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# STUDIES ON THE CURING KINETICS OF EPOXY RESINS USING SILICON CONTAINING AMIDE-AMINES

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## Abstract

Curing kinetics of diglycidyl ether of bisphenol-A (DGEBA) in the presence of novel silicon containing amide-amines were investigated by the dynamic differential scanning calorimetry. Silicon containing amide-amines were prepared by reacting 2.5 moles of 4,4'-diaminodiphenyl ether (E)/4,4'-diaminodiphenyl methane (M)/3,3'-diaminodiphenyl sulfone (mS)/bis(*m*-aminophenyl) methyl phosphine oxide (B) with one mole of bis(4-chlorobenzoyl) dimethyl silane. The multiple heating rate method (5, 10, 15 and 20°C $min^{-1}$) was used to study the curing kinetics of epoxy resins in the presence of stoichiometric amounts of amide-amines having molecular masses in the range of 660 to 760 g $mol^{-1}$. The peak exotherm temperature depends on the heating rate as well as on the structure of amide-amines. Activation energy of curing reaction as determined in accordance to the Ozawa's method was found to be dependent on the structure of amine. The thermal stability of the isothermally cured resins was also evaluated using dynamic thermogravimetry in a nitrogen atmosphere. The char yield was the highest in case of resins cured with amide-amines having both phosphorus and silicon atoms.

**Keywords:** curing kinetics, DGEBA, epoxy resins, silicon containing amide-amines, thermosetting resins

## Introduction

Epoxy resins have been used in many industrial applications such as in surface coatings, adhesives, structural composites, printed circuit boards and insulating materials for electronic devices because of their good chemical resistance and superior mechanical and electrical properties [1, 2]. These resins also possess excellent processability. However, the conventional epoxy resins are inefficient to satisfy the required properties in the field of advanced materials which require higher thermal and flame resistance [3, 4].

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Several approaches were used in the past to improve the thermal stability and flame retardancy of the epoxy resins. The properties can be varied by the modification of the epoxy backbone i.e. either at the time of synthesis or during cure using curing agents of varying structure. Improvement in the thermal properties of epoxy resin by the incorporation of polynuclear aromatic structures such as naphthalene, biphenyl, anthracene, pyrene etc. [5–7] or phosphorus containing moieties [8–21] has been reported in literature. Another approach used to develop flame resistant epoxy formulations involves the incorporation of additives having flame retarding elements such as halogens, boron, silicon, arsenic or antimony compounds or their combination [22–27]. Apart from the structure of resins and curing agents, properties of epoxy formulations can also be varied to a large extent by the choice of curing conditions. Kinetic characterisation of thermoset resins is therefore of a great importance in understanding the structure–property–processing relationship in order to manufacture high performance materials.

In order to develop flame resistant epoxy resins, the curing and thermal behaviour of epoxy resin (DGEBA) in the presence of phosphorus containing amines, amide-amines and imide-amines was carried out in our laboratory [28–34]. A synergistic effect was observed when phosphorus is used in combination with nitrogen or other flame retarding elements [35–36]. It was therefore considered of interest to investigate systematically the curing behaviour of DGEBA in the presence of silicon containing amines/amide-amines of varying molecular mass (660 to 760 g $mol^{-1}$) and structure. The amide-amines having ether, methylene, sulfone and phosphine oxide moieties were used in the present work. The paper describes the curing kinetics of DGEBA in the presence of stoichiometric amounts of novel amide-amines having silicon in the backbone. Thermal behaviour of the isothermally cured resins have also been investigated using dynamic thermogravimetry in a nitrogen atmosphere.

## Experimental

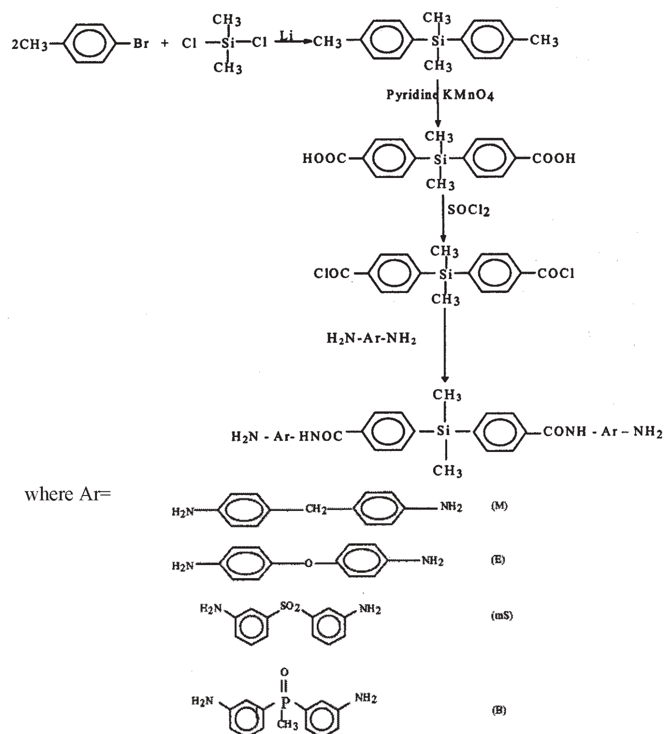
### *Materials*

Diglycidyl ether of bisphenol-A (DGEBA, grade LY 556 having an epoxy equivalent 177) was procured from Hindustan Ciba Geigy Ltd. 4,4'-diaminodiphenyl ether (E), 4,4'-diaminodiphenyl methane (M), 3,3'-diaminodiphenyl sulfone (mS) were purchased from Aldrich. Bis(*m*-aminophenyl) methyl phosphine oxide (B) was synthesised in the laboratory in accordance with the procedure reported in the literature [1]. Dimethyl dichlorosilane (Merck), 4-bromotoluene (Merck), lithium metal (Aldrich), pyridine (CDH), potassium permanganate (Qualigens), thionyl chloride (Thomas Baker) were used as such.

Dimethyl acetamide (CDH) was dried over phosphorus pentaoxide for 24 h followed by vacuum distillation. It was then stored in a dark flask over molecular sieves. Methyl ethyl ketone (Merck) was used as such. Diethyl ether (Qualigens) was dried with sodium wire.

Amide-amines used for the curing studies were synthesised in accordance with the following reaction scheme:

The alphabets within the parenthesis represent the letter designation of amide-amines. The detailed procedure for their preparation and characterisation have been reported elsewhere [37].




**Scheme 1**

*Curing studies*

A Rheometric Scientific Model DSC SP was used to record DSC scans at a heating rate of 5, 10, 15 and 20°C $min^{-1}$. For curing studies, samples were obtained by mixing DGEBA with stoichiometric amounts of appropriate amide-amines dissolved in a minimum amount of low boiling solvent. After thorough mixing, the solvent was removed under vacuum and the freshly prepared samples were used for recording DSC traces in static air atmosphere. Dynamic heating scans were recorded at different heating rates by heating the samples at a programmed heating rate from room temperature to 300°C. 5±2 mg of samples were used in each experiment. The samples have been designated by adding a prefix E to the letter designation of amide-amines. Epoxy resin cured with mS, B, M and E amide-amines have been designated as EmS, EB, EM and EE, respectively.

*Thermal stability*

The thermal stability of the resins cured isothermally (at 200±20°C for 2 h) in an air oven was evaluated by recording TG/DTG traces in a nitrogen atmosphere (flow rate 60 $cm^3$ $min^{-1}$) using a TA 2100 thermal analyser having a 951 TG module. A heating rate of 10°C $min^{-1}$ and powdered samples of 10±2 mg were used in each experiment.

## Results and discussion

Figure 1 shows the DSC scans of epoxy resins in the presence of different aromatic amide-amines obtained at a heating rate of 10°C $min^{-1}$. The curing of epoxy resin depends upon the structure of amine and its stoichiometry with the curing agent used. In the present work we have investigated the effect of structure of amine by taking stoichiometric amounts of curing agent. The molecular mass of amide-amines used in the present work was in the range of 660–760 g $mol^{-1}$. A broad curing exotherm was observed in all the samples. The curing exotherm was characterised by noting the following temperatures:

$T_i$=kick-off temperature where the curing starts.

$T_o$=temperature of onset of exotherm obtained by extrapolating the steepest portion of the exotherm to the base line.

$T_p$=peak exotherm temperature.

$T_f$=temperature at the end of the exotherm. This was taken as the temperature where the exotherm levels off with the base line.

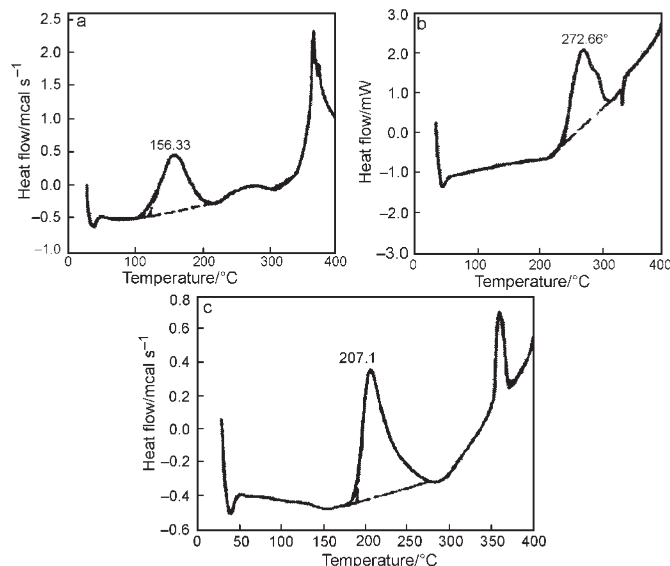



**Fig. 1** DSC scans of epoxy resin cured with stoichiometric amounts of different amide-amines (heating rate 10°C $min^{-1}$) a – E; b – M; c – mS

$\Delta H$=heat of curing reaction. This is obtained from the area under the exothermic transition.

The results are summarised in Table 1. All the characteristic curing temperatures i.e. $T_i$, $T_o$, $T_p$ and $T_f$ showed the effect of amine structure. All these temperatures are the lowest in the presence of amide-amine having the ether linkage (E) and the highest in case of amine having the methylene linkage (M). The following trend was observed in the peak exotherm temperatures: E<mS<B<M.

**Table 1** Results of DSC scans of DGEBA in the presence of different amide-amines at varying heating rates

| Sample designation | Heating rate/ °C $min^{-1}$ | $T_i$/°C | $T_0$/°C | $T_p$/°C | $T_f$/°C | $E_a$/ kJ $mol^{-1}$ |
|---|---|---|---|---|---|---|
| EM | 5 | 198.8 | 229.1 | 258.1 | 197.9 | 103.9 |
| | 10 | 212.9 | 240.6 | 272.6 | 315.7 | |
| | 15 | 219.6 | 249.1 | 282.5 | 326.4 | |
| | 20 | 223.5 | 253.0 | 288.4 | 334.3 | |
| EE | 5 | 96.4 | 105.6 | 139.1 | 193.8 | 50.7 |
| | 10 | 100.6 | 118.3 | 156.3 | 211.6 | |
| | 15 | 103.2 | 125.9 | 168.9 | 224.5 | |
| | 20 | 106.0 | 132.9 | 175.4 | 227.9 | |
| EmS | 5 | 166.6 | 174.9 | 193.0 | 266.7 | 95.8 |
| | 10 | 174.9 | 188.3 | 207.1 | 277.6 | |
| | 15 | 171.6 | 194.2 | 213.7 | 286.9 | |
| | 20 | 187.1 | 199.6 | 218.3 | 303.4 | |
| EB | 5 | 195.3 | 209.2 | 232.7 | 262.2 | 72.9 |
| | 10 | 210.4 | 222.4 | 251.1 | 277.1 | |
| | 15 | 217.4 | 233.7 | 263.2 | 292.1 | |
| | 20 | 224.5 | 237.4 | 271.6 | 300.5 | |

Curing characteristics are dependent upon the nucleophilicity of amines. In the present work, amide-amines have been derived from bis(4-chlorobenzoyl) dimethyl silane and corresponding diamines such as 4,4'-diaminodiphenyl ether (E)/4,4'-diaminodiphenyl methane (M)/3,3'-diaminodiphenyl sulfone (mS)/bis(*m*-aminophenyl) methyl phosphine oxide (B) and the amide-amines thus differ by the presence of ether, methylene, sulfone or a methyl phosphine oxide groups in the amine moiety. B and mS amide-amines have the meta linkage whereas E and M amide-amines have the para linkage. It is well known that sulfone is a strong electron withdrawing group both by negative induction (–I) and negative mesomeric (–M) effects, thus its nucleophilicity is considerably reduced. On the basis of nucleophilicity one would have expected the highest curing temperatures with sulfone based amide-amines; however, in the present work the highest curing temperature was observed with amide-amines having the methylene linkage which has a positive induction effect and has no mesomeric effect. These results are therefore difficult to explain on the basis of nucleophilicity. The other parameter which can affect the curing tempeartures are

the diffusion. The higher curing temperature observed with M in the present work could be restricted by diffusion.

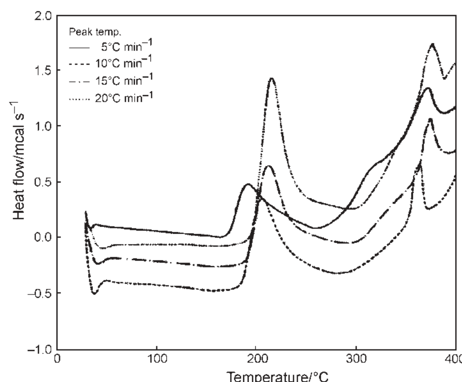



**Fig. 2** DSC scans of EmS sample at different heating rates (5, 10, 15 and 20°C $min^{-1}$)

If one compares the DSC scans of EM and EE samples, it is very clear that in case of EE sample after the first exotherm a second exotherm was observed at a higher temperature which may be due to the etherification reaction whereas in case of EM a shoulder was observed towards the completion of exotherm. EB sample also clearly showed two exotherms whereas in EM and EmS samples only one exotherm was observed and the samples start degrading immediately after the completion of the exotherm. All the samples gave symmetrical exothermic peaks whereas EM sample showed large changes upon curing and did not show well defined symmetrical exothermic transition.

*Curing kinetics*

Kinetic parameters of the curing reaction can be obtained from dynamic DSC scans or isothermal experiments. The dynamic method was used in the present study and the DSC scans were recorded at different heating rates for the samples. Figures 2 and 3 show DSC scans for resin samples EmS and EE using different heating rates. The characteristic curing temperatures for the DGEBA at different heating rates in the presence of different amide-amines are summarised in Table 1. As expected in all the samples, curing temperatures increased with the increase in heating rate. The activation energy of the curing reaction was calculated using the Ozawa's method [38, 39] assuming that:

1. The peak exothermic temperature ($T_p$) represents a point of constant conversion.
2. The reaction follows the first order kinetics.
3. The temperature dependence of the reaction rate constant obeys Arrhenius equation.

The data from dynamic DSC measurements are analysed in accordance with the following equation:

$$\log\phi = 1/2.303\text{X} \ln\phi = -0.4567E/RT + (\log AE/R - \log F(\alpha) - 2.315)$$

where $\phi$ is the heating rate, $E$ the activation energy, $R$ the gas constant and $F(\alpha)$ – the conversion dependent term.

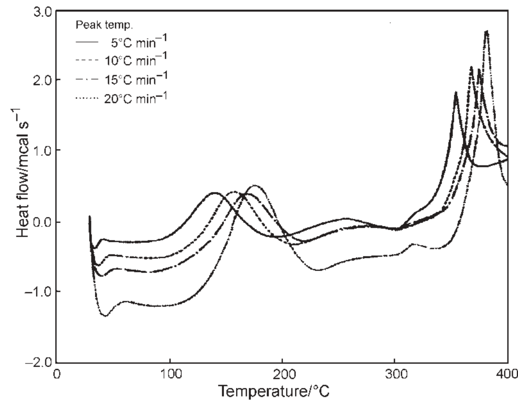



**Fig. 3** DSC scans of EE sample at different heating rates (5, 10, 15 and 20°C min$^{-1}$)

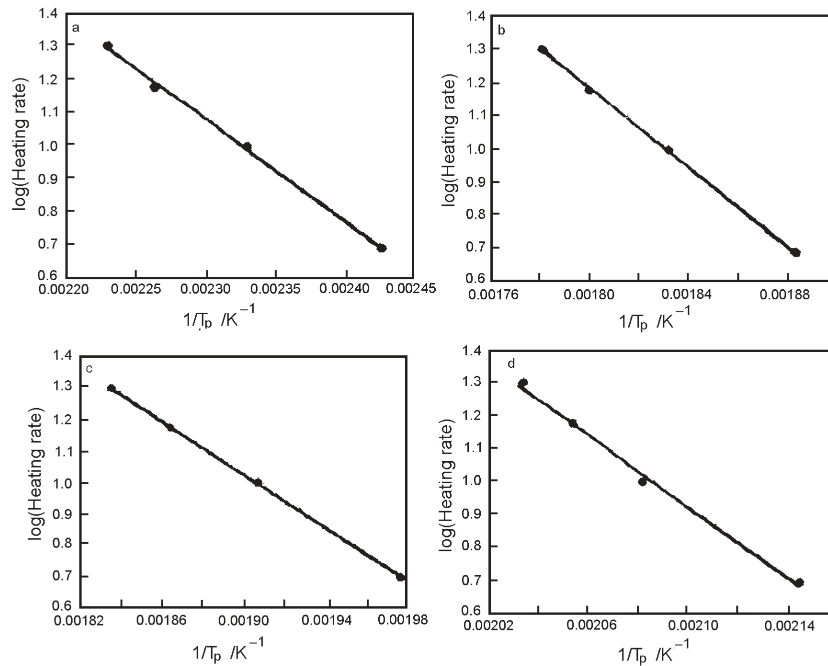



**Fig. 4** Plots of log$\phi$ *vs.* $1/T_p$ for EE, EM, EB and EmS samples

Assuming a constant conversion at the peak exotherm temperature, a plot of log$\phi$ *vs.* $1/T_p$ was obtained and are shown in Fig. 4. From the slope of these lines activation energy was calculated for the first exotherm and the results are given in Ta-

ble 1. Activation energy was the lowest in case of EE sample and was the highest in case of EM. Thus the activation energy of curing showed the following trend in the presence of amide-amines of varying structure:

EE< EB<EmS<EM

*Thermal stability*

Figure 5 shows TG/DTG traces of isothermally cured epoxy resins in the presence of different amide-amines. The relative thermal stability of the cured resins was evaluated by comparing initial decomposition temperature (*IDT*), temperature of maximum rate of mass loss ($T_{max}$), final decomposition temperature (*FDT*) and percent char at 800°C. The results are summarised in Table 2. All the samples were stable upto 350±15°C. A single step degradation was observed in case of EE and EmS whereas EM and EB showed two-step degradation. In case of EE and EmS samples almost no mass loss observed after 600°C whereas EM and EB showed a mass loss of 7.4 and 7% respectively in the temperature range of 600–800°C. Char yield was the highest in case of the cured resins having both phosphorus and silicon in the backbone. The following trend was observed in char yield of the resins:

EB>EM>EE>EmS

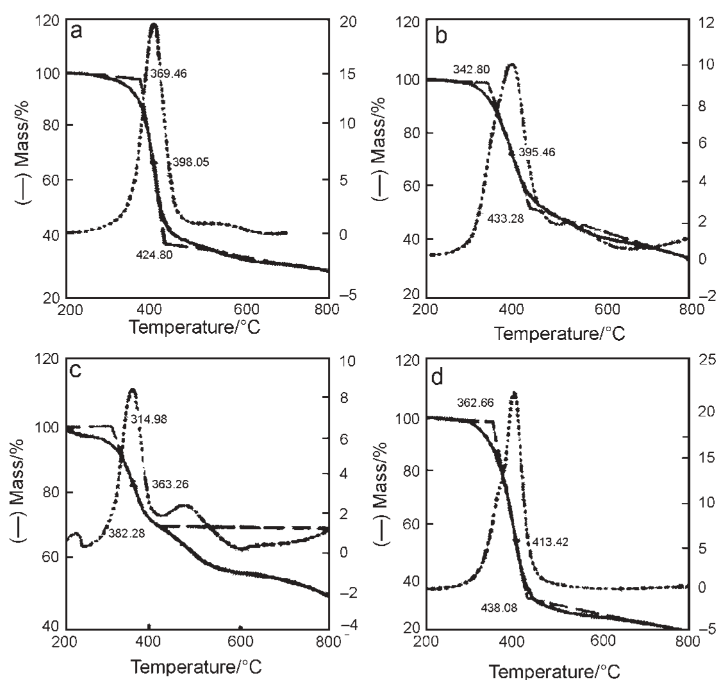



**Fig. 5** TG/DTG traces of cured epoxy resins in nitrogen atmosphere (heating rate 10°C min$^{-1}$) a – EE; b – EM; c – EB; d – EmS

The trend in char yield was the same at 600°C but the char yield in case of EB and EM resins was found to be 57 and 42% respectively whereas char yield in case of EE and EmS samples at 600°C was the same as reported at 800°C in Table 2. Char yield can be used as a criteria for evaluating limiting oxygen index (*LOI*) of the resins in accordance with Van Krevelen and Hoftyzer equation [40].

$$LOI=17.5+0.4CR$$

**Table 2** Results of thermal stability of isothermally cured epoxy resins

| Sample designation | $IDT$/°C | $T_{max}$/°C | $FDT$/°C | Char at 800°C/% |
|---|---|---|---|---|
| EM | 342.8<br>490.0 | 395.5<br>563.0 | 433.3<br>631.8 | 34.9 |
| EE | 369.5 | 398.0 | 424.8 | 27.8 |
| EmS | 362.7 | 413.4 | 438.1 | 22.2 |
| EB | 314.9<br>382.3 | 363.3<br>477.3 | 382.3<br>554.5 | 50.8 |

It was found to be 37.8(EB), 31.5(EM), 28.6(EE) and 22.2(EE). These results thus clearly show that flame resistant DGEBA resin can be obtained by using curing agents having a combination of phosphorus and silicon as flame retarding elements.

## Conclusions

Novel silicon containing curing agents showed the effect of structure on curing kinetics as well as on the thermal stability. Synergism in char yield was observed when amide-amines having both phosphorus and silicon elements in the backbone was used as curing agent.

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