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Multi-scale structural changes of starch-based material during microwave and conventional heating

Jie Zhu [a,*], Lin Li [b], Shuyan Zhang [b], Xiaoxi Li [b], Binjia Zhang [c]

[a] College of Chemistry and Environmental Engineering, Dongguan University of Technology, Dongguan 523808, China
[b] 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 Light Industry and Food Sciences, South China University of Technology, Guangzhou 510640, China
[c] College of Food Science and Technology, Huazhong Agricultural University, Wuhan 430070, China

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ABSTRACT

This work revealed the influence of thermal processing on the microstructural, mesoscopic and molecular scale structures and thus the plasticizer migration of the starch ester films. Thermal processing promoted the permeation of water molecules to hinder the shrink of the amorphous macromolecules. That is, the swelling of the amorphous macromolecules diminished the ordered regions to a certain degree, resulting in the enlarged amorphous regions. Along with slight degradation of the macromolecules, the crystallites were partially disorganized, as indicated by a reduced relative crystallinity. These multi-scale structural changes of the films and the thermally enhanced mobility of plasticizer molecules synergistically enhanced the plasticizer migration. This study not only enables a well understanding of how thermal treatment alters the plasticizer migration of starch-based films from a multi-scale structural view, but also hints to our future work that rationally modulating the structural features of starch-based film may effectively control the migration of chemicals.

1. Introduction

Due to the environmental concerns and the shortage of fossil resources, starch and other biopolymers have been used as replacements for synthetic polymeric plastics in the food industry following various modifications and processes [1]. However, starch-based materials are known to have tremendous limitations such as poor processability and properties due to the intense macromolecular interaction of starch [2,3]. With the introduction of plasticizer, the major drawbacks in the application of starch-based materials are overcome to a great extent [4,5]. The gelatinization occurs with plasticizer and elevated temperature, which results in the disruption of the net-like structure of native starch to generate the homogeneous amorphous thermoplastic starch [6,7].

For starch-based materials, the content of plasticizer affects the crystalline structure and the formation of an entangled starch matrix with starch chain-to-chain associations [8], and further causes the changes of the available packaging performance [9,10]. The multi-scale structure within the starch-based film matrix, including the crystalline structure and the amorphous region, could be affected by increasing the addition of plasticizer [11,12]. However, the migration of plasticizer and other chemicals from food packaging materials is inevitable, which has been demonstrated for years [13]. The decrease of plasticizer content due to the migration could cause relevant structural changes and subsequent reduction of protect function [14]. In addition, the absorption of food systems could give rise to the swelling of the polymer matrix [15,16].

The thermal processing including microwave technology has gained acceptance in domestic usage and is gaining popularity in industrial applications [17–19]. However, the thermal processing could accelerate the migration of chemicals from the packaging materials [20–22]. The food-packaging interactions and the structure of the packaging material were also affected to get changed [23]. Siripatrawan et al. [24] have characterized that the degree of crystallinity of the polypropylene as package material was increased after the repeatedly heated in the microwave oven, resulting to the decrease in the impact resistance. Other researchers have found that the microwave heating caused the significant polymer degradation, and consequently increased the specific migration from the packaging materials matrix [21,22]. From the point of view of the structure-property relation, the multi-scale structural changes of the packaging material determine the migration of chemicals from the material matrix [16,25]. In this

* Corresponding author at: No. 1, Daxue Rd., Songshan Lake, Dongguan, Guangdong Province, China.
E-mail address: zhujie@dgut.edu.cn (J. Zhu).

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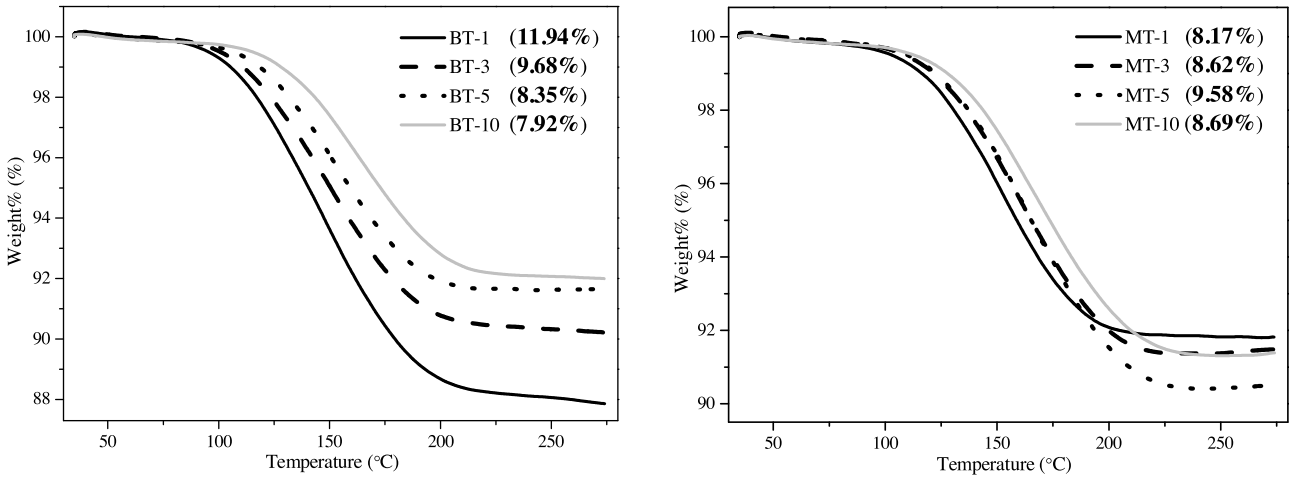

Fig. 1. TG curves of starch ester films heated with boiling water and microwave.

research, we attempted to acquire the relationship between the structural changes and the plasticizer migration of the starch-based films during thermal processing. The findings from the present study enable a well understanding of the reasonable design of the novel starch-based materials for the food packaging application.

2. Materials and methods

2.1. Materials

Starch ester (DS = 2.49) was prepared by acetyl esterification from native starch G50 (Penford, Australia) according to our previous study [26,27]. Triacetin (AR, M_w = 218.20) was purchased from Aladdin Chemistry Co. Ltd. (Shanghai, China) and applied as plasticizer. Distilled water was selected as heating medium (food simulant for water-based products) [28].

2.2. Film preparation and thermal processing

Starch ester film with 30% triacetin content (w/w, starch acetate db) was prepared by a solvent-cast method using acetone as the solvent [11]. The thickness of the film (83.6 ± 7.4 μm) was measured using micrometer caliper. According to the ratio between contact area of packaging material and food volume (1:5) described in American Society for Testing and Materials (ASTM) standard D4754-11 [29], starch ester film (2 × 0.7 cm^2) was immersed in 7 mL boiling distilled water for 1, 3, 5 and 10 min, which was defined as conversational thermal processing. A microwave heating device Ethos Sel (Milestone, Italy) (maximum power 1000 W) was used to heat the starch ester film with the same size immersed in 7 mL distilled water in the vessels. The samples were heated from 30 °C to 100 °C within 1 min, 3 min, 5 min and 10 min according to the procedure, respectively. Then the water on the surface was wiped out, and the films were stored in resealable bags at constant temperature (26 °C) and humidity (40%) for 24 h before analysis.

In the following, codes typically as BT-10 and MT-10 will be used, in which "BT" and "MT" mean thermal processing with boiling water and microwave, respectively, and "10" means the treatment time (min).

2.3. Thermogravimetric analysis (TGA) test

The change of triacetin content within the film was obtained according to the weight loss of the film in thermogravimetric analysis 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. Nitrogen was used as the purge gas at a flow rate of 20 mL/min. According to the determined thermal stability of triacetin, the migration quantity of triacetin was monitored until the equilibrium at 250 °C was attained.

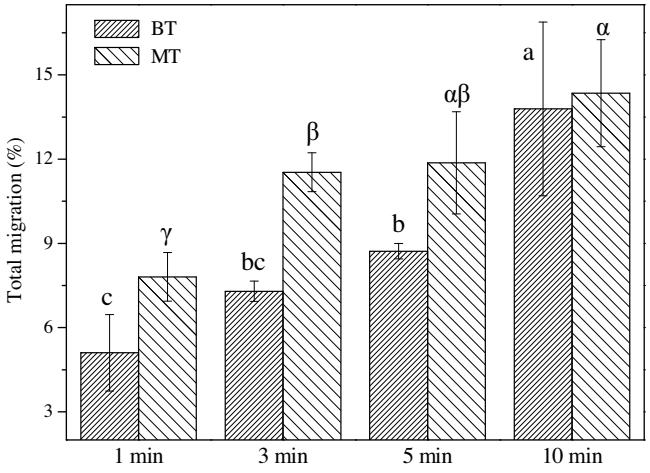

Fig. 2. Total migration of starch ester films heated with boiling water and microwave. Data are means of three replications; means with the same letter are not significantly different ($p < 0.05$).

2.4. Total migration of starch ester film

The total migration of treated starch ester film was analyzed by calculating the mass changes of the film after thermal treatment with the electronic scale (0.00001 g, BP211D, Sartorius, Germany). The migration rate (M%) was calculated with the following eq:

$$M\% = \frac{M0 - M1}{M0} \times 100\%$$

where M_0 is the weight of the initial film and M_1 is the weight of the treated film.

2.5. Scanning electron microscope (SEM) observation

The cross-section of the treated starch ester films were observed with a EVO 18 scanning electron microscope (Carl Zeiss Microscopy,