

Polyurethane-Polyacrylate Interpenetrating Polymer Networks. II

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Synopsis

Two component topologically interpenetrating polymer networks of the SIN type (simultaneous interpenetrating networks) composed of a melamine-cured polyacrylate and three different polyether-based polyurethanes were prepared. The linear polymers and prepolymers were combined in solution, together with the necessary crosslinking agents and catalysts, films were cast and subsequently chain extended and crosslinked *in situ*. In all cases, maxima in tensile strength significantly higher than the tensile strengths of the component networks occurred at 50% polyurethane:50% polyacrylate. This was explained by an increase in crosslink density resulting from interpenetration. One of the interpenetrating polymer networks showed only one glass transition temperature (T_g) (measured calorimetrically) intermediate in temperature to the T_g 's of the components and as sharp as the component T_g 's. This is indicative of phase mixing and indicates at least partial chain entanglement (interpenetration). Some enhancement of other physical properties was also noted.

INTRODUCTION

Ever since the concept of chemical topology was introduced¹ a number of investigators have prepared molecules involving topological isomerism²⁻¹⁸ most of which were catenanes, i.e., interlocking rings with no chemical bonds between them. Construction of space-filling models of such catenanes has demonstrated that the minimum ring size (if a carbon sp^3 ring) is 20 atoms. In recent years, the attention has turned to interpenetrating polymer networks (IPN's).⁷⁻¹⁸ These materials are produced, in general, by mixing two initially linear polymers in the liquid state (dispersion, solution, or bulk liquid prepolymers), fabricating them into the desired form (i.e., casting films, molding sheets, etc.), and then crosslinking them *in situ*. Permanent entanglements will then occur, depending on the relative cohesive energy densities of the two materials. If these energies differ too greatly, total phase separation will result. In selecting the polymers, it must be borne in mind that little or no reaction between the differing polymers must occur during cure; otherwise true chemical topology will not result (analogous to covalent bonds between the rings described above). Previous studies in this laboratory^{7-10, 14-18} have indicated that it is desirable to select the polymers

such that one is a rubbery material and the other is glassy. In this manner, additional reinforcement of the composite structures is achieved.

In two of these studies,^{15,17} a number of IPN's were made by combining solutions of linear prepolymers (together with crosslinking agents and catalysts) of various polyurethanes and a polyacrylate. Enhancement of a number of physical properties, including tensile strength, thermal resistance, and impact strength was noted. A morphological study of one of these IPN's¹⁷ showed that extensive interpenetration occurred. This was evidenced by a single glass transition temperature (T_g) intermediate in temperature to the T_g 's of the component networks and by electron micrographs showing no phase separation.

In the present study, a number of IPN's of this melamine-cured polyacrylate and several other polyurethanes have been produced by mixing solutions of the linear polymers, together with crosslinking agents and catalysts, then casting films and curing them *in situ*. These materials have similar cohesive energy densities so that total phase separation might not be expected. The degrees of crosslinking were chosen so that statistical threading could easily be accomplished. Since the melamine cure involves reaction with pendent hydroxyl groups on the acrylic chain, and can react with isocyanate on the polyurethane, the prepolymer was blocked with 2-butanone oxime, thereby rendering the isocyanate nonreactive at the temperature necessary to cure the polyacrylate. Higher temperature curing results in deblocking and crosslinking of the polyurethane. However, the acrylic cure is very rapid at this temperature and occurs before the urethane is deblocked, thus reducing the chances of co-reaction between the two polymers.

The stress-strain properties, hardness, impact strength, and thermal resistance of these IPN's as well as of the constituent networks were measured to determine any enhancement in properties resulting from interpenetration. The glass transition of one of the IPN's was also measured in order to determine the extent of interpenetration.

EXPERIMENTAL

Materials

The materials used and their descriptions are listed in Table I. All polyols were dried at 80°C for 10 hr under a vacuum of 0.1 mm Hg. The solvents used were reagent grade and dried over molecular sieves. 2-Butanone oxime was dried by refluxing under a vacuum of 1.5 mm Hg for 6 hr. All other materials were used without further purification.

Preparation

Polyacrylate (PA)

The polymer used is commercially available as a 50% solution in xylene and cellosolve acetate. It is a random copolymer of butyl acrylate, styrene, and hydroxyethyl methacrylate and crosslinks by reaction of the pendent hydroxyl groups on the chain with a butylated melamine-formaldehyde resin, also commercially available as a 60% solution in xylene and cellosolve acetate. It also contained a small amount (<1%) of methacrylic acid which was present as a catalyst for the melamine cure. To 14 g of the acrylic solution were added 5 g

TABLE I
Materials

Designation	Description	Source
Polymeg 660	poly(1,4-oxybutylene)glycol [poly(tetramethylene glycol)]; mw = 661; hydroxyl no. = 169.8	Quaker Oats Co.
TMP	trimethylolpropane	Celanese Chem. Corp.
H ₁₂ MDI	4,4'-methylene bis(cyclohexyl isocyanate)	Allied Chem. Co.
PeP 450	polyoxypropylene adduct of pentaerythritol; hydroxyl no. = 55.8; equiv. wt. = 100.5	BASF Wyandotte
Mondur S	a phenol-blocked triisocyanate made from tolylene diisocyanate and trimethylolpropane	Mobay Chem. Co.
T-12	dibutyltin dilaurate	M & T Chemicals Inc.
T-9	stannous octoate	M & T Chemicals Inc.
Acrylic 342-CD725	random copolymer of butyl acrylate, styrene, methacrylic acid, and hydroxyethyl methacrylate; 50% solution in xylene:cellosolve acetate—1:1; hydroxyl no. = 60.0; acid no. = 13.5	Inmont Corp.
Melamine RU 522	butylated melamine-formaldehyde resin; 60% solution in xylene:cellosolve acetate—1:1;	Inmont Corp.
Silicone L-522	poly(dimethylsiloxane)-poly(oxyalkylene) copolymer	Union Carbide Corp.
CAB	cellulose acetate butyrate EAB-381-2; ASTM viscosity 15	Eastman Chem. Corp.
2-But. ox.	2-butanone oxime	Matheson, Coleman & Bell

of the melamine solution. After thoroughly mixing, films were cast on glass and aluminum panels with a doctor blade and cured at 150°C for 4 hr.

Polyurethane (PU)

A number of different polyurethanes were synthesized in order to better determine structure-property relationships in the IPN's. The prepolymer route was selected in which an isocyanate-terminated urethane prepolymer is first prepared by reacting two equivalents of a diisocyanate with one equivalent of a diol or triol. The hydroxy-containing compound may or may not be polymeric. This prepolymer is then simultaneously chain extended and crosslinked by reacting with another polyfunctional alcohol (again it may or may not be polymeric).

Prepolymer. Two different isocyanate-terminated urethane prepolymers (both polyether based), were prepared: Poly(tetramethylene glycol), mol wt = 661 (PM 660) + 4,4'-methylene bis-(cyclohexyl isocyanate)(H₁₂MDI) and trimethylolpropane (TMP) + H₁₂MDI. A resin kettle equipped with nitrogen inlet, stirrer, thermometer, and reflux condenser was charged with a 50% solution of two equivalents of isocyanate in a 1:1 mixture of cellosolve acetate and xylene. To this was added slowly, with stirring, a 50% solution of polyol in the above solvent mixture. The reactions were carried out under nitrogen at 80°C until the theoretical isocyanate contents (as determined by the di-*n*-butyl amine method)¹⁹ were reached.

Blocking. A 50% solution (in the above solvent mixture) of a slight equivalent excess of 2-butanone oxime and 0.2% by weight dibutyltin dilaurate (T-12) were added to the prepolymer solutions in a 3-necked flask equipped with a stirrer, reflux condenser, thermometer, and nitrogen inlet. The reaction was carried out under nitrogen at 80°C until the isocyanate content reached zero (complete blocking).

Chain extension and curing. An equivalent weight of a polyoxypropylene adduct of pentaerythritol (mol wt = 402) (PeP 450) (in a 50% solution as above), 0.1% by weight stannous octoate (T-9) and 1% by weight flow agent composed of a 1:1 mixture of cellulose acetate butyrate, and a poly(dimethylsiloxane)-polyoxyalkylene copolymer (L-522) were added to the prepolymer of PM 660 and H₁₂MDI. Films were cast and cured at 150°C for 4 hr. At this temperature, deblocking occurs followed by chain extension and crosslinking. To the prepolymer of TMP and H₁₂MDI were added an equivalent weight of PM 660 (in a 50% solution as above) and catalyst and flow agent as above. Films were cast and cured at 150°C for 4 hr. An additional polyurethane was prepared by mixing a phenol-blocked triisocyanate of tolylene diisocyanate and TMP (Mondur S) with an equivalent weight of PM 660 in a 50% solution, adding flow agent and catalysts, and casting films and curing them at 150°C for 4 hr. Thus three crosslinked polyurethanes were produced.

IPN's

The polyurethane solutions (containing crosslinking agents and catalysts) were thoroughly mixed with the polyacrylate-melamine solution. Combinations containing 25%, 50%, and 75% PU were made. Films were cast and cured as above. All films were absolutely clear. Thus, three IPN's were produced:

IPN 1: PA-PU (Polymeg 660-H₁₂-MDI-PeP 450)

IPN 2: PA-PU (TMP-H₁₂ MDI-Polymeg 660)

IPN 3: PA-PU (Polymeg 660-Mondur S)

Measurements

Stress Strain

The tensile strengths and elongations at break were measured on an Instron Tensile Tester at room temperature and a crosshead speed of 2 in./min (ASTM testing method D-2370-68). Specimens were 0.125-in.-wide dumbbells. The results reported were the average of 10 specimens.

Impact Strength

The resistance of coatings to high velocity impact was measured by the Gardner method using aluminum-coated panels. (ASTM testing method D-2794-69).

Hardness

The hardness of the coatings was measured by the Sward hardness rocker method. (ASTM test method D-2134-26).

Thermal Resistance

Thermogravimetric measurements were made on a DuPont 950 Thermogravimetric Analyzer (TGA) at a heating rate of 20°C/min under nitrogen at a flow rate of 1.5 ft³/hr.

Calorimetric Measurements

In addition to a physical properties determination, the T_g of IPN 3 was determined on a Perkin-Elmer Differential Scanning Calorimeter, DSC-1B. Measurements were carried out from -100°C to +150°C under nitrogen at a scanning rate of 10°C/min. Specimen sizes were on the order of 25 mg. Measurements were repeated several times, and the average was reported to ensure accuracy.

RESULTS AND DISCUSSION

Stress-Strain Properties

In all cases, maxima in tensile strength (Fig. 1) occur at 50% polyurethane, in agreement with the results of the previous studies on IPN's of polyurethanes and polyacrylates.^{8,15-17} This behavior is typical of all IPN's made in this laboratory and is not restricted to polyurethane-polyacrylate IPN's. The

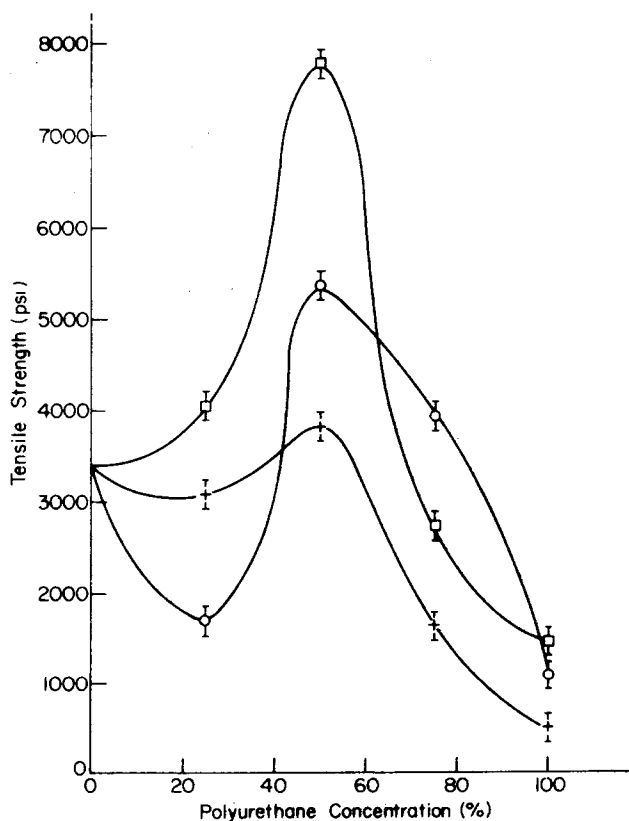


Fig. 1. Tensile strength vs. polyurethane concentration: (+) IPN 1; (O) IPN 2; (□) IPN 3.

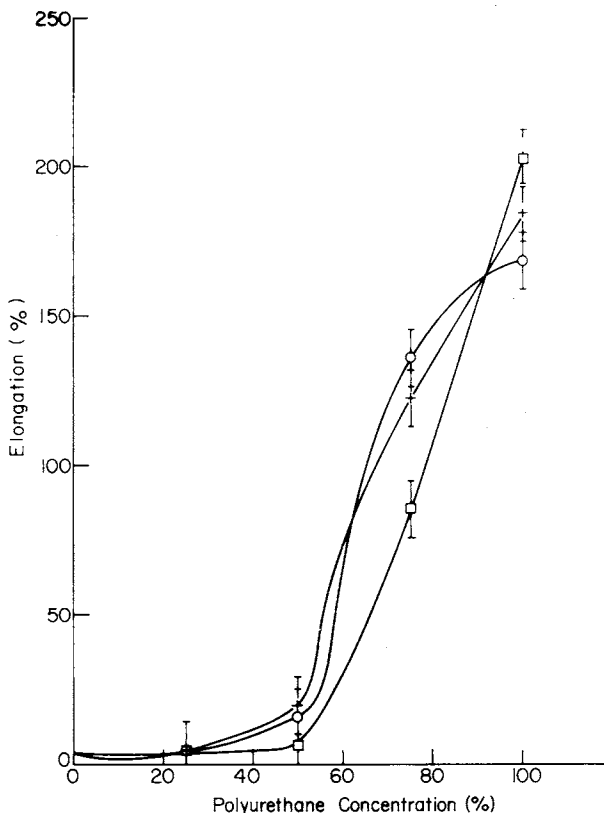


Fig. 2. Elongation vs. polyurethane concentration: (+) IPN 1; (O) IPN 2; (□) IPN 3.

maximum is a result of an increase in crosslink density resulting from interpenetration. Previous studies on other IPN's showed that there is a maximum in crosslink density corresponding to the maximum in tensile strength. This maximum in tensile strength (which is significantly higher than the tensile strengths of the components in all cases except IPN 1) is not only evidence of interpenetration, but is also an indication of the enhancement in properties possible through IPN formation. The minimum occurring at 25% polyurethane in IPN's 1 and 2 may be attributed to initial weakening of hydrogen bonding at small values of interpenetration (more of one component than the other) and is also typical of IPN behavior. After about 25% of one component, the crosslink density becomes larger than the weighted mean crosslink density of the component networks, raising the tensile strength to a maximum.

There is another possibility for this observed enhancement in tensile strength. This is intermolecular crosslinking occurring between the polyurethane and polyacrylate networks to result in a "better" cured system. One possible reaction is between the isocyanate-terminated prepolymer and the acid groups in the polyacrylate. However, since the concentration of acid is extremely low and the rate of this reaction is much less than that of the isocyanate-hydroxyl reaction, this would not be expected to take place. Another possibility is reaction of the isocyanate and the small amount of secondary amine present on the melamine-formaldehyde resin. Again, this is expected to be minimal since

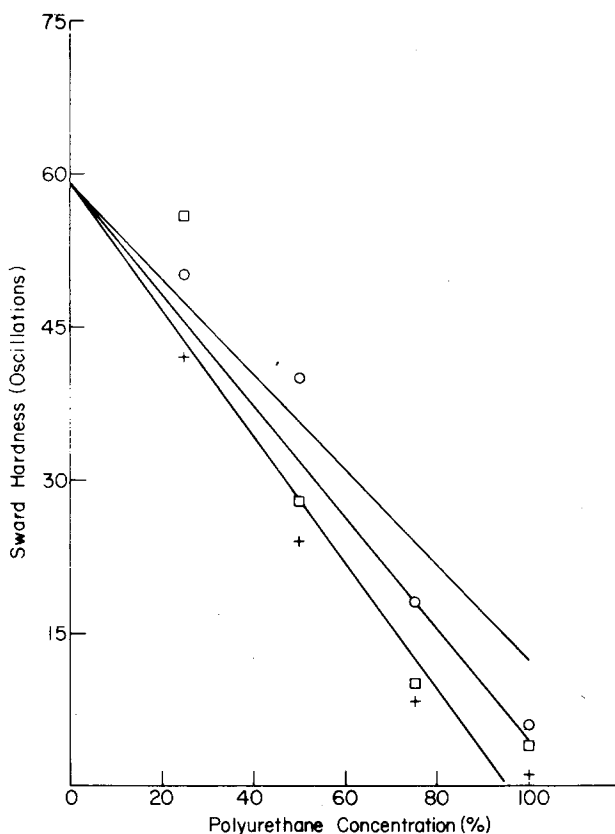


Fig. 3. Sward hardness vs. polyurethane concentration: (+) IPN 1; (O) IPN 2; (□) IPN 3.

this amine participates in the melamine cure of the polyacrylate. The free methylol and secondary amine groups in the butylated melamine-formaldehyde resin react very rapidly under the influence of acid catalysis to form methylene and methylene ether bridges with simultaneous splitting off of butyl alcohol by reaction with the hydroxyl groups on the polyacrylate. Thus, the active hydrogens from the secondary amine are used up before the isocyanate deblocks. Therefore, this reaction, just as in the isocyanate-acrylic hydroxyl reaction, is expected to be minimized as a result of the blocking. That is, the melamine cure occurs before the isocyanate deblocks (this reaction proceeds quite readily at 100°C, while the deblocking occurs slowly even at 150°C). Thus, no amine hydrogen or hydroxyl groups remain to react with the isocyanate. However, more extensive interreaction could be expected between the butylated melamine resin and the hydroxyl-terminated chain extender for the polyurethane. This would result in the formation of a combination of chemically linked polymer networks and interpenetrating polymer networks. However, infrared studies, carried out on similar IPN's produced earlier,¹⁵ suggest that the degree of chemical inter-reaction is less pronounced than the formation of IPN's.

The elongations (Fig. 2) also behave in a manner typical of IPN's made from solution.^{8,14-18} They decrease rapidly with acrylic concentration until about 50% polyurethane, at which point they reach the value of the pure acrylic.

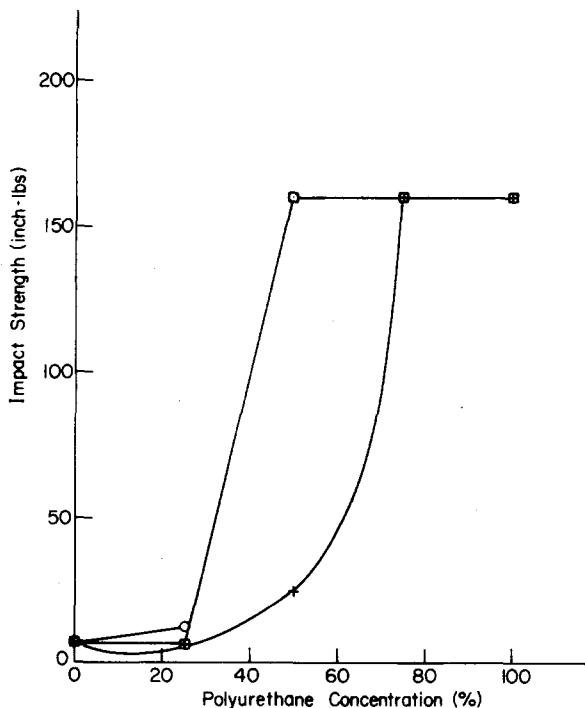


Fig. 4. Impact strength vs. polyurethane concentration: (+) IPN 1; (O) IPN 2; (□) IPN 3.

Hardness

Figure 3 shows the Sward hardness versus concentration. The hardness drops approximately linearly with polyurethane concentration, as would be expected.

Impact Strengths

Figure 4 shows the impact strength as a function of polyurethane concentration. The three IPN's have similar behavior. They show high impact strengths until the composition is mostly acrylic. IPN 1, however, loses impact strength at a higher polyurethane content than do IPN's 2 and 3. This IPN also shows the smallest maximum in tensile strength (see Fig. 1). This IPN might be expected to exhibit the least enhancement in physical properties since it has a very high crosslink density (based on tetrafunctional pentaerythritol). IPN's 2 and 3, however, have lower degrees of crosslinking and are, in fact, very similar, the only difference being that IPN 2 is aliphatic and IPN 1 is aromatic. This behavior is similar to that seen in the previous study of IPN's made from the acrylic 342-CD725.¹⁵ The IPN made from the highly crosslinked polyurethane (TMP-H₁₂MDI-TMP) showed no enhancement in properties. High degrees of crosslinking lower the probability of statistical threading and would be expected to result in low degrees of interpenetration.

Thermal Resistance

No enhancement in thermal resistance (see Figs. 5-7) results from interpenetration for these IPN's. The thermograms of the IPN's fall between those of the polyurethane and the polyacrylate.

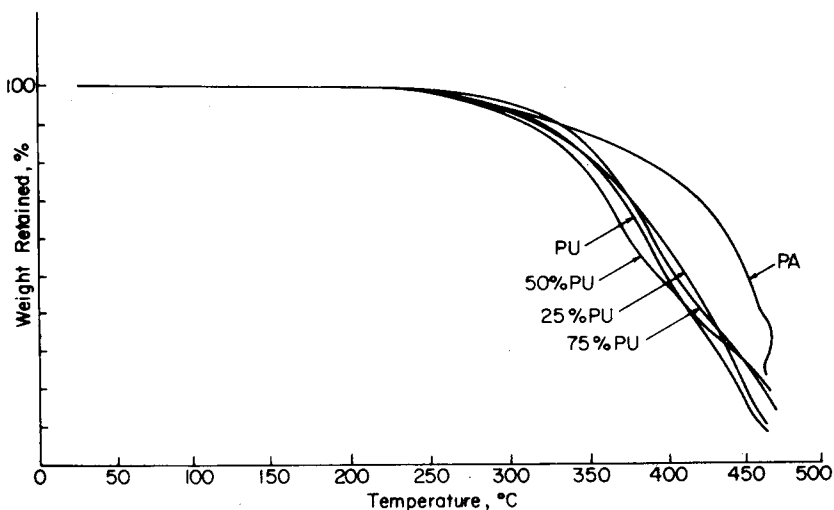


Fig. 5. Thermogram: % weight retained vs. temperature: IPN 1.

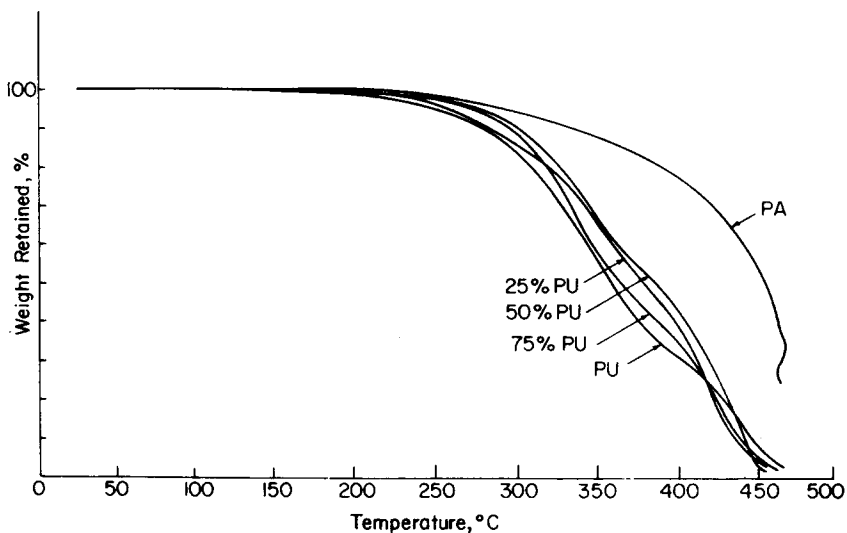


Fig. 6. Thermogram: % weight retained vs. temperature: IPN 2.

Glass Transitions

The DSC scans are shown in Figure 8. Table II shows the T_g 's of IPN 3 and the component networks. Also shown are the values of the calculated T_g 's according to the Fox copolymer equation²⁰ and the arithmetic mean of the T_g 's of the components. In all cases the IPN's show one T_g intermediate in temperature to the T_g 's of the constituent networks. This indicates that total phase separation is not occurring. If two distinct phases were present, the IPN would exhibit two T_g 's, one from each component. This fact is supported by the clarity of the IPN films. Were this a multiphase system, the domains would scatter light, which would result in cloudy films. That the films are clear is not proof that complete interpenetration is occurring, since the dispersed phase may be composed of particles much smaller than the wavelengths of visible light

(microphase separation). However, even this situation must result in extensive interpenetration (at the phase boundaries). The fact that in all cases, the T_g 's were greater than those calculated according to the copolymer equation suggests that these IPN's were not merely random copolymers, i.e., there was no reaction

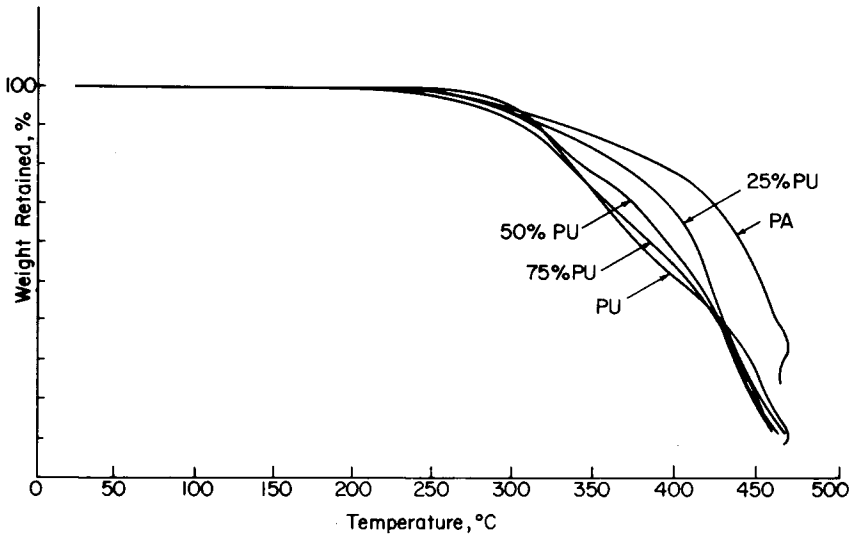


Fig. 7. Thermogram: % weight retained vs. temperature: IPN 3.

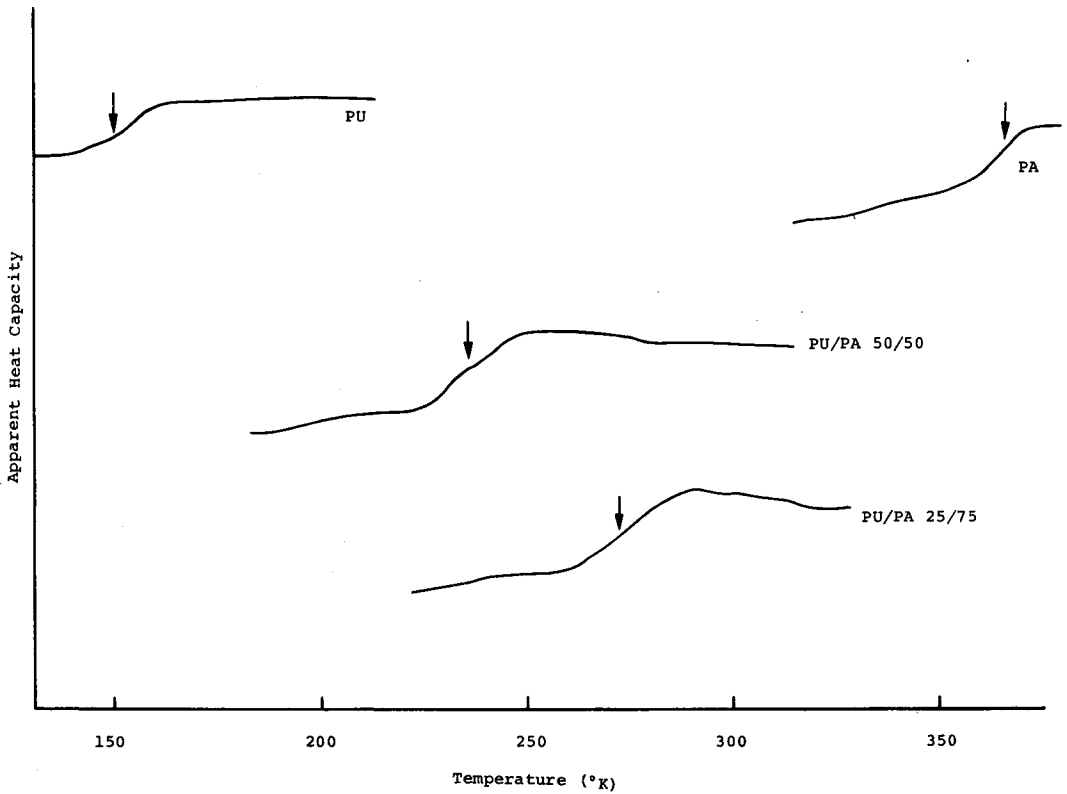


Fig. 8. DSC scan for IPN 3.

TABLE II
 Glass Transition Temperatures of IPN 3

Composition	T_g , °K (Found)	T_g , °K ^a (Calcd)	T_g , °K ^b (Av)	Θ ^c
100% PU	150	—	—	—
75% PU + 25% PA	—	—	—	—
50% PU + 50% PA	236	213	258	0.0933
25% PU + 75% PA	272	270	313	0.159
100% PA	367	—	—	—

^a Calcd: $1/T_g = W_1/T_{g1} + W_2/T_{g2}$.

^b Av: $T_g = W_1T_{g1} + W_2T_{g2}$.

^c $T_g - T_g(\text{Av})/T_g(\text{Av}) = -\Theta/1 + \Theta$.

between the two networks. Infrared spectra of similar IPN's made in a previous study¹⁵ support this conclusion. The measured T_g 's were lower than the average T_g 's of the components, in agreement with previous studies.^{17,18} The amount of lowering is given by Θ (its significance is discussed elsewhere—in ref. 18).

CONCLUSIONS

Partial interpenetration (possibly to a high extent) is occurring in these IPN's as evidenced by the improvement of some of the physical properties (tensile strength in particular), the clarity of the films, and the single T_g . It is also quite evident that IPN's could be quite desirable engineering materials. They show maxima in tensile strength at concentrations at which the impact strength is still as high as that of the pure polyurethane. The hardness at these concentrations is still great enough for the materials to be useful as protective coatings and in other similar applications.

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