



Inhibition of plasticizer migration from packaging to foods during microwave heating by controlling the esterified starch film structure



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ABSTRACT

Plasticizer migration from packaging films to foods can raise health concerns especially when foods are heated in microwaves with their packaging. To inhibit the plasticizer migration, starch-based films were prepared by controlling the micro-structure of esterified starch films with various degrees of substitution (DS), and diethyl phthalate (DEP) was added. The DEP migration after microwave heating, and the interaction between the plasticizer and starch molecules, and the aggregation structure of starch films at nanometer scales were investigated. The data showed that the esterified starch film with the DS of 1.81 had the lowest amount of DEP migration compared with other films (DS 1.17, 1.42, 2.27, and 2.61). The starch films with higher DS showed increased X-ray scattering intensity with a B-type starch scattering pattern. The high DS enhanced the order and compactness in both crystalline and amorphous regions of the film, and increased the distance between crystalline regions. In addition to the change in its aggregation structure, the increase of DS weakened intermolecular interaction between starch molecules, but increased the interaction between DEP and starch–ester molecules. Our approach offered a balance of structural integrity and intermolecular interaction. Plasticizer migration was successfully reduced by controlling the DS of esterified starch film with a strong interaction between DEP and starch–ester molecules, better organized crystalline structure, and more compact and better ordered micro-region aggregation structures with suitable distance between them.

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1. Introduction

It is common to add plasticizers in food packaging to enhance mechanical performance, processing functions and film forming properties. For example, the presence of plasticizers decreases the melting point of packaging films allowing for lower processing temperatures, facilitating thermoplastic processing and improving film quality. Though there are several benefits, plasticizers can migrate into the packaged foods and raise health concerns (Bomfim, Zamith, & Abrantes, 2011; Fasano, Bono-Blay, Cirillo, Montuori, & Lacorte, 2012; Grob et al., 2010; Preeti Singh, Ali Abas Wani, & Horst-Christian Langowski, 2012; Triantafyllou, Akrida-Demertzi, & Demertzi, 2007; Von Goetz et al., 2013). The migration of plasticizers becomes a greater concern when foods are

heated with their packaging materials, such as microwave-meals (Huang, Zhu, Chen, Li, & Li, 2014; López-Cervantes, Sánchez-Machado, Simal-Lozano, & Paseiro-Losada, 2003). During microwave heating, plasticizer molecules gain more energy for migrating. Additionally, the molecular structure of packaging materials and the interaction between food and packaging molecules change. These changes lead to a higher degree of migration during microwave heating (Guillard, Mauricio-Iglesias, & Gontard, 2010; Huang et al., 2014). Previously, we heated milk with its packaging in a microwave, and we observed similar structural changes in packaging, which was starch-based films. The crystalline structure of the starch films became loss during microwave heating, and it resulted in a higher degree of plasticizer migration from the film to the milk. To avoid risking consumers' health, it is crucial to minimize their migration into foods.

Several strategies have been reported to reduce the migration of plasticizers. Organic/inorganic composites were used as coatings to prevent plasticizer leaching from the polymer substrates (Amberg-Schwab et al., 2003; Messori et al., 2004). These coatings are usually

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made from organic oligomers with reactive groups and liquid precursors, such as metal alkoxides, and are prepared by sol–gel processes (Brinker & Scherer, 1990). Nanoclay particles have been considered in postponing mobility of gas, water and plasticizers (Adame & Beall, 2009; Lu & Mai, 2007; Motahari, Dornajafi, & Fotovat Ahmadi, 2012; Pavlidou & Papispyrides, 2008; Xu, Zheng, Song, & Shanguan, 2006). Three organically modified nanomontmorillonite formed intercalated and exfoliated structures, which helped polymer chains penetrate between silicates and thus created a longer, more tortuous path for migration (Motahari et al., 2012). Other nanoparticles, such as silica dioxide (SiO₂), starch nanocrystals and cellulose nanocrystals, were added to films to prevent molecular migration (Kristo & Biliaderis, 2007; Voon, Bhat, Easa, Liong, & Karim, 2012; Xiong, Tang, Tang, & Zou, 2008). A surface cross-linked layer formation, which was obtained by gamma, plasma or ultraviolet irradiation on films, generated highly compact structures and hindered migration (Duvis, Karles, & Papispyrides, 1991; Parra, Rodrigues, & Lugão, 2005). Covalent linking plasticizers to a PVC chain were another method to prevent the migration of plasticizers (Navarro, Pérez Perrino, Gómez Tardajos, & Reinecke, 2010). Though some strategies have been successful to modulate migration, we, focusing on developing renewable and environmentally friendly packaging, proposed a new approach using starch-based films in this study.

We hypothesized the generation of aggregation structures within starch-based films would solve the problem of plasticizer migration into food. An aggregation structure can affect the diffusion coefficient of molecules and change the mobility of small molecules in materials (Alin & Hakkarainen, 2011, 2012; Helmroth, Rijk, Dekker, & Jongen, 2002; Hernandez, Selke, & Culter, 2004). Our previous study about microwave heating milk within starch-based films supports this hypothesis. During microwave-heating, loss of organized crystalline structure and enlarging amorphous structure greatly promoted plasticizer migration (Huang et al., 2014).

In this study, starch films were made with starch–ester powders to generate aggregating structure. The degree of aggregation was controlled by the interaction between starch molecules and ester groups, and the interaction was determined by the degree of substitution (DS). The plasticizer migration from starch-based films with different DS was evaluated by thermal gravimetric (TG) analysis. Furthermore, the multi-structural changes at micro- and nanometer scales and intermolecular interactions were characterized in details by attenuated total reflectance - Fourier transform infrared spectroscopy (ATR-FTIR), wide and small angle X-ray scattering (WAXS/SAXS), and scanning electron microscopy (SEM).

2. Materials and methods

2.1. Materials

Starch–ester powders with the DS values of 1.17, 1.43, 1.81, 2.27 and 2.49 were prepared following the method used in our previous study (Pu et al., 2011). The plasticizer, Diethyl phthalate (DEP), was purchased from Fuchen Chemistry Co. (Tianjing, China). Mineral water, used as the food system, was purchased from Nongfu Spring Co. Ltd. (Heyuan, China).

2.2. Film preparation

Starch–ester films were prepared using a solvent-cast method described in our previous studies (Zhu, Li, Huang, Chen, & Li, 2013; Zhu, Li, Huang, Chen, & Li, 2014).

2.3. Microwave heating treatment

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 films (2 cm × 0.7 cm²) were immersed in 7 mL of mineral water and added to the closed vessels of the microwave heating device (Ethos Sel, Milestone, Italy; maximum power 1000 w). The samples were heated from 25 °C to a maximum temperature of 100 °C. The heating rate was 15 °C/min based on the temperature of the mineral water. Heated films were cooled to 30 °C and then washed with distilled water. The films were dried, sealed in re-sealable bags, and then were stored at 26 °C with a constant humidity (40%) for 24 h before analysis.

2.4. Migration measurement

The DEP contents of the original and processed starch–ester films were determined by thermal gravimetric (TG) analysis using a Perkin Elmer Pyris 1 TGA system (Perkin Elmer Inc, USA) with aluminum oxide (Al₂O₃) as a reference material. The heating temperature was in the range of 30–500 °C with a heating rate of 10 °C/min. Nitrogen was used as the purge gas at a flow rate of 20 mL/min. Three repetitions were performed. The mass loss before reaching 100 °C and between 100 °C and 300 °C were attributed to the evaporation of water and DEP, respectively. The amount of migrating DEP was the difference between the weight at 100 °C and 298 °C, and it was obtained by subtracting the value of DEP content of the heated film from the value before microwave-heating.

2.5. Morphology of starch–ester film surface

Films were frozen by liquid nitrogen, then there were fractured, subsequently fixed on sample stages, and coated with gold. An EVO 18 scanning electron microscope (Carl Zeiss Microscopy, GmbH, Oberkochen, Germany) was used to examine the morphology of films at 20.0 kV.

2.6. Intermolecular interactions

FTIR, a Tensor 37 spectrometer (Bruker Optik, Germany), in the Attenuated Total Reflectance (ATR) mode was applied to obtain information about the chemical groups on the film surface (below 5.0 μm) to interpret the intermolecular interactions (Koenig, 1999; Torregrosa-Coque, Álvarez-García, & Martín-Martínez, 2011). The wavenumber was between 600 and 2000 cm⁻¹ and 32 scans were taken at a resolution of 4 cm⁻¹. The spectra were subjected to a baseline correction using OPUS 6.5 software (Bruker Optik, Germany). An open beam background spectrum of the clean crystal was recorded before each sample analysis. Three repetitions were performed. Data analysis was performed with Peak Fit 4.12 (SYSTAT Software Inc., Richmond, CA, USA), and the AutoFit peaks III deconvolution method was applied. The deconvolution filter constant was 75 for all samples.

2.7. Aggregation structures examination

The SAXS/WAXS experiments for the starch–ester films were carried out by a simultaneous small- and wide angle scattering system (SAXSess, Anton Paar GmbH., Graz, Austria). WAXS was applied to examine the crystalline structure in starch–ester films, and SAXS was used to examine the micro-region aggregation structure at larger nanometer scale. A PW3830 X-ray generator operated at 40 kV and 50 mA was used to obtain a Cu-K α intense monochromatic primary beam with a wavelength of 0.1542 nm as

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