

Stress-Strain Properties and Thermal Resistance of Polyurethane-Polyepoxide Interpenetrating Polymer Networks

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Synopsis

Two-component interpenetrating polymer networks (IPN) of the SIN type (simultaneous interpenetrating networks) were prepared from three different polyurethanes and two epoxies. The linear prepolymers were combined in solution, together with cross-linking agents and catalysts, films cast, and subsequently chain extended and crosslinked in situ. Two of the IPN's showed significant improvement in thermal resistance, as measured by thermogravimetric analysis (TGA). All of the IPN's showed maxima in tensile strength significantly higher than the tensile strengths of the component networks at 25% polyurethane and minima at 75% polyurethane. The minima were explained by an initial dilution of the strong polyurethane hydrogen bonds by the epoxies, and the maxima, by an increase in crosslink density due to interpenetration.

INTRODUCTION

Interpenetrating polymer networks (IPN) made in this¹⁻⁵ and other laboratories⁶⁻⁹ have, in many cases, shown enhancement in stress-strain properties. IPN's have shown tensile strengths significantly higher than those of the component polymer networks. In fact, this has been interpreted as an evidence for interpenetration.² There have been to date, however, little or no measurements of any of the other properties of IPN's which may make them valuable engineering materials. In the present study, a number of polymer combinations have been produced by mixing in solution the linear prepolymers (polyurethane and epoxies) together with crosslinking agents, casting films, and subsequently curing them in situ, thereby hypothetically producing IPN's. The systems were selected such that reaction between the two polymers during curing would be minimized, thereby preserving chemical topology.¹⁰ The stress-strain properties as well as thermal resistance of these materials were measured.

EXPERIMENTAL

Materials

The materials used and their descriptions are listed in Table I. All polyols were dried at 80°C for 5 hr under a vacuum of 0.1 mm Hg. The

TABLE I
Materials

Designation	Description	Source
TDI	tolylene diisocyanate; 80/20 mixture of 2,4 and 2,6 isomers; NCO = 87.0	BASF Wyandotte Corp.
Elastonol JX2057	hydroxyl-terminated polyester of 1,4-butanediol and adipic acid; hydroxyl no. = 55.1; acid no. = 0.02	North American Urethanes
Pluracol TP 440	poly(oxypropylene) adduct of trimethylolpropane; MW = 420; hydroxyl no. = 401	BASF Wyandotte Corp.
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(dimethylaminomethylphenol)	Rohm & Haas Co.
Catalyst T-9	stannous octoate	M & T Chemicals Inc.
CAB	cellulose acetate butyrate EAB-381-2; ASTM viscosity = 15 *	Eastman Chemical Co.
Silicone L-522	poly(dimethylsiloxane)-poly(oxyalkylene) copolymer	Union Carbide Corp.
Polymeg 1000	poly(1,4-oxybutylene glycol) [poly(tetramethylene glycol)]; MW = 1004; hydroxyl no. = 111.8	Quaker Oats Co.
BD	1,4-butanediol, urethane grade	GAF Corp.
TMP	trimethylolpropane	Celanese Chemical Co.

solvents used were reagent grade and stored over molecular sieves. All other materials were used without further purification.

Preparation of Networks

Polyurethanes

Three urethane networks were prepared, one polyester and two polyethers:

PU 1. The prepolymer was prepared under nitrogen at 80°C. A resin kettle, equipped with a nitrogen input, thermometer, reflux condenser, and stirrer, was charged with 348 g (4 equivalents) tolylene diisocyanate (TDI). A poly(oxypropylene) adduct of trimethylolpropane, MW = 420 (TP-440), 280 g (2 equivalents), was slowly stirred in. The reaction was carried out until the theoretical isocyanate content (as determined by the di-*n*-butylamine method¹¹) was reached (2 hr). An equivalent weight of poly(tetramethylene glycol), MW = 1004 (PM 1000), was added to 50 g of the prepolymer and the mixture was diluted to 50% with cellosolve acetate. To this solution was added 0.1% by weight flow agent composed of a 1:1 mixture of cellulose acetate butyrate and a poly(dimethylsiloxane)-poly(oxyalkylene) copolymer (L-522 silicone). Films were then cast on glass using a doctor blade and cured at 85°C for 16 hr and 135°C for 2 hr.

PU 2. To 50 g prepolymer prepared above was added an equivalent weight of a hydroxy-terminated polyester of 1,4-butanediol and adipic acid, hydroxyl number 55.1 (Elastonol JX2057), and 0.1% stannous octoate (T-9). A solution was made and films were cast and cured as above.

PU 3. This prepolymer was also prepared under nitrogen at 80°C. PM 1000, 502 g (1 equivalent), was slowly stirred into 174 g (2 equivalents) TDI. The reaction was carried out until the theoretical isocyanate content was reached (2 hr). An equivalent weight of a 1:1 (molar) mixture of 1,4-butanediol and trimethylolpropane was added to 50 g of the prepolymer. A solution was made and films were cast and cured as described previously.

Polyepoxides

Two epoxy resins were employed:

Epon 828. A 50% by weight solution of Epon 828 (bisphenol A-epichlorohydrin resin) in cellosolve acetate was made. To this was added 1% by weight flow agent (see above) and 0.5% by weight 2,4,6-tris(dimethylaminomethylphenol) (DMP-30). Films were cast and cured as above.

Epon 152. A 50% by weight solution of Epon 152 (novolac-epichlorohydrin resin) was made and films were cast and cured as above.

IPN's

Six different polymer combinations were made by mixing each of the three polyurethane solutions (containing flow agent, curing agents, and catalyst) with each of the two epoxy solutions (also containing flow agent and curing agent). Films were then cast and cured in situ as previously described, thereby hypothetically producing IPN's. Combinations of 25%, 50%, and 75% polyurethane were made, except for the IPN's with PU 2. Here, an additional combination of 20% urethane was made. Thus, the IPN's were: IPN 1: PU 1 + Epon 828, IPN 2: PU 1 + Epon 152, IPN 3: PU 2 + Epon 828, IPN 4: PU 2 + Epon 152, IPN 5: PU 3 + Epon 828, and IPN 6: PU 3 + Epon 152

Measurements

Stress-Strain

The tensile strengths and elongations at break were measured on an Instron tensile tester at room temperature and a cross-head speed of 2 in./min. Specimens were 0.125-in-wide dumbbells. Results reported were the average of ten specimens.

Thermal Resistance

Thermogravimetric measurements were made on a du Pont 950 thermogravimetric analyzer (TGA) at a heating rate of 20°C per minute under nitrogen at a flow rate of 0.75 liters per minute.

RESULTS AND DISCUSSION

Thermal Properties

In most cases, the thermograms of the IPN's fall in between those of the epoxy (generally the more thermally stable network) and the polyurethane (see Figs. 1-4). Thus, these IPN's show no enhancement in thermal resistance over the individual components. However, IPN's 5 and 6 (see Figs. 5 and 6) show significant improvement in thermal stability. Their thermograms fall significantly to the right of those of the component networks. The 25% epoxy IPN shows the least enhancement, while the 50% and 75% epoxy IPN's show the greatest, and are about the same. The biggest difference between these two IPN's and the other four is that the polyurethane component shows much greater stability than the other polyurethanes. In fact, the PU has a thermal resistance equal to or greater than the epoxies.

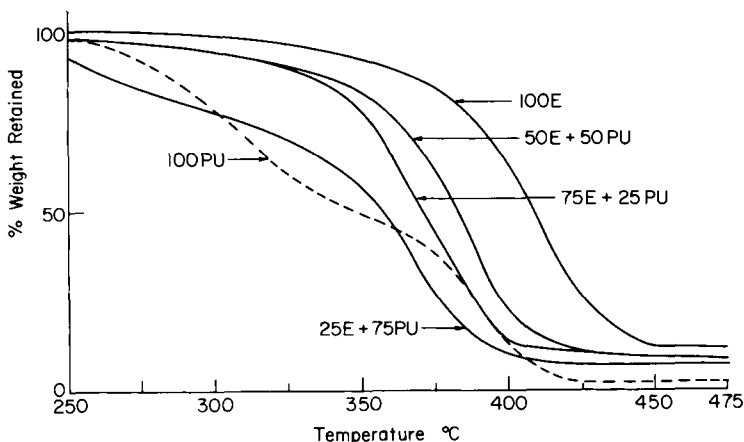


Fig. 1. Thermogravimetric analysis of IPN 1 and component networks.

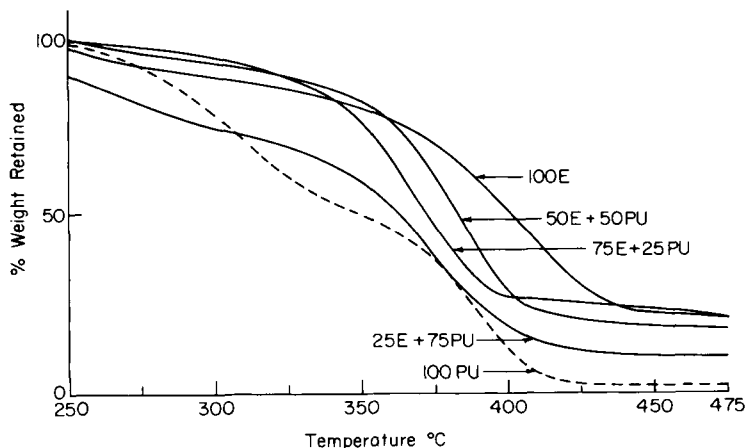


Fig. 2. Thermogravimetric analysis of IPN 2 and component networks.

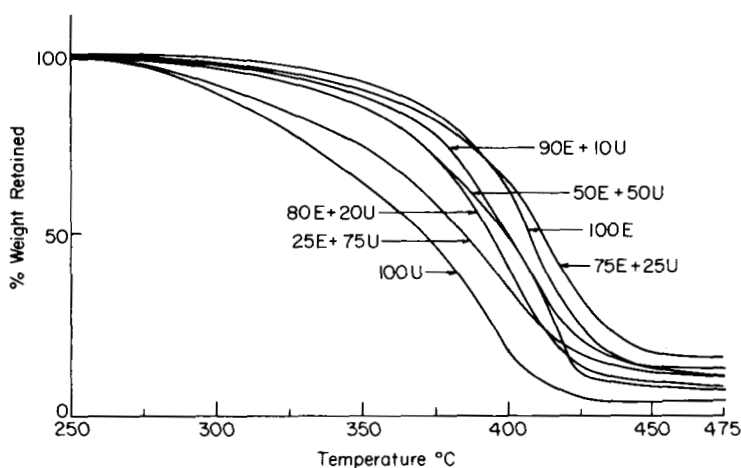


Fig. 3. Thermogravimetric analysis of IPN 3 and component networks.

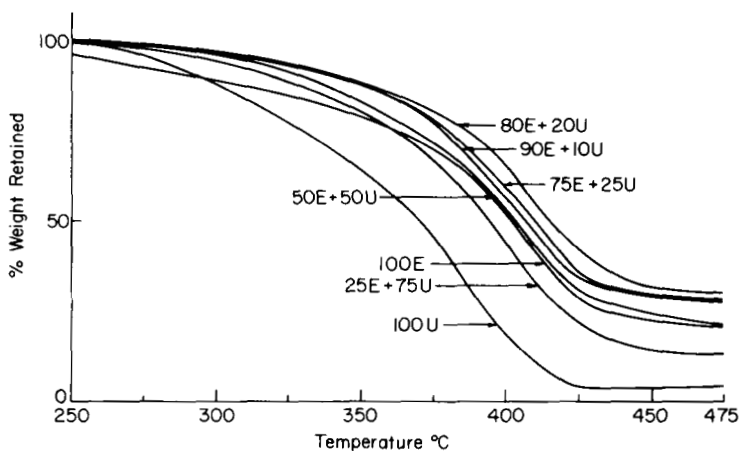


Fig. 4. Thermogravimetric analysis of IPN 4 and component networks.

Stress-Strain Properties

It is here that we note the most dramatic characteristic of IPN's (see Table II and Figs. 7 and 8). In all cases, a minimum in tensile strength (see Fig. 1) occurs at 75% polyurethane, and a maximum, significantly higher than the tensile strength of either component, occurs at 25% polyurethane. This is in agreement with results obtained previously on IPN's of a polyurethane and acrylic made by mixing dispersions of these two polymers.² The maximum may be attributed to an increase in crosslink density due to additional physical entanglement crosslinks (from interpenetration). Previous IPN's made by the latex technique² also exhibited maxima in tensile strength. In fact, these maxima corresponded to maxima in the measured crosslink density. The tensile strength σ of conventional polymers is known to increase with X_c^α , $1/2 \leq \alpha \leq 1$ up to its maximum value

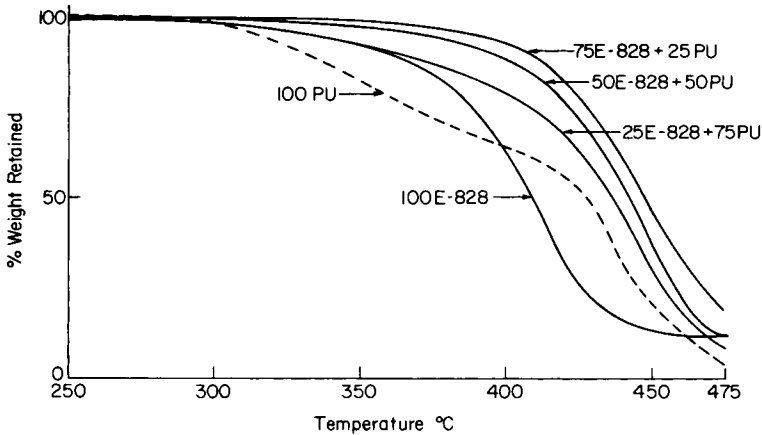


Fig. 5. Thermogravimetric analysis of IPN 5 and component networks.

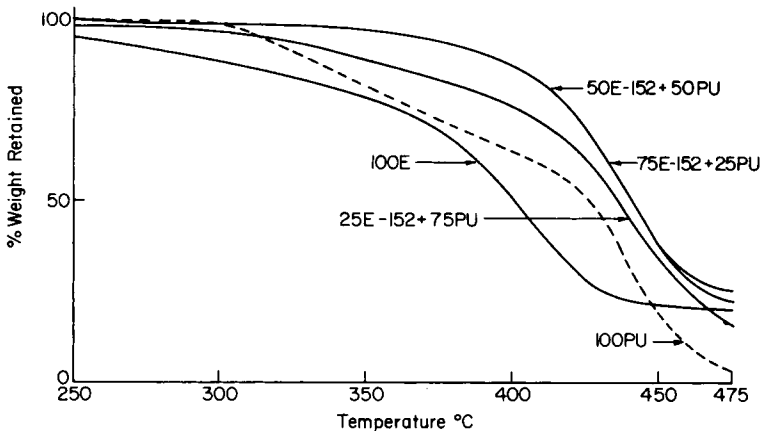


Fig. 6. Thermogravimetric analysis of IPN 6 and component networks.

(12). Here, X_c , the mole fraction of monomer units which are crosslinked, includes contributions from both chemical and physical (entanglement) crosslinks.

The tensile strength of an IPN would be expected to similarly vary with the entanglement mole fraction (interpenetration) as we have observed here. The minimum is most likely due to initial weakening of the polyurethane structure due to disruption of hydrogen bonding at small values of X_c . This maximum in tensile strength may not only be taken as evidence of interpenetration, but is also indicative of the enhancement in properties possible through IPN formation. There are two possible alternative explanations for the maximum in tensile strength. The tensile strengths of the pure epoxies were somewhat lower than those of well-cured commercial epoxies. This is presumably because the films were cast from solution or that they were cured with DMP-30, a tertiary amine, which does not generally yield polymers with the highest tensile strengths.

TABLE II
Stress-Strain Data

PU, %	Epoxy, %	Tensile at break, psi	Elongation at break, %
IPN 1: PU 1 + E-828			
100	0	1260	130
75	25	1020	55
50	50	4360	5
25	75	6220	5
0	100	2230	5
IPN 2: PU 1 + E-152			
100	0	1260	130
75	25	1270	30
50	50	5320	10
25	75	7040	10
0	100	3630	10
IPN 3: PU 2 + E-828			
100	0	2560	225
75	25	1090	50
50	50	2430	25
25	75	6700	5
20	80	5870	5
0	100	2230	5
IPN 4: PU 2 + E-152			
100	0	2560	225
75	25	1650	20
50	50	2990	10
25	75	4980	5
20	80	7370	5
0	100	3630	10
IPN 5: PU 3 + E-828			
100	0	1190	615
75	25	850	100
50	50	3650	5
25	75	6340	5
0	100	2230	5
IPN 6: PU 3 + E-152			
100	0	1190	615
75	25	1050	50
50	50	3870	5
25	75	7670	5
0	100	3630	10

(Normally, active hydrogen-containing diamines or polyamines are used which would, however, react instantaneously with the isocyanate groups. Hence, a tertiary amine was selected which would not enter into reaction with the isocyanate group.)

If the former was the explanation, then possibly better solvent removal due to slower curing reactions caused by a diluting effect of the two com-

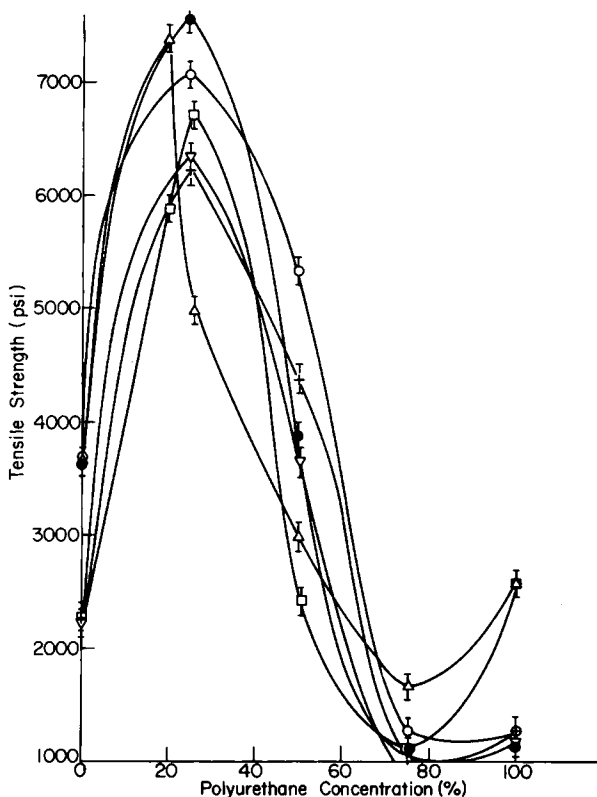


Fig. 7. Tensile at break vs. polyurethane concentration: (+) IPN 1 (PU 1 + E 828); (O) IPN 2 (PU 1 + E 152); (□) IPN 3 (PU 2 + E 828); (Δ) IPN 4 (PU 2 + E 152); (▽) IPN 5 (PU 3 + E 828); (●) IPN 6 (PU 3 + E 152).

ponent system could result in stronger films. If the latter were the case, then side reaction between the two polymers during cure could result in a better-cured material with greater strength. One possible side reaction would be reaction of the isocyanate terminated prepolymer with pendant hydroxyls on the epoxy. Epon 828 does contain some free hydroxyl (0.06 equivalent hydroxyl/100 g resin¹³). However, Epon 152 is a pure novolac-epichlorohydrin adduct and contains no free hydroxyl. Since the behavior of the IPN's with both epoxies was very similar, although there may be some intermolecular epoxy hydroxyl-isocyanate crosslinking in IPN's 1, 3, and 5, it is probably not the cause for the enhancement in tensile strength.

Another possibility is the reaction of the isocyanate with terminal hydroxyls on the epoxy. Since the epoxy cure consists of attack by a phenoxide ion from DMP-30,¹⁴ the reaction could be terminated by hydrogen to produce a hydroxyl. However, the concentration would probably be extremely low, much less than the concentration of diol and triol hydroxyls.

Another possible reaction is between the hydroxyls on the chain extender for the polyurethane system and the epoxy itself. Although the concentration of epoxy groups is greater than isocyanate groups, the isocyanate-hydroxyl reaction in the presence of tin (T-9) and tertiary amine (DMP-30) (which exhibits a well-known synergism¹⁵) would be expected to proceed to a much greater extent. A final possibility is reaction of the epoxy with the urethane group itself, since epoxies are known to react with amides in the presence of amines.¹⁴ However, this reaction is generally slow if no active amine hydrogens are present (much slower than the ionic cure for DMP-30). Also, a urethane group is not a true amide group and would not be expected to react to any great extent.

Thus, while there are several possibilities of intermolecular crosslinking between the polyurethane and epoxy systems, the kinetics are such that they would be minimized and that the interpenetrating effect accounts for the enhancement in tensile strengths.

Inspection of Figure 8 shows that the elongation of all the IPN's drops off rapidly as the concentration of the epoxy component (the more rigid material) increases. This behavior is different from that of latex IPN's²

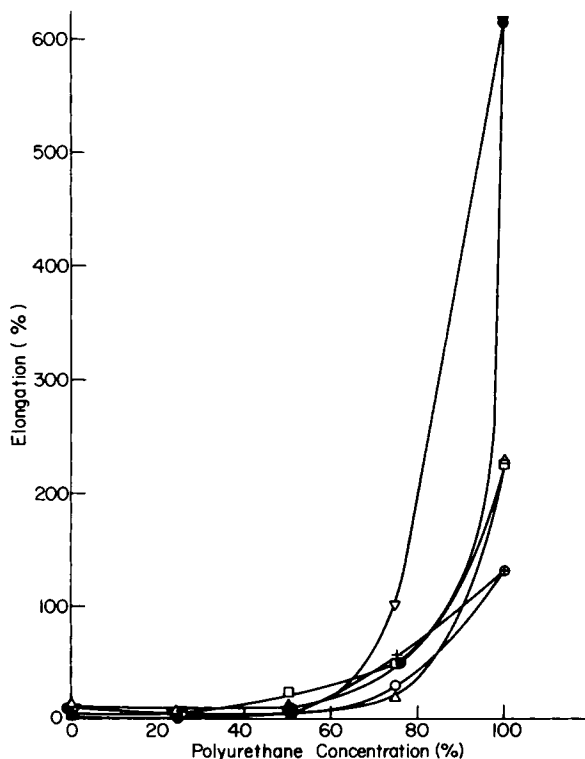


Fig. 8. Elongation at break vs. polyurethane concentration: (+) IPN 1 (PU 1 + E 828); (O) IPN 2 (PU 1 + E 152); (□) IPN 3 (PU 2 + E 828); (Δ) IPN 4 (PU 2 + E 152); (▽) IPN 5 (PU 3 + E 828); (●) IPN 6 (PU 3 + E 152).

and from other polyurethane-acrylic IPN's made in this laboratory by solution techniques where the elongation remained relatively high and did not start dropping until about 75% of the more rigid component. This is probably because in the present study, the rigid component (epoxy) shows very low extensibility ($\sim 5\%$), whereas in previous studies^{1,2,16} the rigid component (acrylic) was much more extensible ($\sim 100\%$).

Conclusions

The maximum in tensile strength exhibited by all these IPN's is partial evidence that interpenetration is occurring here. One of these IPN's, IPN 3 was shown in a previous study¹⁷ to possess one glass transition (as measured by differential scanning calorimetry) intermediate in temperature to that of the component networks. This is additional evidence that total phase separation has not occurred and that at least some interpenetration must occur.

The fact that these networks show enhancement in mechanical properties, with some exhibiting improved thermal properties, could make them desirable engineering materials. Indeed, further studies may show enhancement in other properties as a result of topologic interpenetration.

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