

## Thermal Conductivity, Specific Heat, and Dynamic Mechanical Behavior of Diglycidyl Ether of Bisphenol A Cured with *m*-Phenylenediamine

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### Synopsis

The thermal conductivity, specific heat, and dynamic mechanical behavior of an epoxide system have been investigated over a relatively wide temperature range. Effects of nonstoichiometric amine concentrations and postcure heat treatments were included in the study. The thermal conductivity behavior was found to be related to the extent of cure of the epoxy system, but in general the results were typical of an amorphous polymer. Calorimetric determinations were used to study the curing reaction and the glasslike transition temperature for the various systems. Dynamic mechanical results were employed to delineate the various internal relaxations of the cured materials and in some instances to permit correlation of relaxations with the thermal conductivity and the specific heat results. From comparison of present results to those of a previous paper, the activation energy for the relaxation process occurring near 270°K has been estimated to be 16 kcal/mole.

### INTRODUCTION

There are relatively few reports in the scientific literature concerning studies of the thermal conductivity, specific heat, and dynamic mechanical behavior of crosslinked systems. Thermal conductivity data above room temperature have been reported for epoxy resins by Cherkasova,<sup>1</sup> Knappe,<sup>2</sup> and Kline.<sup>3</sup> A linear increase in conductivity with increasing temperature from a value of  $4.2 \times 10^{-4}$  cal/cm-sec-C° at 0°C to  $4.5 \times 10^{-4}$  cal/cm-sec-C° at 60°C for a diglycidyl ether of bisphenol A-based epoxy (Epon 828, Shell Chemical Co.) cured with *m*-phenylenediamine was reported by Kline.<sup>3</sup> Cherkasova<sup>1</sup> reported a more rapid increase of conductivity with temperature ( $4.3 \times 10^{-4}$  cal/cm-sec-C° at 25°C to  $5.8 \times 10^{-4}$  cal/cm-sec-C° at 90°C); however, no description of the epoxy compound was given. The work of Knappe<sup>2</sup> was based on a higher molecular weight bisphenol A-type resin (Araldite B, Ciba Chemical Co.). For this material an approximately constant conductivity over the temperature range of 0° to 100°C was observed (no description of the curing procedure was given).

Specific heat data above room temperature for several thermosetting polymers have been reported by Warfield, Petree, and Donovan.<sup>4</sup> The

exact variation of  $c_p$  with  $T$  was found to depend upon the curing agent for a given epoxide polymer. An abrupt change in specific heat was observed in the region of the glass transition.

Studies of the dynamic mechanical behavior for some cured epoxy resins have been reported by Kline and Sauer,<sup>5</sup> May and Weir,<sup>6</sup> Kwei,<sup>7</sup> Kaelble,<sup>8</sup> Kline,<sup>9</sup> and Dammont and Kwei.<sup>10</sup> For a bisphenol A-based epoxy (Epon 828) cured with *m*-phenylenediamine, four internal friction peaks were observed between 80° and 580°K.<sup>9</sup> The principal  $Q^{-1}$  maximum was observed at approximately 440°K, corresponding to the temperature of the glasslike transition. A secondary peak centered at approximately 240°K has been associated with the diglycidyl ether portion of the cured resin.<sup>6,7</sup> Two other secondary peaks were suggested as being associated with unreacted ends of the bisphenol units (370°K) and with decomposition products (540°K).<sup>9</sup>

Most of the above work<sup>5-10</sup> was carried out using a stoichiometric amount of amine. Data were generally not reported for different curing temperatures. Most of the previous studies were conducted on commercial epoxy resins having a distribution of molecular weights. The present report is based on an investigation of the thermal conductivity, specific heat, and dynamic mechanical behavior of an epoxy system composed of relatively well-purified diglycidyl ether of bisphenol A cured with *m*-phenylenediamine (*m*-PDA).

## EXPERIMENTAL PROCEDURES

### Thermal Conductivity

In the thermal conductivity apparatus a thin foil heater is placed between two identical specimens (3 in. in diameter by ~0.06 in. thick).<sup>11</sup> The sample-heater system is pressed between two copper plates that serve as heat sinks.

A quasi-steady-state temperature regime was used for the determination of the thermal conductivity over the range of 100° to 400°K. An analysis of the method<sup>11</sup> shows that, if the temperature of the heat sinks is increased linearly at a rate  $h$  (C°/sec) and no current is applied to the central heater, there will be a temperature drop,  $\Delta T_0$ , across the sample. The value of  $\Delta T_0$  is dependent upon the heating rate  $h$ , the thickness  $Z_0$  (cm), and the thermal diffusivity  $\alpha$  (cm<sup>2</sup>/sec) of the sample as follows:

$$\Delta T_0 = \frac{hZ_0^2}{2\alpha}. \quad (1)$$

If the foil heater power is turned on, a new equilibrium condition will be reached and the temperature drop  $\Delta T$  across the sample after a sufficient time interval will be given by

$$\Delta T = \frac{qZ_0}{k} - \frac{hZ_0^2}{2\alpha} \quad (2)$$

where  $q$  is the heater power per unit area (cal/cm<sup>2</sup>-sec) and  $k$  is the thermal conductivity of the sample (cal/cm-sec-C°).

Substitution of eq. (1) into eq. (2) gives the relation for the determination of the thermal conductivity

$$k = \frac{qZ_0}{\Delta T + \Delta T_0} \quad (3)$$

The measurement of  $k$  at a given temperature  $T$  involves three steps. First,  $\Delta T_0$  is measured immediately before the power to the foil heater is turned on. After equilibrium is reached, the total  $\Delta T$  is measured. The heater power is turned off and  $\Delta T_0$  is again measured when equilibrium is reached. Linear interpolation between the two measurements of  $\Delta T_0$  is used to obtain a value of  $\Delta T_0$  at the temperature  $T$ . The third equation is used to calculate the thermal conductivity.

### Calorimetric Determinations

A Perkin-Elmer Model DSC-1 differential scanning calorimeter (DSC) was used for the determination of the specific heat, the heat of polymerization, and the endothermic transition energy. The details of this instrument have been described in the literature.<sup>12-14</sup>

Samples and reference materials were enclosed in aluminum sample pans which weigh approximately 20 mg. Heats of polymerization for the epoxide-amine reaction were obtained by filling a previously weighed sample pan with the epoxide-amine mixture immediately after the two components were combined. This sample pan was placed in one sample holder and an aluminum pan containing a previously polymerized epoxy-amine of approximately the same mass was placed in the other holder. The temperature was increased at the rate of 2.5 C°/min until the reaction was completed, as indicated by the return of the recorder pen to the zero position. The maximum temperature attained was usually between 400° and 450°K. A second scan of the same sample indicated no further reaction occurred in this temperature range; i.e., no exotherm was observed. The heat of reaction was determined from the area under the exotherm curve.

The specific heat measurements were obtained in three steps.<sup>13</sup> First, empty sample pans were placed in both sample holders and the temperature was scanned over the desired range to obtain a baseline. Second, a disk of synthetic sapphire with known specific heat characteristics was placed in one sample holder and the temperature range was scanned. Third, the sapphire was replaced by the sample to be measured and the temperature range was scanned again.

The specific heat of the sapphire had previously been determined<sup>15</sup> over the temperature range of 0° to 1200°K and served as a calibration standard. At any temperature the specific heat is obtained from the relation

$$c_p = \left( \frac{m'}{m} \frac{D}{D'} \right) c'_p \quad (4)$$

where  $c_p$  is the specific heat,  $m$  is the mass, and  $D$  is the deflection of the pen from the baseline. The primed quantities refer to the sapphire while the unprimed quantities refer to the sample.

### Dynamic Mechanical Measurements

The values of internal friction and dynamic elastic modulus were obtained from 80° to 500°K from experiments utilizing the transverse vibration of a cylindrical specimen (4.4 in.  $\times$  0.25 in. in diameter). The frequency of vibration for these measurements was in the range of 200 to 1500 Hz. The details of this apparatus have been previously described.<sup>16</sup>

The internal friction was determined from the relation

$$Q^{-1} = \frac{\Delta f}{f_1} \quad (5)$$

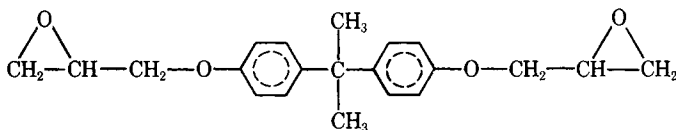
where  $\Delta f$  is the bandwidth at the half-power level of the amplitude-frequency curve and  $f_1$  is the resonance frequency of the fundamental vibration mode. The elastic modulus was calculated from the resonance frequency by the relation

$$E' = \frac{0.3154 l^4 \rho f_1^2}{r^2} \quad (6)$$

where  $l$ ,  $r$ , and  $\rho$  are, respectively, the length, radius, and density of the specimen.<sup>17</sup>

### Specimen Preparation

For the present study a relatively well-purified epoxide was obtained. This epoxide, diglycidyl ether of bisphenol A, termed X22, (Shell Development Co., Emeryville, Calif.), had a molecular weight of 340. The molecule has the following structure:



To form the cured epoxy system, the above epoxide was combined with *m*-phenylenediamine (*m*-PDA).

The mixing of the epoxide and the amine was accomplished in the following manner. The desired amount of epoxide was melted in a glass beaker by heating to 50°C. When the epoxide had cooled to approximately 40°C, the required amount of solid amine was added. The epoxide-amine mixture was heated to 70°C, which is slightly above the melting point of the amine, then stirred for about 5 min. When the mixture had cooled to about 60°C, it was poured into molds.

Samples for the thermal conductivity measurements were molded between two glass plates with a confining aluminum ring spacer. Specimen size was about 3 in. (diameter) by 0.06 in. (thickness). Before the epoxide-

amine mixture was poured, the glass and aluminum surfaces were sprayed with a fluorocarbon release agent. Samples for the DMP measurements were molded in Teflon tubing of  $1/4$ -in. inside diameter.

All specimens used in this study were given a basic two-stage heat treatment. First the material was cured at room temperature until the gel point was reached. Then the specimens were placed in an oven at  $345^{\circ}\text{K}$  for 24 hr. This is a typical primary curing cycle for the epoxy-*m*-PDA system.

## RESULTS

Thermal conductivity data for epoxide X22 cured with a stoichiometric amount of *m*-phenylenediamine (*m*-PDA) are presented in Figure 1. The first curve (open circles) was obtained after the specimen had received a heat treatment of 24 hr at  $345^{\circ}\text{K}$ . The second run of this specimen (after heating to  $400^{\circ}\text{K}$ ) yielded higher values of conductivity (solid full circles) at all temperatures below  $390^{\circ}\text{K}$ . Figure 1 also shows values of  $k$  at room temperature (R.T.) for four other samples.

Specific heat data for a specimen of epoxide X22 cured with the stoichiometric amount of *m*-PDA are shown in Figure 2 for the temperature range  $320^{\circ}$  to  $470^{\circ}\text{K}$ . The dynamic mechanical properties of this mixture are presented as a function of temperature in Figures 3 and 4. Data presented were obtained from different specimens of the epoxy-amine system.

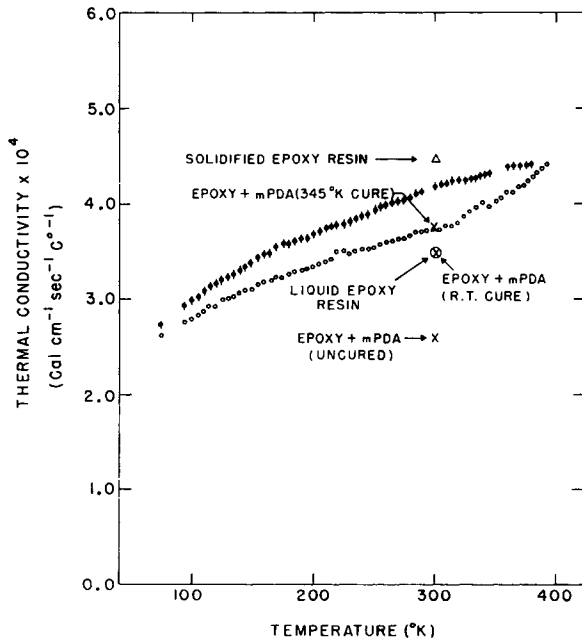


Fig. 1. Thermal conductivity of diglycidyl ether of bisphenol A cured with stoichiometric amount of *m*-phenylenediamine: (○) 24 hr at  $345^{\circ}\text{K}$ ; (●) rerun after heating to  $400^{\circ}\text{K}$ .

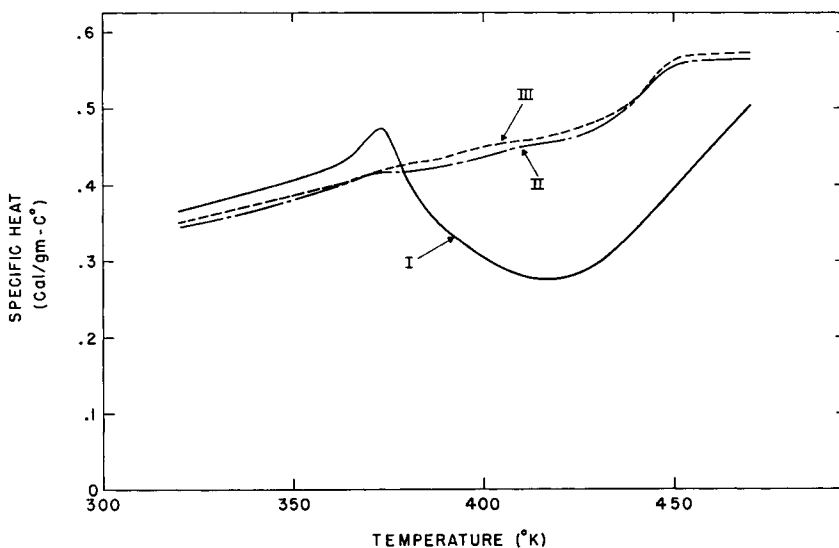


Fig. 2. Specific heat of diglycidyl ether of bisphenol A cured with stoichiometric amount of *m*-phenylenediamine: (I) first run after 345°K cure; (II) second run; (III) third run.

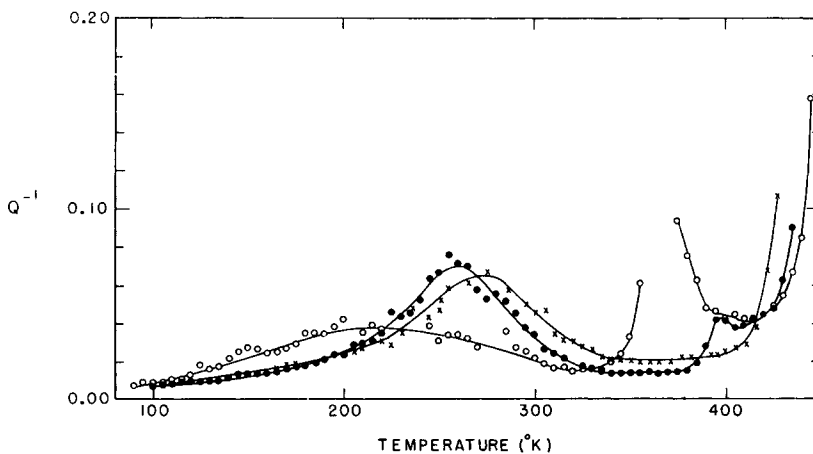


Fig. 3. Internal friction of diglycidyl ether of bisphenol A cured with stoichiometric amount of *m*-phenylenediamine for three different heat treatments: A(O) 24 hr at 345°K; B(●) 24 hr at 375°K; C(×) 24 hr at 400°K.

Similar results were obtained upon retesting of each specimen. If a specimen originally cured at 345°K was tested to 400°K, a retest of this sample resulted in equivalent data to that originally obtained from a sample cured at 400°K.

Figure 5 presents the thermal conductivity data for epoxide X22 cured with 10 g of *m*-PDA per 100 g epoxide (62% stoichiometric). To illustrate the effect of a substoichiometric amount of *m*-PDA as compared to a stoi-

chiometric amount of *m*-PDA, the curves for the second runs (following testing to 390°K) presented in Figures 1 and 5 are reproduced in Figure 6. The conductivity of the substoichiometric specimen reaches a maximum value of 325°K while the stoichiometric specimen exhibits a monotonically increasing conductivity up to 400°K.

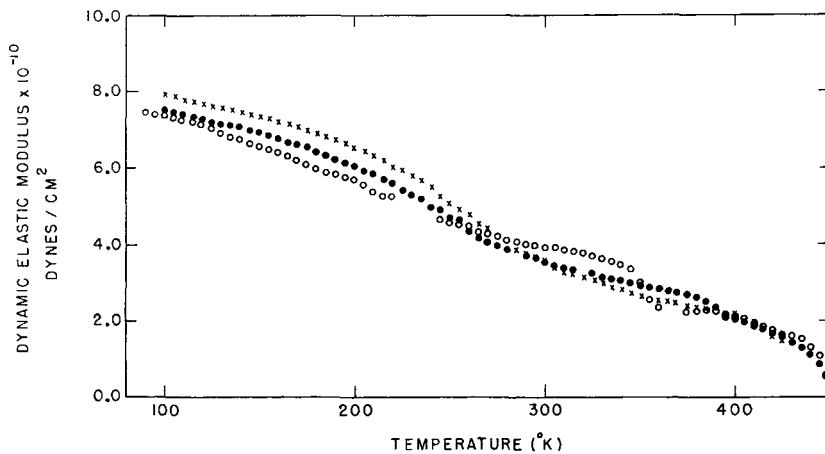


Fig. 4. Dynamic elastic modulus of diglycidyl ether of bisphenol A cured with stoichiometric amount of *m*-phenylenediamine for three different heat treatments: A(○) 24 hr at 345°K; B(●) 24 hr at 375°K; C(×) 24 hr at 400°K.

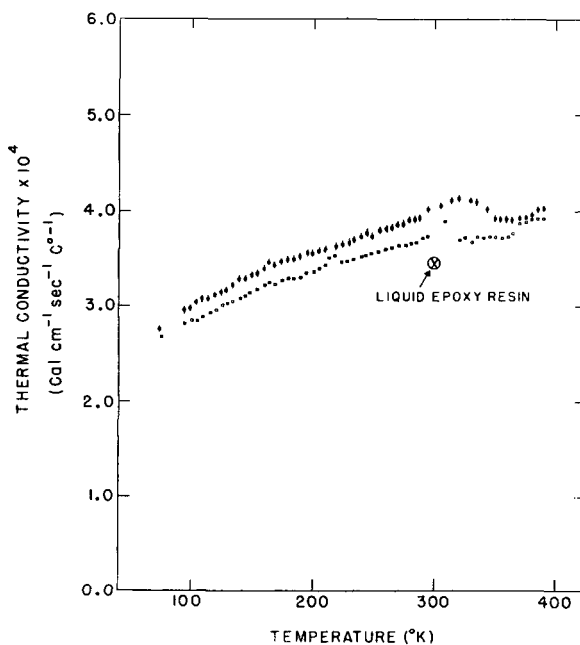


Fig. 5. Thermal conductivity of diglycidyl ether of bisphenol A cured with 62% of the stoichiometric amount of *m*-phenylenediamine: (□) 24 hr at 345°K; (●) rerun after heating to 400°K.

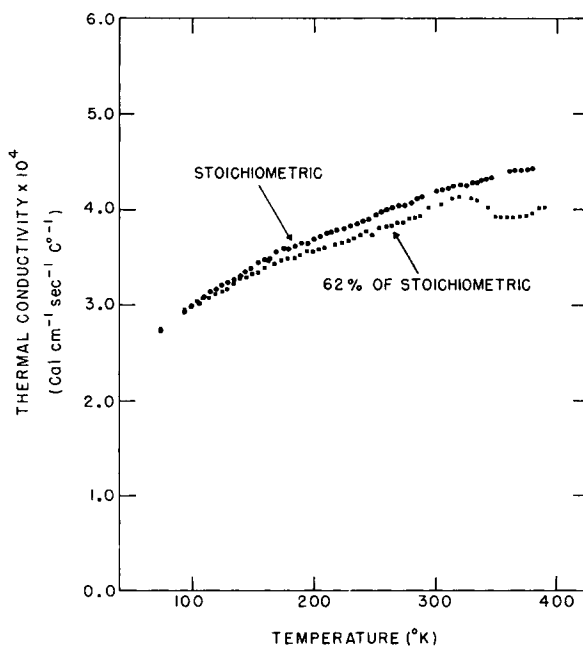


Fig. 6. Thermal conductivity of diglycidyl ether of bisphenol A cured with *m*-phenylenediamine (specimens heat treated to 400°K).

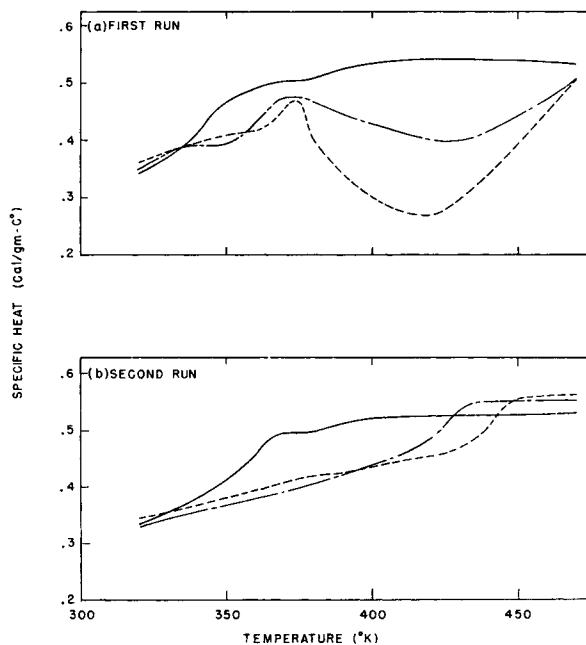


Fig. 7. Specific heat of diglycidyl ether of bisphenol A cured with *m*-phenylenediamine for different amounts of amine: stoichiometric amts of *m*-PDA: (—) 62%; (— · —) 86%; (----) 100%.



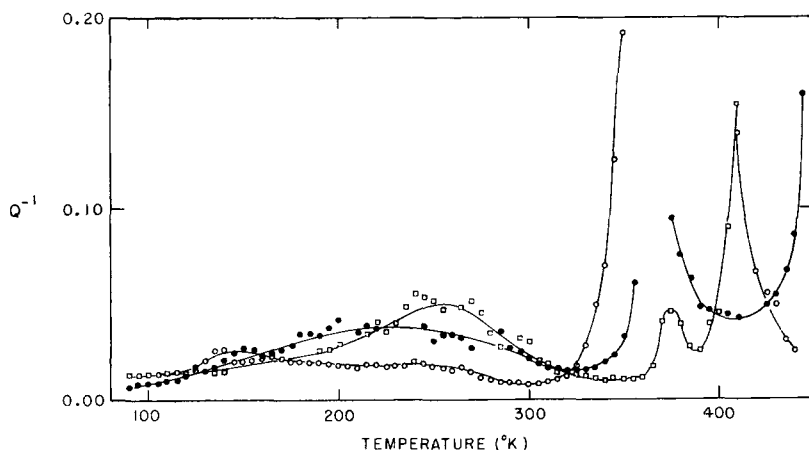


Fig. 8. Internal friction of diglycidyl ether of bisphenol A cured with different amounts of *m*-phenylenediamine (specimens heat treated 24 hr at 345°K): stoichiometric amts of *m*-PDA: (○) 62%, H; (●) 100%, C; (□) 141%, E.

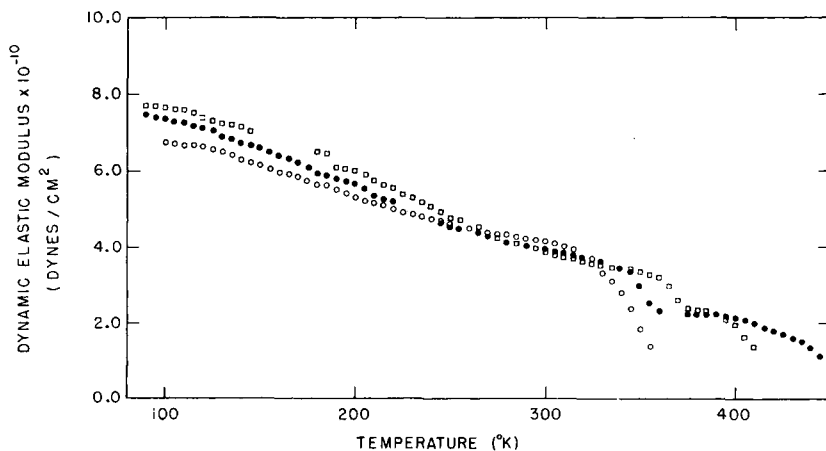


Fig. 9. Dynamic elastic modulus of diglycidyl ether of bisphenol A cured with different amounts of *m*-phenylenediamine (specimens heat treated 24 hr at 345°K): stoichiometric amts of *m*-PDA: (○) 62%, H; (●) 100%, C; (□) 141%, E.

In Figure 7 specific heat curves for epoxide cured with substoichiometric amounts of amine are presented. The data of Figure 7a were obtained after a heat treatment of 24 hr at 345°K. Figure 7b presents the data obtained for the second or repeat run of the three specimens of Figure 7a. The inflection in the  $c_p$  curve, which is generally an indication of a glasslike transition, moves to lower temperatures with decreasing amine content. The value of the specific heat above the glass transition appears to increase as the amine content is increased toward the stoichiometric amount.

The effect of varying the amount of amine used in the curing of epoxide X22 on the relaxation behavior is demonstrated by the DMP data of Figures

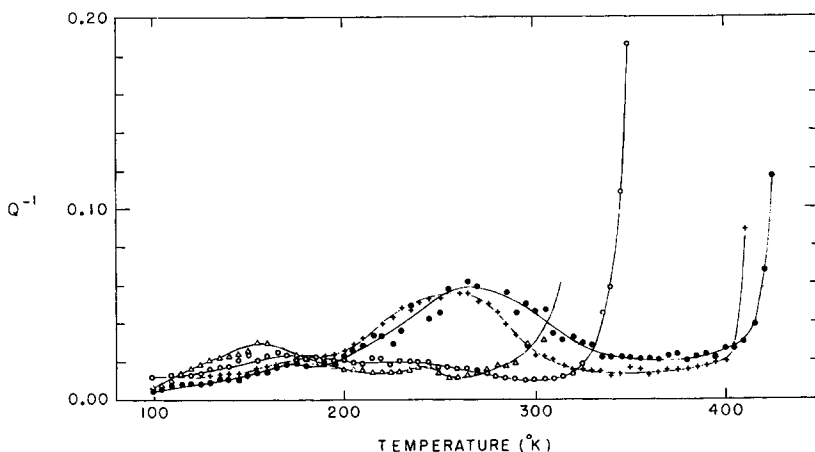


Fig. 10. Internal friction of diglycidyl ether of bisphenol A cured with different amounts of *m*-phenylenediamine (specimens heat treated to 400°K): stoichiometric amt of *m*-PDA: ( $\Delta$ ) 43%, G; ( $\circ$ ) 62%, H; (+) 81%, I; ( $\bullet$ ) 100%, C.

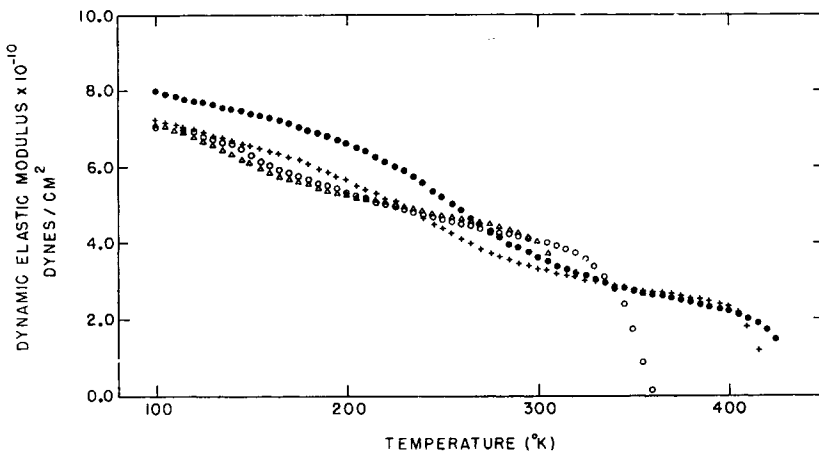


Fig. 11. Dynamic elastic modulus of diglycidyl ether of bisphenol A cured with different amounts of *m*-phenylenediamine (specimens heat treated to 400°K); stoichiometric amt of *m*-PDA: ( $\Delta$ ) 43%, G; ( $\circ$ ) 62%, H; (+) 81%, I; ( $\bullet$ ) 100%, C.

8 and 9 for specimens cured 24 hr at 345°K. Data are given for specimens H, C, and E cured respectively with 62%, 100%, and 141% of the stoichiometric amounts of *m*-PDA. The onset of the main glasslike transition occurs at about 420°K for the stoichiometric specimen (C). When the proportion of amine is either increased or decreased, this transition occurs at lower temperatures.

For specimens cured at a higher temperature (400°K), Figures 10 and 11 present the dynamic mechanical properties of epoxide X22 samples G, H, I, and C cured respectively with 43%, 62%, 81%, and 100% of the stoichiometric amount of *m*-PDA. As the amount of amine decreases through the

values of 100%, 81%, 62% and 43%, the temperature of the onset of the glasslike transition occurs near 420°, 400°, 325°, and 290°K, respectively.

## DISCUSSION

### Effect of Heat Treatment on the Properties of the Epoxide-Amine System

Several studies of the reaction of epoxides with amines have been reported.<sup>18-21</sup> The results of these studies suggest that the room temperature cure of the X22-*m*-PDA system is largely related to the reaction of primary amines with the epoxide groups. At higher temperatures the reaction of the secondary amines with epoxy groups is responsible for the formation of crosslinking. The room-temperature-cured polymer is soluble while the high-temperature-cured material exhibits swelling behavior typical of a crosslinked system. Data obtained from the DSC and the DMP apparatus are consistent with those of a crosslinked system following heat treatment to >345°K.

DSC scans for specimens having varying percentages of stoichiometric values of amine and cured at 345°K are shown in Figure 12. These results along with the specific heat curves of Figures 2 and 7 show that an irreversible exothermic reaction is observed above the heat treatment temperatures (345°K) for samples having 86% or 100% of the stoichiometric mixture. Evidence of a slight endothermic transition is also observed for three of the samples at a temperature below the exotherm. The temperature of the latter transition decreases with decreasing amount of amine. The occurrence of an endotherm at a temperature just below the exotherm has also been reported for an epoxy-anhydride system.<sup>22</sup>

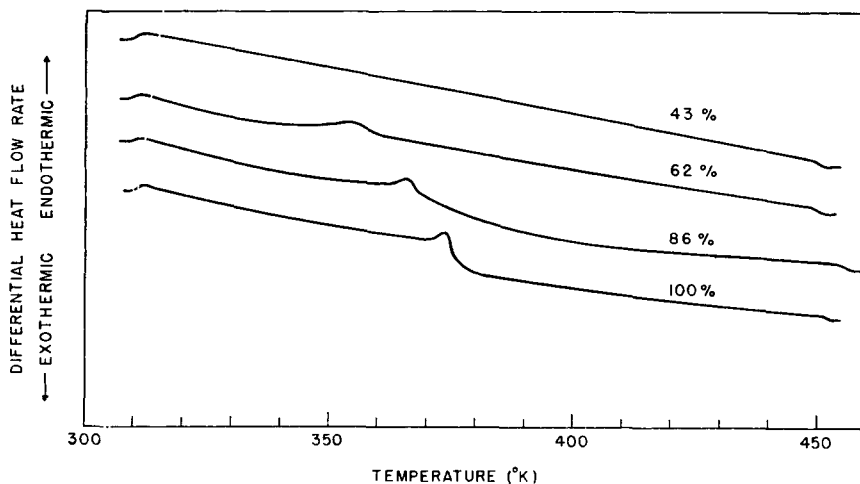


Fig. 12. DSC scans for the diglycidyl ether of bisphenol A and *m*-phenylenediamine system after heat treatment at 345°K: numbers indicate the % stoichiometric amt of amine.

As noted in the DMP data for the stoichiometric specimen (Figs. 3 and 4), several aspects of the internal friction and elastic modulus curves are changed as a result of higher cure temperatures. The relaxation centered at 365°K for the 345°K cure is eliminated by curing at 400°K. The modulus associated with the 345°K cure also drops significantly near the onset of the 365°K DMP relaxation. The modulus values (Fig. 4) also show a slight increase with temperature between 360° and 380°K, suggesting further curing with increasing temperature. Results for higher temperature cures do not exhibit either the sharp drop near 340°K or the subsequent slight rise. The observed effects are a result of a softening process followed by increased curing of the system, but following higher cure temperatures this softening process is largely eliminated.

The low-temperature relaxation process (200° to 300°K) is also related to the extent of cure. The value of the modulus below about 200°K increases as higher heat treatment temperatures are employed. Slightly above room temperature the modulus levels are reversed and the specimen with the highest heat treatment temperature has the lowest modulus value.

May and Weir<sup>6</sup> have attributed the above low-temperature relaxation to processes involving the diglycidyl ether portion of the cured resin. It is interesting to note that a similar relaxation also occurs in polyethylene terephthalate (PETP) in the same temperature range.<sup>23</sup> The PETP linkage  $-\text{OC}_2\text{H}_4\text{O}-$  has some similarity to the ether segment in the cured epoxy. At lower temperatures, higher modulus values are noted to accompany higher cure temperatures (Fig. 4).

The irreversible increase in thermal conductivity observed above 325°K for the stoichiometric specimen cured at 345°K (first run of Fig. 1) is considered to be a result of further crosslinking accompanying the additional high-temperature exposure. The thermal conductivity of polystyrene (PS) crosslinked with divinylbenzene (DVB) is also reported to increase as the degree of crosslinking is increased.<sup>24</sup> Further, for polyethylene,<sup>25</sup> the thermal conductivity above the crystalline melting point is reported to increase as the amount of radiation-induced crosslinking is increased. The dependence of thermal conductivity on the extent of crosslinking can be related to the increased concentration of primary chemical bonds, as opposed to secondary forces between adjacent molecules.<sup>29</sup>

The above argument is given further support by the results of the repeat run after prior exposure to 400°K in the first run. Increased curing causes the conductivity to increase more rapidly with increasing temperature in the 80° to 300°K temperature range. The thermal conductivity of crosslinked PS shows similar behavior.<sup>24</sup> Between 20° and 60°C, the conductivity of PS increases linearly with temperature; however, the rate of conductivity rise is higher for the specimen crosslinked with 15% DVB as compared to a specimen with 5% DVB.<sup>24</sup>

The ratio of the thermal conductivity value for various cure times to the conductivity of the room temperature-cured material for the X22-*m*-PDA

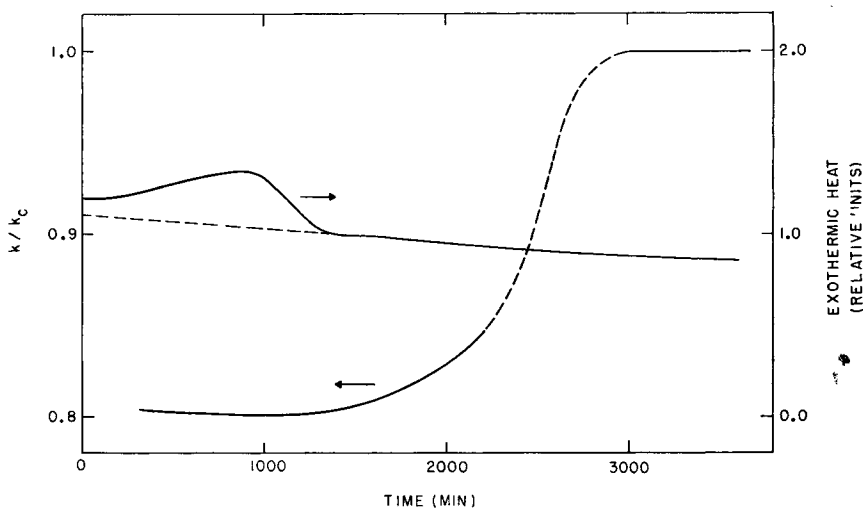


Fig. 13. Thermal conductivity and heat evolution as a function of time during the room temperature cure of diglycidyl ether of bisphenol A with *m*-phenylenediamine.

system is plotted as a function of time in Figure 13. The heat evolved during the curing reaction, as determined by the differential scanning calorimeter, is also plotted. The ratio of the conductivities is seen to increase by about 20% between 1000 and 3000 min after the epoxy and amine are mixed. The peak exotherm occurs at about 1000 min after mixing and appears to be largely completed by about 1200 min. Observations taken on material from the same batch as the above specimen indicate that the material remains soft up to about 1500 min after mixing. The material then hardens rapidly and becomes brittle by the time 3000 min have elapsed.

Data presented in Figure 1 for both an epoxide sample and for the epoxide-*m*-PDA mixture illustrate that the low value of room temperature conductivity of the epoxy-amine mixture ( $2.7 \times 10^{-4}$  cal/cm-sec- $C^\circ$ ) as compared to the pure resin ( $3.5 \times 10^{-4}$  cal/cm-sec- $C^\circ$ ) is probably related to the dilution of the epoxide by the *m*-PDA molecule. After the room temperature cure is completed the conductivity value increases to that of the pure resin. Further curing at  $345^\circ\text{K}$  raises the conductivity value to that of the corresponding  $345^\circ\text{K}$ -cured specimen, whose conductivity-temperature curve is given in Figure 1.

Upon heat treatment to  $470^\circ\text{K}$ , the specific heat of the stoichiometric specimen (Fig. 2) cured at  $345^\circ\text{K}$  is found to decrease by 6% in the  $320^\circ$  to  $350^\circ\text{K}$  temperature range. This is not the behavior expected from increased crosslinking. For instance, Überreiter and Otto-Laupenmühlen<sup>24</sup> found that, for polystyrene crosslinked with divinylbenzene, the value of  $c_p$  below the glass temperature increased as the concentration of DVB was increased.

In comparing the effects associated with additional curing for the different properties, it is important to note that the data were obtained at

different heating rates for the different experiments. The thermal conductivity data were obtained at a heating rate of 0.25 K°/min, the DMP data at a heating rate of 1.0 K°/min, and the specific heat data at a heating rate of 10 K°/min.

### Relationship of Molecular Relaxations to the Measured Properties

The thermal conductivity curve (Fig. 6) for the specimen cured with the stoichiometric amount of *m*-PDA after the 400°K heat treatment exhibited a pattern typical of amorphous polymers.<sup>26</sup> A decrease in the conductivity curve is expected to occur in passing through the region of the glass transition because of the abrupt decrease in the van der Waals forces<sup>27</sup> and the increased free volume. The specific heat and DMP data for the above material indicate that the glass transition is centered near 450°K. The gradual decrease in slope of the *k*-versus-*T* curve near 400°K is thus consistent with the onset of the glass transition.

For the specimen cured with only 62% of the stoichiometric amount of *m*-PDA, a maximum in the thermal conductivity curve is observed at 325°K (Fig. 6). The DMP (Figs. 10 and 11) and the specific heat data (Fig. 7) for this specimen indicate that the glass transition begins near this temperature. The shape of the thermal conductivity curve in the region of the glasslike transition is similar to the conductivity curves for several types of rubber in the temperature region of the respective glasslike transitions as reported by Eiermann and Hellwege.<sup>28</sup>

From the DMP data of Figures 10 and 11, the relaxation process below room temperature is found to depend upon the amount of amine used in the reaction of the epoxide. The decrease in height of the 270°K peak with decreasing amine content is consistent with a decrease in concentration of chain segments associated with the opened epoxy rings which are believed responsible for the relaxation.<sup>6</sup> Comparison of the present DMP data with that of May and Weir<sup>6</sup> (with regard to shift of the temperature of the relaxation with shift in frequency of measurement) indicates that the process has an activation energy of about 16 kcal/mole.

The internal friction peak which occurs in the region near 370°K for stoichiometric specimens cured at 345°K (Figs. 3 and 8) is assumed to be associated with unreacted molecular segments. Upon curing to higher temperatures (400°K), this peak disappears as can be observed from specimen C of Figure 3 or specimens C and I of Figure 10.

For the low amine concentration samples, the development of the peak at about 150°K may be associated with the chain segments formed when only one oxirane ring of the epoxide molecule has reacted. Evidence of a low-temperature relaxation appears to be present in the thermal conductivity curve of both specimens of Figure 6, as a noticeable change in slope occurs near 170°K. Figure 3 also gives some evidence of a 150°K transition in the incompletely cured stoichiometric sample heat treated at 345°K. The interpretation given is consistent with the fact that for completely cured samples, as Figures 3 and 4 show, or for samples of high

amine content, as Figures 8 and 9 show, no transition is present in this temperature range.

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