

## Study of curing kinetics of ladder-like polyepoxysiloxane

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### Summary

We report on the curing kinetics of three ladder-like polyepoxysiloxanes synthesised by us, namely, AC (with the alkyl groups and epoxy groups grafted to the ladder like main chain), ACP (with the alkyl group, phenyl groups and epoxy groups grafted to the ladder like main chain) and AP (with the phenyl groups and epoxy groups grafted to the ladder like main chain). We also describe the curing behavior of these three polyepoxysiloxanes studied, both in the absence and presence of a curing agent, 1,3-bis(3-aminopropyl)tetramethyldisiloxane. The apparent activation energy required for curing was calculated using the Ozawa method, and was further verified by the Kissinger method. The activation energies follow the order: AC > ACP > AP. The apparent activation energy for AP-CA (AP in the presence of the curing agent) was found to be a little lower than for AP. The curing behavior was also observed using the FTIR technique. Following the curing, the IR bands at 940, 930 and 834 cm<sup>-1</sup> that are associated with the epoxy groups disappeared and a new peak appeared at 920 cm<sup>-1</sup>, which suggests that the epoxy groups reacted completely.

### Introduction

It is well known that epoxy resins are important adhesives and composite matrix materials. A persistent demand for the miniaturisation and thinness of electronic packaging has led to a quest for epoxy resins with increased thermal stability and lower thermal stress, which are essential properties for moulding materials for electronic packaging [1-4]. Siloxane has been known to possess many unique properties, such as low glass transition temperature ( $T_g$ ), low surface energy, high resistance to thermal oxidation, and imparting non-flammability to the resins [4]. Polyepoxysiloxanes, a class of epoxy containing siloxanes, are expected to have mechanical and thermal properties well suited for electronic packaging applications. Compared to single chain polysiloxanes, the double chain polysiloxanes, also called ladder-like polysiloxanes have better properties such as higher heat-resistance and better thermal stability apart from possessing good physical properties such as flame retardancy. Therefore, they are suitable for passivation film or interlayer insulating film in integrated circuits [4-6].

The epoxy resin becomes brittle after curing due to self-polymerisation, which results in the formation of a highly cross-linked network. Details of curing kinetics including

the curing rate at various temperatures and reaction activation energies are usually required for industrial process modelling, so their accurate description is very important. These data on kinetics, collected under dynamic and isothermal conditions, provide us with a knowledge of the mechanisms of curing reactions [7-9]. Many researchers have studied various mechanisms and the kinetics of curing reactions for different epoxy resins [10-13], to the best of our knowledge no work has been published on the evaluation of the kinetics of curing reactions for ladder-like polyepoxysiloxanes. Extensive investigations of improvements in the flexibility of epoxy resins have resulted in a better understanding of their structure-property relationships.

In the present study we report on three types of epoxies labelled as AC, ACP and AP synthesised by us. Further, we have chosen the (AP) epoxy for a study incorporating a curing agent (AP-CA), as it exhibits highest thermal stability among the three epoxies. There are several ways to improve the thermal and other properties of epoxy resins. Modification is one among them and is usually done by blending the conventional epoxy resins with epoxy containing polysiloxanes. Such blends may be expected to combine the higher thermal stability property associated with polysiloxanes and with the desirable properties that conventional epoxy resins possess. A study of the blend and a stoichiometric study of the curing agent are part of an work in progress and may be reported separately. The aim of the present work report results from using dynamic DSC to evaluate the curing kinetics of a new polyepoxies synthesised by us.

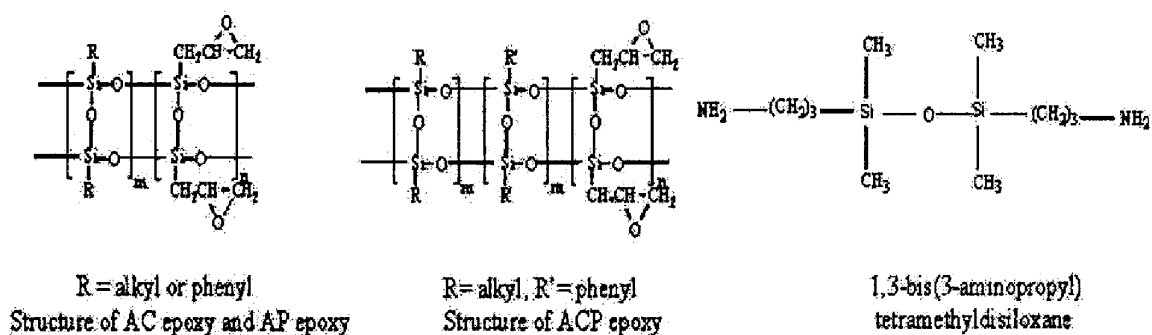
## Experimental

### Materials

We synthesised the following three polyepoxysiloxanes in our laboratory:-

- AC (with alkyl group and epoxy group grafted to the ladder-like polysilsesquioxane chain),
- ACP (with alkyl group, phenyl group and epoxy group grafted to the ladder-like chain) and
- AP (with phenyl group and epoxy group in the ladder-like side chain).

The detailed synthesis procedure is described elsewhere [14]. The chemical structure of ladder-like polyepoxysiloxanes is shown in Figure 1 along with the curing agent, 1,3-bis(3-aminopropyl)tetramethyldisiloxane.



**Fig. 1** Schematic structural diagram of the ladder-like polyepoxysiloxanes and the curing agent, 1,3-bis(3-aminopropyl)tetramethyldisiloxane.

**Table 1** Molar ratio of ladder-like polyepoxysiloxanes

	Epoxy (mol%)	Alkyl (mol%)	Phenyl (mol%)
AC	30	70	0
ACP	30	35	35
AP	30	0	70

The reaction mixture for the AP epoxy with the curing agent was prepared by dissolving the reactants in dichloromethane followed by solvent evaporation. Following this, it was dried under vacuum at room temperature. Table 1 gives the molar ratio of side groups in the ladder like main chains.

#### *DSC (Differential Scanning Calorimetry)*

A Perkin-Elmer Pyris 1 DSC was used after calibrating the instrument with high purity melting standards (Indium and Zinc). All measurements were made in a dried nitrogen environment. The samples were heated from 50°C to 340°C at various heating rates in different runs. In our study we used heating rates of 10, 15, 20 and 30°C/min. The peak temperature,  $T_p$ , and enthalpy values were measured for each run.

#### *FTIR (Fourier Transform Infra-red)*

The FT-IR spectra of ladder-like polyepoxysiloxanes were scanned using a Perkin-Elmer Spectrum 2000 FTIR spectrometer both before and after the curing process, which was monitored using dynamic DSC. The sample was first heated to 340°C at 10°C/min and held at that temperature for 3 minutes and then cooled down to 50°C. For the AP epoxy cured with 2% 1,3-bis(3-aminopropyl)tetramethyldisiloxane as the curing agent the FTIR spectra was taken after mixing with the amine as well as after the curing was completed during the dynamic DSC scan.

## **Results and Discussion**

### *Cure kinetics of ladder-like polyepoxysiloxanes without any curing agent*

The curing behavior of an epoxy resin depends upon the curing conditions, which can greatly affect not only the curing kinetics but also the physical properties of the resulting material. There is a wide variety of factors such as the epoxy structure, molecular weight, and properties of the curing agent that influence the curing kinetics [1,2].

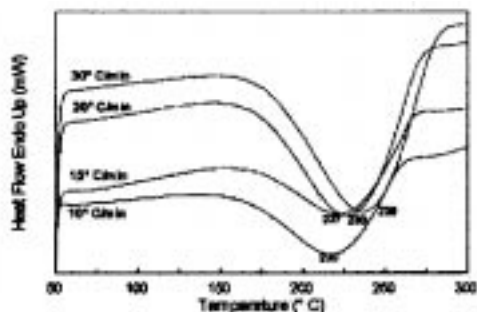
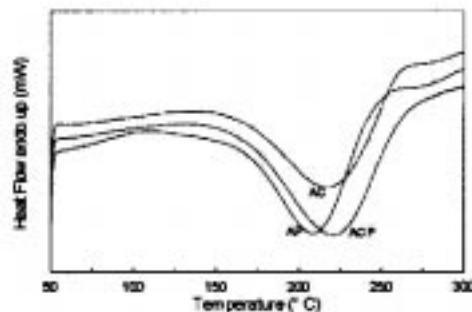
The apparent activation energy required for curing was calculated using the Ozawa method, and was further verified by the Kissinger method. In order to determine the activation energy we used the dynamic DSC method. The dynamic DSC method is based on a simple but accurate relationship between activation energy ( $E_a$ ), heating rate ( $\beta$ ), and temperature of the exothermic peak ( $T_p$ ), as derived by Ozawa. The experimentally obtained peak temperature and enthalpy values for the complete cure of the three epoxies under different heating rates are tabulated in Table 2. It may be noted that the variations in heating rate do not have a significant effect on the enthalpy values, which were found to be 135, 195 and 162 J/g for the AC, ACP and AP epoxies, respectively. Figure 2 shows the dynamic mode DSC curves of AC ladder-like polyepoxysiloxanes under four different heating rates of 10, 15, 20 and 30°C/min. The higher the heating rate is the higher is the exothermic peak temperature. Figure 3

**Table 2** The peak temperature and the enthalpy values for ladder-like polyepoxysiloxanes for various heating rates

Sample Code	Heating Rate (°C/min)	$T_p$ (°C)	$\Delta H$ (-J/g)
AC	10	220.0	135.2
	15	226.0	117.3
	20	230.0	123.5
	30	238.0	127.5
ACP	10	221.9	195.4
	15	228.6	177.4
	20	233.9	187.8
	30	240.8	181.5
AP	10	209.6	161.7
	15	216.4	150.3
	20	220.9	167.7
	30	227.8	163.8
AP-CA	10	212.0	79.0
	15	218.0	82.1
	20	224.0	92.0
	30	230.8	98.4

shows the DSC thermograms for AC, ACP and AP, at the heating rate of 10°C/min. A single exothermic peak was observed for the epoxy self-polymerisation process. The area under the DSC curve is related to the magnitude of exothermic heat during the reaction. The curing characteristics of ladder-like polyepoxysiloxanes are summarised in Table 2.

Curing reactions for all the samples could be safely completed below 340°C without any decomposition during the curing. The subsequent heating of these samples following quenching from 340°C showed no traces of any exotherm indicating that the curing reaction was completed during the first dynamic DSC scan.

**Fig. 2** DSC thermograms of AC epoxy for heating rates of 10, 15, 20, and 30°C/min.**Fig. 3** DSC thermograms of AC, ACP, AP at the heating rate of 10°C/min.

Moreover, it demonstrates that though there are silanes at the terminals of the double chains, they cannot be condensed at high temperature under our experimental conditions. In other words, the exothermic peaks are solely due to the epoxy

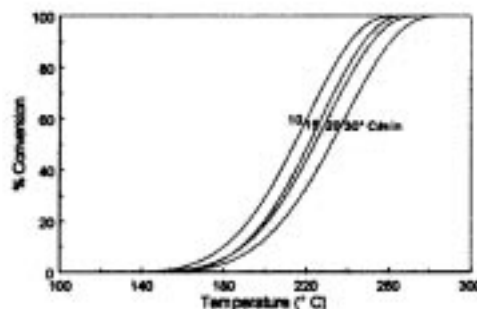
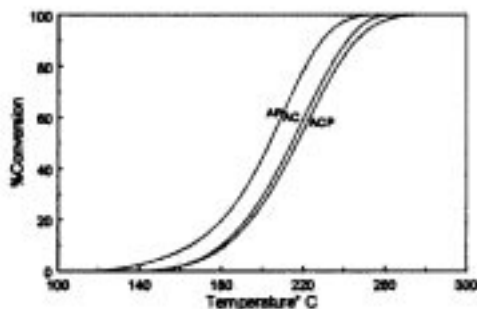
functionality. This was further confirmed by FTIR studies reported later in this paper. Peak temperature,  $T_p$ , is the temperature at which the maximum rate of reaction can be deduced. The extent of reaction at the peak temperature is constant and independent of the heating rate for many epoxy systems [11-13, 15]. One can see that for the same heating rate, the exothermic peak temperature follows the order  $ACP > AC > AP$ . Furthermore, the difference in peak temperatures of AC and ACP is relatively small ( $\sim 3^\circ\text{C}$ ) compared to that between AP and ACP ( $\sim 12^\circ\text{C}$ ).

The fractional conversion at various temperatures was calculated from the following equation:

$$\alpha = \frac{H_T}{H_{total}} \quad (1)$$

Where  $H_{total}$  is the total amount of exothermic heat evolved, and  $H_T$  is the heat evolved at temperature  $T$  [7]. Figure 4 shows the fractional conversion as a function of the curing temperature. The curing characteristics in terms of the fractional conversion as a function of the curing temperature can be visualized as follows: the rate of conversion of AP is faster than of AC or ACP throughout the curing process. However, at an initial lower conversion stage the curing rates for the AC and ACP are quite close to each other; while at the higher conversion stage the rate of conversion of AC is faster than of ACP. The curing reaction rate of epoxy is directly related to the probability of mutual diffusion of the reactants. The reaction rate of AP is fast possibly due to the fact that the phenyl group contributes less steric hindrance and makes AP molecules diffuse fast [15]. Between AC and ACP, the latter is slower. It is possible that intramolecular and intermolecular interactions between the alkyl chain and phenyl groups, and the molecular orientation of the ladder-like polymers in ACP cause its molecules to diffuse slowly during the curing process.

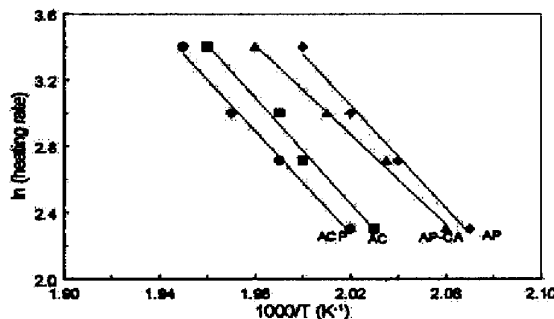
The fractional conversion of epoxy as a function of the curing temperature for four different heating rates of 10, 15, 20, and 30  $^\circ\text{C}/\text{min}$  is shown in Figure 5. One phenomenon is particularly noteworthy here: though the initial cure temperatures are the same, the temperature at constant conversion increases with the heating rate.



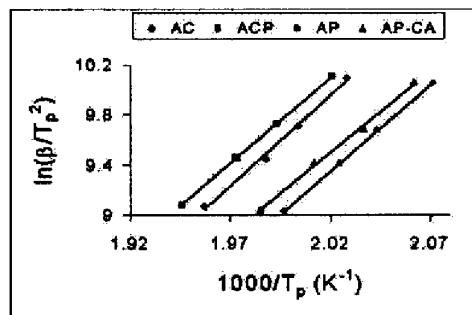
**Fig. 4** Fractional conversion of AC, ACP, and AP epoxies for the heating rate of  $10^\circ\text{C}/\text{min}$ . **Fig. 5** Fractional conversion of AP-CA for the heating rate of 10, 15, 20 and  $30^\circ\text{C}/\text{min}$ .

The graphical plot of  $\ln(\beta)$  versus  $(1/T_p)$  is a straight line as shown in Figure 6 (a), and one can estimate the apparent activation energy required for curing from its slope. The value of the activation energy for curing is about 122 kJ/mol for AC-epoxy but is only about 116 and 115 kJ/mol for ACP and AP epoxies, respectively. Thus, the AC epoxy

has the highest activation energy. When comparing its activation energy to that of poly(dimethylsiloxane) (118 kJ/mol) [16], we found that ours is relatively high. This may be due to the presence of long alkyl chains in the AC epoxy that may tend to exclude the hydroxy groups from reaching the epoxy rings and thus suppressing the reaction, which leads to an increase in the apparent activation energy. However, in the present case, comparing ACP and AP, the bulky phenyl group is a little far away from the epoxy group and therefore, causes less or no effect on the steric factor.



**Fig. 6(a)** Apparent activation energy determination by Ozawa method



**Fig. 6(b)** Apparent activation energy determination by Kissinger method

The apparent activation energy estimated based on Ozawa's method was further verified using Kissinger's method and the two values were found to be in good agreement. The pre-exponential factor, A, is calculated and are tabulated in Table 3. The relation between the peak temperature and the heating rate in the case of Kissinger's method are as given in equation (b) [see Fig. 6 (b)]. The values calculated using the Kissinger method are shown in Table 3 along with the values obtained using the Ozawa method.

**Table 3** The apparent activation energy and the Pre-exponential factor for the ladder-like polyepoxysiloxanes

Sample Code	$T_p$ (°C)	Ozawa method <sup>a*</sup>			Kissinger method <sup>b*</sup>		
		$E_a$ (kJ/mol)	A (min <sup>-1</sup> ) <sup>c*</sup>	$R^2$	$E_a$ (kJ/mol)	A (min <sup>-1</sup> ) <sup>d*</sup>	$R^2$
AC	220.0	122.0	$5.63 \times 10^{12}$	0.9866	120.0	$3.08 \times 10^{12}$	0.9936
ACP	221.9	116.3	$1.14 \times 10^{12}$	0.9914	113.9	$5.89 \times 10^{11}$	0.9996
AP	209.6	115.7	$2.28 \times 10^{12}$	0.9914	113.5	$1.13 \times 10^{12}$	0.9997
AP-CA	212.0	112.1	$5.56 \times 10^{11}$	0.9956	109.8	$2.69 \times 10^{11}$	0.9964

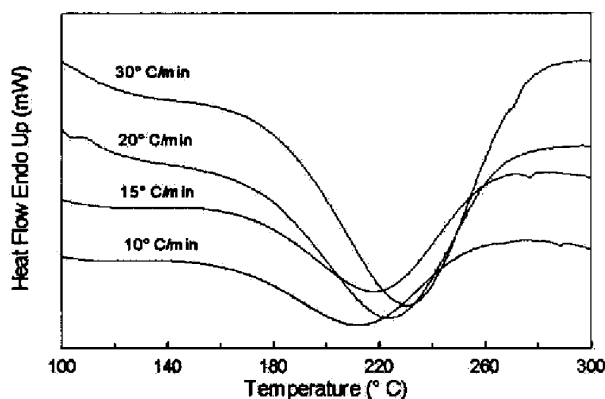
$$a^* E_a = \frac{-R}{0.4567} \frac{\partial \log \beta}{\partial (1/T_p)} = \frac{-R}{1.052} \frac{\partial \ln \beta}{\partial (1/T_p)} \quad b^* \frac{d[\ln(\beta/T_p^2)]}{d(1/T_p)} = -\frac{E_a}{R}$$

$$c^* \log A = \ln(-\ln(1-\alpha_p)) - \log E + \log \beta + \log R + 2.315 + 0.4567 \left( \frac{E}{RT_p} \right)$$

$$d^* A = \frac{\beta E \cdot \exp(E/RT_p)}{RT_p^2 \cdot [n(1-\alpha_p)^{n-1}]} \equiv \frac{\beta E \cdot \exp(E/RT_p)}{RT_p^2}$$

### *Cure kinetics of ladder-like polyepoxysiloxanes with curing agent*

In this section we examine the role of a curing agent in the curing kinetics of ladder-like polyepoxysiloxanes. For this purpose we have chosen the AP epoxy treated with 2 wt. % of 1,3-bis(3-aminopropyl)tetramethyldisiloxane as its curing agent. Its kinetics were studied as in the previous cases where no curing agent was used. A single exothermic peak was observed in this case too. The dynamic DSC thermograms of different heating rates for AP epoxy in the presence of the curing agent are shown in Figure 7. It is clear that in the presence of the curing agent the exothermic maximum shifted slightly towards a higher temperature. This may be due to the high reactivity of the primary amines. The early stage of the reaction might have occurred at room temperature soon after mixing AP with the curing agent.



**Fig. 7** DSC thermogram of AP epoxy with curing agent for various heating rates

Thus, the observed exothermic peaks in the figure correspond to the remaining epoxy groups. Although the peak temperature did not increase significantly compared to that of AP epoxy without any curing agent, its enthalpy reduced to half indicating that a large portion of the epoxy reacted with the curing agent before the DSC scan.

The calculated apparent activation energy is about 112 kJ/mol, which is slightly lower than that of AP epoxy with no curing agent. This may be due to the following reasons:

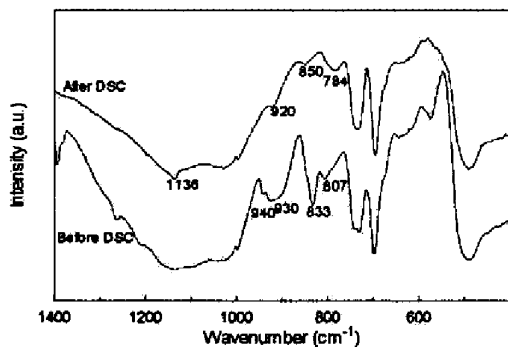
- Epoxy-hydroxy reaction takes place at higher temperature compared to the amine-epoxy reaction, implying that higher activation energy is required.
- In the AP-CP system, the secondary amine-epoxy reaction lowers the overall activation energy because of the higher reactivity of the amine-epoxy reaction.

### *FTIR*

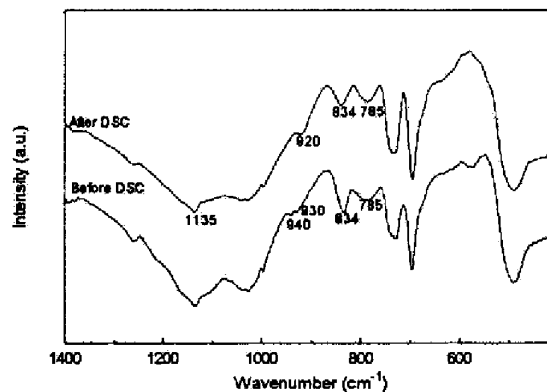
Figure 8 shows the FT-IR spectra of the AP epoxy (in the absence of any curing agent) before and after the dynamic DSC scan. The peak at 1135  $\text{cm}^{-1}$  represents the vibration of the Si-O-Si bond. The peaks at 940, 930 and 834  $\text{cm}^{-1}$  are associated with the epoxy groups. Following the curing these peaks disappeared, and a new peak appeared at 920  $\text{cm}^{-1}$  in the cured sample. This suggests that the epoxy groups reacted

completely during the curing process, so the system can be considered as a self-polymerization system.

Figure 9 shows the FT-IR spectra of AP epoxy cured with 2 wt. % 1,3-bis(3-aminopropyl)tetramethyldisiloxane before and after the dynamic DSC scan. As in the previous case, the peak at  $1135\text{ cm}^{-1}$  represents the vibration of the Si-O-Si bond, and the peaks at  $940$ ,  $930$  and  $834\text{ cm}^{-1}$  are associated with the epoxy groups. Comparing the IR spectra of the pre-DSC scan from figures 8 and 9, one can deduce the influence of the curing agent. Though the amount of curing agent is low (i.e. only 2 wt. %), a significant difference is observed between the IR spectra of the samples with and without the curing agent. Compared to those in figure 8 the intensities of the IR bands corresponding to  $940$ ,  $930$  and  $834\text{ cm}^{-1}$  in figure 9 are reduced noticeably, which indicates that parts of the epoxy groups have reacted with the curing agent before IR measurement. The IR spectra of the AP epoxy with curing agent following its DSC scan shows a new peak at  $920\text{ cm}^{-1}$ . Simultaneously, the IR bands at  $940$  and  $930\text{ cm}^{-1}$  disappear, and the intensity of the  $834\text{ cm}^{-1}$  peak decreases. This suggests that a majority of the epoxy groups reacted during curing.



**Fig. 8** FTIR spectra of AP epoxy without any curing agent before and after DSC treatment.



**Fig. 9** FTIR spectra of AP epoxy with 1,3-bis(3-aminopropyl) tetramethyldisiloxane, as curing agent, before and after DSC treatment.

## Conclusions

The ladder-like polyepoxysiloxanes synthesised by us could be cured with and without a curing agent. The experimental results demonstrate that the curing reaction occurred via the epoxy functionality. The apparent activation energies of these polyepoxysiloxanes, as determined by our experiments, are in the order of  $AC > ACP > AP$ . The long alkyl chains may tend to exclude the hydroxy groups from reaching the epoxy rings and thus suppressing the reaction, thereby contributing to an increase in the apparent activation energy. There is no drastic change in the activation energy between AP epoxy with and without any curing agent, as the amount of curing agent is relatively low. The FTIR results suggest that the curing was completed during the dynamic DSC scan.



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