

Curing of an Epoxy Resin Modified with Nanoclay Monitored by Dielectric Spectroscopy and Rheological Measurements

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ABSTRACT: Dielectric and rheological measurements have been performed in “real-time” to follow curing reaction on blends of a diglycidyl ether of bisphenol-A epoxy resin with 4,4-methylene bis(2,6-diethylaniline) hardener and different amounts of organically modified nanoclay (Nanofil 919) as modifier. The effect of the modifier and its amount on the curing reaction, as well as that of the curing temperature has been studied. Changes in molecular mobility in the reaction mixture have been investigated by dielectric relaxation spectroscopy. Evolutions of ionic conductivity and main relaxation have been analyzed and vitrification times have been obtained and compared with

those obtained by rheological measurements. The relaxational behavior has been analyzed through curing in the frequency domain, being the displacement of the main relaxation indicative of the cure reaction advancement. Gelation and vitrification times for the nanocomposite systems have been found to be lower than for the neat resins, indicating a catalytic effect of the clays on the curing reaction. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 5927–5933, 2006

Key words: dielectric properties; relaxation; rheology; thermosets; organoclay

INTRODUCTION

Polymer-clay nanocomposites based on layered silicates like montmorillonite have been widely studied during the last 10 years. Nanocomposites are usually prepared by adding a silicate to a polymer during its polymerization, or to a solvent-swollen polymer, or to the polymer melt.^{1–3} Polymer-clay nanocomposites can show remarkable property improvement (increased tensile properties, decreased gas permeability, decreased solvent uptake, increased thermal stability, and flame retardance) when compared with conventionally-scaled composites.^{2,4}

While thermoplastic polymer nanocomposites have been widely studied, thermoset polymer ones are beginning to receive considerable attention as well.^{5–7} For both systems, the precise mechanism(s) by which the reported property enhancements are achieved remains a matter of ongoing debate. The ability to process thermoset nanocomposites into useful forms

depends upon the ability to control the interplay of the thermoset composition (resin, curing agent, clay, etc.) and its effect on the curing process (gelation, vitrification, kinetics, or crosslink density) and the morphology development.⁸ Concerning the curing process, gelation and vitrification are the most significant phenomena. Gelation is defined as the point at which an infinite molecular weight forms, while vitrification takes place when the increasing glass transition temperature of the system reaches the value of the isothermal cure temperature.

Dielectrometry has been developed by many authors as a nondestructive and convenient method for monitoring of thermosets curing. Many dielectric studies of epoxy-amine systems have been reported.^{9–13} Several groups^{14–17} have tried to relate the changes in dielectric properties to chemical and physical phenomena that occur during reaction. Rheological measurements have been widely used to monitor the cure process of epoxy/amine systems,^{18–20} determining adequate criteria to obtain gelation and vitrification times.

The main objective of this work is to monitor *in situ* and in “real-time” the cure of nanoclay-modified epoxy thermosets by using dielectric relaxation spectroscopy and rheological measurements. Gelation, vitrification, ionic conductivity evolution, and relaxational behavior have been analyzed. The effect of

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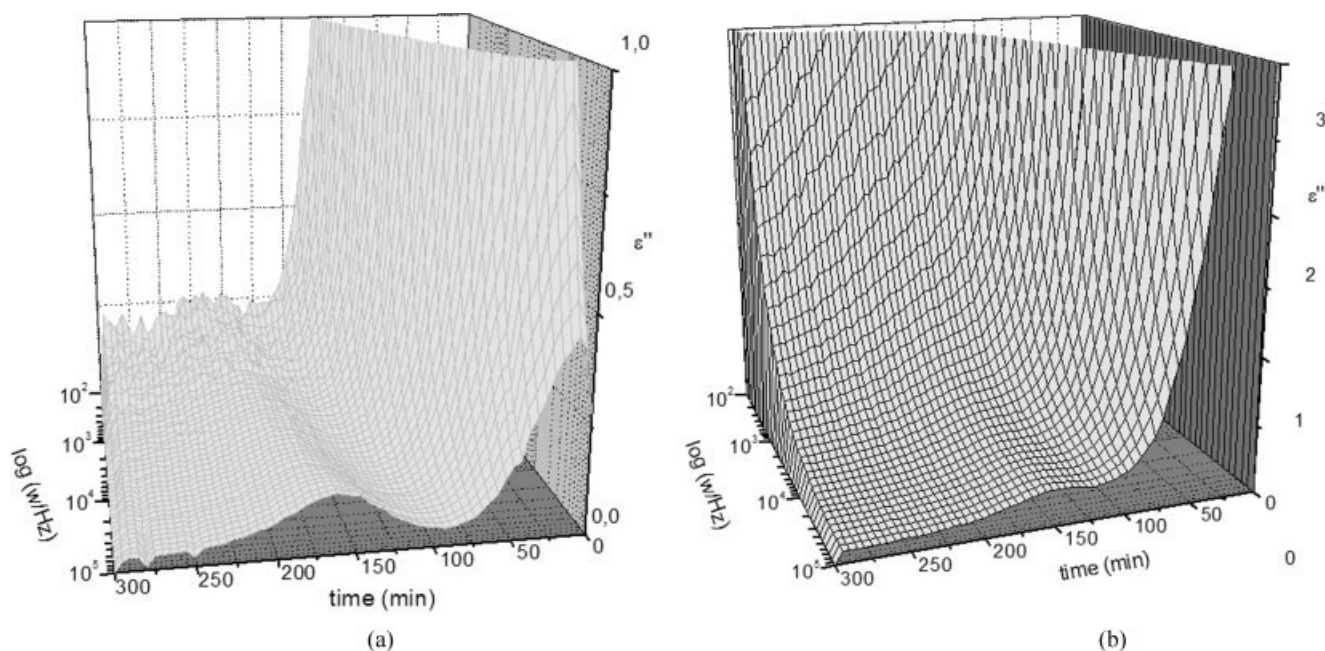


Figure 1 Three-dimensional dielectric loss-frequency-cure time plots for curing at 120°C of (a) neat epoxy matrix and (b) epoxy matrix modified with 1 wt % clay.

modifier and its amount and that of the cure temperature have also been analyzed, comparing results obtained from both techniques.

EXPERIMENTAL

The layered silicate used in this study (Nanofil 919) was kindly supplied by Süd Chemie España (Madrid, Spain). It is a montmorillonite organically modified with a benzyltallowdimethyl ammonium salt ($[\text{CH}_3]_2\text{N}^+\text{CH}_2\text{PhHT}$, where HT is 65% C18, 30% C16, 5% C14), with an interlayer distance of 2.0 nm, an average particle size of about 35 μm , and a loss on ignition of 35%. A diglycidyl ether of bisphenol A (DGEBA Gy250) epoxy resin provided by Ciba Resins was used as matrix. The curing agent was 4,4-methylene bis(2,6-diethyl aniline) (MDEA) of Lonzacure.

For the nanocomposite preparation, the organoclay, previously dried for 24 h at 80°C, was mixed with the matrix for 30 min at room temperature. Then the mixture was degassed at this temperature under vacuum for 2 h. Stoichiometric mixtures of epoxy-amine were prepared by dissolving the amine in the epoxy-silicate mixture for 5 min at 90°C.

Dielectric measurements have been performed on a Solartron 1260 impedance gain-phase analyzer operable in the range from 0.1 Hz to 10 MHz, interfaced with a computer to the reaction cell used. The measuring cell consists of two glass slides separated by a 1-mm-thick Teflon spacer. Thin aluminum electrodes, with a surface area of 4 cm^2 are placed on

each glass plate. The cell constant $K = 25$ cm. At each frequency f , a 5 mV AC excitation wave is applied to the metallic electrodes located in the sample cell and the overall impedance is measured. Using the cell constant, the machine transforms the impedance values in complex permittivity values, which are used in this work. Further information about these transformations and used equation can be found elsewhere.²¹⁻²³ The excitation frequency was varied from the maximum of 10 MHz to a minimum value that depends on time and temperature of the measurement and was chosen to be representative of the migrating charge region, but high enough that electrode blocking effects might be excluded. The used frequency range was from 10 Hz to 10 MHz, because between 0.1 and 10 Hz the impedance reached too high values in our experimental equipment. The time scale of each experiment (about 1 min) was negligible in comparison with the time scale of the changes in the polymer-forming network, and hence each measurement can be taken to represent a structural state.

Rheology and cure transition measurements were carried out with a TA instrument AR1000 amplitude control. Plate-plate geometry (25 mm) was used. Multiwave time sweeps were used to examine both gelation and vitrification transitions. Multiwave tests allow the dynamic response to different frequencies to be analyzed at the same time,²⁴ which is essential in characterization of reacting systems. Because the viscosity of the system changes significantly during the curing process, a control program was used in

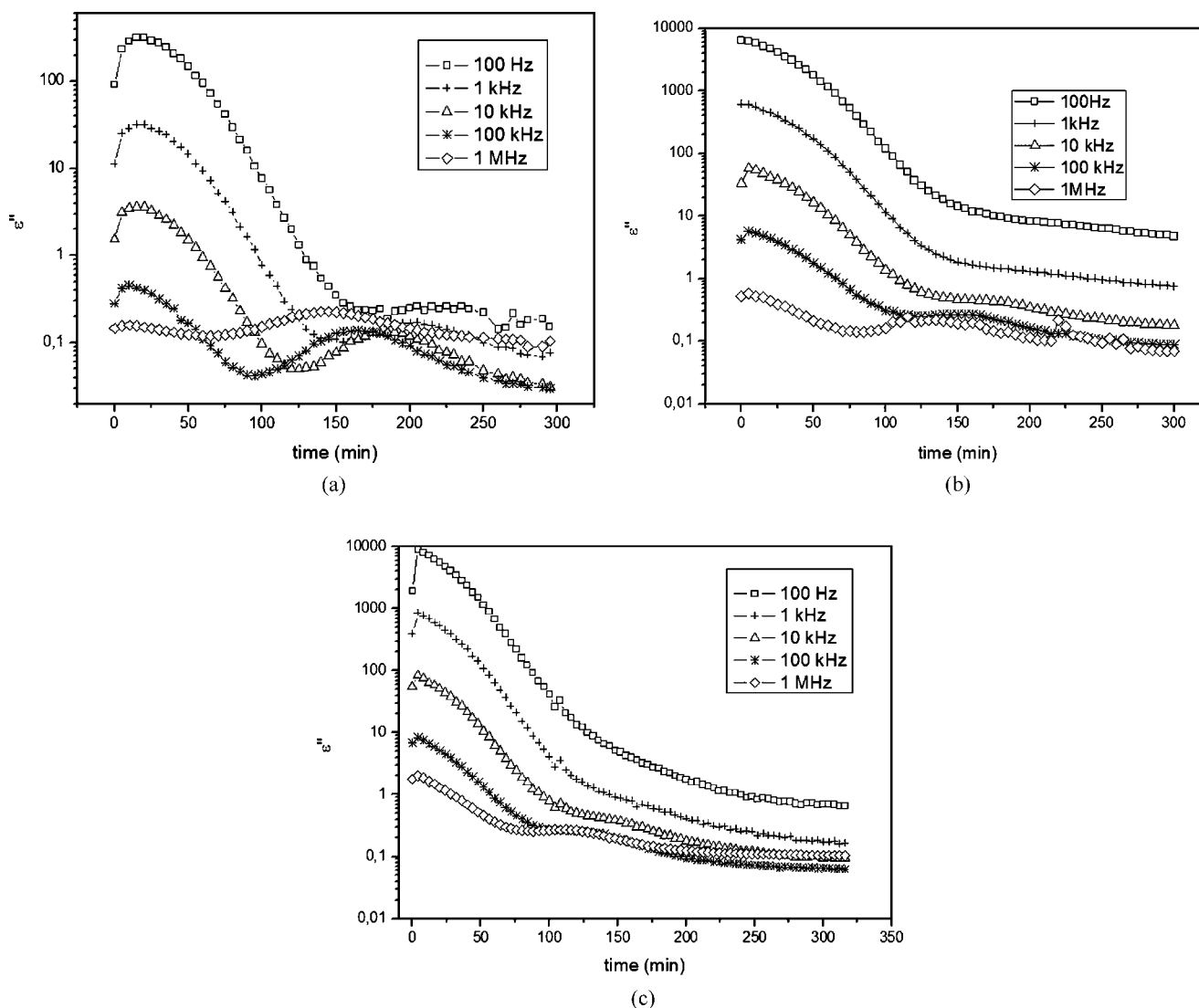


Figure 2 Dielectric loss versus cure time plots at several frequencies for curing at 120°C of (a) neat epoxy matrix, (b) epoxy matrix modified with 1 wt% clay, and (c) epoxy matrix modified with 2 wt % clay.

which the oscillation stress increased by diminishing the applied amplitude. This allows cure characterization in the whole conversion range. Prior to these tests dynamic strain sweep tests were conducted to ensure the systems were within the linear viscoelastic region.

RESULTS AND DISCUSSION

Dielectric measurements

Cure monitoring of clay-modified epoxy matrices has been developed by DRS for systems with different amounts of clay (from 1 to 5 wt %) at different cure temperatures from 120 to 160°C. Evolution of dielectric complex permittivity (ϵ^*) with cure time and frequency and the behavior of ionic conductivity (σ) with cure time are analyzed for each system. The

effect of the clay and its amount on cure and that of the cure temperature is studied.

Complex dielectric permittivity has a capacitive component (dielectric constant, ϵ') and a resistive one (dielectric loss, ϵ''). Since the permittivity and loss are related by the Kramers-Kronig transform,²⁵ only the loss data are presented in the figures. Figure 1(a, b) shows 3D plots of dielectric loss (ϵ'') versus frequency and cure time for isothermal cure at 120°C of the neat epoxy matrix and matrix modified with 1 wt % clay, respectively. Ionic conductivity and electrode polarization due to ionic species gives the increase in ϵ'' at low frequencies and cure times (note that values are cut to follow the main relaxation). For the clay-modified matrix, the increase in ϵ'' is higher than that for the neat system during all the cure process. The ionic species of the clay increase the conductivity (and consequently the

TABLE I
Vitrification Times (min) for Neat Epoxy Matrix and Modified with 1 and 2 wt % Clay at Several Temperatures between 120 and 160°C, as Obtained from Dielectric Relaxation Spectroscopy

T (°C)	Neat	1 wt %	2 wt %
120	250	225	210
140	160	140	140
160	110	90	90

loss factor ϵ'') of the mixture as shown below in the section dedicated to conductivity. The importance of these effects due to ions decreases with increasing cure time, since ion mobility decreases as the local viscosity of the mixture increases. At longer cure times, when dipolar contribution dominates the response, ϵ'' shows a well-defined peak in the frequency domain because of the α -relaxation process, which arises from the large-scale motions of dipoles associated with polymeric species present in the mixture.^{23,26} The peak appears from the high frequency region and moves to lower frequencies as the cure advances.^{13,16,17,21-23} During the cure, as the glass transition temperature (T_g) of the resin becomes higher and the medium becomes more viscous, the chain segments have more difficulties to move, and consequently dipoles need longer times for their orientation and relaxation. It has to be noted that the frequency at which the dipolar contribution begins to dominate the response is higher for the clay-modified matrix due to the presence of ionic species of the clay, so higher frequencies are needed to obtain well-defined peaks, as it is shown below.

To analyze more precisely the evolution of the α -process, it becomes interesting to study its behav-

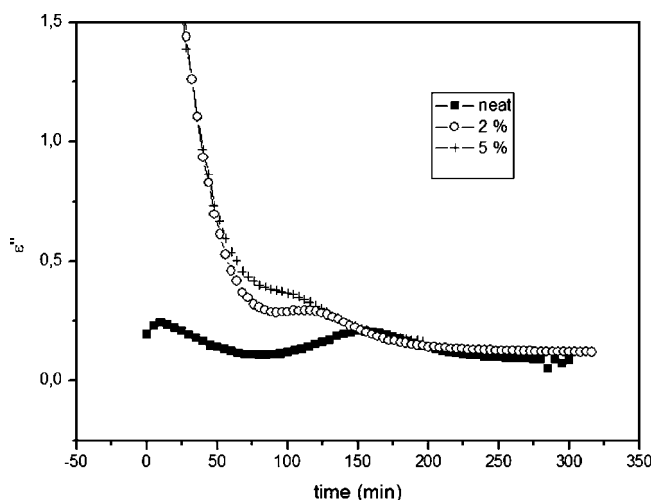


Figure 3 Dielectric loss versus cure time plots at 250 kHz for curing at 120°C of neat epoxy matrix and modified with 2 and 5 wt % clay.

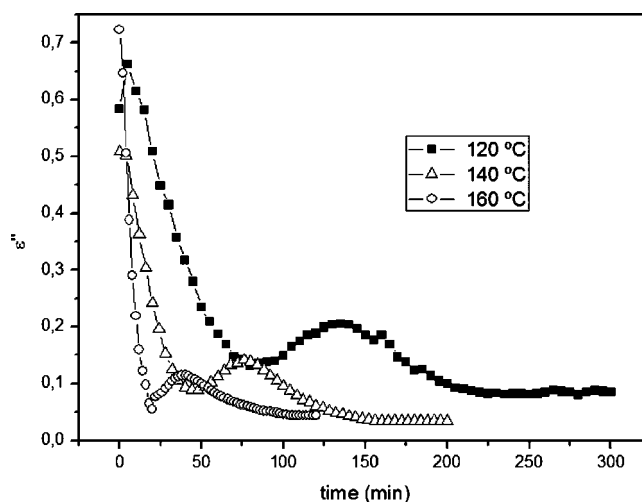


Figure 4 Dielectric loss versus cure time plots at 1 MHz for curing at temperatures between 120 and 160°C of epoxy matrix modified with 1 wt % clay.

ior with cure time at different frequencies. In this way, the frequency of appearance of the loss peak and vitrification times of the curing systems are analyzed. Figure 2(a-c) shows the ϵ'' versus cure time plots at different frequencies for the unmodified epoxy matrix and those modified with 1 and 2 wt % clay, respectively, at 120°C. Logarithmic scale is used to include all the frequencies in one plot.

It can be clearly seen that the maximum of the ϵ'' peak (which corresponds with the main relaxation and T_g of the system) moves steadily to longer times with decreasing frequency, as shown for other glass-forming thermosetting systems.²⁷ In the case of the neat matrix, the peak begins to appear at around 100 Hz as shown for other epoxy/amine systems,^{21-23,27} while for clay-modified matrices the peak is well-defined at frequencies higher than 10 or even 100 kHz. The higher the clay content the higher the frequency of appearance is, due to the higher contribution of the conductive component of the loss. The clay increases the conductivity of the matrix (ϵ'' values are higher for modified ones) due to its ionic species, higher frequencies being needed to be in the dipolar domain and appreciate the peak. For the matrix modified with 5 wt % clay, the strong conductivity component masks the dipolar one and the peak is not well defined at the used frequency range.

Vitrification occurs when the resin changes from the liquid to the glassy state. When the cure proceeds at a constant temperature, the time at which the increasing T_g of the system reaches the cure temperature defines this physical event. Vitrification times can be obtained from ϵ'' versus cure time plots as follows: ϵ'' shows a transition presented like a peak, related to the increasing hindrance that the dipoles feel as the reaction progresses and the network

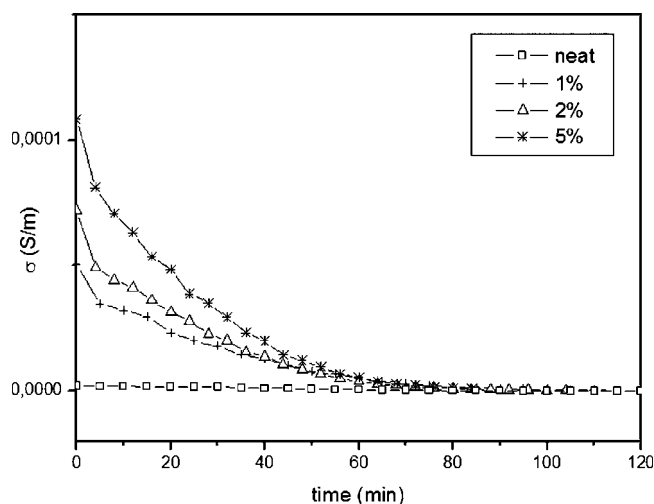


Figure 5 Ionic conductivity versus cure time plots for curing at 120°C of neat epoxy matrix and modified with 1, 2, and 5 wt % clay.

expands, their relaxation time will lengthen, shifting the dielectric loss peak to lower frequencies.²⁸ After this transition ε'' reaches an asymptotic value indicating that the system does not change any more at this temperature. Times at which these asymptotic values are reached can be considered as times for which the mobility of the dipoles (related to the T_g of the system) have reached the minimum and the T_g of the system has reached the cure temperature, being the system vitrified.^{21-23,28} To calculate vitrification times, first tangents to the plots are drawn both in the final constant region and in the decreasing region (after the maximum of the peak), and the intersection of the tangents gives the vitrification times.^{21-23,29,30} Table I shows vitrification times obtained in that way for all the systems except for that containing 5 wt % clay, in which the absence of a well-defined peak makes impossible the determination of a feasible vitrification time.

To study the effect of the clay amount and cure temperature on the curing process, Figure 3 shows ε'' versus cure time plots for the unmodified matrix and modified with 2 and 5 wt % clay at 120°C and 250 kHz, while Figure 4 shows ε'' versus cure time plots for the matrix modified with 1 wt % clay at 120, 140, and 160°C and 1 MHz.

It is worth to note that the clay content increases loss values due to the higher conductivity produced by its ions and makes the cure reaction to be faster, being vitrification times shorter with higher clay contents, as shown by other authors for very similar clays.^{31,32} The catalytic effect could be possibly due to the existence of attractive forces between the clay and the growing prepolymer. The cation-exchange capacity of the layered silicate possibly influenced the polymerization of the epoxy resin between the

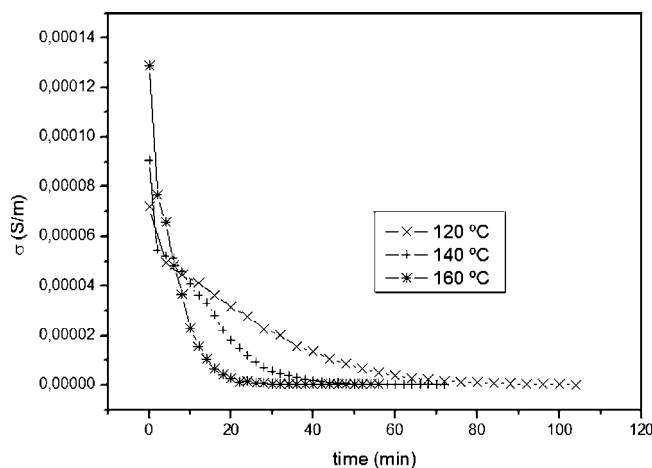


Figure 6 Ionic conductivity versus cure time plots for curing at temperatures between 120 and 160°C of epoxy matrix modified with 2 wt % clay.

silicate layers induced by the organic alkylammonium ions that contains.^{33,34} For constant clay content, the higher the cure temperature the faster the reaction advances and the shorter vitrification times are.

Evolution of ionic conductivity with cure time has been analyzed to quantify the highest conductivity of systems modified with the clay and its evolution during cure process. The ionic conductivity is given by

$$\sigma = \omega \varepsilon_0 \varepsilon_c'' \quad (1)$$

where ω is the angular frequency, ε_0 is the air permittivity, and ε_c'' is the conductive component of the dielectric loss. Ionic conductivity is calculated from dielectric loss data during the first stages of the cure process, when ionic conductivity dominates the response.^{21-23,28}

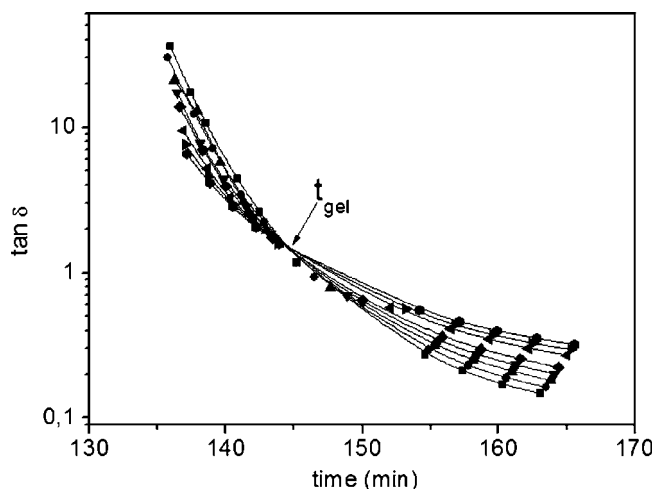


Figure 7 Loss tangent ($\tan \delta$) in logarithmic scale, obtained from multiwave tests for curing of neat epoxy matrix at 120°C.

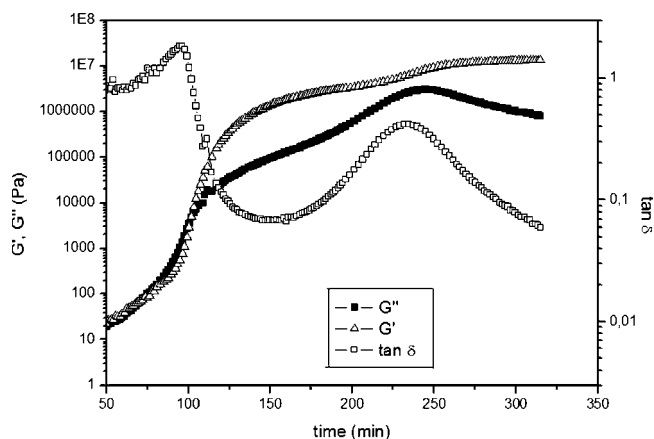


Figure 8 Storage modulus, G' , loss modulus G'' , and loss tangent ($\tan \delta$) during cure of epoxy matrix modified with 5 wt % clay at 120°C.

Figure 5 shows the evolution of ionic conductivity during cure process for the neat epoxy matrix and modified with 1, 2, and 5 wt % clay at 120°C. It can be clearly seen that the clay increases conductivity strongly due to the presence of ions, obtaining higher conductivity values for higher clay contents. Furthermore, the fall in conductivity, related with the increase in viscosity due to reaction advance, occurs faster for higher clay contents due to its catalytic effect on cure reaction. Cure reaction advances faster with higher clay contents, with the consequent increase in viscosity and decrease in conductivity.

The effect of temperature on conductivity can be seen in Figure 6, which shows the ionic conductivity evolution for the matrix modified with 2 wt % clay at different temperatures from 120 to 160°C. Conductivity becomes higher with the increase of temperature due to the higher mobility of the ions, but it also falls faster due to the advance of the reaction, favored at high temperatures.

Rheological measurements

The continuous monitoring of the viscoelastic behavior of the samples during network formation allows to monitor events that take place during cure process. At a critical extent of reaction, the epoxy/amine

system undergo a pseudophase transition from liquid to solid as network formation proceeds. The gelation point of a chemically crosslinked system is clearly defined as the time at which the weight-average molecular weight diverges,^{35–37} leading to a sharp increase in the loss modulus, G'' . At this moment, covalent bonds connect across the whole volume of the curing material, and a macroscopic network is formed. On the basis of the Winter-Chambon criterion at the gelation point, $\tan \delta$ is independent of the frequency, and storage modulus G' and loss modulus G'' have the same power-law frequency dependence.^{35,36,38} In this work, the Winter-Chambon criterion has been applied to determine the gelation point, as can be seen in Figure 7 for the neat matrix cured at 120°C. After the sharp increase of G'' due to gelation, a maximum appears related with the vitrification of the system.^{39–41} In this work, vitrification times from rheological measurements have been taken as the time at which the maximum in G'' appears.

As an example, Figure 8 shows G' , G'' , and loss tangent ($\tan \delta$) at 1 kHz during cure for 5 wt % clay modified matrix at 120°C. Table II summarizes gelation and vitrification times obtained for 0, 1, 2, and 5 wt % clay modified matrices at various cure temperatures from 120 to 160°C. The catalytic effect of the clay can be clearly seen, being gelation and vitrification times shorter by increasing the clay content. Although they are not shown in the present work, conversion data obtained from calorimetric measurements (yet to be published) show that the conversion at gelation and vitrification depend on the clay content, indicating that the interfacial region between the clay and the polymer may dominate the properties.

Vitrification times obtained from rheological measurements are in quite good agreement with those obtained from dielectric measurements, validating the dielectric spectroscopy as a suitable technique to determine vitrification times for these systems as was shown by the authors for epoxy/amine systems modified with elastomers and thermoplastics,^{22,23} in which dielectric measurements were carried out simultaneously with near infrared spectroscopy and results validated with rheology.

TABLE II
Vitrification Times (min) for Neat Epoxy Matrix and Modified with 1, 2, and 5 wt % Clay at Several Temperatures between 120 and 160°C, as Obtained from Rheological Measurements

T (°C)	Gelation				Vitrification			
	0 wt %	1 wt %	2 wt %	5 wt %	0 wt %	1 wt %	2 wt %	5 wt %
120	145	140	130	100	244	230	220	210
140	65	60	58	47	160	154	150	–
160	31	29	27	20	120	110	100	–

CONCLUSIONS

In this article, the curing reaction of nanoclay-modified epoxy resins has been *in situ* monitored. The dielectric results have been generated using an experimental setup assembled in our laboratory for real-time monitoring of cure reactions.

Vitrification of the reacting blends and the evolution of their main α -relaxation process with cure time and frequency have been studied by dielectrometry. The effects of curing conditions, such as temperature and amount of modifier, on the curing reaction are also reflected in this relaxation. The evolution of the peak towards lower frequencies reflects the reaction advance. Conductivity data extracted from ϵ'' show that the clay leads to a sharp increase in ionic conductivity, masking the dipolar component and increasing the frequency of appearance of a well-defined peak corresponding to the main relaxation.

Gelation and vitrification times have been obtained by rheological measurements, finding a good agreement with vitrification times obtained from dielectrics. Both techniques show the catalytic effect of the clay, accelerating cure reaction probably due to the attractive forces between the clay and the growing prepolymer. The cation-exchange capacity of the layered silicate possibly influences the polymerization of the epoxy resin between the silicate layers as induced by the alkylammonium ions that contains.

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