

# Silicon Secondary Crosslinked IPN Based on Poly(methyl acrylate-co-acrylic acid) and SiO<sub>2</sub>

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**ABSTRACT:** Silicon secondary crosslinked interpenetrating polymer networks (IPNs) of poly(methyl acrylate-co-acrylic acid) (PMAA) and SiO<sub>2</sub> were prepared and characterized. The effects of composition, water content, and substrate plate on the phase morphology of the IPNs of PMAA/SiO<sub>2</sub> have been studied by scanning electron microscopy, and the glass transition temperature measured by differential scanning calorimetry. By controlling the synthetic conditions an optically transparent film was obtained, which shows a remarkably high degree of mixing between the two chemically dissimilar phases. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 903–909, 1997

**Key words:** IPNs; PMAA; tetraethyl orthosilicate; scanning electron microscopy

## INTRODUCTION

Interpenetrating polymer networks (IPNs) represent an interesting approach to the blending of two polymers.<sup>1–3</sup> In these materials, the constituents are physically entangled in the form of their networks. In contrast with other polymer blends, the state of phase separation obtained at the end of their synthesis cannot change significantly by aging or under applied stresses, so that the properties are not influenced by such parameters. IPNs are therefore well suited when a combination of two polymers is necessary to obtain a material with a specific range of properties. Silicon-containing polymers are particularly incompatible with other polymers, and a classical mechanical blend would be most unstable, whereas the corresponding IPN provides stable morphology and properties.

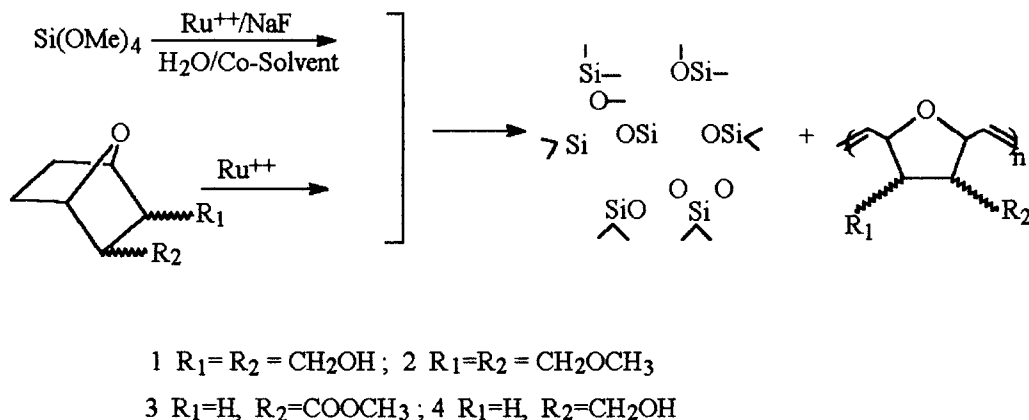
In the field of new inorganic–organic IPNs, aspects such as phase continuity, domain size, and molecular mixing at the phase boundaries greatly

influence the optical, physical, and mechanical properties of the composite materials.<sup>3</sup> In an effort to improve the degree of mixing between the two chemically dissimilar phases, some transparent IPN composites have been synthesized through a synchronous application of the aqueous ring-opening metathesis polymerization (aqueous ROMP)<sup>4,5</sup> of cyclic alkenyl monomers and the hydrolysis and polycondensation of tetraalkyl orthosilicate (the sol–gel process).<sup>4–6</sup> The mild conditions offered by the sol–gel process allow for the incorporation of performed organic polymers into the glass matrix to form composites possessing properties of both inorganic and organic polymers.<sup>5</sup> However, due to the poor solvating properties of typical sol-gel formulations, homogeneous polymer solutions can be obtained only by using a limited number of polymers.<sup>4,5,7,8</sup> To compound this limitation and to circumvent the solubility and homogeneity problems associated with performed polymers/sol-gel formations, Ellsworth and Novak<sup>9,10</sup> prepared organic–inorganic simultaneous interpenetrating networks via incorporation of a crosslinked polymer formed *in situ* within sol-gel derived tetraalkoxy silane glasses through both radical and ring-opening metathesis polymerization. Scanning electron microscopy

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**Figure 1** Formation of organic–inorganic simultaneous interpenetrating networks.

(SEM) shows a remarkably high degree of mixing between the two chemically dissimilar phases of these new composite materials (see Fig. 1).

Here we report on the synthesis and characterization of novel organic–inorganic IPNs, i.e., silicon secondary crosslinked IPNs, based on poly(methyl acrylate-*co*-acrylic acid) (PMAA) and  $\text{SiO}_2$  formed via the hydrolysis and polycondensation of tetraethyl orthosilicate.

## EXPERIMENTAL

### Materials

The raw materials used and their descriptions are listed in Table I. Methyl acrylate (MA) and acrylic acid (AA) were distilled under vacuum before use. 2,2'-Azobisobutyronitrile (AIBN) was dissolved in anhydrous ethanol at 35°C, recrystallized, and dried under vacuum at room temperature. Dodecyl benzene sulfonic acid (DBSA) was purified through a rotary evaporator. Ethyl acetate, anhydrous ethanol, benzene, and cyclohexane (Beijing Chemical Factory, Beijing, China) were used as received. Tetrahydrofuran (THF)

and tetraethyl orthosilicate (TEOS) were also used as received.

### Synthesis of Poly(methyl acrylate-*co*-acrylic acid)

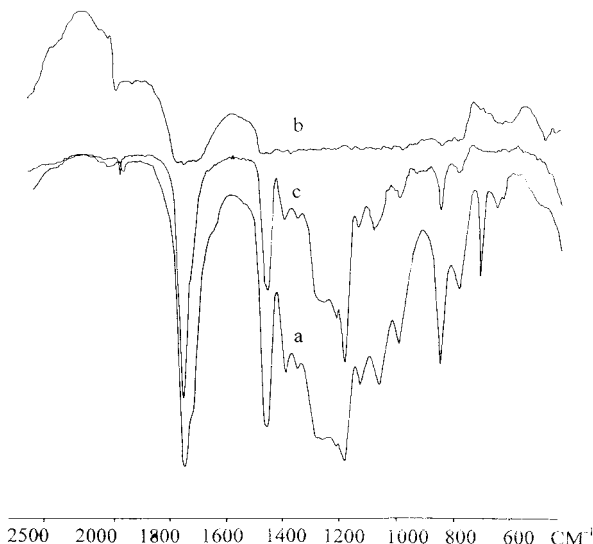
MA, 42 g, was dissolved in an 80-g mixture of ethyl acetate, benzene, and anhydrous ethanol (ratio, 16 : 3 : 1). AA, 5.8 g, and 0.8 g of AIBN in 20 g the mixture solvent was added dropwise at 70°C, and the reaction mixture was stirred under a nitrogen atmosphere for 6 h. To terminate the reaction, the copolymer was precipitated in cyclohexane and the precipitate was dried in a bake oven to constant weight.

### Preparation of Silicon Secondary Crosslinked IPNs

The well-defined amount of copolymer, TEOS, and deionized water, and 0.01 g DBSA were dissolved in 10 g THF. The mixture was refluxed for 1 h, poured into a substrate plate, and placed at room temperature under moisture atmosphere for 24 h. The final film was soaked in water, peeled off, and dried at 40°C in a bake oven for another 1 h.

**Table I** Materials

Abbreviation	Description	Source
MA	Methyl acrylate	Beijing Chem. Co., China
AA	Acrylic acid	Beijing Chem. Co., China
THF	Tetrahydrofuran	Beijing Chem. Fact., China
AIBN	2,2'-Azobisobutyronitrile	Beijing Chem. Fact., China
TEOS	Tetraethyl orthosilicate	Beijing Chem. Fact., China
DBSA	Dodecyl benzene sulfonic acid	DuPont, Philadelphia, PA



**Figure 2** IR spectra of (a) PMAA, (b) PMAA/TEOS/DBSA, and (c) PMAA/DBSA.

**Etching of the IPNs**

The freestanding film was etched with 10% H<sub>2</sub>SO<sub>4</sub> at room temperature for 24 h, washed with distilled water several times, and dried at 35 to 45°C.

**Measurements**

**Infrared Measurement**

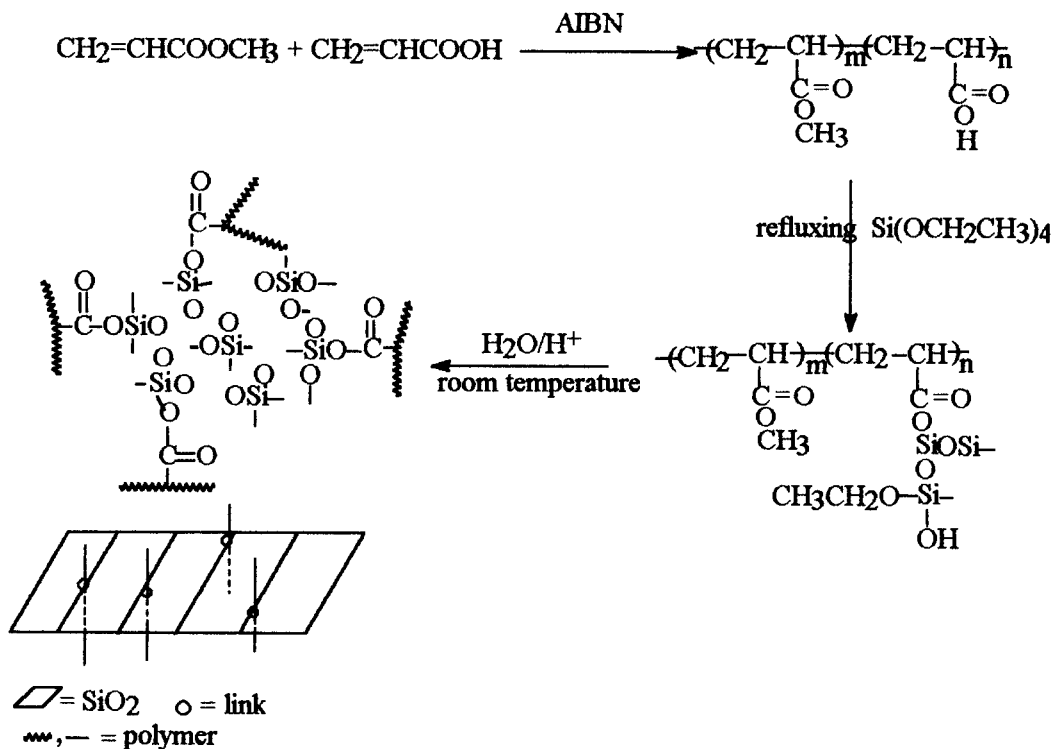
The freestanding film and the film cast from the solution on the KBr plate were measured with a Hitachi model 270-30.

**Electron Microscopy**

The phase morphologic characteristics of the samples were studied by SEM. The specimens for SEM were frozen in liquid nitrogen, fractured, mounted, and coated with gold. They were then observed with a Hitachi S-530.

**Calorimetric Measurements**

The glass transitions (*T<sub>g</sub>s*) were measured by differential scanning calorimetry (DSC) (PE, 7 series thermal analysis system). Measurements were carried out from -25 to 150°C under nitrogen at a scanning rate of 20°C/min. Specimen sizes were of the order of 14 mg.



**Figure 3** Formation of silicon secondary crosslinked IPN.

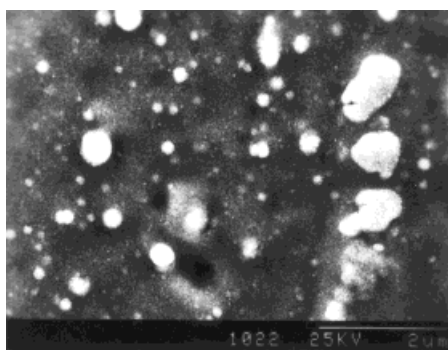
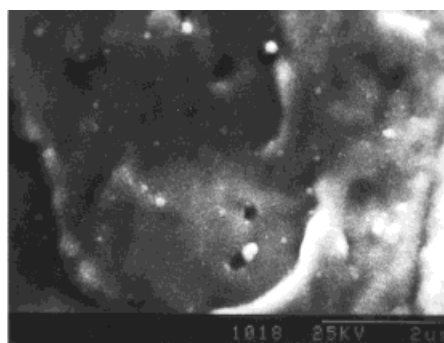
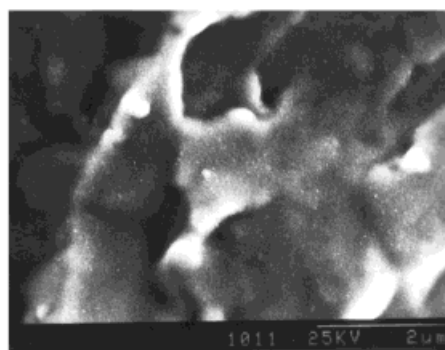
**Table II Results of DSC Measurement ( $T_g$ ) and Properties of the IPN Films**

Sample	Composition TEOS/ TEOS + PMAA	$T_g$ (°C)	Remarks on the Samples <sup>a</sup>
PMAA	0/100	16.0	soft, TP, sol. in A and T
P <sub>2</sub>	10/100	—	soft, TP, sol. in A and T
P <sub>4</sub>	20/100	—	soft, TP, spot, partly sol. in A and T
P <sub>5</sub>	50/100	—	soft, TP, spot, swollen in A and T
P <sub>H</sub> <sup>+b</sup>	5/100	22.2	soft, TP, sol. in A and T (slow)
P <sub>2H</sub>	10/100	—	soft, TP, sol. in A and T (slow)
P <sub>4H</sub>	20/100	27.7	soft, TP, partly sol. in A and T
P <sub>5H</sub>	50/100	32.1	brittle, TP, less spot, swollen in A and T
P <sub>4H-5</sub> <sup>++</sup>	20/100	—	soft, TP, swollen in A and T
P <sub>4H-5</sub> <sup>c</sup>	20/100	—	brittle, TP, LY, swollen in A and T
P <sub>5H-5</sub>	50/100	—	less soft, OP, swollen in A and T

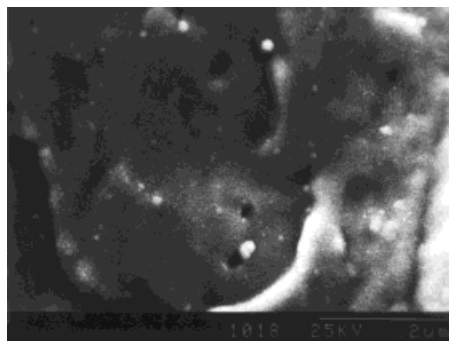
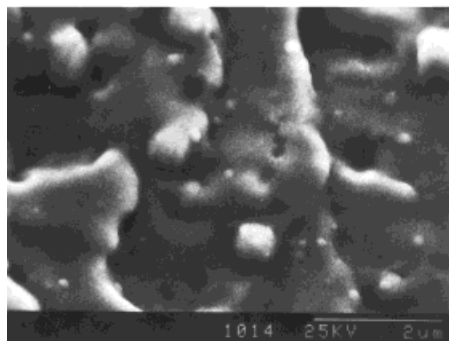
<sup>a</sup> TP, transparent; sol., soluble; A, acetone; T, THF; LY, light yellow; OP, opaque.

<sup>b</sup> + and ++ with H and H-5 means with 0.1% and 0.5% water respectively; all others without water.

<sup>c</sup> Substrate plate is iron; for all others, Teflon.

P<sub>4</sub>P<sub>4H</sub>P<sub>4H-5</sub>

**Figure 4** SEM of the fracture sections of IPNs for P<sub>4</sub> (0% water), P<sub>4H</sub> (0.1% water), and P<sub>4H-5</sub> (0.5% water).

P<sub>4H</sub>P<sub>5H</sub>

**Figure 5** SEM of the fracture sections of IPNs for P<sub>4H</sub> (20% TEOS) and P<sub>5H</sub> (50% TEOS).

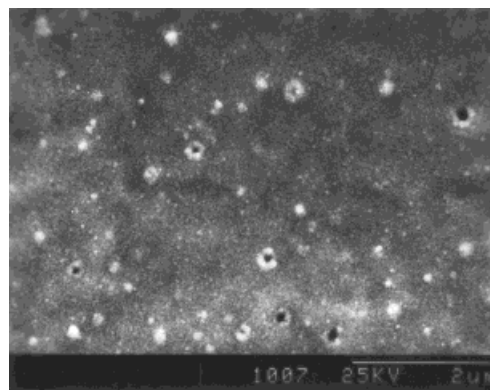
## RESULTS AND DISCUSSION

Siloxane can readily be self-condensed with the product of a Si—O—Si network via hydrolyzation with acid as catalyst.<sup>11,12</sup> The formation of Si—O—CO via siloxane reacting with PMAA plays an important role in the preparation of silicon secondary crosslinked IPNs in this study. Therefore it is necessary to verify whether or not the Si—O—CO link is formed. The infrared (IR) spectra of PMAA, PMAA/TEOS/DBSA, and PMAA/DBSA are given in Figure 2. The IR spectrum of PMAA/TEOS/DBSA [Fig. 2(b)] shows a sharp decrease in absorption from 1800 to 1700  $\text{cm}^{-1}$  with formation of a short absorption tail and another long absorption tail from 1500 to 800  $\text{cm}^{-1}$  compared with that of PMAA [Fig. 2(a)]. The decrease in carbonyl absorption may result from PMAA reacting with TEOS to form a Si—O—CO link, so the former tail suppresses the C=O absorption of COOCH<sub>3</sub>, COOH, and Si—O—CO stretching mode absorption at about

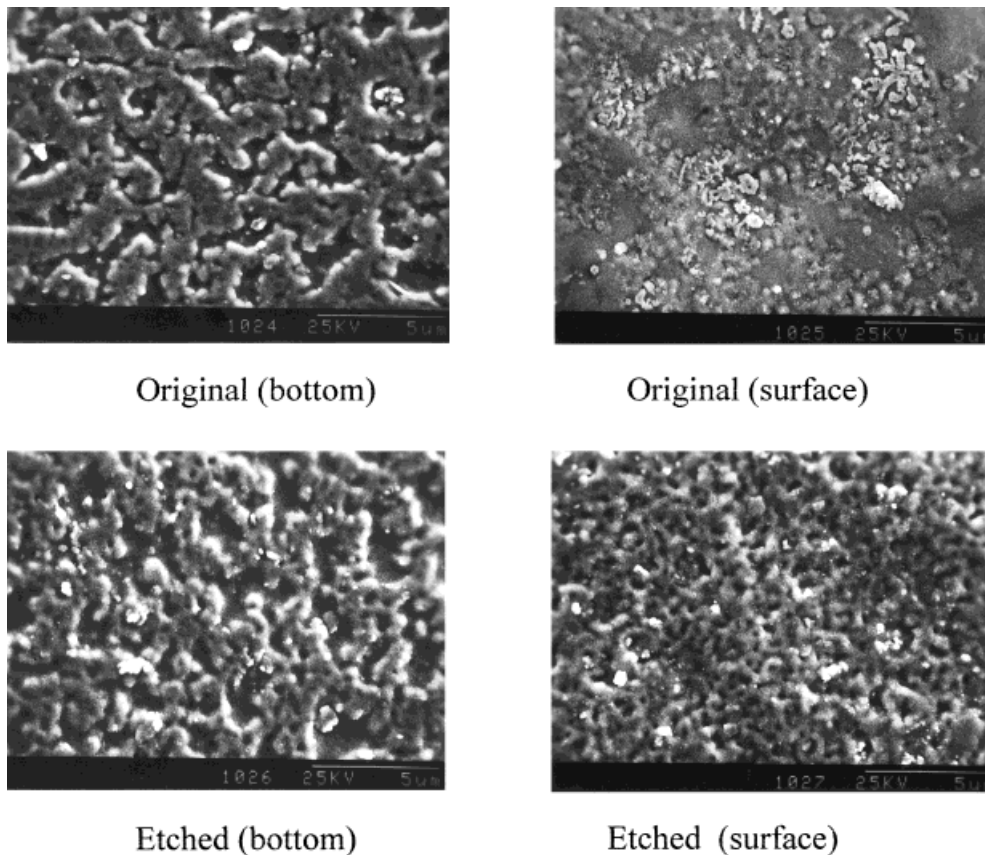
1720, 1740, and 1720  $\text{cm}^{-1}$ ,<sup>13,14</sup> respectively. On the other hand, the IR spectrum of PMAA/DBSA [Fig. 2(c)] shows no feature change in absorption from 1800 to 800  $\text{cm}^{-1}$ , denying the possibility of carbonyl absorption tail formed by PMAA interacting with DBSA. Therefore the fact that the Si—O—CO link is present in the composite film is reasonably substantiated, and this is well indicative of secondary crosslinked network formation in the PMAA/SiO<sub>2</sub> IPN. The possible way to form the silicon secondary crosslinked IPN is shown in Figure 3.

$T_g$  obtained from P<sub>H</sub>, P<sub>4H</sub>, and P<sub>5H</sub>, and solubility obtained for P<sub>4</sub>, P<sub>5</sub>, P<sub>H</sub>, P<sub>2H</sub>, P<sub>4H</sub>, P<sub>5H</sub>, P<sub>4H-5</sub>, and P<sub>5H-5</sub> are given in Table II. Except P<sub>5H-5</sub>, all films were soft and transparent. With increase of TEOS from 0 to 50%, the solubility of these films in acetone and THF became poor gradually; at 50%, only swollen. Moreover, without water for P<sub>4</sub> and P<sub>5</sub> in refluxing, there existed some spots in their films showing phase separation between the two components. With increased content of water from 0 to 0.5%, the spots decreased or even disappeared and the IPN film became brittle and insoluble. This suggests an increase of the crosslink density in the film. The addition of mild water content can fasten the formation of Si—OCO link upon PMAA reacting with TEOS,<sup>15</sup> and this renders the two chemically dissimilar phases compatible so that a homogeneous, transparent film can be obtained. Interestingly, the P<sub>4H-5</sub> film cast from Teflon plate is different from that cast from iron plate. The former is soft and transparent, and the latter is brittle, transparent, and light yellow.

From Table II, we can also observe only one  $T_g$  for P<sub>H</sub>, P<sub>4H</sub>, and P<sub>5H</sub>, among which there exists a trend of increase with the increase of TEOS. The results show a single-phase morphology but can-



**Figure 6** SEM of the fracture section of P<sub>4H-5</sub> (cast on iron plate).



**Figure 7** SEM comparison of the bottom and surface of original  $2P_{4H-5}$  and etched  $2P_{4H-5}$  ( $P_{4H-5}$  with 2 h of refluxing remarked as  $2P_{4H-5}$ ).

not explain the spots in the IPN film. Therefore, it is suggested that the spots disappearing with the increase of water result from the small “cage” structure of Si—O—Si<sup>17</sup> without or with a little Si—O—CO link, which cannot lead to an individual  $T_g$ .

SEM fracture studies of  $P_4$ ,  $P_{4H}$ , and  $P_{4H-5}$  revealed the number of spherical particles lessening with increased water, confirming the films’ characteristic that the spots disappeared from  $P_4$  to  $P_{4H-5}$  gradually (Fig. 4). Phase-separated  $P_{4H}$  exhibited dispersed phase particles, submicrometer-sized particles, and holes in the micrographs, just like other phase-separated IPNs mentioned in literature,<sup>18</sup> indicating particles not imbedded in the bulk phase. The SEM observation of  $P_{4H}$  and  $P_{5H}$  (Fig. 5) showed a larger phase size and more spherical particles for  $P_{5H}$  than for  $P_{4H}$ , consistent with the result that there were spots in  $P_{5H}$  and no spots in  $P_{4H}$ .

$P_{4H-5}$  cast onto iron plate (with high surface tension) showed a different morphology from that cast onto Teflon plate (with low surface tension)

(Fig. 6). There were many particles and holes in the former; none in the latter. These findings may result from the difference in surface tension between the two substrate plates due to migration of siloxane to the surface with lower surface tension.<sup>19</sup>

The surface morphology was different from that of the bottom for  $2P_{4H-5}$  (Fig. 7), in good agreement with the result of Figure 6. After  $2P_{4H-5}$  was etched with 10%  $H_2SO_4$ , the morphology of the bottom and surface was obviously changed, displaying clear network structure. However, in contrast to the bottom, larger change occurred in the surface morphology resulting from the uncrosslinked and partly crosslinked PMAA dissolved in 10%  $H_2SO_4$  solution.

In summary, the formation of a Si—O—CO link plays an important role in the preparation of the silicon secondary IPNs. The characteristics of the IPN film are in agreement with the glass transition behavior and the SEM fracture studies for this PMAA/SiO<sub>2</sub> system and indicates that the IPN phase-mixing ability corresponds to a definite

composition range of PMAA and TEOS and to water content. With addition of 0.5% water, the IPNs exhibited no phase separation between the two chemically dissimilar phases up to 20 wt % of the TEOS component. At and above 50 wt % of TEOS content, evidence of phase separation has been observed, e.g., by SEM and the characteristics of the film. The phase separation of the component network in the IPNs increased as the weight percentage of TEOS content increased, and also increased as the weight percentage of water content decreased. In addition, the surface morphology strongly depends on the substrate plate.

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