

NOTES

Thermoset Polyurethanes from Hydroxyl-Terminated Natural Rubber

Telechelic liquid prepolymers that yield rubbery products upon end-to-end linking are well known in modern technology. The telechelic polymeric diols are the most important ingredients in many kinds of modern polyurethanes. Considerable amount of work has been done on the degradation of natural rubber (NR) under various experimental conditions¹⁻⁶ to prepare different functional natural rubber. Gupta et al.⁷ reported the preparation of hydroxy-terminated natural rubber (HTNR) using hydrogen peroxide as the reagent at high temperature and pressure. In the present investigation, the HTNR was prepared by the procedure reported by Ravindran et al.^{8,9} A series of thermoset polyurethanes were prepared using HTNR and toluene diisocyanate (TDI) or hexamethylene diisocyanate (HMDI). Their thermal and mechanical properties were investigated.

EXPERIMENTAL

Materials

Natural crumb rubber (ISNR-5, M_n 820,000, intrinsic viscosity in benzene at 30°C; 4.45 dL/g; Wallace plasticity [Po] 39.0) was supplied by the Rubber Research Institute of India, Kottayam. Toluene, methanol, and tetrahydrofuran (THF) were of reagent grade and were dried and distilled before use.

Preparation of HTNR

The HTNR was prepared by the procedure given in Ravindran et al.⁸

Preparation of Polyurethanes

HTNR (4.53 g) was reacted with TDI (0.057 g) to maintain a NCO/OH ratio of 1 : 2 using 2-3 drops of dibutyl tin dilaurate as catalyst. The reaction was carried out at 60-65°C with continuous stirring for 2 h. Then, the reaction product was casted on a mercury pool. Following

the above procedure, other prepolyurethanes with varying NCO/OH ratios were prepared. The experiments were also repeated with HMDI.

The molecular weight distribution of the HTNR was measured by gel permeation chromatograph (GPC) (Water Associates with RI detector using THF as carrier solvent). IR spectrum was recorded with a NICOLET Fourier transform infrared spectrophotometer. The mechanical properties are measured according to ASTM D 638 (1977). The thermal stability (Tonset) was measured on a Perkin-Elmer differential scanning calorimeter (DSC) in nitrogen atmosphere at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

The IR spectra of the HTNR shows bonds at 3600-3400 (broad, O-H str. 3035 (m), 2961 (S), 2928 (S), 2855 (S), (C-H str.), 1664 (m; C=C, *cis*-vinylene); 1450 (S), 1375 (S), (-H def.), 1310 (m; C-O str., aliph. prim. alcohol); 837 (m; CH₃ def.); 836 cm⁻¹ (S, C-H out-of-plane deformation in -CH=CCR). The characteristic urethane peaks at 1690, 1510, 700, and 620 cm⁻¹ indicate the urethane formation.

The GPC trace of HTNR shows $\overline{M}_n = 8.40 \times 10^3$, $\overline{M}_w = 1.51 \times 10^4$, Z-avg. = 3.01×10^4 , Vis-avg. = 1.44×10^4 , and dispersity = 1.80. The thermosetting polyurethane elastomers prepared from the above HTNR was subjected to mechanical properties, and the results are given in Table I.

The effect of structure of diisocyanate on physical properties have been analyzed by many workers.¹⁰⁻¹³ The

Table I Mechanical Properties of Polyurethane Elastomers Prepared from HTNR

Diisocyanate	NCO/ OH	Tensile Strength (kg/cm ²)	Percent Elongation
2,4/2,6-Toluene diisocyanate	1.2	29.79	431.82
	1.3	33.58	338.32
	1.4	48.53	295.45
Hexamethylene diisocyanate	1.2	4.34	174.99
	1.3	6.47	272.72
	1.4	11.86	204.95

Table II Thermal Stability of Polyurethane Elastomers

Diisocyanate Used	R Value	Tonset (°C)
TDI	1.1	357.50
TDI	1.2	370.45
TDI	1.3	379.31
TDI	1.4	382.88
HMDI	1.1	360.25
HMDI	1.2	378.11
HMDI	1.3	387.13
HMDI	1.4	389.04

tensile strength and percent elongation is more for TDI/HTNR-based polyurethanes than for HMDI/HTNR-based polyurethanes. This may be due to the hard segmented nature of TDI. In TDI polyurethanes, the tensile strength increases with an increase in the R value and a corresponding decrease in percent elongation was observed, whereas in HMDI-based polyurethane, the tensile strength increases with the R value and the percent elongation is maximum at $R = 1.3$.

The oxidative thermal stability (Tonset) was measured using DSC, and the values are given in Table II. From the table it is clear that the TDI-based polyurethane elastomers are thermally less stable than are the corresponding HMDI-based polyurethanes, which is in agreement with the results reported earlier.¹⁴ The thermal stability of all the films are almost in the same range. The R value has a slight effect on the thermal stability. The increase in the R value increases the thermal stability, which may be due to the formation of more thermally stable cross-link (allophanate and biurett).

In conclusion, (i) the TDI-based polyurethane elastomers have higher tensile strength and lower thermal stability than does the HMDI-based polyurethane elastomer, and (ii) the increase in the R value increases the tensile strength and the oxidative stability of the polyurethane elastomers.

References

1. L. M. K. Tillekeratne, P. V. A. G. Perera, M. S. C. DeSilva, and G. Scott, *J. Rubber Res. Inst. Sri Lanka*, **54** (2), 501 (1977).
2. R. Rautrat, *Rer. Gen. Caoutch. Plast.*, **600**, 91 (1980).
3. V. V. Voronenkov, G. V. Bobykina, Yu. F. Shapiro, and E. A. Lazurin, *Vysokomol. Soedin.*, **20**, 724 (1978).
4. S. K. Gupta, B. John, and M. R. Kurup, in *Proceedings of International Rubber Conference*, Rubber Research Institute, Kottayam, India, Nov., 1980.
5. Jpn. Kokai Pat. 75,117,881 (1975) (to Japan Synthetic Rubber Co. Ltd.); O. Nabora, E. Hiroyi, N. Yozo, *Chem. Abstr.*, **84**, 1326985 (1976).
6. P. Kitzmantel, *Allg. Prakt. Chem.*, **24**, 93 (1973).
7. S. K. Gupta, M. R. Kurup, E. Devadoss, Rm. Muthiah, and S. Thomas, *J. Appl. Polym. Sci.*, **30**, 1095 (1985).
8. T. Ravindran, M. R. G. Nayar, and J. D. Francis, *Makromol. Chem. Rapid Commun.*, **7**, 159 (1986).
9. T. Ravindran, M. R. G. Nayar, and J. D. Francis, *J. Appl. Polym. Sci.*, to appear.
10. G. Trappe, in *Advances in Polyurethane Technology* J. M. Buist and H. Gudgeon, Eds., MacLaren, London, 1968, Chap. 3.
11. C. S. Schollenberger, in *Polyurethane Technology* P. Bruins, Ed., Wiley, New York, 1969, Chap. 10.
12. J. H. Saunders, *Rubber Chem. Tech.*, **35** (5), 1259 (1960).
13. K. Pigott, B. F. Frye, K. R. Allen, S. Steingiser, W. C. Darr, and J. H. Saunders, *J. Chem. Eng. Data*, **5** (3), 391 (1960).
14. Y. Norimuchi, *Ariake Kogyo Koto Senmon Gakko Kiyo*, **16**, 105-110 (1980), *Chem. Abstr.*, **93**, 240335b (1980).

PONSWAMY RAJALINGAM
GANGA RADHAKRISHNAN

Polymer Division,
Central Leather Research Institute,
Madras 600020, India

JOSEPH D. FRANCIS

Department of Polymer Science
& Rubber Technology,
Cochin University of Science
& Technology,
Cochin, India

Received July 28, 1989

Accepted November 30, 1990