

TOPOLOGICALLY INTERPENETRATING POLYMER NETWORKS

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ABSTRACT

Topologically interpenetrating polymer networks (IPNs) were prepared in bulk or in solution by the simultaneous crosslinking of two different pre-polymers in the presence of suitable crosslinking agents and catalysts. The polymers selected were such that one consisted of a glassy and the other of an elastomeric network, and conditions were chosen to minimize or altogether avoid any chemical interreaction between the two networks, thus forming truly topological IPNs whenever possible.

The elastomeric networks in these IPNs consisted of various polyurethanes and the glassy networks of polystyrene, polyacrylates, polyepoxides and unsaturated polyesters.

Mechanical and thermal properties of the IPNs were investigated and the morphology of these systems studied by means of electron microscopy and glass transition measurements. A significant enhancement of a number of mechanical and thermal properties of the IPNs resulted when compared with those of the constituent networks.

In all cases studied so far, maxima in tensile strength occurred at some intermediate concentration of the two constituent networks. This has been assumed to be the consequence of interpenetration, which manifests itself by an apparent higher crosslink density. In some instances a similar enhancement in thermal resistance was observed in IPNs as measured by thermal gravimetric analysis.

I. INTRODUCTION

Since the introduction of the concept of chemical topology in 1961¹, a number of systems exhibiting topological isomerism have been prepared²⁻¹⁶, most of them catenanes, i.e. interlocking rings with no chemical bonds between them. These materials are topological isomers of their non-threaded counterparts.

In recent years attention has turned to polymeric catenanes or interpenetrating polymer networks (IPNs)⁷⁻¹⁶. A number of methods may be employed for the preparation of these materials. One consists of the sequential polymerization in which one crosslinked network is formed first, and is then swollen in another liquid monomer in the presence of a crosslinking agent and a polymerization initiator to form another crosslinked network. Polymerization and crosslinking of the imbibed system takes

place *in situ* to yield a sequential interpenetrating polymer network (SIPN)¹¹⁻¹³. Another type of IPNs is referred to as latex interpenetrating polymer networks (LIPN), and involves the mixing and coagulation of two different polymer lattices followed by fusion of the particles and simultaneous crosslinking⁷⁻¹⁰. Still another type of IPNs is known as simultaneous interpenetrating networks (SIN), produced by mixing two monomers or prepolymers with crosslinking agents followed by simultaneous polymerization of the two networks via different crosslink mechanisms¹⁴⁻¹⁶. Permanent entanglements will form, depending upon the mode of synthesis and the relative cohesive energy densities. If the latter differ very much, total phase separation will occur. In order to obtain truly chemical topology in these polymer systems, it is necessary to select the two polymers in such a way that little or no reaction occurs between them, i.e. that the formation of any covalent bonds between the two networks is minimized or avoided altogether. Previous studies in our laboratory⁷⁻¹⁰ have indicated that it is desirable to select a combination of polymers consisting of a glassy and a rubbery polymer. In this manner additional reinforcement of the composite structures can be achieved and a morphological analysis by means of glass transition measurements carried out. The purpose of this paper is to present the synthesis, properties and morphologies of some of the IPNs which were recently produced in our laboratories. In every instance a polyurethane was used as the rubbery system while the glassy system employed was selected from polyepoxides, polyacrylates, polymethacrylates, unsaturated polyesters and styrene. The IPNs were prepared by mixing the linear prepolymers in the presence of crosslinking agents and catalysts, either in bulk or in solution. The resulting mixtures were then cast in the form of sheets or films, crosslinking them thermally *in situ*, thus forming SIN polymers.

II. EXPERIMENTAL

A. Materials

Table 1 lists the raw materials used in these studies. All polyols (hydroxyl-terminated polyethers or polyesters) were dried at 80°C for five hours under a vacuum of 0.1 mmHg. Styrene and divinylbenzene (DVB) monomers were washed with five per cent aqueous potassium hydroxide solution, followed by distilled water, dried over Linde 4A molecular sieves and distilled at 40°C under 2 mmHg pressure. Methyl methacrylate was distilled at 50°C under a vacuum of 1 mmHg pressure. 2-Butanone oxime was dried by refluxing under a vacuum of 1.5 mmHg for six hours. The solvents used were reagent grade and were dried over molecular sieves. All other materials were used without any further purification.

B. Procedures

(1) Polyurethanes (PU)

(a) *Preparation of prepolymers*—Nine different isocyanate-terminated prepolymers were prepared from hydroxyl-terminated polyethers or polyesters at a NCO/OH ratio of 2/1. The composition and designation of these prepolymers are shown in Table 2. Two equivalents of the diisocyanate were charged into a resin kettle. One equivalent of the polyol was added with

INTERPENETRATING POLYMER NETWORKS

Table 1. Materials

Designation	Description	Source
Polymeg 660	Poly(1,4-oxybutylene)glycol (Poly[tetramethylene glycol]) mol. wt. = 661, hydroxyl no. 169.8	Quaker Oats Co.
Polymeg 1000	Poly(1,4-oxybutylene)glycol (Poly[tetramethylene]glycol) mol. wt. = 1004, hydroxyl no. 111.8	Quaker Oats Co.
Niax D560	Poly(caprolactone)glycol, mol. wt. = 1978, hydroxyl no. 56.7	Union Carbide Corp.
TMP	Trimethylolpropane	Celanese Chem. Corp.
2-But. Ox	2-Butanone oxime	Matheson Coleman & Bell
Pluracol TP 440	Poly(oxypropylene) adduct of trimethylolpropane, mol. wt. = 420, hydroxyl no. 401	BASF Wyandotte
H ₁₂ MDI	4,4'-Methylene bis(cyclohexyl isocyanate)	Allied Chem. Co.
MDI	4,4'-Diphenylmethane diisocyanate	Mobay Chem. Co.
XDI	Xylylene diisocyanate; 70/30 mixture of meta and para isomers NCO = 94.1	Takeda Chem. Co.
TDI	Tolylene diisocyanate; 80/20 mixture of 2,4 and 2,6 isomers; NCO = 87.0	BASF Wyandotte
T-12	Dibutyltin dilaurate	M & T Chem. Co.
T-9	Stannous octoate	M & T Chem. Co.
Acrylic 342-CD 725	Random copolymer of butyl acrylate, methacrylic acid, styrene and hydroxyethyl methacrylate; 50% solution in xylene: cellosolve acetate (1:1); hydroxyl no. 60; 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(dimethyl siloxane)-poly (oxyalkylene) copolymer	Union Carbide Corp.
CAB	Cellulose acetate butyrate EAB-381-2; ASTM viscosity 15	Eastman Chem. Corp.
BD	1,4-Butanediol	GAF Corp.
Elastonol JX 2057	Hydroxyl-terminated polyester of 1,4-butanediol and adipic acid, mol. wt. = 2036, hydroxyl no. 55.11	North American Urethane
Epon 828	Bisphenol A-epichlorohydrin resin; Epoxy 189	Shell Chemical Co.
Epon 152	Novolac-epichlorohydrin resin; Epoxy 175	Shell Chemical Co.
DMP-30	2,4,6-tris-(Dimethylaminomethyl) phenol	Rohm & Haas Co.
Polyester P-373	Unsaturated polyester; dipropylene glycol maleate	W. R. Grace & Co.
Styrene		Dow Chemical Co.
DVB	Divinyl benzene	Dow Chemical Co.
Adipic acid		Monsanto Chem. Co.
Maleic anhydride		Monsanto Chem. Co.
DEG	Diethylene glycol	Dow Chemical Co.
DPG	Dipropylene glycol	Dow Chemical Co.
MMA	Methyl methacrylate	Fisher Chemical Co.
TMPTMA	Trimethylolpropane trimethacrylate	Polyscience Inc.
BPO	Benzoyl peroxide	Fisher Scientific Co.

Table 2. Prepolymer composition and polyurethane curing conditions

Designation	Curing agent	Prepolymer composition	Temperature, °C	Time, hours
PU 1	TP 440	PM 660 + TDI	100	16
PU 2	Elastonol	TP 440 + TDI	85	16
	JX		130	2
PU 3	BD + TMP (1:1)	PM 1000 + TDI	85	16
PU 4	TMP	PM 660 + H ₁₂ MDI	150	4
PU 5	TMP	PM 1000 + H ₁₂ MDI	150	4
PU 6	TMP	PM 660 + MDI	150	4
PU 7	TMP	PM 660 + XDI	150	4
PU 8	TMP	TMP + H ₁₂ MDI	150	4
PU 9	BD + TMP	Niax D560 + MDI	110	16

TP 440—Poly(oxypropylene) adduct of trimethylolpropane

PM 660 and PM 1000—Poly(tetramethylene) glycols

Elastonol JX 2057—Poly(1,4-butanediol) adipate

Niax D560—Poly(caprolactone) glycol

BD—1,4-Butanediol

TMP—Trimethylolpropane

TDI—Tolylene diisocyanate

H₁₂MDI—4,4'-Methylene bis(cyclohexyl isocyanate)

MDI—4,4'-Diphenylmethane diisocyanate

XDI—Xylylene diisocyanate

stirring, maintaining a nitrogen sparge throughout the reaction and keeping the temperature at 60°C for the MDI-based prepolymers and at 80°C for the TDI, XDI and H₁₂MDI-based prepolymers.

(b) *Blocking of isocyanate-terminated prepolymers*—A number of IPNs were prepared from some of the above prepolymers and a melamine cured polyacrylate copolymer. The latter crosslinks via the pendant hydroxyl groups present in the polyacrylate copolymer. Therefore, it was necessary to block the isocyanate group of the prepolymers to prevent a chemical reaction between the isocyanate and the hydroxyl group in the polyacrylate. Blocking was carried out with the following prepolymers: PM 660 + H₁₂MDI, PM 1000 + H₁₂MDI, PM 660 + MDI, PM 660 + XDI, and TMP + H₁₂MDI. A slight excess of 2-butanone oxime and 0.2 per cent by weight of dibutyltin dilaurate catalyst (T-12) were added to each of the prepolymer solutions (50 per cent in cellosolve acetate). The reactions were carried out at 80°C with nitrogen sparging until the isocyanate content reached zero, indicating complete blocking of the isocyanate group¹⁷. Deblocking of the isocyanate group takes place at about 159°C, while the melamine cure of the polyacrylate takes place at about 100°C. Hence, it is expected that the latter will cure first before deblocking of the isocyanate occurs with subsequent chain extension and crosslinking of the urethane polymer, thus reducing the possibility of chemical interaction between the two polymer systems.

(c) *Chain extension and curing*—For the preparation of moulded sheets, an equivalent weight of the curing agent(s) was mixed with the prepolymer and cured in a sealed mould.

In the preparation of films, an equivalent weight of the curing agent in 50 per cent cellosolve acetate solution and 0.1 per cent weight of stannous

octoate were added to the 50 per cent solution of the prepolymer in cellosolve acetate. Films of 0.002–0.003 inch thickness were cast on glass and were heat cured. Table 2 shows the curing conditions as well as the composition and designation of the fully cured polyurethanes.

(2) Polyepoxides (E)

Two epoxy resins were employed, Epon 828 (bisphenol-A-epichlorohydrin resin) (E-1) and Epon 152 (novolac-epichlorohydrin resin) (E-2). Films of both were cast and cured with 2,4,6-tris(dimethylaminomethyl) phenol (0.5 per cent) (DMP-30). Epon 828 contains a small amount of free hydroxyls which may possibly react with the isocyanate during IPN formation. Epon 152 has none.

(3) Polyesters (PE)

Two unsaturated polyesters were used, one of which was highly unsaturated (dipropylene glycol maleate) (PE-2) while the other was more flexible, containing adipate units in addition to the maleate units in the polyester moiety (PE-1). Both polyesters were crosslinked with styrene monomer.

(a) *PE-1*—To 100 g of polyester prepared from 0.2 mol of maleic anhydride, 0.8 mol of adipic acid, 0.2 mol dipropylene glycol and 0.9 mol of diethylene glycol, were added 30 g styrene and 1.3 g (one per cent) of benzoyl peroxide. The mixture was stirred and castings made, between glass plates sealed with rubber gaskets in order to prevent monomer evaporation. The polyester was cured at 85°C for sixteen hours.

(b) *PE-2*—This unsaturated polyester (dipropylene glycol maleate) (P-373) was mixed with styrene and benzoyl peroxide and castings made as described above.

(4) Polyacrylates and polymethacrylates (PA)

(a) *PA-1*—This was a random copolymer consisting of butyl acrylate, styrene, methacrylic acid and hydroxyethyl methacrylate, which was used as a 50 per cent solution in cellosolve acetate and xylene. Only a small amount (less than one per cent) of methacrylic acid was present and served as catalyst for the curing reaction. Crosslinking took place by reaction of the pendant hydroxyl groups of the acrylate copolymer with a butylated melamine formaldehyde solution (60 per cent solids in xylene and cellosolve acetate). 5 g of the modified melamine resin solution was added to 149 g of the acrylate copolymer solution. The films were cured at 150°C for four hours.

(b) *PA-2*—A crosslinked polymethyl methacrylate (PMMA) was prepared by reacting methyl methacrylate monomer (MMA) and trimethylolpropane trimethacrylate (TMPTMA) in the presence of one per cent by weight of benzoyl peroxide (BPO)²³. The reaction was carried out at 80°C in a water-jacketed resin kettle. A PMMA prepolymer syrup was obtained by stopping the reaction at 10–20 per cent conversion. Crosslinking was accomplished by further reacting the PMMA prepolymer syrup in a sealed mould at 80°C for sixteen hours and at 110°C for four hours. The TMPTMA level was chosen to give a crosslink density of 0.5×10^{-4} mol/cm³ in the cured polymer.

(5) *Styrene copolymer (PS)*

A styrene copolymer was prepared by reacting styrene monomer and divinyl benzene (DVB) in the presence of one per cent BPO catalyst. The preparation of the PS prepolymer syrup was carried out at 80°C and was stopped when a 20 per cent conversion was reached. Crosslinking was accomplished by further reacting the PS prepolymer syrup in a sealed mould at 80°C for sixteen hours and at 110°C for four hours. The DVB level was chosen to give a crosslink density of 0.5×10^{-4} mol/cm³ in the cured polymer²³.

(6) *Interpenetrating polymer networks (IPNs)*

All IPNs were binary systems and were prepared by blending the appropriate prepolymers together with crosslinking agents (if not already present in the prepolymers) and catalysts. Films were cast from solution and then heat cured or sheets moulded in a closed mould. The designation, composition and curing conditions for the IPNs are listed in *Table 3*.

C. Measurements

(1) *Stress/Strain*

The tensile strengths and elongations at break were measured on an Instron Tensile Tester at a crosshead speed of 2 in/min. An exception was IPN 11 (PU 9 + PS) when the crosshead speed was 20 in/min.

Table 3. IPN composition and curing conditions

Description	Composition	Temperature, °C	Time, hours
IPN 1 (Urethane-polyester)	PU 1 + PE 1	110	16
IPN 2 (Urethane-polyester)	PU 1 + PE 2	110	16
IPN 3 (Urethane-epoxy)	PU 2 + E 1	85	16
		130	2
IPN 4 (Urethane-epoxy)	PU 3 + E 1	85	16
		130	2
IPN 5 (Urethane-epoxy)	PU 3 + E 2	130	2
IPN 6 (Urethane-polyacrylate)	PU 4 + PA 1	150	4
IPN 7 (Urethane-polyacrylate)	PU 5 + PA 1	150	4
IPN 8 (Urethane-polyacrylate)	PU 6 + PA 1	150	4
IPN 9 (Urethane-polyacrylate)	PU 7 + PA 1	150	4
IPN 10 (Urethane-polyacrylate)	PU 8 + PA 1	150	4
IPN 11 (Urethane-polystyrene)	PU 9 + PS	80	16
IPN 12 (Urethane-polymethyl methacrylate)	PU 9 + PA 2	110	4

PU—Polyurethane

PE—Polyester

PS—Polystyrene

E—Epoxy

PA-1—Polyacrylate copolymer

PA-2—Polymethyl methacrylate copolymer

(2) *Calorimetric measurements*

The glass transitions (T_g) were determined on a Perkin-Elmer differential scanning calorimeter, DSC-1 b. Measurements were carried out from -100°C to $+150^\circ\text{C}$ under nitrogen at a scanning rate of $10^\circ\text{C}/\text{min}$.

(3) *Infra-red analysis*

Infra-red spectra were obtained on a Perkin-Elmer Model 457 infra-red spectrophotometer at room temperature.

(4) *Electron microscopy*

Samples were stained in osmium tetroxide for two weeks, after which they were embedded in epoxy resin¹⁸, sectioned on an LKB Ultratome III and observed with an AEI 6B and a Phillips 300 electron microscope.

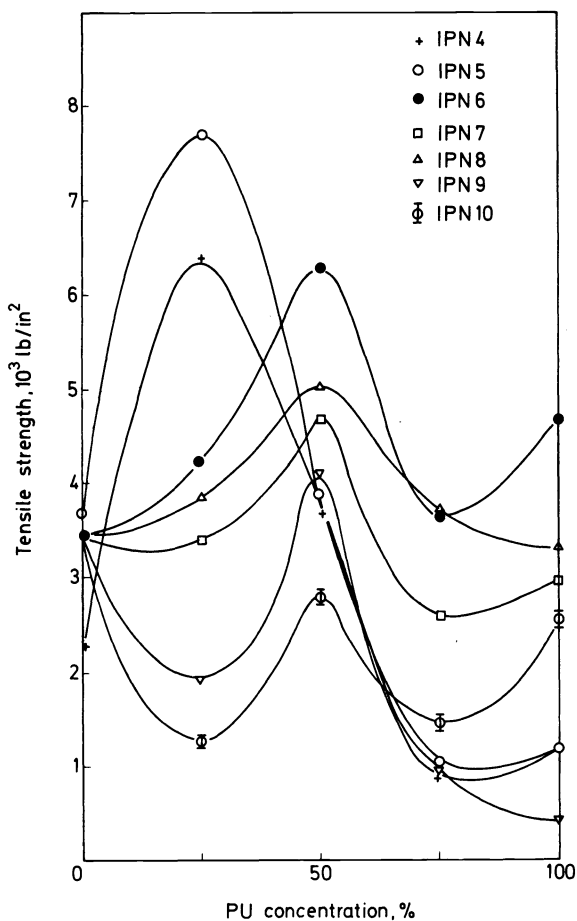


Figure 1. Tensile strength versus polyurethane concentration.

III. RESULTS AND DISCUSSION

A. Stress/strain properties

The tensile strengths and breaking elongations as a function of the urethane polymer content in some IPNs are shown in *Figures 1* and *2* (IPNs 4–10) and in *Tables 4* and *5* (IPNs 11–12), respectively. In all cases shown in *Figure 1*,

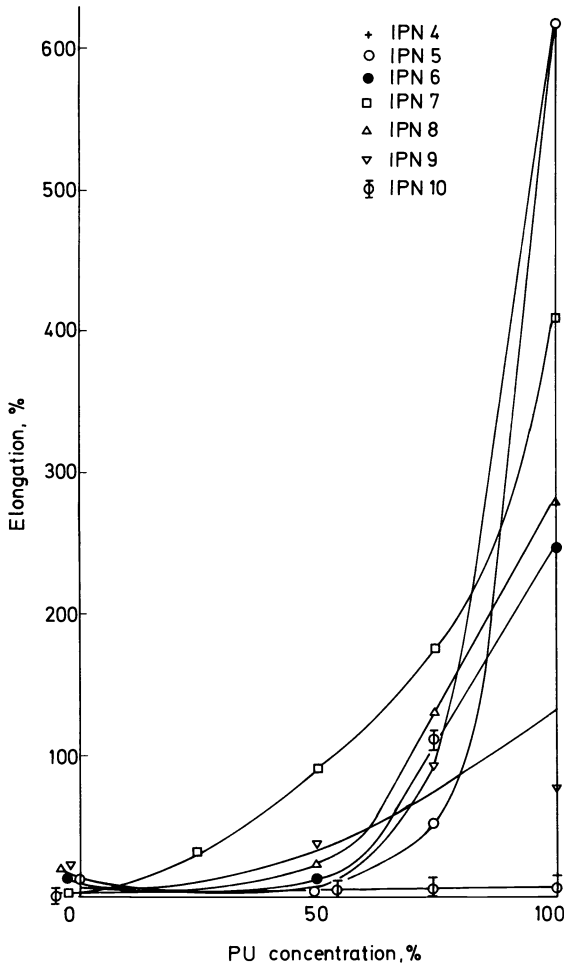


Figure 2. Elongation versus polyurethane concentration.

except for IPN 10, a maximum in tensile strength significantly higher than the tensile strength of the components occurred. This behaviour is typical of latex IPNs made previously in this laboratory^{7–10}. In the cases of the IPNs 4–9 where no phase separation was observed the maximum may be attributed to an increase in the crosslink density due to interpenetration, since it is well

INTERPENETRATING POLYMER NETWORKS

 Table 4. Properties of IPN 11 (PU-9 + PS)
 (Crosshead speed—20 in/min)

Composition, %	Tensile strength, lb in ⁻²	Elongation at break, %	Tear strength, Die C, lb in
100 PU	1654	768	246
95 PU/5 PS	1811	871	262
90 PU/10 PS	2124	859	242
85 PU/15 PS	2354	862	270
75 PU/25 PS	2486	668	180

PU = Niox D-560 + MDI + BD + TMP.

PS = Styrene-divinylbenzene copolymer.

known that the tensile strength of a crosslinked rubber goes through a maximum as the crosslink density increases. IPN 10, made from a very highly crosslinked polyurethane (trifunctional prepolymer as well as a trifunctional chain extender) showed no such enhancement in tensile strength, as would be expected. This high degree of crosslinking lowers the statistical probability of threading, thereby precluding the reinforcing effect of interpenetration. IPNs 4, 5, 6 and 7 showed minima at 75 per cent polyurethane, and IPN 8 showed no minimum. The minima presumably may be attributed to initial weakening of hydrogen bonding at small values of interpenetrating (more of one component than the other). After about 25 per cent of one component, the crosslink density effect takes over, thus raising the tensile strength to a minimum. IPNs 6 and 7 (minima at 75 per cent polyurethane) are made from polyurethanes with H₁₂MDI (cycloaliphatic) as the isocyanate, while IPN 9 used XDI (an aralkyl) and IPN 8, MDI (an aromatic). Thus, it appears from this work that aliphatic polyurethanes yield IPNs with tensile strength minima near the pure polyurethane, while aromatic (and aralkyl) polymers result in either no minima or minima near the pure polyacrylate. IPNs 4 and 5 (made from an aromatic polyurethane and polyepoxides, a relatively non-polar polymer) showed minima near the pure polyurethane.

Another possible reason for the maximum in tensile strength is intermolecular crosslinking occurring between the two networks to result in a better cured system. Specifically, Epon 828 does contain a small amount of free hydroxyls which could react with the isocyanate-terminated prepolymer.

 Table 5. Properties of IPN 12 (PU-9 + PA-2)
 (Crosshead speed—2 in/min)

Composition, %	Tensile strength, lb in ⁻²	Elongation at break, %	Tear strength, Die C, lb in
100 PU	5159	780	258
85 PU/15 PA-2	6096	667	294
75 PU/25 PA-2	5127	874	355
60 PU/40 PA-2	3265	300	381
40 PU/60 PA-2	2592	43	—

PU = Niox D-560 + MDI + BD + TMP

PA-2 = Methylmethacrylate + trimethylolpropane trimethacrylate copolymer

However, Epon 152 contains none. Since the behaviour of IPNs 4 and 5 was quite similar, we may assume either that this reaction does not occur, or, that if it does, it has a minimal effect on the properties of the IPN. Also, the isocyanate-terminated prepolymer may possibly react with excess hydroxyl on the polyacrylate backbone, or with a small amount of amine hydrogen possibly present on the melamine polymer. However, infra-red analysis of IPNs 6-10 (below) suggests these side reactions to be minimal.

Table 6. Glass transition temperatures

Sample	Percentage composition	T_g , K (found)	T_g , K (avg)*	θ^\dagger
IPN 1	50 PU1/50 PE1	252	257	0.020
IPN 2	50 PU1/50 PE2	306	330.5	0.080
IPN 3	50 PU2/50 E1	283	302.5	0.060
	25 PU2/75 E1	304	336.75	0.108
IPN 6	75 PU4/25 PA1	246	249	0.012
	50 PU4/50 PA1	274	288	0.051
	25 PU4/75 PA1	321	327	0.019
IPN 11	80 PU9/20 PS	228, 369	254	
	60 PU9/40 PS	226, 366	284	
	25 PU9/75 PS	226, 372	337	
IPN 12	60 PU9/40 PA2	226, 366	287	
	40 PU9/60 PA2	227, 367	319	
	25 PU9/75 PA2	225, 371	343	
PU 1	100	266		
PU 2	100	234		
PU 4	100	209		
PU 9	100	224		
PE 1	100	248		
PE 2	100	395		
E 1	100	371		
PA 1	100	367		
PS	100	375		
PA 2	100	382		

* Avg.: $T_g = W_1 T_{g1} + W_2 T_{g2}$

† $\frac{T_g - T_{g(av)}}{T_{g(av)}} = \frac{-\theta}{1 + \theta}$

Except for IPN 10 (made from the highly crosslinked rigid polyurethane) the elongations behave basically in the same way (see *Figure 2*). They all decrease rapidly as the polyurethane content decreases until about 50 per cent at which point they approach the value of the pure polyacrylate or polyepoxide.

Tables 4 and 5 list the tensile and tear strengths together with breaking elongations for IPN 11 (PU 9 + PS) and IPN 12 (PU 9 + PA-2), both cases where phase separation was observed. The enhancement of the tensile strength in IPN phase separated systems is a combined result of reinforcement by the glassy dispersed phase and increased physical entanglement and adhesion of phase boundaries due to interpenetration. In these instances, reinforcement is most probably a result of the accepted mechanism of rein-

forcement of rubber with high modulus fillers, enhanced by phase adhesion and small domain sizes due to interpenetration occurring at the boundaries. As can be seen from *Table 4*, the tensile strength of the IPNs (IPN 11) increases with increasing polystyrene content. Data on the higher PS-containing polymers are not presented due to the brittleness of the cast sheets. The elongation at break shows a slight increase from 100% PU to 85% PU/15% PS and then drops at 75% PU/25% PS. This drop in the elongation at 75% PU also suggests that phase inversion occurs at about 75% PU/25% PS (where the continuous matrix changes from the elastomeric PU to the rigid PS). The tear strength also shows a slight enhancement in high PU-containing IPNs and drops at 75% PU/25% PS, which is consistent with the elongation and the morphology results.

Table 5 shows the corresponding data for IPN 12 (PU 9 + PA-2). As in the case of IPN 11, an enhancement of the stress/strain properties at high PU content was observed. A sharp drop in these properties was noted in the region from 75% PU/25% PA-2 to 60% PU/40% PA-2. However, in contrast to IPN 11, the tear strength of IPN 12 increases from 75% PU/25% PA-2 to 60% PU/40% PA-2.

B. Infra-red analysis

Infra-red spectra of IPNs 6–10 showed all the bands of the constituent networks with no new ones appearing. The positions of all the bands in the IPNs were the same as in the components. This is an indication that within the limitations of this technique, little interreaction between component polymers has taken place during cure.

C. Calorimetric measurements

Table 6 shows the T_g s of IPNs 1, 2, 3, 6, 11 and 12 and their component networks. Also shown are the arithmetic means of the T_g s of the components. For IPNs 1, 2, 3 and 6 one T_g intermediate in temperature to the T_g s of the components and as sharp as the T_g s of the components resulted. This supports the possibility of interpenetration of at least a similar extent as that found for the latex IPNs made previously by us. In fact, interpenetration is probably more extensive now since the T_g s are much sharper than those of the latex IPNs in which the transition of one component ran into that of the other¹⁰. Also, the enhancement in tensile strength of these IPNs was much greater than that of the latex IPNs. In these IPNs, some intermolecular reaction might be expected. In IPNs 1 and 2, the isocyanate terminated prepolymer may possibly have reacted with the terminal hydroxyls on the polyester. In IPN 3, the isocyanate may react with the small amount of pendant hydroxyls on the epoxy. In IPN 6, the isocyanate might react with excess hydroxyl on the polyacrylate backbone, or with a small amount of amine hydrogen present on the melamine-formaldehyde resin. This small chemical interaction, which probably could not be seen in the infra-red spectra, most likely contributes to the apparent single phase morphology, since IPNs 11 and 12 (in which no interreaction is possible) show a multiphase behaviour. In IPNs 11 and 12, two T_g s corresponding to the T_g s of the component networks were observed. However, these T_g s were shifted inwards. This agrees with the existence of two phases observed by electron microscopy (below). The shifting of T_g s is

solely attributed to the interpenetration in these cases, since there is little or no possibility for chemical interaction between component networks. The shifting is more apparent in IPN 12 (PU 9 + PA 2) than in IPN 11 (PU 9 + PS) which indicates less phase separation (smaller phase domain sizes) in IPN 12. This agrees with the closer solubility parameter of PA2 (9.3)²⁰ than PS (9.1)²¹ to polyurethane (10.0)²². A complete theory of the thermal properties of IPNs has not up to this time been developed due to the mathematical difficulties of handling the details of topological constraints imposed by the extensive permanent entanglements present in these materials. The usual assumption made in the theory of conventional crosslinked polymers (containing only small amounts of permanent entanglements) is that permanent entanglements act effectively like chemical crosslinks. If this assumption is valid for IPNs, then we can employ simple modifications of an existing theory for conventional crosslinked polymers to explain or correlate the observed DSC glass transition temperatures.

In examining the T_g s of the IPNs (*Table 6*) we see immediately that the T_g of the IPN is always lower than the $T_{g(av)}$ defined by

$$T_{g(av)} = W_1 T_g(1) + (1 - W_1) T_g(2) \quad (1)$$

where W_1 is the weight fraction of component 1 and $T_g(1)$ and $T_g(2)$ are the T_g s of components 1 and 2 respectively.

This observation may be consistent with a modification of a theoretical equation of DiBenedetto (unpublished result quoted in ref. 19) relating the shift in glass transition temperature to degree of crosslinking. Ordinarily, chemical crosslinking in conventional polymers raises the T_g . If T_g is the glass temperature of the crosslinked polymer, $T_{g,0}$ the glass temperature of the uncrosslinked polymer, X_c the mole fraction of monomer units which are crosslinked in the polymer, ϵ_x/ϵ_m the ratio of the lattice energies for crosslinked and uncrosslinked polymer and F_x/F_m the ratio of segmental mobilities for the same two polymers, then the DiBenedetto equation reads

$$\frac{T_g - T_{g,0}}{T_{g,0}} = \frac{(\epsilon_x/\epsilon_m - F_x/F_m)X_c}{1 - (1 - F_x)/(F_m)X_c} \quad (2)$$

Any copolymer effect due to crosslinking is to be accounted for by modifying $T_{g,0}$. For chemically crosslinked polymers $\epsilon_x/\epsilon_m \sim 1$ (DiBenedetto estimates this to be about 1.2) and the mobility of a chemically crosslinked segment $F_x \ll F_m$ so that $F_x/F_m \sim 0$. Hence equation 2 can be simplified in a first approximation to

$$\frac{T_g - T_{g,0}}{T_{g,0}} \simeq \frac{1.2 X_c}{1 - X_c} \quad (3)$$

which exhibits the often experimentally observed increase of T_g with X_c .

In the case of an IPN we must modify equation 2 by replacing $T_{g,0}$ with $T_{g(av)}$. This should account in a first approximation for the copolymer effect which is obviously present with the IPNs. Next we note that $\epsilon_x/\epsilon_m = 1$ since the monomer units of both networks are not chemically modified on forming an IPN as a result of forming permanent entanglements by topological

INTERPENETRATING POLYMER NETWORKS

interpenetration. Thus, equation 2 now becomes

$$\frac{T_g - T_g(\text{av})}{T_g(\text{av})} = \frac{[1 - F_x/F_m]X_c}{1 - (1 - F_x)/(F_m)X_c} \quad (4)$$

with X_c the entanglement mole fraction. In general, secondary intramolecular bonding of a network, van der Waals or hydrogen bonding (if present), are reduced by the permanent entanglement of portions of two different networks; hence the mobilities of the segments of an IPN, F_x , are larger than in the non-interpenetrating separate network, F_m , i.e. $F_x/F_m > 1$. Setting

$$\theta = [F_x/F_m - 1]X_c \geq 0, \quad 1 \geq X_c \geq 0 \quad (5)$$

we can rewrite equation 4 as

$$\frac{T_g - T_g(\text{av})}{T_g(\text{av})} = \frac{-\theta}{1 + \theta}$$

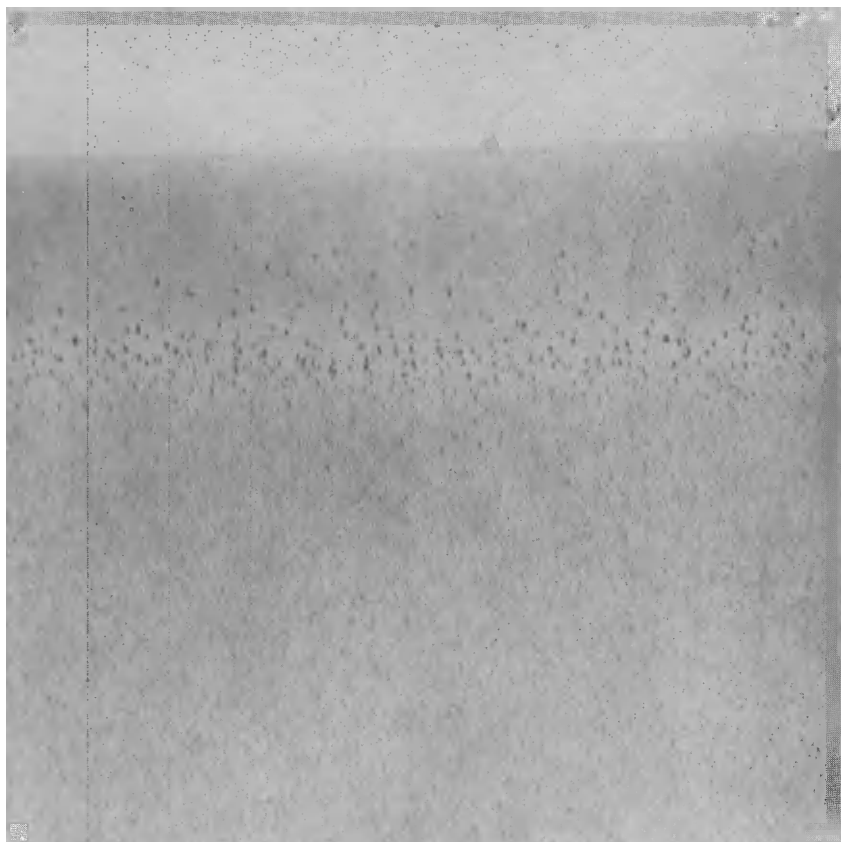


Figure 3. Electron micrograph of IPN 6: 50/50 polyurethane (PU-4) and polyacrylate (PA-1); $\times 78\,000$; reduced to $\frac{6}{10}$ on reduction.

which would predict that the T_g of an IPN would be less than or equal to $T_g(av)$, the relative negative shift being given quantitatively by $\theta/(1 + \theta)$ which increases monotonically from zero to $(F_x - F_m)F_m$ as X_c goes from zero to one. θ values for the IPNs are listed in *Table 6*.

The values of F_x/F_m and X_c depend on the chemical nature, crosslink densities and weight fraction W , of the constituent networks of the IPN.

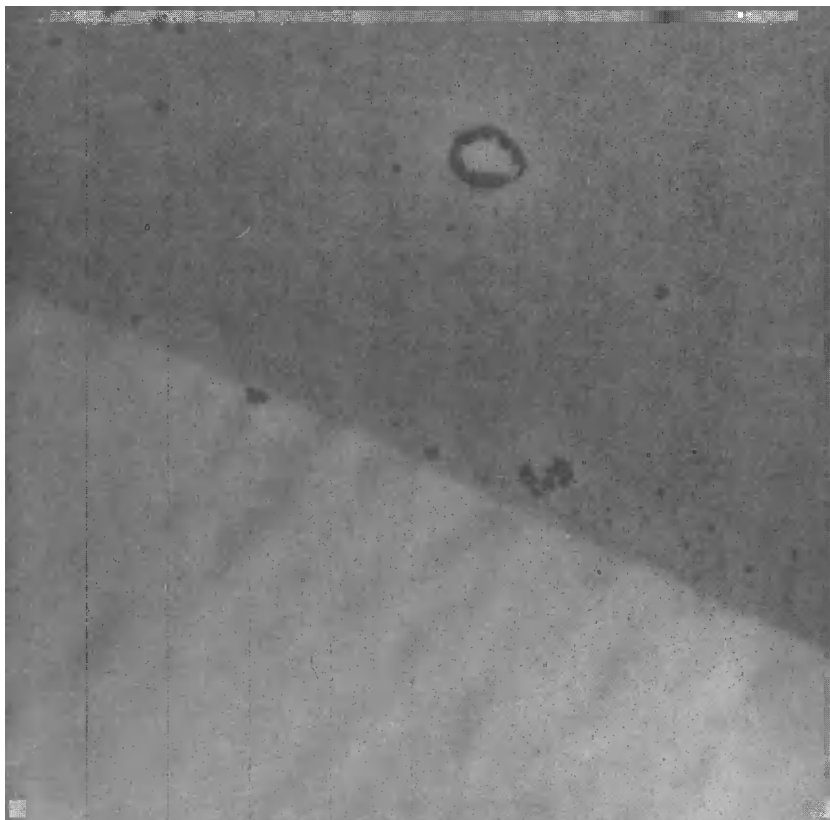


Figure 4. Electron micrograph of IPN 6: 75/25 polyurethane (PU-4) and polyacrylate (PA-1); $\times 78\,000$; reduced to $\frac{6}{10}$ on reproduction.

For a series of IPNs of differing W made from the same two constituent networks θ is expressed to reach a maximum of X_c as a function of W .

Inspection of *Table 6* shows that for the PU/PA IPN series, θ reaches a maximum at 50% PU. This IPN also exhibits a maximum in tensile strength (*Figure 1*) at 50% PU. Since this has already been separately theorized to be due to maximum in crosslink density, the two theories are self-consistent. We thus have strong support for the occurrence of extensive interpenetration.

D. Electron microscopy*(1) IPN 6*

Inspection of the electron micrographs of IPN 6 (see *Figures 3 and 4*) shows that mixing appears to have occurred as evidenced by the absence of any microstructure. At higher magnifications, some granularity is visible in the high-polyurethane IPNs, but this is present in highest quantity in the pure polyurethane sample and so is probably not a characteristic of the IPNs themselves.



Figure 5. Electron micrograph of IPN-11 : 90/10 polyurethane (PU-9) and polystyrene; $\times 75\,000$; reduced to $\frac{2}{3}$ on reproduction.

This single phase situation that occurs between normally incompatible polymers is most probably due to topological interpenetration, which does not allow thermodynamic equilibrium (phase separation) to be achieved. Intermolecular reaction is probably a partial explanation for this single phase behaviour.

(2) IPN 11

The electron micrographs of IPN 11 (PU 9 + PS) (Figures 5 and 6) show phase separation with polyurethane one phase (black) and polystyrene the other phase (white). The sizes of the dispersed phase range from 200 to

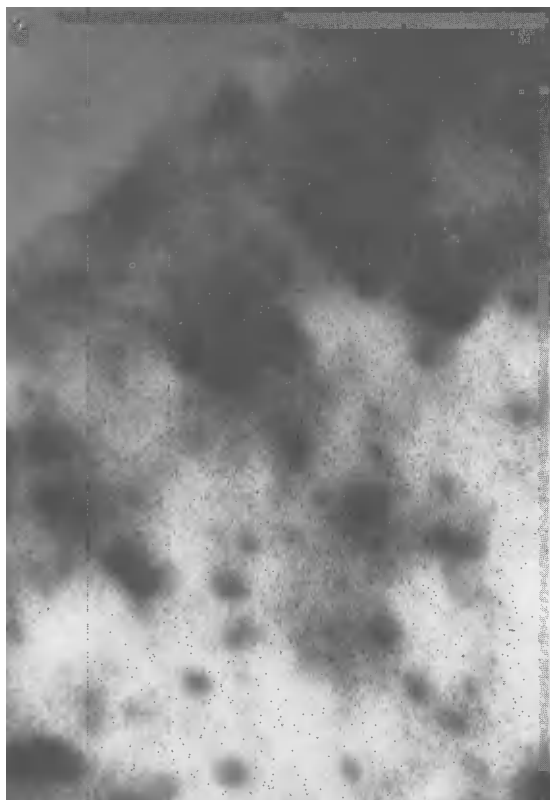


Figure 6. Electron micrograph of IPN 11: 75/25 polyurethane (PU-9) and polystyrene; $\times 75\,000$; reduced to $\frac{2}{3}$ on reproduction.

5000 Å. The same granularity in the polyurethane phase is also observed. Initially (high polyurethane), the polyurethane is the continuous phase (90% and 85% PU). At about 75% polyurethane, a phase inversion occurs. The polyurethane is now the dispersed phase.

IV. CONCLUSIONS

The electron microscopy correlated well with the glass transition behaviour of the IPNs (DSC). One sharp T_g intermediate in temperature to the T_g s of

the components resulted in completely phase mixed IPNs, while two inwardly shifted T_g s corresponding to each component network resulted in the phase separated IPNs. The single intermediate T_g was observed to be lower than the arithmetic mean of the component T_g s and was theorized to be a result of permanent entanglement due to interpenetration.

A maximum in tensile strength was observed in completely phase mixed IPNs and was explained by the increase of the apparent crosslink density due to permanent chain entanglements. In the two cases where phase separation occurred (IPNs 11 and 12), the electron microscopy again agreed well with the glass transition behaviour. Two T_g s were seen corresponding to the T_g s of the component networks. The electron micrographs showed a dispersed and a continuous phase. The inward shifting of the T_g s (which implies less phase separation and more interpenetration) was greatest with the acrylic polymer, as would be expected from their solubility parameters. There exist several possible reasons for phase separation occurring here with none occurring in the earlier cases with similar polymers. There is little or no possibility for grafting between the networks to occur here while there was in the single phase IPNs. This would reduce the differences in cohesive energy density of the two polymers and allow phase mixing. Also, the chemical nature of the polymers in the phase mixed and phase separated IPNs was not exactly the same. It is well known that small differences in the chemical composition of polymers results in grossly different morphologies. For example, poly(2,6-dimethyl phenylene oxide) (PPO) was found by MacKnight and co-workers²⁴ to be completely compatible with polystyrene. However, poly(α -methylstyrene) does not exhibit this behaviour with PPO.

Further studies with the linear counterparts of these polymers should further elucidate the role played by interpenetration in the morphology and properties of these IPNs.

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