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Structural changes and triacetin migration of starch acetate film contacting with distilled water as food simulant

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ABSTRACT

This work studied the structural changes and the migration of triacetin plasticizer in starch acetate films in the presence of distilled water as food simulant. Fourier-transform infrared spectroscopy result showed that the macromolecular interaction was enhanced to form compact aggregation of amorphous chains. The characterization of aggregation structures via wide and small angle X-ray scattering techniques indicated that the orderly microregion was compressed and the crystallites inside were "squeezed" to form interference and further aggregation. The compact aggregation structures restricted the mobility of macromolecules, triacetin and water molecules. The overall kinetic and the diffusion model analysis manifested that Fick's second law was the predominant mechanism for the short-term migration of triacetin. The increasing relaxation within film matrix caused the subsequent migration to deviate from Fick's law. The safe and reasonable application of the starch-based materials with restrained plasticizer migration could be accomplished by controlling the molecular interaction and aggregation structures.

1. Introduction

Starch-based food packaging materials have attracted many interests because of their biodegradability (Chandra & Rustgi, 1998; Tharanathan, 2003; Siracusa, Rocculi, Romani, & Rosa, 2008; Von Goetz et al., 2013). However, the intense macromolecular interaction of starch led to higher melting temperature and glass–rubber transition temperature than its degradation temperature (Hoover, Hughes, Chung, & Liu, 2010; Jiang, Jiang, Gan, Zhang Xi Dai, & Zhang, 2012). In consequence, the plasticizer is necessarily introduced to decrease the melting and processing temperatures, and the thermoplastic processing was facilitated to improve the packaging properties of starch-based materials (Mathew & Dufresne, 2002; Avérous & Halley, 2009). On the other hand, the natural water uptake of starch-based material (Shogren, 1992) because of the hydrophilicity of starch restricts the application as food packaging materials, especially in food system with moisture. Previous researchers have stated that native starch can be converted to hydrophobic starch ester with high degree of substitution (*DS*) through esterification (Fringant, Rinaudo, Foray, & Bardet, 1998; Nejad, Ganster, & Volkert, 2010), which enhances the water-resistance of starch-based films.

The starch-based food packaging materials are used to contain the foods and prevent them from quality deterioration (Arvanitoyannis, 1999). These primary functions depend on the mechanical and barrier properties, which could be improved by controlling and modifying the structure of the polymeric material (Viera, Da Silva, Dos Santos, & Beppu, 2011). Plasticizer usually endows starch-based materials with available packaging performance that are clearly related to the content of plasticizer (Mali, Grossmann, García, Martino, & Zaritzky, 2005; Chen & Lai, 2008; Tang, Alavi, & Herald, 2008). Other researchers have clarified that the plasticizer content affects the crystalline structure and the formation of an entangled starch matrix with starch chain-to-chain associations (Van Soest & Knooren, 1997). Our previous study also proved that the increased plasticizer content enhanced the mobility of macromolecular chain and enlarged the amorphous region, resulting in multiple structural changes within the starch acetate film (Zhu, Li, Huang, Chen, & Li, 2013).

The chemical compounds inevitably migrate from traditional packaging materials into the contacted food products (Tovar, Salafranca, Sánchez, & Nerín, 2005; Poças & Hogg, 2007; Sanches-Silva et al., 2009), and the plasticizer would also migrate from the starch-based film into the food system. Previous researches have reported that the redistribution of plasticizer in bio-polymer films led to the changes of mechanical and water barrier properties,

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and thus affected the protective function (Anker, Stading, & Hermansson, 2001; Hernández, Rubio, Del Valle, Almenar, & Gavara, 2004). Therefore, the decrease of plasticizer content due to the migration could cause relevant structural changes in the starch-based film matrix and subsequent reduction of packaging performance. The film materials could lose the protect function to packaged food with gradual quality deterioration. In addition, the absorption of food systems causes swelling of the polymer matrix (Reynier, Dole, & Feigenbaum, 1999; Helmroth, Rijk, Dekker, & Jongen, 2002b), which could aggravate the structural changes.

The eco-friendly starch-based food packaging material has been considered as one of the most promising biodegradable materials in food industry (Ma, Chang, Yu, & Stumborg, 2009). The starch ester further facilitates the application in food system with moisture. Therefore, the in-depth understanding of the relationship between the detailed structural changes, as well as the food/packaging interaction, and the plasticizer migration will be crucial for the development of this novel hydrophobic packaging material. Based on the prepared starch acetate films plasticized with triacetin in our previous study. The present research aimed to evaluate the structural changes and plasticizer migration of our prepared hydrophobic starch acetate film (Zhu et al., 2013) during contacting with aqueous food simulant. Further, on the basis of the experimental results, the probable mechanism of interactions between these aspects was also proposed.

2. Materials and methods

2.1. Materials

In this study, starch acetate powder ($DS = 2.49$) was prepared according to the method of our previous study (Pu et al., 2010). Triacetin (AR, $M_w = 218.20$) as plasticizer was purchased from Aladdin Chemistry Co. Ltd. (Shanghai, China). Distilled water prepared with a Milli-Q filter system (Millipore, Bedford, MA) was selected as food simulant (for water-based products) according to (EC, 1997) and National Standard of China (GBT 5009.156-2003).

2.2. Starch-based film preparation and processing

Starch acetate film with 30% triacetin content (w/w, dry base) was prepared by a solvent-cast method described in our previous study (Zhu et al., 2013). The prepared film was cut into strips (1 cm × 2 cm) and totally immersed in the tightly sealed vials with 20 mL distilled water. Strips were taken out for structural characterizations after different immersion time. The migration quantity of triacetin was monitored until the equilibrium was attained. The content change of triacetin within the film was obtained according to the weight loss of the immersed films in thermogravimetric analysis test. The immersion of the starch acetate film was performed at 26 °C and did not adversely affect the integrity of the film.

2.3. Fourier-transform infrared spectroscopy (FTIR) detection

The starch acetate films were immersed in distilled water for 20 s up to 30 h. The IR spectra of the starch acetate film were determined using a Tensor 37 spectrometer (Bruker Optik, Madrid, Spain), in Attenuated Total Reflectance mode (ATR) between 600 and 2000 cm^{-1}, with 32 scans at a resolution of 4 cm^{-1}. Three times of repetition were performed. Before sample analysis, an open beam background spectrum of clean crystal was recorded. Data analysis was performed with Peak Fit 4.12 (SYSTAT Software Inc., Richmond, CA, USA) program. Spectra were deconvoluted with the AutoFit peaks III deconvolution method.

2.4. Small and wide angle X-ray scattering (SAXS/WAXS) experiment

The starch acetate films were immersed in distilled water for 2 h up to 19 day. SAXS/WAXS experiments were performed using a SAXSess camera (Anton-Paar, Graz, Austria). A PW3830 X-ray generator with a long fine focus sealed glass X-ray tube (PANalytical) was operated at 40 kV and 50 mA. A focusing multilayer optics and a block collimator provide an intense monochromatic primary beam (Cu-K_α, $\lambda = 0.1542$ nm). A semi-transparent beam stop enables measurement of attenuated primary beam at zero scattering vector. The film trip was fixed with a sample holder and placed in a TCS 120 temperature-controlled unit along the line shaped X-ray beam in the evacuated camera housing. The sample-to-detector distance was 261.2 mm, and the temperature was kept at 26 °C. The 2D scattered intensity distribution recorded by an imaging-plate (IP) detector was read out by a Cyclone storage phosphor system (Perkin Elmer, USA). 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: $q = 4\pi \sin\theta/\lambda$, where λ is the wavelength and 2θ is the scattering angle. Each measurement was collected for 10 min. All $I(q)$ data were normalized to have the uniform primary intensity at $q = 0$ for transmission calibration. Desmearing is necessary because of the line collimation.

2.5. Thermogravimetric analysis (TGA) test

TGA data were collected using a PerkinElmer Pyris 1 TGA Thermogravimetric system (Perkin Elmer Inc, USA). The film samples were subjected to a heating rate of 10 °C/min in a heating range of 30–500 °C with Al_2O_3 as reference material. Nitrogen was used as the purge gas at a flow rate of 20 mL/min. According to the determined thermal stability of triacetin, the total weight loss at 250 °C is related to the triacetin content in the starch ester film.

2.6. Kinetic analysis of triacetin migration

The migration of triacetin from the starch acetate film was analysed using two data analysis treatments: the overall kinetic and the diffusion model (Crank, 1975; Cran, Rupika, Sonneveld, Miltz, & Bigger, 2010). The migration of plasticizer into the food simulant was initially analysed for the fit to first-order kinetic model. For this model, Eq. (1) is used:

$$\ln\left(1 - \frac{m_t}{m_\infty}\right) = -k_1 t \quad (1)$$

where m_t is the amount of triacetin migrated at time t, m_∞ is the amount of triacetin migrated from the film at equilibrium and k_1 is the first-order rate constant.

The mechanism involved in the diffusion model can be determined by fitting the release curve ($m_t/m_\infty < 0.67$) to Eq. (2):

$$\frac{m_t}{m_\infty} = kt^n \quad (2)$$

where k is a constant which characterizes the polymer network system, and n is the diffusional exponent characteristic of the release mechanism. A value of $n \leq 0.5$ is referred to as Fickian diffusion. For values of $0.5 < n < 1.0$, anomalous (non-Fickian) transport is the predominant mechanism. Values of $n > 1.0$ define Super Case II transport. Values of n and k can be obtained from the slope and intercept of the $\ln(m_t/m_\infty)$ versus $\ln(t)$ plot.

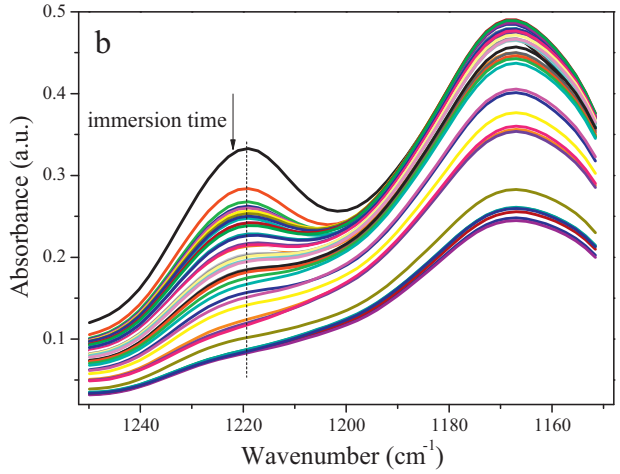

Fig. 1. (a) IR spectra of plasticized starch acetate films immersed in distilled water; (b) IR spectra between 1250 and 1150 cm^{-1}.

3. Results and discussion

3.1. Changes of interaction between triacetin and starch acetate

When compounds are mixed, physical bonds and chemical interactions are reflected by the changes in characteristic IR spectra peaks (Cerqueira, Souza, Teixeira, & Vicente, 2012). Our previous research has demonstrated that the band of stretching vibration of ether bond shifted to high wavenumbers due to the interaction between starch acetate and triacetin (Zhu et al., 2013). Consequently, this research focused on the changes of the mentioned bands during the immersion of starch ester film in distilled water.

Other researchers said when the starch-based film contacted with the distilled water, the water molecules might be absorbed by the polymer to some extent (Reynier et al., 1999; Helmroth, Dekker, & Hankemeier, 2002a; Helmroth et al., 2002b). The absorption of solvent could cause swelling of the polymer matrix, thereby enlarging the gaps and facilitating plasticizer migration during the initial immersion. The observed decreasing peak at 1220 cm^{-1} in Fig. 1 proved the gradual migration of triacetin from starch acetate film matrix into distilled water. Fig. 2 presents the specific peak positions for the stretching vibration of C–O after the deconvolution of area bands. It was displayed that the band of stretching vibration of ether bond shifted to lower wavenumber, indicating that the stability of C–O in triacetin and starch acetate molecules was weakened.

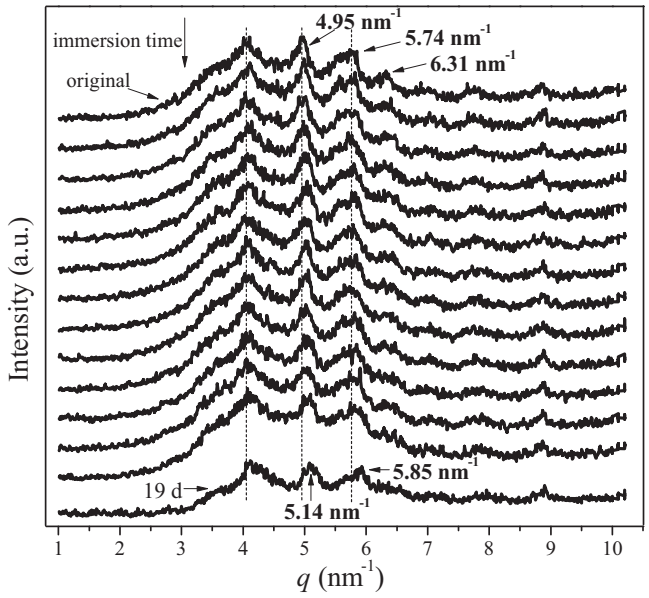

Fig. 3. WAXS data of starch acetate films after immersion in distilled water (the curves have been shifted vertically to avoid overlapping).

According to the gel theory (Suyatma, Tighzert, Copinet, & Coma, 2005), plasticizers break polymer–polymer interactions such as hydrogen bonds and Van der Waals or ionic forces. Along with the gradual plasticizer migration, the inter-molecular interaction between triacetin and starch acetate was weakened and thus, the inter- and intra-molecular interaction of starch acetate molecules was directly enhanced. In consequence, the macromolecular chains shrank to generate more compact aggregation structure within the film matrix, which could exert more intense forces on triacetin molecules.

3.2. Crystalline structural changes

Fig. 3 shows the WAXS patterns of immersed starch acetate films. Several characteristic diffraction peaks of untreated film were observed. The peaks at $q = 4.95\ nm^{-1}$ ($2\theta = 6.96°$) and $q = 5.74\ nm^{-1}$ ($2\theta = 8.08°$) shifted to $q = 5.14\ nm^{-1}$ ($2\theta = 7.23°$) and $q = 5.85\ nm^{-1}$ ($2\theta = 8.23°$) (19 days) with the increasing immersion time, respectively, which indicated that the inter-planar spacing of associated crystallites was reduced. Simultaneously, these two peaks became

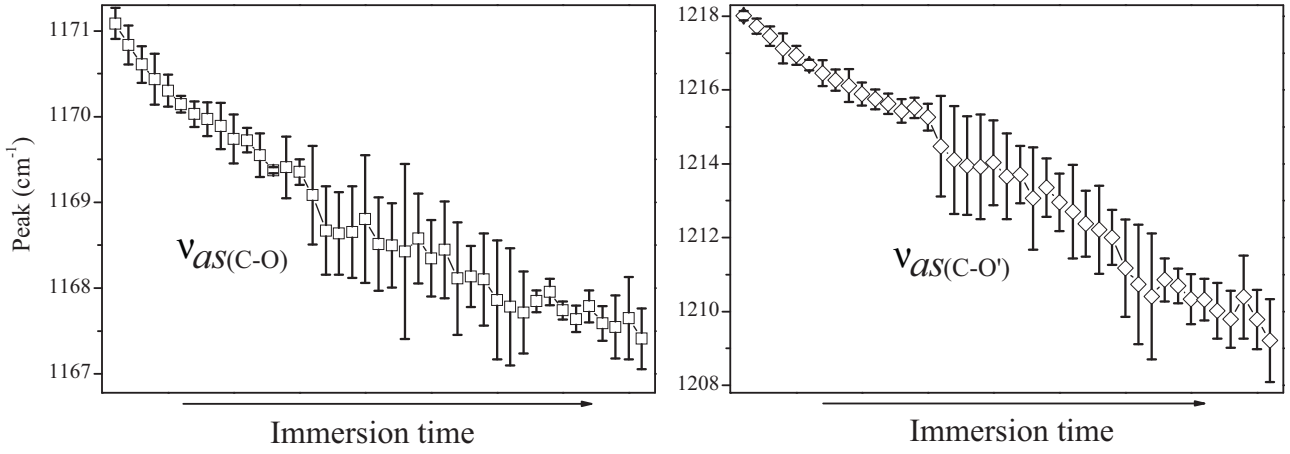

Fig. 2. The variation of characteristic peaks from the stretching vibration of C–O after deconvolution with Peak Fit 4.12 (ν_{as}(C–O) and ν_{as}(C–O′) stand for the stretching vibration of C–O in starch acetate and triacetin molecules, respectively).

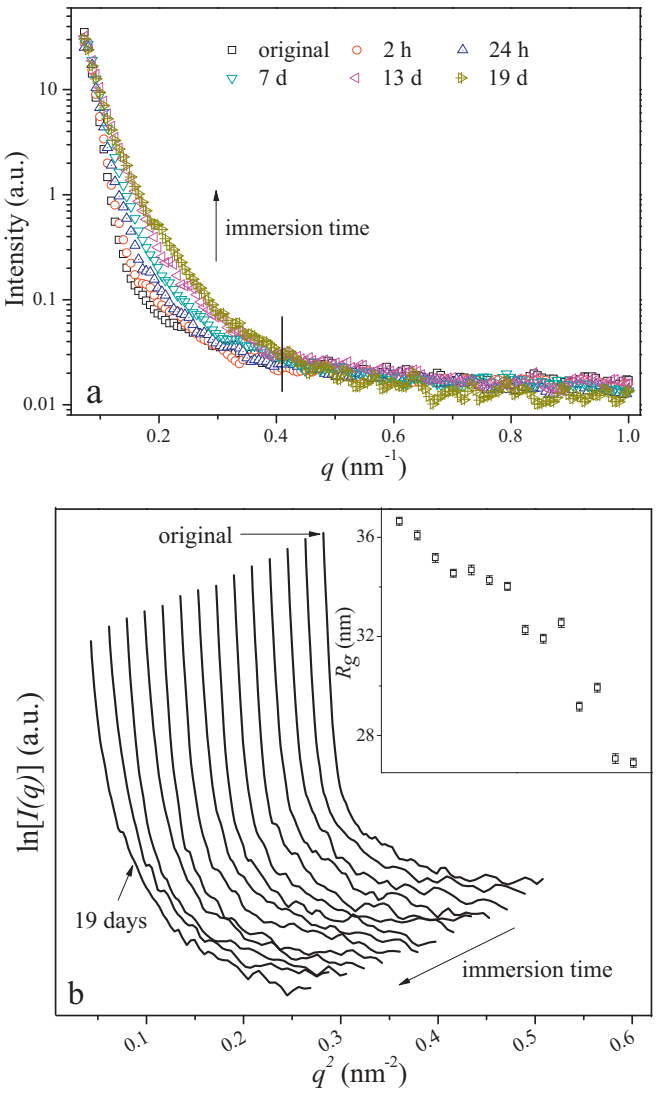

Fig. 4. SAXS data of starch acetate films with immersion in distilled water. (a) Plotted in the form of log[$I(q)$] versus q; (b) Guinier curves plotted in the form of ln[$I(q)$] versus q^2 (Waterfall from OriginPro 8).

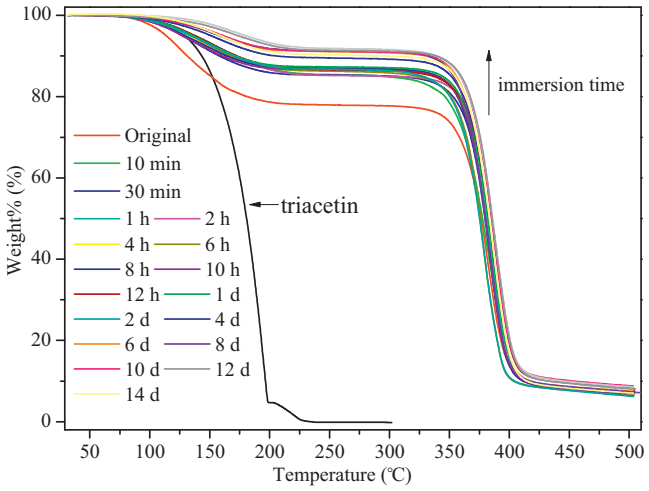

Fig. 5. TG curves for starch acetate films immersed in distilled water.

less well-defined with lower height and larger width, and another peak at $q = 6.31\ nm^{-1}$ ($2\theta = 8.88°$) gradually vanished. The migration of triacetin directly resulted in enhanced interaction between starch acetate molecule chains and led to more compact macromolecular aggregation structure. The interplanar spacing in crystallite was therefore moved closer with smaller d-spacing values and even disappeared.

3.3. Changes of microstructure and domain size

SAXS is powerful for analyzing not only the phase behaviors in condensed and solution states, but also the perturbed or nonperiodic structures of amorphous and mesormorphic materials (Chu & Hsiao, 2001), which could provide the information about the overall shape and dimension of microphases (Baldini et al., 1999).

Fig. 4(a) shows the changes of scattering intensity of starch acetate films in small q regions which should result from the structural changes due to the permeation of water molecules and the migration of triacetin. It is obvious that the scattering intensity between 0.1 and 0.4 nm^{-1} increased during the gradual immersion, indicating the changes of microstructure with the dimension of ca. 16–63 nm ($2\pi/q$). The small angle scattering intensity is related to the electron density difference between the crystalline and amorphous region with nano-scale features within the starch acetate films. It was before-mentioned that the crystalline structure was changed with smaller inter-planar spacing, which generated more compact macromolecular region with higher electron density. On the other hand, because of the lower resistance in the amorphous region, the water molecules mainly permeated into the amorphous regions, and the swelling effect could defer the macromolecular aggregation to some extent. In consequence, the electron density difference between crystalline and amorphous regions was increased, which was reflected in the enhanced scattering intensity.

For a two-component system, the scattering intensity can be then approximated by the equation below (Baldini et al., 1999):

$$I(q) = I(0)e^{-q^2R_g^2/3} \quad (3)$$

$I(0)$ is the scattering intensity at zero angle ($q = 0$) and R_g is the radius of gyration. Fig. 4(b) shows the Guinier plots and all R_g values estimated from the slope value of the regression line according to Guinier equation $\ln[I(q)] = \ln[I(0)] - R_g^2q^2/3$ (Glatter & Kratky, 1982). The R_g value was decreased along with the immersion in distilled water (inset in Fig. 4(b)), which agreed with the slight decrease of d value (WAXS result). In addition, a gradual decrease of linearity of the regression line (i.e. an increased curvature) was observed. This result suggested the interference and some aggregation between crystalline structures. It could be indicated that the crystalline structure was "squeezed" and the distance between crystalline domains was reduced due to the macromolecular shrink. Crystalline domains could act as cross-links to play the anti-plasticization (Mathew & Dufresne, 2002) and consequently restricted the mobility of macromolecular chains in amorphous regions. The characteristic interference and aggregation between crystalline domains should exert more intense restriction on macromolecular motion. Zygoura, Paleologos, and Kontominas (2011) have stated that the enlargement of the gaps between the polymer molecules could enhance additive migration. Consequently, the further permeation of water molecules and the migration of triacetin molecules were supposed to be restricted to greater extent by the formed compact structure.

3.4. Migration of triacetin into food simulant

Fig. 5 shows the initial thermograms for starch acetate films immersed in distilled water for different time values. According to the thermal stability of triacetin, the first stage of weight loss before 250 °C is related to the triacetin evaporation. The weight

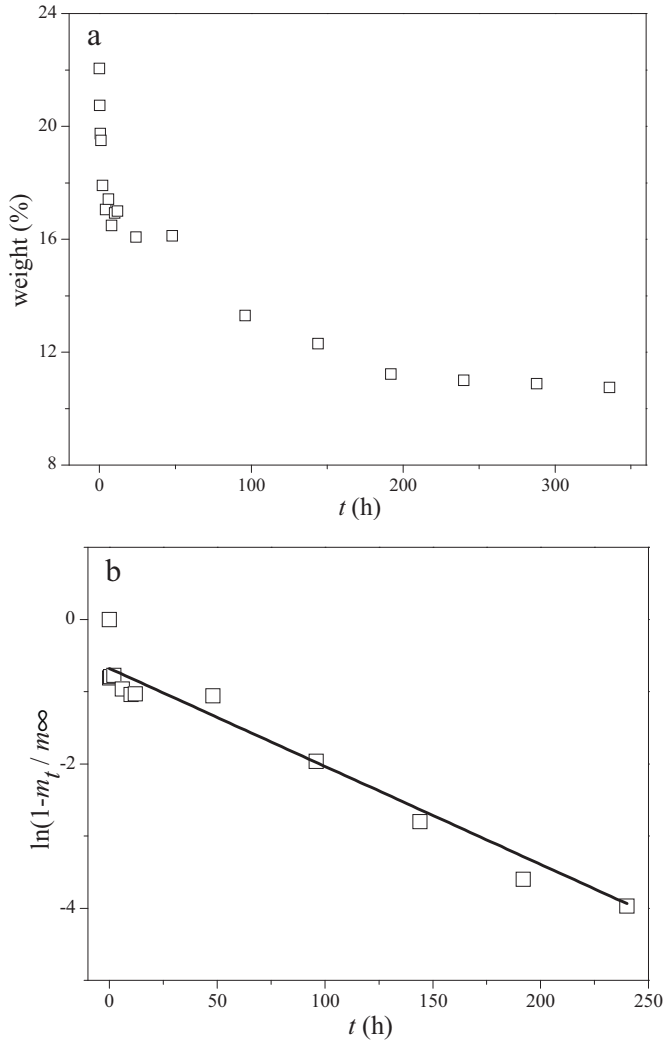

Fig. 6. (a) Change of triacetin content in starch acetate films immersed in distilled water; (b) Plot of $\ln(1 - m_t/m_\infty)$ versus t for the migration of triacetin into distilled water.

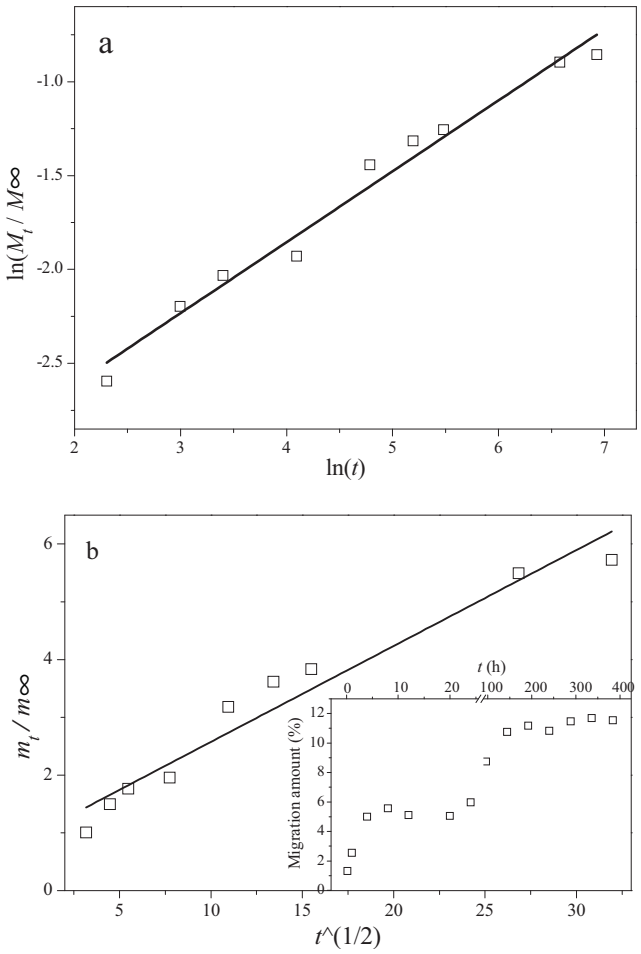

Fig. 7. Plots of (a) $\ln(m_t/m_\infty)$ versus $\ln(t)$ and (b) m_t/m_∞ versus $t^{1/2}$ for the short-term migration of triacetin from starch acetate films into distilled water.

loss of triacetin gradually becomes unconspicuous along with the extended immersion, indicating the decreased residual plasticizer in starch acetate film.

Fig. 6(a) shows the change of triacetin content of starch acetate film immersed in distilled water. It is evident that the migration of triacetin was retarded gradually and reached equilibrium within ca. 200 h. The data of content change for the triacetin were further analysed in terms of an overall kinetic model and the analysis plot was shown in Fig. 6(b). The overall first-order rate constant k_1 obtained from the slope of the linear fitting is 0.0136 h^{-1}. The fitting degree (R^2 = 0.9324) demonstrated that, in general, an overall first-order kinetic model could describe the migration of triacetin into distilled water from the hydrophobic starch acetate systems. Other researchers have reported that the overall first-order kinetic model adequately describe the migration of three antimicrobial agents into isooctane from the starch-based films (Kuorwel, Cran, Sonneveld, Miltz, & Bigger, 2013). However, the correlation coefficient of regression (R^2) of their fitting was not shown. When starch-based film was contacted with different food simulants presenting high or low affinity (intense or weak interaction) with the film matrix, the different interaction between the film materials and the food simulants affected the migration of chemical components from the film matrix. On the other hand, the aggregation structure of film, including the crystalline structure, degree of cross-linking, degree of branching, and etc, determines the migration of plasticizer through the macromolecular matrix (Zygoura et al., 2011). The interior structure of starch acetate film was changed during the immersion and therefore, the migration of triacetin was influenced to present fluctuant migration rate at different immersion stage.

3.5. Diffusion model analysis of triacetin migration

The experimental results were also analysed by the diffusion model. The migration of triacetin into distilled water from starch acetate film could be considered in two domains: the short-term ($m_t/m_\infty < 0.67$) and the long-term migration ($m_t/m_\infty > 0.67$) (Crank, 1975).

Fig. 7(a) shows plots of $\ln(m_t/m_\infty)$ versus $\ln(t)$ for the short-term migration of triacetin from starch acetate film. The estimated n value 0.3776 (R^2 = 0.9765) demonstrated that Fickian diffusion was the predominant mechanism for the short-term migration of triacetin; the initial migration of triacetin was scarcely affected by the relaxational phenomena due to the diffusion of solvent and plasticizer within the film matrix. As Fig. 7(b) shows, the initial part of the diffusion curves was found to be linear with the square root of diffusion time (R^2 = 0.9540), from which it could be indicated that the short-term migration of triacetin further followed Fick's second law of diffusion (Crank, 1975).

According to the theoretical swelling-controlled model (Armand et al., 1987; Malley, Bardon, Rollet, Taverdet, & Vergnaud, 1987), water first enters the film matrix and dissolves the organic

molecules, thus allowing their subsequent migration from the polymer. The migration of triacetin increased with the increasing penetration of water and finally reached a plateau when the starch acetate film matrix was saturated with water. The liquid uptake swelled the starch acetate film to some extent and the time-dependant relaxation process occurred during the diffusion of liquid. As a result, the migration rate of triacetin changed continuously. In addition, the observed sigmoidal shape of the curves (see the inset in Fig. 7(b)) for subsequent migration of triacetin suggested the evidence of the non-Fickian diffusion, as previously mentioned by Lim and Tung (1997). The change of the diffusion model indicated that the subsequent migration of triacetin was affected by the aggravated structural changes of starch acetate film matrix.

4. Conclusion

The distilled water molecules permeated the starch acetate film to cause the film matrix swelling and dissolve the triacetin molecules. Along with the permeation of water and the migration of triacetin, the inter- and intra-macromolecular interaction was enhanced to facilitate the shrink of amorphous chains and the compression of orderly microregion; the crystallite inside the microregions presented further interference and aggregation. These formed compact aggregation structures exerted more intense restrictions on the mobility of macromolecular chains and micromolecules through the film matrix. In consequence, it was more difficult for the further permeation of water and thus, the migration of triacetin by dissolution and passing through the network structure within the film matrix was retarded to display decreased migration rates. Meanwhile, the relaxation process of the film due to the aggravated swelling affected the subsequent migration of triacetin to obey the changed diffusion rule. The discussion about the correlations between the multiple structural changes and the migration of plasticizer in the starch-based film is significant for the safe application of this novel food packaging material. It could be accomplished to control the migration of plasticizer by the further structural modification of the film materials.

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