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HEAT OF REACTION AND CURING OF EPOXY RESIN

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The heat of reaction and kinetics of curing of diglycidyl ether of bisphenol-A (DGEBA) type of epoxy resin with catalytic amounts of ethylmethylimidazole (EMI) have been studied by differential power-compensated calorimetry as a part of the program for the study of process monitoring for composite materials. The results were compared with those from 1 : 1 and 1 : 2 molar mixtures of DGEBA and EMI. A method of determination of heat of reaction from dynamic thermoanalytical instruments was given according to basic thermodynamic principles. The complicated mechanism, possibly involving initial ionic formation, has also been observed in other measurements, such as by time-domain dielectric spectroscopy. The behavior of commercially available DGEBA resin versus purified monomeric DGEBA were compared. The melting point of purified monomeric DGEBA crystals is 41.4 °C with a heat of fusion of 81 J/g. The melt of DGEBA is difficult to crystallize upon cooling. The glass transition of purified DGEBA monomer occurs around −22 °C with a ΔC_p of 0.60 J/K/g.

Epoxy resins are the most widely used polymer matrices for composite materials. Epoxy resins are commonly cured by amines or anhydrides, with or without the use of catalysts and accelerators. Phenolic curing agents are sometimes used. Epoxies may also be cured by means of catalysts alone. The catalytic curing process produces crosslinked epoxy homopolymers composed mainly of ether linkages rather than amide or ester linkages as in amine or anhydride cured epoxies. Epoxies cured by phenolic crosslinking agents will also consist of ether linkages. The resultant polymer from the relatively low temperature catalytic cure possesses superior thermal stability and chemical resistance than most epoxies made from other processes. The chemical stability of the ether linkage is higher than either the amide or ester linkages which may be subject to hydrolysis by strong acidic or alkaline agents. The glass transition temperature of catalytically cured epoxies is generally higher than 150°.

2-Ethyl-4(5)-methylimidazole, EMI, has been used widely in the curing of epoxies either as an accelerator for a curing agent in the amounts of below 1 phr (parts per hundred-part of resin) or as a catalyst alone for curing in the amounts

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between 2 to 10 phr. The curing mechanism of EMI and the most popular epoxy resin, diglycidyl ether of bisphenol-A (DGEBA), has been studied mainly through the use of the model compound phenyl glycidyl ether as well as other imidazoles [1–3]. The initial rapid reaction was considered to be the formation of 1 : 1 epoxy-EMI adduct and the subsequent formation of the 2 : 1 epoxy-EMI adduct in the form of imidazolium alkoxide. The alkoxide ion was considered as an effective catalytic center to attack another epoxy group and to continue the polymerization reaction [1] with the EMI incorporated in the polymer. Further investigation [3] indicated that an inherent instability of the imidazolium system led toward the regeneration of imidazoles during the curing process by at least two routes. The major path was the N-dealkylation via a substitution process with the formation of ethers. Imidazoles could also be regenerated by the β-elimination of an N-substituent from either the adducts or the polymer leading to the formation of ketones.

The heat of reaction of the catalytic curing system was not well studied. The curing reaction of DGEBA with EMI was quoted to be complex and yielding a double peak exotherm but without any further description [2]. The heat of reaction for the formation of the 2 : 1 phenyl glycidyl ether-EMI adduct was observed isothermally to be about 460 J/g at 80–100° [4], as corrected from an earlier observation of about 380 J/g [2]. The heat of reaction for the adduct formation of DGEBA–EMI polymer was given as 410 J/g [2] which may require a similar correction.

As a part of the effort in correlating the cure monitoring techniques for the processing of composite materials in polymer matrices, we are studying the cure behaviour on identical resin system with thermal, dielectric, viscosity, dynamic mechanical, ultrasonic attentuation, and spectroscopic measurements. We report here in detail the observations from the use of a dynamic thermal analytical instrument to study the polymer formation by catalytic amounts of EMI on a low molecular weight resin of the DGEBA type. Results from other cure-monitoring techniques studied in this laboratory may be introduced as appropriate. The heat of reaction is erelated to the bonding energy released and is directly proportional to the degree of crosslinking reaction, thus this information may be used as a common basis to compare with other measurements. A method of determination of the heat of reaction based on the fundamental thermodynamic principles is described. The heat of reaction so obtained is well defined at specified temperature and thus alleviates the ambiguity associated with the commonly employed method of integration of the exothermic peak over a wide temperature region of a single scanning curve.

The reaction kinetics for the catalytic curing of DGEBA seems to be rather complicated. Isothermally, two exothermic peaks may be resolved. The earlier one may correspond to the increase in the electrical conductivity from a time-domain dielectric spectroscopic study. This early peak is presumed to be due to the alkoxide ion formation. A study in the scanning mode of differential scanning calorimetry of the reaction reveals at least three distinctive reactions.

Experimental detail

Materials

Diglycidyl ether of bisphenol-A, DGEBA, is the major type of epoxy resin produced among all epoxies. Three commercially available low molecular weight resins: Dow Chemical DER332, Shell Chemical EPON825 and EPON828* were used. The first two products contain 97–99% of monomeric DGEBA, $C(CH_3)_2(C_6H_4OCH_2\overline{CHCH_2O})_2$, and tend to crystallize in some degree on long standing at room temperature. For most experiments reported here, these resins and the catalyst, EMI, 99% 2-ethyl-4(5)-methylimidazole, were used without further purification. In preparing the resin mixture, EMI is allowed to melt at about 40–45°. After cooling, appropriate amount of DGEBA is added. The resin mixture is run in DSC within 30 min of preparation. Long standing at room temperature will cause partial reaction to occur.

In order to find out whether the purer monomer produces noticeable difference in the heat of reaction or the reaction kinetics, purified DGEBA samples were prepared as described in the following paragraphs. Thermally there is little difference that can be detected at high EMI concentrations. However, in the dielectric measurements, the first peak (presumed to be ionic adduct formation) is somewhat sharper and more distinguishable. At low EMI concentrations, the magnitude and the rate of reaction for purer DGEBA are somewhat reduced from a typical low molecular weight resin such as EPON828.

Several methods have been described in the literature to enrich the monomeric content of DGEBA. The best fraction from a centrifugal molecular distillation yielded a material with a MW of 355 from an original material with a MW of 381 [5]. Several patents describe methods of crystallization from solutions in ethanol, methanol or methanol-acetone mixtures. We have recrystallized DGEBA monomer from methanol, ethanol, and a mixture of 4-methyl-2-pentanol and 4-methyl-2-pentanone [6]. The purification process involves the dissolution of the

* Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply necessarily the best available for the purpose.

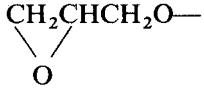
resin in the solvent at room or slightly elevated temperatures, followed by cooling at 0°. The crystals are washed by ethanol or methanol and then dried in vacuum.

The results of size exclusion chromatography, SEC, and calorimetric studies of m.p. and heat of fusion for purified DGEBA as well as some of the characteristics of raw materials are summarized and compared in Table 1. DER332X is the crystallized fraction from DER332 without the use of solvents. The raw material of DER332 has been crystallized from the mixed solvents of 4-methyl-2-pentanol and 4-methyl-2-pentanone, and twice in methanol. EPON825 has been recrystallized from the same mixed solvents and then followed by once in ethanol or in methanol. When recrystallize in methanol or ethanol, only the solvent-rich phase at room temperature, about 10–15% DGEBA, is used for the purification purposes. Large single crystals can easily be obtained from unstirred ethanol or methanol solutions.

The general formula for DGEBA monomer ($n=0$, MW$=340.4$) and its oligomers may be represented as:

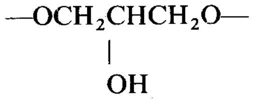
$$E—[B—EHO]_n—B—E$$

where E =



$$CH_2CHCH_2O— \text{ (with } CH_2 \text{ and } CH \text{ bridged by O)}$$

EHO =



$$—OCH_2\underset{\displaystyle OH}{\underset{|}{C}}HCH_2O—$$

and $$B = —C_6H_4C(CH_3)_2C_6H_4—.$$

From the SEC results, in 0.1% tetrahydrofuran solutions, the only oligomers that are detectable are the dimer ($n=1$, $MW=624.7$) and the trimer ($n=2$, $MW=909.0$). Only two oligomer peaks, at retention volumes 46.3 and 48.3 ml, are observed before the main monomer peak at 50.2 ml. As an indication for relative purity, the peak heights of these two peaks are normalized to that of the main peak and listed in Table 1. The dimer appears to be easily removed by fractional crystallization of the raw material or by any of the recrystallization procedures. However, the trimer content seems to be little effected by the recrystallization procedures. The trimer may have rather low solubility in the solvents and thus co-precipitate with the monomer upon cooling.

The melting point of the best crystallized sample of DGEBA as determined by DSC is 41.4° with a heat of fusion of 81 J/g. Once the crystals are melted, the liquid does not crystallize easily when cooled below the m.p. A few references [5, 7] gave the m.p. of DGEBA as 42° without any detail. DGEBA melt can easily be supercooled to temperatures below its m.p. and forms a vitreous state. The glass

Table 1 Purification of DGEBA

Material	SEC peak height ratio $\frac{p48.3}{p50.2}$	$\frac{p46.3}{p50.2}$	T_m, °C	ΔH_m, J/g	MW, g/mol
DER332	0.019	0.012			364
DER332X	—	0.009			
mixed solvents	—	0.007	39.5	78	360
methanol once	—	0.010	38.2	78	
methanol twice	—	0.010	40.4	81	350
Epon825	0.004	0.003			384
mixed solvents	—	0.003	40.3	79	350
ethanol	—	0.002	40.2	81	
methanol	—	0.002	41.2	81	

transition temperature of the melt from all crystallized DGEBA from the above list is $-22°$ with a ΔC_p of 0.60 J/K/g. A value of $-23°$ for T_g with a ΔC_p of 0.51 J/K/g for an unspecified DGEBA resin was reported [8]. Cycling between the T_g and some temperature below T_m, a common technique to increase the probability of nucleation and hence crystal growth, does not seem to produce DGEBA crystals in reasonable times.

Differential calorimetry

A commercial differential power-compensated calorimeter, Perkin–Elmer DSC–7 and its associated Perkin–Elmer 7500 series computer*, was used for this study. Although the noise level in the differential power is in the order of a few microwatts, the reproducibility of the differential power in the middle of a long scan is at times in the order of a 0.1 mW. This type of uncertainty is produced as a consequence of a change in the heat-loss pattern between the sample and the reference holders, as caused by a change in the environmental conditions during the experiment. This random uncertainty can neither be corrected by subtracting a blank baseline nor be compensated by the changes in the beginning and the end isothermal differential power levels. The reproducibility of the temperature reading is believed in the order of 0.1 K. With the power scale and the temperature scale calibrated by 99.99% pure indium (m.p. 156.63°, ΔH_m 28.4±0.4 J/g) at a scan rate of 10 deg/min, the heat capacity of a sapphire disc is observed to be within 1–2% of the literature value [9] between 100–300°, obtained from the net scanning differential power and the scanning rate in either long or short scans. The melting points and heats of fusion of organic compounds, such as Calorimetry Conference Standard benzoic acid [10] and *o*-terphenyl [11], have also been used to check the reliability of the calibration.

A more realistic method of obtaining the heat capacity from the dynamic measurements is to mimic the classical method of determining the energy required to produce a unit temperature difference. The heat capacity of the same sapphire disc mentioned above, obtained by integrating the net enthalpy, Q divided by the small temperature increment of 5 to 10 K as programmed in a short scan, is usually within 1% of the literature values. These magnitudes of uncertainty are in the same range of 1–3% as those found by other studies on similar instruments [12].

Heat of reaction

Isothermally, the heat of reaction at the isothermal reaction temperature can simply be obtained by integrating the area of an exothermic event from that of an assumed steady state baseline without any thermal events. Assuming a 10 mg sample and a noise level of 5 μW, the uncertainty is at best 2 J/g per hour. As the baseline in the present system drift often more than 50 μW within one hour, the estimated uncertainty is assumed in the order of 2–20 J/g per hour.

In the scanning mode, the heat of reaction from the reactant A to the product B is often estimated in the thermal analysis in the same way as that for the estimation of the transitional energy from state A to state B at the transition temperature T_t, i.e., simply by integrating the thermogram from a temperature in state A to a temperature in state B, for the area over or under a baseline which is supposed to take care of the heat capacity contribution from mainly lattice vibrations. In practice, a baseline is often taken as the linear interpolation at two points between T_a and T_b. The linear baseline should yield a reasonably correct result for a transition, where A and B phases are stable at both points chosen, especially if the temperature range chosen is symmetrical about T_t and the temperature coefficients of the changes in heat capacity of A and B are small or equal. The error created by any asymmetry is relatively small when the transitional energy is large in comparison to the difference caused by the small change in the specific heat over the temperature range of concern, such as in fusion and other well-defined first order transitions.

The heat of reaction generally does not occur in a specific narrow temperature range and changes depending on the reaction temperature. A schematic enthalpy diagram is shown in Figure 1 for a scanning curing path R from the raw material A to the product B between temperatures T_a and T_b. The material may continue to cure to certain extent at highest temperature of scan T_b. $T_{g,\mathrm{A}}$ and $T_{g,\mathrm{B}}$ denote the glass transition temperatures for the raw material A and the product B, respectively. A scan for raw material A may be extended to lower temperature T_a' to

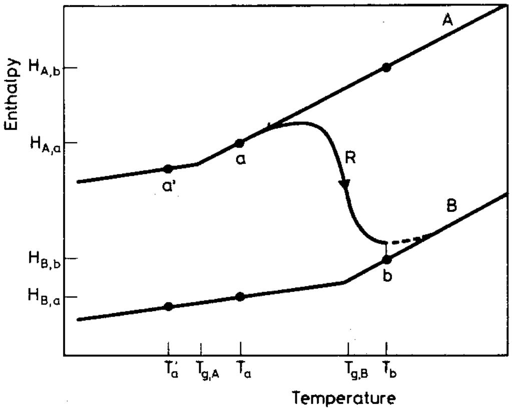


Fig. 1 Schematic enthalpic diagram of epoxy cure reaction. A – Raw material, B – Cured epoxy, R – Curing path

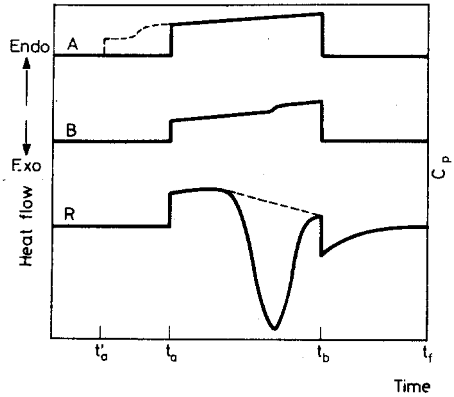


Fig. 2 Schematic DSC curves of epoxy cure reaction. A – Raw Material, B – Cured epoxy, R – Curing path

show its T_g, Curve A in Figure 2. A corresponding thermal curve, R, for the curing reaction is shown schematically in Figure 2, where times t_a and t_b correspond to the scan from temperature T_a to T_b in Figure 1. For the reaction run R, residual curing is still observable on at end of scan at t_b until sometime t_f isothermally held at T_b. A scan of the cured resin, Curve B in Figure 2, will show the T_g of the resin. In most instruments, the exothermic heat is obtained by integrating the area between the scan curve and a straight line (shown as dash in Curve R of Figure 2) between two somewhat arbitrary chosen points. Even if the reaction is complete at T_b, the above integration method yields an observed heat of reaction ΔH_{obs}, occurred not at a specific temperature but over an unspecified wide temperature range somewhere between T_a to T_b, as the difference between the heat integrated under the curve ΔH_{int} minus contributions from lattice vibration, ΔH_{vib}, as approximated by a mean heat capacity $(C_b+C_a)/2$.

$$\begin{aligned}\Delta H_{\text{obs}} &= \Delta H_{\text{int}} - \Delta H_{\text{vib}} \\ &\simeq [H_{\text{B},b} - H_{\text{A},a}] - (C_b + C_a)(T_b - T_a)/2\end{aligned}$$

By repeating a scan on the cured resin over the same temperature range as that of the curing experiment, precise heat of reaction at defined temperatures may be obtained. Large error in the above estimation of exothermic heat can result in the case where the end of the scan curve still contains residual exothermic heat effect from the reaction.The entire amount of heat involved from T_a to T_b, integrated between time t_a at T_a and t_f at T_b, ΔH_{int}, may be decomposed into either

$$\begin{aligned}\Delta H_{\text{int}} = H_{\text{B},b} - H_{\text{A},a} &= [H_{\text{B},b} - H_{\text{A},b}] + [H_{\text{A},b} - H_{\text{A},a}] \\ &= [H_{\text{B}} - H_{\text{A}}]_b + [H_b - H_a]_{\text{A}}\end{aligned}$$

or

$$\begin{aligned}&= [H_{\text{B},a} - H_{\text{A},a}] + [H_{\text{B},b} - H_{\text{B},a}] \\ &= [H_{\text{B}} - H_{\text{A}}]_a + [H_b - H_a]_{\text{B}}\end{aligned}$$

Thus it is possible to calculate the heat of reaction at either temperature T_a or T_b from the enthalpy changes observed during the reaction from A at T_a to B at T_b and incorporating either the enthalpy increment for B or A over the same temperature interval:

$$\begin{aligned}\Delta H_{rxn,a} &= [H_{\text{B}} - H_{\text{A}}]_a = \Delta H_{\text{int}} - \Delta H_{\text{B}} \\ \Delta H_{rxn,b} &= [H_{\text{B}} - H_{\text{A}}]_b = \Delta H_{\text{int}} - \Delta H_{\text{A}}\end{aligned}$$

where ΔH_{A} and ΔH_{B} represent the enthalpy increments for A and B, as $\int C_{\text{A}}\,dt$ and $\int C_{\text{B}}\,dt$, respectively, over the same temperature range of T_a to T_b without undergoing any chemical reaction. ΔH_{B} is easily obtainable after the curing process. In the present case, ΔH_{A} may be obtained from DGEBA alone, without the addition of EMI. For most organic materials containing C, H, O and N only, the specific heats are all in the order 1.5–2.5 J/g. Thus by neglecting the differences in the specific heats contributed by a few per cent of EMI from that of DGEBA will not cause any significant error. Heat of reaction at any temperature between T_a and T_b can be estimated from either $\Delta H_{rxn,a}$ or $\Delta H_{rxn,b}$ by incorporating the heat capacity differences between A and B.

This scheme of subtracting the integrals of two scanning curves produces more definable heat of reaction values than that practiced commonly in differential scanning calorimetry. The precision is also higher as the baseline correction is taken care of, assuming the changes in the baseline drift is minimal between the reaction run and the non-reaction run. This scheme is especially useful if the reaction is not quite complete when the scan ends at T_b. In such a case the scan curve may have significant contribution from the residual exothermic energy release, and thus the integration of the scan curve alone may yield rather large errors. In the proposed method, ΔH_{int} will be integrated up to a time t_f isothermally at T_b, when the exothermic heat release becomes insignificant. The heat of reaction is then obtained as the differences between ΔH_{int} and ΔH_{vib} as stated above. For this purpose, both scan curves for curing and cured resin are required and are shown in the following experiments.

In comparison to isothermal curing, the total experimental time for scan is shorter, therefore the error in integration is also smaller. We believe the error in the difference of two scans is in the order of 10 J/g for a typical 10 mg sample.

Results and discussion

Scan curing at 1 deg/min

At least three distinctive processes are observed when DGEBA–EMI resin mixtures are scanned at a relatively low rate of 1 deg/min as shown in Figure 3. At the end of the scan from 50 to 250°, the sample is held at 250° for 45 to 60 min until the isothermal rate of heat release is within the nominal background isothermal drift rate of about 0.1 mW/hr of the instrument. The major exothermic peak occurs

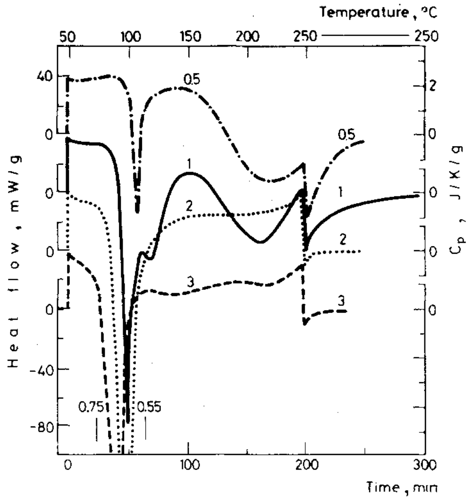


Fig. 3 Cure of DGEBA/EMI resins at 1 deg/min. Numbers denote phr EMI content

in the temperature range of 93 to 110°. The peak temperature is increased as the amount of catalyst is decreased. The amount of heat released in this process is also strongly dependent on the amount of catalyst used, varying from 50 J/g at 0.5 phr of EMI to 380 J/g at 4 phr of EMI. The peak temperature T_1, maximum rate of energy release $\dot{q}_1$ and the amount of energy released Q_1 are all listed in Table 2. The weak second process may be seen in some of the catalyst compositions. It is barely visible at 0.5 phr EMI. It is most pronounced in 1 phr of EMI. The peak temperature is about 124° with an energy release of about 100 J/g. The second peak may also be discerned in the 4 phr EMI resin, with a maximum rate of energy release of 0.02 W/g at 138°. A third peak which is rather broad and occurs in the high temperature region is observed at 0.5 and 1 phr EMI and continues to release significant amount of heat at 250°. Because of the broadness of the peak, the amount of heat released is fairly large, about 250–350 J/g. This third process is less well observed at 2–4 phr of EMI, presumably most of the active groups have already reacted in the first process, thus leaving only a small amount of groups available for the third process. The glass transition temperature of the resultant polymer is a function of the catalytic content as shown in Figure 4. The heat of reaction at 50°, calculated as above mentioned, for all four compositions are reasonably constant, within 15% of 520 J/g. The low T_g material from low catalytic contents can be improved by further heat treatment of the polymer as described in the following section.

Table 2 Curing of DGEBA by EMI at 1 deg/min

EMI phr	T_1, °C	$\dot{q}_1$, $\bar{W}$/g	Q_1, J/g	T_3, °C	$\dot{q}_3$, $\bar{W}$/g	Q_3, J/g	ΔH_{int}, J/g	ΔH_B, J/g	$\Delta H_{rxn,50}$, J/g	T_g, °C
0.5	109	0.1	− 50	237	0.08	−350	0	463	−463	80
1	100	0.19	−120	205	0.07	−250	−139	451	−590	132
2	98	0.57	−400	210	0.01	− 60	− 50	425	−475	180
4	93	0.77	−380	215	0.02	− 40	−100	451	−551	160

Scan curing at 10 deg/min

A scan rate of 10 deg/min is more commonly used in DSC than the rate of 1 deg/min, not only the elapsed time is shorter but the signal-to-noise ratio also improves drastically. The behaviour of the scan at higher speed is very similar to that of the slow scan except that all occurrences are now shifted to higher temperatures due to kinetic reasons as shown in Figure 5. After the scan, the samples are held for

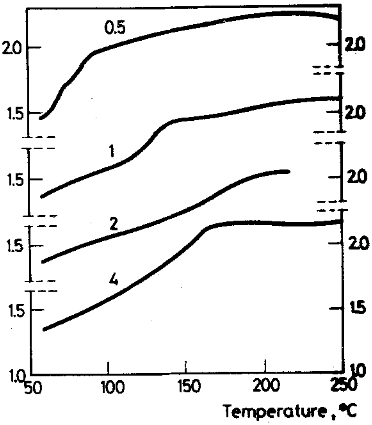


Fig. 4 Specific heat and glass. Transition of resins cured at 1 deg/min. Numbers denotes phr EMI content

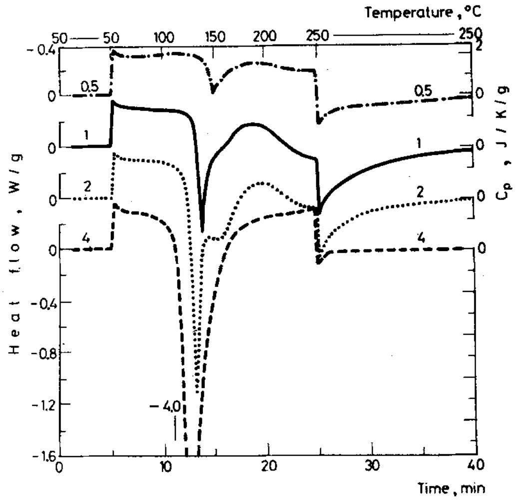


Fig. 5 Cure of DGEBA/EMI resins at 10 deg/min. Numbers denote phr EMI content

15 min, to allow temperature equilibration in the sample and to allow for a relatively large reduction of isothermal heat flow. The first process remains to be the most pronounced exothermic peak, occurring between 130–151°. The relatively weak second peak is observed only as a shoulder at 1 phr of EMI, but as a pronounced peak at 2 phr of EMI at 155° with a rate of heat release at about 0.6 W/g and may involve a heat released in the order to 100 J/g. The broad third peak is shifted to 240–250° at 0.5–2 phr of EMI. The third peak at 4 phr of EMI

cannot be distinguished from the long tail of the main peak. The occurrence of these peaks and their magnitudes are listed in Table 3. The higher rate of scan produces materials cured at higher temperatures for less time. The resultant material appears less reacted than that obtained by the slow scan as described earlier. The heat of reaction at 50° is also less constant versus the catalytic content in comparison to those of the slow scans.

Table 3 Curing DGEBA by EMI at 10 deg/min

EMI phr	T_I, °C	$\dot{q}_I$, °C	T_{II}, °C	Q_I	T_3, °C	$\dot{q}_3$, W/g	Q_3, J/g	$\Delta H_{rxn,50}$, J/g	T_g, °C
0.5	150	−0.3	—	− 35	240	−0.12	− 25	−155	—
1	139	−1.0	155	80	250+	−0.40	−185	−369	77
2	133	−1.6	155	−100	243	−0.45	−190	−440	112
4	127	−4.0	—	−460	—	—	—	−535	165

The glass transition temperature of the resultant polymers is a function of the composition, with lower T_g for lower EMI content as shown in Figure 6. However, the low T_g polymer may be improved to certain degree by further heat treatment as shown in Figure 7. The original T_g of the 1 phr EMI resin at 77° is increased to 87° by the second scan of 50 to 250°, to 107° by holding for 4 hours at 200°, and to 120° by holding for another 16 hours at 200°. Small amount of heat release can still be detected in the 77° and 87° T_g samples at temperatures above 200 and 230° (curves a and b, Figure 6). By annealing the material in the state with a T_g of 107° at 100° for 4 hours, the material is not changed chemically but shows up with a relaxation peak

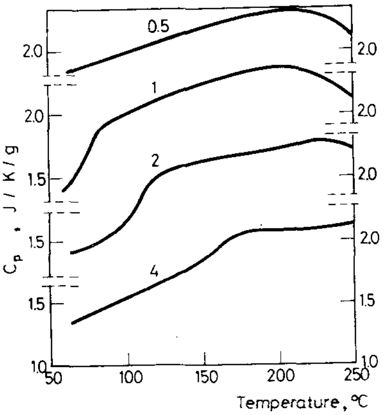


Fig. 6 Specific heat and glass transition of resins cured at 10 deg/min. Numbers denote phr EMI content

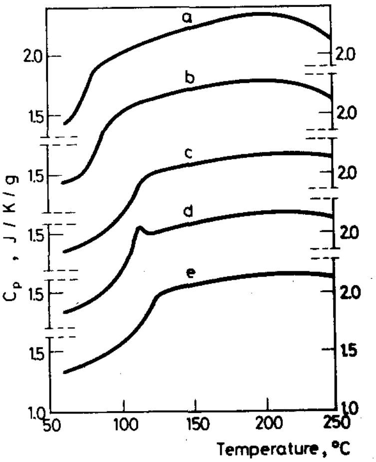


Fig. 7 Glass transition temperature of DGEBA–1 phr EMI resin. Each curve down shifted by 0.3 J/K/g from curve a. a – first scan after cure, b – second scan after cure, c – scan after 4 hours at 200°, d – scan after 4 hours at 100°, e – scan after 16 hours at 200°

at about 115° (Curve d, Figure 6). The T_g of the annealed polymer is estimated to be 106° from the intersection in a enthalpy versus temperature plot (curve e, Figure 6).

Isothermal curing at 80°

Two mechanisms are visible in the isothermal curing of DGEBA by catalytic amounts of EMI as shown in Figure 8. The first one may be associated with the initial ion formation and involves relatively small amounts of energy. This peak appears as shoulders in thermograms for 2–4 phr EMI. It is well separated in

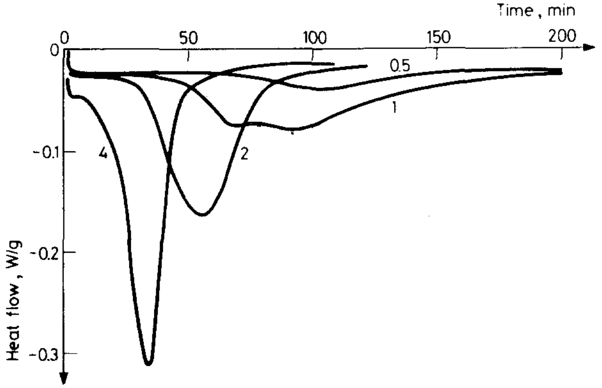


Fig. 8 Isothermal cure of DGEBA EMI resins at 80°. Numbers denote phr EMI content

samples containing 1-phr of EMI or less. The time at which the rate of energy release reaches a peak, t_a, is a strong function of the catalytic content. The magnitude of this peak, $\dot{q}_a$ remains relatively constant as the concentration of EMI is varied, as listed in Table 4. It is believed that this peak is not resolved in the scanning mode of operation as described above.

Table 4 80° isothermal curing and post-curing of DGEBA by EMI

EMI phr	t_a, min	$\dot{q}_a$, W/g	t_b, min	$\dot{q}_b$, W/g	ΔH_{80}, J/g	$\Delta H_{pc,50}$, J/g	$\Delta H_{rxn,50}$, J/g	T_g, °C
0.5	104	0.015	—	—	− 44	− 76	−120	—
1	53	0.045	80	0.035	−220	−120	−340	125
2	44	0.08	55	0.15	−274	−120	−394	168
4	20	0.05	34	0.28	−273	− 95	−368	166

The mechanism of ion formation associated with this first peak may be confirmed by the increase in the conductance at 50 Hz at early times using a time-domain dielectric spectrometer [13], as shown in Figure 9. The maximum increase in the conductance of DGEBA–1 phr EMI, after the sample reaches a temperature equilibrium, appears at some earlier time than t_a of calorimetric studies. The peak of the conductance increase is cut short at about 1 hr when the conductance begins to decrease drastically as the material crosslinks and loses its mobility. Although the kinetics of the curing (decreasing in conductance) differ among various origins of DGEBA, the magnitude of the conductivity increase appears to be relatively independent of the raw material used, e.g., EPON828 and DER332X, as well as of

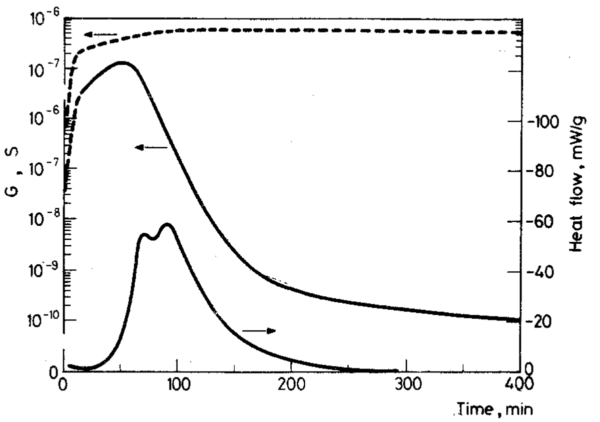


Fig. 9 Conductance and heat flow during isothermal curing of DGEBA–1 phr EMI at 80°. – – – DGEBA only. Conductance, G, unit in Siemens, S

the EMI content varying from 1 to 3 phr. The detail of the dielectric studies will be published elsewhere. The dashed-line indicates the change of conductance for DGEBA alone. An initial rapid rise in conductance shows that the system reaches near thermal equilibrium at about 10 min, and is followed by a slow rise for about 2 h.

The magnitude of the second peak, $\dot{q}_b$ at t_b, is much greater than that of the first peak at high EMI content. The second peak is a strong function of the EMI content. The rate of energy release is higher and the reaction is faster for higher EMI content. This peak is believed to be the part of the main peak as observed in the scanning mode. The enthalpy ΔH_{80} released at 80° remains relatively constant above an EMI content of 1%. This indicates that the amount of epoxy ring opening and crosslinking reaction which has taken place are about the same irrespective of the EMI content, although the time for the completion of the reaction is strongly dependent on the EMI content.

Post-curing of isothermally cured samples

The post-curing is performed by scanning the above isothermally cured sample from 50 to 250° at a rate of 10 deg/min and with a holding time at 250° for 15 min. Release of heat may be noticed at just below 100°, indicating that T_g of samples isothermally cured at 80° are all less than 100°. As T_g is raised from the monomeric value toward the temperature of isothermal cure, the rate of crosslinking reaction is greatly reduced or quenched by the isothermal vitrification process as described by time-temperature-transformation diagram of Gillham [14]. The first peak for the scanning post-curing occurs in the temperature range of 120–125°, regardless of the EMI content as shown in Figure 10. This peak is presumed to be the remainder of the isothermal process, and is the remaining part of the process I occurred in the scanning mode described earlier. The amount of energy released diminishes as the catalytic content is reduced. The long tail of process I at 4 phr of EMI indicates the possible presence of the process II which appears as a shoulder at 153°. The process III occurs at 240–250° in a similar magnitude as seen in other scanning runs. By combining the isothermal energy release ΔH_{80} and the enthalpy decrement for the post-curing $\Delta H_{pc,50}$, it is apparent that the heat of reaction is relatively constant above 1 phr of EMI content as shown in Table 4. The glass transition temperature of post-cured samples varies from less than 60° for 0.5 phr EMI sample to about 165° for 2–4 phr EMI samples (Figure 11). Further thermal treatments on the 0.5 phr EMI sample can improve the T_g to about 120° as shown in Figure 12. No improvement in T_g was observed after holding at 150° for 3 h. After holding at 200° for overnight, the T_g increased to 70°. By holding at 250°, the T_g increased to 93° after 3 h and to 120° after overnight.

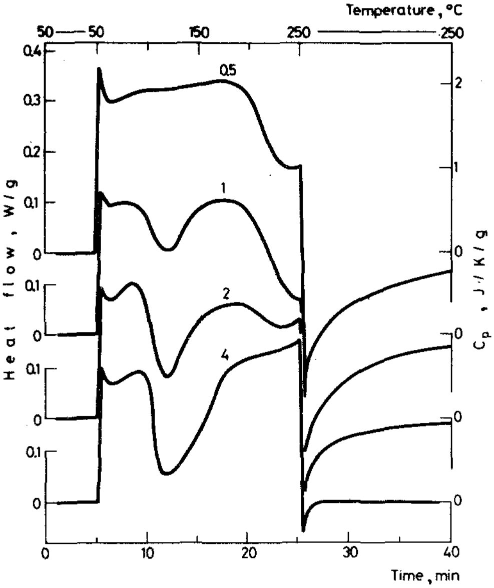


Fig. 10 Post-cure of DGEBA/EMI resins after 80° isothermal cure. Numbers denote phr EMI content

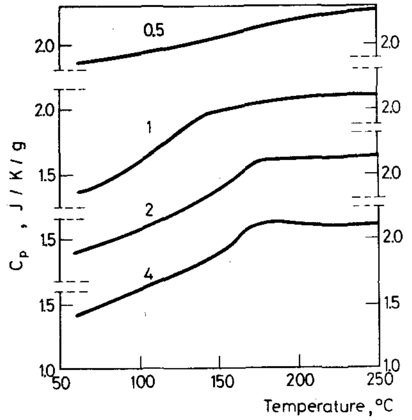


Fig. 11 Specific heat and glass transition of resins cured isothermally at 80° and post-cured. Numbers denote phr EMI content

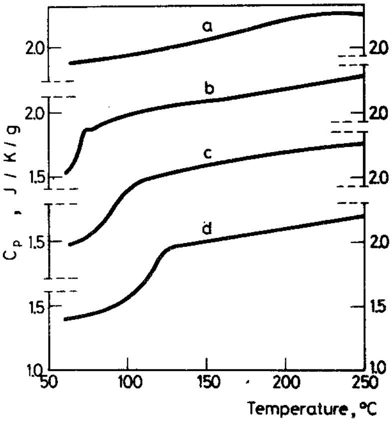


Fig. 12 Specific heat and glass transition of isothermally cured DGEBA-0.5phr EMI. a – second scan after isothermal curing, b – scan after 200°, 16 h, c – scan after 250°, 3 h, d – scan after 250°, 16 h

DGEBA-EMI polymer

The composition of the 1 : 1 molar mixture for producing DGEBA-EMI polymer is 31 phr of EMI per 100 parts of DER332X. The curing behaviour for this high EMI content polymer is slightly structured with a hint of perhaps two different mechanisms and thus is somewhat similar to those with catalytic amounts of EMI.

In scan curing at a rate of 10 deg/min from 50 to 150°, the major exothermic peak occurs at about 103° with a maximum rate of heat release of 2.2 W/g. There is a shoulder on the major peak at 112°. The heat of reaction at 50° is estimated to be 425 J/g, or at 100 kJ/mole of epoxy, very close to the value of about 94 kJ/mole of epoxy, as estimate from the results of Barton and Shepherd [2]. Values of heat of crosslinking reactions for other system may be found in a review of thermal characterization of thermosets [15].

The isothermal heat release at 80° is observed to be 350 J/g. However, by the time the sample approaches 80° from room temperature (within one minute), some reaction has already taken place. The exothermic peak occurred at 2.5 min with a maximum rate of heat release of 0.6 W/g. There appears a slower reaction at about 8 min. The reaction is more or less completed at 30 min. An additional 50 J/g of energy is released between 100 and 140° during the scan post-curing.

The glass transition temperature of the resultant polymer appears reasonably stable at about 95°.

DGEBA–2EMI adduct

The composition of the 1:2 molar mixture used for the study of the DGEBA–2EMI adduct reaction is 63 phr of EMI for 100 part of DER332X. The 80° isothermal curing curve indicates that the reaction has already proceeded to certain degree by the time the sample is stabilized at 80° in about 1 min. The maximum rate of heat release is about 0.7 W/g occurring at 3 min. The rate of heat release drops to near zero after 30 min. The amount of isothermal release at 80° is about 400 J/g. T_g of the resultant adduct is estimated to be 77° with a relaxation peak at 90°.

In scan curing at 10 deg/min, a maximum rate of heat release of 2.3 W/g is observed at 100°. The rate of heat release drops to a minimum value at about 140°. The amount of heat released in this region is 410 J/g or about 120 kJ per mole of epoxy, somewhat higher than that reported elsewhere [2]. Both isothermal and scan curves for the adduct formation are simple and uncomplicated, indicating perhaps a single mechanism.

The resultant adduct appears relatively unstable at temperatures above 150°, as revealed by thermogravimetric analysis at a heating rate of 5 deg/min. In DSC traces, there appears a small exothermic peak at 175–180° and followed by rather noisy curves, due perhaps to the evaporation of decomposed products. In contrast to this DGEBA–2EMI adduct, polymers produced with low catalytic amounts of EMI are stable to 300° under similar condictions of thermogravimetric analysis. The T_g of the adduct drops from 77 to 62°, and then to 56°, by successive heating to 250°. Thus the relative instability of the adduct supports the idea of imidazole regeneration as part of the cure mechanism [3].

Conclusion

The heat of reaction from dynamic calorimetry should be obtained not just from the single scan include the reaction, but should be evaluated in combination with the scan of the product, or the reactant if the reaction can be prevented. The products of different catalytic content from scan-curing process are quite different as seen from the resultant T_g's. The products obtained by first isothermal curing at 80° and subsequently post curing by scanning up to 250° indicated a relatively constant heat of reaction of around 400 J/g. In slow scans, the raw material is allowed sufficient time to more or less complete the faster reactions before the other mechanism sets in. The highest heat of reaction at 50° is observed to be near 550 J/g or about 109 kJ/mole of epoxy group.

The reaction mechanism of EMI on epoxy groups is quite complicated with at least three distinct reactions. The first stage of ion formation may have been confirmed by dielectric measurements. The low thermal stability of the DGEBA–2EMI adduct supports the proposed mechanism of imidazole regeneration [3]. The details of the other two mechanisms occurring at higher temperatures may require bond specific techniques, such as various forms of spectroscopy, to identify the particular bond cleavage and formation.

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Zusammenfassung — Reaktionswärme und Kinetik der Härtung von Diglycidylether des Bisphenol-A-Typs (DGEBA) von Epoxidharzen mit katalytischen Beimengungen von Ethylmethylimidazol (EMI) wurden als Teil eines Programms zur Untersuchung der Prozeßführung für Verbundstoffe untersucht. Die Ergebnisse werden mit den von DGEBA/EMI-Mischungen im molaren Verhältnis 1 : 1 und 1 : 2 verglichen. Eine Methode zur Bestimmung der Reaktionswärmen mit dynamischen thermoanalytischen Geräten nach grundlegenden thermodynamischen Prinzipien wird angegeben. Der komplizierte, möglicherweise durch eine Bildung von Ionen eingeleitete Mechanismus wurde ebenfalls bei anderen Messungen beobachtet, wie z. B. bei dielektrischer Spektroskopie. Das Verhalten von handelsüblichen DGEBA-Harzen wurde mit dem von gereinigtem monomerem DGEBA verglichen. Der Schmelzpunkt gereinigter Kristalle von monomerem DGEBA liegt bei 41,4 °C, die Schmelzwärme beträgt 81 kJ $\cdot$ g^{-1}. Die Schmelze ist durch Abkühlung schwer zu kristallisieren. Der Glasübergang von gereinigtem DGEBA-Monomer erfolgt bei etwa -22 °C mit einem ΔC_p-Wert von 0,60 J K^{-1} g^{-1}.

Резюме — Как часть программы по изучению управления процессом получения композитных материалов, методом дифференциальной калориметрии с энергетической компенсацией была изучена теплота яеакции и кинетика отверждения эпокси смолы на основе двойного эфира эпигидринового спирта и бис-фенола-А (ДГЕБА) в присутствии каталитических количеств этилметилимидазола (ЭМИ). Результаты были сопоставлены с таковыми для полярных смесей ДГЕБА : ЭМИ равным 1 : 1 и 1 : 2. В соответствии с основными термодинамическими принципами, приведен метод определения теплоты реакции, исходя из данных динамических термоаналитических приборов. Сложный механизм, возможно включающий начальное ионное образование, наблюдался также и в других методах, таких как диэлектрическая спектроскопия с временной компенсацией. Сопоставлено поведение продажных образцов смол ДГЕБА и очищенных мономерных образцов ДГЕБА. Для очищенных мономерных кристаллов ДГЕБА точка плавления 41,4 °C, а теплота плавления 81 дж/г. Расплав ДГЕБА трудно кристаллизуется при охлаждении. Температура стеклообразования очищенного мономера ДГЕБА наблюдается около −22 °C с ΔC_p равным 0,60 дж/К/г.