

# Interpenetrating Polymer Networks of Polyurethane and Polystyrene Ionomers

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## Synopsis

Interpenetrating polymer networks (IPNs) and linear blends of polyurethane (PUN) and poly(styrene-acrylic acid) (PSAA), which contain mutually opposite charge groups, i.e., tertiary amine and carboxyl groups, respectively, were synthesized through simultaneous bulk polymerization. Physical and mechanical properties of these IPNs and linear blends are discussed in the present paper. The tensile strength of both PUN/PSAA IPNs and linear blends has shown to increase with an increase of acrylic acid (AA) content in PSAA in any PUN/PSAA composition. A maximum value emerged in both polymer systems with 30 mol % AA in PSAA and the PUN/PSAA ratio of 25/75. A minimum swelling ratio as well as a maximum density was also observed in the IPNs and linear blends, respectively, related to this PUN/PSAA ratio. From dynamic mechanical analysis, two distinct relaxation transitions for the IPN or linear blend without AA in the system have merged into a single broad transition as the AA was introduced into PSAA. Two-phase morphology was observed from scanning electron microscopy studies for the polymer systems in the absence of charge groups; however, one-phase morphology was observed when the charge groups were introduced.

## INTRODUCTION

The interpenetrating polymer network (IPN) is a new type of polyblend having interlocking structure without covalent bond between the polymers. According to Sperling and Frisch,<sup>1,2</sup> it is defined as a combination of two or more polymers in network form, at least one of which is synthesized and/or crosslinked individually in the presence of the others. Since research on the subject of IPN is always associated with two or more different polymer systems, the compatibility between the polymers in the IPNs is an important role to be investigated and determined for their applications. In highly incompatible polymer systems, phase separating owing to thermodynamic effects can be so great that phase separation may take place prior to the formation of interlocking between the two polymers, and eventually result in obscured interpenetrating effect.<sup>3</sup>

There are many ways available to improve the compatibility between two polymers. Introducing opposite charge groups into the polymer components is one of the most effective ways among them,<sup>4-9</sup> because the opposite charge groups in the two polymers can interact with each other to achieve a lower enthalpy of mixing. Thus, the free energy of the mixing decreases to a negative or zero value. Hence the compatibility between the polymers has been increased and has resulted in an increase of interpenetrating networks in the IPNs.

The polyurethane/polystyrene IPNs had been found of significant phase separation owing to discrepancy of solubility parameters between them.<sup>7</sup> In order to improve their compatibility, the tertiary amine group in *N*-methyl diethanolamine (MDEA) as well as the carboxyl group in acrylic acid (AA) was introduced into polyurethane (PUN) and poly(styrene-acrylic acid) (PSAA), respectively, to prepare PUN/PSAA IPNs and linear blends through simultaneous bulk polymerization. The effect of the charge groups on the physical and mechanical properties and morphology of the resultant IPNs and linear blends will be discussed in the present paper.

## EXPERIMENTAL

### Preparation of PUN/PSAA IPNs and Linear Blends

PUN prepolymers were prepared from the reaction of 2 eq 4,4'-methylenebis(phenyl isocyanate) (MDI) and 1 eq poly(tetramethylene oxide) glycol (PTMO) of molecular weight 998 at 70°C under nitrogen atmosphere. One equivalent chain extender, *N*-methyl diethanolamine (MDEA), or crosslinking agent, triethanolamine (TEA), was agitated with a mixture of suitable composition for styrene (S), acrylic acid (AA), benzoyl peroxide (BPO), and/or divinyl benzene (DVB) at room temperature for 3 min. At this stage, the tertiary amine group of MDEA or TEA interacted with the carboxyl group of AA in the mixture, as proved in Figure 1, to form a complex molecule. The mixture was then stirred vigorously with the PUN prepolymer. The whole mixture was poured into an aluminum mold after it was degassed under vacuum for 30 s. Simultaneous bulk polymerization was performed in the oven at 80°C for 24 h, and then post-cured for another 24 h at 100°C. Due to interaction between AA and MDEA or TEA, both the PUN and PSAA chains could grow intimately and result in more interpenetrating or entangling structures in the resultant polymers. In the preparation of linear blends, the crosslinking agent, DVB for PSAA, had to be omitted and TEA for PUN be replaced by MDEA in the preparation procedure described above. The sam-

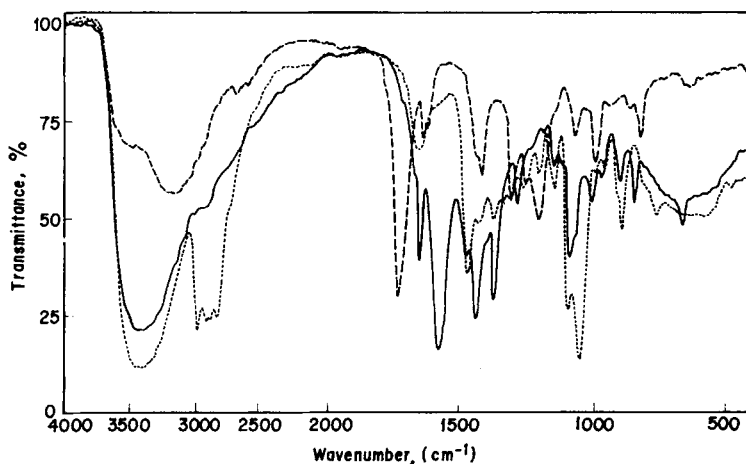


Fig. 1. Infrared spectra of AA (---), MDEA (···), and AA/MDEA mixture (—).

ples of PUN/PSAA IPNs and linear blends of various ratios were kept in a container at 50% RH for at least 3 days before they were tested on their mechanical properties.

### Testing Methods

The stress-strain properties were determined on an Instron table Model 1130 testing machine according to ASTM D638 with strain rate at 1 cm/min.

Dynamic mechanical studies were performed by employing Rheovibron Model DDV-IIC at temperatures between  $-80$  and  $160^{\circ}\text{C}$ . The frequency was set at 110 Hz. The measurements were made at a heating rate of  $1^{\circ}\text{C}/\text{min}$  in transition regions and of  $3\text{--}5^{\circ}\text{C}/\text{min}$  in nontransition regions. The specimens used were in the shape of 1.6 cm long, 0.15 cm wide, and 0.05 cm thick.

Morphological studies were performed by employing scanning electron microscopy (SEM). Microphotographs had been taken on the surface by fracturing the specimen in liquid nitrogen and then coating with gold powder.

The swelling property was determined with a known weight of the specimen ( $W_0$ ) immersed in benzene as solvent at room temperature. Until constant weight of the swollen specimen ( $W'$ ) had been obtained, the swelling ratio ( $q$ ) could be calculated as follows:

$$q = 1 + \frac{(W' - W_0) \cdot \rho_0}{W_0 \cdot \rho_s}$$

where  $\rho_s$  and  $\rho_0$  are the densities of benzene and the specimen, respectively.

## RESULTS AND DISCUSSION

### Infrared Spectroscopy

Figure 1 shows IR survey spectra for MDEA, AA, and the mixture of equimolar ratio of MDEA and AA. It clearly shows that the strong  $\text{—COOH}$  peak emerged at  $1748\text{ cm}^{-1}$  in the IR spectrum of AA. This  $\text{—COOH}$  peak disappeared completely and converted into carboxylic salt peak at  $1580\text{ cm}^{-1}$

in the spectrum of the MDEA and AA mixture, and the formation of  $\text{—N}^+\text{H}$  peaks could also be detected in the stronger peaks at  $1659$  and  $1485\text{ cm}^{-1}$ . This is evidence that strong interactions existed resulting from proton transfer from carboxylic acid in AA to the tertiary amine group in MDEA, as shown in Figure 2(a).

This strong interactions between MDEA and AA would result in very intimate growing in both PUN and PSAA chains during polymerization. Meanwhile, hydrogen bonding would be possibly involved<sup>6</sup> between polyurethane chains and the excess carboxylic acid in PSAA as shown in Figures 2(b) and (c).

### Stress-Strain Properties

The tensile strength of PUN/PSAA IPNs and linear blends with various AA content in PSAA are shown in Figures 3 and 4, respectively. The results



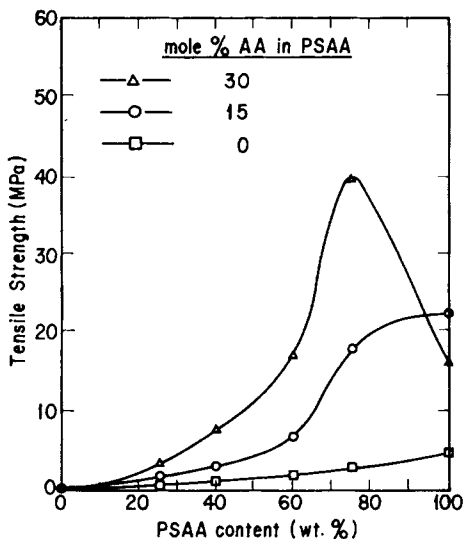


Fig. 4. Variation of the tensile strength with compositions of PUN/PSAA linear blends with varying AA concentration.

PSAA, the swelling ratio was measured and is shown in Figure 5. It is noted that the swelling ratio decreases to a minimum value at the same PUN/PSAA ratio of 25/75 as that maximum tensile strength observed before.

This indicates that more interpenetrating networks would be formed through continuously increasing intermolecular interactions in the IPNs. For linear blends of 30 mol % AA in PSAA, the density increases, as shown in Figure 6, to a maximum value at the same PUN/PSAA ratio of 25/75 as that

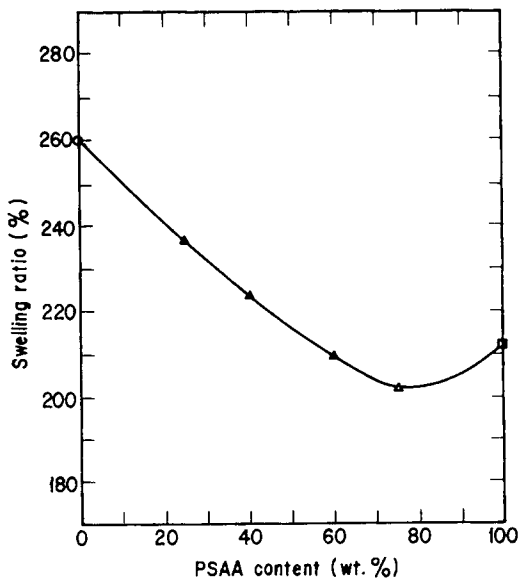


Fig. 5. Variation of the swelling ratio with PSAA content in PUN/PSAA IPNs with 30 mol % AA in PSAA.

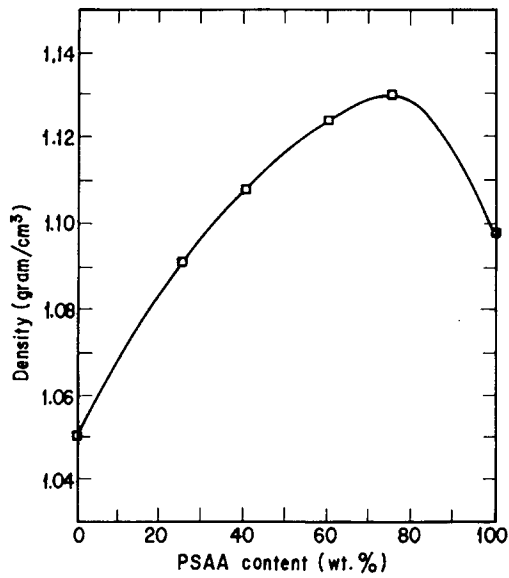


Fig. 6. Variation of the density with PSAA content in PUN/PSAA linear blends with 30 mol % AA in PSAA.

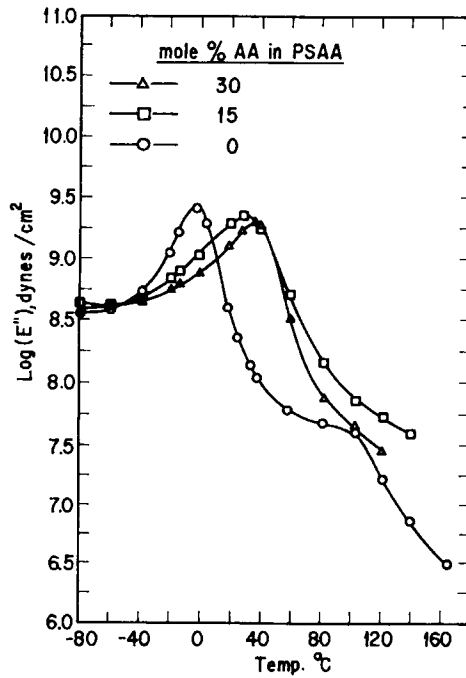


Fig. 7. Variation of the loss modulus ( $E''$ ) with temperature for PUN/PSAA IPNs at 60/40 ratio with varying AA concentration.

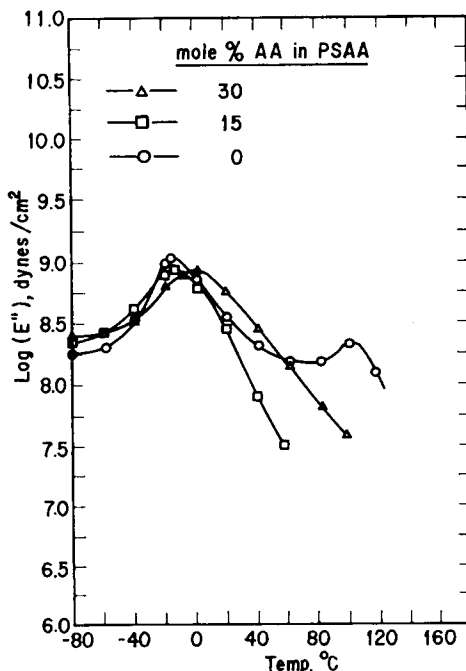


Fig. 8. Variation of the loss modulus ( $E''$ ) with temperature for PUN/PSAA linear blends at 60/40 ratio with varying AA concentration.

maximum tensile strength emerged. Those are similar to the results shown in different IPN systems<sup>12,14</sup> and polyblends.<sup>15</sup> In summary, intermolecular interactions increased due to the fact that the introduction of opposite charge groups into two individual polymers would lead to more interpenetrating networks or entanglements and hence result in an increase of tensile strength for both the IPNs and linear blends.

### Dynamic Mechanical Properties

The effect of charge groups on dynamic mechanical properties of IPNs and linear blends was studied at a PUN/PSAA ratio of 60/40, and the results are shown in Figures 7 and 8, respectively. It is clearly seen that two distinct relaxation transitions emerge for both PUN/PSAA IPNs and linear blends in the absence of AA in PSAA. While in the presence of AA in the alloys, it is clearly observed that a single relaxation transition peak emerges and shifts inwardly to a temperature between the two transition peaks of PUN and PSAA. In addition, the more AA was introduced into PSAA in the alloys, the more shifting of the transition peak to a high temperature is seen in Figures 7 and 8. Furthermore, this tendency of shifting is more effective in the IPN system than in the linear blend system. It concludes that the compatibility between PUN and PSAA in both systems could be greatly enhanced by introducing opposite charge groups into the polymer alloys and had been improved more in the IPN system than in the linear blend system.

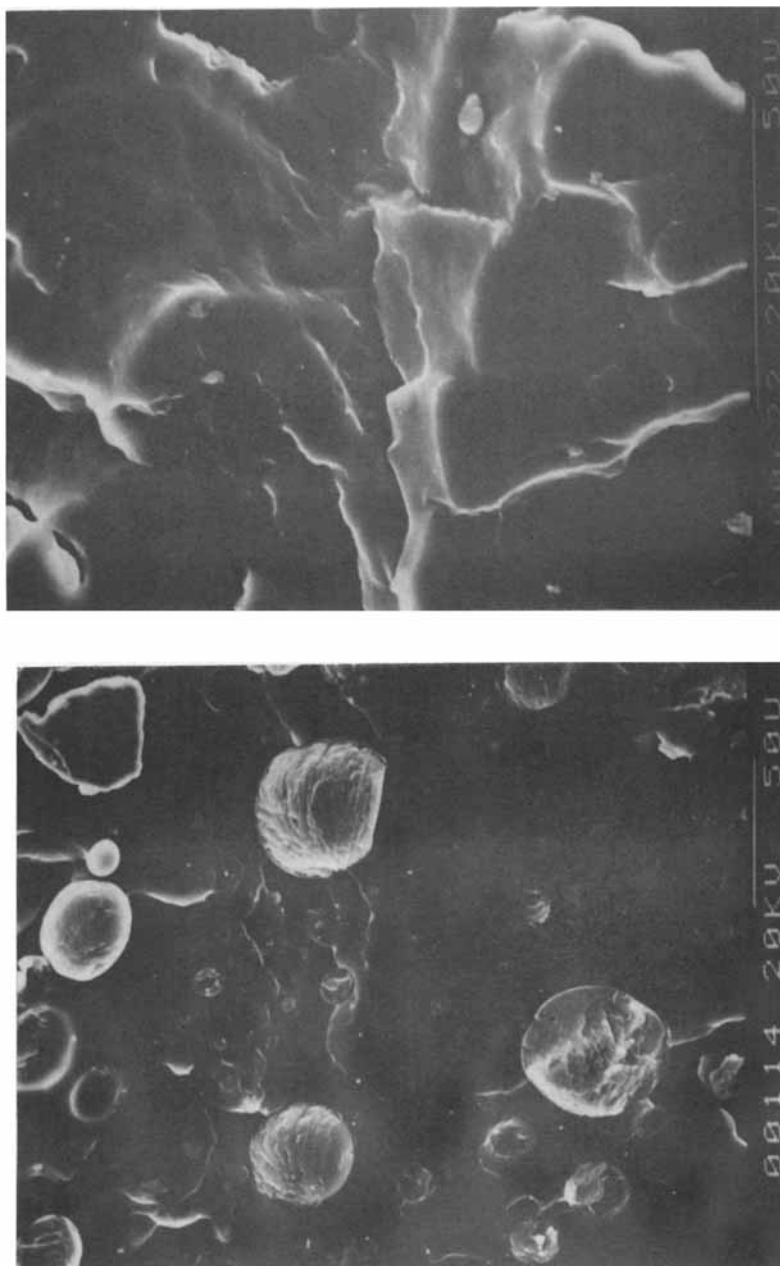


Fig. 9. Microphotographs of SEM for PUN/PSAA IPNs at 60/40 ratio with varying AA concentration: (a) 0 mol % AA and (b) 15 mol % AA in PSAA.



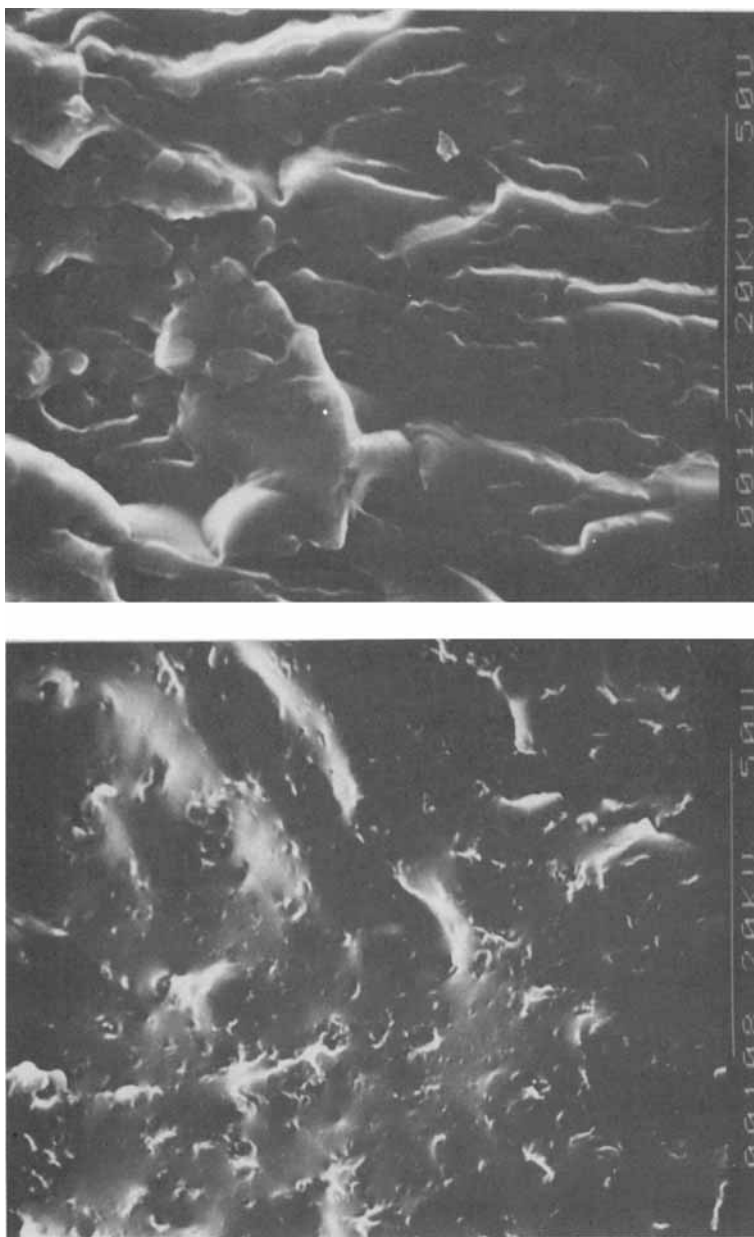


Fig. 10. Microphotographs of SEM for PUN/PSAA linear blends at 60/40 ratio with varying AA concentration: (a) 0 mol % AA and (b) 15 mol % AA in PSAA.

### Scanning Electron Microscopy

Microscopic structures of the IPN and linear blend at a PUN/PSAA ratio of 60/40 are shown in Figures 9 and 10, respectively. Two-phase morphology is clearly seen in both the IPN and linear blend containing no opposite charge groups in the system, whereas a uniform morphology has been seen as the AA (or carboxyl group) was introduced into both alloy systems. This is evidence that the phase separation has been eliminated through increasing intermolecular interaction between polymers.

### CONCLUSIONS

Introduction of opposite charge groups into incompatible polyurethane and polystyrene IPNs or linear blends would result in a compatible polymer system with increasing mechanical strength, crosslinking density or density. A maximum value in tensile strength was observed for the IPNs or linear blends with 30 mol % AA in PSAA and at a PUN/PSAA ratio of 25/75.

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