Effect of Mica on the Curing Behavior of an Amine-Cured Epoxy System: Differential Scanning Calorimetric Studies

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Synopsis

Differential scanning calorimetry has been used to follow the cure behavior of mica filled epoxy system using an aromatic diamine (4,4′-diaminodiphenylmethane) as a crosslinking agent. Both dynamic and isothermal methods have been adopted. The effect of mica on the kinetic parameters and the T_g of the cured system has been studied. It was found that mica accelerates the curing process, and decreases the T_g of the fully cured system to some extent.

INTRODUCTION

Mica is an abundant, naturally occuring mineral with high strength, good thermal stability, good corrosion resistance, and also excellent dielectric properties. Besides cost reduction, due to its outstanding dielectric properties, mica is often used as a special filler for thermosetting resins which are used in the electronics or electrical appliance industries. Finely divided mica when employed as a filler for epoxy resins in concentrations up to 100 phr, confers greater arc resistance, a higher dielectric constant, high resistivity, improved chemical and moisture resistance, reduced coefficient of thermal expansion, reduced shrinkage after curing, and increased modulus. It has been observed that the addition of micronized mica to adhesive formulations increases the lap shear strength,[1] and substantial improvement in rigidity by the incorporation of mica has been confirmed.[2]

Extensive literature is available on the cure behavior of epoxy resins with various hardeners[3-5] and also with fillers.[6] Though mica is being considered as one of the widely used fillers, its effect on the cure behavior of the epoxy resins has not been studied in detail. It has been reported in the literature[7] that any hydrogen bond donor molecule present in the amine–epoxy system might act as an accelerator, increasing the initial rate of curing and shifting the exothermic peak to earlier times. Since mica (muscovite–$K_2Al_4(Al_2Si_6O_{20})(OH)_4$) has —OH groups in its structure, it is expected to accelerate the epoxy cure when it is added as a filler. Hence, an attempt has been made to study the effect of mica on the epoxy cure.

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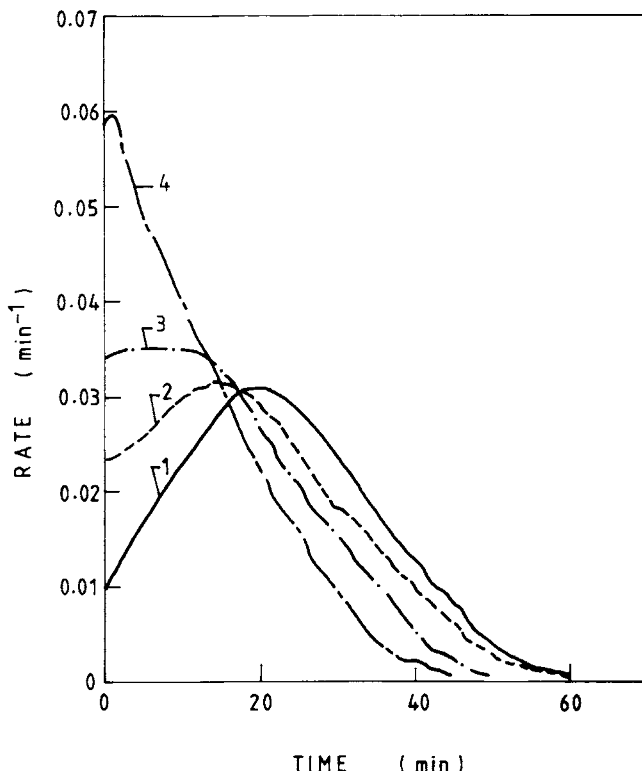
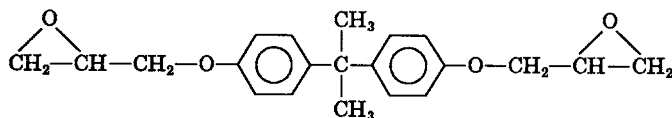


Fig. 1. Plots of rate of cure vs. time for epoxy resin systems containing different mica loadings: (1) unfilled; (2) 30 phr; (3) 60 phr; (4) 100 phr (100°C).

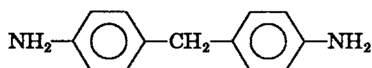
EXPERIMENTAL

Materials. The epoxy resin used was the diglycidyl ether of bisphenol A supplied by Hindustan Ciba-Geigy Ltd., commercial name Araldite LY 556 whose molecular weight is 340 and epoxy equivalent 189.



Diglycidyl ether of bisphenol A

The crosslinking agent used was 4,4′-diaminodiphenylmethane.



4,4′-Diaminodiphenylmethane

Micronized mica was supplied by Export Linkers, Bihar (India). It is a dry ground product of muscovite type. The particle size was 44 μm and the loading was from 30 to 100 phr (parts by weight per hundred parts of the resin).

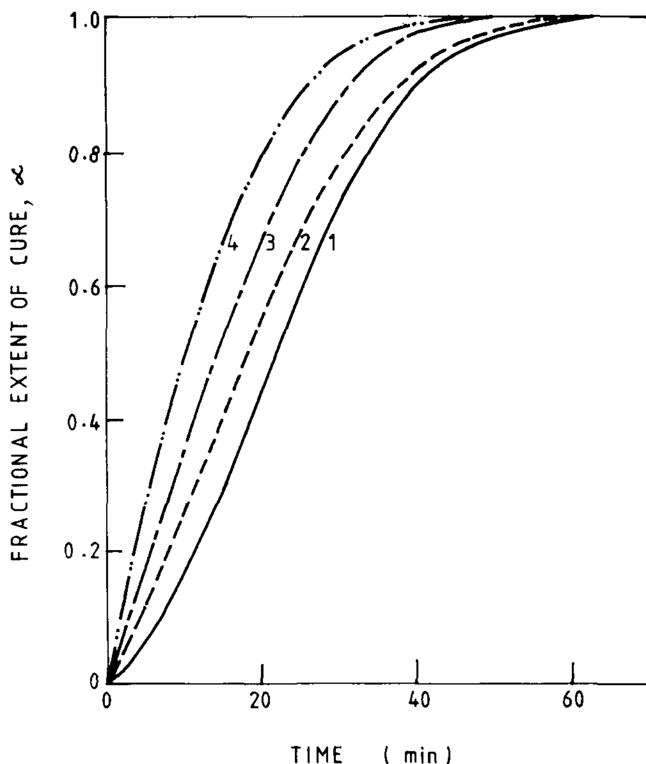


Fig. 2. Fractional extent of cure vs. time plots for systems containing different mica loadings: (1) unfilled; (2) 30 phr; (3) 60 phr; (4) 100 phr (100°C).

Mica/Resin/Hardener Mixture

The mica powder (30–100 parts) was dried and mixed with the hot resin (100 parts) at about 90°C thoroughly. This mixture was then mixed with the molten hardener, diaminodiphenylmethane (27 parts, 1 : 1 stoichiometry) and cooled down immediately.

Differential Scanning Calorimetry

DSC measurements were made using resin/mica/hardener mixture samples of about 5–15 mg on a Mettler TA 2000 DSC instrument, operating in a nitrogen atmosphere. Isothermal runs were carried out between 90 and 140°C. The reaction was considered to be complete when the exotherm leveled off. The base line for these the isothermal traces were obtained by the negative extrapolation of the horizontal portion of the end of the reaction.

Dynamic scans were obtained using a heating rate of 10°C/min in the temperature range 35 and 250°C. The base line was obtained by joining the beginning and the end of the exothermic peak by a straight line. Indium was used as a reference for the DSC instrument.

The isothermally cured samples were subjected to post-curing at 200°C for 5 h and the T_g was measured by DSC with a heating rate of 10°C/min. The midpoint of the transition zone of the DSC scan was taken as T_g.

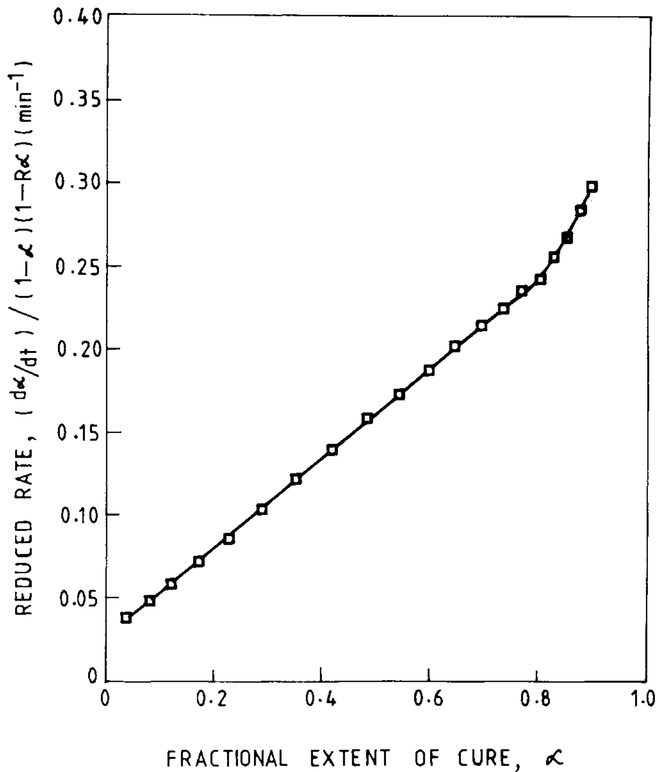
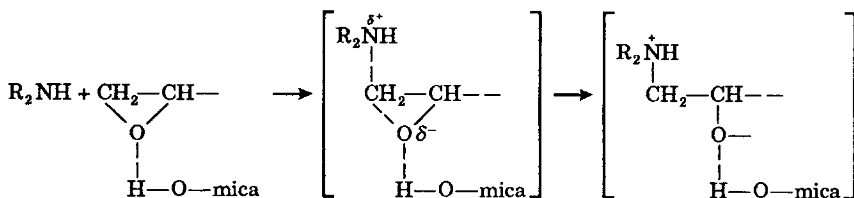


Fig. 3. Plots of reduced rate vs. fractional extent of cure for 100 phr mica filled system at 120°C.

Epoxy/mica mixture (100 : 100 parts without hardener) and hardener/mica were also subjected to DSC which gave no observable exothermic peak.

RESULTS AND DISCUSSION

Isothermal Studies. In Figure 1, rate of cure vs. time plots have been shown for resin mixtures with different mica loadings. As the mica content increases, the initial reaction rate increases considerably and also the peak reaction rate ($d^2\alpha/dt^2 = 0$) occurs earlier, which shows that mica acts as an accelerator without taking part in the reaction itself. Similar observations have also been made by Horie et al.[7] for the aliphatic amine-cured systems with n-butyl alcohol as an accelerator. Probably mica, like other hydrogen-bond donors, participates in the opening of epoxy ring in the transition state as shown below:



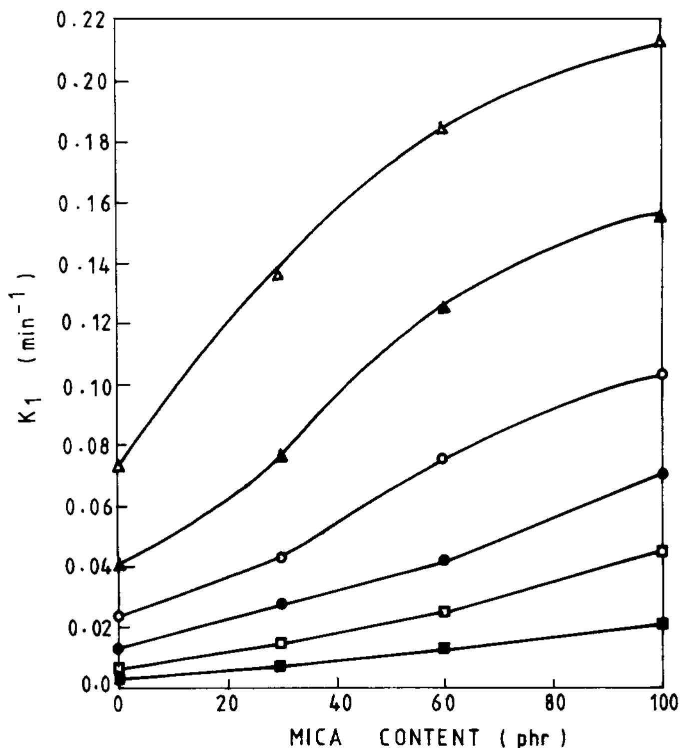


Fig. 4(a). Plots of K_1 vs. mica content at various temperatures (°C): (■) 90; (□) 100; (●) 110; (○) 120; (▲) 130; (△) 140.

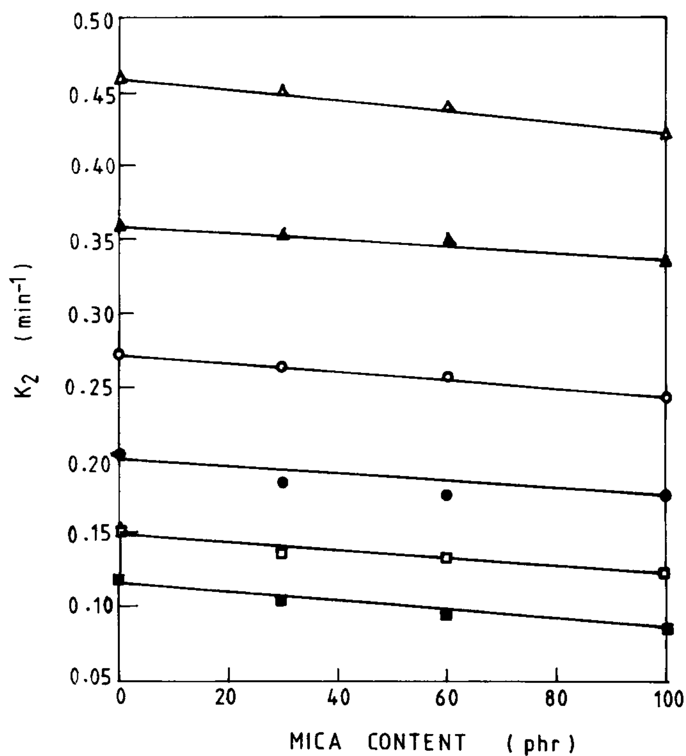


Fig. 4(b). Plots of K_2 vs. mica content at various temperatures (°C): (■) 90; (□) 100; (●) 110; (○) 120; (▲) 130; (△) 140.

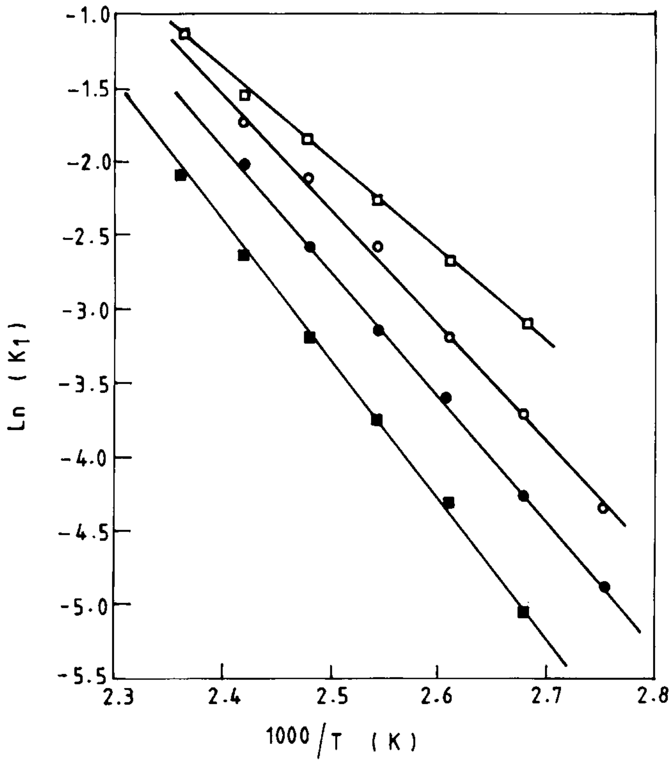


Fig. 5(a). Plots of K_1 vs. 1/temperature for systems containing different mica loadings: (1) unfilled; (2) 30 phr; (3) 60 phr; (4) 100 phr.

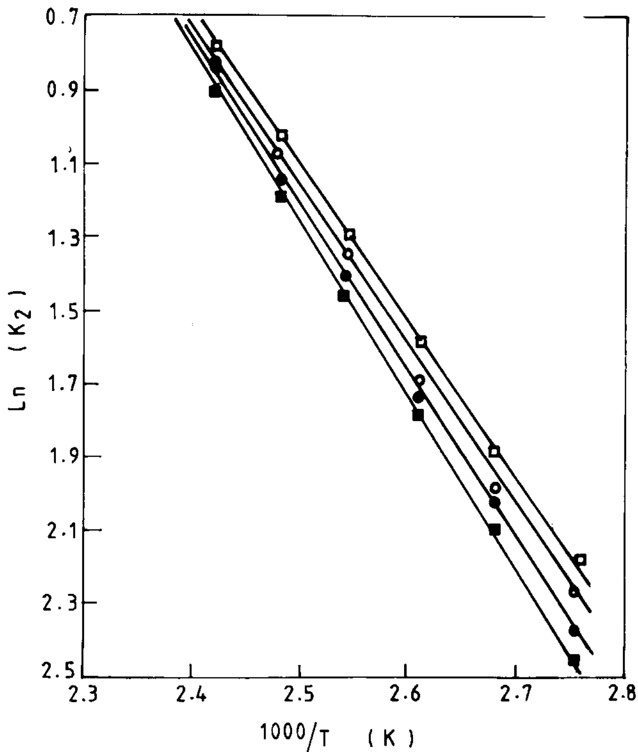


Fig. 5(b). Plots of K_2 vs. 1/temperature for systems containing different mica loadings: (1) unfilled; (2) 30 phr; (3) 60 phr; (4) 100 phr.

TABLE I
Temperature Dependence of Kinetic Parameters Obtained from the Isothermal Cure Studies

Mica content (phr)	K_1	K_2
0	$3.9 \times 10^8 \times \exp(18.5/RT)$	$10.4 \times 10^3 \times \exp(8.3/RT)$
30	$1.9 \times 10^8 \times \exp(17.4/RT)$	$7.5 \times 10^3 \times \exp(8.1/RT)$
60	$1.4 \times 10^8 \times \exp(16.8/RT)$	$3.2 \times 10^4 \times \exp(9.3/RT)$
100	$2.4 \times 10^7 \times \exp(15.1/RT)$	$7.8 \times 10^4 \times \exp(9.9/RT)$

Figure 2 shows the fractional extent of cure vs. time plots for different mica loadings.

The overall kinetic equation[8] for an isothermal process can be given as under:

$$\frac{d\alpha}{dt} = (K_1 + K_2\alpha)(1 - \alpha)(1 - R\alpha) \tag{1}$$

where $K_1 = k_1 a_0 c_0$, $K_2 = k_2 a_0 c_0$, and $R = e_0/2a_0$, α = the fractional extent of cure at time t, a_0 = initial amine concentration, e_0 = initial epoxy concentration, c_0 = initial concentration of hydrogen bond donor molecules present in the system.

The plots of the reduced rate $(d\alpha/dt)/(1 - \alpha)(1 - R\alpha)$ against fractional extent of cure (Fig. 3) were found to be linear (correlation coefficient $R^2 \geq 0.97$) up to about 70% of cure, after which the process becomes diffusion controlled due to increase in the viscosity, as reported by Horie et al.,[7] and hence the rate falls.

The plots of K_1 and K_2 against mica content are shown in Figures 4(a) and 4(b). It has been observed that K_1 values increased markedly with the increase in mica content and the change is also sensitive to the temperature. The activation energy values calculated from Figs. 5(a) and (b), show a decreasing trend as the mica content is increased (Table I). On the contrary, K_2 values seem to decrease with the mica content and also with the rise in temperature, though the effect was not as pronounced as in the case of K_1 values.

Mica seems to have a significant effect on the t_{50} (time taken to reach 50% cure) values [Fig. 6(a)] irrespective of the temperature of cure.

Dynamic DSC Studies. The dynamic DSC data was treated with the following equation[8]:

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n = A \exp(-E_a/RT)(1 - \alpha)^n \tag{2}$$

where n = order of the reaction and k = overall rate constant. The kinetic parameters, namely, the overall activation energy E_a, reaction order n, and the preexponential factor A were obtained and have been listed in Table II. All the three parameters were found to have a decreasing trend as the mica content increased. The exothermic peak temperature ($d^2\alpha/dt^2 = 0$) also decreased markedly with increasing mica content as in the case of isothermal DSC traces.

Post-Curing Studies. The post-cured samples were subjected to DSC for T_g measurement (Fig. 7). It was found that there was a slight fall in T_g (5°C

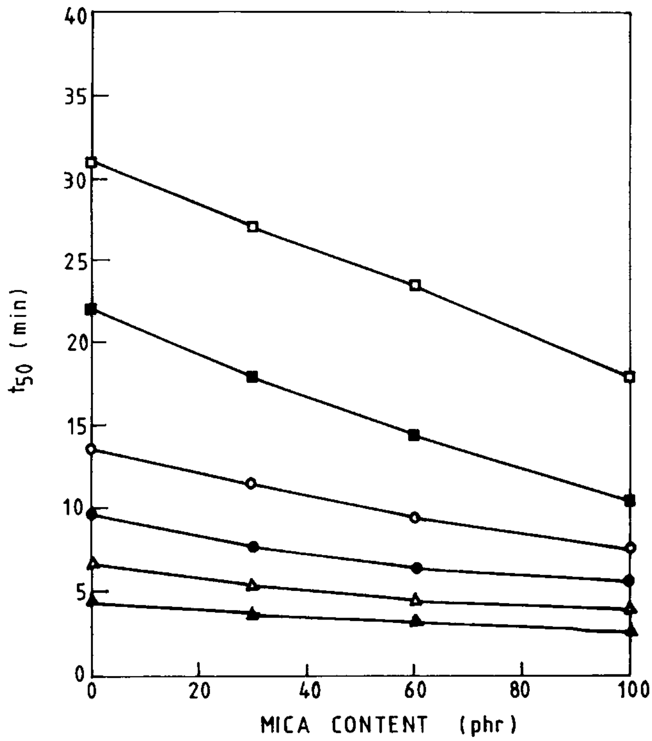


Fig. 6(a). Plots of t_{50} vs. mica content at various temperatures (°C): (■) 90; (□) 100; (●) 110; (○) 120; (▲) 130; (△) 140.

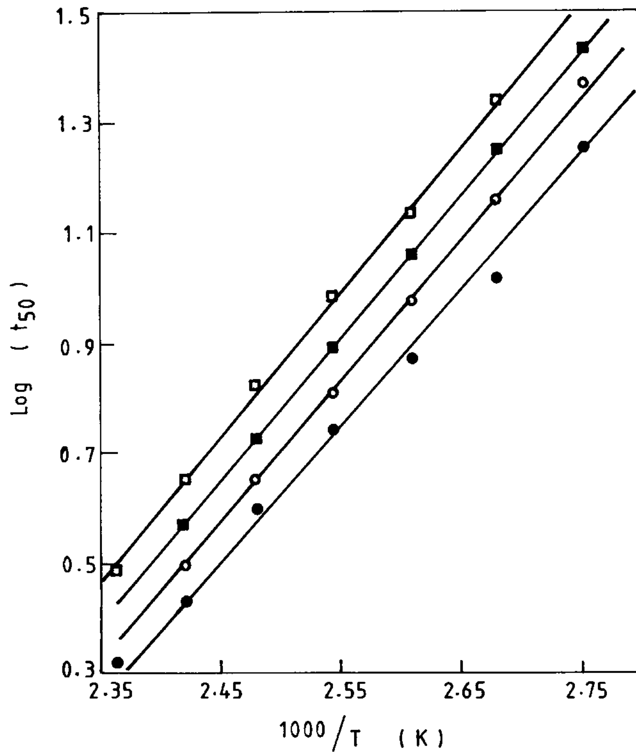


Fig. 6(b). Plots of log(t_{50}) vs. 1/temperature for systems containing different mica loadings: (1) unfilled; (2) 30 phr; (3) 60 phr; (4) 100 phr.

TABLE II
Kinetic Parameters Obtained from the Dynamic DSC Data

Mica content (phr)	E_a (kcal/mol)	n (order)	ln(A)	ΔH (cal/g)	Exothermic peak temp. (°C)	T_g (°C)
0	20.2	1.33	21.8	104	168	170
30	18.0	1.27	19.5	110	164	170
60	15.9	1.22	17.3	106	160	168
100	13.2	1.10	14.3	109	156	165

for 100 phr mica loading) in the mica filled samples, which may be due to the following reason: Mica dispersed in the 3-dimensional network could have possibly reduced the crosslink density, thereby causing a reduction in T_g. However, the ΔH (exothermic heat of curing) values calculated for the filled and unfilled systems did not show any trend (Table II).

CONCLUSION

The following conclusions have been arrived at from the above study.

(i) The presence of mica accelerates the epoxy–amine cure considerably especially at high loadings. The reason for this could be that the —OH

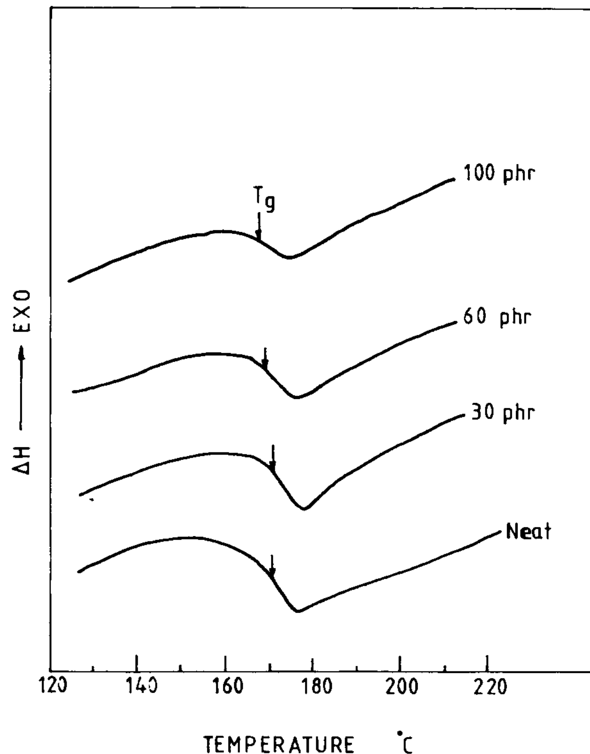


Fig. 7. DSC traces of the post-cured samples.

groups present in the mica structure act as hydrogen bond donors, thereby accelerating the curing process.

(ii) A slight reduction in the T_g of the fully cured epoxy resin was observed as the mica content increased, which can be attributed to the reduction in crosslink density due to the presence of mica in the network.

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