Structural changes and plasticizer migration of starch-based food packaging material contacting with milk during microwave heating

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**A B S T R A C T**

The effect of microwave treatment on the plasticizer migration and the changes in multi-scale structures of starch ester films for food packaging were evaluated, and the relationship between these structural changes and plasticizer migration was revealed. The plasticizer migration from the starch ester film to the milk system was accelerated during microwave heating compared with during simple immersion at 30 °C without microwave. After microwave heating, the water and/or fat molecules of the milk system rapidly permeated the film interface to enlarge the interchain spaces. The plasticizer molecules distributed near the boundary more readily migrated out than those located in the matrix interior. The changes in the plasticizer/starch ester interaction and film structures weakened the stability of the ether bond both in the plasticizer and starch ester molecules. The crystalline structure of the film was changed with a certain degree of destruction and the relevant interplanar spacing was decreased. The milk permeation into the amorphous region of the film impeded the shrinkage and aggregation of amorphous starch ester chains and even enlarged the inter-chain distances in this region. However, the ordered microaggregations were shrunk with reduced polydisperse size distribution. In consequence, the aggregation structure showed less restriction to the activated plasticizer molecules as a result of microwave treatment. These structural changes, including the expanded amorphous region and shrunk ordered microregions, could be the reason for the greater plasticizer migration during the microwave treatment. This knowledge will help us in further designing the starch-based materials with restrained plasticizer migration by controlling the molecular interaction, crystalline structure and ordered aggregation structure within the film matrix for safe and reasonable application of this type of packaging materials.

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1. Introduction

The principal roles of food packaging are to protect food products from external influence or damage and provide consumers with ingredient and nutritional information (Marsh & Bugusu, 2007). However, food packaging materials usually contain chemical additives (Singh, Saengerlaub, Wani, & Langowski, 2012), which could migrate into foodstuffs inside and thus be ingested by the consumer (Bomfim, Zamith, & Abrantes, 2011; Fasano, Bono-Blay, Cirillo, Montuori, & Lacorte, 2012; Grob et al., 2010; Singh et al., 2012; Triantafyllou, Akrida-Demertzis, & Demertzis, 2007; Von Goetz et al., 2013).

As a popular and efficient processing method applied in the field of food processing, especially for the “ready-to-eat” meals (Chandrakeran, Ramanathan, & Basak, 2013; Salazar-González, San Martín-González, López-Malo, & Sosa-Morales, 2012), microwave heating aggravates molecules movement and decreases the activation energy (Vadivambal & Jayas, 2010), and consequently, the chemical migration from the packaging material during microwave heating would be different from that during conventional heating (López-Cervantes, Sánchez-Machado, Simal-Lozano, & Paseiro-Losada, 2003). On the other hand, food/packaging interactions and the packaging material structure were affected by microwave treatment (Guillard, Mauricio-Iglesias, & Contard, 2010). For the packaging polymers, the multi-scale structure plays an important role in the diffusion coefficient of migration (Hernandez, Selke, & Culter, 2004), which determines the migration of chemical components added in the materials (Helmoth, Rijk, Dekker, & Jongen, 2002). However, little work has been performed for the determination of the rearrangement of aggregation structure in the packaging material during microwave treatment. The structural changes can significantly affect the additive migration from the packaging material matrix to the food system.

Starch-based food packaging materials have attracted much interest because of its biodegradability to ease the environmental
crisis and the petroleum shortage arising from the consumption of traditional plastics (Chandra & Rustgi, 1998; Siracusa, Rocculi, Romani, & Rosa, 2008). The potential application in the food industry has been investigated extensively (Jiménez, Fabra, Talens, & Chiralt, 2012). However, the water-sensitivity of starch-based materials (Shogren, 1992) because of the inherent hydrophilicity of starch greatly restricts their application in food packaging, especially in food systems containing moisture. Many researches have focused on chemical modification of starch to improve the hydrophobicity of starch-based materials for expanding their application. It has already been reported that esterification of starch with a high degree of substitution (DS) can convert native starch into hydrophobic starch ester (Fringant, Rinaudo, Foray, & Bardet, 1998; Hassan Nejad, Ganster, & Volkert, 2010), which could be an effective solution to produce water-resistant starch-based materials.

While plasticizer is indispensable in thermal processing of starch-based materials (Li, Xie, Yu, Chen, & Li, 2009; Xie, Halley, & Averous, 2012) and in improving the mechanical and barrier properties of them (Averous & Halley, 2009; Mathew & Dufresne, 2002), the inevitable migration of plasticizer from starch-based materials to the packaged foods generates concerns about food safety, especially when starch-based packaging materials with improved hydrophobicity are used (Munroa, Haightona, & Lyncha, 2009). This is further especially the case with microwave heating which could accelerate the motion of molecules (foods and plasticizer) and result in structural changes of the starch-based packaging materials. Therefore, the study of the relationship between the structural changes and the plasticizer migration during microwave treatment of foods packaged with starch-based films is of great significance for the safe application and the rational design of water-resistant starch-based films.

Based on our previous study (Zhu, Li, Huang, Chen, & Li, 2013) where the hydrophobic starch ester films plasticized with triacetin were successfully prepared, this paper aims at evaluating the plasticizer migration from this water-resistant starch-based film into aqueous foods such as whole milk and skimmed milk by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) and thermal gravimetric analysis (TGA). The changes in the molecular interaction between the plasticizer and starch ester, crystalline structure and ordered aggregation structure of the starch ester film during microwave heating were characterized in detail by utilizing ATR-FTIR and wide-small angle X-ray scattering (WAXS/SAXS).

2. Materials and methods

2.1. Materials

Starch ester with the degree of substitution (DS) value of 2.49 was prepared according to the method in our previous study (Pu et al., 2011). Triacetin (AR, Mn = 218.20) as the plasticizer was purchased from Aladdin Chemistry Co. Ltd. (Shanghai, China). The whole milk with 3.4 g/mL fat content and the skimmed milk with 0.1 g/mL fat content, purchased from Parmalat Australia Ltd. (Australia), were selected as food systems according to Grob (Koni Grob, 2008).

2.2. Film preparation

Starch ester films were prepared by a solvent-cast method as described in our previous study (Zhu et al., 2013).

2.3. Microwave treatment

A microwave heating device Ethos Sel (Milestone, Italy) (maximum power 1000 W) was used. According to the ratio between food volume and contact area of packaging material in American Society for Testing and Materials (ASTM) standard D4754-11 (ASTM, 2011), each starch ester film (2 × 0.7 cm²) was immersed in 7 mL of either whole milk or skimmed milk in the vessels. The samples were heated from 30 °C at a heating rate of 2 °C/min for different heating times (15 min, 20 min, 25 min, 30 min, and 35 min). After treatment, all the samples were taken out and washed with distilled water. Then the water on the surface was wiped out, and the films were stored in resealable bags at constant temperature (26 °C) and humidity (40%) for 24 h before analysis. The corresponding control starch ester films without microwave treatment were immersed in whole milk and skimmed milk at 30 °C.

2.4. Attenuated total reflectance-Fourier transform infrared spectroscopy

ATR-FTIR spectroscopy is an analytical method to obtain the structure information of the surface (below 5.0 μm) of a sample. Therefore, the migration of low molecular weight plasticizer around the film–milk interface could be detected (Koenig, 1999; Torregrosa-Coque, Álvarez-García, & Martín-Martínez, 2011). The IR spectra of the films were characterized using a Tensor 37 spectrometer (Bruker Optik, Germany) in the Attenuated Total Reflectance (ATR) mode with the scanning range between 600 and 2000 cm⁻¹ by 32 scans at a resolution of 4 cm⁻¹. Three times of repetition were performed. The spectra were subjected to baseline correction using the OPUS 6.5 software (Bruker Optik, Germany). An open beam background spectrum of clean crystal was recorded before each sample analysis. The Peak Fit 4.12 (SYSTAT Software Inc., Richmond, CA, USA) program was then performed to obtain peak positions and areas for further analysis. The AutoFit peaks III deconvolution method was applied. The deconvolution filter constant was 75.0 and was kept consistent for all samples.

2.5. Thermal gravimetric analysis

Thermal gravimetric analysis of starch-ester films was carried out using a PerkinElmer Pyris 1 TGA system (Perkin Elmer Inc, USA) with Al₂O₃ as the reference material. The heating rate was 10 °C/min and the heating range was 30–500 °C. Nitrogen was used as the purge gas at a flow rate of 20 mL/min. According to the thermal stability of triacetin, the mass loss before 250 °C arose from the triacetin evaporation. The triacetin contents of original and processed starch ester films were determined. Three times of repetition were performed.

2.6. Wide and small angle X-ray scattering experiment

A SAXSess camera (Anton-Paar, Austria) and a PW3830 X-ray generator with a long fine focus sealed glass X-ray tube (Panalytical) operating at 40 kV and 50 mA were used to carry out the SAXS/WAXS experiment for the starch ester films. An intense monochromatic primary beam (Cu-Kα, λ = 0.1542 nm) was obtained. The film sample was placed in the sample holder along the line shaped X-ray beam in the evacuated camera housing. The sample-detector distance was 261.2 mm, and the temperature was kept at 26 °C. The 2D data were integrated into the one-dimensional scattering function I(q) as a function of the magnitude of the scattering vector q defined as: q = 4 π sin θ/λ, where λ is the wavelength and 2θ is the scattering angle. Each measurement was collected for 5 min. All I(q) data were normalized and de-averaged. Three times of repetition were performed.
Fig. 1. (a) IR spectra of starch ester films with different triacetin contents; (b) Linear regression between the ratio of peak areas and corresponding triacetin contents ($A_{CeO}$ and $A_{CeO0}$ represent the peak areas of stretching vibration of C–O in triacetin and starch ester molecules, respectively).

Fig. 2. (a) Changes in the IR spectra of starch ester films immersed in milk systems with microwave treatment; (b) changes in the triacetin content in film surface calculated from the linear regression equation according to $A_{CeO}/A_{CeO0}$ variation (data not shown).
3. Results and discussion

3.1. Changes in plasticizer content on the surface of starch ester film

Fig. 1(a) shows the IR spectra of starch ester films with different triacetin contents. The bands at ca. 1220 cm\(^{-1}\) and 1169 cm\(^{-1}\) were attributed to the stretching vibration of the ether bond (C-O) in the alcoxyl group (C-O-C) of triacetin and starch ester molecules (Zhu et al., 2013). As presented in Fig. 1(b), by further deconvolution of these two characteristic bands, the change in the peak area ratio \(A_{C-O}/A_{C-O0}\) yielded a straight line as a function of the triacetin content \(R^2 = 0.9962\), indicating that the changes of characteristic peaks could be utilized to calculate the plasticizer migration in the film surface region.

Fig. 2(a) shows the changes of IR spectra of starch ester films immersed in whole milk and skimmed milk heated by microwave. The peak area at 1220 cm\(^{-1}\) decreased obviously in both whole milk and skimmed milk with an increase in the microwave heating time, suggesting that the plasticizer migrated rapidly from the film surface under microwave treatment. Accordingly, the changes in the plasticizer content in the film surface were presented in Fig. 2(b). Compared to the controlled samples, the plasticizer content of microwave heated films decreased more dramatically, which signified that the microwave treatment accelerated the plasticizer migration from the starch ester film surface. However, no obvious difference was observed between the migration into whole milk and skimmed milk.

3.2. Changes in plasticizer migration from starch ester film

Fig. 3(a) shows the initial thermograms of starch ester films immersed in whole milk and skimmed milk heated by microwave. The weight loss related to triacetin evaporation became unconspicuous with an increase in the microwave heating time, which indicated that the triacetin migration was enhanced. As seen from Fig. 3(b), the films after microwave heating showed greater plasticizer migration than those of the corresponding control films. However, the difference of migration between the films immersed in whole milk and in skimmed milk at 30 °C was comparatively small, while the microwave treatment enhanced the plasticizer migration into whole milk which had a higher fat content. The property of food affects the migration of the additive(s) in the packaging material if the food component has a high affinity with the additive(s) (Helmroth et al., 2002). Here, the larger amount of

![Fig. 3](image-url)
plasticizer migration was attributed to the better affinity among triacetin, starch ester film and the fat molecules in whole milk.

On the other hand, it was obvious that the amount of plasticizer migration on the film surface was larger than that within the whole film. The milk system first interacted with the surface of starch ester film to enlarge the distances between the macromolecular chains; therefore, the plasticizer distributed in the surface region was more likely to migrate from the film matrix into the milk. During the microwave treatment, the interaction between the milk system and the surface was also preferentially enhanced to facilitate the plasticizer migration. The difference of plasticizer content between the surface and interior of the starch ester film led to the redistribution of plasticizer molecules within the film matrix. Combined with the permeation of milk, the plasticizer/starch ester interaction and the film structure were supposed to be changed accordingly.

3.3. Changes in the interaction between triacetin and starch ester molecules

As shown in Fig. 4, the specific peak positions of starch ester films immersed in whole milk and skimmed milk with/without microwave treatment shifted to lower wavenumbers, indicating the stability of C–O–C was weakened, which was supposed to arise from the structural changes within the film matrix during the immersion in the milk systems caused by the plasticizer migration and milk permeation.

Obviously, the peak positions decreased to a greater degree during the microwave treatment compared to immersed at 30 °C without the microwave treatment. In addition to the large amount of traction migration, the microwave treatment promoted the milk permeation to occupy the interspaces of the film matrix. Consequently, the inner structure was changed more significantly during the microwave treatment to provide triacetin and starch ester molecules with a different chemical environment.

3.4. Changes in crystalline structure

WAXS data presented in Fig. 5 reveals the changes in the crystalline structure. Four well-defined scattering peaks at 4.02, 4.93, 5.69 and 6.32 nm\(^{-1}\) respectively were observed in the diffractogram of untreated starch ester film. With an increase in the microwave heating time, these peaks became first weakened and then enhanced to a certain extent. Especially, the peak at 4.93 nm\(^{-1}\) was vanished after 35 minutes' treatment. Moreover, the peaks at 4.02 and 5.69 nm\(^{-1}\) were shifted to a larger q range (indicated by the arrows). In comparison, all the mentioned changes were not observed for the starch ester films immersed at 30 °C (data not shown).
shown). Previous paper has reported that rapid microwave heating accelerated the destruction of the V-type single helix in starch granules (Fan et al., 2013). Analogously, the observed changes indicated that the microwave treatment led to the macromolecular rearrangement within crystallites, including a certain degree of destruction to the crystalline structure and a decrease in the interplanar spacing, which arose from the greater plasticizer migration and milk permeation resulting from the microwave treatment.

Fig. 6. SAXS data of starch ester films immersed in milk systems with microwave treatment.

Fig. 7. (a) Guinier curves of starch ester films immersed in milk systems with microwave treatment plotted in the form of \( \ln[I(q)] \) versus \( q^2 \); (b) according changes of \( R_g \) values.
3.5. Changes in aggregation structure and size

The changes in aggregation structure and size within starch ester films during microwave treatment were detected by SAXS. Fig. 6 shows the changes in the scattering intensity of starch ester films at a low q range. For the films heated with microwave, the scattering intensity between 0.1 and 0.5 nm\(^{-1}\) was increased with the microwave treatment, identifying the structural changes at the corresponding dimension of ca. 13–63 nm (d = 2π/q). For the films microwave heated in whole milk, the scattering intensity was mainly increased at a wider q range of 0.1–0.8 nm\(^{-1}\) (8–63 nm) except the film microwave heated for 35 min. In addition, compared with the films in skimmed milk, those in whole milk showed a significant increase in the scattering intensity for the same microwave heating time.

WAXS results revealed that the crystalline structure was destroyed slightly, leading to present lower electron density. Considering the increased scattering intensity at small angle, the electron density in the amorphous region should be reduced to a greater degree, which was caused by the plasticizer migration and permeation of milk components. Plasticizer migration resulted in the aggregation of macromolecular chains by gradually increasing permeation of milk components. Plasticizer migration resulted in destroyed slightly, leading to present lower electron density. Although certain absorption to generate more structural changes. Although certain changes in the starch ester film (35 min) of microwave heating in the whole milk, the whole crystalline structure was changed with decreasing integrity and electron density. Thus, the electron density difference between these two regions within the film was weakened after 35 minutes' treatment (Fig. 6).

Fig. 7 shows the Guinier plots (Glatter & Kratky, 1982) and all the \(R_g\) values estimated from the slope of the linear regression. With the microwave treatment, a decrease in linearity of the regression line with a greater curvature was observed, implying that the original uniform size of ordered aggregation structure was gradually changed to present polydisperse size distribution. The decreased \(R_g\) values (Fig. 7b) means that the entire ordered aggregation structure was affected. According to the above discussions, it could be deduced that the microwave treatment not only led to direct destruction to the crystallite structure, but also caused the overall shrinkage of the ordered aggregation structure, which was due to the fact that the macromolecules at the edge of ordered regions were rearranged into an amorphous state, i.e. the amorphous region was expanded after the microwave treatment.

4. Conclusion

Compared to simple immersion in the milk at 30 °C, the additional microwave treatment could lead to multiple structural changes in the starch ester film and to the migration of a greater amount of plasticizer into the milk system. When used was whole milk which had a better affinity with triacetin and starch ester film, the microwave treatment intensified the plasticizer migration to a greater degree. With the permeation of water and/or fat molecules from the milk system, the inter-chain spaces in the film surface region was enlarged and therefore the plasticizer distributed in the surface region was more likely to migrate out than from the interior region, which resulted in continual movement of plasticizer molecules within the film matrix. Consequently, the redistributed plasticizer and permeation of milk component molecules caused the changes in the plasticizer/starch ester interaction and the film structures, providing triacetin and starch ester molecules a different chemical environment which weakened the stability of C—O—C. During the microwave treatment, the crystalline structure was changed with a certain degree of destruction and the interplanar spacing was decreased to some extent. The water and/or fat molecules mainly permeated the amorphous region to impede the shrinkage and aggregation of macromolecular chains due to the increasing polymer—polymer interaction in this region. The amorphous interchain distances were even enlarged. In addition, the ordered aggregation structure gradually shrank to present reduced and polydisperse size distribution.

The expanded amorphous region provided larger space for the motion of plasticizer and milk component molecules, and simultaneously, the shrunk ordered aggregation structure with less crystallites could pose fewer obstacles for the kinetic plasticizer molecules with greater average energy provided by microwave. Therefore, the plasticizer migration was accelerated during microwave treatment. Discussing about the relation between structural changes and plasticizer migration is of practical significance for the application of this novel hydrophobic starch-based food packaging material. It could be accomplished to restrain the plasticizer migration by controlling the molecular interaction, crystalline structure and ordered aggregation structure within the film matrix, which will guide the rational design and safety application of this novel packaging material.

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