesterol (Wan et al., 2001), improved endothelial function (Engler et al., 2004; Hermann et al., 2006), lowered blood pressure (Grassi et al., 2005), increased insulin sensitivity (Grassi et al., 2005) and improved platelet function. A recent 15-year epidemiological study of elderly Dutch men showed that blood pressure was significantly lowered in the group
Nutritional and health benefits of cocoa and chocolate consumption

Cocoa polyphenols

Oxidative stress

Arginine

eNOS

NO

Peroxinitrite

Endothelial dysfunction

Lipoprotein oxidation

Platelet aggregation

Inflammation

Cardiovascular risks

Fig. 6.3 The role of cocoa polyphenols on the vascular system, with nitric oxide as target. eNOS = endothelial nitric oxide synthase.

Consuming cocoa/chocolate. The groups with the highest cocoa and chocolate consumption were also reported to have a lower incidence of death due to CVD compared to men who did not consume cocoa or chocolate (Buijsse et al., 2006). Taubert et al. (2007) also stated that small amounts of commercial cocoa confectionary conveyed similar blood pressure-lowering potential compared with comprehensive dietary modifications that have proved efficacy to reduce cardiovascular event rate. They explained that whereas long-term adherence to complex behavioural changes is often low and required continuous counselling (McCullough et al., 2000; Appelm et al., 2003), adoption of small amounts of flavanol-rich cocoa into the habitual diet is a dietary modification that is easy to adhere to and therefore may be a promising behavioural approach to lower blood pressure in individuals with above-optimal blood pressure.

Although chocolate and cocoa consumption have been reported to have favourable effects on lipid peroxidation ex vivo and on serum concentration of HDL (Arora et al., 2000; Engler & Engler, 2006), very few long-term studies of the effects on lipid peroxidation in vivo have been published. Previous studies have shown that the concentration of serum HDL cholesterol and the oxidative modification of LDL play important roles in the pathogenesis of atherosclerosis (Lamuela-Raventos et al., 2005; Buijsse et al., 2006; Gu et al., 2006), with reports that the consumption of cocoa or chocolate may have beneficial effects on both of these factors in humans. In many of these studies, consumption of cocoa and dark chocolate was reported to increase the concentration of HDL cholesterol and plasma antioxidant capacity and decreased the formation of lipid oxidation products (TBARS) (Rein et al., 2000b; Wang et al., 2000).
In another study, Mursu et al. (2004) found that the concentration of HDL cholesterol increased in healthy humans receiving chocolate that contained cocoa mass. The increase in HDL cholesterol was 11% after the consumption of dark chocolate and 14% after the consumption of dark chocolate enriched with cocoa polyphenols, whereas no effect was observed after the consumption of white chocolate. The ratio of LDL/HDL also changed in a similar manner, suggesting that because the fatty acid content in the study chocolates was identical, the compounds in the cocoa mass were responsible for the increase in HDL cholesterol.

Data documenting a beneficial effect on HDL concentration are supported by a reported, long-term, crossover study. Wan et al. (2001) found that after daily consumption of 22 g of cocoa powder and 16 g of dark chocolate for 4 weeks, the concentration of HDL cholesterol was 4% higher compared to the control diet (average American diet). The higher amount of chocolate ingested (75 g or the equivalent of two candy bars) might explain the greater increase in the HDL cholesterol (11–14%) reported by Mursu and colleagues (2004). A high concentration of HDL cholesterol has been shown to decrease the risk of CVDs (Castelli et al., 1986). As well, concentration of HDL cholesterol can usually be increased by 10–15% by changing lifestyle behaviour, but this strategy is not suitable for everyone, since it can only be meaningfully achieved by vigorous exercise or moderate alcohol consumption (Safeer & Cornell, 2000).

The consumption of chocolate also inhibited significantly the oxidation of LDL in vivo, as measured in the formation of conjugated dienes. The decrease in LDL peroxidation in these study groups indicated the likelihood of this effect due to the fatty acids in chocolate. It has previously been reported that, compared to polyunsaturated fatty acids, monounsaturated fatty acids inhibit lipid peroxidation (Reaven et al., 1991; Bonanome et al., 1992; Gutteridge and Halliwell, 1994; Eritsland, 2000). Thus, a high consumption of saturated or monounsaturated fat in the form of chocolate may modify the lipid content of LDL to make it more resistant to oxidation by increasing the amount of monounsaturated and saturated fats, and by decreasing the amount of polyunsaturated fatty acids.

6.7 EFFECTS ON INSULIN SENSITIVITY AND CARCINOGENIC PROPERTIES

Cocoa and dark chocolate consumption has been claimed to protect the vascular endothelium by augmenting NO availability and thereby improving endothelium-dependent vasorelaxation (Karim et al., 2000; Ross & Kasum, 2002; Fisher et al., 2003; Engler et al., 2004). In attempt to expand on these findings, Grassi et al. (2005) studied the effects of consuming either dark or white chocolate on the homeostasis model assessment of insulin resistance and the quantitative insulin sensitivity check index in 15 healthy young adults with typical Italian diets that were supplemented daily with 100 g dark chocolate or 90 g white chocolate, each of which provided 480 kcal. The polyphenol contents of the dark and white chocolate were assumed to be 500 and 0 mg, respectively. Dark chocolate ingestion not only decreased blood pressure but also improved glucose metabolism and insulin sensitivity in the subjects. They explained that polyphenol-rich dark chocolate, but not white chocolate (which contains mainly sugar and cocoa butter), decreased their blood pressure and improved their insulin sensitivity.

In another study, Romanczyk et al. (1997) examined anticarcinogenic properties of cocoa extracts, using several human cancer cell lines. Interestingly, the effects were seen only with
oligomeric procyanidins and of these in particular oligomers of 5 ± 12 subunits, with the most effective being the pentamer. It was suggested that the mechanisms by which procyanidins exert anticarcinogenic activity include inhibition of DNA strand breaks, DNA–protein cross-links and free radical oxidation of nucleotides due to their antioxidative activity as well as inhibition of enzyme activities of cyclo-oxygenase 2 (COX-2) and DNA topoisomerase II. Moreover, procyanidins modulate NO production by macrophages, possessing an inducible nitric oxide synthase (iNOS), and thereby affecting ribonuclease reductase, the enzyme that converts ribonucleotides to deoxyribonucleotides necessary for DNA synthesis. Inhibition of DNA synthesis may be an important way in which macrophages and other tissues possessing iNOS can inhibit the growth of rapidly dividing tumour cells or infectious bacteria. These findings indicate that cocoa and dark chocolate consumption may exert anticarcinogenic activity in human cells, and offer protective action on the vascular endothelium, by improving insulin sensitivity, thereby exerting favourable metabolic effects in humans with further protection against CVDs. Obviously, since these findings cannot be generalised for all populations, large-scale trials are needed to confirm these protective actions of dark chocolate or other flavanol-containing foods in populations affected by insulin-resistant conditions such as essential hypertension and obesity.

6.8 COCOA, CHOCOLATE AND APHRODISIAC PROPERTIES

Cocoa and chocolate have been reported to exert several effects on human sexuality, mainly acting as an effective aphrodisiac, increasing sexual desire and improving sexual pleasure (Salonia et al., 2006). They have been claimed to contain a chemical substance known as phenylethylamine, which has been reported to stimulate the hypothalamus, inducing pleasurable sensations as well as affecting the levels of two neurotransmitters – 5-hydroxytryptamine (serotonin) and endorphins in the brain, hence enhancing mood lifting and sexual drive (Kenneth, 1996). These chemicals occur naturally and are released by the brain into the nervous system during situations of happiness, feelings of love, passion and/or lust. This causes a rapid mood change, a rise in blood pressure, increasing the heart rate and inducing those feelings of well-being, bordering on euphoria usually associated with being in love.

In other studies, the cocoa in chocolate was reported to contain several potentially psychoactive chemicals, for instance the sympathomimetic biogenic amines, tyramine and phenylethylamine, and the methylxanthines, theobromine and caffeine (Hurst & Toomey, 1981; Hurst et al., 1982; Max, 1989). Spampinato (2007) noted that each 100 g of chocolate contains 660 mg of phenylethylamine (C₉H₅(CH₂)₂NH₂), a stimulant similar to the body’s own dopamine and adrenaline. Phenylethylamine was noted to raise blood pressure and heart rate, heightening sensations and blood glucose levels (Spampinato, 2007). Since eating chocolate gives an instant energy boost, increasing stamina, it is no wonder why its effects have given it a reputation as an aphrodisiac. In addition, both compounds can be mildly addictive, explaining the drive of chocoholics. However, women are more susceptible to the effects of phenylethylamine and serotonin than men (Salonia et al., 2006), explaining why women tend to be chocoholics more than men.

Chocolate has also been shown to contain unsaturated N-acylethanolamines, which might activate cannabinoid receptors or increase endocannabinoid levels, resulting in heightened sensitivity and euphoria. Researchers believe that chocolate contains pharmacologically
active substances that have the same effect on the brain as marijuana, and that these chemicals may be responsible for certain drug-induced psychoses associated with chocolate craving (Rozin, 1991). Although marijuana’s active ingredient that allows a person to feel ‘high’ is tetrahydrocannabinol, a different chemical neurotransmitter produced naturally in the brain called anandamide has been isolated in chocolate (di Tomaso et al., 1996). Because the amounts of anandamide found in chocolate is so minuscule, eating chocolate will not get a person high, but rather that there are compounds such as unsaturated N-acylethanolamines in chocolate that have been associated with the good and ‘high’ feeling that chocolate consumption provides. In the body, anandamide is broken down rapidly into two inactive sections after production by the enzyme hydrolase found in our bodies (di Tomaso et al., 1996). In chocolate, however, there are other chemicals that may inhibit this natural breakdown of anandamide. Therefore, natural anandamide may remain extensively, making people feel good longer when they eat chocolate. Although chocolate contains chemicals associated with feelings of happiness, love, passion, lust, endurance, stamina and mood lifting, scientists continue to debate whether it should be classified as an aphrodisiac. It is therefore very challenging to say that there is a firm proof that chocolate is indeed an aphrodisiac, but it does contain substances that increase energy, stamina, mood lifting and feelings of well-being. The reality is that a gift of chocolate is a familiar courtship ritual that makes you feel good and induces feelings of being in love.

6.9 CONCLUSION

Cocoa and chocolate flavonoids are compounds that are vital in human health, as evidenced by their influence on a number of findings relating to their biochemical and physiological functions in the body, with identified potent antioxidant effects under in vitro conditions and in vivo after consumption. These antioxidant properties have been related to increases in plasma epicatechin concentrations, endothelial-dependent vascular relaxation as promoted by cocoa flavonoids in part due to increased bioavailability of NO and prostacyclin, and antiatherosclerotic properties of NO combined with a favourable shift towards vasodilation conferring vasculoprotective effect. Blood pressure lowering has also been found after short-term dark chocolate intervention in the presence of mild isolated systolic hypertension. Other known effects from cocoa flavonoids include their suppressive effect on platelet reactivity and platelet-related primary hemostasis, modulation of immune function and inflammation as potential cardioprotective effects. Finally, some aphrodisiac effects, mood liftings and heightened sensitivity have also been reported due to phenylethylamine and N-acylethanolamines compounds in cocoa and chocolates. As consumers become more aware of the potential aphrodisiac effects and health benefits associated with cocoa and chocolate consumption, they would require more information as to whether the intake of these functional compounds and/or their sources is related to measurable effects on human sexual lives, health and/or the development of diseases. As well, it may provide relevant information on their specific sources and products commonly available in the marketplace as a guide to their selection of foods. Consumption of cocoa and chocolate flavonoids therefore still presents an exciting area of further nutritional/clinical/epidemiological research with significant implications for sexual sensitivities and cardiovascular protection in humans.
7 Structure – properties (rheology, texture and melting) relationships in chocolate manufacture

7.1 SUMMARY AND INDUSTRIAL RELEVANCE

Chocolate manufacturing is complex and requires a combination of several ingredients and technological operations to achieve the desired rheological, textural and melting qualities. However, the extent to which the formulated ingredients and the applied processing operations, such as refining and conching, influence these quality characteristics remains quite unclear to processors and therefore requires in-depth investigations to elucidate their effects. This study investigated effects of particle size distribution (PSD) and composition on rheological, textural and melting properties of dark chocolates, and used multivariate statistics to explore their interrelationships. The levels studied were as follows: PSD, D90 (90% finer than this size) – 18, 25, 35 and 50 µm; fat – 25, 30 and 35%; and lecithin – 0.3 and 0.5%. Instruments utilised included a shear rate-controlled rheometer, TA-HD Plus Texture Analyzer and differential scanning calorimeter (DSC). Surface colour was evaluated in terms of CIELAB parameters L*, C* and h° using a HunterLab Miniscan Colorimeter and microstructure of products determined using light microscopy. Levels of PSD, fat and lecithin content significantly affected all rheological parameters, with significant interaction among factors. Increasing particle size (PS) gave significant reductions in all rheological and textural properties, with greatest effect noted at 25% fat and 0.3% lecithin, then inversely related to fat and lecithin contents. PSD and fat concentration also influenced melting characteristics and colour (L*, C* and h°). Micrographs revealed PSD and fat level induced wide variations in sugar crystalline network structure and interparticle interaction: 25% fat yielded more crystal agglomerates, well flocculated with greater particle-to-particle interaction strengths than those with higher (30 and 35%) fat contents. Increasing PSD to 35–50 µm resulted in particles becoming coarser at all fat levels. Fat showed the greatest effect on the variability in each property followed by PSD and lecithin. Analyses showed high correlation ($r = 0.89–1.00$) and regression coefficients ($R^2 = 0.84–1.00$). The newer International Confectionery Association (ICA) technique gave higher correlation and regression coefficients than the Casson model but was highly related and either could effectively quantify dark chocolate viscosity parameters. High correlation ($r = 0.78–0.99$) and regression coefficients ($R^2 = 0.59–0.99$) were observed among rheological, textural and melting index. As PSD, fat and lecithin could be manipulated to control dark chocolate rheology, texture, appearance and melting character, it would be possible to influence quality whilst reducing production cost.
Chocolate is a dense suspension of solid particles, on average 60–70% sugar and non-fat cocoa solids and milk solids (depending on type) dispersed in a fat continuous phase, mostly of cocoa butter. During manufacture, refining and conching determine PS and suspension consistency and viscosity to yield specific textural and sensory qualities (Beckett, 2000; Afoakwa et al., 2007).

Rheologically, molten chocolates behave as non-Newtonian liquids with yield stress (minimum amount of energy to initiate fluid flow) and plastic viscosity (energy to keep fluid in motion), dependent on processing. Quality in finished chocolates is highly dependent on inherent size distribution of solid particles from sugar, milk and cocoa, composition of fat phase and emulsifiers (Ziegleder, 1992; Beckett, 2003). Rheological properties determine efficiency of mixing, pumping and transportation of finished products during processing. Servais et al. (2004) concluded that the control of chocolate rheology is important for quality and exact weight control during enrobing, shell making and moulding processes. Processing parameters such as conching, PSD, fat content, emulsifiers (lecithin and polyglycerol polyricinoleate, PGPR), temper, vibrations and temperature – all influence rheological properties and production cost (Tscheuschner & Wunsch, 1979; Beckett, 1999; Vavreck, 2004; Schantz & Rohm, 2005; Afoakwa et al., 2008).

Of techniques for characterising rheological properties, the ICA (previously IOCCC) suggests the use of rotational viscometers with concentric cylinders (bob and cup geometry) and the Casson equation (IOCCC, 1973; Bouzas & Brown, 1995; ICA, 2000; Sokmen & Gunes, 2006; Afoakwa et al., 2008b), with measurement of stress and viscosity at shear rates between 2 and 50 s$^{-1}$ using up and down curves, preceded by a pre-shear at 5 s$^{-1}$ of more than 5 minutes (Servais et al., 2004). Important are the rheological models of Herschel–Bulkley, Casson and Bingham (Chevalley, 1999; Beckett, 2000; Sokmen & Gunes, 2006), following the equations:

\[
\text{Herschel–Bulkley : } \tau = \tau_0 + \eta_{pl} \dot{\gamma}^n \tag{7.1}
\]
\[
\text{Casson : } \sqrt{\tau} = \sqrt{\tau_{CA}} + \sqrt{\eta_{CA}} \cdot \sqrt{\dot{\gamma}} \tag{7.2}
\]
\[
\text{Bingham : } \tau = \tau_0 + \eta_{pl} \dot{\gamma} \tag{7.3}
\]

where $\tau$ denotes shear stress; $\tau_0$, yield stress; $\eta_{pl}$, plastic viscosity; $\tau_{CA}$, Casson yield value; $\eta_{CA}$, Casson plastic viscosity; $\dot{\gamma}$, shear rate; $\eta$, viscosity of the suspension; $n$, flow viscosity index. Since 1973, the ICA has accepted rheological measurement of molten chocolate using rotational viscometers with concentric cylinders (bob and cup geometry) and Casson equation calculation of the parameters (IOCCC, 1973; Bouzas & Brown, 1995). In 2000, ICA recommended measurement of stress and viscosity at shear rates between 2 and 50 s$^{-1}$ using up and down curves in shear rate, preceded by a pre-shear at 5 s$^{-1}$ lasting 5 or more minutes (ICA, 2000).

The basis for change in 2000 was results from an interlaboratory study (Aeschlimann & Beckett, 2000), which concluded that the Casson’s mathematical model employing only a small set of parameters was limited in accuracy as, at lower shear rates, rheology data do not fit the Casson equation well. The outcome was a low degree of repeatability in interlaboratory analyses, and ICA thus recommended use of interpolation data for chocolate viscosity. Servais et al. (2004) noted that this strategy was simple, accurate and readily applicable to different systems, given a basis of relevant information. In the United States, the current
National Confectioners Association/Chocolate Manufacturers Association (NCA/CMA) method for chocolate rheological properties is to extrapolate concentric cylinder flow data using the Casson equation (Baker et al., 2006) with a correction factor of a gap ratio between the cup and the bob used during rheological measurement. This technique is different from the ICA quantification strategy (ICA, 2000) and therefore requires an understanding of their interrelationships.

PSD, central to rheological properties, has a direct influence on sensory character. The largest particles (D90) are important for mouthfeel notably grittiness, but smaller particles influence flow properties (Beckett, 2000, 2003; Mongia & Ziegler, 2000; Ziegler et al., 2001). A small proportion of particles up to 65 µm give an improved texture for milk chocolate. Good dark chocolate requires a maximum PS of 35 µm (Awua, 2002), and at solids more 61% by volume and PSD more than 35 µm, the quality becomes unacceptable due to high viscosity and poor texture (Beckett, 1999). Limit values are determined by targets for character and product composition. Generally, chocolate viscosity is controlled by addition of cocoa butter and expensive viscosity modifiers (surface-active ingredients, e.g. soy lecithin and PGPR). The optimum for average sugar PS is cultural, in the United States 25–30 µm with a maximum of 50 µm and in Europe 20–23 and 35–40 µm, respectively (Jeffery, 1993). Benefits of PSD optimisation include reductions in viscosity modifiers. There is no general agreement on the central role of PSD in suspension flow properties, with Awua (2002) and Whitefield (2005) arguing that other factors influence rheology. Modification of suspension viscosity by changing PSD merits further investigation together with compositional factors that contribute to rheological properties during manufacture.

Chocolate texture and appearance are key attributes in consumer choice and acceptability even though flavour is frequently judged important in product identification (Beckett, 2003; Whitefield, 2005). Although texture perception is a dynamic oral process before and during mastication, individuals also perceive texture through vision, touch and hearing (Heath & Prinz, 1999; Kilcast, 1999; Wilkinson et al., 2000). Chocolate texture can also be evaluated by instrumental measurements often rationalised as cheap, efficient and objective replacements or complements for sensory evaluations (Lawless & Heymann, 1998) with statistically significant correlations (Mohamed et al., 1982; Christensen, 1984; Meullenet et al., 1997; Rosenthal, 1999; Bourne, 2002). Visual information characterising objects, including gloss, colour, shape, roughness, surface texture, shininess and translucency, is summarised into appearance attributes. Briones et al. (2006) concluded that these emerge from complex interactions of incident light, optical characteristics and human perception. Relevant information can be acquired from modern technologies such as computer vision and calibrated colour imaging analysis, HunterLAB and CIELAB models (Lawless & Heymann, 1998; Jahns et al., 2001; Hatcher et al., 2004; Briones & Aguilera, 2005). Such lab-based models provide close descriptions of colour attributes (Lawless & Heymann, 1998; Taylor & Hort, 2004) although Thai and Shewfelt (1991) found that L (lightness), C (chroma) and H (hue angle) from HunterLAB data were better correlated. Given that chocolates should meet prior acquired consumer expectations, appearance attributes can have significant commercial implications.

Microstructure is a fundamental variable influencing transport phenomenon and physical properties of foods determining perceived quality in terms of mechanical and sensorial attributes (Kulozik et al., 2003). Consequently, microstructure is important for manipulation or regulation of texture and related to composition and physical forces influencing mechanical properties (van Marle et al., 1997; Afoakwa & Sefa-Dedeh, 2002). Varela et al. (2007) noted that successful delivery in new product development requires understanding of factors that
influence texture. Improvement in the quality of existing foods and new product formulations requires interventions at microscopic level. Most elements that critically participate in transport properties, physical and rheological behaviours, textural and sensorial characters are less than 100 µm in diameter (Aguilera, 2005). Bourne (2002) concluded that texture is derived from food structure and relationship between microstructure, and rheological and textural properties have been studied (Kulozik et al., 2003; Pereira et al., 2003; Remeuf et al., 2003; Braipson-Danthine & Deroanne, 2004; Sandoval-Castilla et al., 2004; Christiansen et al., 2006; Baixauli et al., 2007). However, there is limited information on relationship between microstructure and mechanical properties of finished dark chocolates specifically on how PSD and composition affect the microstructure and mechanical properties.

During chocolate manufacture, the crystalline state and the proportion of solid fat present are important in determining the melting character in finished products. DSC has been used to characterise changes in chocolate melting profiles and measures the relative amounts of each crystalline state (Tabouret, 1987; Ziegleder & Schwingshandl, 1998; Walter & Cornillon, 2001, 2002), and peaks corresponding to latent heat are observed in temperature ranges related to melting of specific polymorphs (McFarlane, 1999). Such information is relevant to sensory character and impacts on mechanical and rheological properties of chocolate and confectionery shelf-life (Hartel, 2001).

As demand for dark chocolate products is increasing in global markets, understanding the factors influencing the rheological, textural and melting properties as well as appearance would be of value in predicting changes in quality. The acquired information would impact on process improvement and new product development in dark chocolate manufacture. The objectives of this work were to:

1. investigate effects of PSD and composition (fat and lecithin) on rheological behaviour of molten dark chocolate characterised, using steady shear measurements;
2. study the relationship between the two models (Casson’s model and the new ICA recommendations) for estimating dark chocolate rheological parameters;
3. evaluate effects of PSD and compositional variations on textural properties and appearance of dark chocolates;
4. determine the influence of PSD and fat content on dark chocolate microstructure and how it relates to the rheological and mechanical properties of dark chocolates;
5. characterise the effects of PSD, fat and lecithin content on the crystallinity and melting profiles of finished dark chocolates;
6. explore relationships between rheological, textural and melting properties of dark chocolate as influenced by PSD of solids and composition during processing.

### 7.3 MATERIALS AND METHODS

#### 7.3.1 Materials

Cocoa liquor of Central West African origin was obtained from Cargill Cocoa Processing Company (York, UK); sucrose (pure fine granulated) from British Sugar Company (Peterborough, UK); pure prime-pressed cocoa butter and soy lecithin from ADM Cocoa Limited (Koog aan de Zaan, the Netherlands) and Unitechem Company Ltd (Tianjin, China), respectively.
Table 7.1 Recipes used for the formulation of the dark chocolate

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>25% fat (% w/w)</th>
<th>30% fat (% w/w)</th>
<th>35% fat (% w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sucrose</td>
<td>58.8</td>
<td>59.0</td>
<td>49.7</td>
</tr>
<tr>
<td>Cocoa liquor</td>
<td>35.9</td>
<td>35.5</td>
<td>45.0</td>
</tr>
<tr>
<td>Cocoa butter</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Lecithin</td>
<td>0.3</td>
<td>0.5</td>
<td>0.3</td>
</tr>
</tbody>
</table>

7.3.2 Preparation of chocolate samples

Dark chocolate formulations (Table 7.1) from sucrose, cocoa liquor, cocoa butter and emulsifier (lecithin) used total fat contents between 25 and 35% (w/w) (from cocoa liquor and cocoa butter) and a minimum of 35% total cocoa solids, to ensure conformance with standard of identity for dark chocolate of the Codex Revised Standard (2003) on chocolate and chocolate products, and European Commission Directive 2000/36/EC on cocoa products and chocolate (European Commission Directive, 2000).

Experimental samples (5 kg batch for each formulation) were produced by mixing sucrose and cocoa liquor in a Crypto Peerless mixer (Model K175, Crypto Peerless Ltd, Birmingham, UK) at low speed for 2 minutes and then at high speed for 3 minutes, refining using a three-roll refiner (Model SDX 600, Buhler Ltd, CH-9240 Uzwil, Switzerland), to predetermined PSs (D90: 18 ± 1, 25 ± 1, 35 ± 1 and 50 ± 1 μm) confirmed by PS analysis.

Refined chocolates were stored in plastic containers and conditioned at ambient temperature (20–22°C) for 24 hours prior to conching in a Lipp Conche (Model IMC-E10, Boveristr 40-42, D-68309, Mannhein, Germany) at low speed for 3.5 hours at 60°C. Lecithin and cocoa butter were then added and mixtures were conched at high speed for further 30 minutes for mixing and liquefaction. Samples were stored in sealed plastic containers at ambient temperature (20 ± 2°C), and moisture and fat contents were determined using Karl Fischer and Soxhlet methods (ICA, 1988, 1990), respectively.

7.3.3 Determination of particle size distribution

A MasterSizer® Laser Diffraction Particle Size Analyzer equipped with MS 15 sample presentation unit (refractive index 1.590) (Malvern Instrument Ltd, Malvern, England) was used. About 0.2 g of refined dark chocolate was dispersed in vegetable oil (refractive index 1.450) at ambient temperature (20 ± 2°C) until an obscuration of 0.2 was obtained. Ultrasonic dispersion for 2 minutes to ensure particles were independently dispersed was maintained by stirring. Size distribution was quantified as relative volume of particles in size bands presented as size distribution curves (Malvern MasterSizer Micro Software v 2.19). PSD parameters obtained included specific surface area, largest PS (D90), mean particle volume (D50), smallest PS (D10), Sauter mean diameter (D[3,2]) and mean particle diameter (D[4,3]). The four PSDs used for the study are shown (Table 7.2).

7.3.4 Rheological measurements

The rheological behaviour of molten dark chocolate was characterised using steady shear measurements. All measurements were carried out in shear rate-controlled rheometer (Thermo Haake ViscoTester 550 (VT 550), Thermo Electron Corp., Karlsruhe, Germany).
### Table 7.2  Particle size distribution of the dark chocolates

<table>
<thead>
<tr>
<th>Particle size ($D_{90}$) (µm)</th>
<th>Fat content (%)</th>
<th>Specific surface area (m$^2$ g$^{-1}$)</th>
<th>$D_{(v,0.1)}$ (µm)</th>
<th>$D_{(v,0.5)}$ (µm)</th>
<th>$D_{[3,2]}$ (µm)</th>
<th>$D_{[4,3]}$ (µm)</th>
<th>$D_{(v,0.9)}$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18 ± 1.0</td>
<td>25</td>
<td>1.97 ± 0.04</td>
<td>1.09 ± 0.03</td>
<td>4.72 ± 0.05</td>
<td>2.61 ± 0.04</td>
<td>7.80 ± 0.06</td>
<td>18.71 ± 0.19</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>1.89 ± 0.03</td>
<td>1.04 ± 0.03</td>
<td>4.89 ± 0.05</td>
<td>2.63 ± 0.04</td>
<td>8.02 ± 0.05</td>
<td>18.72 ± 0.46</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>1.54 ± 0.03</td>
<td>1.39 ± 0.04</td>
<td>6.03 ± 0.06</td>
<td>3.17 ± 0.05</td>
<td>8.44 ± 0.03</td>
<td>18.60 ± 0.24</td>
</tr>
<tr>
<td>25 ± 1.0</td>
<td>25</td>
<td>1.65 ± 0.06</td>
<td>1.22 ± 0.04</td>
<td>5.62 ± 0.04</td>
<td>2.92 ± 0.04</td>
<td>10.28 ± 0.07</td>
<td>25.60 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>1.58 ± 0.02</td>
<td>1.24 ± 0.02</td>
<td>5.79 ± 0.06</td>
<td>3.02 ± 0.03</td>
<td>10.32 ± 0.14</td>
<td>25.53 ± 0.65</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>1.45 ± 0.02</td>
<td>1.45 ± 0.05</td>
<td>6.63 ± 0.06</td>
<td>3.43 ± 0.06</td>
<td>10.39 ± 0.08</td>
<td>25.06 ± 0.32</td>
</tr>
<tr>
<td>35 ± 1.0</td>
<td>25</td>
<td>1.46 ± 0.04</td>
<td>1.40 ± 0.04</td>
<td>6.59 ± 0.07</td>
<td>3.36 ± 0.03</td>
<td>13.35 ± 0.08</td>
<td>35.53 ± 0.14</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>1.42 ± 0.02</td>
<td>1.46 ± 0.03</td>
<td>6.70 ± 0.02</td>
<td>3.49 ± 0.02</td>
<td>13.36 ± 0.07</td>
<td>35.59 ± 0.27</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>1.28 ± 0.05</td>
<td>1.68 ± 0.06</td>
<td>7.54 ± 0.06</td>
<td>3.85 ± 0.05</td>
<td>13.55 ± 0.09</td>
<td>35.39 ± 1.14</td>
</tr>
<tr>
<td>50 ± 1.0</td>
<td>25</td>
<td>1.30 ± 0.01</td>
<td>1.59 ± 0.03</td>
<td>7.69 ± 0.03</td>
<td>3.74 ± 0.05</td>
<td>17.46 ± 0.05</td>
<td>50.16 ± 0.65</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>1.26 ± 0.04</td>
<td>1.68 ± 0.03</td>
<td>7.97 ± 0.05</td>
<td>3.80 ± 0.06</td>
<td>17.58 ± 0.06</td>
<td>50.41 ± 0.79</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>1.10 ± 0.04</td>
<td>2.04 ± 0.04</td>
<td>9.08 ± 0.09</td>
<td>4.47 ± 0.06</td>
<td>17.90 ± 0.05</td>
<td>50.08 ± 0.48</td>
</tr>
</tbody>
</table>

Mean values ± standard deviations from triplicate analysis.

*D_{(v,0.1)}, D_{(v,0.5)}, D_{[3,2]}, D_{[4,3]} and D_{(v,0.9)}, respectively, represent 10%, 50%, Sauter mean diameter, mean particle diameter and 90% of all particles finer than this size.*
using bob and cup (recessed end) geometry (sensor SVI and SVII), as for IOCCC method (Aeschlimann & Beckett, 2000) with a ratio of inner to outer radius of 0.92 in the concentric cylinder system. Samples were incubated at 50°C for 75 minutes for melting and transferred, pre-sheared at 5 s⁻¹ rate for 15 minutes at 40°C, before measurement cycles. Shear stress was measured at 40°C as function of increasing shear rate from 5 to 50 s⁻¹ (ramp up) within 120 seconds, and then decreasing from 50 to 5 s⁻¹ (ramp down), within each ramp 50 measurements were taken. Viscosity was also measured as a function of increasing shear rate from 5 to 50 s⁻¹ (ramp down) within 120 seconds, and then decreasing from 50 to 5 s⁻¹ (ramp up), within each ramp 50 measurements were taken. Temperature of the chocolate samples was controlled during the experiment using Haake K20 Thermo-regulator (Thermo Electron Corp., Karlsruhe, Germany). Mean value and standard deviation of triplicate readings were recorded. Casson plastic viscosity and Casson yield values were calculated using Casson model (Eq. 7.2) and interpolation data from the viscosity and shear stress graphs (Fig. 7.1), respectively, using ThermoHaake RheoWin Pro 297 Software by the least square method.

![Fig. 7.1](image_url)  
**Fig. 7.1** Typical rheology graph illustrating measurement of (a) apparent viscosity and yield stress and (b) thixotropy from two dark chocolates containing (a) 50 μm PS, 35% fat and 0.5% lecithin, and (b) 50 μm PS, 25% fat and 0.5% lecithin.
Figure 7.1 (Continued)

Figure 7.1 shows how the new ICA rheological parameters (yield stress and apparent viscosity) and thixotropy were deduced from interpolation data according to recommendations of IOCCC (1973) and Servais et al. (2004) with some modifications. Value of stress during ramp up at a shear rate of 5 s\(^{-1}\) represented yield stress, viscosity during ramp down at a shear of 30 s\(^{-1}\), apparent viscosity (Fig. 7.1(a)), and difference between yield stress at 5 s\(^{-1}\) during ramp up and down, thixotropy (Fig. 7.1(b)).

7.3.5 Tempering procedure

Samples were incubated at 50°C for 4 hours for melting and tempered using an Aasted Mikrovert laboratory continuous three-stage tempering unit (Model AMK 10, Aasted Mikroverk A/S, Farum, Denmark). Chocolate was pumped through the multistage units and a worm screw drove the product through the heat exchangers. Sensors located at specific points in the equipment measured the temperature of both the chocolate and the coolant.
fluid at each stage. The temperatures of each of the three stages were thus set and controlled independently of each other to obtain a final chocolate temperature of approximately 27°C to promote crystal growth of the desired triacylglyceride fractions. Pre-crystallisation was measured using a computerised tempermeter (Exotherm 7400, Systech Analytics, SA, Switzerland). A built-in algorithm was used to ensure an optimal temper regime of slope 0 ± 0.3 (5.0 ± 1.0 chocolate temper unit). The principle of this method has been described by Nelson (1999). The tempered chocolate was moulded using plastic moulds – 80 mm length, 20 mm breadth and 8 mm height – allowed to cool in a refrigerator (12°C) for 2 hours before demoulding onto plastic trays and conditioned at 20 ± 2°C for 14 days before analysis.

7.3.6 Texture measurements

Texture of molten chocolates was evaluated using a TA-HD Plus Texture Analyzer (Stable Micro Systems, Godalming, Surrey, England) with back extrusion rig and a 35 mm diameter compression disk attached to an extension bar using 50 kg load cell (Fig. 7.2(a)). Samples melted at 50°C for 75 minutes were quickly transferred to a standard back extrusion container (50 mm diameter) and work was done in back, extruding 100 mL chocolate determined by measuring force in compression. Eight replications were made at a pre-test 1.0 mm/second, test of 0.5 mm/second and post-test 10.0 mm/second at 50 mm above sample surface, penetrating 30 mm for 60 seconds, then returning to the start position. Mean values were used to obtain a force–time graph (XT.RA Dimension, Exponent 32 software; Stable Micro Systems) as shown in Figure 7.3(a) by calculating as texture parameters:

1. Firmness = maximum compression force in extrusion thrust into sample (g).
2. Consistency = area within curve during extrusion thrust (g.s).

![Fig. 7.2](image-url) Back extrusion rig (a) and puncture test rig (b) used for texture measurements of molten and solid chocolates, respectively. With kind permission from Springer Science and Business Media, Afoakwa et al. (2008b).
Fig. 7.3  Typical (a) back extrusion curve and (b) penetration probe curve used for the measurement of molten and solid dark chocolates, respectively. With kind permission from Springer Science and Business Media, Afoakwa et al. (2008b).
3. Cohesiveness = maximum compression force during withdrawal of probe from sample (g).
4. Index of viscosity = area within negative region of curve during probe withdrawal (g.s).

Hardness of solid tempered chocolate was measured using TA-HD Plus Texture Analyzer with a penetration probe (needle P/2) attached to an extension bar and a 50-kg load cell and a platform (Fig. 7.2(b)). Maximum penetration force through a sample (80 × 20 mm, depth 8 mm) was determined with eight replications at a pre-speed of 1.0 mm/second, test of 2.0 mm/second, post-speed of 1.0 mm/second, penetrating 6 mm for 3 seconds at 20°C, converting mean values into hardness data on a force–time graph using XT.RA Dimension, Exponent 32 software (Stable Micro Systems, Godalming, Surrey, UK) as shown in Figure 7.3(b).

7.3.7 Colour measurements of solid dark chocolate
HunterLab Miniscan™ XE Colorimeter Model 45/0 LAV (Hunter Associates Inc., Reston, VA, USA) calibrated with white ceramic reference standard was used. Colour images of chocolate surfaces were converted into XYZ tristimulus values, which were further converted to CIELAB system: $L^*$, luminance ranging from 0 (black) to 100 (white); and $a^*$ (green to red) and $b^*$ (blue to yellow) with values from $-120$ to $+120$. Information was obtained using a software algorithm (Matlab v. 6.5; The Math-Works, Inc., Natick, MA, USA): hue angle ($h^\circ$) = arctan ($b^*/a^*$); chroma ($C^*$) = [(a*)$^2$ + (b*)$^2$]$^{1/2}$. Mean values from five replicate measurements and standard deviations were calculated.

7.3.8 Microstructure analysis
Microstructures were observed using a high resolution polarised light microscope (Olympus Optical U-PMTVC, Tokyo, Japan). One drop (10 µL) of molten chocolate (previously heated at 55°C to destroy crystal memory) was placed on a pre-heated (55°C) glass slide. A cover slip was carefully placed over the sample, parallel to the plane of the slide and centred to ensure sample thickness was uniform. Specimens were observed immediately at ×20 magnification, and micrographs (black and white images) were captured using a digital camera (Model 2.1 Rev 1, Polaroid Corporation, NY, USA) and observed using Adobe Photoshop (version CS2, Adobe Systems Inc., NJ, USA).

7.3.9 Determination of melting properties of dark chocolates
The differential scanning calorimeter (DSC Series 7, Perkin Elmer Pyris, Norwalk, CT, USA) equipped with a thermal analysis data station was calibrated using indium and octadecane at a scan rate of 5°C/minute using an aluminium pan as reference. Samples (~5 mg) were loaded into 40 µL capacity pans with holes and sealed with lids using a sample press. Pans were heated at 5°C/minute from 15 to 55°C in an N₂ stream. Onset temperature ($T_{\text{onset}}$), peak temperature ($T_{\text{peak}}$), end temperature ($T_{\text{end}}$) and enthalpy of melting ($\Delta H_{\text{melt}}$) were calculated automatically by the software. Melting index ($T_{\text{index}}$) was computed as $T_{\text{end}} - T_{\text{onset}}$, as described by Vasanthan and Bhat (1996). Each sample was analysed in triplicate and mean values and standard deviations were reported.
7.3.10 Experimental design and statistical analysis

Three key experimental variables were PSD, fat and lecithin contents with other variables including refiner temperature and pressure, conching time and temperature, and cocoa butter (5% (w/w)) held constant. A $4 \times 3 \times 2$ factorial experimental design was used with principal factors: PSD ($D_{90}$) 18, 25, 35 and 50 µm; fat content 25, 30 and 35% (w/w); lecithin content 0.3 and 0.5% (w/w).

Statgraphics Plus 4.1 (Graphics Software System, STCC, Inc., Rockville, MD, USA) was used to examine the rheological properties (Casson plastic viscosity and yield values, apparent viscosity, yield stress and thixotropy), textural properties (firmness, consistency, cohesiveness, index of viscosity of molten chocolate and hardness of tempered chocolate), colour – lightness ($L^*$), chromaticity ($C^*$) and hue angle (h°) – and melting properties – melting onset ($T_{\text{onset}}$), melting end ($T_{\text{end}}$), melting index ($T_{\text{index}}$) and peak melting ($T_{\text{peak}}$) and melting enthalpy ($\Delta H_{\text{melt}}$) – using two-way analysis of variance (ANOVA) and multiple range tests to determine effects of PSD, fat and lecithin contents and their interactions. Tukey multiple comparisons at 95% significance level were conducted to determine differences between factor levels. Multivariate statistical techniques comprising regression, correlation and principal component analyses were used to evaluate the relationships between the rheological, textural and melting parameters. All process treatments and analysis were conducted in three replicates and the mean values reported.

7.4 RESULTS AND DISCUSSION

7.4.1 Particle size distribution of molten dark chocolate

The PSD parameters from the four PSs are presented in Table 7.2. Wide variations in PSD were produced with intervals ranging between 18, 25, 35 and 50 µm, using $D_{90}$ (90% finer than this size). The $D_{90}$ value was used as it has been reported to correlate fairly on sensory character with micrometer measurements made of the biggest particles (Beckett, 2000). Figure 7.4(a–d) shows volume histograms of samples with size distributions of narrow bimodal distribution for 18 µm PS (Fig. 7.4(a)), wide bimodal distribution for 25 µm PS (Fig. 7.4(b)), narrow multimodal distribution for 35 µm PS (Fig. 7.4(c)) and a wide multimodal distribution for 50 µm (Fig. 7.4(d)). Such PSD, ranging from fine (18 µm) to coarse particles (50 µm), covers optimal minima and maxima (Ziegler & Hogg, 1999; Beckett, 2000, 2003).

Data from the PSD parameters (Table 7.2) showed variations in specific surface area, mean particle volume $D(v,50)$, Sauter mean diameter ($D[3,2]$) and mean particle diameter ($D[4,3]$) with increasing $D_{90}$ PSs. Increasing $D_{90}$ from 18 to 50 µm led to significant ($p \leq 0.05$) reduction in specific surface area, with increases in Sauter mean and mean particle diameter (Table 7.2) that indicate that the largest PS ($D_{90}$) is directly proportional to the $D_{10}, D_{50}$, Sauter mean diameter ($D[3,2]$) and mean particle diameter ($D[4,3]$), and inversely proportional to specific particle surface area.

Similarly, increasing fat content from 25 to 35% led to significant ($p < 0.05$) reduction in specific surface area, with increases in other PSD parameters (Table 7.3), suggesting fat content at refining had a direct influence on PSD. Reduction in sugar levels, with increased fat content, influences PSD.
Beckett (1999) concluded that the largest PS and specific surface area of solids are the two key parameters: the largest particle diameter impacting on coarseness, and surface area with requirement of fat to obtain desirable flow properties. As size increases, particles become more spherical, leading to broadening of PSD with consequential reduction in solid loading as fat content increases. Reduction in specific surface area with increasing PSs of component PSD has been reported (Beckett, 1999; Ziegler & Hogg, 1999; Sokmen & Gunes, 2006). Analyses showed that total fat values were within the stipulated ranges of 25% ± 1% (w/w), 30% ± 1% (w/w) and 35% ± 1% (w/w), respectively, and moisture contents were within the range 0.8–0.98%.

![Particle size distribution of dark chocolate with D₉₀ of (a) 18, (b) 25, (c) 35 and (d) 50 μm.](image)

*Fig. 7.4* Particle size distribution of dark chocolate with D₉₀ of (a) 18, (b) 25, (c) 35 and (d) 50 μm. With kind permission from Springer Science and Business Media, Afoakwa et al. (2008b).
**Fig. 7.4** (Continued).

**Table 7.3** ANOVA summary of F-ratios from particle size distribution

<table>
<thead>
<tr>
<th>Process variables</th>
<th>Specific surface area</th>
<th>D(v,0.1)</th>
<th>D(v,0.5)</th>
<th>D[3,2](^a)</th>
<th>D[4,3](^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: Particle size (D(_{90}))</td>
<td>302.77(^*)</td>
<td>455.54(^*)</td>
<td>1007.84(^*)</td>
<td>546.01(^*)</td>
<td>8388.61(^*)</td>
</tr>
<tr>
<td>B: Fat</td>
<td>115.88(^*)</td>
<td>312.87(^*)</td>
<td>311.17(^*)</td>
<td>228.10(^*)</td>
<td>23.21(^*)</td>
</tr>
<tr>
<td>A × B</td>
<td>4.37(^*)</td>
<td>6.63(^*)</td>
<td>2.59(^*)</td>
<td>3.52(^*)</td>
<td>2.08</td>
</tr>
</tbody>
</table>

\(^*\) Significant F-ratios at p ≤ 0.05.
7.4.2 Rheological properties of molten dark chocolate

7.4.2.1 Casson plastic viscosity

Plastic viscosity relates to pumping characteristics, filling of rough surfaces, coating properties and sensory character of body (Seguine, 1988). Increasing PS drastically decreased plastic viscosity with 25% fat and 0.3% lecithin samples; while only slight decreases were noted with 30 and 35% fat at all lecithin levels (Fig. 7.5). Plastic viscosity with 25% fat and 0.3% lecithin was reduced from 20.42 to 9.46 Pa·s, respectively, for 18 and 50 µm PS samples representing over 50% reduction but not with 0.5% lecithin at 25% fat. Likewise, changes in PS and lecithin content had no significant effect on plastic viscosity with 30 and 35% fat samples. Higher plastic viscosities in low-fat chocolate can be explained as when distribution of PSs becomes wider with a large specific surface area – the smaller particles fill spaces between larger, reducing viscosity of suspension for any given solid concentration. Increasing fat content reduces specific surface area (Table 7.2), restricting solids, packing ability with no apparent change in plastic viscosity. In addition, as the particles become finer, their number increases with parallel increase in points of contact between particles, thus increasing their plastic viscosities. Servais et al. (2002) reported that viscosity can double with solid content increases of a few percentage for high solid content suspensions.

Increasing fat content from 25 to 30% led to reduced plastic viscosities at all PSs and lecithin concentrations. At 18 µm, 5% increase in fat gave up to tenfold reduction in plastic viscosity, indicating that fat had effects on plastic viscosity especially at lower PS (18–25 µm) and lower lecithin levels. However, at and above 30% fat, differences in plastic viscosity

![Fig. 7.5](image-url) Effect of PSD, fat and lecithin content on Casson plastic viscosity of dark chocolate. With kind permission from Springer Science and Business Media, Afoakwa et al. (2008b).
were small at all PS and lecithin levels. Beckett (1999) also attributed this to free-moving lubricating plastic flow related to forces between solid particles. Fat fills spaces or voids between particles in molten chocolate and reduces resistance to flow, with greatest effect noticeable at lower PS.

Similar reductions in plastic viscosity were noted with increasing lecithin from 0.3 to 0.5%, especially at lower fat contents and PS where up to fourfold reductions were noted. Plastic viscosity reductions from lecithin are attributed to association with sugar particles. Lecithin migrates to sugar/fat interfaces and coats sugar crystals, influencing rheology and aiding dispersion of sugar crystals in the continuous phases (Dhonsi & Stapley, 2006). Chevalley (1999) suggested that lecithin forms a monolayer on sugar particle surfaces, allowing greater mobility in suspensions while increasing fat spreadability. It was concluded that fat content and PSD had the greatest effects on plastic viscosity of dark chocolates.

Casson plastic viscosity values of 2.1 and 3.9 Pa·s have been reported to be the acceptable minimum and maximum for dark chocolates (Aeschlimann & Beckett, 2000). The data showed that the 30 and 35% fat samples fell within range but all the low-fat (25%) chocolates with 0.5% lecithin had values between 5.81 and 5.21 Pa·s. Such high plastic viscosity means these formulations cannot be employed for enrobing or coating with requirements for smoother and thinner chocolates. However, with application of mechanical vibrations, lower fat (25%) chocolates with PS between 25 and 35 µm and 0.5% lecithin could have applications in solid eating chocolates, panned products and chocolate chips/drops with implications for production cost. PSD, fat and lecithin contents significantly \( p \leq 0.05 \) affected Casson plastic viscosity with significant interactions (Table 7.4). Multiple range tests revealed that at low-fat contents, PSD significantly \( p \leq 0.05 \) influenced plastic viscosity but not at fat concentrations of 30 and 35%. This means that the combined influences of PSD, fat and lecithin contents could be manipulated to control plastic viscosity in dark chocolates.

### 7.4.2.2 Casson yield value

Casson yield values showed an inverse relationship with PS, fat and lecithin contents. Increasing PSs caused significant \( p \leq 0.05 \) reductions in the yield values at all fat contents (Fig. 7.6). The greatest reductions were observed with low fat (25%) and 0.3% lecithin, from 408.8 Pa at 18 µm to 57.53 Pa at 50 µm, representing approximately 70-fold reduction

### Table 7.4 ANOVA summary of F-ratios showing the rheological properties

<table>
<thead>
<tr>
<th>Process variables</th>
<th>Casson plastic viscosity</th>
<th>Casson yield value</th>
<th>Apparent viscosity</th>
<th>Yield stress</th>
<th>Thixotropy</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Main effects</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A: PSD (D90)</td>
<td>20.38*</td>
<td>363.58*</td>
<td>464.41*</td>
<td>1364.97*</td>
<td>8381.44*</td>
</tr>
<tr>
<td>B: Fat</td>
<td>1278.85*</td>
<td>1097.87*</td>
<td>2956.29*</td>
<td>6554.36*</td>
<td>53299.17*</td>
</tr>
<tr>
<td>C: Lecithin</td>
<td>413.47*</td>
<td>383.78*</td>
<td>688.96*</td>
<td>2054.07*</td>
<td>12149.36*</td>
</tr>
<tr>
<td><strong>Interactions</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A × B</td>
<td>30.02*</td>
<td>104.72*</td>
<td>197.51*</td>
<td>472.35*</td>
<td>3518.89*</td>
</tr>
<tr>
<td>A × C</td>
<td>21.70*</td>
<td>95.86*</td>
<td>161.22*</td>
<td>475.16*</td>
<td>2928.37*</td>
</tr>
<tr>
<td>B × C</td>
<td>322.96*</td>
<td>275.64*</td>
<td>536.93*</td>
<td>1587.24*</td>
<td>9725.58*</td>
</tr>
<tr>
<td>A × B × C</td>
<td>22.43*</td>
<td>68.72*</td>
<td>123.82*</td>
<td>351.97*</td>
<td>2204.33*</td>
</tr>
</tbody>
</table>

*Significant F-ratios at \( p \leq 0.05 \).
Fig. 7.6 Effect of PSD, fat and lecithin content on Casson yield value of dark chocolate. With kind permission from Springer Science and Business Media, Afoakwa et al. (2008b).

(Fig. 7.6). Similar reductions were noted with 30 and 35% fat with 0.3% lecithin at all PSs, with effects being less pronounced at higher PSs (Fig. 7.6). Higher values with the low (25%) fat and lower (18–25 µm) PSs can be attributed to high particle–particle interactions at lower PS, specific surface area and mean particle diameter, forming spanning stress-bearing paths increasing yield values. Yield value is affected largely by interparticle contacts, and shows a linear dependency on mean PS or, more accurately, specific surface area (Prasad et al., 2003). The yield stress or yield value relates to shape retention, pattern holding, feet and tails, inclined surface coating and presence of air bubbles (Seguine, 1988).

Increasing fat content gave significant \((p \leq 0.05)\) decreases in yield values at all PSs and lecithin levels (Fig. 7.6). At 18 µm, yield values decreased from 408.80 to 32.37 Pa, representing approximately 120-fold reductions with fat increases from 25 to 35%. Similarly, with 50 µm, reductions of up to 90-fold were noted when fat was increased from 25 to 35%. This explains that combined effects of fat content and PSD having greatest influence on the yield values in dark chocolates. This effect is however less pronounced at higher fat and lecithin contents (Fig. 7.6). Fat coats the particle surfaces and reduces their interparticle interaction to induce chocolate flow. Beckett (2000) explained that the effect of an extra 1% fat upon yield value depends on the amount already present. Above fat content of 32%, there is very little change in yield value with any further additions.

Similar significant \((p \leq 0.05)\) reductions in Casson yield value were noted when lecithin was increased from 0.3 to 0.5% as reported previously (Beckett, 1999; Chevalley, 1999). The lecithin molecule has two long fatty acid chains capable of forming a non-polar tail that gives it a good stability in lipids, and its amphiphilic nature promotes deagglomeration of clumps and wetting contributing to lowering of viscosity. Significant \((p \leq 0.05)\) interactions
were observed among all parameters (Table 7.4), indicating complex effects on yield value (Beckett, 1999, 2000; Chevalley, 1999), which remain a challenge.

Casson yield values for dark chocolate have been reported as between 4 and 32 Pa (Aeschlimann & Beckett, 2000). Most (30 and 35%) fat formulations fell within this range (Fig. 7.6) without the addition of PGPR. For industrial application, PGPR could further reduce the yield values of the low-fat (25%) chocolates with 35 and 50 µm PS. Addition of 0.5% PGPR has been reported to affect up to 12-fold and 24% reductions in yield value and plastic viscosity, respectively (Haedelt et al., 2005). PGPR achieves steric stabilisation of sugar particles, thereby reducing interactions on yield values and plastic viscosities in chocolates (Vernier, 1998).

### 7.4.2.3 Apparent viscosity

Apparent viscosity values were determined at 30 s$^{-1}$ shear (Table 7.5). Servais et al. (2004) noted that apparent viscosity could be represented by value of the viscosity at 30, 40 or 50 s$^{-1}$ depending on product, but recommended viscosity value at 40 s$^{-1}$ to represent apparent viscosity through relative reproducibility. In this study, shear at 30 s$^{-1}$ was used to represent the apparent viscosity as obtainable from all formulations. All studied factors significantly ($p < 0.001$) affected apparent viscosity. Generally, increasing PS led to consistent decreases in apparent viscosity, a trend noted at all fat contents (Table 7.5).

#### Table 7.5 Effect of PSD, fat and lecithin contents on apparent viscosity and yield stress of dark chocolates

<table>
<thead>
<tr>
<th>Particle size $D_{90}$ (µm)</th>
<th>Fat content (%)</th>
<th>Lecithin (%)</th>
<th>Apparent viscosity (Pa s)</th>
<th>Yield stress (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18 ± 1.0</td>
<td>25</td>
<td>0.3</td>
<td>61.03 ± 1.60</td>
<td>920.77 ± 6.22</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>20.26 ± 0.40</td>
<td>260.33 ± 4.98</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.3</td>
<td>13.51 ± 0.08</td>
<td>211.63 ± 5.79</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>10.55 ± 0.06</td>
<td>157.77 ± 4.76</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>0.3</td>
<td>5.63 ± 0.05</td>
<td>79.47 ± 1.38</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>4.93 ± 0.08</td>
<td>69.85 ± 1.32</td>
</tr>
<tr>
<td>25 ± 1.0</td>
<td>25</td>
<td>0.3</td>
<td>32.42 ± 1.24</td>
<td>441.50 ± 5.26</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>18.37 ± 0.07</td>
<td>232.37 ± 3.21</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.3</td>
<td>8.53 ± 0.04</td>
<td>123.63 ± 2.54</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>7.88 ± 0.08</td>
<td>113.93 ± 3.10</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>0.3</td>
<td>4.61 ± 0.03</td>
<td>56.43 ± 1.56</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>4.05 ± 0.02</td>
<td>51.02 ± 1.42</td>
</tr>
<tr>
<td>35 ± 1.0</td>
<td>25</td>
<td>0.3</td>
<td>24.74 ± 0.07</td>
<td>346.10 ± 6.24</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>15.78 ± 0.08</td>
<td>193.37 ± 3.16</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.3</td>
<td>6.12 ± 0.05</td>
<td>84.89 ± 1.82</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>6.27 ± 0.06</td>
<td>66.82 ± 1.72</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>0.3</td>
<td>4.28 ± 0.03</td>
<td>49.98 ± 1.61</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>3.84 ± 0.02</td>
<td>44.85 ± 1.26</td>
</tr>
<tr>
<td>50 ± 1.0</td>
<td>25</td>
<td>0.3</td>
<td>15.71 ± 0.17</td>
<td>225.57 ± 4.45</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>11.50 ± 0.13</td>
<td>144.30 ± 3.24</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.3</td>
<td>5.80 ± 0.23</td>
<td>62.60 ± 1.71</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>5.27 ± 0.16</td>
<td>63.10 ± 1.68</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>0.3</td>
<td>3.54 ± 0.02</td>
<td>35.49 ± 1.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>3.45 ± 0.07</td>
<td>38.95 ± 0.82</td>
</tr>
</tbody>
</table>

Mean values ± standard deviations from triplicate analysis.
The trends with apparent viscosity were similar with Casson plastic viscosity; increasing PSs from 18 to 50 µm led to significant decreases in apparent viscosity, more pronounced at low fat (25%). Increasing fat content had similar inverse relationship with apparent viscosity but less effect at both 30 and 35% fat at all PSs, and finally, lecithin increase from 0.3 to 0.5% caused further reductions in apparent viscosity for all PSs and fat contents (Table 7.5). Influence on apparent viscosity of dark chocolates was more dependent on fat and lecithin content. ANOVA showed that PSD, fat and lecithin contents significantly \((p \leq 0.05)\) affected dark chocolate’s apparent viscosity with significant interactions among factors (Table 7.4).

### 7.4.2.4 Yield stress

Yield stress relates to energy required to initiate chocolate flow and is important in keeping small solid particles in suspension and in coating of solid surfaces (Yoo & Rao, 1995). Values were significantly \((p \leq 0.05)\) influenced by PSD, fat and lecithin contents as for Casson yield value. Increases in PSs from 18 to 50 µm caused significant \((p \leq 0.05)\) reductions at all fat contents with the greatest reductions with low-fat (25%) chocolates containing 0.3% lecithin, from 920.77 Pa for 18 µm to 225.57 Pa in the 50 µm (Table 7.5). Trends were similar for 30 and 35% fat and 0.3% lecithin with increasing PSs but less pronounced with 30 and 35% fat contents. Higher yield stress with lower PSs and lower fat levels could result from higher specific surface area with lower PS, showing an inverse relationship. Servais \textit{et al.} (2004) suggested that yield stress depends on proportion of small particles (specific surface area) and on their interactions, originating in mechanical (friction) and chemical effects.

Fat and lecithin content effects on yield stress were comparable to trends noted with the Casson yield values. Increasing fat led to significant \((p \leq 0.05)\) decreases in yield stress at all PS and lecithin levels (Table 7.5), with higher yield stress values noted at 18 µm and lower fat content (25%), decreasing from 25 to 35% fat at all PSs, which could be attributed to coating of fat on particle surfaces, reducing interparticle interaction and inducing flow in a direct relationship with fat content. Similarly, significant \((p \leq 0.05)\) reductions in yield stress were noted when lecithin was increased from 0.3 to 0.5%, at all PSs and fat contents. Significant \((p \leq 0.05)\) interactions were observed among all the processing parameters (Table 7.4). Fat content had the greatest influence in reducing yield stress in dark chocolates followed by lecithin content and then PSD.

### 7.4.2.5 Thixotropy

Thixotropy is when apparent viscosity or shear stress decreases with time of shear at a constant rate (Chhabra, 2007). During shearing, the continuous decrease in apparent viscosity and subsequent recovery of shear stress or apparent viscosity when flow is discontinued creates a hysteresis loop. Thixotropy is quantified from the area of loop or specific point on ramp curves of shear stress or apparent viscosity at a specific shear rate, usually 5 or 40 s\(^{-1}\). A certified method has still to be denoted (ICA, 2000; Cheng, 2003; Servais \textit{et al.}, 2004), but a well-conched chocolate should not be thixotropic. Difference between yield stresses measured at a shear of 5 s\(^{-1}\) during ramp up and down in shear was used to represent thixotropy.

PSD, fat and lecithin content – all had significant effects on thixotropy although this observation was only made on the low fat (25%). The samples containing 30 and 35% fat...
contents exhibited little thixotropy, implying that irrespective of PSD, fat and lecithin content, chocolates of 30% or more fat were not thixotropic (Fig. 7.7).

With the exception of 50 µm, which had reduced thixotropy values, all 25% fat samples exhibited high thixotropic behaviour, suggesting that thixotropy is dependent on PS and fat content (Fig. 7.7), which could be attributed to the crowding of the particulate system during shearing with formation of sample spanning aggregates due to low interaction energy at low fat levels. Prasad et al. (2003) noted that the rates of formation and disruption of aggregates are functions of the flow-induced shear stresses, particle volume fraction and interaction energy. Chevalley (1999) suggested that thixotropy is especially important for thick chocolates, and in this study PSD and lecithin were key factors that could be manipulated to reduce thixotropy in low fat and/or thick chocolates.

### 7.5 RELATIONSHIPS BETWEEN CASSON MODEL AND ICA RECOMMENDATIONS

Multivariate correlation, regression and principal component analyses evaluated relationships between Casson plastic viscosity and Casson yield value and the newer yield stress, apparent viscosity and thixotropy (ICA, 2000; Servais et al., 2004). Effects of PSD and composition on dark chocolate rheology using both models have been reported in Section 7.4.

Correlation and regression analyses conducted on the data revealed high regression and correlation coefficients among all rheological parameters (Table 7.6). Relationships were...
calculated using correlation analysis between Casson plastic viscosity and Casson yield value, and the apparent viscosity and (apparent) yield stress, the ICA-recommended values. High correlation coefficients \( r = 0.95; p < 0.001 \) were observed between the Casson plastic viscosity and apparent viscosity and Casson yield value and yield stress \( (r = 0.98; p < 0.001) \).

Regression analyses (Fig. 7.8(a and b)) showed Casson plastic viscosity and apparent viscosity, and Casson yield value and yield stress were closely related. Contrary to the findings of Servais et al. (2004), Casson plastic viscosity and Casson yield value were highly correlated \( (r = 0.89; p < 0.001) \), with a high and significant regression coefficient, \( R^2 = 0.84 \) (Table 7.6). The regression model is as shown in Figure 7.8(c). Similarly, yield stress and apparent viscosity were highly correlated \( (r = 0.99; p < 0.001) \), with regression coefficient, \( R^2 = 0.99 \) (Table 7.3). Figure 7.8(d) shows the regression model for yield stress and apparent viscosity.

Thixotropy is exhibited in chocolates if its apparent viscosity or shear stress decreases with time when sheared at a constant rate, and relates to degree of conching – well-conched chocolate should not be thixotropic. Interpolation and extrapolation data could be used to characterise thixotropy, but no certified method has been denoted (ICA, 2000; Cheng, 2003; Chhabra, 2007). Servais et al. (2004) suggested that practically thixotropy can be obtained by (i) area differences between ramp up and ramp down in flow curves; (ii) calculating analytically area differences in Casson models between 2 and 50 s\(^{-1}\); (iii) stress differences at 5 s\(^{-1}\) from ramps up and down; (iv) viscosity differences at 40 s\(^{-1}\) from ramps up and down. Using data from four Swiss dark chocolates, viscosity differences at 40 s\(^{-1}\) from ramps up and down in shear rates multiplied by 1600 [s\(^{-2}\)] represented thixotropy. However, provided there are sufficient data points, interpolation data give more robust information and extrapolation should be avoided as giving erroneous results.

Correlation and regression analyses (Fig. 7.8(e)) determined relationships between thixotropy from yield stress differences at 5 s\(^{-1}\) and from calculating the difference between apparent viscosities at 40 s\(^{-1}\), in each case comparing ramps up and down. Significant correlation coefficients of \( r = 0.98 (p < 0.001) \), and regression coefficient of determination of \( R^2 = 0.95 (p < 0.001) \), among the two methods (Table 7.6), suggested that both yield stress

### Table 7.6 Regression and correlation analyses between rheological parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Analysis</th>
<th>Casson plastic viscosity</th>
<th>Casson yield value</th>
<th>Apparent viscosity</th>
<th>Yield stress</th>
<th>Thixotropy (YS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Casson plastic viscosity</td>
<td>Regression</td>
<td>1.0000</td>
<td>0.8368*</td>
<td>0.9053*</td>
<td>0.8919*</td>
<td>0.9021*</td>
</tr>
<tr>
<td></td>
<td>Correlation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Casson yield value</td>
<td>Regression</td>
<td></td>
<td>1.0000</td>
<td>0.9582*</td>
<td>0.9694*</td>
<td>0.9665*</td>
</tr>
<tr>
<td></td>
<td>Correlation</td>
<td></td>
<td>1.0000</td>
<td>0.9786*</td>
<td>0.9844*</td>
<td>0.9823*</td>
</tr>
<tr>
<td>Apparent viscosity</td>
<td>Regression</td>
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<td></td>
<td></td>
<td>1.0000</td>
<td>0.9898*</td>
</tr>
<tr>
<td></td>
<td>Correlation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.9955*</td>
</tr>
<tr>
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<td>Correlation</td>
<td></td>
<td></td>
<td></td>
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<td>1.0000</td>
</tr>
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<td>Thixotropy (AP)</td>
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<td>0.9527</td>
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<td>Correlation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.9761</td>
</tr>
</tbody>
</table>

*Significant at \( p < 0.001 \).
Fig. 7.8  (a) Relationship between Casson plastic viscosity and apparent viscosity using bob and cup (reference) geometry (Afoakwa et al., 2009c). Data points (squares); linear regression (inner solid line); minimum and maximum tolerance intervals (both outer lines); Casson plastic viscosity = $0.477564 + 0.31802 \times$ apparent viscosity. (b) Relationship between Casson yield value and yield stress using bob and cup (reference) geometry (Afoakwa et al., 2009c). Data points (squares); linear regression (inner solid line); minimum and maximum tolerance intervals (both outer lines); Casson yield value = $-8.29934 + 0.458911 \times$ yield stress. (c) Relationship between Casson yield value and Casson plastic viscosity using bob and cup (reference) geometry (Afoakwa et al., 2009c). Data points (squares); linear regression (inner solid line); minimum and maximum tolerance intervals (both outer lines); Casson yield value = $-11.9953 + 18.4325 \times$ Casson plastic viscosity. (d) Relationship between yield stress and apparent viscosity using bob and cup (reference) geometry (Afoakwa et al., 2009c). Data points (squares); linear regression (inner solid line); minimum and maximum tolerance intervals (both outer lines); yield stress = $-14.4174 + 14.8302 \times$ apparent viscosity. (e) Relationship between thixotropy from yield stress and thixotropy from apparent viscosity (Afoakwa et al., 2009c). Data points (squares); linear regression (inner solid line); minimum and maximum tolerance intervals (both outer lines); thixotropy (YS) = $6.42097 + 1.1907 \times$ thixotropy (AP).
and apparent viscosity could be used as reliable interpolation data to measure thixotropy. In contrast, the use of extrapolation data from Casson parameters should be avoided as this gave lower coefficients of determination (Table 7.6).

The principal component analysis (PCA) product space (Fig. 7.9) explained 95.2% variance (74.2, 13.7 and 7.3%) (eigenvalue > 1) and showed rheological parameters very closely related with PSD, fat and lecithin content as key influencing factors. This PCA (Fig. 7.9) product space for Casson parameters (plastic viscosity and yield value) and ICA-recommended parameters (apparent viscosity and yield stress) were closely related and could be used independently to evaluate rheological properties of dark chocolates.

### 7.6 TEXTURAL PROPERTIES

#### 7.6.1 Molten dark chocolate

Firmness, consistency, cohesiveness and index of viscosity were evaluated to ascertain degree of spreadability, consistency and resistance to flow behaviour (viscosity). Ziegler and Hogg (1999) concluded that such flow behaviour is important for moulding and enrobing, for proper cookie drop formation and in design of bulk handling systems. Firmness and consistency correlated with degree of spreadability, and particulate consistency showed similar trends varying PSD and composition (Figs 7.10 and 7.11). Increasing PSs from 18 to 50 µm caused significant ($p < 0.001$) reductions in firmness and consistency at all fat levels, greatest (approximately sixfold reduction) at 25% fat.

Similarly, cohesiveness and index of viscosity, respectively, denoting work of cohesion and viscosity, showed consistent and significant ($p < 0.001$) decreasing trends with increasing PS at all fat levels, causing up to approximately eightfold reductions in cohesiveness (Fig. 7.12) and approximately sixfold reductions in index of viscosity (Fig. 7.13). Samples with
18 µm particles were firmer, more consistent, cohesive and viscous than those with 50 µm: with reduced mean diameter, particle number increases in parallel with specific surface area (Table 7.2), enhancing particle surface–surface contacts yielding higher values for firmness, consistency and cohesiveness, restricting spreadability and viscosity for a specific solid concentration.

The high degree of reductions noticeable with low-fat (25%) chocolate, with increasing PS might be because, as the distribution of PSs becomes more spread out with a large specific surface area, the smaller particles fill the spaces between the larger particles, resulting in drastic reduction in the firmness, consistency, cohesiveness and viscosity. Likewise, increasing the fat content of the chocolates from 25 to 30% led to drastic reductions in all textural parameters at all PSs and lecithin concentrations. At low PS (18 µm), 5% increase in fat content caused up to fivefold reduction, indicating that fat has a marginally greater effect on firmness, consistency, cohesiveness and viscosity of dark chocolates especially at lower PS (18–25 µm) and lower lecithin levels. At 35% fat content, very little differences were observed at all PS and lecithin levels, attributable to fat inducing free-moving lubricating flow, which is more connected with the forces between the solid particles. Beckett (2000) explained that fat fills the spaces or voids between the solid particles in molten chocolate and reduces their resistance to flow, with the greatest effect noticeable at lower PS.

Increasing lecithin from 0.3 to 0.5% significantly decreased firmness, consistency, cohesiveness and index of viscosity especially at lower fat content and lower PS, where up to
twofold reductions were noted, attributable to an association with sugar particles. Lecithin phospholipids migrate to sugar crystal surfaces, making these lipophilic, and thus acts as lubricant, reducing internal friction and firmness, consistency, cohesiveness and viscosity (Beckett, 2000; Bueschelberger, 2004). Chevalley (1999) noted that a monolayer of lecithin on sugar particle surfaces enhances suspension mobility with parallel increases in fat spreadability. Samples with 30 and 35% fat had comparable values for molten chocolate firmness, consistency, cohesiveness and viscosity with implications for manufacturing.

Univariate ANOVA showed that PSD, fat and lecithin contents significantly \((p < 0.001)\) influenced firmness, cohesiveness and viscosity (Table 7.7) with interactions also significant. Duncan’s multiple range tests revealed that at 25% fat, PSD had significant \((p < 0.001)\) effect on spreadability but less at 30 and 35%. Combined effect of PSD, fat and lecithin could be manipulated within stipulated legal regulations to achieve high-fat textural properties, notably spreadability and viscosity, at reduced fat concentrations.

### 7.6.2 Hardness of tempered dark chocolate

Hardness showed inverse relationships with PS, fat and lecithin with significant reductions at all fat contents, but greatest at 25 with 0.3% lecithin (Fig. 7.14). At 25% fat, hardness decreased from 7062 g with 18 µm to 5546 g at 50 µm. Trends in hardness were similar
Fig. 7.12  Effect of PSD and composition on cohesiveness of molten dark chocolate. Reprinted from Afoakwa et al. (2008e), copyright 2008, with permission from Elsevier.

Fig. 7.13  Effect of PSD and composition on index of viscosity of molten dark chocolate. Reprinted from Afoakwa et al. (2008e), copyright 2008, with permission from Elsevier.
Table 7.7  ANOVA summary of F-values of the textural properties

<table>
<thead>
<tr>
<th>Process variables</th>
<th>Firmness</th>
<th>Consistency</th>
<th>Cohesiveness</th>
<th>Index of viscosity</th>
<th>Hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: Particle size (D₉₀)</td>
<td>1595.40*</td>
<td>2340.25*</td>
<td>2027.61*</td>
<td>1018.71*</td>
<td>978.94*</td>
</tr>
<tr>
<td>B: Fat</td>
<td>5971.02*</td>
<td>8583.65*</td>
<td>10547.21*</td>
<td>5919.75*</td>
<td>6921.18*</td>
</tr>
<tr>
<td>C: Lecithin</td>
<td>578.48*</td>
<td>815.85*</td>
<td>988.35*</td>
<td>518.83*</td>
<td>166.74*</td>
</tr>
<tr>
<td>A × B</td>
<td>841.85*</td>
<td>1221.89*</td>
<td>1083.29*</td>
<td>502.72*</td>
<td>160.94*</td>
</tr>
<tr>
<td>A × C</td>
<td>224.58*</td>
<td>317.98*</td>
<td>279.52*</td>
<td>127.12*</td>
<td>7.48*</td>
</tr>
<tr>
<td>B × C</td>
<td>392.59*</td>
<td>534.14*</td>
<td>698.08*</td>
<td>354.23*</td>
<td>17.74*</td>
</tr>
<tr>
<td>A × B × C</td>
<td>156.79*</td>
<td>219.63*</td>
<td>186.26*</td>
<td>81.83*</td>
<td>32.48*</td>
</tr>
</tbody>
</table>

*Significant F-ratios at $p \leq 0.05$.

at 30 and 35% fat with 0.3% lecithin but less pronounced at higher PSs (Fig. 7.14). The greater hardness levels noted with 25% fat and 18–25 µm PSs suggest more particle–particle interactions and spanning of stress-bearing paths. Hardness from particle contacts was a function of mean PS and diameter and specific surface area.

Fat content was inversely related ($p < 0.001$) to hardness at all PSs and lecithin levels (Fig. 7.14). Combined effects of fat content and PSD thus have greatest influences but are less pronounced at higher fat and lecithin contents (Fig. 7.14) where fat coating of particles reduces interparticle interactions, inducing product softening. Significant ($p < 0.001$) reductions were noted when lecithin content was increased from 0.3 to 0.5%. Lecithin has

Fig. 7.14  Effect of PSD and composition on hardness of tempered dark chocolate. Reprinted from Afoakwa et al. (2008e), copyright 2008, with permission from Elsevier.
amphiphilic (both hydrophilic and lipophilic) properties, making the molecule an effective dispersant, promoting deagglomeration and wetting of clumps inducing chocolate softening. Significant \( p < 0.001 \) interactions (Table 7.7) showed that the combined effects of PSD, fat and lecithin could be manipulated to control softness and/or hardness of tempered dark chocolate, with implications for quality control and production cost.

### 7.6.3 Colour measurements

Lightness \( (L^*) \), chroma \( (C^* \) and hue \( (h^\circ) \) followed similar trends with changes in PSD, fat and lecithin contents (Table 7.8). Significant \( p < 0.001 \) and linear effects on \( L^* \) were recorded with increasing particles from 18 to 50 \( \mu \)m, with consequential decreases in \( L^* \), noticeable but dependent on fat contents (Table 7.8). Similar decreases were noted in \( C^* \) and \( h^\circ \) with increasing PSD and fat. Thus, dark chocolate became lighter as \( D_{90} \) decreased from 50 to 18 \( \mu \)m and as PS increased (18–50 \( \mu \)m); \( C^* \) and \( h^\circ \) were significantly decreased, pronounced at 25% fat. Increasing fat content reduced \( C^* \) and \( h^\circ \), but the effects were less marked at 35% fat than at 30%. As lecithin had no noticeable effect on \( L^* \), \( C^* \) and \( h^\circ \) (Table 7.9), appearance data were primarily dependent on PSD and fat content.

#### Table 7.8 Effects of particle size distribution and composition on colour measurements

<table>
<thead>
<tr>
<th>Particle size ( (D_{90}) ) (( \mu )m)</th>
<th>Fat content (%)</th>
<th>Lecithin (%)</th>
<th>( L^* )</th>
<th>( C^* )</th>
<th>( h^\circ )</th>
</tr>
</thead>
<tbody>
<tr>
<td>18 ± 1.0</td>
<td>25</td>
<td>0.3</td>
<td>43.49 ± 0.40</td>
<td>14.36 ± 0.40</td>
<td>43.9 ± 0.24</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>43.52 ± 0.87</td>
<td>14.24 ± 0.46</td>
<td>43.7 ± 0.87</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.3</td>
<td>40.39 ± 1.16</td>
<td>13.15 ± 0.08</td>
<td>42.6 ± 0.49</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>37.43 ± 0.67</td>
<td>13.04 ± 0.52</td>
<td>42.4 ± 0.35</td>
<td></td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>0.3</td>
<td>35.19 ± 0.56</td>
<td>11.60 ± 0.07</td>
<td>40.4 ± 0.15</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>34.73 ± 0.38</td>
<td>11.82 ± 0.34</td>
<td>41.4 ± 0.61</td>
<td></td>
</tr>
<tr>
<td>25 ± 1.0</td>
<td>25</td>
<td>0.3</td>
<td>42.16 ± 0.36</td>
<td>14.11 ± 0.48</td>
<td>42.9 ± 0.87</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>41.72 ± 1.82</td>
<td>14.17 ± 0.57</td>
<td>42.8 ± 0.72</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.3</td>
<td>35.96 ± 0.33</td>
<td>12.70 ± 0.28</td>
<td>42.5 ± 0.77</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>36.43 ± 0.67</td>
<td>12.90 ± 0.75</td>
<td>42.5 ± 0.78</td>
<td></td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>0.3</td>
<td>36.41 ± 0.50</td>
<td>11.65 ± 0.33</td>
<td>40.6 ± 0.60</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>34.01 ± 0.14</td>
<td>11.51 ± 0.19</td>
<td>40.5 ± 0.80</td>
<td></td>
</tr>
<tr>
<td>35 ± 1.0</td>
<td>25</td>
<td>0.3</td>
<td>40.94 ± 0.33</td>
<td>13.79 ± 0.38</td>
<td>42.9 ± 0.31</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>40.38 ± 0.80</td>
<td>13.94 ± 0.15</td>
<td>42.6 ± 0.50</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.3</td>
<td>34.85 ± 0.18</td>
<td>12.38 ± 0.22</td>
<td>42.5 ± 0.10</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>35.27 ± 0.52</td>
<td>12.58 ± 0.27</td>
<td>42.0 ± 0.21</td>
<td></td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>0.3</td>
<td>33.50 ± 0.42</td>
<td>11.50 ± 0.07</td>
<td>39.7 ± 0.40</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>33.86 ± 0.23</td>
<td>11.51 ± 0.06</td>
<td>40.1 ± 0.26</td>
<td></td>
</tr>
<tr>
<td>50 ± 1.0</td>
<td>25</td>
<td>0.3</td>
<td>38.64 ± 0.53</td>
<td>13.42 ± 0.28</td>
<td>42.5 ± 0.39</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>36.93 ± 0.26</td>
<td>13.93 ± 0.16</td>
<td>42.7 ± 0.15</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.3</td>
<td>34.22 ± 1.17</td>
<td>12.24 ± 0.46</td>
<td>41.6 ± 0.95</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>34.90 ± 0.35</td>
<td>12.14 ± 0.26</td>
<td>41.2 ± 0.21</td>
<td></td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>0.3</td>
<td>33.25 ± 1.16</td>
<td>11.27 ± 0.42</td>
<td>39.5 ± 0.83</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>33.42 ± 0.59</td>
<td>11.04 ± 0.15</td>
<td>38.9 ± 0.34</td>
<td></td>
</tr>
</tbody>
</table>

Means ± standard deviation from triplicate analysis.
Hutchings (1994) stated that $L^*$, $C^*$ and $h^\circ$, respectively, represent food diffuse reflectance of light, degree of saturation and hue luminance, which are dependent on particulate distribution, absorptivity and scattering factors or coefficients. In a densely packed medium, scattering factor is inversely related to particle diameter (Saguy & Graf, 1991). Chocolates with varying PSs differ in structural and particulate arrangements (Table 7.2), influencing light-scattering coefficients and thus appearance. Chocolates with finer particles (18–25 $\mu$m) have larger specific surface areas, lower particle diameters and more interparticle interactions, thus tend to be denser, scatter more light, appear lighter and more saturated than those with coarser (35–50 $\mu$m) particles. Such changes result in higher scattering coefficients, with subsequent paleness – higher $L^*$ values. Consequently, increases in saturation effects within suspensions yield higher $C^*$ and $h^\circ$ values. On the other hand, cocoa fat is an inherent crystalline network, which scatters light, reducing luminance and saturation indices in higher fat products.

From ANOVA, PSD and fat content significantly ($p < 0.001$) influenced $L^*$, $C^*$ and $h^\circ$, but lecithin had no significant effect on appearance (Table 7.9). No significant ($p \leq 0.05$) interactions were observed among processing parameters (Table 7.8), with the exception of interaction between PSD and fat content. Fat content had the greatest influence on dark chocolate appearance followed by PSD.

### 7.6.4 Relationships between textural properties and appearance of dark chocolate

Correlation and principal component analyses established the extent that PSD, fat and lecithin contents influence textural properties and appearance with clear correlations. The correlation matrix (Table 7.10) for textural properties (firmness, consistency, cohesiveness, index of viscosity and hardness) and colour ($L^*$, $C^*$ and $h^\circ$) showed that these were directly correlated with a highly significant correlation ($r = 0.99–1.00; p < 0.001$) among textural properties, with high direct correlation ($r = 0.71–0.96; p < 0.001$) between colour measurements. Thus, changes in textural properties in molten and solid tempered dark chocolates could predict finished product appearance although $L^*$ exhibited higher correlation ($r = 0.87–0.96; p < 0.001$) than $C^*$ and $h^\circ$, suggesting a better prediction.

The multivariate PCA product space (Fig. 7.15) explained more than 81% variance in the first two factors and showed that texture and colour parameters were closely related with loadings for PSD, fat and lecithin content influencing factors. Fat content and PSD had polar influences on principal component 2 (PC2) (16.4% variance) score. Further examination
Table 7.10  Correlation between textural properties and colour measurements of dark chocolate

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Firmness</th>
<th>Consistency</th>
<th>Cohesiveness</th>
<th>Index of viscosity</th>
<th>Hardness</th>
<th>L-value</th>
<th>Chroma</th>
<th>Hue</th>
</tr>
</thead>
<tbody>
<tr>
<td>Firmness</td>
<td>1</td>
<td>0.9997*</td>
<td>0.9967*</td>
<td>0.9947*</td>
<td>0.9855*</td>
<td>0.9558*</td>
<td>0.9104*</td>
<td>0.7811*</td>
</tr>
<tr>
<td>Consistency</td>
<td>—</td>
<td>1</td>
<td>0.9928*</td>
<td>0.9845*</td>
<td>0.8814*</td>
<td>0.8691*</td>
<td>0.7069*</td>
<td>0.7287*</td>
</tr>
<tr>
<td>Cohesiveness</td>
<td>—</td>
<td>—</td>
<td>1</td>
<td>0.9982*</td>
<td>0.9865*</td>
<td>0.9584*</td>
<td>0.9099*</td>
<td>0.7834*</td>
</tr>
<tr>
<td>Index of viscosity</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1</td>
<td>0.9861*</td>
<td>0.9563*</td>
<td>0.9086*</td>
<td>0.7841*</td>
</tr>
<tr>
<td>Hardness</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1</td>
<td>0.9470*</td>
<td>0.9275*</td>
<td>0.8107*</td>
</tr>
<tr>
<td>L-value</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1</td>
<td>0.8600*</td>
<td>0.7273*</td>
</tr>
<tr>
<td>Chroma</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1</td>
<td>0.8760*</td>
</tr>
<tr>
<td>Hue</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1</td>
</tr>
</tbody>
</table>

*Significant at \( p < 0.05 \).
suggested that PSD had multiple discrete components (specific surface area, largest PS (D_{90}), smallest PS (D_{10}), mean PS (D_{50}) and Sauter mean diameter (D_{3,2})), together influencing texture and appearance.

### 7.7 MICROSTRUCTURAL PROPERTIES OF MOLTEN DARK CHOCOLATE

Light microscopy was used to characterise the variations in sugar crystalline network, particle–particle interaction strengths and particle-fat phase behaviour from molten dark chocolate with varying PSD and fat concentration. Micrographs (Figs 7.16–7.18) showed clear variations in microstructure among samples from different PSD (Table 7.2) and fat contents.

 Samples containing 25% fat showed high solids packing intensity with extensive particle–particle interaction strengths at all PSs (Fig. 7.16(a–d)) so that the crystalline network was dispersed with large specific surface area (Table 7.2), and with smaller particles filling the spaces between the larger, the result was a high bed density. At lower PS (18 µm), particle numbers increased in parallel with points of contact, particle–particle interactions and greater packing ability. The increased particle–particle interactions, amount of and specific surface area and mean particle diameter, resulted in flocculation and agglomeration, forming spanning stress-bearing paths, restricting mobility and compartmentalisation of the matrix (Fig. 7.16(a and b)).

 With PS ranges between 35 and 50 µm, particles were coarser, leading to PSD broadening into multimodal distributions (Fig. 7.4(c and d)), which reduced solid loading, and specific surface area (Table 7.2). As PSs were increased, the packing ability of solids became restricted, leading to fewer particle–particle interactions (Fig. 7.16(c and d)). Prasad et al. (2003) also noted that rates of formation and disruption of aggregates were functions of flow-induced shear stresses, particle volume fraction and interaction energy. The observed greater flocculation and agglomeration of sugar crystals network and high interparticle interaction with 25% fat explained higher rheological (Beckett, 1999; Chevalley, 1999) and mechanical properties (firmness and hardness) observed with low-fat chocolates. Servais et al. (2004) noted that yield stress depended on amount of small particles (specific
surface area) and interactions, and originated in mechanical (friction) and chemical interactions between particles. Prasad et al. (2003) concluded that yield value was determined by interparticle contacts, with a consequent linear dependence on mean PS or, more accurately, on specific surface area.

With higher fat (Figs 7.17 and 7.18), there were less dense sugar crystalline networks and reduced particle–particle interactions, with more open structures and void spaces between the crystals. This could be related to the higher fat content in the suspension, which tends to wet the matrix with fat, thereby opening up the fat phase, as fat filled the voids within the crystal network. Beckett (1999) attributed this to the free-moving lubricating plastic flow, more connected with forces between solid particles. Fat fills spaces between solid particles in molten chocolate and reduces resistance to flow, with the greatest effect at lower PS. However, the microstructure of D$_{90}$ PSs of more than 35 µm shows very large spherical and dispersed crystalline grains within the suspension (Figs 7.16(c and d), 7.17(c and d) and 7.18(c and d)), which is suggested to be the cause of grittiness associated with chocolates processed with D$_{90}$ of more than 35 µm (Beckett, 2008).

![Microstructure of dark chocolate containing 25% fat with PS (D$_{90}$) of (a) 18 (b) 25 (c) 35 and (d) 50 µm (Afoakwa et al., 2009d).](image)

**Fig. 7.16** Microstructure of dark chocolate containing 25% fat with PS (D$_{90}$) of (a) 18 (b) 25 (c) 35 and (d) 50 µm (Afoakwa et al., 2009d).
The qualitative structural information illustrated by the micrographs thus provides a mechanistic explanation for quantitative differences in rheological, textural and sensory character in dark chocolates with varying PSD and fat content. This knowledge can improve the quality of models developed to optimise PSD influences on the flow, textural and sensory character in chocolate. Release of structural mobility and compartmentalisation can be achieved by controlling microstructure during processing. Aguilera (2005) explained that structure has the largest effect on sound and food behaviour in biting. Structuring of particles within the multiphase chocolate systems during processing could be optimised to enhance resistance to flow, reduce grittiness perceived in chocolate with particle D$_{90}$ of more than 35 µ, with consequential effects on the quality characteristics of finished chocolates.

### 7.8 MELTING PROPERTIES OF DARK CHOCOLATE

Peak onset corresponds to the temperature at which a specific crystal form starts to melt; peak maximum, that at which melting rate is greatest; and end of melting, completion of
liquefaction – all the information is related to the crystal type. Peak height, position and resolution are dependent on sample composition and crystalline-state distribution (McFarlane, 1999). All the samples exhibited similar distinct single endothermic transitions between 15 and 55°C, the range expected for chocolate melting profiles. Figure 7.19 shows a typical DSC thermogram used for evaluating the melting properties of dark chocolates manufactured from varying PSD, fat and lecithin content. It recorded that heat capacity, $c_p$, gradually and consistently increased to onset temperature ($T_{onset}$), and then progressively increased more rapidly until peak temperature ($T_{peak}$), after which it decreased to the end temperature ($T_{end}$), indicating the chocolate was completely melted.

![Microstructure of dark chocolate containing 30% fat with PS (D90) of (a) 18 (b) 25 (c) 35 and (d) 50 µm (Afoakwa et al., 2009d).](image)

**Fig. 7.17** Microstructure of dark chocolate containing 30% fat with PS (D90) of (a) 18 (b) 25 (c) 35 and (d) 50 µm (Afoakwa et al., 2009d).
7.8.1 Effects of particle size distribution

PSD influences chocolate rheological and microstructural properties as well as texture in derived molten and tempered products (Afoakwa et al., 2008b, 2009d). The thermogram (Fig. 7.20) showed similar peak shapes and sizes for dark chocolates manufactured with varying PSD, suggesting no characteristic differences in crystallinity and degree of crystallisation between the products. Table 7.11 shows values for key DSC parameters ($T_{\text{onset}}, T_{\text{end}}, T_{\text{peak}}$, etc.)
Increasing PS from 18 to 50 µm caused no significant ($p = 0.675$) changes in $T_{\text{onset}}$, at all fat and lecithin levels (Table 7.12). Values for $T_{\text{onset}}$ were in the range of 26.5–26.6°C in products containing 25% fat and 0.3% lecithin at 18 and 50 µm PS, respectively. Similar insignificant differences ($p > 0.05$) in $T_{\text{onset}}$ were noted with varying PS at all fat and lecithin levels (Table 7.12). Likewise, $T_{\text{peak}}$ in products with varying PSD, fat and lecithin contents showed only marginal differences.

The results (Table 7.11) showed that $T_{\text{peak}}$ of products with increasing PS from 18 to 50 µm ranged between 32.3 and 32.5°C, respectively, in products containing 25% fat and 0.3% lecithin, and this trend was similar at all fat and lecithin concentrations. These showed that the initiation and maximum temperatures in dark chocolate melting are independent of PSD, with mean values for $T_{\text{onset}}$ and $T_{\text{peak}}$ of approximately 26.5 and 32.4°C, respectively.
Similar non-significant differences ($p > 0.05$) in $\Delta H_{\text{melt}}$ were found between products with varying PS at all fat and lecithin contents (Table 7.12). Values of $\Delta H_{\text{melt}}$ in products with increasing PS from 18 to 50 $\mu$m ranged from 30.07 to 30.62 J/g in products containing 25% fat and 0.3% lecithin, and this marginal and insignificant differences ($p > 0.05$) in trends were similar at all fat and lecithin levels.
The non-significant relationship between PSD and $\Delta H_{\text{melt}}$ implies that enthalpy of melting was similar for chocolates at all PS at specified fat and lecithin levels. This indicates that irrespective of the ingredient (fat or lecithin content) used for the formulation, dark chocolates produced with varying PS would require similar energy to complete melting.

In contrast, varying PSD had significant effects on $T_{\text{end}}$ and $T_{\text{index}}$ of products. Generally, there were inverse relationships between PS and $T_{\text{end}}$ and $T_{\text{index}}$, at all fat and lecithin contents (Table 7.11). Products with smaller PS (18 µm) at 25% fat and 0.3% lecithin content had $T_{\text{end}}$ value of 34.6°C, whilst those with 50 µm had 34.0°C, representing a difference of 0.6°C. Similar marginal but significant ($p < 0.05$) decreasing trends in $T_{\text{end}}$ were observed at all fat and lecithin levels (Table 7.12), suggesting that dark chocolates with larger PS (50 µm) require slightly lower temperatures to complete melting than their corresponding smaller PS (18 µm) products. However, the $T_{\text{end}}$ values in all the products were in the range
Structure – properties (rheology, texture and melting) relationships in chocolate manufacture

33.0–34.6°C, indicating all samples had similar Form V (β₂) polymorphic stability. A similar inverse relationship was observed between $T_{\text{index}}$ and PSD. The data (Table 7.11) showed that increasing PS for 18–50 µm in chocolates containing 25% fat and 0.3% lecithin caused significant ($p \leq 0.05$) reductions in $T_{\text{index}}$ from 8.4 to 7.4°C, respectively. ANOVA showed significant ($p < 0.05$) influence of PSD on $T_{\text{end}}$ and $T_{\text{index}}$ with significant interactions for fat and lecithin contents (Table 7.12).

Multiple range test revealed significant differences ($p = 0.001$) between $T_{\text{end}}$ of products containing 18, 35 and 50 µm, indicating that chocolates with finer particles would take relatively longer time to melt than their corresponding products with larger particles, suggesting their possible relationships with the relative strengths of the interparticle aggregations and floculation in the different products.

Chocolates with smaller PSD ($D_{90}, 18$ µm) have been found to contain higher particle-to-particle strengths with resultant increases in hardness (texture) than their corresponding larger PSD ($D_{90}, 50$ µm) (Do et al., 2007; Afoakwa et al., 2009d). Do et al. (2007) also

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**Fig. 7.20** Typical DSC thermograms for dark chocolate at constant fat and lecithin content with varying PSD: (a) 18, (b) 25, (c) 35 and (d) 50 µm (Afoakwa et al., 2008d). Reprinted from Afoakwa et al. (2008d), copyright 2008, with permission from Elsevier.
Table 7.11  Melting properties of dark chocolate from varying PSD, fat and lecithin content

<table>
<thead>
<tr>
<th>Particle size (Dv₀.9) (μm)</th>
<th>Fat (%)</th>
<th>Lecithin (%)</th>
<th>Melting properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>T&lt;sub&gt;onset&lt;/sub&gt; (°C)</td>
</tr>
<tr>
<td>18 ± 1.0</td>
<td>25</td>
<td>0.3</td>
<td>26.2 ± 0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>26.0 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.3</td>
<td>26.5 ± 0.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>26.3 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>0.3</td>
<td>26.4 ± 0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>26.5 ± 0.2</td>
</tr>
<tr>
<td>25 ± 1.0</td>
<td>25</td>
<td>0.3</td>
<td>26.3 ± 0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>26.3 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.3</td>
<td>26.6 ± 0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>26.5 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>0.3</td>
<td>26.6 ± 0.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>26.5 ± 0.2</td>
</tr>
<tr>
<td>35 ± 1.0</td>
<td>25</td>
<td>0.3</td>
<td>26.3 ± 0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>26.4 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.3</td>
<td>26.6 ± 0.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>26.7 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>0.3</td>
<td>26.8 ± 0.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>26.9 ± 0.4</td>
</tr>
<tr>
<td>50 ± 1.0</td>
<td>25</td>
<td>0.3</td>
<td>26.6 ± 0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>26.7 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.3</td>
<td>26.8 ± 0.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>26.7 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>0.3</td>
<td>26.8 ± 0.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5</td>
<td>26.8 ± 0.3</td>
</tr>
</tbody>
</table>

Mean values from triplicate analysis ± standard deviation.
Table 7.12 ANOVA summary of F-values of the melting properties

<table>
<thead>
<tr>
<th>Process variables</th>
<th>$T_{\text{onset}}$ (°C)</th>
<th>$T_{\text{end}}$ (°C)</th>
<th>$T_{\text{peak}}$ (°C)</th>
<th>$\Delta H_{\text{melt}}$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: Particle size</td>
<td>1.53</td>
<td>11.00*</td>
<td>199.84*</td>
<td>0.84</td>
</tr>
<tr>
<td>B: Fat</td>
<td>12.54</td>
<td>32.32*</td>
<td>2300.26*</td>
<td>0.23</td>
</tr>
<tr>
<td>C: Lecithin</td>
<td>2.43</td>
<td>18.18*</td>
<td>148.84*</td>
<td>3.13</td>
</tr>
<tr>
<td>A $\times$ B</td>
<td>0.89</td>
<td>2.89*</td>
<td>99.22*</td>
<td>0.49</td>
</tr>
<tr>
<td>A $\times$ C</td>
<td>2.16</td>
<td>2.39</td>
<td>31.69*</td>
<td>0.91</td>
</tr>
<tr>
<td>B $\times$ C</td>
<td>2.45</td>
<td>0.53</td>
<td>198.58*</td>
<td>0.66</td>
</tr>
<tr>
<td>A $\times$ B $\times$ C</td>
<td>1.73</td>
<td>1.01</td>
<td>19.76*</td>
<td>2.17</td>
</tr>
</tbody>
</table>

*Significant F-ratios at $p \leq 0.05$.

noted that decreases in the amount of particle aggregation and structure build up in flow affect chocolate meltdown, suggesting that in its crystallised state, the particle skeleton of chocolates with larger PS is less interconnected, providing less resistance to breakage and meltdown. This knowledge is important as it provides information on likely oral melting behaviour with an impact on temporal components of flavour release and also oral epithelial sensation. Beckett (1999) and Ziegler et al. (2001) noted that variations in PS might influence melt, flavour, colour and gloss of chocolates.

7.8.2 Effects of fat content

Data from the DSC (Fig. 7.21) indicated that varying fat content produced changes in crystallinity and melting properties observed in the differences in their peak widths. This suggests that the fat content in dark chocolates during manufacture influences the degree of crystallinity and crystal size distribution (CSD) of their corresponding tempered products. Lonchampt and Hartel (2004) also noted that amount and composition of fat in chocolate production had unpredictable effects on crystal size, and polymorphism and crystallisation rate in products. Hartel (2001) concluded that distribution of crystal sizes in foods plays key roles in final product quality, defined by total and specific characteristics of the crystalline material. Number of crystals and range of sizes, shapes and polymorphic stability, as well as arrangements in network structures, dictate mechanical and rheological properties. Knowledge and control of CSD can be important for optimising processing conditions.

Results from the DSC data on $T_{\text{onset}}$, $T_{\text{end}}$, $T_{\text{peak}}$, $\Delta H_{\text{melt}}$ and $T_{\text{index}}$ with varying fat content are as shown in Table 7.11. ANOVA and multiple mean comparisons showed no significant difference ($p > 0.05$) for $T_{\text{onset}}$ and $T_{\text{peak}}$ in chocolates with different fat contents (Table 7.12), implying limited influence on temperatures for onset and peak melting. There were significant differences ($p < 0.05$) between melting end ($T_{\text{end}}$), index ($T_{\text{index}}$) and enthalpies ($\Delta H_{\text{melt}}$) (Table 7.12). Increasing fat content from 25 to 35% caused consistent reductions in $T_{\text{end}}$ from 34.6 to 33.8°C in products containing 18 µm PS and 0.3% lecithin level.

Similar marginal but significant ($p < 0.05$) decreasing trends in $T_{\text{end}}$ with increasing fat content were noted at all PS and lecithin concentrations (Table 7.12). These suggest that low-fat (25%) chocolates completed melting at higher temperatures than those with more fat (30–35%). Likewise, increasing fat content caused consistent decreases in $T_{\text{index}}$ of products, suggesting an inverse relationship of $T_{\text{index}}$ with fat content (Table 7.11). Products with lower (25%) fat content, 18 µm PS and 0.3% lecithin had $T_{\text{index}}$ of 8.4°C, and this reduced consistently from 7.9 and 7.4°C, respectively, with increasing fat content to 30 and 35%.
Fig. 7.21 Typical DSC thermograms for dark chocolate at constant PS and lecithin content at constant PS and lecithin content with varying fat content: (a) 25, (b) 30 and (c) 35% (Afoakwa et al., 2008d). Reprinted from Afoakwa et al. (2008d), copyright 2008, with permission from Elsevier.

Similar reducing trends in $T_{\text{index}}$ were noted at all PS and lecithin levels. These explain that lower fat chocolates required longer time to melt than similar products with higher fat contents, again with a likely impact on behaviour during consumption. Lower melting duration in high-fat chocolates can be attributed to reductions in interparticle interactions and increased free-moving plastic flow, possibly related to yield value of products (Beckett, 2000; Do et al., 2007). Fat fills voids between particles in molten chocolate and reduces resistance to flow, with a direct relationship between fat content and $\Delta H_{\text{melt}}$, independent of PS. This implies that enthalpy is reduced in products of lower fat contents. From ANOVA and multiple comparison tests, fat content had the greatest influence on melting characteristics in these chocolates (Table 7.12).

### 7.8.3 Effects of lecithin

The amphiphilic nature of lecithin promotes deagglomeration with effects on physical properties (Talbot, 1999; Beckett, 2000; Lonchampt & Hartel, 2004; Dhonsi & Stapley, 2006).
Figure 7.22 shows typical DSC thermograms for dark chocolate manufactured from varying lecithin content (0.3 and 0.5%) at 18 µm PS and 30% fat content. The thermograms (Fig. 7.22) revealed the effect of lecithin concentration on crystallinity of products. The differences observed in peak widths suggest a moderate reducing effect of lecithin addition on degree of crystallinity, with consequential effect on some melting properties of products. Earlier studies reported that lecithin content had significant ($p < 0.001$) effect on the rheological and textural properties of dark chocolates with significance among the interactions with PS and fat content (Afoakwa et al., 2008b, e). Table 7.11 shows the results from the DSC data on $T_{\text{onset}}$, $T_{\text{end}}$, $T_{\text{peak}}$, $\Delta H_{\text{melt}}$ and $T_{\text{index}}$ with varying lecithin. Analysis of the values deduced from ANOVA and multiple mean comparisons showed no significant difference ($p > 0.05$) between $T_{\text{onset}}$ and $T_{\text{peak}}$ for the different lecithin concentrations, but significant differences ($p < 0.05$) between $T_{\text{end}}$, $T_{\text{index}}$ and $\Delta H_{\text{melt}}$ (Table 7.12). Both Johansson and Bergenstahl (1992) and Lonchampt and Hartel (2004) reported that lecithin influences sugar coating, fat crystallisation, crystal growth, polymorphism and oil migration, but has limited effect on solid fat content.
Generally, there were inverse relationships between $T_{\text{end}}$ and $T_{\text{index}}$, independent of PS and fat content (Table 7.11). Thermograms (Fig. 7.22) showed that increasing lecithin content influenced crystal dimensions and melting character in products. Increasing lecithin content of products from 0.3 to 0.5% caused marginal but significant differences in $T_{\text{end}}$ of products, noticeable at all PS and fat concentrations (Table 7.11). The $T_{\text{end}}$ values were between 33 and 34°C, an indication that the crystallisations were in $\beta V$ polymorph, imply limited influence under normal tempering conditions.

On the other hand, $T_{\text{index}}$ decreased consistently with increasing lecithin content, suggesting that products containing lower lecithin levels (0.3%) might require relatively longer residence time to melt than those of their corresponding products with higher lecithin levels (0.5%), with likely impact on the melting residence time of products during consumption. The lower melting index (duration) observed with products containing higher lecithin levels might be attributed to sugar-coating ability of lecithin during processing, and thus reducing their interparticle interaction to induce chocolate melting properties. Dhonsi and Stapley (2006) reported that lecithin migrates to sugar/fat interfaces and coats sugar crystals, influencing rheology and aiding dispersion of sugar crystals in the continuous phases. Chevalley (1999) suggested that lecithin forms a monolayer on sugar particle surfaces, allowing greater mobility in suspensions while increasing fat spreadability. Increasing lecithin content caused significant and consistent decreases in $\Delta H_{\text{melt}}$, trends noted at all PS and fat content (Table 7.11). This implies that products with relatively higher lecithin content would require lower enthalpies to melt than those of their corresponding products with lower lecithin levels. Significant ($p < 0.05$) interactions were observed among all the processing parameters. Multiple comparison tests revealed that fat content had the greatest effect on $T_{\text{index}}$ and $\Delta H_{\text{melt}}$ of dark chocolates, followed by lecithin content and then PSD (Table 7.12).

### 7.9 RELATIONSHIPS BETWEEN RHEOLOGICAL, TEXTURAL AND MELTING PROPERTIES OF DARK CHOCOLATE

The rheological properties (yield stress and apparent viscosity) of chocolate are of crucial importance to the properties of materials and their efficiency of manufacture (Chevalley, 1999; Afoakwa et al., 2007). On the other hand, textural properties (firmness and index of viscosity) determine the degree of consistency and spreadability, and resistance to flow (viscosity) of molten chocolate (Beckett, 2000). Ziegler and Hogg (1999) concluded that knowledge of such flow behaviour is important for moulding and enrobing, for quality control of molten chocolate products, for proper cookie drop formation and in design of bulk handling systems. Hardness determines the physical rigidity (texture) of products and relates directly to sensory properties during consumption. Assessment of both molten and solid tempered chocolate using texture analyser with various probes and procedures has been reported previously (Full et al., 1996; Beckett, 2000; Pereira et al., 2003; Liang & Hartel, 2004).

Multivariate statistical techniques were employed to evaluate relationships between the rheological properties (apparent viscosity and yield stress), textural properties (firmness, index of viscosity and hardness) and melting index of dark chocolate systems. Correlation and regression analyses conducted on the data revealed very high and significant ($p < 0.05$) regression and correlation coefficients among all rheological and textural parameters (Table 7.13). Relationships were calculated using correlation analysis between yield stress and apparent viscosity. As previously discussed, high correlation coefficients ($r = 0.99; p = 0.001$)
Table 7.13  Regression and correlation analyses between dark chocolate rheological, textural and melting parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Analysis</th>
<th>Apparent viscosity</th>
<th>Yield stress</th>
<th>Firmness</th>
<th>Index of viscosity</th>
<th>Hardness</th>
<th>Melting index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apparent viscosity</td>
<td>Regression</td>
<td>1.0000</td>
<td>0.9898**</td>
<td>0.9321**</td>
<td>0.9333**</td>
<td>0.7640*</td>
<td>60.38*</td>
</tr>
<tr>
<td></td>
<td>Correlation</td>
<td>1.0000</td>
<td>0.9941**</td>
<td>0.9654**</td>
<td>0.9661**</td>
<td>0.8567**</td>
<td>77.70*</td>
</tr>
<tr>
<td>Yield stress</td>
<td>Regression</td>
<td>—</td>
<td>1.0000</td>
<td>0.9211**</td>
<td>0.9121**</td>
<td>0.7314*</td>
<td>58.80*</td>
</tr>
<tr>
<td></td>
<td>Correlation</td>
<td>—</td>
<td>1.0000</td>
<td>0.9598**</td>
<td>0.9550**</td>
<td>0.8314*</td>
<td>76.68*</td>
</tr>
<tr>
<td>Firmness</td>
<td>Regression</td>
<td>—</td>
<td>—</td>
<td>1.0000</td>
<td>0.9896**</td>
<td>0.9764**</td>
<td>62.48*</td>
</tr>
<tr>
<td></td>
<td>Correlation</td>
<td>—</td>
<td>—</td>
<td>1.0000</td>
<td>0.9947**</td>
<td>0.9855**</td>
<td>79.05*</td>
</tr>
<tr>
<td>Index of viscosity</td>
<td>Regression</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1.0000</td>
<td>0.9742**</td>
<td>67.92*</td>
</tr>
<tr>
<td></td>
<td>Correlation</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1.0000</td>
<td>0.9861**</td>
<td>82.41**</td>
</tr>
<tr>
<td>Hardness</td>
<td>Regression</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1.0000</td>
<td>82.74**</td>
</tr>
<tr>
<td></td>
<td>Correlation</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1.0000</td>
<td>90.96**</td>
</tr>
<tr>
<td>Melting index</td>
<td>Regression</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1.0000</td>
</tr>
<tr>
<td></td>
<td>Correlation</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>1.0000</td>
</tr>
</tbody>
</table>

*Significant at $p < 0.05$; **significant at $p < 0.001$. 
were observed between the yield stress and apparent viscosity. The rheological measurements indicated that yield stress and apparent viscosity follow the same trend and have a strong linear correlation and regression model (Fig. 7.7(d)) with a highly significant \( p = 0.001 \) regression coefficient, \( R^2 = 0.99 \), indicating the two rheological parameters were highly related and could individually be used to predict rheological behaviour of dark chocolate during manufacture. This confirms observations by Servais et al. (2004) that yield stress and apparent viscosity of chocolates are related, suggesting either of the two rheological parameters could be effectively used to predict chocolate viscosity during processing. Contrary to this observation, Mongia and Ziegler (2000) did not find any relationship between yield stress and apparent viscosity. They interpreted their data based on regression to the Casson model, thus, Casson yield stress and the Casson plastic viscosity. Servais et al. (2004) observed that for the same products a linear correlation could be found between yield stress and apparent viscosity using the new ICA (2000) recommendation, but not between Casson yield value and Casson plastic viscosity using the Casson model.

High correlation coefficients \( (r = 0.96; \ p = 0.001) \) were noted between both yield stress and index of viscosity, and yield stress and firmness (Table 7.13), suggesting their high interrelationships. The regression models developed (Figs 7.23 and 7.24) showed highly significant \( p = 0.001 \) regression coefficient, \( R^2 = 0.92 \) and \( 0.91 \), respectively, for yield stress and firmness, and yield stress and index of viscosity. Servais et al. (2004) noted that yield stress depends on proportion of small particles (specific surface area) and on interactions, originating in mechanical (friction) and chemical effects. As yield stress corresponds to the energy needed for chocolate to start moving and relates to the strength of interparticle aggregates at rest, the observed high interrelationship suggests that both firmness and index of viscosity could be related to strengths of the aggregated particle-to-particle network system of chocolate mass during manufacture (Beckett, 2000; Servais et al., 2004), with the distribution and arrangement of PSs, fat and lecithin contents as the main influential factors dictating their flow behaviour (Afoakwa et al., 2007, 2008b). This knowledge would be useful for engineering purposes such as pumping, mixing, storage and transportation of molten chocolate. Contrary to the high regression coefficients noted between yield stress

\[
\text{Firmness (g force)} \quad \text{Yield stress (Pa)} \\
0 \quad 300 \quad 600 \quad 900 \quad 1200 \quad 1500 \\
0 \quad 200 \quad 400 \quad 600 \quad 800 \quad 1000 \\
R^2 = 0.92
\]

![Fig. 7.23](image-url) Relationship between yield stress and firmness in molten chocolate (Afoakwa et al., 2008f). Data points (squares); linear regression (inner solid line); 95% minimum and maximum tolerance intervals (both outer lines); yield stress = 18.2498 + 0.683086 × firmness. With kind permission from Springer Science and Business Media, Afoakwa et al. (2008f).
and firmness and that of index of viscosity (Table 7.13), yield stress and hardness yielded high and significant, but relatively lower correlation ($r = 0.83; p = 0.001$) and regression coefficient, $R^2 = 0.73$ (Table 7.13), suggesting other processing factors play significant role in defining the texture (hardness) of solid tempered dark chocolate. Afoakwa et al. (2007) and Beckett (1999) noted that several factors including recipe, manufacturing techniques, temper, polymorphism (stability of fat crystals) and cooling temperature controls influence final texture (hardness) of solid tempered chocolate. Keogh et al. (2002) also concluded that hardness is a useful indicator of good tempering, or degree to which a stable fat crystal network has been formed. The regression model forms Figure 7.25.

Apparent viscosity and firmness, and apparent viscosity and index of viscosity were highly positively correlated ($r = 0.97; p = 0.001$), with regression coefficient, $R^2 = 0.93$ (Table 7.13),
indicating strong relationships. Figures 7.26 and 7.27 show the respective regression models.
The observed high positive correlation (>95%) and regression (>94%) coefficients between
yield stress and index of viscosity, and apparent viscosity and index of viscosity suggest that
index of viscosity could be measured by back-extrusion technique using texture analysers to
predict both yield stress and apparent viscosity of dark chocolate systems during manufacture.
This would reflect thickness and uniformity of molten chocolate coatings (Prasad et al., 2003;
Baker et al., 2006), and pumping characteristics, coating properties and sensory character of
the mass (Seguine, 1988). Afoakwa et al. (2008b) reported that apparent viscosity and yield
stress were more dependent on fat and lecithin contents, with PSD showing only marginal
effects. Similar to yield stress and hardness, the R-squared statistic for hardness indicated

![Figure 7.26](image-url)

**Fig. 7.26** Relationship between apparent viscosity and firmness in molten chocolate [Afoakwa et al.,
2008f]. Data points (squares); linear regression (inner solid line); 95% minimum and maximum tolerance
intervals (both outer lines); apparent viscosity = 2.20313 + 0.0460588 × firmness. With kind permission
from Springer Science and Business Media, Afoakwa et al. (2008f).

![Figure 7.27](image-url)

**Fig. 7.27** Relationship between apparent viscosity and index of viscosity in molten chocolate [Afoakwa
et al., 2008f]. Data points (squares); linear regression (inner solid line); 95% minimum and maximum tolerance
intervals (both outer lines); apparent viscosity = 1.5664 + 0.00927351 × index of viscosity.
With kind permission from Springer Science and Business Media, Afoakwa et al. (2008f).
the model as fitted explained 76.4% of the variability in apparent viscosity, with correlation coefficient, \( r = 0.86, p = 0.001 \), indicating a strong relationship between variables (Fig. 7.28). These suggest that although other factors contribute to final product hardness, both rheological parameters (yield stress and apparent viscosity) can predict approximately 75% variability in the final texture of tempered finished dark chocolate products.

The rheological and textural properties of the dark chocolate systems were related to the melting index (duration) of their respective tempered chocolate using regression and correlation analyses. The purpose was to establish the extent to which both rheological and textural properties of dark chocolates manufactured using varying PSD, fat and lecithin content could be used to predict the melting duration of their respective products during consumption. This knowledge would be useful for new product development and process engineering purposes. The results showed moderately high correlation coefficients (\( r = 0.77 \) and 0.78; \( p = 0.001 \)), respectively, between both yield stress and melting index, and apparent viscosity and melting index (Table 7.13), indicating a moderately strong relationship between the variables. Similarly, moderately high regression coefficients were noted between the rheological properties (yield stress and apparent viscosity) of molten chocolate and melting index (Table 7.13). The regression models developed (Figs 7.29 and 7.30) showed relatively lower but significant (\( p = 0.001 \)) regression coefficient, \( R^2 = 0.59 \) and 0.60, respectively, for yield stress and melting index, and apparent viscosity and melting index.

The relationships between the textural properties (firmness and index of viscosity) and melting index showed moderately higher positive correlations, \( r = 0.79, p = 0.001 \) and \( r = 0.82, p = 0.001 \), with regression coefficient, \( R^2 = 0.62 \) and 0.67, respectively (Table 7.13), indicating their moderately strong relationships. Their regression models have been shown in Figures 7.31 and 7.32. These observations suggest that although other factors such as degree of fat crystal stability during tempering, tempering regime and cooling procedures might contribute to the melting behaviour of the products during consumption, both rheological parameters (yield stress and apparent viscosity) and textural properties of molten dark chocolate can be used to predict approximately 60–70% variability in the melting index or duration.
The relationship between hardness of the finished chocolate and melting index showed relatively higher coefficients of regression (Fig. 7.33) and correlation (Table 7.13). Multivariate analyses on the data showed fitting of a linear model to describe the relationship between hardness and melting index. The R-squared statistic indicated that the model as fitted explained 82.74% of the variability in hardness, with correlation coefficient, $r = 0.91$, $p = 0.001$, indicating a relatively strong relationship between the variables. This explains that tempering, a fat crystallisation process, which is used to convert molten chocolate into finished product, plays a very significant role in defining the melting time or duration of the products. Beckett (1999) explained that melting of chocolate in the mouth is defined by
the characteristics of the fat phase, and facilitates the perception of its characteristic taste, flavour and textural attributes. The intensity of perceived flavour changes dynamically over time as the chocolate is melted, manipulated and mixed with saliva for swallowing. Ziegler et al. (2001) also noted that PS and rheology significantly influenced the melting time and sweetness intensity of milk chocolate using time–intensity methodology.

Multivariate PCA evaluated the extent to which PSD, fat and lecithin contents influence rheological, textural and melting properties of dark chocolates. Group A is composed of rheological, textural and melting parameters and B influencing factors comprising PS, fat and lecithin content (Fig. 7.34). The PCA product space (Fig. 7.34) explained more than 82% variance in the first two factors and showed that the rheological and texture parameters

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**Fig. 7.31** Relationship between firmness and melting index in chocolate (Afoakwa et al., 2008f). Data points (squares); linear regression (inner solid line); 95% minimum and maximum tolerance intervals (both outer lines); firmness \(= -2371.11 + 357.237 \times \) melting index. With kind permission from Springer Science and Business Media, Afoakwa et al. (2008f).

**Fig. 7.32** Relationship between index of viscosity and melting index in chocolate (Afoakwa et al., 2008f). Data points (squares); linear regression (inner solid line); 95% minimum and maximum tolerance intervals (both outer lines); index of viscosity \(= -12263.5 + 1850.79 \times \) melting index. With kind permission from Springer Science and Business Media, Afoakwa et al. (2008f).
Melting index

Hardness (g.force)
6.1 6.5 6.9 7.3 7.7 8.1 8.5 8.9

4100 4600 5100 5600 6100 6600 7100

R² = 82.74

Fig. 7.33 Relationship between hardness and melting index in chocolate (Afoakwa et al., 2008f). Data points (squares); linear regression (inner solid line); 95% minimum and maximum tolerance intervals (both outer lines); hardness = \(-4396.97 + 1318.07 \times \) melting index. With kind permission from Springer Science and Business Media, Afoakwa et al. (2008f).

were closely related with loadings for PSD, fat and lecithin content as influencing factors. Fat and lecithin content had polar influences on principal component 1 (PC1) (69.67% variance) score, while PS had marginal influence on PC2 (12.71% variance) score. Afoakwa et al. (2008a) established that PSD had multiple discrete components – specific surface area, largest PS (D₉₀), smallest PS (D₁₀), mean PS (D₅₀) and Sauter mean diameter (D[3,2]) – together influencing rheological properties of dark chocolates. A small number of linear combinations of the nine variables accounted for most of variability (98.7%). In this case, three components were extracted, since 1888 components had eigenvalues 1 or more. The PCA (Fig. 7.34) product space for rheological properties (apparent viscosity and yield stress),

![Fig. 7.34](image) Principal component analysis of rheological, textural and melting properties of dark chocolates (A) as affected by PSD, fat and lecithin content (B) (Afoakwa et al., 2008f). With kind permission from Springer Science and Business Media, Afoakwa et al. (2008f).
textural properties (firmness, index of viscosity and hardness) and melting index were very closely related and could be used to predict the relative processing behaviours during dark chocolate manufacture.

### 7.10 CONCLUSION

Increasing PSs resulted in decreases in Casson plastic viscosity, Casson yield value, yield stress and apparent viscosity, which were more pronounced at lower fat and lecithin levels. Increasing the fat and lecithin levels enhanced the reducing effects of PSD on the rheological properties of the dark chocolates, with the exception of plastic viscosity and thixotropy, where no significant effects were noticed at fat levels at and above 30%. The effectiveness of fat and lecithin in reducing the plastic viscosity and thixotropy of dark chocolate depends on the level of fat already present. Fat content exerts the greatest effect on the variability in the rheological properties, followed by lecithin content and then PSD. The Casson reference parameters (yield value and plastic viscosity) and newer ICA recommendations (yield stress and apparent viscosity) for evaluating chocolate viscosity are very closely related, and could be used independently. The ICA method is relatively more efficient than the Casson model, which has limitations with chocolates with wide variations in viscosity. Both rheological models are dependent on PSD, fat and lecithin as key factors under controlled processing conditions.

Increase in PS resulted in linear decreases in textural properties of both molten and solid tempered dark chocolates, higher at lower fat and lecithin contents. At low (25%) fat contents, 5 and 2% increases in fat and lecithin levels, respectively, enhanced PSD effects on texture, with no significant effects at 30% or more fat. Effects on texture of changes in fat and lecithin depended on base fat content. Increasing PSD and fat inversely influenced appearance parameters (L*, C* and h°). Fat content exerted greatest effect on texture and appearance, followed by PSD and then lecithin with the last having no significant effect on appearance.

PSD and ingredient content were significant factors determining microstructural properties of dark chocolates. Microstructural analysis revealed that the smaller particles (D10, D50), largest particles (D90) and specific surface area had direct influence on packing ability and interparticle interactions. At low (25%) fat concentrations, interparticle interaction of crystals led to flocculation, with an impact on microstructure and behaviour of molten and tempered products. Increasing fat reduced the crystalline network density, created more open and void spaces which fill with fat, reducing resistance to flow, and enhancing spreadability and softening.

Variations in PSD, fat and lecithin content during dark chocolate manufacture influence to varying levels, the degree of crystallinity and melting properties (Tend, Tindex and ΔHmelt) of their derived products. Changes in PSD had no effect on the crystallinity of products. Increasing fat content resulted in consistent increases in crystallinity of products formed during tempering. Products containing 25% fat had the smallest crystal size, followed by those with 30%, with the 35% fat having the largest crystal size, causing significant changes in Tend, Tindex and ΔHmelt of products. Similarly, increasing lecithin content from 0.3 to 0.5% moderately reduced the crystallinity of products with significant variations in Tend, Tindex and ΔHmelt of products. Neither PSD, fat nor lecithin content influenced initiation (Tonset) and maximum (Tpeak) melting temperatures. Chocolates with finer particles, higher fat and
lower lecithin contents, took longer and higher temperatures to complete melting than their corresponding products with larger PS, lower fat and higher lecithin content. This suggests that for chocolate of the same composition, processed under identical conditions, the PSD of the suspended non-fat solid, fat and lecithin contents plays important roles in determining their melting behaviour. These findings would have application in defining chocolate quality as the nature of crystalline material; dimensions of crystals and polymorphic stability dictate the mechanical and rheological properties of chocolate products.

Rheological parameters (apparent viscosity and yield stress), textural parameters (firmness, index of viscosity and hardness) and melting index (duration or time) were highly positively correlated, suggesting effective prediction. Except for hardness which showed relatively lower correlation and regression coefficients with both apparent viscosity and yield stress, all other rheological and textural parameters had high correlation and regression coefficients of more than 90%, suggesting that the rheological parameters and textural properties of molten dark chocolate were very highly related and predictive of character. Similarly, the rheological and textural properties of the molten dark chocolate showed relatively lower correlation and regression coefficients with melting index, while relatively higher correlation and regression coefficients were noted with hardness. PCA revealed that with the exception of melting index, which showed a moderate shift in space, the rheological properties (apparent viscosity and yield stress) and textural properties (firmness, index of viscosity and hardness) were closely related. PSD, fat and lecithin contents – all interact to determine rheological and textural properties, and melting index (duration) of dark chocolates, with significance for manufacturing improvements and quality control.
8 Tempering behaviour during chocolate manufacture: effects of varying product matrices

8.1 SUMMARY AND INDUSTRIAL RELEVANCE

Tempering consists of shearing chocolate mass at controlled temperatures to promote cocoa butter crystallisation in a stable polymorphic form. During industrial processing, multistage heat exchangers are used to control temperature adjustments to promote formation of appropriate stable polymorphic crystals to obtain products with good snap, colour, contraction, gloss and shelf-life characteristics. The process employs varying time-temperature throughputs of the multistage units, making it difficult to obtain standard tempering conditions for products with variable particle sizes and fat content, thus prolonging equipment standardisation periods with consequential effects on processing times and product quality characteristics. Modelling the tempering behaviour of chocolates from varying particle size distribution (PSD) and fat content would enhance our knowledge and understanding on the optimal temperature conditions for obtaining good tempered products during industrial manufacture, with significance for reducing processing (tempering) times and assurances in quality and shelf characteristics.

Central composite rotatable design (CCRD) for $K = 2$ was used to study the combined effects of multistage heat exchangers for Stages 1 (14–30°C) and 2 (12–28°C) coolant temperatures at constant Stage 3 coolant and holding temperatures during tempering of dark chocolates using laboratory-scale mini temperer. Quantitative data on chocolate temper index (slope) were obtained for products with varying PSD ($D_{90}$ of 18, 25, 35 and 50 µm) and fat (30 and 35%) content. Regression models generated using stepwise regression analyses were used to plot response surface curves, to study the tempering behaviour of products. The results showed that both Stage 1 and Stage 2 coolant temperatures had significant linear and quadratic effects on the crystallisation behaviour, causing wide variations in chocolate temper slope during tempering of products with variable PSD and fat content. Differences in fat content exerted the greatest variability in temperature settings of the different zones for attaining well-tempered products. At 35% fat content, changes in PSD caused only slight and insignificant effect on tempering behaviour. No unique set of conditions was found to achieve good temper in dark chocolate with a specified tempering unit. Thus, different combinations of temperatures could be employed between the multistage heat exchangers to induce nucleation and growth of stable fat crystal polymorphs during tempering. Variations in tempering outcomes of the dark chocolates were dependent more on the fat content than on PSD.
8.2 INTRODUCTION

Tempering is a directed pre-crystallisation that consists of shearing chocolate mass at controlled temperatures to promote cocoa butter crystallisation in a thermodynamically stable polymorphic form. During chocolate manufacture, tempering is used to obtain the stable Form V (or $\beta_2$) of cocoa butter having a melting temperature of 32–34°C, which gives the desired glossy appearance, good snap, contraction and enhanced shelf-life characteristics (Seguine, 1991; Beckett, 1999; Talbot, 1999; Timms, 2003; Lonchampt & Hartel, 2006; Afoakwa et al., 2007a). The process involves pre-crystallisation of a small proportion of triglycerides (TAGs), with crystals forming nuclei (1–3% total) for the remaining lipid to set in the correct form. The final crystal form depends critically on the shear–temperature–time process which the material has undergone. The tempered chocolate is then deposited in moulds and cooled so that subsequent crystal growth occurs upon the existing seed crystals (Stapley et al., 1999; Hartel, 2001). Tempering has four key steps: melting to completion (at 50°C), cooling to the point of crystallisation (at 32°C), crystallisation (at 27°C) and conversion of any unstable crystals (at 29–31°C) (Talbot, 1999). Thereby, the tempering sequence is a function of recipe, equipment and the final purpose.

Current industrial tempering machines consist of multistage heat exchangers (Fig. 8.1) through which chocolate passes at widely differing rates and are used to control temperature adjustments to promote formation of appropriate stable crystals. Time–temperature combinations are of paramount importance in process design and in continuous tempering (Beckett, 1999; Nelson, 1999; Tewkesbury et al., 2000; Hartel, 2001). The varying time–temperature throughputs of these units make it difficult to obtain standard tempering conditions for products with variable particle sizes and fat composition, thus prolonging equipment standardisation periods with consequential effects on process times and product quality characteristics. Poorly tempered chocolates result in unstable crystal growth and poor setting characteristics, making products more susceptible to fat bloom, a physical imperfection that often manifests itself as a white or greyish white layer on the surface of the chocolate product during storage. The occurrence of fat bloom is associated with the polymorphic transformation from a lower and unstable crystal Form IV to a higher and more stable Form VI (Bricknell & Hartel, 1998; Beckett, 2000; Lonchampt & Hartel, 2004; Lonchampt & Hartel, 2006). PSD and fat composition during dark chocolate manufacture affect their rheological (Afoakwa et al., 2008b) as well as microstructural and mechanical properties (Afoakwa et al., 2009d), establishing relationships between the rheology and structural character of products; however, their influence on pre-crystallisation and nucleation still remains unclear.

Response surface methodology (RSM) is a collection of statistical and mathematical techniques useful for developing, improving and optimising processes in which a response of interest is influenced by several variables, and the objective is to optimise the response. Baş and Boyacı (2007) noted that RSM has important applications in the design, development and formulation of new products, as well as in the improvement of existing product designs. It defines the effect of the independent variables, alone or in combination, on the processes. In addition to analysing the effects of the independent variables, this experimental methodology generates a mathematical model, which describes the chemical, biochemical or physical processes involved (Myers & Montgomery, 1995; Anjum et al., 1997; Senanayake & Shahidi, 2002; Vohra & Satyanarayana, 2002; Afoakwa et al., 2007b). The objective of this work was to study tempering behaviour of dark chocolates varying in PSD and fat content using RSM.
8.3 MATERIALS AND METHODS

8.3.1 Materials

Cocoa liquor of Central West African Origin was obtained from Cargill Cocoa Processing Company (York, UK); sucrose (pure extra-fine granulated) from British Sugar Company (Peterborough, UK); pure prime pressed cocoa butter and soy lecithin from ADM Cocoa Limited (Koog aan de Zaan, the Netherlands) and Unitechem Company Ltd (Tianjin, China), respectively.

The recipe, formulation and production of samples have been given in Table 8.1, but with only 0.5% lecithin content. Chocolates were formulated with total fat of 25–35% (w/w) from cocoa liquor and cocoa butter with more than 34% total cocoa: composition as specified for dark chocolate by relevant directives (European Commission Directive, 2000; Codex Revised Standard, 2003). Experimental samples (5 kg batch for each formulation) were produced by mixing sucrose and cocoa liquor in a Crypto Peerless mixer (Model K175, Crypto Peerless Ltd, Birmingham, UK) at low speed for 2 minutes and then at high for 3 minutes, then refined using a three-roll refiner (Model SDX 600, Buhler Ltd, CH-9240...
Table 8.1 Process variables and their levels used in the central composite rotatable design for $K = 2$

<table>
<thead>
<tr>
<th>Independent variables</th>
<th>Code</th>
<th>$-1.414$</th>
<th>$-1$</th>
<th>$0$</th>
<th>$1$</th>
<th>$1.414$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stage 1 coolant temp</td>
<td>$X_1$</td>
<td>13.9</td>
<td>16.0</td>
<td>21.0</td>
<td>26.0</td>
<td>28.1</td>
</tr>
<tr>
<td>Stage 2 coolant temp</td>
<td>$X_2$</td>
<td>11.9</td>
<td>14.0</td>
<td>19.0</td>
<td>24.0</td>
<td>26.1</td>
</tr>
</tbody>
</table>

Uzwil, Switzerland) to a specified particle size ($D_{90}$: $18 \pm 1 \mu m$, $25 \pm 1 \mu m$, $35 \pm 1 \mu m$ and $50 \pm 1 \mu m$) conducting particle size analysis, during refining, to ensure $D_{90}$ values. Refined chocolates were placed in plastic containers and conditioned at 50–55$^\circ$C for 24 hours to ensure melting of fat within chocolate mass prior to conching in a Lipp Conche (Model IMC-E10, Boveristr 40-42, D-68309, Mannheim, Germany) at low speed for 3.5 hours at 60$^\circ$C. Lecithin and cocoa butter were added and mixtures were then conched at high speed for 30 minutes to affect adequate mixing and liquefication. Samples were kept in sealed plastic containers at ambient temperature (20–22$^\circ$C). Moisture and fat contents determined using Karl Fischer and Soxhlet methods (ICA, 1988, 1990).

8.3.2 Tempering procedure

Samples were allowed to melt at 50$^\circ$C for 4 hours and tempered using an Aasted Mikrovert laboratory continuous three-stage tempering unit (Model AMK 10, Aasted Mikroverk A/S, Farum, Denmark) as shown in Figure 8.1. Chocolate is pumped through the multistage units, and a worm screw drives the product through the heat exchangers. Sensors are located at specific points in the equipment to measure the temperature of both the chocolate and the coolant fluid at each stage. The temperatures of each of the coolant in each of the three stages were thus set and controlled independently of each other to obtain the temper status of the chocolate.

Pre-crystallisation status of the chocolate was measured as temper slope on cooling curves generated using a computerised tempermeter (Exotherm 7400, Systech Analytics, Neuchâtel, Switzerland) on a temperature–time graphs using Software version 5.0 (Exotherm 7400, Systech Analytics, Neuchâtel, Switzerland) and the readings were recorded. The cooling curve measures the amount of heat released during solidification of chocolate with time. The tempering process generates two inflection points on the cooling curve – first inflection point being the temperature–time at which seed crystals begin to nucleate, and the second inflection point, where the actual nucleation takes place. The slope that is used to evaluate the temper status of the chocolate mass is developed at the second inflection as illustrated in Figure 8.2. This is directly related to the amount of seed crystals formed during the pre-crystallisation or tempering process. Figure 8.2 shows typical pre-crystallisation (cooling) curves and how the temper slopes generated by the computerised tempermeter to evaluate the temper status – optimally tempered, undertempered and overtempered of the chocolate mass is processed. Triplicate measurements were taken for each product composition and the mean values were recorded.

8.3.3 Determination of particle size distribution

A MasterSizer® Laser Diffraction Particle Size Analyzer equipped with MS 15 sample presentation unit (refractive index 1.590) (Malvern Instrument Ltd, Malvern, England) was
Tempering behaviour during chocolate manufacture: effects of varying product matrices

Fig. 8.2 Chocolate pre-crystallisation (cooling) curves showing how (a) optimally tempered (b) undertempered and (c) overtempered temper slopes were determined by the tempermeter. Reprinted from Afoakwa et al. (2008g), copyright 2008, with permission from Elsevier.
used. About 0.2 g of refined dark chocolate was dispersed in vegetable oil (refractive index 1.450) at ambient temperature (20 ± 2°C) until an obscuration of 0.2 was obtained. The sample was placed under ultrasonic dispersion for 2 minutes to ensure particles were independently dispersed and thereafter maintained by stirring during the measurement. Size distribution was quantified as the relative volume of particles in size bands presented as size distribution curves (Malvern MasterSizer® Micro Software v 2.19). PSD parameters were obtained as described previously (Afoakwa et al., 2008b).

8.3.4 Experimental design and statistical analysis

A CCRD of the experiment was set up using the Statgraphics Plus 4.1 software with experimental study variable number \( K = 2 \), for independent variables including Stage 1 coolant temperature \( (X_1) \) and Stage 2 coolant temperature \( (X_2) \). Stage 3 coolant temperature and the temperature of the holding tank (Fig. 8.1) were kept constant at 32 and 45°C, respectively. The variables used in the CCRD for \( K = 2 \) were processed using the software, and provided the dependent variable limits and their values (Table 8.1). The experiments were carried out in two separate sets to optimise these parameters. According to this design, the total number of treatment combinations is \( 2k + 2k + n_o \), where ‘\( k \)’ is the number of independent variables and \( n_o \) is the number of repetitions of the experiments at the centre point. For statistical calculation, the variables \( X_i \) have been coded as \( x_i \) according to the following transformation:

\[
x_i = \frac{X_i - X_0}{\delta X}
\]  

(8.1)

where \( x_i \) is the dimensionless coded value of the variable \( X_i \), \( X_0 \) is the value of the \( X_i \) at the centre point and \( \delta X \) is step change. A \( 2k \)-factorial design with four axial points (\( \alpha = 1.414 \)) and six replicates at the centre point with a total number of 14 experiments was employed for the studied parameters. The number of centre point replications was chosen to verify any change in the estimation procedure, which was also a measure of precision described by the following equation:

\[
no = \lambda_4(\sqrt{F+2})^2 - F - 2k
\]  

(8.2)

where \( F \) is the number of points in factorial portion, i.e. the first four experiments in experimental design (run numbers 1–4 in Table 8.2) and \( \lambda_4 \) is the mixed fourth-order moment. The total number of centre point replications obtained after substituting the values in Eq. (8.2) is five, but six replications were performed to reduce error. The behaviour of the system was explained by the following quadratic model:

\[
Y = \beta_0 + \sum \beta_i X_i + \sum \beta_{ii} X_i^2 + \sum \beta_{ij} X_{ij}
\]  

(8.3)

where \( Y \) is the predicted response, \( \beta_0 \) the offset term, \( \beta_i \) the linear effect, \( \beta_{ii} \) the quadratic effect and \( \beta_{ij} \) is the interaction effect. The dependent variables studied were the chocolate temper index (slope) as measured by the tempermeter, for samples processed from 18, 25, 35 to 50 µm particle sizes, \( D_{90} \) at 35% fat to study the tempering behaviour of samples from varying PSD. The tempering behaviour of samples processed from 25 to 35 µm PSD at 30% fat content were also studied and compared to their respective samples with 35% fat,
Table 8.2 Design matrix and variable combinations in experimental runs

<table>
<thead>
<tr>
<th>Runs</th>
<th>Block</th>
<th>X1</th>
<th>X2</th>
<th>Stage 1 coolant temperature (°C)</th>
<th>Stage 2 coolant temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1.0</td>
<td>1.0</td>
<td>26.1</td>
<td>24.0</td>
</tr>
<tr>
<td>2</td>
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<td>−1.0</td>
<td>−1.0</td>
<td>16.0</td>
<td>14.0</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>1.0</td>
<td>−1.0</td>
<td>26.0</td>
<td>14.0</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>−1.0</td>
<td>1.0</td>
<td>16.0</td>
<td>24.0</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>0.0</td>
<td>0.0</td>
<td>21.0</td>
<td>19.0</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>0.0</td>
<td>0.0</td>
<td>21.0</td>
<td>19.0</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>0.0</td>
<td>0.0</td>
<td>21.0</td>
<td>19.0</td>
</tr>
<tr>
<td>8</td>
<td>2</td>
<td>−1.414</td>
<td>0.0</td>
<td>13.9</td>
<td>19.0</td>
</tr>
<tr>
<td>9</td>
<td>2</td>
<td>1.414</td>
<td>0.0</td>
<td>28.1</td>
<td>19.0</td>
</tr>
<tr>
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</tr>
<tr>
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</tr>
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</tr>
<tr>
<td>14</td>
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<td>0.0</td>
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<td>21.0</td>
<td>19.0</td>
</tr>
</tbody>
</table>

*X1, Stage 1 coolant temperature (°C); X2, Stage 2 coolant temperature (°C).*

to determine the effect of varying fat content. These samples were selected following trends in rheological properties observed from earlier studies (Afoakwa et al., 2008b). The design matrix and variable combinations in experimental runs are as shown in Tables 8.1 and 8.2.

The experiments conducted on the various combinations and the results (temper slopes) obtained are as shown in Tables 8.3 and 8.4. These were analysed using stepwise regression analysis. Analysis of variance tables were generated and the effect and regression coefficients of individual linear, quadratic and interaction terms were determined. The significance of all terms in the polynomial was judged statistically by computing the F-value at a probability (p) of 0.001, 0.01 or 0.05. The regression coefficients were then used to make statistical calculation to generate response plots from the regression models. Table 8.5 shows the coefficients of the variables in the models and their contribution to the model’s variation. A test for the lack of fit and the $R^2$ values were used to judge the adequacy of the models.

The $R^2$ of a model refers to the proportion of variation in the response attributed to the model rather than random error. For a good fit of a model, an $R^2$ of 0.80% was used. Malcolmson et al. (1993) commented that $R^2$ of 0.80% is perfect for a good model study and but recommended that an $R^2$ of 0.60% can be used for a preliminary study.

### 8.4 RESULTS AND DISCUSSION

#### 8.4.1 Particle size distribution of dark chocolates

Variations in PSD were observed for 18, 25, 35 and 50 µm (Fig. 8.3) using D₉₀ values (>90% finer) that relate to chocolate character (Beckett, 2000). Data from the PSD showed variations in specific surface area, mean particle volume D(v,50), Sauter mean (D[3,2]) and mean particle diameter (D[4,3]) with increasing D₉₀ particle sizes. These findings have been previously reported (Afoakwa et al., 2008b). Increasing fat from 25 to 35% led to significant ($p < 0.001$) reductions in specific surface area and to an increase in all other PSD parameters,
Table 8.3  Design matrix, variable combinations temper slopes obtained from experimental runs for dark chocolates containing 35% fat with varying PSD

<table>
<thead>
<tr>
<th>Runs</th>
<th>$X_1$</th>
<th>$X_2$</th>
<th>Stage 1 temperature ($^\circ$C)</th>
<th>Stage 2 temperature ($^\circ$C)</th>
<th>Temper slope for 18 µm</th>
<th>Temper slope for 25 µm</th>
<th>Temper slope for 35 µm</th>
<th>Temper slope for 50 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0</td>
<td>1.0</td>
<td>26.1</td>
<td>24.0</td>
<td>0.62</td>
<td>−0.03</td>
<td>0.75</td>
<td>0.41</td>
</tr>
<tr>
<td>2</td>
<td>−1.0</td>
<td>−1.0</td>
<td>16.0</td>
<td>14.0</td>
<td>−1.72</td>
<td>−1.71</td>
<td>−1.74</td>
<td>−1.73</td>
</tr>
<tr>
<td>3</td>
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<td>0.20</td>
<td>0.01</td>
<td>−0.04</td>
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</tr>
<tr>
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<td>−1.0</td>
<td>1.0</td>
<td>26.0</td>
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<td>0.48</td>
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<tr>
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<td>21.0</td>
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<td>0.01</td>
<td>0.06</td>
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</tr>
<tr>
<td>6</td>
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<td>0.0</td>
<td>21.0</td>
<td>19.0</td>
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<td>21.0</td>
<td>19.0</td>
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<td>0.01</td>
<td>0.06</td>
<td>0.53</td>
</tr>
<tr>
<td>8</td>
<td>−1.414</td>
<td>0.0</td>
<td>28.1</td>
<td>19.0</td>
<td>−0.13</td>
<td>−1.76</td>
<td>−0.09</td>
<td>−0.01</td>
</tr>
<tr>
<td>9</td>
<td>1.414</td>
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<td>28.1</td>
<td>19.0</td>
<td>1.17</td>
<td>1.36</td>
<td>1.73</td>
<td>2.40</td>
</tr>
<tr>
<td>10</td>
<td>0.0</td>
<td>1.414</td>
<td>21.0</td>
<td>26.1</td>
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<td>2.06</td>
<td>1.97</td>
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<tr>
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<td>21.0</td>
<td>11.9</td>
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<td>−1.73</td>
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<tr>
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<tr>
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<td>21.0</td>
<td>19.0</td>
<td>−0.01</td>
<td>0.01</td>
<td>0.06</td>
<td>0.53</td>
</tr>
<tr>
<td>14</td>
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<td>0.0</td>
<td>21.0</td>
<td>19.0</td>
<td>−0.01</td>
<td>0.01</td>
<td>0.06</td>
<td>0.53</td>
</tr>
</tbody>
</table>

$X_1$, Stage 1 coolant temperature ($^\circ$C); $X_2$, Stage 2 coolant temperature ($^\circ$C).
Table 8.4  Design matrix, variable combinations temper slopes obtained from experimental runs for dark chocolates varying in fat content (30 and 35\%) and PSD (25 and 35 \(\mu\)m)

<table>
<thead>
<tr>
<th>Runs</th>
<th>(X_1)</th>
<th>(X_2)</th>
<th>Stage 1 temperature ((^\circ)C)</th>
<th>Stage 2 temperature ((^\circ)C)</th>
<th>Temper slope for PS 35 (\mu)m, fat 30%</th>
<th>Temper slope for PS 50 (\mu)m, fat 30%</th>
<th>Temper slope for PS 35 (\mu)m, fat 35%</th>
<th>Temper slope for PS 50 (\mu)m, fat 35%</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>1.0</td>
<td>1.0</td>
<td>26.1</td>
<td>24.0</td>
<td>0.05</td>
<td>0.57</td>
<td>0.75</td>
<td>0.41</td>
</tr>
<tr>
<td>2</td>
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<td>-1.0</td>
<td>16.0</td>
<td>14.0</td>
<td>-1.89</td>
<td>-2.00</td>
<td>-1.74</td>
<td>-1.73</td>
</tr>
<tr>
<td>3</td>
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<td>-1.0</td>
<td>26.0</td>
<td>14.0</td>
<td>-0.26</td>
<td>-0.20</td>
<td>-0.04</td>
<td>0.00</td>
</tr>
<tr>
<td>4</td>
<td>-1.0</td>
<td>1.0</td>
<td>16.0</td>
<td>24.0</td>
<td>-0.06</td>
<td>0.15</td>
<td>0.59</td>
<td>0.54</td>
</tr>
<tr>
<td>5</td>
<td>0.0</td>
<td>0.0</td>
<td>21.0</td>
<td>19.0</td>
<td>-0.27</td>
<td>-0.02</td>
<td>0.06</td>
<td>0.53</td>
</tr>
<tr>
<td>6</td>
<td>0.0</td>
<td>0.0</td>
<td>21.0</td>
<td>19.0</td>
<td>-0.27</td>
<td>-0.02</td>
<td>0.06</td>
<td>0.53</td>
</tr>
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<td>-0.09</td>
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<td>28.1</td>
<td>19.0</td>
<td>0.56</td>
<td>1.30</td>
<td>1.73</td>
<td>2.40</td>
</tr>
<tr>
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<td>21.0</td>
<td>26.1</td>
<td>1.67</td>
<td>1.82</td>
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<td>1.97</td>
</tr>
<tr>
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<td>11.9</td>
<td>-0.31</td>
<td>-0.35</td>
<td>-1.80</td>
<td>-1.70</td>
</tr>
<tr>
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<td>0.0</td>
<td>21.0</td>
<td>19.0</td>
<td>-0.27</td>
<td>-0.02</td>
<td>0.06</td>
<td>0.53</td>
</tr>
<tr>
<td>13</td>
<td>0.0</td>
<td>0.0</td>
<td>21.0</td>
<td>19.0</td>
<td>-0.27</td>
<td>-0.02</td>
<td>0.06</td>
<td>0.53</td>
</tr>
<tr>
<td>14</td>
<td>0.0</td>
<td>0.0</td>
<td>21.0</td>
<td>19.0</td>
<td>-0.27</td>
<td>-0.02</td>
<td>0.06</td>
<td>0.53</td>
</tr>
</tbody>
</table>

\(X_1\), Stage 1 coolant temperature (\(^\circ\)C); \(X_2\), Stage 2 coolant temperature (\(^\circ\)C).
Table 8.5: Regression coefficients from the second-order polynomials used for the response plots

<table>
<thead>
<tr>
<th>Coefficients</th>
<th>Slope (18 µm PS, 35% fat)</th>
<th>Slope (25 µm PS, 35% fat)</th>
<th>Slope (35 µm PS, 35% fat)</th>
<th>Slope (50 µm PS, 35% fat)</th>
<th>Slope (25 µm PS, 30% fat)</th>
<th>Slope (35 µm PS, 30% fat)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X₁</td>
<td>0.186044**</td>
<td>0.474608**</td>
<td>0.028105*</td>
<td>0.169025**</td>
<td>0.027762*</td>
<td>0.181715**</td>
</tr>
<tr>
<td>X₂</td>
<td>0.228753***</td>
<td>0.359311**</td>
<td>0.40447***</td>
<td>0.659722***</td>
<td>0.25184**</td>
<td>0.0415585*</td>
</tr>
<tr>
<td>X₁²</td>
<td>0.002729*</td>
<td>−0.003763*</td>
<td>0.004770*</td>
<td>0.0023979*</td>
<td>0.002806*</td>
<td>−0.000179*</td>
</tr>
<tr>
<td>X₁X₂</td>
<td>−0.012857*</td>
<td>−0.011378*</td>
<td>−0.007857*</td>
<td>−0.0094898*</td>
<td>−0.005306*</td>
<td>−0.006480*</td>
</tr>
<tr>
<td>X₂²</td>
<td>0.003647*</td>
<td>0.0004209*</td>
<td>−0.002270*</td>
<td>−0.0084183*</td>
<td>−0.003571*</td>
<td>0.004975*</td>
</tr>
<tr>
<td>R²</td>
<td>0.9073</td>
<td>0.8759</td>
<td>0.8992</td>
<td>0.8811</td>
<td>0.9280</td>
<td>0.8636</td>
</tr>
<tr>
<td>F *</td>
<td>0.4220</td>
<td>0.2028</td>
<td>0.5140</td>
<td>0.3189</td>
<td>0.8658</td>
<td>0.3265</td>
</tr>
<tr>
<td>Probability of F</td>
<td>p ≤ 0.001</td>
<td>p ≤ 0.01</td>
<td>p ≤ 0.001</td>
<td>p ≤ 0.001</td>
<td>p ≤ 0.001</td>
<td>p ≤ 0.01</td>
</tr>
</tbody>
</table>

*p ≤ 0.05; **p ≤ 0.01; ***p ≤ 0.001.

*Models have non-significant lack of fit (p > 0.05).
suggesting fat content, inversely correlated with specific surface area, during refining has a direct influence on PSD. Beckett (1999) concluded that the largest particle size and specific surface area of solids are the two key parameters for chocolate manufacture. The largest particle size determines chocolate coarseness and textural character, the specific surface area of solids with desirable flow properties. Specific surface area is inversely correlated with the different components of PSD (Beckett, 1999; Ziegler & Hogg, 1999; Sokmen & Gunes, 2006). Fat contents were 25±1, 30±1 and 35±1%; moisture was within the range 0.80–0.98.

8.4.2 Effect of particle size distribution on tempering behaviour

PSD has been reported as a key determinant of the microstructure, rheological and mechanical properties in dark chocolates with a direct influence on yield stress and plastic viscosity (Afoakwa et al., 2008b, 2009d). Dark chocolates were processed from varying PSD, mainly 18, 25, 35 and 50 µm, at fat content of 35%, to study the effect of varying PSD on degree of fat crystal nucleation and crystallisation during the tempering process using a multistage temperer.

The regression models obtained for temper slope for products with varying PSD at fat content of 35% have respectively been given in Table 8.5. Statistical analyses on the data showed that the models developed for all products showed strong and significant \( p < 0.05 \) influence of both linear and quadratic factors of Stages 1 and 2 coolant temperatures. The models obtained showed coefficient of determination \( (R^2) \) of 0.91, 0.88, 0.88 and 0.88, respectively, for products with PSD of 18, 25, 35 and 50 µm, with a non-significant \( F \)-ratios for lack of fit (Table 8.5), explaining that all the experimental data had good fit of the model.
Stage 1 temperature (°C)  Stage 2 temperature (°C)

<table>
<thead>
<tr>
<th>Slope (18 µm)</th>
<th>14</th>
<th>17</th>
<th>20</th>
<th>23</th>
<th>26</th>
<th>29</th>
<th>32</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
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<td></td>
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<td></td>
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<td>15</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>21</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>27</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

-1.5 -1 -0.5 0 0.5 1 1.5 2 2.5

Fig. 8.4 Response plot showing chocolate temper slope for a sample containing 18 µm PS at 35% fat content. Reprinted from Afoakwa et al. (2008g), copyright 2008, with permission from Elsevier.

and could be used to explain in each case over 87% of the variation in tempering behaviour of the products.

The response plots (Figs 8.4–8.7) showed that both Stage 1 and Stage 2 coolant temperatures had significant effects on the temper slope of the products and could be regulated to obtain optimal temper. From the study, it was observed that at temper slope of −0.5 to +0.3, optimal temper is achieved, above 0.3 is undertempered and below −0.5 is overtempered. Combining Stage 1 coolant temperature between 14 and 20°C and Stage 2 coolant temperature of between 12 and 18°C produced too low cooling temperatures, resulting in unsatisfactory tempered (overtempered) products with temper slopes well below −0.4.

Tewkesbury et al. (2000) noted that chocolate melts over a temperature range, and the presence of lower polymorphs will mean that a greater fraction of the cocoa butter will be liquid at room temperature, thus affecting texture and consumer acceptability. Increasing Stage 1 coolant temperature to between 20 and 26°C, and Stage 2 coolant temperature between 18 and 24°C led to optimally tempered products. This explains that there is no unique set of conditions needed to achieve optimal temper with a given dark chocolate in a given tempering unit, but a wide range of conditions exist, all of which could result in tempered product.

Similarly, at all Stage 1 coolant temperatures (12–32°C), any Stage 2 coolant temperature combination above 24°C (Figs 8.4–8.7) resulted in drastic heat generation within the chocolate system, and these cause complete remelting of all the nucleated stable fat crystals initially formed within the chocolate, thus leaving the product unsatisfactory tempered (undertempered). This temperature combination led to undertempering of the products, and would affect formation of fat bloom in storage. Likewise, at higher Stage 1 coolant temperatures above 30°C, all Stage 2 coolant temperature points resulted in complete remelting of the stable fat crystals formed, thus causing undertempering of products. This observation is particularly true with products processed from lower (18 and 25 µm) PS (Figs 8.4 and 8.7).
Fig. 8.5  Response plot showing chocolate temper slope for a sample containing 25 µm PS at 35% fat content. Reprinted from Afoakwa et al. (2008g), copyright 2008, with permission from Elsevier.

Fig. 8.6  Response plot showing chocolate temper slope for a sample containing 35 µm PS at 35% fat content. Reprinted from Afoakwa et al. (2008g), copyright 2008, with permission from Elsevier.
and at 35% fat content, as products with larger (35 and 50 µm) PS showed quite different tempering behaviour.

A close examination of the response plots (Figs 8.5 and 8.7) showed that at all Stage 1 coolant temperatures, it was possible to find an alternative Stage 2 coolant temperature condition to yield an optimally tempered product. Contrary to the observations made with the 18 and 25 µm (Figs 8.4 and 8.5), setting Stage 1 coolant temperature above 30°C yielded optimal tempered products when a lower corresponding Stage 2 coolant temperature (12–14°C) was used (Figs 8.6 and 8.7), suggesting that with larger (35 and 50 µm) PS, lower coolant temperatures at Stage 2 are required to induce nucleation of the required stable polymorphs in the fat. These findings were probably due to the different apparent viscosities and yield stress values of 4.93, 4.05, 3.84 and 3.45 Pa·s, and 69.85, 51.02, 44.85 and 38.95 Pa, respectively, noted with the 18, 25, 35 and 50 µm samples containing 35% fat and 0.5% lecithin (Afoakwa et al., 2008b), which is suspected to be influencing the pumping and cooling rates of products through the multistage heat exchangers.

Nelson (1999) noted that the Stage 1 coolant temperature in a multistage heat exchangers serves to gently cool the warm chocolate through the tempering machine, gradually reducing the temperature to ‘strike seed’ and initiate the first stages of crystal growth. At this phase the crystals grow very fast, and as the viscosity increases there is the need to raise the chocolate temperature to prevent runaway solidification. Thus, variations in particle sizes, mainly differences in smaller (18 and 25 µm) and larger (35 and 50 µm) particle sizes of dark chocolates, influence the tempering behaviour of products even at higher (35%) fat content as a result of their varying cooling rates or throughputs within the heat exchangers. However, the effect is minimal and does not cause wide changes in the temperature settings for attaining optimal temper in the different PS products at higher (35%) fat content.
8.4.3 Effect of fat content on tempering behaviour

The continuous phase of molten chocolate consists of fat (mainly cocoa butter). During chocolate manufacture, a minimum level of fat is required to maintain its flow properties depending on the solid component PSD, being the void fractions between the packed bed and the specific surface area of the particles (Chevalley, 1999). To study the tempering behaviour of products with varying fat content, dark chocolate containing 30% fat at 25 and 35 µm PS was further tempered using the multistage temperer and the models developed were compared with those processed with 35% fat at 25 and 35 µm PS.

The multiple regression models developed for products containing 30% fat at 25 and 35 µm PS have, respectively, been given in Table 8.5. Statistical analyses revealed that the models developed for products with different fat content (30 and 35%) showed strong and significant ($p < 0.05$) influence of both linear and quadratic factors of Stages 1 and 2 coolant temperatures. The models obtained for products containing 30% fat content at 25 and 35 µm showed coefficient of determination ($R^2$) of 0.93 and 0.86, respectively, with a non-significant $F$-ratios for lack of fit (Table 8.5), explaining that the experimental data had good fit of the model and could be used to explain in each case over 86% of the variation in tempering behaviour of the products at 30% fat content. This was very similar to coefficient of determinations of 0.88 and 0.90% noted for products containing 35% fat at 25 and 35 µm PS (Table 8.5), meaning the all four models have good fit for effective comparative study of their tempering behaviours.

Variations in fat content had the greatest influence in dictating the tempering behaviour of products. The response plots (Figs 8.8 and 8.9) showed that both Stages 1 and 2 coolant temperatures had significant effects on the temper slope. Contrary to observations made with models developed for products containing 35% fat at 25 µm PS where combined coolant temperatures for Stage 1 (14 and 20°C) and Stage 2 (12 and 18°C) resulted in too low cooling temperatures effecting overtempering of products, reducing the fat content of products to 30% showed a different tempering behaviour. The response plots developed for products containing 30% fat at 25 µm PS (Fig. 8.8) showed that at all Stage 1 coolant temperatures there was a corresponding Stage 2 coolant temperature that gave an optimal temper. The model showed that at lower Stage 1 coolant temperature between 17 and 23°C, a corresponding Stage 2 coolant temperature between 18 and 21°C yielded an optimal temper, whereas reducing Stage 2 temperature (12–18°C) caused too high chocolate temperature, resulting in remelting of all the initial nucleated fat crystals, thereby rendering the product undertempered. This explains that at all Stage 1 coolant temperatures, a corresponding Stage 2 temperature could be found to achieve successful nucleation and growth of fat crystals, yielding an optimal temper (Fig. 8.8). It could be observed that at low Stage 1 coolant temperature (14–20°C), a corresponding intermediate Stage 2 coolant temperature between 18 and 21°C was ideal to affect nucleation of the fat crystals and growth; extending the temperature beyond this range would raise the nucleated fat crystal growth temperature beyond the required limit, affecting remelting of the nucleated crystals to unstable poly-morphic state causing undertempering of products. Alternatively, at higher Stage 1 coolant temperature between 21 and 32°C, a corresponding lower Stage 2 coolant temperature between 12 and 21°C was required for an optimal temper, beyond which the products were undertempering.
Similar tempering behaviours were noted between products containing 35 and 30% fat at 35 µm PS, respectively (Figs 8.6 and 8.9). The models explained that for samples containing 30% fat at 35 µm PS, all Stage 1 coolant temperatures could successfully affect nucleation of stable fat crystals and growth independently, when a correct corresponding Stage 2 coolant temperature was identified and used, at constant Stage 3 coolant temperature. Nelson (1999) noted that Stage 3 coolant temperature zone is known as the retention stage, being the period at which crystal maturity is promoted within the equipment.

During progression through the machine, agitation from scraping and mixing blades increases the spread of nuclei in a fine homogeneous structure of small crystals. At this stage,
Fig. 8.9 Response plot showing chocolate temper slope for a sample containing (a) 35 µm PS at 35% fat content and (b) 35 µm PS at 30% fat content. Reprinted from Afoakwa et al. (2008g), copyright 2008, with permission from Elsevier.

Continuous temperature control is applied in conjunction with the period the chocolate attains the transition from the unstable strike seed temperature condition to a mature, completely stable optimum temper. Making the Stage 3 coolant temperature ‘constant’ therefore offers levelled chance of seed maturity, independent of seed crystal nucleation and growth previously occurred within the chocolate as they passed through the Stage 1 and Stage 2 coolant temperature zones. The observed variation in tempering behaviour with products containing varying fat content is suspected to be due to the differences in their effective heat capacity exchanges and the rheological properties of the products (Afoakwa et al., 2008b) as these influence the heating or cooling rate through the multistage heat exchangers during the tempering process. Nucleation of fat crystals, crystal growth and maturity in dark chocolates are therefore dependent, among other factors, on the rheological properties and thermal
Table 8.6  Satisfactory and unsatisfactory temper values and their temper regimes

<table>
<thead>
<tr>
<th>Temper slope</th>
<th>Temper regime</th>
<th>Chocolate temper unit</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Overtempered (unsatisfactory tempered)</td>
<td></td>
</tr>
<tr>
<td>−1.0</td>
<td></td>
<td>−</td>
</tr>
<tr>
<td>−0.9</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>−0.8</td>
<td></td>
<td>9</td>
</tr>
<tr>
<td>−0.7</td>
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<td>8</td>
</tr>
<tr>
<td>−0.6</td>
<td></td>
<td>7.5</td>
</tr>
<tr>
<td>−0.5</td>
<td>Optimally tempered</td>
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</tr>
<tr>
<td>−0.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>−0.3</td>
<td></td>
<td>6.0</td>
</tr>
<tr>
<td>−0.2</td>
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<td>5.6</td>
</tr>
<tr>
<td>−0.1</td>
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<td>5.4</td>
</tr>
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<td>0.3</td>
<td></td>
<td>4.6</td>
</tr>
<tr>
<td>0.4</td>
<td>Undertempered (unsatisfactory tempered)</td>
<td>4.0</td>
</tr>
<tr>
<td>0.5</td>
<td></td>
<td>3.5</td>
</tr>
<tr>
<td>0.6</td>
<td></td>
<td>3.0</td>
</tr>
<tr>
<td>0.8</td>
<td></td>
<td>2.5</td>
</tr>
<tr>
<td>1.0</td>
<td></td>
<td>2.0</td>
</tr>
</tbody>
</table>

history of the samples. Pérez-Martínez et al. (2007) noted that crystallisation conditions such as cooling rate and thermal history (i.e. crystallisation temperature and tempering process) have significant effects on the kinetics and physical properties of the crystallised systems. Fat crystallisation in chocolates is expected to provide the unique characteristics of texture and flavour release in finished products. The three-dimensional crystal network organisation and the polymorphic state of the TAG crystals as affected by the crystallisation conditions have been reported as major factors determining physical (i.e. rheology) and functional (i.e. texture) properties of crystallised TAG systems (Narine & Marangoni, 1999; Herrera & Hartel, 2000; Marangoni & McGauley, 2002; Toro-Vazquez et al., 2004). Following observations made during the tempering processes, satisfactory and unsatisfactory temper regimes and their corresponding temper slopes and chocolate temper units were developed (Table 8.6).

This would enhance the knowledge base of chocolate manufacturers by providing greater understanding and guidance on temper index–temper regime relationships during tempering (pre-crystallisation) of dark chocolates.

8.5 CONCLUSION

Variations in PSD and fat content influenced the crystallisation behaviour, causing wide variations in chocolate temper units during tempering of products. Differences in fat content...
exerted the greatest variability in temperature settings of the different zones for attaining well-tempered products. At 35% fat content, changes in PSD caused only minimal and non-significant effects on tempering behaviour. However, at 30% fat content, the effect of PSD was pronounced. No unique set of conditions was found to achieve good temper with a given chocolate in a specified tempering unit. The models developed showed that a wide range of optimal conditions exist, depending on the attainment of the appropriate temperature settings, all of which would result in tempered chocolate. Thus, different combinations of tempering temperatures could be employed to induce stable fat polymorph formation and are dependent greatly on fat content and partly PSD during dark chocolate manufacture. Optimal satisfactory and unsatisfactory temper regimes and their corresponding temper slopes and chocolate temper units have been provided. These would have great industrial significance for reducing processing (tempering) times during tempering of dark chocolates with assurance in quality control and shelf characteristics.
9 Tempering and fat crystallisation effects on chocolate quality

9.1 SUMMARY AND INDUSTRIAL RELEVANCE

Fat crystallisation behaviours in dark chocolates varying in particle size distribution (PSD) (D$_{90}$ of 18, 25, 35 and 50 µm) were studied, examining influence of temper regimes (optimal, over- and undertemper), and evaluating mechanical properties, appearance, microstructure and melting characteristics. Wide variations in mechanical properties and appearance were noted. Particle size (PS) was inversely related with texture and colour, with greatest effects noted in hardness, stickiness and lightness for all tempers. Overtempering increased product hardness and stickiness but reduced gloss and darkening of surfaces. Undertempering induced fat bloom, yielding defects in texture, colour and surface gloss. The PSD had no influence on crystallinity at all tempers but limited effects on $T_{\text{onset}}$, $T_{\text{peak}}$ and $\Delta H_{\text{melt}}$ independent of temper but significantly influenced $T_{\text{end}}$ and $T_{\text{index}}$. On the contrary, temper influenced crystallinity and melting properties ($T_{\text{end}}$, $T_{\text{index}}$ and $\Delta H_{\text{melt}}$). Undertemper showed as widened crystal size distribution (CSD) with significant changes in $T_{\text{end}}$, $T_{\text{index}}$ and $\Delta H_{\text{melt}}$ with whitening of both surface and internal structures, with other effects on appearance and texture. Overtempering caused moderate increases in CSD and melting properties, with significant effects on $T_{\text{end}}$, $T_{\text{index}}$ and $\Delta H_{\text{melt}}$ but not on $T_{\text{onset}}$, or $T_{\text{peak}}$. Fat–sugar melting profiles were similar for all formulations and tempers. Micrographs revealed variations in surface and internal crystal network structures and interparticle interactions related to temper. From scanning electron micrography, undertemper resulted in rearrangements with recrystallisation of unstable fat crystals to smaller numbers of larger agglomerates with formation of solid bridges between the crystalline network structures. Thus, optimising temper regime is central to achievement of premium quality to avoid defects, affecting mechanical properties, appearance and melting characteristics.

9.2 INTRODUCTION

Tempering is a technique of controlled pre-crystallisation employed to induce the most stable solid form of cocoa butter, a polymorphic fat in finished chocolates. The process consists of shearing chocolate mass at controlled temperatures to promote crystallisation of triacylglycerols (TAGs) in cocoa butter to effect good setting characteristics, foam stability, demoulding properties, product snap, contraction, gloss and shelf-life characteristics. Time–temperature protocols and shearing are employed to induce nucleation of stable polymorphs with the formation of three-dimensional crystal network structure influencing the microstructure, mechanical properties and appearance of products. The crystal network organisation and the
polymorphic state of the TAG crystals as affected by the crystallisation conditions are major factors determining rheological and textural properties of crystallised TAG systems (Narine & Marangoni, 1999; Herrera & Hartel, 2000; Toro-Vazquez et al., 2004; Altimiras et al., 2007; Pérez-Martínez et al., 2007).

Cocoa butter, the only continuous fat phase in dark chocolates, consists of a mixture of approximately 40–50 different TAGs dominated by 2-oleyl glycerides of palmitic and stearic acids, mainly 1-palmitoyl-2-oleoyl-3-stearoylglycerol (POS) 35%, 1,3-distearoyl-2-oleoylglycerol (SOS) 23% and 1,3-disaturated-2-oleoylglycerol-type, 1,3-dipalmitoyl-2-oleoylglycerol (POP) 15% (Lipp & Anklam, 1998; Segall et al., 2005). These occur as symmetric triacylglycerols that contain a central monounsaturated fatty acid, with saturated fatty acids in the 1 and 3 positions, which dominate the crystallisation, polymorphism and phase transformations, thus provide chocolate with its unusual textural and other sensory properties.

PSD influences rheological and textural properties of both molten and tempered dark chocolates, with effects on microstructure, product spread, tempering and pre-crystallisation behaviour, hardness and sensorial qualities (Chevalley, 1999; Beckett, 2000; Do et al., 2007; Afoakwa et al., 2008b, c, e). Smaller particles improve sensory properties (Ziegler et al., 2001), but plastic viscosity and yield stress increase due to changes in surface area of particles in contact with fat phase. Chocolate production processes, such as refining, conching, tempering and crystallisation mechanisms result in physical and compositional attributes, influencing product quality and stability through the supply chain occurring during production, storage, distribution and ultimately sensory character in consumption and product identification.

Instrumental measurements can act as complements for sensory evaluations (Lawless & Heymann, 1998) with statistically significant correlations (Mohamed et al., 1982; Meullenet et al., 1997; Rosenthal, 1999; Ali et al., 2001; Bourne, 2002). Appropriate strategies can objectively assess features of texture and appearance such as gloss, colour, shape, roughness, surface texture, shininess and translucency (Leemans et al., 1998; Jahns et al., 2001; Hatcher et al., 2004; Briones & Aguilera, 2005; Briones et al., 2006; Altimiras et al., 2007). Hartel (2001) noted that the control of crystallisation is critical for texture, melting properties and other quality characteristics. Melting profiles of chocolates have been studied using pulsed nuclear magnetic resonance (pNMR) and differential scanning calorimeter (DSC) (Tabouret, 1987; Walter & Cornillon, 2001, 2002; Smith et al., 2007). Knowledge of tempering effects on product texture and appearance attributes can have significant commercial implications.

With recent innovations and growth in chocolate confectionery industry, understanding the factors influencing chocolate microstructure, texture and appearance would be of value in predicting changes in quality. As well, information on cocoa butter isothermal phase behaviour is important for optimising production processes that maintain product quality. This study was therefore aimed at investigating effects of tempering and fat crystallisation behaviours on mechanical properties, appearance, melting characteristics and crystallised network microstructure in dark chocolates varying in PSD.

### 9.3 MATERIALS AND METHODS

#### 9.3.1 Materials

Cocoa liquor of Central West African origin was obtained from Cargill Cocoa Processing Company (York, UK); sucrose (pure extra-fine granulated) from British Sugar Company (Peterborough, UK); pure prime-pressed cocoa butter and soy lecithin from ADM Cocoa
Limited (Koog aan de Zaan, the Netherlands) and Unitechem Company Ltd (Tianjin, China), respectively.

The recipe, formulation and production of samples have been described in Section 8.3.1. Chocolates were formulated with total fat of 35% (w/w) from sucrose, cocoa liquor, cocoa butter and lecithin. Experimental samples (5 kg batch for each formulation) were produced by mixing sucrose (40.8%) and cocoa liquor (53.7%) in a Crypto Peerless mixer (Model K175, Crypto Peerless Ltd, Birmingham, UK) at low speed for 2 minutes and then at high for 3 minutes, then refined using a three-roll refiner (Model SDX 600, Buhler Ltd, CH-9240 Uzwil, Switzerland) to a specified PS (D 90: 18 ± 1 µm, 25 ± 1 µm, 35 ± 1 µm and 50 ± 1 µm) conducting PS analysis, during refining, to ensure D90 values. The refined chocolates were melted at 50–55°C for 24 hours and the chocolate mass was conched in a Lipp Conche (Model IMC-E10, Boveristr 40-42, D-68309, Mannhein, Germany) at low speed for 3.5 hours at 60°C. Lecithin (0.5%) and cocoa butter (5%) were added and then conched at high speed for 30 minutes to effect adequate mixing and liquefaction. Samples were kept in sealed plastic containers at ambient temperature (20–22°C) and moisture, and fat contents were determined using Karl Fischer and Soxhlet methods (ICA, 1988, 1990).

9.3.2 Determination of particle size distribution

A MasterSizer® Laser Diffraction Particle Size Analyzer equipped with MS 15 sample presentation unit (refractive index 1.590) (Malvern Instrument Ltd, Malvern, England) was used. About 0.2 g of refined dark chocolate was dispersed in vegetable oil (refractive index 1.450) at ambient temperature (20 ± 2°C) until an obscuration of 0.2 was obtained. The sample was placed under ultrasonic dispersion for 2 minutes to ensure particles were independently dispersed and thereafter maintained by stirring during the measurement. Size distribution was quantified as the relative volume of particles in size bands presented as size distribution curves (Malvern MasterSizer® Micro Software v 2.19). PSD parameters obtained included specific surface area, largest PS (D 90), mean particle volume (D 50), smallest PS (D 10) and Sauter mean diameter (D[3,2]).

9.3.3 Tempering experiment

Samples were incubated at 50°C for 4 hours for melting and tempered using Aasted Mikrovert laboratory continuous three-stage tempering unit (Model AMK 10, Aasted Mikroverk A/S, Farum, Denmark). Chocolate was pumped through the multistage units and a worm screw drove the product through the heat exchangers. Sensors located at specific points in the equipment measured the temperature of both the chocolate and the coolant fluid at each stage. Based on our earlier work on modelling temperature controls to study tempering behaviour (Afoakwa et al., 2008g), the temperature of each of the coolant fluids (Zones 1, 2 and 3) was thus set as 26, 24 and 32°C; 21, 19 and 32°C; and 18, 16 and 32°C, respectively, for attaining the undertempered, optimally tempered and overtempered regimes. The degree of pre-crystallisation was measured using a computerised tempermeter (Exotherm 7400, Systech Analytics, Neuchâtel, Switzerland), and a built-in algorithm provided the tempering curves and temper readings in chocolate temper index (slope), corresponding to optimal temper (slope 0), undertemper (slope 1.0) and overtemper regimes (slope −1.0). The principle of this method has been described by Nelson (1999). Chocolates from three regimes were moulded using plastic moulds, 80 mm length, 20 mm breadth and 8 mm height. The final products were allowed to cool in a refrigerator (12°C) for 2 hours before de-moulding onto
plastic trays and conditioned at 20 ± 2°C for 14 days before analysis. Triplicate measurements were taken for each product composition and the mean values were recorded.

9.3.4 Texture measurements

Mechanical properties of chocolates (hardness and stickiness) were measured using TA-HD Plus Texture Analyzer with a penetration probe (needle P/2) attached to an extension bar and a 50-kg load cell and a platform reported by Afoakwa et al. (2008e). Maximum penetration and withdrawal forces through a sample (80 × 20 mm, depth 8 mm) were determined with eight replications at a pre-speed of 1.0 mm/second, test of 2.0 mm/second, post-speed of 10.0 mm/second, penetrating 6 mm at 20°C, converting mean values of the penetration force exerted by the 50 kg load cell into hardness (g force) and the withdrawal force with time into stickiness (g force · s) data, respectively, using XT.RA Dimensions, Exponent 32 software (Stable Micro Systems, Godalming, Surrey, UK) as shown in Figure 7.3(b).

9.3.5 Colour and gloss measurements

HunterLab Miniscan™ XE Colorimeter Model 45/0 LAV (Hunter Associates Inc., Reston, VA, USA) calibrated with white ceramic reference standard was used. Colour images of chocolate surfaces were converted into XYZ tristimulus values, which were further converted to CIELAB system: L*, luminance ranging from 0 (black) to 100 (white); and a* (green to red) and b* (blue to yellow) with values from −120 to +120. Information was obtained using a software algorithm (Matlab v. 6.5; The Math-Works, Inc., Natick, MA, USA): hue angle \( h^\circ = \arctan (b*/a*) \); chroma \( C^* = [(a*)^2 + (b*)^2]^{1/2} \). Mean values from five replicate measurements and standard deviations were calculated.

Gloss of chocolate surface was measured using the multiple angle Tricor Gloss meter (805A/806H Gloss System, Elgin, IL, USA). Reflectance was measured at an incidence light angle of 85° from the normal to the chocolate surface, in accordance with ASTM method D523. A polished black glass plate with a refractive index of 1.567 was used as standard surface (ASTM, 1995) and given a gloss value of 200. Gloss was reported as gloss units (GU) based on determinations (in triplicate) at six positions along a chocolate sample. As a reference, a surface with a gloss value less than 10 GU is considered a low-gloss surface (BYK, 1997; Briones et al., 2006).

9.3.6 Image acquisition and capture

A colour digital camera (Canon Powershot, Model A70, MA, USA) was mounted on a stand inside a large box with internal black surface impervious to light. Images of the optimally tempered, undertempered and overtempered samples were captured before storage and after 14 days in storage. The iris was operated in manual mode, with the lens aperture at \( f = 8 \) and speed 1/20 second (no zoom, no flash) to achieve high uniformity and repeatability. The camera was grey-balanced before each imaging session. Uniform diffuse lighting was used to illuminate the samples. The lighting system consisted of four CIE source D65 lamps (60 cm length and 18 W; Model TLD/965, Philips, Singapore) was placed above the sample at a 45° angle to maximise diffuse reflection responsible for colour. The angle between the camera lens axis and the sample was around 90° to reduce gloss. A Kodak grey card
with 18% reflectance was used as a white reference to standardise the illumination level. The grey-level image (1600 × 1200 pixels) of this card was divided into 192 blocks, each one of 100 × 100 pixels. After calibration, samples were placed in the field of view of the camera and an image of 1600 × 1200 pixels (approximately covering the whole area of the tablet) was acquired and stored in JPEG (Joint Photographic Experts Group, a standard for compressing digital photographic images) format of high resolution and superfine quality.

9.3.7 Determination of melting properties

The differential scanning calorimeter (DSC Series 7, Perkin Elmer Pyris, Norwalk, CT, USA) equipped with a thermal analysis data station was calibrated using indium and octadecane at a scan rate of 5°C/minute using an aluminium pan as reference. Samples (~5 mg) were loaded into 40 µL capacity pans with holes, which were sealed with lids using a sample press. Pans were heated at 5°C/minute from 15 to 55°C in an N₂ stream. Onset temperature ($T_{\text{onset}}$), peak temperature ($T_{\text{peak}}$), end temperature ($T_{\text{end}}$) and enthalpy of melting ($\Delta H_{\text{melt}}$) were calculated automatically by the software. Melting index ($T_{\text{INDEX}}$) was computed ($T_{\text{end}}-T_{\text{onset}}$), as described by Vasanthan and Bhatty (1996). Each sample was analysed in triplicate, and mean values and standard deviations were reported.

Thermal behaviour of fat and sugar components in samples from the different temper regimes was analysed using DSC. Pans containing approximately 5 mg samples were heated at 10°C/minute from 15 to 200°C in an N₂ stream, and melting profiles of the fat and sugar were calculated by the software. To calculate the $\Delta H_{\text{melt Sugar}}/\Delta H_{\text{melt Fat}}$ ratio, the melting enthalpy of the sugar was divided by the melting enthalpy of the fat peak, technique reported to provide information on the possible structural changes in the fat and/or sugar components in bloomed chocolates (Lonchampt & Hartel, 2006). Triplicate analyses were conducted, and mean value and standard deviation were reported.

9.3.8 Microstructural determinations

Chocolate samples were characterised using stereoscopic binocular microscope (Nikon, SMZ-2T, Tokyo, Japan) equipped with a variable removable lens. Micrographs (coloured images) were captured using a digital camera (Model 2.1 Rev 1, Polaroid Corporation, NY, USA) and observed using Adobe Photoshop (Version CS2, Adobe Systems Inc., NJ, USA). Triplicate experiments were conducted capturing six images per sample, and micrographs representing the surface of each temper regime were captured and presented. Samples were then sectioned (cut) into two pieces using a knife, and the internal microstructures were observed.

9.3.9 Scanning electron microscopy

Microstructural studies were carried out on optimally, under- and overtempered chocolates after 14 days in storage using a 1200 EX JEM scanning electron microscopy (SEM; Joel Ltd, Akishima, Japan). Sectioned samples (20 × 20 mm) were lyophilised (Heto Model DW3, Allerød, Denmark), then transferred and separately placed on grids with the help of double-sided tape, sputter-coated with gold (2 minutes, 2 mbar). Microstructures were observed at
5 kV and 9.75 × 10⁻⁵ torr vacuum taking 12 micrographs for each section (500×, 1,500× and 5000×) showing typical micrographs for each temper regime.

9.3.10 Experimental design and statistical analysis

Two experimental variables comprising temper regime and PSD were used. Other variables including refiner temperature and pressure, conching time and temperature were held constant. A 3 × 4 factorial experimental design was used comprising:

1. Temper regime: optimal temper, undertemper and overtemper
2. PSD (D₉₀): 18, 25, 35 and 50 µm

Statgraphics Plus 4.1 (Graphics Software System, STCC, Inc., Rockville, USA) examined mechanical properties (hardness and stickiness), appearance (colour [L, C*, F°] and gloss) and melting properties (Tₙₐₜₜ, Tₚₑₜₚₑₜ, Tₚₑₜₚₑₜ, ΔHₘₑₜ) using two-way analysis of variance (ANOVA) and multiple comparison tests to determine effects of factors and their interactions. Tukey multiple comparisons (95% significance level) determined differences between levels. All experiments were conducted in triplicates and the mean values were reported.

9.4 RESULTS AND DISCUSSION

9.4.1 Particle size distribution of dark chocolates

These findings (Fig. 7.1), previously reported (Afoakwa et al., 2008b), show volume histograms consisting of narrow (18 µm PS) and wide (25 µm PS) bimodal, and narrow (35 µm PS) and wide (50 µm PS) multimodal size distributions. This PSD range 18–50 µm using D₉₀ values (>90% finer) covers optimum minimum and maximum sizes with direct effects on texture and sensory character in manufacture (Ziegler & Hogg, 1999; Beckett, 2000). Data from the PSD as previously described (Afoakwa et al., 2008b) showed variations in specific surface area, mean particle volume D(v, 50), Sauter mean (D[3,2]) and mean particle diameter (D[4,3]) with increasing D₉₀ PSs. Specific surface area was inversely correlated with the different component of PSD. Similar inverse relationships of specific surface area with all the other components of PSD have been reported (Beckett, 1999; Ziegler & Hogg, 1999; Sokmen & Gunes, 2006). Beckett (1999) concluded that largest PS and specific surface area of solids are the two key parameters for chocolate manufacture. The former determines chocolate coarseness and textural character, the latter with desirable flow properties. Fat contents of the products were 35 ± 1% and moisture within the range of 0.90–0.98%.

9.4.2 Fat crystallisation behaviours during tempering of dark chocolate

Four different temper regimes (untempering, undertempering, overtempering and optimal tempering) were characterised (Fig. 9.1) each with its unique characteristic crystallisation behaviour. In optimal tempering, the temperature of the chocolate remained constant for sometime during cooling to initiate formation of stable fat crystals. The crystallisation heat released was then balanced by an equal amount of cooling energy causing the growth of stable crystal nuclei in adequate amounts, which during post-tempering conditioning mature
to affect shelf-stability of the product. The temperature of the chocolate dropped further when the liquid cocoa butter was transformed into solid crystals, resulting in solidification of the products (Fig. 9.1). Beckett (2000) reported that properly tempered chocolate shows formation of Form V, the most desirable polymorphic form, which confers appropriate product snap, contraction, gloss and shelf-life characteristics.

Undertempering (insufficient tempering) was caused by the relatively higher temperatures released between the multistage heat exchangers during tempering. The process caused development of more crystallisation heat within the product during solidification, effecting quick cooling, as more liquid fat was transformed quickly into solid form, resulting in the formation of very few stable fat crystal nuclei (Fig. 9.1). Distinct increase in temperature was observed during the crystallisation period, which declined again after reaching a maximum point where most of the stable crystals formed were remelted prior to cooling. Untempered chocolate produced no stable fat crystals as the heat exchange system generated higher crystallisation heat during cooling, resulting in quick cooling of the completely melted product, with no inflexion point for stable fat crystal formation (Fig. 9.1).

Beckett (2000) explained that the crystallisation processes in both untempered and undertempered chocolates lead to the formation of unstable crystal polymorph, which later transforms into more stable Form VI polymorph during storage. Preliminary studies showed that untempering and undertempering regimes exhibit different crystallisation behaviours but result in similar unstable fat crystal nucleation and growth, with similar associated storage polymorphic transformations and defects in products. Storage of the undertempered products under ambient temperature (20–22°C) for 14 days of conditioning induced blooming in samples, affecting various quality changes in the products as reported in this study. Products from undertempering regime were used in this study.
Overtempering occurred when relatively lower temperatures were exchanged between the multistage heat exchangers of the tempering equipment, causing significant part of the liquid fat to withdraw from the continuous phase of the chocolate, and transformed into solid form leaving less liquid fat available for pumping of the product. The process released little crystallisation heat during cooling, rendering a rather flat and slow cooling curve (Fig. 9.1). This crystallisation process results in too many small stable seed crystal formation, leading to reduced strengths in the polymorphic stabilities of the fat crystals formed during the process (Talbot 1999). As a substantial part of the phase transition (from liquid to solid) took place before the chocolate reached the mould, less contraction occurred in the mould, leading to demoulding problems with defects in final product quality and storage characteristics (Hartel, 2001; Lonchampt & Hartel, 2004).

9.4.3 Effect of temper regime and PSD on mechanical properties

Hardness showed an inverse relationship with PSs, with significant reductions at all temper regimes, and greatest in the undertempered (bloomed) products (Fig. 9.2). Hardness of the optimally tempered products decreased from 5318 g with 18 µm PS to 4259 g at 50 µm. Similar trends in hardness were noted with the overtempered samples, decreasing from 6064 g with 18 µm PS to 4651 g at 50 µm, and from 6533 g with 18 µm PS to 5459 g at 50 µm.

![Fig. 9.2](image_url) Effect of temper regime and PSD on hardness of dark chocolates. Reprinted from Afoakwa et al. (2008c), copyright 2008, with permission from Elsevier.
in the undertempered products (Fig. 9.2), suggesting differences in hardness with varying PS at all temper regimes. PSs have been noted as an important parameter in the hardness of fat crystal networks in many confectionery products (Campos et al., 2002; Marangoni & Narine, 2002; Narine & Marangoni, 2002; Pérez-Martínez et al., 2007). Earlier studies showed inverse relationships of hardness in tempered dark chocolates with PSs at varying fat and lecithin levels (Afoakwa et al., 2008e), attributed to the relative strengths of their particle-to-particle interactions (Campos et al., 2002; Afoakwa et al., 2009d).

Do et al. (2007) also reported consistent reductions in hardness (texture) of milk chocolates with increasing PSs. The results showed that the undertempered products had the greatest hardness (texture), attributable to the recrystallisation process undergone by the fat in the undertempered chocolates resulting in intense hardening of products. This trend in hardness was followed by the overtempered samples with the optimal tempered products possessing relatively lesser hardness levels, suggesting overtempering of dark chocolates leads to increased hardness of samples at all PSs as compared to their respective optimally tempered products.

Chocolate stickiness showed an inverse relationship with PSs at all temper regimes, and the greatest trends were noted in the undertempered products (Fig. 9.3). Stickiness of the optimally tempered products decreased consistently from 380.67 g with 18 µm PS to 325.25 g at 50 µm. Likewise, the levels of stickiness in the overtempered samples decreased from 447.92 g with 18 µm PS to 365.10 g at 50 µm, and from 336.86 g with 18 µm PS to 309.20 g at 50 µm in the undertempered products (Fig. 9.3). These explain that the overtempered products had the greatest stickiness levels, followed by the optimally tempered products with the undertempered samples having the least. Narine and Marangoni (2001) noted that stickiness of confectionery gives information about deformability related to oral sensory characters. ANOVA suggested significant differences ($p \leq 0.05$) in both hardness and stickiness levels with PSs and temper regimes. Significant interactions were observed between all parameters (Table 9.1), suggesting the combined effects of PSD and tempering could be manipulated to

![Fig. 9.3](image-url) Effect of temper regime and PSD on stickiness of dark chocolates. Reprinted from Afoakwa et al. (2008c), copyright 2008, with permission from Elsevier.
reduce hardening and stickiness in dark chocolates. Multiple comparison tests showed that overtempered products were significantly harder and stickier than the optimally tempered – important for quality control and in new product development.

9.4.4 Effect of temper regime and PSD on colour and gloss

Lightness ($L^*$), chroma ($C^*$) and hue ($h^\circ$) followed similar trends with varying PS at all temper regimes (Table 9.2). Significant ($p < 0.001$) and linear effects on $L^*$ were recorded with increasing PSs from 18 to 50 µm, with consequential decreases in $L^*$, noticeable but dependent on temper regime (Table 9.3). Similar decreases in $C^*$ and $h^\circ$ with increasing PS were also noted. Thus, dark chocolate became lighter as $D_{90}$ decreased from 50 to 18 µm and as PS increased (18–50 µm), $C^*$ and $h^\circ$ were significantly decreased, with levels pronounced in the undertempered samples. Similarly, temper regime affected to varying levels all the colour measurements. The undertempered samples attained relatively higher $L^*$-values than both the optimally tempered and overtempered samples. The blooming process resulted from undertempering of samples caused decreases in $L^*$ from 81.47, 80.60, 80.09 and 78.76, respectively, for the products with 18, 25, 25 and 50 µm, an indication that all the undertempered samples had become whiter in colour within the 14 days of conditioning period. As well, the blooming caused great reductions in $C^*$ and $h^\circ$ in the undertempered products at all PSs (Table 9.2). Hutchings (1994) stated that $L^*$, $C^*$ and $h^\circ$, respectively, represent food diffuse reflectance of light, degree of saturation and hue luminance, which are

<table>
<thead>
<tr>
<th>Table 9.2</th>
<th>Effects of temper regime and PS on gloss and colour measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temper regime</td>
<td>Particle size ($D_{90}$) (µm)</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Optimally tempered</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>50</td>
</tr>
<tr>
<td>Overtempered</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>50</td>
</tr>
<tr>
<td>Undertempered</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>50</td>
</tr>
</tbody>
</table>

Means ± standard deviation from triplicate analysis.
Table 9.3 ANOVA summary of F-values of colour and gloss measurements

<table>
<thead>
<tr>
<th>Process variables</th>
<th>L*</th>
<th>C*</th>
<th>h°</th>
<th>Gloss</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: Particle size (D90)</td>
<td>516.04***</td>
<td>80.99***</td>
<td>15.08**</td>
<td>111.46***</td>
</tr>
<tr>
<td>B: Temper regime</td>
<td>2960.75***</td>
<td>17482.54***</td>
<td>2302.96***</td>
<td>10183.49***</td>
</tr>
<tr>
<td>A × B</td>
<td>29.95**</td>
<td>43.86**</td>
<td>12.15*</td>
<td>23.01***</td>
</tr>
</tbody>
</table>

*Significant F-ratios at *p ≤ 0.05, **p ≤ 0.01 and ***p ≤ 0.001.

dependent on particulate distribution, absorptivity and scattering factors or coefficients. In a densely packed medium, scattering factor is inversely related to particle diameter (Saguy & Graf, 1991). Chocolates with varying PSs differ in structure and particulate arrangements, influencing light scattering coefficients, and, thus appearance (Afoakwa et al., 2008e).

Similar decreasing trends in L* were noted in both tempered and overtempered samples with increasing PS. However, the overtempered samples had relatively lower L* values at all PSs as compared to their corresponding optimally tempered products (Table 9.2). These suggest that overtempering reduces the degree of lightness in dark chocolates, effecting product darkening and thus affecting quality. However, no noticeable effect on C* and h° was observed among the optimally and overtempered products (Table 9.2). Thus, changes in colour in dark chocolates were primarily dependent on PS and temper regime. Undertempered (bloomed) dark chocolates tend to scatter more light, appear lighter and less saturated than overtempered and optimally tempered products. The blooming process resulted in higher scattering coefficients, with subsequent paleness (whitening) – higher L* values. Hartel (1999) reported that the whitish haze in bloomed chocolate is caused by the dispersion of light of fat crystals. Similar effects of PS on the degree of whitening during blooming have been reported (Altimiras et al., 2007). Colour of foods may be affected by various optical phenomena, among them scattering and surface morphology; therefore, an accurate understanding of the influence of appearance on measured colour is essential.

Gloss relates to capacity of a surface to reflect directed light at the specular reflectance angle with respect to the normal surface plane (ASTM, 1995). Significant (p < 0.001) and linear effects on gloss were observed with increasing PS from 18 to 50 µm, with consequential decreases in gloss, greatly dependent on the temper regime (Table 9.3). Gloss of dark chocolates was reduced as D90 increased from 18–50 µm at all temper regimes. As well, differences in temper regime influenced the gloss measurements to varying levels. Blooming of the undertempered samples caused drastic reduction in gloss of the products than their respective optimally tempered and overtempered samples. The undertempered samples containing 18 µm PS had gloss value of 7.3 GU, while the corresponding tempered and overtempered products had 158.6 and 142.0 GU, respectively. Similar trends were noticed at all PSs (Table 9.2). Beckett (2000) noted that tempering was important for gloss, a key quality attribute in chocolate. In undertempered chocolates, light scattering is affected by reductions in surface regularity. Gloss stability of edible coating formulations of chocolates has been studied (Trezza & Krochta, 2000; Lee et al., 2002; Briones et al., 2006).

ANOVA showed that both PS and temper regime significantly (p < 0.001) influenced L*, C*, h° and gloss, with significant (p ≤ 0.05) interactions (Table 9.3), all influencing appearance. Multiple comparison tests showed that undertempering had the greatest influence on appearance and gloss of products, but differences between optimally and overtempered products were significant. Attention to tempering is important for consistency in dark chocolate appearance and quality control.
9.4.5 Effect of temper regime and PSD on melting properties

9.4.5.1 Effects of temper regime

Figure 9.4 shows typical DSC thermograms used for evaluating the melting properties of dark chocolates manufactured from the optimally tempered, overtempered and undertempered regimes. All the samples exhibited similar distinct single endothermic transitions between 15 and 55°C, the range expected for chocolate melting profiles. McFarlane (1999) explained that peak onset corresponds to the temperature at which a specific crystal form starts to melt; peak maximum, that at which melting rate is greatest; and end of melting, completion of liquefaction – all the information is related to the crystal type. Peak height, position and resolution are dependent on sample composition and crystalline state distribution.

Data from the DSC (Fig. 9.4) showed that differences in temper regime produced changes in crystallinity and melting properties, observed in the differences in their peaks, suggesting that variations in crystallisation behaviour in dark chocolates during tempering influence the degree of crystallinity and CSD of their derived products. Undertempered (bloomed) chocolates showed the greatest peak width, followed by the overtempered samples having slightly wider CSD than the optimally tempered products with resultant variation in their melting profiles (Fig. 9.4).

Hartel (2001) concluded that distribution of crystal sizes in foods plays key roles in final product quality, defined by the total and specific characteristics of their crystalline material. Number of crystals and range of sizes, shapes and polymorphic stability, as well as arrangements in network structures, dictate mechanical and rheological properties. Knowledge and control of CSD can be important for optimising processing conditions.
### Table 9.4  Effects of temper regime and particle size distribution on melting properties

<table>
<thead>
<tr>
<th>Temper regime</th>
<th>Particle size (D90) (µm)</th>
<th>T\text{onset} (°C)</th>
<th>T\text{end} (°C)</th>
<th>T\text{index} (°C)</th>
<th>T\text{peak} (°C)</th>
<th>∆H\text{melt} (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optimally tempered</td>
<td>18</td>
<td>26.5 ± 0.4</td>
<td>33.6 ± 0.3</td>
<td>7.1 ± 0.2</td>
<td>31.9 ± 0.1</td>
<td>37.73 ± 0.65</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>26.4 ± 0.3</td>
<td>33.3 ± 0.4</td>
<td>6.7 ± 0.4</td>
<td>31.7 ± 0.2</td>
<td>37.56 ± 0.92</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>26.6 ± 0.2</td>
<td>32.7 ± 0.3</td>
<td>6.1 ± 0.2</td>
<td>31.7 ± 0.1</td>
<td>36.87 ± 0.58</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>26.5 ± 0.4</td>
<td>32.5 ± 0.4</td>
<td>6.0 ± 0.4</td>
<td>31.8 ± 0.2</td>
<td>36.76 ± 0.72</td>
</tr>
<tr>
<td>Overtempered</td>
<td>18</td>
<td>26.6 ± 0.2</td>
<td>34.2 ± 0.3</td>
<td>7.6 ± 0.2</td>
<td>32.6 ± 0.2</td>
<td>41.26 ± 0.61</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>26.5 ± 0.4</td>
<td>33.8 ± 0.4</td>
<td>7.3 ± 0.4</td>
<td>32.7 ± 0.1</td>
<td>40.42 ± 0.88</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>26.7 ± 0.2</td>
<td>33.5 ± 0.2</td>
<td>6.8 ± 0.2</td>
<td>32.5 ± 0.2</td>
<td>40.47 ± 0.57</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>26.6 ± 0.3</td>
<td>33.2 ± 0.4</td>
<td>6.6 ± 0.4</td>
<td>32.6 ± 0.2</td>
<td>40.36 ± 0.52</td>
</tr>
<tr>
<td>Undertempered</td>
<td>18</td>
<td>27.4 ± 0.2</td>
<td>36.2 ± 0.3</td>
<td>8.8 ± 0.2</td>
<td>33.8 ± 0.2</td>
<td>44.45 ± 0.88</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>27.3 ± 0.4</td>
<td>36.0 ± 0.4</td>
<td>8.7 ± 0.4</td>
<td>33.7 ± 0.1</td>
<td>44.10 ± 0.51</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>27.2 ± 0.2</td>
<td>35.7 ± 0.3</td>
<td>8.5 ± 0.2</td>
<td>33.6 ± 0.2</td>
<td>43.87 ± 0.86</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>27.4 ± 0.3</td>
<td>35.6 ± 0.4</td>
<td>8.2 ± 0.4</td>
<td>33.6 ± 0.1</td>
<td>43.80 ± 0.58</td>
</tr>
</tbody>
</table>

Means ± standard deviation from triplicate analysis.

Data from the DSC on T\text{onset}, T\text{end}, T\text{peak}, ∆H\text{melt} and T\text{index} in relation to temper regime (Table 9.4) analysed by ANOVA and multiple comparison tests showed significant (p < 0.05) differences for T\text{onset} and T\text{peak} differing in temper regime (Table 9.4) and highly significant differences (p < 0.001) among T\text{end}, T\text{index} and ∆H\text{melt} (Table 9.5). The differences in temper yielded mean T\text{end} values of 33.0, 33.7 and 35.9°C, respectively, for the optimally, over- and undertempered chocolates. There was a significant (p < 0.05) inverse relationship between T\text{end} and PSD (Table 9.5). Such observations suggest that undertempered chocolate completed melting at higher temperatures than optimally and overtempered products. The changing T\text{end} values of the samples revealed that the crystallites in optimally and overtempered were within βV polymorphic status (32–34°C) while that of undertempered had undergone polymorphic transformation into βVI polymorphic status (34–36°C). Similarly, undertempered (bloomed) chocolate had higher T\text{index} values of 8.8, 8.7, 8.5 and 8.2°C, inversely related to PS from 18 to 50 µm, while the optimal and overtempered products had T\text{index} ranges of 7.1–6.0°C, and from 7.6 to 6.6°C, respectively, suggesting that the undertempered chocolate took longer to melt than the optimally and overtempered products. Multiple comparison tests showed that the overtempered samples took longer to melt than the optimally tempered. It is predicted that these would have likely impact on their behaviour during consumption, attributable to the relative strengths of their mechanical properties (hardness and stickiness). Similarly, undertempered chocolate had higher ∆H\text{melt} values at all PSs than the optimally and overtempered products (Table 9.4), with significant (p < 0.05) interactions with PS. Multiple comparison test revealed that overtempered chocolates showed higher T\text{index} and ∆H\text{melt} than the optimally tempered, a significant finding for process quality control.

### Table 9.5  ANOVA summary of F-values of melting properties

<table>
<thead>
<tr>
<th>Process variables</th>
<th>T\text{onset} (°C)</th>
<th>T\text{end} (°C)</th>
<th>T\text{peak} (°C)</th>
<th>T\text{index} (°C)</th>
<th>∆H\text{melt} (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: Particle size (D90)</td>
<td>1.78</td>
<td>12.17*</td>
<td>3.74</td>
<td>34.73**</td>
<td>6.96</td>
</tr>
<tr>
<td>B: Temper regime</td>
<td>198.75***</td>
<td>261.19***</td>
<td>22.57**</td>
<td>1107.80***</td>
<td>462.78***</td>
</tr>
<tr>
<td>A × B</td>
<td>1.18</td>
<td>2.45*</td>
<td>7.26***</td>
<td>160.33***</td>
<td>3.67**</td>
</tr>
</tbody>
</table>

Significant F-ratios at *p ≤ 0.05, **p ≤ 0.01 and ***p ≤ 0.001.
9.4.5.2 Effects of particle size distribution

In dark chocolate, PSD influences rheological and microstructural properties as well as texture in tempered products (Afoakwa et al., 2007, 2008b, 2009d). In this study, peak shapes and sizes were similar with all values for PSD suggesting little differences in crystallinity between them. Examination of important DSC parameters (Table 9.4) – \( T_{\text{onset}}, T_{\text{end}}, T_{\text{peak}}, \Delta H_{\text{melt}} \) and \( T_{\text{index}} \) – suggested that increasing PS from 18 to 50 \( \mu \)m yielded no significant \((p = 0.2782)\) changes in \( T_{\text{onset}} \), for any temper regime (Table 9.5), with values in the ranges of 26.5–26.6°C, 26.5–26.7°C and 27.2–27.4°C, respectively, for the optimally, over- and undertempered chocolates. Similar observations were made for \( T_{\text{peak}} \) (Table 9.4) – ranging from 31.7 to 31.9°C, 32.1 to 32.3°C and 33.6 to 33.8°C for the optimally, over- and undertempered products, respectively (Table 9.4), with insignificant differences \((p > 0.05)\) in PS found at all temper regimes. The lack of significant relationship between PS and \( \Delta H_{\text{melt}} \) implies that enthalpy of melting was similar for chocolates at all PSs, independent of temper regime.

In contrast, varying PS had significant effects on \( T_{\text{end}} \) and \( T_{\text{index}} \), with general inverse relationships between PS and \( T_{\text{end}} \), and \( T_{\text{index}} \), at all temper regimes (Table 9.4). Optimally tempered products with smaller PS (18 \( \mu \)m) had \( T_{\text{end}} \) value of 33.6°C, and decreased consistently to 32.5°C in 50 \( \mu \)m samples, representing a difference of 0.9°C.

Similar marginal but significant \((p < 0.05)\) decreasing trends in \( T_{\text{end}} \) with increasing PS were observed with both the overtempered and undertempered (bloomed) samples (Table 9.5). These findings suggested that dark chocolates with larger PS (50 \( \mu \)m) require slightly lower temperatures to complete melting than the smaller PS (18 \( \mu \)m) products at all temper regimes. Similar inverse relationships were observed between \( T_{\text{index}} \) and PS at all temper regimes. The data (Table 9.4) showed that increasing PS for 18–50 \( \mu \)m in the optimally tempered products caused significant \((p \leq 0.05)\) reductions in \( T_{\text{index}} \) from 7.1 to 6.0°C, respectively, and similar trends were noted with the overtempered and undertempered products. ANOVA showed significant \((p < 0.001)\) influence of PS on \( T_{\text{end}} \) and \( T_{\text{index}} \), with significant interactions with temper regime (Table 9.5). Multiple comparison tests revealed significant differences \((p = 0.001)\) between \( T_{\text{end}} \) of products containing 18, 35 and 50 \( \mu \)m, suggesting that chocolates with finer particles (18 \( \mu \)m) would take relatively longer time to melt than their corresponding products with larger particles (35 and 50 \( \mu \)m) independent of temper regime, attributable to the relative strengths of the interparticle aggregations and flocculation in the different PS products (Narine & Marangoni, 1999; Marangoni & McGauley, 2002; Afoakwa et al., 2009d). Do et al. (2007) noted that quantitative decreases in particle aggregation and structure in chocolate influence melting behaviour, suggesting that in its crystallised state, structures with larger PS are less interconnected, providing less resistance to breakage and melting. This could be important for predicting oral melting behaviour with impacts on temporal components of flavour release and oral epithelial sensations.

9.4.5.3 Thermal behaviours and ratio of sugar/fat melting enthalpies in products

Thermal behaviours and ratio of sugar/fat melting enthalpies in chocolates differing in temper regime were studied using DSC to provide information on differences in structure. The DSC thermograms (Fig. 9.5) showed differences in fat melting profile, resulting from the widened peak width in the undertempered (bloomed) sample, but no differences were noted in the
sugar melting profiles, explaining the structural (polymorphic) transformations in the fat component in the undertempered product.

The DSC data on fat and sugar melting properties \( (T_{\text{onset}}, T_{\text{end}}, T_{\text{peak}}, \Delta H_{\text{fat}}, \Delta H_{\text{sugar}} \text{ and } \Delta H_{\text{sugar}}/\Delta H_{\text{fat}}) \) related to temper regime (Table 9.6) were similar to the trends for fat (Table 9.4). Fat melting profiles suggested the \( \beta \text{V} \) polymorph in both optimally and overtempered chocolates with \( T_{\text{end}} \) of 32.3 and 32.9°C, respectively, and a more stable \( \beta \text{VI} \) polymorph in undertempered samples with \( T_{\text{end}} \) of 35.8°C, showing significant \( (p < 0.001) \) influences (Table 9.7) on \( T_{\text{onset}}, T_{\text{peak}}, \Delta H_{\text{fat}} \) in chocolates.

On the contrary, the results of the sugar melting properties (Table 9.6) showed only marginal differences in all the melting properties with varying temper regime. ANOVA showed no significant differences \( (p > 0.05) \) in all the studied melting properties \( (T_{\text{onset}}, T_{\text{end}}, T_{\text{peak}}, \Delta H_{\text{sugar}}) \) on chocolates from the three temper regimes (Table 9.7), suggesting that no structural change in sugar was found in products from the three temper regimes. Similarly, the ratios of sugar to fat melting enthalpies in products from optimal, over- and undertempered samples were 1.25, 1.24 and 1.17, respectively (Table 9.6), with no significant difference \( (p = 6.853) \) among them (Table 9.7). The lower \( \Delta H_{\text{sugar}}/\Delta H_{\text{fat}} \) ratio noted in the undertempered sample resulted from the higher \( \Delta H_{\text{fat}} \), as a result of recrystallisation of fat (Hartel, 2001; Lonchampt & Hartel, 2004). These findings support the earlier finding that fat and sugar components are present in similar quantities in both bloomed and optimally tempered dark chocolates, but contrast with the report of Lonchampt and Hartel (2006) that the melting peak of fat in untempered (bloomed) chocolate was almost non-existent with \( \Delta H_{\text{fat}} \) being tenfold smaller than that obtained for optimally tempered chocolate, concluding that the whitish spots in bloomed chocolates were mainly composed of sugar crystals and cocoa powder and nearly devoid of fat. Kinta and Hatta (2005) also reported the presence of fat components in bloomed dark chocolate, suggesting mechanisms of bloom development in chocolate involve phase separation associated with the growth of xenomorphic fat crystals.
Table 9.6  Thermal properties of fat and sugar components in dark chocolates from different temper regimes

<table>
<thead>
<tr>
<th>Temper regime</th>
<th>Fat melting properties</th>
<th>Sugar melting properties</th>
<th>Sugar/fat relations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_{\text{onset}}$ (°C)</td>
<td>$T_{\text{end}}$ (°C)</td>
<td>$T_{\text{peak}}$ (°C)</td>
</tr>
<tr>
<td>Optimally tempered</td>
<td>26.2 ± 0.24</td>
<td>32.3 ± 0.44</td>
<td>30.8 ± 1.04</td>
</tr>
<tr>
<td>Overtempered</td>
<td>26.4 ± 0.18</td>
<td>32.9 ± 0.28</td>
<td>31.4 ± 0.83</td>
</tr>
<tr>
<td>Undertempered</td>
<td>27.3 ± 0.53</td>
<td>35.8 ± 0.19</td>
<td>33.5 ± 0.71</td>
</tr>
</tbody>
</table>

Means ± standard deviation from triplicate analysis.
Table 9.7 ANOVA summary of F-values of fat and sugar thermal properties

<table>
<thead>
<tr>
<th>Process variable</th>
<th>Fat melting properties</th>
<th>Sugar melting properties</th>
<th>Sugar/fat relations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_{\text{onset}}$ ($^\circ$C)</td>
<td>$T_{\text{end}}$ ($^\circ$C)</td>
<td>$T_{\text{peak}}$ ($^\circ$C)</td>
</tr>
<tr>
<td>Temper regime</td>
<td>12.41*</td>
<td>42.83***</td>
<td>3.86*</td>
</tr>
</tbody>
</table>

Significant F-ratios at *p ≤ 0.05, **p ≤ 0.01 and ***p ≤ 0.001.

9.4.5.4 Effect of temper regime on product image

Digital images of dark chocolates (18 µm PS) were assembled to show surface appearances of the optimally, under- and overtempered products before and after 14 days of conditioning (Fig. 9.6). Initially, surface appearances were similar and smooth, but after 14 days, clear differences were apparent. Optimally and overtempered chocolates maintained their characteristic glossy appearance and dark brown colour, but the undertempered samples had bloomed, with appearance of surface whitish spots, rendering them dull and hazy in colour (Fig. 9.6). Similar increases in whiteness in undertempered (bloomed) chocolates have been reported (Lonchampt & Hartel, 2004, 2006; Altimiras et al., 2007). Hartel (1999) explained this phenomenon as recrystallisation of fats from a less stable Form IV to a more stable Form VI polymorph, with changes in light dispersion on small surface fat crystals ($\geq 5$ µm), consequently impacting on both appearance and textural attributes. Fat bloom development, mechanisms and effects on chocolate appearance, quality and marketability have been extensively studied (Bricknell & Hartel, 1998; Ali et al., 2001; Hartel, 2001; Walter & Cornillon, 2001, 2002; Timms, 2003; Lonchampt & Hartel, 2004, 2006; Altimiras et al., 2007; Smith et al., 2007).

9.4.6 Effect of temper regime on microstructure

Microstructural examination using stereoscopic binocular microscopy after 14 days of conditioning showed clear variations in both surface and internal peripheries of products from varying temper regimes (Fig. 9.7). Overtempered products had relatively darker surfaces and internal appearances than optimally tempered, confirming the reported relative differences in $L^*$ (Table 9.2). Undertempered products showed both bloomed surface and internal periphery with large whitish and distinct smaller brown spots (Fig. 9.7). The observed whitish appearance on surfaces and internal peripheries appear to be mixtures of fat and sugar crystals, and the small brown spots, cocoa solids. Lonchampt and Hartel (2004, 2006) suggested that these whitish spots were primarily sugar crystals and cocoa powder, nearly devoid of fat. This difference in interpretation is the subject of further studies.

9.4.7 Effect of temper regime on scanning electron microstructure

Microstructural examination using scanning electron microscopy after 14 days of conditioning showed clear variations in crystalline network structure, interparticle interactions and spatial distributions of network mass among optimally, over- and undertempered samples,
Fig. 9.6 Photographic images of (a) fresh and (b) matured (conditioned) optimally tempered, undertempered and overtempered dark chocolates (18 μm PS). Reprinted from Afoakwa et al. (2009a), copyright 2009, with permission from Elsevier.
Fig. 9.7  Micrographs of surface (a) and internal (b) structures, respectively, of (1) optimally tempered, (2) undertempered and (3) overtempered dark chocolates (18 μm PS). Reprinted from Afoakwa et al. (2009a), copyright 2009, with permission from Elsevier.
becoming well defined with increasing magnification from (i) ×800 (ii) ×1500 to (iii) ×2500 (Fig. 9.8(a–c)). Microscopy of the optimally tempered chocolate showed an even spatial distribution of small number of dense crystalline networks with well-defined interparticle connections among crystals, suggesting the stable \( \beta \)-polymorph (Fig. 9.8(a)). Similarly, micrographs of the overtempered chocolate showed a spatial distribution of a dense mass of smaller crystals (relative to those of the optimally tempered) within a network structure of well-defined particle-to-particle crystal connections, suggesting their \( \beta \)-polymorph stability (Fig. 9.8(b)). These larger numbers of small crystalline networks noted in the overtempered samples are suspected to result from early nucleation and growth of seed crystals due to the slow cooling (Fig. 9.1), leading to the formation of submicron primary crystallites from the melt, with the resulting fat crystal network stabilised by van der Waals forces, possibly with steric and Coulombic forces (deMan, 1999; Narine & Marangoni, 2002; Tang & Marangoni, 2008).

Undertempered (bloomed) chocolate showed dissolution, rearrangement and recrystallisation of the numerous small crystals noted in the over- and optimally tempered products to a smaller number of larger (lumps) fat crystals (Ostwald ripening), and polymorphic transformation, nucleation and growth of new large crystals in a more stable polymorphic form, inducing formation of solid bridges with weak and less intercrystal connections within the crystalline structures (Fig. 9.8(c)). Hartel (2001) suggested that this phenomenon is brought about by thermodynamic differences in equilibrium between large and small crystals within a network structure leading to recrystallisation of unstable fat polymorphs. In another study, surface imperfections – pores and pits – in filled chocolates were reported on the microstructure of bloomed chocolate (Rousseau & Smith, 2008). Both reports explained that morphological changes on the surface of the chocolate were dominated by the growth of needle-like crystals and spherulites on the chocolate with large crystals approximately 100 µm in length, and concluded that from a microstructural perspective, both diffusion and capillarity appear to be involved in fat bloom formation and development, though temperature, PSD of the product and the presence of a filling fat strongly dictate the rate and type of mechanism that dominate the process.

These hypotheses suggest that differences in crystallisation behaviour during tempering lead to formation of different microstructural organisations of crystal network structure, with associated physical changes in chocolates. Characterising the nature of crystals in confectionery is an important step in quantifying the physical and sensory properties, as the resulting three-dimensional fat crystal network along with the phase behaviour and structural arrangements impacts on mechanical, rheological and melting properties and shelf-life (Hartel, 2001; Campos et al., 2002; Pérez-Martínez et al., 2007). Parameters such as cooling rate and thermal history (i.e. crystallisation temperature and tempering) influence kinetics and ultimate physical properties of the crystallised fat systems.

### 9.5 CONCLUSION

Fat crystallisation behaviour during tempering of dark chocolate plays vital roles in defining the structure, mechanical properties and appearance of products. Wide variations in mechanical properties and appearance occurred in products from different PS and temper regimes. PS was inversely related with texture and colour, with the greatest effects noted in hardness, stickiness and lightness at all temper regimes. Overtempering caused increases in product hardness, stickiness with reduced gloss and darkening of product surfaces.
Fig. 9.8  Scanning electron micrographs showing crystalline network microstructures at magnifications of (i) ×800 (ii) ×1500 and (iii) ×2500 for (a) tempered, (b) overtempered and (c) undertempered (bloomed) dark chocolates at 18 μm PS. C shows some of the well-defined crystal structures; iC shows some of the ill-defined crystal structures; i shows some of the intercrystal connections. The arrows indicate some of the pores, cracks and crevices; B shows some of solid bridges; L shows some of the large (crystal) lumps on the crystal structure. Reprinted from Afoakwa et al. (2009a), copyright 2009, with permission from Elsevier.
Fig. 9.8 (Continued)
Fig. 9.8  (Continued)
Undertempering induced fat bloom in products with consequential quality defects in texture, colour and surface gloss. Variations in PSD had no influence on crystallinity of chocolates, whether optimally, over- or undertempered. PS had a limited but significant direct relationship with certain melting parameters – $T_{\text{onset}}$, $T_{\text{peak}}$ and $\Delta H_{\text{melt}}$ – independent of temper but significant inverse relationship with others – $T_{\text{end}}$ and $T_{\text{index}}$. Contrariwise, varying temper influenced crystallinity and chocolate melting properties ($T_{\text{end}}$, $T_{\text{index}}$ and $\Delta H_{\text{melt}}$). Undertempering of chocolate resulted in widened CSD with significant changes in $T_{\text{end}}$, $T_{\text{index}}$ and $\Delta H_{\text{melt}}$. Overtempering caused moderate increases in CSD, with significant effects on $T_{\text{end}}$, $T_{\text{index}}$ and $\Delta H_{\text{melt}}$, but no changes were noted in $T_{\text{onset}}$ or $T_{\text{peak}}$. Fat–sugar melting profiles were similar in all chocolates independent of PS and temper regime.

Stereoscopic binocular micrographs revealed clear variations in surface and internal crystal network structure and interparticle interactions among optimally tempered, overtempered and undertempered (bloomed) samples. Blooming caused whitening of both surface and internal periphery of products with consequential effects on texture and appearance. Electron micrographs showed an even spatial distribution of numerous small stable $\beta$-polymorph crystals in a network with well-defined interparticle connections in optimally tempered chocolate. With overtempered chocolate there were large numbers of very small crystals in a network with similar well-defined particle-to-particle connections resulting from formation of a stable $\beta$-polymorph with early nucleation: the outcome was growth of seed crystals from the melt into submicron primary crystallites and a fat crystal network stabilised by van der Waals forces. Undertempering resulted in dissolution of a large number of small crystals, rearrangement and recrystallisation into a small number of larger (lumps) fat crystals (Ostwald ripening). In this process, there were polymorphic transformation, nucleation and growth of new large crystals in a more stable polymorphic form with formation of solid bridges, with weak and fewer intercrystal connections within the chocolate structure. Attainment of optimal temper regime during tempering of dark chocolate is necessary for the achievement of premium-quality products and avoidance of defects in mechanical properties, appearance and melting character.
10 Fat bloom formation and development in chocolates

10.1 SUMMARY AND INDUSTRIAL RELEVANCE

Fat bloom development and associated changes in microstructure, texture, appearance and melting properties were studied. Dark chocolates varying in particle size (PS) (D$_{90}$ of 18, 25, 35 and 50 µm) were processed and pre-crystallised to undertemper regime. Bloom was induced by storing products under ambient conditions (18 ± 2°C, relative humidity 50%), and changes in texture, surface whiteness, gloss and melting properties were evaluated on cooling and after every 24 hours in storage until reaching asymptotic values. Microstructure of products was characterised during blooming using stereoscopic binocular microscopy. Measurements on texture and surface whiteness showed initial rapid increases with consequential reductions in gloss within the first 96 hours, followed by gradually decreasing gradient until reaching asymptotic levels. Storage influenced melting properties ($T_{\text{onset}}$, $T_{\text{end}}$, $T_{\text{peak}}$ and $\Delta H_{\text{melt}}$) in products causing polymorphic transformation from $\beta$IV to $\beta$VI within 72 hours. Micrographs showed similar surface crystalline network structure and interparticle interactions among products from different PS after tempering, and bloom initiation occurred within 24 hours in storage, resulting in appearance of both liquid and unstable fat on the surface of products. The unstable fat then recrystallised during storage into more stable polymorphs and crystal growth was promoted by Ostwald ripening (larger crystals growing at the expense of smaller ones), with the appearance of white crystalline structure, which spread gradually throughout the chocolate mass after 96 hours. Products containing the largest PS (50 µm) showed the fastest fat bloom rate, with the smallest PS (18 µm) the least, attributed mainly to hydrodynamic forces by capillary action. It was hypothesised that fat bloom development was initiated by capillarity, followed by growth of recrystallised fat by diffusion across the entire chocolate mass until fully bloomed.

10.2 INTRODUCTION

Fat crystallisation in chocolates is a complex process induced by tempering (pre-crystallisation) during manufacture. The process promotes crystallisation of triacylglycerols (TAGs) in cocoa butter to effect formation of a large number of small crystals of the $\beta$V polymorph (2–3% of the initial fat content) that act as seeds for further crystal growth. The bulk of the TAGs are deposited on the seeds during cooling, forming crystals and eventually an interconnected fat crystal network. The crystal network organisation and the polymorphic state of the TAG crystals as affected by the crystallisation conditions are major factors
determining the microstructure, rheological and textural properties of the crystallised TAG systems (Narine & Marangoni, 1999; Herrera & Hartel, 2000; Toro-Vazquez et al., 2004; Pérez-Martínez et al., 2007), the stability of which depends on the temper regime attained by the crystals during pre-crystallisation.

Cocoa butter, the only fat phase in dark chocolates, is composed mainly of TAGs of the 1,3-disaturated-2-oleoylglycerol-type with three fatty acids accounting for almost 95% of the attachments to the glycerol backbone. These fatty acids and their approximate proportions are oleic acid (C 18:1, 35%), stearic acid (C 18:0, 34%) and palmitic acid (C 16:0, 26%) (Beckett, 2008). Main TAGs in cocoa butter are palmitoyl-oleoyl-palmitoyl (POP), palmitoyl-oleoyl-stearoyl (POS) and stearoyl-oleoyl-stearoyl (SOS), according to the esterification position of fatty acids in the glycerol molecule. Cocoa butter can exist in six polymorphic forms of which the β Forms V and VI are the most stable. Form V predominates in well-tempered chocolate and slowly transforms into Form VI, during prolonged storage of overtempered chocolate with the physical appearance of fat bloom (Lipp & Anklam, 1998; Talbot, 1999; Aguilera et al., 2004; Segall et al., 2005).

Fat bloom in chocolate products is a major quality defect in modern confectionery industry. This physical phenomenon is manifested by the appearance of whitish haze on the surface of chocolates due to recrystallisation of cocoa butter when chocolate is either insufficiently tempered or exposed to high temperatures during storage and/or distribution in supply chain, depriving it from its smooth appearance, bright colour and gloss (Hartel, 1999; Beckett, 2008). Several studies have attributed this to fat migration, mainly induced by insufficient formation of stable polymorphs (Form V) in cocoa butter during tempering, polymorphic crystalline transition from Form V to VI during prolonged storage of products, melting and recrystallisation of low-melting-point crystals without retempering during fluctuating storage temperatures, and in composite structures such as chocolates with nut-based filings, consequently impacting on microstructure, visual appearance and textural properties (Hartel, 1999; Talbot, 1999; Briones & Aguilera, 2005; Lonchampt & Hartel, 2006; Afoakwa et al., 2008e; Beckett, 2008).

Many hypotheses and mechanisms have been published to explain the kinetics of fat migration in different chocolate and confectionery products, most of which have been attributed to diffusion and capillary rise due to the particulate nature of chocolate structure (Ziegleder et al., 1996; Miquel et al., 2001; Ghosh et al., 2002; Aguilera et al., 2004; Quevedo et al., 2005). Ghosh et al. (2002) explained that the driving force for diffusion was assumed to be affected by the difference in liquid fat content, but recently diffusion has been attributed to a gradient in TAG concentration within some domains of the product, with the explanation that differences in TAGs are less likely to occur in chocolate made with a homogeneous liquid phase of cocoa butter but may occur in composite structures. Although the physical changes associated with fat bloom is well known, available information on the mechanism of the crystallisation phenomenon is confusing, and on the actual complex crystal structures that are formed and the rate of bloom development with products from different PSs as occurs in undertempered dark chocolate systems remain unclear.

To enhance understanding of the mechanism of fat bloom development in dark chocolate systems, it is important to evaluate the structure–appearance relationships leading to the formation and development of fat bloom in products during post-processing handling and storage. Thus, the objectives of this work were to investigate changes in microstructure, appearance, texture and melting characteristics during blooming in undertempered dark chocolates varying in PS distribution and to explain the possible mechanism leading to fat bloom development in products.
10.3 MATERIALS AND METHODS

10.3.1 Materials

Cocoa liquor of Central West African origin was obtained from Cargill Cocoa Processing Company (York, UK); sucrose (pure extra-fine granulated) from British Sugar Company (Peterborough, UK); pure prime-pressed cocoa butter and soy lecithin from ADM Cocoa Limited (Koog aan de Zaan, the Netherlands) and Unitechem Company Ltd (Tianjin, China), respectively.

The recipe, formulation and production of samples have been described previously in Chapter 7, Section 7.3.1, but limited only to products containing 35% fat and 0.5% lecithin. Chocolates were formulated with total fat of 35% (w/w) from sucrose, cocoa liquor, cocoa butter and lecithin. Experimental samples (5 kg batch for each formulation) were produced by mixing sucrose (40.8%) and cocoa liquor (53.7%) in a Crypto Peerless mixer (Model K175, Crypto Peerless Ltd, Birmingham, UK) at low speed for 2 minutes and then at high speed for 3 minutes, then refined using a three-roll refiner (Model SDX 600, Buhler Ltd, CH-9240 Uzwil, Switzerland) to a specified PS (D$_{90}$: 18 ± 1 µm, 25 ± 1 µm, 35 ± 1 µm and 50 ± 1 µm) conducting PS analysis, during refining, to ensure D$_{90}$ values. The refined chocolates were melted at 50–55°C for 24 hours and the chocolate mass was conched in a Lipp Conche (Model IMC-E10, Boveristr 40-42, D-68309, Mannhein, Germany) at low speed for 3.5 hours at 60°C. Lecithin (0.5%) and cocoa butter (5%) were added and then conched at high speed for 30 minutes to affect adequate mixing and liquefaction. Samples were kept in sealed plastic containers at ambient temperature (20–22°C), and moisture and fat contents were determined using Karl Fischer and Soxhlet methods (ICA, 1988, 1990).

10.3.2 Determination of particle size distribution

A MasterSizer$^\text{®}$ Laser Diffraction Particle Size Analyzer equipped with MS 15 sample presentation unit (refractive index 1.590) (Malvern Instrument Ltd, Malvern, England) was used. About 0.2 g of refined dark chocolate was dispersed in vegetable oil (refractive index 1.450) at ambient temperature (20 ± 2°C) until an obscuration of 0.2 was obtained. The sample was placed under ultrasonic dispersion for 2 minutes to ensure that particles were independently dispersed and thereafter maintained by stirring during the measurement. Size distribution was quantified as the relative volume of particles in size bands presented as size distribution curves (Malvern MasterSizer$^\text{®}$ Micro Software v 2.19). particle size distribution (PSD) parameters obtained included specific surface area, largest PS (D$_{90}$), mean particle volume (D$_{50}$), smallest PS (D$_{10}$) and Sauter mean diameter (D[3,2]).

10.3.3 Tempering experiment

Samples were incubated at 50°C for 4 hours for melting and tempered using Aasted Mikrovert laboratory continuous three-stage tempering unit (Model AMK 10, Aasted Mikroverk A/S, Farum, Denmark). Chocolate was pumped through the multistage units and a worm screw drove the product through the heat exchangers. Sensors located at specific points in the equipment measured the temperature of both the chocolate and the coolant fluid at each stage. Based on our earlier work on modelling temperature controls to study tempering behaviour (Afoakwa et al., 2008g), the temperature of each of the coolant fluids (Zones 1, 2, 3) were thus set as 26, 24, 32°C, respectively, for attaining the undertempered regime. The
degree of pre-crystallisation was measured using a computerised tempermeter (Exotherm 7400, Systech Analytics, Neuchâtel, Switzerland) and a built-in algorithm provided the tempering curves and temper readings in chocolate temper index (slope), corresponding to undertemper (slope 1.0). The principle of this method has been described by Nelson (1999). Chocolates were moulded using plastic moulds – 80 mm length, 20 mm breadth and 8 mm height – allowed to cool in a refrigerator (12°C) for 2 hours before demoulding onto plastic trays. Bloom was induced by storing the products under ambient condition (18 ± 2°C, relative humidity 50%), and samples evaluated on cooling and after every 24 hours in storage until reaching asymptotic values. Triplicate measurements were conducted and the mean values were recorded.

10.3.4 Texture measurements

Hardness of products was measured using TA-HD Plus Texture Analyzer with a penetration probe (needle P/2) attached to an extension bar and a 50-kg load cell and a platform as reported by Afoakwa et al. (2008e). Maximum penetration forces through a sample (80 × 20 mm, depth 8 mm) were determined with eight replications at a pre-speed of 1.0 mm/second, test of 2.0 mm/second, post-speed of 10.0 mm/second, penetrating 6 mm at 20°C, converting mean values of the penetration force exerted by the 50 kg load cell into hardness (g) using XT.RA Dimension, Exponent 32 software (Stable Micro Systems, Godalming, Surrey, UK) as shown in Figure 7.3(b).

10.3.5 Surface colour and gloss measurements

HunterLab Miniscan™ XE Colorimeter Model 45/0 LAV (Hunter Associates Inc., Reston, VA, USA) calibrated with white ceramic reference standard was used. Colour images of chocolate surfaces were converted into XYZ tristimulus values, which were further converted to CIELAB system: L*, luminance ranging from 0 (black) to 100 (white), and a* (green to red) and b* (blue to yellow) with values from −120 to +120. Mean surface whiteness (L* values) from five replicate measurements and standard deviations were reported.

Gloss of chocolate surface was measured using the multiple angle Tricor Gloss meter (805A/806H Gloss System, Elgin, IL, USA). Reflectance was measured at an incidence light angle of 85° from the normal to the chocolate surface, in accordance with American Society for Testing and Materials (ASTM) method D523. A polished black glass plate with a refractive index of 1.567 was used as standard surface and given a gloss value of 200 (ASTM, 1995). Gloss was reported as gloss units (GU) based on determinations (in triplicate) at six positions along a chocolate sample. As a reference, a surface with a gloss value less than 10 GU is considered a low-gloss surface (BYK, 1997; Briones et al., 2006).

10.3.6 Determination of melting properties

Differential scanning calorimeter (DSC Series 7, Perkin Elmer Pyris, Norwalk, CT, USA) equipped with a thermal analysis data station was calibrated using indium and octadecane at a scan rate of 5°C/minute using an aluminium pan as reference. Samples (~5 mg) were loaded into 40 µL capacity pans with holes, which were sealed with lids using a sample press. Pans were heated at 5°C/minute from 15 to 55°C in an N₂ stream. Onset temperature (T onset), peak temperature (T peak), end temperature (T end) and enthalpy of melting (ΔH_melt) were
calculated automatically by the software. Each sample was analysed in triplicate, and mean values and standard deviations were reported.

10.3.7 Microstructural determinations

Chocolate samples were characterised using stereoscopic binocular microscope (Nikon, SMZ-2T, Tokyo, Japan) equipped with a variable removable lens. Micrographs (coloured images) were captured using a digital camera (Model 2.1 Rev 1, Polaroid Corporation, NY, USA) and observed using Adobe Photoshop (Version CS2, Adobe Systems Inc., NJ, USA). Triplicate experiments were conducted capturing six images per sample, and micrographs representing the surface of samples during storage were captured and presented in JPEG (Joint Photographic Experts Group, a standard for compressing digital photographic images) format of high-resolution and superfine quality. Samples of products containing 50 µm were also sectioned (cut) into two pieces after every 24 hours during blooming using a knife, and the internal microstructures were observed.

10.3.8 Experimental design and statistical analysis

Two experimental variables comprising storage time (on cooling until reaching asymptotic levels) and PSD (D90) 18, 25, 35 and 50 µm were used. Other variables including refiner temperature and pressure, conching time and temperature, were held constant. Statgraphics Plus 4.1 (Graphics Software System, STCC, Inc., Rockville, MD, USA) examined textural properties (hardness) and appearance (L* and gloss) and melting properties (T onset, T end, ΔH melt) using the two-way analysis of variance (ANOVA), and multiple comparison tests to determine effects of factors and their interactions. Tukey multiple comparisons (95% significance level) determined differences between levels. All experiments were conducted in triplicates and the mean values were reported.

10.4 RESULTS AND DISCUSSION

10.4.1 Particle size distribution of dark chocolates

These findings (Fig. 7.1), previously reported in Section 7.4.1, show volume histograms consisting of narrow (18 µm PS) and wide (25 µm PS) bimodal, and narrow (35 µm PS) and wide (50 µm PS) multimodal size distributions. This PSD range, 18–50 µm, using D90 values (>90% finer) covers optimum minimum and maximum sizes with direct effects on texture and sensory character in chocolate manufacture (Ziegler & Hogg, 1999; Beckett, 2008). Data from the PSD as previously described (Afoakwa et al., 2008b) showed variations in specific surface area, mean particle volume D(v,50), Sauter mean (D[3,2]) and mean particle diameter (D[4,3]) with increasing D90 PSs. Specific surface area (SSA) was inversely correlated with the different components of PSD. Similar inverse relationships of specific surface area with all the other components of PSD have been reported (Ziegler & Hogg, 1999). Beckett (1999) concluded that the largest PS and specific surface area of solids are the two key parameters for chocolate manufacture. The former determines chocolate coarseness and textural character, the latter with desirable flow properties. Fat contents of the products were 35 ± 1% and moisture within the range of 0.90–0.98%.
10.4.2 Changes in textural properties during blooming

Changes in texture (hardness) in the undertempered products with varying PS were investigated during storage to provide information on their rate of hardening during bloom development. Hardness showed an inverse relationship with PSs, prior to storage with the 18 µm sample showing the highest hardness (1081.24 g) and the 50 µm sample the least (1008.75 g) (Fig. 10.1), attributed mainly to the relative strengths of the particle-to-particle interactions within the different particulate structures of products containing different PSD (Campos et al., 2002; Do et al., 2007; Afoakwa et al., 2009d). These values revealed that the undertempered products on cooling were very soft, compared to hardness values of 5318.23 and 4259.48 g for 18 and 50 µm PS, respectively, noted for optimally tempered dark chocolates as previously reported (Afoakwa et al., 2008e).

Storage of the products caused consistent and significant \( p < 0.05 \) increases of approximately fourfold in hardness levels within the first 72 hours (Table 10.1), within which period

![Fig. 10.1](image-url) Changes in hardness during blooming of dark chocolates. Reprinted from Afoakwa et al. (2009e), copyright 2009, with permission from Elsevier.

Table 10.1 ANOVA summary of F-values of texture, whiteness, gloss and melting properties

<table>
<thead>
<tr>
<th>Process variables</th>
<th>Hardness</th>
<th>Whiteness ((L^*))</th>
<th>Gloss</th>
<th>(T_{\text{onset}}) ((\degree C))</th>
<th>(T_{\text{end}}) ((\degree C))</th>
<th>(T_{\text{peak}}) ((\degree C))</th>
<th>(\Delta H_{\text{melt}}) ((J/g))</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: Particle size (D_{90})</td>
<td>11.80*</td>
<td>134.78***</td>
<td>51.73***</td>
<td>0.55</td>
<td>11.41***</td>
<td>0.65</td>
<td>10.85**</td>
</tr>
<tr>
<td>B: Storage time</td>
<td>198.49***</td>
<td>2673***</td>
<td>3312.39***</td>
<td>429.73***</td>
<td>1227.66***</td>
<td>707.84***</td>
<td>53.47***</td>
</tr>
<tr>
<td>A × B</td>
<td>3.75*</td>
<td>45.04***</td>
<td>9.54***</td>
<td>0.91</td>
<td>5.72***</td>
<td>0.72</td>
<td>6.59**</td>
</tr>
</tbody>
</table>

Significant F-ratios at *\( p \leq 0.05 \), **\( p \leq 0.01 \) and ***\( p \leq 0.001 \).
over 90% of the textural changes that occurred during the bloom development of the products were noted at all PSs, before attaining asymptotic levels where only gradual increases were noted. Products with the largest PS (50 µm) showed the fastest increase in hardness levels within 72 hours of storage, followed by the 35 µm PS, and then 25 µm PS, with those containing 18 µm PS showing the least increases (Fig. 10.1), an indication that the rate of structural changes during blooming is directly related to the magnitude of product PSs (D90).

However, this hardening trend was reversed between 72 and 96 hours in storage with the 18 µm PS sample attaining the highest hardness values and the 50 µm PS the least after 96 hours, remaining unchanged at the end of the storage period where asymptotic values were noted. The observed textural changes were suspected to be caused by the restructuring and recrystallisation of unstable fat crystals in the undertempered chocolates inducing blooming in products, and thus increasing their hardness levels.

Variations in microstructure regarding the structural arrangements of particles and inter-particle network in products from different PSD accounted for the varying textural changes during bloom development. Previous work on microstructure of molten dark chocolate (Afoakwa et al., 2009d) showed that at higher (35%) fat content, products with larger PS (50 µm) were less flocculated and contained larger pores and crevices between particles filled with fat, relative to those with smaller PS (18 µm), which tended to be more flocculated and aggregated with higher interparticle network interaction. The presence of these larger pores and crevices in products with 50 µm PS was suspected to facilitate movement of recrystallised fat through them onto the surface of the product, suspected to be by capillary action. Aguilera et al. (2004) noted that capillary penetration into pores is a spontaneous process driven by an interfacial pressure gradient, and may occur at two pore scales in chocolates: that of the interparticle channels when the migrating mass is the total fat phase (liquid and crystals) and that of capillaries between the fat crystals for the liquid fat. The flocculated network provided by the higher inter-particle interaction in the 18 µm PS product might have interfered with the migration of recrystallised fat onto the product surface and consequently reducing their rate of bloom development.

10.4.3 Changes in appearance (surface whiteness and gloss) during blooming

Significant (p < 0.001) and linear effects on surface whiteness (L*) were recorded with increasing storage time, noticeable at all PSs (Table 10.1). Prior to storage, whiteness of products varied between 42.26 for 50 µm PS and 45.54 for the 18 µm PS, suggesting that products with smaller PS (18 µm) appear lighter, decreasing consistently with increasing PS. This confirmed previous findings that chocolates with varying PSs differ in structure and particulate arrangements, influencing light scattering coefficients and thus appearance (Afoakwa et al., 2008e). Generally, storage induced blooming in products causing initial rapid increases in whiteness until reaching asymptotic levels after 96 hours, trends observed in all PSs (Fig. 10.2). Increases in whiteness from 45.54 to 82.46 and 42.26 to 87.62 were noted in the 18 and 50 µm PS products, respectively, showing that over 95% of the change in whiteness occurring during blooming of products took place within 96 hours after processing, rendering the products surface whitish in appearance. Similar increases in whiteness in fat bloomed chocolates have been reported (Lonchampt & Hartel, 2004, Altimiras et al., 2007). Hartel (1999) attributed this phenomenon to recrystallisation of fats, causing changes in light scattering and dispersion effects on small surface fat crystals (≥5 µm), consequently impacting on their appearance attributes.
Contrariwise, gloss of products showed significant ($p < 0.001$) and inverse effects, with increasing storage time at all PSs (Table 10.1). Gloss of undertempered dark chocolates prior to storage showed slightly reducing levels as $D_{90}$ increased from 18 to 50 µm with values of 146.6–130.4 GU, respectively, explaining that differences in particulate arrangements in dark chocolate structure influence the final product gloss after tempering.

Storage of the products induced blooming within 24 hours, causing drastic consistent reduction in gloss until 96 hours in storage where decreases in gradient were observed (Fig. 10.3). No noticeable changes in gloss occurred after 96 hours, and this trend was noted in all PSs. The largest PS (50 µm) showed the fastest rate of reduction in gloss within the 96 hours fast blooming period, and the smallest PS (18 µm), the least (Fig. 10.3). Beckett (2008) noted that tempering was important for gloss, a key quality attribute in chocolate. In undertempered chocolates, light scattering is caused by reductions in surface regularity, as gloss relates to capacity of a surface to reflect directed light at the specular reflectance angle with respect to the normal surface plane and any interference on this plane influences gloss levels (ASTM, 1995). ANOVA showed that both PS and storage time significantly ($p = 0.001$) influenced the levels of whiteness and gloss, with significant ($p \leq 0.05$) interactions (Table 10.1), all influencing appearance. Fat bloom development and effects on chocolate appearance, quality and marketability have been extensively studied (Bricknell & Hartel, 1998; Ali et al., 2001; Walter & Cornillon, 2001, 2002; Timms, 2003; Lonchampt & Hartel, 20042006; Altimiras et al., 2007; Afoakwa et al., 2009e).

Multiple comparison tests revealed that products containing the largest PS (50 µm) showed the fastest rate of change on surface appearance with regards to both increased whiteness and reduced gloss, whilst those with smallest PS (18 µm) showed the least. The rate of fat bloom development in undertempered dark chocolate found in this study was fastest in products
containing the largest (50 \( \mu \text{m} \)) PS, which tended to decrease with decreasing PS, with the smallest PS (18 \( \mu \text{m} \)) showing the slowest blooming rate until 96 hours when no further changes in appearance occurred. These suggested that bloom development in undertempered dark chocolates is caused by hydrodynamic forces exerted on the liquid fat content of unstable fat crystals, forcing its movement under capillary action through interparticle passages and connected pores onto the product surface. The relatively larger capillary pores created within the particulate structures of products containing 50 \( \mu \text{m} \) PS facilitated their rate of bloom development, relative to the smaller pores of their respective smaller PS products (Afoakwa et al., 2009d). Beckett (2008) noted that fat bloom may occur due to insufficient formation of stable polymorphs (Form V) in cocoa butter during tempering, leaving a liquid fraction that is propelled to the surface, particularly if the chocolates have cracks and crevices. These findings confirm predictions from capillary theory that higher migration rates would occur through bigger capillaries (at short times), reaching asymptotic levels with long storage periods (Aguilera et al., 2004).

Contrary to these findings, Altimiras et al. (2007) reported that the rate of fat bloom development was fastest in chocolate with smaller PS as compared to those with medium and larger PSs and attributed the effects to Brownian motion. However, Genovese et al. (2007) explained that three kinds of forces coexist to various degrees in flowing dispersions – Brownian, colloidal and hydrodynamic forces – and their relative magnitude of bulk flow depends on the PSs within the products. Brownian motion and interparticle forces equilibrate for subnanometer-size dispersion (1 nm–10 \( \mu \text{m} \)), while hydrodynamic forces dominate in particles between 10 and 100 \( \mu \text{m} \), such as chocolate, sauces and fruit purees. For such particles as in chocolate, Brownian motion and interparticle forces are negligible compared to hydrodynamic forces, thus defeating Brownian motion as the resultant force during structural–fat migration relationships in chocolates. Lonchampt and Hartel (2006) reported that fat was almost...
non-existence in untempered (bloomed) chocolate, possessing melting enthalpy ($\Delta H_{\text{fat}}$) being about tenfold smaller than that obtained for optimally tempered chocolate, concluding that the whitish spots in improperly tempered (bloomed) chocolates were mainly composed of sugar crystals and cocoa powder, and nearly devoid of fat. Kinta and Hatta (2005) also reported that the presence of fat components in untempered (bloomed) dark chocolate is minimal and suggested that the mechanism of bloom development in bloomed chocolate involves phase separation associated with the growth of xenomorphic fat crystals. These reported structural changes in components in bloomed chocolate require further studies into their microstructure to clarify the changes during bloom formation, blooming rates and their associated mechanisms.

Multivariate regression and correlation analyses were conducted between changes in texture, surface whiteness and gloss to help establish the structural–appearance relationships during blooming of undertempered dark chocolates. The output showed the results of fitting linear models to describe the relationship between surface whiteness and hardness, and gloss and hardness during blooming are as follows:

\[
\text{Whiteness} = 38.9304 + 0.0104 \times \text{Hardness} \quad (10.1)
\]
\[
\text{Gloss} = 166.534 - 0.0342 \times \text{Hardness} \quad (10.2)
\]

Good fit of the models was confirmed graphically by scatter plots, in which high regression coefficient of determination, $R^2 = 94.0\%$ ($p = 0.001$), for whiteness and hardness with very high correlation coefficient, $R = 0.96$ ($p = 0.001$), and also $R^2 = 92.5\%$ ($p = 0.001$) for gloss and hardness with very high correlation coefficient, $R = -0.97$ ($p = 0.001$), were found between the predicted and experimental values (Fig. 10.4). These explained that during bloom development in undertempered dark chocolates, changes in textural properties (hardness) could be used to predict the rate of change in surface whiteness and gloss reduction (blooming) in products. These developments are important in bringing greater understanding on structure–appearance relationships during blooming of dark chocolates and would be useful for further studies on the prevention of fat bloom in chocolates.

### 10.4.4 Changes in melting behaviour during blooming

Typical DSC thermograms used for characterising the melting properties of the undertempered dark chocolates during blooming are as shown in Figure 10.5. All the samples exhibited similar distinct single endothermic transitions between 15 and 55°C, the range expected for chocolate melting profiles. Data from the DSC on $T_{\text{onset}}$, $T_{\text{end}}$, $T_{\text{peak}}$ and $\Delta H_{\text{melt}}$ in relation to storage time and PSD (Table 10.2) analysed by ANOVA and multiple comparison tests showed highly significant differences ($p < 0.001$) of $T_{\text{onset}}$, $T_{\text{peak}}$, $T_{\text{end}}$ and $\Delta H_{\text{melt}}$ for differing storage time (Table 10.2). The differences in storage time yielded mean $T_{\text{end}}$ values of approximately 28.7, 32.4, 33.0, 35.3 and 35.7°C, respectively, after 0, 24, 48, 72 and 96 hours in storage. These observations suggest that bloom development in undertempered chocolate significantly influences their melting temperatures as a result of polymorphic transformations of fat crystals within the products. The changing $T_{\text{end}}$ values of the samples revealed that the crystallites in the undertempered products were in $\beta\text{IV}$ polymorph ($\sim 28.7^\circ\text{C}$) on cooling, and transformed to $\beta\text{V}$ ($\sim 32.4^\circ\text{C}$) within 24 hours in storage, with further transformation to the more stable $\beta\text{VI}$ polymorph ($\sim 35.5^\circ\text{C}$) after 72 hours in storage, stabilising at that polymorphic status until fully bloomed. This finding is very significant as it reveals that
undertempered dark chocolate undergoes a three-stage ($\beta'$, $\beta_2$ and $\beta_1$) polymorphic transformation within 72 hours after processing, during which period fat bloom occurs (Fig. 10.5). PS distribution in products however played significant role as products containing 25, 35 and 50 µm reached Form VI polymorphic status after 72 hours, those with the smallest PS (18 µm) attained Form VI status after 96 hours (Table 10.2) influencing $T_{\text{end}}$ and $\Delta H_{\text{melt}}$ of products during blooming. Similarly, the blooming process influenced the melting enthalpies ($\Delta H_{\text{melt}}$) during storage (Table 10.2), with significant ($p < 0.05$) interactions with PS (Table 10.1).

Multiple comparison tests showed that $\Delta H_{\text{melt}}$ of products measured soon after tempering was relatively lower, and increased with increasing storage time, attributable to the relative strengths of the recrystallised fat network formed during blooming of products, thereby requiring higher enthalpies for melting.

10.4.5 Changes in microstructure during blooming

Microstructural examination using stereoscopic binocular microscopy captured soon after cooling showed similarity in structure on the surface image of products with varying PS (Fig. 10.6). Storage of the products induced bloom development within 24 hours with the
Fig. 10.5  Typical DSC thermograms showing changes in fat melting profile during blooming of dark chocolates with 25 µm PS. Reprinted from Afoakwa et al. (2009e), copyright 2009, with permission from Elsevier.

Table 10.2  Changes in melting properties during storage

<table>
<thead>
<tr>
<th>Storage time (hour)</th>
<th>Particle size (D90) (µm)</th>
<th>T(_{\text{onset}}) (°C)</th>
<th>T(_{\text{end}}) (°C)</th>
<th>T(_{\text{peak}}) (°C)</th>
<th>(\Delta H_{\text{melt}}) (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>18</td>
<td>22.8 ± 0.3</td>
<td>28.9 ± 0.3</td>
<td>27.2 ± 0.2</td>
<td>35.66 ± 0.42</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>22.9 ± 0.3</td>
<td>28.7 ± 0.2</td>
<td>27.4 ± 0.1</td>
<td>34.74 ± 0.39</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>22.9 ± 0.4</td>
<td>28.6 ± 0.2</td>
<td>27.6 ± 0.2</td>
<td>34.56 ± 0.25</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>22.8 ± 0.4</td>
<td>28.6 ± 0.4</td>
<td>27.4 ± 0.2</td>
<td>34.72 ± 0.63</td>
</tr>
<tr>
<td>24</td>
<td>18</td>
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<td>36.3 ± 0.3</td>
<td>33.7 ± 0.1</td>
<td>41.82 ± 0.75</td>
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</table>

Means ± standard deviation from triplicate analysis.
Fig. 10.6  Micrographs showing changes in surface appearance of dark chocolate with (i) 18, (ii) 25, (iii) 35 and (iv) 50 \( \mu \)m after (a) on cooling (0 hour), (b) 24 hours, (c) 48 hours, (d) 72 hours and (e) 96 hours in storage, showing liquid fat (lf), recrystallised fat (rcf) and cocoa solids (cs). Reprinted from Afoakwa et al. (2009e), copyright 2009, with permission from Elsevier.
Fig. 10.6 (Continued)
release and appearance of a colourless fluid and small spots of whitish haze suspected to be liquid and recrystallised fat, respectively, onto the product surfaces. These were more obvious on products containing 50 $\mu$m, with the 35, 25 and 18 $\mu$m showing only little apparent surface changes (Fig. 10.6(b)). Bomba (1993) and Beckett (2008) stated that liquid fat originated from less stable crystals with lower melting points is likely to melt at fairly modest temperatures during chocolate blooming and is separated from the crystal structure migrating to the product surfaces. After 48 hours in storage, blooming was physically induced in all products with the appearance of whitish crystal structures on their surfaces, growing across high–low concentration gradients with storage time and eventually spreading throughout the product surface until 96 hours where no further changes on surface appearances were noticeable in all products, hence the conclusion that the products were fully bloomed. Microscopic images captured after 120–168 hours in storage on products were not shown as they were similar to those presented for 96 hours (Fig. 10.6).

The micrographs showed that the fastest rate of bloom was noticeable in samples containing 50 $\mu$m PS, followed by the 35 and 25 $\mu$m PS, with those with 18 $\mu$m PS showing the least rate of bloom development, confirming the reported relative rates of changes in texture, whiteness and gloss during storage (Figs 10.1–10.3). The relatively larger capillary pores created within the particulate structures of products containing 50 $\mu$m PS were suspected to be the key factor, facilitating their rate of bloom development, relative to the smaller pores with decreasing PS in products. These differences were attributed to the variations in amounts of hydrodynamic forces exerted on the liquid fat content of the unstable fat crystals in the undertempered chocolate, forcing them to move under capillary action through the interparticle passages and connected pores onto the product surface. The unstable fat portion then recrystallised during storage into more stable polymorphs initiating the physical appearance of bloom (whitish haze) in products and crystal growth was promoted by Ostwald ripening (recrystallisation and redistribution of larger crystals growing at the expense of smaller ones). Microstructures showing the internal periphery of the 50 $\mu$m samples revealed that during bloom development crystal growth was noted to be facilitated by mass movement of recrystallised fat through high–low concentration gradient by diffusion as the recrystallised fat redistributes itself across the entire chocolate mass during storage. The surface and internal periphery of the fully bloomed products showed whitish crystals which appear to be mixtures of fat and sugar components of the product, and distinct smaller brown spots made up of cocoa solids (Figs 10.6 and 10.7).

**10.5 CONCLUSION**

The rate of bloom development in undertempered dark chocolate was dependent on solids, PS distribution and storage time. Hardness and surface whiteness showed initial rapid increases with parallel reductions in gloss in the first 96 hours, with subsequent decreases in rate until asymptotic values were reached. Blooming was initiated in products within 24 hours and essentially complete by 96 hours. Changes during blooming were attributed primarily to growth of new fat crystals within the structural network with changes in light reflections, yielding increases in surface whiteness and in hardness. From differential scanning calorimetry on melting properties values for $T_{\text{onset}}$, $T_{\text{end}}$, $T_{\text{peak}}$ and $\Delta H_{\text{melt}}$ suggested polymorphic transformation from $\beta$IV to $\beta$V within 24 hours and further to $\beta$VI after 72 hours. Micrographs showed similar crystal network structure and interparticle interactions in chocolates of
Fig. 10.7  Micrographs showing changes in internal appearance of dark chocolate with 50 μm PS after (i) 0 hour, (ii) 24 hours, (iii) 48 hours, (iv) 72 hours and (v) 96 hours in storage, showing liquid fat (lf), recrystallised fat (rcf), growing recrystallised fat (grcf) and cocoa solids. Reprinted from Afoakwa et al. (2009e), copyright 2009, with permission from Elsevier.
different PS immediately after tempering. Within 24 hours, liquid and unstable recrystallised fat had appeared on surfaces with initiation of bloom. Unstable fat recrystallised during storage into more stable polymorphs and crystal growth was promoted by Ostwald ripening, with the appearance of white crystalline structure that had spread gradually throughout entire chocolate masses after 96 hours. Chocolate of largest PS (50 µm) showed most rapid fat bloom, smallest PS (18 µm) slowest, attributed mainly to hydrodynamic forces of capillary action. It was concluded that bloom development was initiated by movement of liquid and unstable fat onto product surfaces through capillarity created by hydrodynamic forces within the interparticle pores and crevices, followed by growth of new fat crystals promoted by diffusion gradients across the mass until chocolate was fully bloomed. Understanding fat bloom formation and development in dark chocolate has potential applications in new product development.
11 Matrix effects on flavour volatiles character and release in chocolates

11.1 SUMMARY AND INDUSTRIAL RELEVANCE

Influences of matrix particle size distribution (PSD) (18, 25, 35, 50 µm) and fat content (25, 30, 35%) on flavour release of dark chocolate volatiles were quantified by static headspace gas chromatography using gas chromatography–mass spectrometry (GC-MS). Sixty-eight flavour compounds were identified comprising alcohols, aldehydes, esters, ketones, furans, pyrans, pyrazines, pyridines, pyrroles, phenols, pyrones and thiozoles. From gas chromatography–olfactometry (GC-O) 2-methylpropanal, 2-methylbutanal and 3-methylbutanal had chocolate notes. With cocoa/roasted/nutty notes were trimethyl-, tetramethyl-, 2,3-dimethyl-, 2,5-dimethyl-, 3(or 2),5-dimethyl-2(or 3)-ethyl- and 3,5(or 6)-diethyl-2-methylpyrazine and furfuryl pyrrole. Compounds with fruity/floral notes included 3,7-dimethyl-1,6-octadien-3-ol, 5-ethenyltetrahydro-\( R.R \),5-trimethyl-cis-2-furanmethanol. Caramel-like, sweet and honey notes were conferred by 2-phenylethanol, phenylacetaldehyde, 2-phenylethylacetate, 2,3,5-trimethyl-6-ethylpyrazine, 2-carboxaldehyde-1\( H \)-pyrrole, furancarboxaldehyde, furfuryl alcohol and 2,5-dimethyl-4-hydroxy-3(2\( H \))-furanone. There were direct relationships between fat content and 3-methylbutanal and branched pyrazines but inverse with 2-phenylethanol, furfuryl alcohol, methylpyrazine, phenylacetaldehyde, 2,3,5-trimethyl-6-ethylpyrazine and 2-carboxaldehyde-1\( H \)-pyrrole. Particle size influenced higher alcohols, aldehydes, esters, ketones and pyrazines concentrations at all fat contents. A multivariate product space suggested flavour effects of the interacting factors. This knowledge on how variations in PSD and continuous phase fat content affects flavour character and their release would be useful for product development during industrial chocolate manufacture.

11.2 INTRODUCTION

Flavour is central to acceptability in chocolate and is influenced not only by volatile aroma compounds but also by non-volatiles and behaviour of the continuous fat phase, influencing release of volatiles into the mouth headspace and taste perception. Precursor composition depends on bean genotype and environmental effects particularly on contents of storage proteins and polyphenols (Kim & Keeney, 1984; Schwan & Wheals, 2004). Cocoa beans are rich in antioxidants – including catechins, epicatechin and procyanidins – polyphenols similar to those found in wine and tea (Carnesecchia et al., 2002; Hatano et al., 2002; Grassi et al., 2005; Lamuela-Raventos et al., 2005; Hermann et al., 2006). Chocolate manufacture involves complex physical and chemical processes, determining rheological characteristics, flavour development, melting properties and ultimately sensory perceptions of character.
Chocolate Science and Technology (Ziegler & Hogg, 1999; Ziegler et al., 2001; Afoakwa et al., 2007, 2008b; Do et al., 2007). There are a number of studies of precursors for flavour formation in cocoa and chocolate (Misnawi et al., 2003; Counet et al., 2004; Kyi et al., 2005).

An appropriate cocoa bean composition can be converted through controlled post-harvest treatments and subsequent processing technologies to a high-quality chocolate flavour character (Clapperton, 1994). Fermentation is crucial to not only the formation of key volatile fractions (alcohols, esters and fatty acids) but also provision of Maillard flavour precursors (amino acids and reducing sugars) (Buyukpamukcu et al., 2001; Luna et al., 2002; Kyi et al., 2005). Drying reduces levels of acidity and astringency in cocoa nibs, decreasing volatile acids and total polyphenols. Maillard reactions during roasting convert these flavour precursors into two main classes of flavour-active component – pyrazines and aldehydes (Gill et al., 1984; Oberparlaiter & Ziegleder, 1997; Dimick & Hoskin, 1999; Stark et al., 2005; Granvogl et al., 2006; Ramli et al., 2006). Flavour development continues during conching following the elimination of volatile acids, and moisture with associated viscosity changes due to emulsification and tannin oxidation (Mermet et al., 1992; Plumas et al., 1996; Reineccius, 2006). Afoakwa et al. (2008a) reviewed relationships between initial composition and post-harvest treatments of cocoa beans and subsequent processing (roasting and conching) and technological effects on final flavour character in chocolate.

PSD influences dark chocolate structure – specifically interparticle interactions and network microstructure, rheology and texture – with specific surface area and mean particle size influencing yield stress, plastic viscosity, product spread and hardness (Chevalley, 1999; Beckett, 2008; Afoakwa et al., 2008a, 2008b, 2008c, 2009d). Genovese et al. (2007) suggested that non-hydrodynamic parameters such as particle shape, particle size and size distribution, particle deformability and liquid polarity influence food structure and flow behaviours. Such factors dictate the space dimension of a suspension, whether strongly or weakly flocculated, with influence on yield stress and plastic viscosity. Although key flavour compounds of milk and dark chocolates have been reported (Cerny & Fay, 1995; Schnerrmann & Schieberle, 1997; Schieberle & Pfner, 1999; Counet et al., 2002; Taylor, 2002; Taylor & Roberts, 2004; Reineccius, 2006), their abundancy, release and contribution to product character and matrix effects remain unclear.

Modern healthier foods – less fat and low sugar products – require modifications in ingredients and recipe formulation, with impacts on flavour release and product rheology, structure and texture. Knowledge of how variations in PSD and continuous phase fat content influence flavour would be useful for product development and manufacture. The objectives of this study were to characterise and quantify volatile flavour constituents in dark chocolates, and to evaluate matrix effects from varying PSD and fat content on release of flavour volatiles using headspace high-resolution gas chromatography (HRGC), identifying components with GC-MS and flavour notes by GC-O.

11.3 MATERIALS AND METHODS

11.3.1 Materials

Cocoa liquor of Central West African origin was obtained from Cargill Cocoa Processing Company (York, UK); sucrose (pure extra-fine) from British Sugar Company (Peterborough, UK); pure prime-pressed cocoa butter and soy lecithin from ADM Cocoa Limited (Koog aan de Zaan, the Netherlands) and Unitechem Company Ltd (Tianjin, China), respectively.
Matrix effects on flavour volatiles character and release in chocolates

Table 11.1 Recipes used for the formulation of the dark chocolate

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>25% fat (% w/w)</th>
<th>30% fat (% w/w)</th>
<th>35% fat (% w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sucrose (%)</td>
<td>59.0</td>
<td>49.9</td>
<td>40.8</td>
</tr>
<tr>
<td>Cocoa liquor (%)</td>
<td>35.5</td>
<td>44.6</td>
<td>53.7</td>
</tr>
<tr>
<td>Cocoa butter (%)</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Lecithin (%)</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Recipe (Table 11.1) and sample formulations have been described previously (Afoakwa et al., 2008b). Chocolates were formulated with total fat of 25–35% (w/w) from cocoa liquor and cocoa butter with more than 34% total cocoa, composition as specified for dark chocolate (European Commission Directive, 2000; Codex Revised Standard, 2003). Sucrose and cocoa liquor (5 kg per formulation) were mixed in a Crypto Peerless mixer (Model K175, Crypto Peerless Ltd, Birmingham, UK) at low speed for 2 minutes and then at high for 3 minutes, then refined using a three-roll refiner (Model SDX 600, Buhler Ltd, CH-9240 Uzwil, Switzerland) to a specified particle size (D₉₀: 18 ± 1 µm, 25 ± 1 µm, 35 ± 1 µm and 50 ± 1 µm) conducting particle size analysis, during refining, to ensure D₉₀ values. Refined chocolate flakes were placed in plastic containers and conditioned at 50–55°C for 24 hours to ensure melting of fat prior to conching in a Lipp Conche (Model IMC-E10, Boveristr 40-42, D-68309, Mannhein, Germany) at low speed for 3.5 hours at 60°C.

Lecithin and cocoa butter were added and mixtures were conched at high speed for 30 minutes to effect adequate mixing and liquefaction. Samples were stored in sealed plastic containers at ambient temperature (20–22°C) and moisture, and fat contents were determined using Karl Fischer and Soxhlet methods (ICA, 1988, 1990), respectively.

11.3.2 Tempering procedure

Samples were melted at 50°C for 4 hours and tempered using a continuous three-stage tempering unit (Model AMK 10, Aasted Mikroverk A/S, Farum, Denmark) pumping chocolate through multistage units, with a worm screw driving product through heat exchangers. Sensors in equipment measured temperature of both chocolate and coolant fluid at each stage. Based on our previous work on modelling temperature controls to study tempering behaviour (Afoakwa et al., 2008g), the temperature of each of the coolant fluids was thus set and controlled independently to obtain a final chocolate at approximately 27°C to promote crystal growth of the desired triacylglyceride fractions. Pre-crystallisation was measured using a computerised tempermeter (Exotherm 7400, Systech Analytics, SA, Switzerland) using a built-in algorithm to ensure an optimal temper regime of slope 0 ± 0.3 (Nelson, 1999). Tempered chocolate was formed using plastic moulds, 80-by-20-by-8 mm, allowed to cool at 12°C for 2 hours before demoulding onto plastic trays and conditioned at 20 ± 2°C for 14 days before analysis.

11.3.3 Determination of particle size distribution

A MasterSizer® Laser Diffraction Particle Size Analyzer equipped with MS 15 sample presentation unit (refractive index 1.590) (Malvern Instrument Ltd, Malvern, England) was used. About 0.2 g of refined dark chocolate was dispersed in vegetable oil (refractive index 1.450) at ambient temperature (20 ± 2°C) until an obscuration of 0.2 was obtained. Samples
were placed under ultrasonic dispersion for 2 minutes to ensure particles were independently dispersed and suspensions thereafter were maintained by stirring. Size distribution was quantified as the relative volume of particles in size bands presented as size distribution curves (Malvern MasterSizer® Micro Software v 2.19). PSD parameters obtained included specific surface area, the largest particle size (D90), mean particle volume (D50), the smallest particle size (D10) and Sauter mean diameter (D[3,2]).

11.3.4 Quantification of flavour volatiles by gas chromatography

Static headspace isolation of volatile compounds was performed using solid phase micro extraction (SPME) for 30 minutes at 55°C onto a polydimethylsiloxane-divinylbenzene, 65 µm fibre (Supelco, Bellafonte, PA, USA). Chocolate (~4 g) was previously heated to 55°C and intermittently stirred for 60 minutes for headspace equilibration. Each experiment had a system control sample, made by stirring an empty vial under the same conditions. Volatile compounds were desorbed (5 minutes) into the splitless injector (220°C) of Agilent Technologies 6890N-5793 Network GC-MS system (Agilent Technologies, Santa Clara, CA, USA) and separated on a J&W 60 m DB-Wax capillary column (0.22 mm inner diameter and 0.25 µm film thickness). The temperature program was 5 minutes at 40°C, 3°C/minute to 230°C, finally 15 minutes at 230°C. Compounds were fragmented using electron-impact ionisation (70 eV), with a source temperature of 200°C, a scan range of 30–300 amu and a scan rate of 5 s⁻¹. Components were identified based on comparison of mass spectra with those of spectral libraries NIST 05 and Wiley 7N Registry of GC Mass Spectral Data (John Wiley, NY, USA).

11.3.5 Gas chromatography–olfactometry analytical conditions

The GC-O analyses were conducted using Agilent Technologies (6890N Network Systems, CA, USA) with analyses as before, diverting the effluent to a humidified sniffing port. Two chromatographic runs were assessed by two trained assessors (alternating for 20 minutes periods). Only matching descriptors for an aroma attribute were retained.

11.3.6 Experimental design and statistical analysis

Two experimental variables comprising PSD and fat contents were used with other variables including refiner temperature and pressure, conching time and temperature held constant. A 4×3-factorial experimental design was used with PSD (D90) 18, 25, 35 and 50 µm; fat 25, 30 and 35% (w/w). Statgraphics Plus 4.1 (Graphics Software System, STCC, Inc., Rockville, USA) examined quantitative data using the two-way analysis of variance (ANOVA) and multiple range tests to determine effects of factors and interactions. Multivariate techniques comprising PCA and multiple regression analysis were used to evaluate relationships between selected flavour volatiles obtained by quantification of GC-MS data and influential factors. Tukey multiple comparisons at 95% significance level were conducted to determine differences between factor levels. All process treatments and analysis were conducted in duplicates and the mean values were reported.
11.4 RESULTS AND DISCUSSION

11.4.1 Particle size distribution of dark chocolates

PSDs (Fig. 7.1), previously reported, show volume histograms consisting of narrow (18 µm PS) and wide (25 µm PS) bimodal, and narrow (35 µm PS) and wide (50 µm PS) multimodal size distributions. This PSD range, 18–50 µm, using D₉₀ values (>90% finer) covers optimum minimum and maximum sizes with direct effects on texture and sensory character in manufacture (Ziegler & Hogg, 1999; Beckett, 2008). Data from PSD showed variations in specific surface area, mean particle volume D(v,50), Sauter mean (D[3,2]) and mean particle diameter (D[4,3]) with increasing D₉₀ particle sizes. Beckett (2009) concluded that the largest particle size and specific surface area of solids were two key parameters in manufacture. The former determines chocolate coarseness and textural character; the latter, desirable flow properties. Specific surface area was inversely correlated with the different component of PSD (Ziegler & Hogg, 1999; Sokmen & Gunes, 2006; Beckett, 2009). Fat contents were 25, 30 and 35 ± 1% (each) and moisture in the range 0.90–0.98%.

11.4.2 Characterisation of flavour compounds in dark chocolates

Criteria for selection of the key volatiles were (presence in headspaces at >10⁶ abundant units) quantified by GC-MS and also detection and intensities by the GC-O techniques. In all, 68 flavour compounds (Table 11.2) comprising nitrogen and oxygen heterocycles, aldehydes and ketones, esters, alcohols, hydrocarbons, nitriles and sulphides were identified by GC-MS in dark chocolates. A typical chromatogram is as shown in Figure 11.1.

Compounds quantified included 1-pentanol (1), 3-(methylthiol)-propionaldehyde (12), methylbenzene (38), methlypyrazine (41), ethenylpyrazine (47), pyridine (55), 2-methylpyridine (56), 1-(2-furanylmethyl)-1H-pyrrole (62), 1H-indole (63) and dimethyl disulphide (67) (Table 11.2). Two others, benzyl alcohol (5) and dihydro-2-methyl-3(2H)-furanone (30), were only reported in dark chocolates (Counet et al., 2002).

Specific nitrogen heterocycles from Maillard reactions included 3(or 2),5-dimethyl-2(or 3)-ethylpyrazine (50), 3,5-(or 6)-diethyl-2-methylpyrazine (53), 2,3-dimethyl-1H-pyrrole (59), 3-ethyl-2,5-dimethyl-1H-pyrrole (61) and 10(2-furanylmethyl)-1H-pyrrole (furfurylpyrrole) (62) (Table 11.2). All had cocoa, praline, chocolate and roasted notes identified as important. The ethyl group in two pyrazine compounds suggests key roles for alanine and/or its Strecker aldehyde, acetaldehyde, in dark chocolate flavour (Cerny & Fay, 1995).

Flavour-active compounds identified as having strong chocolate characters included 2-methylpropanal (8), 2-methylbutanal (9) and 3-methylbutanal (10). Compounds derived from Maillard reactions were 2,3-dimethylpyrazine (45), 2,5-dimethylpyrazine (42), 2,6-dimethylpyrazine (43), trimethylpyrazine (47), tetramethylpyrazine (51), 3(or 2),5-dimethyl-2(or 3)-ethylpyrazine (50), 3,5(or 6)-diethyl-2-methylpyrazine (53) and furfurylpyrrole (60) exhibiting cocoa/roasted/nutty/cooked notes. Counet et al. (2002) identified such flavour volatiles in dark chocolates after conching, suggesting these are formed during cocoa processing.

Volatile such as 2-phenylethanol (7), phenylacetaldehyde (15) and 2-phenylethylacetate (22), 2,3,5-trimethyl-6-ethylpyrazine (54), 2-carboxaldehyde-1H-pyrrole (60) were characterised by sweet, candy and honey flavours. Furancarboxaldehyde (furural) (31), furfuryl alcohol (furfural) (32), 2,5-dimethyl-4-hydroxy-3(2H)-furanone (Furaneol) (35) were also...
Table 11.2: Key flavour volatiles identified in dark chocolate

<table>
<thead>
<tr>
<th>No.</th>
<th>Flavour compound</th>
<th>Odour descriptiona</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1-Pentanol</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2,4-Hexadien-1-ol</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3-Methyl pentanol</td>
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</tr>
<tr>
<td>4</td>
<td>2-Heptanol</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Benzyl alcohol</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>3,7-Dimethyl-1,6-octadien-3-ol (linalool)</td>
<td>Flowery, floral, fruity (low)</td>
</tr>
<tr>
<td>7</td>
<td>2-Phenylethanol</td>
<td>Caramel-like, sweet, honey</td>
</tr>
<tr>
<td>8</td>
<td>2-Methylpropanal (isobutanal)</td>
<td>Chocolate</td>
</tr>
<tr>
<td>9</td>
<td>2-Methylbutanal</td>
<td>Chocolate</td>
</tr>
<tr>
<td>10</td>
<td>3-Methylbutanal</td>
<td>Chocolate</td>
</tr>
<tr>
<td>11</td>
<td>2-Methyl-2-butenal</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>3-(Methylthio)propionaldehyde (methional)</td>
<td>Potato</td>
</tr>
<tr>
<td>13</td>
<td>Heptanal</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>Benzaldehyde</td>
<td>Nutty</td>
</tr>
<tr>
<td>15</td>
<td>Phenylacetaldehyde</td>
<td>Flowery, sweet, honey</td>
</tr>
<tr>
<td>16</td>
<td>Nonanal</td>
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<tr>
<td>17</td>
<td>2-Phenyl-2-butenal</td>
<td>Cocoa, roasted</td>
</tr>
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<td>2-Phenyl-5-methyl-2-hexenal</td>
<td>Roasted</td>
</tr>
<tr>
<td>19</td>
<td>Ethyl benzoyleformate</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>Ethyl benzoate</td>
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</tr>
<tr>
<td>21</td>
<td>Ethyl octanoate</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>2-Phenylethylacetate</td>
<td>Honey, sweet</td>
</tr>
<tr>
<td>23</td>
<td>Ethyl cinnamate</td>
<td>Fruity, floral (low)</td>
</tr>
<tr>
<td>24</td>
<td>Acetate (acetic acid)</td>
<td>Astringent, vinegar</td>
</tr>
<tr>
<td>25</td>
<td>2,3-Butanedione (diacetyl)</td>
<td>Buttery (low)</td>
</tr>
<tr>
<td>26</td>
<td>2-Heptanone</td>
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</tr>
<tr>
<td>27</td>
<td>4-Methylcyclohexanone</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>3-Hydroxy-2-butanone</td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>3,4,4-Trimethyl-2-cyclopenten-1-one</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>Dihydro-2-methyl-3(2H)-furanone</td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>Furancarboxaldehyde (furfural)</td>
<td>Caramel-like, sweet</td>
</tr>
<tr>
<td>32</td>
<td>Furfuryl alcohol (furfurol)</td>
<td>Caramel-like, sweet</td>
</tr>
<tr>
<td>33</td>
<td>1-(2-Furanyl)ethanone (acetylfuran)</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>5-Methyl-2-furancarboxaldehyde</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>2,5-Dimethyl-4-hydroxy-3(2H)furanone (Furaneol)</td>
<td>Caramel-like, sweet</td>
</tr>
<tr>
<td>36</td>
<td>5-Ethenyltetrahydro-R,R,5-trimethyl-cis-2-furanmethanol (linalool oxide)</td>
<td>Fruity, floral/flowery (low)</td>
</tr>
<tr>
<td>37</td>
<td>3-Phenylfuran</td>
<td>Cocoa, green, nutty</td>
</tr>
<tr>
<td>38</td>
<td>Methylbenzene (toluene)</td>
<td></td>
</tr>
<tr>
<td>39</td>
<td>Benzonitrile</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>3,4-Dihydro-8-hydroxy-3-methyl-1H-2-benzopyran-1-one</td>
<td></td>
</tr>
</tbody>
</table>
Table 11.2 (Continued)

<table>
<thead>
<tr>
<th>No.</th>
<th>Flavour compound</th>
<th>Odour descriptiona</th>
</tr>
</thead>
<tbody>
<tr>
<td>41</td>
<td>Methylpyrazine</td>
<td>Nutty, green</td>
</tr>
<tr>
<td>42</td>
<td>2,5-Dimethylpyrazine</td>
<td>Roasted, cooked</td>
</tr>
<tr>
<td>43</td>
<td>2,6-Dimethylpyrazine</td>
<td>Roasted, cooked</td>
</tr>
<tr>
<td>44</td>
<td>Ethylpyrazine</td>
<td>Nutty, roasted</td>
</tr>
<tr>
<td>45</td>
<td>2,3-Dimethylpyrazine</td>
<td>Cooked, nutty</td>
</tr>
<tr>
<td>46</td>
<td>2-Ethyl-5(or 6)-methylpyrazine</td>
<td>Cocoa, roasted, green</td>
</tr>
<tr>
<td>47</td>
<td>Trimethylpyrazine</td>
<td>Cocoa, roasted, cooked</td>
</tr>
<tr>
<td>48</td>
<td>2-Ethyl-3-methylpyrazine</td>
<td>Hazelnut, roasted</td>
</tr>
<tr>
<td>49</td>
<td>2-Ethenyl-6-methylpyrazine</td>
<td>Roasted, smoky</td>
</tr>
<tr>
<td>50</td>
<td>3(or 2),5-Dimethyl-2(or 3)-ethylpyrazine</td>
<td>Milk coffee, roasted</td>
</tr>
<tr>
<td>51</td>
<td>Tetramethylpyrazine</td>
<td></td>
</tr>
<tr>
<td>52</td>
<td>2,3-Dimethyl-5-ethylpyrazine</td>
<td>Cocoa, chocolate</td>
</tr>
<tr>
<td>53</td>
<td>3,5(or 6)-Dimethyl-2-ethylpyrazine</td>
<td>Cocoa, praline, chocolate</td>
</tr>
<tr>
<td>54</td>
<td>2,3,5-Trimethyl-6-ethylpyrazine</td>
<td>Candy, sweet</td>
</tr>
<tr>
<td>55</td>
<td>Pyridine</td>
<td></td>
</tr>
<tr>
<td>56</td>
<td>2-Methylpyridine</td>
<td>Caramel-like, sweet</td>
</tr>
<tr>
<td>57</td>
<td>2-Pyrinidamine</td>
<td></td>
</tr>
<tr>
<td>58</td>
<td>1-(2-Pyrinidyl)-1-propanone</td>
<td></td>
</tr>
<tr>
<td>59</td>
<td>2,3-Dimethyl-1H-pyrrole</td>
<td>Cocoa, praline, chocolate</td>
</tr>
<tr>
<td>60</td>
<td>2-Carboxaldehyde-1H-pyrrole</td>
<td>Honey, candy (low)</td>
</tr>
<tr>
<td>61</td>
<td>3-Ethyl-2,5-dimethyl-1H-pyrrole</td>
<td>Cocoa, coffee</td>
</tr>
<tr>
<td>62</td>
<td>1-(2-Furanylmethyl)-1H-pyrrole (furfurylpyrrole)</td>
<td>Cocoa, roasted (low)</td>
</tr>
<tr>
<td>63</td>
<td>1H-indole</td>
<td>Chocolate, green (low)</td>
</tr>
<tr>
<td>64</td>
<td>Phenol</td>
<td></td>
</tr>
<tr>
<td>65</td>
<td>4-Methylphenol</td>
<td></td>
</tr>
<tr>
<td>66</td>
<td>3-Hydroxy-2-methyl-4-pyrone (maltol)</td>
<td></td>
</tr>
<tr>
<td>67</td>
<td>Dimethyl disulphide</td>
<td>Meaty (low)</td>
</tr>
<tr>
<td>68</td>
<td>4,5-Dihydro-2-methylthiazole</td>
<td></td>
</tr>
</tbody>
</table>

*Odour quality and intensity at GC-O outlet.

characterised by *caramel-like, sweet* and *honey* notes likely derivatives of Strecker degradation and caramelisation reactions developed during cocoa processing and transformed during chocolate flavour synthesis in conching (Cerny & Fay, 1995).

Eight heterocyclic compounds including 2,3-dimethylpyrazine (45), 2,5-dimethylpyrazine (42), 2,6-dimethylpyrazine (43), trimethylpyrazine (47), tetramethylpyrazine (51), 3(or 2),5-dimethyl-2-(3)-ethylpyrazine (50), 3,5(or 6)-diethyl-2-methylpyrazine (53) and 2,3,5-trimethyl-6-ethylpyrazine (54) were identified (Table 11.2). Characteristic key chocolate flavours such as *fruity* and *floral* likely derived from cocoa were found in 3,7-dimethyl-1,6-octadien-3-ol (*linalool*) (6) and 5-ethenyltetrahydro-\(RR,RR,5\)-trimethyl-\(cis\)-2-furanmethanol (*linalool oxide*) (36). Ethyl cinnamate (23) and acetic acid (24), not previously reported important in dark chocolates, were characterised by *fruity-spicy* and *astringent-vinegar*
notes, respectively. Tetramethylpyrazine (51), the most abundant flavour compound in dark chocolate, exhibited *milk coffee-roasted-cooked* notes, and trimethylpyrazine (47) had *cocoa-roasted-cooked* characters (Table 11.2).

### 11.4.3 Effects of particle size distribution on flavour volatile release

Effects of PSD and fat content on the release of selected abundant (>10<sup>6</sup> units) flavour volatiles characterised by distinct aroma were evaluated using SPME-HRGC with GC-MS detection and reported (Tables 11.3 and 11.4). Data from ANOVA indicated that with the exception of 3,7-dimethyl-1,6-octadien-3-ol (*linalool*) and 2-carboxaldehyde-1-<i>H</i>-pyrrole (<i>p</i> = 0.965 and 0.854, respectively), increasing particle size (PS) caused significant reduction on the release of all selected compounds measured in the sample headspace with <i>p</i> < 0.001 for 3-methylbutanal, 2-phenylethanol, furfuryl alcohol (*furfurol*), acetic acid, methylpyrazine, 2,3-dimethylpyrazine, 2,5-dimethylpyrazine, trimethylpyrazine, tetramethylpyrazine and 2,3,5-trimethyl-6-ethylpyrazine; and <i>p</i> < 0.05 for 2-phenylethylacetate, 2-methylbutanal and 5-ethylenetetrahydro-<i>R</i>,<i>R</i>,5-trimethyl-<i>cis</i>-2-furanmethanol (*linalool oxide*), with significant interactions noted with fat content (Table 11.5).

The decreasing flavour volatiles release with increasing PS could be related to increased matrix retention through structural, rheological and textural differences (Afoakwa *et al*., 2008a, b, c). Beckett (2008) noted that movement of volatiles was related to an initial concentration gradient between phases, and refining (degree of particle sizes) in production may influence release during manufacture. Beckett (2008) also noted that correlated compositional and sensory analyses showed differences in flavour profile with preference for lower
### Table 11.3 Flavour volatiles in dark chocolates varying in PSD and fat content

<table>
<thead>
<tr>
<th>Volatile compound (abundance × 10^6)</th>
<th>25%</th>
<th>30%</th>
<th>35%</th>
<th>50%</th>
<th>25%</th>
<th>30%</th>
<th>35%</th>
<th>50%</th>
<th>25%</th>
<th>30%</th>
<th>35%</th>
<th>50%</th>
</tr>
</thead>
<tbody>
<tr>
<td>3,7-Dimethyl-1,6-octadien-3-ol (linalool)</td>
<td>1.93</td>
<td>1.74</td>
<td>1.24</td>
<td>1.03</td>
<td>2.07</td>
<td>1.72</td>
<td>1.37</td>
<td>0.99</td>
<td>2.66</td>
<td>1.91</td>
<td>1.85</td>
<td>1.26</td>
</tr>
<tr>
<td>2-Phenylethanol</td>
<td>46.84</td>
<td>32.42</td>
<td>26.24</td>
<td>25.22</td>
<td>27.84</td>
<td>24.45</td>
<td>22.33</td>
<td>22.01</td>
<td>26.43</td>
<td>24.01</td>
<td>22.02</td>
<td>17.14</td>
</tr>
<tr>
<td>2-Methylbutanal</td>
<td>2.64</td>
<td>2.24</td>
<td>2.02</td>
<td>2.01</td>
<td>2.92</td>
<td>2.24</td>
<td>2.14</td>
<td>1.99</td>
<td>3.04</td>
<td>2.23</td>
<td>2.25</td>
<td>1.99</td>
</tr>
<tr>
<td>2-Phenylethylacetate</td>
<td>11.89</td>
<td>8.75</td>
<td>7.09</td>
<td>6.82</td>
<td>6.74</td>
<td>6.08</td>
<td>5.86</td>
<td>5.56</td>
<td>6.14</td>
<td>6.01</td>
<td>5.80</td>
<td>5.32</td>
</tr>
<tr>
<td>Furfuryl alcohol (furfural)</td>
<td>4.29</td>
<td>3.21</td>
<td>2.44</td>
<td>2.24</td>
<td>4.08</td>
<td>2.84</td>
<td>2.17</td>
<td>2.05</td>
<td>2.89</td>
<td>2.67</td>
<td>1.99</td>
<td>1.82</td>
</tr>
<tr>
<td>5-Ethenyltetrahydro-(R,R,5)-trimethyl-2-furanmethanol (linalool oxide)</td>
<td>5.58</td>
<td>5.22</td>
<td>4.63</td>
<td>4.60</td>
<td>5.45</td>
<td>5.05</td>
<td>4.73</td>
<td>4.52</td>
<td>5.87</td>
<td>5.32</td>
<td>5.16</td>
<td>5.01</td>
</tr>
<tr>
<td>2-Carboxaldehyde-1-H-pyrrole</td>
<td>2.74</td>
<td>1.53</td>
<td>1.02</td>
<td>1.02</td>
<td>1.21</td>
<td>0.89</td>
<td>0.75</td>
<td>0.68</td>
<td>1.01</td>
<td>0.68</td>
<td>0.54</td>
<td>0.40</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>130.43</td>
<td>78.64</td>
<td>58.83</td>
<td>56.08</td>
<td>112.36</td>
<td>65.26</td>
<td>48.76</td>
<td>42.01</td>
<td>30.77</td>
<td>28.74</td>
<td>28.07</td>
<td>27.15</td>
</tr>
</tbody>
</table>

*aQuantification was by GCMS expressed as mean peak area.*
<table>
<thead>
<tr>
<th>Volatile compound</th>
<th>25%</th>
<th>30%</th>
<th>35%</th>
<th>25%</th>
<th>30%</th>
<th>35%</th>
<th>25%</th>
<th>30%</th>
<th>35%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>18 µm</td>
<td>25 µm</td>
<td>35 µm</td>
<td>50 µm</td>
<td>18 µm</td>
<td>25 µm</td>
<td>35 µm</td>
<td>50 µm</td>
<td>18 µm</td>
</tr>
<tr>
<td>Methylpyrazine</td>
<td>5.48</td>
<td>5.08</td>
<td>3.78</td>
<td>2.92</td>
<td>4.25</td>
<td>3.30</td>
<td>2.94</td>
<td>2.60</td>
<td>3.51</td>
</tr>
<tr>
<td>2,3-Dimethylpyrazine</td>
<td>5.77</td>
<td>6.20</td>
<td>6.16</td>
<td>5.57</td>
<td>6.56</td>
<td>5.88</td>
<td>5.49</td>
<td>5.39</td>
<td>6.89</td>
</tr>
<tr>
<td>2,5-Dimethylpyrazine</td>
<td>9.27</td>
<td>9.04</td>
<td>8.43</td>
<td>8.43</td>
<td>10.09</td>
<td>8.95</td>
<td>7.43</td>
<td>6.60</td>
<td>10.24</td>
</tr>
<tr>
<td>Trimethylpyrazine</td>
<td>28.63</td>
<td>28.87</td>
<td>28.60</td>
<td>28.54</td>
<td>29.50</td>
<td>29.10</td>
<td>28.81</td>
<td>28.80</td>
<td>33.14</td>
</tr>
<tr>
<td>Tetramethylpyrazine</td>
<td>109.61</td>
<td>105.37</td>
<td>96.69</td>
<td>96.43</td>
<td>98.89</td>
<td>96.88</td>
<td>96.79</td>
<td>96.05</td>
<td>112.61</td>
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<tr>
<td>2,3-Diethyl-5-methylpyrazine</td>
<td>4.66</td>
<td>4.59</td>
<td>4.29</td>
<td>3.79</td>
<td>4.80</td>
<td>4.54</td>
<td>4.51</td>
<td>3.89</td>
<td>4.89</td>
</tr>
<tr>
<td>2,3,5-Trimethyl-6-ethylpyrazine</td>
<td>3.86</td>
<td>3.05</td>
<td>2.68</td>
<td>1.93</td>
<td>2.25</td>
<td>2.11</td>
<td>1.82</td>
<td>1.78</td>
<td>1.89</td>
</tr>
</tbody>
</table>

*aQuantification was by GC-MS expressed as mean peak area.*
Table 11.5 ANOVA summary showing F-values and regression coefficients of flavour compounds identified in dark chocolates with varying PSD and fat content

<table>
<thead>
<tr>
<th>Volatile compound</th>
<th>PSD (D90): A</th>
<th>Fat: B</th>
<th>Interactions: A × B</th>
<th>R²a</th>
</tr>
</thead>
<tbody>
<tr>
<td>3,7-Dimethyl-1,6-octadien-3-ol (linalool)</td>
<td>1.81</td>
<td>2.64</td>
<td>1.03</td>
<td>7.11</td>
</tr>
<tr>
<td>2-Phenylethanol</td>
<td>1305.56***</td>
<td>1906.11***</td>
<td>265.68***</td>
<td>75.21***</td>
</tr>
<tr>
<td>2-Methylbutanal</td>
<td>5.83*</td>
<td>0.48</td>
<td>4.76*</td>
<td>21.2</td>
</tr>
<tr>
<td>3-Methylbutanal</td>
<td>32.36***</td>
<td>20.79***</td>
<td>27.92***</td>
<td>84.3***</td>
</tr>
<tr>
<td>Phenylacetaldehyde</td>
<td>8.62***</td>
<td>29.46***</td>
<td>10.28**</td>
<td>81.8***</td>
</tr>
<tr>
<td>2-Phenylethylacetate</td>
<td>3.23*</td>
<td>1.67</td>
<td>3.28*</td>
<td>9.47</td>
</tr>
<tr>
<td>Furfuryl alcohol (furfurol)</td>
<td>70.57***</td>
<td>19.16***</td>
<td>27.82***</td>
<td>87.7***</td>
</tr>
<tr>
<td>5-Ethenyltetrahydro-R,R,5-trimethyl-cis-2-furanmethanol (linalool oxide)</td>
<td>4.89*</td>
<td>5.34*</td>
<td>5.71*</td>
<td>7.86</td>
</tr>
<tr>
<td>2-Carboxaldehyde-1-H-pyrrole</td>
<td>1.15</td>
<td>1.77</td>
<td>0.95</td>
<td>17.9</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>13.67***</td>
<td>26.31***</td>
<td>12.62***</td>
<td>75.0***</td>
</tr>
<tr>
<td>Methylpyrazine</td>
<td>30.15***</td>
<td>34.81***</td>
<td>28.63***</td>
<td>86.4***</td>
</tr>
<tr>
<td>2,3-Dimethylpyrazine</td>
<td>8.93***</td>
<td>11.26***</td>
<td>10.56**</td>
<td>51.6***</td>
</tr>
<tr>
<td>2,5-Dimethylpyrazine</td>
<td>15.62***</td>
<td>12.32***</td>
<td>18.63***</td>
<td>61.4***</td>
</tr>
<tr>
<td>Trimethylpyrazine</td>
<td>13.01***</td>
<td>795.09***</td>
<td>18.52***</td>
<td>81.9***</td>
</tr>
<tr>
<td>Tetramethylpyrazine</td>
<td>13.68***</td>
<td>17.20***</td>
<td>12.29***</td>
<td>51.0***</td>
</tr>
<tr>
<td>2,3-Diethyl-5-methylpyrazine</td>
<td>312.88***</td>
<td>19.24***</td>
<td>48.78**</td>
<td>86.9***</td>
</tr>
<tr>
<td>2,3,5-Trimethyl-6-ethylpyrazine</td>
<td>9.67***</td>
<td>29.59***</td>
<td>13.36**</td>
<td>76.6***</td>
</tr>
</tbody>
</table>

Significant F-ratios at *p ≤ 0.05, **p ≤ 0.01, ***p ≤ 0.001; aR from multiple regression.

PS (thick and pasty) chocolates, rather than the higher PS (thin and runny). These suggest that dark chocolates with finer PS (18 and 25 µm) would release more cocoa-chocolate-praline and caramel-like-sweet-honey notes than those with larger PS (35 and 50 µm), predicting perceived differences in flavour with varying PS. The increase in surface area with decreasing PS (D90) would be predicted to facilitate volatiles release. The lack of significant effects of 3,7-dimethyl-1,6-octadien-3-ol (linalool) and 2-carboxaldehyde-1-H-pyrrole (p = 0.965 and 0.854, respectively) would not be predicted to influence flavour character from headspace contents and odour intensities (Tables 11.3 and 11.4). Voltz and Beckett (1997) and Ziegler et al. (2001) reported that finer (smaller PS) chocolate tend to be sweeter in taste than coarser (larger PS) ones, attributed to relative crystals sizes and melting behaviour. Particle size influences perceptions of creaminess and flavour release in soft model systems (Kilcast & Clegg, 2002; Engelen et al., 2005; Engelen et al., 2008). Concentration of flavour volatiles in headspaces has been reported as a function of diffusion in the solid phase (Guinard & Marty, 1995; Carr et al., 1996; Engelen et al., 2003; Kersiene et al., 2008).

11.4.4 Effects of fat content on flavour volatile release

Fat content influenced headspace concentration of volatiles independent of PSD (Table 11.3). Data from ANOVA showed that 3,7-dimethyl-1,6-octadien-3-ol (linalool), 2-methylbutanal,
2-phenylethylacetate and 2-carboxaldehyde-1-\(H\)-pyrrole lacked significant effects (\(p > 0.05\)). Fat content significantly influenced headspace concentrations of all other quantified volatiles (\(p < 0.001\)) at all PSD with significant interactions among factors studied (Table 11.5). Volatiles characterised by cocoa, chocolate, praline, fruity and roasted notes included trimethylpyrazine, 3-methylbutanal, 2,3-dimethylpyrazine, 2,5-dimethylpyrazine, tetramethylpyrazine, linalool oxide and 2,3,5-triethyl-5-methylpyrazine. All showed a direct relationship with fat content at all PS (Tables 11.3 and 11.4). Volatile release data suggested that chocolates of higher fat content would exhibit greater release of components with cocoa-chocolate-praline notes than those with lower fat. This decreased matrix retention could be related to differences in (micro)structure as interparticle flocculation and aggregates are reduced with higher fat contents (Afoakwa et al., 2008b), releasing more Strecker degradation compounds with cocoa-chocolate notes. Concentrations of less volatile heterocyclic compounds were increased, notably polysubstituted ethyl- and isobutyl pyrazines, tri- and tetramethylpyrazine, and furans (linalool oxide), suggesting structural and rheological effects as major determinants of chocolate character (Do et al., 2007; Afoakwa et al., 2008b, 2009d).

Contrariwise, volatiles with caramel-like, sweet, honey and candy notes included 2-phenylethanol, furfuryl alcohol (furfurol), methylpyrazine, phenylacetaldehyde, 2,3,5-trimethyl-6-ethylpyrazine and 2-carboxaldehyde-1-\(H\)-pyrrole. All showed an inverse relationship with fat content at all PS (Tables 11.3 and 11.4), primarily due to lipophilic matrix–flavour interactions. The major influence of fat content was observed with the most lipophilic compounds (Tables 11.3 and 11.4), particularly with fat contents above 25%. These results are consistent with earlier reports (Jo & Ahn, 1999; Doyen et al., 2001), and are also consistent with the suggestion that the more lipophilic the volatile, the less lipid is needed to reduce its headspace concentration (Roberts et al., 2003). More lipids generally reduce volatility of lipophilic components such as long-chain aldehydes and esters (Kersiene et al., 2008). Lack of a significant effect on overall flavour character from 3,7-dimethyl-1,6-octadien-3-ol (linalool), 2-methylbutanal, 2-phenylethylacetate and 2-carboxaldehyde-1-\(H\)-pyrrole would be predicted (Tables 11.2 and 11.3). Studies from emulsions showed that release of lipophilic compounds is decreased with limited amounts of lipid (Carey et al., 2002; Roberts et al., 2003). Factors such as lipophilicity or hydrophobicity of compounds could modulate the effect of fat content on release, specifically in confectionery (Barylko-Pikielna & Szczeniak, 1994; Hyvonen et al., 2003), as well as mouth-feel (De Wijk et al., 2006) and thermal perceptions (Engelen et al., 2002).

A further key finding was related to headspace acetic acid contents in the products. The data showed very high values in dark chocolates, containing 25 and 30% fat at lower (18 and 25 \(\mu\)m) PS, and inversely related to fat content. Greatest reduction in acetic acid (approximately fourfold) was noted with 35% fat at all PS, relative to similar products with 25 and 30% fat (Table 11.3). Similarly, increasing PS from 25–50 \(\mu\)m reduced contents by approximately two- to threefold with 25 and 30% fat, whereas only minimal (5%) reduction was noted with 35% fat. From ANOVA there were highly significant effects of PSD and fat content (\(p = 0.001\)) on acetic acid release with significant interactions (Table 11.5).

Acetic acid in 25 and 30% fat chocolate headspaces may be related to higher plastic viscosity and yield values (Afoakwa et al., 2008b), and greater flocculation and aggregation of interparticle network structure (Afoakwa et al., 2009d), influencing release and volatilisation in conching. High acetic acid levels in low-fat (25%) chocolates may reduce acceptability scores: effective elimination of volatile free fatty acids (e.g. acetic acid) and moisture during conching is crucial for development of final flavour character and texture in chocolates (Mermet et al., 1992; Pontillon, 1995; Plumas et al., 1996; Kealey et al., 2001; Beckett,
Matrix effects on flavour volatiles character and release in chocolates

As demand for healthier (low-fat) chocolate has increased in recent years, good process optimisation to effect adequate release of acetic acid during manufacture of low-fat (∼25%) dark chocolates would be necessary to obtain well-balanced flavour characters.

### 11.4.5 Relating flavour volatiles release to PSD and fat content: product spaces

Multivariate principal component analysis (PCA) generated a product space, exploring influence of PSD and fat content on headspace volatiles data on dark chocolates. The PCA space (Fig. 11.2) explained more than 91% variance in two factors, and showed two flavour volatile clusters with loadings for PSD and fat content as influential factors. Fat content had polar influences on principal component 1 (PC1) (65.2% variance) score, while particle size had marginal influence on principal component 2 (PC2) (25.6% variance) score. The PCA loading showed distinct relationships. Two components were extracted with eigenvalues 1 or more, and volatiles segregated into two groups were labelled A and B. Group A volatiles were trimethylpyrazine, 3-methylbutanal, 2,3-dimethylpyrazine, 2,5-dimethylpyrazine, tetramethylpyrazine, linalool oxide and 2,3,5-trimethyl-5-methylpyrazine, all characterised by cocoa, chocolate, praline and roasted notes possibly originating in cocoa.

Group B consisted of 2-phenylethanol, furfuryl alcohol (furfurol), acetic acid, methylpyrazine, phenylacetaldehyde, 2,3,5-trimethyl-6-ethylpyrazine and 2-carboxaldehyde-1-$H$-pyrrole, characterised by caramel-like, sweet, honey and candy notes developed during
chocolate manufacture. Both PC1 and to some extent PC2 differentiated chocolate samples with clear groupings characterised by specific flavour notes from GC-O (Table 11.2).

The PCA loadings on PC1 showed that flavour volatiles within Group A characterised by *cocoa, chocolate, praline* and *roasted* notes were highly related in abundancy to fat content. The working hypothesis is that Group A flavour volatiles are primary origins of *cocoa* and *chocolate* notes in dark chocolates, with trimethylpyrazine and 3-methylbutanal central to these characters (Fig. 11.2). Contrariwise, the PCA loading showed a polar relationship of fat content with Group B observed to have *caramel-like, sweet, honey* and *candy* notes (Table 11.2), suggesting that increasing fat content reduces influence of such notes on flavour character in dark chocolates.

Regression models were developed to predict contribution of specific flavour volatiles to overall flavour character. One Strecker aldehyde and two nitrogen heterocycles derived from Maillard reactions had high regression coefficient, respectively: 3-methylbutanal, $R^2 = 0.843$, $P = 0.001$; trimethylpyrazine, $R^2 = 0.819$, $p = 0.001$; 2,3-diethyl-5-methylpyrazines, $R^2 = 0.869$, $p = 0.001$ (Table 11.5). These emerged as probably the most interesting compounds in dark chocolates providing *cocoa, praline-chocolate* and *nutty* flavours. Three other heterocycles − 2,3-dimethylpyrazine, 2,5-dimethylpyrazine and tetramethylpyrazine − showed less but still significant effects with $R^2 = 0.516$, 0.614 and 0.510 ($p < 0.05$), respectively, contributing *cocoa-chocolate* notes. Others, 2-methylbutanal, 5-ethenyltetrahydro-$R$,R,$R$,5-trimethyl-cis-2-furanmethanol (linalool oxide) and 3,7-dimethyl-1,6-octadien-3-ol (linalool), had no significant influence ($p > 0.05$) (Table 11.5), possibly due to their low contents in Central West African cocoa (Tables 11.3 and 11.4).

On the other hand, the regression models developed showed high and significant regression coefficients ($R^2 = 0.75–0.88$; $p = 0.001$) for Group B compounds. These predicted likely contributions of 2-phenylethanol, furfuryl alcohol (*furfurol*), methylpyrazine, phenylacetaldehyde and 2,3,5-trimethyl-6-ethylpyrazine of *caramel-like, sweet, honey* and *candy* notes. Acetic acid had high regression coefficient ($R^2 = 0.75$; $p = 0.001$), and likely contribute *astringent-sour* characters to dark chocolates. Others, 2-phenylacetate and 2-carboxaldehyde-1-$H$-pyrrole, showed no significant effect ($R^2 = 0.095$ and 0.179; $p > 0.05$, respectively), predicting their minimal impacts on flavour character in dark chocolate. This product space from PCA (Fig. 11.2) demonstrated the importance and relationships of the different flavour volatiles and likely effect on flavour character and furthermore the influence of solids PSD and continuous phase matrix fat content on the overall volatiles release into the headspace in dark chocolates.

### 11.5 CONCLUSION

Variations in flavour volatile release in dark chocolate matrices varying in PSD and fat content were noted, suggesting the potential effects of matrix structure and lipophilic–flavour interactions. Increasing PS significantly reduced the release of 3-methylbutanal, 2-phenylethanol, furfuryl alcohol (*furfurol*), acetic acid, methylpyrazine, 2,3-dimethylpyrazine, 2,5-dimethylpyrazine, trimethylpyrazine, tetramethylpyrazine and 2,3,5-trimethyl-6-ethylpyrazine, 2-phenylethylacetate, 2-methylbutanal and 5-ethenyltetrahydro-$R$,R,$R$,5-trimethyl-cis-2-furanmethanol (linalool oxide). Fat content was directly related to headspace concentrations of compounds characterised by *cocoa, chocolate, praline, fruity* and *roasted* notes: trimethylpyrazine, 3-methylbutanal, 2,3-dimethylpyrazine, 2,5-dimethylpyrazine,
tetramethylpyrazine, linalool oxide and 2,3,5-triethyl-5-methylpyrazine at all PSDs. Contrariwise, there was an inverse relationship between matrix fat content and headspace concentration of 2-phenylethanol, furfuryl alcohol (furfurol), methylpyrazine, phenylacetaldehyde, 2,3,5-trimethyl-6-ethylpyrazine and 2-carboxaldehyde-1-\(H\)-pyrrole likely due to lipophilic matrix–flavour interactions.

The PCA and regression models predicted contribution of volatiles to overall flavour character. One Strecker aldehyde, 3-methylbutanal, and two nitrogen heterocycles derived from Maillard reactions, trimethylpyrazine and 2,3-diethyl-5-methylpyrazine, provided cocoa, praline-chocolate and nutty notes, with three others, 2,3-dimethylpyrazine, 2,5-dimethylpyrazine and tetramethylpyrazine, likely making little contribution to showing only minimal effect to cocoa-chocolate flavour. Ethyl groups in pyrazine compounds suggest key role of alanine and its Strecker aldehyde and acetaldehyde in dark chocolate flavour formation. Others, 2-methylbutanal, 5-ethylnitetrahydro-\(R,R,5\)-trimethyl-cis-2-furanmethanol (linalool oxide) and 3,7-dimethyl-1,6-octadien-3-ol (linalool), had likely no effect on dark chocolate flavour character. Likewise, 2-phenylethanol, furfuryl alcohol (furfurol), methylpyrazine, phenylacetaldehyde and 2,3,5-trimethyl-6-ethylpyrazine emerged as compounds contributing caramel-like, sweet, honey and candy notes, with acetic acid contributing to acid-sour sensations. Matrix effects on flavour release in dark chocolate merit attention as new product development and consumers demand a wider range of origins and defined products, and their influence on sensory effects with PSD and fat content remains unclear.
12 Conclusions and industrial applications

12.1 CONCLUSIONS: STRUCTURE–PROPERTIES RELATIONSHIPS IN CHOCOLATE MANUFACTURE

Modifications in particle size distribution (PSD) of suspended solids in chocolates could be employed to influence flow behaviour during industrial manufacture. This potential has not been fully realised due to a lack of pertinent information on the role of PSD in defining rheological behaviour. This study has enhanced understanding on effects of PSD and compositional variations on rheological (flow) properties and related quality characteristics. Research revealed that PSD parameters consist of many discrete components comprising specific surface area, largest particle size (PS) D(v,0.9), Sauter mean diameter (D[3,2]) and mean particle diameter (D[4,3]), all of which exert significant effects on chocolate viscosity. This was confirmed by examination of crystalline network microstructures in molten chocolates varying in PSD and fat content. It was therefore concluded that PSD was a significant factor, but not the only determinant controlling chocolate rheology. Fat content exerted greatest effect on the variability in the rheological properties of molten chocolate, followed by lecithin content and then PSD.

Multivariate procedures were used to explain relationships between the two models (Casson’s and the new International Confectionery Association, ICA, recommendations) used to determine dark chocolate viscosity. From this, it was found that the Casson reference parameters (yield value and plastic viscosity) and new ICA recommendations (yield stress and apparent viscosity) for evaluating chocolate viscosity are very closely related, and could be used independently. However, the ICA method proved to be relatively more efficient than the Casson model, which has limitations with chocolates with wide variations in viscosity. It was therefore recommended that for routine quality control purposes, the calculation of Casson’s reference parameters where the product history is known could be justified while the ICA would be better suited for research purposes with wide variations in component viscosity.

Textural properties of both molten and solid tempered chocolates were noted to decrease linearly with increasing PS, fat and lecithin contents. At low (25%) fat contents, 5 and 2% increases in fat and lecithin, respectively, enhanced PSD effects on texture, with no significant effects at 30% or more fat. Effects on texture of changes in fat and lecithin depended on base fat content. Increasing PSD and fat inversely influenced appearance parameters (L*, C* and h°). Fat content exerted greatest effect on texture and appearance, followed by PSD and then lecithin content, with the last having no significant effect on appearance. Textural parameters (firmness, consistency, cohesiveness, index of viscosity and hardness) and colour measurements (L*, C* and h°) were highly correlated, suggesting prediction. The conclusion
Conclusions and industrial applications

was that PSD, fat and lecithin content all interact to determine texture and appearance in dark chocolates, with significance for new product development and process improvements.

Microstructural analysis revealed that the smaller particles ($D_{10}$, $D_{50}$), the largest particles ($D_{90}$) and specific surface area had direct influence on packing ability and interparticle interactions. At low (25%) fat concentrations, interparticle interaction of crystals led to flocculation, with an impact on microstructure and behaviour of molten and tempered products. Increasing fat reduced the crystalline network density, created more open and void spaces which were filled with fat, reducing resistance to flow, and enhancing spreadability and softening in products. Thus, application of PSD with fat and lecithin could be manipulated to control rheological and mechanical properties of molten and tempered (solid) chocolates, respectively, with importance for new product development and costs of manufacture.

Further work on melting properties using differential scanning calorimetry showed that variations in PSD, fat and lecithin content during dark chocolate manufacture influenced to varying extents, the degree of crystallinity and melting properties ($T_{\text{end}}$, $T_{\text{index}}$ and $\Delta H_{\text{melt}}$) of derived products. It was found that chocolates with finer particles, higher fat and lower lecithin contents, took longer and higher temperatures to complete melting than their corresponding products with larger PS, lower fat and higher lecithin content, suggesting that for chocolate of the same composition, processed under identical conditions, the PSD of the suspended non-fat solid, fat and lecithin contents play important roles in determining their melting behaviour. These findings have applications in defining chocolate quality in terms of nature of crystalline material, dimensions of crystals and polymorphic stability that dictate mechanical and rheological properties of chocolate products.

Rheological parameters (apparent viscosity and yield stress), textural parameters (firmness, index of viscosity and hardness) and melting index (duration or time) were highly positively correlated, suggesting effective prediction. These explain that hardness (texture) could be effectively used to predict melting time (or duration) of finished dark chocolates during consumption. Other processing factors such as temper, polymorphism and cooling temperature controls could contribute to the variability in hardness and melting index of products. Principal component analysis revealed that with the exception of melting index, which showed a moderate shift in space, the rheological properties (apparent viscosity and yield stress) and textural properties (firmness, index of viscosity and hardness) were closely related. PSD, fat and lecithin contents – all interact to determine rheological and textural properties, and melting index (duration) of dark chocolates, with significance for manufacturing improvements and quality control.

12.2 CONCLUSIONS: TEMPERING BEHAVIOUR FROM RESPONSE SURFACE METHODOLOGY

Tempering behaviours of dark chocolates varying in PSD and fat content were studied using models developed by response surface methodology. The models revealed that variations in PSD and fat content of products influenced optimal temperature settings of temperers during pre-crystallisation of products, causing wide variations in chocolate temper units. Differences in fat content exerted greatest variability in temperature settings of the different zones of multistage temperers used, for attaining optimal tempered products. From this work, satisfactory and unsatisfactory temper regimes and corresponding temper
slopes and chocolate temper units were generated to enhance understanding of the different temper regimes and boundaries of identification. Thus, different combinations of tempering temperatures could be employed to induce stable fat polymorph formation and are greatly dependent on fat content and partly PSD of the dark chocolate during manufacture.

### 12.3 CONCLUSIONS: EFFECTS OF TEMPERING AND FAT CRYSTALLISATION ON MICROSTRUCTURE AND PHYSICAL PROPERTIES

Fat crystallisation behaviour during tempering of dark chocolate plays vital roles in defining structure, mechanical properties and appearance of final products. Wide variations in mechanical properties and appearance were noted in products of differing PS and temper regime. PS was inversely related with texture and colour, with the greatest effects noted with hardness, stickiness and visual lightness at all temper regimes. Overtempering caused increases in product hardness, stickiness with reduced gloss and darkening of product surfaces. Undertempering induced fat bloom in products with consequential quality defects in texture, colour and surface gloss. Also, it was noted that variations in PS had no influence on crystallinity of dark chocolates whether optimally-, over- or undertempered. PS had a limited but significant direct relationship with certain melting parameters – $T_{\text{onset}}$, $T_{\text{peak}}$ and $\Delta H_{\text{melt}}$ – independent of temper but significant inverse relationship with $T_{\text{end}}$ and $T_{\text{index}}$. Contrariwise, varying temper influenced crystallinity and chocolate melting properties ($T_{\text{end}}$, $T_{\text{index}}$ and $\Delta H_{\text{melt}}$). Undertempering of dark chocolate resulted in widened crystal size distribution with significant changes in $T_{\text{end}}$, $T_{\text{index}}$ and $\Delta H_{\text{melt}}$. Overtempering caused moderate increases in crystal size distribution, with significant effects on $T_{\text{end}}$, $T_{\text{index}}$ and $\Delta H_{\text{melt}}$, but no changes were noted in $T_{\text{onset}}$, or $T_{\text{peak}}$. Fat–sugar melting profiles were similar in all chocolates independent of PS and temper regime.

Examination using a stereoscopic binocular microscope revealed clear variations in surface and internal crystal network structures and interparticle interactions among optimally tempered, overtempered and undertempered (bloomed) samples. Blooming caused whitening of both surface and internal peripheries with consequential effects on texture and appearance. Scanning electron micrography showed an even spatial distribution of numerous small, stable $\beta$-polymorph crystals in a network with well-defined interparticle connections in optimally tempered chocolate. With overtempered chocolate there were large numbers of very small crystals in network with similar well-defined particle-to-particle connections resulting from formation of stable $\beta$-polymorphs with early nucleation: the outcome was growth of seed crystals from melt into submicron primary crystallites and a fat crystal network stabilised by van der Waal forces. Undertempering resulted in dissolution of a large number of small crystals, rearrangement and recrystallisation into a small number of larger (lumps) fat crystals (Ostwald ripening). In this process there was polymorphic transformation, nucleation and growth of new large crystals in a more stable polymorphic form, with formation of solid bridges with weak and fewer intercrystal connections within chocolate structures. Thus, attainment of optimal temper regime during tempering of dark chocolate is necessary for achievement of premium quality products and avoidance of defects in microstructure, affecting mechanical properties, appearance and melting character.
12.4 CONCLUSIONS: FAT BLOOM FORMATION AND DEVELOPMENT WITH UNDERTEMPERING

The rate of bloom development in undertempered dark chocolate was dependent on solids, PSD and storage time. Blooming was initiated in chocolates within 24 hours and essentially complete by 96 hours. Changes during blooming were attributed primarily to growth of new fat crystals within the structural network with changes in light reflection, yielding increases in surface whiteness and in hardness. From differential scanning calorimetry on melting properties, values for $T_{onset}$, $T_{end}$, $T_{peak}$ and $\Delta H_{melt}$ suggested polymorphic transformation from $\beta IV$ to $\beta V$ within 24 hours and further to $\beta VI$ after 72 hours. Micrographs showed similar crystal network structure and interparticle interactions in chocolates of different PS immediately after tempering. Within 24 hours, liquid and unstable recrystallised fat had appeared on surfaces with initiation of bloom. Unstable fat recrystallised during storage into more stable polymorphs and crystal growth was promoted by Ostwald ripening with the appearance of white crystalline structure that had spread gradually throughout entire chocolate masses after 96 hours. Chocolate of the largest PS (50 $\mu$m) showed most rapid fat bloom, the smallest PS (18 $\mu$m) the slowest, attributed mainly to hydrodynamic forces of capillary action. It was concluded that bloom development was initiated by movement of liquid and unstable fat onto product surfaces through capillarity created by hydrodynamic forces within the interparticle pores and crevices, followed by growth of new fat crystals promoted by diffusion gradients across the mass until the chocolate was fully bloomed. Understanding fat bloom formation and development in dark chocolate has potential applications in new product development.

12.5 CONCLUSIONS: FLAVOUR VOLATILES AND MATRIX EFFECTS RELATED TO VARIATIONS IN PSD AND FAT CONTENT

Variations in flavour volatile release in chocolate matrices, varying in PSD and fat content, suggested potential effects of matrix structure and lipophilic–flavour interactions. Increasing PS significantly reduced release of 3-methylbutanal, 2-phenylethanol, furfuryl alcohol ($furfurol$), acetic acid, methylpyrazine, 2,3-dimethylpyrazine, 2,5-dimethylpyrazine, trimethylpyrazine, tetramethylpyrazine and 2,3,5-trimethyl-6-ethylpyrazine, 2-phenylethylacetate, 2-methylbutanal and 5-ethenyltetrahydro-$R,R,5$-trimethyl-$cis-2$-furanmethanol (linalool oxide). Fat content was directly related to headspace concentrations of compounds characterised by cocoa, chocolate, praline, fruity and roasted notes: trimethylpyrazine, 3-methylbutanal, 2,3-dimethylpyrazine, 2,5-dimethylpyrazine, tetramethylpyrazine, linalool oxide and 2,3,5-triethyl-5-methylpyrazine at all PSDs. Contrariwise, there was an inverse relationship between matrix fat content and headspace concentration of 2-phenylethanol, furfuryl alcohol ($furfurol$), methylpyrazine, phenylacetaldehyde, 2,3,5-trimethyl-6-ethylpyrazine and 2-carboxaldehyde-1-$H$-pyrrole likely due to lipophilic matrix–flavour interactions.

The principal component analysis and regression models predicted contribution of volatiles to overall flavour character. One Strecker aldehyde, 3-methylbutanal, and two nitrogen heterocycles derived from Maillard reactions, trimethylpyrazine and 2,3-diethyl-5-methylpyrazine, provided cocoa, praline-chocolate and nutty notes, with three others, 2,3-dimethylpyrazine,
2,5-dimethylpyrazine and tetramethylpyrazine, likely making little contribution and showing only minimal effects on cocoa-chocolate flavours. Ethyl groups in pyrazine compounds suggest a key role of alanine and its Strecker aldehyde and acetaldehyde in dark chocolate flavour formation. Others, 2-methylbutanal, 5-ethenyltetrahydro-\textit{R, R, 5}-trimethyl-\textit{cis}-2-furanmethanol (linalool oxide) and 3,7-dimethyl-1,6-octadien-3-ol (linalool), had likely no effect on dark chocolate flavour characters. Likewise, 2-phenylethanol, furfuryl alcohol (furfurol), methylypyrazine, phenylacetaldehyde and 2,3,5-trimethyl-6-ethylpyrazine emerged as compounds contributing \textit{caramel-like}, \textit{sweet}, \textit{honey} and \textit{candy} notes, with acetic acid contributing to acid-sour sensations. Matrix effects on flavour release in chocolate merit attention for new product development with consumer demand for a wider range of origins and defined products: sensory influences of PSD and fat content remain unclear.

12.6 INDUSTRIAL RELEVANCE AND APPLICATIONS OF RESEARCH FINDINGS IN THIS BOOK

The research findings in this book would be valuable to the chocolate confectionery industry as it brings greater understanding on the applicability of PSD and ingredient composition to optimise flow behaviour and consequently textural and melting properties of finished chocolates. PSD could be manipulated with the combined action of fat and lecithin to control rheological properties of chocolates, with significance for quality control and reductions in production costs. This understanding would allow manufacturers to lower the viscosity of chocolates without changing the composition or cost, or to lower fat content without affecting viscosity and quality.

In addition, findings on crystalline network microstructure of the molten chocolate explained the defining role of PSD and fat content on the rheological, textural and melting properties of chocolates. These revealed that for chocolate of the same composition and processed under identical conditions, the PSD of the suspended non-fat solid, fat and lecithin contents play important roles in determining their melting behaviour. These findings would have application in defining chocolate quality during manufacture in terms of nature of crystalline material, dimensions of crystals and polymorphic stability that dictate mechanical and melting properties.

Results from models developed to study tempering behaviour revealed that PSD and fat content of products influenced crystallisation behaviour during tempering of products, causing wide variations in chocolate temper units. From these, satisfactory and unsatisfactory temper regimes and their corresponding temper slopes and chocolate temper units have been provided. These would limit the trial and errors currently used to identify appropriate temper regimes for chocolates, with industrial significance for reducing processing (tempering) times with assurance in quality control and shelf characteristics.

Finally, findings from the tempering and fat crystallisation behavioural studies showed that attaining optimally tempering during pre-crystallisation of chocolate is necessary and plays vital roles in defining the structure, mechanical properties and appearance of finished products. As well, information from the flavour studies showed that differences in product matrices varying in PSD and fat content result in variations in flavour volatile release in chocolate systems, suggesting potential effects of matrix structure and lipophilic–flavour interactions. These findings would help processors predict contribution of individual flavour volatiles and suggest how these can be regulated to attain defined flavour characters during
manufacture. This knowledge is necessary for the achievement of premium quality products, manufacturing improvements, new product development and quality control.

12.7 RECOMMENDATIONS FOR FURTHER RESEARCH STUDIES

A number of points have been noted throughout this book that suggest the need for further in-depth investigations in chocolate research. These could include the following:

1. Further studies are required to integrate sensory and instrumental analyses of texture and flavour release from chocolate products varying in PSD and fat content, and establish relationships using multivariate analyses.

2. Time–intensity procedures could be employed to characterise the effects of optimal temper and overtemper regimes on the melting behaviour of products during consumption. It could also be deployed to study effects of varying PSD and fat content on reported variations in melting character of derived chocolates.

3. Some scientific findings from this book have revealed that the finer the chocolate, the sweeter the taste, since small crystals dissolve more rapidly than larger ones. However, there is no published systematic research on the effect of particle fineness on the flavour of chocolate. Further studies are required to elucidate the relationship between ingredient composition, PSD and its textural effects on the release of chocolate flavour volatiles and their perceived intensity during consumption.

4. Comparison of flavour characters in chocolate is complicated by variations caused by different genotypes, geographical origin, pod differences, fermentation and drying methods, and subsequent processing (roasting, alkalisation and conching). Although some major steps have been made to identify the causes of these variations, it is still premature to conclude that this is fully understood. To fully understand variations in chocolate character, further research is required to optimise post-harvest treatments (pod storage, pulp pre-conditioning, depulping, fermentation and drying) of cocoa beans differing in genotype, subsequent manufacturing processes (roasting, alkalisation and conching) during chocolate manufacture as well the sensory evaluation of final flavour character in chocolate.

5. Milk chocolate solids comprise particles from sugar, non-fat milk components and cocoa. This study investigated PSD of solids from only sugar and cocoa, which cannot be related directly to milk chocolate products. Changes in the sizes of particles from the other two particulate ingredients should also be investigated for effects on the physical and sensory character in milk chocolates.

6. The effectiveness of conching could be studied using response surface methodology to optimise conching efficiency in terms of time and temperature that are best suited for the different types of chocolate products (white, milk and dark) during industrial manufacture. This will help reduce the inconsistencies in conching conditions.
References


References


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# Appendix 1: Abbreviations used and their meanings

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AEDA</td>
<td>Aroma extract dilution analysis</td>
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<tr>
<td>ANOVA</td>
<td>Analysis of variance</td>
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<td>ASTM</td>
<td>American Society for Testing and Materials</td>
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<tr>
<td>CBE</td>
<td>Cocoa butter equivalent</td>
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<td>CBR</td>
<td>Cocoa butter replacer</td>
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<tr>
<td>CBS</td>
<td>Cocoa butter substitute</td>
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<tr>
<td>CCRD</td>
<td>Central composite rotatable design</td>
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<tr>
<td>cDNA</td>
<td>Complementary deoxyribonucleic acid</td>
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<tr>
<td>CSD</td>
<td>Crystal size distribution</td>
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<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
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<td>EC</td>
<td>European Commission</td>
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<td>EU</td>
<td>European Union</td>
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<tr>
<td>FID</td>
<td>Flame ionisation detection</td>
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<tr>
<td>GC</td>
<td>Gas chromatography</td>
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<tr>
<td>GC-MS</td>
<td>Gas chromatography–mass spectrometry</td>
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<td>GC-O</td>
<td>Gas chromatography–olfactometry</td>
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<td>GMS</td>
<td>Glycerol monostearates</td>
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<tr>
<td>GU</td>
<td>Gloss units</td>
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<tr>
<td>HRGC</td>
<td>High-resolution gas chromatography</td>
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<tr>
<td>ICA</td>
<td>International Confectionery Association</td>
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<td>ICCO</td>
<td>International Cocoa Organisation</td>
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<tr>
<td>IOCCC</td>
<td>International Office of Cocoa, Chocolate and Confectionery</td>
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<tr>
<td>NCA/CMA</td>
<td>National Confectioners Association/Chocolate Manufacturers Association</td>
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<td>PC</td>
<td>Principal component</td>
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<tr>
<td>PCA</td>
<td>Principal component analysis</td>
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<tr>
<td>PGPR</td>
<td>Polyglycerol polyricinoleate</td>
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<tr>
<td>PS</td>
<td>Particle size</td>
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<tr>
<td>PSD</td>
<td>Particle size distribution</td>
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<tr>
<td>RSM</td>
<td>Response surface methodology</td>
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<td>SDS-PAGE</td>
<td>Sodium dodecyl sulfate polyacrylamide gel electrophoresis</td>
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<td>SEM</td>
<td>Scanning electron microscopy</td>
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<td>SPME</td>
<td>Solid phase micro-extraction</td>
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<td>SSA</td>
<td>Specific surface area</td>
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## Appendix 2: Abbreviations, acronyms and websites of organisations related to cocoa and chocolate industry

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<td>Codex Alimentarius Commission</td>
<td><a href="http://www.codexalimentariuscommission.net">http://www.codexalimentariuscommission.net</a></td>
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<td>CMAA</td>
<td>Cocoa Merchants’ Associations of America</td>
<td><a href="http://www.cocoamERCHANTS.com">http://www.cocoamERCHANTS.com</a></td>
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<tr>
<td>ED&amp;F Man</td>
<td>Cocoa trader (cocoa statistics, free registration)</td>
<td><a href="http://www.edfman.com/cocoa.php">http://www.edfman.com/cocoa.php</a></td>
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<tr>
<td>FAO</td>
<td>Food and Agriculture Organization of the United Nations</td>
<td><a href="http://www.fao.org/">http://www.fao.org/</a></td>
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<td>FCC</td>
<td>Federation of Cocoa Commerce</td>
<td><a href="http://cocoa">http://cocoa</a> federation.com</td>
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<tr>
<td>FDA</td>
<td>US Food and Drug Administration</td>
<td><a href="http://www.fda.gov/">http://www.fda.gov/</a></td>
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<td>FLO</td>
<td>Fairtrade Labelling Organizations International</td>
<td><a href="http://fairtrade.net">http://fairtrade.net</a></td>
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<td>ICA (formerly IOCCC)</td>
<td>International Confectionery Association (source of ICA/IOCCC analytical methods)</td>
<td><a href="http://www.international-confectionery.com/">http://www.international-confectionery.com/</a></td>
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<tr>
<td>ICCO</td>
<td>International Cocoa Organization</td>
<td><a href="http://www.icco.org">http://www.icco.org</a></td>
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<td>ICE</td>
<td>Intercontinental Exchange</td>
<td><a href="http://www.theice.com/cocoa.jhtm/">http://www.theice.com/cocoa.jhtm/</a></td>
</tr>
<tr>
<td>LIFFE</td>
<td>London Intercontinental Financial Future and Options Exchange</td>
<td><a href="http://www.liffe.com">http://www.liffe.com</a></td>
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<td>NYBOT</td>
<td>New York Board of Trade World Cocoa Foundation</td>
<td><a href="http://www.nybot.com">http://www.nybot.com</a></td>
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<tr>
<td>WCF</td>
<td>World Cocoa Foundation</td>
<td><a href="http://www.worldcocoafoundation.org/">http://www.worldcocoafoundation.org/</a></td>
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<td>WHO</td>
<td>World Health Organisation</td>
<td><a href="http://www.who.int">http://www.who.int</a></td>
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<tr>
<td>WTO</td>
<td>World Trade Organisation</td>
<td><a href="http://www.wto.org">http://www.wto.org</a></td>
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Appendix 3: Glossary of chocolate terminologies

Bittersweet chocolate Also referred to as ‘dark chocolate’, this chocolate is manufactured by blending a minimum amount of 35% cocoa liquor with variations of sugar, cocoa butter, emulsifiers and flavourings.

Bloom The appearance of fat or sugar on the surface of chocolate giving it white sheen or sometimes individual white blobs.

Casson equation $\sqrt{\tau} = \sqrt{\tau_{CA}} + \sqrt{\eta_{CA}} \cdot \sqrt{\dot{\gamma}}$

$\tau$, yield stress; $\tau_{CA}$, Casson yield stress; $\eta_{CA}$, Casson plastic viscosity; $\dot{\gamma}$, shear rate.

Cocoa butter A natural fat that is present in cocoa beans and obtained by pressing cocoa liquor.

Cocoa butter equivalent These are vegetable fats that are totally compatible with cocoa butter and can be mixed with it in proportions stipulated by regulation.

Cocoa butter replacer These are vegetable fats that may be mixed with cocoa butter but only in a limited proportion by regulation.

Cocoa liquor, cocoa mass Also known as chocolate liquor, this is composed of roasted and ground cocoa nibs.

Cocoa nibs Similar to cocoa cotyledons, these are cocoa beans with shells removed.

Cocoa powder A product obtained by grinding or pulverising pressed cocoa cake and available in different fat levels. It can be natural or manufactured by the Dutch process.

Compound This is a confectionery product in which vegetable oil has been substituted for cocoa butter.

Dextrose Also known as glucose or cornstarch, it is a sweetener which is commercially made from starch by the action of heat and acids or enzymes, resulting in the complete hydrolysis of cornstarch. It is a reducing sugar that produces high-temperature browning effects in baked foods. Industrially, it is used in ice-cream bakery products, confections and chocolate cookie drops. The sugar helps maintain the shape of the cookie drop during baking and reduces smearing of the chocolate after baking.

Dutching process This is an alkaline treatment of cocoa nibs prior to grinding, or the liquor prior to pressing. It facilitates darkening of the resultant cocoa liquor, modifies the chocolate flavour and also helps keep the cocoa solids in uniform suspension in chocolate beverages.

Emulsifier A surface-active agent that promotes the formation and stabilisation of an emulsion. Examples are lecithin and polyglycerol polyricinoleate that are used in chocolate manufacturing to help control flow properties.

Enrobing The act of coating a candy centre by covering it with chocolate. This could be done by either hand or mechanical means.

Fat bloom This is the visually undesirably white cast that appears on chocolate products as a result of poor or insufficient tempering or exposure of the chocolate to high temperatures without retempering.

Fermentation A process by which complex microbial interaction naturally modifies the composition of cocoa beans so that upon roasted it yields characteristic chocolate flavour.
Appendix 3: Glossary of chocolate terminologies

**Grinding** A mechanical process by which roasted cocoa bean nib is reduced to a smooth liquid known as cocoa liquor.

**Hard butter** This is a class of specialty fats with physical properties similar to cocoa butter. They are typically solid to semisolid at ambient temperatures and melt relatively rapidly at higher temperatures depending on application.

**Lauric fat** A vegetable fat typically containing 40–50% lauric fat acid and mainly obtained from coconut and palm-kernel origin. Compound coatings containing lauric fats usually require appropriate tempering.

**Lecithin** A natural food additive which acts as an emulsifier and surface-active agent. Most commercial lecithin products are derived from soybean. In chocolate manufacture, it controls flow properties by reducing viscosity and it is typically used in ranges between 0.1 and 0.5%.

**Milk chocolate** A chocolate product made by the combination of about 10% cocoa liquor, 12% milk with cocoa butter, sugar or sweeteners, emulsifiers and some flavourings.

**Natural process** Non-alkalised cocoa liquor processed into cocoa powder without alkaline treatment.

**Non-lauric fat** This is an edible fat which does not contain lauric fatty acids. Examples are cottonseed oil, soybean oil and palm oil. Manufacture of confectionery products containing non-lauric fat typically requires no tempering and will possess a higher melting point.

**Non-Newtonian liquid** A liquid such as molten chocolate whose viscosity varies according to rate of stirring (shear).

**Origin liquor** Cocoa mass manufactured in country of bean origin.

**Particle fineness** This is the measurement of average particle size of component solids in a chocolate mix and is expressed in ten-thousandths of an inch or in microns.

**Plastic viscosity** Amount of energy required to keep a non-Newtonian liquid moving once motion has been initiated.

**Press cake** The product that remains after most of the cocoa butter has been expressed from the cocoa liquor. Press cake is pulverised for making cocoa powder.

**Pressing** The process of partially removing cocoa butter from cocoa liquor by means of hydraulic presses. The two products obtained after pressing are cocoa butter and pressed cake.

**Roasting** A cooking or heating process applied to cocoa beans using dry heat at high temperatures to facilitate winnowing of the beans into nibs and also help develop the chocolate flavour.

**Semisweet** See ‘Bittersweet chocolate’, another name for semisweet.

**Sweet chocolate** A chocolate product prepared by blending a minimum of 15% cocoa liquor with varying amounts of sweeteners and cocoa butter. Flavourings may sometimes be added.

**Tempering** The process of fat crystallisation during chocolate manufacture so that the finished product solidifies in a stable crystal form. Proper tempering when followed provides good contraction from moulds, good setting properties, good surface gloss and shelf-life characteristics. Tempering is a critical step in chocolate manufacture and certain confectionery products.

**Unsweetened baking chocolate** This is a consumer term for cocoa or chocolate liquor.

**Vanillin** An artificial substitute for vanilla.

**Viscosity** A measure of the resistance to flow of molten chocolate and determines its ability to be pumped through pipes during industrial manufacture, and the extent to which
the chocolate could be used to cover the centre of confectionery, cake, cookie or ice cream. Chocolate viscosity is influenced by process, solids particle size distribution and formulation variations.

**White chocolate** A chocolate product composed of sugar, cocoa butter, whole milk and flavourings. In the United States, this product cannot be called chocolate since it does not contain cocoa solids. It is sometimes referred to as white cocoa butter-based confectionery coating.

**Winnowing** The process of cracking and removing the cocoa bean shell to reveal the inner part of the bean, the ‘nibs’.

**Yield value** Amount of energy required to initiate motion in a non-Newtonian liquid, for example molten chocolate.
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Photographs showing chocolate manufacture from cocoa seedling to final product

Plate 1  Nursery of cocoa seedlings for planting.

Plate 2  Young cocoa plantations intercropped with plantain.

Plate 3  Flowering cocoa tree.
Plate 4  Growing (immature) Trinatario-type cocoa pods.

Plate 5  Typical cocoa plantation in Ghana with trees bearing unripe pods.

Plate 6  Unripe cocoa pods.
Plate 7  Cocoa tree with ripe and unripe pods.

Plate 8  A ripe (Forastero) cocoa pod from Ghana.

Plate 9  Ripe (Arriba) cocoa pods from the Ecuadorian region.
Plate 10  A researcher harvesting cocoa pods from trees.

Plate 11  A typical sharp-edged tool used for harvesting cocoa pods from trees.

Plate 12  A researcher carrying ripe and unripe cocoa pods.
Plate 13  Ripe, unripe and over-ripe cocoa pods (from left to right).

Plate 14  Vertical sections of unripe and ripe cocoa pods showing arrangements and colour of fruits and seeds.

Plate 15  An opened unripe cocoa pod showing longitudinal arrangement of fruits.
Plate 16  Researchers opening cocoa pods in Ghana, West Africa.

Plate 17  Cocoa beans undergoing heap fermentation system in Ghana, West Africa.

Plate 18  Cocoa beans covered with plantain leaves undergoing heap fermentation in Ghana.
Plate 19  Cocoa beans undergoing basket fermentation in Ghana, West Africa.

Plate 20  Cocoa beans undergoing tray fermentation in Ghana, West Africa.

Plate 21  A researcher arranging cocoa beans for tray fermentation.
Plate 22  Typical set-up for box fermentation system.

Plate 23  Researchers drying cocoa beans on raised platforms at the Cocoa Research Institute of Ghana.

Plate 24  Dried cocoa beans.
Plate 25  A typical chocolate manufacturing factory.

Plate 26  Stages in the chocolate manufacturing process.
Plate 27  Malvern Mastersizer used for measuring chocolate particle size during processing.

Plate 28  The three stages of chocolate conching during manufacture.
Plate 29  Molten milk chocolate after conching.

Plate 30  Determination of chocolate viscosity (experimental set-up and data curves).
**Plate 31**  AMK 50 Aasted Mikrovert Mini-temperer. Reprinted from Afoakwa et al. (2008g), copyright 2008, with permission from Elsevier.

**Plate 32**  Depositing of molten chocolate on moulds.
Plate 33  Depositing plant in a chocolate manufacturing factory.

Plate 34  Demoulded chocolate bars.

Plate 35  Handmade chocolate truffles with white, milk and dark types.
Plate 36  Delicious chocolate pralines with different shapes from the same production line.

Plate 37  Chocolates with different flow wrap countlines.
Plate 38  Cadbury Roses (UK), Nestlé Quality Street (UK) and Golden Trees (Ghana) chocolate products.

Plate 39  Assorted brands of chocolate products.

Plate 40  Assorted brands of chocolate products in the global market showing different packaging materials.
Fig. 4.7  Cocoa powders alkaliised into different colour shades.