

Properties of Hydroxyl-Terminated Polybutadiene-Urethane Systems

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Synopsis

The properties of liquid hydroxyl-terminated polybutadiene (HTPB) stocks cross-linked with isocyanates of different functionalities were intensively investigated. The stocks were modified by inclusion of small proportions of various low molecular weight diols to increase the urethane concentration. The following studies were carried out: (1) the system functionality was varied at a low and relatively constant urethane concentration; (2) the system functionality was varied with the urethane concentration constant but at a higher level; (3) at a constant crosslink density, the urethane concentration was varied by adding low molecular weight diols; and (4) the structure of the diols used in the previous experiments was varied.

A correlation between the per cent functional groups reacted, the average functionality of the system, and the mechanical properties of simple HTPB stocks was attained. Furthermore, a correlation was found between mechanical properties and urethane concentration at constant crosslink density. The properties of the stocks could be varied enormously by addition of low molecular weight diols in relatively small proportions by weight. The structure and concentrations of these diols caused significant variations in the elongation-at-break and tensile strength values.

INTRODUCTION

Polyurethanes have been studied in great detail.¹ For the most part, investigations reported were on systems where the segments between urethane groups were highly polar polyester structures or were polyethers of moderate chain length. By incorporation of trifunctional reactants during the preparation of these materials, crosslinks could be introduced, but more often they were prepared as linear polymers relying on the rigidity or polarity of the structures to produce useful products.

It seems clear that the physical properties of these linear polyurethanes result largely from the formation of hydrogen bonds between C=O and NH groups on the polymer chains,²⁻⁶ although the influence of the chemical structure cannot be neglected.⁷ The mechanical behavior of such stocks has been interpreted as resulting from the presence of hard domains of ordered segments dispersed in amorphous segments of the same polymer chains.¹⁴

Recently, there have become available a number of liquid hydroxyl-terminated polybutadienes (HTPB) which can be formed into elastomers by reaction with polyisocyanates. These contain amorphous, elastomeric,

and nonpolar segments of molecular weight 2500 to 6000 between the urethane structures.⁸ The properties of these elastomers have been discussed by Verdal et al.⁹ Since one must regard these stocks as amorphous, the question has remained as to whether the characteristics of these materials are due mainly to the presence of crosslinks, of hydrogen bonds between chains, or of bulky or polar groups contributed by the crosslinking agent or other additives. The present work was undertaken to determine the mechanical properties of HTPB systems, with and without low molecular weight diol additives, while accounting for or eliminating formulation and network variables.

EXPERIMENTAL

Materials

The prepolymers used in the work were HTPB of molecular weights in the range of 1500–6000. Samples were obtained from Phillip's Petroleum Company (Butarez HT series), General Tire and Rubber Company (Tela-gen HT series), and Arco Chemical Company (R45M). These prepolymers were used without further purification. The crosslinking agents were polyfunctional isocyanates, Isonate 390P, Isonate 143L, and Papi, obtained from the Upjohn Company, and a difunctional isocyanate, Isophorone diisocyanate, IPDI, obtained from Scholven Chemie AG. Some properties of the isocyanates are reported in Table I.

Diethanol cyclohexylamine was obtained from the Ames Laboratories,

TABLE I
Compounding Ingredients

Abbreviation or trade name	Chemical name	Func- tional- ity	Equiv. wt.	Reac- tive group concs., meq/g	Supplier
Isonate 390P	unknown	2.50	129	7.77	Upjohn
Isonate 143L	unknown	2.00	125	8.00	Upjohn
PAPI	polymethylene polyphenylisocyanate	3.0	132	7.58	Upjohn
IPDI	isophorone Diisocyanate	2.00	111	9.02	Scholven
CHDM	1,3-cyclohexanedimethanol	2.00	72.2	13.87	Eastman
BHMTD	4,8-bishydroxymethyltricyclo-[5.2.1.0 ^{2,6}]decane	2.00	98.0	10.2	Aldrich
DECHA	N,N-diethanol cyclohexylamine	2.00	93.5	10.7	Ames Labs
DEPD	2,2-diethyl-1,3-propanediol	2.00	116.0	8.62	Aldrich
C-1	2,3-dihydroxypropylbis-2-cyanoethylamine	2.00	98.5	10.14	Aerojet
DOS	dioctyl sebacate	—	—	none	Rohm & Haas
Tufflo Oil 6024	naphthenic hydrocarbon oil	—	—	none	Arco
Oronite 6	liquid polybutene	—	—	none	Chevron

Inc., and 1,4-cyclohexane dimethanol from the Eastman Chemicals Products, Inc. Both 2,2-diethyl-1,3-propanediol and 4,8-bis(hydroxymethyl)-tricyclo[5.2.1.0^{2,6}]decane were obtained from Aldrich Chemical Company, while 2,3-dihydroxypropyl(bis-2-cyanoethyl)amine was obtained from Aerojet General Corp. All the low molecular weight diol chain extenders were used without further purification. (See Table I).

The plasticizers employed in the study were dioctylsebacate from Rohm and Haas, Tufflo Oil 6024 (a naphthenic-type hydrocarbon oil) from Arco Chemical Company, and Oronite 7 (a polybutene) from Chevron Chemical Company.

Characterization of the HTPB

The characterization of several HTPB resins was reported in an earlier publication.¹⁰ Determination of molecular weight, equivalent weight, and functionalities of the prepolymers were discussed.

Determination of Isocyanate Content

The isocyanate content of the curing agents was determined by the standard method of reacting an excess of di-*n*-butylamine with the isocyanates.¹¹

Functionality of the Isocyanates

The functionality of the isocyanates was calculated by dividing the molecular weight by the equivalent weight. Molecular weight determinations were made using the Hitachi Perkin Elmer Model 115 vapor pressure osmometer. (See Table I).

Preparation of Stocks

Gumstocks were prepared by reaction of the prepolymers with isocyanates and curing at 80°C for 48 hr in a closed Teflon-coated mold. Isocyanate-to-hydroxyl ratios were 1.00 and 1.10. Various systems were studied to follow the effect of plasticizers, urethane concentration, and structure of chain extenders on the mechanical properties of the gumstocks.

Swelling Tests

Swelling tests were run to determine the state of cure of the crosslinked binder stocks. Samples of gumstocks weighing approximately 200–250 mg were covered with reagent-grade mixed xylene and sealed in a container for seven days at room temperature. The swollen stock was removed from the solvent and weighed to determine the solvent uptake. After drying the swollen stock under vacuum, the stock was reweighed to obtain the dry weight, and the RNB number, the relative number of crosslinking bonds, was calculated from the equation

$$\text{RNB number} = V_2^{1/2} \times \text{per cent gel}$$

where V_2 = volume fraction of polymer in the solvent-swollen gel.

RESULTS AND DISCUSSION

Gel Point and Maximum Extent of Cure

The extent of reaction of the HTPB resins at the gel point and the final maximum extent of reaction with several polyfunctional isocyanates were determined using previously published methods.^{10,12} The maximum extent of reaction was determined by extrapolation of the nearly flat extent-of-reaction-versus-time curve. Results are shown in Table II. When prepolymers which are approximately difunctional are reacted with Isonate 143L, whose functionality is 2.0, almost 100% of the functional groups are reacted. However, as the average functionality of the system increases from 1.97 to 2.52, as measured by the per cent reacted at the gel point, the final extent of reaction decreases to 68%. That is, the higher the average functionality of the system, the lower the maximum degree of reaction of the functional groups.

The average functionality of the system was calculated using the relationship

$$f_{AV} = \frac{(1+r)f_1f_2}{rf_1+f_2}$$

where f_1 = average functionality of the hydroxyl-containing moles, f_2 = average functionality of the isocyanate containing moles, and r = initial equivalents isocyanate per equivalent of hydroxyl.

Variation With Functionality

Variations in mechanical properties of HTPB stocks were observed when different structured isocyanates, chain extenders, and plasticizers were employed. The properties can also be varied by changing the average functionality of the system and thereby establishing a correlation between mechanical properties and the average system functionality or urethane concentration. However, different prepolymer systems cannot be compared with one another without taking all variables into account. For example, Butarez HTS is different in molecular weight and functionality from R45M. Since the molecular weight of the prepolymers vary, the molecular weight between crosslinks and the concentration of urethane groups in cured stocks will also vary, affecting mechanical properties and making a correlation between different prepolymer systems difficult. In this work, only the R45M systems were studied in great detail.

Gumstocks were made using Arco R45M with various ratios of the following isocyanates; Isonate 143L, Papi, and Isophorone diisocyanate (IPDI). These stocks gave an average functionality in the range of 2.25 to 2.78, as shown in Table III. A plot of both elongation at break and tensile strength versus average functionality of the system gave curves as illustrated in Figure 1.

TABLE II
Extent of Reaction and Functionality

Prepolymer	Crosslinking agent	Reactant ratio ^a	Funct. crosslinking agent	Funct. prepolymer	Per cent reacted at gel point	Final per cent reacted	Average funct. of system
HTPB D	Isonate 143L	1.15	2.00	1.94	96	98	1.97
HTPB F	Isonate 143L	1.15	2.00	1.99	94	95	2.00
HTPB I	Isonate 143L	1.10	2.00	2.10	91	95	2.04
HTPB C	Isonate 390P	1.0	2.50	1.94	84	83	2.18
HTPB G	Isonate 390P	1.0	2.50	1.99	82	83	2.22
HTPB H	Isonate 390P	1.0	2.50	2.54	65	68	2.52

^a Equivalents crosslinking agent reactive groups per equivalent prepolymer reactive groups.

TABLE III
Variation of the Average Functionality

Arco R45M	92.12	91.28	91.16	91.09	91.02	90.96	90.89	90.83	90.74	90.68	90.60	90.53
Isonate 143L		8.72	7.96	7.13	6.29	5.42	4.56	3.67	2.78	1.86	.94	
Papi			.88	1.78	2.69	3.62	4.55	5.50	6.48	7.46	8.46	9.47
IPDI	7.88											
NCO/OH	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Average functionality of system	2.25	2.25	2.29	2.33	2.38	2.42	2.47	2.52	2.58	2.62	2.70	2.77
Isocyanate content, meq/g	0.709	0.698	0.702	0.701	0.701	0.700	0.700	0.698	0.699	0.698	0.698	0.697
Tensile strength, psi	77	98	87	82	102	116	110	94	94	108	100	108
Elongation at break, E_b , %	238	250	226	271	167	167	173	150	125	167	157	147

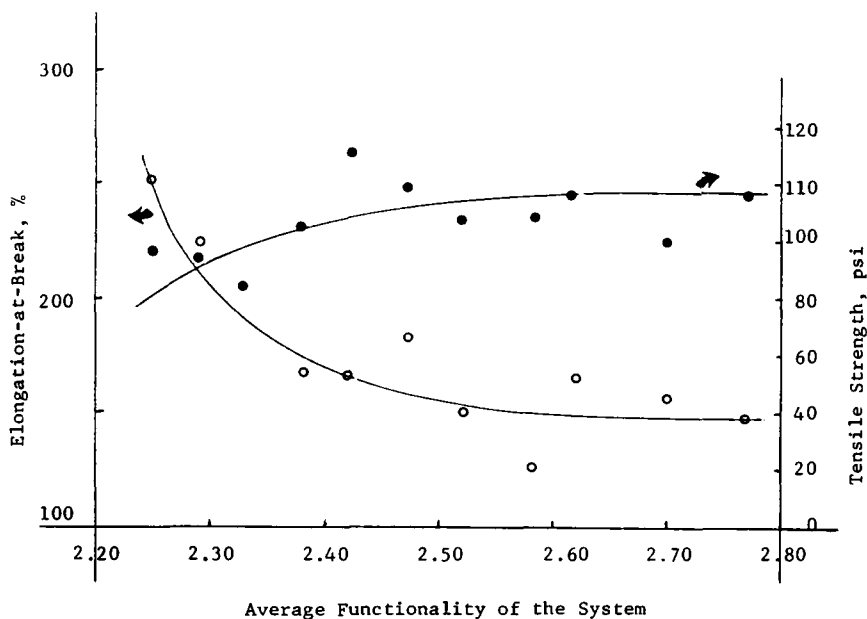


Fig. 1. Correlation of the average functionality with mechanical properties.

It is observed that tensile strength rises with increasing average system functionality and reaches a rather low maximum at 110 psi, while the elongation at break continuously decreases. This behavior is characteristic of amorphous elastomeric gumstocks.

Variation with Functionality in Presence of Added Urethane Groups

The mechanical properties of hydroxyl-terminated polybutadiene systems may be varied by addition of low molecular weight diols. If the level of isocyanate curative is raised to accommodate this addition, the result is an increase in urethane concentration in the cured stocks. Since urethane groups are strongly hydrogen bonded, the stocks will exhibit increased stiffness and tensile strength. Furthermore, since the diols to be employed as additives would have a functionality of 2, chain extension will take place during cure if the HTPB prepolymer has a functionality greater than 2, as is true with R45M. The proportion of diol needed in a binder stock to change the properties will be less than 10% since the molecular weights of the diols will generally be less than one tenth that of the prepolymer.

Diols employed as additives are shown in Table I. A series of gumstocks were made using cyclohexanedimethanol to increase the concentration of urethane groups and curing with various isocyanates as shown in Table IV. The total isocyanate group concentration was 1.23 meq/g for the stocks in Table IV, and 0.70 meq/g for the stocks in Table III. Results are shown in Tables III and IV and Figure 2. A comparison of the two curves in

TABLE IV
Effect of the Addition of a Diol on Mechanical Properties

Arco R45M	80.12	79.95	79.99	79.80	79.63	79.27	79.16	79.08
Isonate 143L	15.43	11.87	11.93	8.10	4.16			
Isonate 390P		3.74		7.67	11.80		4.21	
Papi			3.65			8.17	12.24	16.54
1,4-Cyclohexanedimethanol	4.45	4.44	4.43	4.43	4.41	4.39	4.39	4.38
R45M/Diol	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
NCO/OH	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Average functionality of system	2.12	2.17	2.20	2.23	2.29	2.46	2.51	2.57
Isocyanate content, meq/g	1.234	1.233	1.223	1.229	1.226	1.220	1.232	1.217
Tensile strength, psi	292	288	322	261	249	251	215	210
Elongation at break, E_b , %	256	263	343	213	173	206	193	243

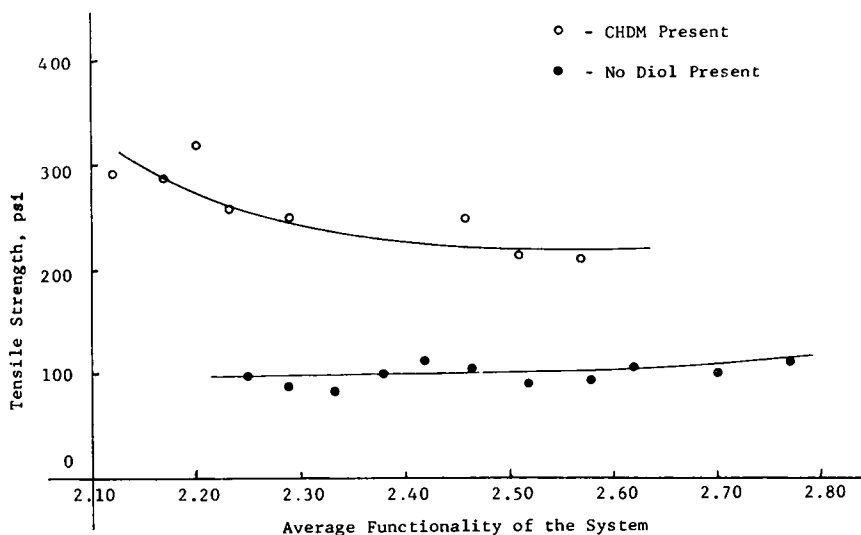


Fig. 2. Variation of tensile strength with crosslink density.

Figure 2 shows that similar-shaped tensile strength curves are obtained with and without the diol. However, both higher elongation-at-break and tensile values were obtained when CHDM was incorporated in the system. This increase in mechanical properties when the chain extenders were used can be attributed to an increase in the concentration of urethane groups and to the structure of the diol additive.

It should be noted that addition of less than 5% of CHDM more than doubled the tensile strength while maintaining the same elongation range and in some cases increasing the elongation-at-break.

Variation in Urethane Concentration at Constant Crosslink Density

Table V show stocks prepared with various amounts of the five diols listed in Table I and plasticized with dioctyl sebacate at a 30% level. These stocks were so formulated that the diol concentration, and hence the urethane concentration, varied but the covalent crosslink density as predicted from formulation parameters was fairly constant in all cases. To check on the uniformity of the crosslink density, swelling tests were run.

Swelling tests have been used extensively in determining the state of cure of crosslinked binder stocks. We have calculated from the results of such tests what we call the RNB number. The RNB value is the relative number of crosslinking bonds. It is calculated as follows:

$$\text{RNB} = V_2^{4/3} \times \text{per cent gel}$$

where V_2 = volume fraction of polymer in the solvent-swollen gel, excluding filler. The RNB number is approximately proportional to the number of chemical bonds at the branch points. This treatment is derived from the modified equation of Flory¹³ relating solvent swelling and crosslink density.

Average functionality of system	2.24	2.11	2.15	2.17	2.18	2.19	2.22
Isocyanate content, meq/g	0.538	0.926	0.747	0.680	0.646	0.625	0.610
Tensile strength, psi	80	59	58	52	56	49	45
Elongation at break E_b , %	166	189	182	170	179	172	161
Arco R45M	63.28	54.50	58.57	60.06	60.83	61.31	61.63
Isonate 143L	6.72	11.58	9.32	8.50	8.08	7.81	7.64
DOS	30.00	30.00	30.00	30.00	30.00	30.00	30.00
DECHA ^c	—	3.92	2.11	1.44	1.09	0.88	0.74
R45M/DECHA	—	1.00	2.00	3.00	4.00	5.00	6.00
NCO/OH	1.10	1.10	1.10	1.10	1.10	1.10	1.10
Average functionality of system	2.24	2.11	2.15	2.17	2.18	2.19	2.19
Isocyanate content, meq/g	0.538	0.926	0.746	0.680	0.646	0.625	0.611
Tensile strength, psi	80	57	54	48	36	37	32
Elongation at break E_b , %	166	640	532	524	428	354	264
Arco R45M	63.28	54.36	58.48	60.00	60.79	61.28	61.83
Isonate 143L	6.72	11.54	9.31	8.49	8.07	7.80	7.63
DOS	30.00	30.00	30.00	30.00	30.00	30.00	30.00
BHMTD ^d	—	4.10	2.21	1.15	1.14	0.92	0.78
R45M/BHMTD	—	1.00	2.00	3.00	4.00	5.00	6.00
NCO/OH	1.10	1.10	1.10	1.10	1.10	1.10	1.10
Average functionality of system	2.11	2.15	2.17	2.18	2.19	2.204	2.210
Isocyanate content, meq/g	0.538	0.923	0.745	0.679	0.646	0.624	0.600
Tensile strength, psi	80	75	66	44	38	26	61
Elongation at break E_b , %	166	393	402	552	606	642	195
RNB	2.66	2.20	2.39	2.65	2.65	2.70	2.46
							2.50
							2.40
							2.47

^a 2,2-Diethyl-1,3-propanediol.

^b 2,2-Dihydroxypropyl(bis-2-cyanoethyl)amine.

^c Diethanolylohexylamine.

^d 4,8-Bis(hydroxymethyl)tricyclo[5.2.1.0^{2,5}]decane.

The use of swelling data to show the constant nature of the covalent crosslink density in these stocks assumes that in the swollen state the polymer chains are separated from each other and that hence extra effects due to the added diol such as steric hindrance, hydrogen bonding, etc., are not operative. On the other hand, the unswollen solid stock would be expected to show the effects of secondary factors, as is well known to occur in urethane systems.

The series of stocks employing CHDM and BHMTD as chain extenders shown in Table V were selected for swelling tests. An average deviation of 7.5% was obtained for the RNB values of the two series, thus indicating that the crosslink density is fairly constant. On the other hand, elongation-at-break varied from 166% to 642%, a total variation of 118% of the median.

Results are plotted in Figures 3 and 4 in terms of tensile strength and elongation-at-break against the concentration of isocyanate. Since the stocks were mixed at a constant isocyanate-to-hydroxyl ratio, the concentration of isocyanate will be proportional to the urethane concentration in the cured stocks. This will be nearly true since according to previously obtained results the final extent of reaction in these stocks will show a total variation of from 78% to 86% only.

The elongation curve for CHDM, Figure 3, reaches a maximum and then drops off, while the tensile curve, Figure 4, increases as the urethane concentration is increased.

Effect of Diol Structure

A result of the present work was the great differences found among stocks made with various diol additives, as shown in Figures 3 and 4. Considering all the diols, C_1 was least effective. The elongation-at-break values for the C_1 system were only slightly higher than those for the stock containing plasticizer and no additive. A possible explanation for this difference can be attributed to the structure of C_1 , which contains adjacent hydroxy groups shielded by two cyanoethyl groups. The adjacent groups can sterically hinder both hydroxyl groups from forming a urethane linkage. Employment of C_1 as a chain extended did not increase the elongation-at-break over that of the nonchain extended, as evidenced by the curve in Figure 3. It was assumed that the reaction of both hydroxyl groups did not take place.

The structures of 4,8-hydroxymethyltricyclo[5.2.1.0^{2,6}]decane (BHMTD) and cyclohexanedimethanol (CHDM) are similar to each other in that both compounds contain hydroxymethyl groups on a ring.

Elongation curves for BHMTD and CHDM reach a peak and then decline, as shown in Figure 3. This is in direct contrast to the elongation curves for 2,2-diethylpropanediol and diethanol cyclohexylamine, which do not peak in the range studied but just increase. One may assume that the bulky rings prevent close packing of the polymer chains. At high con-

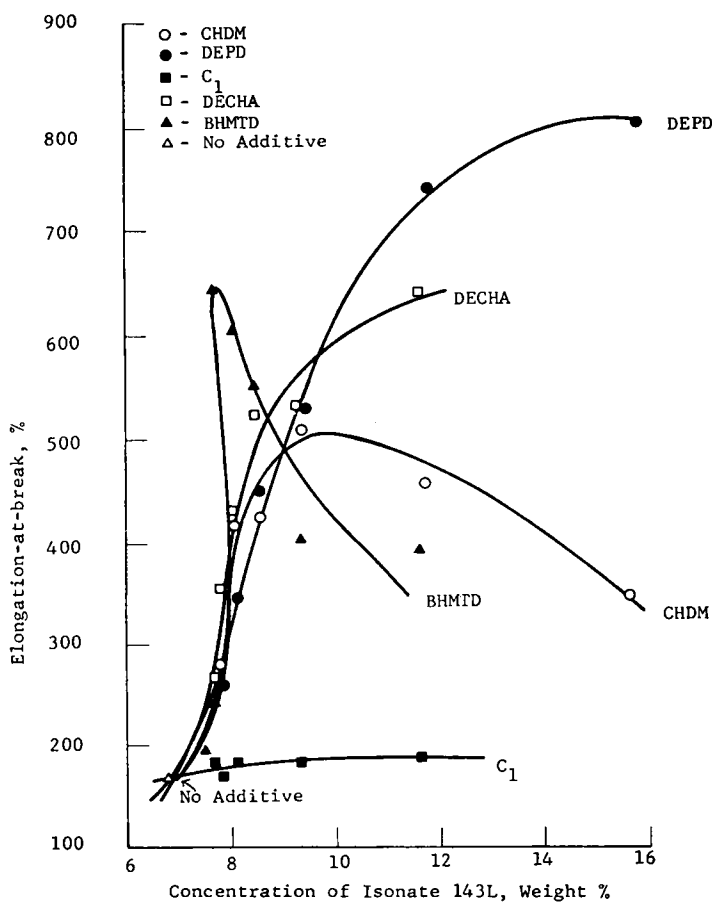


Fig. 3. Variation of E with urethane group concentration at constant crosslink density—effect of various diol structures.

centrations, when the ratio of R45M/diol is 1, the high number of bulky rings present may prevent the polymer chains from readily slipping by one another. An increase in elongation was observed as the bulkiness of the chain extenders increased; below an Isonate 143L concentration of 8 wt-%. Above 8 wt-%, DEPD and DECHA continued to increase in elongation, while the stocks with more rigid or bulky groups decreased.

In regard to tensile strength, as we examine Figure 4, which relates tensile strength and concentration of Isonate 143L, we find at particular isocyanate concentrations marked differences between the curves resulting from the use of different diols in the formulation. The differences must result in some way from the different structures of the diols. Only the CHDM system gave a significantly higher tensile strength than when no diol was employed.

Additional stocks for the BHMTD system were made where the R45M/

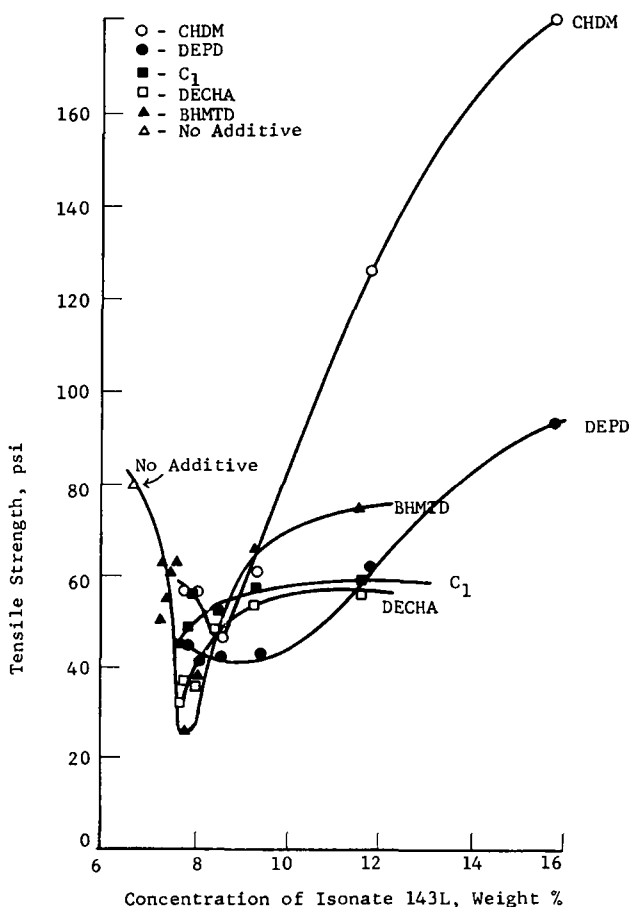


Fig. 4. Variation of tensile strength with urethane group concentration at constant crosslink density—effect of various diol structures.

diol ratio was increased to 10. These high-ratio stocks were made to see what effect low concentrations of diol would have on the tensile strength and elongation at break. On the elongation curve for BHMTD system, the elongation-at-break values decrease as we lower the diol concentration below 8%, approaching the point where no diol was present. On the tensile curve, a minimum is reached at about 7.75 wt-% Isonate 143 L and then the tensile strengths increase in value below this point, approaching the point where no diol was present. The minimum in the tensile strength curves corresponds to the maximum in the elongation-at-break curves. From Figures 3 and 4, it is apparent that R45M/diol ratios in the range of 5 to 10 are very significant in that sharp declines in tensile strength and sharp increases in elongation-at-break values were observed. One can assume that small decreases in the average functionality of the system and small increases in molecular weight between crosslinks are much more

important than small increases in urethane concentrations and are therefore responsible for the initial sharp slopes in the tensile and elongation-at-break curves. At approximately 8 wt-% of Isonate 143L, the effect of urethane concentration and diol structure became significant. The tensile values for all systems began to increase owing to the rise in urethane concentration, but the shape of the curves varied greatly. We can attribute the variation of the shape of the tensile and elongation-at-break curves, above 8 wt-% Isonate 143L, to the variation in the structure of the low molecular weight diols, as this was the only variable known to be present.

CONCLUSIONS

In conclusion, a correlation between the per cent of functional groups reacted, the average functionality of the system, and the mechanical properties of simple HTPB stocks has been attained. Furthermore, a correlation has been established between mechanical properties and urethane concentration at constant crosslink density for HTPB stocks containing low molecular weight diols. However, this correlation is dependent on the structure and type of additives employed in the formulation of the cured system as well as the effect of hydrogen bonding. There appears to be no essential contradiction between this idea and an interpretation based on the formation of domains of ordered structures,¹⁴ since one may regard the domains as resulting from hydrogen bonding. It is believed that crystalline structures were not present in the soft stocks examined here.

The authors wish to thank the sponsor of this work, the Naval Ordnance Systems Command, Task Assignment ORD-331-001-067-//UF19-332-303, for permission to publish this work; Morgan King, John E. Woodall, and Dr. Albert S. Tompa of this laboratory, for help in some of the work; and the General Tire and Rubber Company, The Phillips Petroleum Company, the Arco Chemical Company, the Upjohn Company, and the Schloven-Chemie AG for some samples of material and much advice and information.

The opinions or assertions made in this paper are those of the authors and are not to be construed as official or reflecting the views of the Department of the Navy or the naval service at large.

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Revised June 30, 1971.