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1979

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# A Dynamic Mechanical Study of the Curing Reaction of Two Epoxy Resins

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The curing behavior of two commercially formulated epoxy resins composed of the tetrafunctional amine dicyandiamide and with differing epoxy components, 4,4'-bisglycidylphenyl-2,2'-propane and the tetraglycidyl ether of methylene dianiline, is characterized by dynamic spring analysis. This supported viscoelastic technique is well suited to the determination of the onset of gelation under isothermal conditions but the method is not useful for monitoring later stages of reaction when the resins become more rigid. The activation energy for the curing of the two resins is about 87 kJ/mole (20.7 kcal/mole). Rate constants for the first order curing reaction are given. Additional studies of films cured below the ultimate  $T_g$  show that two relaxations can be observed upon heating. The first relaxation occurs near the original isothermal cure temperature with a low activation energy, about 250 kJ/mole, whereas the second relaxation occurs near the ultimate  $T_g$ , under the conditions used here, with an activation energy of 500-650 kJ/mole. It is believed that these activation energies provide a unique method of characterizing the molecular mobility of epoxy resins at various states of cure.

## INTRODUCTION

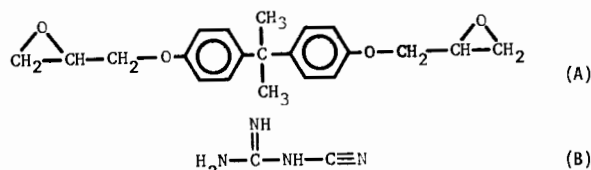
Several techniques are available which allow the dynamic mechanical properties of epoxy resins to be determined during the actual curing process. Torsional braid analysis, TBA, has been shown by Gillham (1, 2) to be a useful method for characterizing the curing behavior of epoxy resins through both the gelation and vitrification stages of the reaction. Viscosity and dynamic shear measurements have been employed by Mussatti and Macosko (3) to determine the order, rate constants and activation energy for a network forming epoxy reaction. The method of dynamic spring analysis, DSA, was proposed by Naganuma and coworkers (4) as a viscoelastic technique employing the Rheovibron dynamic viscoelastometer with the sample coated on small metal springs. The technique was initially applied to the study of a butylated melamine resin but subsequent work by the same authors showed the versatility of the method by examining the crosslinking of commercial adhesives (5) as well as the curing of modified phenolic resins and tung oil (6). The present work fo-

cuses on the extension of the DSA technique to a study of the crosslinking of two epoxy resins. Applications of a model described elsewhere by Senich and MacKnight (7, 8) allowed both storage and loss moduli to be obtained as a function of time for the curing system. Additional characterization of unsupported resin films cured at several temperatures was also carried out on the Rheovibron employing conventional methods of analysis.

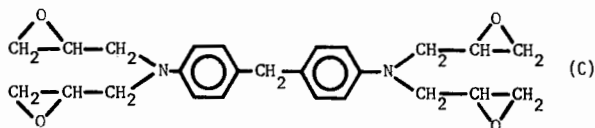
## EXPERIMENTAL

### Samples

Two commercially formulated epoxy resins are the same as those used in recent DSC and TBA study (9, 10), where more detailed sample composition information can be found. Resin I consists of novolac resin, a phenol-formaldehyde prepolymer, a difunctional epoxy, 4,4'-bisglycidylphenyl-2,2'-propane (A), a tetrafunctional amine, dicyandiamide (Dicy, B), and a urea type accelerator.



Resin II consists of a tetrafunctional epoxy, the tetraglycidyl ether of methylene dianiline (C) and the tetrafunctional amine Dicy, in addition to a urea type accelerator.



The recommended cure for both resins is two hours at 127°C with no postcure. Epoxy resin II was supplied as a 50 percent by weight solution in methylene chloride.

### Measurements

The curing reaction was followed by the technique of dynamic spring analysis (DSA) in conjunction with the Rheovibron DDV-IIB dynamic viscoelastometer, as described previously (7, 8). A spring 3.3 mm in outer diameter of 0.30 mm diameter steel wire, twenty turns in length was placed in the Rheovibron and stretched to achieve a pitch of 0.1 mm. The Rheovibron temperature chamber was then brought to a constant cure temperature,  $T_c$ , and the sample applied with a hypodermic syringe as a 50 percent by weight solution in methylene chloride. The viscoelastic response of the composite was followed in a dry nitrogen atmosphere as a function of time from the moment of sample application. About 15 mg of epoxy sample was required for each curing study.

Thin film epoxy samples were prepared by compression molding 0.25 mm thick samples under a pressure of 3 MPa at a constant cure temperature. Resin II was subjected to room temperature drying in a vacuum oven to remove most of the methylene chloride before molding. The epoxy films were air quenched after the desired time at  $T_c$  had been attained. These samples were analyzed in the Rheovibron DDV-IIB by standard procedures at nominal heating rates of 1.5°C/min in a dry nitrogen atmosphere. DSA and Rheovibron measurements were made sequentially at frequencies of 3.5, 11, 35 and 110 Hz with the exact time or temperature noted when the measurement was made.

## RESULTS AND DISCUSSION

### Isothermal Cures

Several cures of each resin system were examined over the temperature range of 80 to 110°C by the DSA technique. Figure 1 shows the storage and loss modulus of resin I at several frequencies as a function of the natural logarithm of time for a cure at 80.2°C. The analysis required to obtain the storage and loss modulus of the epoxy as discussed previously (7, 8) was modified slightly by elimination of the volume fraction terms from the parallel model assumed. For this case, the defining parallel model equation can be written as:

$$M_c = M_p + M_s \quad (1)$$

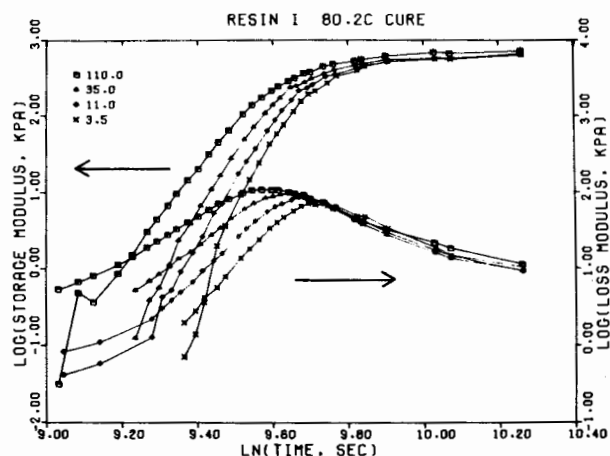


Fig. 1. Storage and loss modulus of resin I as a function of logarithmic time for an 80.2°C cure.

where  $M_c$  is the composite modulus,  $M_s$  the spring modulus, and  $M_p$  the polymer modulus. The frequency dependence of the loss peaks in Fig. 1 indicates that the phenomenon occurs first at high frequency and last at the lowest frequency studied. Corresponding to the loss peak in  $M_p''$ , the storage modulus  $M_p'$  shows an increase from about 0.1 kPa to 1000 kPa, over a relatively short time interval. The final level of the storage modulus is about that expected for a lightly crosslinked rubbery network.

The existence of a loss process associated with curing can be explained by the rapid increase in viscosity of the epoxy resin as its molecular weight increases. Recent DSA studies on low molecular weight polystyrene samples (11) have shown that a loss maximum occurs at a critical viscosity for composite samples in the liquid region, which can be attributed to a coupling between the support and the liquid sample. The same process is thought to be occurring during the curing reaction. An increasing degree of cure causes the resin viscosity to rise and achieve a critical level at the relaxation maximum. A model for this phenomenon asserts that the product of sample viscosity and forced oscillation frequency is a constant for a particular composite system. For an isothermal experiment, the loss maximum should occur at a longer time for a lower frequency determination as the viscosity, or alternatively the molecular weight, must be greater in order that constancy of the viscosity-frequency product be maintained. Such behavior can be noted for the loss maximum associated with curing. The relaxation shown in Fig. 1 is not of molecular origin, however it can be used to characterize the curing reaction of epoxy resins, which will subsequently be discussed.

In the study of the gelation of an epoxy resin, Gillham (1) observed two loss maxima in a torsional braid experiment. The first peak was attributed to gelation and the second to vitrification. In the DSA studies previously described, no well defined relaxation attributable to vitrification was observed. This can perhaps be explained by the lack of sensitivity of the DSA technique to changes in modulus of a high modulus material, as discussed in ref. (7) and (8). It was assumed, therefore, that

the loss peak observed in the present work was due to an increase in viscosity caused by the curing reaction and not to the network glass transition.

In isothermal cures at fixed frequency, the position of the loss maximum was found to vary with the temperature at which the epoxy sample was cured. Figure 2 shows a plot of the composite  $\tan(\delta)$  at 110 Hz for four resin II samples cured at temperatures between 80 and 110°C. It is apparent that the highest  $T_c$  results in the earliest onset of the loss peak associated with the curing process. This information can be used to calculate an activation energy for the epoxy curing process in the following manner. The velocity constant  $k$  for a chemical reaction varies with temperature according to the Arrhenius relation:

$$\ln(k) = -H_a/RT + C \quad (2)$$

where  $H_a$  is the activation energy of the reaction. Since the velocity constant is inversely proportional to the time of reaction independent of the order of the reaction, the elapsed time to the loss modulus maximum was used as a convenient measure of the rate of reaction at each temperature and for each frequency. The slope of a plot of  $\ln(t_{max})$  vs  $1/T$  can then be used to determine the activation energy. Such a plot is shown in Fig. 3 for resin I. For each frequency, the data can be seen to fit a straight line quite well. A linear least squares fit was used to determine the activation energy for both resins at each frequency. These results are summarized in Table 1 for both materials. Chemical activation energies determined by DSA are in good agreement with determinations by other methods on the same samples, as indicated in Table 2, as well as with the results obtained from other studies of epoxy resins cured with Dicy (12, 13).

A rate constant for the curing reaction can be evaluated by a method proposed by Mussatti and Macosko (3) in which the viscosity is plotted against the reaction time required to reach that viscosity at a constant temperature. Since DSA experiments were conducted at four frequencies and the viscosity frequency product is constant at the loss maximum, four reaction times to a known viscosity level are available. From this

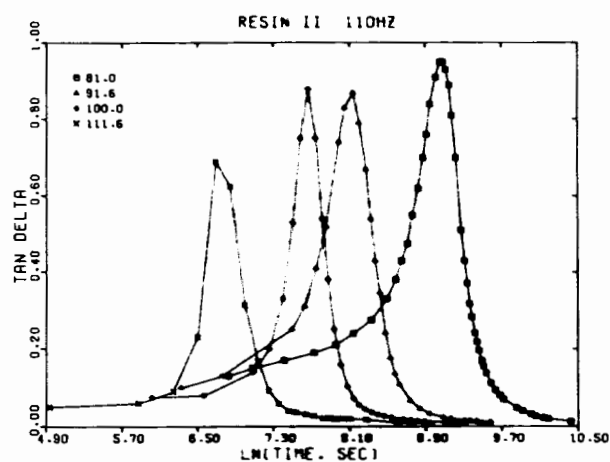


Fig. 2. Loss tangent at 110 Hz vs logarithmic time for resin II at several cure temperatures.

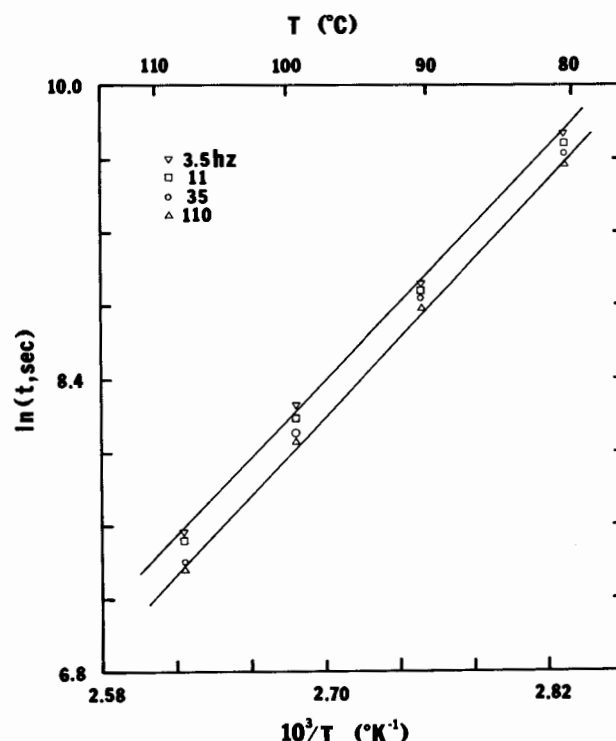


Fig. 3. Arrhenius plots at four frequencies for the determination of activation energies of the Resin I curing reaction.

data, plots of logarithmic viscosity, determined from data given in ref. (11), as a function of reaction time for each isothermal cure were constructed, as shown in Fig. 4 for resin II. A logarithmic variation of viscosity with time indicates that the reaction is first order and the slope of such a plot is equal to the overall rate constant. The rate constant measured is thought to be complex in nature as it is dependent upon particle size, solubility and degree of mixing of the Dicy component (13) as well as the extent of various side reactions which are possible in the system (14). Rate constants determined for each resin at each cure temperature by a linear least squares fit are given in Table 3.

Table 1. Chemical Activation Energy from DSA for Epoxy Cures

Frequency, Hz	Resin I $H_a$ , kJ/mole	Resin II $H_a$ , kJ/mole
110	$88.5 \pm 4.1^a$	$81.8 \pm 5.0^a$
35	$89.4 \pm 4.7$	$85.0 \pm 4.5$
11	$86.8 \pm 2.3$	$86.0 \pm 4.3$
3.5	$86.8 \pm 4.2$	$86.6 \pm 5.2$
Avg	$87.9 \pm 2.8$	$84.9 \pm 4.6$

<sup>a</sup> From the loss modulus maximum, to the 95 percent confidence level.

Table 2. Comparison of the Chemical Activation Energy of Curing Determined by Several Methods

Analysis	Resin I $H_a$ , kJ/mole	Resin II $H_a$ , kJ/mole
DSA	87.9	84.9
TBA <sup>a</sup>	81.6	85.4
DSC <sup>a</sup>	84.9	84.9

<sup>a</sup> From ref. 9.

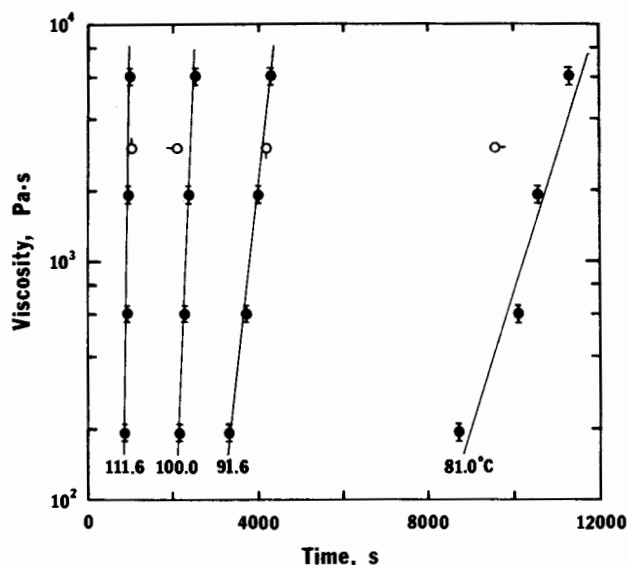


Fig. 4. Logarithmic viscosity vs time for several resin II isothermal cures. Filled points from DSA, open points from TBA ( $\circ$  112,  $\circ$  102,  $\circ$  92,  $\circ$  82°C).

The time to the TBA gelation loss maximum can be seen to coincide well with the DSA curing loss process in cases where the cure temperatures are similar, as can be noted in Fig. 4. The viscosity at the TBA gelation maximum was calculated to be about 3 kPa·s from  $T_{II}$  relaxation data for low molecular weight polystyrene (15) with the aid of an empirical relation of polystyrene melt viscosity to temperature and molecular weight (16). The frequency of measurement was assumed to be the same at both polystyrene  $T_{II}$  and TBA gelation maxima, about 0.3 Hz. TBA cure times at the gelation maximum of 70 and 17.6 min for resin II at 92 and 112°C respectively (17) fall quite closely to the DSA isothermal cure data obtained at 91.6 and 111.6°C. This indicates that the TBA loss maximum attributed to gelation is identical in nature to the DSA loss process associated with sample-support coupling at a critical sample viscosity.

The rate constants for isothermal curing can be used to determine the activation energy of the curing reaction from a plot of the logarithm of the rate constant vs the inverse cure temperature as indicated in Eq 2. A linear least squares fit of the data in Table 3 gave an activation energy to the 95 percent confidence level of  $104 \pm 17$  kJ/mole for resin I and  $111 \pm 26$  kJ/mole for resin II. The greater degree of error in the activation energies obtained from the rate constants compared to those obtained from the time to the loss maxima can be attrib-

Table 3. Rate Constants for Epoxy Cures from DSA

Sample	Cure temp, °C	Rate constant $k \times 10^3, s^{-1}$
Resin I	108.0	$8.5 \pm 4.3^a$
	99.4	$3.2 \pm 0.6$
	90.2	$1.8 \pm 0.2$
	80.2	$0.59 \pm 0.11$
Resin II	111.6	$11.0 \pm 2.0$
	100.0	$3.9 \pm 0.3$
	91.6	$1.6 \pm 0.2$
	81.0	$0.57 \pm 0.21$

<sup>a</sup> Calculated from time to reach  $\tan \delta_{max}$  to the 95 percent confidence level.

uted to the necessity of performing two least squares fits in the former procedure.

### Partially Cured Thin Films

Data were collected on cured epoxy films to characterize the behavior of the partially cured resin beyond its gel point. Figure 5 shows the dynamic mechanical relaxation behavior of a sample of resin I cured at 79°C for 260 min. Two relaxations were observed upon initial heating, the first at about 80°C and a second at 128°C, both at 3.5 Hz. Upon cooling, the same sample showed a relaxation at 140°C, again at 3.5 Hz, and no lower temperature relaxation. This behavior agrees with Gillham's observation (1) that the glass transition temperature of a thermoset system is equal to the temperature of the cure if the sample is cured below its ultimate  $T_g$ . The  $T_g'$  relaxation observed at 80°C, both as a maximum in the loss modulus  $E''$  as well as by a drop in the storage modulus  $E'$ , corresponds closely to the isothermal cure temperature. As the temperature increases the polymer network becomes increasingly rubbery and further curing takes place, thereby raising  $T_g'$ . Although the crosslinking reaction occurs more rapidly as the temperature increases the number of unreacted functional groups continually decreases, limiting the upper value of the glass transition temperature that can be attained. The effect of this continuous curing process can be seen in the width of the  $E''$  peak, which extends over a 100°C range of temperature for each frequency studied. The first softening loss peak gives an apparent activation energy, determined from the dependence of  $\ln(\text{frequency})$  on  $1/T$ , of 330 kJ/mole while the process near 130°C has an activation energy of about 500 kJ/mole. These approximate values of the activation energy characterize the network mobility in different states of cure assuming that the measurement procedure results in a state of cure at  $T_g$  which is independent of frequency. As the degree of crosslinking increases, the free volume of the network decreases leading to an increasingly cooperative relaxation process at the glass transition. This is reflected as an increase in both the temperature and activation energy of the  $T_g'$  relaxation as the extent of cure increases. Similar effects of an increase in

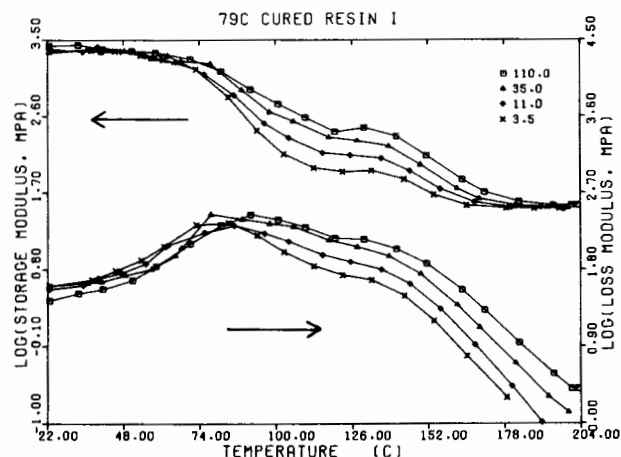


Fig. 5. Storage and loss modulus as a function of temperature for resin I cured at 79°C.

crosslink density on the glass transition in vulcanized natural rubber have been found by Scott and co-workers (18) in a dielectric relaxation study. The sample was continuously heated to over 200°C, then cooled while observing its dynamic mechanical response. Upon cooling only a single relaxation in the vicinity of 145°C was observed. The value of  $T_{g\infty}$  for resin I, the limiting  $T_g$  which could be reached with a network cured for long times at high temperatures, appeared to be 140°C at 3.5 Hz and 148°C at 110 Hz based on results from several determinations.

The dynamic mechanical behavior of a resin II sample cured at 83°C is shown in Fig. 6. A  $T_g'$  relaxation at 84°C (3.5 Hz) is indicated in the figure by a broad maximum in  $E''$ . The storage modulus also shows a gradual drop of about an order of magnitude followed by a gradual rise as the sample undergoes additional reaction and forms a more highly cured network structure during heating. The high magnitude of  $E''$  throughout this region confirms the occurrence of a reaction process. Kline (19) has previously observed an increase in the modulus of uncured bisphenol A resins as the test temperature was increased above the initial cure temperature. The modulus increase was attributed to a further degree of reaction at these temperatures. A second relaxation is indicated at 197°C, this time by the sharp decline in both  $E''$  and  $E'$ . The first relaxation has an activation energy of 180 kJ/mole while the second process has an  $E_a$  of about 570 kJ/mole. When the sample was cooled from the upper temperature limit of 250°C, only a single relaxation near 190°C was observed with  $E_a$  equal to 725 kJ/mole. For Resin II,  $T_{g\infty}$  equals 210°C at 3.5 Hz and 218°C at 110 Hz.

A comparison of samples cured at several temperatures is evidence for the occurrence of additional reaction that takes place above the initial  $T_g$ . Figure 7 gives a comparison of the loss tangent at 11 Hz as a function of temperature for resin II samples cured from 83 to 112°C while Table 4 summarizes transition temperature and activation energy data. As the temperature of curing increases, the temperature of the  $T_g'$  maximum can be seen to increase. The height of this loss maximum decreases as  $T_c$  increases until it becomes extremely small

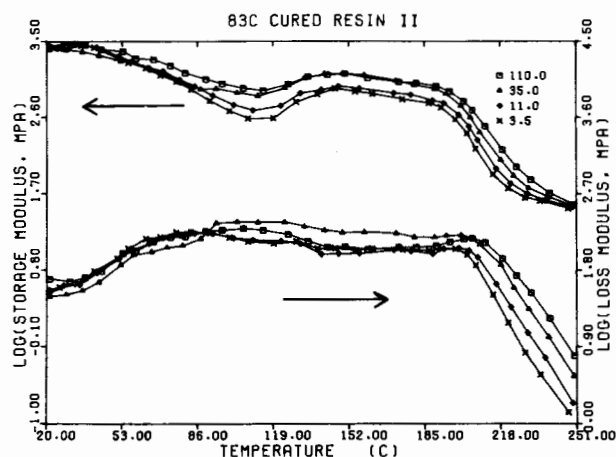


Fig. 6. Storage and loss modulus as a function of temperature for resin II cured at 83°C.

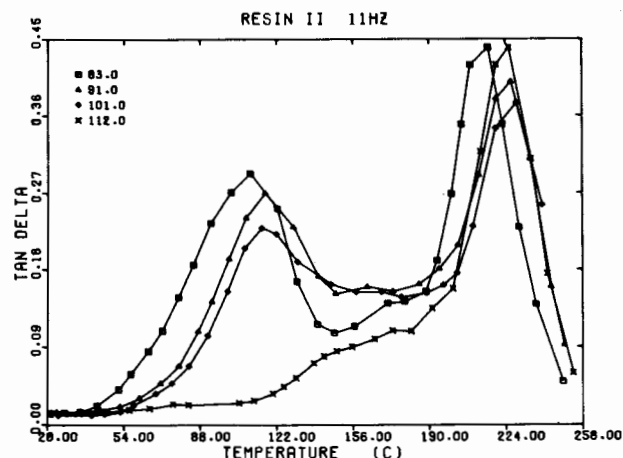


Fig. 7. Temperature variation of the loss tangent at 11 Hz of resin II for several cure temperatures.

for the 112°C cure. This effect can be attributed to the greater coherence of the network which achieves a higher degree of crosslinking as  $T_c$  increases. Furthermore, less unreacted material is available above the initial softening temperature as  $T_c$  is increased, and the small degree of additional reaction possible also contributes to the decline in intensity of the first loss maximum with increasing  $T_c$ . The second loss peak in resin II, corresponding to  $T_{g\infty}$  for the fully developed network structure, is observed in all cases at about 220°C. The activation energy for the  $T_{g\infty}$  relaxation is much greater than that of the  $T_g'$  relaxation, as the fully developed network requires a greater degree of cooperativity for long range main chain motion.

## CONCLUSIONS

Studies of the curing behavior of two epoxy resins by DSA show that the technique is well suited to the determination of the onset of gelation under isothermal curing conditions but that the method is not useful for monitoring later stages of reaction when the resin becomes more rigid. The activation energy for the curing of two commercially formulated resins is determined from time to time to the onset of gelation and reaction rate constants as 87.9 kJ/mole for resin I and 84.9 kJ/mole for resin II, in good agreement with results of DSC and TBA studies on the same materials. The loss maxima associated with the onset of gelation in DSA and TBA experiments result from the rapid increase in resin viscosity, with increasing conversion, to a critical level which depends on the frequency of the experiment. Films cured at temperatures below the ultimate  $T_g$  dis-

Table 4. Transition Temperatures and Associated Activation Energies for Partially Cured Resin II Films

Cure temperature, °C	Cure time, min	$T_g'$ , °C	$E_{a1}$ , kJ/mole	$T_{g\infty}$ , °C	$E_{a2}$ , kJ/mole
83 ± 3	340	92 <sup>a</sup>	180 ± 95 <sup>b</sup>	200 <sup>a</sup>	725 ± 280 <sup>b</sup>
91 ± 1	150	99	230 ± 50	213	440 ± 130
101 ± 2	90	104	300 ± 90	210	590 ± 170
112 ± 2	75	—	—	213	460 ± 100

<sup>a</sup> At 11 Hz from  $E''_{max}$ .

<sup>b</sup> To the 95 percent confidence level.

play two relaxation processes during the initial heating run. The first relaxation occurs near the original isothermal cure temperature and has an apparent activation energy on the order of 250 kJ/mole. Following this relaxation the resins softened and additional curing occurred, producing a more highly crosslinked structure. A second relaxation associated with the ultimate  $T_g$  of the epoxy networks occurs at about 140°C for resin I and 215°C for resin II with an activation energy of 500-650 kJ/mole. The large increase in activation energy for the  $T_g$  relaxation is attributed to the reduction in molecular mobility caused by increasing crosslink density.

#### ACKNOWLEDGMENTS

We are grateful to the Army Materials and Mechanics Research Center, Watertown, Massachusetts, for support of this research under contract no. DAAG 46-77-C-0031. We are also grateful to Professor J. Gillham for helpful discussions.

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