

Semi- and Fully Interpenetrating Polymer Networks Based on Polyurethane-Polyacrylate Systems. X. Polyurethane-Poly(ethyl Acrylate) Interpenetrating Polymer Networks

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Synopsis

A series of polyurethane-poly(ethyl acrylate) interpenetrating networks (IPNs) containing 40 wt% polyurethane were prepared, in which the cross-link density of the polyurethane component was varied by altering the ratio of diol/triol. Decreasing the molecular weight between crosslinks from 9500 to 1200 g/mol brought about an increase in the tensile strength accompanied by a decrease in elongation at break. The tensile properties of the IPNs are, however, poorer than those of the equivalent polyurethane homopolymers. Electron microscopy showed that the polyurethane was present as distinct phases, connected by a cellular fine structure, in the poly(ethyl acrylate) matrix. Dynamic mechanical analysis as well as sonic velocity studies gave results which were consistent with this morphological picture.

INTRODUCTION

The morphology and attendant properties of interpenetrating polymer networks (IPNs) have received increasing attention in recent years.¹⁻³ IPNs can be formed in a variety of ways^{1,2,4} but must involve the crosslinking of at least one of the components in the presence of the other one. If a solution of both monomers and their cross-linking agents are polymerized by noninterfering methods, the product is known as a simultaneous interpenetrating network (SIN). More commonly, IPNs are made by swelling a cross-linked polymer with a second monomer containing appropriate cross-linking agents, followed by polymerization of the second monomer. If only one of the polymers in an IPN is crosslinked, the material is referred to as a semi-1 or semi-2 IPN depending on whether the first or second formed polymer is crosslinked.

In the ideal case of total mutual solubility, interpenetration will occur on a molecular scale. However, most IPNs show limited miscibility and phase separate to a greater or lesser extent, depending on the compatibility,⁵ extent of crosslinking,⁶⁻⁸ method of synthesis,^{1,6} and composition.^{9,10} The morphology of these two-phase materials plays an important role in determining the properties of the IPN⁶ and as such has been extensively investigated.^{1-4,6} Traditionally, electron microscopy was the major tool used, but more recently it has been recognized that it is best to complement such direct examination with other methods such as dynamic mechanical analysis.¹¹

This paper investigates the effect on the morphology and properties of increasing the cross-link density in the polyurethane (PU) component of a PU-poly(ethyl acrylate) (PEA) IPN. Previous papers in this series have investigated the effect of cross-link density in PU-poly(methyl acrylate) (PMA) semi-1,¹² semi-2,¹³ and full IPNs,^{8,14} the effect of grafting in a PU-PMA semi-1 IPN¹⁵ as well as isomerically related systems,^{16,17} copolymers,¹⁸ and the PU network alone.¹⁹ Sperling and co-workers^{5,20-23} have investigated other IPNs containing PEA as one of the components.

EXPERIMENTAL

Sample Preparation

IPNs containing 40% PU and 60% PEA were prepared with varying cross-link densities in the PU phase. The molecular weight between cross-links (\bar{M}_c) in the PU network was varied between 1200 and 9500 g/mol by using the appropriate amounts of toluene diisocyanate (BDH Chemicals), polypropylene glycol (Aldrich Chemicals) and trimethylol propane (Aldrich Chemicals). The details of composition are given in reference 8. The polypropylene glycol had a \bar{M}_n of 2000 g/mol and a \bar{M}_w/\bar{M}_n of 1.1.⁸ Dibutyl tin dilaurate (BDH Chemicals) was added (2% w/w of PU) to promote the urethane reaction. The NCO:OH ratio was kept constant at 1.1. The ethyl acrylate (BDH Chemicals) contained 5% w/w of divinyl benzene (Cambrian Chemicals) as a network former and was initiated with 0.2% (w/w of monomer) azobisisobutyronitrile (Aldrich Chemicals).

All the ingredients were dissolved in the ethyl acrylate, dibutyl tin dilaurate was added, and the mixture carefully degassed and poured into a metal mould.¹⁹ The PU network was allowed to form at room temperature for 24 h. The mould was then heated to 60°C for 18 h followed by 6 h at 90°C to allow the PEA network to form. The resultant sheets were placed in a vacuum oven at 30°C for at least one week to remove any residual monomer.

Characterization

Dynamic mechanical data were obtained with a Rheovibron dynamic mechanical viscoelastometer (model DDV-II-B) at a heating rate of approximately 1°C/min and a frequency of 11 Hz. The activation energies were also determined.⁸ The longitudinal sonic velocity, V_L , was measured at 20°C with a Morgan pulse propagation meter (PPM-5R).²⁴

Transmission electron micrographs were obtained with a Hitachi electron microscope (model HU-11B) after the samples had been stained with osmium tetroxide vapor.^{9,11,25}

Tensile tests were carried out using standard dumb-bell test pieces on a Howden tensometer at 20°C and a crosshead speed of 2.5 cm/min.

RESULTS AND DISCUSSION

The composition of all the IPNs was kept constant at 40 PU-60 PEA (w/w). The PU networks of the IPNs are identical to those discussed previously.⁸

TABLE I
Properties of the PU Networks^a

Code	\bar{M}_c (g/mol)	T_g (°C)	Tensile strength (MPa)	Elongation at break (%)	100% Modulus (MPa)	V_L (km/s)
PU 1	9500	-3	0.8	280	0.3	0.15
PU 2	3300	15	2.6	265	0.6	0.30
PU 3	2000	30	6.8	245	1.8	0.47
PU 4	1200	108	18.5	150	14.0	1.00

^aFrom Ref. 8.

Increasing the cross-link density in the PU network by increasing the triol/diol ratio increases the glass transition temperature, modulus, tensile strength, and sonic velocity while decreasing the elongation at break (see Table I.) These property changes are readily explained in terms of the increased cross-link density and hard segment content of the polyurethanes.⁸

Figure 1 is a transmission electron micrograph of a PU/PEA IPN in which the \bar{M}_c of the PU is 1200 g/mol. It shows dark regions in a continuous matrix. The dark areas are PU-rich regions since OsO₄ is known⁹ to stain preferentially the PU component. Close inspection of the micrograph reveals a fine structure in the matrix which is typical of IPNs,⁵ indicating that even the apparently dispersed PU phase is continuous. Since PU is the first formed network, this result is consistent with expectation. The PU-PMA IPNs discussed in Ref. 8 also had the acrylate as the major component. Increasing

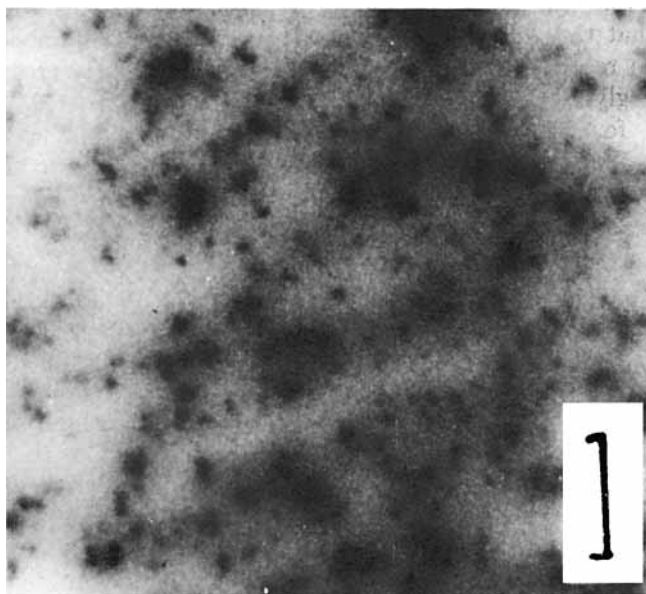


Fig. 1. Transmission electron micrograph of IPN 4. Scale mark represents 500 nm.

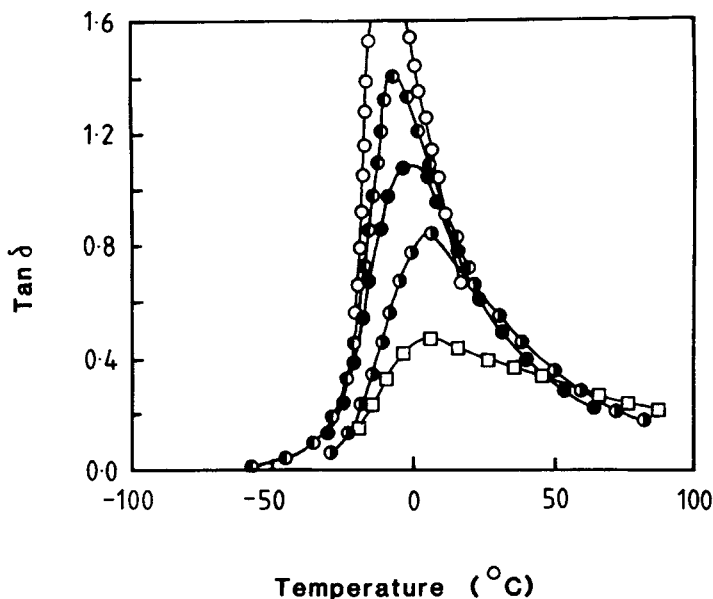


Fig. 2. $\tan \delta$ -temperature plots for IPN 1 (\circ), IPN 2 (\bullet), IPN 3 (\circ), IPN 4 (\square), and PEA (\circ).

levels of crosslinking in the PU component lead to a finer morphology for that system.

Dynamic mechanical data for the IPNs are shown in Figures 2–4. They should be viewed in conjunction with Table I listing the glass transition temperatures (T_g) of the PU components. The T_g data in Table I were obtained at a frequency (35 Hz) which is slightly higher than that used to test the IPNs. From the known activation energy of the transition, it can be calculated that this difference in frequency raises the T_g by about 3°C. The PEA used to record the $\tan \delta$ plot in Figure 2 was lightly crosslinked with tetraethyleneglycol dimethacrylate (0.5% w/w). Hence, it would be expected that the T_g for PEA crosslinked with 5% DVB would be several degrees higher. The T_g of linear PMA for instance is increased by 10°C when it is crosslinked with 5% divinyl benzene.¹³ The $\tan \delta$ -temperature plot (Fig. 2) shows a single transition which shifts by only 14°C as the PU network becomes progressively tighter. For the same variation of \bar{M}_c , the T_g of the PU homonetwork increases by 111°C.

The IPNs are coded IPN 1 to IPN 4 where the numbers indicate the PU composition. For example, IPN 1 is an IPN in which the nominal value of \bar{M}_c for the PU network is 9500 g/mol. IPN 1 displays only one glass transition which has a $\tan \delta_{\max}$ of 1.4 at -6°C. This almost certainly arises from simultaneous relaxations of the PEA and PU components, as their respective relaxations are close to this temperature. A further indication of this is the broadening and skewing on the high temperature side of the transition. The half-peak width is 37°C. The $\tan \delta_{\max}$ of IPN 2 is shifted to a higher temperature, 0°C, accompanied by a reduction in its magnitude to 1.08. The transition is flatter than IPN 1, reflecting the contribution of the PU component whose transition as a homopolymer is at a slightly higher temperature (12°C). In IPN 3 the trend is continued, $\tan \delta_{\max}$ being 0.85 at 5°C. The half

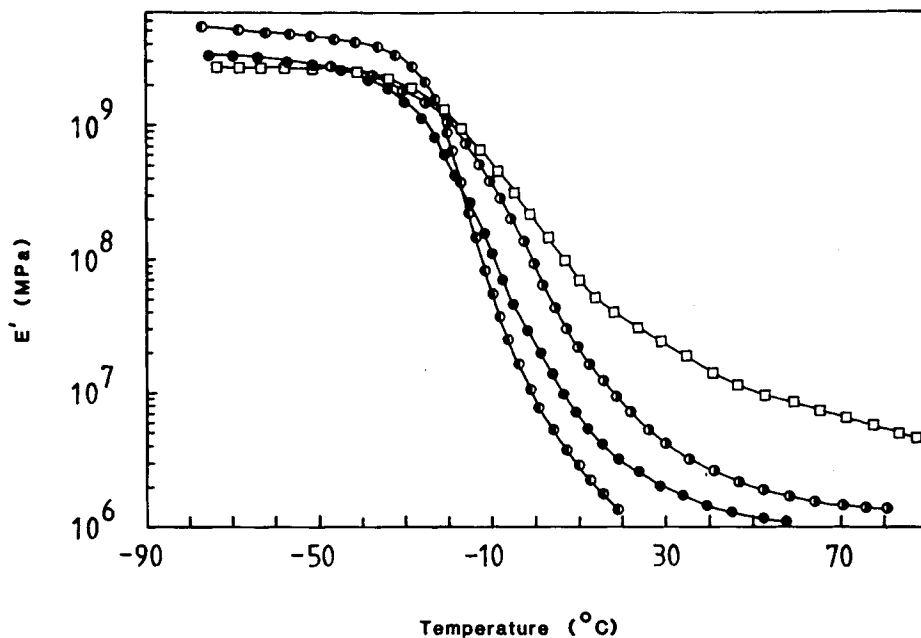


Fig. 3. E' -temperature plots for IPN 1 (○), IPN 2 (●), IPN 3 (○), and IPN 4 (□).

peak width is now 54 $^{\circ}\text{C}$. IPN 4 has a $\tan \delta_{\max}$ of 0.46 at about 8 $^{\circ}\text{C}$. The damping transition of the more rubbery component in a polymer blend can be severely suppressed by the presence of the glass-like second component.^{8,12} The fact that the PEA-damping transition remains the main transition even when the PU component has a T_g about 100 $^{\circ}\text{C}$ higher indicates that it is not only the major component but also the more continuous phase. The PU phase,

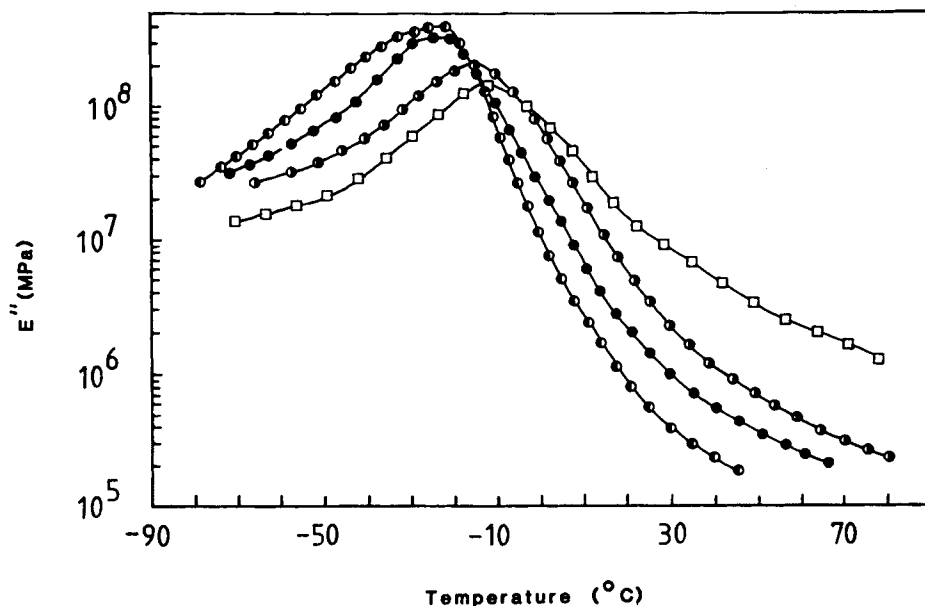


Fig. 4. E'' -temperature plots for IPN 1 (○), IPN 2 (●), IPN 3 (○), and IPN 4 (□).

TABLE II
Dynamic Mechanical and Sonic Velocity Data of PU-PEA IPNs

Code	T_g (°C)	Tan δ_{max}	Half-peak width (°C)	Energy of activation (kJ/mol)	V_L (km/s)
IPN 1	-6	1.41	37	97	0.23
IPN 2	0	1.08	45	130	0.35
IPN 3	5	0.85	54	141	0.43
IPN 4	8	0.46	94	146	0.65

although continuous on the molecular level, to all intents and purposes acts as though it were a dispersed phase. As the PU network is tightened, the discrete PU-rich zones gradually disappear,⁸ resulting in a more effective continuous phase. This in turn leads to more enforced mixing and a decrease in the $\tan \delta_{max}$. The increases in half-peak width and activation energy are consistent with this interpretation.

This is also consistent with the electron microscopy results and is readily explained by the model of interpenetration proposed by Huelck et al.⁵ They postulate a morphology consisting of small cells connected by a fine network. Segments from the cell contents penetrate the cell walls to form a continuous

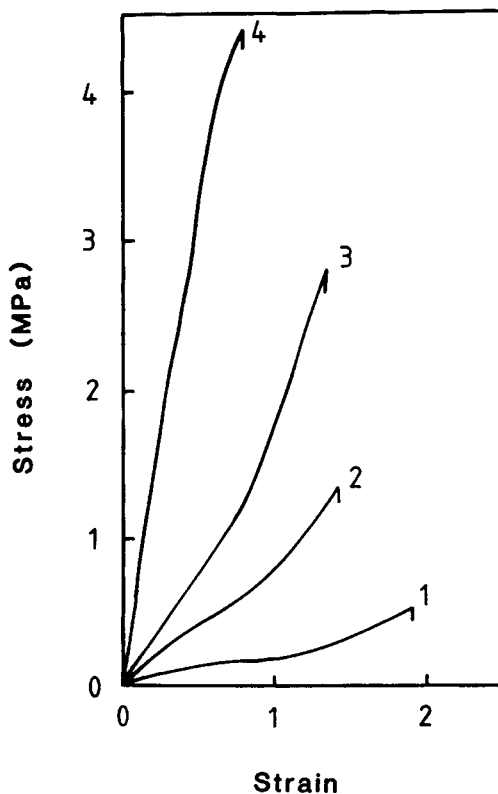


Fig. 5. Stress-strain curves (20°C) for IPN 1 (1), IPN 2 (2), IPN 3 (3), and IPN 4 (4).

TABLE III
Stress-Strain Properties of PU-PEA IPNs

Sample	Tensile strength (MPa)	100% Modulus (MPa)	Elongation at break (%)
IPN 1	0.5	0.16	184
IPN 2	1.35	0.74	144
IPN 3	2.81	1.70	134
IPN 4	4.41	—	78

network. In the present work the cells of PEA are virtually indistinguishable from the fine structure of the walls. PU is present in the fine structure of the matrix as well as in discrete PU-rich zones.

The storage modulus-temperature profiles of the four IPNs are shown in Figure 3. As the cross-linking level of the PU is increased, the moduli fall more slowly with increasing temperature. This suggests that the PEA segment motion is increasingly more restricted in the highly cross-linked networks. In all the samples only one relaxation is apparent.

The loss moduli versus temperature plots of the four IPNs are shown in Figure 4. All the IPNs possess relatively broad loss modulus profiles. IPN 4 shows a particularly broad distribution of relaxation times. Again, this is entirely consistent with a substantial level of enforced mixing.

The dynamic mechanical data are summarized in Table II.

The stress-strain profiles of the four materials are shown in Figure 5, and the results summarized in Table III. In all samples the elongation to break and tensile strength are significantly reduced as compared to the equivalent PU homonetworks (Table I). This is not unexpected, since PEA is a highly rubbery material of relatively low modulus and is present as the major component. As the level of crosslinking in the PU increases, there is an increase in the tensile strength and a decrease in the elongation to break.

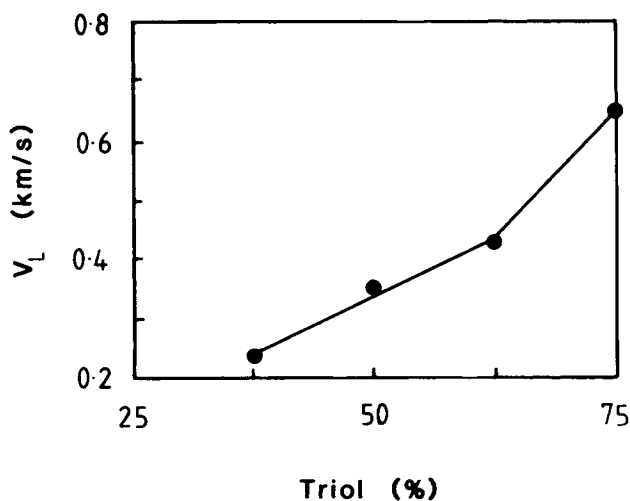


Fig. 6. Longitudinal sonic velocity (20°C) of the IPNs as a function of triol content.

Figure 6 shows the longitudinal sonic velocities of the IPNs as a function of triol content in the PU component. The four IPNs have V_L values in the range 0.23–0.65 km/s (Table II), whereas in the corresponding PU homonetworks the sonic velocities vary from 0.15 to 1.0 km/s (Table I). As the IPNs consist of 60 wt% of relatively rubbery PEA, a decrease in V_L for the IPNs containing the high T_g PU components is as expected.

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