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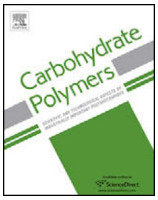

Interfacial modification on polyhydroxyalkanoates/starch blend by grafting *in-situ*

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ABSTRACT

The interfacial adhesion between polyhydroxyalkanoates (PHAs) and native starch is poor. To improve the interfacial adhesion, PHAs were *in-situ* grafted onto starch using dicumyl peroxide (DCP) as a free radical initiator. The grafting reaction was carefully characterized and confirmed by gel analysis and Fourier transform infrared spectroscopy (FT-IR). The gel yield of the PHAs/starch/DCP blend increased with the DCP concentration up to 2 wt%. Meanwhile, obvious plastic deformation (stretched fibrils) was observed at the interface in the PHAs/starch/DCP blend in comparison with complete interfacial debonding in the PHAs/starch physical blend. The improved interfacial adhesion after grafting was further confirmed by a reduction in adhesion factor (A_f) obtained from dynamic mechanical analysis (DMA). The mechanical strength and the crystallization rate of the PHAs were deteriorated after incorporation of starch, and were backed up by the interfacial improvement. A linear relationship between the mechanical properties and the gel yield was discovered. In addition, the PHAs/starch/DCP blend exhibited higher decomposition active energy (E_a) and thus better thermal stability in comparison with the PHAs and the PHAs/starch physical blend. Therefore, this study provides a simple route to utilize low-cost starch as a component in biopolymer blend.

1. Introduction

Moldable, lightweight and strong plastics are used widely enhancing the quality and convenience of our lives. However, at least 40% of these traditional petroleum-based plastics are used in short-run applications such as supermarket bags, sanitary cups and utensils, and after being disposed the resulting wastes quickly lead to both terraneous and marine environmental pollution (Chen & Patel, 2011; Halden, 2010). In brief, the environmental issues drive the efforts to more environmentally friendly plastics and materials. The most commonly eco-friendly plastics from renewable resources include polyhydroxyalkanoates (*e.g.*, polyhydroxybutyrate), poly(lactic acid) (PLA), thermoplastic starch, protein plastics (*e.g.*, soy protein plastics), cellulose derivatives and so on (Garlotta, 2001; Mekonnen, Mussone, Khalil, & Bressler, 2013). PHAs have attracted special interests due to the bacterially synthesized and fully degradable characters. However, PHAs still have some shortages such as the low melt elasticity, poor thermal stability, brittleness, low crystallization rate and high cost (Lunt, 1998; Rasal, Janorkar, & Hirt, 2010; Yamaguchi & Arakawa, 2006). Comprehensive application of PHAs may occur after overcome some shortages.

Blending PHAs with other materials is an effective and frequently-used way to overcome these shortages. In recent years, PHAs-based biopolymer blend has been successfully fabricated by blending with starch and lingo-cellulosic biomass such as wood flour, coir fiber, wheat straw and bamboo fiber *via* melt extrusion or injection molding (Berthet, Gontard, & Angellier-Coussy, 2015; Fernandes, Pietrini, Chiellini, 2004; Javadi et al., 2010; Singh, Mohanty, Sugie, Takai, & Hamada, 2008; Srubar et al., 2012).

Starch, one of the most abundant natural products, has been regarded as a promising biopolymer due to its low cost, low density, biodegradability, and so on. Starch is primarily composed of amylose and amylopectin. Amylose is a largely linear polymer of α-1,4-linked glucose units, with a small number of long-chain branches, while amylopectin is a highly branched polymer of α-1,4-linked chains connected by 1,6-linkages (Whistler, Bemiller, & Paschall, 1984). Griffin in 1975 pioneered to blend granuliform starch with plastics materials (Griffin, 1975). Unfortunately, native starch generally exists in a granuliform state because of the inherent hydrogen bonding between adjacent molecules. This in turn

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fails to disperse starch in an extremely fine scale of size into the plastic matrix. Efforts to solve this problem have led to the recent progress of thermoplastic starch (TPS) prepared by mixing appropriate amounts of plasticizers, a process termed "gelatinization" (Wittwer & Tomka, 1987). The mechanical properties had been considerably improved for traditional plastics to blend with gelatinized or TPS since then (Bikiaris & Panayiotou, 1998), however, a complete degradability of the resulting blends was often questioned. Thus, numerous works have been moved to the blending of starch with biodegradable polymers including PLA (Park, Im, Kim, & Kim, 2000), polycaprolactone (John, Tang, Yang, & Bhattacharya, 1997; Wu, 2003), poly(butylene succinate) (Lai, Huang, & Shen, 2005; Mani & Bhattacharya, 2001), and PHA (Godbole, Gote, Latkar, & Chakrabarti, 2003; Innocentini-Mei, Bartoli, & Baltieri, 2003; Koller & Owen, 1996). However, it is still a challenge to fine disperse starch into the polymeric matrix because of the poor interfacial adhesion.

Therefore, we intend to explore a straightforward approach in this paper to improve the interfacial adhesion and consequently the performance of PHAs/starch blend *via in-situ* peroxide-induced grafting. The mechanism of grafting reaction was carefully characterized and confirmed.

We assume that PHAs was grafted *in-situ* onto starch using dicumyl peroxide as a free radical initiator and the chemistry grafting would not only improve the interfacial adhesion but also the physical and mechanical properties.

To the best of our knowledge, the *in-situ* grafting in the PHAs/starch blend is not well applied and understood yet, although it is eco-friendly and economic since it is just with minor amount of chemicals. Moreover, neither special equipment nor extra purification is required, thus it may be easily scaled up. This reported approach may enable a wider utilization of low-cost starch in biopolymer blend.

2. Experimental section

2.1. Materials

Bacterially synthesized poly(3-hydroxybutyrate) (PHB, containing ~1 mol% of hydroxyvalerate) with a M_w of 350 KDa was provided by Tianan Biopolymer Inc., Ningbo, China. Bacterially synthesized poly(3-hydroxybutyrate-co-4-hydroxybutyrate) (P3HB4HB containing 10 mol% of 4HB) with a M_w of 750 KDa were provided by Ecomann Biologic Technology Inc., Shenzhen, China. In order to get balanced physical properties, a mixture of the PHB and the P3HB4HB with a weight ratio of 60/40 was used and marked as PHAs in this work. Native corn starch with an initial moisture content of 10 wt% was obtained from Changchun Dacheng Industrial Group Co., Ltd., Changchun, China. Dicumyl peroxide (DCP, 98% purity) was received from J&K Chemical Ltd., Shanghai, China. Phenol, acetone, dimethylsulfoxide and 1,1,2,2-tetrachloroethane were HPLC grade and used as received. All materials were used as received. The detailed information of the chemicals was listed in Table S1.

2.2. PHAs/starch blend preparation

To make a better dispersion of DCP in PHAs and starch, a small amount of DCP was physically coated on the surface of PHAs and starch, respectively, prior to the melt compounding. The coating process was schematically illustrated in Fig. S1. Taking PHAs/DCP-0.5 for example, 50 g PHAs were first dispersed in an acetone solution of DCP (2.5 mg/mL, 100 mL) under stirring, and then acetone was evaporated and vacuum dried prior to melt processing to get DCP-coated PHAs. The DCP-coated starch was prepared by using the same way. The DCP contents in the PHAs, starch and their blends were shown in Table 1.

PHAs/starch blend with different amount of DCP (marked as PHAs/starch/DCP-i, where i indicates the weight percentage of DCP) was prepared by compounding 45 g of the DCP-coated PHAs and 5 g of the DCP-coated starch (*i.e.*, 90/10, wt/wt) in a Haake mixer (HAAKE Polylab-OS, Germany) at 170 °C for 8 min. The rotation speed was fixed at 50 rpm. Thus, 50 g materials were used in total for each sample preparation, and the yield of each sample was almost 100%. Then, the samples were compression molded into sheets with 1 mm (and 0.5 mm) in thickness at 170 °C for 3 min. The shape and thickness of the sheets were determined by the mold without accurate measurement since they are not important parameters to the further characterizations. For comparison, PHAs, PHAs/DCP-0.5 and PHAs/starch blend without DCP (noted as PHAs/starch) were also prepared under the same conditions. The compression molded samples were used for characterizations.

2.3. Gel fraction

The gel yields of the PHAs/starch/DCP blends were measured *via* solvent extraction to determine the extent of grafting as a function of DCP content. The samples (~1 g) were immersed in a solvent mixture (phenol/1,1,2,2-tetrachloroethane 1/1, wt/wt, 100 mL) for 24 h to swell and dissolve non-reacted PHAs, and then filtered through a nylon screen (200 μm openings) to collect the pre-product. The pre-product was then dissolved with dimethylsulfoxide to remove the non-reacted starch and filtered to collect the final product. The final product (free of non-reacted starch and PHAs) was washed and dried in vacuum to a constant weight, which was defined as "gel" in this work. The gel yield was calculated as:

$$\text{gel} = W_{gel}/W_0 \times 100 \tag{1}$$

where W_{gel} and W_0 are the dry weights of extracted gel and the initial sample prior to extraction, respectively.

2.4. Mechanical properties

Tensile properties of all samples were measured in accordance with ISO 527 at room temperature by using a tensile tester (Instron 5967, Instron, US). The crosshead speed was 10 mm/min and five replicates of each sample were tested. The averaged values and standard deviation were presented.

DMA (Q800, TA Instruments, US) measurement on all samples was carried out in a tensile-film mode. The samples ($15 \times 5.3 \times 0.5\ \text{mm}^3$) were tested from 30 °C to 150 °C at 2 °C/min. The amplitude and frequency were set as 20 μm and 1 Hz, respectively. Storage modulus and *Tan* δ were measured as a function of temperature for each sample.

2.5. Fourier Transform Infrared Spectroscopy (FT-IR)

The samples were analyzed on FT-IR spectrometers (Nicolet 6700, Thermo Fisher Scientific, US) in an attenuated total reflection mode (ATR). The final spectrum of each sample was an average of 64 scans at a resolution of 2 cm^{-1} in the wavenumber range of 400–4000 cm^{-1}.

2.6. Scanning electron microscopy (SEM)

The microstructure of the samples was observed by using a scanning electron microscope (S-4800, HITACHI, Japan) at an accelerating voltage of 1 kV. The cryo-fractured surfaces of the samples were coated with a thin gold layer before the observation.