

The Curing of a Bisphenol A-Type Epoxy Resin with 1,8-Diamino-p-Menthane

THOMAS DONNELLAN

Naval Air Development Center
Warminster, Pennsylvania 18974

and

DAVID ROYLANCE

Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Differential Scanning Calorimetry (DSC), Torsional Braid Analysis (TBA), and Fourier Transform Infrared Spectroscopy (FT-IR) were used to study the cure characteristics of an epoxy system that utilized a sterically hindered amine curing agent. The apparent activation energy was found to be 13.3 kCal./Mol. by DSC and 12.8 kCal./Mol. by FT-IR. Resin volatility hindered useful application of conventional TBA techniques. The resin was found to react to a partially cured (52%) state at room temperature and then vitrify. Samples stored for a two-month period showed no advance in cure state. Subsequent application of heat caused resin devitrification and advance to a more fully cured state. The isothermal curing behavior was studied in a temperature range from 100° to 150°C.

INTRODUCTION

The growing use of composite materials in commercial and military equipment has led to concern over field repair or patching of damaged components. Field level repair has some unique materials requirements in terms of storage and curing characteristics. Since the presence of freezer storage space is not guaranteed, the resin used in the composite patch would necessarily require room-temperature stability. Also, since cure facilities are very limited, the resin system must be curable at low temperatures and times (i.e., 150° for one hour). Unfortunately, commercially available "prepregs" (partially cured resins) typically require both freezer storage and higher temperature cures.

One approach toward the development of ambient storage repair systems is through resins that vitrify at room temperatures before any substantial curing reaction occurs. Rinde, *et al* (1), have shown that a resin composed of diglycidyl ether of bisphenol A (DGEBA) epoxy and 2,5 dimethyl, 2,5 hexane diamine (DMHDA) hardener (*Fig. 1*) forms a linear glassy pre-polymer at room temperature. The linear nature of the glass is a result of the steric hindrance of the methyl groups adjacent to the amines. Upon mixing, primary amino hydrogens may react very slowly, but local crowding inhibits the secondary amino hydrogen reaction. As a result, DMHDA at room temperature essentially reacts as if it were difunctional. As the reaction proceeds, the molecular weight of the resin increases until vitrification occurs. Heating the resin during subsequent cure imparts sufficient energy to overcome the steric con-

straints so that the secondary aminohydrogens react, and the cure proceeds to completion.

The kinetic curing characteristics of potential resin systems are an important consideration. Field repair applications require simple cure schedules. A schedule

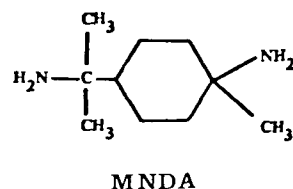
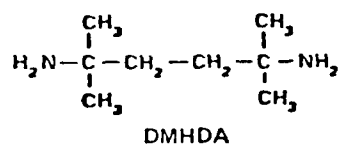
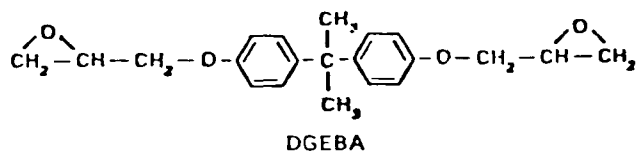


Fig. 1. Chemical structures of resin components.

currently in use, for instance, calls for a one-h cure at 150°C (2). This schedule reduces the number of candidate systems. DGEBA/DMHDA has been found to cure almost to completion under these conditions, but other systems based on DMHDA react to a lower extent. Buckley and Roylance (3), investigated a resin system composed of 86 mole percent DGEBA, 14 mole percent epoxy cresol novolac (CIBA ECN 1299), and DMHDA. They found that this system reacted to 80 percent conversion when cured at 150°C and ascribed the incomplete cure to the loss of mobility of functional groups at high extents of reaction. The consequences of incomplete cure may be reduced thermal stability and degraded mechanical properties.

Resin development work to date has emphasized DMHDA-cured systems, and the extension of this type of chemistry to other curing agents has not been widely investigated. One potential alternate curing agent is 1,8 diamino-p-menthane or menthane diamine (MNDA). MNDA is a cycloaliphatic primary amine that contains the same type of hindrance present in DMHDA (Fig. 1). Also, Kolb, *et al* (4), have found that MNDA-cured DGEBA has mechanical properties superior to those of DMHDA-cured DGEBA.

The considerations mentioned here form the background and basis of the present study. In this work, the storageability and cure characteristics of a DGEBA/MNDA system have been investigated in order to evaluate MNDA as an alternate curing agent for field repair applications. The approach taken has been a determination of both the activation energy of the reaction and the extent of cure attainable at various cure times and temperatures, so as to quantify the reaction kinetics. We assume that the only reaction occurring is the epoxy-amine reaction. This assumption is supported in the literature (5), but the possibility of other reactions, of course, exists.

A number of experimental techniques have been developed for the study of the curing behavior of reacting systems. The techniques that have been utilized in this work include Differential Scanning Calorimetry, Torsional Braid Analysis, and Infrared Spectroscopy.

MATERIALS

The resin system studied consisted of a stoichiometric mixture of DGEBA (Dow Der 332) and MNDA (Aldrich). No attempt was made to purify either constituent. The resin mixture obtained was optically homogeneous and fluid enough to use in wet lamination of composites. The resin is reported to possess a pot life in excess of 21 h, and the glass transition temperature of the fully cured system was found to be 155°C (4).

RESULTS AND DISCUSSION

Differential Scanning Calorimetry (DSC)

DSC has been used by a number of workers (6-8) to study the kinetics of epoxy curing reactions. In these analyses, the assumption is usually made that the heat evolved during cure is proportional to the extent of cure. For dynamic (constant heating state) experiments, this implies that the extent of cure at the peak exotherm

is a constant, although the temperature at which the peak exotherm occurs depends on the heating rate. The relation between the heating rate and the peak exotherm temperature is of the form (7-8):

$$\text{Log } Q = - \frac{E_a}{2.303RT_p} + B$$

where Q is the heating rate in °C/min, T_p is the absolute peak exotherm temperature, B is a constant related to an Arrhenius frequency factor, and R is the gas constant. The activation energy, E_a , can be obtained from the slope of a plot of $\text{Log } q$ vs. $1/T_p$.

In the present work, testing was conducted with a Dupont 990 Thermal Analyzer with a 910 DSC attachment. The resin samples were contained in hermetically sealed pans, and the scans were performed in a static atmosphere. Dynamic DSC scans were run at heating rates of .5, 2, 10, and 20°C/min. The plot of $\text{Log } Q$ vs. $1/T_p$ for these data is shown in Fig. 2, and the activation energy determined from the slope is 13.3 Kcal/mol. This value falls within the range usually cited for amine-epoxy reactions. (9)

DSC scans can also be used to illustrate the chemical changes that occur upon staging. In Fig. 3, a scan of a freshly mixed sample is compared to that of a staged one. The freshly mixed sample exhibits two exothermic peaks that roughly correspond to primary and secondary aminohydrogen reactions. As the sample is B-staged at room temperature, the primary amines are reacted, and the first exothermic peak in the subsequent scan disappears. The scan of the B-staged sample also shows an endothermic peak at approximately 40°C. The origin of this peak is unclear, but it may be related to the melting point of small DGEBA crystallites in the melt.

Torsional Braid Analysis (TBA)

Torsional braid analysis provides a means of monitoring the mechanical response of a curing thermosetting system. Two physical transitions are usually observable with TBA as cure proceeds isothermally. The first, gelation, corresponds to a transition from linear or branched molecules to an infinite network. The second, vitrification, corresponds to a transition from a rubbery to a glassy state. Each of these phenomena is accompanied by an increase in rigidity and by a maximum in mechanical damping. The use of TBA for the

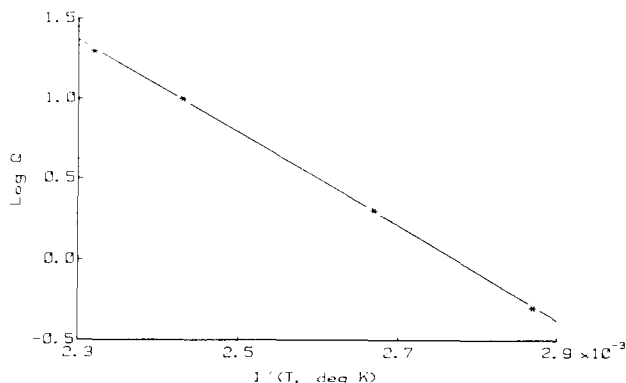


Fig. 2. Arrhenius plot of log heating rate vs. reciprocal temperature at peak exotherm.

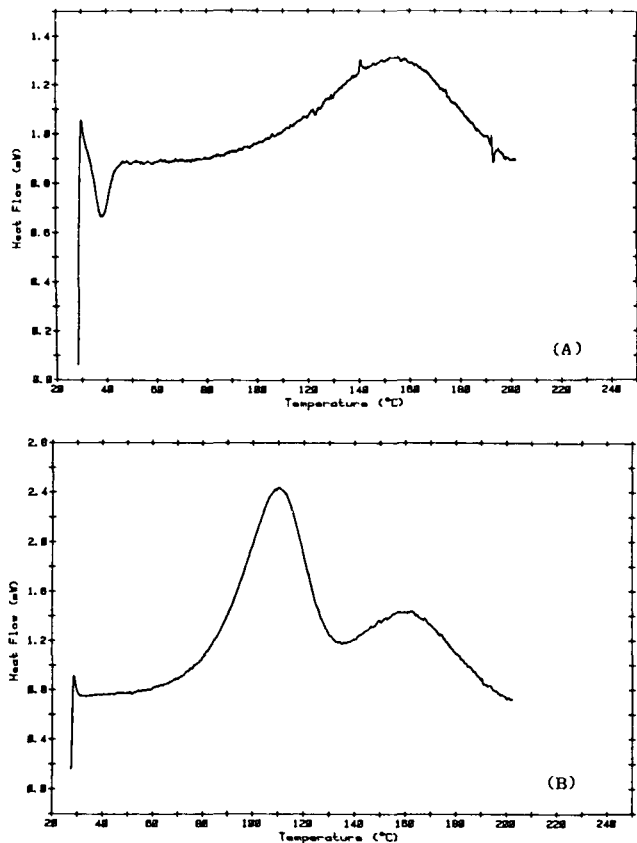


Fig. 3. DSC plots of DGEBA/MNDA in (a) freshly mixed condition and (b) B-staged condition.

study of thermoset curing reactions has been described in detail by Gillham, *et al* (10-12).

TBA can be used to obtain the activation energy of the curing reaction. Assuming Arrhenius kinetics, the time to reach a given extent of cure (i.e., the gel point) can be described by an expression of the form:

$$t_{gel} = t_0 \exp\left(\frac{E_a}{RT}\right)$$

where t_0 is a constant.

In this study, isothermal TBA runs were performed at a frequency of approximately 1 Hz with an automated apparatus in a helium atmosphere. Specimens were prepared by impregnating a glass braid with neat resin, and tests were conducted in a temperature range of 80 to 150°C.

Initially, TBA runs were attempted with fresh resin samples. Poor correlation was found between these results and those of FT-IR and DSC, which were being run concurrently. The activation energy found by TBA was less than 10 Kcal/mol, while the other techniques yielded as E_a of approximately 13 kcal/mol. Furthermore, the TBA results indicated that the $T_{g\infty}$ of this resin occurred at 120°C. As mentioned earlier, the T_g of this system has been found by other means to be 155°C. These discrepancies were eventually attributed to differences in sample containment in the techniques used. In both the FT-IR and the DSC tests, the curing reaction took place in a closed environment. However, the curing resin in the TBA was exposed to a flowing stream of helium, so any vaporization of the system's compo-

nents could be expected to produce error in the TBA results.

In order to evaluate the volatility of the system, thermogravimetric analysis (TGA) was performed on freshly mixed resin samples. These tests were conducted with a Perkin Elmer TGS-2 system. Samples were heated at a rate comparable to the maximum rate attainable with TBA and held for two h. The results of three runs are shown in Fig. 4. At 150°C, almost 10 percent of the resin is lost by vaporization. The amount of resin lost depends on the test temperature, so comparison of different isothermal TBA runs does not provide useful information on the reaction kinetics.

TGA runs of DGEBA and MNDA separately showed that the resin volatility was due exclusively to the MNDA. The volatility problem could, therefore, be reduced by allowing the MNDA to react with the DGEBA. This reaction occurs as the resin advances to a B-stage at room temperature. In Fig. 5, the weight loss of a fresh resin sample is compared to that of a B-stage one. B-staging the resin effectively eliminates the curing agent volatility.

The TGA results prompted a new direction in the TBA study. Braids were impregnated with resin, sealed in polyethylene, and allowed to vitrify for two days. The braids were then placed in the apparatus and

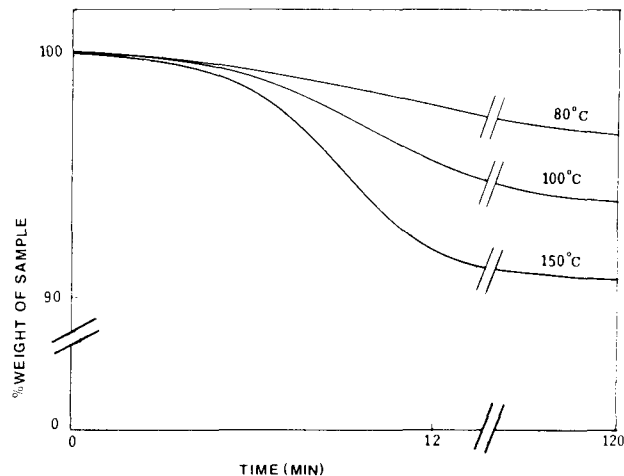


Fig. 4. TGA plot of resin samples in freshly mixed state.

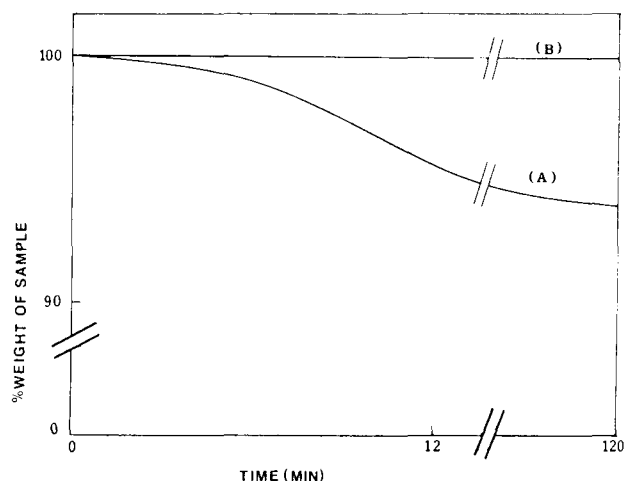


Fig. 5. Comparison of TGA response of freshly mixed sample to that of a B-staged sample.

heated to temperatures above 60°C. In this temperature region, the B-staged resin devitrified, and instrument alignment was accomplished. The braids were then run isothermally at temperatures of 80°, 90°, 95°, and 100°C. An Arrhenius plot of time to gel versus $1/T^{\circ}k$ is shown in Fig. 6. As seen from the data, only a qualitative comparison can be made to FT-IR and DSC results. The dotted line in the figure corresponds to the activation energy found by FT-IR. It is possible that the technique may only be useful at temperatures sufficiently above the staged devitrification region. At these temperatures, the resin viscosity is low, and instrument alignment can be achieved easily. At temperatures close to the devitrification region, resin viscosity is high, its response is sluggish, and alignment is difficult. This may explain the inconsistent results obtained at the lower temperatures.

Fourier Transform Infrared Spectroscopy (FT-IR)

A number of authors (13-15) have used FT-IR to study the curing behavior of epoxies. The absorbance at 910 cm^{-1} has been assigned to the epoxide peak, and the extent of reaction can be monitored by the decrease in peak height as a function of time. Variation in epoxide absorbance caused by differences in specimen thicknesses can be eliminated by normalizing the epoxide peak height to an internal reference peak. Absorbance at 1610 cm^{-1} is due to the phenyl groups in the DGEBA molecule, and this peak was used as the internal standard.

Using this technique, a plot of extent of isothermal cure vs. time at various temperatures can be generated. These data can be used to determine the time to reach a given extent of conversion for each temperature. Then, assuming Arrhenius kinetics, a plot of \ln time vs. $1/T$ will have a slope equal to E_a/R . Thus, FT-IR can be used to find the activation energy of the reaction.

In this study, fresh resin specimens were heated between aluminum pans for various times at different temperatures. Spectra of specimens that remained liquid were obtained by spreading a thin film on a potassium bromide (KBr) plate, while those of specimens that vitrified were obtained from KBr pellets. The spectra were recorded with a Fourier Transform Spectrometer (Digilab FTS-10m). Spectral resolution was 4

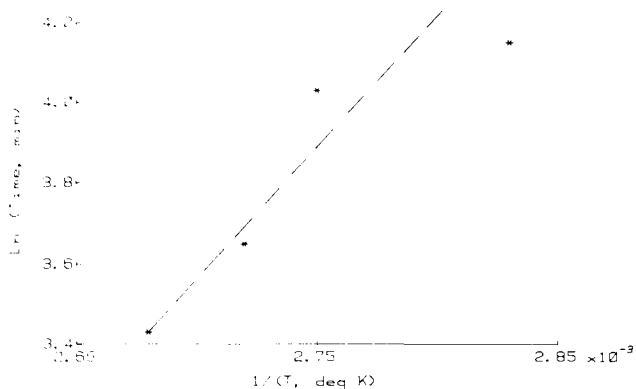


Fig. 6. Arrhenius plot of \ln time to gelation vs. reciprocal temperature for the TBA results.

cm^{-1} and averaged over 120 scans. All specimens were run under a nitrogen purge.

A plot of the decrease in epoxy peak height as a function of time at temperature is shown in Fig. 7, and the corresponding Arrhenius plot of time to reach 50 percent conversion vs. $1/T^{\circ}k$ is shown in Fig. 8. The value of the activation energy obtained from these data is 12.8 kcal/mol. This value is in good agreement with that obtained from the DSC tests. This value is also slightly higher than that previously reported for DMHDA (3). This indicates that MNDA is more temperature-sensitive than DMHDA. The value of the rate constant, and thus the reactivity, will depend on both the activation energy and the pre-exponential frequency factor. Assuming that the frequency factors are comparable, DGEBA/MNDA resin could be expected to cure at a slower rate than DGEBA/DMHDA resin. Comparison of the data shown in Fig. 7 with those previously reported for DGEBA/DMHDA (1) shows that the extent of cure at any particular time at temperature is lower in DGEBA/MNDA resins.

FT-IR was also used, in conjunction with some simple experiments, to verify the room temperature storage-ability of the DGEBA/MNDA resin. Spectra run on specimens that were "freshly vitrified" showed that 52 percent of the epoxy groups had reacted. Spectra of specimens that were stored in a dessicator for one- and two-month periods indicated that no real change had

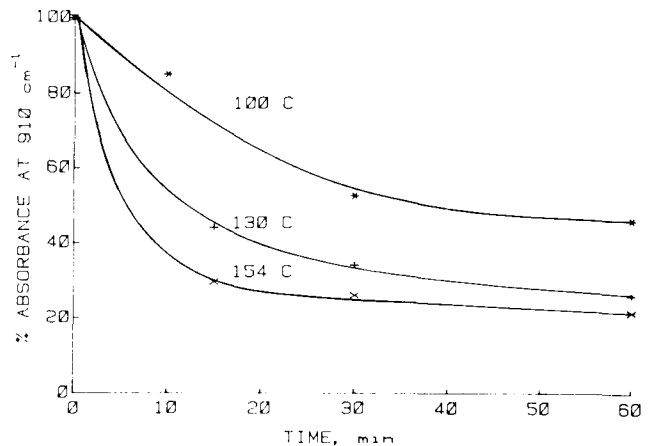


Fig. 7. Plot of percent absorbance at 910 cm^{-1} vs. time from the FT-IR data.

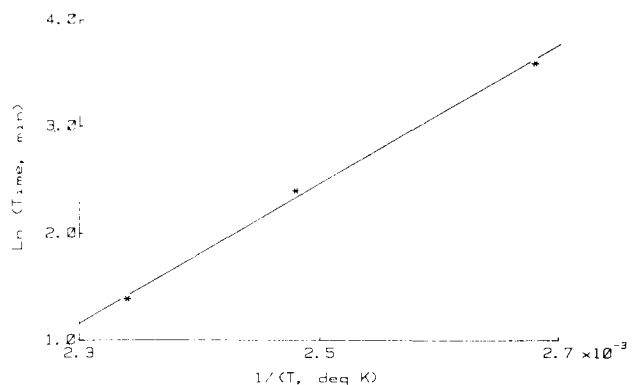


Fig. 8. Arrhenius plot of \ln time to reach 50 percent conversion vs. time for the FT-IR results.

occurred (i.e., the resin had not advanced). The "B-staged" nature of these samples was tested by placing them on a hot plate. All of the specimens devitrified and flowed freely, and thus were not crosslinked to gelation.

A similar experiment was performed to determine the gel point of the resin. Assuming equal reactivity of all functional groups, gelation occurs at 57 percent conversion (16). Differences between primary and secondary amino hydrogen reactivities can alter the extent of conversion at gel. A characteristic of any gel point is that the system viscosity approaches infinity. The test for the experimental gel point involved short-time exposure of a number of resin samples at 125°C. Samples were removed at two-min intervals, quenched, and reheated on a hot plate. It was found that the sample exposed for 24 min was the earliest in which the reheat did not induce flow. The corresponding extent of reaction as measured by FT-IR was 60 percent. This value can only serve as a semi-quantitative estimate of the gel point, since the experimental technique was simplistic.

Perhaps the single most significant result obtained in this study is shown in Fig. 7. The data indicate that the DGEBA/MNDA system reacts rapidly at each temperature until some limiting reaction extent is reached. At this point, the rate slows considerably. This levelling trend can be attributed to loss of mobility of the reactive groups in the resin. The curve representing the 154°C isotherm is seen to approach 80 percent conversion. As mentioned previously, DGEBA/DMHDA reacts to nearly 100 percent conversion under these conditions. Also, the addition of small amounts of a high-viscosity resin to DGEBA/DMHDA reduced the limiting extent of cure at 150°C to 80 percent. Modifications of this type on DGEBA/MNDA can be expected to further reduce the extent of cure attainable at any temperature. Thus, temperatures above 155°C are required for complete cure in MNDA-based resins.

CONCLUSIONS

The results of this study show that the cure characteristics of DGEBA/MNDA are similar to those of DGEBA/DMHDA. The resin vitrifies at room temperature prior to gelation, and thus can be stored at room temperature. Upon application of sufficient heat, the resin will advance into a fully cured state. The activation energy of the DGEBA/MNDA reaction was found to be approximately 13 kcal/mol. This value is higher

than that found for a similar DMHDA-cured resin, and thus it can be implied that MDNA-cured systems react at a slower rate than DMHDA-cured systems. It was also found that the DGEBA/MNDA resin cured to only 80 percent completion in the cure schedule used the DGEBA/DMHDA system. Resins based on MNDA, therefore, require higher temperatures to effect complete cure than those found sufficient in DMHDA-based systems. Further study is required to ascertain whether or not the addition of supplemental curing agents that have been employed with some success with DMHDA-cured systems (2) would be effective in the MNDA-cured systems.

ACKNOWLEDGEMENTS

The authors wish to thank the Army Materials and Mechanics Research Center for the use of their equipment and many consultations and the Naval Air Development Center, which supported this work.

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