

The Thermal Analyses of Polymers. V. Effects of Crosslinking and Hard Block Crystallinity on the Mechanical Behavior of Polyurethane Elastomers

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Synopsis

Linear expansion measurements have been used to correlate the degree of molecular ordering of a polyurethane elastomer with the increase in hard block content. The lower the value of the linear coefficient of expansion, α_L , the higher the degree of molecular fit. The soft block exerts the major influence on the coefficient of expansion below its fusion temperature (45°C), and the value usually decreases as the hard block content increases. Extension with aromatic diols causes the α_L to decrease at 100°C as the hard block content increases. Crosslinking a urethane prepolymer with triol increases the expansivity over the diol-extended elastomer. Keeping the NCO/OH ratio in the range 0.975 to 1.06 causes the lowest coefficient of expansion. For elastomers of low crystallinity, no correlation can be made between hard block content and enthalpy.

INTRODUCTION

Crystallinity and crosslinking are two of the more dominant factors affecting the mechanical behavior of polymers. Stiff chains and structural regularity promote the formation of definite areas of molecular alignment or order, causing the phenomena of polymer crystallinity. This molecular ordering in linear polymers leads to physical property changes similar to those induced by crosslinking, e.g., decrease in solubility, flexibility, and elongation. Crosslinking will usually inhibit crystallinity by restricting the chain motions for proper orientation and, in amorphous polymers, will increase hardness, tensile strength, and softening points in a similar manner for increases in crystallization. Crystallinity is readily reversed by heat, whereas the crosslinking of a polymer tends to make it practically infusible.

Kline, Sauer, and Woodward¹ and Nielsen² have shown that the modulus behavior and the loss factor are greatly influenced by both branching and crystallinity in polyethylene. Saunders³ has illustrated that crosslinking in polyurethane elastomers significantly affects the torsional modulus. Heijboer⁴ has pointed out the generalities that exist in the modulus-temperature profile for a polymer as it is affected by crosslinking and crystallinity. According to his model, there are a minimum of four major transitions to be expected in the shear modulus for any linear polymer, and a minimum of three for highly crosslinked polymers. At some temperature

above absolute zero, T_1 , rotational or torsional motions may begin with the groups on the polymer chain; T_2 is probably the T_g ; and T_3 and T_4 involve translational motion of significant magnitude, such as crystal-crystal transformations and fusion of molecular order.⁵

The thermal response of crosslinked and highly crystalline polymers has been shown for a wide variety of polymers, using the techniques of differential thermal analysis or differential scanning calorimetry. Thermodynamically, the greater the crystalline content, the greater the enthalpy change for the fusion of the polymer under study.⁶ On the other hand, if a polymer is sufficiently crosslinked, there is no endotherm which occurs, for the polymer does not melt. Fava⁷ has shown that exotherms and endotherms occur via DSC for both partially cured and uncured epoxy resins. On the other hand, when the material is fully crosslinked, there is no endothermal effect because no fusion is possible. Usually, thermogravimetric techniques have not correlated with crosslinking or degree of crystallization.

Ke⁸ has shown that the degree of crystallinity in a series of polyethylenes affects the fusion temperature, and generally, within limits, the higher the crystalline content, the higher is the fusion temperature. The effects of methyl and ethyl branching in polymethylenes have been illustrated by DTA measurements to show that the greater the number of branch points in the polymer, the lower is the melting temperature.⁹ These data are generally in agreement with that of Kline, Sauer, and Woodward¹ for the shear modulus behavior. Stehling and Mandelkern¹⁰ have shown that T_g is independent of crystallinity for polyethylene and that increasing the crystallinity decreases the linear coefficient of expansion.

Some properties of polymers have been shown to change as a function of crosslinking or crystallinity, but for the most part available techniques usually do not show a property change for small changes in crystalline content or crosslinking of a polymer. In cases where there are no endothermal maxima for the fusion of thermoplastic polyurethane elastomers, changes in the coefficient of expansion can be easily determined for these types of polymers. This report relates the effects of crystallinity and crosslinking of polyurethane elastomers as measured by changes in the coefficient of expansion as a function of temperature. With this technique, even subtle changes in the crystalline morphology or crosslinking content can be determined.

EXPERIMENTAL

All of the polyols required in this study had a molecular weight of 2000. In the studies of the effect of triol content on the linear expansion coefficient, prepolymers were made from polyethylene adipate and MDI (4,4'-diphenylmethane diisocyanate) with a slight excess of diisocyanate. These prepolymers were then reacted stoichiometrically with a quantity of diol-triol mix in order to form a crosslinked network. In examining the effect

of NCO/OH ratio, the same prepolymers were extended with 1,4-butanediol. The polyurethane elastomers with varying hard block content were prepared as described previously.⁶ Those elastomers made from prepolymers were heated to 110°C and degassed for 15 min at 50 mm pressure prior to mixing and casting. The cast slabs were approximately 0.050 in. thick and were cured at 110°C for 16 hr.

The measurements for linear expansion were made on the du Pont 941 TMA using an expansion probe whose tip diameter was 0.250 in. The ΔH values were obtained with the du Pont DSC cell using the usual calorimetric calibrations. All runs were made in duplicate to assure reproducibility. Linear expansion measurements were made at a heating rate of 5°C/min, whereas the DSC and DTA runs were made at heating rates of 10°C/min.

RESULTS AND DISCUSSION

It is a commonly accepted practice to determine the relative degrees of crystallinity in polymers by measuring changes in the enthalpy value for the fusion of polymers. This effect is readily shown for highly crystalline polymers, such as polyacetal, polyethylene, polypropylene, and others. Previous work has shown that polyurethane elastomers can exhibit crystalline fusion, depending upon the type of diisocyanate and polyol backbone.¹¹ For example, the ΔH_f values are higher for urethane elastomers employing a diisocyanate which can order, such as MDI or hexamethylene diisocyanate (HMDI), whereas the use of those diisocyanates which exhibit geometric isomerism and poor molecular fit, such as tolylene diisocyanate (TDI), hydrogenated TDI (STD), and hydrogenated MDI (SMDI), produces a very low value of ΔH_f .

Triol-Extended Elastomers

When a prepolymer is made from a polyol and a slight excess of diisocyanate, there is an insufficient amount of diisocyanate available for forming a hard block sequence within the urethane elastomer. Extension of the prepolymer with diol produces an elastomer which has a very small endotherm near 175°C, but as the triol content is increased and approaches 15%, the endotherm diminishes in intensity and disappears. Any amount of branching or crosslinking occurring above this limit would not be observed by DTA or DSC methods.

However, changes in the coefficient of linear expansion for varying contents of triol extension (Table I) indicate that the behavior of the backbone of the polyols is influenced by the triol content. The coefficient of expansion at 25°C is indicative of the polyol behavior, for the fusion of the polyester occurs at 45°C.¹¹ The α_L shows the expected behavior in that as the triol content is increased, it increases. This is caused by the lack of fit of the polyol backbone when extended with triol. Better molecular ordering occurs on complete extension with diol, and α_L is smaller than with

TABLE I
Effect of Triol Content on α_L for the Extension of PEA-MDI Prepolymers

1,4-Butanediol, %	Trimethylolpropane, %	$\alpha_L \times 10^4, ^\circ\text{C}^{-1}$ at 25°C
0	100	2.92
25	75	4.86
80	20	2.51
90	10	2.20
100	0	2.00

triol. The large value of α_L for 25/75 triol is real and is not easily explainable.

Effects from NCO/OH Variation

The NCO/OH ratio is always a necessary criterion for maximizing the properties of a urethane elastomer. These ratios also significantly influence the molecular weight of the polymer which exerts its own influence on the polymer property. The data in Table II illustrate that the coeffi-

TABLE II
Effect of NCO/OH Ratio on the α_L of PEA-MDI-BD Urethane Elastomers

NCO/OH	$\alpha_L \times 10^4, ^\circ\text{C}^{-1}$	
	25°C	100°C
0.90	2.30	2.05
0.95	2.19	1.51
0.975	1.87	1.90
1.00	1.80	1.60
1.03	1.82	1.83
1.06	1.80	1.63
1.10	2.50	2.30
1.20	2.14	2.30

cients of expansion, both at 25° and 100°C, go through a minimum when equivalent ratios of diisocyanate to diol are used for making a urethane elastomer. The high coefficients of expansion for both low and high NCO/OH ratios are due in part to the fact that the molecular weight of the polymer initially is low, and the probability of segments aligning themselves one with another cannot be obtained until sufficient molecular weight is possible. Moreover, upon extensive curing, excess NCO groups form allophanate structures causing crosslinks which inhibit crystallization. Hence, the preferred range of NCO/OH is near 1.00.

Hard Block Sequences

With Polyester Soft Block

The effect of extender in the hard block can be shown by the coefficients of expansion in Table III. In using a polybutylene adipate-MDI mix with

four different diol extenders, that is, ethylene glycol, 1,4-butanediol, 1,4-bishydroxyethylhydroquinone, and 1,4-hydroxyethylbisphenol-A, the fusion response of increasing the MDI content was examined, and it is apparent that there is no correlation between the amount of MDI in the hard block and the enthalpy values derived from that elastomer. On the other hand,

TABLE III
Effect of Increasing Hard Block Content for Poly(butylene Adipate)-MDI-Diol Polyurethanes on α_L and ΔH^a

Diol	MDI, parts/100 parts polyester	$\alpha_L \times 10^4, ^\circ\text{C}^{-1}$		$\Delta H,$ cal/g
		40°C	100°C	
Ethylene glycol	60	2.37	1.90	1.21
	80	2.30	2.05	1.54
	90	1.77	2.54	4.88
1,4-Butanediol	40	2.79	2.18	3.28
	60	2.01	2.05	1.95
	80	1.90	1.99	4.38
	90	1.31	2.03	3.22
1,4-Bishydroxyethylhydroquinone	40	1.39	21.0	3.00
	60	1.83	1.38	3.38
1,4-Hydroxyethylbisphenol-A	60	0.473	0.95	3.74

^a NCO/OH = 1.0.

if the coefficient of expansion is measured at two temperatures, one in the temperature range in which the polybutylene adipate (soft block) exhibits a dominant influence (40°C) and one in which the soft block exhibits no apparent influence (100°C), the observed behavior can be summarized as follows:

1. Aliphatic glycol extension decreases the coefficient of expansion at 40°C as the hard block or MDI content increases; α_L (100°C) increases with MDI content when extended with ethylene glycol but shows little change with 1,4-butanediol extension.
2. Rigid aromatic diols tend to increase α_L at 40°C and decrease α_L at 100°C as the MDI content increases.
3. Increasing the rigidity of the aromatic diol tends to decrease α_L at 40° and 100°C.

From these results, it would seem that extension of the hard block with an aliphatic glycol increases the molecular fit or order of the polyester soft block since α_L decreases. On the other hand, the increases in α_L at 100°C for ethylene glycol extension may indicate that the hydrogen bonding occurring between the urethane block and the polyester backbone with short-chain diol extension is a more dominant influence than the hydrogen bonding between the hard blocks themselves.

The lack of change at 100°C in α_L for butanediol extension may be due to a combination of a better fit of the hard block sequence than with ethylene glycol extension offset by the influence of the hydrogen bonds between the hard block and the polyester. The aromatic extenders show a definite increase in order in the hard block sequence, as the α_L at 100°C decreases and at 40°C increases with increasing MDI content. Increasing the planar structure or susceptibility to molecular stacking in the aromatic diol will tend to decrease α_L at 40°C and 100°C, as evidenced by extension with 1,4-hydroxyethylbisphenol-A.

There was no clear correlation of hard block structure with enthalpy values derived from the fusion of the polymer with any of the extenders in this work.

With Polyether Soft Block

When the polyol backbone is switched from a polyester to a polyether, such as that of polytetramethylene glycol, we see from Table IV that in-

TABLE IV
Effect of Increasing the Hard Block Content in Poly(tetramethylene Glycol)-MDI-Diol Polyurethanes on α_L ^a

Diol	MDI, parts/100 parts polyester	$\alpha_L \times 10^4, ^\circ\text{C}^{-1}$		$\Delta H,$ cal/g
		40°C	100°C	
1,4-Butanediol	50	2.38	3.09	—
	60	1.79	2.50	1.07
	70	1.19	2.05	2.16
	80	0.80	1.99	0.40

^a NCO/OH = 1.0.

creasing the MDI content decreased the coefficient of expansion both at 40°C and 100°C, indicating that the molecular fit of both the soft block and hard block increased as the MDI content increased. These decreases in the coefficient of expansion as the hard block content is increased are typical of a polymer whose expansion behavior is not affected substantially by the block behavior, but exhibits more the general behavior of a random block or homopolymer. The polyurethane elastomers made from the polytetramethylene glycol were transparent, whereas those made from the polyester were translucent or opaque, depending on the MDI content. The heats of fusion for the poly(ether-urethanes) showed no correlation with increases in the hard block content.

CONCLUSIONS

Linear expansion measurements readily lend themselves to determining the degree of molecular order in semicrystalline block copolymers as well

as assessing the changes in structure with varying amounts of crosslinking. This suggests that linear expansion measurements may be used to determine the cure of both thermoplastics and the degree of cure for thermosetting resins. The linear expansion measurements point out quite markedly the effect of aromatic and aliphatic diol extenders on block polymer behavior of poly(ester-urethanes), illustrating that with the use of aliphatic glycol extenders, the expansion behavior at 40°C or lower is governed by the mechanical motions of the soft block backbone. Those elastomers extended with the aromatic diols are influenced predominantly by the hard block segment. An increased amount of hydrogen bonding between the urethane hard blocks and the polybutylene adipate with ethylene glycol extension is manifested by an increase in α_L . Apparently, for the polyether glycol there is a lesser opportunity for hydrogen bonding between the polyurethane backbone and the segmental hard block, and the expansion characteristics are typical of a polymer whose crystalline content or rigidity is less dependent on segmental interactions.

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