

Relation of Structure to Properties in Polyurethanes

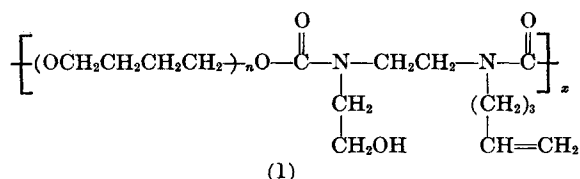
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The present work was undertaken to assess the effect of crosslink structure on the properties of an elastic network derived from a linear polyetherurethane elastomer. In order to study this effect, a polyetherurethane was synthesized which contained two types of reactive sites suitable for establishing crosslinks: pendant hydroxyl groups for reaction with diisocyanate curatives and pendant double bonds for vulcanization with sulfur. Incorporation of both types of curing sites within the same linear polymer served to hold constant variables which might otherwise influence vulcanizate properties. Thus, the elastic networks formed by both curing systems were produced from the same polymer, and such factors as polymer molecular weight and molecular weight distribution, interchain forces and cure site distribution remained constant. Furthermore, the curing sites have been placed on pendant groups well removed from the main polymer chain in order to avoid degradation of the polymer by side reactions which may accompany sulfur vulcanization.

It is recognized that common elastomers with internal unsaturation, such as SBR and natural rubber, can be crosslinked by more than one method (e.g., with sulfur, peroxides, or high energy radiation), but the extent and nature of side reactions which may occur is not known with certainty. There are possibilities of polymer degradation reactions with all of these curing systems, and the occurrence of such degradation reactions would cloud any conclusions concerning the relation between crosslink structure and vulcanizate properties.

Polyetherurethane I was synthesized for the present study:

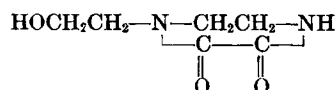


Reaction of the pendant hydroxyl groups with diisocyanates leads to the formation of bisurethane crosslinks, and by proper choice of the diisocyanate curative, the length of the crosslink can be altered readily. Vulcanization through the pendant double bonds with accelerated sulfur systems leads to sulfur-containing crosslinks.

EXPERIMENTAL

Polytetramethyleneether Glycol. This compound was synthesized by an acid-catalyzed polymerization of tetrahydrofuran.¹ The various samples used in this work had hydroxyl numbers ranging from 105.0 to 110.7, corresponding to molecular weights of 1068 to 1014. This glycol was stabilized against oxidation by adding 1 wt.-% phenyl- β -naphthylamine.

***N*-(2-Hydroxyethyl)-*N'*-4-Pentenylethylenediamine.** Alkylation of



with $\text{CH}_2=\text{CH}-(\text{CH}_2)_3\text{Br}$ followed by hydrolysis yielded *N*-(2-hydroxyethyl)-*N'*-4-pentenylethylenediamine. Details of this synthesis are to be reported elsewhere.⁸

Polyetherurethane (I). Polyetherurethane was synthesized by reacting the bischloroformate of polytetramethyleneether glycol with *N*-(2-hydroxyethyl)-*N'*-4-pentenylethylenediamine in chloroform solution with aqueous sodium carbonate as the acid acceptor.² The average spacing of cure sites along the chain was approximately 1200 molecular weight units. Weight-average (light scattering) and number-average (osmotic) molecular weights were 195,000 and 54,000, respectively.

Curing of the elastomers was effected by the three following reagents.

(a) 3,3'-Dimethoxy-4,4'-biphenylene diisocyanate was obtained from The Carwin Company and

purified by vacuum sublimation. Titration with di-*n*-butylamine indicated a purity of 98%.

(b) The isocyanate-terminated polyetherurethane (molecular weight, approximately 5500) was prepared by reacting 4 moles of polytetramethylene glycol and 5 moles of 3,3'-dimethoxy-4,4'-biphenylene diisocyanate.

(c) An accelerated sulfur recipe was used which consisted of: sulfur, 1.0 part phr; mercaptobenzthiazole disulfide, 4.0 parts phr; mercaptobenzthiazole, 2.0 parts phr; mercaptobenzthiazole disulfide·ZnCl₂, 0.7 parts phr; and cadmium stearate, 1.0 part phr. When the sulfur level was varied the other constituents of the recipe were changed in the same relative proportion.

Compounding was carried out on a 2 × 6 in. rubber mill. Stocks were cured at 150°C. for 2 hr. in standard laboratory presses. Vulcanizate physical properties measured were: Yerzley resilience (ASTM D945-52T), compression set (ASTM D395-53T), Shore A hardness (ASTM D676-49T), and modulus on the Instron tensile testing machine at a crosshead speed of 20 in./min.

Crosslink densities were calculated from modulus measurements carried out on samples swollen in toluene. Moduli were measured either in extension or compression. Crosslink densities were computed from eq. (1):

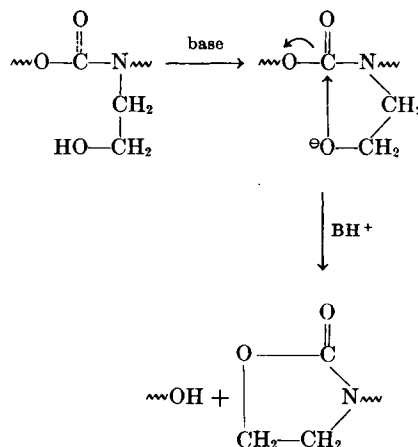
$$\nu_e/V = FV_r^{1/3}/[ART(\alpha - \alpha^{-2})] \quad (1)$$

where ν_e/V represents the moles of effective network chains per milliliter of polymer, F is the force in grams required to obtain an extension ratio of α , V_r is the volume fraction of elastomer in the swollen sample, A is the cross-sectional area of the unswollen sample, R is the gas constant, and T is the absolute temperature. Equation (1) has been shown to be valid in systems where V_r is less than 0.25.³

The sulfur crosslinks introduced by the curing system described above were characterized as follows. A reagent solution was prepared by dissolving 0.65 g. of xylyl mercaptan in 130 ml. of tetrahydrofuran (THF) and adding 1 ml. of 0.5 *M* benzyltrimethylammonium butoxide in *tert*-butanol or 25% benzyltrimethylammonium hydroxide in methanol. Sulfur vulcanizates immersed in this solution dissolved on standing overnight at room temperature. The solutions were filtered to remove traces of insolubles and poured into a

large excess of water to precipitate the solubilized polymers and to remove tetrahydrofuran. The recovered polymers were washed with additional water, dried on a mill at 100°C., and their intrinsic viscosities in a 86.2:13.8 tetrahydrofuran-dimethylformamide mixture (w/w) were determined at 30°C.

Control experiments showed that diisocyanate vulcanizates of polyetherurethane I were insoluble in this basic mercaptan solution. However, both the sulfur and diisocyanate vulcanizates dissolved in a tetrahydrofuran-quaternary ammonium base mixture which was free of mercaptan. Both of these vulcanizates contain unreacted hydroxyl groups so located that a base-catalyzed cleavage of the urethane linkage is likely:



The fact that no high molecular weight polymer could be recovered from the solutions lends support to this hypothesis. Furthermore, a sulfur vulcanizate of a polyether elastomer which was free of urethane linkages was not solubilized by the solution of quaternary ammonium base in tetrahydrofuran, although it did dissolve when mercaptan was present also.

Thioglycolic acid was an effective crosslink cleavage reagent also, although it was much slower in its action than xylyl mercaptan. Seven days were required for solution of the vulcanizates. Thioglycolic acid, however, has the advantage that it is more readily removed from recovered polymer by washing with water. Recovered polymer, redissolved in tetrahydrofuran, was crosslinked and insolubilized instantly upon addition of a small amount of iodine to the solution. Gelation occurred also if the solution was allowed to stand exposed to air for several hours. Results are summarized in Table I.

TABLE I

Reagent mixture	Polyetherurethane I ^a -S vulc.		Polyetherurethane I ^a -DI cure		Polyether ^b	
	Behavior toward reagent	Characteristics of recovered polymer	Behavior toward reagent	Characteristics of recovered polymer	Behavior toward reagent	Characteristics of recovered polymer
THF + xylyl mercaptan + quat. NH ₄ ⁺ base	Dissolved	[η] = 1.70	Insol.	—	Dissolved	[η] = 1.54
THF + thioglycollic acid + NH ₄ ⁺ base	Dissolved	Gelled in air	Insol.	—	Dissolved	Gelled in air
THF + quat. NH ₄ ⁺ base	Dissolved	Low mol. wt. ^c	Dissolved	Low mol. wt. ^c	Insol.	—
THF	Insol.	—	Insol.	—	Insol.	—

^a Intrinsic viscosity of uncured polymer = 1.24.

^b Intrinsic viscosity of uncured polymer = 1.35. Polymer prepared from tetrahydrofuran, diethyloxetane and 2-(pen-tenoxymethyl)-2-methyloxetane by an acid-catalyzed polymerization.⁹

^c A stable, milky suspension was formed when the solution was drowned in water in contrast to the other precipitations where the high molecular weight polymer coalesced.

DISCUSSION

(a) Crosslink Structure and Vulcanizate Properties

The concentration of effective network chains has been used as a parameter to correlate physical properties and crosslink structure. Concentration of effective network chains, rather than crosslink density, was used to avoid ambiguities which can arise in defining a crosslink once the network has been established. If the crosslinks are short, such ambiguities do not appear; there are two network chains per crosslink. However, in systems where long bifunctional molecules are used to crosslink a structurally similar linear polymer, the relationship between the number of crosslinks and the number of network chains becomes obscure. It is then more convenient to use network chain concentration as the correlating parameter. If the molecule used to crosslink the linear polymer is long enough to exert an effect upon the equilibrium modulus, it will be counted properly as a network chain. If not, it will not be so counted.

The vulcanization of polyetherurethane I with 3,3'-dimethoxy-4,4'-biphenylene diisocyanate and accelerated sulfur systems provides crosslinks of different chemical structure. Reaction of the diisocyanates with the pendant hydroxyl groups produces urethane linkages, while sulfur vulcanization at the double bond gives a sulfur-containing bridge between pendant pentenyl groups. Use of a long-chain, isocyanate-terminated polyurethane as the crosslinking agent introduces a segment which is about 19 times longer than that of the former diisocyanate reagent. In this case, the length of the crosslinking agent approaches the length of the network chains themselves.

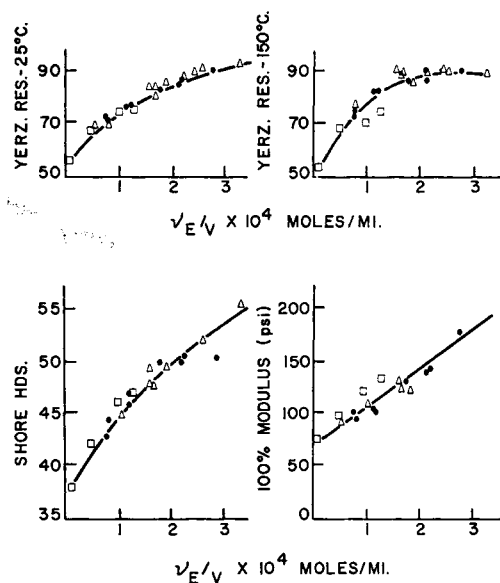


Fig. 1. Dependence of resilience, modulus, and hardness on network chain concentration: (Δ) vulcanization by sulfur; (\bullet) vulcanization by diisocyanate; (\square) vulcanization by isocyanate-terminated polyetherurethane.

Modulus, hardness, and resilience (25 and 150°C.) of the cured polyetherurethane I were found to be essentially independent of both the chemical nature and the chain length of the curing agent. Results are shown in Figure 1, where these properties are plotted as functions of effective network chain concentration.

The results described above were obtained by tests which are nondestructive in nature. That is, the tests were either so short in duration or mild in nature that the specimen was essentially unchanged by subjection to the test. A more destructive test is the measurement of compression set, wherein

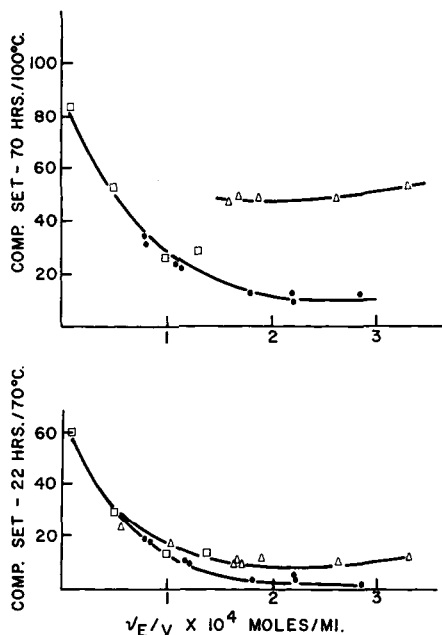


Fig. 2. Dependence of compression set on network chain concentration: (Δ) vulcanization by sulfur; (\bullet) vulcanization by diisocyanate; (\square) vulcanization by isocyanate-terminated polyetherurethane.

the vulcanizate is subjected to high temperatures for relatively long periods of time, thus permitting chemical effects to come into play.

The response of the vulcanizates containing different crosslinks to the compression set conditions distinguished between the two chemically different types of crosslinks. In both tests (22 hr. at 70° and 70 hr. at 100°) the sulfur cures showed consistently higher compression sets than the diisocyanate cures at equivalent crosslink densities (Fig. 2). This difference was due, at least in part, to the thermal instability of the sulfur crosslink formed by the curing system utilized in this study.

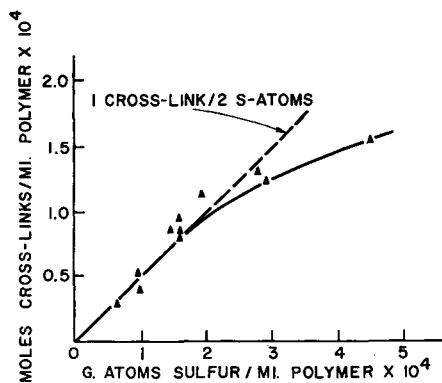
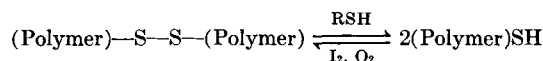


Fig. 3. Dependence of crosslink concentration ($2v_e/V$) on sulfur concentration: (—) experimental; (---) theoretical.

Both chemical and physical evidence is available to show that the sulfur crosslink consists predominantly of disulfides.

The physical evidence is shown in Figure 3, where crosslink concentration is plotted against moles of elemental sulfur per milliliter of elastomer for the polyetherurethane I. Up to a crosslink concentration of approximately 1×10^{-4} moles/ml., which is equivalent to 24% of the double bond curing sites available, two moles of elemental sulfur are required for the formation of one mole of crosslinks. At higher sulfur usages, formation of a crosslink requires more than two moles of sulfur, possibly because the concentration of available cure sites is reduced to the point where the coupling reaction becomes less efficient. The data, however, do not rule out the possibility of a change in the curing mechanism at these high sulfur levels.

Chemical evidence for the formation of disulfide crosslinks is provided by the behavior of these vulcanizates when treated with mercaptans. Thus, when the vulcanizates are treated with either xylyl mercaptan or thioglycollic acid in basic tetrahydrofuran solution, they dissolve to form clear solutions from which high molecular weight polymer can be recovered, and the recovered polymer is crosslinked readily by oxidation (see Experimental). These observations are consistent with the reaction scheme:



The higher compression set of the sulfur vulcanizates is attributable to the lability of the disulfide crosslinks. Application of stress at high temperatures induces rearrangement of the original disulfide crosslinks to relieve the applied stress. Similar behavior of disulfide linkages has been observed in other systems, particularly the polysulfide elastomers.⁴

(b) Equation of State for Rubbery Elasticity

In a polymer of infinite primary molecular weight the introduction of each crosslink results in the formation of two effective network chains. However, in crosslinking elastomers of finite molecular weight some chains are produced which are secured at only one end, the free end being the terminus of the primary molecule. This type of chain is not elastically effective in providing a restoring force for equilibrium deformations, since it is free to flow and relieve the imposed strain. Flory⁵ has

derived a relationship between the numbers of loose chain ends, total chains, and effective chains:

$$\nu_e/V = (\nu/V) - (2N/V) = (\nu/V)[1 - (2N/\nu)]$$

or

$$(2)$$

$$\nu_e/V = (\nu/V)[1 - (2M_c/\bar{M})]$$

where ν/V is the total moles of all types of chains per unit volume, N/V is the moles of uncrosslinked primary molecules per unit volume, M_c is the molecular weight of a network chain, and \bar{M} is the primary molecular weight of the uncrosslinked polymer.

Tests of the validity of the network-statistical theory of rubber elasticity require a method for measuring the degree of crosslinking. Thus, if the efficiency of the cross-linking reaction can be determined, the effective network chain concentration for a polymer of known molecular weight can be computed from eq. (2). Flory, Rabjohn, and Schaffer³ used bisazodicarboxylates as bifunctional coupling agents in natural rubber and obtained apparently good agreement between the statistical theory and the degree of cross-linking. However, the assumption that the coupling reaction was quantitative has been questioned by Moore and Watson.⁶ The latter workers used di-*tert*-butyl peroxide as the curing agent and determined the extent of crosslinking by analyzing the volatile decomposition products. The degree of crosslinking, as measured physically [eq. (1)], was always greater than that measured chemically. The discrepancy was ascribed to the presence of chain entanglements which acted as crosslinks.

In the present work, polyetherurethane I was crosslinked with 3,3'-dimethoxy-4,4'-biphenylene diisocyanate through its pendant hydroxyl groups. The isocyanate-hydroxyl reaction is known to produce urethanes in essentially quantitative yields in nonpolymeric systems,⁷ and on the basis that this reaction retains its quantitative character in the polymer it offers a means for an additional test of the network equation. Note also that the diisocyanate curative was always the limiting reagent. Even at the highest state of cure only 40% of the available hydroxyls would have been utilized for complete reaction with the diisocyanate.

The chemical degree of crosslinking was calculated from the amount of diisocyanate used and the primary molecular weight ($M_n = 54,000$) by means of eq. (2). The physical degree of crosslinking was determined from the equilibrium

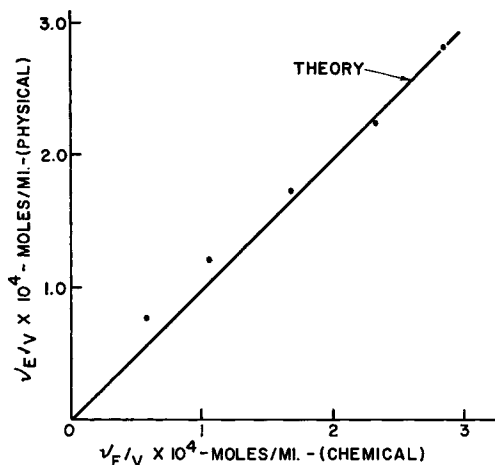


Fig. 4. Comparison of physical and chemical values of degree of crosslinking for diisocyanate cures.

compression modulus of samples swollen in toluene by use of eq. (1). In all cases V_r was less than 0.25.

Physical values of ν_e/V determined from modulus measurements are plotted in Figure 4 against chemical values of ν_e/V derived from the amount of curing agent used by use of eq. (2). The solid line is that required by elastic theory. The agreement is excellent and provides further verification of the network-statistical theory of rubbery elasticity in highly swollen systems ($V_r < 0.25$). That no chain entanglement was observed as in the case of Moore and Watson may be due to differences in primary molecular weight of the polymers used (54,000 in the present work vs. 250,000 for the natural rubber used by the English workers).

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References

- OTS Report P.B. 22697, P.B. 717; K. Hamann, *Angew. Chem.*, **63**, 231 (1951).
- Wittbecker, E. L., P. W. Morgan, and M. Katz, paper presented at 134th National American Chemical Society Meeting, September 1958, Chicago, Ill.
- Gee, G., *Trans. Faraday Soc.*, **42**, 585 (1946); P. J. Flory, N. Rabjohn, and M. C. Schaffer, *J. Polymer Sci.*, **4**, 225 (1949).
- Leandri, G., and A. Tundo, *Ann. chim. (Rome)*, **44**, 63 (1954); E. R. Bertozzi, F. O. Davis, and E. M. Fettes, *J. Polymer Sci.*, **19**, 17 (1956); A. V. Tobolsky, *J. Appl. Phys.*, **27**, 673 (1956).
- Flory, P. J., *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, N. Y., 1953, p. 462.
- Moore, C. G., and W. F. Watson, *J. Polymer Sci.*, **19**, 237 (1956).

7. Parker, J. A., J. J. Thomas, and C. L. Zeise, *J. Org. Chem.*, **22**, 594 (1957); N. G. Gaylord and J. J. O'Brien, *Rec. trav. chim.*, **74**, 218 (1955).

8. Cluff, E. F. and H. F. McShane, to be published.

9. Walter, H. C., Italian Patent 585,572 (to E. I. duPont de Nemours and Co., Inc.).

Synopsis

A polyurethane bearing pendant hydroxyl groups and carbon-carbon double bonds was prepared. Curing was carried out by diisocyanates of different lengths and by an accelerated sulfur recipe. The vulcanizate properties of modulus, hardness, and resilience were found to be independent of both the length and chemical nature of the crosslink. Compression set, however, was always higher for the sulfur cures, an effect which can be attributed to the disulfide structure of this particular crosslink. Both physical and chemical evidence support this structure. Diisocyanate curing of the polyurethane via the hydroxyl groups is a clean-cut, essentially quantitative reaction which provided an absolute method for determining the degree of crosslinking. Excellent agreement was obtained between the physical degree of crosslinking as determined by equilibrium modulus and the chemical degree of crosslinking. This agreement provides further verification of the network-statistical theory of rubber elasticity in highly swollen systems. No chain entanglement was observed.

Résumé

On a préparé un polyuréthane portant un hydroxyle latéral et des doubles liaisons carbone-carbone. Le traitement est effectué au moyen des diisocyanates de différentes longueurs et par un traitement accéléré au soufre. Les propriétés de vulcanisation, dureté et rebondissement sont avérées être indépendantes de la longueur et de la nature chimique du pontage. La compression était toujours plus élevée après traitement au soufre, effet qui peut être attribué

à la structure disulfure de ce pontage. Des évidences autant physiques que chimiques appuient cette structure. Le traitement du polyuréthane au diisocyanate via le groupe hydroxylique est une réaction spécifique et essentiellement quantitative qui fournit une méthode absolue pour la détermination du degré de pontage. On a obtenu un excellent accord entre le degré physique de pontage déterminé par le module d'équilibre et le degré de pontage chimique. Cet accord fournit une vérification supplémentaire à la théorie statistique de l'élasticité du caoutchouc dans les systèmes à haut degré de gonflement. Aucune constriction de chaînes n'a été observée.

Zusammenfassung

Ein Polyurethan mit Hydroxylseitengruppen und Kohlenstoff-Kohlenstoffdoppelbindungen wurde dargestellt. Eine Nachbehandlung mit Diisocyanaten von verschiedener Länge und nach einem Schwefel-Beschleunigerrezept wurde ausgeführt. Die Eigenschaften des Vulkanisats bezüglich Modul, Härte und Rückfederung wurden als unabhängig von der Länge und der chemischen Natur der Vernetzungsstelle gefunden. Der Kompressionseinfluss war aber für die Schwefelvulkanisate immer stärker, ein Effekt, der der Disulfidstruktur dieser speziellen Vernetzungsstelle zugeschrieben werden kann. Sowohl physikalische als auch chemische Befunde stützen diese Struktur. Vulkanisation der Polyurethane mit Diisocyanat über die Hydroxylgruppen ist eine ohne Nebenreaktionen und im wesentlichen quantitativ verlaufende Reaktion und liefert daher eine Möglichkeit zur Absolutbestimmung des Vernetzungsgrades zwischen dem physikalischen Vernetzungsgrad, wie er sich aus dem Gleichgewichtsmodul ergibt, und dem chemischen Vernetzungsgrad besteht ausgezeichnete Übereinstimmung. Diese Übereinstimmung liefert eine weitere Bestätigung der statistischen Netzwerktheorie der Kautschukelastizität hochgequollener Systeme. Es wurde keine Kettenverschlingung beobachtet.

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