



Morphology and mechanical properties of poly(butylene adipate-co-terephthalate)/potato starch blends in the presence of synthesized reactive compatibilizer or modified poly(butylene adipate-co-terephthalate)

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ABSTRACT

The biodegradable poly(butylene adipate-co-terephthalate)(PBAT)/thermoplastic starch (TPS) composite has received considerable attention because of the environmental concerns raised by solid waste disposal. However, the application of PBAT/TPS blends was limited due to the poor mechanical properties originating from the incompatibility between PBAT and TPS. In this work, two approaches were developed to improve the mechanical properties of PBAT/TPS blends. One approach is to use compatibilizers, including the synthesized reactive compatibilizer – a styrene–maleic anhydride–glycidyl methacrylate (SMG) terpolymer, and the commercial compatibilizer (Joncryl-ADR-4368). The chemical structures of SMG were analyzed with ¹H NMR and FT-IR. The other approach is to use the modified PBAT (M-PBAT) to replace part of PBAT in the PBAT/TPS blends. M-PBATs with higher molecular weight were obtained via reactive extrusion of PBAT in the presence of a chain extender. The better dispersion of TPS in PBAT was observed in SEM images when using M-PBAT, leading to the higher tensile strength and elongation at break of PBAT/TPS blends. However, the elongation at break decreased in the presence of compatibilizer (SMG or 4368), though the tensile strength remained in a similar level or slightly higher. Overall, the tensile strength and the elongation at break of the resulting biodegradable PBAT/M-PBAT/TPS blends (TPS = 40 wt%) were above 27.0 MPa and 500%, respectively, which is promising for various applications, including packaging and agricultural mulching films.

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1. Introduction

Because of the significant environmental concerns over solid wastes, the sustainability, industrial ecology, biodegradability and recyclability are becoming major consideration in the package products, especially in the disposable packaging, and in the agricultural mulching film. Biodegradable polymeric materials (BPMs) become an ideal choice in these applications. There is a strong market need to develop biodegradable plastic packaging products and mulching films, which can be safely and effectively disposed in soil or in compost (eco-friendly), but retaining the satisfied performance.

According to the raw materials, BPMs can be distinguished based on renewable or petrochemical sources. Poly(butylene adipate-co-terephthalate) (PBAT), an aromatic–aliphatic copolyester, is a typical example of BPMs from petrochemical resources (Witt, Yamamoto, Seeliger, Müller, & Warzelhan, 1999). The physical and mechanical properties of PBAT are close to those of polyethylene. However, the application of PBAT in some fields is limited due to the high cost.

Starch, an example of BPMs from renewable resources, has been considered as a polymer with a high potential to be blended with synthetic biodegradable polymers to reduce cost in the past years (Stagner, Alves, & Narayan, 2012). Thermoplastic starch (TPS) is often applied in the polymer blends, where the starch granules are plasticized using plasticizers (such as water or glycerol) under heating. So far a number of research have focused on the PBAT/TPS composites (Brandelero, Grossmann, & Yamashita,

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2011; Brandelero, Grossmann, & Yamashita, 2012; Brandelero, Yamashita, & Grossmann, 2010; Garcia et al., 2014; Hablot et al., 2013; Mohanty & Nayak, 2010; Nayak, 2010; Olivato, Grossmann, Yamashita, Eiras, & Pessan, 2012; Olivato, Grossmann, Bilck, Yamashita, & 2012; Olivato et al., 2011; Olivato et al., 2013; Raquez, Dubois, & Narayan, 2005; Raquez, Nabar, Narayan, & Dubois, 2008; Silva et al., 2013; Stagner & Narayan, 2011). However, the incompatibility between the hydrophilic starch and the hydrophobic biodegradable polyester PBAT resulted in the poor mechanical properties of PBAT/TPS composites, such as tensile strength, compressibility, resilience, and flexibility. Developing a blend with satisfied overall physicochemical behavior depends on the ability to control the interfacial tension, in order to generate a uniformly dispersed phase size and strong interfacial adhesion, which is able to improve the stress transferring between the component phases (Raquez et al., 2005).

The compatibilizer has been mostly used to improve the interfacial adhesion between PBAT and TPS, and to further enhance the mechanical properties of PBAT/TPS blends. Maleated TPS (MTPS) (Hablot et al., 2013; Raquez et al., 2008; Stagner et al., 2012), maleated PBAT (Mohanty & Nayak, 2010; Raquez et al., 2005), soybean oil (Brandelero et al., 2012), adipic acid (Silva et al., 2013), tartaric acid (Olivato et al., 2013), maleic anhydride and citric acid (Olivato, Grossmann, & Yamashita, 2012; Olivato, Grossmann, & Bilck, 2012; Olivato et al., 2011) are the typical compatibilizers used in PBAT/TPS blends. It seems that the anhydride group of maleic anhydride, the epoxy group of GMA, the carboxyl group of acrylic acid and citric acid are efficient in the improvement of the mechanical properties of PBAT/TPS blends. However, MTPS had lower molecular weight compared to TPS because of some hydrolysis and glucosidation reactions (Raquez et al., 2008). Also, the grafting efficiency of MA onto PBAT was relatively low in the maleated PBAT (Raquez et al., 2005). Acids in small molecules have the ability to promote the esterification or transesterification reactions in the PBAT/TPS system, which might further improve the compatibilization between PBAT and TPS, or have a chance to decrease the molecular weight of PBAT.

In this work, we focused on improving the mechanical properties of PBAT/TPS blends using two different approaches. One approach is to use the synthesized reactive terpolymers (marked as SMG), containing anhydride group and epoxy group, as the compatibilizer, to improve the interfacial adhesion between PBAT and TPS. It is reasonable to expect that the compatibilization between PBAT and TPS would be improved by the reactions between the anhydride and epoxy groups of SMG with the hydroxyl groups of TPS and the carboxyl groups of PBAT, respectively. The other approach is to use the modified PBAT (M-PBAT) to replace part of PBAT in the PBAT/TPS blends, which changes the PBAT/TPS blends into the PBAT/M-PBAT/TPS blends. Different types of M-PBATs were prepared via reactive extrusion in a twin-screw extruder using the different chain extenders, such as 2,2'-(1,3-phenylene)-bis(2-oxazoline) (PBO), poly(propylene glycol) diglycidyl ether (PPGDE), or Joncryl-ADR-4368 (a commercial compatibilizer). The molecular weights of M-PBATs were expected to be higher than that of the original PBAT, and consequently resulted in a better dispersion of TPS in the PBAT/M-PBAT/TPS blends, and the improvement of the mechanical properties.

2. Experiments

2.1. Materials

Potato starch (food grade) and poly(butylene adipate-co-terephthalate) (PBAT)(Ecoflex BASF) were kindly provided by Aroostock Co. (Maine, USA) and Al Pack Co. (Moncton, Canada),

respectively. Styrene (St), maleic anhydride (MA), glycidyl methacrylate (GMA), butanone, petroleum ether, deuteriochloroform (CDCl_3), benzoyl peroxide (BPO), poly(propylene glycol) diglycidyl ether (PPGDE, number-average molecular weight 640), and glycerol were purchased from Sigma-Aldrich. 2,2'-(1,3-phenylene)-bis(2-oxazoline) (PBO) was purchased from TCI America. The commercial compatibilizer (Joncryl-ADR-4368) was provided by BASF America. St-MA-GMA terpolymers (SMG) were synthesized using free radical copolymerization. The chemical structures of PBAT, PPGDE, PBO, Joncryl-ADR-4368 and SMG are shown in Fig. 1.

2.2. Synthesis and characterization of St-MA-GMA (SMG) terpolymers

A typical preparation process is as follows: according to the designed molar ratio, St, MA, GMA and BPO were added to a three-neck flask under constant stirring, followed by adding 2.5 times volume of butanone as the solvent, stirring, and nitrogen bubbling to remove oxygen for 20 min. The system was heated and remained at $69.0 \pm 1.0^\circ\text{C}$ until the polymerization reaction ended. The product solution was precipitated using petroleum ether. After removing the solvent by filtering, the sample was dried under vacuum to a constant weight. The obtained terpolymer was marked such as SMG₉₀₀₁₀₉ (the subscript representing $n_{\text{St}}:n_{\text{MA}}:n_{\text{GMA}} = 90.0:1.0:9.0$). A series of terpolymers with different molar ratios were further synthesized.

The FTIR spectra of the terpolymers were obtained by scanning from 400 cm^{-1} to 4000 cm^{-1} using a Perkin-Elmer model 2000 FTIR. Terpolymer samples and KBr were mixed and ground in the mortar before scanning.

The terpolymer was dissolved in CDCl_3 and the concentration ranged from 12 mg/ml to 20 mg/ml. The ^1H NMR spectra were recorded using a Varian Unity 400 spectrometer operated at 300 MHz.

2.3. Preparation and GPC test of modified PBAT (M-PBAT)

The preparation of M-PBAT was conducted in the ZSK 18 MEGAlab laboratory extruder system (twin-screw extruder, D : 18 mm, L/D : 40:1, Coperion). The weight ratio of PBAT to the chain extender (PPGDE, PBO or 4368) was fixed at 100.0:1.0. The screw speed was set at 150 rpm. The temperature profile was $90/110/130/155/170/180/170^\circ\text{C}$ from the barrel to the die. The extrudate was cooled in the water, and dried in the oven at 80°C for at least 4 h.

Molecular weight was determined by dissolving SMG and PBAT samples in tetrahydrofuran (THF) and then injecting the sample solution into a multi-measurement gel permeation chromatograph (GPC, Waters Model 244). The GPC was equipped with the Wyatt Technology DAWN EOS small-angle light scattering (LS) and differential refractometer (DRI) detectors. The measuring range of the molecule weight was from 10^3 to 10^6 . THF was used as the eluent, with a sample content of 5–15 mg/ml, and the test was carried out at 25°C .

2.4. Preparation of different PBAT/TPS films

The preparation of TPS is as follows: the plasticization of starch was conducted in the same extruder system. The weight ratio of potato starch:glycerol:water was fixed at 100:30:20. The screw speed was set at 150 rpm. The temperature profile was $80/100/120/135/155/175/165^\circ\text{C}$ from the barrel to the die. The extrudate was cooled in air, and then sealed to prevent the moisture.

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