

Anomalous Depression of Rubbery Modulus through Crosslinking

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Synopsis

Introduction of primary covalent crosslinks into linear, segmented elastomers was followed by observing their modulus-temperature behavior. The behavior of the linear segmented polymers is explained by association of glassy segments into regions which act as filler and quasi-crosslink. In several cases crosslinkage disrupts these regions and thereby lowers the "plateau" modulus.

INTRODUCTION

Previous investigations¹⁻³ in these laboratories have indicated that in certain linear, amorphous segmented elastomers their unusual properties were derived from association of glassy and rubbery segments with themselves in the solid state. Two glass transitions are seen to exist; T_g , a major transition due to the rubbery segments, and T_g' , a subsidiary higher-temperature transition due to the stiffer segments. Between T_g and T_g' a region of enhanced rubbery modulus exists caused by association of the stiffer, glassy segments which act as filler and as quasi-crosslink.

In an attempt to learn more about the intermolecular bonding in these systems we have systematically introduced crosslinking agents into previously linear elastomers. Upon curing, both the effect of the level of crosslink density and the site of the crosslink were studied by observing modulus-temperature behavior.

Our results reveal that both the chemical structure of the crosslink and the site of crosslinking influence the mechanical properties of the elastomers. These results can not be explained in terms of the kinetic theory of rubber elasticity and hence may be considered anomalous crosslinking effects.

EXPERIMENTAL

Two systems of linear elastomers, one a polyester-urethane (Estane),⁴⁻⁷ and a second, a polybutadiene-styrene block copolymer (Kraton, Shell Chemical Co.), were used in this study. Both were readily soluble in

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tetrahydrofuran (THF), and a solution technique was used to incorporate the crosslinking agents. Another series of polyester-urethane samples were kindly supplied by Drs. E. C. Haag, Jr. and J. H. Saunders of Mobay Chemical Company. These were crosslinked with increasing amounts of triol.⁸ The Mobay samples were supplied in the form of cast sheets.

Incorporation of Crosslinking Agent

Approximately 15 g. of linear elastomer was placed in 200 cc. of THF. The polymer was stirred in a Teflon-coated pan until complete solution was obtained. At this stage while still at room temperature, quantitatively weighed amounts of crosslinking agent were added with stirring. The crosslinking agents were benzoyl peroxide (Bz_2O_2), and 4,4'-diphenylmethane diisocyanate (MDI). These were used in varying concentrations as shown in Table I.

TABLE I

No. ^a	Elastomer	Crosslinking agent	Amount crosslinking agent, %	Curing conditions
1	Polybutadiene-styrene block copolymer	Benzoyl peroxide	0.4	45 min., 120°C. 40,000 psi
2			1.0	
3			2.3	
4			3.5	
1	Estane 5740-070	Benzoyl peroxide	0	3 hr., 120°C.
2			0.5	
3			2.0	
4			3.9	
5			8.3	
6			15.5	
7			29.3	
1	Estane 5740-070	MDI	5.1	1 hr., 150°C. 40,000 psi
2			18.6	
3			25.1	
4			50.6	
5			99.3	
A	Mobay polyester-urethane	Triol	0 Triol	16 hr., 110°C.
B			10.0/90 Triol/diol	
C			20/80 " "	
D			50/50 " "	
E			100 Triol	

^a These numbers correspond to curve numbers in Figs. 2-5.

Curing of Samples

After complete solution of both the curing agent and polymer, the solvent (THF) was slowly evaporated at room temperature over a period of several days. To accomplish this a cover of perforated aluminum foil was placed over each pan of polymer. The curing of the polyester-urethane with

Bz_2O_2 was carried out at $120^\circ C.$ for 3 hr., the polymer still in the cast form. The Kraton samples were also cured at $120^\circ C.$ but were simultaneously compression-molded at 40,000 psi for 45 min. The cure of Estane 5740-070 with MDI was also done with compression molding under conditions of 40,000 psi for 1 hr. at $150^\circ C.$ The above information is summarized in Table I.

Modulus-Temperature Experiments

Modulus measurements as a function of temperature were made by using a Clash-Berg⁹ and Gehman¹⁰ torsional testing apparatus. Silicone oil was used as a heat transfer medium and a heating rate of $1^\circ C./min.$ was used. The modulus plotted is 3 times the 10-sec. shear modulus which is comparable to modulus data obtained in tensile experiments.^{11a} Data were taken at $5^\circ C.$ intervals.

RESULTS AND DISCUSSION

The linear segmented elastomers discussed in this paper were all characterized by an enhanced modulus, or extended "rubbery plateau" region, above a major glass transition temperature. This phenomena was most easily observed in measurements of modulus versus temperature and experiments of this nature were used throughout this study.

In Figure 1 are presented modulus-temperature curves of some of the un-

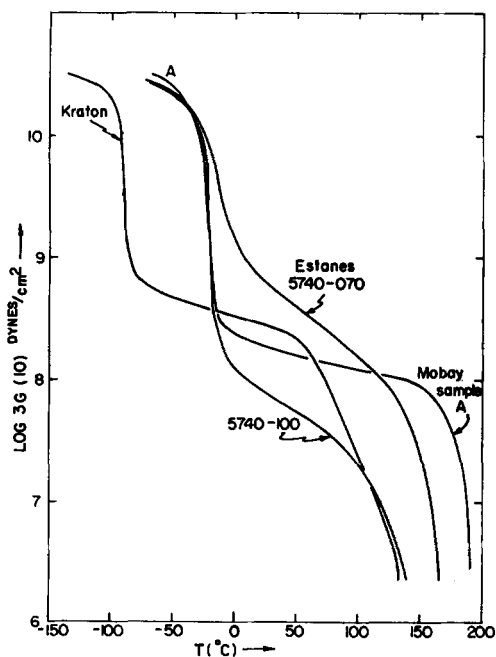


Fig. 1. Modulus-temperature curves of linear elastomers.

modified materials investigated. All are linear, noncrystalline polymers. Estane 5740-070 is a well-characterized polyester-urethane sample containing aromatic linkages,² and Kraton is a polystyrene-butadiene block copolymer. In each case the low temperature T_g is characteristic of the "rubbery" segments present while the more rigid segments retain their glassy character, reinforcing the structure until they also pass through a softening region at a T_g' . Crosslinking of the systems displayed in Figure 1 revealed markedly different effects depending upon the structure of the crosslink, as well as the region of the polymer chain where the covalent tie points were made. These results plotted as modulus versus temperature are summarized in Figures 2-5.

Kraton Crosslinked with Bz_2O_2

In the case of Kraton crosslinked by Bz_2O_2 (Fig. 2) the results show two transitions in the modulus-temperature behavior; one is associated with the butadiene segments, a second with the polystyrene segments. Above the transition due to the styrene, a rubberlike behavior was observed with a slight increase of modulus with temperature at each level of crosslink density. This behavior is predicted by the kinetic theory of rubber elasticity^{11b} shown in the form of eq. (1)

$$f = N(0)KT(\alpha - 1/\alpha^2) \quad (1)$$

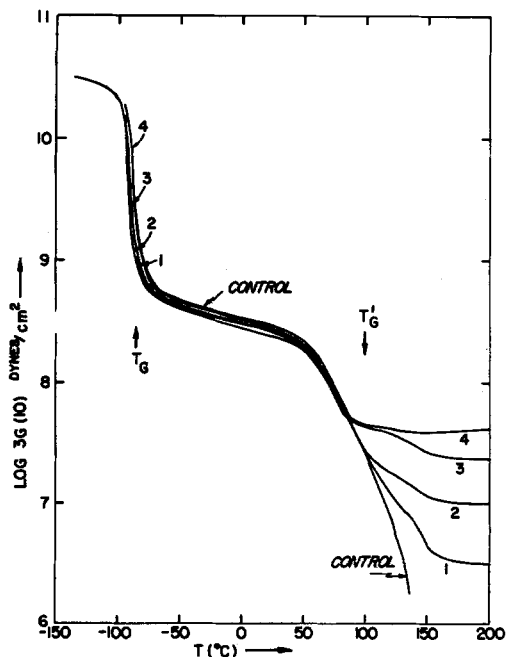


Fig. 2. Kraton crosslinked with benzoyl peroxide: (1) 0.4% Bz_2O_2 ; (2) 1.0%; (3) 2.3%; (4) 3.5% Bz_2O_2 .

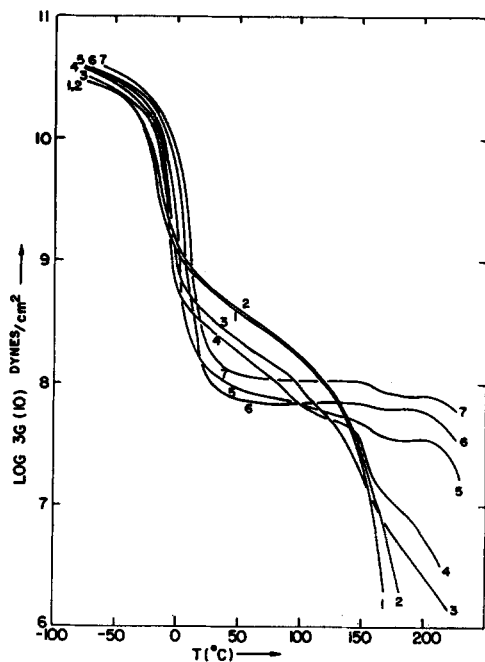


Fig. 3. Estane 5740-070 crosslinked with benzoyl peroxide: (1) control; (2) 0.54%; (3) 1.98%; (4) 3.94%; (5) 8.25%; (6) 15.5%; (7) 29.3% Bz_2O_2 .

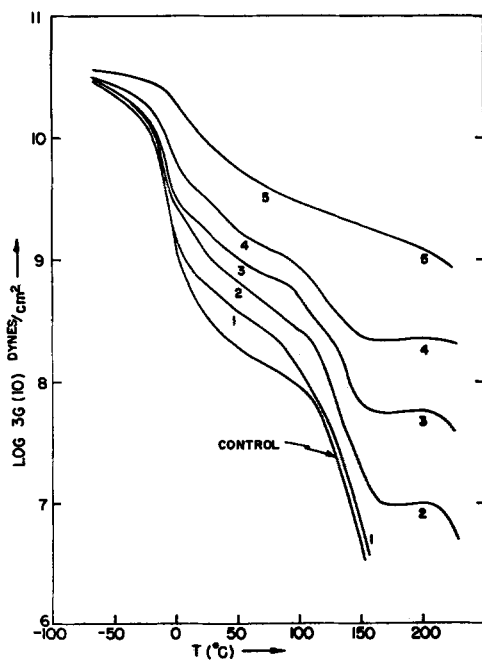


Fig. 4. Estane 5740-070 crosslinked with MDI: (1) 5.1% MDI; (2) 18.6%; (3) 25.1%; (4) 50.6%; (5) 99.3% MDI.

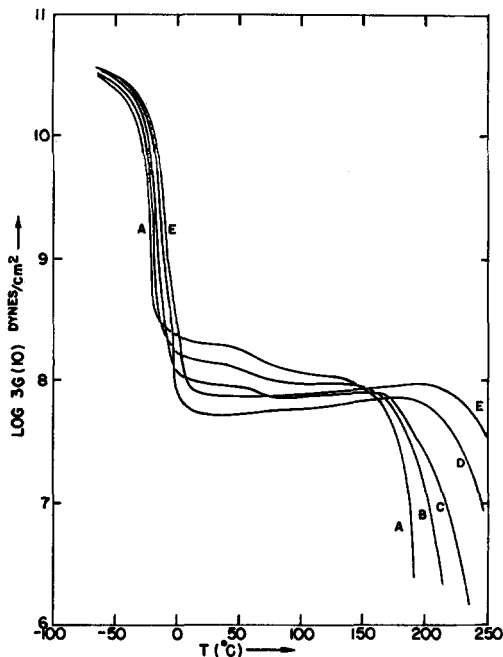


Fig. 5. Mobay polyurethane crosslinked with triol: (A) 100% diol; (B) 90/10% diol/triol; (C) 80/20%; (D) 50/50%; (E) 100% triol.

where f is the stress and α the ratio of stretched to unstretched length at absolute temperature T , K is Boltzmann's constant, and $N(0)$ is the crosslink density in terms of network chains per cubic centimeter. It is significant that the stress, or modulus (when appropriately rearranged) is directly proportional to the degree of crosslinking and to the absolute temperature. Our results of Figure 2 show this to be the case only at elevated temperature. At temperatures below which the styrene segments are glassy, all the curves lie in the same region as the control and all have an enhanced modulus.

An important consideration in the interpretation of this behavior is the actual site of the crosslink. In the Kraton system, it is believed benzoyl peroxide produces free radicals which are predominantly formed by abstraction of allylic hydrogen from the butadiene segments.

Thus, crosslinking occurs in the rubbery segments and no disruption of the packing or the intermolecular bonding occurs within the glassy regions. This explanation reveals why the unusual plateau modulus is unaffected by the crosslinking in this instance.

Estane Crosslinked with Bz_2O_2

Crosslinking with benzoyl peroxide gives somewhat different results in the polyester-urethane system, Estane 5740-070. Bayer¹² has stated that peroxides form free radicals on the methylene linkage of the MDI segments.

In this case then, the crosslinking occurs primarily within the hard segment region and produces a different result than observed in the case of Kraton. These results are presented in Figure 3.

Of importance in Figure 3 is the observation that as the amount of crosslinking increases, the plateau modulus is decreased to some extent. At still higher levels of crosslinking this trend is reversed. These data can be interpreted as a decrease in packing efficiency of the aromatic urethane segments due to crosslinking. At elevated temperatures the Estane system seems to approach the behavior predicted by the kinetic theory. The results at high temperatures are not as conclusive as those with the Kraton elastomer, which can be partly be ascribed to interchange reactions and hydrolytic degradation of the polymer backbone.¹³⁻¹⁶ This is indicated by a rapid decrease in modulus of the crosslinked samples above 175°C.

In conclusion to these sets of experiments it could be said that crosslinking within the hard segments of linear elastomers affects the plateau modulus, primarily decreasing it, while crosslinking in the rubbery segments shows itself only above the glass transition of the hard segments.

Estane Crosslinked with MDI

In this series of experiments MDI was used as a crosslinking agent. The crosslinking reaction in this case proceeds through reaction of the isocyanate with the urethane hydrogen. This produces a crosslinked structure, but also one with an increased content of aromatic linkages. The results shown in Figure 4 can be interpreted in this light. An increase in the "plateau" modulus with increasing MDI used is the result of a greater percentage of bulky groups present to act as glassy tie points through this region. Samples 2, 3, and 4 of this group show a tendency to follow the behavior predicted by the kinetic theory at elevated temperatures while sample 5 behaves and looks like a very highly crosslinked sample of phenolic or epoxy resin.

Triol Crosslinked Polyester-Urethane

A series of curves presented in Saunders and Frisch's text¹⁷ on polyurethanes now seems explainable in terms of the conclusions so far presented in this work. In this earlier study originating at Mobay,⁸ modulus-temperature behavior of a series of polyester-urethanes was investigated as a function of crosslink density. The control was in the "linear state," although actually it was lightly crosslinked via allophanate linkages. Upon adding amounts of diol and triol rather than pure diol in the chain-extending step, crosslinking was produced. Modulus-temperature curves of the products revealed a drastic decrease of modulus in what we have been calling the plateau region. This decrease can be attributed to a poor association of hard segments, since in the triol cure the packing of these segments is disrupted at every branch point.

Figure 5 extends the experiment described above. Modulus-temperature behavior of five samples of varied triol-cured polyester-urethanes were obtained. The data agrees with the earlier study,^{8,17} and shows a similarity to the Bz₂O₂-cured Estane in that the plateau modulus first decreases and then, at high levels of crosslinking, does begin to increase.

CONCLUSIONS

In our previous investigations^{1,2} we found that an external plasticizer could affect both the glass transition and the level of enhanced modulus above this T_g . Similarly the decrease of the plateau modulus in Figures 3 and 5 can be attributed to disruption of the glassy tie points as crosslinks are introduced. In the case of Bz₂O₂ an increase of disorder is probably due to the steric difficulty of crosslinking through the methylenic linkages of the MDI segments. Similarly, in the triol cure the mechanism is most likely also a disordering, rendering the aromatic linkages less continuous and hence less able to assert their glassy character for reinforcement.

In contrast, the addition of MDI as a crosslinking agent (Fig. 4) increases the modulus. In this case new aromatic molecules are added to regions already in the glassy state augmenting these regions and increasing their effect as reinforcement.

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Résumé

L'introduction de ponts covalents primaires entre des élastomères linéaires a été suivie en observant le comportement module-température. Le comportement des polymères linéaires est expliquée par association de segments vitreux au sein des régions qui agissent comme charge et comme des ponts. Dans beaucoup de cas, la rupture détruit ces régions et dès lors diminue le module au plateau.

Zusammenfassung

Die Einführung von primären, covalenten Vernetzungen in lineare Segmentelastomere wurde durch Messung ihres Modul-Temperaturverhaltens verfolgt. Das Verhalten linearer Segmentpolymerer wird durch eine Assoziation der glasartigen Segmente zu Bereichen erklärt, welche als Füllstoffe und Quasivernetzungsstellen wirken. In einigen Fällen stört die Vernetzung diese Bereiche und erniedrigt dadurch den "Plateau"-Modul.

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