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# THE EFFECT OF CASTOR OIL ON THE STRUCTURE AND PROPERTIES OF POLYURETHANE ELASTOMERS (TDI SYSTEM)*

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## ABSTRACT

Segmented polyurethane elastomers, based on a mixture of castor oil and polypropylene glycol, toluene diisocyanate and 1,4-butanediol were prepared. The physical, thermal, dynamic mechanical behaviour, and x-ray diffraction have been studied. The use of castor oil shifts the main transition of the soft phase to higher temperature (glass transition temperature Tg increases),improves hardness, tensile strength, modulus and tear strength. Elongation and abrasion resistance decrease as ratio of castor oil increases. X- ray diffraction patterns show elastomers are amorphous. Trifunctionality of castor oil leads to the crosslinking of soft segments and a decrease of solubility and swelling of elastomers.

## INTRODUCTION

Polyurethane (PU) elastomers are well known for their high strength, resiliency and good resistance to abrasion. The main constituents of polyurathane elastomers are a long chain oligomeric polyol, a diisocyanate and a low molecular weight diol or diamine as a chain extender. The polyol may be a polyester or a polyether oligom-

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TABLE 1

COMPOSION AND PROPERTIES OF PREPOLYMERS

| Sample | $P_1$ | $P_2$ | $P_3$ | $P_4$ | $P_5$ | $P_6$ |
|---|---|---|---|---|---|---|
| Composition pbw | | | | | | |
| Castor oil | 0.00<br>(0.00) | 23.00<br>(0.20) | 54.40<br>(0.40) | 61.20<br>(0.60) | 136.00<br>(0.08) | 340.00<br>(1.00) |
| PPG | 333.00<br>(1.00) | 266.66<br>(0.80) | 240.00<br>(0.60) | 120.00<br>(0.40) | 100.00<br>(0.20) | 0.00<br>(0.00) |
| TDI | 130.00 | 116.00 | 121.80 | 80.37 | 116.14 | 200.00 |
| NCO/OH | 4.49 | 3.98 | 3.50 | 3.08 | 2.67 | 2.29 |
| Colour | cl | cl | ly | ly | y | y |
| % NCO | 10.60 | 9.50 | 10.37 | 9.36 | 9.87 | 9.55 |
| Eq. wt. | 396.20 | 442.12 | 405.00 | 448.7 | 425.5 | 439.7 |

pbw = parts by weight, parentheses ( ) indicate equivalent ratios, cl= colourless, ly= light yellow, y= yellow, Eq. wt.= equivalent weight.

er. Efforts have been made during the past few decades to replace these expensive polyols with low cost natural vegetable oils or their derivatives in the production of urethane products.

Among the vegetable oils, castor oil possessing hydroxyl groups is a good polyol for the synthesis of urethane elastomers.[1-7] Cast polyurethane elastomers based on castor oil and diisocyanates are highly crosslinked, hard and have low elongation at break. We have observed that castor oil possesses excellent compatibility with polypropylene glycols (PPG) in all proportions so that PPG can be effectively blended with castor oil to obtain polyurethane elastomers.

In the present study we report blends of castor oil,PPG for producing castable urethane elastomers. Effect of the different ratios of two polyols on the physical, thermal, dynamic mechanical properties and x-ray diffraction of these urethane elastomers have been studied.

## EXPERIMENTAL

Materials: Polypropylene glycol of $M_n$= 1930 (BASF Wyandotte Corporation U. S. A.), castor oil (I.P. grade) having hydroxyl number 165 mg KOH/g were used. 1,4-butanediol was obtained from M/s. Koch Light Lab. England. Toluene diisocyanate (TDI) having 80/20 blends of

TABLE 2

COMPOSITION OF ELASTOMERS

| Sample | $E_1$ | $E_2$ | $E_3$ | $E_4$ | $E_5$ | $E_6$ |
|---|---|---|---|---|---|---|
| Composition pbw | | | | | | |
| CO/PPG | 0.0/1.0 | 0.2/0.8 | 0.4/0.6 | 0.6/0.4 | 0.8/0.2 | 1.0/0.0 |
| PP | 43.40 | 46.32 | 42.77 | 47.09 | 44.68 | 46.17 |
| 1,4-BD | 4.5 | 4.5 | 4.5 | 4.5 | 4.5 | 4.5 |
| NCO/OH | 1.05 | 1.05 | 1.05 | 1.05 | 1.05 | 1.05 |
| $T_g$ °C | -43.5 | -42.1 | -33.5 | -28.2 | -11.7 | 15.1 |

CO = Castor oil, PP = Prepolymer, $T_g$= Glass transition temperature.

the 2,4- and 2,6- isomers of 48.2 % NCO was obtained from M/s. BASF Wyandotte Corporation, U.S.A.

Preparation of prepolymers: In a four-neck flask, equipped with a mechanical stirrer, thermometer, nitrogen gas inlet and outlet, calculated quantity of TDI was taken in the flask. The required quantity of mixture of castor oil and PPG (Table 1) was added gradually to TDI maintaining temperature of the reactants at 20°-25°C till the addition of polyol is completed. Later the reactants were heated to 80° C and maintained at 80°-85° C for one hour to complete resinification reaction. The isocyanate content (% NCO) of the prepolymers were determined as per the procedure mentioned in the literature.[8]

Preparation of elastomers: Castable polyurethane elastomer was prepared by taking the required quantity of prepolymer, 1,4-butane diol (Table 2) and the catalyst dibutyltin dilaurate (0.01 wt.% of total charge). The reactants were weighed in a beaker, degassed under reduced pressure (2-5 mm of Hg) and poured into a heated sheet mould maintained at 80° C, having silicone release agent. Elastomer sheets of size 140x100x2 mm size were produced. The cast sheets were cured to solidify at $80^{\circ}$ C in about 2-3 hours, and finally cured at $110^{\circ}$C for additional 12 hours. All the samples were aged at room temperature 27 ± $2^{\circ}$ C for 30 days, prior to evaluation of properties.

*Physical testing*: The tensile strength, 100 % modulus, hardness and elongation at break were determined according to ASTM -D 412. Tear strength was determined according to ASTM-D 624-54 using die C.

*Dynamic mechanical behaviour*: The dynamic shear modulus $G^{*}(w) = G' + G''$ where $G'$ and $G''$ are the storage and loss moduli respectively was measured using a Rheometrics system four apparatus, at Institute of Macromolecular Chemistry (IMC), Prague, Czechoslovakia. The measurements were made at frequency w = 1 Hz in the temperature range $-60^{\circ}$ and 200 $^{\circ}$C.

*Glass transition temperature Tg*: Differential scanning calorimetry measurements were carried out with a Rigaku Thermal Analyser Model DSC- 8230, using sample weight of 17-18 mg. The heating rate was kept at $10^{\circ}$ C per minute in nitrogen atmosphere.

*Thermogravimetric analysis(TGA)*: Perkin Elmer 7 series, thermal analyser was used in the study. The samples were tested at the heating rate of $10^{\circ}$C per minute under nitrogen atmosphere, at IMC, Prague.

*Abrasion resistance*: Abrasion resistance studies were carried out using Taber Abrasion tester model 503 and H-18 abrading wheels for 1000 g load for 1000 cycles.

*Solvent swelling and soluble extract*: The samples were kept in solvent benzene for one week, and volume swell % was determined from the increase in weight of the sample. The samples were kept in dimethyl formamide (DMF) for a week and soluble fractions (%) were determined.

*X-ray diffraction*: X-ray diffraction patterns of PU elastomers were determined using Philips X-ray unit (Philips generator PW-1730) and Ni-filtered $CuK_{\alpha}$ radiations.

## RESULTS AND DISCUSSION

Several vegetable oils and their derivatives have been employed in the preparation of urethane products. Goldblatt[9] has reported the use of castor oil with PPG of molecular weight 400 and 2000 with toluene diisocyanate using 4-4 -methylene-bis-2-chloroaniline (MOCA) as chain extender. The elastomers thus obtained have high tensile strength, hardness and moderate elongation at break.

In the present study prepolymers $P_1$ to $P_6$ were prepared having isocyanate content (% NCO) 9.0 to 10.0. Part of PPG was replaced successfully by castor oil (0.2 to 0.8 equivalent weight). TDI quantities were also varied accordingly. The average molecular weight of polyols mixture decreases as castor oil content increases from $P_1$ to $P_6$. All the prepolymers were free flowing viscous liquids possessing satisfactory storage stability.

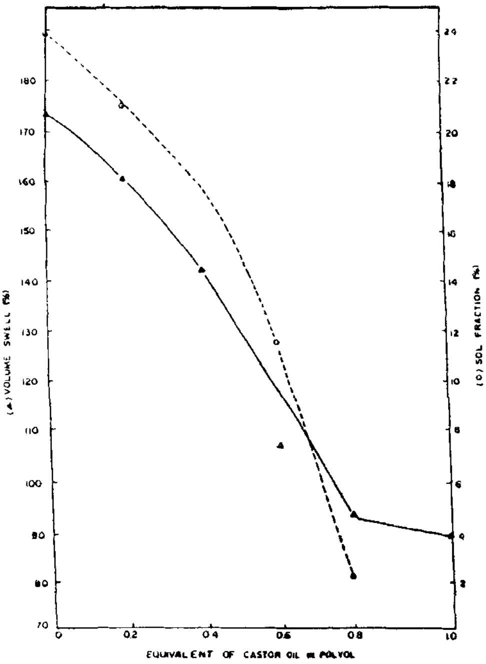

FIG. 1 VOLUME SWELL AND SOLUBLE FRACTION OF PU ELASTOMERS

The elastomer samples were prepared with NCO/OH ratio 1.05/1.0. The mixed resins provided sufficient time for mixing, degassing and casting. Increase in castor oil ratio in the blend, resulted in higher viscosity of the prepolymers. Cast sheets were tested after one month aging at room temperature.

These elastomers may be visualized as copolymers having randomly distributed soft segments of castor oil and PPG and hard segments of TDI and BD. Elastomer based on only PPG has 23.8 % solubility whereas elastomer based on only castor oil has negligible solubility. However , solubility of elastomers $E_1$ to $E_6$ decreases with the increasing ratio of castor oil (Fig.1). The degree of swelling is dependent on the amount of castor oil and it decreases from 173.5 % in $E_1$ to 89.9 % in $E_6$ .

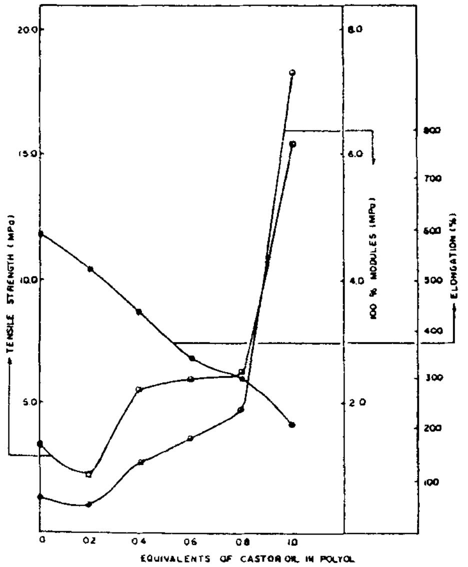

FIG. 2 PHYSICAL PROPERTIES OF PU ELASTOMERS

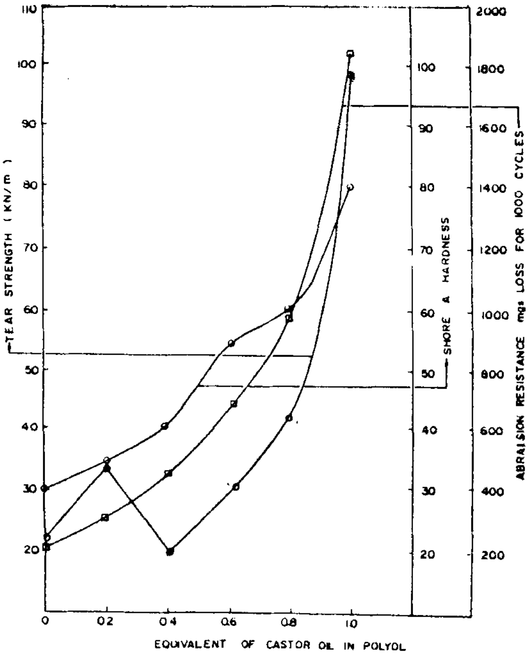

FIG. 3 PHYSICAL PROPERTIES OF PU ELASTOMERS

**Physical and thermal properties**: The physical properties of samples were dependent on the amount of castor oil in the polymer. The tensile strength increases from 2.09 to 15.46 MPa for elastomers $E_2$ to $E_6$ (Fig.2). Initially it declines from 3.34 to 2.09 MPa for samples $E_1$ to $E_2$. 100 % modulus also shows similar behaviour.
It decreases from 0.529 to 0.389 for $E_1$ to $E_2$. But increases from 0.389 to 7.31 MPa for $E_2$ to $E_6$. Elongation at break decreases from 590 % for $E_1$ to 210 % for $E_6$ indicating that as castor oil polyol increases, higher cross-linking occurs due to its trifunctional nature.

With increasing content of castor oil in the blend glass transition (Tg) of soft segment increases from $-43.5^{\circ}$ to $15.1^{\circ}C$ for elastomers $E_1$ to $E_6$ (Table 2). Tear strength for samples $E_1$ to $E_2$ increases from 22.05 to 32.94 KN/m respectively. Then the tear strength value for sample $E_3$ decreases to 20.73 KN/m.

## TABLE 3
## THERMOGRAVIMERTIC ANALYSIS OF POLYURETHANE ELASTOMERS

| Sample | $E_1$ | $E_2$ | $E_3$ | $E_4$ | $E_5$ | $E_6$ |
|---|---|---|---|---|---|---|
| $T_0$ °C | 272 | 264 | 267 | 272 | 259 | 261 |
| $T_{10}$ °C | 308 | 300 | 305 | 314 | 305 | 308 |
| $T_{30}$ °C | 357 | 351 | 339 | 343 | 333 | 333 |
| $T_{50}$ °C | 380 | 386 | 393 | 397 | 389 | 389 |
| $T_{max-1}$ °C | 321 | 319 | 322 | 333 | 328 | 328 |
| $T_{max-2}$ °C | 389 | 394 | 404 | 411 | 408 | 464 |

Again it increases steadily as ratio of castor oil increases (Fig. 3). Shore A hardness increases from 30 for $E_1$ to 80 for $E_6$. On the other hand weight loss due to abrasion increases as castor oil content increases. This shows abrasion properties deteriorate as crosslinking increases with increasing ratio of castor oil.

According to Apukhtina[10] et al.,abrasion resistance of PU elastomers decreases as the length of the flexible diol chain increases from $(CH_2)_2$ to $(CH_2)_6$. The least abrasion resistance of elastomer $E_6$ based on castor oil with high crosslinking may be attributed to the triglyceride structure of castor oil containing ricinoleate and $CH_2$ alkyl chains.

Weight loss of the elastomers have been recorded from 250° C to 600° C. Initial decomposition temperature($T_0$) and temperature at 10 % ($T_{10}$), 30 % ($T_{30}$), and 50 %($T_{50}$) weight loss occurred are given in Table 3 and Fig. 4. $T_0$ for all the samples is between 259° to 272° C. $T_{10}$, $T_{30}$ and $T_{50}$ temperature for elastomer samples are 305° to 314°, 333° to 357°, and 380° to 397° C respectively.

Temperature $T_{max-1}$(decomposition temperature at first stage) and $T_{max-2}$(decomposition temperature at second stage) are between 319°to 328° C and 394° to 463° C respectively. These elastomers have lower thermal stability irrespective of the higher crosslinking as ratio of castor oil is increased .Thermal data of MDI based PU

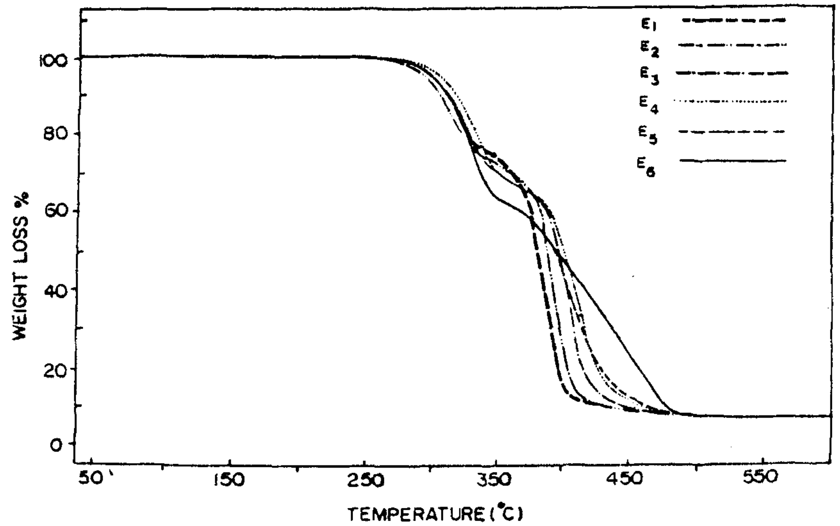

FIG 4 THERMOGRAVIMETRIC ANALYSIS OF POLYURETHANE ELASTOMERS

rubbers of PPG/castor oil blends has shown higher thermal stability than the PU elastomers of TDI system$^{11}$.

Dynamic mechanical behaviour: The dynamic mechanical behaviour of samples E$_2$, E$_4$ and E$_6$ is shown in Fig. 5-7. The graphs of elastomers have a shape typical for amorphous system (Fig.6).

Increasing castor oil content shifts the main transition zone to higher temperatures. Thus, as expected the main transition region of polyether chain based on PPG is located at about $40^{o}$ C lower temperature than the main transition of castor oil.

Due to higher functionality of castor oil (about 2.7) and increasing oil content, the modulus G$'$ in the rubber region increases (Fig.5).

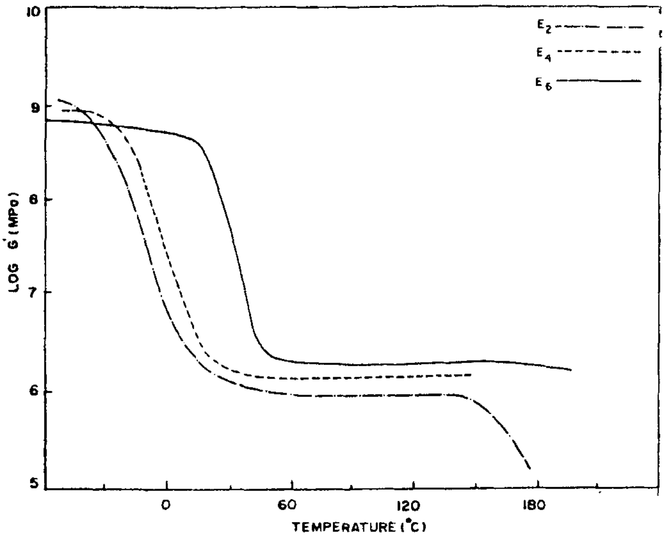

FIG.5 TEMP. DEPENDENCE OF TENSILE STORAGE (G') MODULUS FOR POLYURETHANE ELASTOMERS

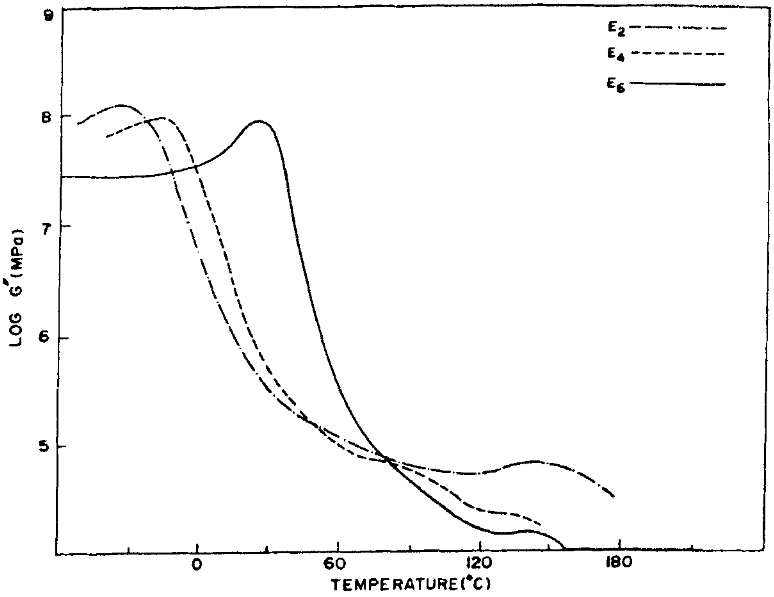

FIG.6 TEMP. DEPENDENCE OF TENSILE STORAGE(G'') MODULUS FOR POLYURETHANE ELASTOMERS

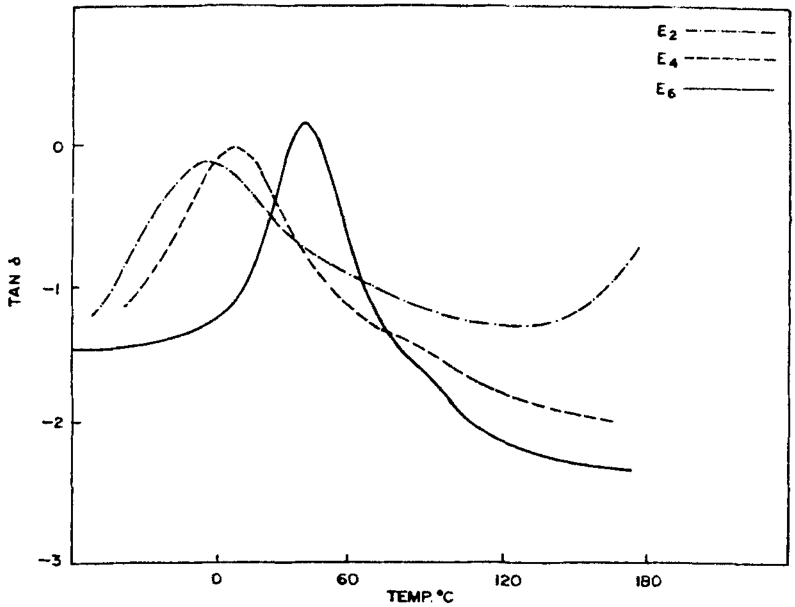

FIG. 7. TEMPERATURE DEPENDENCE OF TAN δ FOR POLYURETHANE ELASTOMERS

From the value of $G'$ for sample $E_6$ at $110^0$ C ($G'$=2 MPa) it is possible to calculate the molecular weight $M_c$ between the crosslinks.

$$M_c = \rho RT/G'$$

where $\rho$ is the density, R is the gas constant and T is the temperature. One can find the value $M_c$ = 1800 which qualitatively correlates with the estimated value of $M_c$ (2/3 CO + TDI) 800.

For sample $E_2$ with higher content of PPG transition to flow region on $G'$ and log $\delta$ can be observed (Fig.5 and Fig. 7). This means that chemical network was not formed in this case. From Fig.7 one can see, that broadening of main transition takes place with increasing content of PPG. X-ray diffraction patterns of PU elastomer samples $E_1$ to $E_6$ do not show significant variation on the spectra (Fig. 8). The spectra consisted of one broad halo in the region between $2\theta = 19^\circ$ and $21^\circ$, indicating that major portion of the polymer is amorphous in character.

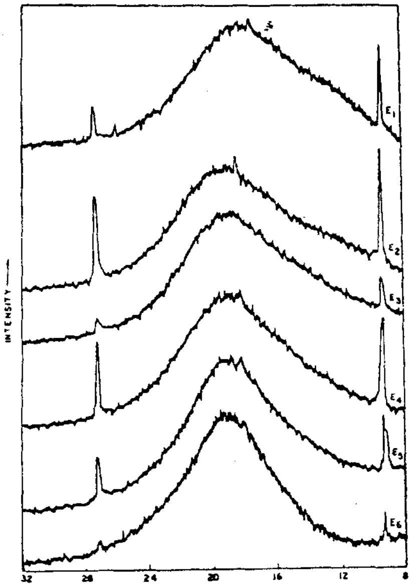

FIG 8 X-RAY DIFFRACTION PATTERN OF PU ELASTOMERS

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