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Bio-based blends of starch and poly(butylene succinate) with improved miscibility, mechanical properties, and reduced water absorption

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ABSTRACT

Poly(butylene succinate) (PBS) was blended with thermoplastic starch (TPS) to improve the mechanical properties and reduce water absorption of the resulting starch-based plastics. In order to enhance the miscibility between TPS and PBS, reactive PBS (RPBS) with terminal NCO group was synthesized first and then blended with TPS. The mechanical properties of the TPS were greatly improved after blending with RPBS, the tensile strength was increased to 10 times more than TPS even only 10 wt% RPBS was introduced. The water absorption of the blend was significantly reduced with increasing RPBS content. SEM results suggest RPBS to be uniformly distributed in the TPS matrix, and the size of the RPBS phase was decreased with reducing intrinsic viscosity of RPBS. The study of contact angle indicated that the hydrophobicity of the blend was largely enhanced toward TPS. With improved mechanical properties and reduced water absorption, the materials could find more extensive applications.

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1. Introduction

A growing awareness of the negative impact of indiscriminate use of fossil resources, on the environment, has led to a renewed and increased interest in bio-based polymers like starch, cellulose and lignin. Their attractiveness stems from their annual renewability and biodegradability (Chiellini, Cinelli, Chiellini, & Imam, 2004; Gandini & Belgacem, 2002; Ganjyal, Weber, & Hanna, 2007; Guan & Hanna, 2006; Karlsson & Albertsson, 1998; Li et al., 2009; Wang, Cao, & Zhang, 2006; Wu, Wang, Wang, Bian, & Li, 2009; Yu, Yang, Liu, & Ma, 2009). However, these polymers often cannot be directly used in plastics applications due to their poor processability and water sensitivity (Chandra & Rustgi, 1998). Starch for example, is completely biodegradable and annually renewable inexpensive polymer (Galliard, 1987). Nevertheless, with very strong intra- and inter-molecular hydrogen bonds (Ma, Yu, & Jin, 2004), the thermal decomposition temperature of starch is lower than its melting point, which leads to poor processability of starch. It must be plasticized with low molecular weight compounds such as polyols to form thermoplastic starch (TPS) for processing on conventional processing equipment, which would further increase the water sensitivity and decrease mechanical strength of the resulting materials (Mathew & Dufresne, 2002; Souza & Andrade, 2002). These are some of the problems, which need to be solved, before these attractive materials can find meaningful applications in various products.

In order to improve the properties and explore the applications of these polymers, several approaches have been developed to modify these polymers, among which blending with aliphatic polyester was found to be an effective method (Ratto, Stenhouse, Auerbach, Mitchell, & Farrell, 1999; Dubois & Narayan, 2003). Aliphatic polyesters are usually biodegradable thermoplastic polymers with good processability, thermal stability, excellent mechanical properties, good water resistance, and dimensional stability (Gupta, Revagade, & Hilborn, 2007). In addition, some aliphatic polyesters such as poly(lactic acid) (PLA) (Maharana, Mohanty, & Negi, 2009), poly(butylene succinate) (PBS) (Song & Lee, 2006), and poly(3-hydroxyalkanoates) (PHA) (Sudesh, Abe, & Doi, 2000) could also be derived from renewable resources. So blending with these bio-renewable aliphatic polyesters could improve performance without negatively influencing the biodegradability and reduce dependence on fossil resources for production of these materials. While natural polymers are usually hydrophilic, aliphatic polyesters are hydrophobic polymers, so these two polymers are usually thermodynamically immiscible, which would result in poor adhesion between the two components and hence poor performance (Yu, Dean, & Li, 2006).

To achieve improved properties of blends, the compatibility between natural polymers and aliphatic polyesters has to be enhanced, and considerable progress has been made in this regard (Li, Zeng, Wang, Yang, & Wang, 2008; Nabar, Raquez,

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Dubois, & Narayan, 2005; Ohkita & Lee, 2004; Raquez, Nabar, Narayan, & Dubois, 2008). Taking starch/aliphatic polyester blends as examples, Maliger, McGlashan, Halley, and Matthew (2006) have reported on a compatible blend of starch and polyester through reactive extrusion using maleic anhydride (MA) and dicumyl peroxide (DCP) as compatilizer and initiator, respectively. The tensile properties of the blend were superior to that of the incompatible one. Chen et al. (2006) prepared a compatible PLLA/starch blend with improved performance by using poly(L-lactide)-g-starch as a compatilizer, without affecting the biodegradability of the blend. Wu (2003) synthesized maleated-polycaprolactone (PCL-g-MAH) as a compatibilizer for PCL–starch blends. The resulting blend showed better physical and mechanical properties than untreated PCL/starch blend. Diisocyanates were used as compatilizers in blends of PCL or PBSA and starch. It was found that distributing diisocyanate in polyester phase prior to blending resulted in better mechanical properties than distributing in starch phase (Yu, Dean, Yuan, Chen, & Zhang, 2007).

In this study, we report a simple and efficient way to prepare PBS/starch blends with improved compatibility through reactive extrusion of NCO terminated PBS with thermoplastic starch. The processing conditions, mechanical properties, phase morphology, hydrophobic character, and water resistance of the blends have also been studied systematically.

2. Materials and results

2.1. Materials

Corn starch (industrial grade) was procured from Guowei Starch Plant (Xian, China) and dried at 110 °C for 8 h to remove the moisture prior to use. Glycerol, succinic acid and 1,4-butanediol (AR grade) were obtained from Kelong Chemical Plant (Chengdu, China) was used as received. Toluene-2,4-diisocyanate (TDI) (AR grade) was procured from Bodi Chemical Plant (Tianjin, China) and used without further purification.

2.2. Preparation of reactive poly(butylene succinate) (RPBS)

RPBS was prepared via a two-step process. Firstly, HO–PBS–OH (hydroxyl terminated PBS) was synthesized through the procedures we reported previously (Zeng et al., 2009a, 2009b). Typically, 1.2 mol 1,4-butanediol and 1 mol succinic acid were introduced into a 500 mL three-neck round-bottom flask equipped with a Dean-Stark trap, mechanical stirrer, and nitrogen inlet pipe. The esterification was carried out at 190 °C for 4 h, then the catalyst tetrabutyl titanate (0.1 wt% of total amount of the reactants) was introduced into the flask, and HO–PBS–OH was obtained after vacuum polycondensation at 220 °C under 30 Pa for 45 min. The resulting prepolymer was used without further purification. Secondly, RPBS was formed through reaction of HO–PBS–OH with predetermined amount of TDI. The reaction was carried out in a two-neck round-bottom flask at 140 °C for 1 h. The resulting RPBS was cooled down to room temperature and kept in a silica gel desiccator prior to use.

2.3. Preparation of TPS/RPBS blends

To prepare TPS/RPBS blend, TPS was first produced by extrusion of dry starch with 30 wt% glycerol through a twin-screw extruder (CTE-20, China). The temperatures from feed throat to die of the extruder were 110, 120, 130, 130, 120, 110, and 100 °C, respectively, and the screw speed was 100 rpm. TPS/RPBS blend was prepared by reactive extrusion of TPS with RPBS. The processing conditions were identical to those employed for the synthesis of TPS. The blend was injection-molded into standard test samples using a HAAKE MiniJet injection molder. The zone and mold temperature were maintained at 150 and 40 °C, respectively. The standard sample was used for mechanical testing.

2.4. Characterization

2.4.1. Intrinsic viscosity

The intrinsic viscosities of HO–PBS–OH and RPBS were measured with an Ubbelohde viscometer at a concentration of 0.1% (w/v) in chloroform at 25 °C. The intrinsic viscosity values of polymers were determined by Solomon–Ciuta equation $[\eta] = \sqrt{2(\eta_{sp} - \ln \eta_r)}/C$, where $\eta_r = t/t_0$, $\eta_{sp} = \eta_{r-1}$; t and t_0 are elution times of polymer solution and pure solvent, respectively.

2.4.2. Nuclear magnetic resonance (NMR) spectroscopy

Chemical structure characterization of HO–PBS–OH and RPBS were conducted under ambient temperature on a 400 MHz Brucker spectrometer using $CDCl_3$ and tetramethylsilane (TMS) as the corresponding solvent and internal chemical shift standard.

2.4.3. Fourier transform infrared (FTIR) spectroscopy

FTIR spectra of the HO–PBS–OH and RPBS were recorded on a Fourier transform infrared spectrometer (NICOLET 6700) in a range of wave numbers from 4000 to 400 cm^{-1}. The specimens were milled into powder and then mixed with KBr and laminated. The resolution and scanning time were 4 cm^{-1} and 32 times, respectively.

2.4.4. Scanning electron microscopy (SEM)

The phase morphologies of blends were examined by scanning electron microscopy (SEM; JSM-5900LV, JEOL, Japan) at an accelerating voltage of 20 kV. The injection-molded tensile specimens were cryofractured in liquid nitrogen, after which the fractured surfaces were extracted with chloroform for several seconds to get a better observation of the phase structure. All the surfaces were dried and sputter coated with gold prior to examination.

2.4.5. Tensile testing

All samples were balanced in 50% relative humidity (RH) at 20 °C for 48 h prior to testing. The tests were performed on a Sansi Universal Testing Machine (CMT, Shenzhen, China) at a crosshead speed of 20 mm/min at room temperature according to ASTM D638. Six measurements were conducted for each sample, and the results were reported as averaged values.

2.4.6. Contact angle

The contact angles for the surfaces of TPS and blend sheets were tested with a contact angle analyzer (Model DSA-100 TC40-MK1, Germany). The surface of the sample sheets were cleaned with ethanol and dried prior to testing. The samples were glued to a movable sample stage horizontally; then about 4 μL probe water was introduced on the surface of the sheet using a microsyringe.

2.4.7. Water absorption

Sample sheets of rectangular shape with dimensions of 15 mm × 15 mm × 0.5 mm were dried in a vacuum oven at 60 °C for 48 h and weighed prior to testing. The vacuum dried rectangular sheets were immersed in distilled water at 20 °C to determine the water absorption and soluble ratio. The sample was taken out to measure the water absorption and soluble ratio in a certain time, and then the same sample was vacuum dried to measure the weight loss of the sample. The weights of the original sample and the sample after water absorption were designated as W_0 and W_1, and the dry weight of the water extracted sample was designated as W_2. The value of water absorption was obtained by

$(W_1 - W_2)/W_2 \times 100\%$, and the value of soluble ratio was derived from $(W_0 - W_2)/W_0 \times 100\%$. Three measurements were performed for each sample, and the result was reported as average value.

3. Results and discussion

3.1. Preparation of RPBS

RPBS was prepared with a two-step process as shown in Scheme 1. In the first step, HO–PBS–OH was prepared by condensation polymerization between 1,4-butanediol and succinic acid including two steps of esterification and subsequent polycondensation with tetrabutyl titanate as a catalyst. In order to obtain dihydroxyl terminated PBS, the feed molar ratio of 1,4-butanediol to succinic acid was fixed at 1.2:1. The molecular weight of HO–PBS–OH was controlled by the polycondensation time. The chemical structure of HO–PBS–OH was confirmed with NMR spectrum as shown in Fig. 1A. The peaks at 1.67 (δH^b), 2.65 (δH^a), and 4.10 (δH^c) ppm with the same integral area are assigned to the three different of methylenes in the repeat units of PBS. The peak at 3.65 (δH^d) ppm could be ascribed to the methylene group linked to the terminal hydroxyl group of PBS molecular chain. The degree of polymerization and number-average molecular weight of HO–PBS–OH can be calculated according to the intensity of methylene groups at 3.65 ($I_{3.65}$) and 4.10 ($I_{4.10}$) ppm by the following equation:

$$M_{n,NMR} = \frac{I_{4.10}}{I_{3.65}} \times 172 + 90$$

where 172 is the molecular weight of repeat unit of PBS, and 90 is the gross mass of end chains of HO–PBS–OH. HO–PBS–OH with $M_{n,(NMR)}$ of 4300 g/mol was prepared in this study, and the intrinsic viscosity was 0.21 dL/g as shown in Table 1.

In the second step, RPBS was prepared through melt bulk reaction of HO–PBS–OH with TDI. In order to obtain RPBS, the mol number of TDI should be in excess of HO–PBS–OH. Four mol ratios of HO–PBS–OH to TDI with 1:1.3, 1:1.5, 1:1.7, and 1:2 were chosen to synthesize RPBS and the four RPBS samples were marked as RPBSI, RPBSII, RPBSIII, and RPBSIV, respectively. After reaction, the intrinsic viscosity of the resulting RPBS increased in comparison to that of HO–PBS–OH, and the $[\eta]$ value of RPBS gradually decreased in going from RPBSI, to RPBSIV. The reaction of the –NCO group with the –OH group could lead to a chain-extension reaction or an end-capping reaction. When the mol ratio of –OH to –NCO is 1:2, the

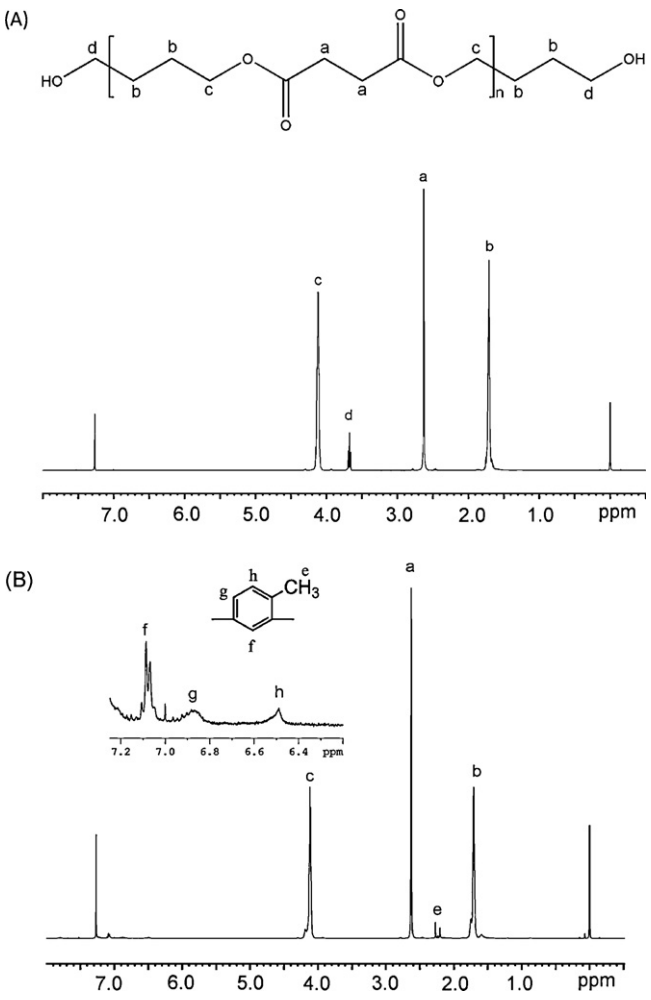
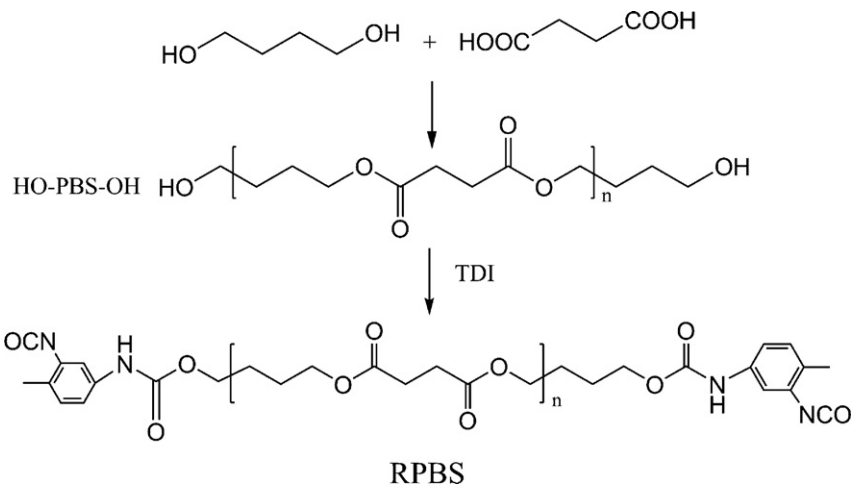


Fig. 1. ^{1}H NMR spectra of HO–PBS–OH (A) and RPBS (B).

Table 1
The effect of [NCO]/[OH] on the $[\eta]$ of RPBS.

Polymer	[NCO]/[OH]	$[\eta]$ (dL/g)
PBS	–	0.21
RPBSI	1.3	0.52
RPBSII	1.5	0.31
RPBSIII	1.7	0.29
RPBSIV	2.0	0.28



Scheme 1. Synthetic route for RPBS.

blocking reaction is expected to be the predominant reaction, thus the [η] of RPBSIV was the smallest. As the mol ratio decreases to 1:1.3, chain-extension is expected to be predominant. The intrinsic viscosity of the resulting polymer would then increase to a higher value.

Fig. 1B gives the ^{1}H NMR spectrum of RPBS. Except for the three main peaks (δH^b, δH^a, and δH^c) attributed to HO–PBS–OH, four new peaks belong to TDI unit were also observed at 2.21(δH^e), 6.49(δH^h), 6.88(δH^g), and 7.10(δH^f) ppm in the spectrum of RPBS. In addition, the peak at 3.65 ppm in the NMR spectrum of HO–PBS–OH are absent in the spectrum of RPBS due to reaction of terminal hydroxyl group of HO–PBS–OH with the –NCO group of TDI. The results suggest that the reaction between TDI and HO–PBS–OH has indeed happened.

FTIR is an effective way to characterize functional groups present in polymers (Zeng et al., 2009a, 2009b). Fig. 2 shows the FTIR spectra of HO–PBS–OH and RPBS. It could be found that the peak appearing around 3500 cm^{-1} (O–H vibration) in the spectrum of HO–PBS–OH shifted to lower wavenumber (around 3400 cm^{-1}, N–H vibration), which was ascribed to the conversion of hydroxyl to urethane group because of the reaction between hydroxyl and isocyanate. Besides this change, a significant difference was that a strong absorption peak at 2250 cm^{-1} emerged in spectrum of RPBS which was caused by the existence of NCO group. These results suggest that reactive PBS containing isocyanate was successfully prepared via melt bulk reaction of HO–PBS–OH with TDI.

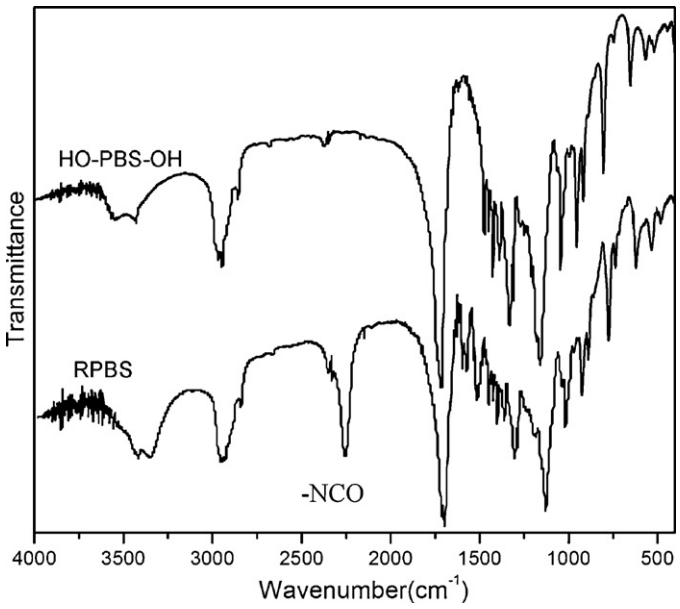


Fig. 2. FTIR spectra of HO–PBS–OH and RPBS.

3.2. Phase morphologies of the blends

It is known that the properties of blends are strongly dependent on the phase morphologies. Fig. 3 shows the SEM micrographs for the etched surface of the blends with different kind of PBS. For TPS/HO–PBS–OH blend (Fig. 3A), very large voids were formed when HO–PBS–OH was etched, and starch still retained in its granular shape, which suggests that the two phases are immiscible. The results indicate that simple blending of PBS with TPS cannot give rise to miscible blend system, which should be caused by the different polarities between the two polymers; starch is hydrophilic with strong polarity while PBS is hydrophobic with relatively poorer polarity. When HO–PBS–OH is reacted with TDI

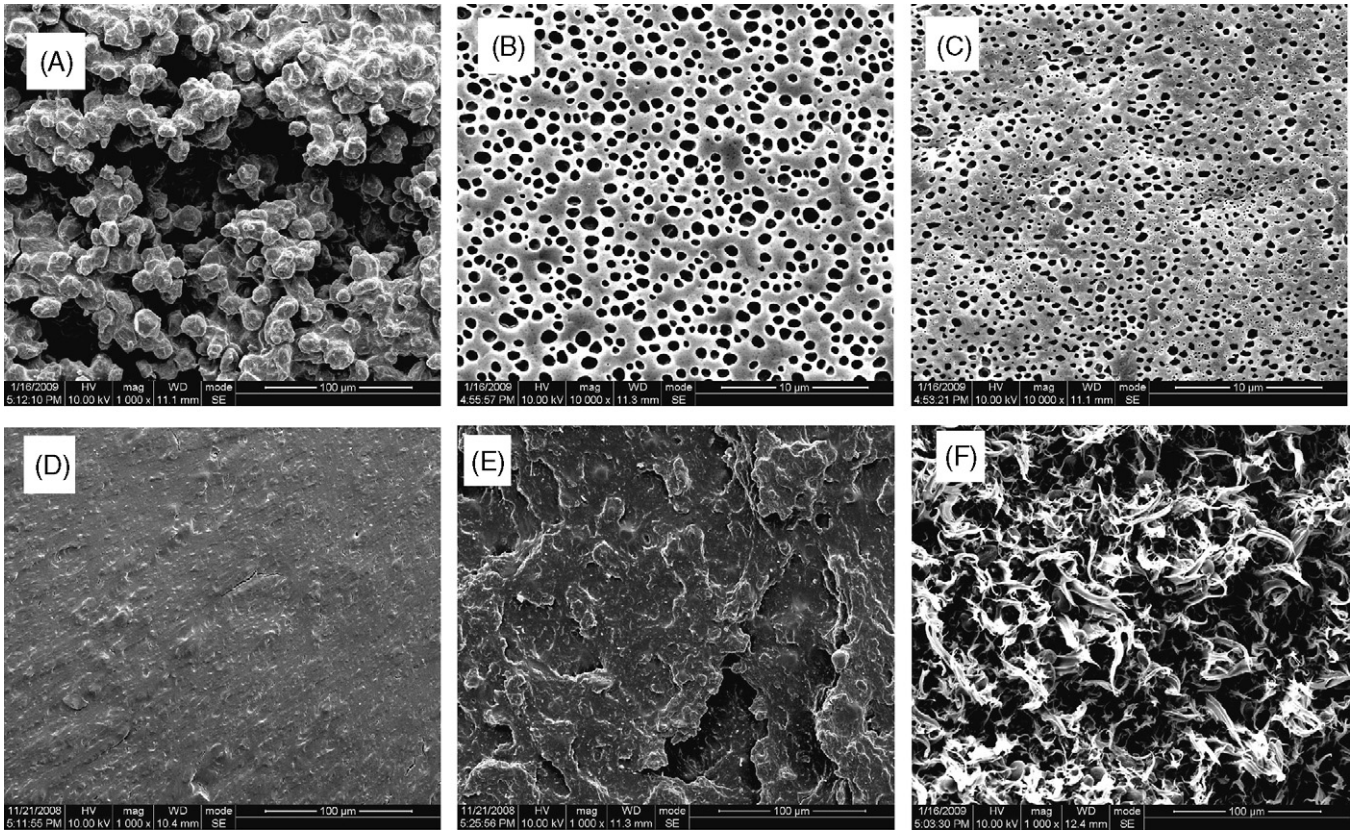


Fig. 3. SEM micrographs of the etched surfaces for starch/HO–PBS–OH (A), starch/RPBSI (B), and starch/RPBSIII (C), and tensile fracture surfaces for starch/HO–PBS–OH (D), starch/RPBSI (E), and starch/RPBSIII (F).

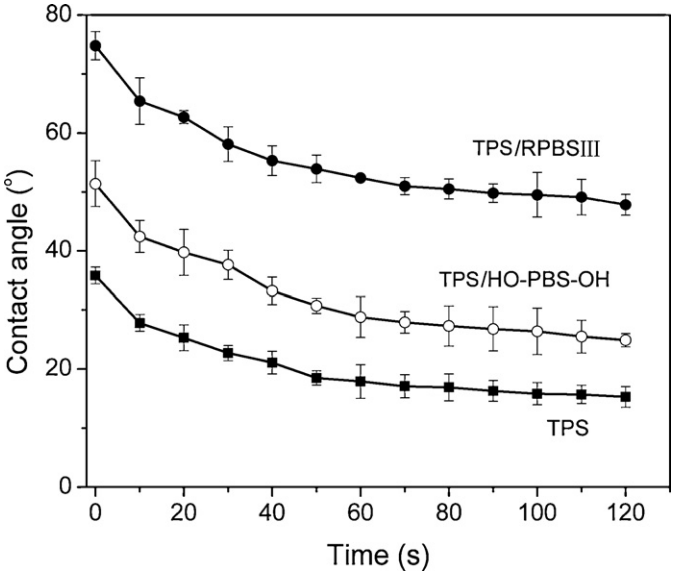


Fig. 4. Dynamic changes in contact angle of water drops on TPS and blends.

and terminated with an –NCO group, the resulting polymer blends with starch showed very fine phase structures. Uniform holes of small size were left in the blend after extraction of PBS, which suggested that starch formed a continuous phase of the blend, while PBS formed a fine dispersed phase distributed uniformly in the starch matrix. The results prove that the miscibility of starch and PBS was improved through introducing NCO group to the chain end of PBS molecules. Thus NCO group played a very important role in improving the miscibility of the two phases, since NCO group can react with hydroxyl groups of both starch and glycerol. The reaction between NCO and hydroxyl of starch could improve the compatibility of the blends directly; and the reaction between NCO and hydroxyl of glycerol could also enhance the compatibility indirectly, since glycerol acts as a plasticizer for starch phase and thus exists between the molecules of starch. Comparing Fig. 3B with Fig. 3C, we find that the size of dispersed phase increases with the intrinsic viscosity of RPBS, and the average values for the cell size in Fig. 3B and C were around 0.86 and 0.45 μm, respectively. So we can conclude that the size of the dispersed phase increases and thus the miscibility decreases with the increasing intrinsic viscosity of RPBS. It was because that the molecular size of higher intrinsic viscosity of RPBS was larger than that of the lower one.

3.3. Tensile properties

Table 2 summarizes the tensile testing results for TPS and the blends of TPS with different kinds of PBSs and blend compositions. The tensile strength of TPS was less than 1 MPa, and slightly increased after blending with 30 wt% HO–PBS–OH. However, the elongation at break was dramatically decreased from 83.1 to 3.0%, which should be a result of the poor compatibility between starch and HO–PBS–OH phases as discussed previously. When HO–PBS–OH was modified with TDI, the tensile strength of the blend was considerably enhanced with 30 wt% RPBS introduced. The value of tensile strength was at least 20 times more than that of TPS; meanwhile the elongation at break decreased gradually. It can be seen from the tensile properties of the samples TPS/RPBSI, TPS/RPBSII, TPS/RPBSIII, and TPS/RPBSIV in Table 2 that the tensile strength and elongation at break showed trends of increasing first and then decreasing with the increase of NCO group in RPBS. The maximum values appeared when blending with RPBSIII which was synthesized with [NCO]/[OH] of 1.7. The results were caused by the combination of the content of –NCO group and intrinsic viscosity of RPBS. More linking points should be formed thus stronger cohesive force would be obtained between PBS and starch phases with increase of –NCO group's content. Consequently the mechanical properties should be improved with the increase of –NCO group's content. The mechanical properties of the blends should also increase with the intrinsic viscosity of RPBS. However, the content of –NCO group in RPBS increases while intrinsic viscosity of RPBS decreases with the increase of [NCO]/[OH]. When [NCO]/[OH] is 1.7, the best balance NCO group and intrinsic viscosity was achieved thus the best mechanical properties were obtained. The Young's modulus of the blend always increased with the increase of [NCO]/[OH], indicating that the interaction between starch and RPBS increased with increasing –NCO content.

Since TPS/RPBSIII showed the best tensile properties, the effect of weight ratio of TPS to RPBSIII on the tensile properties of the blends was investigated. The sample name TPS/RPBSIII10 represents the weight fraction of RPBSIII in the blend (10%), shown in Table 1. Both the tensile strength, elongation at break, and Young's modulus of the blends increased gradually with the weight fraction of RPBS. This is because the mechanical property of RPBS is superior to that of TPS and increasing compatibility between the two polymers occurs, with the increasing content of RPBS the blends. The results also prove the good compatibility between TPS and RPBS indirectly.

Tensile fracture surface morphologies could give more information for tensile properties of blends. The SEM micrographs for tensile fracture surfaces of the blends are shown in Fig. 3. The surface for starch/HO–PBS–OH (Fig. 3D) was almost smooth, suggesting the sample underwent a brittle fracture, which was caused by the weak interaction between starch and HO–PBS–OH. The fracture surface (Fig. 3E) turned rough when RPBSI was blended with starch, which indicated the interaction between starch and RPBS was enhanced due to the introduction of NCO group to PBS molecule. But a visual inspection of the fracture surface suggests, NCO groups in RPBSI were not sufficient enough and the interac-

Table 2
The effects of PBS kinds and blend compositions on the tensile properties of the blends.

Sample	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
TPS	0.68 ± 0.04	83.1 ± 15.9	1.46 ± 0.02
TPS/HO–PBS–OH[a]	2.4 ± 1.0	3.0 ± 1.1	131 ± 33
TPS/RPBSI[a]	14.8 ± 0.5	24.3 ± 7.5	97 ± 26
TPS/RPBSII[a]	15.2 ± 3.1	32.9 ± 10.3	174 ± 33
TPS/RPBSIII[a]	22.9 ± 2.0	46.6 ± 6.4	419 ± 27
TPS/RPBSIV[a]	20.2 ± 1.3	36.7 ± 5.4	472 ± 35
TPS/RPBSIII10[b]	7.2 ± 0.4	43.5 ± 3.8	160 ± 35
TPS/RPBSIII20[b]	12.8 ± 0.9	47.6 ± 5.4	214 ± 28
TPS/RPBSIII40[b]	26.3 ± 0.5	63.4 ± 6.9	435 ± 30
TPS/RPBSIII50[b]	30.1 ± 0.5	74.4 ± 3.7	441 ± 41

[a] The weight ratio of TPS to PBS with different kinds is 70:30.
[b] The number represents the weight fraction of RPBSIII.

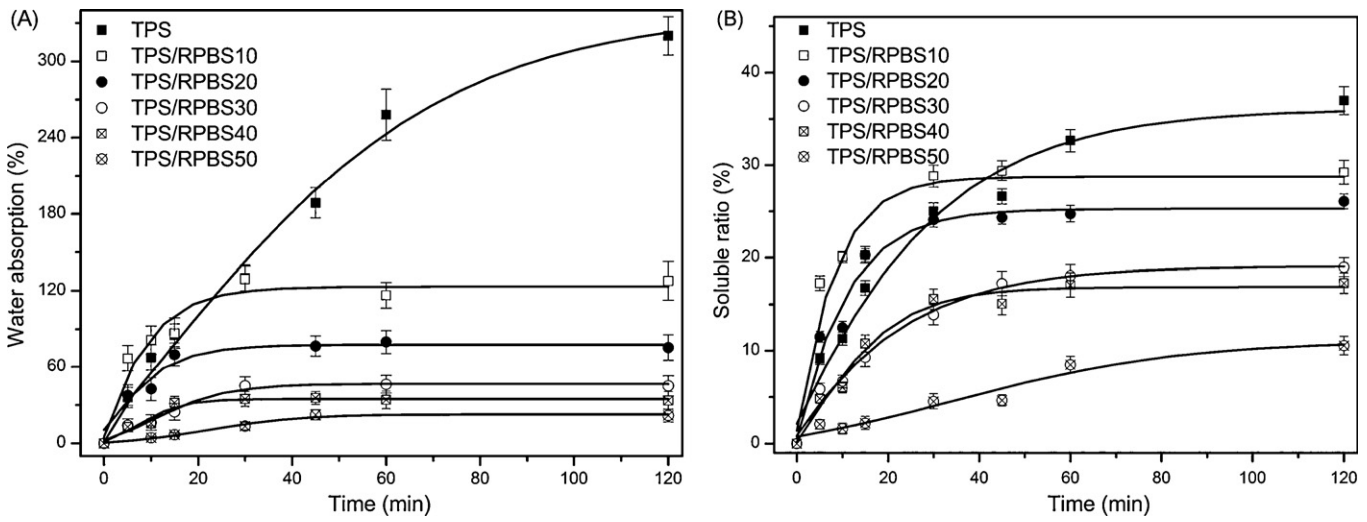


Fig. 5. Water absorption (A) and soluble ratio (B) as functions of time for the samples immersion in water.

tions between the two phases could be further improved if more NCO groups could be introduced. Consequently, as the content of NCO group in RPBS increased, the interaction between starch and RPBS increases, thus many deformation bands emerge at the tensile fracture surface of starch/RPBSIII, which proved the fracture for sample starch/RPBSIII (Fig. 3F) to be a ductile fracture. Moreover, the sample also had the largest tensile strength among all the blends. The study on the morphology of tensile fracture surface confirmed that the interaction and hence the compatibility between starch and PBS phases could be improved significantly with increasing content of NCO group. The result was in good agreement with that obtained by cryofractured surface analysis.

3.4. Contact angle

Contact angle of water usually reflects the hydrophilic/hydrophobic character of the surface. Generally, hydrophobic materials have relatively higher water contact angle. Natural polymers such as starch, cellulose, and soy protein are usually hydrophilic and water sensitive. Fig. 4 shows the dynamical change in contact angles of water drop on TPS and blends. The initial contact angle for TPS was 35.8°. The value was increased to 51.4° after blending with HO–PBS–OH, suggesting that the introduction of PBS could improve the hydrophobicity of starch although the miscibility of the two phases was not very good. The initial contact angle for starch/RPBSIII was increased to 74.8°, which was caused by the improvement of miscibility between starch and PBS through introducing NCO group to PBS molecule. In addition, we could find that all the samples showed decreased contact angles only over a short time period, which could be as a result of the water absorption of the sample. The value of contact angle decreased rapidly in the beginning, and then nearly leveled off in the end. The contact angle of the blend remained at a higher value than TPS during entire test, which suggests that blending with PBS could enhance the hydrophobicity of the material.

3.5. Water absorption

Water absorption is one of the main shortcomings that restricts the application of starch-based materials. As we have mentioned previously that one main objective of this study was to improve the water resistance of TPS after blending with PBS. So we studied the water resistance of the blends systematically in the present paper. The water absorption and soluble ratio of the samples were tested by immerging in distilled water for a certain time period. The results are shown in Fig. 5. It was hard for TPS to acquire equilibrium of water absorption because of the constant dissolution of the material. The water absorption and the soluble ratio of TPS in the time period of measurement was more than 300% (Fig. 5A) and 30% (Fig. 5B), respectively. After blending with RPBS, the samples could reach absorption and dissolution equilibrium in a time of about 30 min to an hour. Furthermore, the values of water absorption and soluble ratio of the blends were much less than those of TPS and decreased dramatically with increasing weight fraction of RPBS. As the weight fraction of RPBS increased to 50%, the water absorption and soluble ratio of the blend were decreased to 21.2% and 10.5%, respectively. The results also demonstrate that the water absorption of the sample decreases with the increase of weight fraction of RPBS.

4. Conclusion

Biodegradable starch-based thermoplastic was successfully produced through reactive blending of TPS and RPBS. The blends exhibited improved mechanical properties, the tensile strength approaching PE and PP, which were remarkably superior to those of TPS and improved with the increase of RPBS content. Hydrophobicity was enhanced and water absorption was reduced significantly in comparison with TPS and immiscible blend. With enhanced mechanical properties and reduced water absorption, the blends could find more applications and be able to partially substitute non-degradable and non-renewable fossil-based polymers such as PE and PP.

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