Synthesis and Characterization of Castor Oil Urethane Triamine Networks

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Synopsis

Castor oil was polymerized with diisocyanate and crosslinked with primary triamine (Jeffamine T-403) to form networks. The effect of triamine as a crosslinking agent on rubbery castor oil urethane elastomer was determined by measuring network parameters such as average molecular weight between crosslinks (MC) number of polymer chains per unit volume (N), tensile strength, and modulus of the networks. The crosslinking density was varied by varying the ratio of $NCO:NH_2$ from 0.60 to 0.95. The results indicated the formation of highly crosslinked elastomers at all $NCO:NH_2$ ratios employed. The tensile strength and modulus increased with increasing crosslink density up to a value of $NCO:NH_2$ 0.85 and after this there was no significant change, indicating the maximum limit of improvement attainable in terms of network characteristics.

INTRODUCTION

Castor oil-based polyurethanes form a variety of elastomers and plastics useful for many applications.[1] Castor oil-based polymers find use as elastomeric components in rubber-toughened interpenetrating network (IPN) plastics. Polymerization and crosslinking of castor oil leads to rather soft elastomers.[2-4] In all these instances, the castor oil is polymerized and crosslinked either by sulfur or by diisocyanates.

There is however no report on the use of a primary triamine as a crosslinking agent for rubbery elastomers based on castor oil. Since the reaction between an amine and an isocyanate results in the formation of stiffer urea linkage, some *in situ* toughening of elastomer is possible.[5-7] With this objective in view, the present study on the synthesis and characterization of castor oil urethane triamine networks was undertaken. Networks with different crosslink densities were prepared by varying the $NCO:NH_2$ ratios from 0.60 to 0.95. The $NCO:NH_2$ ratios were chosen according to values corresponding to various degrees of gelation. The networks were characterized by swelling experiments, stress–strain analysis, and modulus temperature study to determine the effect of amine crosslinking on the rubbery castor oil elastomers.

EXPERIMENTAL

Materials

Castor oil [Indian Pharmacopia OH.No. (KOH/mg/g) 163-164, Acid No (KOH/mg/g) 1.51], 2,4-toluene-di-isocyanate (Fluka-AGS), amine equivalent

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TABLE I
Castor Oil Urethane Triamine Networks

Sample no.	Prepolymer composition NCO/OH	Wt. Jeffamine (g.)	Final NCO/NH_2 ratio
1	2:1	24.25	0.60
2	2:1	26.00	0.65
3	2:1	28.01	0.70
4	2:1	29.91	0.75
5	2:1	31.82	0.80
6	2:1	34.00	0.85
7	2:1	36.16	0.90
8	2:1	37.88	0.95

[(%) 81.4], Jeffamine T-403 (equivalent weight (g/mol) 136.4, functionality 2.96) were all used as received.

Procedures

Synthesis of Castor Oil Urethane Triamine Networks

A known weight of the castor oil was mixed with excess 2,4-toluene diisocyanate (to give a ratio of NCO:OH 2:1) at 50°C in an oil bath to produce an isocyanate-terminated prepolymer. The mixture was stirred vigorously at this temperature for one hour and degassed for 15 minutes by applying vacuum to produce a clear bubble-free liquid prepolymer.

The degassed prepolymer was mixed and crosslinked with enough primary triamine to give a final predetermined NCO/NH_2 ratio. The mixture was stirred vigorously for 10 minutes, degassed for another 10 minutes, and poured into a Teflon-coated mould and heated for 6 h at 80°C to complete the reaction. The resulting network was tough, pale reddish, and translucent. The several samples are described in Table I.

Instrumentation and Measurements

Swelling experiments. Several specimens of known dimension and weight were cut from the samples and swollen in several solvents of known solubility parameters from value 4 $(cal/cm^3)^{1/2}$ to 14 $(cal/cm^3)^{1/2}$ for two weeks at ambient conditions. From this experiment the number of polymer network chains per unit volume and the average molecular weight between crosslinks were measured.

Stress-strain measurements. This was conducted on an Instron tester at room temperature; a cross-head speed of 0.2 in./min was used. The force required to break the sample and the displacement at this point were recorded and the yield and tensile strengths and elongation at break calculated. The specimens were cut with minimum widths of 7.0–14.0 mm, thickness of about 1.0 mm, and gauge lengths of 30–50 mm. The results reported are an average of four specimens for each composition.

TABLE II
Parameters from Swelling Test for Castor-Oil Urethane Triamine Networks

NCO/NH_2 ratio	Maximum swelling in CCl_4 δp. $(cal/cm^3)^{1/2}$	$N \times 10^4$	Polymer chains / Unit volume	MC g/mol
0.60	8.6	1.62		7287
0.65	8.6	1.77		6281
0.70	8.6	2.03		5383
0.75	8.6	2.49		4208
0.80	8.6	2.77		3695
0.85	8.6	3.61		2787
0.90	8.6	4.90		1989
0.95	8.6	5.20		1831

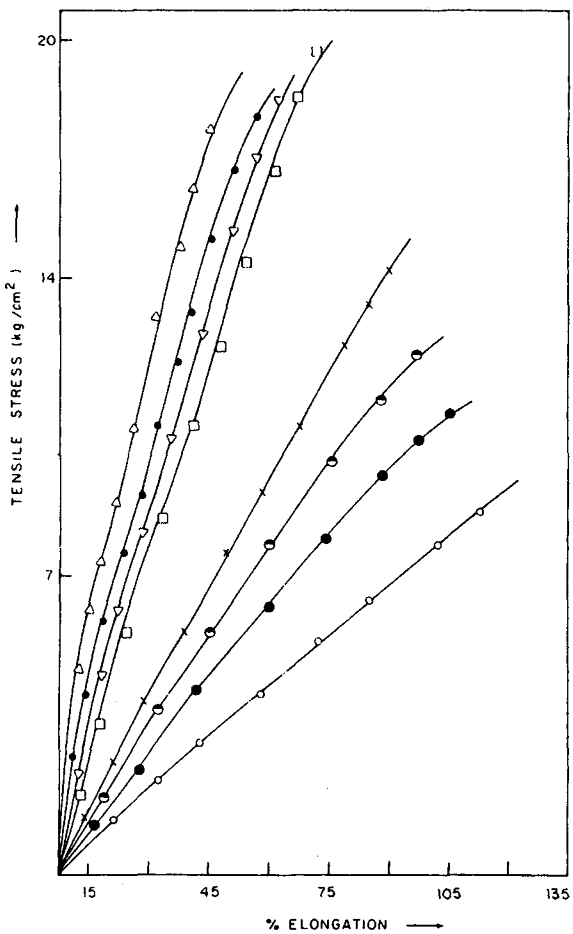

Fig. 1. Stress-strain behavior of castor-oil urethane triamine networks. NCO/NH_2 ratio: ○–0.60; ●–0.65; ⊖–0.70; ×–0.75; □–0.80; ▽–0.85; ●–0.90; △–0.95.

Modulus-temperature study. The shear modulus G as a function of temperature was measured by means of Gehman torsion stiffness tester.[8,9] E was calculated using the Young's modulus approximation $E \simeq 3G$.

RESULTS AND DISCUSSION

The degree of crosslinking determines many of the polymer network properties.[10,11] The chemical effects of the crosslinking agent on the ultimate properties of networks were reported earlier.[12,13] Since the castor oil forms rather soft elastomers, the triamine crosslinking is expected to produce *in situ* toughening and an elastoplastic-type network. The results of swelling tests for networks are given in Table II. The maximum swelling was taken to correspond to the solubility parameter of the polymer network[14,15] and the number of average molecular weight between crosslinks (MC) was determined using modified Flory-Rehner equation.[16-20] From a knowledge of densities of the network, the number of polymer network chains per unit volume (N) was determined, through the relationship $N = d/MC$.

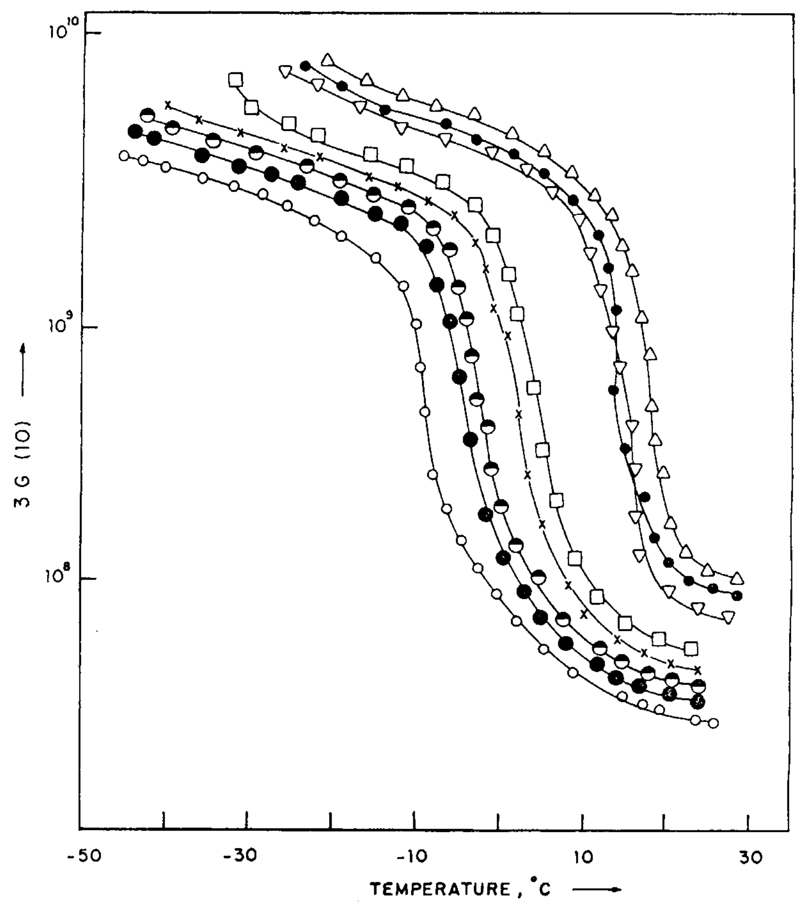

Fig. 2. Glass-rubber transition behavior of castor-oil urethane triamine networks NCO/NH_2 ratio: ○–0.60; ●–0.65; ◓–0.70; ×–0.75; □–0.80; ▽–0.85; ●–0.90; △–0.95.

It is clear from the values in Table II that a high degree of crosslinking was achieved for networks prepared at all $NCO:NH_2$ ratios.

The number of polymer chains per unit volume (N) increases and the MC values decrease with increasing crosslinking densities.

The tensile behavior of the networks are shown in Figure 1. It can be seen that the higher the crosslink density the higher the tensile strength, but the elongation tends to be lower. The maximum strength and elongation were noted up to an intermediate value of crosslink density of $NCO:NH_2 = 0.85$. Recovery from the strained state was also found to be faster for these networks. The tensile strength values were higher with little effect on the elongation, which indicates that urea crosslinkage contributes to the toughening of the elastomers.

Shear modulus (10 s) versus temperature data are presented in Figure 2. The glass transition temperature of the networks improves gradually and ranges between $-10°C$ to $+10°C$ as seen from Figure 2. It can be seen from Figure 2 that networks corresponding to $NCO:NH_2$ ratios of 0.85 to 0.95 show similar kinds of transition, and the values of glass transitions overlap. The transition curves point to the retention of rubbery behavior of the networks while showing improved toughening.

CONCLUSION

The use of primary triamine as crosslinking agent for rubbery soft castor oil urethane elastomers results in highly crosslinked networks even at lower levels of crosslink density. Further, the networks exhibit superior physical and mechanical properties without losing the rubbery nature. The maximum value of these properties was achieved at an intermediate level of crosslink density viz. $NCO:NH_2 = 0.85$. All these results suggest that the nature of the crosslinking agent affects the properties of the networks, and the required amount of reinforcement of networks could be achieved by careful control of crosslink density and choice of crosslinking agent.

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