Viscoelastic Properties and Heat Generation in Urethane Elastomers

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Synopsis

Static and dynamic properties were studied in a series of polyurethane elastomers as a function of selected compositional variables such as curative system, curative level, catalyst level, and curing temperature. A number of physical properties including swelling ratio, density, glass transition temperature, stress–strain behavior, and thermal conductivity were also measured on these elastomers. The selected variables affect dynamic mechanical properties as well as heat buildup. A good correlation was noted between the loss modulus and the heat generation. The loss modulus and the heat generation decrease with decreasing curative level. The elastomers cured with a mixture of triol and diamine give lower loss modulus and heat buildup than those cured with diamine alone. These responses are believed due to the increase in covalent crosslinks. The observed low heat generation of the elastomer cured with 0.2 phr azelaic acid as a catalyst level was also attributed to the high crosslink density. The curing temperature, in the range investigated, appears to have very little effect on the properties. Thus, the choice of formulation variables, especially the use of diamine–triol blends, provides an effective means of minimizing heat generation in dynamic applications of polyurethane elastomers.

INTRODUCTION

Polyurethane elastomers are block copolymers built up of relatively short urethane hard segments separating long, flexible polyether or polyester soft blocks. As a result of microphase separation or domain formation,[1] the soft blocks impart extensibility, whereas the hard segments give physical crosslinks mainly through hydrogen bonding. These elastomers exhibit mechanical properties superior to those of conventional vulcanizates. Because of their superior strength and abrasion resistance, polyurethane elastomers are finding increasing use for industrial trucks, aircraft wheels, and materials handling equipment.[2]

Elastomers are viscoelastic materials, that is, they are characterized by both a viscous and an elastic behavior. The dynamic properties of elastomers are a complex of their viscous and elastic properties. When a linear viscoelastic material is subjected to a sinusoidal tensile strain, the stress response is also sinusoidal, but is out of phase with the strain. As a consequence of the phase difference between stress and strain, a part of the energy put into the elastomer during deformation is dissipated as heat.[3] Thus, the heat generation occurring in an elastomer subjected to periodic deformation can be predicted from a knowledge of the dynamic mechanical properties.

TABLE I
Formulas of Curing Agents

Name	Abbreviation	Formula
4,4'-Methylenebis(2-chloroaniline)[a]	MOCA	
2,6-Dichloro-1,4-phenylenediamine[b]	DCPPD	
Isobutyl 4-chloro-3,5-diaminobenzoate[c]	ICDB	
Methylenedianiline	MDA	
1,1,1-Tris(hydroxyethoxymethyl)propane[d]	THMP	$(HOCH_2CH_2OCH_2)_3CCH_2CH_3$
1,4-Butanediol	BDO	$HO—(CH_2)_4—OH$

[a] Cyanaset M, American Cyanamid Company, Bound Brook, New Jersey.
[b] Cyanaset 26, American Cyanamid Company, Bound Brook, New Jersey.
[c] Curative DD 1604, Bayer AG, Leverkusen, Germany.
[d] Isonol 93, a 3:1 adduct of ethylene oxide and trimethylolpropane, Upjohn Company, Kalamazoo, Michigan.

TABLE II
Compositions of Polyurethane Elastomers Prepared from
Cyanaprene A-8 Prepolymer[a]

Sample	Curative	TCP,[b] phr	Stoichiometry, %	Azelaic acid, phr	Curing temp, °C
1	70/30 DCPPD/THMP	—	95	0.3	100
2	85/15 DCPPD/THMP	—	95	0.3	100
3	80/20 DCPPD/MDA	—	95	0.1	100
4	DCPPD	—	95	0.3	100
5	DCPPD	4	70	0.3	100
6	DCPPD	4	80	0.3	100
7	DCPPD	4	95	0.3	100
8	DCPPD	4	95	0.2	100
9	DCPPD	4	95	0.1	100
10	DCPPD	4	95	—	100
11	70/30 DCPPD/THMP	4	95	0.3	100
12	70/30 DCPPD/BDO	4	95	0.3	100
13	DCPPD	4	95	0.3	110
14	DCPPD	4	80	0.3	110
15	DCPPD	4	95	0.3	120
16	DCPPD	4	110	0.3	100
17	MOCA	—	95	—	100
18	ICDB	—	95	—	100

[a] All samples were cured for 1 hr and postcured at 100°C for 16 hr.
[b] Tricresyl phosphate.

TABLE III
Swelling of Polyurethane Elastomers in DMAC at Room Temperature[a]

	Sample 5	6	7	8	9	10	11	12[b]	13	14	15	16[b]
Wt. of sample, g	0.5200	0.5321	0.5155	0.5284	0.5173	0.5160	0.5310	0.5310	0.5051	0.5168	0.5312	0.5238
Density of sample, g/cm³	1.2500	1.265	1.263	1.263	1.263	1.257	1.253	1.243	1.257	1.265	1.263	1.2723
Wt. of sample after swelling	2.6000	3.0854	4.4557	3.5438	4.3844	5.2167	2.2773	—	4.7448	4.3900	3.9481	—
$\phi_r = \dfrac{V_2}{V_2 + V_s}$	0.158	0.134	0.088	0.115	0.090	0.076	0.185	—	0.082	0.090	0.1035	—

[a] V_2 is the volume of polymer and V_s is the volume of solvent at equilibrium swelling state.
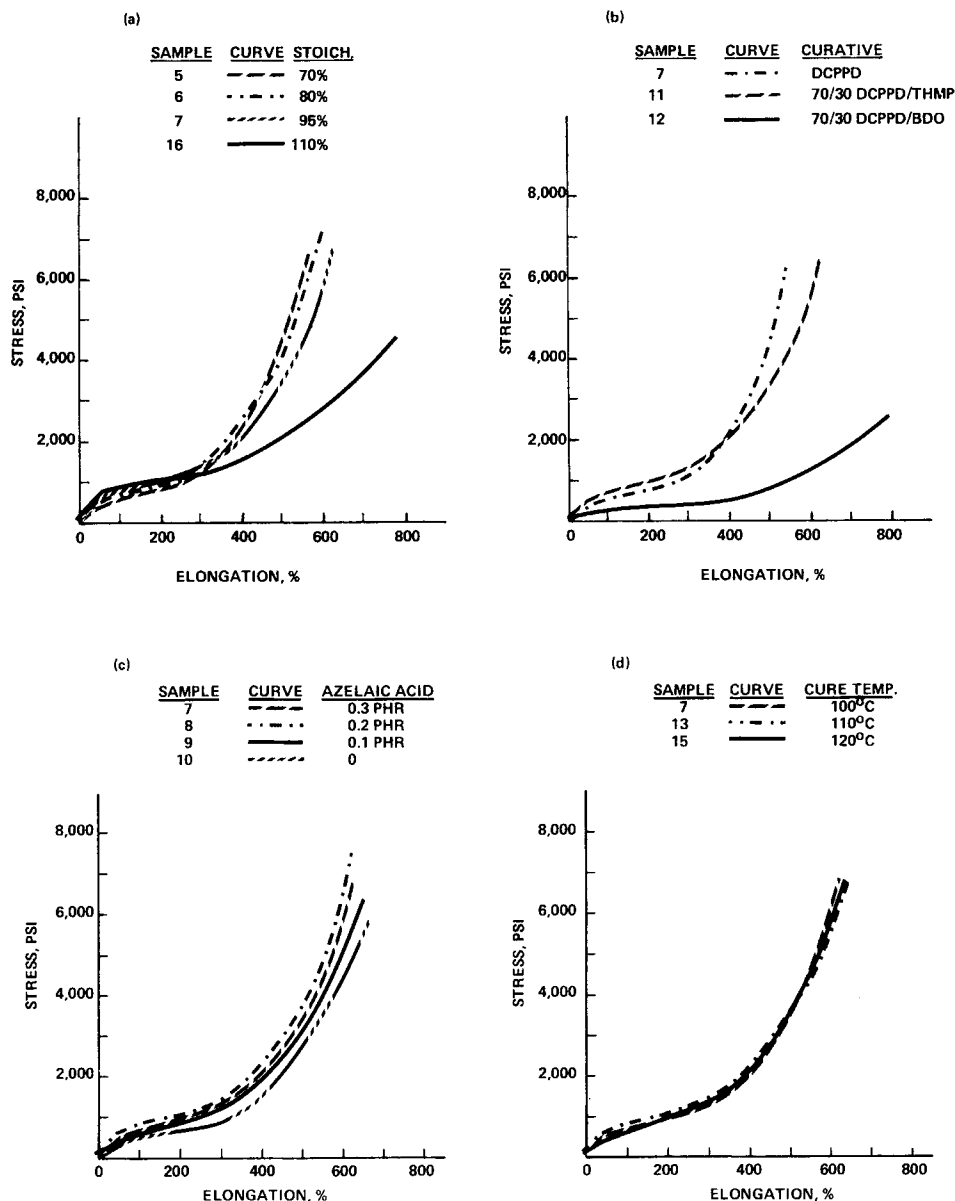Density of DMAC = 0.937 g/cm³.
[b] The sample dissolves in DMAC.

Fig. 1. Stress–strain curves of different polyurethane formulations: (a) effect of stoichiometry; (b) effect of curative; (c) effect of azelaic acid catalyst; (d) effect of cure temperature.

Polyurethane elastomers display considerable damping, i.e., a high proportion of the energy of deformation is dissipated as heat. Therefore, these materials are not suitable for prolonged use with heavy strain of high frequency because of heat buildup within the material. In an attempt to keep pace with dynamic applications for urethane elastomers, experiments have been conducted to relate curative type, curative level, catalyst level, and curing temperature to viscoelastic properties, heat buildup, and other physical properties.

TABLE IV
Thermal Conductivity of Polyurethane Elastomers

Sample	Curative	Stoichiometry, %	Thermal conductivity λ, cal-cm/cm^2-sec-°C
5	DCPPD	70	5.33×10^{-4}
7	DCPPD	95	5.37×10^{-4}
16	DCPPD	110	5.15×10^{-4}
17	MOCA	95	5.45×10^{-4}
18	ICDB	95	5.04×10^{-4}

EXPERIMENTAL

Materials

The polyester-based polyurethane elastomers investigated in this work were prepared in a two-step process. The prepolymer was formed from poly-(ethylene adipate) glycol and toluene diisocyanate (TDI) (Cyanaprene A-8 urethane prepolymer, American Cyanamid Company, Bound Brook, N.J.). Chain extension of the prepolymer was achieved by reaction with a curing agent such as a diol, a triol, a diamine, or combinations thereof. The structural formulas of the curing agents used are shown in Table I. These curatives are likewise commercially available. In selecting curing agents for study, emphasis was placed on 2,6-dichloro-1,4-phenylenediamine (DCPPD), which was developed as a replacement for the more traditional 4,4'-methylenebis(2-chloroaniline) when the latter was asserted[4] to be a cancer suspect agent. DCPPD is often used with an acidic promoter or catalyst such as azelaic acid. The compositions of the elastomers studied are listed in Table II. All samples were compression molded at 100°, 110°, or 120°C for 1 hr, followed by a 16-hr postcure at 100°C to yield sheets about 75 mils in thickness.

TABLE V
Effect of Formulation Variables on Collapse Time[a]

(A)	Sample 5	6	7	16
Stoichiometry, %	70	80	95	110
Collapse time, min	18	15	6	2.5

(B)	Sample 7	8	9	10
Azelaic acid, phr	0.3	0.2	0.1	0
Collapse time, min	6	20	5	4.5

(C)	Sample 7	11	12	17	18
Curative	DCPPD	70/30 DCPPD/THMP	70/30 DCPPD/BDO	MOCA	ICDB
Collapse time, min	6	19	4.5	7	3

(D)	Sample 7	13	15
Curing temp, °C	100	110	120
Collapse time, min	6	4.5	5

[a] Collapse time is the time to reach a 5% vertical deflection.

Measurements

Equilibrium Swelling. Small pieces of the elastomers, approximately 0.5 g, were weighed, and each of these specimens was placed in a flask filled with dimethylacetamide (DMAC) until equilibrium swelling was reached (about three days). The swollen pieces were removed, blotted with filter paper, and reweighed. The volume fraction of elastomer at equilibrium swelling state was calculated from the equation

$$\phi_r = (W_2/d_2)/(W_1/d_1) \tag{1}$$

where W_1 and W_2 are the weight of the solvent and the weight of the elasto-

(a)

SAMPLE	CURVE	CURATIVE
1	– – –	70/30 DCPPD/THMP
3	· – · ·	80/20 DCPPD/MDA
4	——	DCPPD
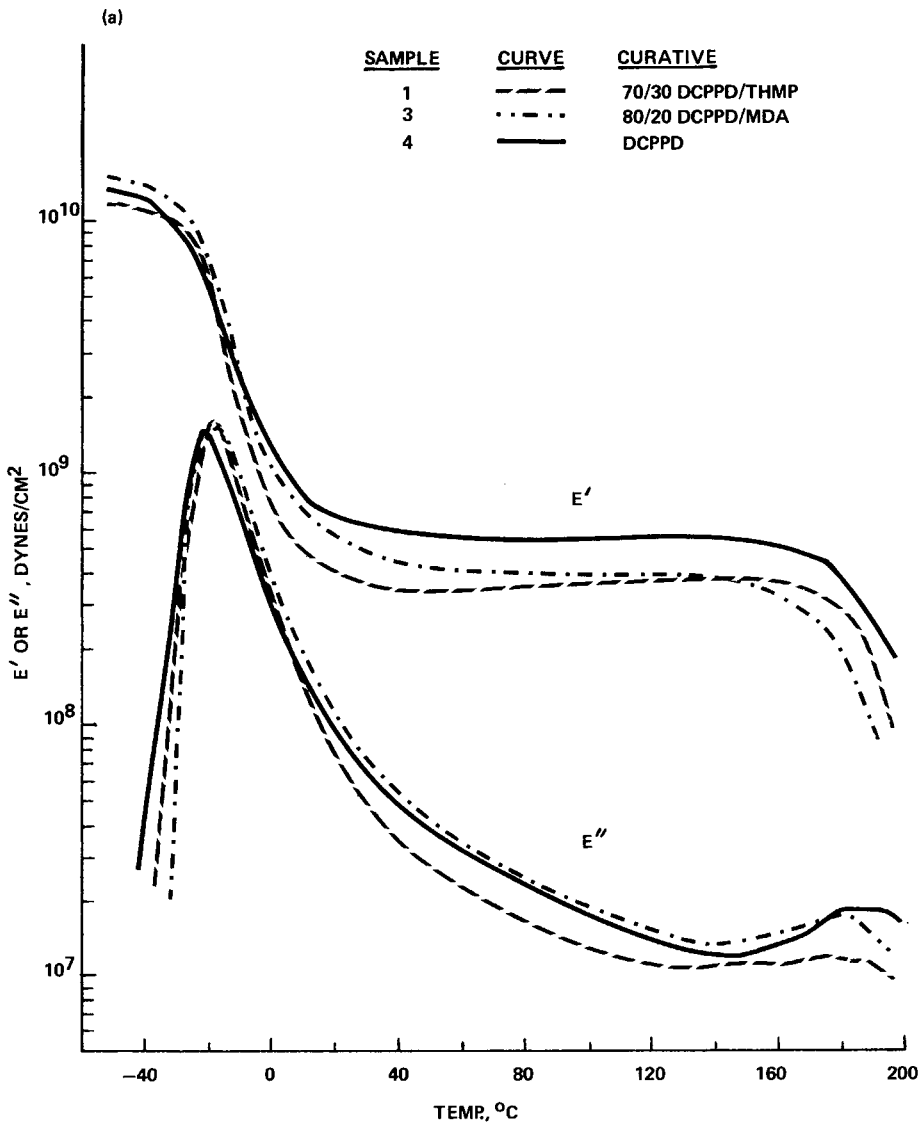
Fig. 2 (*continued*)

mer, respectively, and d_1 and d_2 are the density of the solvent and the elastomer.

Tensile Testing. The stress–strain behavior of the elastomers was measured on an Instron tensile tester at room temperature and a constant extension speed of 20 in/min. Dumbbell-shaped specimens were cut from the sheets of the elastomers (ASTM Method D 412, Die C).

Dynamic Mechanical Testing. The dynamic mechanical properties, namely, the storage or elastic modulus (E'), the loss modulus (E''), and the loss tangent (tan δ) were measured as a function of temperature using a Rheovibron viscoelastometer[5] at a frequency of 110 Hz. The samples were heated at 1–2°C/min, under dry nitrogen, from −80°C to melting point.

Thermal Conductivity. The thermal conductivity of the elastomers was measured using a Colora thermoconductometer[6] using water and trichloro-
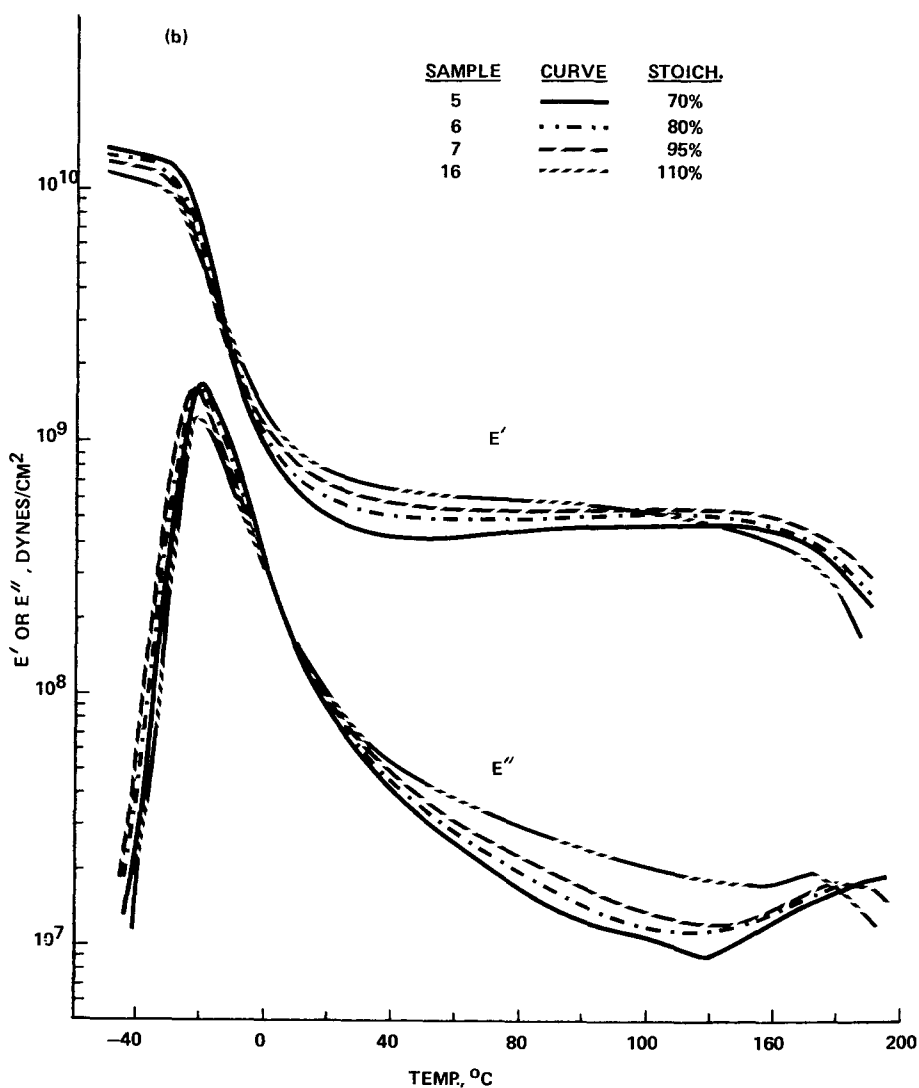
Fig. 2 (*continued*)

ethylene as the liquid pair. Cylindrical test samples were die-cut from the test sheets.

Heat Buildup. The evaluation of heat generation during compression flex was carried out using a Goodrich flexometer.[7] The test specimens were compression molded and cylindrical in shape, having a diameter of 0.7 in. and a height of 1 in. The tests were conducted at 40°C with a compression stroke of 0.175 in. In order to measure the heat buildup in the elastomers under conditions closer to practical application, another set of experiments was also carried out on the Goodrich flexometer with a definite compression preload of 236 psi applied to the test piece. The temperature of the sample was determined by means of a thermocouple inserted at the center of the specimen. It should be noted that this placement is not the same as in the ASTM method (D 623 Method A); but, as the temperature rise is necessarily greatest in
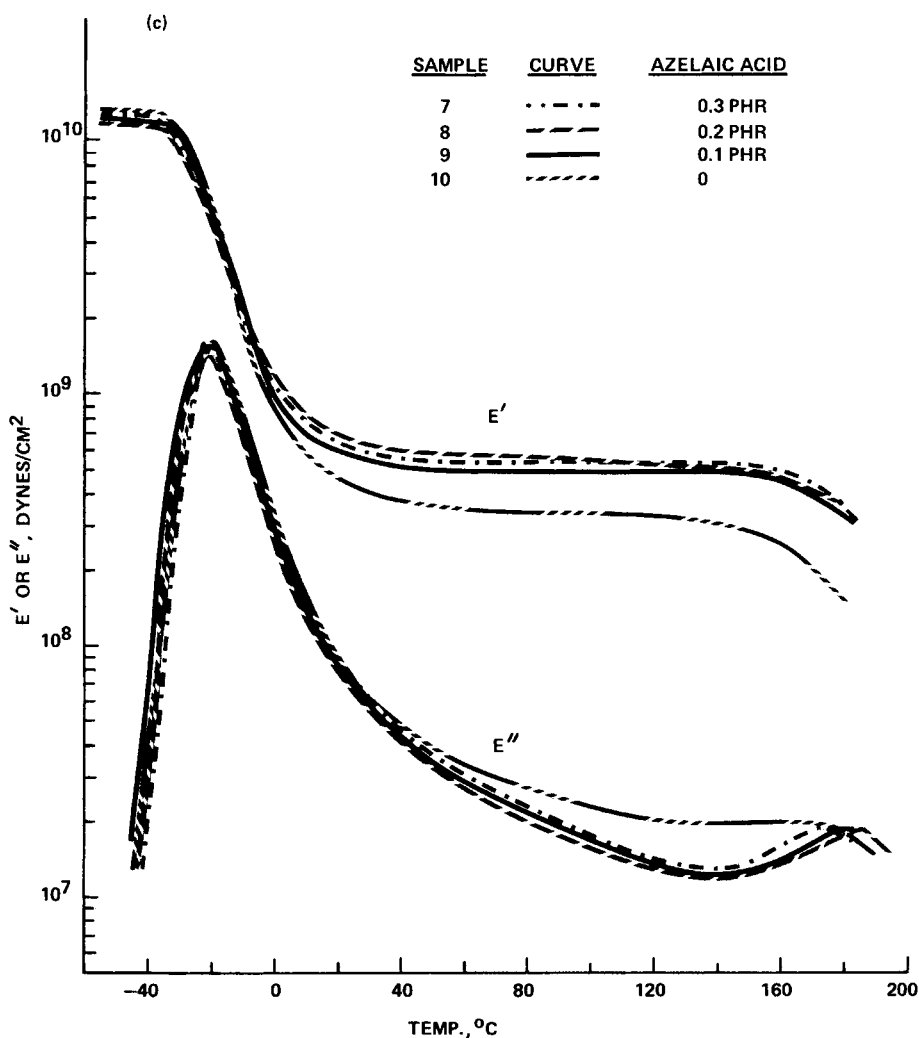

Fig. 2 (*continued*)

the center of the specimen, placing the thermocouple there was judged to be a worthwhile modification.

RESULTS AND DISCUSSION

Degree of Crosslinking

The results of the swelling measurements are summarized in Table III. The crosslink density of a polymer can be obtained from equilibrium swelling data by use of the Flory-Huggins relationship[8]

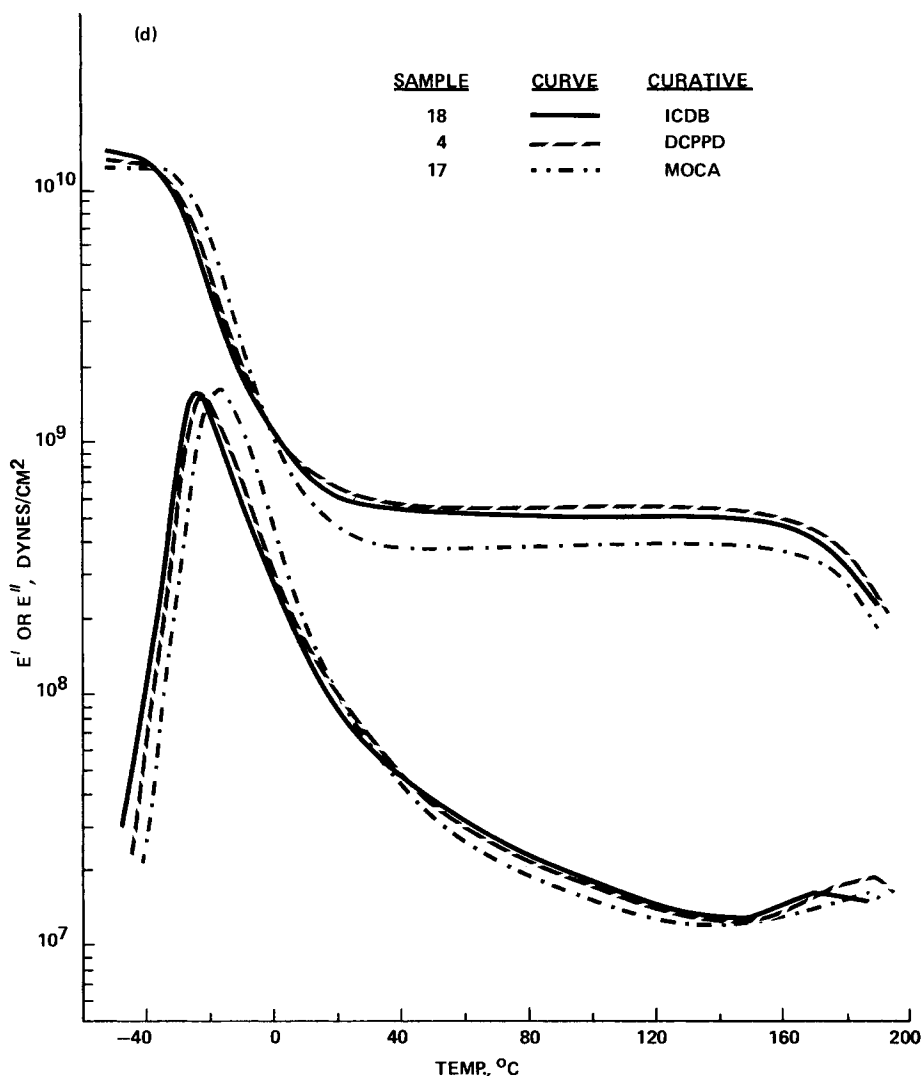$$-[\ln (1 - \phi_r) + \phi_r + \mu\phi_r^2] = V_e V_1(\phi_r^{1/3} - \phi_r/2) \qquad (2)$$

Fig. 2. Temperature dependence of E' and E'' for urethane elastomers cured (a) with DCPPD and DCPPD-containing mixed curatives; (b) at different levels of curative (DCPPD); (c) with DCPPD at different azelaic acid concentrations; (d) with various curatives. Measurements at 110 Hz. In each chart, E' is given by the upper family of curves, E'' by the lower family.
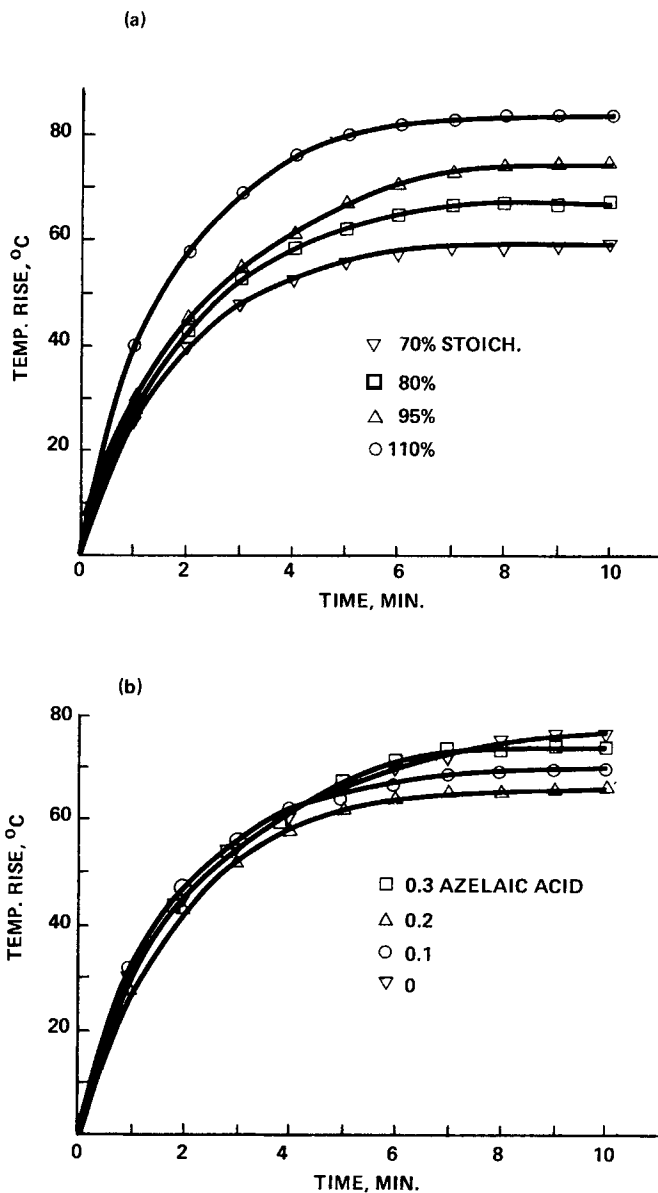
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(a)

(b)

Fig. 3 (continued)

where ϕ_r is the volume fraction of polymer at equilibrium swelling state, μ is the solvent–rubber interaction coefficient, V_e is the number of network chains per unit volume, and V_1 is the solvent molar volume. At high degree of swelling, where ϕ_r is small, eq. (2) can be simplified as follows:

$$\phi_r{}^{5/3} = V_e V_1 \bigg/ \left(\frac{1}{2} - \mu\right). \tag{3}$$

Thus, V_e may be deduced from eq. (3) by measurements of the degree of swelling when the values of V_1 and μ are known. Because the value of μ can-
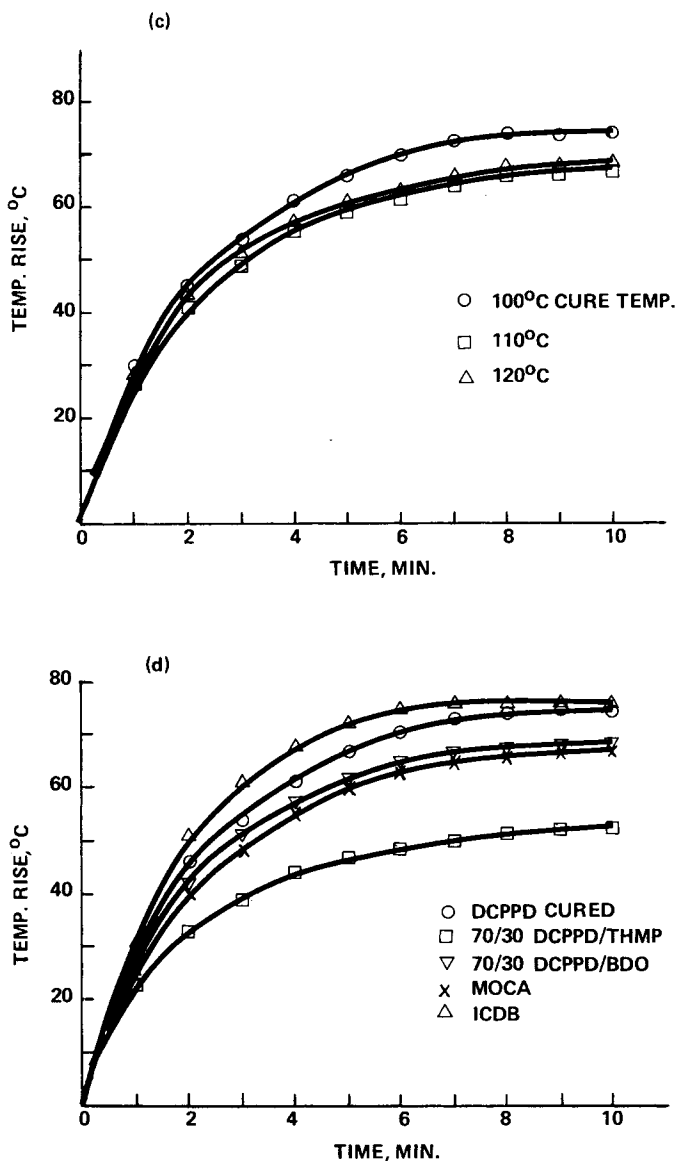
Fig. 3. Effect of formulation variables on temperature rise in a flexometer, tested at constant strain amplitude without preload: (a) effect of stoichiometry; (b) effect of azelaic acid concentration; (c) effect of curing temperature; (d) effect of curative.

not easily be determined experimentally, the degree of crosslinking can best be obtained in a relative way from the volume fraction of elastomer at the equilibrium swelling state. If the solvent–rubber interaction coefficient μ is constant for the systems investigated, the crosslink density is proportional to $\phi_r^{5/3}$. The effect of stoichiometry (curative equivalent/NCO equivalent) on crosslink density can be observed by comparing samples 5, 6, 7, and 16 in Table II. As expected, the crosslink density increases with decreasing stoichiometry of the curative. The crosslinks observed in these samples are
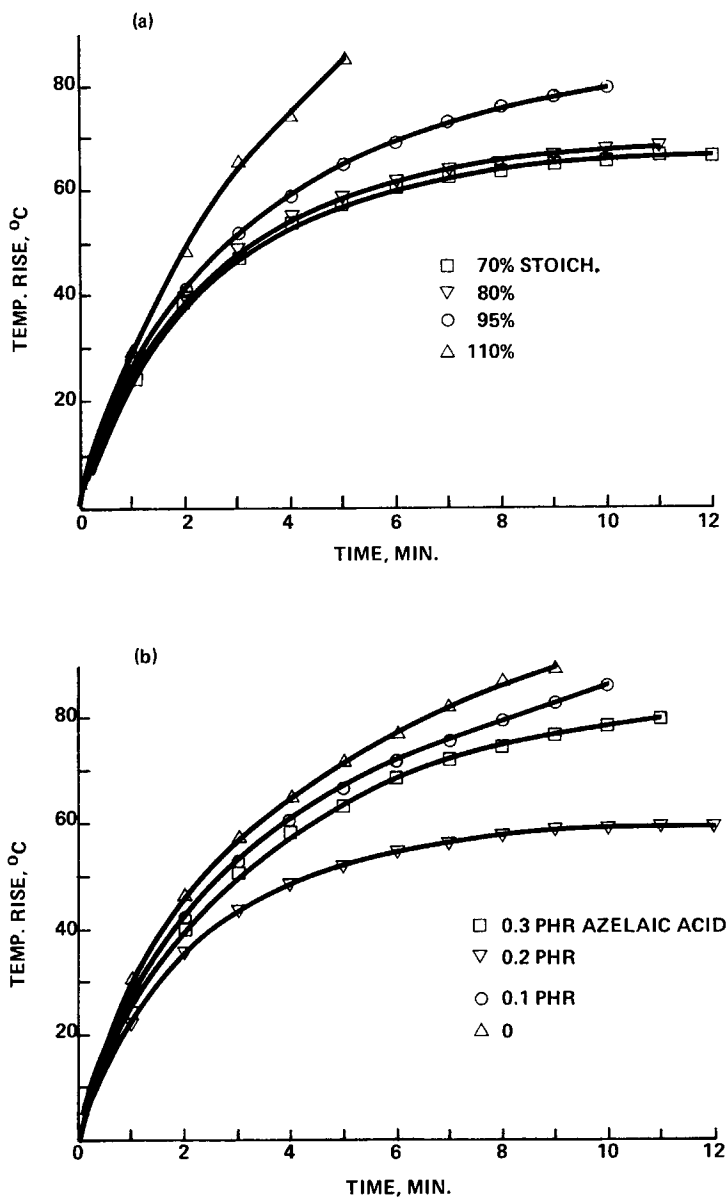
Fig. 4 (continued)

formed through the reaction of excess isocyanate with urea or urethane groups. At 110% stoichiometry, essentially linear polymer was obtained. Trifunctional curatives, such as THMP, also lead to crosslinked polymers (compare sample 7 with sample 11). It was further observed that at 95% stoichiometry and curing temperature of 100°C, the crosslink density exhibits a maximum at an azelaic acid concentration of about 0.2 phr. At 95% stoichiometry and 0.3 phr azelaic acid level, the curing temperature appears to have very little effect on crosslinking.
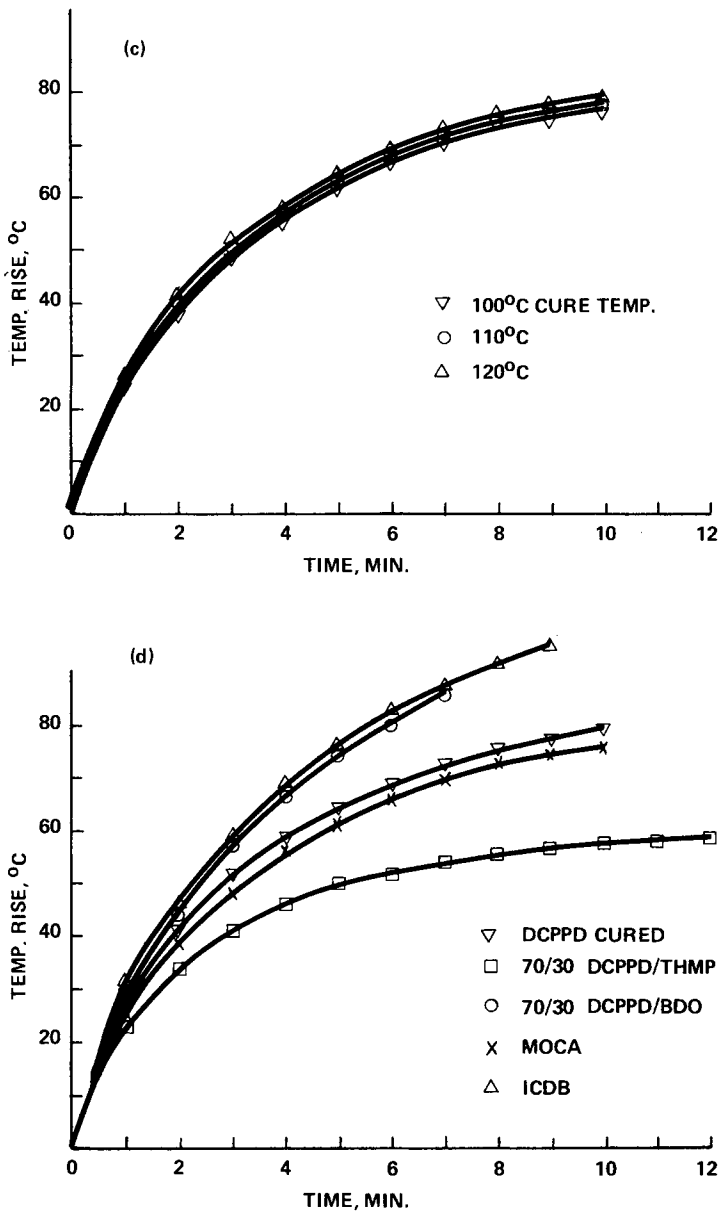
Fig. 4. Effect of formulation variables on temperature rise in a flexometer, tested at constant strain amplitude with a preload: (a) effect of stoichiometry; (b) effect of azelaic acid concentration; (c) effect of curing temperature; (d) effect of curative.

Stress–Strain Behavior

Stress–strain relationships observed for these elastomers are illustrated in Figure 1. As can be seen in Figure 1a, for a curative stoichiometry of less than unity the modulus at low strain increases with stoichiometry, resulting from an increase in the concentration of hard segments or urea linkages. In this region, the modulus is due to the elastic deformation of hard segments.

However, at high elongation, in the region of rubber-like elasticity, the modulus values increase as the curative stoichiometry decreases, presumably due to an increase in covalent crosslinks which restrict the slippage of the segments. The stress in this region is probably transmitted primarily through the elastomeric matrix, that is, the soft segment domain. The tensile strength exhibits a maximum at 80% stoichiometry. Similar effects are also observed with different curative systems as shown in Figure 1b, namely, an increase of covalent crosslink density results in a steep rise in stress at high strain. It is also noticed that at the same curative stoichiometry level the initial modulus decreases when the concentration of THMP increases, indicating a decrease in rigidity. It is believed that the addition of the triol, THMP, not only reduces urea concentration but also provides more chemical crosslinks which disrupt the hard segment interaction. The specimens cured with DCPPD give better tensile strength than those cured with a mixture of this amine and a diol or triol. The tensile properties appear to be independent of curing temperature in the range investigated (see Fig. 1d).

Dynamic Mechanical Properties

The elastic modulus–temperature and loss modulus–temperature profiles are shown in Figure 2. The addition of THMP to the prepolymer has very little effect on the soft segment behavior of the resulting elastomer; that is, there is little change in the glass transition temperature, as shown in Figure 2a. However, the modulus in the rubbery plateau, which is associated with the hard segment contribution, is decreased by the introduction of THMP. The loss modulus–temperature profiles of these systems are quite similar to one another, except that the loss modulus of the sample cured with a mixture of DCPPD and THMP is lower than that of the other two systems above room temperature. Figure 2b shows the temperature profiles of E' and E'' for the prepolymer cured at different levels of DCPPD. A decrease in curative only slightly increases the glass transition temperature (loss modulus peak temperature). This result indicates that crosslinks were developed in the region of hard segments and have little effect on the mobility of soft segments. However, both the elastic modulus (E') and the loss modulus (E'') in the rubbery region increase as the concentration of curative increases. These results are, as already discussed under stress–strain behavior, due to a change in the concentration of urea linkages and the density of chemical crosslinking. Without catalyst, the elastomer shows very high loss modulus and very low elastic modulus in the rubbery region (see Fig. 2c).

The concentration of azelaic acid in the range studied seems to have little effect on these dynamic properties. However, 0.2 phr seems to give somewhat low values for loss modulus, presumably due to the high chemical crosslinking density obtained at this catalyst level. The loss modulus shows very little change with curing temperature. For prepolymers cured with DCPPD and ICDB, the elastic modulus and the loss modulus are essentially identical in the rubbery plateau. However, these moduli for the prepolymer cured with MOCA are relatively lower (see Fig. 2d). The glass transition temperature of the MOCA-cured elastomer is slightly higher than that of the elastomer cured with DCPPD or ICBD.

Heat Buildup

The results of heat generation on the elastomers during compression flex using a Goodrich flexometer without a preload are given in Figure 3. The temperature rise in a sample under cyclic load in a flexometer is proportional to the loss modulus[9] and inversely proportional to the thermal conductivity[10] as follows:

$$\Delta T \propto \frac{\gamma_0^2 \omega E''(\omega)}{\lambda} \tag{4}$$

where γ_0 is the strain amplitude, ω is the frequency, and λ is the coefficient of thermal conductivity. The thermal conductivity values of the elastomers are listed in Table IV. With DCPPD at different stoichiometry levels, no significant difference was observed. Of the curatives evaluated, ICBD shows a slightly lower value of thermal conductivity than those with other curing agents at 95% stoichiometry. The effect of curative stoichiometry on temperature rise in flexometer test is illustrated in Figure 3a. The temperature rise increases markedly with stoichiometry. This behavior is in line with the earlier finding concerning loss modulus. The effect of azelaic acid concentration is presented in Figure 3b. Although the difference in temperature rise is larger than that expected from the magnitudes of the loss modulus, the relative order is in good agreement.

Figure 3d shows the effect of the choice of curative system. It is obvious that the heat generation can be reduced by increasing the chemical crosslinking through the addition of a multifunctional curative. Among the three curatives, DCPPD, MOCA, and ICDB, the heat buildup shows only slight differences. The somewhat lower thermal conductivity of the elastomer cured with ICDB may be responsible for the slightly higher heat buildup in this case. Figure 4 shows the results of the flexometer test with a compression preload. The heat generation data are similar to those observed without a preload, except that the elastomer cured with ICDB shows a much higher heat buildup than it does without a preload.

The collapse time, which was chosen as the time to reach a 5% vertical deflection during the dynamic flexing test, is reported in Table V. As would be expected, the higher the heat buildup, the shorter the collapse time. Thus, collapse time can be regarded as an index for heat buildup.

CONCLUSIONS

The compositional variables of a polyurethane elastomer have an important influence on dynamic properties. A good correlation was observed between the loss modulus and heat generation in the elastomers. The viscoelastic properties can be affected by curative type, curative level, and catalyst level, which would result in a change in covalent crosslink density. These properties are almost independent of curing temperature in the range investigated. Similar effects are also observed on heat buildup in dynamic tests. These observations suggest that the heat generation is reduced in cases where the chemical crosslink density is increased. Thus, proper formulation can provide a means of minimizing heat generation in dynamic applications for polyurethane elastomers.

References

1. R. Bonart, L. Morbitzer, and G. Hentze, *J. Macromol. Sci.-Phys.*, **B3**, 337 (1969).
2. *Mod. Plast.*, *36*, 101 (1959).
3. P. Kainradl and F. Handler, *Rubber Chem. Technol.*, **28**, 153 (1955).
4. *Federal Register*, **39**, 3756 (1974).
5. M. Takayanegi, *Proc. 4th Int. Rheol. Congr.*, **1**, 16 (1965).
6. J. Schroder, *Rev. Sci. Instruments*, **34**, 615 (1963).
7. E. T. Lessig, *Ind. Eng. Chem., Anal. Ed.*, **9**, 582 (1937).
8. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, N.Y., 1953.
9. K. Ninomiya and I. Furuta, *Rubber Chem. Technol.*, **44**, 1395 (1971).
10. A. Payne, *Rubber J.*, **146** (1), 36 (1964).