

Improvements in the Stress-Strain Behavior of Urethane Rubbers by Bimodal Network Formation

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Synopsis

Urethane rubbers find increasing application as binders for composites. Typical examples are solid propellants. The rubber networks are formed by end linking hydroxy-terminated prepolymers with tri- or higher functional isocyanates. A recent trend in solid propellant technology is the replacement of the traditional low-energy binders with "energetic" binders containing nitro, nitrate, or azido groups. Since these energetic polymers create relatively short interchain lengths between the cross-link points, the binders give notoriously poor mechanical properties. Our study demonstrates that significant improvements in the stress-strain behavior are attained with bimodal modifications of the energetic binders, that is, by blending these energetic short chains with very long chains prior to curing into rubbers.

Molecular aspects of the improvement have been examined in terms of polymer types, cross-linkers, viscoelastic factors, and solid filler content. Results indicate that the improvement is primarily due to the extent of nonaffine deformation of the bimodal rubber network.

INTRODUCTION

Urethane rubbers find increasing application as binders for composites. Typical examples are solid propellants. The binder networks are formed by end linking hydroxy-terminated prepolymers with di- or higher functional isocyanates. This reaction takes place after the liquid slurry has been cast into a rocket motor chamber. The molecular weights of the prepolymers are usually 2000–4000, which ensures low enough viscosity so that pourable propellant slurries can be prepared.

A recent trend in solid propellant technology is the replacement of the traditional low-energy prepolymers, such as polybutadienes, polyethers, and polyesters, with "energetic" prepolymers in which nitro, nitrate, and/or azido groups are attached to the polymeric chain. The number of skeletal atoms is far less for these energetic polymers than for the traditional polymers. [Compare energetic polydinitropropylacrylate (PDNPA) with conventional polymers in Table I.] Since the strain capabilities are primarily a function of the load-bearing skeletal atoms,^{1,2} the mechanical properties obtained with these polymers are notoriously poor (Table II).

This study involves the evaluation of potential improvements in the stress-strain behavior of energetic propellant binders by bimodal network formation; that is, by blending these energetic short chains with long-chain prepolymers prior to cure into rubbers.

TABLE I
 Some Prepolymers Used in Urethane Rubbers

Prepolymer	Structure	Weight % of skeletal atoms
Polybutadiene (PBD)	$\left\{ \text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2 - \underset{\begin{array}{c} \\ \text{CH} \\ \\ \text{CH}_2 \end{array}}{\text{CH}} \right\}_n$	72 ^a
Polyethylene glycol (PEG)	$\left\{ \text{CH}_2 - \text{CH}_2 - \text{O} \right\}_n$	91
Polypropylene glycol (PPG)	$\left\{ \text{CH}_2 - \underset{\begin{array}{c} \\ \text{CH}_3 \end{array}}{\text{CH}} - \text{O} \right\}_n$	69
Polycaprolactone (PCP)	$\left\{ \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_2 - \overset{\text{O}}{\parallel} \text{C} - \text{O} \right\}_n$	77
Polydinitropropyl acrylate (PDNPA)	$\left\{ \text{CH}_2 - \underset{\begin{array}{c} \\ \text{C} = \text{O} \\ \\ \text{OCH}_2 - \underset{\begin{array}{c} \\ \text{CH}_3 \end{array}}{\text{C}} (\text{NO}_2)_2 \end{array}}{\text{CH}} \right\}_n$	12

^a Vinyl content ranges from 10 to 25%. The value is based on 19%.

EXPERIMENTAL

Plasticizers and Solids

Diethylene glycol dinitrate (DEGDN) and triethylene glycol dinitrate (TEGDN) were purchased from Trojan Company (Spanish Fork, Utah) and used as received. Cyclotetramethylene tetranitramine (HMX) was purchased from Trojan Company and ground to average particle size of 2 μm and vacuum dried at 60°C.

 TABLE II
 Stress-Strain Properties of Monomodal Network of Short Chains [29% Polymer, 43% Plasticizer, 28% Solids (2 μm HMX)]^a

Polymer	MN ^b	OH Eq wt ^c	f ^d	Estimated skeletal atoms between cross-link points	66°C, 4.2 × 10 ⁻⁴ m/s crosshead speed ^e		
					σ (MPa)	ϵ (%)	E ₀ (MPa)
PEG 600	600	294	~2	40	0.71	33	4.0
PEG 1000	1000	500	~2	70	0.61	42	3.0
PDNPA(F-1)	4400	990	~4	20	0.24	12	2.6
PDNPA(M-13)	9000	3020	~3	50	0.18	34	0.8

^a Cured with Desmodur N-100 (see Experimental). Plasticizer was diethylene glycol dinitrate. HMX: see Experimental.

^b Number-average molecular weight.

^c Number-average OH equivalent weight.

^d Average functionality.

^e See Experimental.

Cure Catalyst

Ferric acetylacetonate ($\text{Fe}(\text{AA})_3$) was purchased from Aldrich Chemical Company.

Prepolymers

Polyethylene glycols (PEG) were acquired from Union Carbide. Polydi-nitropropyl acrylates (PDNPA) were synthesized in this laboratory. Detailed background and the synthetic procedure of PDNPA have been reported.³

Isocyanates

Desmodur N-100 was obtained from Mobay Chemical Company. It is a mixture of aliphatic isocyanates with an average functionality greater than 3, according to the GPC analysis.⁴ Synthesis of 1,3,5-pentane triisocyanate (PTI) has been reported.⁴

Preparation of Rubber Samples

Prepolymers predissolved in plasticizer and the other ingredients of the composite [isocyanate, solid filler, and $\text{Fe}(\text{AA})_3$] were mixed thoroughly while degassing under vacuum and then cast on a plate. The samples were cured for 2 days at 45°C. A longer cure time did not change the swelling ratio of the rubber; hence the cure reaction is as complete as the system allows. Some of the possible side reactions are intramolecular ring formation,⁵ urea formation from isocyanates and water, and homopolymerization of isocyanates. To compensate for these side reactions, 5–10% excess isocyanates were used. It is assumed that the cure reaction of the polymer is nearly complete and the extent of the cure is the same for the monomodal and the bimodal systems being compared.

Stress-Strain Properties

The cast samples, approximately 3×10^{-3} m thick, were stamped out using a cutting die. Tensile properties of these minibone specimens were tested according to ASTM D1708-79. The properties obtained were ultimate nominal stress σ , percentage elongation ϵ , and initial modulus E_0 .

RESULTS AND DISCUSSION

Improvements of the ultimate properties of bimodal urethane rubbers were examined in terms of (1) types of short-chain polymers; (2) cross-linkers; (3) chain lengths of short chains, and (4) solid filler.

Bimodal Networks of PDNPA-PEG and PEG-PEG at Different Compositions

The blended prepolymers were reacted with isocyanates having functionality greater than 3.0 (Desmodur N-100). Hence, the resulting networks should have the same interchain length as the number of skeletal atoms

TABLE III
Transition Temperatures of Bimodal Rubbers [43% Plasticizer, 28% Solids (2 μm HMX)]

Weight % PEG 8000 of polymer blend	Transition temperatures ($^{\circ}\text{C}$)	
	PEG 1000-PEG 8000	PDNPA-PEG 8000
0	-55	-55
20	-55	-55
30	-55, -5	-50, -15
50	-55, 0	-45, 0
65	+15	+15
100	+28	+28

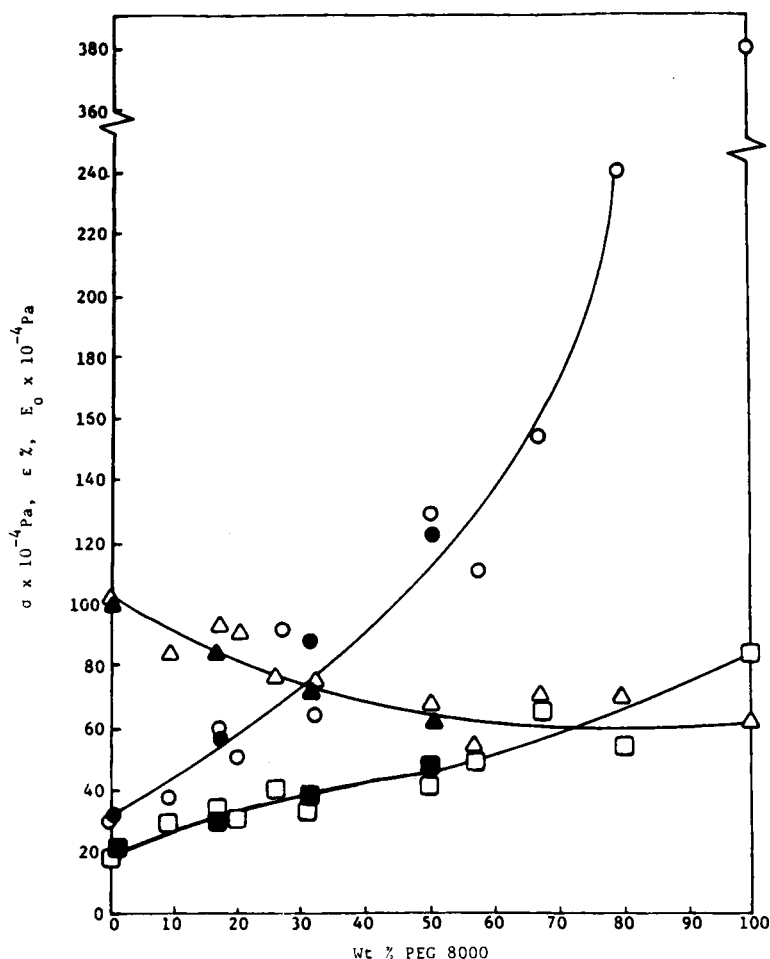


Fig. 1. Ultimate stress-strain properties of PDNPA (M-13)-PEG 8000 bimodal systems versus weight percentage PEG 8000 at 66°C ; strain rate: open symbols are at 4.2×10^{-4} m/s; filled symbols are at 4.2×10^{-5} m/s; \square σ , \circ ϵ , \triangle E_0 .

between the hydroxyl groups of the prepolymers. These plasticized and partially filled rubber samples had transition temperatures (softening points) below 0°C , provided the weight fraction of PEG 8000 was less than one-half of the total polymer (Table III). Stress-strain data were obtained at 66°C to minimize the effect of strain-induced crystallization of PEG 8000.

Ultimate stress-strain properties of the PDNPA (M-13)-PEG 8000 systems are plotted against the weight percentage PEG 8000 (Fig. 1). At 66°C , both ultimate stress and percentage elongation steadily increase with the weight percentage of PEG 8000, although the initial modulus decreases because of lower cross-link density. However, the extent of improvement appears to be strongly dependent on the type of polymer system. The PEG-PEG systems under the same deformation conditions show little improvement when the weight percentage of PEG 8000 is less than one-half of the total polymer, as shown in Figs. 2 and 3.

The bimodal systems of short chains with comparable chain lengths between the cross-links are compared at various mole percentage of PEG 8000. Monomodal systems of these short chains with about the same interchain

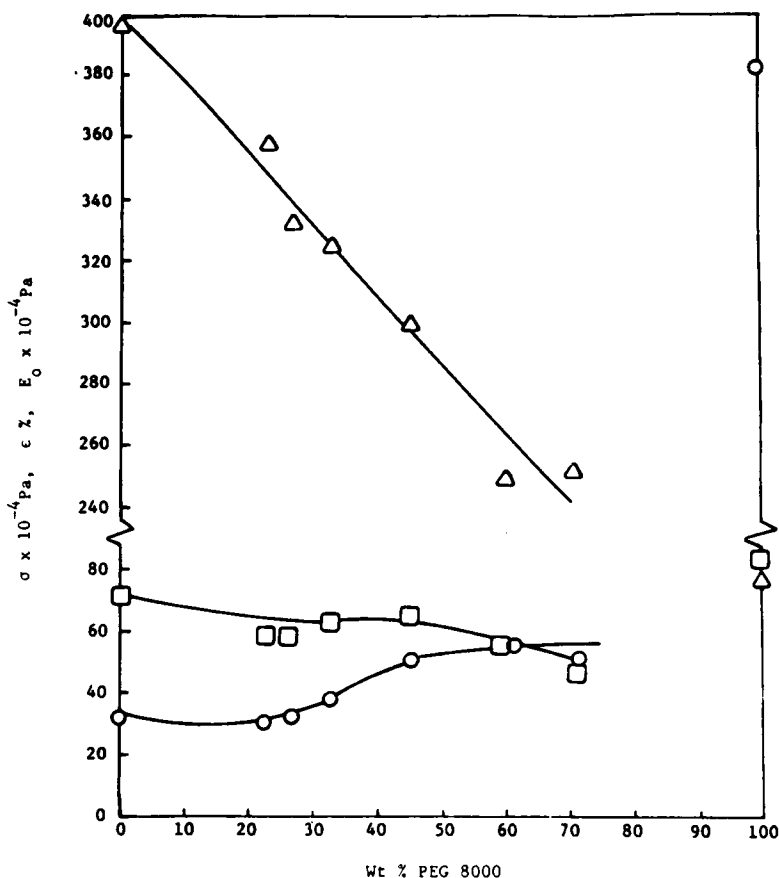


Fig. 2. Ultimate stress-strain properties of PEG 600-PEG 8000 bimodal systems versus weight percentage PEG 8000 at 66°C ; strain rate 4.2×10^{-4} m/s; \square σ , \circ ϵ , Δ E_0 .

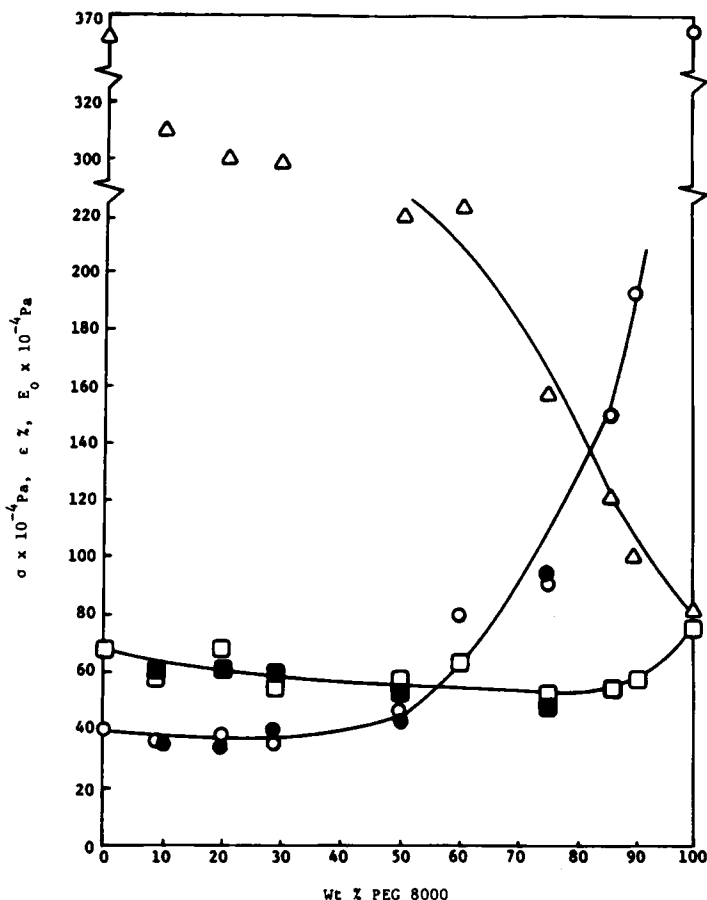


Fig. 3. Ultimate stress-strain properties of PEG 1000-PEG 8000 bimodal systems versus weight percentage PEG 8000 at 66°C; strain rate: open symbols are at 4.2×10^{-4} m/s; filled symbols are at 4.2×10^{-5} m/s; \square σ , \circ ϵ , \triangle E_0 .

length have about the same elongation at rupture, indicating that the strain capability is mainly a function of the number of load-bearing skeletal atoms between the cross-link points (Table II). However, the percentage elongation at rupture of the bimodal networks of PDNPA-PEG 8000 more than triples when 20 mol% of PEG 8000 is incorporated, whereas that of the PEG-PEG system increases at most two times (Fig. 4). This difference indicates that the improvement under these conditions is due to nonaffine deformation, rather than to long chains (PEG 8000) acting as inhibitors of the growth of rupture nuclei,⁶ and/or PEG 8000 undergoing strain-induced crystallization. The degree of nonaffine deformation in these bimodal systems may be influenced by (1) different degree of H bonding (around the cross-link points) and (2) additional plasticization by the side groups in PDNPA. In PEG-PEG systems the acidic hydrogen atoms of the urethane groups and urea groups (from N-100) at the cross-link points would undergo extensive intra- and intermolecular H bonding with PEG, whereas in the PDNPA-PEG systems,

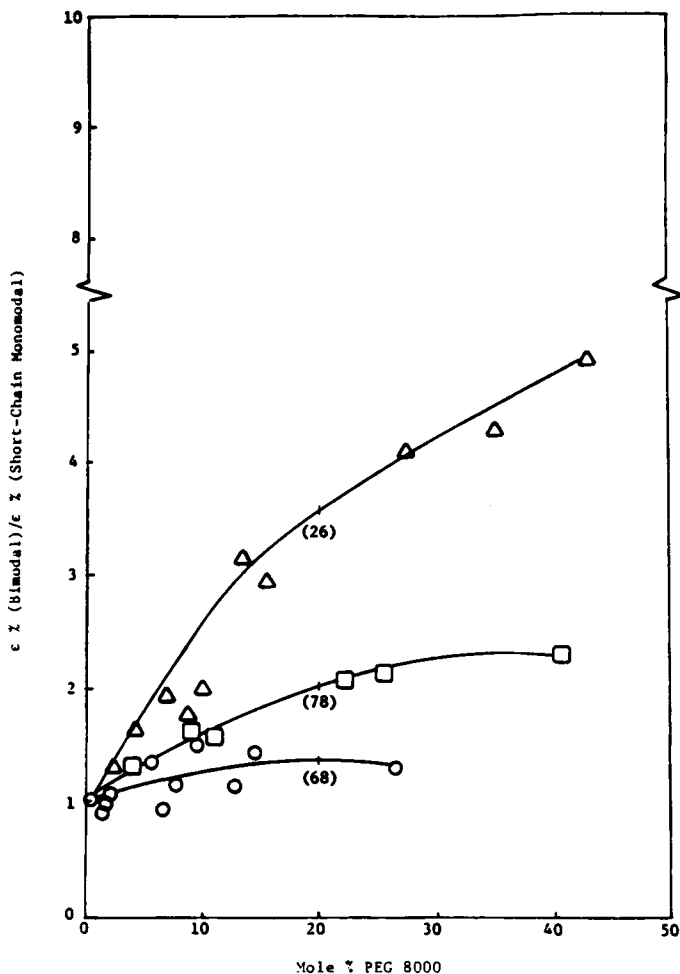


Fig. 4. Improvement of ultimate strain properties of various polymer-PEG 8000 bimodal systems versus mole percentage PEG 8000 at 66°C; strain rate 4.2×10^{-4} m/s; ○ PEG 600 (40 skeletal atoms), □ PEG 1000 (70 skeletal atoms), △ PDNPA (50 skeletal atoms); numbers in parentheses are the weight percentage PEG 8000.

the H bonding is substantially reduced by the interference of the dangling side groups and the reduced number of ether-oxygen atoms. The H bonds would restrict the mobility of the polymeric chains, especially that of cross-link points, during the deformation of the network and thus minimize the degree of nonaffine deformation.

The lack of significant change in the ultimate properties of the bimodal systems when changing the temperature or the strain rates by 10-fold (Figs. 1 and 3) indicates that the difference between the PEG-PEG and PDNPA-PEG systems may not be contributed by the difference in the degree of plasticization, that is, the free-volume effect. It appears that once these polymers are sufficiently plasticized (1.5–2.0 plasticizer-polymer ratio) to create enough free volume to make the system reasonably flexible, addi-

tional free-volume effect by the side chains does not significantly increase the extent of nonaffine deformation in the range of strain rates tested. The difference in the improvement, therefore, is most likely due to the difference in the degree of H bonding. This hypothesis is supported by a significant improvement of the PEG-PEG bimodal system when the samples were deformed under near equilibrium conditions (Fig. 5). Under the near equilibrium conditions, H bonds are allowed to reequilibrate after each small deformation to create more stable conformations of the network, thus allowing more extensive nonaffine deformation. The significant upturn of the curve prior to rupture is likely due to strain-induced crystallization. Little improvement in the properties is expected with the monomodal PEG 1000 under the near equilibrium conditions (Fig. 6), since no extensive nonaffine deformation is possible here.

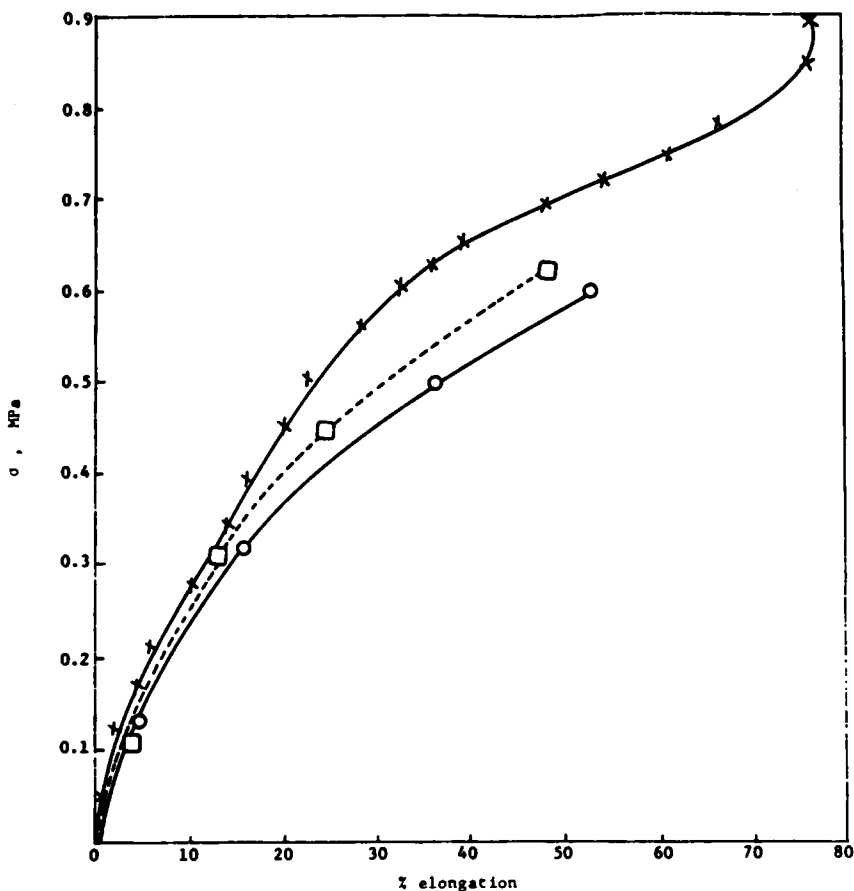
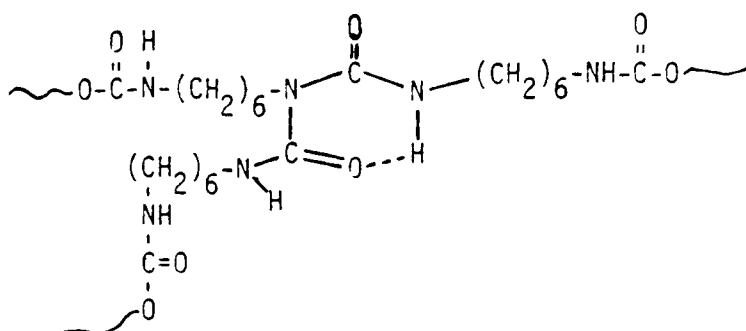


Fig. 5. Effect of Strain Rate on Ultimate Properties of PEG 1000/PEG 8000 (26 wt% PEG 8000) Bimodal System; Strain Rate: X Under Near Equilibrium, \square 4.2×10^{-5} m/s, \circ 4.2×10^{-4} m/s, at 66°C.

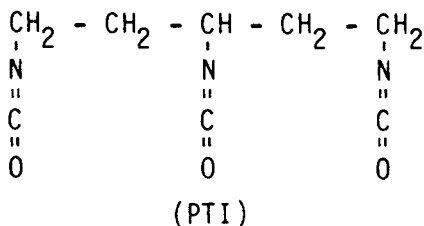
Effect of Cross-linker

All the previous rubber networks were prepared using Desmodur N-100. N-100 is a mixture of aliphatic isocyanates of functionality greater than 3.0

and contains significant amounts of urea ($-\text{N}-\overset{\text{O}}{\parallel}{\text{C}}-\text{N}-$) groups. Furthermore, many of these components would cause additional rigidity by forming intramolecular H bonding to create stable six-membered rings at the cross-link points as illustrated below:



On the other hand, our newly synthesized 1,3,5-pentane triisocyanate (PTI) is 100% trifunctional and does not contain amide groups.



The above analysis leads us to believe that the bimodal systems with PTI would create far more flexible cross-link points than with N-100, thus allowing more extensive nonaffine deformation.

Solid-filled and plasticized binders of PDNPA-PEG 8000 bimodal systems were prepared using PTI and N-100. The effect of variation of the cross-linkers on the ultimate properties of monomodal short-chain PDNPA is negligible. However, the properties of bimodal PDNPA-PEG 8000 systems are strongly influenced by the type of cross-linker, as predicted previously (Table IV). The differences in the improvement are dramatic: PTI is far superior to N-100.

Effect of the Chain Length of Short Chains

Studies of the bimodal systems PEG-PEG 8000 and PDNPA-PEG 8000 indicate that the short chains should be as long as the overall system allows,

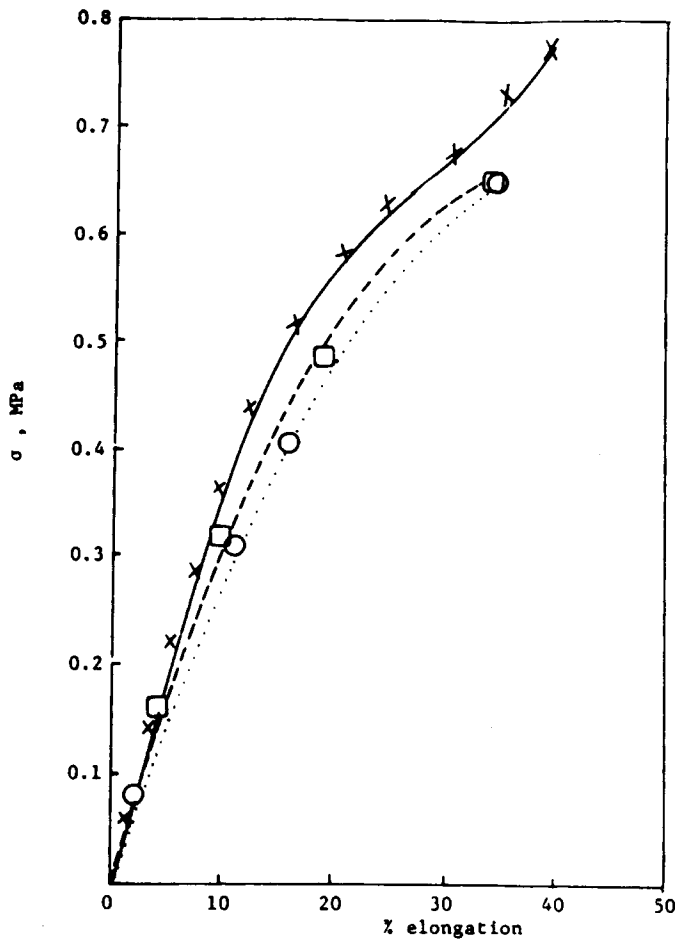


Fig. 6. Effect of Strain Rate on Ultimate Properties of PEG 1000 monomodal system; Strain rate: X under near equilibrium, \square 4.2×10^{-5} m/s, \circ 4.2×10^{-4} m/s, at 66°C.

TABLE IV
Stress-Strain Properties of PDNPA-PEG 8000 Bimodal System (50% TEGDN; 20% 2 μ m HMX; NCO-OH = 1.1)^a

Cross-linker	0% PEG 8000			35% PEG 8000			45% PEG 8000		
	σ (MPa)	ϵ (%)	E_0 (MPa)	σ (MPa)	ϵ (%)	E_0 (MPa)	σ (MPa)	ϵ (%)	E_0 (MPa)
PTI	0.17	8.8	2.0	0.41	73	0.9	0.70	93	0.9
N-100	0.18	9.0	2.1	0.25	24	1.2	0.33	38	1.0

^a Minibones; strain rate 4.2×10^{-4} m/s at 66°C.

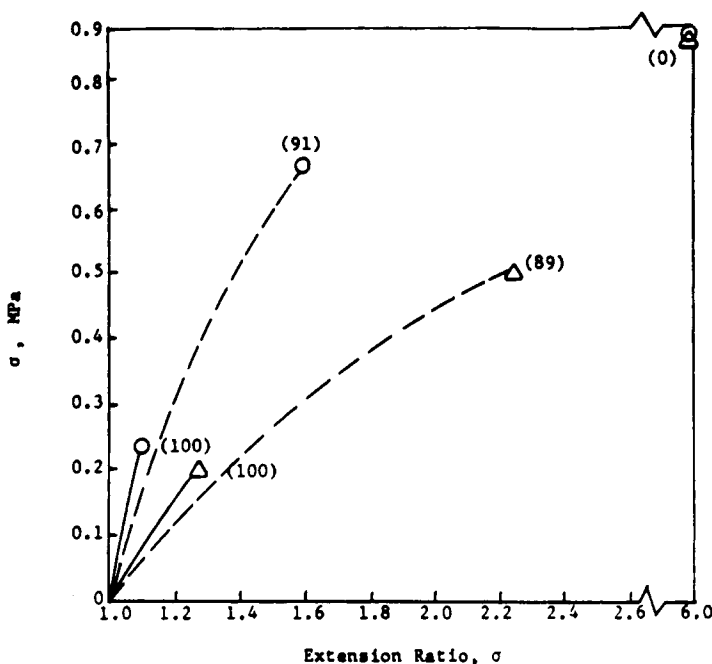


Fig. 7. Bimodal PDNPA/PEG 8000 Systems at 66°C; X-head speed 4.2×10^{-4} m/s; the values in () are the mole percent of short chains; \circ PDNPA (20 sk. atoms), \triangle PDNPA (50 sk. atoms), PEG 8000 (550 sk. atoms); solid curves (monomodal), dotted curves (bimodal).

in order to attain best stress-strain properties (Figs. 4 and 7). Furthermore, properties of all the bimodal systems studied under the test conditions never surpassed those of monomodal PEG 8000. This is contradictory to the observations of Mark on his unfilled and unplasticized polydimethylsiloxane (PDMS) systems.⁷ Energy of rupture E_r for PDMS bimodal systems was the greatest when the chain length of short PDMS was the shortest. Furthermore, E_r values of the bimodal PDMS systems were always greater than the monomodal systems of both short and long chains, thus negating the "weakest link" theory.⁸ Mark's result was attributed to limited chain extensibility.⁹ This discrepancy between our results and Mark's is most likely because monomodal PEG 8000 undergoes strain-induced crystallization, whereas his PDMS does not undergo strain-induced crystallization.¹⁰

Effect of Solid Filler

Unfilled bimodal systems show appreciable improvements in both stress and strain properties over the short-chain monomodal system, whereas the solid-filled systems mainly provide improvement in the strain capabilities (Table V). The reinforcing effect of small filler particles may overshadow the increased stress by nonaffine deformation.

TABLE V
Effect of Solids on PDNPA-PEG Bimodal Systems (6:4 Plasticizer-Polymer Weight Ratio)^a

PDNPA-PEG 8000 (wt% PEG)	Volume % solids	σ (MPa)	ϵ (%)	E_0 (MPa)
0	0	0.07	18	0.6
30	0	0.24	80	0.9
0	23	0.31	43	1.4
30	23	0.46	100	1.3
0	40	0.35	48	1.6
30	40	0.42	95	1.5

^a Crosshead speed, 4.2×10^{-4} m/s at 66°C.

SUMMARY AND CONCLUSION

The practical importance of the bimodal systems for improving the stress-strain properties is clearly demonstrated. For example, a 65:35 PDNPA-PEG 8000 system shows an eightfold increase in strain over monomodal PDNPA. Experimental results indicate that the improvement at 66°C is primarily due to the extent of nonaffine deformation of the bimodal rubber rather than the effect of long chains as growth inhibitors of rupture nuclei. The most important factors in these systems appear to be the type of polymer and cross-linker; flexible cross-link points allow more extensive nonaffine deformation, thus improving the ultimate properties further.

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