

Effect of Interfacial Crosslinking on Miscibility Behavior Between Isocyanate-Functionalized Poly(*n*-butyl methacrylate) Particles and Carboxylic Alkali-Soluble Resin

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ABSTRACT: The effect of interfacial crosslinking on miscibility behavior in blend systems of isocyanate-functionalized poly(*n*-butyl methacrylate) (PBMA) and a carboxylic alkali-soluble resin, poly(styrene/alpha-methylstyrene/acrylic acid) (SAA), was studied with different dimethyl meta-isopropenyl benzyl isocyanate (TMI) concentrations. For the blend films of pure PBMA and SAA, both theoretical analysis and direct observation showed immiscibility between PBMA and SAA. For the blend systems of isocyanated PBMA and SAA, Fourier transform infrared spectra and gel permeation chromatography analyses qualitatively showed the crosslinking between the isocyanate group in isocyanated PBMA and the carboxylic group in SAA. Two $\tan \delta$ peaks were shown in the blend system of SAA and

isocyanated PBMA containing low concentrations of TMI (from 0 to 5 wt %), and the span of the two peaks became shorter as the TMI concentration increased. For a high TMI concentration (7 wt %), only one $\tan \delta$ peaks was observed. This result means the interfacial crosslinking between isocyanated PBMA and SAA occurred fully, and thus the miscibility between two polymers was significantly improved. As these results showed, the tensile strength of the blend film of isocyanated PBMA and SAA was higher than that of pure PBMA and SAA. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 792–798, 2003

Key words: interfacial crosslinking; isocyanate-functionalized; miscibility; dynamic mechanical; tensile strength

INTRODUCTION

Polymer blend systems play an important role in the plastic industry because they can be made to have a better combination of physical properties than homopolymers. Nevertheless, the major problem of polymer blends has been their very unstable quality because of the large interfacial tension between the components of the polymer blends.¹ Immiscible blend film usually accompanies phase separation during film formation, and thus such a phenomenon reduces the mechanical properties of films. A critical and determinant aspect of the properties of polymer blends is the miscibility between their individual components. The driving force for miscibility is the specific interactions between polymeric components. If the specific

interactions are strong enough, they could be miscible and possessed of special mechanical properties.

Polymer latices capable of undergoing latent crosslinking after film formation are of paramount importance from an industrial point of view.² Such systems are designed by introducing functional groups capable of forming a crosslink upon thermal treatment or catalysis.^{2,3} Crosslinking improves the integrity of polymer films and enhances desirable properties such as impact strength, tensile strength, peel strength, and water, alkali, and chemical resistance. Because of their improved properties, crosslinkable latices have found many applications in areas such as fabric coating and backing, textile finishing, fire-resistant coating, and ink binders. Interfacial crosslinking can be a more effective method to strengthen latex film and allows for more process control by varying the type, concentration, and distribution of the crosslinkable functional groups within the latex particles.⁴ Functional groups are capable of associating with one another through ionic, hydrogen, or covalent bond mechanisms.⁵ However, a relatively high-temperature thermal-curing period (usually higher than 100°C and longer than 20 min) is required

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for interfacial crosslinking. The synthesis of interfacially crosslinkable latex films under a mild curing condition has been of great interest. Such systems can be developed by incorporating functional monomers that can undergo crosslinking reactions at room temperature.⁶ One such functional monomer is dimethyl meta-isopropenyl benzyl isocyanate (TMI).⁷ TMI is a novel bifunctional monomer and has a double bond. The isocyanate group reacts with a variety of functional groups such as carboxyl and hydroxyl moieties.

Carboxylic alkali-soluble resin (ASR) contains both hydrophobic groups and a large number of carboxyl groups that can stabilize polymer particles electrostatically.⁸ In a recent article we compared the dynamic mechanical properties of PBMA latex films that were post-added with poly(styrene/alpha-methylstyrene/acrylic acid) (SAA) with those latex films prepared by emulsion polymerization in the presence of SAA (SAA-fortified latex).⁹ The dynamic properties of PBMA latex films post-added with SAA showed two distinct damping peaks, corresponding to those of PBMA and SAA, respectively, in the phase-separated state. SAA tended to desorb and migrate to interparticle spaces with its own domain in a phase-separated state during film formation,⁹ and the driving force for such a migration of SAA resin was the immiscibility between PBMA and SAA.¹⁰⁻¹² On the other hand, the SAA-fortified films exhibited a single damping peak. This improvement in miscibility between PBMA and SAA resulted from the grafting reaction between PBMA and SAA.⁹

This article describes the improvement in miscibility between PBMA and SAA by the reaction of an incorporated isocyanate group into PBMA with a carboxylic group in SAA. The effect of the interfacial crosslinking on miscibility behavior in blend systems of isocyanate-functionalized PBMA and carboxylic alkali-soluble resin, SAA, was studied with different TMI concentrations.

EXPERIMENTAL

Materials

Twice-distilled water was used throughout. *n*-Butyl methacrylate was purchased from Junsei Chemical Co. (Japan). It was purified by vacuum distillation under reduced pressure and refrigerated at 4°C. The dimethyl meta-isopropenyl benzyl isocyanate (TMI) was donated from Cytec Ind. (USA) and used as received. The SAA, with $M_n = 4300$ g/mol, $M_w = 8600$ g/mol, acid number = 190, and $T_g = 115^\circ$, was received from Morton Inc. (USA) and used as received. Reagent-grade potassium persulfate (KPS) and sodium bisulfate, from Samchun Pure Chemical Ind., Ltd. (Korea), were used as received. Ammonium iron(II) sulfate hexahydrate and sodium lauryl sulfate

TABLE I
Recipe for Seeded Emulsion Polymerization of Isocyanated-PBMA Latexes

Components	Stage I amount (g)	Stage II amount (g)
PBMA seed latex (20 wt % solid)		400
BMA	600	variables ^a
TMI	0	variables ^b
Potassium persulfate	1.826	0.949
Sodium bisulfate	0.720	0.375
Ammonium iron(II) sulfate hexahydrate	0.018	0.011
DDI water	2400	100
Sodium lauryl sulfate	3.034	0

^a Variables are 20, 19.8, 19.4, 19, 18.6.

^b Variables are 0, 0.2, 0.6, 1, 1.4.

(SLS), from Aldrich Chemical, Inc. (USA), were recrystallized before use.

Preparation of isocyanated PBMA latexes

The basic recipe for seeded emulsion polymerization is given in Table I. Redox initiators comprising potassium persulfate (oxidant), sodium bisulfate (reductant), and ammonium iron(II) sulfate hexahydrate (activator) were used. The surfactant was introduced into the bottles, along with DDI water. Separate aqueous solutions of the oxidant, reductant, and activator were prepared with the remainder of the water charge. The activator solutions and the monomers were added to the bottles and the contents purged with nitrogen. The agitation rate was maintained at 290 rpm throughout the reaction. They were charged into a double-jacketed glass reactor equipped with stirrer, thermometer, condenser, and nitrogen inlet and were polymerized at 40°C. For the second-stage emulsion polymerization, seed latex was introduced into the reactor, along with some of the DDI water charge, and purged with nitrogen. The second-stage monomers were then introduced, and the seed latex swelled for 30 min at 40°C with constant stirring. Thirty-three percent of the reductant and oxidant were added as aqueous solutions at 15-min intervals to start the polymerization. A syringe pump was used to feed the remaining initiator as two separate streams (of reductant and oxidant) over a period of 5 h. The polymerization was then continued for an additional hour. Additional surfactant was not added during the second-stage polymerization.

Preparation of blend films

A known weight of a 10 wt % SAA solution, obtained by dissolving the SAA resin in DDI water, was added slowly to 100 g of isocyanated PBMA latex at 25°C,

TABLE II
Sample ID for Prepared Film Samples

Composition	Sample ID
PBMA containing 0 wt % TMI ^a	IP-TMI-0
Isocyanated PBMA containing 1 wt % TMI ^a	IP-TMI-1
Isocyanated PBMA containing 3 wt % TMI ^a	IP-TMI-3
Isocyanated PBMA containing 5 wt % TMI ^a	IP-TMI-5
Isocyanated PBMA containing 7 wt % TMI ^a	IP-TMI-7
Blend of IP-TMI-0 and 20 wt % SAA ^b	IP-TMI-0-S
Blend of IP-TMI-3 and 20 wt % SAA ^b	IP-TMI-3-S
Blend of IP-TMI-5 and 20 wt % SAA ^b	IP-TMI-5-S
Blend of IP-TMI-7 and 20 wt % SAA ^b	IP-TMI-7-S

^a TMI weight % based on second-stage monomer.

^b SAA weight % based on isocyanated PBMA (IP-TMI).

and then mixed under moderate magnetic stirring for 24 h. Homogeneous transparent solid films were prepared by the dehydration of the dispersions according to the following procedure. First, the dispersions were degassed at room temperature, and then they were cast on a nonsticking, smooth Teflon substrate. All films dried and were annealed in an oven at 60°C for 24 h. Table II summarizes the composition of the PBMA film samples containing SAA that were prepared in this study.

Characterizations

The average particle size and polydispersity of the latex particles was determined using the capillary hydrodynamic fractionation (CHDF). A Fourier transform infrared (FTIR) spectrophotometer with an attenuated total reflectance (ATR) accessory was used to obtain the spectra. The penetration depth of the measurements was 5–10 μm from the film surface. A total of 128 scans at a resolution of 4 cm^{-1} were accumulated. The isocyanate (NCO) groups resulting from the incorporation of the TMI in the copolymer latex films were identified. Molecular weights and distributions of the isocyanated PBMA with SAA were obtained using a gel permeation chromatograph (Waters Co., USA) equipped with a series of μ Styragel[®] columns (pore sizes of 10^4 , 10^5 , and 10^6 Å), HPLC pump (Waters 501), RI detector (Waters 410), and an integrator at 40°C. Polystyrene standards and universal calibration were adapted to reduce measuring error. Sampling of the latex was carried out to investigate the inclination of molecular weight. Tetrahydrofuran (THF) was used as an eluent at 1.0 mL/min of flow rate and 1.0×10^3 Pa of the pump pressure.

The dynamic mechanical behavior of sample films was investigated using a dynamic mechanical thermal analyzer (Polymer Laboratories, Model MK-III, UK) equipped with an attachment for temperature control. This apparatus enabled us to measure the extension storage modulus (E'), the loss modulus (E''), and the loss tangent ($\tan \delta$) over a wide range of temperatures

(from -50°C to 200°C). The isochronal temperature dependence of the moduli and $\tan \delta$ were obtained for a frequency of 10 Hz at a constant heating rate of $2^\circ\text{C}/\text{min}$ under a nitrogen atmosphere. Accuracy of the data values was confirmed by repeating measurements twice in the same temperature range, and reproducibility was found to be satisfactory. Tensile strength measurements were done in a universal test machine (LR10K; Lloyd Instruments, Ltd., UK) with a crosshead speed of 10 mm/min. The tensile strength, yield stress, and strain at fracture were calculated. At least five specimens were tested for each sample, and the average values were determined.

RESULTS AND DISCUSSION

Particle size and size distribution

The particle size characterization and polydispersity of the latices are shown in Table III. The average seed particle diameter was 61 nm, and the final particle diameter obtained in all four runs ranged from 71 to 75 nm. The final particle size was almost the same regardless of the concentration of TMI, implying no secondary particle formation during the seeded emulsion polymerization.

FTIR analysis on crosslinking between isocyanated PBMA and SAA

Isocyanated PBMA latex films and blend films of isocyanated PBMA and SAA were analyzed using FTIR spectroscopy in order to evaluate qualitatively the crosslinking of the NCO groups from TMI with the COOH groups from SAA. In Figure 1 the FTIR spectra of the isocyanated PBMA latex films, which dried at room temperature for 24 h, show that the isocyanate group apparently appeared at 2270 cm^{-1} .¹³ For the isocyanated PBMA films, the NCO was still active, and the NCO peak was also detected clearly as TMI concentration increased.

The blend films of isocyanated PBMA and SAA did not reveal any peak at 2270 cm^{-1} , which was the

TABLE III
Particle Size Analyses of Isocyanated-PBMA Latices

TMI concentration ^a	D_n (nm)	D_w (nm)	PDI (D_w/D_n)
Seed	60	80	1.33
PB-TMI-0	71	96	1.35
IP-TMI-1	71	92	1.29
IP-TMI-3	72	96	1.33
IP-TMI-5	75	95	1.26
IP-TMI-7	75	94	1.25

PDI: polydispersity index; D_n : number-average diameter; D_w : weight-average diameter.

^a wt % based on second-stage monomer.

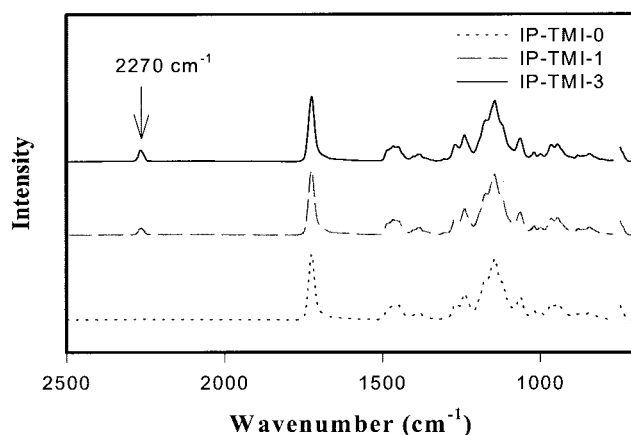


Figure 1 The FTIR spectra of the isocyanated PBMA as a function of TMI concentration.

characteristic region of the isocyanate group, shown in Figure 2. This indicates that at room temperature the isocyanate groups were consumed by the crosslinking reaction with the carboxylic groups.

Crosslinking density

The crosslinking reaction was also confirmed using the swelling technique. These gel fraction measurements were carried out using the solvent extraction technique. Briefly, this method involves dissolving 0.2 g of a series of blend films cast at room temperature and dried under vacuum for 10 h in 25 mL of 1,4-dioxane with stirring for 24 h. The dissolved portion, that is, the nongel part, is determined gravimetrically from the amount of solids remaining in the supernatant after the centrifugation of the swollen system at 5000 rpm for 30 min. The gel fraction is the percentage of the insoluble polymer in the total film sample. The swelling ratio of a latex film is deter-

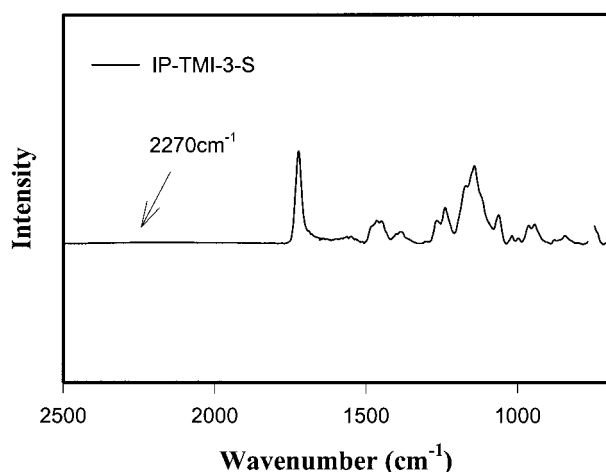


Figure 2 The FTIR spectra of the blend film of isocyanated PBMA latex and 20 wt % SAA based on PBMA.

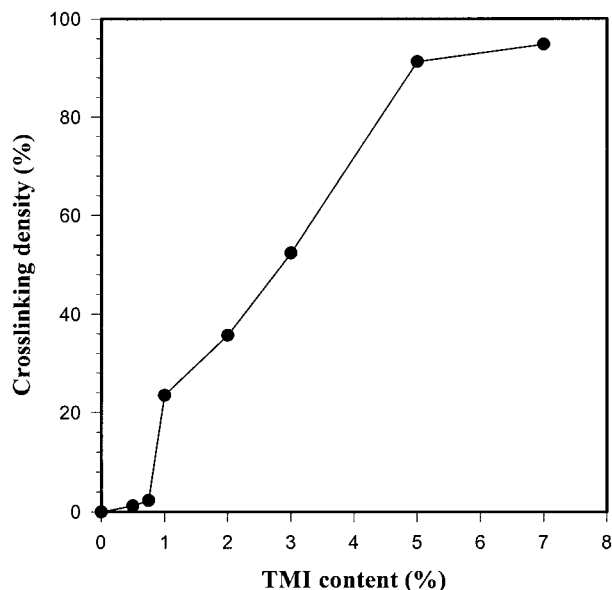


Figure 3 The crosslinking density of blend films of isocyanated PBMA and 20 wt % SAA as a function of the TMI concentration in isocyanated PBMA.

mined from the weight ratios of the film samples before and after a 24-h swelling process at room temperature. The weight (W_0) of film specimen before immersion into the solution is measured. The swollen film is then dried in a vacuum oven to a constant weight (W_1). The gel content (%) is calculated from the following expression:

$$\text{Gel content (\%)} = (W_1/W_0) \times 100\% \quad (1)$$

Figure 3 showed that the crosslinking density of blends of isocyanated PBMA and SAA increased with the increase of TMI offering NCO groups. Both isocyanated PBMA and SAA films were soluble in 1,4-dioxane. When SAA solution was added to the isocyanated PBMA latex and the blend films were dried at room temperature, these films did not dissolve in 1,4-dioxane. These results indicate that the reaction between NCO groups and carboxylic groups occurred either in the dispersion stage or during the air-drying and aging stage, which resulting in a crosslinking reaction to resist 1,4-dioxane.

When the TMI concentration was more than 5 wt %, the gel content reached more than 90%. This tendency showed that interfacial crosslinking increased with an increase in TMI concentration.

Molecular weight and molecular weight distribution

In Figure 4 the molecular weight distributions are shown for a series of blends of SAA and isocyanated

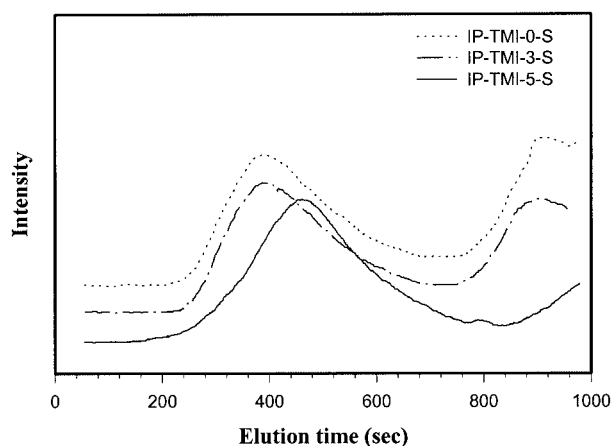


Figure 4 The molecular weight and distribution of blends of the isocyanated PBMA and 20 wt % SAA (based on PBMA) as a function of TMI concentration.

PBMA (IP) containing different TMI concentrations. There were two distinct molecular weight peaks for the blend of IP-TMI-0 and SAA. The low molecular weight peak (ca. 4300 g/mol) was from SAA polymer and the peak on the high-molecular-weight side was from PBMA polymer (ca. 420,000 g/mol). This implied that crosslinking between the two polymers had not occurred. In the blends of isocyanated PBMA and SAA, however, as the TMI concentration increased, the low-molecular-weight peak decreased. This result implied that the partial crosslinking reaction between isocyanated PBMA and SAA occurred, and the more sufficient isocyanate group in isocyanated PBMA could make SAA molecules graft more into isocyanated PBMA molecules.

Dynamic mechanical properties

The miscibility of different polymer blends through various specific interactions can be predicted theoretically with solubility parameters, whose components may be predicted from group contribution using the method of Hoftzyer and Van Krevelen.¹⁴ The solubility parameter for a random copolymer can be calculated using the Hildebrand equation.¹⁵ To achieve molecular-level mixing of the blend constituents, the value of the interaction parameter (χ) should be < 0.002 , which can be calculated by using the Hildebrand equation, as follows¹⁶:

$$\chi = V_R/RT(\delta_A - \delta_B)^2 \quad (2)$$

where V_R is the reference volume, δ_A and δ_B are the solubility parameters of the two blend constituents, T is the temperature, and R is the molar gas constant.

Using the data given in Table IV, the miscibility of the binary blend system of PBMA and SAA was predicted. With the solubility parameters, δ_A and δ_B , ob-

TABLE IV
Physical Parameters of Pure Constituents of the Blend

	Molar volume (cm ³ /mol)	Molecular weight (g/mol)	Solubility parameter (J ^{1/2} cm ^{-3/2})
Poly(<i>n</i> -butyl methacrylate)	86.79		17.9
Polystyrene	99	103.95	18.01
Poly(alpha-methylstyrene)	111	118.22	18.49
Poly(acrylic acid)	38	72.06	30.36
SAA			20.91

tained from the group contribution and a reference volume of 86.79 cm³/mol at 25°C, the interaction parameter (χ) was calculated and found to be 0.32, which is well above the 0.002 predicted by the Hildebrand approach. This value substantiates that the blends of PBMA and SAA are completely immiscible.

For the blend film (IP-TMI-0-S) of PBMA and SAA, the phase separation was confirmed by direct observation after film formation. The spectrum in Figure 5 shows two distinct $\tan \delta$ peaks, corresponding to those of the PBMA and SAA resin, respectively, in the phase-separated state. These results were interpreted from immiscibility between PBMA and SAA, as predicted theoretically. The presence of two well-defined peaks in the blend film established the immiscibility of the two phases. The SAA resin was phase-separated from PBMA during film formation, and as a result, SAA resin preserved its own domains in the matrix phase, showing two distinct $\tan \delta$ peaks in the DMA spectrum. This interval between two distinct $\tan \delta$ peaks in the DMA spectrum decreased as the TMI concentration in isocyanated PBMA increased. Both IP-TMI-3-S and IP-TMI-5-S also had the two δ peaks; however, the dynamic mechanical properties of the blend films were affected by the crosslinking reaction

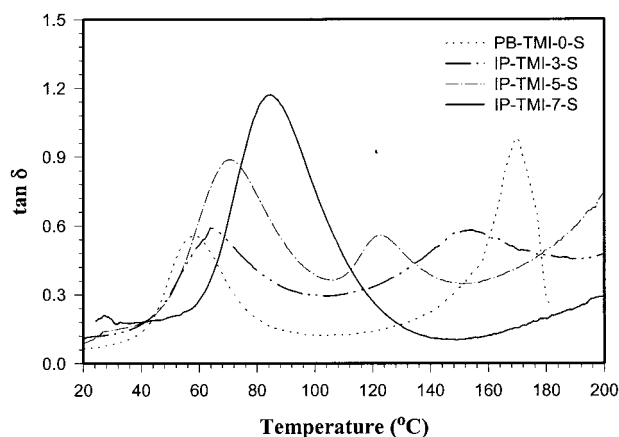


Figure 5 Dependence of $\tan \delta$ on the temperature for the blend films of the isocyanated PBMA latex and 20 wt % SAA (based on PBMA) as a function of TMI concentration.

between isocyanated PBMA and SAA. The peak for the former had originated in PBMA and the other in SAA. Because of the crosslinked molecules between isocyanated PBMA and SAA, the $\tan \delta$ peaks were shifted from 64.2°C to 72.4°C at the lower temperature and from 154.3°C to 122.0°C at the upper temperature. The shifts resulted from the crosslinking reaction between isocyanated PBMA and carboxylic groups in SAA and indicated partial improvement in compatibility between PBMA and SAA (Fig. 5).

As the TMI concentration increased, the span of two peaks decreased. For IP-TMI-7-S, in which sufficient TMI content was incorporated in PBMA particles, one $\tan \delta$ peak was observed on the middle range of the previous two $\tan \delta$ peaks, as shown in Figure 5. This result meant that the crosslinking between isocyanated PBMA and SAA had fully occurred and thus that the miscibility between two polymers was significantly improved.

The Hildebrand equation showed immiscibility theoretically between PBMA and SAA. However, these results showed that the miscibility between PBMA and SAA could be improved through a crosslinking reaction between the isocyanate and carboxylic groups.

Tensile strength properties

Tensile strength buildup of polymer films prepared from aqueous dispersion of latex particles was dependent not only on the nature of the bulk material property but also on the degree of interfacial crosslinking, that is, the extent of interdiffusion of the chain segments across the particle boundary.¹⁶ The tensile properties were determined after curing the films at room temperature for 24 h. Figure 6 shows the tensile properties of blend films with and without the incorporation of TMI. In the presence of TMI in PBMA particles, higher stress and longer elongation were observed than for the blend film of IP-TMI-0 and SAA. This result was similar to the general results of the modulus increase as the degree of crosslinking increased.¹⁷ Therefore, the crosslinking between isocyanated PBMA and SAA was found to induce improvement both in the miscibility of two polymers and in mechanical properties.

CONCLUSIONS

The miscibility behavior of blend films of isocyanated PBMA particles and carboxylic alkali-soluble resin, SAA, was studied. The chemical reaction between the isocyanate groups on PBMA particles and carboxylic groups in SAA occurred during film formation. This showed that the development of a continuous crosslinked network at the boundaries between individual particles occurred as a result of interfacial

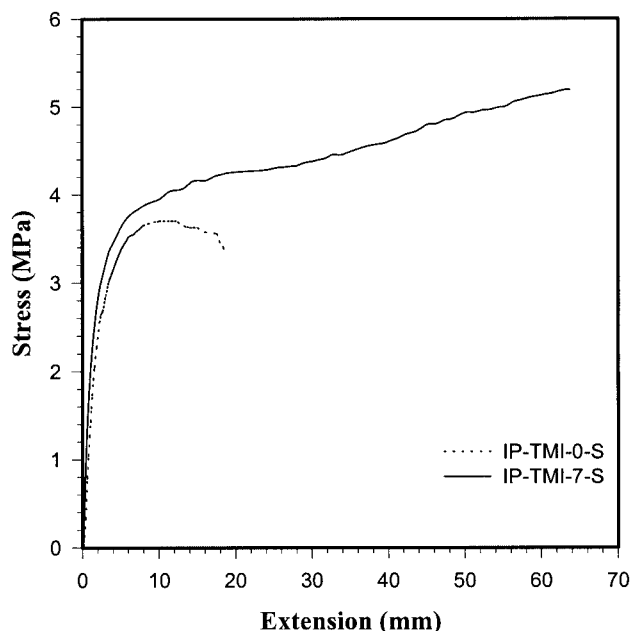


Figure 6 Stress-strain plots for blend films composed of isocyanated PBMA with 20 wt % SAA based on PBMA as a function of TMI concentration.

crosslinking and the miscibility enhancement of incompatible polymer blends. On the FTIR spectra the isocyanate group apparently appeared at 2270 cm^{-1} for the isocyanated PBMA. For the blends of isocyanated PBMA and SAA, however, the isocyanate peak disappeared because of the interfacial crosslinking reaction. As the concentration of TMI increased, the crosslinking density increased. The GPC analysis showed that the peak of the SAA molecules decreased with an increase of TMI concentration in the blend of isocyanated PBMA and SAA. Two $\tan \delta$ peaks were observed in the blend film of isocyanated PBMA and SAA; however, the span of the two $\tan \delta$ peaks was decreased with an increase of TMI concentration (0–5 wt %) in the PBMA particles. On the 7 wt % TMI concentration, only one peak, whose temperature was about 84°C, was observed. These results show that the miscibility between PBMA and SAA apparently had improved. In the absence of TMI, the blend film of PBMA latex and SAA was very brittle because of the immiscibility between PBMA and SAA. However, the blend film of isocyanated PBMA and SAA had higher stress and longer extension than did blend film of pure PBMA and SAA. The interfacial crosslinking reaction between isocyanated PBMA and carboxylic SAA enhanced the miscibility between PBMA particles and SAA, which resulted in the improvement of tensile strength.

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