

Stress-Strain Properties of Polyurethane-Polyacrylate Interpenetrating Polymer Networks

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Synopsis

Two-component interpenetrating polymer networks (IPN) of the SIN type (simultaneous interpenetrating networks) were prepared from two different polyurethanes (a polyester type and a polyether type) and a polyacrylate of two different crosslink densities. The linear polymers and prepolymers were combined in solution, together with crosslinking agents and catalysts, films cast, and subsequently chain extended and crosslinked in situ. In all cases, maxima in tensile strengths significantly higher than the tensile strengths of component networks occurred. This was explained by an increase in crosslink density due to interpenetration.

INTRODUCTION

Interpenetrating polymer networks (IPN) made previously in this laboratory¹⁻⁴ from polyacrylate and poly(urethane-urea) dispersions exhibited tensile strengths greater than either component. It has been hypothesized that this maximum occurs because of increased crosslink density.² The IPN's were shown to have crosslink densities higher than that of either component. In this study, a number of IPN's of polyurethanes and polyacrylates have been made from solutions rather than dispersions. Solutions of the linear polymers were combined and films were cast and then cured to form IPN's. The polymers were selected such that there would be no reaction between them during cure, thus preserving chemical topology.^{1,2} The stress-strain properties were measured at room temperature and a simple theory developed to explain the gross behavior.

EXPERIMENTAL

Materials

The materials used and their descriptions are shown in Table I. All polyols were dried at 80°C for 5 hr under a vacuum of 0.1 mm Hg. All other materials were used without further purification.

Preparation of Networks

Polyurethanes

Two urethane networks, an ester and an ether, were synthesized:

PU 1 (Polyester). The prepolymer (NCO/OH = 2) was prepared at 60°C under N₂. A poly(oxypropylene) adduct of trimethylolpropane (MW = 420) (TP-440), 280 g (2 equivalents), was added slowly with stirring to 348 g (4 equivalents) of tolylene diisocyanate (TDI) in a 1-liter resin kettle. The reaction was carried out until the theoretical isocyanate content (determined by the di-*n*-butylamine method⁵) was reached. An equivalent weight of a hydroxy-terminated polyester of 1,4-butanediol

TABLE I
Materials

Designation	Description	Source
Pluracol TP 440	poly(oxypropylene) adduct of trimethylolpropane; MW = 420; hydroxyl no. = 401	BASF Wyandotte Corp.
TDI	tolylene diisocyanate; 80/20 mixture of 2,4, and 2,6 isomers; NCO = 87.0	BASF Wyandotte Corp.
Elastonol JX2057	hydroxy-terminated polyester of 1,4-butanediol and adipic acid; hydroxyl no. = 55.1; MW = 2036	North American Urethanes
Polymeg 1000	poly(1,4-oxybutylene glycol) [poly(tetramethylene glycol)]; MW = 1004; hydroxyl no. = 111.8	Quaker Oats Co.
Ethyl acrylate		Rohm & Haas Co.
Methyl methacrylate		Rohm & Haas Co.
EGDMA	ethylene glycol dimethacrylate	Sartomer Resins, Inc.
Benzoyl Peroxide		Lucidol Corp.
T-9	stannous octoate	M & T Chemicals Co.
CAB	cellulose acetate butyrate EAB-381-2; ASTM viscosity = 15	Eastman Chem. Co.
Silicone L-522	poly(dimethylsiloxane)-poly(oxyalkylene) copolymer	Union Carbide Corp.

and adipic acid (MW = 2036) (Elastonol JX2057) was added to 25 g of the prepolymer. A 50% solution of this mixture in cellosolve acetate was made, and 0.02% by weight stannous octoate (T-9) and 5% by weight flow and bodying agent (composed of a 1:1 mixture of a poly(dimethylsiloxane)-poly(oxyalkylene) copolymer and cellulose acetate butyrate) were added. Films were cast on glass using a doctor blade and cured at 60°C for 12 hr, at 80°C for 3 hr, and at 115°C for 2 hr. Films 2-3 mils thick resulted.

PU 2 (Polyether). An equivalent weight of poly(tetramethylene glycol) MW = 1004 (PM 1000) was added to 25 g of the above prepolymer. A solution was made and films were cast and cured as above.

Polyacrylate (PA)

Only one polyacrylate, a copolymer of one part methyl methacrylate and two parts ethyl acrylate, was employed. Networks with two different crosslink densities were made by adding 5% and 10% ethylene glycol dimethacrylate (EGDMA). Ethyl acrylate, 200 g (2 moles), 100 g (1 mole) methyl methacrylate, and 0.3 g (0.1%) benzoyl peroxide were heated with stirring in a 500-cc three-necked flask equipped with a reflux condenser and nitrogen inlet. The reaction was carried out at 80°C until a prepolymer of syrupy consistency was obtained (1 hr). Two 50% solutions of the prepolymer in cellosolve acetate were made. EDGMA was added to both solutions, 5% by weight to one and 10% to the other. Films were cast on glass and the solvent was removed under a low vacuum (10^{-1} mm Hg) at room temperature. They were then sealed between glass plates (to prevent monomer evaporation) and cured at 60°C for 12 hr, at 80°C for 3 hr, and at 110°C for 2 hr.

IPN's

Four combinations were made. Each polyurethane casting solution was mixed thoroughly with each polyacrylate casting solution. Combinations composed of 25%, 50%, and 75% PU were made. Films were cast and cured as above. Thus, the IPN's were: PU 1/PA (10% EGDMA), PU 2/PA (10% EGDMA), PU 1/PA (5% EGDMA), and PU 2/PA (5% EGDMA).

Stress-Strain Properties

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

RESULTS AND DISCUSSION

The tensile strengths and elongations of the IPN's and their component networks are shown in Table II and Figures 1 and 2. In all cases, the tensile strengths of the IPN's were higher than those of the individual components. Previous studies² have shown that the maximum in tensile strength is most likely a result of the increase in crosslink density due to increased physical crosslinks caused by interpenetration. No minimum in tensile strength was found with these IPN's, contrary to previous studies on latex IPN's.² This indicates a greater degree of entanglement, as would be expected to result from this method of IPN synthesis (solutions as opposed to dispersions). The tensile strength σ of crosslinked conventional polymers is known to increase with X_c^α , $1/2 \leq \alpha \leq 1$, up to its maximum value.⁶ Here, X_c , the mole fraction of monomer units which are crosslinked, includes contribution from both chemical and physical (entanglement) crosslinks. The tensile strength of an IPN should similarly vary with X_e , the entanglement mole fraction.

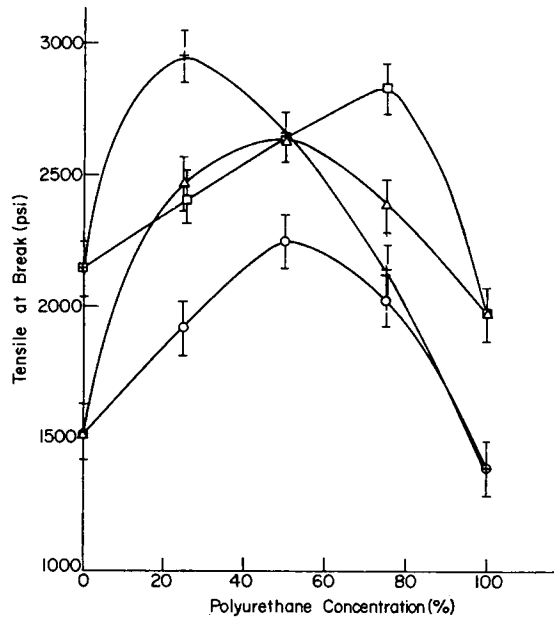


Fig. 1. Tensile at break vs. polyurethane concentration: (+) IPN 1; (O) IPN 2; (□) IPN 3; (Δ) IPN 4.

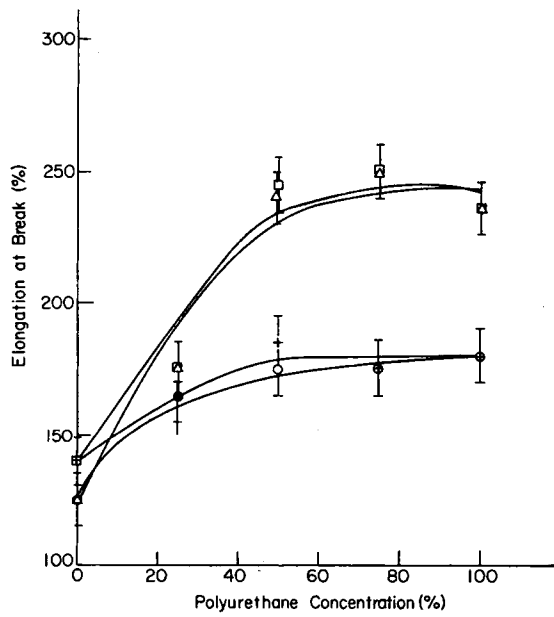


Fig. 2. Elongation at break vs. polyurethane concentration: (+) IPN 1; (O) IPN 2; (□) IPN 3; (Δ) IPN 4.

TABLE II
 Stress-Strain Data

PU, %	PA, %	Tensile at break, psi	Elongation at break, %
IPN 1: PU 1/PA (10% EGDMA)			
100	0	1390	180
75	25	2140	175
50	50	2650	185
25	75	2900	160
0	100	2140	140
IPN 2: PU 1/PA (5% EGDMA)			
100	0	1390	180
75	25	2030	175
50	50	2250	175
25	75	1920	165
0	100	1520	125
IPN 3: PU 2/PA (10% EGDMA)			
100	0	1970	235
75	25	2830	250
50	50	2630	245
25	75	2410	175
0	100	2140	140
IPN 4: PU 2/PA (5% EGDMA)			
100	0	1970	235
75	25	2390	250
50	50	2640	240
25	75	2470	175
0	100	1520	125

Further inspection of Figure 1 shows that, in all cases, IPN's made from the more highly crosslinked acrylic network (10% EGDMA) have the higher tensile strengths. This implies a greater degree of interpenetration, as might be expected in these cases. IPN's made from the less crosslinked acrylic (5% EGDMA) have maxima at the same urethane concentration (50%). The maxima for the more highly crosslinked IPN's occur at different concentrations. This may be due to the difference in tensile strengths of the urethane component of these two IPN's. The IPN made from the stronger PU (IPN 3) has its maximum occurring at the greater concentration of PU. This effect only occurs with IPN's made from the stronger acrylic (the tensile strength of the PA is greater than that of either PU). When the pure acrylic had a tensile strength lower than one of the urethane components, the maxima occurred at the same point.

Inspection of Figure 2 shows that the elongation of the IPN's was about the same as that of the polyurethane (the more extensible component) up to about 50% PA. It then dropped off rapidly to the elongation of pure PA. This behavior was similar to that of the latex IPN's.² Since the elongation was constant in the region in which the tensile strength was

increasing, it is probable that additional permanent entanglements (topological interpenetration) must be present in the IPN's.

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