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A d.s.c. kinetic study on the effect of filler concentration on crosslinking of diglycidylether of bisphenol-A with 4,4′-diaminodiphenylmethane

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The kinetics of formation of epoxy resin composites was studied using an epoxy matrix of diglycidylether of bisphenol-A (DGEBA) and 4,4′-diaminodiphenylmethane (DDM) as curing agent in the presence of quartz flour as filler. The curing reactions of these systems were kinetically followed by differential scanning calorimetry (d.s.c.) at different scanning rates. The activation energies of the curing reactions were obtained using non-isothermal methods: the single scanning rate method of Barrett as well as the multiple scanning rate methods of Kissinger, Osawa and half-width. The crosslinking process is characterized by an average activation energy of 54.2–62.7 kJ mol^{-1} despite different methods or filler concentrations being used to obtain it. The reaction rate for the systems with filler concentrations higher than 10 wt% showed a considerable decreasing at higher temperatures at conversions higher than 50%. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: epoxy systems; inorganic filler; crosslinking)

INTRODUCTION

Many theoretical and experimental studies of the network formation of epoxy resins have been published by several authors: on crosslinking diglycidylether of bisphenol-A (DGEBA) either with an aromatic amine (DDM)[6,7] or with an aliphatic amine[8,9], on the effect of tertiary amines as accelerators in crosslinking of DGEBA with DDM[10,11] on the crosslinking of epoxy resins with anhydrides in the absence[12,13] or in the presence of tertiary amine[14–16].

The knowledge of the kinetics of curing reactions of epoxy resins is very important for the processing of composite materials[13] since for example the highest possible processing time is determined by the gel point[7]. However, to our knowledge, there are only a few studies which treated the reaction kinetics in the presence of fillers: Antoon and Koenig[16], for example, reported silica filler had a slight accelerating effect whereas a high-surface-area E-glass seemed to retard the reaction rate. The technique employed was Fourier transform infrared spectroscopy (*FT*i.r.). Unfortunately the authors did not mention which concentration of filler was used in their work.

This study intends to systematically examine the effect of filler concentration on the crosslinking kinetics of DGEBA with DDM by means of differential scanning calorimetry (d.s.c.) in the non-isothermal mode through the use of differential methods of Barrett[1], Kissinger[2], Osawa[3] and half-width[4,5]. In our laboratory the former method has been used systematically in order to achieve information on the behaviour of the matrix system, i.e. without the presence of filler[15,17]. The latter one was recently introduced and applied to d.s.c. measurements[4,5].

EXPERIMENTAL

The epoxy system in this study is diglycidylether of bisphenol-A, DGEBA(CY-205, Ciba-Geigy) cured with a stoichiometric amount of a tetrafunctional aromatic diamine, 4,4′-diaminodiphenylmethane, DDM (HT-972, Ciba-Geigy). The chemical structures of both reactants are shown in *Figure 1*. The epoxy monomer is a viscous resin with an epoxide equivalent weight (EEW) of 182–196 g eq^{-1} and $n' = 0.14$ (data furnished by manufacturer). The amine curing agent is a crystalline solid (melting point of 90°C) with an amine equivalent weight of 99 g eq^{-1}. The diamine (DDM) was added in the liquid epoxy (DGEBA, pre-heated at 90°C) in a molar ratio 2/1 (DGEBA/DDM).

The quartz flour (99 wt% SiO_2, 200 mesh, mean diameter 17 μm, commercialized by Ciba-Geigy) was oven dried for 24 h at 120°C prior to the mixing procedure. It was added in the epoxy system at concentrations 2, 4, 6, 8, 10, 20 and 30 wt% and mixtures were obtained. Accurately weighed samples were cured in aluminium pans by submitting them to a d.s.c. temperature scan from 50 to 300°C at temperature scanning rate (ϕ) of 10°C min^{-1} under dry N_2 flux.

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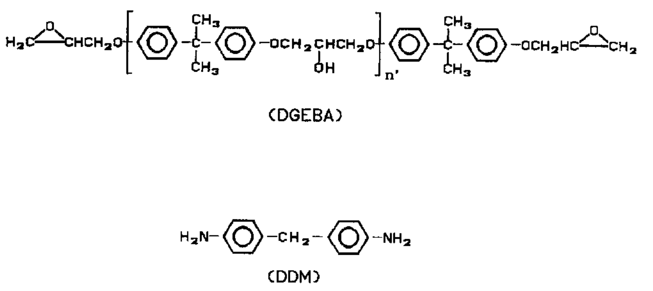

Figure 1 Chemical reactants

Additionally the unfilled and the 10 wt% samples were studied at different temperature scanning rates (ϕ: 5, 7.5, 10, 20 and 30°C min^{-1}) in order to apply multiple scanning rate methods. The d.s.c. scannings were obtained using a Perkin–Elmer DSC-4 differential scanning calorimeter. The minimum temperature (T_{min}), the total and partial areas under the peaks were obtained using the standard Perkin–Elmer DSC-4 software.

RESULTS AND DISCUSSION

The behaviour of two thermal parameters T_{min} were studied experimentally of these composites (for 2, 4, 6, 8, 10, 20 and 30 wt%) and the total enthalpy evolved in the curing process. Both parameters remained practically constant with increasing filler concentration in the matrix. *Figure 2* shows a thermogram for the unfilled and the 10, 20 and 30 wt% samples. T_{min} shows an average value of 164.5 ± 1°C and total enthalpy an average value ($\langle \Delta H_{\mathrm{T}} \rangle$) of 322 ± 21 J $\mathrm{g}^{-1}_{\mathrm{epoxy\ sys}}$. The values of T_{min} and ΔH can be seen in *Table 1*. Thus, T_{min} seems to be better than ΔH as a prior parameter to follow the effects of filler concentrations in the matrix and, at least at low concentrations, the presence of filler unaffects kinetically the curing reaction studied.

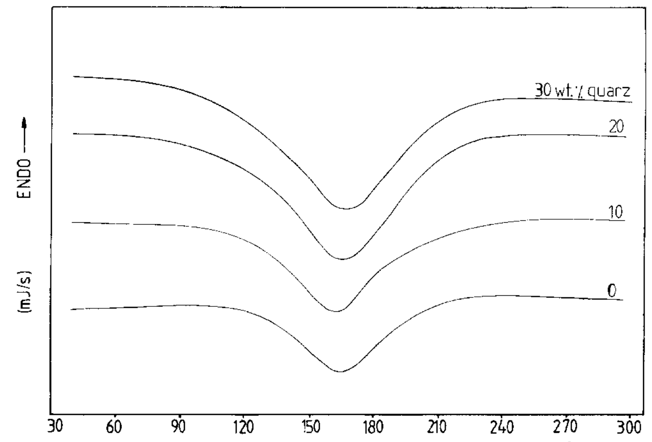

Figure 2 D.s.c. curves of cured filled (10, 20 and 30 wt%) and unfilled epoxy systems measured at 10°C min^{-1}

Table 1 T_{min} and ΔH characteristics of cured filled and unfilled epoxy systems

	$\phi = 10°\mathrm{C\ min}^{-1}$	
wt% quartz	ΔH (J $\mathrm{g}^{-1}_{\mathrm{epoxy\ sys.}}$)	T_{min} (°C)
Unfilled	301	161.5
2	326	164.3
4	301	163.3
6	347	164.1
8	326	164.9
10	330	163.7
20	343	165.3
30	301	165.3
	$\langle \Delta H \rangle = 322 \pm 21$	$\langle T_{\mathrm{min}} \rangle = 164.5 \pm 1$

Applying the Barrett method

In order to obtain kinetic parameters such as activation energies (E_{a}) and study the crosslinking reaction behaviour we used relations, where a single scanning rate is necessary (Barrett method), as well as multiple scanning rates are required (Kissinger, Osawa and half-width methods). The activation energies were estimated using these methods mentioned above and their respective equations are listed in *Table 2*. The Barrett method was applied to determine the activation energies in the epoxy system when filler concentration was varied (10, 20 and 30 wt%) and unfilled with a single temperature scanning rate (10°C min^{-1}). *Table 3* shows the results obtained. It was observed that at filler contents higher than 10 wt% the activation energy data behave constantly and the average value is 53.5 ± 2.1 kJ mol^{-1}. Furthermore the Barrett method provides additional information about network formation, i.e. on initiation, gelation and vitrification processes. As shown in *Figures 3* and *4* the system with 10 wt% filler concentration behaves in the same way as the unfilled one. An initiation stage can be identified from 135°C until *ca.* 152°C; this temperature range corresponds to extents of reaction between 0.05 and 0.25. A second stage can be seen until 170°C (extent of reaction 0.60). According to Flory's theory of gelation[18], the gel point for a diepoxide and a tetrafunctional diamine occurs at the extent of reaction 0.58. Since there is a good agreement between the experimental and theoretical gel points, the observed second stage can be assigned to gel formation. At temperatures higher than 170°C the rate constant increases again. If the line of second stage is extended up to this high temperature region, one sees that the rate constants observed experimentally show lower values. This means the reaction suffers a slowdown and this third stage can be assigned to vitrification. For the 20 and 30 wt% filler concentrations the cure reactions show clearly only two stages. The first stage extends until about 167°C (extent of reaction 0.54). For temperatures higher than 167°C the rate constant increases with values markedly smaller than those of the unfilled and of the 10 wt% samples.

Table 2 Parameters plotted in the ordinate (y) and abscissa (x) axis and slope (m) of the straight line for different non-isothermal methods (ϕ, scanning rate; T_{min}, peak temperature; $t_{1/2}$, half-width time; linear plots, $y = mx + c$)

Method	Y	X	Slope = m	Reference
Kissinger	$\ln[\phi/(T_{\mathrm{min}})^2]$	$1/T_{\mathrm{min}}$	$-E/R^{a}$	2
Osawa	$\ln \phi$	$1/T_{\mathrm{min}}$	$-E/R$	3
Half-width	$\ln t_{1/2}$	$1/T_{\mathrm{min}}$	E/R	4, 5
Barrett	$\ln k^{b}$	$1/T$	$-E/R$	1

[a] $R = 8.3 \times 10^{-3}$ J K mol^{-1}
[b] $k = \mathrm{d}H/\mathrm{d}t\ (H_{\mathrm{T}} - H)$

Table 3 Activation energy characteristic of cured filled and unfilled epoxy systems applying the Barrett method ($\phi = 10°\mathrm{C\,min}^{-1}$)

wt% of quartz flour	Unfilled	10	20	30
Activation energy ($\mathrm{kJ\,mol}^{-1}$)	60.2 ± 2	54.2 ± 2.5	51.4 ± 2.9	55.1 ± 1.7

This means that at higher filler concentrations (20 and 30 wt%) a more accentuated reaction slowdown arises at higher temperatures. Therefore in the high temperature range, where the vitrification process takes place and diffusional effects arise, the curing rate constant is deeply affected by the high amount of quartz flour present in the matrix. On the other hand in *Figure 4* it can be seen that the systems with high filler concentrations (20 and 30 wt%) always show a lower reaction rate constant than the unfilled and 10 wt% filled systems, if equal conversions are considered. These behaviours suggest that structural and morphological differences must be present in the epoxy matrix when high-filled composites are carried out.

Applying Kissinger, Osawa and half-width methods

The determination of the activation energies at different scanning rates was carried out using the methods of Kissinger, Osawa and half-width analysis. These non-isothermal multiple scanning methods can be summarized in *Table 3*. The scanning rates (5, 7.5, 10, 20 and $30°\mathrm{C\,min}^{-1}$) were used for the unfilled and 10 wt% quartz flour concentrations. *Figure 5* shows the typical thermograms for the different temperature scanning rates of 10 wt% filled systems.

The half-width method can be experimentally obtained when at each different scanning rate a thermogram is carried out through d.s.c. experiments. A curing reaction of an epoxy composite gives thermograms with exothermic peaks characterized by the temperature minimum (T_{min}) at half-height. The half-width at the half-height of the thermogram can be experimentally determined. *Figure 6* shows the behaviour of half-width (in minutes), converted from Celsius degree (°C) to

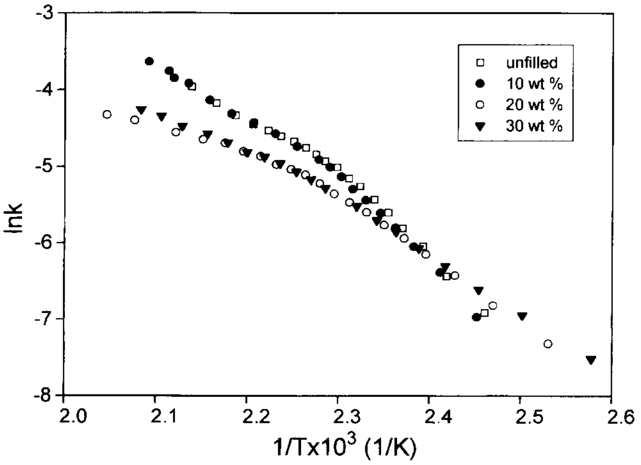

Figure 3 Plot of $\ln k$ vs T^{-1} (K^{-1}) (Barrett method) for the cured filled (10, 20 and 30 wt%) and unfilled epoxy systems measured at $10°\mathrm{C\,min}^{-1}$

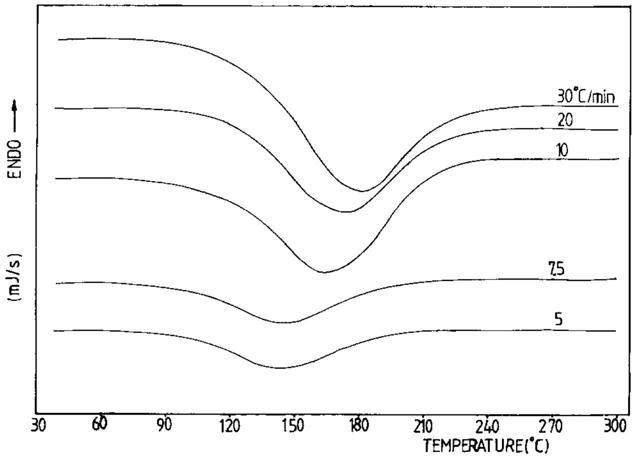

Figure 5 D.s.c. curves of cured filled (10 wt%) epoxy systems at 5, 7.5, 10, 20 and $30°\mathrm{C\,min}^{-1}$

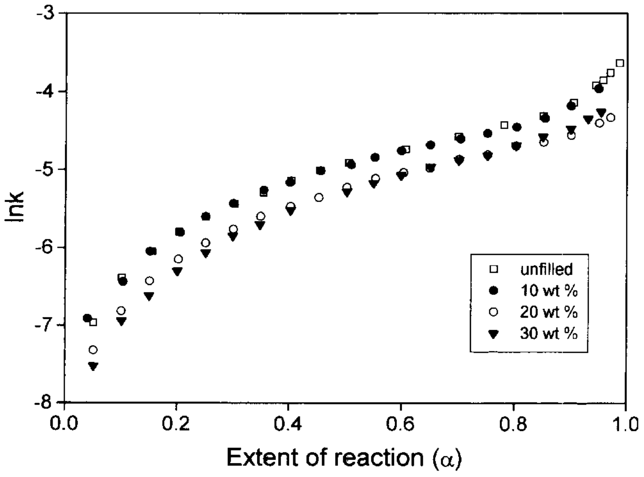

Figure 4 Plot of $\ln k$ vs extent of conversion (Barrett method) for the cured filled (10, 20 and 30 wt%) and unfilled epoxy systems measured at $10°\mathrm{C\,min}^{-1}$

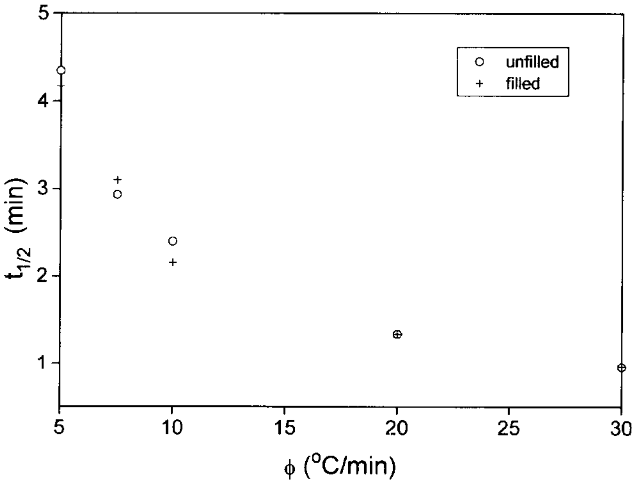

Figure 6 Half-width time ($t_{1/2}$) vs different scanning rates (ϕ) for filled (10 wt% quarz flour) and the unfilled system

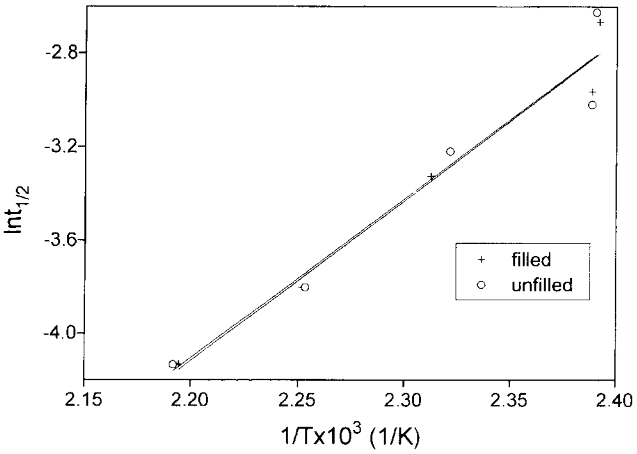

Figure 7 Plot of $\ln t_{1/2}$ vs T^{-1} (K^{-1}) for filled (10 wt% quartz flour) and the unfilled system applying half-width method

Table 4 Activation energy characteristic of cured filled (10 wt% quartz) and unfilled epoxy systems applying different kinetic methods

Method	Unfilled activation energy ($kJ\,mol^{-1}$)	Filled (10 wt%) activation energy ($kJ\,mol^{-1}$)
Kissinger	61.0 ± 7.9	62.7 ± 8.4
Osawa	65.2 ± 7.9	65.2 ± 3.8
Half-width	56.8 ± 7.9	56.8 ± 5.4
Barrett	60.2 ± 2.1	54.2 ± 2.5

minutes by using the relation (ϕ) by $\phi = \Delta T / \Delta t$ where ϕ is the temperature scanning rate, ΔT is the temperature interval and Δt is the time interval at different scanning rates for the systems filled (10 wt%) and unfilled. At higher heating rates, an exponential behaviour arises and the half-width becomes considerably shorter.

For an activation controlled reaction mechanism, the temperature dependence of the rate constant is generally given by an Arrhenius relationship

$$k = A \exp(-E/RT) \qquad (1)$$

and which can be rewritten as

$$\ln(1/t_{1/2}) = \ln A - E/RT \qquad (2)$$

as well as

$$\ln t_{1/2} = E/RT - \ln A \qquad (3)$$

where all parameters have the usual Arrhenius significance and T is the absolute temperature. In this way equation (3) can be used to calculate the Arrhenius activation energy using half-width time ($t_{1/2}$) after the half-width method. *Figure 7* shows a linear regression in order to obtain the activation energies by half-width method for filled (10 wt% quartz flour) and for the unfilled systems. An advantage of this method over the Barrett one is the fact it circumvents difficulties which arise from vitrification processes. The obtained activation energies are shown in *Table 4* where the half-width method provides similar results to the usual non-isothermal methods of Kissinger, Osawa and Barrett and seems to be an excellent method for calculating activation energies.

CONCLUSIONS

Filler presence in diamine-cured epoxy systems at higher concentrations affects the reaction rate constant of the network formation, which is found to follow in good agreement with the kinetic methods, both single scanning and multiple scanning rate. At filler concentrations lower than 10 wt% the d.s.c. technique did not detect any significant effect. At 20 and 30 wt% filler concentrations a marked reaction slowdown arises suggesting structural and morphological differences in epoxy matrix. The half-width, a new non-isothermal kinetic method, has been applied. The half-width follows an Arrhenius-type kinetics and furnished expected results of activation energy in the range 54.2–62.7 $kJ\,mol^{-1}$. Having in mind kinetic data are important for the manufacturing of composites, the present study demonstrates that the simple application of reaction parameters obtained without the presence of fillers may lead to unsatisfactory predictions for the optimization of processing conditions. The classical kinetic Barrett method and the new half-width method seem to be excellent ways to investigate crosslinking epoxy processes in the presence of fillers.

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