Effect of Glycerol and Reactive Compatibilizers on Poly(butylene succinate)/Starch Blends

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ABSTRACT: A one-step process in an internal mixer was used to prepare Poly(butylene succinate) (PBS)/high-loading modified tapioca starch (30–40 wt%) blends with low glycerol content (10–20 wt% of starch) as a plasticizer. To promote a good compatibility, two reactive agents, maleic anhydride (MA)/peroxide and methylene diphenyl diisocyanate (MDI), were selected and compared. The mechanical properties, morphology, and Molau test of the blends were investigated. The compatibility of PBS/starch blends was improved by both reactive agents at the suitable plasticizer loading (glycerol 10 wt% of starch). It was demonstrated that increasing mechanical properties resulted in good adhesion of PBS/starch interface and small evenly dispersed starch particles. MA/peroxide of 0.20/0.01 phr/phr and MDI of 0.2 phr were sufficient to improve the mechanical properties of PBS/starch (60:40 and 70:30) blends at 10 wt% glycerol (of starch). The results from the Molau test confirmed the formation of graft-copolymer at the interface when compatibilizers were added.

KEYWORDS: Poly(butylene succinate), tapioca starch, compatibilizer, reactive blend

1 INTRODUCTION

Biodegradable products from renewable resources have seen a dramatic increase in attention for replacing conventional nonbiodegradable plastics. Among biodegradable polymers, poly(butylene succinate) (PBS) has emerged as one of the popular choices for the substitution of the commercial article due to its availability on a large industrial scale. It is a renewable and fully-degradable plastic and has good processibility and mechanical properties [1–3]. To be able to commercially compete in the market, the price of PBS should be reduced. Therefore, PBS can be blended with low-cost renewable polymers such as starch to provide an attractive and competitive cost and adjustable mechanical properties. Native starch generally exists in a large granular state; it may be added as filler to improve the modulus of the biopolymer matrix, e.g., polycaprolactone (PCL) [4, 5]. Adding suitable amounts of a plasticizer like glycerol and water into starch with heat and shear leads to the formation of thermoplastic starch (TPS), which becomes softer

and tougher as the amount of plasticizers increase [6]. There are many authors who have attempted to blend TPS with biopolymers, e.g., PBS/TPS [1, 7] and poly(lactic acid) (PLA)/TPS [6, 8].

It is known that blending hydrophobic biopolymers with hydrophilic TPS leads to poor distribution and interfacial adhesion. Mechanical properties of polymer blends are reliant on the interfacial adhesion. Therefore, the effective compatibilizers must be located at the interface for giving a low interfacial tension and a fine morphology of blends [9]. The superior compatibility of biopolymer and starch blends could be produced by grafting maleic anhydride onto starch [10] or biopolymer backbone [8]. Jean-Marie Raquez et al. [11] modified TPS with maleic anhydride (MA) using glycerol as a plasticizer (20 wt% by starch). They found that MA played an important role in reducing TPS viscosity, destroying the granular structure of starch and reducing molecular weight by promoting the transester reaction of glycerol with starch. In another work of theirs [10], in blown film applications maleated thermoplastic starch (MTPS) was used to

blend with poly(butylene adipate-co-terephthalate) (PBAT). The tensile properties of MTPS and PBAT blend were much higher than the TPS/PBAT/MA reactive blend when containing 70 wt% polyester and had much finer dispersed phase morphology. Maliger *et al.* [9] also prepared starch/polyester blends in a two-step process. The first step was preparation of maleated polyester by using Dicumyl peroxide (DCP) as initiator. In the second step, maleated polyester and TPS were blended. They reported that MA and DCP can enhance the compatibility of starch/polyester blends and improve mechanical properties.

Alternatively, diisocyanates were also used as reactive compatibilizers in starch/polyester blends [6, 12–14]. Isocyanate groups are highly reactive to hydroxyl groups, further forming urethane linkages [6]. Kweon *et al.* [14] prepared starch-g-PCL using three types of diisocyanates including 2,4-tolylene diisocyanate (TDI), 4,4-diphenylmethane diisocyanate (MDI), and hexamethylene diisocyanate (HDI) as grafting agents. Starch-g-PCL using MDI showed a higher initial thermal degradation temperature than those using TDI and HDI. For systems of PCL or PBSA and starch blends, using MDI as a compatibilizer enhanced the mechanical properties of blends [12]. However, distributing the diisocyanate in polyester phase before blending with starch resulted in good mechanical properties when compared to those distributed in the starch phase directly.

Starch can either be used as a dry starch and blended directly to biopolyesters or used as a thermoplastic starch (TPS) prior to blending with biopolyesters. The compatibility between the two polymers can be improved using physical and chemical (or reactive) compatibilizers. Choice of blending procedure is also important, as it will eventually affect the final properties of the products. In many cases TPS is preferred, as it can be melted and reprocessed more easily. However, forming TPS before blending with other biopolymers is cumbersome, time-consuming and costly.

As mentioned above, the one-step nonreactive and reactive blend process between PBS and starch can be advantageous, as it offers cost-effectiveness and easy-to-handle features. Owing to our lack of knowledge, research into the one-step process to create a PBS/starch blend with the addition of plasticizer and reactive agents is still in its infancy.

Therefore, the one-step process for the preparation of PBS/starch blends was carried out in this work. Tapioca acetate modified starch was used in a blending process in order to improve the compatibility with PBS. The effect of glycerol (at low contents) and reactive compatibilizers (methylene diphenyl diisocyanate [MDI] and maleic anhydride [MA] with peroxide) on mechanical and morphological properties of PBS/

starch blends were investigated. A graft copolymer at the interface of PBS and starch was also characterized using FTIR and Molau test.

2 EXPERIMENTAL

2.1 Materials

Poly(butylene succinate) (PBS) extrusion grade FZ91PD was purchased from Mitsubishi Chemical Corp. (Japan). Tapioca acetate modified starch (PD 12179, moisture content 11.5–14.5%, 0.8% deacetylation) was kindly supplied by Siam Modified Starch (Thailand). Glycerol (99.5%) as a plasticizer for starch was purchased from Ajax Finechem Pty (Australia). The reactive compatibilizations were performed using maleic andhydride (MA)/peroxide (Di(tert-butylperoxyisopropyl)benzene (Perkadox 14-40B-PD) and Methylene diphenyl diisocyanate (MDI). The MA and MDI were purchased from Merck Schuchardt (Germany) and Sigma-Aldrich (United States), respectively. Perkadox was purchased from Akzo Nobel (Netherlands). The peroxide initiator was adsorbed on silica and calcium carbonate powder having reactive content of about 40%.

2.2 Preparation of PBS/Starch Blends

The PBS and starch were first dried at 60°C and 80°C for 12 h respectively before further use. PBS, starch, glycerol, and reactive agents were premixed and then melt-blended together in an internal mixer (MX 105-D40L50, Chareon TUT, Thailand) at 150°C and 100 rpm for 5 min, also called the one-step process. The effects of glycerol content were studied in PBS/starch (60:40) by varied glycerol loading of 0, 10, 15 and 20 wt% of starch. Two reactive systems: (1) condensation reaction (methylene diphenyl diisocyanate (MDI)) and (2) free radical reaction (maleic anhydride (MA) and peroxide) were used for comparison. The weight ratios between PBS and starch used to compare the effect of compatibilizers were 60:40 and 70:30 by weight. Reactive compatibilizers at various loading per 100 g of PBS/starch blend were 0.20/0.01, 0.20/0.02, 0.20/0.04, and 0.50/0.20 phr/phr for MA/peroxide system and 0.20, 0.50, and 1.00 phr for MDI system. For convenience, it should be noted that PBS/starch(10) 60:40 refers to the blend containing 10 wt% of glycerol (by starch weight) with the blend percentage-ratio of 60 (PBS) and 40 (starch).

2.3 Characterization

The tensile properties, e.g., Young's modulus, tensile strength, and % elongation at break of the blends, were

determined using an Instron universal testing machine (model 5969) with a 5 KN load cell and a crosshead speed of 1 mm/min. All samples were tested according to ASTM D-638 type V.

Scanning electron microscopy (SEM) (CAMSCAN MX-2000) was used to characterize the phase morphology and compatibility of PBS/starch blends. The fractured surfaces of samples were coated with spluttered gold.

To investigate the change in physical properties due to possible reactions, the Molau test was conducted; 1 g of PBS/starch blends (with various compatibilizers) was thoroughly shaken with 20 ml dichloromethane and then left to rest at room temperature for 14 h. A digital camera was used to observe the emulsifying effect of the polymer blends solution. The PBS was extracted from PBS/starch blends by dichloromethane solvent. Afterwards, starch was removed from extraction residues with 1 M HCl. In each step, the residues were filtered through a 120-mesh sieve. Finally, the obtained residues were dried in an oven before calculating gel contents in each sample and performing FTIR analysis.

3   RESULTS AND DISCUSSION

3.1   Mechanical Properties

The stress/strain curves of PBS/starch 60:40 physical blends with different glycerol concentration are shown in Figure 1. All samples exhibited no yield point and neck characteristics. The effects of glycerol addition on elongation at break and toughness were considered from the stress/strain curve. The addition of glycerol of 10 wt% (by starch) into the blend resulted in an increased elongation at break and toughness. The sample between the gauge lengths became white and opaque during the extension test. At 15 wt% glycerol, elongation at break and toughness of polymer blends were decreased. The blend sample became brittle at 20 wt% glycerol loading.

The effect of glycerol concentrations on tensile properties of PBS/starch 60:40 (with and without reactive agents), including Young's modulus, tensile strength and elongation at break, were summarized in Table 1. Young's modulus of blends was decreased as glycerol contents increased. This was probably due to an increase of glycerol in the TPS phase. The tensile strength of PBS/starch 60:40 blend was around 24 MPa and lower than that of PBS (40.2 MPa). The presence of 10 wt% glycerol (of starch) yielded the highest elongation at break of PBS/starch 60:40 blends. An overdose of glycerol, higher than 10 wt%, had an adverse effect on elongation at break. To improve the interfacial adhesion between PBS and starch, MA and peroxide (MA0.20/P0.02, phr/phr) were added. Young's
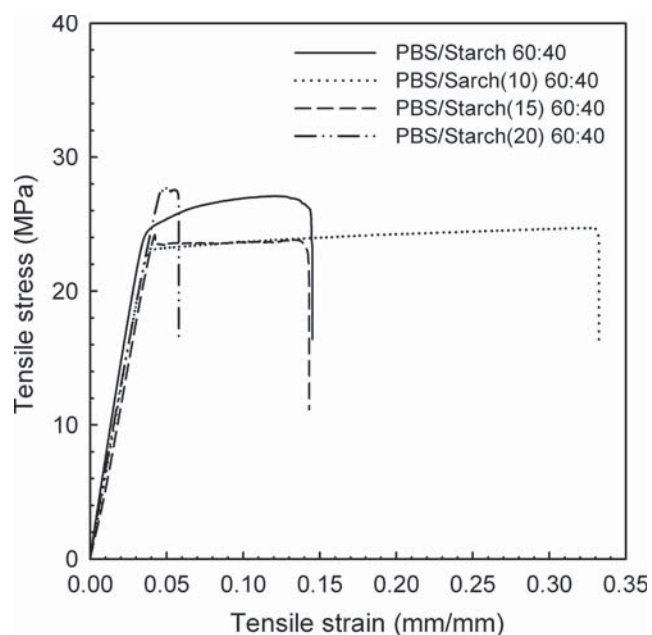

Figure 1 Stress/stain curves of PBS/starch 60:40 at different glycerol contents.

Table 1 Tensile properties of PBS/starch 60:40 at different glycerol contents without and with MA0.20/P0.02 phr/phr.

Sample	Tensile strength (MPa)		Young's modulus (MPa)		Elongation at break (%)	
	Non reactive	MA0.2/P0.2 (phr/phr)	Non reactive	MA0.2/P0.2 (phr/phr)	Non reactive	MA0.2/P0.2 (phr/phr)
PBS/starch 60:40	27.7±1.1	28.4±0.8	740±11	709±4.1	16.8±1.1	13.6±1.5
PBS/starch(10) 60:40	24.8±0.4	24.6±0.3	621±18	648±14	31.1±1.7	32.7±3.4
PBS/starch(15) 60:40	27.5±0.4	23.5±0.3	658±9.1	631±12	10.9±2.3	11.0±2.3
PBS/starch(20) 60:40	27.0±0.4	27.1±0.7	628±4.7	628±6.5	5.1±0.1	5.50±0.3

modulus, tensile strength and elongation at break of all samples of PBS/starch 60:40 blends were insignificantly different from that of their nonreactive blend. However, PBS/starch 60:40(10) possessed the highest elongation at break due to the plasticizing effect. Therefore, 10 wt% glycerol (of starch) was selected to demonstrate the effect of reactive compatibilizer agents on PBS/starch 60:40 and PBS/starch 70:30 blends.

According to two selected reactive systems, the effect of reactive compatibilizers on the mechanical properties of the PBS/starch blends was investigated for the two polymer compositions. The tensile strength and Young's modulus were characterized as shown in Figure 2. Young's modulus was increased with increasing starch contents while tensile strength decreased. In the case of reactive compatibilized blends, Young's modulus was slightly increased. A reactive MA/peroxide system, for fixed MA content of 0.20 phr and varying peroxide contents between 0.01 and 0.04 phr, clearly improved the tensile strength of PBS/starch(10) 70:30, whereas for the MDI system, tensile strength remained unchanged with increasing MDI contents. The effect of reactive compatibilizers on elongation at break is shown in Figure 3. In the case of PBS/starch(10) 60:40, elongation at beak strongly increased for the system consisting of MA0.2/P0.01 phr/phr, after that it decreased with increasing peroxide and MA. In the case of PBS/starch(10) 70:30, elongation at beak increased upon increasing peroxide concentrations (MA0.2/P0.01-0.04 phr/phr). The blends containing MA0.5/P0.02 phr/phr had lower elongation at break than those of the blends containing 0.2 phr of MA. For the MDI system with PBS/starch(10) 70:30, elongation at break of all samples had relatively high value (about 45%) and were very close to a value of the system consisting of MA0.2/P0.04 phr/phr loaded in this same blend ratio. However, for MDI system with a higher starch content of PBS/starch(10) 60:40, elongation at break was very low except for MDI of 0.2 phr loading.

3.2 Morphological Observations

SEM micrographs of starch granules and fractured surface of PBS/starch 60:40 blends at various glycerol contents are showed in Figure 4. An average particle size of starch granules was approximately 20–30 μm and they remained spherical in shape (as seen in Figure 4a). For PBS/starch 60:40 (without glycerol), starch particles were dispersed in PBS continuous phase with the same size or slightly smaller than the original starch granules and retained their shape (Figure 4b). Many starch particles were pulled out from PBS matrix
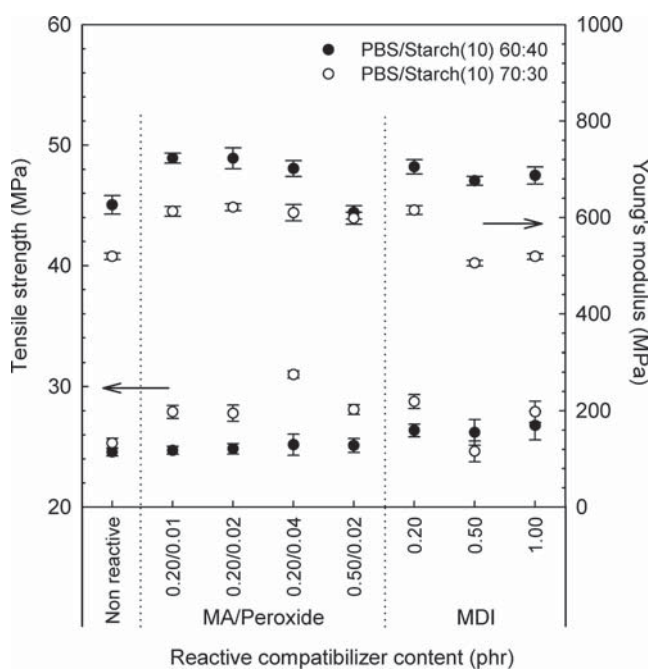
Figure 2 Tensile strength and Young's modulus of PBS/starch(10) 60:40 and PBS/starch(10) 70:30 at different reactive agent concentrations.
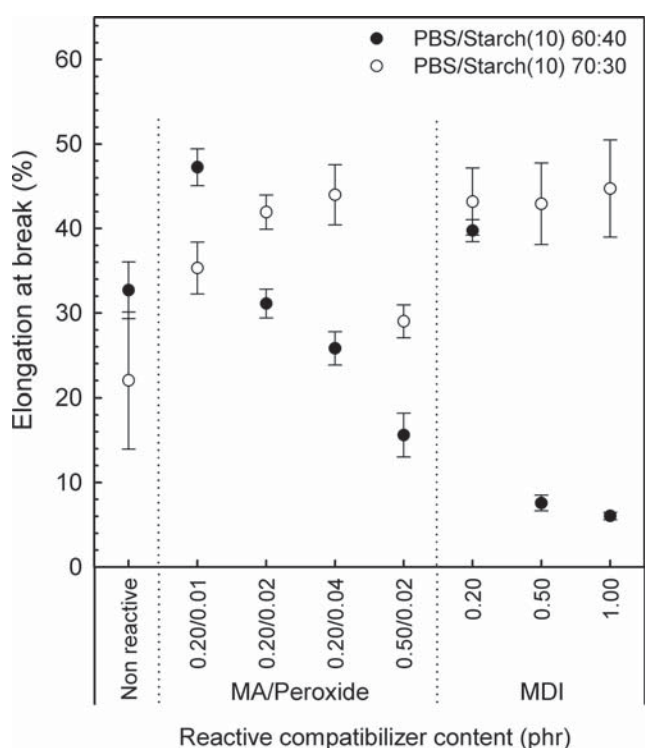
Figure 3 Elongation at break of PBS/starch(10) 60:40 and PBS/starch(10) 70:30 at different reactive agent concentrations.
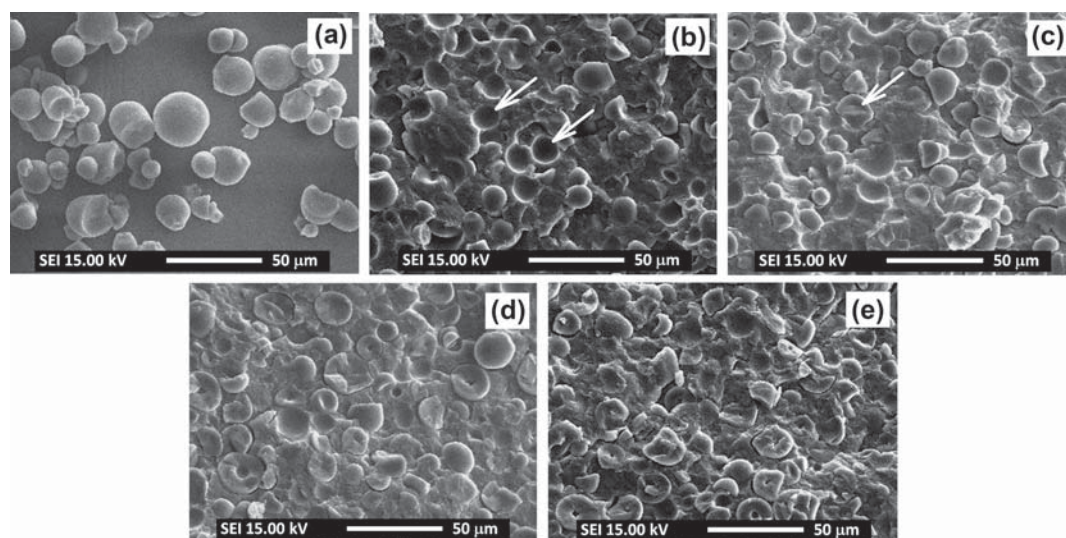
Figure 4 SEM images of (**a**) starch granules and fractured surface PBS/starch 60:40 blends at various glycerol contents: (**b**) 0 , (**c**) 10, (**d**) 15, and (**e**) 20 wt% (by starch).
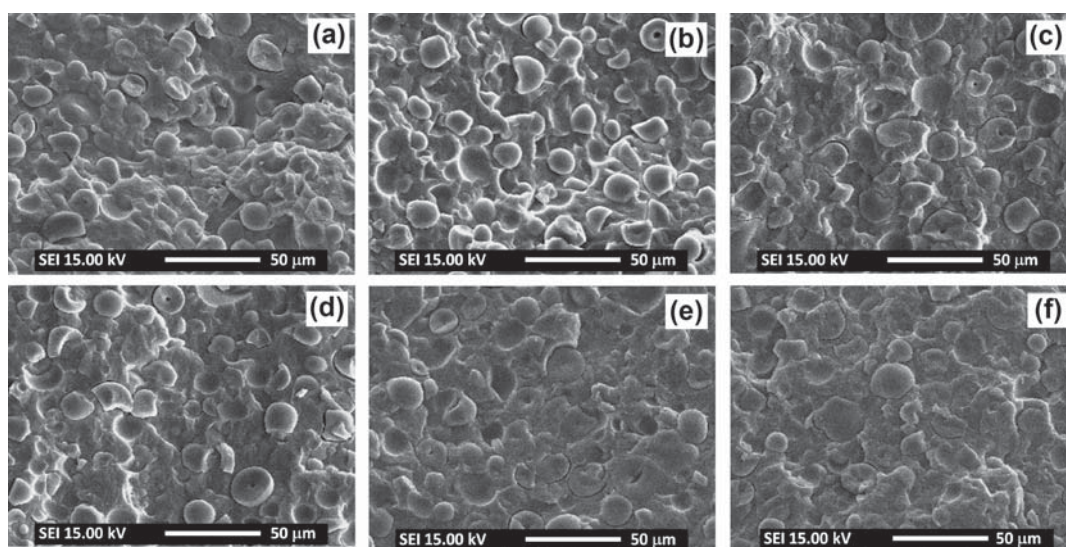

Figure 5 SEM micrographs of the fractured surface of PBS/starch(10) 60:40 with (**a**) MA0.20/P0.01 phr/phr, (**b**) MA0.20/P0.04 phr/phr, (**c**) MA0.50/P0.02 phr/phr, (**d**) MDI 0.20 phr, (**e**) MDI 0.50 phr, and (**f**) MDI 1.00 phr.

resulting in empty holds (arrow signs), implying a poor adhesion between PBS and starch. In the blend of PBS/starch (10) 60:40 (Figure 4c), the starch particle sizes were decreased and had better interface adhesion. In Figure 4(d), when glycerol was increased to 15 wt% of starch, the SEM micrograph showed the disruption of long shape phase, implying that the dispersion phase was not dried starch particles. These indicated that some thermoplastic starch was formed. Some of the TPS phase was greater than the original starch granule. This might be due to a high viscosity of TPS produced during blending. Figure 4(e) shows

that TPS could form co-continuous phase with PBS. Some visual cavity can be observed around plasticized starch phase, reflecting a lack of interactions between PBS and starch.

The chemical reaction at the interface of polymer blends is expected to decrease interfacial tension in melt leading to a smaller dispersion phase, therefore enhancing the adhesion bonding strength. The MA/peroxide and MDI as reactive agents used in this study were expected to react across the polymer interface. The results of interface modification are shown as SEM images in Figure 5 and Figure 6.

Figure 5 shows the fractured surface of PBS/ starch(10) 60:40 with MA/peroxide (Figure 5a–c) and MDI (Figure 5d–g) at various concentrations. All of the PBS/starch(10) 60:40 blends with or without reactive compatibilizers showed blended morphology, consisting of starch particles and disrupted plasticized starches. The blending of PBS/starch(10) 60:40 with MA0.2/P0.01 phr/phr exhibited the best interfacial adhesion and a fine dispersion phase similar to those with 0.2 phr MDI reactive system. They gave a better interfacial adhesion between PBS and starch than that of the nonreactive blend. When increasing peroxide or MA contents, large dispersion phases were obtained.

The fractured surface of PBS/starch(10) 70:30 with MA/peroxide and MDI at various concentrations are shown in Figure 6. For the MA/peroxide reactive system, the best morphology was obtained for the condition using MA0.20/P0.01 phr/phr (Figure 6b). In the case of the MDI reactive system, the starch phase sizes were decreased with increasing MDI loads, as observed by SEM micrographs (Figure 6e–g). MDI 1.0 phr loading expressed the best interfacial adhesion

and fine morphology in MDI-PBS/starch(10) 70:30 system.

3.3 Molau and Gel Content Tests

Figure 7a and b show the emulsifying effect of the graft copolymer in PBS/starch(10) 60:40 and PBS/starch(10) 70:30 called the Molau test. PBS/starch(10) 60:40 and PBS/starch(10) 70:30 with and without compatibilizers were dissolved with dichloromethane (CH_2Cl_2). PBS phase is soluble in CH_2Cl_2, whereas the starch phase is insoluble. PBS/starch(10) 60:40 and PBS/starch(10) 70:30 blends showed a complete phase separation and clear CH_2Cl_2 solution. On the other hand, in cases of polymer blends reactive with MA/peroxide and MDI, the solution was less clear. The emulsifying effects of PBS/starch(10) 60:40 and PBS/starch(10) 70:30 blends were similar in all cases of MA/peroxide system. The peroxide concentrations had no significant effect on the turbidity of solution. However, for MDI system, it showed some colloidal suspension when compared to MA/peroxide system at the same concentration. Therefore, the appearance of turbidity in CH_2Cl_2 solution possibly
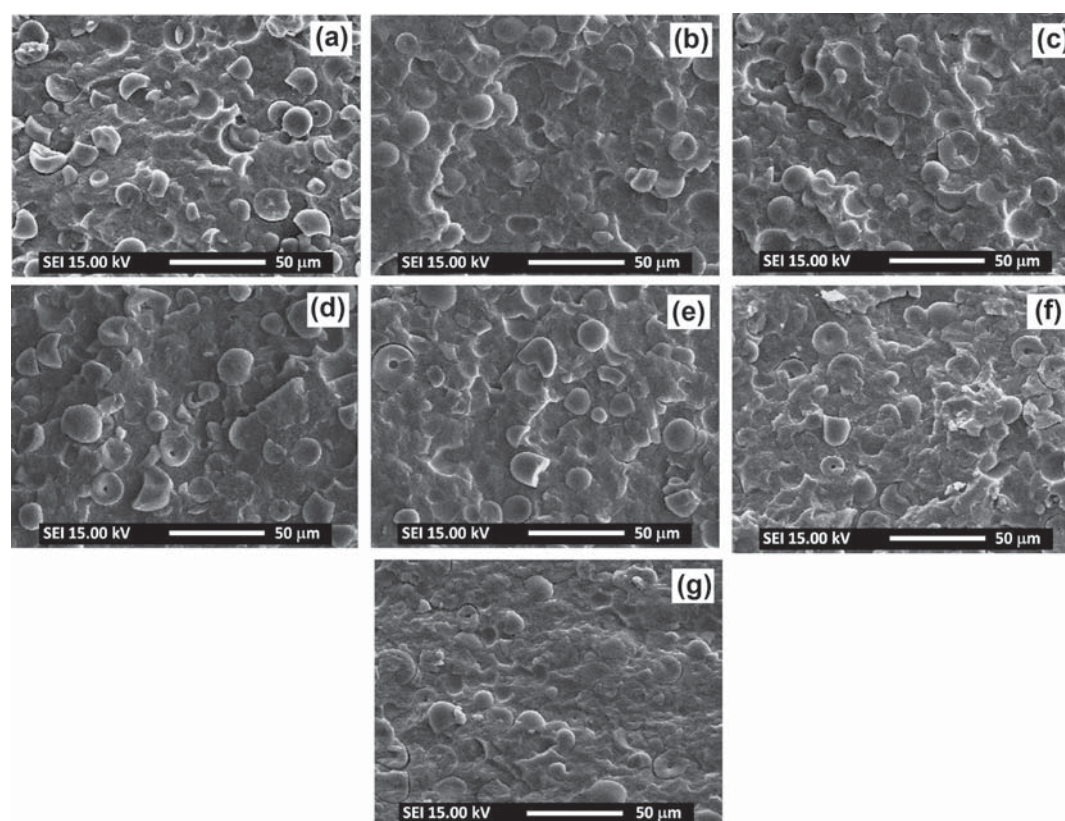

Figure 6 SEM micrographs of the fractured surfaces of PBS/starch(10) 70:30 (**a**) without and with reactive compatibilizers: (**b**) MA0.20/P0.01 phr/phr, (**c**) MA0.20/P0.04 phr/phr, (**d**) MA0.50/P0.02 phr/phr, (**e**) MDI 0.20 phr, (**f**) MDI 0.50 phr, and (**g**) MDI 1.00 phr.
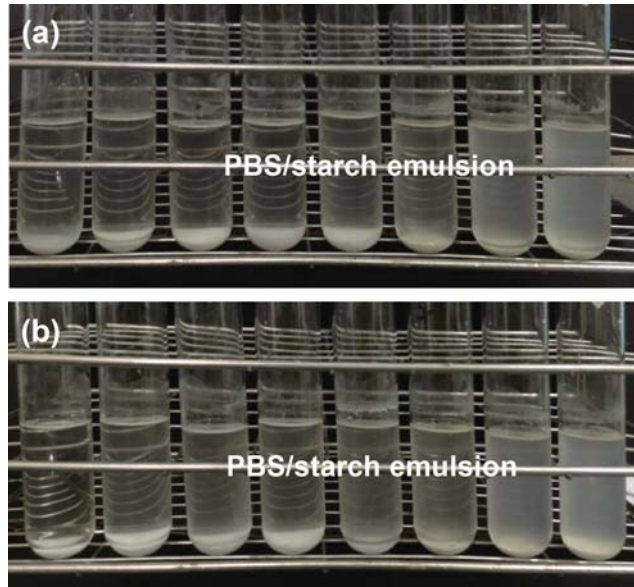
Figure 7 Photographs obtained from the Molau test of (**a**) PBS/starch(10) 60:40 and (**b**) PBS/starch(10) 70:30 with no compatibilizers; MA0.20/P0.01 phr/phr, MA0.20/P0.02 phr/phr, MA0.20/P0.04 phr/phr, MA0.50/P0.02 phr/phr, MDI 0.20 phr, MDI 0.50 phr, and MDI 1.00 phr, respectively, from left to right tube.

Figure 8 Gel contents of PBS/starch(10) 60:40 and PBS/starch(10) 70:30 with reactive compatibilizers after extraction by dichloromethane and HCl.

implied the occurrence of co-polymer between the two polymer components.

For both reactive systems, a side reaction such as crosslinking could occur. Crosslinked polymers give more gel contents in polymer blends, which are obtained after removing PBS and starch by CH_2Cl_2 and HCl (1 M), respectively. In each step, the residues were filtered through a 120-mesh sieve according to ASTM D2765. The gel was not dissolved in both CH_2Cl_2 and HCl. The gel contents (%) of PBS/starch(10) 60:40 and PBS/starch(10) 70:30 with reactive compatibilizers are presented in Figure 8. All of the blends showed low gel content (less than 4%), but it increased with the amount of added reactive agents. A small gel fraction indicated possible crosslinked phase and some graft copolymer in the blends. PBS/starch(10) 70:30 with reactive compatibilizers showed higher gel fraction than that of PBS/starch(10) 60:40 system.

The gel fractions of PBS/starch(10) 70:30 from the extraction method were characterized by FTIR, and compared with the starch and PBS as shown in Figure 9. The FTIR spectrum of PBS showed the characteristic at peak 1726 cm^{-1} and 1175 cm^{-1} assigning to carbonyl (C=O) groups and C-O stretching, respectively. The FTIR characteristic peaks of starch were about 3400 cm^{-1}, 1640 cm^{-1}, and 1041 cm^{-1} corresponding to -OH stretch, -OH bending, and C-O in alcohol, respectively. The FTIR spectra of the gel fractions from the reactive blends showed both
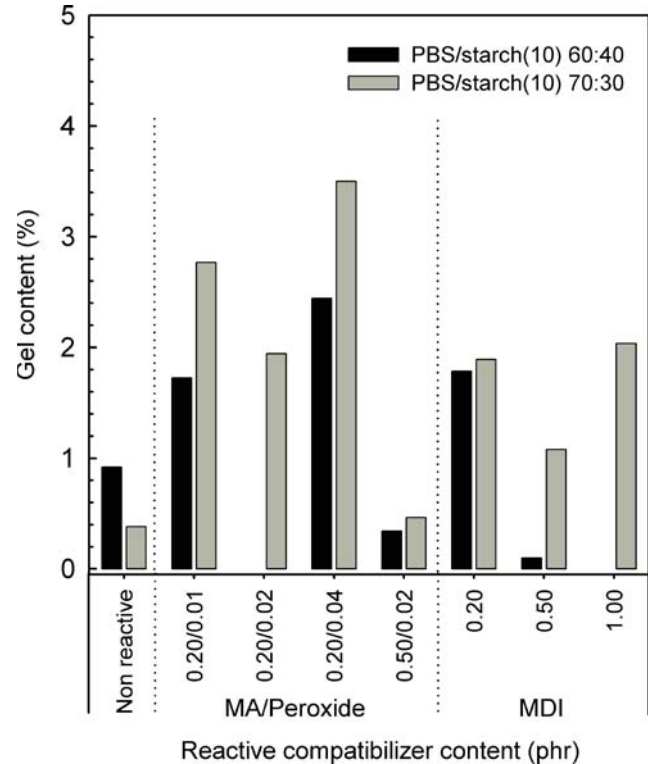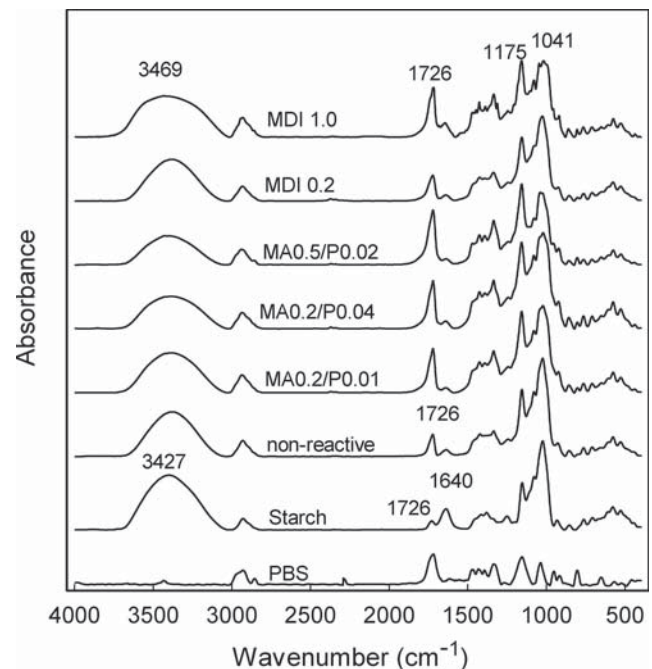

Figure 9 FTIR spectra of PBS/starch(10) 70:30 with reactive compatibilizers after extraction by dichloromethane and HCl.

characteristics of PBS and starch. It indicated that the gel fraction contained PBS-g-starch (graft copolymer). This suggested that the graft copolymer occurred at the interface of PBS and starch.

4   CONCLUSIONS

The one-step process was convenient for preparing the biopolymer blends such as PBS/starch blends. The glycerol content has an effect on the starch's state (from starch granule to thermoplastic starch) and interfacial adhesion. Therefore, it was an important factor resulting in the mechanical properties and morphology of polymer blends for both nonreactive and reactive systems. The glycerol of 10 wt% of starch was enough to obtain dispersed small-starch-particle morphologies and the highest elongation at break among all plasticized blends. The compatibility of PBS/starch blends were improved by both MA/peroxide and MDI, demonstrated by increasing mechanical properties, good adhesions of PBS/starch interface, and the small evenly dispersed starch particles. MA0.20/P0.01 (phr/phr) and MDI of 0.2 phr were sufficient to improve the mechanical properties of PBS/starch(10) 60:40 and PBS/starch(10) 70:30. The results from the Molau test and FTIR spectra confirmed the formation of graft-copolymer at the interface of PBS and starch when reactive compatibilizers were added. The lightly crosslinked polymers could be formed as suggested by very low % gel content.

ACKNOWLEDGMENTS

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