

Processing and Characterization of Epoxy–Anhydride-Based Intercalated Nanocomposites

L. Torre,¹ E. Frulloni,¹ J. M. Kenny,¹ C. Manfredi,² G. Camino²

¹Materials Engineering Center, University of Perugia, Loc. Pentima bassa 21, 05100 Terni, Italy

²Politechnic of Turin, Center for the Engineering of Plastic Materials, Viale T. Michel 5, 15100 Alessandria, Italy

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ABSTRACT: A study of the kinetic and thermal characterization of an epoxy resin (DGEBA) polymerized with a methyl tetrahydrophthalic anhydride reinforced with montmorillonite-layered silicates is presented. The nanoreinforcement used was compatibilized by exchanging the cations between the silicate layers with alkylammonium salts, containing long hydrocarbon chains. The aim of this study was to develop new nanocomposites based on thermoset resins with improved thermal stability, suitable for electronic applications. Differential scanning calorimetry was used here

to produce the polymerization kinetics data, while thermogravimetric analysis was used to evaluate the effects of the nanoreinforcements on the thermal stability and to analyze the degradation kinetics. Unexpected strong effects of the nanocomposite on the polymerization kinetics of the epoxy–anhydride system were detected and evaluated. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2532–2539, 2003

Key words: nanocomposites; kinetics; thermoset

INTRODUCTION

Nanocomposites represent a relatively new interesting class of composite materials with huge potential applications. The possibility of improving the mechanical, thermal, and barrier properties of pure resins, through the insertion of small amounts of nanoreinforcements, is very attractive for several industrial sectors, leading to increasing research efforts in many fields.

Since their introduction, nanocomposites have shown a great potential for application as a substitute for pure resins and composites. As a consequence, the use of polymer-layered silicate nanocomposites has significantly increased over the last 10 years, especially at the laboratory level, and as a result of such an increase, many industries are considering the possibility of introducing nanocomposites in their production cycles.

The introduction of a small amount of a nanoreinforcement can produce a dramatic increase of the mechanical properties of the resins. Other interesting properties which are improved by the use of nanocomposite techniques are, for example, barrier properties, fire resistance, and thermal stability.^{1–3} It is therefore clear that, with such a potential, interest in nanocomposites is increasing and their application

seems to be suitable in many fields of applications, ranging from the automotive to the electrical and packaging industries.

The first introduction of nanoreinforcements in a plastic matrix for potential industrial applications was reported by Toyota researchers using Nylon 6.⁴ Since then, other thermoplastic and thermosetting polymers have also been used as a matrix for nanocomposites and many different compatibilizers, modified clays, and other nanofillers have been developed. The main advantage of using thermosetting (TS) nanocomposites over thermoplastics lies in the lower viscosity of the matrix resins that enhances the process of intercalation and exfoliation of the silicate layers. Since monomer intercalation is very important to have an effective nanocomposite, the clay is generally compatibilized using alkylammonium salts, to improve monomer penetration. Ammonium groups coming from the salt can react with epoxy functional groups of the resin monomers, contributing to an improvement in the resin intercalation.⁵

Except for the intercalation process, the processing of TS nanocomposites is similar to the traditional processing of TS resins involving the cure of a resin at a controlled temperature. As soon as the polymerization reaction starts, the three-dimensional growth of the polymeric chains causes the exfoliation of the reinforcement, yielding the final product with the reinforcement dispersed in the matrix at a nanoscale level. Only if the exfoliation is complete will the nanocomposite be effective.

The cure of the resin and the intercalation and exfoliation processes are the most important steps of the

Correspondence to: L. Torre (torrel@unipg.it).

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processing of TS nanocomposites and knowledge of the kinetic processes that take place during the cure is of fundamental importance. In particular, it is necessary to be able to evaluate the effects of nanoreinforcements on the reaction kinetics. It is known, for example, that the organic salts which are used to compatibilize a fillosilicate can act as a catalyst for epoxy ring opening⁶; this catalyzing effect can affect both the reaction kinetics and the microstructure of the nanocomposite. Zones with a higher degree of crosslinking can be found between the clay layers with respect to the bulk. On the other hand, exfoliation can be obtained only if the intercalated monomer polymerizes faster than does the monomer laying outside the clay galleries; otherwise, the latter would squeeze out the intercalated species by shrinking due to polymerization.

Many researchers have reported that the exfoliated clay nanocomposites present an improved flame resistance and better thermal stability.^{5,7,8} This phenomenon is generally due to the creation of a ceramic protective layer on the surface of the burning material by reassembling the dispersed layers of clay. This provides a barrier to heat and mass transfer across the flame, leading to cooling of the polymer and hindrance to oxygen penetration in the polymer and to the evolution of combustible volatiles feeding the flame. The overall result is improved flame retardancy.⁹ To evaluate this effect, thermogravimetric studies seem to be the most appropriate^{5,7,8}; in particular, the possibility of developing models of degradation kinetics related to the weight loss of the material exposed to high temperatures offers a valid tool for designing the material's properties, allowing the simulation of the thermal degradation behavior.

This work presents a preliminary study on the thermal characterization of a nanocomposite based on an epoxy resin (DGEBA) polymerized with a methyl tetrahydrophthalic anhydride and reinforced with montmorillonite-layered silicates. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used in this work to evaluate the effect of nanoreinforcement on the cure and on the thermal stability. The development of the polymerization and degradation kinetics here was performed to produce an integrated methodology for nanocomposite design, which could range from processing to simulation of the performances. The intended applications for the materials used in this work are for the casting and coating of electronic circuit boards where the temperature can reach high levels, but the methodology is general and can be proposed for different applications.

EXPERIMENTAL

The resin used for the research was a diglycidyl ether of bisphenol A (DGEBA), produced by Vantico, spe-

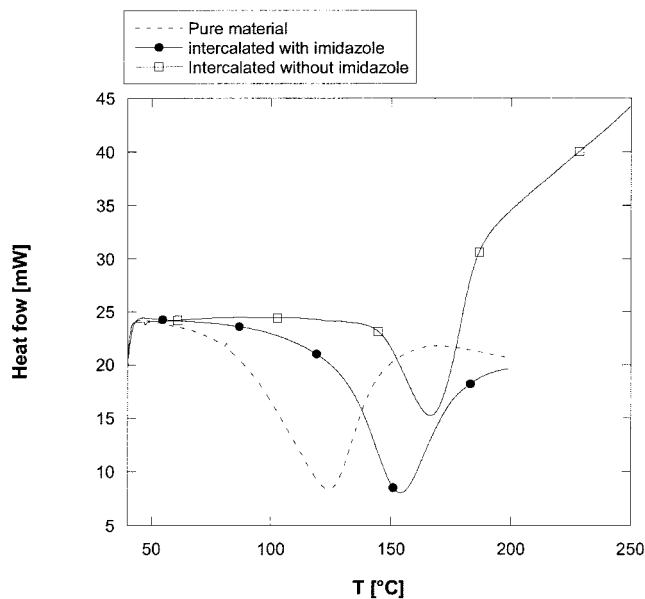


Figure 1 DSC dynamic scan for studied mixtures. All performed at 20°C/min.

cifically for electronic applications LY575 (epoxide equivalent 185 g/equiv). It was polymerized using methyl tetrahydrophthalic anhydride Vantico HY 917 (Basel, Switzerland). The selected weight fractions of the pure mixture were 100 parts of DGEBA and 90 parts of anhydride. Eventually, the crosslinking reaction was catalyzed adding 1% imidazole with respect the total weight of the mixture.

A montmorillonite commercially available, Nanofil 848, compatibilized with an alkyl ammonium linear salt, was used as the nanoreinforcement. The filler was first intercalated within the pure epoxy, and then the anhydride was added. The final concentration of the nanoreinforcement in the composite was 10% in weight.

DSC was performed using a Perkin-Elmer Pyris DSC. Tests were performed both in an isothermal and in a dynamic mode.

TGA was performed using a Seiko ESTAR 2000 TGA. Tests on pure materials and on the nanocomposites produced were performed in a dynamic mode until the complete degradation temperature of the resin was reached (800°C) and at different heating rates ranging from 2 to 20°C/min.

RESULTS AND DISCUSSION

Calorimetric analysis

DSC tests on pure resin and on the nanocomposite were performed to obtain information about the reaction heat and the processing window of the material. In Figure 1, three dynamic scans at 20°C/min are shown; the first two are related to the pure resin and

the intercalated resin polymerized, respectively. In both cases, the right concentration of the catalyst was used. The third thermogram reports the behavior of the intercalated resin without the catalyst. While the heat of reaction calculated in all the cases ranged around 314 J/g, indicating that no difference was observed in the final degree of polymerization, the main difference observed in the thermograms was of the peak temperature. In fact, the inclusion of the nanocomposite in the catalyzed resin produces a slight shift of the reaction peak to higher temperatures for the nanocomposite without the accelerator and a strong shift (+20°) for the nanocomposite with the accelerator, indicating that the presence of the intercalated filler affects somehow the kinetics of the crosslinking reaction.

So, an important feature of the presence of the nanoreinforcement is related to its catalytic effect on the polymerization reaction. Dynamic DSC tests performed on the same formulation of DGEBA and anhydride without the catalyst did not show any reaction peak up to 250°C, close to the degradation temperature of the epoxy resin used, confirming the absolute need of the catalyst to promote the resin polymerization. On the other hand, the DSC scan of the nanocomposite formulation without imidazole in Figure 1 shows clearly that the presence of the nanofiller and its compatibilizer have catalyzed the reaction. The reaction peak is, in this case, at a temperature higher than that of the catalyzed formulations but much lower than 250°C.

To determine the effective influence of the reinforcement on the reaction process of the pure resin, a kinetic analysis was performed. Previous studies on the reaction kinetics of epoxy systems^{10,11} showed that the evolution of the degree of reaction can be fairly modeled using DSC data through the development of a phenomenological model.

Using DSC experiments, the degree of reaction α can be obtained as the ratio of the heat developed during the test and the total enthalpy of the reaction as expressed by eq. (1):

$$\alpha = \frac{Q(t)}{Q_{\text{TOT}}} \quad (1)$$

The total enthalpy of the reaction was calculated as the value of the exothermal peak obtained in dynamic tests at different heating rates and an average value of 314 J/g was obtained for the pure resin. In Figure 2, dynamic tests at different heating rates, performed on the nanocomposite formulation containing imidazole, are presented.

Considering a general reaction model, it is possible to express the derivative of the reaction extent, $d\alpha/dt$, as a function of α and the temperature:

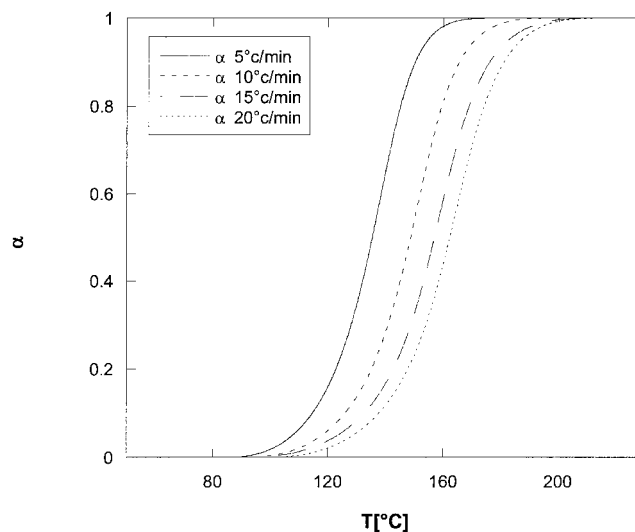


Figure 2 Extent of reaction versus temperature, for tests performed at different heating rates, for nanocomposite prepared adding imidazole.

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E_{\text{att}}}{RT}\right) f(\alpha) \quad (2)$$

To evaluate the influence of the reinforcement on the reaction kinetics, the activation energies E_{att} for the pure resin with imidazole and for the nanocomposite with different formulations were calculated. Starting with the experimental data collected during the dynamic tests, at different heating rates, the activation energy was calculated using the Friedman method,¹² applying logarithms to both sides of eq. (2), yielding the following equation:

$$\ln\left(\frac{d\alpha}{dt}\right) = -\frac{E_{\text{att}}}{RT} + \ln A + \ln [f(\alpha)] \quad (3)$$

By plotting $\ln[(d\alpha)/(dt)]$ versus $1/T$ as a constant α , it is possible to calculate the activation energy E_{att} , since the slope resulting from a linear regression of the $\ln[(d\alpha)/(dt)]$ data gives $-(E_{\text{att}}/R)$, as shown in Figure 3. The results of the kinetic analysis are reported in Table I. It is noticeable that the values of the activation energy found in all the cases are comparable, confirming the strong catalytic role played by the nanoreinforcement.

Thermal degradation

Besides curing kinetic studies, an analysis of the thermal behavior of the nanocomposite was also carried out to determine the degradation kinetics and evaluate the thermal stability. TGA tests were performed in a dynamic mode at different heating rates, and from the thermogravimetric curves, the degree of conver-

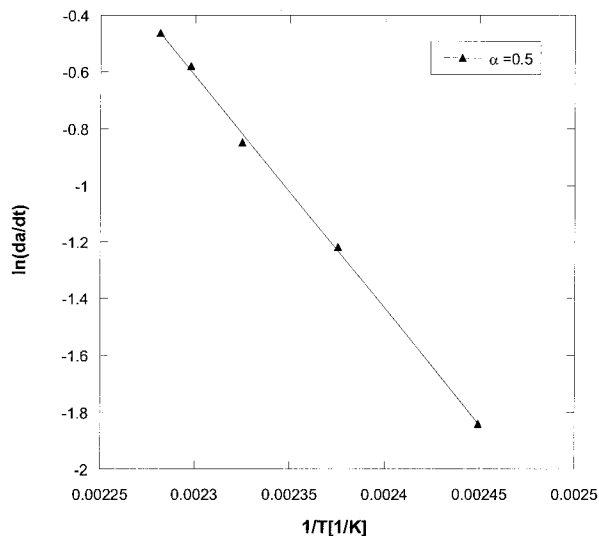


Figure 3 Friedman plot, for the determination of the activation energy of the reticulation process, of nanocomposite mixture prepared adding imidazole.

sion for the degradation process was calculated, this time as

$$\alpha = \frac{W_0 - W}{W_0 - W_f} \tag{4}$$

TABLE I
Results of the Kinetic Analysis for the Three Different Formulations

Formulation	E_{att} (kJ/mol)
Intercalated without imidazole	92
Intercalated with imidazole	68
Pure material	72

where W is the actual weight, W_0 , the initial weight, and W_f , the final weight at the end of the test.

Samples made of pure resin, nanocomposites polymerized with imidazole, and nanocomposites polymerized without adding the accelerator were analyzed. In Figure 4, a dynamic scan in nitrogen at 20°C/min for the three kinds of samples analyzed is presented. The first effect that can be noticed is that the presence of the accelerator in the nanocomposite formulation causes a decrease of the degradation performance of the material at lower temperatures in an inert atmosphere. This phenomenon can be attributed to the effect of the surfactant, which, on the nanocomposite polymerized with imidazole, exposes more surface and can catalyze the decomposition as observed with other systems.⁸ Furthermore, the overall degradation process in N₂ appears not to be strongly affected by the presence of the nanoreinforcement. Very

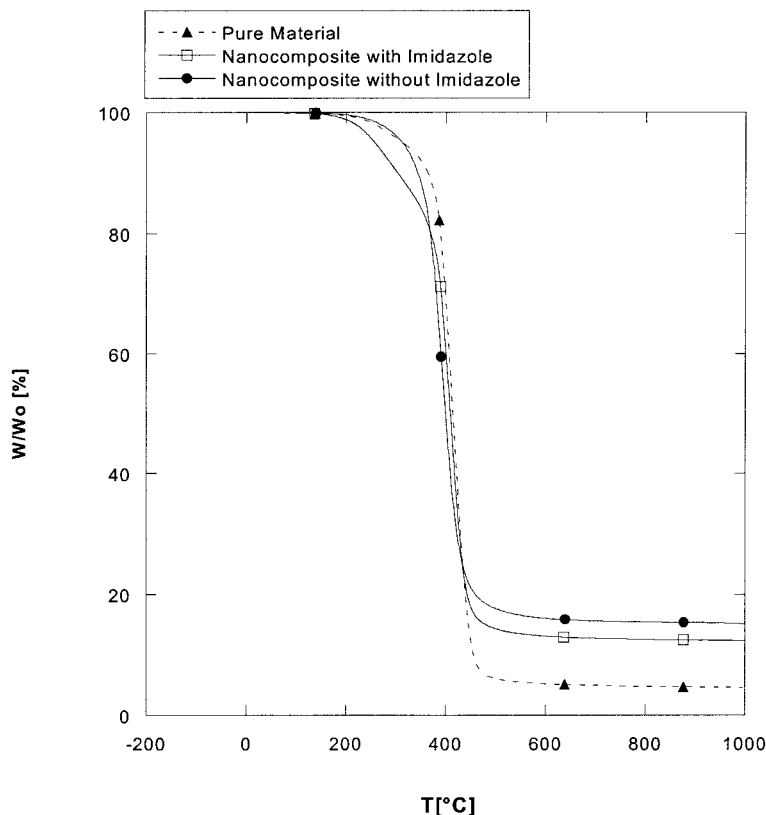


Figure 4 Percent weight loss during a TGA dynamic test in nitrogen for the different mixtures. Heating rate, 20°C/min.

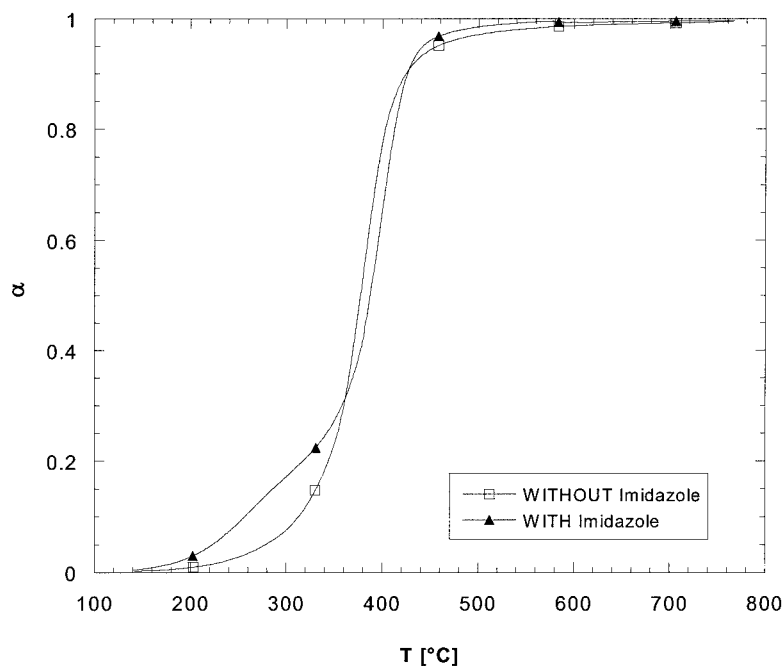


Figure 5 Comparison of the extent of reaction for degradation process in nitrogen for nanocomposite formulations prepared with and without imidazole.

little improvement of the thermal stability in N_2 of the nanocomposite formulations in respect to that of the neat resin was, in fact, observed; this could be explained by the fact that the barrier effect is ineffective in an inert atmosphere, where no oxidizing gases are present.

For all the samples, the degradation reaction appears to be a multistep process; in particular, for the nanocomposite prepared with imidazole, the degradation process occurs at lower temperatures compared to the samples prepared without the catalyzing salt as shown in Figure 5, where the extent of the reaction α versus the temperature is plotted. This effect can be attributed to the action of the catalyst that promotes resin crosslinking outside the borders of the nanolayers, reducing, therefore, the barrier effect.

The presence of two main reactions taking place during degradation is clearly visible in the curve obtained for the derivative of the weight loss with respect to the temperature (DTG), as shown in Figure 6, where the DTG thermogram for pure resin, of a test performed at $20^\circ\text{C}/\text{min}$, is presented. Similar behavior was also observed in the DTG curves obtained during dynamic tests of the nanocomposite prepared with imidazole. In Figure 6, the results of the deconvolution for the DTG curve, considering the shape of the curve as a result of the overlap of two different peaks, is also shown.

To analyze the degradation behavior of the nanocomposites, peak deconvolution was used to produce the conversion curves related to each single peak. In particular, the study was focused on the peak related

to the second process, which corresponds to the highest amount of weight loss.

It has been shown¹³ that, in many degradation processes, the rate of degradation $d\alpha/dt$ can be related to the extent of degradation α and the temperature according with the following model:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_{\text{att}}}{RT}\right) (1 - \alpha)^n \alpha^m \quad (5)$$

To determine the kinetic parameters and the activation energy using dynamic experiments, the Friedman

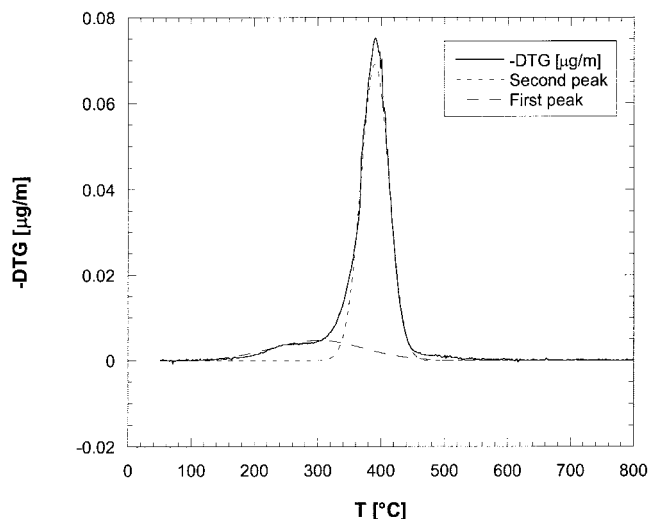


Figure 6 DTG curve for pure resin degradation in nitrogen. Dotted lines represent peaks found in curve deconvolution.

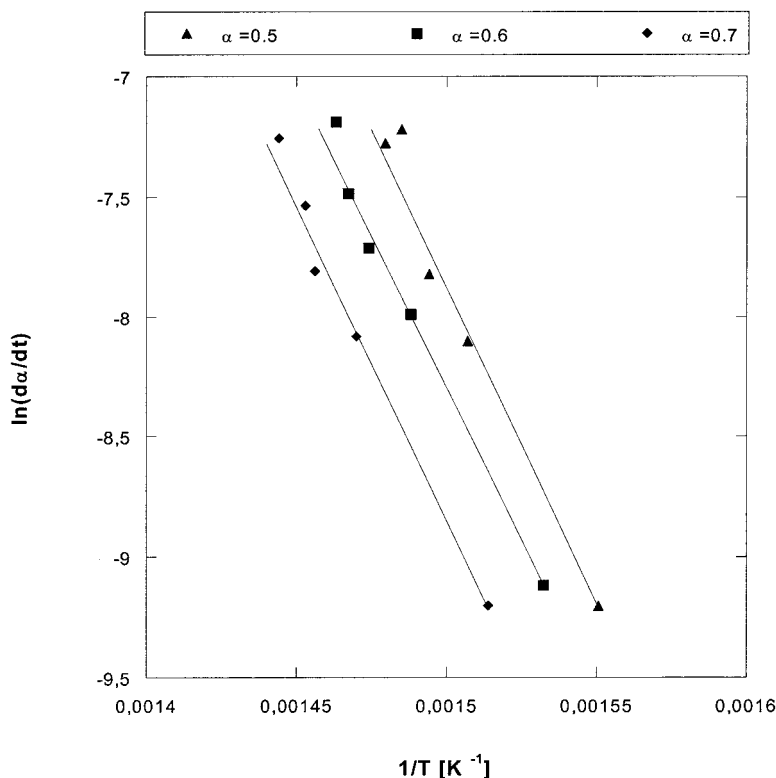


Figure 7 Friedman plot for activation energy determination, for degradation of nanocomposite prepared without adding imidazole.

method was used.¹² Combining eq. (3) and eq. (5), the following expression was obtained:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln A + n\ln(1 - \alpha) + m\ln(\alpha) - \frac{E_{att}}{RT} \quad (6)$$

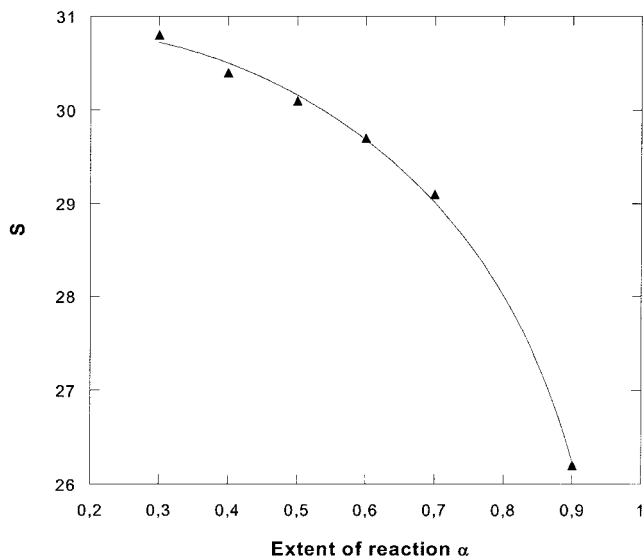


Figure 8 S versus α plot for the determination of the other reaction parameters for nanocomposite prepared without adding imidazole.

As shown previously, by plotting $\ln[(d\alpha)/(dt)]$ versus $1/T$ for a constant α , it is possible to obtain the activation energy E_{att} as the slope of the interpolating line, as shown in Figure 7. The reaction order m and n and the preexponential factor A were then found in the following fashion¹³: In the Friedman analysis, the first three terms of the right-hand side of eq. (6) are not a function of the heating rate and temperature. From the value of the sum S , of these three terms, which represents the intercept with the y axes of each of the Friedman plots, it is possible to write the following equation:

$$S = \ln A + n\ln(1 - \alpha) + m\ln(\alpha) \quad (7)$$

By plotting the term S versus α and performing a nonlinear regression analysis on the data, the values of

TABLE II
Results of the Kinetic Analysis of the Degradation Process in Nitrogen

Formulation	E_{att} (kJ/mol)	$\ln A$ [$\ln(s^{-1})$]	m	n
Pure material	176	24.1	0.05	1.4
Intercalated with imidazole	214	31.7	0.19	1.8
Intercalated without imidazole	194	30.0	0.65	2.7

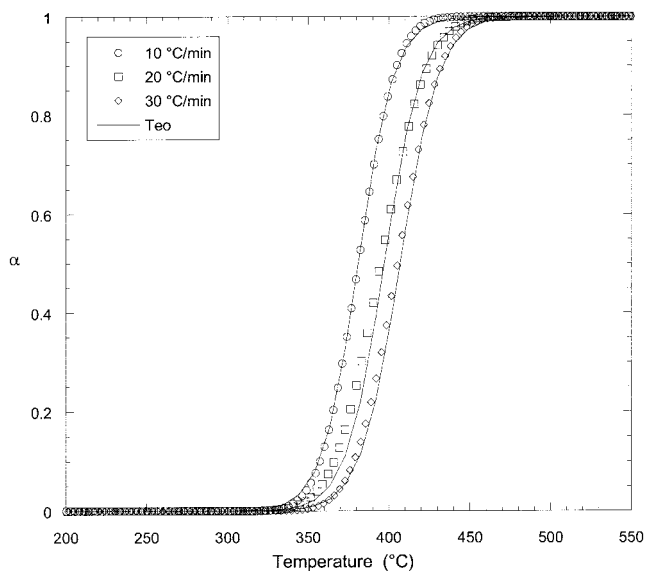


Figure 9 Comparison of the experimental data and the predicted values for degradation kinetic of nanocomposite prepared without imidazole.

A , n , and m can be easily calculated. In Figure 8, the graphic representation of this analysis is shown. The results of such an analysis are summarized in Table II, while in Figure 9, the agreement between the model and the experimental data of the intercalated nano-

composites prepared without the use of imidazole, at different heating rates, is shown. It is possible to observe that, for tests done in nitrogen, the value of the apparent activation energy of the main degradation process of the different samples changes little in the presence of the nanofiller.

Better performances for nanocomposites, with respect to pure resin, were found when testing the materials in the presence of oxygen. In Figure 10, where dynamic TGA, at 10°C/min, plots are presented, it is possible to observe that the main degradation process of the nanocomposites prepared without the catalyst is shifted to a higher temperature, compared with the neat resin. While nanocomposites prepared with imidazole also in the presence of oxygen appear to degrade earlier, in the first stage of degradation, their behavior is worse than that of the pure resin. This behavior seems quite general for polymer-layered silicate nanocomposites, for which a mechanism was proposed based on the creation of a ceramic insulative skin on the surface of the degrading composites.^{8,9,14} Furthermore, the different behavior observed of the nanocomposites, when they are produced with and without a catalyst, confirms what was previously stated about the catalytic effect of the nanofiller. The presence of a catalyst in this case promotes resin crosslinking outside the borders of the nanolayers, reducing, therefore, the barrier effect.

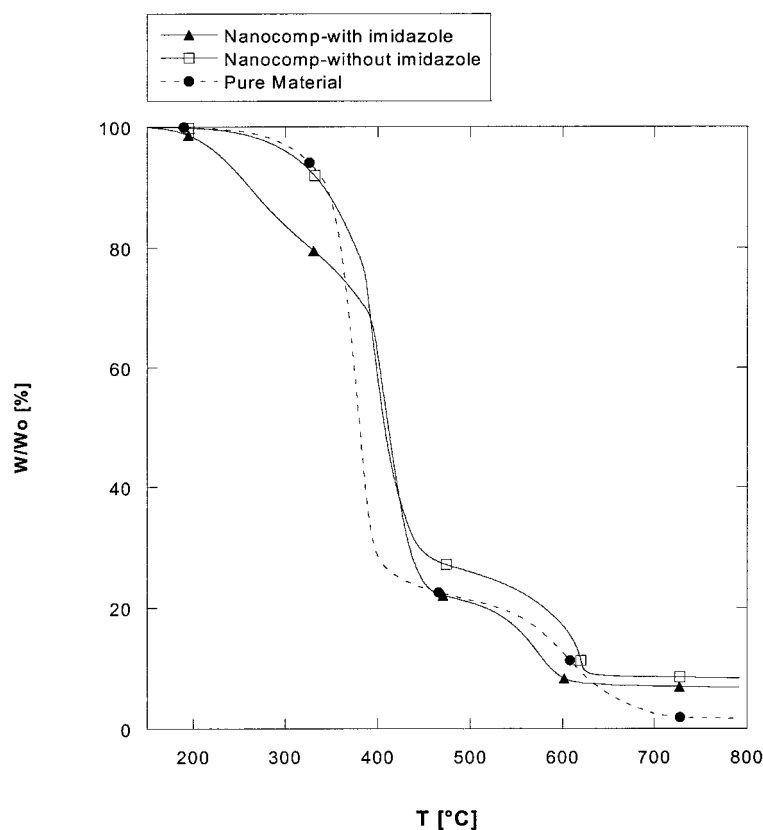


Figure 10 Percent weight loss during a TGA dynamic test in air for the different mixtures. Heating rate, 20°C/min.

CONCLUSIONS

A thermal characterization study of a DGEBA-anhydride-montmorillonite nanocomposite system was presented. In particular, the research focused on the processing aspect to determine the cure kinetics and the effects of the incorporation of a nanoreinforcement on the thermal stability of the system. The study showed that the nanofiller behaves as a catalyst for the crosslinking reaction, affecting both the activation energies and the curing temperature. The results of a kinetic analysis, performed to calculate the activation energy for the process for different starting mixtures, confirmed the catalyzing effect of the nanofiller. The pyrolysis of the selected nanocomposite system was modeled by TGA for tests performed in nitrogen and no better results were found for nanocomposites in these conditions. By performing the same dynamic tests in the presence of oxygen, it was possible to demonstrate the enhancement of the performance in the nanocomposites, especially for the sample prepared without imidazole. Thermograms in this case revealed a higher thermal stability of the nanocomposite with respect to the pure resin. Both the cure kinetic study and the degradation study confirmed that an increase of the properties is obtained, passing from pure resin to a nanocomposite. The better degradation performances of the nanocomposite prepared

without the catalyst confirmed the results obtained on the catalytic effect of the nanofiller.

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