Effect of cure temperature on urethane networks

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Stress relaxation was used over a wide temperature range (−70° to 160°C) to characterize two similarily prepared but differently cured polyurethane networks. Polymer A was cured at 140°C and polymer B was cured at 80°C. The differences in physical properties and responses of the two polymers to the applied strain were consistent with the hypothesis that high cure temperatures produce a more chemically (biuret) crosslinked structure whereas low cure temperatures favour a domain-separated structure. Polymer A (high cure temperature) strain-crystallized below 0°C, had a longer rubber-modulus than that of polymer B, and showed a load–deflection curve more typical of a chemically crosslinked polymer.

INTRODUCTION

The two-step polymerization in the production of urethane elastomers consists of (1) the reaction of a moderately low molecular weight diol with an excess of diisocyanate to form a prepolymer:

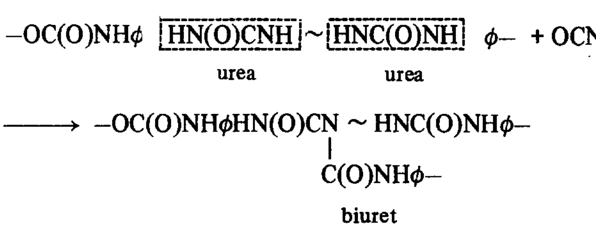
$$HO-OH + 2\,OCN\phi NCO \rightarrow \underset{\text{(prepolymer)}}{OCN\phi NHC(O)O-O(O)CHN\phi NCO} \qquad (1)$$

and (2) the reaction of the prepolymer with a low molecular weight diamine or diol (the chain extension step) to give the polyurethane product:

$$\text{Prepolymer} + H_2N \sim NH_2 \rightarrow$$
$$-\ \{OC(O)NH\phi NHC(O)NH \sim NHC(O)NH\phi NHC(O)O\}\ - \qquad (2)$$

where —— and { } are the soft and hard segments, respectively. Reaction (1) has been examined both theoretically[1] and experimentally[2]. Reaction (2) has received some attention[1,3,4], particularly the products, when they are thermoplastic polyurethanes[3,5–8].

The present study is concerned with the preparation and effect of cure temperature on the structure and physical properties of a diamine-cured thermosetting elastomer. In this case, owing to the influence of cure temperature, there is a second reaction in the chain extension step (2) in which the isocyanate reacts with one of the urea portions of the hard segment to form a biuret (3) (chemical crosslinks):



$$-OC(O)NH\phi\ \underbrace{\boxed{HN(O)CNH}}_{\text{urea}}\sim\underbrace{\boxed{HNC(O)NH}}_{\text{urea}}\ \phi-\ +OCN\phi-$$
$$\longrightarrow -OC(O)NH\phi HN(O)\underset{\substack{|\\ C(O)NH\phi-\\ \text{biuret}}}{CN} \sim HNC(O)NH\phi- \qquad (3)$$

EXPERIMENTAL

Preparation

One equivalent of degassed poly(tetramethylene glycol) ether (DuPont, Teracol 3000) was reacted with two equivalents of 2,4 toluene diisocyanate (DuPont, Hylene-T) for 12 h at room temperature (22°C). A ~15°C temperature rise was observed after about 30 min. Following heating and degassing at 80°C, the isocyanate content of the reaction mixture was found to be the theoretical value of 3.19%. N.m.r. analysis of the prepolymer, by Chokki's procedure[2], indicated that 95% of the diisocyanate was end-capped. The prepolymer was reacted with 3,3′-dichloro-4,4′diaminodiphenyl methane (MOCA), at an amine to unreacted isocyanate ratio of 0.95. The mixture was reacted and cured at the following temperatures:

Sample A 140°C (upper limit of MOCA stability)
Sample B 80°C (MOCA crystallizes below 80°C)

The samples were equilibrated at room temperature for two weeks.

Physical testing

Standard techniques, referred to in *Table 1*, were used to collect the physical characterization data that are listed in *Table 1*. Stress-relaxation measurements were carried out for 10^3 sec with strip samples at about 10% elongation over the

Table 1 Physical properties of polymers A and B

Cure temperature (°C)	A 140	B 80
Soft segment glass transition[a] (°C)	−77	−76
Crystalline melting point[a] (°C)	16	14
Density[b] (Mg/m^3)	1.044	1.043
Hysteresis (%) (1st cycle 300% elongation)	55	59
Tensile strength[c] (273/*T* MPa)	29.5	28.3
Elongation at break[c] (%)	570	640
Crescent tear[d] (kN/M)	44.5	56.9
DeMattia flex life[e] (cycles)	2654	544 × 10^3
25% compression set[f]	20	23

[a] DuPont DTA; [b] ASTM D297; [c] ASTM D412; [d] ASTM D624; [e] ASTM D813; [f] ASTM D395 (Method B)

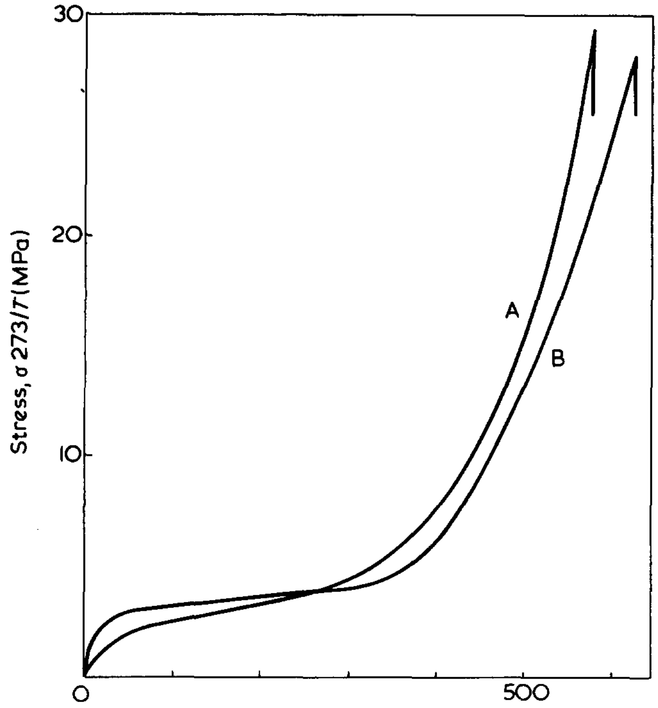


Figure 1 Stress–elongation curves for polymers A and B

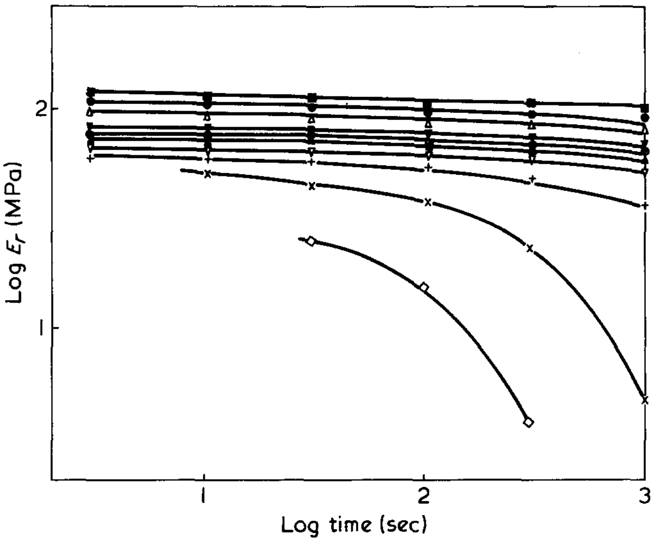


Figure 2 Reduced tensional stress relaxation modulus curves for polymer A. Temperature (°C): ■, 10; ●, 24; △, 40; ▼, 55; ⊕, 70; ▲, 100; ▽, 120; +135; X, 150; ◇, 160

temperature range from –70° to 160°C using Instron equipment. The rate of sample elongation was 8.3 x 10^{-2} m/sec.

RESULTS AND DISCUSSION

Table 1 presents a number of physical properties and *Figure 1* shows the stress–strain curves for polymers A and B. These data give an initial indication that cure temperature has an effect on structure, as the polymers behave quite differently. For example, Young's modulus (initial slope of *Figure 1*), elongation at break, tear strength, and flex life of polymer B (low cure temperature) are noticeably superior to those of polymer A (high cure temperature).

Figures 2 and *3* show the reduced tensional moduli E_r (reference temperature T_0 = 24°C) plotted as a function of relaxation time over the temperature range –70° to 160°C for polymers A and B, respectively. The responses of the two polymers to the applied strain were quite different. For example, below experimental temperatures of about 0°C the retractive force of polymer A rapidly approached zero with decreasing temperature, indicating that polymer A strain-crystallized below about 0°C; polymer B showed no such behaviour. *Figures 4* and *5* show, respectively, the strain-induced crystallization isotherms and crystallization half-lives (time taken for the retractive force normalized by the initial force F/F_0 to attain 50% of its original value) for polymer A.

Figure 6 shows the viscoelastic master curves for the two polymers, where the reduced modulus E_r is plotted against the reduced relaxation time t/a_T. It was found that the shift

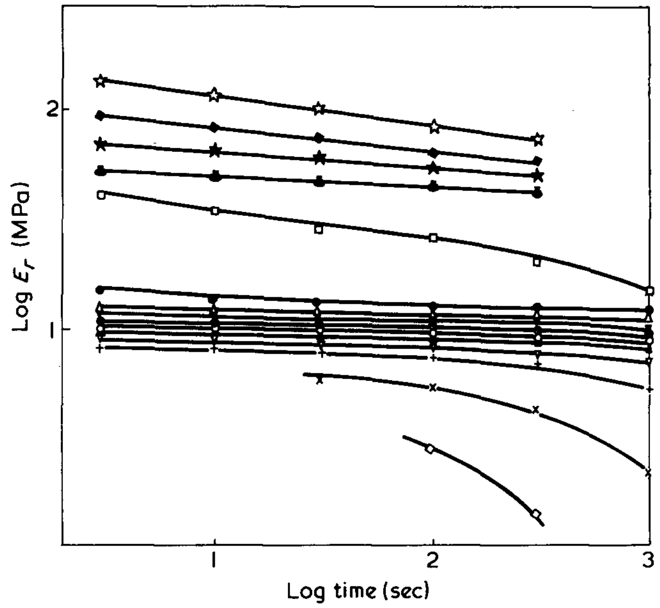


Figure 3 Reduced tensional stress relaxation modulus curves for polymer B. Temperature (°C): ☆, –70; ◆, –55; ★, –40; ♠, 30; □, –10; ●, 24; △, 40; ▼, 55; ⊕, 70; ○, 85; ▲, 100; ▽, 120; +, 135; X, 150; ◇, 160

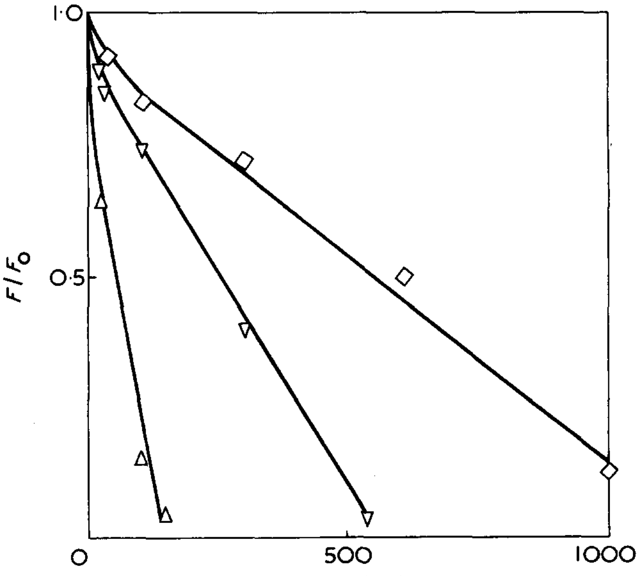


Figure 4 Strain-induced crystallization isotherms for polymer A. Temperature (°C): ◇, –5; ▽, –10; △, –30

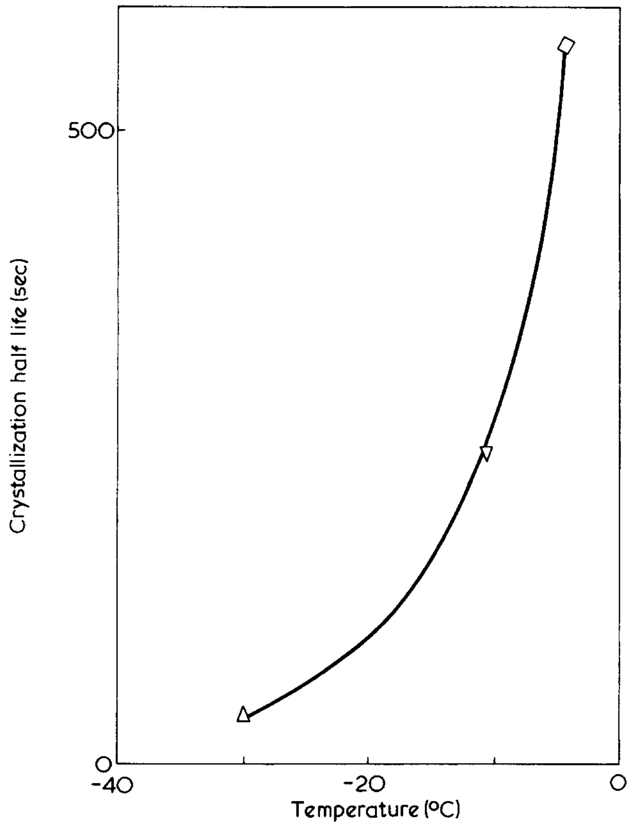


Figure 5 Crystallization half-life as a function of crystallization temperature for polymer A

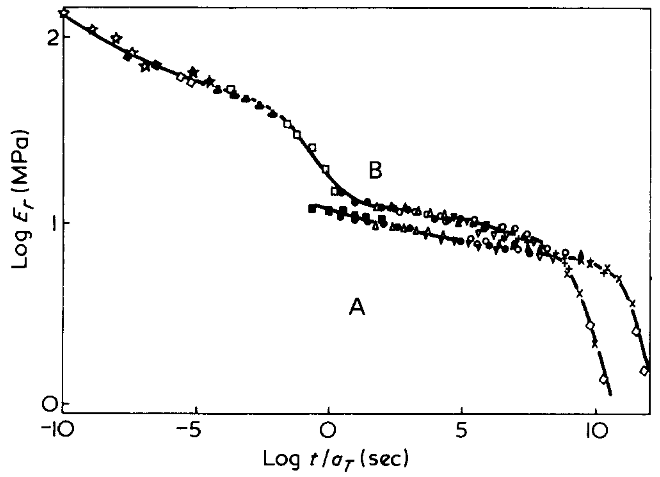


Figure 6 Stress relaxation mastercurves for polymers A and B. Temperature lengend as for *Figure 2* and *3*

factors log a_T used to construct the high temperature (above 24°C) portions of these mastercurves conformed to an Arrhenius-type equation:

$$\log a_T = \frac{\Delta H}{2.303R}(1/T - 1/T_0) \qquad (1)$$

rather than a WLF-type equation. This type of agreement is perhaps not surprising because the polyurethane polymers can be morphologically complex[9–11]. *Figure 7* shows the Arrhenius plots for polymers A and B. The straight lines give constant, but different, activation enthalpies ΔH for the two polymers, $\Delta H_A = 161$ and $\Delta H_B = 129$ kJ/mol, again indicating a structural difference due to cure temperature. Roth *et al.*[12] found that a single activation enthalpy of 154.5 kJ/mol resulted from the construction of compliance mastercurves of pure gum natural rubber vulcanizates that had been cured at different times. In the natural rubber[12], the constancy of the activation enthalpy indicates that no structural changes occurred during vulcanization that affected the timescale of the molecular processes. Copper *et al.*[13] have shown, from the reaction of model compounds, that cure temperature affects structure, as the rates of urea (reaction 2) and biuret (reaction 3) formation are dependent on the cure temperature. At high reaction temperatures the rate of biuret (network) formation is greater than that of urea formation.

Thus, in the present case, polymer A (high cure temperature) may be expected to have a different structure, i.e. more chemical crosslinks, than polymer B (low cure temperature). The hypothesis that polymer A is more crosslinked than polymer B is consistent with the observed physical behaviour.

First, consider the stress–elongation behaviour of the two polymers (*Figure 1*). Polymer A exhibits a stress–elongation curve of a typical moderately crosslinked elastomer[14] while polymer B exhibits a curve more typical of a system showing phase (or domain) separation[15–17], i.e. high initial modulus, followed by a region of low stress and high elongation, prior to a high stress/high elongation failure region. Domain separation is well documented in polyurethane structure studies[9–11].

Next, consider the response of the two polymers to an applied strain (*Figure 6*) where the reduced modulus E_r is plotted against the reduced relaxation time t/a_T over a wide temperature range. Both polymers contain a crystallizable soft segment, *low* molecular weight poly(tetramethylene oxide), and so show a melting point probably due to diffu-

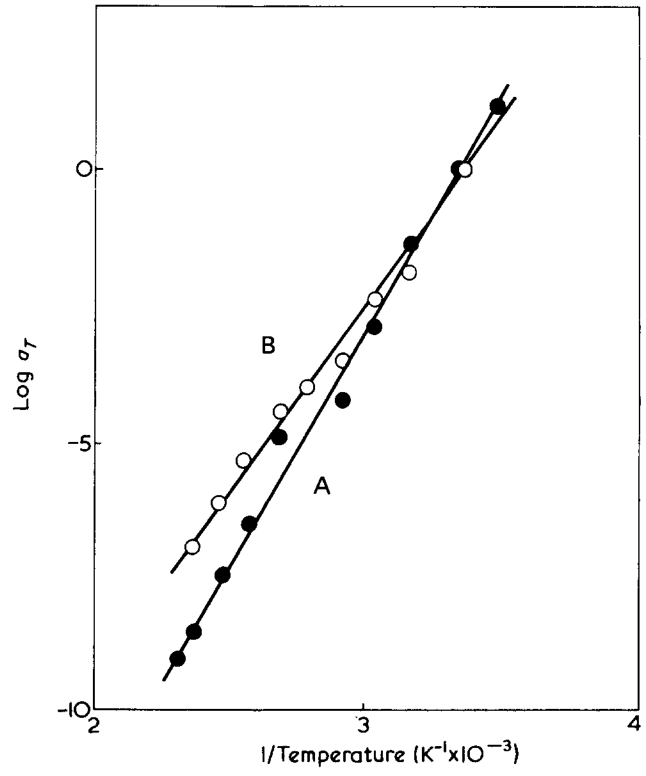


Figure 7 Arrhenius plot of the shift factors used to construct the mastercurve in *Figure 6*; ○, polymer A; ●, polymer B

sional crystallization of this region (see *Table 1*). The fact that polymer A exhibits strain-induced crystallization, whereas polymer B does not, can also be explained by the network hypothesis. It is well known[18] that a certain degree of crosslinking can aid strain-induced crystallization by limiting interchain slippage and thereby allowing an orientational stress to act upon the (network) chains. In the present case polymer B, which is considered to be less crosslinked than polymer A, could permit such slippage. Whereas, the only means in which polymer A, which is considered to contain 'hard' chemical crosslinks between the so-called hard segments, could relieve the stress is via crystallization (of the soft segments).

Two other experimental observations which may suggest that polymer A is structurally different from polymer B, i.e. more chemically crosslinked, are the following. First, the enhanced length of the rubbery plateau of polymer A over that of polymer B is an indication that polymer A contains a more stable network structure than polymer B. Second, a reduction in chain segmental mobility due to biuret-type crosslinking may be reflected by the higher activation enthalpy that was observed for polymer A (ΔH_A = 161, ΔH_B = 129 kJ/mol).

CONCLUSION

The effect of cure temperature on the physical properties of two diamine-cured thermosetting polyurethanes was explained by differences in structure. The polymer cured at the higher temperature (140°C) exhibited properties more typical of a stable *crosslinked* elastomer, whereas the behaviour of the polymer cured at the lower temperature (80°C) was more typical of a *domain-separated* system.

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