

# Dynamic Mechanical Spectrometry Analysis of Modifications in the Cure Kinetics of Polyepoxy Composites with Particulate Fillers

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**ABSTRACT:** We have performed an analysis of the modifications of a polyepoxy cure kinetics due to the introduction of organic and inorganic particulate fillers. In a previous work<sup>1</sup> we have studied by differential scanning calorimetry the rates of reaction of a polyepoxy system reinforced with particulate fillers. This work revealed very important differences between the kinetics of the polyepoxy and those of the composites (polyepoxy reinforced). As a matter of fact, the results obtained with the composites do not fit with any literature models. For this reason, we have decided to focus our work on the various possible interactions between the polyepoxy system and the fillers. In order to bring to light elements of understanding to the origins of cure kinetics modifications, several factors have been examined by turns. On one hand, the influence of residual curing stresses, water content, variations in thermal conductivity, and viscosity has been observed. This let us show that any modification of these parameters can induce important cure kinetic modifications, but none of them is at the origin of the observed modifications. On the other hand, several TTT diagrams obtained for various fillers contents by mechanical spectrometry have been constructed. The analysis of those diagrams revealed that the presence of particulate fillers is of a great influence on the main phase transitions that occur during the crosslinking reaction. The set of results shows that some physical bonds develop between the polyepoxy network and the organic particles. None but those latter can occasion the consequent modifications of cure kinetics that have been observed. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 745–760, 1997

**Key words:** composite; particulate fillers; cure kinetics; dynamic mechanical spectrometry; TTT diagrams

## INTRODUCTION

The addition of particulate reinforcements to polymers is a very widely used technique, particularly when polymer properties need to be modified. The presence of reinforcements leads in prac-

tice to more or less significant changes in the rheological and chemical structure of polymers that receive them. In nearly every case, it is, therefore, necessary to carry out a new characterization of a material once filled.

Our study is part of the ongoing research to develop a new structural filler that consists of small spheres (5 mm diameter) and is designed to have similar applications to honeycombs. This composite materials developed by ATECA RDM

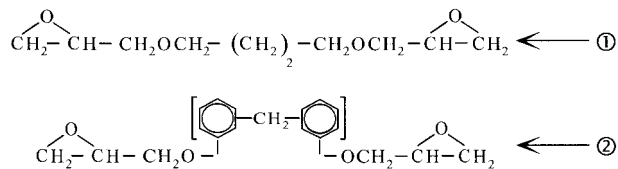
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consists of a mixture of polyepoxy resin and polyamide 12 powder (average granulometry  $50\ \mu\text{m}$ ). A preliminary study of the manufacturing process and an optimization of the material characteristics revealed the influence of the initial stages of the manufacturing process on the final mechanical characteristics. It also established the existence of optimum operating conditions influenced by the presence of the polyamide 12 filler.<sup>1</sup> Our work consisted initially in establishing the cure kinetics of the polyepoxy system alone (prepolymers and crosslinking agents), followed by the polyepoxy and the polyamide 12 mixture. To obtain other elements of comparison, we decided next to use another type of filler, which in terms of size and morphology resembles closely polyamide 12 particles. For this, we chose a chemically inert powdery ceramic filler having no effect on the polyepoxy system. The granulometry of this ceramic filler is identical to that of polyamide 12. The results obtained from this kinetics study enabled us to set up optimal conditions for manufacturing polyepoxy polyamide 12 materials.<sup>1</sup> As a consequence, the temperature for manufacturing the samples has been calculated and set at  $125^\circ\text{C}$ .<sup>1</sup> These results have further revealed significant changes in the rate of the reaction of polyepoxy in contact with the two types of particulate fillers. In particular, correlation obtained using various kinetics models (of phenomenological kind) set up for filled and unfilled<sup>2-7</sup> polyepoxy systems are far from being acceptable. Our study will analyze these modifications.

Numerous studies have been carried out in the field of composites with particulate reinforcements. In the majority, these have had as a goal the study of the changes in the physicochemical and thermomechanical properties of the matrices when filled. The best and most widely used method<sup>8-12</sup> appears to be mechanical spectrometry. Among the studies carried out to date on this subject, some concerned directly with composites of a polyepoxy matrices coupled with various particulate reinforcements.<sup>13,14</sup> All agree on the fact that molecular mobility is reduced near the fillers. This reduction is attributed either to the adsorption of chain segments on the filler surface,<sup>15,16</sup> or to an increase in the matrix degree of cure near the fillers,<sup>17</sup> or in the last resort to residual stresses curing.<sup>18</sup> Generally speaking, all authors, as we have already indicated, are essentially concerned with analyzing changes in the physicochemical and thermomechanical properties. But few of them have analyzed and identified the ori-



**Figure 1** Molecular structure of two polyepoxy prepolymers. The aliphatic diglycidyl ether (circled 1) and the aromatic Novolac (circled 2).

gins of the cure kinetics modifications that will occur when fillers are added to polyepoxy resin.

It is also for this last reason, that we have decided to analyze in detail the behavior of filled mixtures and unfilled resin, in order to bring elements of understanding to changes in the reaction of the polyepoxy system in the presence of organic and ceramic fillers. For this we have decided to use differential scanning calorimetry on the one hand, and a technique using mechanical spectrometry on the other. The latter has not been used with a view to measuring mechanical characteristics, but in order to show and understand behavioral changes brought about by particulate fillers. We shall begin by recalling the main results obtained from the cure kinetics of polyepoxy and polyepoxy-polyamide 12 mixtures. This will enable observation of the phenomena actually modified by the presence of polyamide 12 and ceramic particles. This is followed by a behavioral study of these materials in order to bring out the elements necessary to identify the causes of changes in the cure kinetics.

## PRELIMINARY STUDIES

### Constituent Materials

The polyepoxy used comes in the form of two liquid components. The polyepoxy prepolymer is made up of Novolac and butanediol diglycidyl ether (BDE). It is manufactured by Ciba-Geigy under the trade reference number LY 5052. Note that the BDE is aliphatic and can crosslink quickly at room temperature in the presence of an aliphatic diamine, whereas Novolac (Fig. 1) is aromatic and must be subject to high temperatures in order to crosslink.<sup>19</sup> Ciba-Geigy has not given the proportion of BDE and Novolac in the LY 5052. The crosslinking agent is of a polyaminoamide (aliphatic type) (PAA) and is also produced by Ciba-Geigy under the trade designation HY 5052. The mass ratio between the polyepoxy

**Table I** Main Physical Characteristics of Materials

Materials	$\rho$ (g/cm <sup>3</sup> )	$E$ (MPa)	$\lambda$ (W m <sup>-1</sup> K <sup>-1</sup> )	CTE (K <sup>-1</sup> )	$C_p$ (J g <sup>-1</sup> K <sup>-1</sup> )	$\phi$ ( $\mu$ m)
EP	1, 1	1,300	0, 20	$11 \times 10^{-5}$	1, 02	/
PA 12	1, 01	1,500	0, 35	$12 \times 10^{-5}$	0, 72	50
CM	1, 12	153,000	5	$9 \times 10^{-6}$	1, 10	50

polymer and the crosslinking agent is fixed throughout the study at 100 : 38. This system will be called “polyepoxy” and referred to henceforth as EP. The organic filler is made up of polyamide 12 (referred to as PA12), with an average granulometry of 50  $\mu$ m. It is important to point out that PA12 used in this study (produced by Hüls, trade reference VESTOSINT) is almost entirely crystalline. In fact, some measurements performed on the PA12 by DSC and FTIR have revealed that the crystalline phases are of  $\beta$  and  $\gamma$  types, knowing that they are usually of  $\alpha$  type. Those elements lets us assume that the PA12 crystalline phases are not obtained by simple cooling. This is the reason why the PA12 crystallinity ratio is very high. The ceramic filler is composed of 90% mullite or glass–alumino–silicate (Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–CaO–MgO–BaO) and muscovite (potassium alumino-silicate). Its granulometry is the same as that for the polyamide (50  $\mu$ m on average). This filler will be referred to as CM. In order to avoid any subsequent subjection to humidity, the materials are conserved in airtight packs containing desiccating salts.

The physical properties of the materials used for this study are given in Table I. Except for the density of the ceramic filler, the coefficient of thermal conductivity and the coefficient of thermal expansion of the EP, which have been obtained experimentally, all the other values are those of the manufacturers (Ciba–Geigy and Hüls). Note that the particulate fillers PA12 or CM have received no surface treatment that could induce possible chemical bonds with the polyepoxy matrix.

Last, we must specify that in this study the polyepoxy matrix is considered as a whole. In the resin “as received” the Novolac and the BDE are already mixed by Ciba–Geigy. Thus, those prepolymers cannot be here studied separately.

### Preparing the Materials

Into a beaker are successively poured 100 parts of polyepoxy prepolymer, 38 parts of the crosslink-

ing agent, and a suitable amount of filler representing 0, 20, 40, or even 60% of the total mass of polyepoxy and the crosslinking agent. Then the ingredients are mixed by hand with spatula for 2 min. This operation is carried out at room temperature and followed by degassing in a vacuum bell jar. To check the homogeneity of the mixtures, samples are taken from each batch after each preparation, then placed under an optical microscope. No major evidence of heterogeneity has been detected, apart from slightly higher than average concentrations of particulate fillers in certain zones. For each test carried out by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), or dynamic mechanical thermal analysis (DMTA), the polyepoxy–particulate filler system is mixed just before starting measurements in order to prevent any possible reaction within the system. For the EP–PA12 mixtures, a preliminary study has revealed the total absence of chemical bonding<sup>20</sup> between the constituents. Moreover, it is important to point out that the ceramic filler (mullite and muscovite) is chemically inert. Therefore, chemical bonding between the polyepoxy resin and the fillers could not be the cause of changes in the cure kinetics, which we will describe and then analyze.

### Residual Curing Stresses

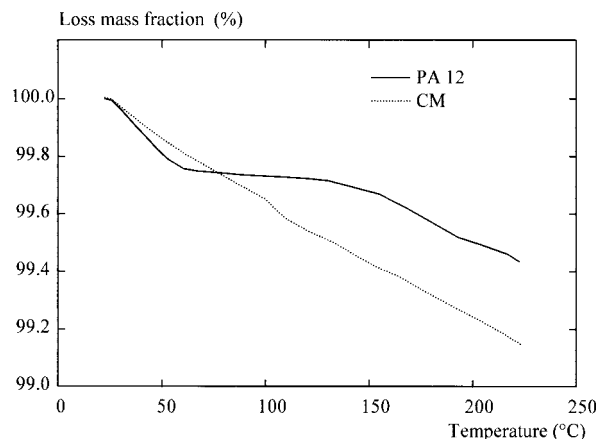
In the manufacture of composites, slow cooling is essential. Indeed, the presence of particulate fillers in polyepoxy matrix can cause internal stresses in their immediate vicinity. Coefficients of thermal expansion of EP matrix and the PA12 or CM fillers are relatively different (cf. Table I) and under the effects of thermal gradients linked to cooling generally give rise to internal stresses called “residual curing stresses.” The level of these stresses depends essentially on the differences between coefficients of thermal expansion, matrix and filler modulus and the thermal gradients.<sup>21,22</sup> It can, in some cases, cause localized cracking in the matrix.<sup>23–25</sup> Because of the visco-

elastic nature of the materials considered, the level of residual curing stresses depends on the cooling rate.<sup>26,27</sup> Physically speaking, the presence of cracks reduces adhesion between the polymer and reinforcement fillers. The cracks caused by residual curing stresses act like voids that increase the molecular mobility of the polymer, thus lowering the temperature of glass transition of the filled materials.<sup>18</sup>

Referring to Table I, it is understandable that the presence of residual curing stresses may adversely affect EP–CM composite between the EP matrix and the ceramic filler. The cooling rate chosen must be sufficiently slow to prevent the level of residual curing stresses from causing cracks in the matrix and debonding of the reinforcement particles. Thus, the material has enough time to relax the residual stresses. For EP–PA12 composites, coefficients of thermal expansion of EP and PA12 are widely different, but the PA12 modulus is relatively low. The stress level which could develop should not cause matrix damage. For EP–CM materials, after a plate has been manufactured, a sample is cut out and submitted to an observation by scanning electron microscope. This check revealed no cracking around the ceramic particles, even in some zones of high concentration particulate fillers. This does not mean that there are not stresses, merely that the level is such that the polyepoxy matrix is not damaged.

### Thermogravimetric Analysis (TGA)

Numerous studies have shown the influence of water on thermodynamic, dielectric, and thermo-mechanical properties of aliphatic polyamides,<sup>28–33</sup> in particular PA12.<sup>34,35</sup> The behavior of epoxy resins is similarly affected.<sup>36,37</sup> For this reason, before any other study, thermogravimetric measurements have been performed on PA12, CM, the polyepoxy prepolymers, and the crosslinking agent. These measurements carried out on a Perkin-Elmer TGA7 apparatus, consisted in raising the temperature from room temperature to 230°C at the rate of 5°C/min. The mass fraction of water contained in all the constituents can thus be calculated. This fraction is lower than 0.8 wt % for PA12, 0.6 wt % for the ceramic filler (see Fig. 2), and 0.8 wt % for the other components (HY 5052 and LY 5052). The mass fraction of water contained in particular in PA12 is here relatively small, and should not, if we take into account the results shown in the above-mentioned studies,



**Figure 2** TGA loss mass curves for the PA12 and CM fillers.

have a noticeable effect on the reaction and relaxation mechanisms of EP–PA12 mixtures.

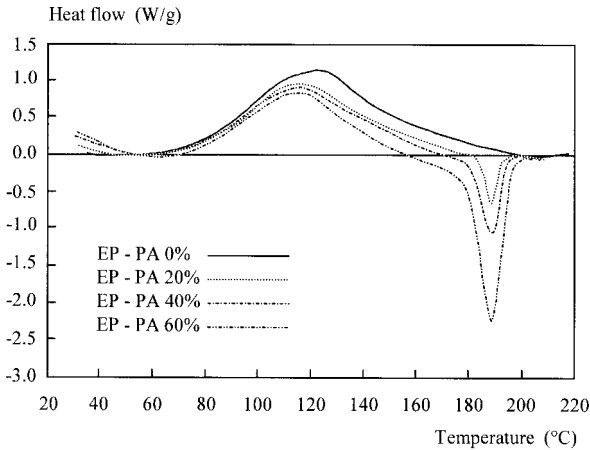
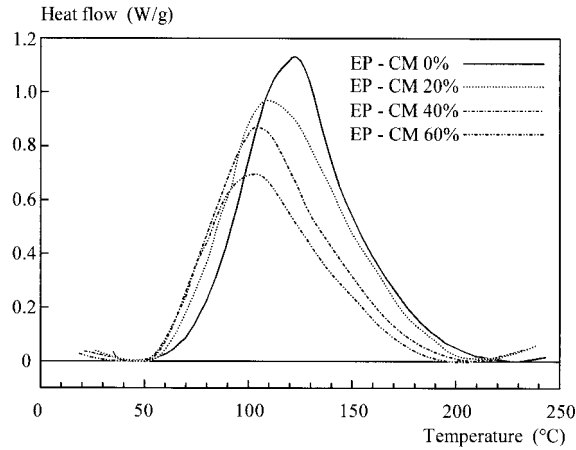
## DIFFERENTIAL SCANNING CALORIMETRY (DSC)

### Samples Preparation

The mass of prepared samples contains 10 mg of polyepoxy + crosslinking agent for each type of sample: polyepoxy alone (EP), polyepoxy–polyamide 12 mixture (EP–PA12) and polyepoxy–ceramic mixture (EP–CM). EP–PA12 mixtures containing 0, 20, 40, and 60% PA12 particles by mass were then prepared, followed by EP–CM mixtures in the same proportions. This mixtures will be referred to as EP–PA12 X% and EP–CM Y%.

### Intermediate Experiments and Results

Tests on the three materials EP, EP–PA12, and EP–CM have been carried out using a DSC apparatus from Polymer Laboratories DSC. The experimental procedure is that traditionally used and will not be described here.<sup>3–5,38–43</sup> From tests in scanning mode we first obtained the total heat of reaction  $H_{tot}$  for materials EP, EP–PA12 20%, EP–PA12 40%, EP–PA12 60%, EP–CM 20%, EP–CM 40%, and EP–CM 60%. Results are shown in Figure 3. Note that in any cases the heat of reaction is determined per mass unit of EP. Total heat of reaction  $H_{tot}$  is given by integrating heat flow compared with temperature (1).



**Figure 3** DSC curves of total heat of reaction  $H_{\text{tot}}$  for the EP-PA12 and EP-CM mixtures with different mass fraction of fillers.

$$H_{\text{tot}} = \int_{T_{\text{initial}}}^{T_{\text{final}}} \frac{dQ}{dt} \left( \frac{dT}{dt} \right)^{-1} dT \quad (1)$$

It is important to point out that the total heat of reaction  $H_{\text{tot}}$  value is always calculated in relation to the mass fraction of polyepoxy and that filler mass does not consequently have a bearing. Results obtained from average of 10 measurements are grouped together in Table II. A whole range of tests in isothermal mode at 125°C (Fig. 4) have enabled us to determine heat of reaction of these materials at this temperature as a function of time  $t$  eq. (2).

$$H(t) = \int_{t_0}^{t_1} \frac{dQ}{dt} dt \quad (2)$$

From results obtained in scanning and isothermal mode we have been able to calculate values

of degree of cure  $\alpha$  eq. (3) and reaction rate  $d\alpha/dt$  derived from the expression of degree of cure  $\alpha^{41-43}$  eq. (4).

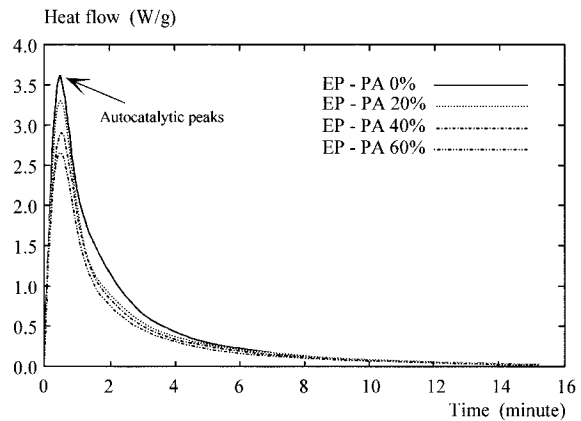
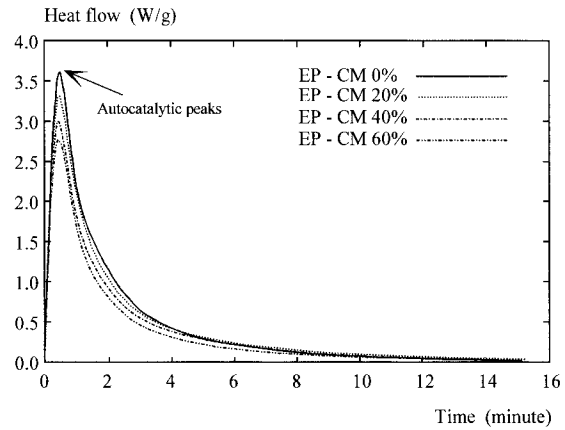
$$\alpha = \frac{H(t)}{H_{\text{tot}}} \quad (3)$$

$$\frac{d\alpha}{dt} = \frac{1}{H_{\text{tot}}} \frac{dH(t)}{dt} \quad (4)$$

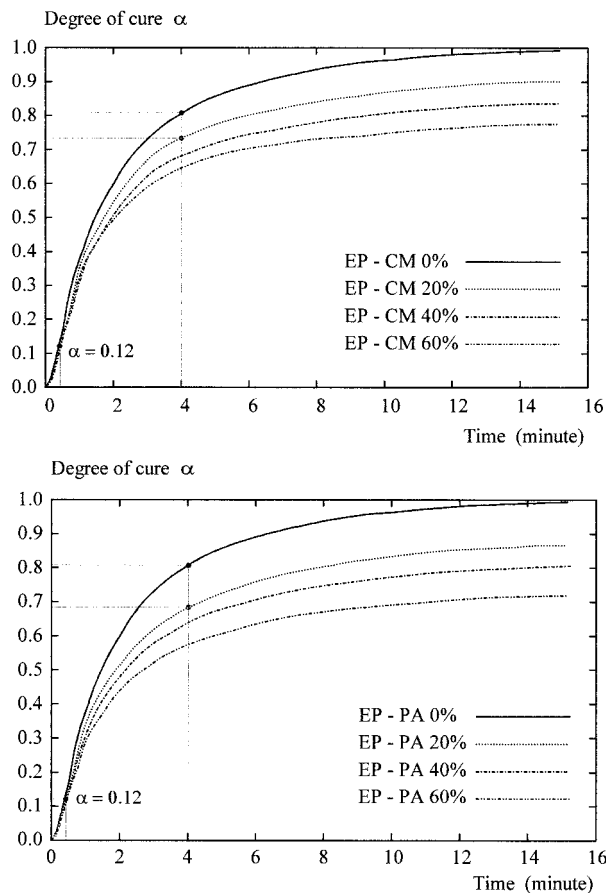
The evolution of degree of cure  $\alpha$  as a function of time  $t$  for all materials is shown in Figure 5, while Figure 6 shows the reaction rate  $d\alpha/dt$  of the materials as a function of degree of cure  $\alpha$ .

#### N.B.

Although we may be stating the obvious, we consider it useful to point out that a relative scale of degree of cure has been used. For us, as in fact for many other authors,<sup>2-6,41-43</sup> the degree of cure is defined in eq. (3) from the heat of reaction val-



**Figure 4** DSC curves of heat flow  $dQ/dt$  for EP-PA12 and EP-CM mixtures with different mass fraction of fillers as a function of time at 125°C.



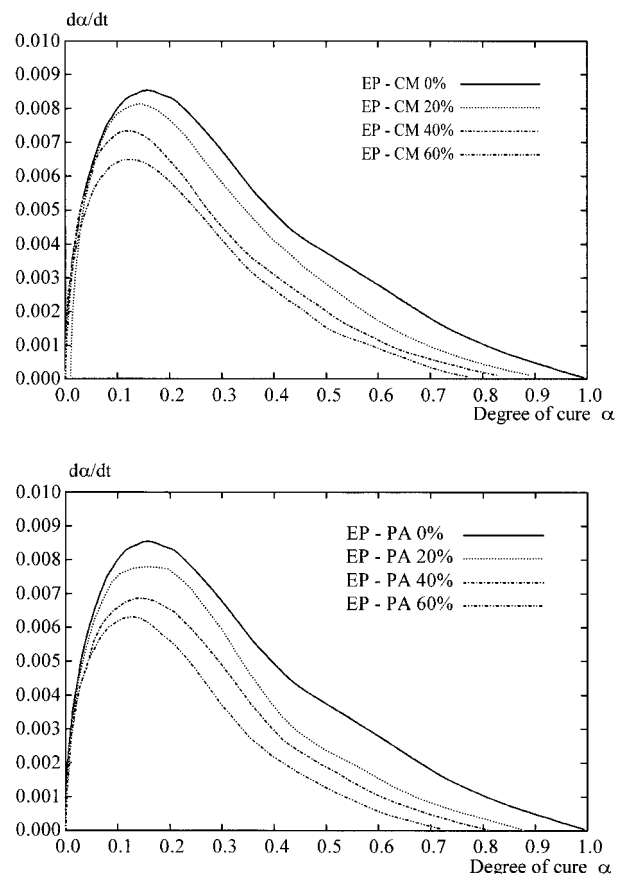
**Figure 5** Evolution of the degree of cure for EP-PA12 and EP-CM mixtures with different mass fraction of fillers as a function of time at 125°C.

ues measured by DSC. “Total heat of reaction” does not mean that the crosslinking reaction is complete, i.e., that all reactive function of the polyepoxy prepolymer have been consumed, but, it is rather the maximum reaction that can be reached whatever the thermal treatment undergone by the considered material. It is for this reason that the degree of cure have values of up to 99% (otherwise improbable from a practical and absolute viewpoint).

#### Remarks Concerning Dynamic Mode Testing

It can be observed from the DSC curves in Figure 3 (dynamic tests) that all materials react quickly as soon as 60°C is reached. The presence of a single exotherm peak indicates a single reaction process between the polyepoxy and the crosslinking agent. As could be expected, the DSC curves in Figure 3 concerning EP-PA12 mixtures show that the endotherm peak characteristic of polyam-

ide 12 fusion appears before the end of the exotherm peak associated with crosslinking of the polyepoxy-polyaminoamide system. Consequently, to determine the total heat of reaction  $H_{tot}$  of polyepoxy present in the EP-PA12 mixtures, we have been obliged to consider that the presence of PA12 in powder form in the polyepoxy matrix in no way changes the total heat of reaction and that its values remains the same as the unfilled polyepoxy. It could be thought that to determine the total heat of reaction of the EP-PA12 mixtures the melting enthalpy of the PA12 particles could have been taken in account. The problem is that the PA12 melting and the polyepoxy degradation occur simultaneously. Thus, no baseline<sup>42</sup> can be determined. As a result, total heat of reaction  $H_{tot}$  for EP-PA12 is considered resistant to variation in the mass fractions of the filler. Various studies<sup>3,5</sup> of composites materials of polyepoxy matrix with carbon filament reinforcements compared with nonreinforced matrices have not



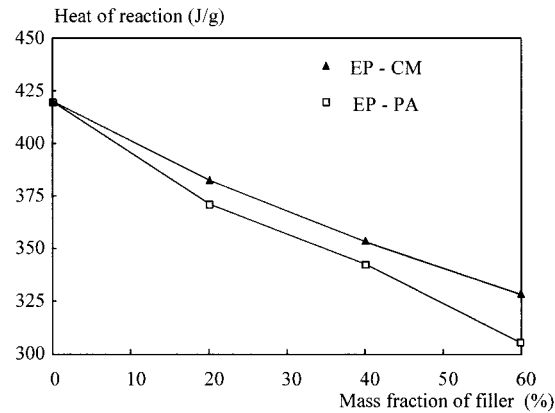
**Figure 6** Cure rate  $da/dt$  for EP-PA12 and EP-CM mixtures with different mass fraction of fillers after 15 min at 125°C treatment.

revealed any  $H_{\text{tot}}$  variation. A clear decrease in  $H_{\text{tot}}$  when filler mass fraction are increased has been observed in EP–CM mixtures. This reduction in  $H_{\text{tot}}$  linked to ceramic filler mass fraction can attain 28.5% for 60% filler mass.

After scanning tests and cooling down to room temperature of each materials, a second scan is carried out. The object is to determine the glass transition temperature of the materials and to verify the subsequent presence of renewed crosslinking in the form of residual heat of reaction. First of all, it can be stated that for EP alone as well as for EP–PA12 and EP–CM mixtures, there is no detectable renewal of crosslinking, leading to the initial supposition that crosslinking is completed during the first scan (cf. preceding N.B.). Even for polyepoxy alone, no renewed crosslinking has been detected. Everything tends to the belief that, in fact, there is no complete crosslinking of the nonfilled materials. The diffusion process is, however, hindered by the appearance of glass in the EP material even before the end of gelation.<sup>44–46</sup> As we shall see below in the remarks concerning isotherm tests, crosslinking reaction depends, in the final stage, on a diffusion mechanism. The blocking of this process prevents a renewed crosslinking reaction when materials are subject to any further heat treatment. In the case of EP, the glass transition has not been detected by DSC. In fact, no glass transition can be detected by DSC. This last remark is inspired by the fact that polyepoxy is made up of an aliphatic prepolymer that can crosslink at room temperature and an aromatic prepolymer that can only crosslink at high temperature ( $\cong 100^\circ\text{C}$ ). It is, consequently, very likely that once the two prepolymers have crosslinked they form locally two micronetworks types where glass transition occurs at different temperatures. The two networks have different glass transition temperatures and exist side by side. This configuration can induce internal prestresses in the whole unreinforced material. This accounts for the fact that no glass transition can be detected in the polyepoxy and the composite. Anyway, the assumption of the presence of a distribution of two micronetworks in the whole polyepoxy matrix has to be verified by other technics, and nether constitute the aim of the present work.

### Isothermal Test Mode and Analysis

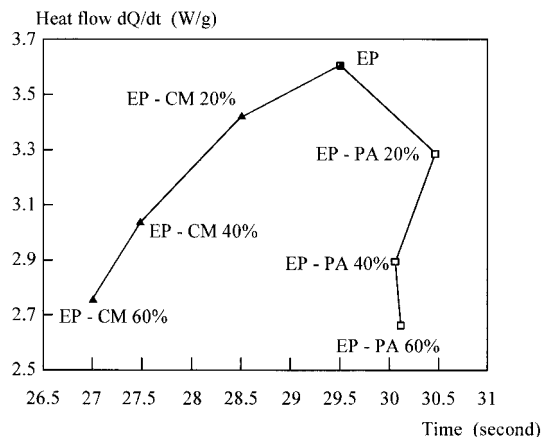
DSC curves obtained from isothermal tests at  $125^\circ\text{C}$  (Fig. 4) reveal the presence of an exotherm



**Figure 7** Heat of reaction for EP–PA12 and EP–CM mixtures with different mass fraction of fillers after 15 min at  $125^\circ\text{C}$  treatment.

peak in all materials. This is usually associated with autocatalytic effect of hydroxyl groups in epoxy systems<sup>2</sup> and is generally called the autocatalytic peak. Note that this peak take place very soon after the start of isotherm treatment. After this peak, the reaction, which is then governed by a diffusion process,<sup>19</sup> decreases more or less quickly, depending on the filler mass fraction. For EP alone, this decrease is generally speaking associated with a rise in viscosity linked to the formation of three-dimensional network.<sup>47</sup> Figure 7 shows the evolution of the heat of reaction value  $H(t)$  during isotherm testing where  $t = 15$  min (with identical heat treatment, i.e., always after  $t = 15$  min at  $125^\circ\text{C}$ ), depending on the mass fraction of the filler added to the polyepoxy system. In the first place, a difference in the overall behavior can be noted between the materials filled with PA12, and that filled with ceramic particles. For EP–CM mixtures, the decrease in  $H(t)$ , depending on filler mass fraction, is linear. This is not the case for EP–PA12 mixtures. If we look at Figure 4, we can see a significant changes in the intensity and time at which autocatalytic peaks occur (see also Fig. 8). On one hand, the intensity of autocatalytic peaks decreases significantly when the particulate fillers (PA12 or CM) mass fraction is increased. On the other hand, for the EP–CM mixtures only, as the filler mass fraction increases, the autocatalytic peaks appear earlier.

Generally speaking, it seems obvious that the introduction of particulate fillers in EP (as yet not crosslinked) increases the initial viscosity of the mixtures: the greater the amount of filler, the greater the increase (this point will be verified in the following section). It is, therefore, more than



**Figure 8** Evolution of autocatalytic peaks for EP-PA12 and EP-CM mixtures with different mass fraction of fillers at 125°C treatment.

probable that increase in the initial value of the apparent composite viscosity, due to the addition of filler, leads to a change in the molecular mobility of the reactants. The increase of the initial apparent composite viscosity probably depends on interfacial interactions between fillers and matrix. This decrease in initial mobility could be the cause of the “blocking” of the self-catalyzing reaction observed in the EP-PA12 and EP-CM mixtures. This “blocking” is premature compared with observations carried out the EP alone. Some authors, who have noticed similar phenomena in composite with fiber reinforcements, attribute this to a reduction in mobility of the reactants due to the presence of fibers.<sup>48</sup> Figure 8 shows, in a system of heat flow ( $dQ/dt$ ) and time axes ( $t$ ), the evolution of autocatalytic peaks<sup>2</sup> in the materials EP-CM  $Y\%$  and EP-PA12  $X\%$ . The relative peak intensity decrease is similar for the two types of materials EP-PA12  $X\%$  and EP-CM  $Y\%$  being  $-0.94$  mW/mg and  $-0.85$  mW/mg, respectively. In relation to the time scale, these peaks seem also to be slowed down in a different way. For the materials EP-CM, they take place earlier with the increase in filler ( $-2.03$  s). In contrast, for the EP-PA12 mixture, the addition of filler only appears to have a slight effect ( $+0.85$  s) on the time differences of appearance of the peaks. In spite of this, it can be pointed out that the time differences are relatively small, and in all cases lower than 2.5 s.

### Thermal Conductivity

Beyond the aspect of mobility reduction, and subsequent modification of the cure kinetics due to the

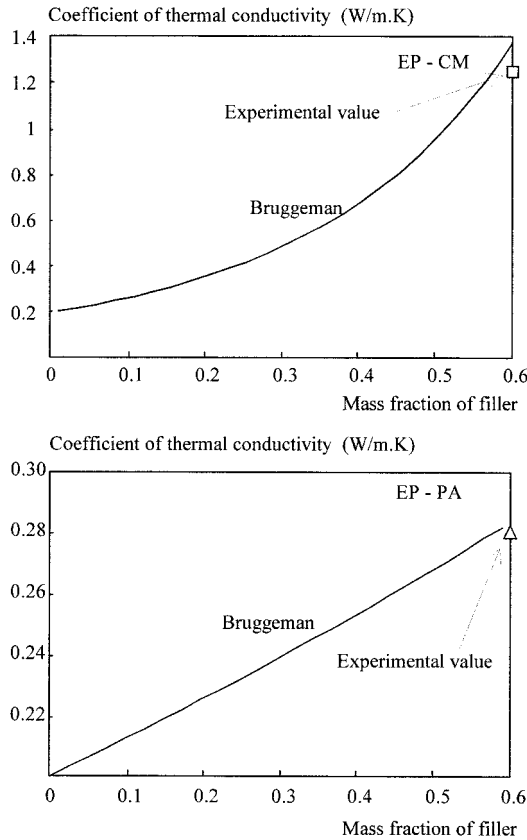
evolution in composite viscosity, heat exchanges play an important point in changing composite kinetics. Several studies of composite materials with carbon fiber reinforcements and epoxy matrix have shown that  $H(t)$  decreases without modifying the cure mechanisms. This decrease is essentially linked to the presence of carbon fibers.<sup>3,5</sup> Equally comparable results have been obtained from composites with an epoxy matrix containing particulate reinforcement (glass balls).<sup>49</sup> In these materials, the coefficient of thermal conductivity of carbon fibers or glass balls is much greater than that of the matrix ( $\lambda_{\text{carbon}} = 200 \cdot \lambda_{\text{epoxy}}$ ). This caused a significant increase in thermal conductivity of the composite materials compared with the nonreinforced matrix. For the materials used in our study, the situation is different, because the differences between the coefficient of thermal conductivity of polyepoxy and the particulate filler used are reduced (cf. Table I). However, we calculated a theoretical evolution of this coefficient as a function of the volume fraction  $v_r(\%)$  of filler introduced into the polyepoxy matrix. To this end, we have used Bruggeman's equation [relation (5)], which gives a good correlation between experimental measurements, and is independent of polymer structure.<sup>50</sup>

$$1 - v_r = \frac{\lambda_r - \lambda_c}{\lambda_r - \lambda_m} \left[ \left( \frac{\lambda_m}{\lambda_c} \right)^{1/2} \right] \quad (5)$$

where  $\lambda_r$  is the coefficient of thermal conductivity of reinforcement (here particles) ( $\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ ),  $\lambda_m$  is the coefficient of thermal conductivity of the matrix ( $\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ ),  $\lambda_c$  is the coefficient of thermal conductivity of the composite ( $\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ ),  $v_r$  is the volume fraction of filler (reinforcement particles) (%).

Results are shown in Figure 9. Note that the coefficient of thermal conductivity of the composite  $\lambda_c$  is, in fact, sensitive to addition of PA12 in the polyepoxy matrix and increase by 42%. However, it is vital to keep this variation in perspective, because only 42%, in fact, represents  $0.085$   $\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ . It is not, therefore, reasonable to suppose that the slowing down of the crosslinking reaction associated with the addition of the PA12 in the polyepoxy matrix is due to a change in thermal conductivity. In the case of the EP-CM mixtures, the coefficient of thermal conductivity increases by 530% when the filler mass fraction goes from 0 to 60%. This increase corresponds to a variation of  $1.26$   $\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ . We are a long way off from reaching  $\lambda$  ratios encountered in carbon or





**Figure 9** Evolution of thermal conductivity  $\lambda_c$  by Bruggeman and Springer models as a function of volume fraction of fillers.

glass epoxy composites. It is, therefore, highly unlikely that in this case, the decrease in  $H(t)$  (where  $t = 15$  min at  $125^\circ\text{C}$ ) can be attributed, even in the smallest degree, to a change in thermal conductivity. Moreover, the surface treatment that reinforcement generally undergo may lead, in certain cases, to periods of slowing down in the cure kinetics in the interfaces.<sup>51</sup> For the materials used in this study, the situation is different because they have received no prior surface treatment.

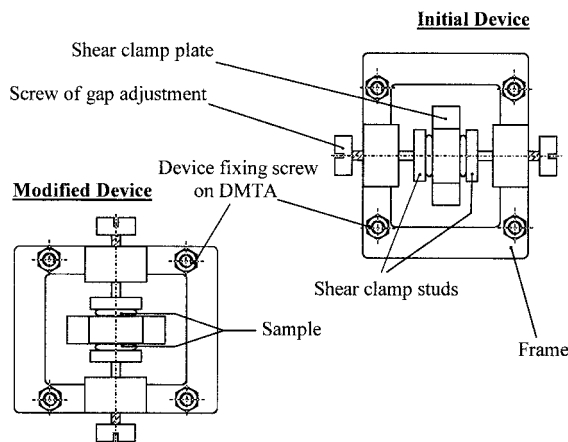
### Cure Kinetics Analysis

For all samples tested, the reaction rate  $d\alpha/dt$  is very high. As can be seen from Figure 5, the degree of cure  $\alpha$  reaches 12% in about 27 s at  $125^\circ\text{C}$ , whatever the fillers mass fractions are. Below this value ( $\alpha < 12\%$ ),  $\alpha$  appears to be indifferent to the presence of filler. In fact, from the onset of reaction, the active functions of polyepoxy prepolymers (BDE and Novolac) only react with nearly polyaminoamides (PAA),<sup>6,46</sup> and there is no high molecular transport in this phase of the reaction. Beyond these instants (where  $\alpha > 0.12$ ), the reaction rate depends greatly on the filler mass fraction. In similar heat treatment circumstances (15 min at  $125^\circ\text{C}$ ) the greater the mass fraction of filler in the polyepoxy, the lower the reaction rate and degree of cure. For the EP-PA12 mixture with 60% mass fraction, the degree of cure is merely 72% after 15 min at  $125^\circ\text{C}$  compared with 99% for EP alone. Similarly, for the EP-CM mixtures with 60% ceramic filler mass fraction, the degree of cure reaches 79% under the same thermal treatment conditions. Let us take another example: after 4 min at  $125^\circ\text{C}$ , with a fillers mass fraction of 20%, the degree of cure reaches 81% for EP alone while it is only 68% for the EP-PA12 and 71% for the EP-CM. All the results obtained are presented in Table II.

It is, thus, clear that with identical filler mass fraction, polyamide 12 slows the reaction down much more than the ceramic filler. All this is, in fact, just another way in which the phenomena observed on the DSC curves manifest themselves. Values for degree of cure  $\alpha$  and reaction rate  $d\alpha/dt$  have been directly calculated from these charts, which indicate measurements taken during isotherm tests. Because the granulometry and the morphology of the PA12 and the CM particles are identical and the modifications that the fillers induce in the material thermal conductivity are relatively small, it can be thought that the pres-

**Table II** Heat of Reaction and Degree of Cure of EP-PA12 and EP-CM Mixtures for Different Mass Fraction of Fillers

Materials		Mass Fraction of Filler (%)			
		0	20	40	60
EP-PA12	H (J/g)	420	372	342	304
	$\alpha$ (%)	99	88	81	72
EP-CM	H (J/g)	420	387	355	335
	$\alpha$ (%)	99	91	84	79



**Figure 10** Experimental shearing device—parallel plates of the DMTA Mk II Polymer Laboratories.

ence of the PA12 particles does not result in a simple steric hindrance of molecular movements. For this reason we have decided to perform further investigations on the cure kinetics modification.

## DYNAMICAL MECHANICAL THERMAL ANALYSIS (DMTA)

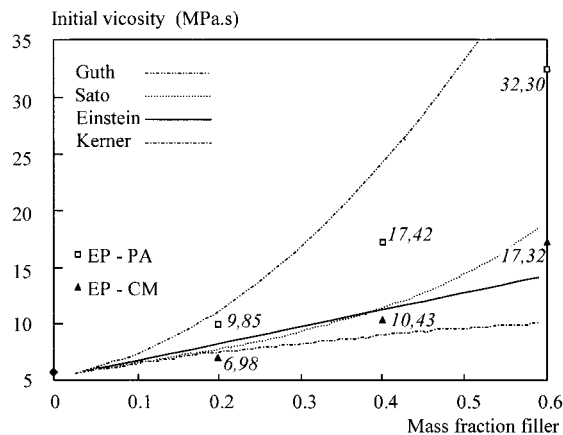
### Initial Viscosity of the Mixtures

Our objective is here to analyze the causal factor of changes observed in reaction kinetics.

For this purpose we have tried to use theoretical models to predict the initial viscosity of the different mixtures (EP-PA12 X% and EP-CM Y%) at room temperature before any thermal treatment. In these models,<sup>52-59</sup> the reinforcement particles have to present a purely elastic behavior while the resin is assumed to behave as a fluid. It is important to point out that all theoretical and numerical models for determining composite viscosity apply to suspensions of particles in the fluid, and do not, therefore, take into account the possible existence of bonding between the matrix and the filler. Furthermore, it must be remembered that particles are not generally supposed to interact with one another. Remember that, from the point of view of their mechanical behavior, the two particulate fillers used are different in kind. The ceramic filler has purely elastic behavior with a high Young's modulus (153,000 MPa), which is radically different from the elastic modulus of the polyamide 12, which is (in static mode at room temperature) 1500 MPa

(cf. Table I). In the case of the EP-PA12 X% composite, it, therefore, seems difficult to use theoretical models to predict viscosity. However, viscosity measurements made at room temperature before any curing on the polyepoxy resin have shown that this latter always remains relatively fluid (5 Pa s) and its  $G'$  modulus is about 2.5 Pa. So this enable us to consider that in relation with the polyepoxy resin modulus, the PA12 particles have an elastic behavior. Thus, the whole material can be considered as a suspension of particles in a fluid whatever the particles are (PA12 or CM). The most recent developments in determining the viscosity of composites with particulate reinforcements have recourse to numerical models, which present practical difficulties beyond the scope of this article.<sup>60-62</sup>

Figure 11 shows the theoretical evolution of polyepoxy initial viscosity (at room temperature and prior to any heat treatment) depending on filler mass fraction by various models. Using a dynamic thermomechanical analyzer from Polymer Laboratories MK II with a dynamic rheometer configuration of parallel plates (Fig. 10), we have determined the initial viscosity values of EP-PA12 X% and EP-CM Y% mixtures at room temperature before any thermal treatment. The samples were subjected to a shear stress of 1 Hz with a 64  $\mu\text{m}$  displacement of the plates. Results obtained have been grouped together on Figure 11. Generally speaking, the mass fraction increase of particulate fillers results in large increase of initial viscosity values of the composites. Regardless of the fillers mass fraction value, the EP-PA12 mixtures continue to present a higher



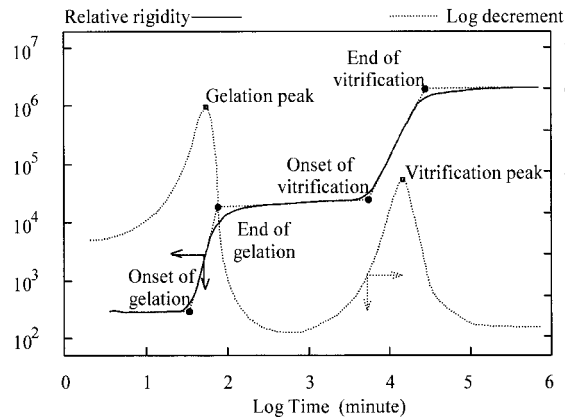
**Figure 11** Comparison of different viscosity models and experimental values of EP-PA12 and EP-CM mixtures with different mass fraction of fillers.

apparent initial viscosity than EP–CM mixtures. In fact, for a filler mass fraction of 60%, the initial viscosity levels are 5 Pa s for the nonreinforced polyepoxy system and 17 Pa s for the EP–CM mixture as opposed to 32 Pa s for the EP–PA12 mixture. Note that only Sato's<sup>55,56</sup> and Einstein's<sup>57</sup> models present an acceptable correlation with the experimental points obtained on the EP–CM Y% materials. For EP–PA12 X% mixtures, the experimental values do not fit with the theoretical curves. In all events, because the modulus of the CM particles is higher than the one of the PA12 particles, the initial viscosity of the EP–PA12 X% mixtures should be lower than the one of the EP–CM Y% mixtures. It is, thus, obvious that the important value of the EP–PA12 X% mixtures initial viscosity can only be due to interactions between the polyepoxy and the PA12 particles. In all cases, it could be expected that the initial viscosity increase of the composite resulting from the addition of particulate reinforcement result in a change in the initial molecular mobility of those reactants present (polyepoxy prepolymer and crosslinking agent). Results observed from the degree of cure (Fig. 5), which in all cases remains at 12% after 1 min at 125°C, leads to the opposite conclusion. In fact, we have seen that during the first seconds of the curing reaction (less than 1 min at 125°C) there were no high molecular transport, and whatever the fillers mass fraction are, the kinetics is not modified. Thus, at that time the analysis performed on the cure kinetics do not reveal any differences between PA12 and CM effects. It is not the case with the initial viscosity.

### Dynamic Mechanical Spectrometry Curves Analysis

In order to study the influence of particulate fillers on the phenomena of gelation and vitrification of EP, we have decided to establish time–temperature–transformation diagrams (TTT diagrams). To this end, we have carried out a series of isotherm tests on EP, EP–PA12 60%, and EP–CM 60%, and by analyzing the evolution of storage shear modulus  $G'$  we have been able to demonstrate the presence of gelation and vitrification. Samples have been subject to a temperature increase at 20°C/min followed by six 1-h isotherms between 80 and 170°C. The results shown come from at least five different tests.

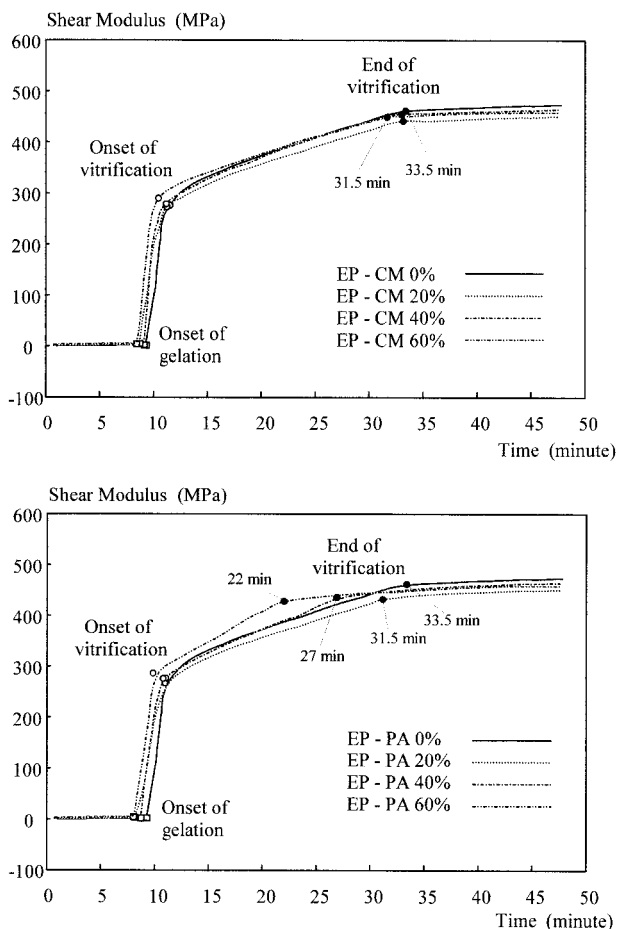
It is important to specify that the curves reported on Figure 12 are only a classical example of the results that could be obtained by DMTA on



**Figure 12** Classical example of DMTA curve for epoxy cure reaction.

epoxy systems during their curing.<sup>63</sup> We are going to use this figure to clearly detail the phase transitions occurring during the curing of epoxies, after which we will perform our own tests. Phase transitions are analyzed from the  $G'$  modulus curves (cf. Fig. 12), whereas generally gelation and vitrification times are determined either from damping peaks visible on the loss factor curve  $\tan(\delta)$ <sup>63</sup> or from the criterion  $G' = G''$ .<sup>64</sup> From these analyses we can determine the beginning and the end of phase transition, both for gelation as well as vitrification. This is in contrast to descriptions carried out from the loss factor curve (cf. Fig. 12), which for gelation only enable the time at which the maximum of molecules reach critical size to be determined (gelation peak on Fig. 12). For the vitrification, only the time at which the maximum of linear molecules bond together to form a glass network (vitrification peak on Fig. 12) can be determined. We have reported on Figure 13 the results of the DMTA tests performed on the EP–A12 X% and EP–CM Y% mixtures while they are cured. Figure 13 shows the evolution of shear modulus  $G'$  of materials while the crosslinking reaction proceeds during isotherm 100°C. Whatever the mass fraction of particulate fillers used, only three mechanical manifestations of the crosslinking process can be observed. The results are relatively different from those traditionally encountered. In fact, on evolution curve  $G'$ , four distinct phases can be observed<sup>40,65,66</sup>: (1) beginning of gelation, (2) end of gelation, (3) beginning of vitrification, and (4) end of vitrification or “full cure.”

Those phases are marked off by different dots directly on the experimental curves (Fig. 13). In the case of the polyepoxy used for our study, vitri-



**Figure 13** Experimental mechanical spectrometry curves at 100°C for different mass fraction of fillers.

fication starts before gelation ends, when the temperatures are, of course, lower than the maximum temperature of glass transition  $T_{g^*}$ . Gillham has already observed this type of reaction.<sup>67</sup> The cause of this phenomenon lies in the fact that the polyepoxy used is a mixture of two distinct prepolymers (cf. Fig. 1). Because of its low steric obstruction the aliphatic prepolymer (BDE) is more mobile than the Novolac. This means that at high temperatures, the aliphatic prepolymer begins to vitrify before Novolac has entirely gelled.

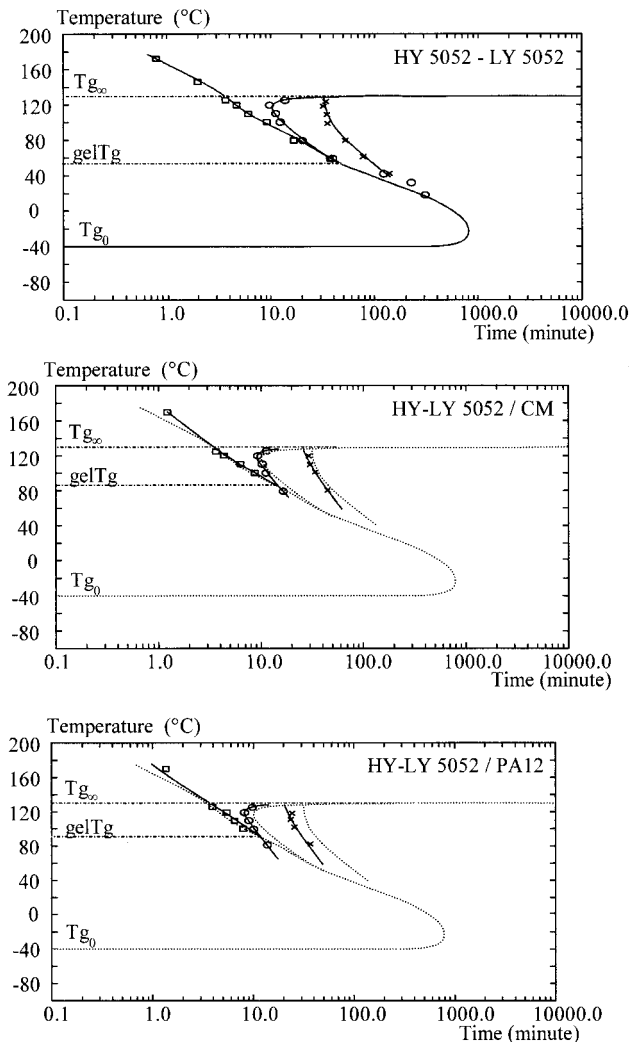
During the first few minutes of reaction (Fig. 13), we notice that regardless of the volume fraction filler, the shear modulus  $G'$  remains constant. It is evident that during the initial reaction phases we are dealing with relatively short molecules (@2 nm), which are unaffected by few longer particulate fillers ( $\cong 50 \mu\text{m}$ ). This situation goes on until the onset of vitrification. After the onset of vitrification, observations reveal that the presence of the PA12 particulate fillers as well as the

increase of the mass fraction of PA12 result in an earlier apparition of the end of vitrification. With isotherm 100°C, vitrification ends, in fact, after 33.5 min for EP alone compared to 22 min for EP-PA12 60%. For the ceramic filler, under the same conditions, the time difference is only 2 min (31.5 min). Given that the amount of particulate fillers PA12 and CM are the same, it is clear that the earlier end of vitrification observed in EP-PA12 is not linked to steric hindrance. If the PA12 particles induced only a steric hindrance, there would be no major differences between the results obtained with the EP-PA12 60% and EP-CM 60% mixtures. So the end of vitrification for the EP-PA12 60% mixture would appear 31 min after the cure cycle beginning instead of 22 min.

### TTT Diagrams

Plotting the point of the start of gelation and the start and end of vitrification on dynamic mechanical spectrometry curves for a series of temperatures (see dots on Fig. 13) has enabled us to determine the evolution of phase transitions. These evolution transferred onto a time-temperature graph form TTT diagrams for each of the materials EP, EP-PA12 60%, and EP-CM 60%. The TTT diagrams show the evolution of the onset of gelation and the onset and the end of vitrification for any temperature, depending on curing time. In other words, this means that the analysis performed hereafter apply to any curing temperature. The construction of TTT diagrams is clearly exposed by Enns and Gillham.<sup>63</sup>

Those diagrams show that the introducing the fillers does not modify gelation onset curves (cf. Fig. 14). At the beginning of gelation, a few chains (made up of bonded prepolymers and polyaminoamide monomers) have reached sufficient size for their mobility to be reduced and for large molecular movements to be impossible.<sup>40</sup> Nevertheless, most part of the chains are still short. As a result, the introduction of fillers on the one hand by steric hindrance produced, and the increase in induced viscosity on the other, only slightly affect the onset of gelation. This explains why, for a degree of cure  $\alpha < 12\%$  the influence of the filler mass fraction is not apparent. In fact, at 125°C, referring to Figure 14, it can be seen that the onset of gelation appears in any cases at least 2 min 30 s after the isotherm beginning. So when  $\alpha = 12\%$  (27 s after the 125°C isotherm beginning) none of the molecules has reached the critical size and the molecular movements remain large. Thus, at that time,



**Figure 14** TTT diagrams for EP, EP–CM 60%, and EP–PA12 60% mixtures.

due to the differences between the particles and molecules sizes there are no steric hindrance.

The onset of vitrification takes place slightly earlier when the filler mass fraction increases. The explanation for this may be as follows. From the moment that gelation begins, reaction takes place between entities with greater and greater molecular mass. The molecular movements that are necessary for the reaction are, therefore, significant (whole molecule displacement). The introduction of filler in the matrix results in an increase in initial viscosity (cf. Fig. 11). Because viscosity is greater, the size of molecules capable of large movements is reduced, which causes the end of gelation, and, thus, an earlier onset of vitrification. Of course, these last remarks find their consequences in the lower degree of cure found in

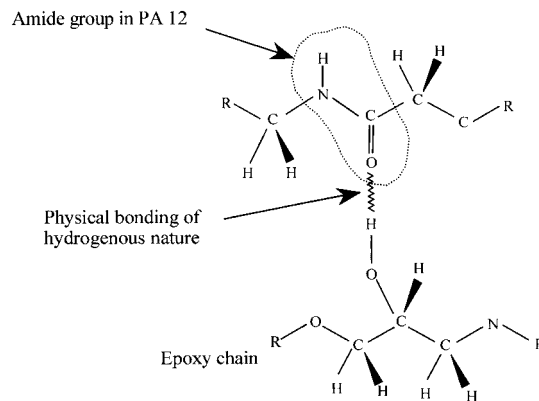
DSC. We can notice, moreover, on TTT diagrams, that the onset of vitrification for EP–PA12 mixture takes place earlier than for the polyepoxy with ceramic filler.

The direct consequence of these two phenomena, i.e., unchanged onset of gelation and earlier onset of vitrification can be found on the TTT diagrams. On these diagrams (Fig. 14) it is to be noted that a significant change occurs in the value of gelTg. The value of gelTg is defined as the temperature at which gelation and vitrification onset coincide. The value of gelTg are for EP alone  $gelTg_{EP} = 52^{\circ}\text{C}$ , for EP–CM  $gelTg_{EP-CM} = 86^{\circ}\text{C}$ , and for EP–PA12  $gelTg_{EP-PA12} = 91^{\circ}\text{C}$ .

During the end of vitrification (“full cure”), molecular movements are severely restricted, and reactions are localized. The introduction of ceramic filler leaves the end of vitrification practically unchanged, as compared with that of the unfilled HY–LY system. For the EP–PA12 60% mixture on the other hand, the end of vitrification takes place really earlier. Viscosity is not a relevant factor here, because the material is, in fact, solid from the moment that vitrification begins. Another phenomenon must be taken into account, therefore, in order to explain the local “blocking” of the reaction. We attributed this to physical bonds between the EP network and PA12. These bonds, suspected elsewhere,<sup>68,69</sup> which can be set up between the epoxy network and PA12, are probably of hydrogenous nature (cf. Fig. 15).

## CONCLUSIONS

Determining the cure kinetics of polyepoxy unfilled resin HY-LY 5052 and the same resin with



**Figure 15** Bonding between epoxy network and amide group of PA 12.

the addition of organic (PA12) and ceramic filler in powder form, in proportions of 0 to 60% by mass, has led us to the following conclusions. The polyepoxy resin reactivity is very high and induces a rapid onset and development of crosslinking reaction. Operational procedure using the mixture take this into account and, consequently, are quick. The fact that the polyepoxy system under observation is a mixture of two distinct prepolymers (cf. Fig. 1), an aliphatic and a Novolac, may explain the absence of crosslinking renewal and of detection of glass transition by DSC regardless of the mass fraction and type of filler, or the degree of cure attained during isothermal treatment. Indeed, if the difference in mobility of two prepolymers is considered to be sufficiently great, it can be thought that the aliphatic prepolymer (BDE) begins to vitrify, thus creating locally its own network with the amine hardener, before the Novolac prepolymer has completely gelled. The material is, thus, made up of a distribution of two micronetworks that cohabit, on the one hand, by the completely crosslinked aliphatic prepolymer (BDE-PAA), and on the other by the partially crosslinked Novolac (Novolac-PAA). The local existence of the micronetwork formed by BDE-PAA, induces a limitation of molecular mobility in the whole material. Consequently, this limitation will prevent further crosslinking of the Novolac-PAA micronetwork. It is probable that both micronetworks have different glass transition temperatures, which leads to a temperature in the transition of the material as a whole, so becoming undetectable by DSC.

Generally speaking, the presence of particulate fillers (PA12 or CM) slows down significantly the cure kinetics and reduces the maximum degree of cure by around 25% for 60% filler by mass. This reduction in the degree of cure, caused by the presence of high proportion of filler, may be explained by hindering of molecular mobility.<sup>46</sup> From a thermal point of view, the presence of particulate fillers does not result in consequent modifications of the composite conductivity. From a rheological point of view, the initial viscosity of the EP-PA12 and EP-CM mixtures always increase with the fillers mass fraction. For example, the initial viscosity of the EP-CM Y% mixtures goes from 5 Pa·s for the polyepoxy alone, up to 17 Pa·s for EP-CM 60%. This corresponds to an increase of 340%. The TTT diagrams established by DMTA reveal time changes in the phase transitions of the EP-PA12 and the EP-CM mixtures. The onset of gelation does not seem to be modified

by the presence of fillers. In fact, at the onset of gelation, the average size of the molecular chains is not sufficiently great for their mobility to be reduced by the introduction of particulate fillers. On the contrary, the vitrification is sensitive to the presence of fillers. Effectively, the increase in initial viscosity due to the introduction of particulate fillers in the matrix reduces the size of molecules capable of large movements, thus advancing the onset of vitrification.

The comparison of the different results obtained on one hand on the polyepoxy system alone and on the other hand on composites with particulate fillers enables to show particular effects of the polyamide 12 fillers with respect to the ceramic fillers. First, for a given fillers mass fraction the polyamide particles induce a greater slow down in the cure kinetics of the polyepoxy system. Consequently, after the same curing the EP-PA12 composites have a degree of cure lower than the EP-CM composites. Effectively after the composites have been cured 15 min at 125°C the degree of cure is only 72% for the EP-PA12 60% versus 79% for the EP-CM 60%. Second, prior to any thermal treatment the EP-PA12 X% mixtures are always more viscous than that of the EP-CM Y%. The experimental results obtained on EP-CM Y% mixtures can always be correctly fitted with theoretical prediction models. This is never the case with the EP-PA12 X% mixtures. Because those models do not take in account the interactions between matrix and fillers, it can be thought that there are some interactions between the polyepoxy network and the polyamide 12 particles. Last, the TTT diagrams show that the end of vitrification take place really earlier in EP-PA12 X% mixtures when increasing the PA12 mass fraction. This phenomenon has not been recorded with the ceramic fillers. This means that the PA12 particles induce a reduction in the mobility of the macromolecules that are in their close vicinity.

These three last points can only be explained by a reduction in the molecular mobility in the EP-PA12 mixtures. As this reduction is never detected in the EP-CM Y% mixtures, it cannot be due to a difference of steric hindrance because the CM and PA12 particles have the same size. The reduction in molecular mobility can only originate from the existence of interfacial interactions between the polyepoxy network and the PA12 particles. Furthermore, because there are no chemical bonds between EP and PA12, those interactions are attributed to physical bonds between the poly-

amides particles and the polyepoxy matrix (Fig. 15).

In our ongoing work we are trying to confirm the existence of physical bonds, probably of hydrogenous type, between epoxy and PA12, by thermally stimulated creep experiments.

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