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Properties of soy protein isolate/polycaprolactone blends compatibilized by methylene diphenyl diisocyanate ☆

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Abstract

Blends of soy protein isolate with 10, 20, 30, 40, and 50% polycaprolactone (SPI/PCL) alone or with addition of 0.5, 1.0, 2.0 and 5.0% methylene diphenyl diisocyanate (MDI) were prepared by using an intensive mixer at 160°C for 10 min, and then milled through a 1 mm sieve. The blends and SPI were compression-molded at 150°C for 5 min, cooled to 30°C, and removed from the mold. Thermal and mechanical properties and water absorption of the blends were studied by a differential scanning calorimeter (DSC), a dynamical mechanic analyzer (DMA), an Instron, a water absorption test, and a scanning electron microscope (SEM). The glass transition temperature (T_g) of SPI was found to decrease with increasing PCL contents in the blends containing 2 wt% MDI. For 50/50 (SPI/PCL) blends, the T_g of SPI decreased with increases in MDI content. Both DSC and DMA results showed that compatibility between SPI and PCL was improved with the addition of MDI. Mechanical properties of the 50/50 (SPI/PCL) blends increased with increasing MDI concentrations. Strength of the SPI/PCL blends with 2 wt% MDI decreased, and elongation of the blends increased with increasing PCL concentration. Water resistance of the blends was improved significantly by increasing PCL concentration and by incorporating MDI.

Keywords: Soy protein isolate; Polycaprolactone; Methylene diphenyl diisocyanate

1. Introduction

The development of synthetic petroleum polymer materials has resulted in not only profitable industry but also serious problems. Every year, hundreds and thousands tons of plastic wastes are discarded [1]. Disposal of these wastes is expensive and has led to environmental problems. Incineration can generate toxic air pollution, and satisfactory landfill sites for burying are limited. Alternative disposal methods are insufficient. The use of biodegradable materials in plastics could help solve these problems, because they can be degraded in the environment by means of humidity and the action of microorganisms.

Soy protein has been considered recently as an alternative to petroleum polymer in the manufacture of adhesives, plastics, and various binders. Soybean protein, the major component of the soybean [2], is readily available from renewable resources and agricultural processing by-products. Utilizing these proteins for biodegradable resins will help alleviate environmental problems and add value to agricultural by-products. Research on soy proteins and their utilization in plastics has received more and more attention [3–26]. Plastics made from soy protein have high strength and good biodegradable performance. However, the brittleness and water sensitivity of soy protein plastics have not been resolved thoroughly although many efforts have been made [8–26], including blending soy protein with starch [15–23].

Blending is an important method in polymer manufacture and has received increasing attention because of the strong economic incentives arising from the use of polymer blends [27–29]. These blends may combine the advantages of both components and may have better properties than either component. Therefore, blending soy protein with other polymers obviously has practical importance. However, the properties of polymer blends depend greatly on their morphology and on interactions between components. Therefore, selection of the blending component or reagent is important.

Polycaprolactone (PCL) is biodegradable synthetic aliphatic polyester. Blending PCL with natural polymers, such as protein [30,31], cellulose [32,33], and starch [34–36], has been particularly interesting. However, most

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Table 1
Characteristics and amino acid composition of two major components (11S- and 7S-rich globulin) in soy protein [2]

	11S	7S
Molecular weight	360,000	175,000
Isoelectric point	6.4	4.8
Amide ammonia	17.39	1.7
Carbohydrate (%)	0	5
Tryptophan	0.75	0.30
Isoleucine	4.24	6.40
Tyrosine	2.81	3.60
Phenylalanine	3.85	7.40
Proline	6.85	4.30
Leucine	7.05	10.30
Valine	4.83	5.10
Lysine	4.44	7.00
Methionine	0.98	0.30
Cysteine	1.44	0.00
Alanine	5.16	3.70
Arginine	5.81	8.80
Threonine	3.91	2.80
Glycine	7.50	2.90
Serine	6.66	6.80
Histidine	1.89	1.70
Aspartate	11.88	14.10
Glutamate	19.97	20.50

natural polymers are hydrophilic and are not miscible with synthetic hydrophobic polymers. The blends consist of two distinctive phases whose interfaces are bounded weakly with a poor interaction, and this results in inferior physical properties. A third component (compatibilizer) usually is added to an immiscible blend to increase the compatibility and/or to modify the interfacial adhesion of the blend and, hence, to improve the mechanical properties. Bhattacharya and his group used maleated PCL (PCLMA) as a compatibilizer and found that a small amount of PCLMA improved the mechanical properties of blends of soy protein/PCL and wheat gluten/PCL [30,31].

The objective of this work was to use methylene diphenyl diisocyanate (MDI) as a compatibilizer for a soy protein isolate (SPI)/PCL blend. MDI is a small molecule and its isocyanate group is more reactive than maleic anhydride, thus it is expected that MDI is a better compatibilizer than PCLMA.

2. Experimental

2.1. Materials and preparation of samples

SPI (PRO-Fam 970) with moisture content of 6.5%, prepared by acid precipitation and containing more than 90% protein (dry basis), was provided by Archer Daniels Midland (Decatur, IL). Soy proteins contain 18 different amino acids, which are connected through peptide bonds, forming primary backbone. The primary polypeptides are further folded into three-dimensional complex protein body, forming secondary, tertiary, and quaternary structure. Two major components of soy proteins are 11S- and 7S-rich globulin, which represent about 80% of soy proteins. The major properties and amino acid composition of 11S and 7S are listed in Table 1 [2]. The SPI was dried at 50°C for 24 h before use. PCL (TONE P-767E) were obtained from Union Carbide Chemicals and Plastics Co. Inc. (Danbury, CT). MDI (RUBINATE 1840) was purchased from ICI Polyurethanes Group (West Deptford, NJ).

Mixtures of SPI with 10, 20, 30, 40, and 50% PCL alone or with addition of 0.5, 1.0, 2.0, and 5.0% MDI were mixed mechanically for 10 min at room temperature, followed by melt blending with an intensive mixer (Rheomix600, HB Instruments Inc., Paramus, NJ) at 160°C and 120 rpm for 10 min. Then the blends were milled into small particles, by passing through a 1 mm sieve in a Model 4 Laboratory Mill (Thomas–Wiley Company, PA). After that, the ground blend was placed in a dumbbell-shaped tensile bar mold (type IV) and compression-molded using a Hot Press (Model, 3890 Auto 'M', Carver Inc., Wabash, IN) according to ASTM standard D638-91 [37]. The specimen was molded at 150°C for 5 min and then cooled to 30°C before removal from the mold. Flash was removed carefully by sanding off the edges of the specimen with grade 180 abrasive sandpaper. The moisture content of these specimens was about 1.5%.

2.2. Differential scanning calorimetry

Thermal properties of SPI and the SPI/PCL blend with and without various MDI additions were measured with a Perkin–Elmer Pyris-1 differential scanning calorimetry (DSC) (Perkin–Elmer, Norwalk, CT). The instrument was calibrated with indium and zinc standards before official measurements, and all measurements were conducted under a nitrogen atmosphere. All samples first were quenched to −60°C and heated to 200°C, then quenched again to −60°C and heated to 200°C at 10°C/min. All data reported in this study were obtained from the second DSC scan.

2.3. Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) was carried out using a DMA-7e dynamic mechanical analyzer (Perkin–Elmer, Norwalk, CT) with the three point bending-rectangle method at 1 Hz. The heating rate was 3°C/min. Size of the samples for DMA testing was about $15 \times 6 \times 3$ mm^3.

2.4. Mechanical property tests and morphology

Mechanical properties were measured using an Instron testing system (Model 4466, Canton, MA) according to ASTM standard D638-91 [37]. Each specimen was preconditioned at 23°C and 50% relative humility for 48 h and tested at a crosshead speed of 5 mm/min. Tensile strength, elongation, and Young's modulus were obtained from the

Table 2
Glass transition temperature (T_g), melting temperature (T_m), heat of fusion (ΔH_f), and crystallinity (X_c) of the SPI/PCL blends with 2 wt% MDI

PCL content (%)	DSC				DMA	
	T_g (°C)	T_m (°C)	ΔH_f (J/g PCL)	X_c of PCL (%)	T_g (°C)	T_m (°C)
0	108.4	–	–	–	114.2	–
10	102.9	56.2	34.9	26	111.8	56.0
20	97.8	57.5	39.5	29	108.0	56.2
30	92.3	57.9	44.4	33	101.7	56.3
40	88.6	58.5	46.1	34	96.3	57.3
50	84.0	58.7	48.7	36	93.0	59.2

test. Toughness was calculated as the area under the stress–strain curve. The values presented here are averages of five specimens.

The fracture surface of tensile test specimens was observed using a scanning electron microscope (SEM) (S-3500N, Hitachi, Japan) at an accelerated voltage of 20 kV. The specimens were coated with thin layers of gold of 200 Å before observation.

2.5. Water absorption

Water absorption was measured using the ASTM standard D570-81 [38]. The specimens were preconditioned by drying in an air oven at 50°C for 24 h. Then they were cooled in a desiccator for a few minutes, weighed, and submerged in distilled water at 25°C for 2 and 26 h. The extra water on the surface of the specimen after water soaking was removed with a paper towel, and the specimen then was weighed again. Dry matter from the plastics left in the water during soaking also was included in the water absorption calculation. The values presented are averages of three specimens.

3. Results and discussion

3.1. Thermal properties

Thermal properties of the SPI/PCL blends with 2 wt% MDI changed as PCL content varied (Table 2). Because of the temperature limitation of the experiment, the glass transition of PCL was not detected, and the glass transition temperature (T_g) presented in Table 2 should correspond to the glass transition of SPI. The melting temperature of the blend was caused by PCL, because the denaturation temperature of SPI with 1.5% moisture content would be above 150°C. The T_g of SPI in the blends decreased as PCL content increased. This indicated that some extent of compatibility existed between SPI and PCL in the presence of 2 wt% MDI, because the T_g of SPI should remain constant if SPI was completely incompatible with PCL. The decreases in melting temperature (T_m) of PCL with increasing SPI content (Table 2) further supported the existence of some extent of compatibility between SPI and PCL in the presence of MDI. The DMA data showed similar results (Table 2) and confirmed the speculation from the DSC data.

The crystallinity of PCL was calculated from the following equation:

$$X_c = (\Delta H_f - \Delta H_c)/\Delta H_f^0, \quad (1)$$

where X_c is percent crystallinity, ΔH_f and ΔH_c are the heats of fusion and crystallization of PCL, respectively, and $\Delta H_f^0 = 136$ J/g [39] is the heat of fusion of 100% crystalline PCL. No crystallization exotherm was observed during the second DSC scan, suggesting that the crystallization was fast and completed during quenching. The X_c of PCL decreased as SPI content increased (Table 2), indicating that the crystallization of PCL in the blend became difficult, which was attributed to the T_g of SPI being higher than PCL and to their partial miscibility.

The thermal properties of the blend were affected significantly by MDI content, for example, the data at 50/50 (SPI/PCL) ratio are presented in Table 3. With increasing MDI content, T_g of SPI decreased, indicating that the compatibility between SPI and PCL was improved, and that interfacial

Table 3
Glass transition temperature (T_g), melting temperature (T_m), heat of fusion (ΔH_f), and crystallinity (X_c) of the 50/50 (SPI/PCL) blends with various MDI contents

MDI content (%)	DSC				DMA	
	T_g (°C)	T_m (°C)	ΔH_f (J/g PCL)	X_c of PCL (%)	T_g (°C)	T_m (°C)
0	109.7	59.7	55.0	40	–	62.7
0.5	94.6	59.4	53.7	39	–	61.3
1.0	87.8	59.0	49.9	37	–	60.8
2.0	84.0	58.7	48.7	36	93.0	59.2
5.0	84.7	58.4	42.7	31	93.3	58.1

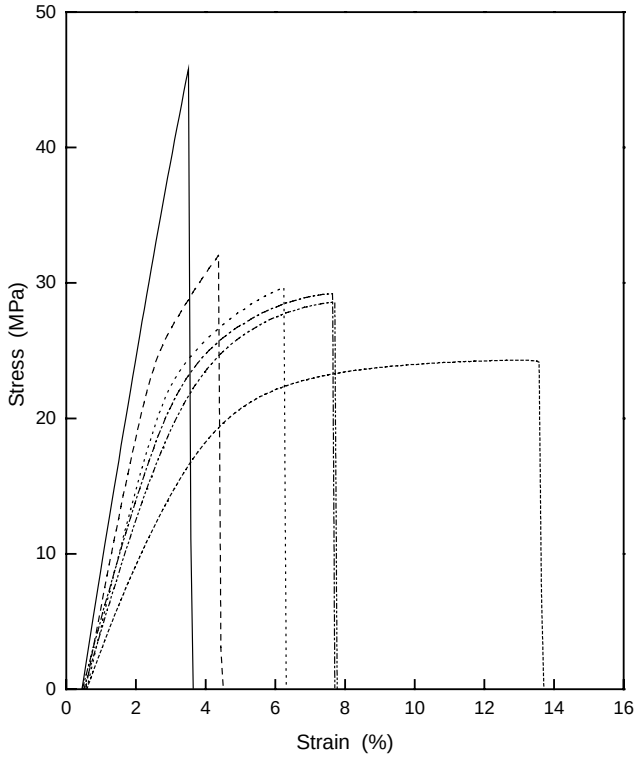

Fig. 1. Typical stress–strain curves of the SPI/PCL blends with 2 wt% MDI. PCL content: (—) 0 wt%, (– – –) 10 wt%, (···) 20 wt%, (–·–·–·) 30 wt%, (–··–··–·) 40 wt%, and (- - -) 50 wt%.

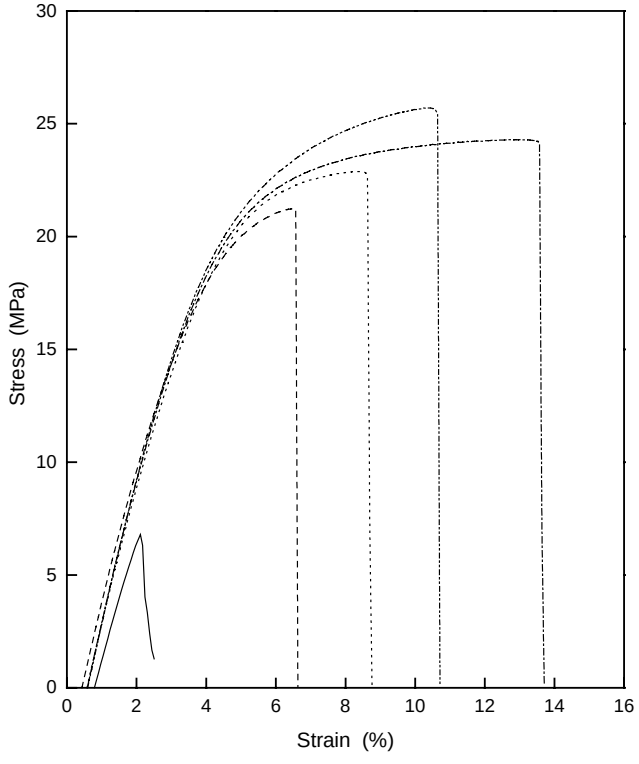

Fig. 2. Typical stress–strain curves of the 50/50 (SPI/PCL) blends added with (—) 0 wt%, (– – –) 0.5 wt%, (···) 1 wt%, (–·–·–·) 2 wt%, and (–··–··–·) 5 wt% MDI.

adhesion between SPI and PCL phases increased. The T_m and X_c data from DSC and the T_g and T_m data from DMA (Table 3) supported this conclusion.

The observations from DSC and DMA data indicated that a reaction or interaction among MDI, SPI, and PCL might occur. MDI has two isocyanate groups, which are very reactive with hydroxyl, amino, carboxyl, and other groups from SPI and the hydroxyl end group from PCL. The reactions of MDI with both SPI and PCL resulted in an enhanced interaction between SPI and PCL, which improved their compatibility and modified phase structure of the blends. In order to understand fully the compatibilization mechanism of MDI, further study of these reactions is needed.

3.2. Mechanical properties

Typical stress–strain curves of SPI/PCL blends with 2 wt% MDI are shown in Fig. 1. The blend of SPI alone with 2 wt% MDI typically showed brittle fracture and no yield. However, some characteristics of ductile fracture were observed as PCL content in the blends increased. For example, the blend with 50% PCL had a yield point and demonstrated ductile fracture compared to other blends with lower PCL content (Fig. 1). The fracture mode for the 50/50 SPI/PCL blends changed from brittle without MDI to ductile with MDI (Fig. 2).

Young's modulus (E) of the SPI/PCL blends with 2 wt% MDI decreased as PCL content increased (Fig. 3), because pure PCL has a low modulus (203 MPa). The E value of the 50/50 SPI/PCL blends was found to increase at first from 579 MPa with 0 wt% MDI to 657 MPa with 2 wt% MDI and then decrease slightly with the further increase of MDI to 5 wt% (Fig. 4). These findings were consistent with our previous conclusion that addition of MDI improved the compatibility between SPI and PCL, which led to improvement of the mechanical properties. The decrease in E at 5 wt% MDI content was probably due to the potential poor MDI dispersion problem. Because PCL is in pellet form, SPI is in powder form, and MDI is in liquid form, it is difficult to achieve uniform dispersion of MDI in the blends, which, is expected to be exacerbated at high MDI concentration (5 wt%).

As PCL content in the blends with 2 wt% MDI increased, tensile strength (σ) decreased greatly at first and then decreased slightly (Fig. 5). After 40 wt% PCL, the σ decreased rapidly again. The elongation (ϵ) of the blends increased as PCL increased (Fig. 5). These phenomena would be related to the changes in morphology of the blends, which are discussed in Section 3.3. The σ value of the 50/50 (SPI/PCL) blends increased sharply as MDI content increased from 0 to 0.5 wt% and then leveled off (Fig. 6). The variation of ϵ with MDI content for the 50/50 (SPI/PCL) blends (Fig. 6) was similar to that for the E of the

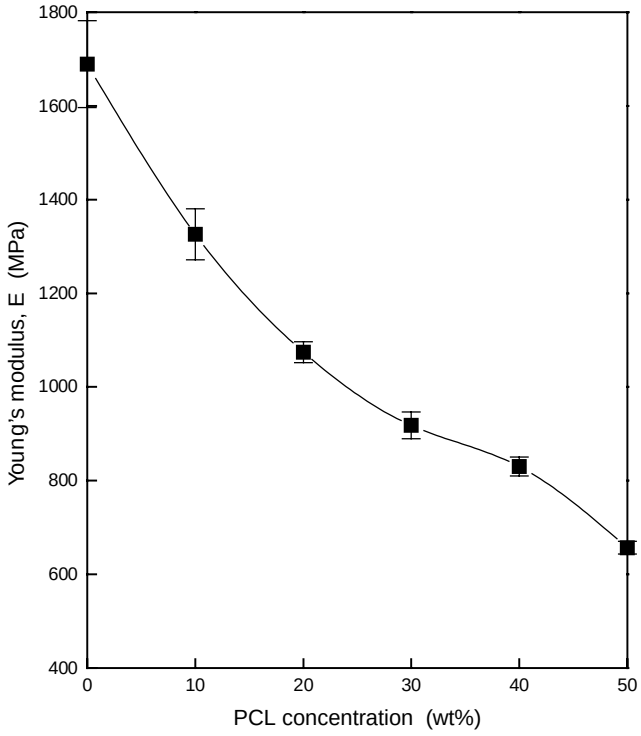

Fig. 3. Effect of PCL concentration on Young's modulus of the SPI/PCL blends with 2 wt% MDI.

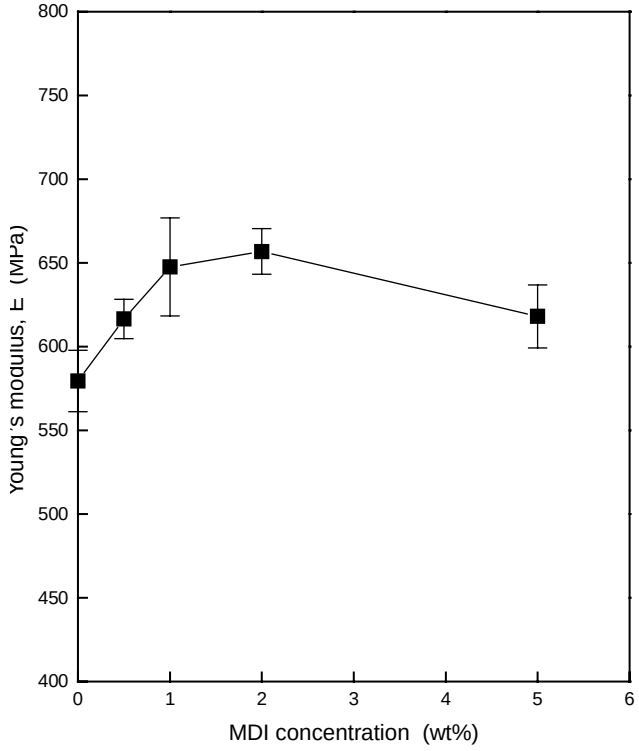

Fig. 4. Effect of MDI concentration on Young's modulus of the 50/50 (SPI/PCL) blends.

blends (Fig. 4). The explanation provided above for the E would be applicable.

The σ values for the SPI/PCL blends with 2 wt% MDI were higher than those for the SPI/PCL blends with PCLMA [30] and were much higher than those for the wheat gluten/PCL blends with PCLMA [31]. For examples, Bhattacharya et al., obtained a σ value of 24.14 MPa for the 65/35 (SPI/PCL) blend with 5% PCLMA [30] and a σ value of less than 20 MPa for the 65/35 (Gluten/PCL) blend with 2.5% PCLMA [31]. The higher σ values for the SPI/PCL blends with MDI obtained from this research were probably because MDI has smaller molecule size than PCLMA and higher reactivity.

The energy of unit volume absorbed by a specimen before fracture, which is simply the area under the stress–strain curve [40], can be used as a measure of toughness of a material. The toughness of the SPI/PCL blends with 2 wt% MDI increased obviously with the increase of PCL content (Fig. 7), and the toughness at 50 wt% PCL content was four times that at 0 wt% PCL content. The toughness also increased sharply as MDI content increased to 2 wt% and then decreased as the MDI increased further (Fig. 8). Therefore, blending PCL into SPI improved the toughness of SPI, and addition of MDI was necessary in order to obtain good mechanical properties.

3.3. Morphology

The SPI sample showed a smooth, homogeneous fracture surface (Fig. 9A). However, a rough and heterogeneous fracture surface was observed as PCL content increased in the SPI/PCL blends with 2 wt% MDI (Fig. 9). For the blends with high PCL content, plastic flow was obvious (Fig. 9E

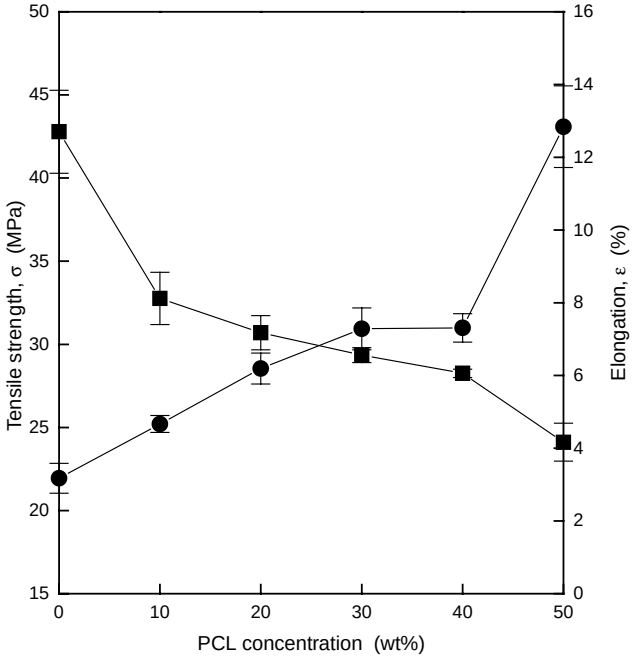

Fig. 5. Effect of PCL concentration on tensile strength (■) and elongation (●) of the SPI/PCL blends with 2 wt% MDI.

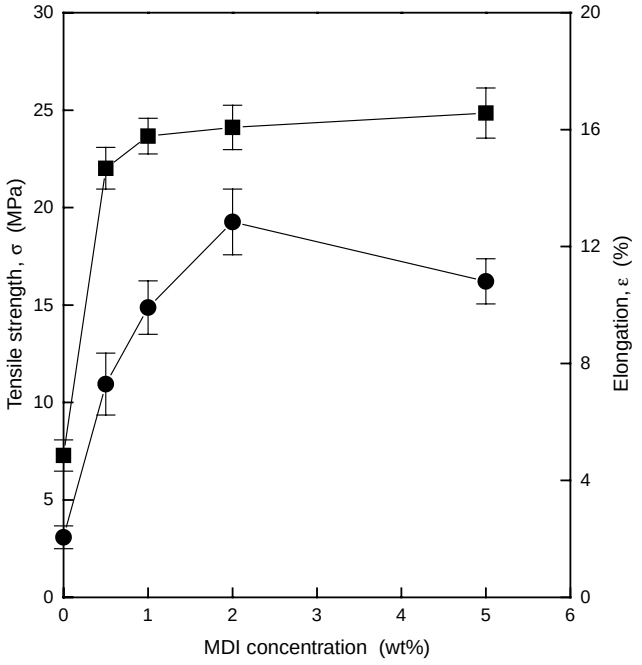

Fig. 6. Effect of MDI concentration on tensile strength (■) and elongation (●) of the 50/50 (SPI/PCL) blends.

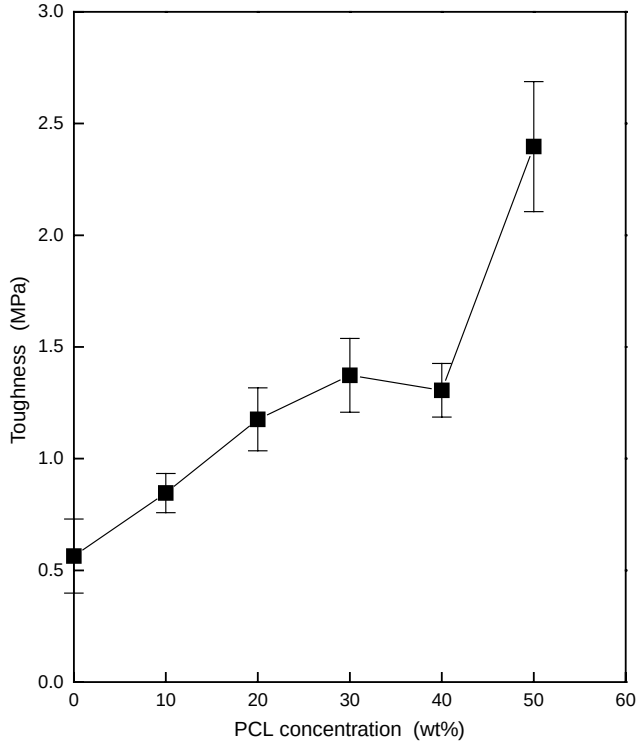

Fig. 7. Effect of PCL concentration on toughness of the SPI/PCL blends with 2 wt% MDI.

and F). Therefore, the morphology observed confirmed that the toughness of the blends increased with increasing PCL content. The phase behavior of the blends with 2 wt% MDI changed as PCL content increased (Fig. 9). The SPI formed a continuous phase at low PCL content, whereas PCL became the continuous phase at 50 wt% PCL. The 60/40 (SPI/PCL) blend showed characteristic of bi-continuous phases (Fig. 9E). Therefore, a phase reversal occurred in the vicinity of 40 wt% PCL content and, consequently, the mechanical properties of the blends changed greatly at the range of 40–50 wt% PCL (Fig. 5).

The 50/50 (SPI/PCL) blends without MDI exhibited an obvious phase separation and large SPI particles distributed in the PCL matrix (Fig. 10A). The surface of the SPI particles was smooth, and there was no evidence of a marked interaction between the SPI and PCL phases. As MDI content increased, however, the interface between SPI and PCL became ambiguous (Fig. 10B), and no evident SPI particles were observed at higher MDI contents (Fig. 10C–E). Clearly, adhesion between SPI and PCL was enhanced and compatibility between them was improved with increasing MDI content. Plastic flow was observed for the fracture surface of the blends with high MDI content (Fig. 10C–E).

3.4. Water absorption

One of major shortcomings of SPI plastics is its water sensitivity. Water absorption of pure SPI plastics was 165% at room temperature for 26 h. Because PCL is a hydrophobic polymer, water resistance of the blends was expected to

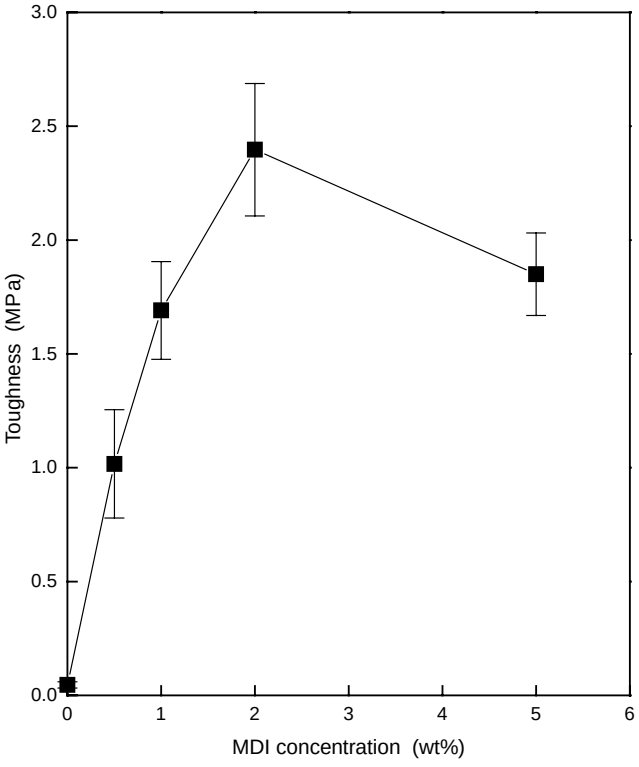

Fig. 8. Effect of MDI concentration on toughness of the 50/50 (SPI/PCL) blends.

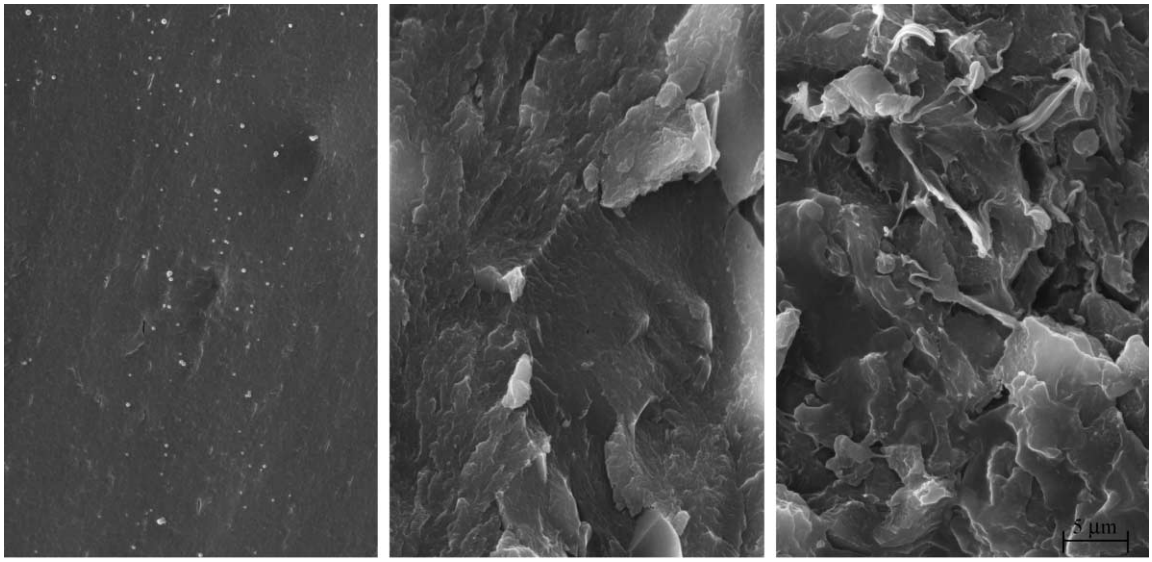

Fig. 9. SEM photographs of the SPI/PCL blends with 2 wt% MDI. PCL content: (A) 0 wt%, (B) 10 wt%, (C) 20 wt%, (D) 30 wt%, (E) 40 wt%, and (F) 50 wt%.

increase. Indeed, the water absorption for 26 h of the blends with 2 wt% MDI decreased significantly from 74% for 0 wt% PCL to 36% for 40 wt% PCL and to 12% for 50 wt% PCL (Fig. 11). This large reduction of the water absorption from 40 to 50 wt% PCL was attributed to phase reversal of the blends, and relatively lower water absorption of SPI with 2 wt% MDI than of the pure SPI was due to a crosslinking reaction of MDI with SPI. The water absorption for 2 h was lower than that for 26 h, and also decreased as PCL content increased (Fig. 11).

The reactions of MDI with SPI and PCL increased the compatibility of SPI and PCL, which increased the water resistance of the blends. For example, the water absorption for 26 h of the 50/50 (SPI/PCL) blends decreased significantly as MDI content increased from 0 to 2 wt% (Fig. 12). The further increment of MDI to 5 wt% increased the water absorption, and this result was similar to the variations in modulus, elongation, and toughness of the blends (Figs. 4, 6, and 8), and it is probably due to a poor MDI dispersion at 5 wt% content. The water absorption for 2 h gave similar results.

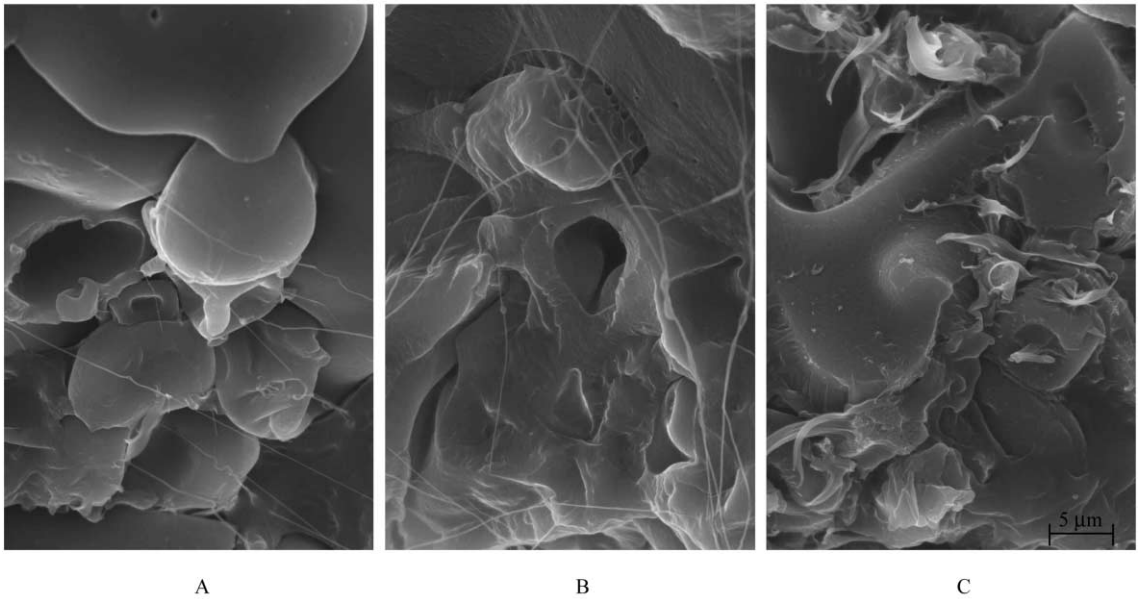

Fig. 10. SEM photographs of the 50/50 (SPI/PCL) blends added with (A) 0 wt%, (B) 0.5 wt%, (C) 1 wt%, (D) 2 wt%, and (E) 5 wt% MDI.

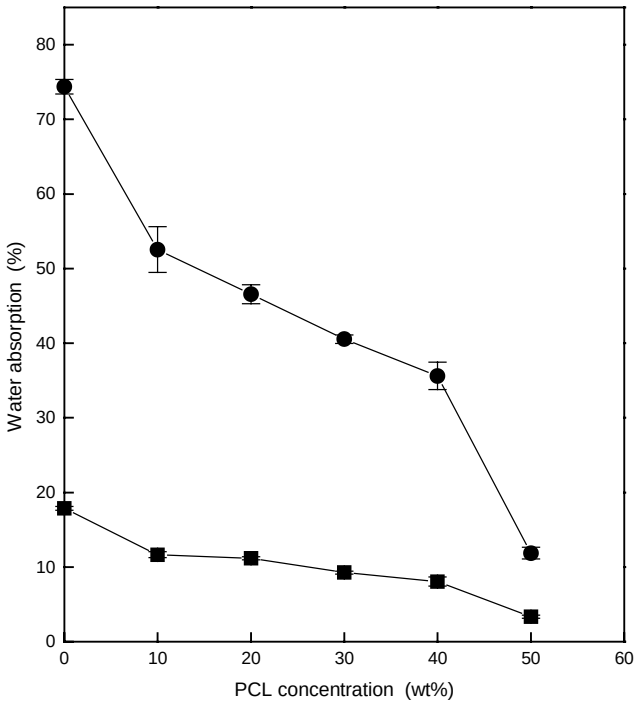

Fig. 11. Effect of PCL concentration on water absorption for 2 h (■) and 26 h (●) of the SPI/PCL blends with 2 wt% MDI.

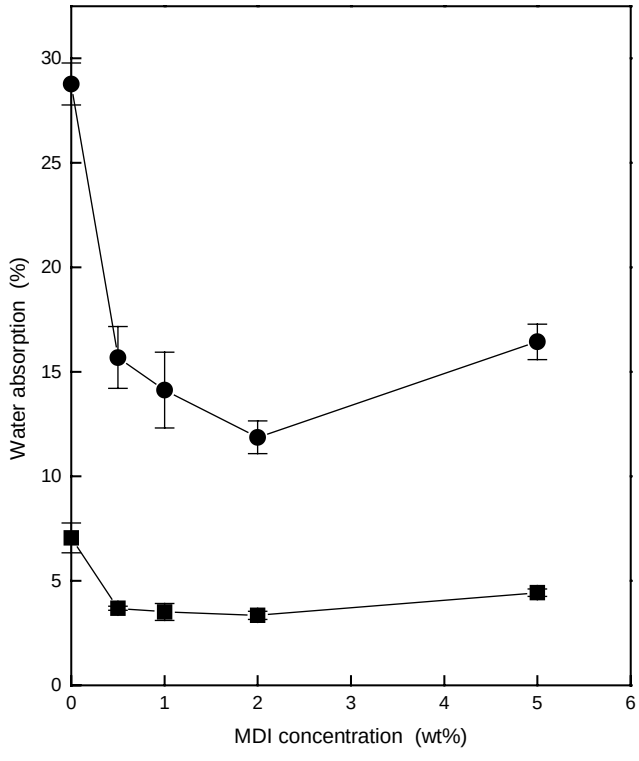

Fig. 12. Effect of MDI concentration on water absorption for 2 h (■) and 26 h (●) of the 50/50 (SPI/PCL) blends.

4. Conclusions

In conclusion, MDI reacted with both SPI and PCL and acted as a compatibilizer in the SPI/PCL blends. The thermal properties and morphology of the blends changed with increasing PCL and MDI concentrations. Incorporating PCL decreased E and σ, while increasing ϵ and improved the toughness and the water resistance of the SPI plastics. The SPI phase became discontinuous when PCL content was 50 wt% or above. Addition of MDI improved the mechanical properties and water resistance of the SPI/PCL blends.

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