

Properties of Soy Protein Isolate/Poly(ethylene-*co*-ethyl acrylate-*co*-maleic anhydride) Blends

Zhikai Zhong, Susan X. Sun

Department of Grain Science and Industry, Kansas State University, Manhattan, Kansas 66506

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ABSTRACT: Blends of soy protein isolate (SPI) with 10, 20, 30, 40, and 50% poly(ethylene-*co*-ethyl acrylate-*co*-maleic anhydride) (PEEAMA), with or without addition of 2.0 wt % methylene diphenyl diisocyanate (MDI), were prepared by mixing with an intensive mixer at 150°C for 5 min, and then milling through a 1-mm sieve. Blends were then compression-molded into a tensile bar at 140°C. Thermal and mechanical properties and water absorption of the blends were studied by differential scanning calorimetry (DSC), dynamical mechanic analysis (DMA), a test of modulus and tensile strength (with an Instron tensile tester), a water absorption test, and scanning electron microscopy (SEM). The blends showed two composition-dependent glass transition temperatures. Furthermore, as the SPI content increased, the melting temperature of PEEAMA remained constant but the

heat of fusion decreased. These results indicate that SPI and PEEAMA were partially miscible. Morphology observations support these results. Increasing the PEEAMA content resulted in decreases in the modulus and tensile strengths and increases in the elongation and toughness of the blends. Water absorption of the blends also decreased with increased PEEAMA content. Incorporating MDI further decreased the water absorption of the blends. The mechanism of water sorption of SPI was relaxation controlled, and that of the blends was diffusion controlled. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 407–413, 2003

Key words: thermal properties; mechanical properties; absorption; biopolymers; blends

INTRODUCTION

Plastics made from soy protein are strong, with tensile strengths up to 40 MPa,^{1–3} but they can also be brittle and water sensitive.^{1–22} Two major approaches are widely used to improve the toughness and water resistance of the soy protein plastics. Chemical processes can be used to improve the properties of soy protein-based plastics; for examples, acetylation and esterification²³ can modify soy protein side chains, and denaturation can alter the configuration of soy protein.²⁴ The second approach is to incorporate other materials into soy protein; for examples, adding plasticizer to improve toughness and processibility,^{4, 8} incorporating filler to improve water resistance,^{21, 22} or blending with other polymers to improve properties.^{11–20, 25, 26}

In our previous work,²⁷ we used polycaprolactone (PCL) to improve the toughness and water resistance of soy protein isolates (SPI). PCL is a hydrophobic synthetic polymer and it is incompatible with SPI. Therefore, methylene diphenyl diisocyanate (MDI) was used as a compatibilizer, and the mechanical properties and water resistance were greatly improved. The improvement was attributed to reactions

between the isocyanate group of MDI and the hydroxyl/amino groups of SPI and PCL.^{27, 28} In this study, we used poly(ethylene-*co*-ethyl acrylate-*co*-maleic anhydride) (PEEAMA) to expand potential polymers that can be used to modify SPI plastics and to study its compatibilization effect. We also compared the SPI/PEEAMA/MDI system with the SPI/PCL/MDI system used in our previous study.²⁷

Poly(ethylene-ethyl acrylate) (PEEA) is one of the most important ethylene-based copolymers. It has been widely used in automobile industry, packaging industry, adhesive industry, and other fields for its superior properties,^{29, 30} such as toughness, flexibility, and resistance to environmental stress cracking and radiation (ultraviolet). Also, its price (\$0.33/lb) is much lower than that of PCL.²⁹ However, PEEA is incompatible with SPI because of its hydrophobic nature, and poor mechanical properties are expected for SPI/PEEA blends. PEEAMA, containing a reactive group of maleic anhydride, was thus chosen. Maleic anhydride is a reactive functional group that can react with amino and hydroxyl groups of protein. Some studies already showed that synthetic polymers with the maleic anhydride group had improved compatibility with soy protein and starch.^{25, 26} John and Bhattacharya²⁵ found that small amounts of maleated polyester significantly improved the mechanical properties of soy protein/polyester blends. Vaidya and Bhattacharya²⁶ used maleated ethylene-propylene copolymer and styrene-maleic anhydride copolymer as

Correspondence to: S.X. Sun (xss@wheat.ksu.edu).

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TABLE I
Thermal Properties of the SPI/PEEAMA Blends Determined by DSC and DMA

SPI/PEEAMA	DSC Results				DMA Results	
	T_g (°C) PEEAMA	T_m (°C) PEEAMA	ΔH_f (J/g) PEEAMA	T_g (°C) SPI	T_g (°C) PEEAMA	T_g (°C) SPI
100/0	—	—	—	103.1 ^a	—	114.2 ^a
90/10	-39.3 ^a	65.0 ^{ab}	8.30 ^c	100.2 ^b	-37.1 ^a	103.0 ^b
80/20	-39.2 ^a	65.3 ^{ab}	8.53 ^c	98.3 ^{bc}	-36.3 ^a	102.6 ^b
70/30	-39.9 ^a	65.3 ^{ab}	8.41 ^c	96.4 ^{cd}	-38.2 ^{ab}	100.3 ^c
60/40	-40.6 ^{ab}	65.0 ^{ab}	9.90 ^{bc}	94.2 ^{de}	-40.0 ^{bc}	ND*
50/50	-41.8 ^{bc}	65.8 ^a	10.02 ^b	92.0 ^e	-39.6 ^{bc}	ND*
0/100	-43.1 ^c	64.7 ^b	11.89 ^a	—	-40.6 ^c	—

^{a-e} Means in the same column followed by different superscript letters are significantly different using least significant differences (LSD) and a probability level of $\alpha = 0.05$.

* ND, not detected.

the second component in a blend with soy proteins, and their results showed improved flexibility and water resistance of the protein plastics.

MDI was used as an additive in the SPI/PEEAMA system to determine if addition of MDI could further improve the properties of the plastic and to compare this system with the SPI/PCL/MDI system used in our previous studies.^{27, 28} The objective of this work was to characterize the thermal and mechanical properties and measure water absorption ability of the SPI/PEEAMA blends with or without the addition of MDI.

EXPERIMENTAL

Materials and preparation of samples

SPI (PRO-Fam 970), prepared by acid precipitation, was provided by Archer Daniels Midland (Decatur, IL). The SPI had a moisture content of 6.5%, was >90% protein, and was dried at 50°C for 24 h before use. PEEAMA, with a melt index of 7 g/10 min (190°C/2.16 kg) and containing 32 wt % ethyl acrylate and 1.5–2.5 wt % anhydride, was purchased from Aldrich Chemical Company, Inc. (St. Louis, MO). MDI

(RUBINATE 1840) was purchased from ICI Polyurethanes Group (West Deptford, NJ).

Mixtures of SPI with 10, 20, 30, 40, and 50% PEEAMA with or without the addition of 2.0 wt % 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 150°C and 120 rpm for 5 min. Blends were then milled into small particles by being passed through a 1-mm sieve in a Model 4 Laboratory Mill (Thomas-Wiley Company, PA). 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 D638-91.³¹ The specimen was molded at 140°C for 5 min and then cooled to 30°C before removal from the mold. Flash was removed by carefully sanding the edges of the specimen with grade 180 abrasive sandpaper. The moisture content of these specimens was ~2%.

Differential scanning calorimetry (DSC)

Thermal properties of the SPI and SPI/PEEAMA blends with or without MDI were determined with a

TABLE II
Thermal Properties of SPI/PEEAMA Blends with 2% MDI Determined by DSC and DMA

SPI/PEEAMA	DSC results				DMA results	
	T_g (°C) PEEAMA	T_m (°C) PEEAMA	ΔH_f (J/g) PEEAMA	T_g (°C) SPI	T_g (°C) PEEAMA	T_g (°C) SPI
100/0	—	—	—	103.1 ^a	—	114.2 ^a
90/10	-31.2 ^a	65.3 ^{bc}	2.68 ^e	101.5 ^{ab}	-36.3 ^{ab}	106.2 ^b
80/20	-35.6 ^b	65.0 ^{bc}	6.65 ^d	99.0 ^{bc}	-35.5 ^a	102.7 ^c
70/30	-37.6 ^{bc}	65.8 ^{ab}	8.37 ^c	96.7 ^{cd}	-37.7 ^{bc}	101.9 ^c
60/40	-38.2 ^{bc}	66.5 ^a	8.98 ^c	94.5 ^{de}	-38.6 ^{cd}	97.7 ^d
50/50	-39.6 ^c	65.2 ^{bc}	10.17 ^b	92.7 ^e	-39.6 ^{de}	ND*
0/100	-43.1 ^d	64.7 ^c	11.89 ^a	—	-40.6 ^e	—

^{a-e} Means in the same column followed by different superscript letters are significantly different using least significant differences (LSD) and a probability level of $\alpha = 0.05$.

* ND, not detected.

differential scanning calorimeter (Pyris-1, 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 were quenched to -70°C and scanned to 180°C at $10^{\circ}\text{C}/\text{min}$ two successive times. All data reported in this study were obtained from the second DSC scan. The values reported are averages of two replications.

Dynamic mechanical analysis (DMA)

Dynamic mechanical properties were determined using a DMA-7e dynamic mechanical analyzer (Perkin-Elmer, Norwalk, CT) according to the 3-point bending-rectangle method at 1 Hz. The heating rate was $3^{\circ}\text{C}/\text{min}$. The dimension of the specimens for the DMA testing was $\sim 15 \times 6 \times 3 \text{ mm}^3$. The values reported are averages of two replications.

Mechanical property tests and morphology

Mechanical properties were measured with an Instron testing system (Model 4466, Canton, MA) according to ASTM standard D638-91.³¹ Each specimen was preconditioned at 23°C and 50% relative humidity for 48 h and tested at a crosshead speed of 5 mm/min. Tensile strength, elongation, and Young's modulus were determined from the test. Toughness was calculated as the area under the stress-strain curve. The values presented in the results are averages of five specimens. The fracture surface of the tensile test specimens was observed with 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 (200 \AA) before observation.

Water absorption

Water absorption was measured following ASTM standard D570-81.³² The specimens were preconditioned in an air oven at 50°C for 24 h. Following preconditioning, they were cooled in a desiccator for a few minutes, weighed, and submerged in distilled water at 25°C for various lengths of time. The extra water on the surface of the specimen after water soaking was removed with a paper towel, and the specimen was then weighed again. Dry matter leached from the specimens into the water during soaking was also included in the water absorption calculation. The values presented are averages of three specimens.

Statistical analysis

Statistical analysis of DSC and DMA data was performed with SAS software (Version 6.12, SAS Institute Inc., Cary, NC). The average values thus obtained were labeled with lower case letters (i.e., a, b, c, etc.)

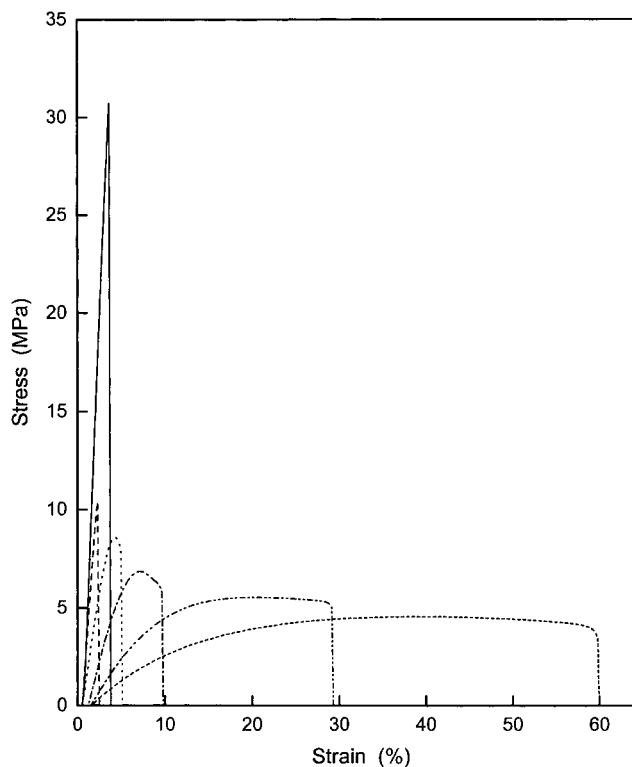


Figure 1 Typical stress-strain curves of the SPI/PEEAMA blends. Key to PEEAMA content: (—) 0 wt %, (---) 10 wt %, (···) 20 wt %, (-·-·-) 30 wt %, (- - - -) 40 wt %, and (—) 50 wt %.

from maximum to minimum, using least significant differences at a probability level of $\alpha = 0.05$. For mechanical properties, mean value and standard deviation were obtained directly from Instron software during the test, and they are shown in the corresponding figures as data points and error bars. For water absorption, the average standard deviation of the data presented in the figure was calculated to avoid crowded graphs, and the error bar given in the figure is twice the average value.

RESULTS AND DISCUSSION

Thermal properties

Thermal properties of the SPI/PEEAMA blends without MDI were influenced by PEEAMA content (Table I). SPI is amorphous and has a glass transition temperature (T_g) of $\sim 103^{\circ}\text{C}$. PEEAMA is semicrystalline and has a melting temperature (T_m) of 64.7°C and a T_g of $\sim -43^{\circ}\text{C}$ (DSC results). After blending, the T_g of both SPI and PEEAMA shifted toward each other (Table I), indicating that SPI and PEEAMA are compatible to some degree. The heat of fusion (ΔH_f) of PEEAMA was calculated based on PEEAMA weight. It decreased significantly with increasing SPI content (Table I), indicating that crystallization of PEEAMA in the blend becomes progressively difficult with increased SPI content. The T_m of PEEAMA in the blends

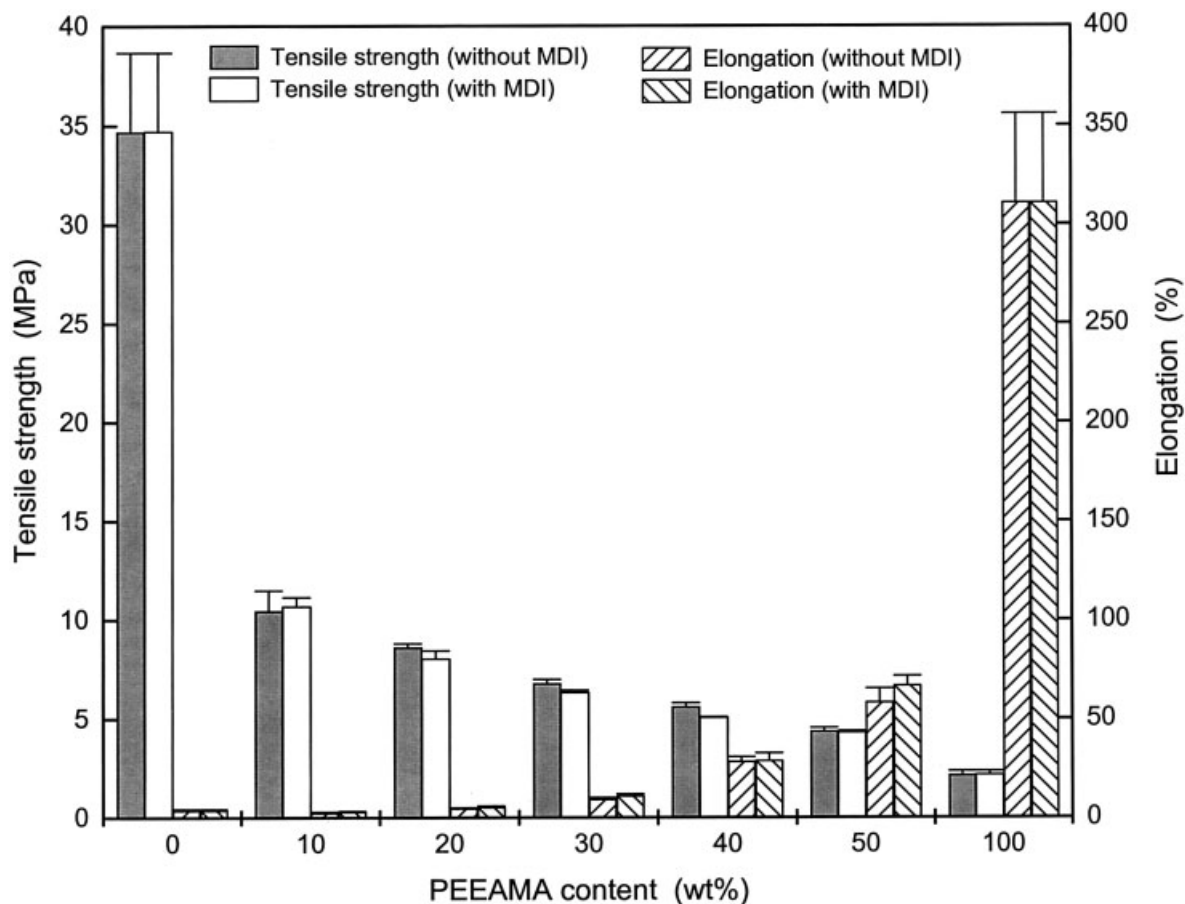


Figure 2 Effect of PEEAMA concentration on tensile strength and elongation of the SPI/PEEAMA blends with or without 2 wt % MDI.

remained nearly constant. These results further support the argument that SPI and PEEAMA are partially miscible. DMA data showed similar results (Table I) and confirmed the speculation from the DSC data.

SPI is hydrophilic and is not compatible with synthetic hydrophobic polymers. However, if the hydrophobic polymer contained reactive functional groups, which would react with some functional groups from SPI, or if a compatibilizer is added, then interaction between SPI and the hydrophobic polymer would occur and, hence, some degree of compatibility would be achieved. PEEAMA contains the maleic anhydride group, which could react with the amino group of SPI, forming an amide or imide linkage, and/or react with the hydroxyl group of SPI, forming an ester linkage.²⁶ These reactions occurred during the melt blending and/or the hot pressing. However, these reactions were not enough to alter the hydrophobic nature of PEEAMA and could not make the SPI/PEEAMA blend completely compatible.

The SPI/PEEAMA blends with 2 wt % MDI exhibited similar thermal properties as those without MDI (Table II). There also were two composition-dependent T_g 's. The ΔH_f value of the blends decreased as SPI content increased, whereas the T_m of the blends re-

mained the same. Therefore, the SPI/PEEAMA blend with MDI was still partially compatible.

Mechanical properties

Typical stress-strain curves of the SPI/PEEAMA blends are presented in Figure 1. The pure SPI and the 90/10 SPI/PEEAMA blend were brittle and showed no yield fracture. As PEEAMA content in the blends reached 20 wt % or more, the blends became ductile. For example, the stress-strain curve of the latter blends had an obvious yield point (Figure 1).

As PEEAMA content increased, the tensile strength (σ) of the SPI/PEEAMA blends decreased, whereas elongation (ϵ) increased (Figure 2) because SPI has high strength and low elongation and PEEAMA has low strength and high elongation. The tensile strength value of the 60/40 SPI/PEEAMA blend was 5.6 MPa, which was comparable with results obtained by Vaidya and Bhattacharyn on blends of SPI with maleated ethylene-propylene copolymer (6.4 MPa for 60% SPI).²⁶ However, the σ value for the 80/20 SPI/PEEAMA blends was 8.6 MPa, which was almost two times that of Vaidya and Bhattacharyn's result (4.5 MPa) for the blend with the same SPI content.²⁶ Com-

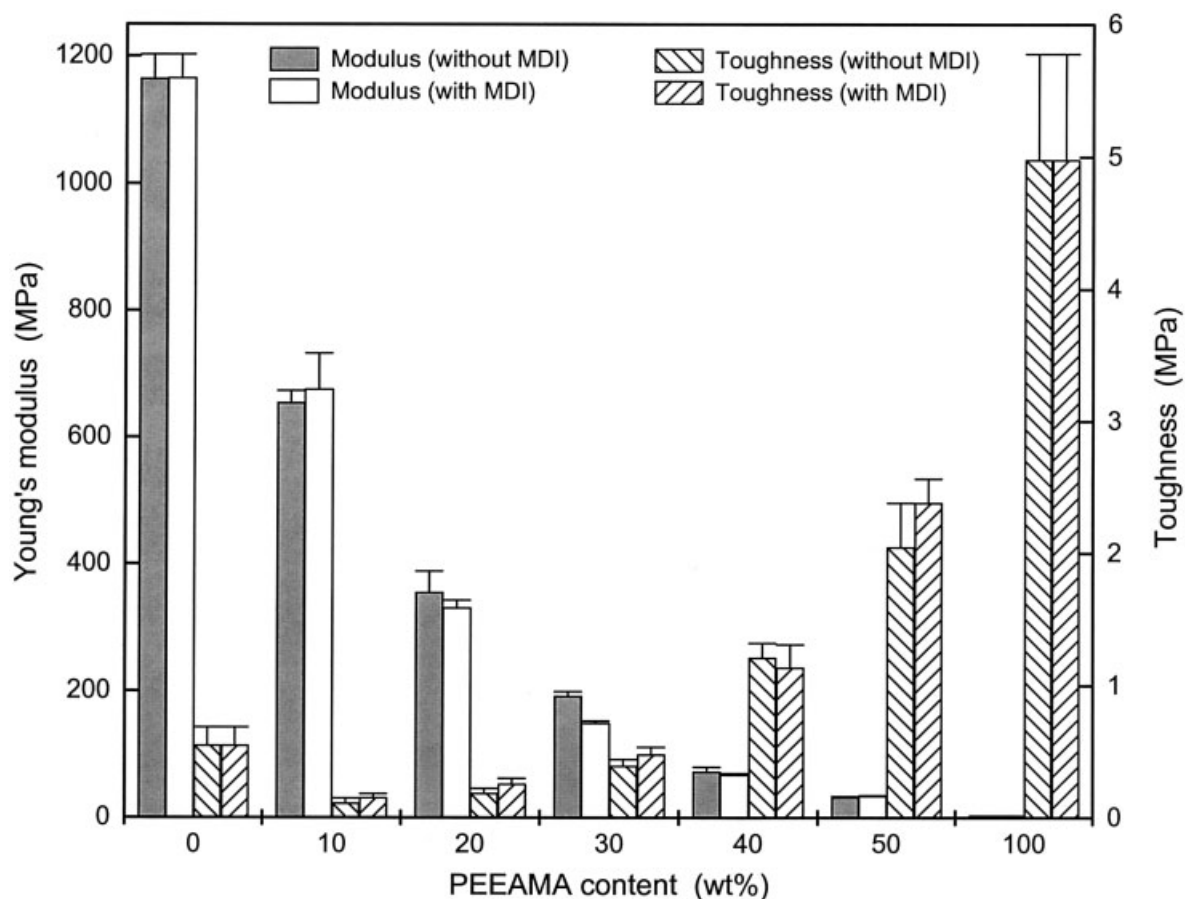


Figure 3 Effect of PEEAMA concentration on Young's modulus and toughness of the SPI/PEEAMA blends with or without 2 wt % MDI.

pared with the SPI/PCL/MDI system,²⁷ the strength of the SPI/PEEAMA blends was much lower. This difference was probably due to the lower strength of PEEAMA ($\sigma = 2.1$ MPa) than that of PCL ($\sigma = 14.8$ MPa). Furthermore, the different reactivities of the maleic anhydride and isocyanate groups in these two systems might cause different compatibilization effects and thus the mechanical properties.

When MDI (2 wt %) was added into the SPI/PEEAMA system, the values of σ and ϵ for the SPI/PEEAMA/MDI were not significantly different from those of the blends without MDI (see Figure 2). The isocyanate groups of MDI are very reactive with hydroxyl, amino, carboxyl, and other groups. In our previous study,^{27, 28} MDI compatibilized the SPI/PCL blends by reacting with both components, and the mechanical properties of the blends were improved significantly. In this study, however, it seems that MDI predominantly reacted with SPI and, hence, had little effect on compatibilization of the SPI/PEEAMA blend. The thermal properties of the blends support this speculation (Table II).

The energy per unit volume absorbed by a specimen before fracture, which is simply the area under the stress-strain curve,³³ can be used as a measure of

material toughness. The toughness of the SPI/PEEAMA blends increased with an increase in PEEAMA content (Figure 3). In contrast, the Young's modulus (E) of the blends decreased as PEEAMA content increased (Figure 3). Incorporating MDI into the SPI/PEEAMA blends did not significantly improve the toughness or Young's modulus of the blends (Figure 3).

Morphology

The pure SPI sample shows a relative smooth and homogeneous fracture surface (Figure 4A). However, a rough and heterogeneous fracture surface is observed after incorporating PEEAMA into the SPI (Figure 4B). Although a contrast between the SPI and PEEAMA phases is not clear, some voids left by some phase materials pulled out during tensile testing are clearly observed. As shown in Figure 4B, particle surfaces are not smooth, which could be caused by the interaction between SPI and PEEAMA. For the blends containing PEEAMA, long stretched materials are observed (Figure 4B), which resulted from PEEAMA plastic flow during tensile test. The morphologic characteristics of the SPI/PEEAMA blends containing 2 wt

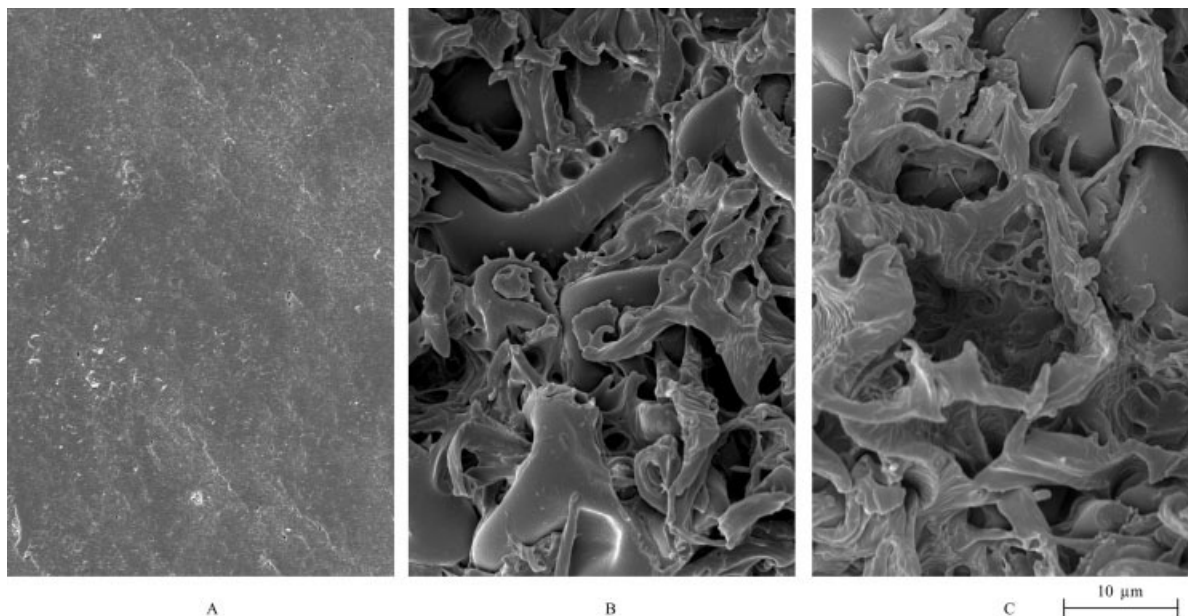


Figure 4 SEM photographs of (A) 100/0 and (B) 70/30 SPI/PEEAMA blends, and (C) 70/30 SPI/PEEAMA blends with 2 wt % MDI.

% MDI are similar to those of the blends without MDI (Figure 4C). These observations are consistent with the results of thermal and mechanical properties (Tables I and II, and Figures 1–3).

Water absorption

Water absorption by the pure SPI plastics was 178% at room temperature after 24 h of soaking. Water absorption by SPI was very rapid and reached equilibrium in 1–2 days. Because PEEAMA is a hydrophobic polymer, the water resistance of the blends was expected to increase with PEEAMA content. The water absorption by blends with various PEEAMA contents as a function of soaking time is shown in Figure 5. Water absorption by all specimens increased quickly at the beginning and then leveled off as soaking time increased. Water absorption ability and absorption rate of the blends decreased significantly after blending with PEEAMA. For example, the water absorption by the 50/50 SPI/PEEAMA blend was reduced to 24.5% following 1 week of soaking. The blends with 2 wt % MDI had lower water absorption ability than the corresponding blends without MDI (Figure 5).

Soy proteins, composed of amino acids, have not only polar groups such as the hydroxyl, amino, and carboxyl groups, but also ionic groups. All of these groups have a positive effect on the interaction of soy proteins with water. Carboxyl and amino groups are mainly responsible for binding with water. During blending with PEEAMA, reactions between SPI and PEEAMA reduced the amount of functional groups in SPI that could bind with water. A shielding effect of the hydrophobic PEEAMA molecules also reduced the

interaction of SPI with water. These two factors decreased water absorption of the blends. MDI could react with the amino, carboxyl, and hydroxyl groups

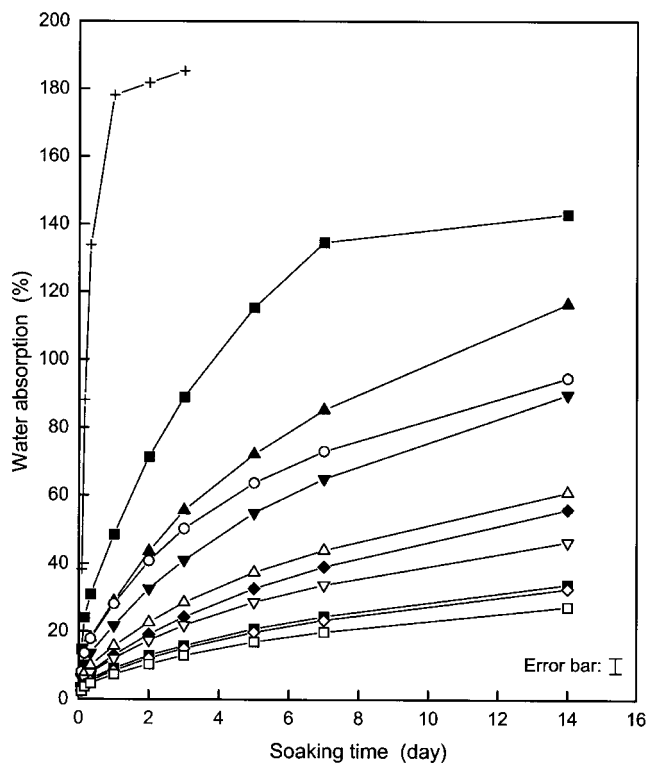


Figure 5 Water absorption of the SPI/PEEAMA blends with or without 2 wt % MDI as a function of soaking time. Key to SPI/PEEAMA ratio: (+) 100/0; (●, ○) 90/10; (▲, △) 80/20; (▼, ▽) 70/30; (◆, ◇) 60/40; and (■, □) 50/50. Solid symbols represent the blends without MDI and open symbols represent the blends with 2 wt % MDI.

TABLE III
Slopes (n) of Logarithmic Plot of the Ratio of Water Absorption to Soaking Time for the SPI/PEEAMA Blends

SPI/PEEAMA blend	Slope (n) at PEEAMA Content of					
	0 wt %	10 wt %	20 wt %	30 wt %	40 wt %	50 wt %
Without MDI	0.90	0.46	0.51	0.51	0.52	0.47
With 2 wt% MDI	—	0.47	0.49	0.48	0.49	0.47

of SPI; therefore, addition of MDI into the blends further decreased water absorption.

The kinetics of water absorption for polymers can be described by eq. 1:³⁴

$$\frac{M_t}{M_\infty} = k \cdot t^n \quad (1)$$

where M_t is the amount of water absorbed at time t , M_∞ is the amount of water absorbed at long time, and k and n are constants. When the ratio of water uptake (M_t/M_∞) is proportional to $t^{0.5}$, then the mechanism is diffusion controlled. A logarithmic plot of the ratio of water uptake to time gave slopes (n), which are summarized in Table III. The pure SPI had an n value of 0.9, indicating that the water sorption mechanism was mainly relaxation controlled. All the SPI/PEEAMA blends, including the blends with MDI, had n values of ~ 0.5 , suggesting that the sorption mechanism of the blends was diffusion controlled. The mechanism change was probably due to the reactions between SPI and PEEAMA and/or MDI.

CONCLUSIONS

SPI and PEEAMA were partially compatible. Two glass transitions were observed, and T_g values of both SPI and PEEAMA decreased as PEEAMA increased. Heat of fusion of PEEAMA decreased, but its T_m remained the same as SPI increased. Blending PEEAMA decreased E and σ , increased ϵ , and improved the toughness and the water resistance of the SPI plastics. MDI did not affect the thermal or mechanical properties of the SPI/PEEAMA blends, but increased water resistance of the blends. The water sorption mechanism of pure SPI was mainly relaxation controlled, but it was diffusion controlled for the SPI/PEEAMA blends with or without MDI.

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