

The Effect of Castor Oil on the Structure and Properties of Polyurethane Elastomers*

P. K. SAXENA, S. R. SRINIVASAN,^{†,1} J. HROUZ, and M. ILAVSKÝ²

¹ Division of Polymer Chemistry, National Chemical Laboratory, Pune-411008, India and ²Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences Heyrovsky sq 2, 162 06 Prague 6, Czechoslovakia

SYNOPSIS

Segmented polyurethane elastomers based on a mixture of castor oil and poly(propylene glycol), 4,4'-diphenylmethane diisocyanate, and 1,4-butanediol were prepared. The ultimate, thermal, dynamic mechanical behavior and morphology were studied. The use of castor oil shifts the main transition region of the soft phase to higher temperatures (the glass transition temperature T_g increases) improves abrasion resistance and the tensile strength. The multifunctionality of castor oil leads to the crosslinking of the soft segments and a decrease of the sol and swelling of elastomers.

INTRODUCTION

Synthetic polyurethane elastomers are characterized by their high mechanical strength, resiliency, and good resistance to abrasion. The essential constituents of polyurethane elastomers are a long chain oligomeric polyol, a diisocyanate, and low molecular diol or diamine as chain extender. The polyol may be a polyether or polyester oligomer. 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, appears to be a good polyol for the synthesis of urethane elastomers.¹⁻⁷ Cast polyurethane elastomers based on castor oil and diisocyanate are highly crosslinked, hard, and have low elongation at break. We have observed that castor oil possess excellent compatibility with the poly(propylene glycol)s (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 and PPG for producing castable urethane elas-

tomers. Effects of the different ratios of two polyols on the physical, thermal, and dynamic mechanical properties and the morphology of these urethane elastomers have been studied.

EXPERIMENTAL

Materials Used. Poly(propylene glycol) (PPG), having molecular weight $M_n = 1930$, was obtained from M/s. BASF Wyandotte Corporation U.S.A. Castor oil (I. P. grade) having hydroxyl number 165 mg KOH/gm was used. 1,4 Butanediol (BD) was obtained from M/s. Koch Light Lab., U.K.

4,4'-Diphenylmethane diisocyanate (MDI) was obtained from M/s. BASF Wyandotte Corporation, U.S.A. The isocyanate was freshly distilled at 195°C (1 mm Hg) prior to use.

Preparation of Prepolymers. In a four-necked flask, equipped with a mechanical stirrer, thermometer, nitrogen inlet, and outlet, a calculated quantity of MDI was added and melted. The desired amount of mixture of PPG and castor oil (Table I) was added to the molten MDI at 45–55°C. Necessary cooling was applied when required. The reactants were heated at $65 \pm 5^\circ\text{C}$ for 0.5 h to complete the reaction. The isocyanate contents (% NCO) of prepolymers were determined as per literature method.⁸

Preparation of Elastomers. The required amount of prepolymer, 1,4 BD (Table II) and cat-

* NCL Communication No. 4759.

† To whom correspondence should be addressed.

Table I Composition and Properties of Prepolymers^a

Sample	P ₁	P ₂	P ₃	P ₄	P ₅
Composition (part by weight)					
Castor Oil	— (0.0)	4.95 (0.2)	11.37 (0.4)	20.04 (0.6)	32.38 (0.8)
PPG	62.18 (1.0)	56.19 (0.8)	48.14 (0.6)	37.92 (0.4)	22.98 (0.2)
MDI	37.82	38.86	40.21	42.04	44.69
NCO/OH	4.70	4.27	3.85	3.43	3.00
Properties					
Color	Colorless	Yellow	Yellow	Yellow	Yellow
NCO Content	9.90	9.87	9.95	9.80	9.78
Eq. wt per NCO group	424.2	425.5	422.1	428.8	429.50

^a Parentheses indicate the equivalent ratios.

alyst dibutyltindilaurate (0.01 wt % of reactants) were weighed in a beaker, stirred vigorously, degassed, and poured in a heated sheet mold at 80°C, which was treated with silicone release agent. The sheets of elastomers produced were 140 × 100 × 2 mm size. The samples were cured at 80°C for 2 h and finally at 110°C for an additional 12 h. All the samples were postcured at room temperature for 30 days prior to testing.

Mechanical Testing. The tensile strength, 100% Young's modulus, and elongation at break were determined according to ASTM D 412. Tear strength was determined according to ASTM D 624-54 using die-c. Specific gravity was determined as per ASTM D 297-55T.

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

Glass-Transition Temperature T_g . Differential scanning calorimetry was carried out with a

Rigaku thermal analyzer Model DSC-8230 using a sample weight of 17–18 mg. The heating rate was kept at 10°C/min in a nitrogen atmosphere.

Thermogravimetric Analysis (TGA). A Perkin-Elmer 7 series, thermal analyzer was used in the study. The samples were tested at a heating rate of 10°C/min under nitrogen atmosphere, at IMC, Prague.

Scanning Electron Microscopy (SEM). The elastomer samples were examined under a SEM of JEOL, JSM35 at IMC, Prague.

Abrasion Resistance. Taber abrasion tester Model No. 503, using H-18 abrading wheel for 5000 cycles.

Solvent Analysis and Soluble Extract. The samples were kept in dimethylformamide (DMF) for a week and sol fractions (%) were determined. The volume swell (%) was determined in benzene from the increase in weight of the sample after keeping it in benzene for a week.

RESULTS AND DISCUSSION

Several vegetable oils and their derivatives have been employed in the preparation of urethane products.

Table II Composition of the Elastomers

Sample	E ₁	E ₂	E ₃	E ₄	E ₅
Composition (part by weight)					
Prepolymer	90.82 (P ₁)	90.85 (P ₂)	90.77 (P ₃)	90.90 (P ₄)	90.92 (P ₅)
1,4 BD	9.18	9.15	9.33	9.10	9.08
NCO/OH	1.05	1.05	1.05	1.05	1.05
Urethane (%)	17.9	18.34	18.92	19.84	21.07
Glass Transition temperature (T_g °C)	-53.2	-48.2	-40.0	-38.6	-30.0

Goldblatt⁹ 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 (P₁-P₅) were prepared having the same isocyanate contents. Part of the PPG was replaced successively by castor oil (20-80 parts by eq weight). Quantities of MDI were also varied accordingly. The average molecular weight of polyol mixture decreases as castor oil content increased and thus the amount of MDI required increases to obtain prepolymers having the same isocyanate content. All the prepolymers were free-flowing viscous liquids possessing satisfactory storage stability.

The elastomer samples were prepared with an NCO/OH ratio 1.05/1 in the final polymers. The mixed resins were provided with sufficient time for mixing, degassing, and casting. Increase of castor oil content in the prepolymers blends, resulted in higher viscosity. Cast sheets were tested after 1 month aging at room temperature. The infrared spectra showed absence of the isocyanate peak at 2270 cm⁻¹.

These elastomers may be visualized as copolymers having randomly distributed soft segments of castor oil and PPG and hard segments of MDI and 1,4 BD. The castor oil acts as a crosslinker due to its higher functionality. Elastomers based on only PPG are

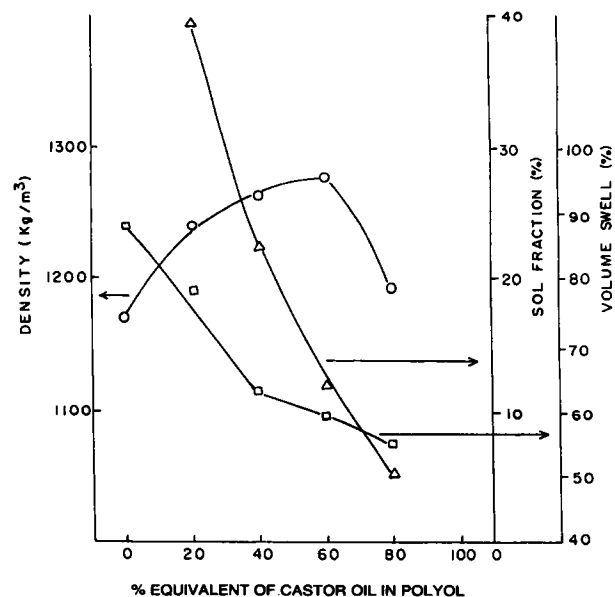


Figure 1 Density and soluble extract analysis of Pu elastomers.

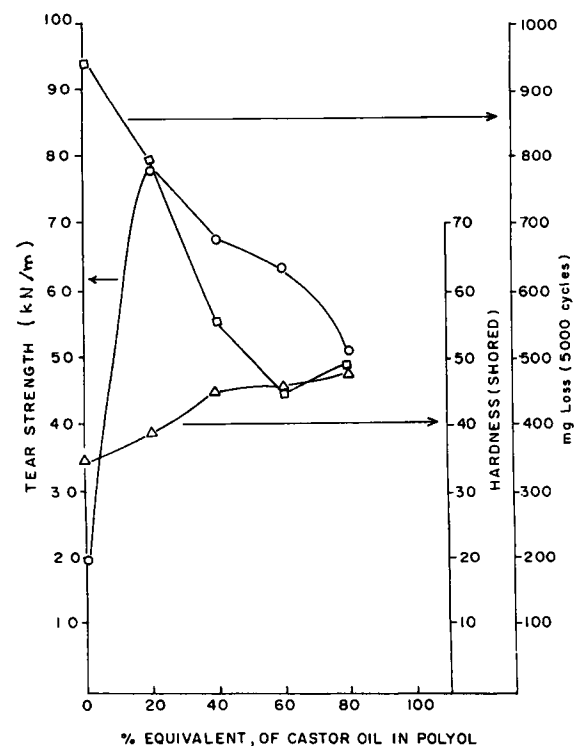


Figure 2 Mechanical properties of Pu elastomers.

soluble in DMF. However, the solubility of elastomers E₁-E₅ decreases with increasing castor oil content in the polyol blends. The degree of swelling (Fig. 1) is dependent on the amount of castor oil and it decreases from 87.7% in E₁ to 54.7% in E₅. This gives a measure of crosslinking in the polymer.

Mechanical and Thermal Properties. The mechanical properties of samples were dependent on the amount of castor oil in the polymer. The weight loss determined by the abrasion tester decreases from elastomer E₁ (950 mg) to E₄ (450 mg) (Fig. 2) indicating that abrasion resistance improves as the castor oil component increases. The tensile strength shows improvement from E₂ to E₅ (Fig. 3). Initially it declines from 17.8 to 15.3 MPa for samples E₁-E₂. The 100% modulus shows a progressive increase from E₁ to E₅. Tear strength also shows sharp increase from E₁ (19.9 kN/m) to E₂ (78 kN/m) but then progressively decreases in elastomers E₂-E₅. Shore D hardness shows a continuous increase with increasing castor oil content in the polyol mixture. Elongation at break decreases from 800 to 175% for E₁-E₅ as polyether decreases (Fig. 3). As expected, with increasing content of castor oil. The glass transition temperature (T_g) of the soft segment increases from E₁ to E₅ (Table II) from -53 to -30°C.

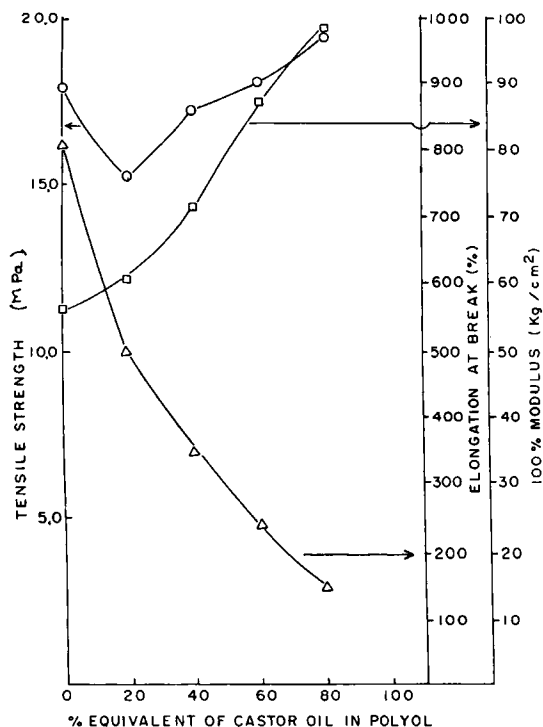


Figure 3 Mechanical properties of Pu elastomers.

Weight losses of the elastomers have been recorded from 250 to 600°C. Initial decomposition temperature T_0 and temperature at 10 (T_{10}), 30 (T_{30}) and 50% (T_{50}) weight loss are given in Table III and Figure 4. T_0 marginally increases and then decreases. T_{10} and T_{30} temperatures decrease as castor oil content increases in the polyol blend, whereas T_{50} increases as castor oil part increases. Temperature $T_{\max-1}$ (decomposition temperature at the first stage) are practically the same for all elas-

Table III Thermogravimetric Analysis of Polyurethane Elastomers

Sample	E ₁	E ₂	E ₃	E ₄	E ₅
T_0 (°C)	289	292	290	276	285
T_{10} (°C)	325	325	319	312	314
T_{30} (°C)	370	359	364	343	346
T_{50} (°C)	386	389	392	383	397
$T_{\max-1}$ (°C)	330	333	327	326	326
$T_{\max-2}$ (°C)	390	396	403	400	410

tomers samples. Finally temperature $T_{\max-2}$ (decomposition temperature at second stage) increases steadily as PPG content decreases.

Dynamic Mechanical Behavior and Morphology. Dynamic mechanical behavior of samples E₁, E₃, and E₅ have been shown in Figures 5 and 6. The temperature dependence of the storage G' and loss G'' moduli shows a typical two-phase behavior with the soft polyether-castor oil and hard MDI-butanediol phase. The soft phase transition zone of sample E₁ is located roughly at -40°C (the main transition region of polyether). Increasing the castor oil content shifts the transition zone to higher temperatures due to increasing crosslinking of the soft phase. From the temperature dependences of both components, G' and G'' , we infer that the hard phase transition is located around 160°C and that in the case of samples E₃ and E₅ the network structure has already been formed (in accord with swelling experiments) (Fig. 1).

The temperature dependence of moduli G' and G'' in the rubbery plateau region (from 30 to 120°C) is affected by the crosslinking of the soft phase (given

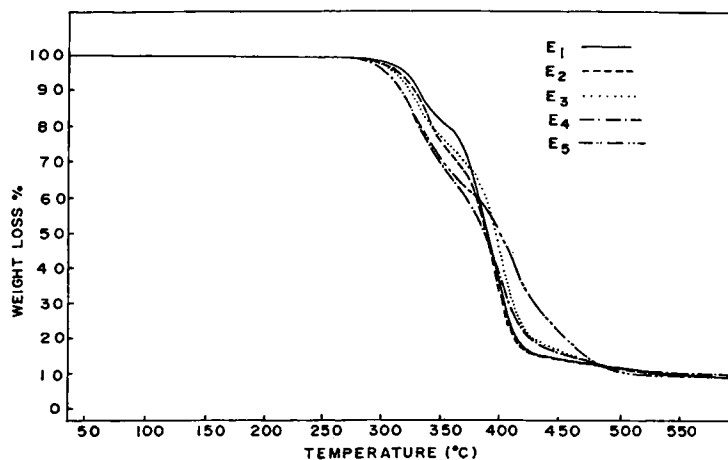


Figure 4 Thermogravimetric analysis of polyurethane elastomers.

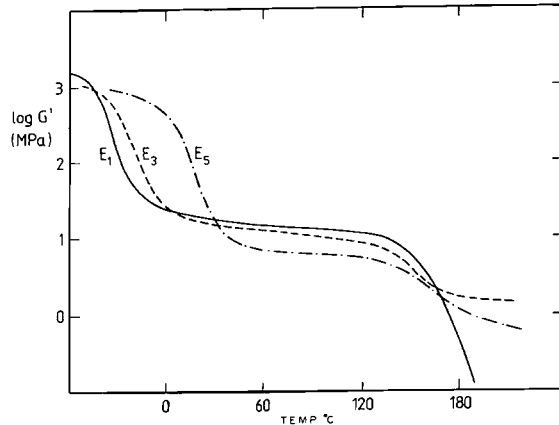


Figure 5 Temperature dependence of tensile storage (G') modulus for polyurethane elastomers.

by the castor oil content) and also by the amount and structure of the hard phase. As the weight fraction of the hard phase for all measured samples is roughly constant (50%), the decrease in the storage G' and loss G'' modulus at 120°C with decreasing content of PPG suggests that castor oil makes the hard less perfect. Values of the G' modulus of our samples at 120°C (from the 5 MPa sample, E_5 , to the 10 MPa sample, E_1) lie in a region found for the PU system¹⁰ based on polycaprolactone diol–MDI–1,4 butane diol and are lower by 1 order of magnitude than those for the polyurethaneimide system¹¹ based on poly(ethylene adipate) glycol–MDI–pyromellitic dianhydride.

The photograph of the sample E_4 (PPG-0.4–castor oil-0.6) was taken at 2000 times magnification at 60° angle by SEM (Fig. 7). The photo shows that the elastomer possesses fine uniform structure of single phase with homogeneity.

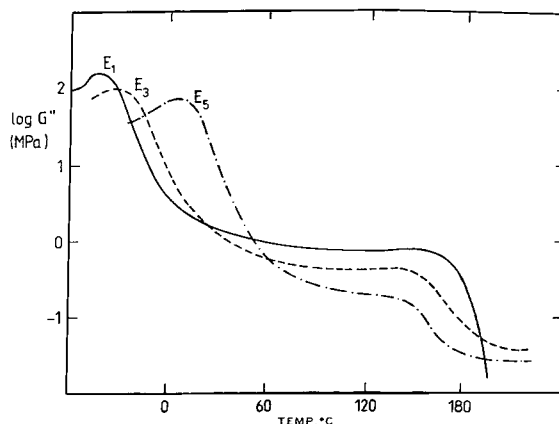


Figure 6 Temperature dependence of tensile loss (G'') modulus for polyurethane elastomers.

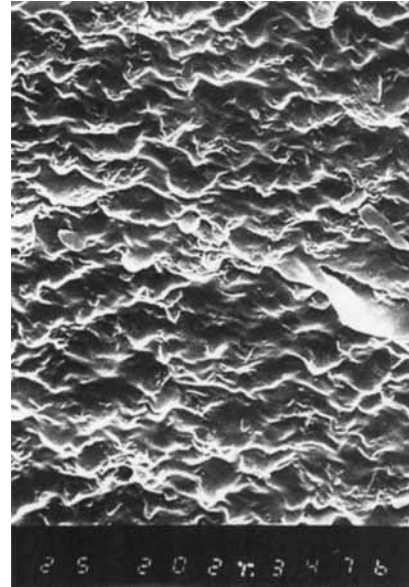


Figure 7 SEM photograph of polyurethane elastomer.

We thank Shri R. R. Katti, Assistant Manager M/s. I. R. Technology Services Pvt. Ltd, Bombay for painstaking efforts to get the DSC data of polyurethane samples from Rigaku Corporation, Japan. The authors also thank Dr. S. Sivaram, Deputy Director and Head, Division of Polymer Chemistry, N.C.L., Pune for his keen interest and encouragement.

REFERENCES

1. H. L. Heiss, *Rubber Age*, **88**(1), 89 (1960).
2. P. K. Saxena, S. K. Menon, and S. R. Srinivasan, *J. Polym. Mater.*, **3**, 251 (1986).
3. T. L. Smith and A. B. Magnusson, *Rubber Chem. Technol.*, **35**, 1753 (1962).
4. N. D. Ghatge and V. B. Phadke, *J. Appl. Polym. Sci.*, **11**, 629 (1967).
5. G. C. Toone and G. S. Wooster, *Off. Dig.*, **32**, 230 (1960).
6. Z. S. Petrovic and D. Fajnik, *J. Appl. Polym. Sci.*, **29**, 1031 (1984).
7. C. K. Lyon and V. H. Garrett, *J. Am. Oil Chem. Soc.*, **50**, 112 (1973).
8. D. J. David and H. B. Staley, *Analytical Chemistry of Polyurethanes. Vol. XVI. Part III, High Polymer Series*, Wiley-Interscience, New York, 1969, pp. 87–89.
9. L. A. Goldblatt, *J. Am. Oil Chem. Soc.*, **39**, 506 (1962).
10. C. G. Seefried, Jr., J. V. Koleske, and F. E. Critchfield, *J. Appl. Polym. Sci.*, **19**, 2503 (1975).
11. B. Masiulanis, J. Hrouz, J. Baldrian, M. Ilavský, and K. Dušek, *J. Appl. Polym. Sci.*, **34**, 1941 (1987).

Received May 17, 1990

Accepted May 14, 1991