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Effect of amylose/amylopectin ratio of esterified starch-based films on inhibition of plasticizer migration during microwave heating

Yiping Zhong [a], Siyuan Liu [a], Chen Huang [a], Xiaoxi Li [a, *], Ling Chen [a, **], Lin Li [a, b], Jie Zhu [b]

[a] Ministry of Education Engineering Research Center of Starch & Protein Processing, Guangdong Province Key Laboratory for Green Processing of Natural Products and Product Safety, College of Food Sciences and Engineering, South China University of Technology, Guangzhou 510640, China
[b] School of Chemical Engineering and Energy Technology, Dongguan University of Technology, Dongguan 523808, China

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ABSTRACT

Plasticizer, as a necessary processing aid in producing packaging materials, migrated into food stuffs, which caused food safety problems. In order to restraint plasticizer migration, the hydrophobic esterified starch-based films with different multi-scale structures were prepared by regulation the ratio of amylose and amylopectin. The influence of multi-scale structures including molecular interactions between plasticizer and esterified starch, crystalline structure and aggregation structure on inhibition of diethyl phthalate (DEP) migration during microwave heating was studied. As the strongest molecular interactions between starch and DEP, the amount of plasticizer migration in waxy film was lower than that of G50 film and G80 film. Even the largest size of micro-ordered region impeded the DEP movement in G50 film, the serious further amorphization in G50 film amorphous region in microwave process and weaker molecular interactions led to higher DEP migration compared with that of waxy film. The amount of DEP migration in G80 film were the largest which resulted from weaker molecular interactions, damaged crystalline structure during microwave process and the smallest size of micro-ordered region. This study provided a new method to control DEP migration which favored the application of esterified starch-based biodegradable material for food packaging.

1. Introduction

The processing agents such as stabilizer, antioxidant, lubricant, and plasticizer were inevitable in order to improve food packaging applications. However, in the process of packaging materials contacting with food, some processing agents migrated into food stuffs which caused serious food safety problems (Pocas & Hogg, 2007; Singh, Saengerlaub, Wani, & Langowski, 2012). Especially during the process of microwave heating, the microwave heating aggravates molecules movement and further strengthens the interactions between packaging materials and food ingredients (Guillard, Mauricio-Iglesias, & Gontard, 2010).

Factors that influence the migration of plasticizer into food packaging materials mainly include the structure of the matrix material and plasticizer, the property of the food system, the temperature and contacting time (Selke & Culter, 2016). Researchers had put forward some methods to inhibit the migration of plasticizer. For example, using the large molecular weight plasticizer with slow migration rate (Fei, Jiang, Lu, & Hang, 2005), coating the un-migrating substance on the surface of the materials, forming the network structures inside the materials by coating (Amberg-Schwab et al., 2003; Breme, Buttstaedt, & Emig, 2000; Messori et al., 2004) and using the ionic liquid instead of plasticizer (Scott, Rahman, & Brazel, 2003). However, most of the researches on inhibition plasticizer migration concentrated on traditional plastic polymers, which caused serious environmental problems. Starch-based food packaging materials have attracted much interest because of its biodegradability which eases the environmental crisis and the petroleum shortage problems (Siracusa, Rocculi, Romani, & Dalla Rosa, 2008). The plasticizer is added into starch matrix to improve its thermoplastic and mechanical properties (Jimenez, Fabra, Talens, & Chiralt, 2012). But it

* Corresponding author. College of Food Sciences and Engineering, South China University of Technology, Guangzhou 510640, China.
** Corresponding author. College of Food Sciences and Engineering, South China University of Technology, Guangzhou 510640, China.
E-mail addresses: xxlee@scut.edu.cn (X. Li), felchen@scut.edu.cn (L. Chen).

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Abbreviations

Waxy	Esterified starch with amylose content of 0%
G50	Esterified starch with amylose content of 50%
G80	Esterified starch with amylose content of 80%
DEP	Diethyl phthalate

also brought some food safety problems due to the migration of plasticizer into foodstuffs.

In the film forming process, starch molecules formed semi-crystalline network structures, which are influenced by the molecular structure of starch, the types of plasticizer and the film forming conditions (Jimenez et al., 2012). The ratio of amylose and amylopectin plays an important role in the multi-scale structures of starch-based films including molecular interactions, crystalline structure and aggregation structure. The amylose chain is mainly liner structure while most of the amylopectin chain is branch structure. It is more difficult for amylopectin chains to move and form crystalline structure in the film forming process, thus the amylopectin is completely in the amorphous state. The crystalline structure in high amylose content film contributed to the surface roughness (Rindlav-Westling & Gatenholm, 2003; Rindlav-Westling, Stading, Hermansson, & Gatenholm, 1998). Moreover high amylose films have greater mechanical strength and smaller breaking elongation, also it is more resistant to hydrolysis, acid and enzyme solutions (Wu, 2008). García found that the oxygen, carbon dioxide and water vapor penetration rates of normal maize starch films are higher than high amylose maize starch films (Garcia, Martino, & Zaritzky, 1999).

Our previous study proved the loss of organized crystalline structure, increase of amorphous region and shrinkage of micro-ordered region during microwave heating greatly favored DEP migration (Huang, Zhu, Chen, Li, & Li, 2014). Also plasticizer migration was successfully reduced by controlling the degree of substitution of esterified starch film. The strong molecular interactions between DEP and starch ester molecules, better organized crystalline structure and more compact aggregation structure helped inhibit the migration of the plasticizer (Li et al., 2016). The molecular interactions between starch and DEP, film crystalline structure and aggregation structure could affect the migration of plasticizer in the films. In this study, the hydrophobic esterified starch-based films with different multi-scale structures were prepared by regulation the ratio of amylose and amylopectin. The DEP migration from esterified starch-based films with different ratios of amylose and amylopectin were evaluated by thermal gravimetric (TG) analysis. Furthermore, the molecular interactions and multi-scale structures changes at micro- and nanometer scales were characterized in details by attenuated total reflectance - Fourier transform infrared spectroscopy (ATR-FTIR), wide and small angle X-rayscattering (WAXS/SAXS) and scanning electron microscopy (SEM).

2. Materials and methods

2.1. Materials

Esterified starch powders with amylose content of 0% (Waxy), 50% (G50), and 80% (G80) 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. (Tianjin, China). Mineral water, used as the food system, was purchased from Nongfu Spring Co. Ltd. (Heyuan, China).

2.2. Film preparation

Esterified starch films were prepared using a solvent-cast method described in our previous studies (Zhu, Li, Huang, Chen, & Li, 2013, 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), films (2 cm × 0.7 cm^2) were immersed in 7 mL of mineral water and added to 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. DEP migration

The DEP contents of the original and processed esterified starch films were determined by thermal gravimetric (TG) analysis using a Perkin Elmer Pyris 1 TGA system (Perkin Elmer Inc, USA) with aluminum oxide (Al_2O_3) 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. Each of the tests was carried out in triplicate. The boiling points of water and DEP are 100 °C and 300 °C, respectively. Thus, 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 esterified starch film fracture surface

Films were frozen by liquid nitrogen, then they 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. Molecular 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 molecular interactions (Torregrosa-Coque, Alvarez-Garcia, & Martin-Martinez, 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