Development of Cast Urethane Elastomers for Ultimate Properties

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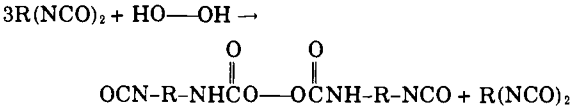
WITH THE ADVENT OF commercially available organic diisocyanates, great interest has been aroused in the preparation of useful products from them, particularly in the field of foams, coatings, and elastomers. Extensive research has been reported on the variables that influence foam properties and structure (*3*), but relatively little has been reported on the influence of structure on the physical properties of the solid urethane elastomers used today. This article is concerned with variations in properties that can be obtained by structural changes arising from the use of different polyesters, diisocyanates, chain extenders, and cross linking. As a result, an improved insight into the prediction of urethane elastomer properties and design of elastomers for specific applications is anticipated.

A preliminary study of the effects of certain variations in diisocyanate and polyester in the "water cross-linked" Vulkollan (Farbenfabriken Bayer, A.G.) was reported by Bayer and coworkers (*2*). Further research led to the "glycol extended" system, which is widely used today (*7, 8, 9*). Some of the original work with this glycol extended system has been repeated and other aspects have been investigated here.

To facilitate understanding the variations introduced in this work, a brief discussion of the chemistry as reported by Bayer is desirable (*2*). In the preparation of these elastomers, a linear hydroxyl-terminated polyester reacts with excess diisocyanate to yield a prepolymer:



$$3\mathrm{R(NCO)_2} + \mathrm{HO}\text{—}\mathrm{OH} \rightarrow \mathrm{OCN\text{-}R\text{-}NH}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{O}\text{—}\mathrm{O}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{NH\text{-}R\text{-}NCO} + \mathrm{R(NCO)_2} \qquad (1)$$

The prepolymer containing excess diisocyanate then reacts under controlled conditions with a polyfunctional compound of low molecular weight—for example, an aliphatic glycol—so that long-chain isocyanate terminated molecules are formed.

$$2\,\mathrm{OCN\text{-}X}\text{—}\mathrm{X\text{-}NCO} + \mathrm{HO\text{-}R\text{-}OH} \rightarrow \mathrm{OCN\text{-}X\text{—}X\text{-}X\text{-}R\text{-}X\text{-}X}\text{—}\mathrm{X\text{-}NCO} \qquad (2)$$

In the simplified formulas, *X*'s are included to indicate the presence of urethane groups, although the actual number is not indicated.

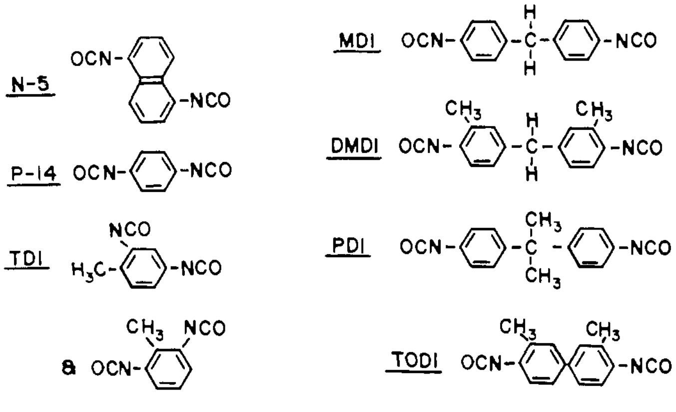
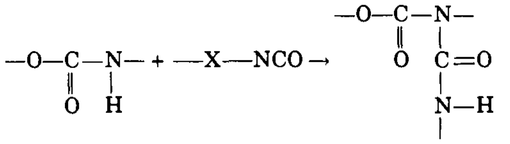


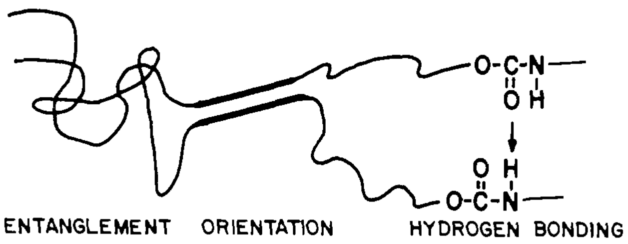
Figure 1. Structure of diisocyanates studied

The extended chains are then cross-linked under the influence of heat by reaction of the isocyanate groups with urethane groups to form allophanate linkages (*2*).



$$-\mathrm{O}-\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-\underset{\underset{\mathrm{H}}{|}}{\mathrm{N}}- + -\mathrm{X}-\mathrm{NCO} \rightarrow \begin{array}{l} -\mathrm{O}-\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{N}- \\ \qquad\quad \mathrm{C{=}O} \\ \qquad\quad \mathrm{N{-}H} \end{array} \qquad (3)$$

While solidification resulting from the chain extension and cross-linking is usually rapid, final cure is promoted by further heating of the polymer for several hours. Some of the possible occurrences other than cross linking which may account for the final properties of the elastomer are chain entanglement, hydrogen bonding, and orientation of molecules.



EXPERIMENTAL

The elastomers were all prepared in the same way (*8, 9*), with only minor variations where necessary for individual materials. Prepolymer was prepared by adding diisocyanate to molten polyester at approximately 130° C. A pressure of 50 to 75 mm. of mercury was maintained to remove entrapped air or gases evolved during the reaction. Chain extension was accomplished by adding liquid extender to the prepolymer at 125° C. with stirring.

The liquid mixture was cast into test sample molds and cured for 20 to 30 minutes at 110° C., removed from the molds, and cured in a 110° C. oven overnight. In all experiments 0.1 equivalent of polyester, 0.32 equivalent of diisocyanate, and 0.2 equivalent of chain extender were used. Test methods were standard ASTM methods, except tear strength, which was measured by Federal Testing Method FTMS-601/M4221 (*4*). Solvent swelling was measured by immersing a 1.0 × 1.0 × 0.1-inch sample in the solvent at room temperature until maximum swelling had been reached and maintained for several hours.

Influence of Diisocyanate. The techniques indicated above were used to prepare elastomers from the diisocyanates illustrated in Figure 1. In these experiments the polyester was polyethylene adipate (hydroxyl number 56, acid number 1), and the extender was 1,4-butanediol. Table I shows the physical properties of these elastomers. The elastomers prepared do not necessarily represent the optimum balance of starting materials for each isocyanate. The experiments were designed to use equivalent stoichiometric amounts of the various diisocyanates in order to be able to draw conclusions on the effect of molecular structure on properties.

Assuming essentially the same degree of polymerization in each case, some possible effects of isocyanate structure are suggested as follows. The influence of bulky, rigid molecules was demonstrated by a comparison of the

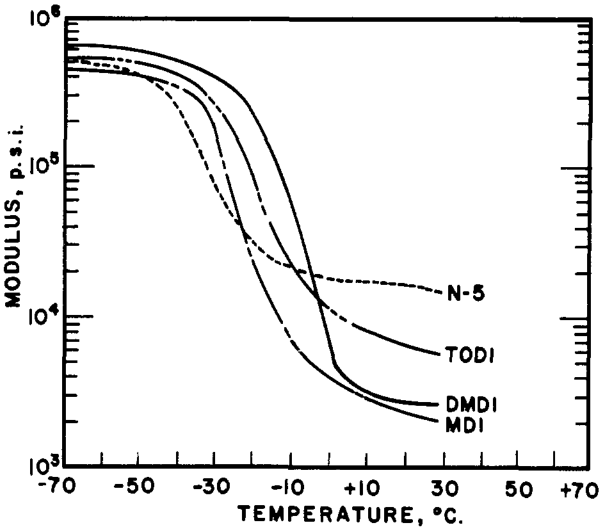


Figure 2. Influence of dissocyanate on modulus-temperature variation of elastomers made from poly(1,4-ethylene adipate)

naphthalene diisocyanate (N5) elastomer with that from *p*-phenylene diisocyanate (P-14). With the increased bulkiness and rigidity, substantial increases in hardness and 300% modulus were noted. A comparison of the elastomers from tolylene (TDI) and *p*-phenylene diisocyanates readily demonstrated the effect of reduced symmetry combined with methyl substituents. Where methyl substituents were present, and symmetry was reduced, a general decrease in tensile, modulus, tear, and hardness was found. A similar effect of methyl groups was shown in a comparison of these diisocyanates: diphenylmethane (MDI), dimethyldiphenylmethane (DMDI), and diphenylisopropylidene (PDI). This effect of methyl groups can very likely be attributed to the induced spatial separation of adjacent polymer chains, resulting in an increased mobility of local segments. The result of increased flexibility within the diisocyanate molecule was indicated by a comparison of the dimethyldiphenylmethane diisocyanate elastomer with that from bitolylene diisocyanate (TODI). There is probably less flexibility associated with the carbon-carbon bond of the bitolylene molecule than with the methylene bridge in the diphenylmethane nucleus. The apparently decreased flexibility resulted in increased hardness, tear strength, and modulus. At the same time ultimate tensile and elongation were decreased.

Table I. Physical Properties of Cast Urethane Elastomers as Influenced by Diisocyanate

Diisocyanate	Tensile Strength, P.S.I.	Elongations %	Elongations Set, %	Modulus, P.S.I., 300% Elong.	Tear Strength, Lb./In.	Hardness, Shore B
N-5	4300	500	85	3000	200	80
P-14	6400	600	25	2300	300	72
TDI	4600	600	1	350	150	40
MDI	7900	600	10	1600	270	61
DMDI	5300	500	0	600	40	47
PDI	3500	700	10	300	90	56
TODI	4000	400	10	2300	180	70

Generally, polymers of higher tensile strength, tensile modulus, tear strength, and hardness are associated with diisocyanate molecules of greatest symmetry and rigidity.

Flexibility of the molecule and spatial separation by methyl side chains were associated with softer, more elastic polymers. These observations indicate that the diisocyanate structure plays a major part in governing the tendency of chains to orient within the polymer. The diisocyanate structure thus exhibits an important influence on the van der Waals forces and hydrogen bonding potential within the polymer.

The influence of the diisocyanate on low temperature properties of these urethane elastomers is shown in Figure 2, a plot of Clash-Berg torsional modulus against temperature. This figure indicates that the glass transition temperature was affected only moderately by the structure of the diisocyanate when compared to other changes.

Influence of Polyesters. Previous investigations showed an optimum molecular weight of 2000 for the polyester in naphthalene diisocyanate–poly(ethylene adipate) elastomers (*8*). Approximately this molecular weight was used in these studies.

Gross changes in the properties of the urethane elastomers can be most readily introduced by varying the structure of the major component of the polymer—i.e., the polyester. The structure of the various polyesters examined are shown in Figure 3. In all cases the elastomers were prepared from diphenylmethane diisocyanate and extended with 1,4-butanediol. Physical properties of the elastomers prepared from these polyesters are listed in Table II. These data do not necessarily represent the optimum obtainable for the individual polyesters, but rather are those obtained from stoichiometrically equivalent formulations.

The following explanations are considered appropriate for polymers containing both ester groups and hydrogen donor groups—e.g. urethane—so that the ester groups may participate in hydrogen bonding. Thus, the relations are somewhat different from that expected for pure polyesters.

Generally, tensile strength and 300% modulus were more nearly functions of the presence of side chains than of ester group separation. This was shown by a comparison of the data for the first four polyesters listed. The tensile and modulus of the elastomer prepared from poly(1,3-butylene adipate), a polyester containing methyl side chains, were significantly lower than for the elastomers prepared from strictly linear polyesters. There was little significant difference noted between the tensile strength and modulus in elastomers of linear adipate polyesters. A similar observation may be made for the polyesters of succinic acid.

Tear strength was apparently dependent on both the presence of methyl side chains and ester group separation, because it decreased significantly in the elastomers made with poly(1,5-pentylene adipate) and with poly(1,3-butyl-

Table II. Physical Properties of Cast Urethane Elastomers as Influenced by Polyester

	Tensile Strength, P.S.I.	Elongation %	Elongation Set, %	Modulus, P.S.I., 300% Elong.	Tear Strength, Lb./In.	Hardness, Shore B	Specific Gravity
Polyester	6900	590	15	1550	240	60	1.25
Ethylene adipate	6000	510	15	1900	280	70	1.21
1,4-Butylene adipate	6300	450	10	1800	60	60	1.17
1,3-Butylene adipate	3200	520	15	1100	100	58	1.19
Ethylene succinate	6800	420	40	3200	200	75	1.32
2,3-Butylene succinate	3500	380	105	[a]	520	85	1.24
Neopentyl succinate	2600	400	70	2000	230	67	1.22

[a] Exhibited cold drawing.

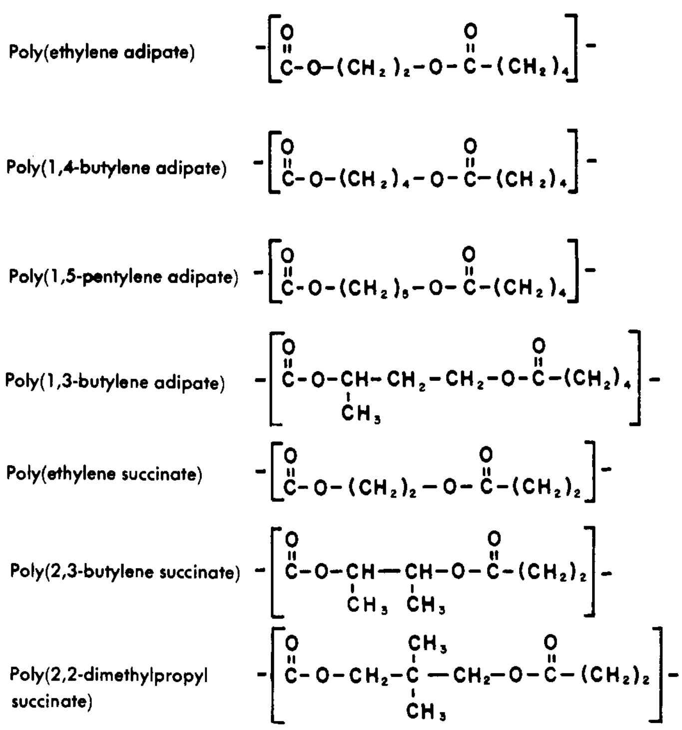


Figure 3. Structure of polyesters studied

ene adipate) as compared to those made from poly(ethylene adipate).

The specific gravity appeared to be a function of either the glycol chain length or the percentage of ester groups present. Where linear polyesters were used, there appeared to be a relation indicated between glycol chain length and specific gravity, with longer chain glycol polyesters yielding elastomers of lower specific gravity.

The torsional modulus for these elastomers was plotted as a function of temperature in Figure 4. The stiffening at low temperatures varied and was apparently dependent on the ester group separation within the polyester. Curves 1 and 2 represent poly(1,4-butylene adipate) and poly(1,5-pentylene adipate) elastomers. These showed a significant decrease in the glass transition temperature compared to the poly(ethylene adipate) elastomer, shown as curve 3. Closer spacing of ester groups as in the polyesters of succinic acid (curves 4, 5, and 6) resulted in the transition occurring at a higher temperature.

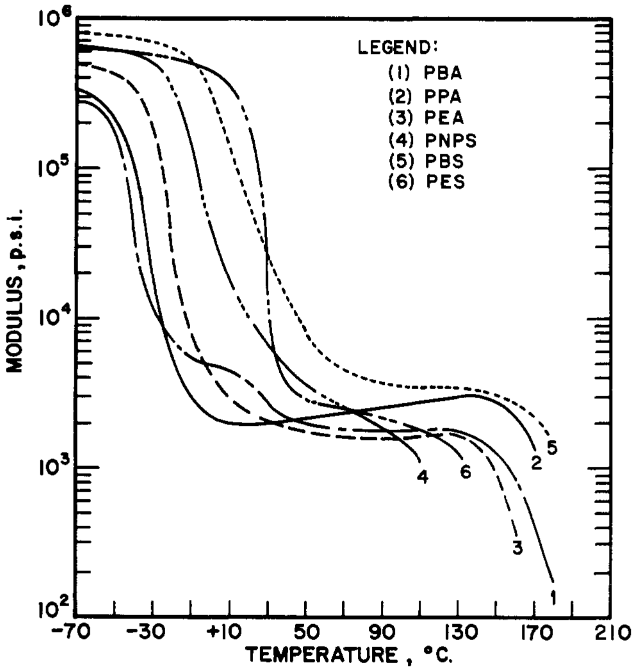


Figure 4. Polyester influence on modulus-temperature of elastomers prepared with 4,4′-diphenylmethane diisocyanate and extended with 1,4-butanediol

1. Poly(1,4-butylene adipate)
2. Poly(1,5-pentylene adipate)
3. Poly(ethylene adipate)
4. Poly(2,2-dimethylpropyl succinate)
5. Poly(2,3-butylene succinate)
6. Poly(ethylene succinate)

Generally, this study of variations in structure of polyesters showed that greater ester group separation yielded improved low temperature flexibility and lower tear strength. Closer ester group spacing reduced flexibility at low temperatures, and at room temperature favored higher hardness values, higher modulus, and a marked increase in permanent elongation. These results may be attributed to increased van der Waals attractive forces.

Influence of Chain Extenders. While investigation of diisocyanates and polyesters was limited by the comparatively small number of compounds available, the opposite was true with low molecular weight glycols used as extenders. For this phase of the investigation, elastomers were prepared from poly(ethylene adipate), diphenylmethane diisocyanate, and the extender to be evaluated.

Table III lists the physical properties of elastomers extended with a homologous series of aliphatic glycols.

Table III. Physical Properties of Cast Urethane Elastomers as Influenced by Aliphatic Glycols

Glycol	Tensile Strength, P.S.I.	Elongation %	Elongation Set, %	Modulus, P.S.I., 300% Elong.	Tear Strength, Lb./In.	Hardness, Shore B
Ethylene glycol	6500	500	20	2000	230	61
1,3-Propanediol	6600	600	15	950	270	61
1,4-Butanediol	7900	600	10	1000	270	61
1,5-Pentanediol	7100	600	10	900	280	62
1,6-Hexanediol	7400	500	5	850	170	60

While not listed in the table, data are available showing that the compression deflection characteristics of all five elastomers were essentially equal. Examination of the data shows that, generally, the optimum balance of properties was obtained with 1,4-butanediol.

The physical properties of elastomers extended with two aromatic glycols, Multrathane XA (Mobay Chemical Co.) and α, α'-dihydroxyxylene are as follows:

	Multrathane XA	α, α'-Dihydroxyxylene
Tensile strength, p.s.i.	4500	6600
Elongation, %	550	500
Elongation set, %	45	20
Modulus, p.s.i. at 300% elongation	2500	2200
Tear strength, lb./in.	350	300
Hardness, Shore B	75	73

Generally, the properties shown indicated lower tensile and higher tear, modulus, and hardness than for specimens extended with aliphatic glycols. These changes may be attributable to the greater rigidity of the aromatic glycols.

The influence of chain extenders was not as pronounced as that of either polyesters or diisocyanates. This was undoubtedly due to the relatively small quantity of extender used in comparison to the other constituents, but within the limits noted, useful changes were obtained by varying the extender.

Influence of Chemical Cross Linking. To this point, the influence of structural changes within the elastomeric polymer chain has been studied while maintaining essentially constant the type and amount of the primary cross linking present. Also studied was the effect of type and amount of chemical cross linking in the polymer. Normal cross linking in the urethane polymer is reported to occur by reaction of terminal isocyanate groups with urethane groups to form allophanate linkages (*2*). Chemical cross linking can be obtained and controlled in another manner. Cross linking by way of urethane groups can be easily accomplished by substituting a trifunctional hydroxyl compound for the glycol extender. In this case the degree of cross linking is a function of the amount of triol used.

Data for samples prepared by substituting trimethylolpropane for 1,4-butanediol are listed in Table IV in order of increasing average molecular weight per branch point, $\bar{M}_c$, or decreasing degree of cross linking, calculated from the triol content of the polymer. In general, decreased $\bar{M}_c$ values in the range of 21,000 to 5300 resulted in decreased physical properties with two exceptions: compression set and permanent elongation. Both of these values decreased, indicating greater elasticity.

These observations are contrary to results of similar work with hydrocarbon elastomers (*5*), where increased cross linking results in increased physical properties, especially modulus. In the case of the polyester-urethane elastomers increased chemical cross linking of this type apparently causes a general weakening of the polymer. This is probably due to a reduction in orientation of chains and hence a reduction in probability of obtaining hydrogen bonding and benefit of other intermolecular attractive forces. In other words, with increased chemical cross linking, a spatial separation of chains is obtained which reduces intermolecular attractions. This observation in part confirms the belief that a major portion of the strength of urethane elastomers is due to forces other than primary valence bonding. In this series, in the $\bar{M}_c$ range of 5300 to 2100, the modulus increased with lower $\bar{M}_c$ values, indicating that the primary cross links eventually became dominant in controlling modulus.

Table IV. Physical Properties of Cast Urethane Elastomers as Influenced by Chemical Cross Linking

$\bar{M}_c$	Tensile[a] P.S.I.	Elongation[a] %	Elongation[a] Set, %	Modulus, P.S.I. 100% Elong.[a]	Tear[b] Lb./In.	Hardness,[c] Shore B	Compression[d]
2,100	1800	170	0	570	30	57	1.5
3,100	1750	200	0	420	25	53	16
4,300	1450	280	0	300	30	49	10
5,300	2800	350	0	270	30	46	5
7,100	4500	410	0	330	40	50	25
10,900	5600	490	5	460	60	55	40
21,000	5500	510	10	500	140	56	45
∞	6750	640	15	630	300	61	55

[a] ASTM 412 (*1*). [b] FTMS-601/M 4221 (*4*). [c] ASTM 676 (*1*).
[d] ASTM 395, Method A, 158° F. for 22 hours.

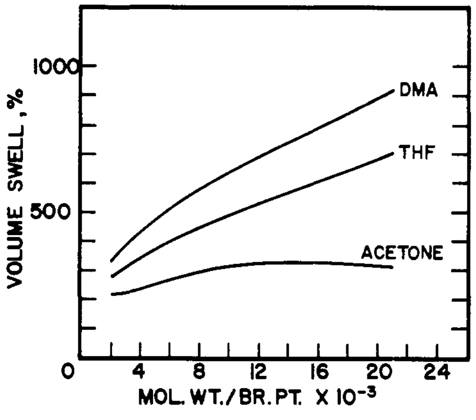


Figure 5. Volume swell of elastomers as influenced by cross linking and solvent

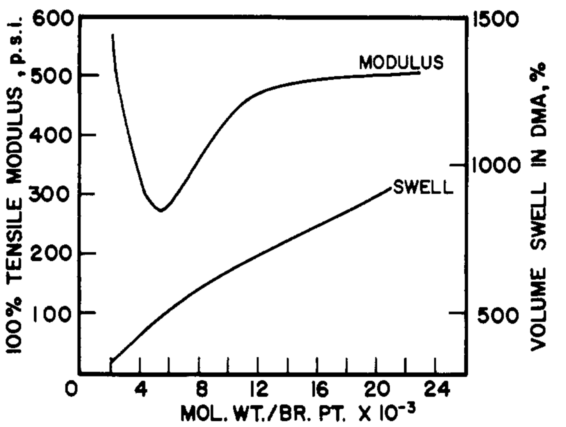


Figure 6. Volume swell and 100% modulus of elastomers as a function of molecular weight per branch point

To test these premises, a series of volume swell measurements was made on the elastomers made from poly(ethylene adipate) diphenylmethane diisocyanate, and 1,4-butanediol and trimethylolpropane. A very strong solvent was necessary to obtain significant changes in volume for the specimens of varying cross linking. Figure 5 shows the effect of three solvents tested—acetone, tetrahydrofuran, and dimethylacetamide. Dimethylacetamide was the most powerful in overcoming intermolecular attractions. Figure 6 shows both the volume swell and 100% modulus as functions of the calculated $\bar{M}_c$. The curve for volume swell increased with decreased cross linking in conformity with theoretical considerations. This confirms qualitatively that changes in the degree of cross linking had been obtained as expected.

The modulus curve showed a decrease with increased cross linking, passed through a minimum, and then increased to a maximum value for the highest degree of cross linking studied. The decreased modulus is contrary to general behavior of this type for hydrocarbon elastomers. If the modulus were only a function of chemical cross linking, as was the volume swell, then the modulus curve would be opposite in slope to the volume swell curve, and would not display a minimum. This set of experiments indicates that hydrogen bonding and other intermolecular

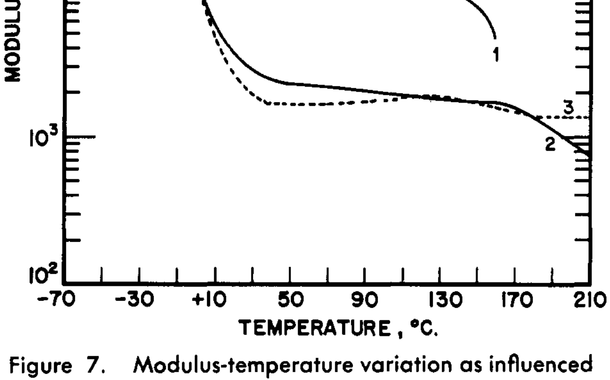


Figure 7. Modulus-temperature variation as influenced by triol cross linking

forces contribute greatly to the ultimate properties of the polyester urethane elastomers. Modulus apparently is affected primarily by intermolecular attractions at high $\bar{M}_c$ values, and by primary cross links at low $\bar{M}_c$ values.

Temperature dependence of the torsional modulus of elastomers cross linked with trimethyolpropane [3-(hydroxymethyl)-1,5-pentanediol] was also determined. Figure 7 shows the Clash-Berg torsional modulus for a series of Multrathane XA–trimethylolpropane cured elastomers. The modulus of a specimen containing no cross linking through triol extension, curve 1, was highest but fell off rapidly at 130° to 150° C. When 70% of the diol extender was replaced with the triol, curve 2, the room temperature modulus was lower but did not exhibit a significant decrease until a temperature of 170° to 190° C. had been reached. Complete substitution of triol for diol resulted in a still further extension of the temperature at which loss of modulus occurred (curve 3). This may be explained by the fact that hydrogen bonding and van der Waals forces are more readily disrupted by thermal means than is primary valence bonding. Where the hydrogen bonding and van der Waals forces were present in the greatest amount, as for curve 1, a material stronger and harder at room temperature was obtained, although its thermal stability was not as great as was that of the triol cross-linked elastomers. While the foregoing explains to a large extent the reasons for improved thermal stability of the polymers containing more cross linking obtained from the triol, it does not appear to be a complete explanation. Part of the improvement is believed due to the greater thermal stability of the urethane linkages (in the triol cross link) compared to that of the allophanate cross link (*6*).

As expected, increases in the degree of cross linking shifted the glass transition region somewhat toward higher temperatures.

ACKNOWLEDGMENT

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Urethane Polyether Prepolymers and Foams

Influence of Chemical and Physical Variables on Reaction Behavior

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"A New Process Control for Making Polyether Urethane Foams" by these authors appears in the July 1960 issue of *Industry and Engineering Chemistry* on page 613.

Three other articles from the May 1959 meeting of the Division of Rubber Chemistry appear on pages 605 to 612 of the July *I/EC*.

OVER THE LAST several years the urethane idustry has seen a major shift in emphasis from polyester-based foams to polyether or polyglycol systems. This has led to successful production techniques for manufacturing flexible and rigid polyether urethane foams and elastomers primarily through trial and error procedures. Reproducibility of the chemical and physical properties of raw materials and their consistency in polymerization have been of prime importance to the industry. The Raw Materials Subcommittee of the Society of Plastic Industry (SPI), Cellular Products Division, has sponsored test methods which have been accepted by ASTM (*1*) and data-exchange programs on a continuing basis in recognition of this need. In addition, raw material suppliers have introduced formulations and technology regarding processing conditions for prepolymer and one-shot techniques for urethane foam manufacture. The prepolymer method lends itself more readily to quantitative reaction rate determination and the conclusions of this study can be applied directly to this technology. By extrapolation, one-shot techniques warrant similar scrutiny.

Factors considered as affecting polyether prepolymer technology are outlined in Table I. Process refinements have materially improved the chemical and physical characteristics of both the polyglycols and aryl diisocyanates currently in use, particularly with respect to water content and unsaturation level of the polyol. The latter is

Table I. Factors Considered in Evaluation of Prepolymer Reaction

Raw Materials	Conditions
Polyglycol	Hydroxyl number, pH, water content, unsaturation, alkali metals as sodium and potassium, carbonyl, saponification value, and total chloride
TDI	Total hydrolyzable chloride, % isomer ratio, and assay
Process conditions	Temperature, reactor design, OH/NCO ratio, agitator design and r.p.m., purging technique, and absence of air or moisture

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[1] E.R. Carpenter Co., Richmond, Va.