Cure Kinetics of Epoxy/Anhydride Nanocomposite Systems with Added Reactive Flame Retardants

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ABSTRACT: Montmorillonite nanocomposite systems obtained from epoxy cured using anhydride and the addition of a reacting flame retardant are studied in this paper. In particular, a thermokinetic analysis of the behavior of five different compounds was performed, using a differential scanning calorimeter. The isothermal tests showed double reaction peaks, due to the cure reactions of DGEBA/acid anhydride systems. The comparisons between dynamic thermograms (and between isothermal ones, too) for the different mixtures also showed that the addition of other active substances (such as a nanofiller or a flame retardant additive) does not change the mechanism of crosslinking from a qualitative point of view, but both the nanoreinforcement and the flame retardant seemed to exert an evident catalytic action on the cure reactions. A model describing the cure behavior of the aforementioned materials is proposed in this work. This model takes into account the fact that the reaction mechanism of each analyzed system is composed of a couple of parallel phenomena: the fast opening of anhydride ring (corresponding to a first exothermic peak and characterized by "*n*-th order" kinetics) and resin networking (corresponding to a second exothermic peak and characterized by an "auto-catalytic with zero initial velocity" behavior). The verification of the proposed model was performed by means of a comparison between experimental data (normalized curves derived from DSC thermograms) and theoretical data (derived from a numerical integration—using the second order Runge–Kutta method—of the model-representative equation) and provided very good results. This allows one to apply such a model to any engineering process problem concerning the cure of DGEBA/acid anhydride/ phyllosilicate nanocomposite systems. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 1676–1689, 2004

Key words: nanocomposites; differential scanning calorimetry (DSC); thermosets; epoxy; montmorillonite

INTRODUCTION

Nanocomposites based on polymers and inorganic layered clays have been the subject of increased interest in the scientific and industrial community due to their potential and promising properties. Common polymer composites usually involve a relative high amount of inorganic filler (in the order of 10% in weight) for imparting desired characteristics. However, this content of inorganic filler causes a deterioration of material properties, such as an increase in product density and a loss of tenacity due to the lack of interfacial compatibility between the organic polymer and inorganic filler. Moreover, the poor dispersion of the inorganic filler (with the increase in relative filler content) requires a high torque level of the mixing equipment, worsening processability.

In nanocomposites, however, a small amount of clay may produce enhanced mechanical and thermal properties due to the large contact area between the polymer and clay through a nanoscaled hybrid. In addition, the layered structure of clay with a high aspect ratio provides enhanced barrier properties, such as low gas permeability, high chemical resistance, and flame retardance.[1]

Nanocomposites can represent a valid alternative to traditional materials in electronic applications, where a combination of mechanical, thermal, and physical properties are required. In particular, thermosetting materials used for circuit boards and other applications (such as high quality LED production or IC encapsulation) can gain benefits from nanocomposite technology. The rising interest in epoxy/silica nanocomposites is, therefore, a consequence of the fact that this new class of materials can assure better electrical insulation and good fire resistance, while keeping the same processing characteristics of pure casting resins and mechanical properties that are similar to traditional short fiber-reinforced composites.

Cyclic acid anhydrides are used as curing agents in many important applications of epoxy resins owing to the advantages that they offer in comparison to traditional amine-based curing agents[2,3]:

lower toxicological hazard;
lower heat release during polymerization;
longer working life;

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TABLE I
Theoretical Compositions of Analyzed Compounds (every 100 g of resin)

Mixture	DGEBA	Montmorillonite	MTHPA	Imidazole	Flame retardant
1	100 g	/	90 g	1.92 g	/
2	100 g	/	90 g	2.24 g	11.23 g
3	100 g	21.06 g	90 g	/	/
4 (Nano)	100 g	21.06 g	90 g	2.24 g	11.23 g
5 (Micro)	100 g	21.06 g	90 g	2.24 g	11.23 g

better thermal stability of cured systems: only when using acid anhydrides is it possible to obtain epoxy resins with a heat distortion temperature (HDT) higher than 250°C and maintain some electrical and physical properties up to 150°C; high compatibility with epoxy resins, which leads to a strong reduction of the viscosity of the resin system.

Acid anhydrides are also preferred to organic acids, since the latter are generally less soluble in resins and also release more water during the cure process, which leads to the product foaming. Care must be taken, however, during storage due to the hygroscopic characteristics of anhydrides.

The chemical reactions that take place during the cure process affect resin morphology, which in turn determines the behavior of the cured system. For this reason, in the last few years, the relationships between processing, morphology, and properties of a wide range of epoxy systems have been intensely investigated.[1,4] Such investigations pointed out that the key for optimal cure is represented by a deep understanding of curing mechanisms and cure kinetics, which allows one to model the reaction processes as accurately as possible. In this framework, the elaboration of an appropriate kinetic equation and therefore the evaluation of reaction orders, activation energies, and frequency factors of the cure process are of fundamental importance. Since the behavior of a thermosetting polymer is strongly affected by the curing process, poorly controlled cure can produce unwanted variations in the thermal and rheological properties of the system during the manufacturing processes and of the final product.[4] Therefore, an accurate model not only helps to monitor the evolution of the curing system (to plan and/or to control single processes), but it can also be used in material design to compare the behaviors of different formulations, obtained mixing several resins, catalysts, additives, or fillers.

Although several studies have been carried out on the modeling of the kinetic behavior of thermosetting resins, the variety of resin formulations actually implies a continuous study and introduces new experimental difficulties and complexities. For example, a complete understanding of the cure mechanisms and kinetics of epoxy resin/cyclic anhydride systems is not yet available, despite the consistent number of models proposed to date in open literature.[1–4,5,6] Moreover, switching to nanocomposites introduces a further variable in the complexity of the modeling problem, as the effects of the nanofillers and the compatibilizer somehow affect the reaction kinetics.

This article proposes a model based on thermal analysis experiments to describe the cure mechanisms and cure kinetics of a nanocomposite based on epoxy matrix (DGEBA)/phyllosilicate (montmorillonite) cured with methyl-tetrahydrophtalic anhydride (MTHPA). The model was developed mainly using differential scanning calorimetry (DSC) to produce data related to the evolution of the cure process both in isothermal and in dynamic tests. Dynamic scans at different heating rates were performed on five different compounds (listed in Table I) to make a comparison between the different cure reactions and consequently to determine possible variations induced by the addition of a flame retardant or by the use of a specific type of nanofiller. Thereafter, the isothermal cure processes at different temperatures for each aforementioned system were analyzed to calculate the temperature dependence of the kinetic parameters and to consider the effects of diffusion control phenomena during the isothermal reaction.

All collected data were then processed to determine a kinetic model for the cure reaction, which could also take into account the fact that the epoxy systems cured in isothermal conditions with acid anhydrides showed two exothermic peaks (unlike DGEBA/diamine systems, which are characterized by only one exothermic peak during isothermal cure). The developed model (consisting, as will be seen, in a simple superposition of two elementary models) was finally verified comparing the model predictions and the experimental data.

REACTION KINETICS

The cure of epoxy matrices for composites is characterized by complex reactions that depend upon many concurrent factors, such as temperature, type of hardener, and catalysts. In the last few years, several empirical equations describing the behavior of such sys-
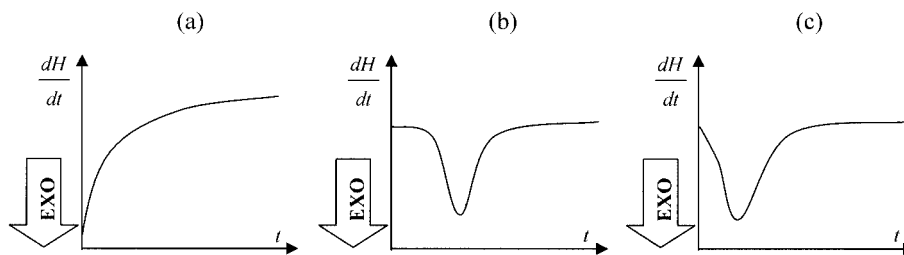
Figure 1 DSC thermograms produced by a curing system: (a) *n*-th order kinetics; (b) auto-catalytic behavior; (c) generalized auto-catalytic behavior.

tems during the cure cycle were published in open literature.

Dynamic and isothermal DSC analyses are widely used to obtain an indirect estimation of the degree of cure of a thermosetting system, assuming that the heat released during polymerization is always proportional to the consumption rate of reactive groups (which actually describes the extent of the reaction). Calorimetric data can therefore be used to create and verify both theoretical and empirical kinetic models and, obviously, to calculate kinetic parameters.[4]

A fundamental step for the interpretation of experimental DSC data is represented by the definition of the degree of cure, α:

$$\alpha = \frac{H(t)}{\Delta H_R} \tag{1}$$

where $H(t)$ is the total heat released between the start of reaction and the time t, and ΔH_R is the total heat of reaction, determined through the integration of a thermogram obtained during a dynamic scan at a controlled heating rate. The DSC provides indeed the heat flow (dH/dt), or instantaneous heat, released or absorbed by the reactive system as a function of the absolute temperature or time.

An expression of the reaction rate can be obtained by differentiating eq. (1):

$$\frac{d\alpha}{dt} = \frac{1}{\Delta H_R} \cdot \frac{dH}{dt} \tag{2}$$

Combining dynamic and isothermal calorimetric analyses, it is therefore possible to determine the variations of the degree of cure and the rate of cure as a function of time and/or temperature. DSC data may in turn be used to develop a kinetic model able to describe the cure process. In a polymerization process, the most general kinetic model can be expressed by the following equation:

$$\frac{d\alpha}{dt} = K(T) \cdot f(\alpha) \tag{3}$$

where $K(T)$ is a temperature-dependent parameter and $f(\alpha)$ is a function of the degree of cure that contains all the necessary information regarding the running process (to be determined by best fitting the experimental results).[4]

The kinetic constant $K(T)$ is generally characterized by an Arrhenius-type temperature dependence:

$$K(T) = K_0 \cdot \exp\left(-\frac{E_a}{RT}\right) \tag{4}$$

where K_0 is a pre-exponential temperature-independent factor (frequency factor), R the universal gas constant, T the absolute temperature, and E_a the activation energy of the process (which may also be seen as the energy barrier to be overtaken to start the reaction).

The shape of the $f(\alpha)$ depends upon the behavior of the cure reaction, that is, whether it follows *n*-th order kinetics or is an auto-catalytic reaction. Figure 1 represents schematically the isothermal thermograms given by three different types of reacting systems. A reaction following *n*-th order kinetics (Fig. 1a) is characterized by a single peak of the $d\alpha/dt$, which is obtained at the beginning of the reaction (always corresponding to a null value of the $\alpha(t)$). Such an identification derives from the fact that for this class of reaction, the shape of the $f(\alpha)$ is given by the following equation:

$$f(\alpha) = (1 - \alpha)^n \tag{5}$$

where n is a parameter simply dependent upon the cure mechanism.

The evolution of the degree of cure for an *n*-th order kinetics reaction can therefore be described by combining eqs. (3), (4), and (5):

$$\frac{d\alpha}{dt} = K_0 \cdot \exp\left(-\frac{E_a}{RT}\right) \cdot (1 - \alpha)^n \tag{6}$$

The term "auto-catalytic reaction," on the contrary, means that the molecules formed in the first steps of
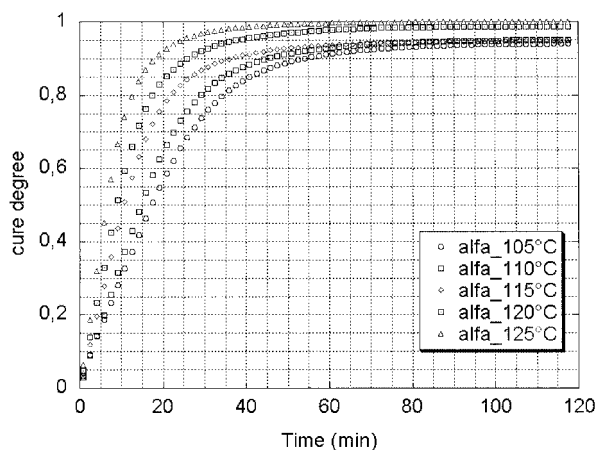
Figure 2 Degree of cure versus time for a DGEBA/MTHPA system cured under isothermal conditions at different temperatures.

the reaction catalyze successive steps, so that the rate of polymerization increases with time. An auto-catalytic reaction is therefore characterized by a peak of the heat flow (proportional by hypothesis to the rate of polymerization) corresponding to a degree of cure strictly higher than zero, and the corresponding kinetic model can be written in the following form:

$$\frac{d\alpha}{dt} = (K_1 + K_2 \cdot \alpha^m) \cdot (1 - \alpha)^n \tag{7}$$

where K_1 and K_2 are kinetic parameters related to temperature by an Arrhenius-type law (similar to that described in eq. (4)).

It is worth pointing out that in an auto-catalytic reaction, the initial rate of cure (i.e., the value of $d\alpha/dt$ when $\alpha = 0$) is usually different from zero (Fig. 1c). A reaction characterized by a zero initial velocity should have an identically null K_1 parameter (Fig. 1b); and a null K_2 parameter, on the contrary, means a return to n-th order kinetics.

Eq. (7) does not perfectly describe the polymerization of a thermosetting system in isothermal conditions. As shown in Figure 2, the complete cure of the resin is not always reached during isothermal polymerization. This behavior depends upon the fact that

during polymerization the glass transition temperature (T_g) of the system increases progressively, so that molecular mobility diminishes as the T_g of the networking system reaches the cure temperature and the reaction becomes diffusion controlled. At lower temperatures, the reaction therefore ends before the complete consumption of all reactive groups. The maximum degree of polymerization (α_{max}) reached by a polymeric system during an isothermal cure can be empirically related to curing temperature by a linear function[3]:

$$\alpha_{max} = a + b \cdot T \tag{8}$$

where a and b are constants, and α_{max} reaches unity at every T higher than a critical temperature $T_{g\infty}$ close to the glass transition temperature of a complete cured resin.

It can therefore be assumed that the rate of cure d_α/dt is zero when $\alpha = \alpha_{max}$, this condition corresponding to a stop of the reaction. With these assumptions, an auto-catalytic kinetic model can be more correctly described as follows:

$$\frac{d\alpha}{dt} = (K_1 + K_2 \cdot \alpha^m) \cdot (\alpha_{max} - \alpha)^n \tag{9}$$

EXPERIMENTAL

All the calorimetric tests were carried out on a Mettler-Toledo DSC822e400 differential scanning calorimeter, controlled by a computer and connected to an intracooler unit that allowed the rapid cooling of the samples. Theoretical compositions of all the analyzed compounds are shown in Table I. Every compound was based on a mixture of 90 parts of MTHPA (commercial name: HY917, produced by VANTICO Ag, Basel, Switzerland) for every 100 parts of DGEBA (commercial name: LY575, produced by VANTICO Ag), to which 5 wt % of phosphorous-based reactive flame retardant (namely BIS-P, synthesized by the University of Catania, whose formula is shown in Fig. 3) was added. In some formulations, 1 wt % of a cure accelerator (imidazole) was eventually added.
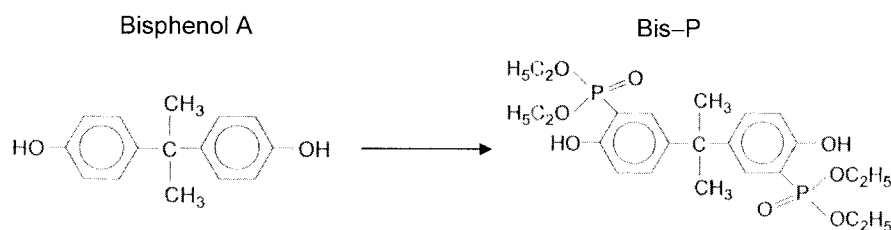

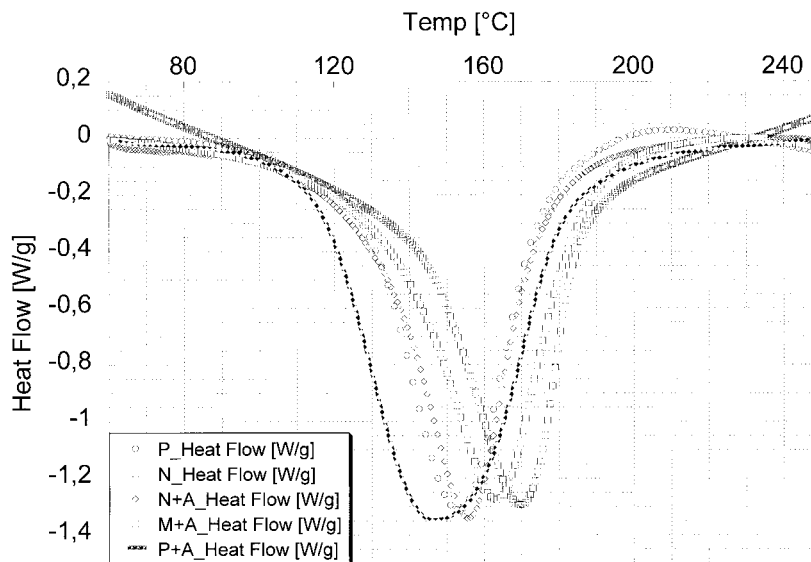**Figure 3** Bis-P flame retardant as a by-product of Bisphenol A.

Figure 4 DSC dynamical thermograms (heating rate: 10°C/min) produced by five different mixtures: pure resin (P, mixture 1), pure resin with flame retardant (P+A, mixture 2), nanocomposite without flame retardant (P+A, mixture 3), nanocomposite with flame retardant (N+A, mixture 4), and microcomposite with flame retardant (M+A, mixture 5).

Nanocomposites were obtained adding organo-modified montmorillonites (Nanofil® 848 by Süd Chemie, Ag, Munich, Germany to obtain a fully exfoliated structure, i.e., a "nanocomposite," or Nanofil® 757 by Süd Chemie to obtain a "microcomposite" structure) to the above-mentioned formulations. The mixture was kindly prepared by the University of Turin in a preintercalated form obtained by means of a sonication treatment at 80°C. In each case, the nanoreinforcement was added to the resin with a mixing ratio of 17.4 wt % to obtain an overall content of about 10 wt % of nanofiller in the composite.

Every compound, once prepared, was immediately submitted to both isothermal and dynamic scans, to avoid any secondary effect due to the hygroscopic and/or environmental aging of the nonreacted compound. All tests were performed in a nitrogen atmosphere, at temperatures varying from 60 to 250°C. Every sample had a mass of about 20 mg, which ensured a good signal of the heat flux without losing the homogeneity of the temperature field within the DSC crucible.

RESULTS AND DISCUSSION

Figure 4 shows a comparison between the dynamic thermograms obtained by heating the aforementioned analyzed formulations from 60 to 250°C, at a heating rate of 10°C/min. Two main indications are provided by those thermograms. First, although the polymerization of epoxy/anhydride systems is characterized by very complex reactions, a single exothermic peak is observed for all the formulations. Second, the shape of the thermograms is slightly influenced by the composition of the relative mixture. To evaluate the effect of the components on the reaction kinetics, it is therefore necessary to analyze the parameters of all the reactions, such as total heat released during polymerization (ΔH_R), the initial and the final cure temperatures (T_s, T_f), and the reaction peak temperature (T_{peak}). These parameters have been listed in Table II for each analyzed compound.

To develop an appropriate kinetic model, the heat flow and the total heat released during the polymerization were normalized by dividing them by the mass

TABLE II
Average Experimental Data Relative to Dynamical Test

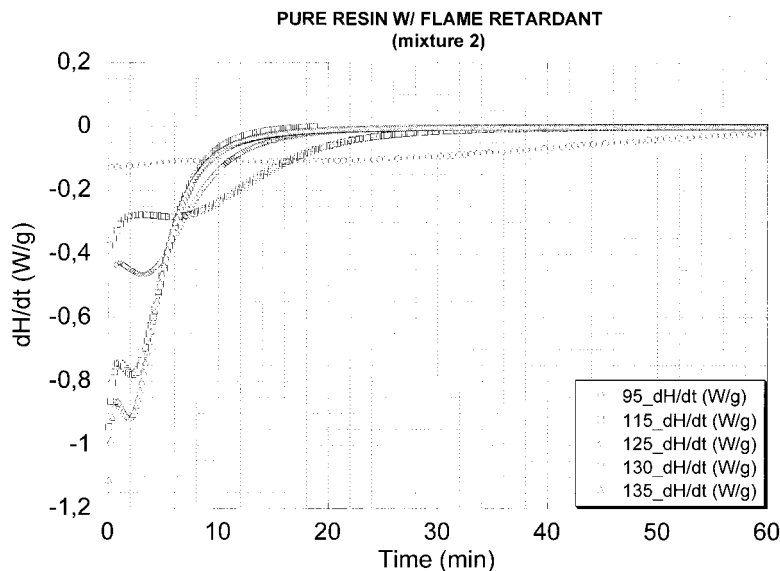| Mixture	Cure start temperature T_i [°C]	Cure end temperature T_f [°C]	Reaction peak temperature T_{peak} [°C]	Total heat of reaction ΔH_R [J/g]
1 (P, pure)	~ 90	~ 205	~ 155	~ 290
2 (P + A, p. w/ f.r.)	~ 80	~ 210	~ 150	~ 325
3 (N, n. w/o f.r.)	~ 120	~ 200	~ 170	~ 300
4 (N + A, n. w/ f.r.)	~ 50	~ 230	~ 155	~ 300
4 (M + A, m. w/ f.r.)	~ 60	~ 225	~ 165	~ 320

Figure 5 Heat flow versus time for isothermal tests performed at 95°C, 115°C, 125°C, 130°C, and 135°C, respectively, on a system containing pure resin with flame retardant.

of reactive species such as the resin, the curing agent, the accelerator, and the flame retardant.

It has been shown[7] that for the pure DGEBA/anhydride system, the crosslinking reaction only starts at temperatures higher than 300°C. Since this behavior is not compatible with the most common manufacturing processes, it is necessary to include at least one more component, which can act as a catalyst in the formulation. The systems studied in this work contained imidazole (mixture 1) or the nanofiller (mixture 3) that could catalyze the anhydride-epoxy systems. Even though it does not take part in the matrix networking, the phyllosilicate, in fact, plays an important role in the control of the cure reaction.

Analyzing Table II, it is evident that the addition of a flame retardant to the pure resin (mixture 2) leads to the following considerations:

a reduction of both the starting temperature and the reaction peak temperature, in comparison with mixture 1. These effects may also be associated with some of the catalytic effects of BIS-P, due to the presence of two hydroxyl groups in its molecule;

the end of the cure is shifted at higher temperatures, probably because of lower chain mobility, which in turn may be ascribed to the presence of a reacted phase that prevents the formation of further chemical bonds. It is therefore necessary to reach higher temperatures to complete the cure;

a steep increase in the total heat of reaction, which is a consequence of the participation of the catalytic behavior of the flame retardant in the crosslinking reaction.

The latter two observations were also valid for the nanocomposite (mixture 4) and for the microcomposite (mixture 5), even though the aforementioned effects appeared more bland. The flame retardant and the phyllosilicate kept their catalytic action (as testified by both the reduction of the curing start temperature and the increase of total heat of reaction with respect to those of the pure resin), but at the same time an intensification of the obstacles to chain mobility as the reaction proceeds could be observed (so that the cure reaction reaches its maximum rate later than in the case of the pure resin of the same composition).

The microcomposite has also shown a T_s and a T_{peak} higher than those of nanocomposites, as the lack of nanofiller exfoliation causes a dispersion of reactants no longer balanced by a surface increment of the reactive substrate in the system. On the other hand, the presence of dispersed phases in the micrometer range favors molecular mobility at the end of the networking process, so that a reduction of the T_f and an increase of ΔH_R may be observed for the microcomposite with respect to the fully exfoliated structure.

To complete the modeling of the reaction kinetics and to take into account the autocatalytic behavior of the studied system, isothermal tests were also performed. Figures 5 to 9 show the thermograms obtained for each studied compound in a temperature range that is typical of the most common manufacturing processes.

Before analyzing the information given by each single thermogram, it should be emphasized that the double peak that is visible in the isothermal scan does not represent instrument settling.[4,6,8,9] All the epoxy-anhydride mixtures studied in this work, in fact, presented this double peak, which was also shifted at
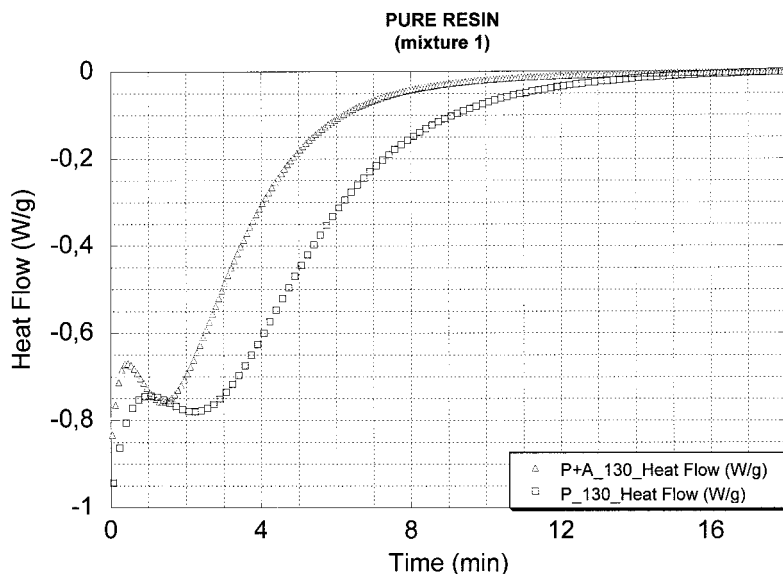
**PURE RESIN
(mixture 1)**

Figure 6 A comparison between DSC isothermal tests at 130°C performed on a pure resin system (mixture 1) and on a pure resin system containing flame retardant, respectively. Note the catalytic effect produced by the flame retardant, which speeds up the achievement of the limit degree of conversion.

higher times at lower temperatures, thereby indicating the effect of the sample reaction kinetics and not of the instrumental apparatus. The presence of two exothermic peaks (easily detectable at temperatures lower than 160°C) has been interpreted as a result of two simultaneous reactions, which could correspond to the anhydride ring opening and to the polymer networking by esterification, respectively, in a mechanism which is schematized in Figure 10.

A comparison between the behaviors of the analyzed compounds also showed that the morphology of

different thermograms is not affected by the addition of a nanofiller and/or flame retardant. However, calorimetric measurements exhibited a strong dependence of peak width (i.e., of the duration of both reactions) not only on cure temperature, but also on the characteristics of the analyzed compound:

The presence of a flame retardant alone (mixture 2, Fig. 6) favors an anhydride ring opening process (as shown by the increase of heat flow of the first peak), and speeds up the resin crosslinking (the
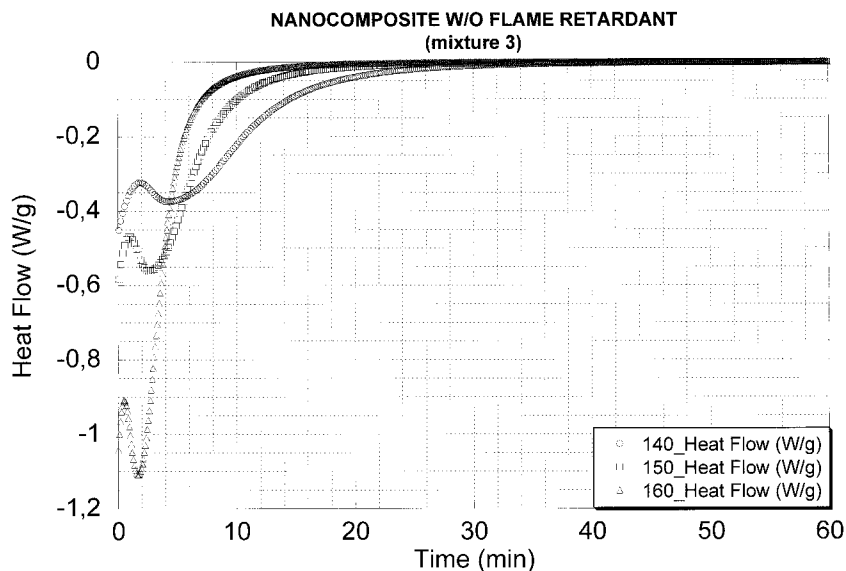
**NANOCOMPOSITE W/O FLAME RETARDANT
(mixture 3)**

Figure 7 Heat flow versus time for isothermal tests performed at 140°C, 150°C, and 160°C, respectively, on a nanocomposite system cured without imidazole (mixture 3). The system reacts in a similar manner, but it is necessary to reach higher temperatures to finish the cure within a reasonable time.
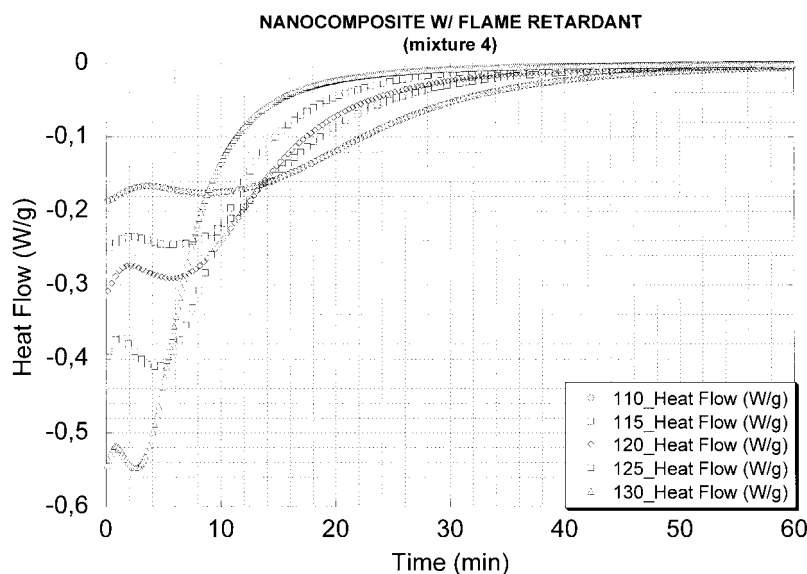
Figure 8   Heat flow versus time for isothermal tests performed at 110°C, 115°C, 120°C, 125°C, and 130°C, respectively, on a nanocomposite system containing flame retardant.

second peak appears at lower times). Neither of these phenomena depend on the cure temperature;
The presence of fully exfoliated Nanofil® 848 does not provide a noticeable increase in anhydride reactivity (mixtures 2–4, Figs. 5–8) and slightly worsens the reactivity of the epoxy resin;
In the system containing intercalated Nanofil® 757 (mixture 5, Fig. 9), the reactivity of the anhydride remains unchanged in comparison to the nanocomposite system, while a substantial worsening of resin reactivity in the former stages of the cure process is observed. Furthermore, the end of the

reaction takes place at approximately the same time as the case shown in Figure 8 (nanocomposite, mixture 4). This confirms the fact that the reduction in catalytic effects due to the lack of nanopowder exfoliation is fully compensated by a higher chain mobility because of the reduced effective volume fraction of dispersed particles.

THERMOKINETIC MODELING

It has already been observed[6,9] that an incomplete networking process during an isothermal cure may be
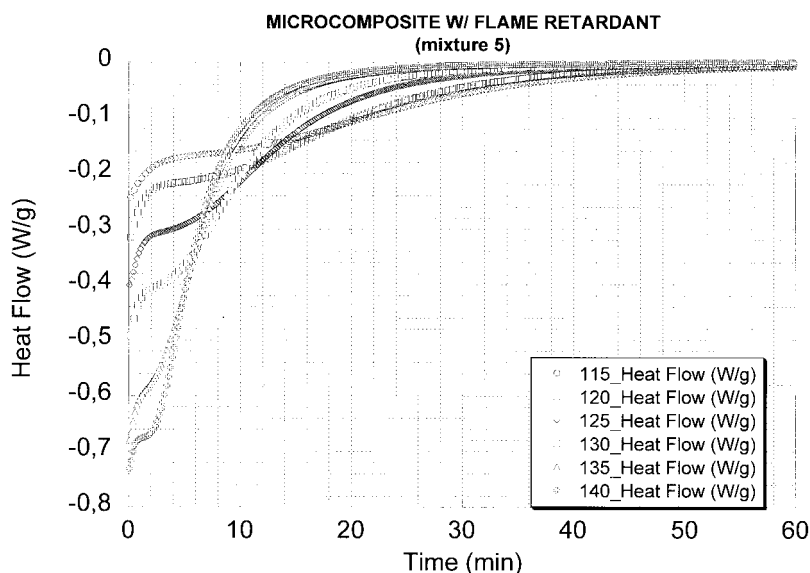

Figure 9   Heat flow versus time for isothermal tests performed at 115°C, 120°C, 125°C, 130°C, 135°C, and 140°C, respectively, on a microcomposite system containing flame retardant.
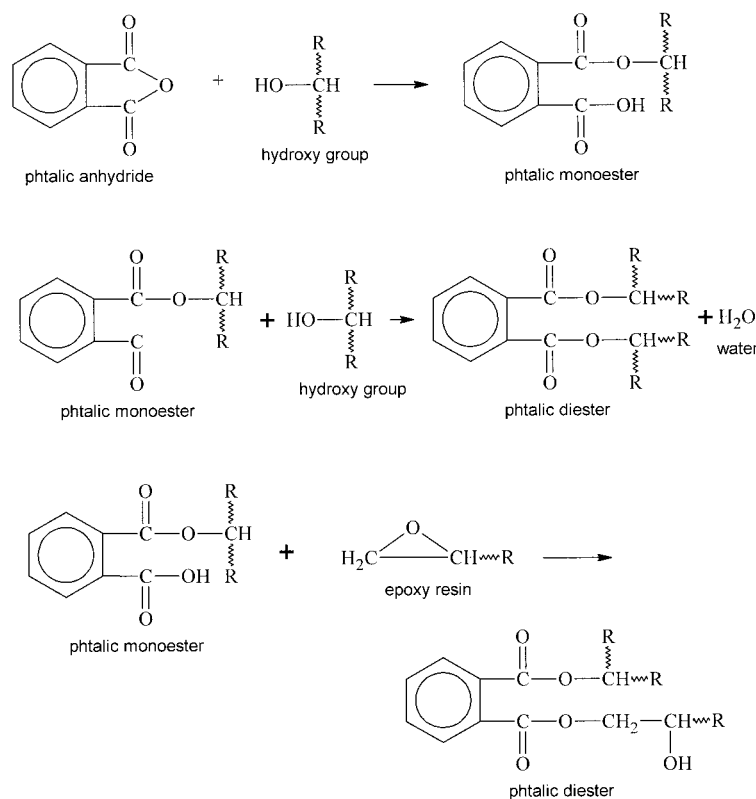
Figure 10 Top: anhydride ring opening through a hydroxylic group to give a monoester. Center: reaction between the monoester and another hydroxylic group to give a diester. Bottom: reaction between the monoester and an epoxy group to form a diester.

justified by the rising of diffusion control effects, which in turn are a consequence of the diminishing molecular mobility in the forming network (i.e., the glass transition temperature of the forming system falls just above the cure temperature). For this reason, it is necessary to characterize the evolution of a polymeric system through the degree of cure $\alpha(t)$, defined as the ratio between the total heat released up to the time t in isothermal conditions and a reference value (usually taken as the total heat ΔH_R released during a dynamic scan):

$$\alpha(t) = \frac{\Delta H(t)}{\Delta H_R} = \frac{1}{\Delta H_R} \cdot \int_0^t \frac{dH}{dt} \cdot dt = \int_0^t \frac{d\alpha}{dt} \cdot dt \quad (10)$$

Following the above-mentioned procedure, it is possible to determine the maximum degree of cure (α_{max}) reached by the system as a function of the cure temperature. The different values are listed in Table III and graphically represented in Figure 11, where a linear dependence of α_{max} on temperature T, as described by eq. (8), can be assumed.

A reliable thermokinetic model should therefore contain some element accounting for the substantial impossibility of the system to reach complete conver-

sion at low curing temperatures. An option to take into account the above considerations consists of considering the reaction rate ($d\alpha / dt$) as a direct function of the term ($\alpha_{max} - \alpha$).[9] With this assumption, the reaction rate becomes zero when the degree of cure reaches its actual maximum value. This means, for example, that the velocity of a generalized auto-catalytic reaction can be described by eq. (9).

However, the aforementioned solution introduces a parameter (α_{max}) in the model that not only depends upon the cure temperature and the system composition, but is also affected by a great uncertainty deriving from the complexity of steps to be taken to determine the degree of cure $\alpha(t)$. For this reason, in the present work, the method described by Dusi et al.,[10,11] who defined an "isothermal" or "normalized" degree

TABLE III
Maximum Degree of Reaction at Different Temperatures

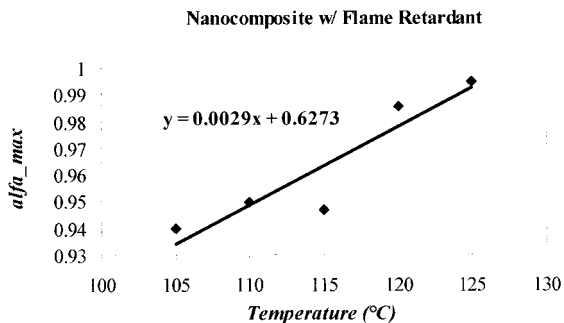| Temperature (°C)	α_{max} (Nanocomposite—Mixture 4)
105	0.940
110	0.950
115	0.947
120	0.985
125	0.995

Figure 11 Maximum degree of cure versus temperature and relative trend-line for the nanocomposite system containing flame retardant.

of cure (α_{norm}) taking the total heat released during an isothermal polymerization as a reference, is preferred:

$$\Delta H_{iso} = \int_0^t \frac{dH_{iso}}{dt} \cdot dt \qquad (11)$$

The analysis of the reaction kinetics was carried out using nonlinear regression analysis. The heat flow was first of all numerically time-integrated to determine the shape of the curve $H_{iso}(t)$. This curve was divided by the total heat of reaction ΔH_R to obtain the function $\alpha(t)$, which represents the degree of cure. Thereafter this curve was divided by its maximum value (obviously corresponding to the end of the cure) to obtain the normalized reaction degree $\alpha_{norm}(t)$. This parameter was finally time-differentiated to obtain the isothermal cure velocity $d\alpha_{norm}/dt$.

In this way the reaction rate of the previous example may again be expressed in a simplified form:

$$\frac{d\alpha_{norm}}{dt} = (K_1 + K_2 \cdot \alpha_{norm}^m) \cdot (1 - \alpha_{norm})^n \qquad (12)$$

The effective and the normalized cure rates are related by a linear correlation as follows:

$$\frac{d\alpha}{dt} = \frac{H_{iso}(T)}{\Delta H_R} = \frac{\Delta H_{iso}}{\Delta H_R} \cdot \frac{d\alpha_{norm}}{dt} = \alpha_{max}(T) \cdot \frac{d\alpha_{norm}}{dt} \qquad (13)$$

The normalized reaction degrees at different temperatures are plotted in Figure 12 as functions of time for the nanocomposite system containing the flame retardant. It must be emphasized that in this case, a temperature rise only causes an increase in the slope of the first portion of any curve.

In the second stage of elaboration, the isothermal cure velocity has been drawn as a function of the normalized conversion degree α_{norm}. It is clear that the presence of a couple of reaction peaks does not allow the application of simplified models, such as the auto-catalytic model represented in eq. (9),[12] which is based on a linear fitting of experimental curves represented in a log-log plot (i.e., [da/dt] versus ln [a]).

In our case, it was therefore necessary to use a nonlinear regression analysis under the hypothesis that the experimental curves can be described as a simple addition (parallel model) of two peaks, the first represented by a "n-th order reaction" kinetic model:

$$\frac{d\alpha_1}{dt} = K_1 \cdot (1 - \alpha_{norm})^{n_1} \qquad (14)$$

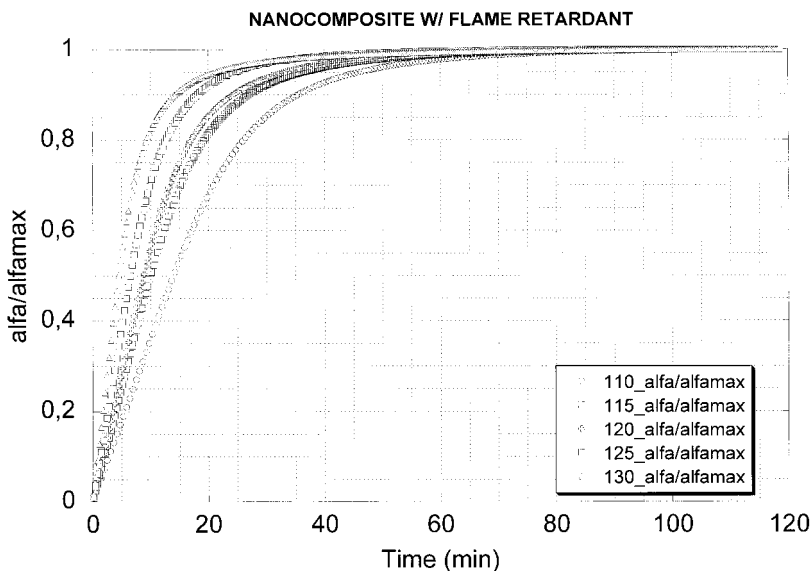and the second corresponding to an "auto-catalytic reaction with a zero initial velocity":

Figure 12 Normalized degree of cure for the nanocomposite system containing flame retardant.
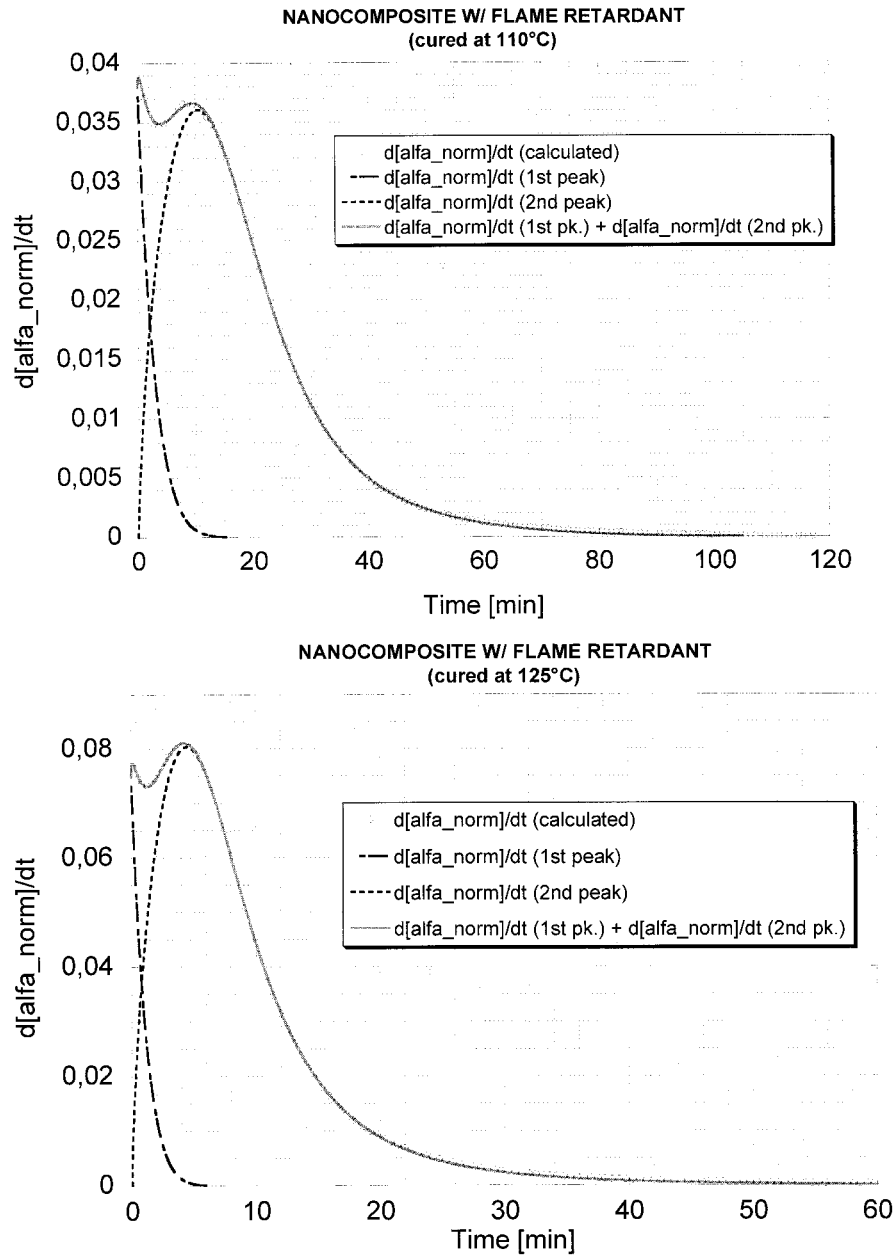
Figure 13 Examples of peak separation at different temperatures for the nanocomposite system containing flame retardant.

$$\frac{d\alpha_2}{dt} = K_2 \cdot \alpha_{norm}^{m_2} \cdot (1 - \alpha_{norm})^{n_2} \qquad (15)$$

For kinetic constants, an Arrhenius-type temperature dependence has been assumed:

$$\ln[K_i(T)] = \ln[K_{0i}] - \frac{E_{ai}}{R} \cdot \frac{1}{T} \qquad (16)$$

Once having found the reaction pseudo-orders and the kinetic constants for both peaks, a numerical integration of the relative functions was performed to obtain a first outline of the curve representing a nor-

malized α versus time (which is conventionally recognized as the "numerical track"):

$$\frac{d\alpha_{norm\_num}}{dt} = \frac{d\alpha_1}{dt} + \frac{d\alpha_2}{dt} \Rightarrow \alpha_{norm\_num} = \alpha_1(t) + \alpha_2(t)$$

$$(17)$$

Examples of peak separation at different temperatures for the flame-retarded nanocomposite system are given in Figure 13. The good correspondence between the experimental curve $(d\alpha_{norm}/dt)$ and the one derived from the application of the proposed model $[(d\alpha_1/dt) + (d\alpha_2/dt)]$ must be emphasized.
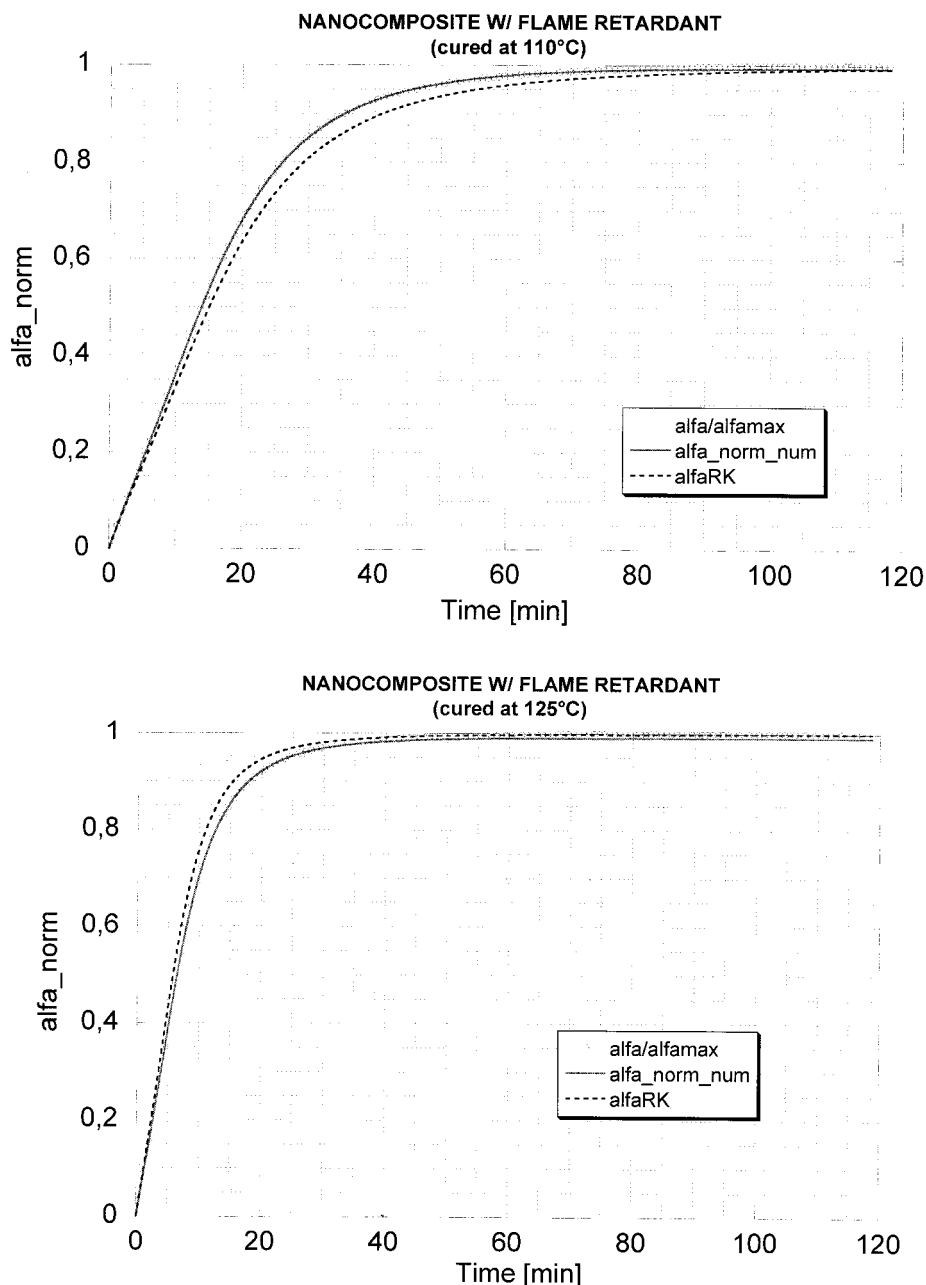
Figure 14 A comparison among the normalized experimental degree of cure, the normalized numerical integration of the heat flow curve, and the Runge–Kutta integration of the proposed model, for isothermal cures performed at 110°C. The reference system is still a nanocomposite containing flame retardant additive.

The temperature dependence of the intersection point between the theoretical peaks has also been investigated, finding once again an exponential dependence:

$$t_{\text{int}} = t_\infty \cdot \exp\left(\frac{\beta}{T}\right) \Rightarrow \ln[t_{int}(\text{min})] = \ln[t_\infty] + \frac{\beta}{T} \quad (18)$$

The average kinetic parameters of the pure resin and the nanocomposite (with or without the flame retardant additive) are listed in Table IV.

Previous considerations are not, however, sufficient to confirm the validity of the proposed thermokinetic model. A correct model should, in fact, be able to

TABLE IV
Average Kinetic Parameters

Mixture	ln [t_∞]	β
2 (P+A, p. w/f.r.)	−35.599	14007
4 (N+A, n. w/f.r.)	−21.249	8405
5 (M+A, m. w/f.r.)	−21.973	8664

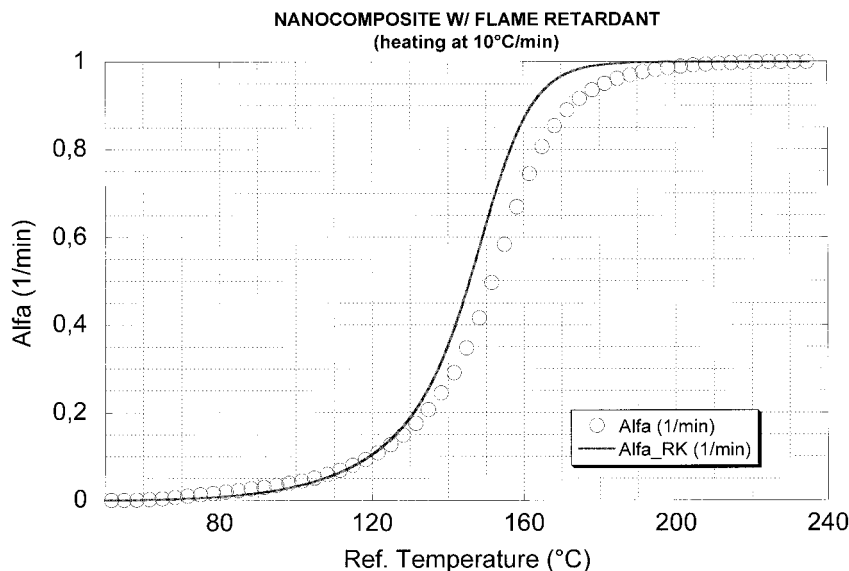**NANOCOMPOSITE W/ FLAME RETARDANT**
(heating at 10°C/min)

Figure 15 A comparison between the normalized experimental and the Runge–Kutta integration of the proposed model, for a dynamical cure (heating rate: 10°C/min).

foresee the behavior of a given polymeric system not only for a particular combination of temperature and cure time, but also for a wide range of conditions to which the system may be exposed. For this reason, the model should describe the evolution of the cure degree $\alpha(t)$ once both the properties of the reactive system (e.g., activation energies, kinetic constants, etc.) and the environmental conditions have been defined. In other words, the correctness of the model must be confirmed through the integration of the theoretical curves:

$$\begin{cases} \dfrac{d\alpha_{norm}}{dt} = K_1 \cdot (1 - \alpha_{norm})^{n_1} + K_2 \cdot \alpha_{norm}^{m_2} \cdot (1 - \alpha_{norm})^{n_2} \\ \ln[K_1] = \ln[K_{01}] - \dfrac{E_{a1}}{R \cdot T}; \quad \ln[K_2] = \ln[K_{02}] - \dfrac{E_{a2}}{R \cdot T} \end{cases}$$

(19)

starting from a set of characteristic parameters of the analyzed compound for each reaction peak (n_1, m_2, n_2, $\ln[K_{01}]$, $\ln[K_{02}]$, E_{a1}, E_{a2}) and for user-defined curing conditions (temperature and cure time).

Since an algebraic integration of the differential eq. (19) was impossible, it was necessary to implement an algorithm for its numerical integration, based on the second order Runge–Kutta method. In Figure 14, a comparison between the shapes of the numerical track $\alpha_{norm\_num} = \alpha_1(t) + \alpha_2(t)$, the numerically integrated curve a_{RK} (t), and the normalized experimental curve $\alpha_{norm}(t) = \alpha(t)/\alpha_{max}$ has been shown for the flame-retarded nanocomposite system. Good concurrence among the three curves can be noticed, within the limits of experimental uncertainty.

A further verification consists of checking the ability of the model to predict the behavior of the polymeric system during dynamic cure at a constant heating rate. The above-mentioned algorithm has been modified to analyze the evolution of the degree of cure starting from the same characteristic parameters of the materials, still allowing the user to choose test conditions (i.e., the start and finish temperatures and heating rate). Figure 15 shows an application of this procedure to the flame-retarded nanocomposite.

CONCLUSION

A complete thermokinetic analysis of the behavior of five different mixtures (pure and flame-retarded resin, pure and flame-retarded nanocomposite, and flame-retarded microcomposite) has been performed using a differential scanning calorimeter. In every case, the isothermal tests have shown the presence of a couple of reaction peaks due to typical cure reactions of DGEBA/acid anhydride systems (which request the presence of a catalyst or a reaction accelerator at least to react at a reasonable temperature).

The comparisons between the dynamic and between isothermal thermograms for the different mixtures also showed that the addition of other active substances (such as the nanofiller or the flame retardant additive) does not change thermogram morphology under a qualitative point of view, but both the nanoreinforcement and the flame retardant seem to exert an evident catalytic action on the cure reactions. Furthermore, in the microcomposite, the permanence of the filler in an intercalated state slowed the former

stages of the cure, providing however at the same time a noticeable acceleration of the last stages (due to the higher mobility of polymer chains).

The most important part of the work is represented by the definition of a model describing the cure behavior of the aforementioned materials. It has been chosen to represent the reaction kinetics of each resin, dividing it into a couple of parallel phenomena, that is, the fast opening of the anhydride ring (corresponding to a first exothermic peak and characterized by n-th order kinetics) and the resin networking (corresponding to a second exothermic peak and characterized by an auto-catalytic with zero initial velocity behavior). The verification of the proposed model has been performed through a comparison between experimental data (normalized curves derived from DSC thermograms) and theoretical data (derived from a numerical integration, using the second order Runge–Kutta method, of the model-representative equation) and has provided very good results. This allows one to apply such a model to any process engineering problem concerning the cure of DGEBA/acid anhydride/phyllosilicate nanocomposite systems.

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