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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.

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 destructurize 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 & Bhattachazya, 1998a), thermal and morphological properties (Mani & Bhattachazya, 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 ~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

2.7. Dynamic mechanical analysis (DMA)

Dynamic mechanical properties were determined as a function of temperature using a DMA testing machine (Q800, TA Instruments) in three-point bending mode. The sample size was 60 × 10 × 3.9 mm, prepared by hot compression moulding with 3 MPa at 160 °C for 3 min using a Flat Sulfuration Machine. The test was carried out in a single cantilever bending mode at a frequency of 3.33 Hz and a strain of 2 N, corresponding to a maximum displacement amplitude of 30 μm. The range of temperature was from 30 to 120 °C. The standard heating rate was 3.0 °C/min.

2.8. Water absorption

The moulded samples (size: 10 × 10 × 4 mm) were immersed in water at room temperature. The samples were then removed at specific intervals, gently blotted with tissue paper to remove the excess water on the surface, and the weight recorded. This process was repeated at several time intervals. The water absorption ratio was calculated by the formula below:

$$\chi = \frac{Mx - Mo}{Mo} \times 100\% \quad (1)$$

Mx indicates the weight of the samples in the *X* day; *Mo* indicates the initial weight of the samples; χ indicates the water absorption ratio.

3. Results and discussion

3.1. Mechanical properties

The tensile strength and elongation at break of TPS/polyester samples are shown in Fig. 1a. When a small amount of compatibilizer was added to the blend, increases in both tensile strength and elongation at break were observed over the whole composition range. These increases could be ascribed to the poor interfacial adhesion between TPS and polyesters being improved after the compatibilizer was added.

For the non-compatibilized blends, there was a decrease in the tensile strength of the blends with increasing PBAT content. The tensile strength decreased slowly with PBAT content increasing from 0 to 20 wt%, but it decreased sharply at a PBAT level between 20 and 30 wt%, where the tensile strength of the blend decreased by about 30% (from 12.22 to 7.60 MPa) compared to the strength of the nc-PBAT0 blend (17.99 MPa). The decreasing rate of the tensile strength slowed down again when PBAT content increased to more than 30 wt%. This could be ascribed to the main phase changing from TPS/PLA (comparatively rigid) to TPS/PBAT (comparatively flexible) at PBAT content between 20 and 30wt%. For the compatibilized blends, as PBAT content increased, the tensile strength of the blends first decreased, and then increased (with the inflexion at 30 wt% PBAT content). This might be caused by the phase separation of PLA and PBAT. As PBAT content increased, the elongation at break of blends increased. At higher concentrations of PBAT (>30 wt%) the increase was dramatic; the elongation at break increased by many times compared to the elongation of the nc-PBAT0 blend (1.28%). This behaviour occurred in both compatibilized and non-compatibilized blends.

The flexural strength and flexural modulus of TPS/polyester samples are shown in Fig. 1b. It can be seen from Fig. 1b that both flexural strength and flexural modulus of TPS/polyester blends were decreased gradually with increasing PBAT content. This is because PBAT is flexible polyester, as its content increasing the blends became much softer, thus resulting in a decrease in flexural strength and flexural modulus. The compatibilized blends showed higher flexural strength and flexural modulus comparing to the non-compatibilized blends. The reaction of the anhydride groups from the compatibilizer with the hydroxyl groups from the TPS granules formed ester linkages (Fig. 2). Therefore, the core of the hydrophilic TPS granules was wrapped by the hydrophobic shell formed by the compatibilizer which has better compatibility with PLA and PBAT. So compatibilized blends have better interfacial adhesion between the blend components, thus resulting in a relatively compact phase structure and an increase in flexural strength and flexural modulus.

3.2. Morphology

The morphology of the blends has been performed by SEM and Table 2 shows the starch granules distributing in the polymer matrix. Large starch phase domains could be found for the non-compatibilized blends. The TPS phase that formed from agglomerated starch granules, was partially plasticized, and could not totally flow as a thermoplastic. While after compatibilized, the starch granules were mostly melted and formed a continuous phase with synthetic polymer matrix. Therefore, the non-compatibilized blends showed poor mechanical properties compared to those of compatibilized ones as described earlier. These results confirm that the anhydride functionalized polymer acted as compatibilizer and increases the interfacial adhesion between the blend components and thereby produces a finer and more uniform morphology, hence, resulting in significantly improvement of mechanical properties. Better distributions of starch granules could be seen when PBAT content increased.

3.3. Melt flow index

Melt flow index (MI) is an assessment of average molecular mass and is an inverse measure of the melt viscosity. In other words, the higher a MI, the more flows of polymer under test conditions. Knowing the MI of a polymer is vital to anticipating and controlling its processing. Generally, higher MI polymers could be used in blow moulding, and lower MI polymers could be used in injection moulding or extrusion processes. Fig. 3 shows the MI values for various blends under a certain condition. The MI values for non-compatibilized and compatibilized blends both increased (from 0.94 to 2.63 and 1.56 to 9.26 g/10 min, respectively) with PBAT content. The compatibilized blends had much higher MI values than the non-compatilized blends. The difference could be attributed to the better interfacial interaction between synthetic polymer and starch since the anhydride groups of the compatibilizer could react with the hydroxyl groups of starch to form ester bonds between these components, thus increased the melt flow properties of the blends.

3.4. Thermal properties of blends

The storage modulus (G'), loss modulus (G'') and loss factor ($tan\delta$) of TPS/polyester are showed in Fig. 4. Storage modulus is a measure of the energy stored and recovered in a cyclic deformation whereas the loss modulus is a measure of the energy dissipated. $Tan\delta$ is the ratio of the energy lost to the energy stored in a cyclic deformation. DMA studies revealed that all binary and ternary blends had a decreasing G' over the glass transition temperature of PLA from 40 to 60 °C. The decrease in G' suggested that the material was becoming less elastic or conversely more permanently deformable. As PBAT content increased, the value of G' of the blends decreased (Fig. 4a), which indicated that the blends with less PBAT content were more elastic than those with more PBAT content. It was noticed that these results were similar to those of tensile strength, percentage elongation, flexural strength and flexural modulus results (Figs. 1 and 2). The storage modulus

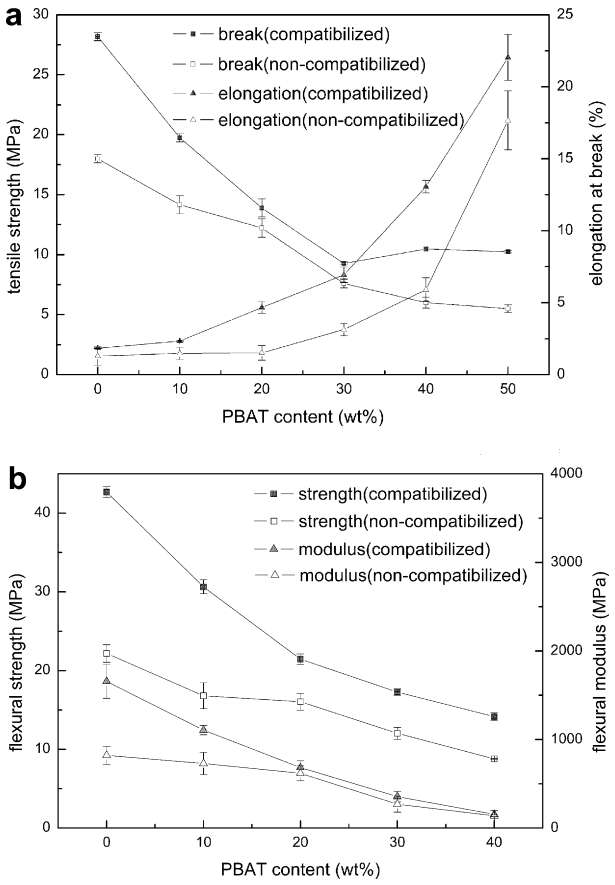


Fig. 1. Mechanical properties of TPS/polyester blends as a function of PBAT content, (a) Tensile strength and elongation at break; (b) Flexural strength and flexural modulus.

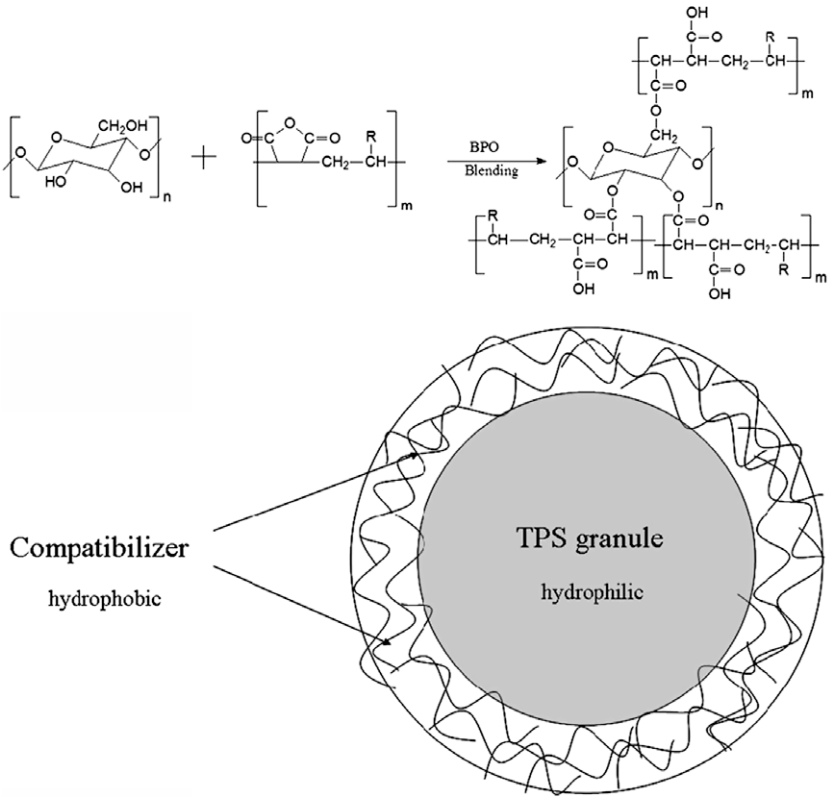
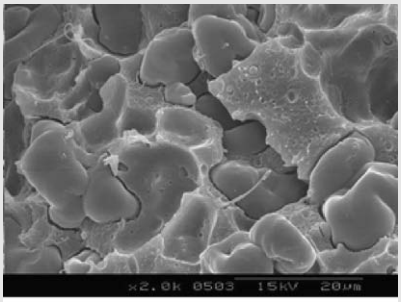
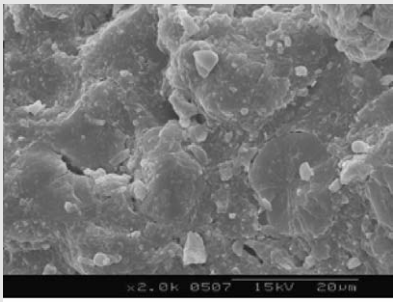
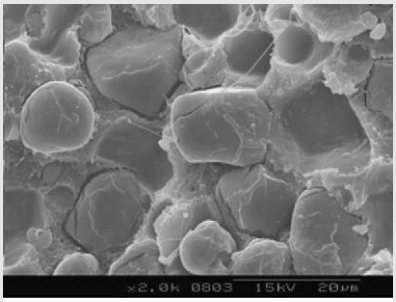
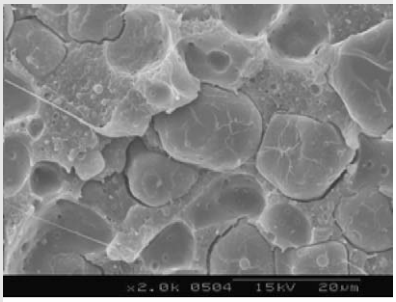
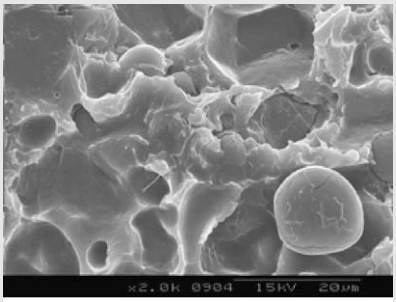
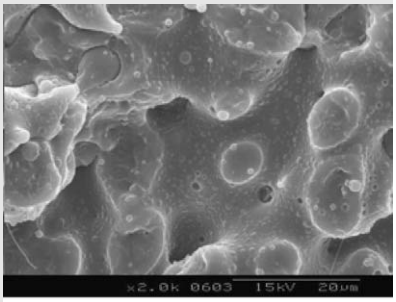
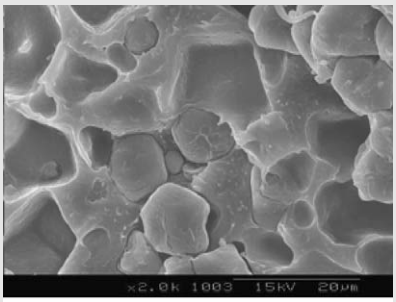
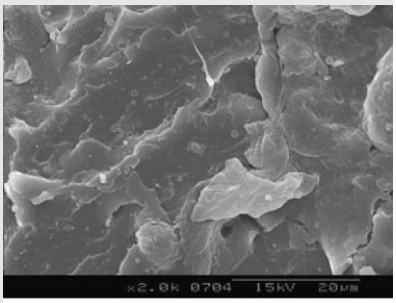


Fig. 2. Formation of TPS and compatibilizer and the reaction between them.

Table 2
SEM micrographs of various TPS/polyester blends.

Samples	SEM image (magnification = 2000×, Scale bar = 20 μm)	
	Non-compatibilized blends	Compatibilized blends
TPS/PLA 50/50	 nc-PBAT0	 c-PBAT0
TPS/PLA/PBAT 50/40/10	 nc-PBAT10	 c-PBAT10
TPS/PLA/PBAT 50/20/30	 nc-PBAT30	 c-PBAT30
TPS/PBAT 50/50	 nc-PBAT50	 c-PBAT50

and the loss modulus correlated positively to the tensile strength, percentage elongation, flexural strength and flexural modulus respectively.

In DMA studies a peak in G'' and $tan\delta$ are usually used as indicators of glass transition. The T_g of PLA measured by the peak of G'' (Fig. 4b) and $tan\delta$ (Fig. 4c) both showed a slight decrease with increasing PBAT content.

Vicat softening temperature (VST) is the temperature at which a flat-ended needle penetrates the specimen to the

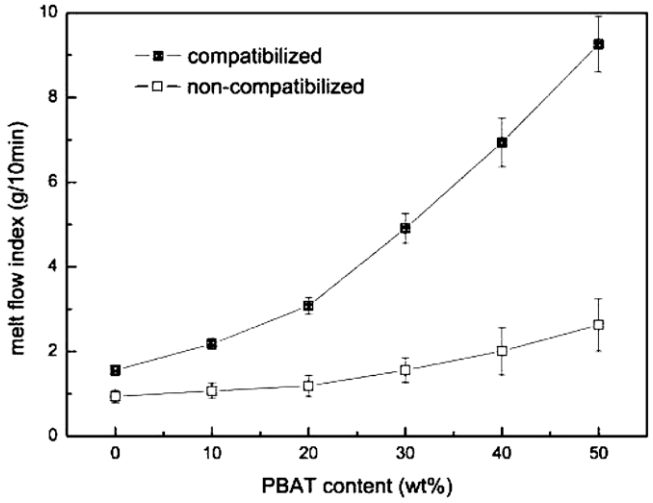


Fig. 3. Melt flow index curves of TPS/polyester blends, as a function of PBAT content.

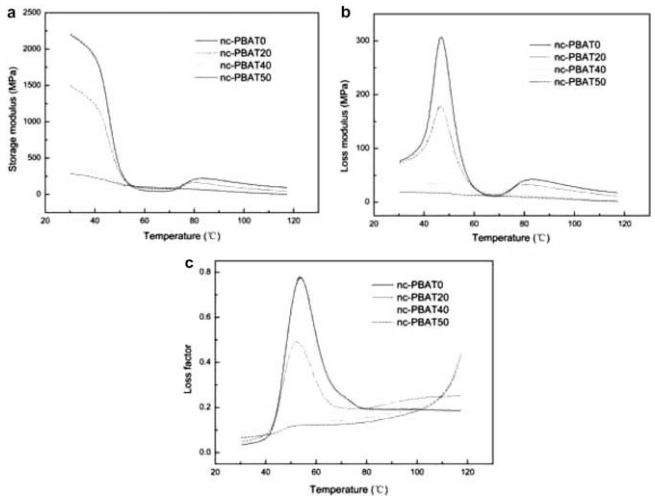


Fig. 4. DMA thermograms of TPS/polyester blends: (a) storage modulus, (b) loss modulus, (c) loss factor.

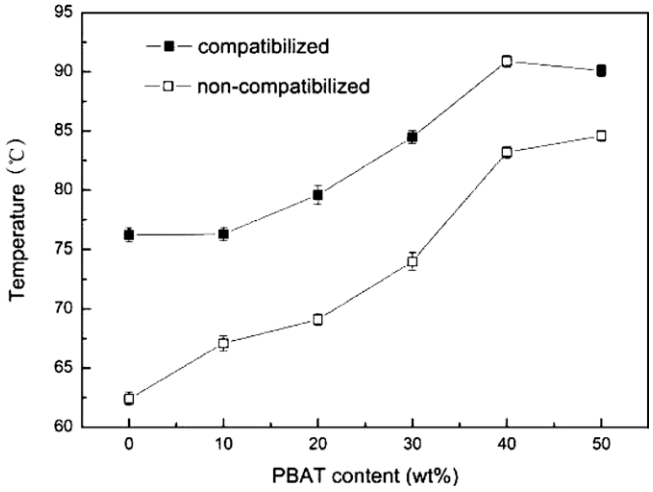


Fig. 5. VST of blends with various PBAT content.

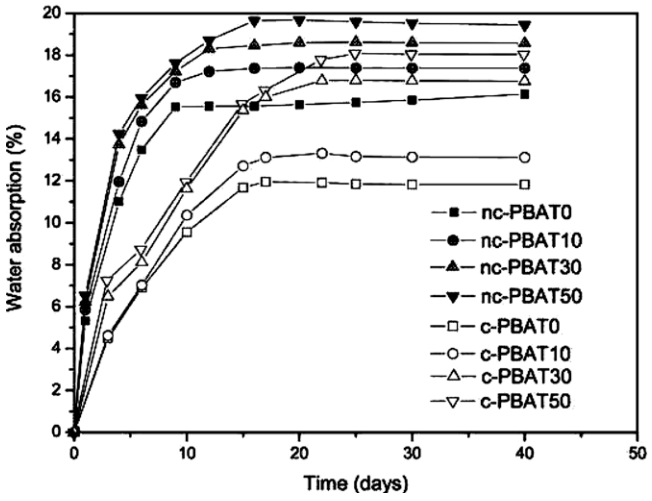


Fig. 6. Water absorption of non-compatibilized and compatibilized blends.

depth of 1 mm under a specific load. The temperature reflects the point of softening to be expected when a material is used in an elevated temperature application. VST was tested for both binary and ternary blends with or without compatibilizer. It can be seen in Fig. 5 that as PBAT content increased, the value of VST increases gradually. It is because PBAT has higher VST than PLA. Comparing to the non-compatilized blends, the VST of the compatilized blends were about 10 °C higher. This is probably because the addition of the compatibilizer increased the interfacial adhesion of the blends, thus caused a higher value of VST.

3.5. Water absorption of blends

The hydroxyl groups in starch can form a hydrogen bond with water, so it is important to study the water absorption properties of blends contenting starch. The water absorption characteristics of non-compatibilized and compatibilized blends are shown in Fig. 6. For all the non-compatilized blends, the time taken to reach the equilibrium water content is about 10 days, which did not change very much as PBAT content increased. The equilibrium water content increased from 16% to 20% as the PBAT content increased from 0% to 50%. This trend is similar to that observed for starch/PBAT blends reported by John and Bhattacharya (1999) before. PBAT has lower crystallinity than PLA and this would account for the higher water absorption of blends with higher PBAT content. For the compatilized blends, there is a comparatively slow uptake of water and the equilibrium absorption value is also lower than non-compatilized blends.

4. Conclusion

Biodegradable binary and ternary blends of TPS, PLA and PBAT give excellent properties when small amount of compatibilizer (an anhydride functionalized polyester) is added. For the TPS/PLA and TPS/PBAT binary blends the tensile strength increased about 30% and 100% each after compatibilized. The elongation is drastically increased as the percentage of PBAT is increased; this is particularly true of the compatibilized blend where at 50% PBAT content the value of the elongation reached 22.04%. The anhydride functionalized polyester reduces the size of the dispersed phase, thus enhancing the interaction between

the two phases between TPS and polyesters. Better properties could also be found for the compatibilized blends in the results of MI and VST. DMA results showed a decrease of the T_g of PLA as PBAT content increased, and storage modulus and loss modulus also showed a decrease as PBAT contents increased. Comparing to those containing more PLA, blends containing more PBAT had higher water uptake and took a longer time to reach equilibrium, which is in inverse proportion to the crystallinity of the polyester in the blend. After compatibilized, the water uptake of the blends is lower and the time required to reach the equilibrium water uptake is longer than those non-compatibilized blends.

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