



Hierarchical structure and thermal behavior of hydrophobic starch-based films with different amylose contents

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ABSTRACT

This work discloses the multi-level structure and thermal behaviors of hydrophobic, propionylated starch-based films as affected by the amylose contents of starch materials used. Scanning electron microscopy results showed that amylose promoted the formation of more compact structure within the film matrices. Also, small and wide angle X-ray scattering analysis revealed that higher amylose content was preferable for the formation of new orders on nanoscale and crystallites. With these structural changes, the viscoelasticity of amorphous short chains was enhanced and the glass transition temperature was reduced by the increased amylose content; but the depolymerization of macromolecules and the decomposition of molecular bonds were postponed, since the increase in starch crystallites restricted the motion of adjacent amorphous regions. Hence, this work provides valuable information for rational design of hydrophobic starch-based films with desired thermal features by simply regulating the amylose content of starch raw materials.

1. Introduction

To address global sustainability, biopolymers, principally being cellulose, hemicellulose, chitin, starch, and lignin, are increasingly selected for the design and development of bio or 'green' materials (Chandra & Rustgi, 1998). Biopolymers are not only widely available and renewable but also can be biodegradable and biocompatible. Starch, a typical biopolymer existed in various plants, has attracted huge interest in cost-effective production of eco-friendly materials for replacing petroleum-based plastics (Siracusa, Rocculi, Santina, Romani, & Rosa, 2009). In particular, starch-based materials have shown their broad utility and versatility in diverse areas, e.g., food package, drug carriers and bioengineering (Tharanathan, 2003). Nevertheless, despite enormous potentials of starch materials, the inherent features of starch such as strong hydrophilicity may limit the application of starch-based products.

Regarding this, chemical modifications have been practiced to tailor the hydrophilicity of starch (Kaur, Ariffin, Bhat, & Karim, 2012; Sandhu, Kaur, Singh, & Lim, 2008). Especially, acylation and esterification are widely used because of the high performance at enhancing

the hydrophobicity of starch and derived starch-based materials. The hydrophobic modification destroys the crystalline structure of starch (Colussi et al., 2014; Garg & Jana, 2011; Luo & Shi, 2012; Whitney, Reuhs, Martinez, & Simsek, 2016) and enhances the thermal stability (Garg & Jana, 2011; Winkler, Vorwerk, & Rihm, 2014; Zhu et al., 2017) and thermoplasticity (Adak and Banerjee, 2016), which advocates the usefulness of the modified starch in food and biopolymer sectors. Besides, the swelling power, water binding capacity and viscosity have been reported to be decreased at a higher DS (degrees of substitution) (Colussi et al., 2014; Garg & Jana, 2011; Luo & Shi, 2012). Since the hydrophobic starch derivatives with high DS ($1.5 < DS < 3$) could be used as bio-based film-forming materials (Luo & Shi, 2012; Winkler et al., 2014), it is important to further explore the structures and thermal behaviors of the starch-based films.

In fact, the native starch granules has a multi-level hierarchical structure, which is assembled by linear amylose or/and hyperbranched amylopectin from molecular to granule levels. These macromolecules with structural differences display characteristic features. For native starch, amylose and amylopectin play different roles to form compact physical granule structure (Hung, Maeda, & Morita, 2007; Jane et al.,

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1999; Schirmer, Hochstotter, Jekle, Arendt, & Becker, 2013; Varatharajan, Hoover, Liu, & Seetharaman, 2010) and crystalline structure (Cheetham & Tao, 1998; Tan, Flanagan, Halley, Whittaker, & Gidley, 2007). Different amylose-amylopectin ratios result in different phase transition behaviors (Liu, Yu, Simon, Dean, & Chen, 2009; Liu, Yu, Chen, & Li, 2007; Liu, Yu, Xie, & Chen, 2006; Xue, Yu, Xiu, Chen, & Li, 2008), rheological properties (Chen, Yu, Kealy, Chen, & Li, 2007; Valle, Vergnes, & Lourdin, 2007; Xie et al., 2009), viscoelasticity (Li, Prakash, Nicholson, Fitzgerald, & Gilbert, 2016a, 2016b; Schirmer et al., 2013), extrusion processing (Li et al., 2011) and in vitro digestion rate (Syahariza, Sar, Hasjim, Tizzotti, & Gilbert, 2013). For starch-based films, the properties, such as mechanical properties, oxygen permeability, water binding capacity *etc.*, also depend on the amylose-amylopectin ratio since the different behavior of these macromolecules contributes to microstructures of starch network (Matta, Silveira, de Oliveira, & Sandoval, 2011). The high content amylose films exhibit higher glass transition temperature, higher tensile strength, higher modulus of elasticity and lower elongation at break (Li et al., 2011; Muscat, Adhikari, Adhikari, & Chaudhary, 2012), and amylose gave rise to films with stiffness, more resistant to fracture, lower oxygen permeability and greater water binding capacity (Cano, Jiménez, Cháfer, González, & Chiralt, 2014). Besides, other materials involved starches also have been discussed. The polyvinyl acetate-starch composites with higher content of amylopectin produced by co-grinding show higher glass transition temperature and water uptake (Bolat & Molina-Boisseau, 2014). Zou et al. (2012) have found that amylopectin reduced the mobility of starch-based biodegradable superabsorbent polymer chains and increased the viscosity. Kim, Patel, and Bemiller (2013) previously revealed that the amylose was a significant determinant of paste and gel properties of the starch-hydrocolloid complex.

Obviously, the fine structure of amylose and amylopectin determine the structure and corresponding properties of starch and end-use starchy products. As for the further development of starch-based films, especially the hydrophobic materials, it is important to understand how the hierarchical structure can be altered by starch structure. However, there are no reported systematic investigations in regard to the effects of amylose or/and amylopectin on the structures and thermal behavior of hydrophobic starch-based films. Our previous work has characterized the multi-level structures of starch acetate film under plasticization (Zhu, Li, Huang, Chen, & Li, 2013), and further studied the relation between plasticizer migration and structural changes of this material (Li et al., 2016; Huang, Zhu, Chen, Li, & Li, 2014; Zhu, Li, Zhang, Li, & Zhang, 2016; Zhu, Li, Huang, Chen, & Li, 2014). Recently, we also reported that propionylated starches prepared from high-amylose starch displayed more ordered region and enhanced thermal stability to greater degree (Zhu et al., 2017).

The polymer network primarily defined the material property of highly plasticized starch film. Based on our previous work, this paper prepared hydrophobic starch-based films with starches from the same source (corn) containing variant amylose contents. In this research, the relation between the multi-scale structures and the thermal behaviors of the films was discussed to reveal how amylose or/and amylopectin tailored the resultant starchy films.

2. Materials and method

2.1. Materials

Commercially available corn starches with different amylose contents were used as model materials, viz.: Waxy ($0.67 \pm 0.07\%$) was supplied by Lihua Starch Co., Ltd. (Qinhuangdao city, China). Maize ($23.74 \pm 0.08\%$) was supplied by Huanglong Food Industry Co., Ltd. (Jilin, China). Gelose 50 (G50, $47.31 \pm 0.05\%$) and Gelose 80 (G80, $81.28 \pm 0.14\%$) were obtained from Penford Australia Pty Ltd. (Lane Cove, NSW, Australia).

The propionylated starches were prepared and DS was determined

according to the recent work (Zhu et al., 2017), viz.: Propionylated Waxy (PW, $DS = 2.61 \pm 0.03$), Propionylated maize (PM, $DS = 2.35 \pm 0.01$), Propionylated G50 (PG50, $DS = 2.40 \pm 0.02$), Propionylated G80 (PG80, $DS = 2.50 \pm 0.03$).

2.2. Preparation of starch-based films

The propionylated starch-based films were prepared by a solvent-cast method using acetone as the solvent (Zhu et al., 2013). 1 g starch ester powder was dissolved in 30 g acetone and was stirred for 4 h. Triacetin (Aladdin Chemistry Co. Ltd., Shanghai, China) used as plasticizer was added in 0, 5, 15 and 30% (w/w, db), and the mixture was stirred for another 2 h. The solution was then cast in a polypropylene mold (casting area. $6 \text{ cm} \times 10 \text{ cm}$). The solvent was allowed to evaporate at 45°C for 12 h. All the films were stored in resealable bags at 4°C and constant humidity (40%).

2.3. Scanning electron microscope (SEM) observation

The cross-section of the prepared films were observed with a EVO 18 scanning electron microscope (Carl Zeiss Microscopy, LLC., Germany) operating at 20.0 kV high voltages. The specimens were frozen under liquid nitrogen and then fractured, mounted, coated with a thin gold film. The observation of magnification is $1000 \times$.

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

The films were cut into strips ($2 \text{ cm} \times 0.8 \text{ cm}$) for SAXS/WAXS experiment using a SAXSess camera (Anton-Paar, Graz, Austria). X-ray generator was operated at 40 kV and 50 mA and provide an intense monochromatic primary beam ($\text{Cu-K}\alpha$, $\lambda = 0.1542 \text{ nm}$). Samples were fixed and placed in a 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 26.0°C . The 2D scattered intensity distribution was recorded by an imaging-plate detector and integrated into the one-dimensional scattering function $I(q)$ as a function of the magnitude of the scattering vector q defined as:

$$q = |\vec{q}| = (4\pi\sin\theta)/\lambda$$

where λ is the wavelength and 2θ is the scattering angle. Each measurement was collected for 10 min. All $I(q)$ data were normalized and desmeared.

2.5. Dynamic mechanical analysis (DMA)

DMA tests were carried out using a Pyris Diamond DMA (Perkin Elmer Inc., USA) under the tensile mode. The analyzer measured the complex tensile modulus E^* , i.e., the storage component E' and the loss component E'' . The ratio between the two components, $\tan\delta = E''/E'$, was also determined. Measurements were performed at 1 Hz, and temperature was increased by steps of 2°C between -100 and $+200^\circ\text{C}$.

2.6. Thermogravimetric analysis (TGA)

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 $10^\circ\text{C}/\text{min}$ in a heating range of $30\text{--}510^\circ\text{C}$. Nitrogen was used as the purge gas at a flow rate of $20 \text{ mL}/\text{min}$.

2.7. Statistical analysis

The DMA and TGA data were analyzed using SPSS 22.0 Statistics software (IBMCo., New York, USA). Analysis of variance (ANOVA) was

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