Ultrasonic properties of some diamine cured aliphatic epoxy polymers

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Longitudinal sound speed and absorption were measured from 0° to 100°C at a frequency of 2 MHz on an aliphatic epoxy resin (butanediol diglycidyl ether) crosslinked with four different curing agents — three aliphatics of differing chain lengths and one aromatic. The ultrasonic properties were found to be dominated by the glass transition in a manner qualitatively similar to linear polymers. In the aliphatic series, the ultrasonic properties all fell on the same master curves when plotted as functions of $T - Tg$, but the aromatic curing agent was qualitatively different. For a single relaxation time model, the sound absorption peak for the aliphatic series would be 55 dB cm^{-1}. The measured peak of 28 dB cm^{-1} shows that the glass transition involves a distribution of relaxation times.

INTRODUCTION

This paper presents the results of sound speed and absorption measurements as a function of temperature at a frequency of 2 MHz on an epoxy resin crosslinked with four different curing agents. The resin used was butanediol diglycidyl ether (BDGE). While some torsional pendulum measurements have been reported[1] on BDGE polymers, no ultrasonic measurements are available.

BDGE is an aliphatic (straight chain) monomer. Of the four diamine curing agents used, three were aliphatics of differing chain length and one was aromatic (containing a benzene ring). Thus, the effect of inserting an aromatic component into an otherwise aliphatic polymer can be determined.

Crosslinked polymers such as these can be characterized by the crosslink density which is the reciprocal of the molecular weight between crosslinks. In the aliphatic curing agent series, the varying chain lengths give polymers of varying crosslink density. This series enables us to determine the effect of crosslink density on the properties of a purely aliphatic system.

It will be shown that the ultrasonic properties of these polymers are dominated by the glass transition, and this transition is qualitatively similar to the glass transition in linear polymers. The ultrasonic properties are shown to depend both on crosslink density and aromaticity. In the aliphatic series, the ultrasonic properties are functions of $T - Tg$.

EXPERIMENTAL

Materials

The epoxy resin (BDGE) was reacted with three different aliphatic curing agents: propanediamine (PDA), hexanediamine (HDA) and dodecanediamine (DDA). The aromatic curing agent was *m*-phenylenediamine (MPDA). All of the starting materials were commercial products that were carefully distilled before use. Details of the polymer synthesis are given in the Appendix.

Crosslink densities for the four polymers are listed in the first row of *Table 1*. There is a progression of crosslink densities in the aliphatic series, and the aromatic (MPDA) has essentially the same crosslink density as one of the aliphatics (HDA).

Room temperature densities of the cured polymers are listed in the second row of *Table 1*. As can be seen, the shorter the aliphatic chain, the higher the polymer density, but in no case does an aliphatic curing agent give as high a density as the aromatic one. In other words, in the aliphatic series, the higher the crosslink density, the higher the polymer density. Comparing MPDA and HDA, at constant crosslink density, the aromatic has higher density than the aliphatic.

Ultrasonic apparatus

The ultrasonic apparatus used has already been described in detail[2]. In brief, the specimen and two transducers are immersed in silicone liquid. Pulses are sent from one transducer to the other, both with and without the specimen in the path of the sound beam. All measurements were made at 2 MHz in the temperature range from 0° to 100°C. Longitudinal sound speed and absorption were determined using this apparatus. Sound speed measurements are estimated to be accurate within $\pm 1\%$ while absorption is within $\pm 5\%$. For each polymer measurements were made on two specimens of different thickness. The nominal specimen sizes, except for DDA,

Table 1 Properties of BDGE polymers

	DDA	HDA	PDA	MPDA
Crosslink density, mol kg^{-1}	1.49	1.70	1.83	1.72
Polymer density at 20°C, g cm^{-3}	1.094	1.152	1.179	1.227
Glass transition temperature, °C	−10	5	12	49
Sound speed at 20°C, m s^{-1}	2040	2310	2430	2580
Absorption at 20°C, dB cm^{-1}	26	23	21	9

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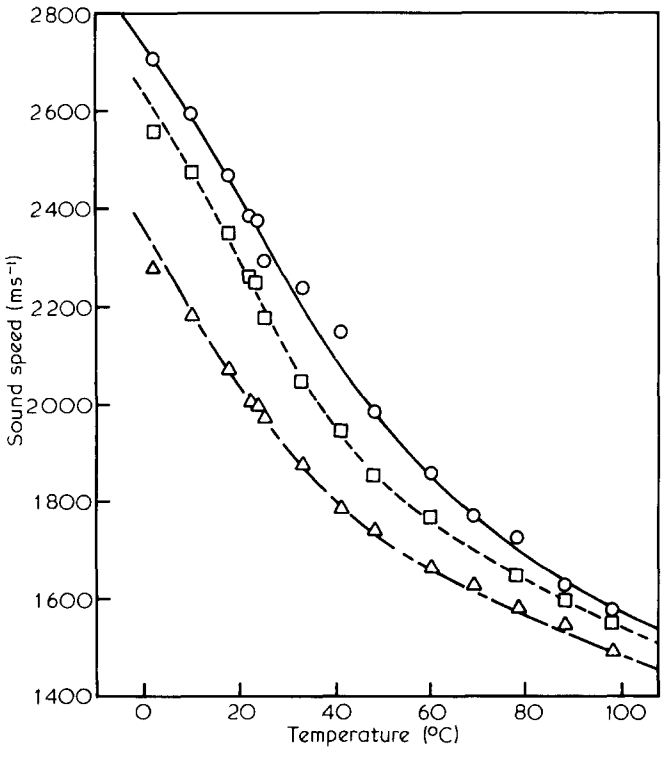

Figure 1 Temperature dependence of sound speed at 2 MHz for aliphatic curing agents. ○, PDA; □, HDA; △, DDA

were 5 cm diameter by 1.3 and 1.9 cm thick. For DDA, the specimens were 2.5 cm diameter by 0.6 and 0.8 cm thick.

Thermal measurements

Two types of thermal measurements were made on the polymers using a Dupont 990 Thermal Analyzer. First, in making ultrasonic measurements as a function of temperature, there is a small correction for the specimen thickness as a function of temperature. Therefore, the cubic coefficient of thermal expansion was estimated. All of the polymers had approximately the same value at room temperature, 6.5×10^{-4} deg^{-1} and this value was used. Second, the ultrasonic measurements will be shown to be dominated by a major structural relaxation, namely the glass transition. The glass transition temperature was determined from Differential Scanning Calorimeter measurements. The values are given in *Table 1*. As expected, *Tg* increases with crosslink density in the aliphatic series, and *Tg* is higher for the aromatic than an equally crosslinked aliphatic.

ULTRASONIC MEASUREMENTS

Room temperature

Sound speeds at room temperature are given in *Table 1*. These values are generally low when compared with values reported for other epoxy polymers[2,3] because these other epoxies had an aromatic backbone.

It has been pointed out by Wada[4] and others[5-7] that sound speed increases approximately linearly with density. The four epoxies are in the expected order, DDA < HDA < PDA < MPDA with the highest density polymer having the highest sound speed and so on.

Absorptions at room temperature are also given in *Table 1*. The values are generally high (except for MPDA) when compared with other polymers. The absorptions are in the order usually observed, with the polymer of highest sound speed having the lowest absorption and so on.

Temperature dependence

Sound speed vs temperature from 0° to 100°C at 2 MHz for the three aliphatic curing agents is shown in *Figure 1* and sound absorption results are shown in *Figure 2*. Both sound speed and absorption results for the aromatic are shown in *Figure 3*.

The ultrasonic properties of all four polymers are seen to be dominated by a major structural relaxation, the glass transition. While the effect of crosslinking is to

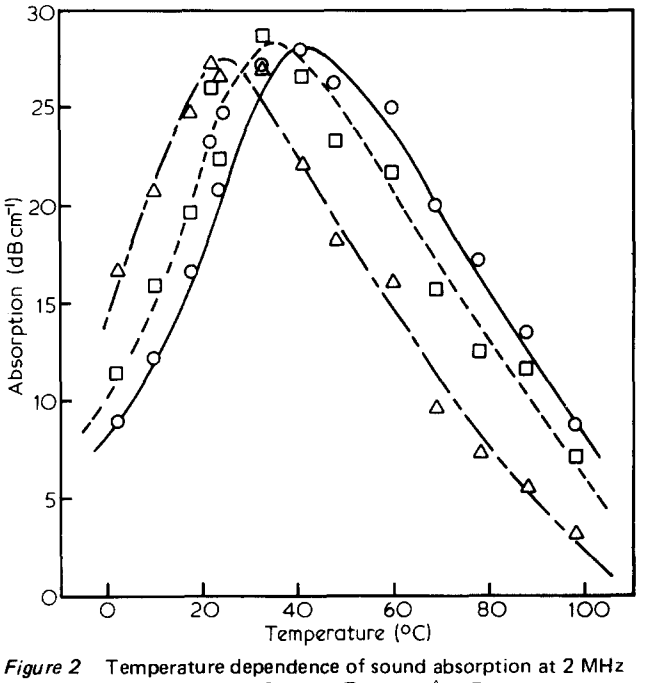

Figure 2 Temperature dependence of sound absorption at 2 MHz for aliphatic curing agents. ○, PDA; □, HDA; △, DDA

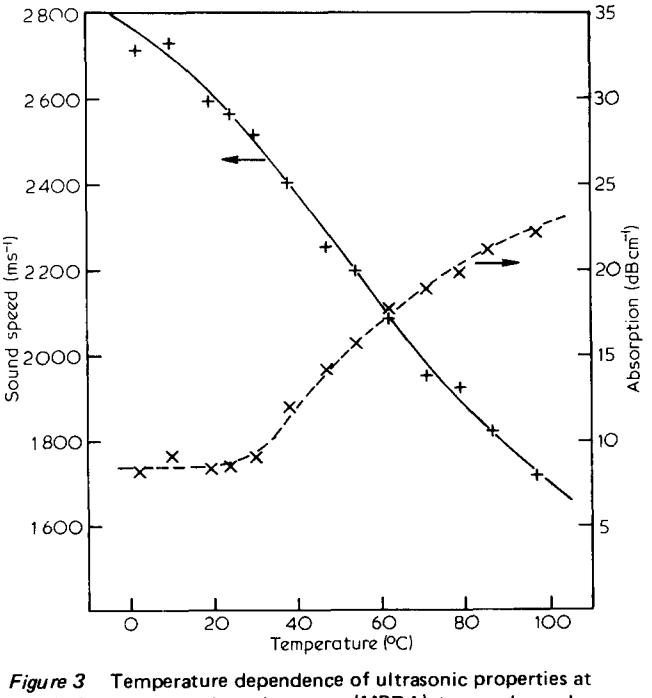

Figure 3 Temperature dependence of ultrasonic properties at 2 MHz for the aromatic curing agent (MPDA) +, sound speed; x, sound absorption

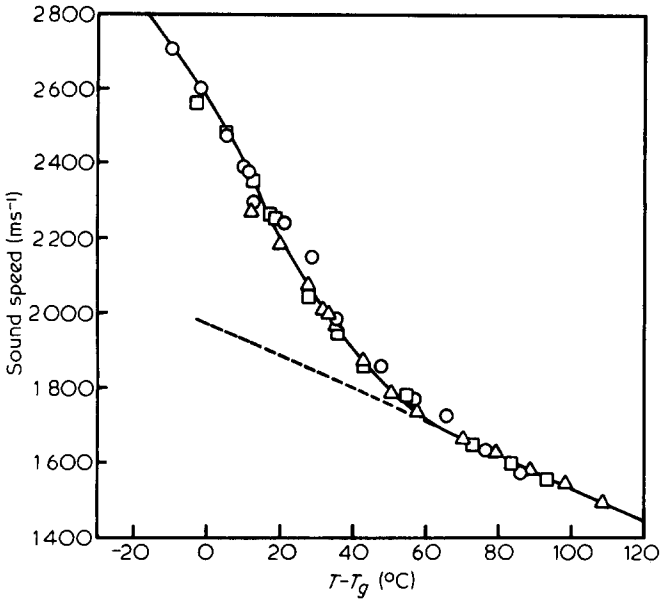

Figure 4 Sound speed vs shifted temperature at 2 MHz. ○, PDA; □, HDA; △, DDA

suppress this transition, for these polymers the ultrasonic properties behave qualitatively the same as observed with linear polymers. It should also be noted that the existence of this transition explains the high values of room temperature absorption mentioned above.

By inspection of *Figures 1* and *2*, it can be seen that the sound speed and absorption curves for the three aliphatics are very similar in shape but shifted in temperature. Since, from *Table 1* the transition temperatures for the three are in the same order, this observation suggests re-plotting the data from *Figures 1* and *2* as a function of $T-Tg$. Sound speed vs $T-Tg$ for the aliphatics is shown in *Figure 4* and absorption in *Figure 5*. Within the experimental uncertainty of the measurements, all the data shift onto the same master curves. However, no temperature shift can superimpose the aromatic data, *Figure 3*, onto the master curves. The aromatic data is shifted by more than its glass transition temperature and the absorption curve is lower and broader than for the aliphatics. It is worth emphasizing that the aliphatic curves were not shifted arbitrarily to obtain the best superposition. They were shifted by the values of their glass transition temperatures, which were determined independently from calorimeter measurements.

The sound speed measurements are interpreted in the following manner. The glass transition is a structural relaxation in which the sound speed varies from its (temperature dependent) unrelaxed value to its (temperature dependent) relaxed value through a broad transition region. The measurements reported here on the aliphatics map out the majority of this relaxation, from the unrelaxed state, indicated by a broken line in *Figure 4*, and through the transition region. Unfortunately, insufficient data was available to determine the unrelaxed value. For the aromatic, only the transition region was determined.

Sound absorption goes through a peak in the transition region, *Figure 5*. If the glass transition involved a single relaxation time, the maximum value of the absorption per wavelength would be given by[8]

$$\alpha\lambda_m = \frac{\pi}{2}\left(\frac{v_U^2 - v_R^2}{v_U v_R}\right)_{T_m} \qquad (1)$$

where subscript U refers to the unrelaxed state and R refers to the relaxed state. T_m is the temperature of the absorption peak (30°C). v_R is given by the broken line in *Figure 4* and v_U can be estimated by assuming that

$$v^2(T_m) \simeq v_U(T_m) v_R(T_m) \qquad (2)$$

where v is the measured sound speed, with the result that $v_U(T_m) = 2260\ \mathrm{m\,s^{-1}}$ and $\alpha_m(\mathrm{calc}) = 55\ \mathrm{dB\,cm^{-1}}$. The single relaxation time model is known to result in a higher, narrower peak than does a distribution of relaxation times. Thus, the observed value of the absorption peak, $\alpha_m(\mathrm{meas}) = 28\ \mathrm{dB\ cm^{-1}}$, shows that the glass transition involves a distribution of relaxation times.

In the aliphatic series, an increase in crosslink density shifts the distribution of relaxation times without change of shape by an amount equal to the increase in glass transition temperature. As a result, the absorption curve has the same peak value and width for all crosslink densities, and the curves can all be superimposed. This implies that all of the same molecular motions occur but at a higher temperature.

When an aromatic component is inserted into the polymer, the distribution of relaxation times not only shifts to higher temperature (by more than the change in glass transition temperature) but also changes in shape. The absorption curve is now lower and broader than before so that superposition is not possible. Presumably, there is now an even broader distribution of relaxation times.

CONCLUSIONS

Qualitatively, the ultrasonic measurements made here are dominated by a structural relaxation, the glass transition. This transition occurs over a broad temperature range and involves a distribution of relaxation times. The majority of the relaxation was mapped out at one frequency in the aliphatic series. Only the transition region was covered for the aromatic.

The following specific observations can be made:

(1) The glass transition in these crosslinked polymers has a qualitatively similar effect on ultrasonic properties as does the glass transition in linear polymers

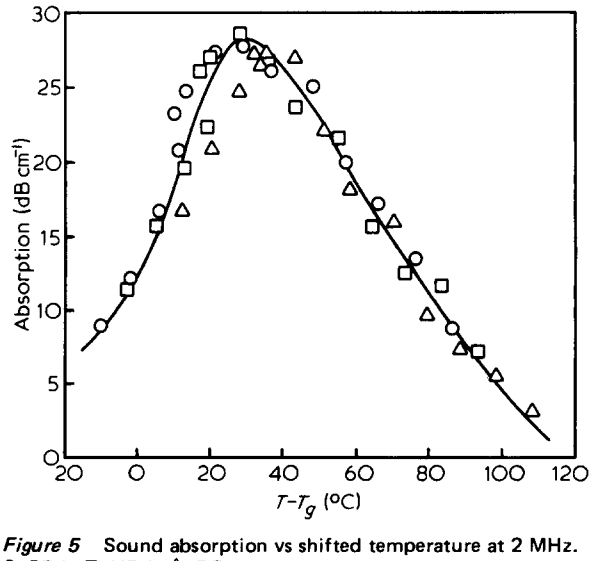

Figure 5 Sound absorption vs shifted temperature at 2 MHz. ○, PDA; □, HDA; △, DDA

(2) In the aliphatic series, a change in crosslink density shifts the ultrasonic properties, unaltered in shape, by the change in glass transition temperature

(3) Inserting an aromatic component in the polymer shifts the ultrasonic properties by more than the change in glass transition temperature and alters the shape.

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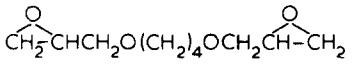
APPENDIX

Polymer synthesis

The epoxy resin used was 1,4-bis(2,3 epoxypropoxy)-butane, commonly known as butanediol diglycidyl ether (BDGE) with the idealized structure:



Three aliphatic diamine curing agents were used: 1,3 propanediamine (PDA), $NH_2(CH_2)_3NH_2$; 1,6 hexanediamine (HDA), $NH_2(CH_2)_6NH_2$; 1,12 dodecanediamine (DDA), $NH_2(CH_2)_{12}NH_2$. One aromatic curing agent was used: *m*-phenylenediamine (MPDA), $NH_2(C_6H_4)NH_2$.

The resin was characterized by measuring its epoxy equivalent weight (*EEW*). This quantity is the molecular weight per reactive site in the polymer. There are two reactive sites in BDGE so the theoretical *EEW* is one half the molecular weight of the structure given above. The *EEW* of the multiply distilled BDGE was measured using the pyridinium chloride–pyridine method[10] with the result that $EEW = 118$ g mol^{-1} compared with the theoretical value of 101 g mol^{-1}, indicating the presence of some lower molecular weight impurity, probably epichlorohydrin.

Stoichiometric amounts of curing agent were used in all cases (i.e. just the amount required for complete reaction). Since there are four reactive sites on the diamine curing agents, four times the *EEW* of the resin (472 g mol^{-1}) are required for each molecular weight of curing agent.

Cure cycles were as follows: DDA — the BDGE at 60°C and DDA at 80°C were mixed and poured into moulds that were alternately cooled and heated (at 80°C). After gelling, the samples remained at room temperature for one day and then were cured for one h at 60°C. HDA — the BDGE at room temperature and HDA at 70°C were mixed and poured into moulds at 5°C, cured overnight at 10°C, then held one day at room temperature, and 2 h at 60°C. PDA — the BDGE and PDA were mixed at room temperature and poured into moulds at 5°C and held overnight, then held for 3 h at 15°C, 4.5 h at 20°C, overnight at room temperature, 2 h at 60°C, and 0.5 h at 80°C. MPDA — the BDGE and MPDA were mixed at room temperature and poured into moulds at 5°C and held overnight, then held for 4 h at 55°C and 2 h at 100°C.