

# Preparation and Properties of Castor Oil-Based Polyurethanes

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## Synopsis

Four series of polyurethane elastomers were synthesized using diphenylmethane diisocyanate (MDI) and castor oil as the polyol. Two types of MDI (crude and distilled) were used. The temperature of reaction and the effect of excess isocyanate above stoichiometric were also varied. The structure of the polyurethanes was analyzed using wide-angle X-ray diffraction, scanning electron microscopy, and density and differential scanning calorimetry (DSC). Thermomechanical and dynamic mechanical (TMA and DMA) as well as mechanical measurements were carried out. The results have shown considerable influence of the type of MDI, excess of isocyanate, and temperature of preparation on the properties of the polyurethanes synthesized.

## INTRODUCTION

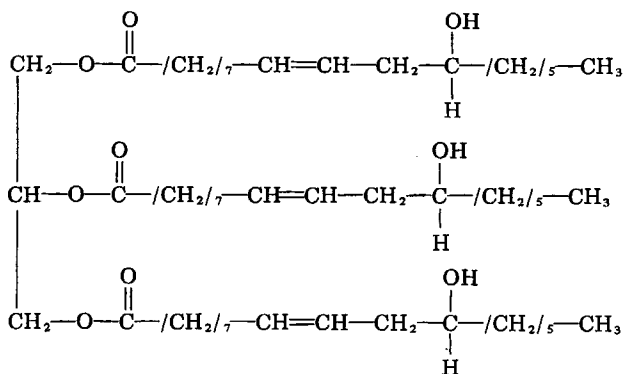
Use of castor oil as a polyol in the preparation of polyurethanes is becoming more and more widespread, especially in the electrical industry for casting compounds. However, very few references exist on the structural properties of these compounds.

Crude MDI is a liquid at 20°C and can be mixed with castor oil at ambient temperature to obtain a castable compound. However, it has been noticed that the properties of the casting depend on the temperature at which the reaction is carried out. Pure MDI ("distilled") is solid at room temperature and, usually during preparation of polyurethanes, is heated to 60–100°C. Due to its well-defined structure, distilled MDI usually gives better mechanical properties in the polyurethanes than crude MDI. Since castor oil is a triol, the polyurethanes synthesized using it are crosslinked. The degree of crosslinking depends on the excess of isocyanate due to its ability to react with the urethane bond, giving allophanate crosslinks.

In this work, three series of polyurethanes based on crude MDI and castor oil were prepared by casting test samples at room temperature (series A), at 90°C (series B), and 120°C (series C). A fourth series (D) was obtained with distilled MDI and castor oil at 100°C.

Castor oil is the triglyceride of ricinoleic acid whose idealized structure can be represented by the formula shown in Scheme 1.

Its molar mass is 933. Industrial castor oils have varied composition, with 5–15% ricinoleic acid being replaced with other fatty acids.<sup>1</sup> Secondary hydroxyl groups react considerably more slowly than primary ones, thus making castor oil a slow reacting polyol. In a fully crosslinked model polymer, the molar mass



Scheme 1

of chains between two nodes is high enough so that these polymers possess fairly high elasticity and can be of considerable commercial interest.

### EXPERIMENTAL

**Materials.** The castor oil used in this work had a hydroxyl number of 180 mg KOH/g. Crude MDI (Desmodur 44V from Bayer) was a dark brown liquid having NCO content of 32%. Distilled MDI (Suprasec MPR from ICI) having a NCO content of 33% was used as delivered. Zeolith T paste (from Bayer) is a 50% dispersion of ground molecular sieves in castor oil. It was dried at 110°C for 2 h before use.

**Synthesis.** The polymers were prepared by mixing castor oil and Zeolith T paste (10%) and the calculated amount of MDI in a beaker. Mixing was continued for about 0.5 h until a homogeneous mixture was obtained which was cast into a mold to produce 2–3 mm thick plates. The temperature of mixing and heating of the mold was varied from room temperature to 120°C. Designation of samples is given in Table I.

**Methods.** X-ray diffraction was carried out using a Philips diffractometer at a scanning rate of 1°/min, from  $2\theta = 3\text{--}39^\circ$ . A scanning electron microscope (Jeol JSM 35) was used to observe the features of the broken surfaces. Shore A and C methods were used to determine hardness of the samples. The density was measured using a Mohr balance. DSC measurements were carried out in nitrogen at a heating rate of 10°C/min, using a DuPont DSC 910. DuPont TMA 943 was used at 5°C/min with 2 g load to carry out thermomechanical measurements. Dynamic mechanical measurements were carried out using the DuPont DMA 981 at a heating rate of 5°C/min and an amplitude of 0.2 mm. An Instron tensile machine (Model 1122) was used for the mechanical measurements.

TABLE I  
Designation of Polyurethanes

Temp. of casting (°C)	Excess of MDI (%)				
	0	5	10	15	20
25	a1	a2	a3	a4	a5
90	b1	b2	b3	b4	b5
120	c1	c2	c3	c4	c5
100 (with pure MDI)	d1	d2	d3	d4	d5

## RESULTS AND DISCUSSION

X-ray diffraction patterns of MDI/castor oil polyurethanes did not vary significantly from sample to sample. Two broad amorphous peaks at  $2\theta \sim 20^\circ$  and  $2\theta = 8^\circ$  were observed, the second being fairly weak. Similar peaks have been seen in a range of amorphous polymers.<sup>2,3</sup> Skrishevskiy<sup>4</sup> has explained the appearance of these peaks by the existence of short range ordering corresponding to the first and second sphere of coordination i.e. the intermolecular distances at about 0.55 nm and 1.4 nm. In that respect, these polyurethanes do not differ from other amorphous polymers as the same positions of the maxima were found in other linear segmented partly crystalline polyurethanes.<sup>5</sup> Since in this case no melting was observed by DSC, it was concluded that these polyurethanes were completely amorphous.

Due to the differences in polarity of the castor oil and MDI, intense stirring is required to obtain a homogeneous mixture. Incompatibility of the components in the mixture decreases as synthesis progresses, but, still, a local excess of MDI may be visualized which causes an inhomogeneous network density. This is particularly true in compositions produced with crude MDI at room temperature. The existence of an inhomogeneous structure in crosslinked polymers is a consequence of the mechanism of crosslinking and is rather a rule than an exception. It is proposed that due to the dominance of intramolecular over intermolecular structure, "gel balls" are formed which at the end of the reaction have the form of globules (nodules) embedded in a matrix of the same polymer of lower crosslinking density.<sup>6-8</sup> The size of the globules may be controlled by the reaction temperature.<sup>9</sup> As the polymerization progresses, the glass transition rises also. Kargin and Slonimskiy suggest that globular structures are formed, especially when polymerization is carried out below final  $T_g$ .<sup>10</sup>

Examination of the broken surface by scanning electron microscope at a magnification of 700 and 5000 times did not reveal any structural features. This was still not proof of a homogeneous structure since, during the swelling experiments, samples based on crude MDI were observed to desintegrate. It was assumed that microcracks were formed at the boundaries of the "gel balls." By increasing the temperature of synthesis, a more homogeneous structure and thus an increase in mechanical properties should have been obtained. This was indeed the case, but the properties of these systems were also affected by the degree of crosslinking which was controlled by the excess of MDI and temperature variation. Thus the effects of both morphology and crosslinking density were responsible for the change in properties.

A qualitative assessment of crosslinking density was done by examining the change in density. Figure 1 shows the effect of excess of MDI on density of all four series. As can be seen from Figure 1, density increases both with excess of MDI and temperature of preparation.

Calculated density of stoichiometric mixture of MDI and castor oil, having densities of 1190 kg/m<sup>3</sup><sup>11</sup> and 950 kg/m<sup>3</sup>,<sup>12</sup> respectively, is about 1020 kg/m<sup>3</sup>.

As the reaction progresses, density increases to about 1130 kg/m<sup>3</sup> for the system with lowest degree of crosslinking (a1) and 1210 kg/m<sup>3</sup> for the system based on distilled MDI (d1).

If MDI in excess is considered as an inert additive, the density of D series polymers should decrease compared to that of the sample with stoichiometric ratio of castor oil and MDI (sample d1). However, that was not the case, meaning

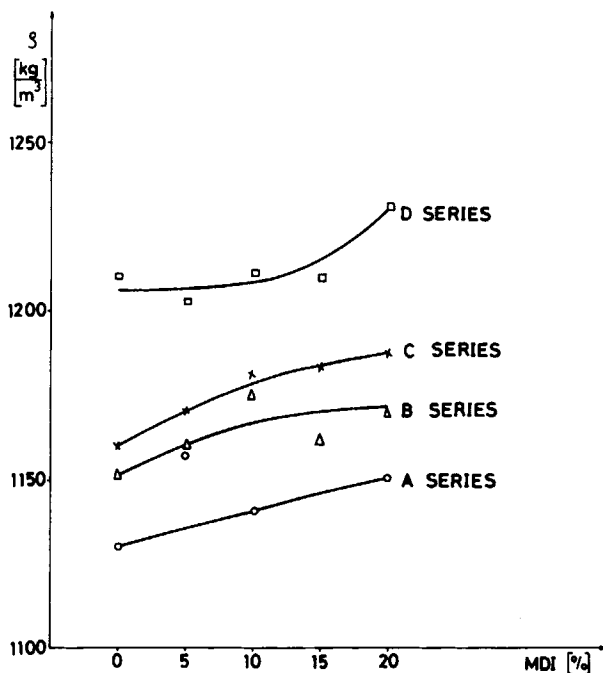


Fig. 1. The effect of excess of MDI on density.

that MDI reacted causing volume contraction. Similar behavior was observed in other three series as an excess of MDI caused the increase of density greater than it should be if MDI was inert.

The effect of reaction temperature is also clearly demonstrated by this increase of density. If it is taken that density increases linearly with conversion and that the highest obtained value of 1231 kg/m<sup>3</sup> represents 100% conversion, then the conversion varies in the A series from 52% to 62%, in the B series from 62% to 71%, in the C series from 66% to 75% and in the D series from 90% to 100%. In the case of the first three series, the increase in temperature has a significant effect on conversion, especially when the temperature is increased from 25°C to 90°C. In the case of the D series, it is evident that the primary effect was obtained from the structure of the MDI, pure MDI being more reactive even at lower temperature (D vs. C series). These figures designating degree of conversion should be taken as very rough estimate.

A more direct measure of crosslinking density can be obtained from swelling experiments. Degree of swelling, measured as the increase of sample weight after immersion in dimethylformamide (DMF), was strongly dependent on preparation temperature. Figure 2 illustrates the change of the degree of swelling ( $\alpha$ ) with casting temperature for samples obtained at a stoichiometric ratio of MDI/castor oil. Although some difficulties were encountered when the swelling of samples based on crude MDI was assessed, due to disintegration as described earlier, Figure 2 qualitatively shows the effect of the preparation temperature on the reaction completion (conversion) and thus the degree of crosslinking. By changing the excess of MDI in the D series from 0% to 20%, the degree of swelling decreased linearly from 93% to 81%. A fully crosslinked polymer should give a trifunctional network, the secondary C-atom in glycerine from castor oil being

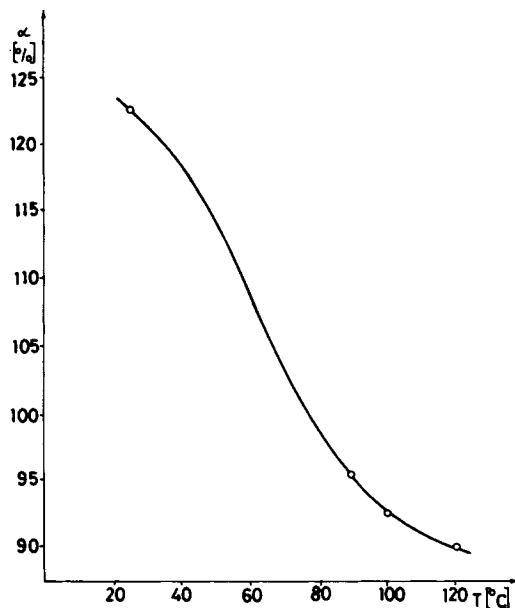


Fig. 2. Variation of degree of swelling ( $\alpha$ ) with casting temperature.

the branching point. The molar mass of the network chain in such a polymer, which should contain two ricinoleic chains and one MDI moiety, is about  $2 \times 311 + 250 = 872$ . This size of network chains produces a semirigid polymer at room temperature. If reaction is not completed, due to unreacted components and free chain ends which act as plasticizers and lower crosslinking density, the

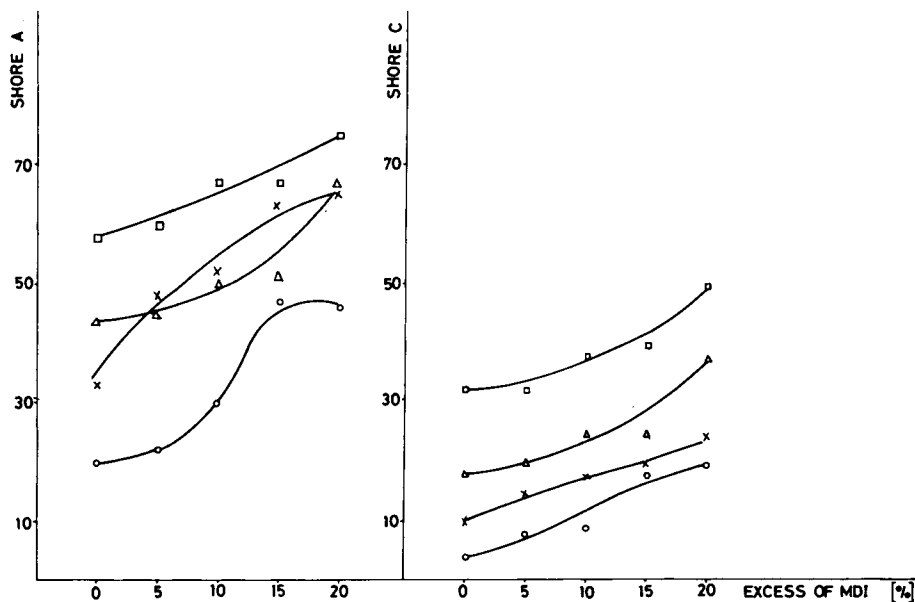


Fig. 3. The effect of excess of isocyanate on Shore A and Shore C hardness: (□) series A; (X) series B; (Δ) series C; (O) series D.

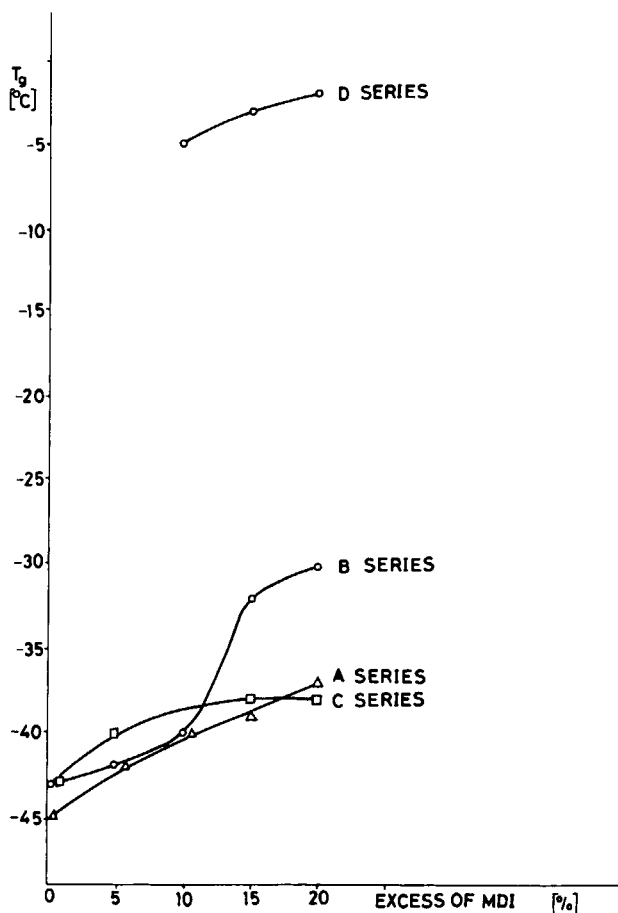


Fig. 4. Change of  $T_g$ , measured by DSC, with excess of MDI.

polymer is softer, as can be seen from the hardness measurements. The variation of Shore A and C hardness represented in Figure 3 shows that samples in the A series are soft and in the D series considerably harder than those based on crude MDI (other three series). Such polymers are interesting for many practical applications. In each case, the increasing MDI content over stoichiometric has the same effect as increasing preparation temperature. By adding 20% excess of MDI, Shore A hardness increases by about 250% in the A series and by 130% in the D series. Variation in the temperature of preparation from 25°C to 120°C causes an increase of Shore A hardness by about 220%.

Crosslinking density also affects glass transition temperature if the length of network chains is comparable with that of segments. Change of  $T_g$  with excess of MDI in all four series is shown in Figure 4. Glass transition temperatures of polymers with crude MDI (A, B, and C series) increases about 15°C with 20% excess of MDI. Whereas these polymers are evidently elastomers at room temperature, the D series polyurethanes have a transition region near room temperature. Such polymers can be considered for artificial leathers. A 40° difference in  $T_g$  between polymers prepared with distilled and crude MDI suggests that there are major structural differences and differences in the degree of crosslinking. Although preparation temperature affects hardness and

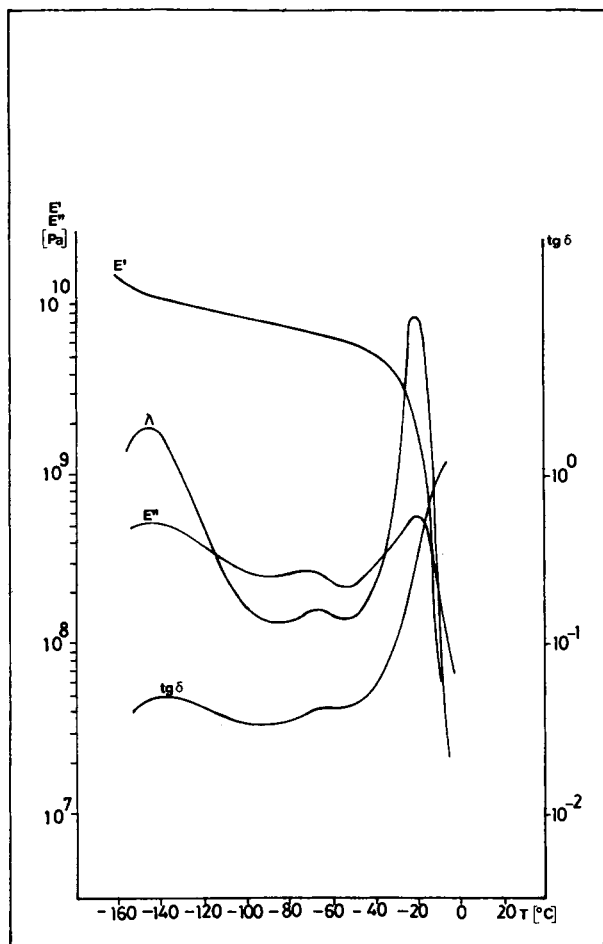


Fig. 5. Change of storage modulus  $E'$ , loss modulus  $E''$ ,  $\tan \delta$ , and damping ( $\lambda$ ), with temperature for the sample a4.

swelling, it has no effect on  $T_g$ . This can be explained by the relatively small number of crosslinks so that the network chains were longer than the segments. Dynamic mechanical analysis revealed three relaxation transitions in the glassy state, one occurring at  $T_g$  (coinciding with the drop of storage modulus  $E'$  by about four decades), the second ( $\beta$ -peak) being at  $-60^\circ\text{C}$  and the third ( $\gamma$ -peak) was located at  $-140^\circ\text{C}$  (Fig. 5). The temperatures of the  $\beta$  and  $\gamma$  transitions in all series coincided. As in polyethylene, the  $\gamma$ -transition was supposed to reflect relaxation involving a crankshaft mechanism as proposed by Schatzki and Boyer.<sup>13</sup> The mechanism of the  $\beta$ -relaxation is still to be elucidated. Variation of the  $\alpha$ -transition temperature ( $T_\alpha$ ) within each series was small. However, the difference in  $T_\alpha$  between A and D series was about  $40^\circ\text{C}$  (as difference in  $T_g$ 's obtained by DSC).  $T_\alpha$  for D series polymers was about  $20^\circ\text{C}$ , i.e., the midpoint of the leathery region occurred at room temperature. These measurements show that D series polymers cannot be used as elastomers below room temperature as polymers in other three series can, in spite of their much

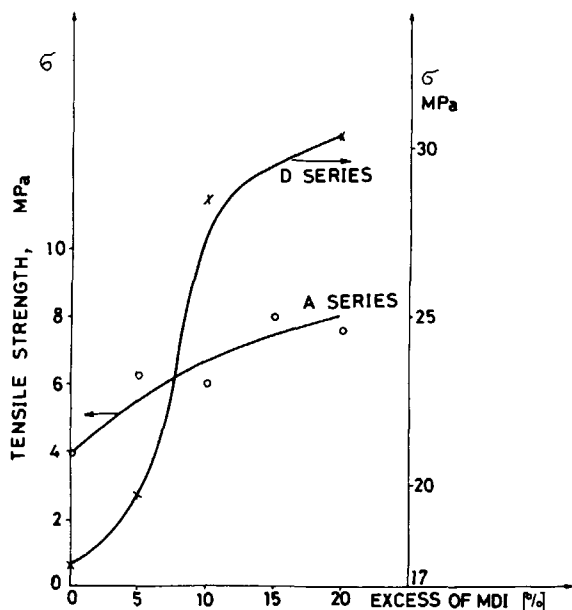


Fig. 6. Variation of tensile strength with excess of MDI of A and D series.

better mechanical properties. The tensile strength of the D series polymers was an order of magnitude higher than in A series polymers (Fig. 6). An especially dramatic effect was observed when an excess of over 10% of MDI was used. Tensile strengths obtained were almost an order of magnitude higher than that reported in the technical literature of the Bayer company.<sup>14</sup> Increasing the excess of MDI from 0% to 20% caused a doubling of tensile strength. As Figure 7 shows, the D series polymers have elongations at break which are two times greater than those of the A series polymers. An interesting fact is that elongation increases with excess of MDI in a similar way as strength does (Fig. 7). The low tensile strength coupled with the relatively low elongation at break of the A series polymers points to the existence of weak spots in the samples caused by incomplete crosslinking and probably structural inhomogeneities (or globular struc-

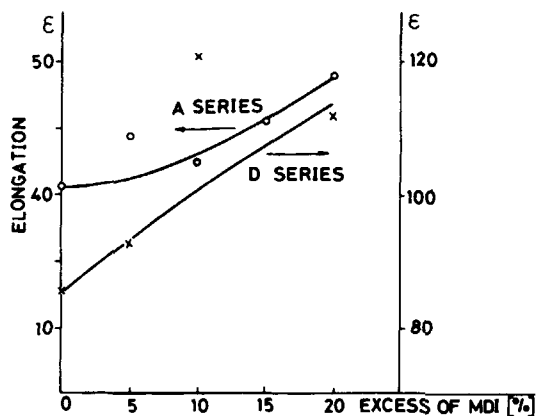


Fig. 7. The effect of excess of MDI on elongation at break of A and D series.



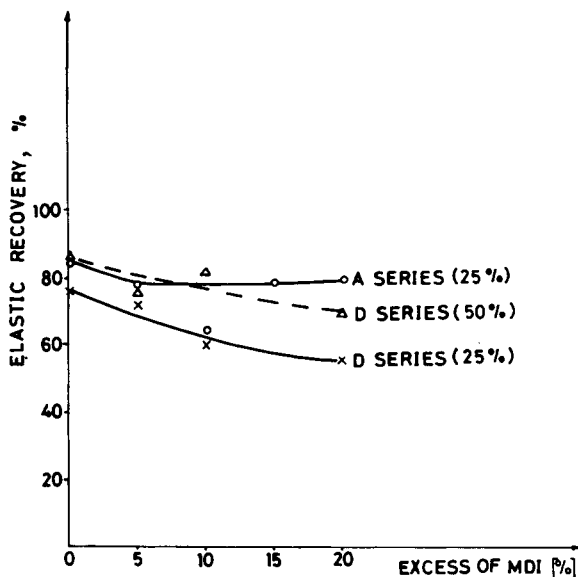


Fig. 8. Variation of elastic recovery with excess of MDI at extension of 25% (A and D series).

ture). By using excess of MDI, the network is "improved" by additional crosslinking so that both tensile strength and elongation at break increase.

Elastic recovery at 25% elongation was better with polyurethanes based on crude MDI. Unfortunately, these polymers could not be tested at 50% extension as polymers in D series. The latter polymers show improvement of elastic recovery with the increase of extension. It is evident from Figure 8 that the elastic recovery of the A series polymers was better, which is to be expected, taking into account that the tests were carried out well above  $T_g$ , whereas relaxation phenomena in the D series near the  $T_g$  were pronounced.

A study of reactivity of castor oil with MDI, carried out in our laboratory, has shown that even when a large excess of castor oil was used, isocyanate peaks in IR spectra of the liquid mixture could be observed after several weeks storage. It is reasonable to assume that the reaction will be even slower in the solid state as in this instance. Thus, the positive effect of temperature on conversion is predictable. Although all samples were tested at least 2 weeks after preparation, it is clear that the reaction was incomplete in most polymers. Unreacted NCO groups may be consumed in reaction with moisture, leaving some hydroxyl-terminated chains which are inoperative during mechanical stress. Excess of isocyanate "mends" the network by linking dangling chains together or reacting with urethane groups through allophanate formation. At high temperatures, allophanate formation seems to dominate, introducing additional crosslinking. Since  $T_g$  is not significantly affected by excess of MDI but density, swelling, and mechanical properties are, it follows that the quantity added causes "improvement" of the network but does not affect segment mobility.

The difference in properties of pure and crude MDI based polyurethanes suggests qualitative structural differences as well as differences in crosslinking density.

Since most of the tests were carried out at room temperature, i.e., in the rubbery region of A, B, and C series and near the transition region of the D series,

the effect of intermolecular attraction could have contributed to the strength of the latter polymers. Polymers with crude MDI failed much before full extension of the chains occurred, suggesting that imperfections and inhomogeneous structure existed in the samples.

Generally speaking, all these polymers possess a high elastic recovery, characteristic of some linear segmented polyurethanes and can be classified as elastomers.

## CONCLUSIONS

Four series of polyurethanes based on castor oil and MDI were synthesized by varying type of MDI and the temperature of preparation.

It was demonstrated that, although the temperature of preparation plays an important role, the effect of the type of MDI was more pronounced. The difference in properties between polymers with crude and pure MDI was explained by structural differences.

The glass transitions of crude MDI based polyurethanes were about  $-40^{\circ}\text{C}$  whereas pure MDI produced harder rubbers, having  $T_g$  at about  $-5^{\circ}\text{C}$ .

It has been shown that crosslinking density varies regularly with temperature of synthesis.

Addition of 20% of MDI above stoichiometric quantity increased  $T_g$  by about  $5^{\circ}\text{C}$ , Shore A hardness by about 20 units, tensile strength by about 80%, elongation at break by about 20%, density for about 2%, and decreased swelling in DMF by about 15% and elastic recovery by 10–30%.

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