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.

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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:

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

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):

$$\frac{m_t}{m_\infty} = kt^n \tag{2}$$

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.