



Preparation, characterization and properties of binary and ternary blends with thermoplastic starch, poly(lactic acid) and poly(butylene adipate-co-terephthalate)

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ABSTRACT

Binary and ternary blends of thermoplastic starch (TPS), poly(lactic acid) (PLA) and poly(butylene adipate-co-terephthalate) (PBAT) were prepared using a one-step extrusion process. The concentration of TPS in both binary and ternary blends was fixed at 50 wt%, with the rest being PLA and PBAT. A compatibilizer with anhydride functional groups was used to improve the interfacial affinity between TPS and the synthetic polyesters. The addition of a small amount of compatibilizer greatly increased the mechanical properties of the blends. Mechanical properties of the blends exhibited a dramatic improvement in elongation at break with increasing PBAT content. Compared to the non-compatibilized blends, the morphology analysis of the blends showed that most of the TPS particles were melting and were well dispersed in the polyester matrix for the compatibilized blends. The water absorption data of the non-compatibilized blends increased more significantly than the compatibilized blends when PBAT content increased.

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1. Introduction

As people's growing concern for environmental protection, biodegradable materials have attracted considerable attention as interesting sustainable plastics. Starch is a naturally occurring biopolymer that can be extracted from many crops including corn, wheat, rice, potato and so on (Tester & Karkalas, 2002). As an inexpensive and renewable source, it has been used as filler (Chandra & Rustgi, 1997; Griffin, 1977; Tang, Zou, Xiong, & Tang, 2008a) for environmentally friendly plastics for about three decades. However, native starch has to be modified in order to be melt-processed as a thermoplastic because the melting temperature (T_m) of pure dry starch is close to 220–240 °C and the onset temperature of starch degradation is around 220 °C (Sarazin, Li, Orts, & Favis, 2008; Souza & Andrade, 2002; Stepto, 2003).

In order to obtain thermal plastic starch (TPS), both physically and chemically methods of modification of starch have been widely studied. Physical modification of starch can be prepared by extrusion using various plasticizers (Da Roz, Carvalho, Gandini, & Curvelo, 2006; Forssell, Mikkila, Suortti, Seppala, & Poutanen, 1996; Graaf, Karman, & Janssen, 2003; Ma, Yu, & Wan, 2006). Water (Teixeira, Da Roz, Carvalho, & Curvelo, 2007) and glycerol

(Tang, Alavi, & Herald, 2008b) are two of the most widely used plasticizers. The role of plasticizers is to destructure granular starch by breaking hydrogen bonds between the starch macromolecules, accompanying with a partial depolymerization of starch backbone. Chemical modification of starch such as esterification (Raquez et al., 2008) is the other well known methods to get TPS. Acetylated starch that can be obtained through changing part of the hydroxyl groups into acetyl groups has been extensively studied over the last two decades (Reinisch, Radics, & Roatsch, 1995; Wang & Wang, 2002). Although various methods have been tried to modify native starch in the last few years, it is still difficult to completely overcome its moisture absorption nature and poor mechanical properties of the final products.

Polymer blending is an important way to obtain new materials that can meet different needs. Blending of TPS with other polymers represents an important route to overcome the limitations of TPS. Poly(lactic acid) (PLA), which is a hydrophobic and semicrystalline polyester, is a renewable material that can be utilized by microbes within 30–40 days (Hakkarainen, Karlsson, & Albertsson, 2000; Itavaara, Karjomaa, & Selin, 2002). Its good physical properties and commercial availability make it very attractive, not only as a substitute of non-biodegradable polymers for commodity applications, but also for specific applications in medicine and in agricultural areas. The main limitation of PLA is its high price which caused by its complicated production process. Blending of PLA with TPS is a good way to balance the cost-effective issue and get a new material that has good performances. However, previous studies

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have shown that TPS/PLA blend have rather poor mechanical properties due to the poor interfacial affinity of starch and PLA (Ke & Sun, 2000; Kim, Chin, Yoon, Kim, & Jung, 1998; Ren, Liu, & Ren, 2007; Wang, Yu, Chang, & Ma, 2008). Thus, compatibility is the vital problem that has to be dealt with when blending hydrophilic starch granules and hydrophobic PLA together. In order to increase the interfacial adhesion between TPS and PLA, polymers having functional groups capable of interacting with the hydroxyl groups on starch are desirable. Huneault and Li (2007) found that MAH-grafted PLA/starch blend showed much finer dispersed phase and exhibited a dramatic improvement in ductility than pure PLA/starch blend. Wu (2005) found that acrylic acid grafted PLA and starch composite had much better mechanical and thermal properties than PLA/starch blend. Bhattacharya et al. prepared starch/synthetic polymer blends by injection moulding and studied the effect of processing parameters on blends physical properties (Ramkumar, Vaidya, Bhattacharya, & Hakkarainen, 1996), evaluation of mechanical properties (Ramkumar, Bhattacharya, & Vaidya, 1997), effect of amylopectin on amylose ratio in starch (Mani & Bhattacharya, 1998a), thermal and morphological properties (Mani & Bhattacharya, 1998b). Their research showed that maleated synthetic polymers such as SMA, EPMA and EVAMA are effective compatibilizers for starch/synthetic polymer blends.

Sarazin et al. (2008) studied binary and ternary blends with PLA, polycaprolactone (PCL) and TPS, it was found that the addition of PCL greatly increased the ductility of PLA/TPS blends. So blending PLA/TPS binary blend with another flexible polymer could be a useful way to obtain a new kind of materials with excellent integrated performances. Poly(butylene adipate-co-terephthalate) (PBAT) is a flexible copolyester which can fully degrade within a few weeks with the aid of naturally occurring enzymes. PLA/PBAT blends were studied by Jiang, Wolcott, and Zhang (2006). The blends showed decreased tensile strength and modulus, however, elongation and toughness dramatically increased. The failure mode changed from brittle fracture of the neat PLA to ductile fracture of the blends. In this respect, PBAT could be considered as a good candidate for the toughening of rigid polymers such as TPS/PLA binary blend.

Here, TPS/PLA/PBAT binary and ternary blends were prepared via a one-step melt-processing. Then, the morphology and properties of both compatibilized and non-compatibilized blends were investigated. To keep the study manageable the TPS content of the blend was fixed at 50% by weight, the remaining being the synthetic polymers PLA and PBAT which were varied in different ratios. One anhydride functionalized polymer which has very high content of maleic anhydride was used as compatibilizer, and for the compatibilized blends its content was fixed at 1 wt% of the blends.

2. Experimental

2.1. Materials

The following materials were obtained from commercial suppliers and used as received. The corn starch was supplied by Ju-Neng-Jing Corn Co., Ltd. (Shandong, China). Poly(lactic acid) (PLA, $M_w = 180,000$, $M_w/M_n = 1.7$, L/D isomer ratio is $\sim 96:4$, $T_g = 58$, $T_m = 155$ °C) was supplied by Tong-Jie-Liang Biomaterial Co., Ltd. (China). Poly(butylene adipate-co-terephthalate) (PBAT, $T_g = -29$ °C, $T_m = 110-115$ °C, Ecoflex F BX 7011) was supplied by BASF.

2.2. Processing

TPS can be obtained by processing granular starch at low water or other plasticizer content using thermal and mechanical forces (Myllarinen, Partanen, Seppala, & Forssell, 2002). In this paper,

TPS was prepared by a high speed mixer (SHR-10A, 2880 r/min, Zhong-Yun machinery Co., Ltd., China) in the following proportions: 80 wt% of starch and 20 wt% of glycerol. The mixing time was kept at 20 min and the temperature of the mixer was kept at 120 °C. TPS/polyester binary and ternary blends were prepared by melt mixing TPS, PLA and PBAT using a twin-screw extruder (F: 27 mm, L/D: 40, LEISTRITZ: Germany). The compositions of the blends are shown in Table 1. Before extrusion, PLA and PBAT pellets were dried under vacuum at 60 °C for 12 h, respectively. The extrusion temperature was independently controlled at eight zones along the extruder barrel and a strand die to achieve a temperature profile in the range of 155–175 °C. The screw speed was set at 80 rpm and feed rate was 30 g/min.

Injection moulding was accomplished in a JN55E injection moulding machine (Ning Bo Zhen Xiong Machinery Co., Ltd., China). Test specimens for tensile testing were obtained according to GB1040-79 (China). The binary and ternary blends follow the following processing conditions: barrel temperature 170 °C, mould temperature 30 °C, back pressure 4 MPa, and injection pressure 12 MPa. All samples were conditioned at room temperature at 50% relative humidity for at least 2 weeks before testing.

2.3. Mechanical properties

All the mechanical property measurements were performed at room temperature on injection moulded blends. Both tensile and flexural properties were measured on a tensile testing machine (DXLL-5000, Shanghai D&G Instruments Co., Ltd., China) according to GB1040-79 (China). A crosshead speed of 5 mm/min was used. At least five specimens were used for each blend condition.

2.4. Blend morphology and image analysis (SEM analysis)

Impact samples were gold coated and observed under a Hitachi S-2360 N scanning electron microscope (SEM).

2.5. Melt flow index (MI)

MI measurements of various blends were obtained using a model MI-1 plastometer (Tanhor, RZY-400, China). The test was carried out according to GB/T 3682-2000 (China).

2.6. Vicat softening temperature (VST)

A Vicat softening temperature testing machine (SWB-300C/D, Si-Yu-Da Co., Ltd., China) was used to measure the VST of the blends. Test specimens for VST testing were obtained according to GB1633-79 (China).

Table 1
Compositions of various TPS/polyester blends.

Samples	TPS	PLA	PBAT	Compatibilizer
nc-PBAT0	50	50	–	–
nc-PBAT10	50	40	10	–
nc-PBAT20	50	30	20	–
nc-PBAT30	50	20	30	–
nc-PBAT40	50	10	40	–
nc-PBAT50	50	–	50	–
c-PBAT0	50	50	–	1
c-PBAT10	50	40	10	1
c-PBAT20	50	30	20	1
c-PBAT30	50	20	30	1
c-PBAT40	50	10	40	1
c-PBAT50	50	–	50	1

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