Effect of Compatibilizer Distribution on the Blends of Starch/Biodegradable Polyesters

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ABSTRACT: Various blends of gelatinized cornstarch and two biodegradable polyesters, PCL or PBSA, were prepared via melt processing using a twin-screw extruder. Distribution of a compatibilizer MDI (methylenediphenyl diisocyanate) was controlled through the processing conditions employed and its effect on the resultant microstructure and mechanical properties of the blends were studied by SEM, DSC, TGA, and mechanical testing. When the MDI was distributed in the starch phase, the highly reactive isocyanate groups in MDI were most probably consumed by water that resulted in an overall weakening of its compatibilizing effect. Modulus, yield strength, and impact strength were increased by more than 35, 40, and 300%, respectively, when MDI was distributed in the polyester phase first rather than in the starch phase prior to blending. SEM observation showed that the interface between starch and the polyesters was improved significantly while DSC and TGA investigation also confirmed the microstructural difference. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 812–818, 2007

Key words: starch; PCL; PBSA; blend; compatibilizer; MDI; distribution

INTRODUCTION

The use of petrochemical-based polymers for disposable items have attracted more and more attention due to ecological concerns. Development of biodegradable plastics, especially for short-term applications, has become increasingly important to reduce the impact on the environment. Starch has been considered as a low-cost alternative and has attracted great attention.[1–3] However, the moisture sensitivity of thermoplastic starch limits many of its potential applications. On the other hand, various biodegradable aliphatic polyesters have been developed,[4] such as polylactic acid (PLA), polycaprolactone (PCL), poly(butylene succinate adipate) (PBSA), etc., which have good water resistance. So far, the high price of these biodegradable aliphatic polyesters has limited their general application. Blending these two kinds of polymers together is of significant interest, since it could lead to the development of a new range of biodegradable polymeric materials.

The blend of starch/PCL is one of the well studied biodegradable polymer blends, since both materials are commercially available and widely produced.[5–14] Koening and Huang[6,7] studied the blends of high-amylose and waxy starch granules with PCL. The blends were found to be mechanically compatible but phase-separated. Averous et al.[13] reported the blend of wheat thermoplastic starch with PCL. Addition of PCL to a thermoplastic starch matrix overcomes some weaknesses of pure thermoplastic starch, such as moisture sensitivity and size stability. Thermal and hydrophobicity studies have shown a fairly low compatibility between these two polymers. Another promising blend is that of cornstarch and poly(butylene succinate adipate) (PBSA, commercial name PBSA).[15–19] In the range of starch content 5–30%, increasing the content of starch granules led to an increase in modulus and a decrease in tensile strength and elongation. SEM revealed that the starch granules were embedded in the continuous-phase PBSA.

Hydrophobic aliphatic polyesters and hydrophilic starches are thermodynamically immiscible, which leads to poor adhesion between the two components, and poor and irreproducible performance. Various compatibilizers and additives have been evaluated to improve the interface between starch and the biodegradable polyesters. Methylenediphenyl diisocyanate (MDI) is one of the well studied compatibilizers, in particular, for the blends of starch/PLA.[20–23] Blends containing MDI have been shown to exhibit enhanced

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mechanical properties, which may be explained by the *in situ* formation of a block copolymer acting as a compatibilizer. Recently, Kweon et al.[24] studied starch-*g*-polycaprolactone copolymerization using diisocyanate (DI) intermediates. By introducing DI to PCL, the melting temperature was decreased.

Starch is a highly hydrophilic material that contains anhydro-glucose units linked by α-D-1,4-glycosidic bond. The water absorbed by starch granules is mainly bound in the amorphous phase.[25] Under a certain temperature, shear stress and pressure in an extruder, the gelatinization processing disrupts the crystalline and ordered structure in starch granules to produce an amorphous phase. Previous research has shown that the highly reactive isocyanate group in MDI could be consumed by the water absorbed in starch granules,[26] which results in weakening the coupling function at the interface between starch and polyester phases.

In this work, various blends of gelatinized cornstarch and two biodegradable polyesters, PCL or PBSA, were used to demonstrate the effect of compatibilizer, especially its distribution, on the microstructure and mechanical properties. The blends were prepared through compounding via twin-screw extrusion followed by injection molding. Methylenediphenyl diisocyanate (MDI) was used as a compatibilizer to improve the interface between starch and polyesters. The distribution of MDI was controlled through processing, and its effect on microstructure and mechanical properties were studied by SEM, DSC, TGA, and mechanical testing.

EXPERIMENTAL

Materials and compounding

High amylose cornstarch, supplied by Penford, Australia, with moisture content 13.1% was used in the experimental work. Two commercial biodegradable ali-phatic polyesters were used: (1) polybutylene succinate adipate (PBSA, commercial name Bionolle[TM]) supplied by Showa Polymers Japan; (2) polycaprolactone (PCL, commercial name CAPA, grade 650) supplied by Solvay caprolactones, with a M_w of 50,000. The preparation of the blends involved (1) gelatinization of starch; (2) premixing of the gelatinized starch and polyester; and (3) compounding gelatinized starch with polyester. Initially 70 wt % cornstarch (dry based) was pregelatinized with 30% water using a twin-screw extruder with the highest temperature reaching 170°C (60, 100, 150, 170, 170, 170, 170, 170, and 150°C for zone 1 to 9 and 130°C for the die). The pellets of gelatinized starch were premixed with polyester in various ratios of starch/polyester than compounded using the extruder with the highest temperature of 110°C and 180°C for starch/PLC and starch/PBSA blends, respectively. Table I lists the blends with various ratios of starch/polyester used in the experimental work.

The compatibilizer, methylenediphenyl diisocyanate (MDI) (purity 99.9%), was added into the blends at different stages to control its distribution. The compatibilizer was added to the blends in three different ways: (1) adding it into the starch phase during starch gelatinization, labeled (starch/MDI)/polyester; (2) adding it into the polyester phase through compounding the polyester with MDI first, than compounding the polyester containing the MDI with gelatinized starch, labeled starch/(polyester/MDI); (3) adding it into the blends of starch/polyester during premixing gelatinized starch and polyester, labeled as starch/MDI/polyester. In this work, 0.5 and 1.0% MDI was used in various blends. Table I lists the blends containing the MDI distributed in different phases.

Specimen preparation and mechanical testing

The specimens used for testing mechanical properties were prepared using a Battenfeld injection molder.

TABLE I
Blends Contain MDI Distributed in Different Phase

No.	Code	Formulation (%)	Add MDI into
1	Starch/PCL	Starch 50/PCL 50	N/A
2	Starch/MDI-0.5/PCL	Starch 49.75/MDI-0.5/PCL 49.75	Blend
3	Starch/MDI-1.0/PCL	Starch 49.5/MDI-1.0/PCL 49.5	Blend
4	(Starch/MDI-0.5)/PCL	(Starch 49.75/MDI-0.5)/PCL 49.75	Starch
5	(Starch/MDI-1.0)/PCL	(Starch 49.5/MDI-1.0)/PCL 49.5	Starch
6	Starch/(MDI-0.5/PCL)	Starch 49.75/(MDI-0.5/PCL 49.75)	PCL
7	Starch/(MDI-1.0/PCL)	Starch 49.5/(MDI-1.0/PCL 49.5)	PCL
8	Starch/PBSA	Starch 50/PBSA 50	N/A
9	Starch/MDI-0.5/PBSA	Starch 49.75/MDI-0.5/PBSA 49.75	Blend
10	Starch/MDI-1.0/PBSA	Starch 49.5/MDI-1.0/PBSA 49.5	Blend
11	(Starch/MDI-0.5)/PBSA	(Starch 49.75/MDI-0.5)/PBSA 49.75	Starch
12	(Starch/MDI-1.0)/ PBSA	(Starch 49.5/MDI-1.0)/PBSA 49.5	Starch
13	Starch/(MDI-0.5/ PBSA)	Starch 49.75/(MDI-0.5/PBSA 49.75)	PBSA
14	Starch/(MDI-1.0/ PBSA)	Starch 49.5/(MDI-1.0/PBSA 49.5)	PBSA

N/A, Not applicable.

TABLE II
Mechanical Properties of Starch/Polyesters Blends in Different Ratio

Formulation	Modulus (MPa)	Yield strength (MPa)	Impact strength (MPa)	Moisture content (%)
Pure PCL	390.0	17.6	144.9	0.6
PCL 90/starch 10	447.0	14.9	100.5	1.8
PCL 80/starch 20	434.0	15.0	76.6	3.3
PCL 70/starch 30	429.9	14.2	46.5	4.2
PCL 60/starch 40	253.4	12.8	39.8	5.9
PCL 50/starch 50	215.8	11.2	27.9	8.5
Pure PBSA	386.9	22.5	300.0	0.4
PBSA 90/starch 10	476.5	18.7	145.0	1.5
PBSA 80/starch 20	463.1	15.8	81.7	2.8
PBSA 70/starch 30	544.5	13.3	65.9	4.0
PBSA 60/starch 40	466.6	13.6	34.5	5.4
PBSA 50/starch 50	249.2	12.3	36.3	7.1

The injection temperature used for the blends of PCL/starch and starch/PBSA was 80 and 120°C, respectively. Tensile properties were evaluated in accordance with ASTM D5938 standard on an Instron tensile testing apparatus (5565). Tensile strength and elongation were measured at a crosshead speed of 50 mm/min. An external extensometer was used for independent modulus measurement at a crosshead speed of 0.5 mm/min. Impact testing was carried out according to ASTM 256 on a Radmana IRT 2000 instrumented impact tester in Izod mode with impact strain rate 3.5 m/s.

Microstructure characterization

A Leica Stereoscan 360FE SEM was used to investigate the fracture surfaces and morphologies of the blends. The fracture surface was obtained from impact testing and coated with gold. Morphologies of the blends were studied using cryo surfaces in which starch had been removed. Cryo fracture surfaces were prepared by immersing the specimens in liquid nitrogen for 3 min followed by manual fracture. The broken specimens were then immersed in water and placed in an ultrasonic bath for 30 min at a temperature of about 45°C to dissolve and remove the starch phase on the surface. A lower voltage of 2 K was used in the experimental work to avoid damaging the surface.

A PerkinElmer Diamond-1 DSC apparatus was used to study the effect of MDI on the melting properties of the polyesters. Samples were cut from impact specimens and a heating rate of 10°C/min was used in the experimental work. A PerkinElmer Diamond-TGA apparatus was used to study the effect of MDI on the thermal stability of the blends. Samples were heated to 650°C at a rate of 20°C/min. The results of weight loss were converted into divination weight percentage.

RESULTS AND DISCUSSION

Table II lists the mechanical properties and moisture content for a series of PCL/starch and PBSA/starch blends, in which the ratio of starch to polyester has been changed incrementally. It is seen that the modulus of these two kinds of blends were increased initially with the addition of starch, but reaches a maximum, after which increasing the starch content further resulted in a reduction of the modulus value. Yield strength and impact strength were decreased with increasing addition of the incompatible starch, in particular at high starch loadings. Similar results were also reported by others.[5–19]

The 50 : 50 wt : wt blend of starch/polyester was used to demonstrate the effect of the compatibilizer MDI on the mechanical properties, in particular the distribution of MDI. Figure 1 shows the mechanical
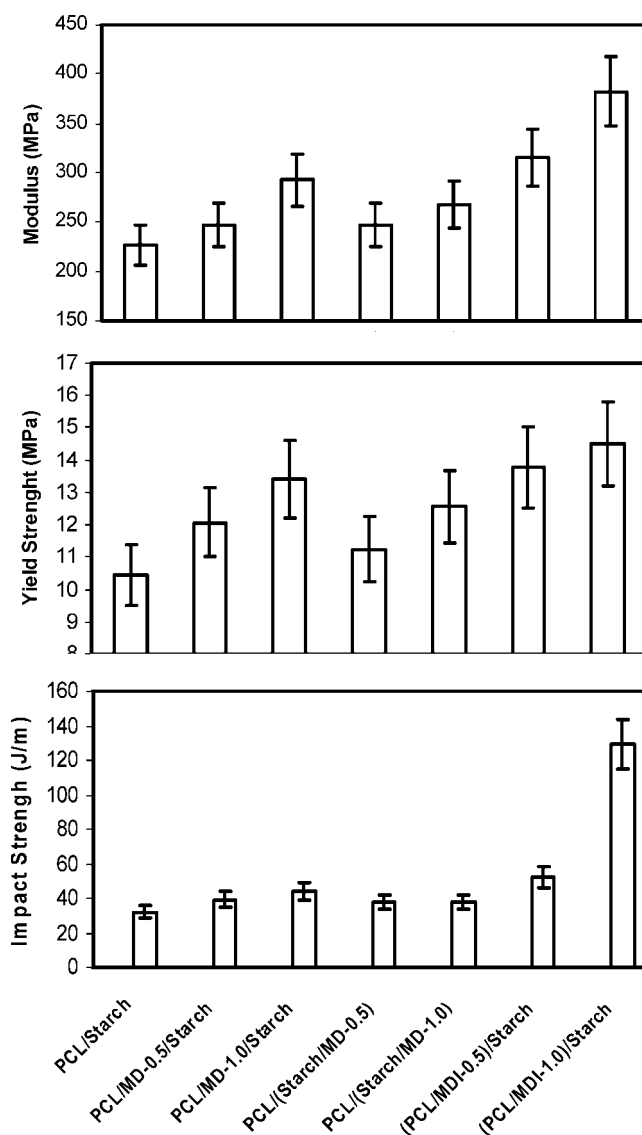

Figure 1 Mechanical properties of PCL/starch blends containing MDI distributed in different phase.

properties of PCL/starch blends containing MDI distributed in the different phases. It is seen that the mechanical properties, modulus, yield strength, and impact strength, were increased with addition of compatibilizer MDI. Increasing the content of MDI from 0.5 to 1% showed a better result. Similar improvement and trends have been reported in starch/PLA blends.[20–23] This improvement may be explained by the *in situ* formation of a compatibilizing block copolymer formed between the MDI isocyanate groups, and the hydroxy groups associated with the starch and the polyester. It is important to note that the distribution of MDI had a significant effect on mechanical properties. The modulus, yield strength, and impact strength were increased ∼30, 40, and 300%, respectively, when MDI was distributed into the PCL phase rather than in the starch phase. Similar results were also observed in PBSA/starch blends (Fig. 2). Modulus, yield strength, and impact strength are increased about 30, 45, and 350%, respectively, when MDI is distributed in the PBSA phase rather than in the starch phase. This phenomenon can be explained by the preference of the highly reactive isocyanate group in MDI to react with the water absorbed in starch, which is shown in eq. (1).

$$O=C=N-\bigcirc-CH_2-\bigcirc-N=C=O \ + H_2O \longrightarrow$$

$$O=C=N-\bigcirc-CH_2-\bigcirc-NH_2 + CO_2 \quad (1)$$
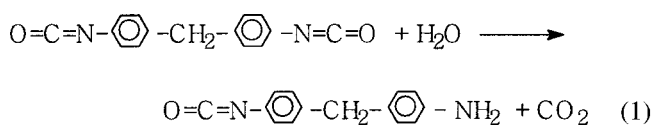
When MDI was first compounded with the starch containing 30% water, it is expected that the dominant interaction would be between the MDI and water because of the higher content of free water. Gelatinized starch (contained about 17% water) not only has a lower concentration of water, but also the water molecules may also have a reduced mobility since they are bound (via hydrogen bonding) to the numerous hydroxyl groups present in the starch. A small amount of bubbles produced by the NCO/H$_2$O reaction were observed in the compounded pellets, however these were removed in the injection molding process. When the MDI was first combined with the polyester phase prior to blending with the gelatinized starch, the most pronounced effect on improving properties occurred, which could be explained by a number of different mechanisms. When the MDI is first extruded with the polyester, it may react with the hydroxy groups present at the end of the polyester chains producing a MDI grafted polyester to extend the chain length or it may also remain unreacted, but well dispersed within the polyester matrix. The isocyanate groups on the MDI grafted polyester could react with the hydroxyl groups in the starch, producing the compatibilizing starch/polyester block copolymer. It is also possible that the free dispersed isocya-
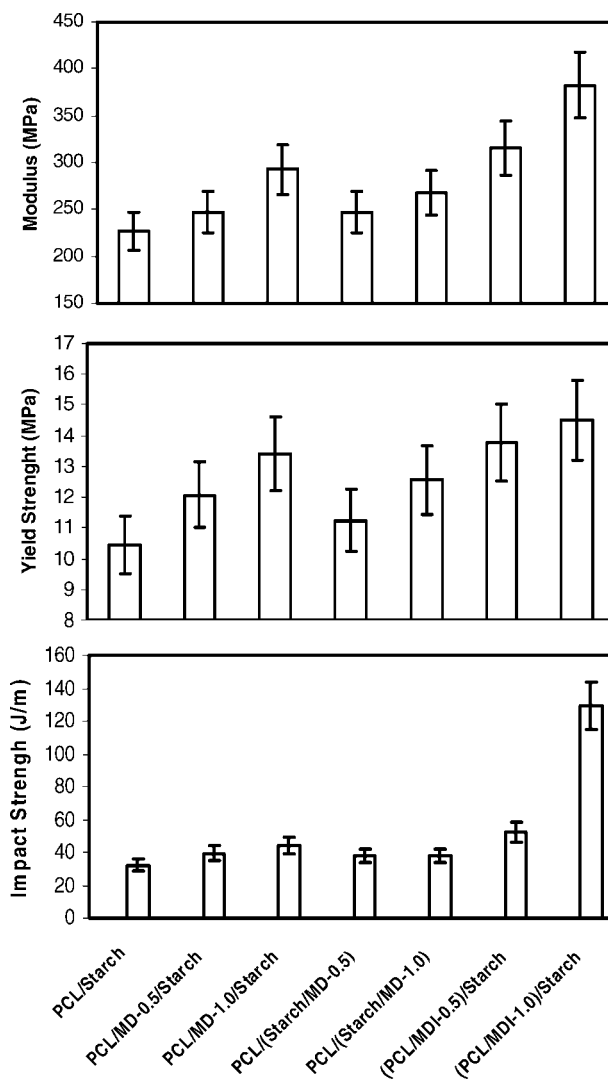

Figure 2 Mechanical properties of PBSA/starch blends containing MDI distributed in different phase.

nate could also react with the hydroxyl groups in the starch and the polyester during the second extrusion. The second extrusion of MDI/polyester with gelatinized starch may result in further hydrolysis of the ester groups of the polyester via the water bound in the gelatinized starch producing more hydroxyl end groups for the isocyanate to react with.

Figure 3 shows the fracture surfaces of 50 : 50 wt : wt blend of starch/PCL after impact testing observed by SEM. The blend of PCL/starch without the compatibilizer MDI [Fig. 3(a)] showed that PCL was a continuous phase with starch distributed as spherical particles with the largest particle diameter being about 5 μm. The interface between starch and PCL was poor, and the phase separation between starch and PCL could be clearly observed, which may be expected since hydrophilic starches and hydrophobic aliphatic polyesters are thermodynamically immiscible. Figure 3(b) shows the PCL/starch blend with
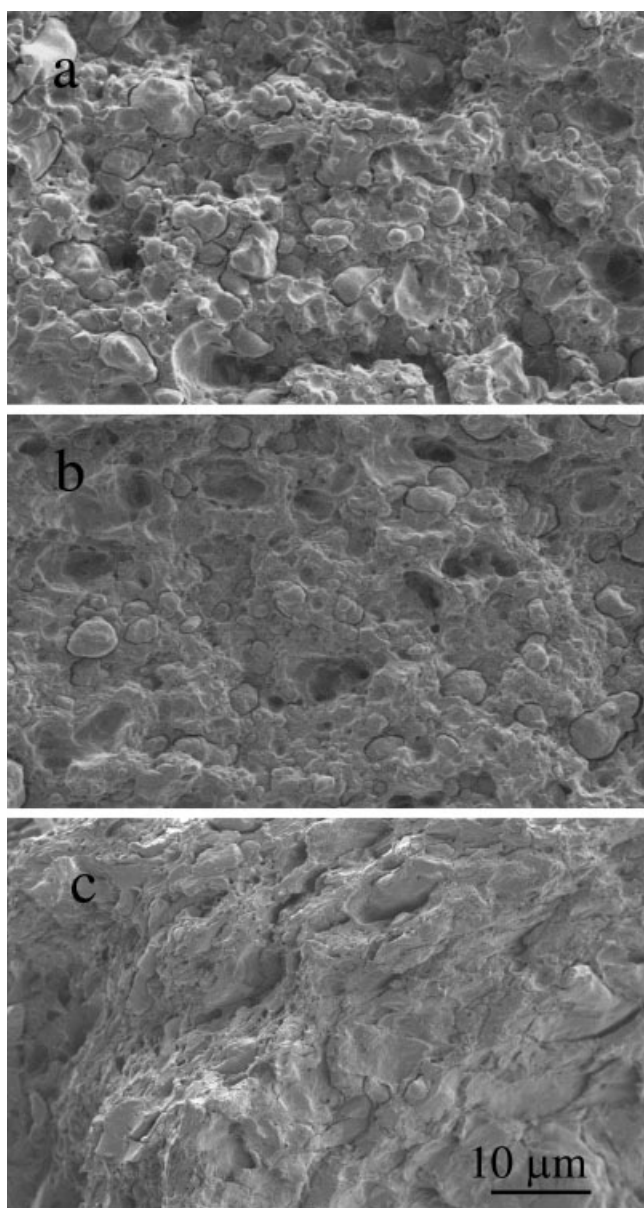
Figure 3 Fracture surfaces of starch 50/PCL 50 blends observed by SEM. (a) Starch/PCL; (b) (Starch/MDI-1.0)/PCL; and (c) Starch/(PCL/MDI-1.0).

MDI distributed in the starch phase. The fracture surface in Figure 3(b) was similar to that shown in Figure 3(a), which indicated that little reaction had occurred between the isocyanate and the starch/polyester. As discussed previously, the MDI was more likely consumed by the water absorbed in starch. Figure 3(c) illustrates the PCL/starch blend where MDI is distributed in the PCL phase. Clearly, the interface has been improved significantly by the addition of MDI since the spherical particles disappeared and the interface became unclear. Similar results were also observed for PBSA/starch blends (Fig. 4). In the PBSA/starch blend, MDI distributed in the starch phase decreases the size of starch particles but does not improve the

interface between starch and PBSA [Fig. 4(a, b)]. The fracture surface has been improved significantly when MDI is distributed in the PBSA phase [Fig. 4(c)]. The improvement in compatibility (as observed in the fracture surfaces) when the MDI was initially distributed in polyester phase correlates to the improved mechanical properties observed and can be explained in terms of the formation of a compatibilizing block copolymer between the isocyanate group and the hydroxy groups of the starch and the hydroxy end groups of the polyester.

Figure 5 shows the SEM images of PCL/starch blends, in which the starch phase has been removed.
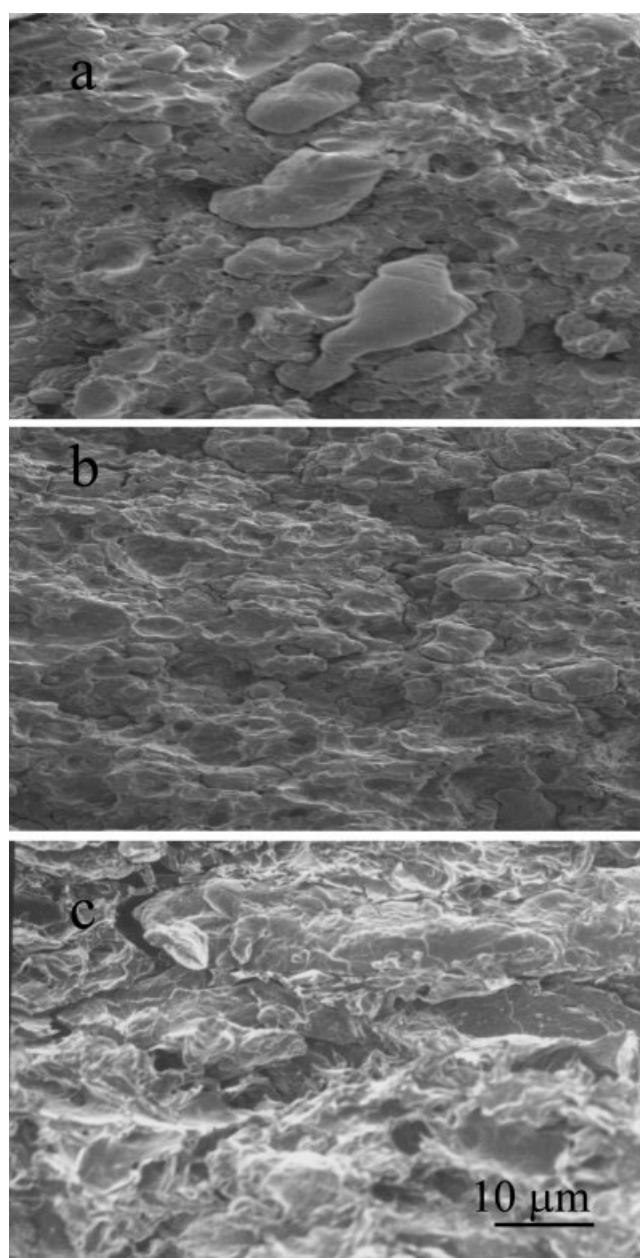

Figure 4 Fracture surfaces of starch 50/PBSA 50 blends observed by SEM. (a) Starch/BIO; (b) (Starch/MDI-1.0)/BIO; and (c) Starch/(BIO/MDI-1.0).
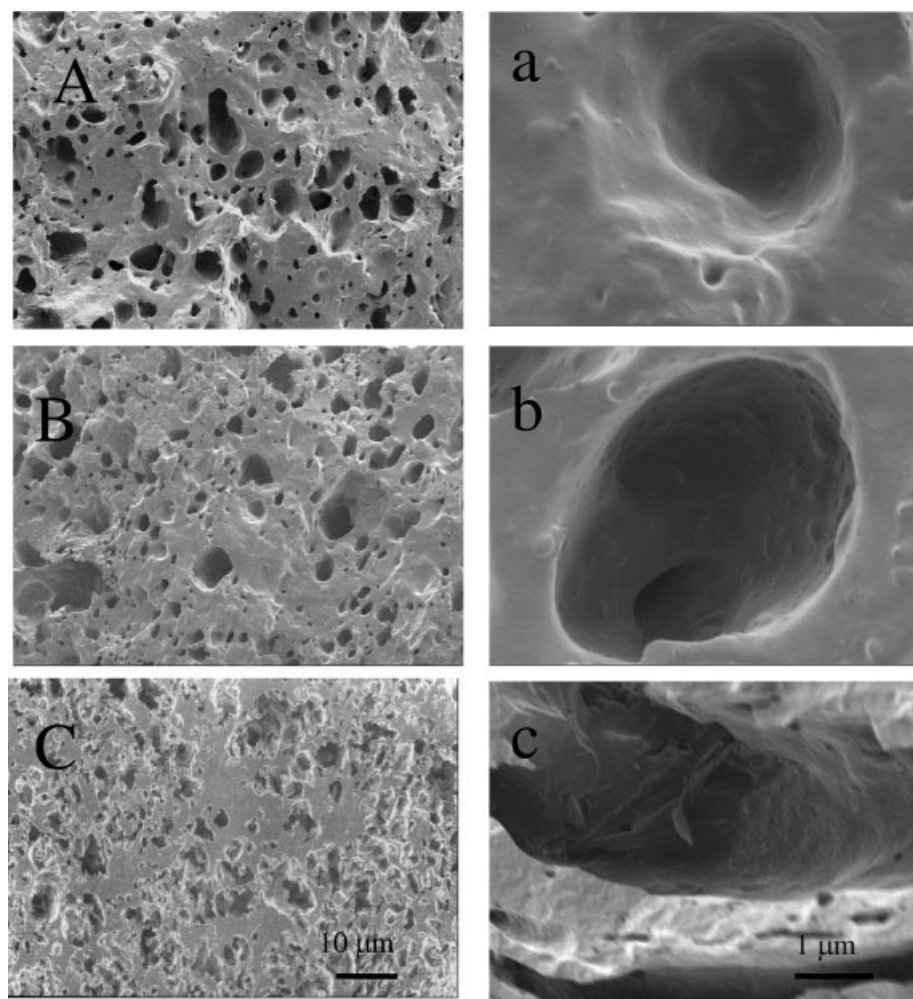
Figure 5 SEM of PCL 70/starch 30 blends containing MDI (1%) distributed in different phase. (A) and (a) are PCL/starch blend without MDI as an refereed; (B) and (b) are the (starch-MDI)/PCL blend; and (C) and (c) are starch/(PCL-MDI) blends.

In this image, the PCL was a continuous phase and the removed starch appears as dark holes with the largest diameter of these holes being about 5 μm. Figure 5(A) shows the PCL/starch blend without MDI. It is seen that the removed starch appears as spherical holes with smooth edges. Similar microstructure was also observed when MDI was distributed in the starch phase [Fig. 5(B)]. When the MDI was distributed in the PCL phase, the shape of the holes became irregular [Fig. 5(C)]. The spherical holes became random and the edges became rough and unclear. Figure 5(a–c) show the enlarged holes from SEM images on the left [Fig. 5(A–C)]. It can be observed that the surface and edge of the holes are very smooth when the MDI was distributed in starch phase or without MDI [Fig. 5(a, b)]. The surface of the holes became rough and some broken pieces appear on the surface when MDI was distributed in PCL phase, giving a clear indication that the interface between starch and PCL has been improved through addition of MDI into the PCL phase. The results correspond with the mechanical properties.

The effect of changing the distribution of MDI was also confirmed by the thermal behaviors of different blends characterized by DSC and TGA. Figure 6
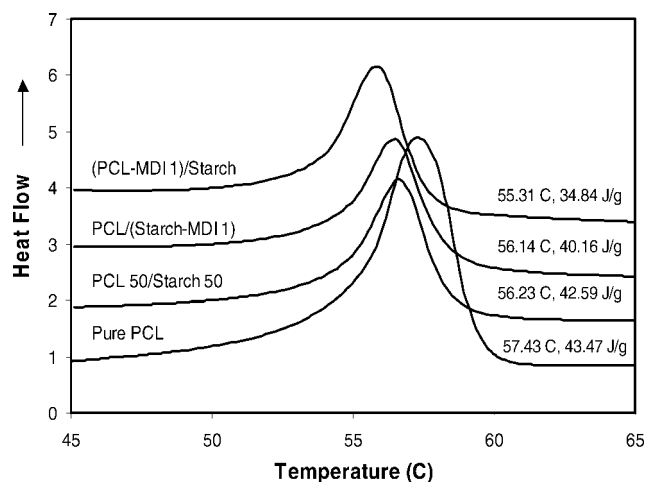

Figure 6 Effect of MDI distribution in PCL/starch blends on the melting properties of PCL measured by DSC.
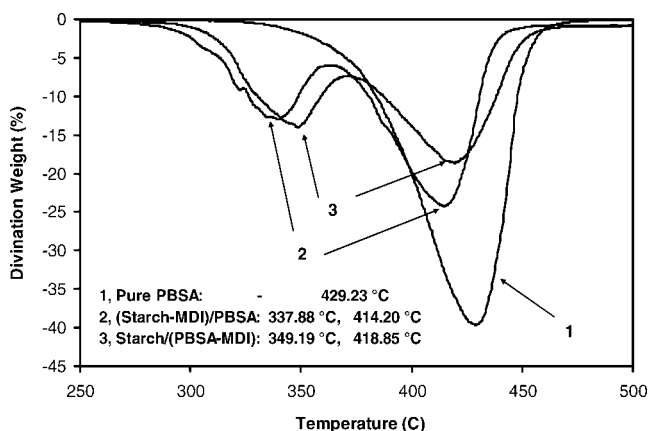
Figure 7 Effect of MDI distribution in PBSA/starch blends on the decomposition temperature of PCL.

shows the DSC thermograms of the PCL/starch blends. The addition of starch to PCL appeared to decrease the melting temperature and melting enthalpy of PCL, possibly due to a reduction in molecular weight of the PCL and hydrolysis of the ester groups by the water in the gelatinized starch similar to previously reported work.[13] The addition of MDI to the blend enhanced the effect of starch, further decreasing the melting temperature and melting enthalpy of PCL, in particular, when MDI was distributed in the PCL phase. The effect of MDI distribution on PBSA/starch blends was also observed. Figure 7 shows the effect of MDI distribution on the decomposition temperature of starch and PBSA in their blends. Two decomposition peaks were observed: the first is the decomposition of starch (at about 340°C) and the other is the decomposition of the PBSA (at about 425°C). Starch decreases the decomposition temperature of the PBSA slightly. It may be noted that the decomposition temperatures of both starch and PCL are higher when MDI is distributed in the PBSA phase rather than in starch phase. Similar results were also observed for PCL/starch blends.

CONCLUSIONS

Various blends of gelatinized corn starch and biodegradable polyesters, PCL or PBSA (Bionolle™), were prepared through melt blending using a twin-screw extruder. The distribution of the compatibilizer MDI was controlled through processing. Thermal analysis

by DSC and TGA confirmed the difference when the MDI was distributed in different phases. Modulus, yield strength, and impact strength were increased significantly when MDI is distributed in the polyester phase rather than in the starch phase. SEM observation also showed that interface between starch and polyesters was improved when MDI was distributed in the polyester phase. This improvement in mechanical and interfacial properties was possibly because of the formation of a compatibilizing block copolymer formed between the isocyanate group and the hydroxy groups of the starch, and the hydroxy end groups of the polyester.

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