

Correlation between Viscoelastic Behavior and Cooling Stresses in a Cured Epoxy Resin System

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ABSTRACT: This work deals with the study of the rheological behavior of an epoxy system subjected to three cooling processes referred to as the normal, air-, and water-cooling processes. The system was set up by a difunctional epoxy resin (DGEBA) mixed with a tetrafunctional diamine (mPDA) in stoichiometric proportions. Different samples of (1) neat and cured polymers and (2) alumina—epoxy composites were prepared. The first part of this work was devoted to optimizing the cure cycle of the neat samples using differential scanning calorimetry and rheometry. The best cure cycle is based on a first heat step at 110°C during 10 min followed by a crosslinking stage of 75 min at 180°C. In the second part of the study the influence of the cooling cycle on the thermomechanical behavior of polymer and composite samples was investigated. Measurement of loss modulus, G'' , and loss factor, $\tan \delta$, versus temperature showed that an intermediate relaxation α' peak arose between the main and

secondary relaxations (resp. α and β). The position and amplitude of the α' peak increased with the cooling rate. This rheological phenomenon is related to the presence of nonequilibrium stresses frozen in the sample during cooling. The effect of thermal aging on the α' peak also is reported. Our work also showed the presence of an α' peak for the composites. However, the amplitude of this peak was more pronounced in the composites because of additional stresses induced by the difference between the resin and the ceramic in thermal expansion coefficients. We showed that a calculation based on a thermoelastic model was useful for qualitative comparison of rheological data on the influence of the cooling process. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 679–690, 2006

Key words: viscoelastic properties; relaxation; differential scanning calorimetry (DSC)

INTRODUCTION

Epoxy resins linked with amine hardeners are widely used as structural adhesives because they have good thermal and mechanical properties, easy processing, weak shrinkage (<0.08%), and low cost. But epoxy networks also are known to exhibit a complex chemical structure in particular because of the production of secondary species during the reaction of epoxy end caps with amine functions. For this reason, the characteristics of the epoxy cure reaction have to be precisely defined in order to obtain a crosslinked sample with optimal properties. In particular, it is well known that a high crosslinking temperature produces a strong exotherm and a short cure time, whereas a low cure temperature induces opposite effects. In theory, the total heat given out does not depend on the temperature of the curing. In reality, an excessive temperature produces a fast increase in viscosity, which limits the mobility and reactivity of the molecules. A

lower temperature enables a crosslinking reaction with better diffusion of the reactants in the medium involving a more homogeneous network that has a reduced number of dangling chains but a low rate of densification. Consequently, the choice of cure temperature is often a compromise between quality of the product and industrial exigencies. Calorimetric studies have shown that two-step thermal cycles enhance the mechanical properties of the final cured system. The first step, temperature, must be judiciously chosen in order to have the viscosity of the resin low enough and the cure limited so that satisfying impregnation of the fillers is enabled. The purpose of the second step is to develop the polymer crosslinking. Polymerization is achieved by a postcure that reduces the number of unreacted epoxy end caps.

After cooling to below its glass-transition temperature (T_g), a polymer is not in thermodynamic equilibrium, whatever the cure process. In other words, internal or residual stresses develop in the polymer bulk that induce physical aging of the material, in which the frozen-in structure tends to relax toward its equilibrium state.^{1–4} Moreover, internal stresses are superimposed on stresses from external forces or environ-

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mental effects (pressure, chemical attack, etc.), leading to premature failure of the polymer. As a consequence, the thermal history of a thermoset polymer is very important because it affects its mechanical properties in the glassy state, properties such as hardness and stress-cracking resistance. In composite materials, this phenomenon is accentuated by the difference in the thermal expansion coefficients of the polymer matrix and the fillers. Indeed, the latter show reduced shrinkage during cooling, which creates additional stresses.

Several experimental techniques can be used to measure residual stresses. Although a full review of these techniques is beyond the scope of this article, here we note the most important ones. Some of these techniques are based on the use of destructive tests such as the hole-drilling, layer removal, and surface hardness tests. Others such as stress relaxation and photoelastometry show the real advantage of not requiring breakage of the studied sample. These latter methods are sometimes used for characterization of complex systems. For example, Rutherford et al.⁵ performed stress relaxation experiments on a composite made with a bisphenol A-type epoxy matrix bonding Ti-6Al-4V tubular substrates. Their experimental results showed that when an adhesive bond is submitted to a nondestructive stress, the measured stress can be larger than the applied stress. So, Rutherford et al. estimated that the value of the residual stresses in the polymer bulk was between 8 and 18 MPa. This seems reasonable because it agrees with the range of stress values (10–20 MPa) proposed in the literature on the basis of results obtained from the use of other experimental methods.^{6–11}

Residual stresses accelerate the physical aging of a material, which for thermoplastic and thermoset polymers is detected by differential scanning calorimetry with sub- T_g heat flow transitions.^{12–16} This mechanism is based on the very slow relaxation of polymer chains. Then these stresses also should be observed with rheometry, in particular, with thermomechanical analysis consisting of measurement of the evolution of the shear complex modulus, $G^* = G' + jG''$, according to temperature. It is well known that in this kind of analysis, relaxation phenomena are detected by the peaks on the G'' loss modulus curve that are representative of the dissipative energy in the material. This parameter is quite sensitive to the long-range molecular motion that occurs during the glass transition of the polymer (α relaxation). At a lower temperature, it also enables a description of more localized segmental motion in the polymer chain, which is representative of secondary relaxation (designated as β , γ , ... on a decreasing temperature scale). Studying these relaxations is often because their changes are sensitive both to the cooling process and to physical aging.^{7,8,10,16–25}

In the framework of an industrial project, the structural bonding of a ceramic (alumina) with an epoxy resin (DGEBA–mPDA) was studied. The objective of this work was to analyze the influence of the cooling process on the rheological properties of the cured resin and the ceramic-filled epoxy composite. The first part of the study was devoted to optimizing the cure cycle (curing and cooling) of the DGEBA–mPDA system. Differential scanning calorimetry (DSC) and rheometry were used to study the curing of the resin–hardener mixture in stoichiometric proportions. In a second step, rheometric analysis also was used to characterize the mechanical properties of the cured system. More precisely, we focused on the influence of the thermal gradients that occurred during the curing cycle, especially during the cooling step. We found that these gradients generate internal stress in the polymer bulk and at the polymer–ceramic interface. The effects of three cooling processes were compared on the two series of samples, a series of neat and cured polymer samples and a series of samples filled with alumina.

EXPERIMENTAL

Materials used

The epoxy resin used was a bifunctional prepolymer resin based on diglycidylether of bisphenol A (DGEBA). It is marketed as DER 331 by Dow Chemical Company (Midland, MI). The theoretical molar weight of the resin was 368.4 g/mol and the melting temperature was 60°C. The curing agent used was meta-phenylene diamine (mPDA), a tetrafunctional molecule supplied by Sigma-Aldrich (Munich, Germany). It had a molecular weight of 108.14 g/mol and a melting temperature of 60°C. The chemical structures of DGEBA and mPDA are shown in Figure 1. As mPDA is tetrafunctional, each molecule reacts with four units of resin to form a tridimensional network (Fig. 2). To take into account the respective molar weights of the resin and the diamine, the stoichiometric composition of mPDA and DGEBA required a weight-to-weight ratio of 14.5:100. This polymer system is widely used as an adhesive because it is easy to make and has good resistance to aging in an aggressive chemical medium.

Alumina, a high-temperature, high-purity (>99.97%) sintered porous α - Al_2O_3 ceramic, was supplied by the Société des Céramiques Techniques (Bazet, France). Its mechanical properties were determined by ultrasound. The elastic modulus, E , was about 84 GPa, and the shear modulus, G , was 36.6 GPa. Consequently the Poisson's coefficient was estimated to be close to 0.14. The density, ρ , the thermal conductivity, λ , and the thermal expansion coefficient, α , were 2624 kg/m³, 25 W m⁻¹ °C⁻¹, and 8.16

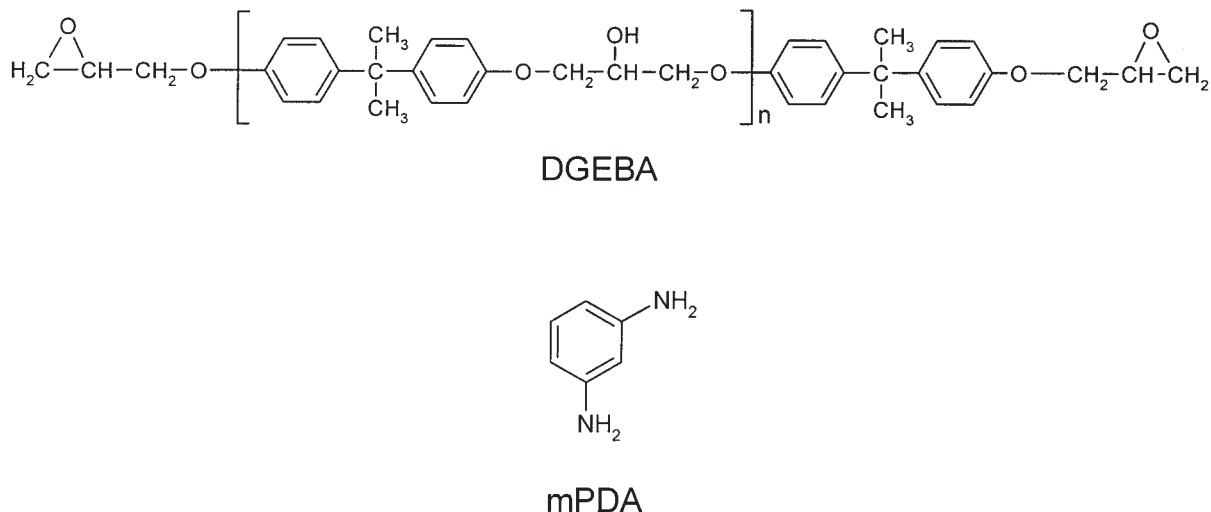


Figure 1 Chemical structure of the DGEBA resin and the mPDA hardener.

$\times 10^{-6}/\text{m}$, respectively. These weak mechanical moduli are a result of the high porosity of the alumina. For our study, the ceramic was furnished as a rectangular tablet ($15 \times 5 \times 2 \text{ mm}^3$).

Apparatus

Differential scanning calorimetry (DSC)

The calorimetric study of the DGEBA–mPDA system was performed using a Perkin–Elmer DSC 7 (Wellesley, MA) and a Shimadzu DSC 50 (Kyoto, Japan). First, 10 mg of the uncured mixture was set in an aluminum cell that was placed in a measurement heating cell. An empty cell was used as reference. The temperature increased $5^\circ\text{C}/\text{min}$, and a microcomputer automatically registered the different points of the reaction of enthalpy versus temperature. All experiments were performed under a nitrogen atmosphere in dynamic mode at a heating rate ranging from $0.5^\circ\text{C}/\text{min}$ to $5^\circ\text{C}/\text{min}$.

Rheometry

Rheological characterization of the DGEBA–mPDA system was performed with a strain-imposed dynamic

rheometer (Rheometrics[®] RDA II, Piscataway, NJ). First, kinetic experiments were performed in order to examine the progressive transformation of the prepolymer in the crosslinked system by registering the isothermal evolution of the shear modulus, G^* , which can be defined by $G^* = G' + j G''$ where G' is the storage modulus and G'' is the loss modulus. We used cup–plate geometry, in which the diameter of the upper plate is much smaller than the diameter of the cup ($\phi = 30 \text{ mm}$), in order to prevent side effects and slippage. The resin crosslinking induced an important increase in G^* between the first liquid state and the last glassy state. Taking into account the sensibility range of our apparatus, we employed two different upper plates in order to get the complete G^* curve. The larger plate ($\phi = 20 \text{ mm}$) was conveniently below the gel state, whereas the smaller one ($\phi = 5 \text{ mm}$) was used until sample vitrification. Before measuring, the epoxy resin was mixed with diamine (see the section on sample preparation for more details). Then the solution was quickly poured into the cup, and the upper plate was lowered until contact was made with the sample. Angular frequency was fixed at 1 rad/s , and the temperature of the kinetic experiment ranged between 70°C and 120°C .

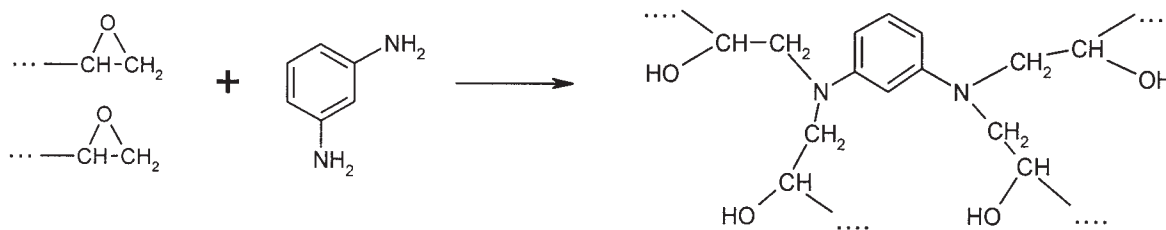


Figure 2 Chemical reaction of mPDA with DGEBA units.

Thermomechanical characterization of the crosslinked samples was performed with the same apparatus equipped with rectangular torsion geometry. The temperature ranged from -70°C to 190°C , and angular frequency was kept constant at $\omega = 1$ rad/s, and the temperature increased at a rate of $2^{\circ}\text{C}/\text{min}$.

In addition to these rheological measurements, kinetic evolution of the viscosity of the DGEBA–mPDA mixture was registered at a constant shear gradient (55 s^{-1}) for temperatures between 70°C and 120°C . The viscometric experiments, performed with a Contraves® Rheomat 30 equipped with Couette geometry, were useful for determining the influence of temperature on the gel time of the system. To prevent shearing from affecting the kinetics of the crosslink reaction, the motor was turned off between two measurement points, and a delay of 5 s was set in order to obtain the shear equilibrium regime before the viscosity measurement.

Photoelastometry

Most elastic isotropic transparent polymers become birefractive under stress (σ) or strain (ε). Thus, the elastic stressed sample was anisotropic according to two perpendicular directions, D_1 and D_2 . When a light wave passes through such a product, it is split into two beams with coherence and nearly equal amplitudes according to D_1 and D_2 . The two light waves so created interfere with each other, generate an optical path difference, δ , between the two waves, given by

$$\delta = Ce(\sigma_1 - \sigma_2) \quad (1)$$

where e is the thickness of the sample, C is a constant for a given material, and σ_i is the stress value in the D_i direction.

The photoelastometric method in transparency mode allows the measurement of the stress effects on the crossing light wave according to eq. (1). In the present study, a sample lightened by a monochromatic source was set between a polarizer and an analyzer. Then interference fringes alternately black and white appeared inside the sample. These curves were characteristic of a state of stress. The more important was the density of the fringes, the more stressed was the material.

Sample preparation

Curing

To prepare the samples, the resin and diamine first were heated in separate containers in a thermostated oven at 110°C until mPDA was completely melted. Then the diamine was poured into the resin, and the

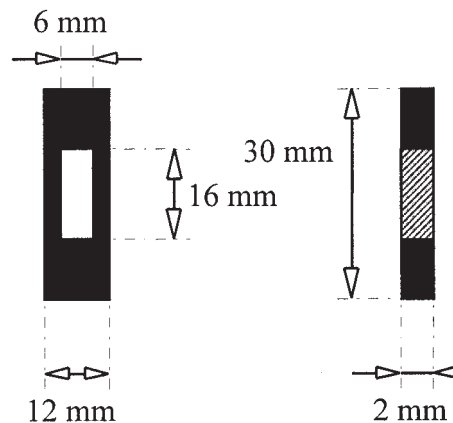


Figure 3 Schematic representation of a composite sample for the thermomechanical studies.

mixture for the reaction was vigorously stirred for 30 s at room temperature. Then the mixture was vacuum-degassed for 10 min at room temperature. The choice of a temperature of 110°C is explained in the section on rheological kinetic experiments. The mixture was prepared in stoichiometric proportions because this leads to a cured polymer with a glass-transition temperature²⁶ that is higher than that in systems with mPDA or epoxy in excess.

For investigation of the kinetics of the crosslinking reaction, the compound was used without further treatment. But to obtain a crosslinked sample for future analyses, the prepolymer mixture was poured into a flexible aluminum cup. Then it was placed between the heating plates of a laboratory press and cured at 180°C for 1 h, 15 min. The choice of this temperature is detailed in the section on determination of cure cycle parameters, below.

For the manufacture of the composite samples (polymer–alumina), a ceramic tablet ($16 \times 6 \times 2\text{ mm}^3$) was introduced into the epoxy–amine solution after mixing at 110°C . The use of an aluminum cup to produce molded cured samples is very useful because it can be easily peeled. All cured samples (pure polymer and composite) were thin and cylindrical in form ($\phi = 55\text{ mm}$, thickness = 2 mm). They were cut into a parallelepipedic form ($30 \times 6 \times 2\text{ mm}^3$) in order to be characterized in rectangular torsion mode on the RDA II rheometer. For the alumina-based products, the filler was in the central part of the tablet (Fig. 3). Each sample was 27% (w/w) alumina and 73% (w/w) cured resin.

Cooling

After curing at 180°C for 1 h, 15 min, the samples were cooled to room temperature (RT). Three specific cooling processes were used to study the effects of the cooling rate on the production of the thermal gradient

between the ceramic and the polymer. Two cooling systems were integrated into the laboratory heating press, one based on the circulation of water in the core of the heating plates and the other on using compressed air as cooling gas. A last cooling process was obtained by keeping the samples in the press after having switched off the heating of the plates.

To determine the characteristics of each cooling process, we used two thermocouples in contact with the upper and lower sides of a pure polymer sample (used as the control). Then it was possible to measure the exact temperatures, T_1 and T_2 , of the heating plates. Consequently, the average temperature in the sample

$$\left(T_a = \frac{T_1 + T_2}{2}\right)$$

and in the thermal gradient, $\Delta T = |T_2 - T_1|$, were determined all along the cooling step. This gradient was fully artificial and was inherent to the press: it occurred mainly because of the difference in cooling between the two plates.

Following are the characteristics of each cooling process. Water cooling was the fastest process. The time necessary to decrease the temperature of a sample from 180°C to room temperature (T_f) was close to 12 min. During this operation the thermal gradient can reach $\Delta T = 8^\circ\text{C}$. Air cooling required 50 min to decrease the temperature of a cured sample from 180°C to ambient temperature, with a maximum temperature of the thermal gradient also close to 8°C. In the last cooling process, designated as normal cooling, the time necessary to cool a sample to room temperature was about 8 h, and the thermal gradient was very reduced because it did not exceed 2°C.

Whatever the cooling process used, the reduced temperature, $T - T_f$, seemed to vary with time by obeying a quasiexponential law:

$$T - T_f = A \exp\left(-\frac{t}{\tau}\right) \quad (2)$$

The origin of the equation is not hazardous because it can be obtained from the heat equation

$$T - T_f = (T_o - T_f) \exp\left(-\frac{hSt}{mC}\right) \quad (3)$$

where T_o and T_f are the initial and final temperatures, respectively; h is the thermal exchange coefficient; C is the calorific capacity; S is the exchange surface; and m is the weight of the system (product + mold). As a consequence, the thermal relaxation time, τ , can be expressed by:

TABLE I

Values of Parameters A and τ for Each Cooling Process

Cooling process	A (°C)	τ (s)
Water	170	182
Air	159	800
Normal	157	7969

$$\tau = \frac{mC}{hS} \quad (4)$$

The values of parameters A ($= T_o - T_f$) and τ , obtained by numerical adjustment for each cooling process, are shown in Table I. Note that in the three cases studied, preexponential factor A was close to 160, in agreement with the theoretical value. In contrast, the value of τ strongly depended on the cooling process. Thus, this parameter enabled us to establish to distinguish between the different processes. The smallest value was obtained for water (fastest cooling) and the highest value for normal cooling (slowest cooling). The important differences in τ values indicated that the different cooling processes had very different profiles.

RESULTS AND DISCUSSION

Rheological kinetic experiments

In the isothermal kinetic analysis of the epoxy polymer, performed in dynamic mode, it was interesting to investigate the effects of the temperature on the gelation and vitrification phenomena. In particular, the results were useful for determining the critical gelation temperature (T_{gel}), which was defined as the minimal temperature at which gelation of the system is reached before vitrification. During the crosslinking process, the glass-transition temperature (T_g) of the polymer increases with an increased degree of cure reaction, implying that the system will vitrify as soon as its T_g value becomes higher than the cure temperature, T . As a consequence, if the latter is lower than a specific T_{gel} , vitrification of a polymer will be observed before gelation.²⁷⁻²⁸ In rheology gelation and vitrification can be detected by the presence of a damping peak in the representation of $\tan \delta = G''/G'$ versus time. It can be seen in Figure 4 that at $T = 80^\circ\text{C}$, the curve $\tan \delta = f(t)$ only had a single damping peak. This reveals the direct transformation of the system from the fluid to the glassy state, creating a mixing of crosslinked chains and prepolymer. In contrast, the two damping peaks on the curve obtained at 120°C proves that the reactive system gelled before vitrification. On the basis of these results, we assessed that 80°C was a temperature close to T_{gel} . The other iso-

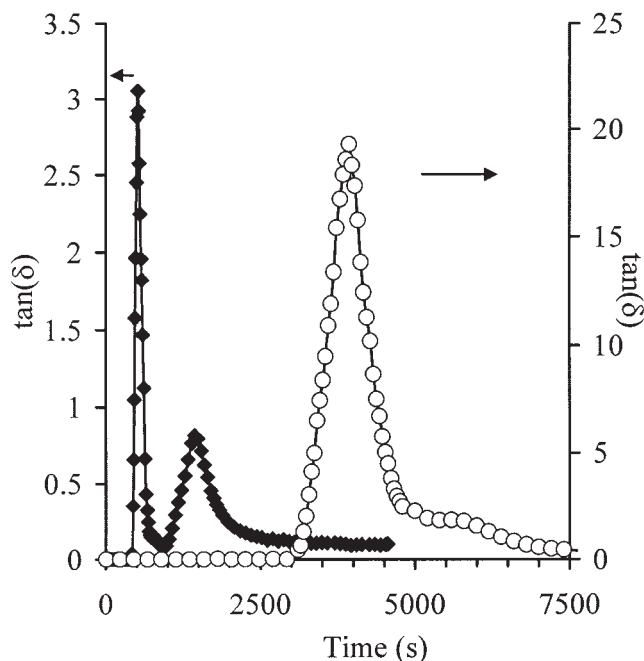


Figure 4 Effect of temperature on the loss angle curve in the isothermal rheological studies: $T = 80^{\circ}\text{C}$ (○), 120°C (◆).

thermal studies, at temperatures between 90°C and 110°C , confirmed that 80°C was close to T_{gel} .³³

As evidence, the previous crosslinking reaction required excellent mixing of the two components, hardener and resin. This means that to research minimal viscosity, the characteristics (temperature and time) of the first step of the cure cycle must be defined precisely in order to measure the period during which this viscosity decreases. With this objective, a kinetic viscometric analysis of DGEBA–mPDA system was performed (Fig. 5). It was clearly shown that the gel time, measured at the divergence with viscosity, strongly depended on the temperature used in the kinetic. In the framework of our project, 110°C seemed a reasonable choice for the first plateau of the cure cycle because at this temperature, the viscosity of the DGEBA–mPDA system was low for 10 min. This was sufficient time to ensure good impregnation of the alumina in the manufacture of a composite sample without degrading the curing agent.

It is clear that these results did not provide reliable information about advancement in the degree of the cure reaction. Thus, the experiments were completed with calorimetric measurement.

DSC study of DGEBA–mPDA system

As mentioned in the Experimental section, DSC was performed on DGEBA–mPDA samples subjected to a three-stage procedure corresponding to the three temperature ramps beginning at ambient temperature. In

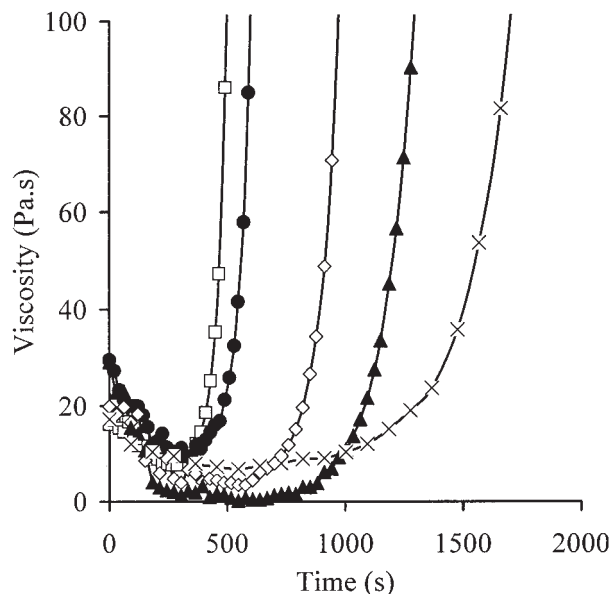


Figure 5 Kinetic studies of the steady viscosity at different temperatures: $T = 90^{\circ}\text{C}$ (×), 100°C (▲), 110°C (◆), 120°C (●), 130°C (□).

the first stage, five of the samples each had a different constant heating rate of $0.5^{\circ}\text{C}/\text{min}$, $1^{\circ}\text{C}/\text{min}$, $3^{\circ}\text{C}/\text{min}$, $4^{\circ}\text{C}/\text{min}$, and $5^{\circ}\text{C}/\text{min}$; the other two had the same heating rate of $10^{\circ}\text{C}/\text{min}$. The ramps were separated by free cooling to the ambient temperature, and the samples were kept in a closed oven. During the first stage the crosslinking reaction of the DGEBA resin with the mPDA hardener occurred; in the other two stages (of postcuring) measurement of the glass-transition temperature (T_g) was carried out. In these conditions, two T_g values were measured.

Thus, in the first stage, as expected, all heat flow via programming temperature curves showed an exothermic peak corresponding to the crosslinking reaction, with a sharper profile for high heating rates (Fig. 6). In the first approach, the main cure reaction was considered complete at the exothermic peak end—when this

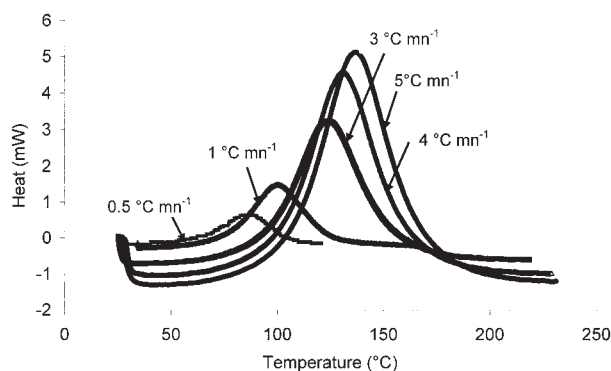


Figure 6 Effect of the heat rate on the exothermal crosslinking reaction of the DGEBA–mPDA system.

TABLE II
 ΔH Reaction Enthalpy and T_{g1} and T_{g2} glass-temperature
 Temperatures after Postcure, Obtained for Different
 Temperature Ramps(r)

Scanning rate (°C/min)	0.5	1	3	4	5
ΔH (J/g)	293 ± 5	409 ± 5	410 ± 5	435 ± 5	411 ± 5
T_{g1} (°C)	131 ± 1	163 ± 1	166 ± 1	167 ± 1	167 ± 1
T_{g2}	140 ± 1	165 ± 1	167 ± 1	168 ± 1	167 ± 1

peak became symmetrical—even for slow heating rates such as 0.5°C/min and 1°C/min. During the first stage of curing, the samples heated at 0.5°C/min, 1°C/min, 3°C/min, 4°C/min, and 5°C/min were then subjected to maximal temperatures of 122°C, 170°C, 220°C, 230°C, and 233°C, respectively. If these temperatures are compared to glass-transition temperatures T_{g1} and T_{g2} (Table II), it can be seen that only samples heated at 3°C/min, 4°C/min, and 5°C/min had a maximal programming temperature that clearly was higher than the glass-transition temperature of the DGEBA–mPDA system ($T_g = 167.1^\circ\text{C} \pm 0.6^\circ\text{C}$; T_{g2} average of experiments carried out at 3°C, 4°C, and 5°C/min). Consequently and according to previous works about DGEBA–amine systems relating curing temperature and $T_{g'}$,³⁴ only experiments performed at 3°C, 4°C, and 5°C/min corresponded to conditions in which the crosslinking reaction between DGEBA and mPDA could be considered complete, despite the high reaction enthalpy still obtained at 1°C/min ($\Delta H_r \sim 410$ J/g; Table II).

Determination of different parameters of the cure cycle

This experimental study of an DGEBA–mPDA system aimed to determine the best values of the parameters of the cure cycle for thick samples (Fig. 3) used in rheological experiments and isothermally cured. The next objective was to produce a massive crosslinked system with a glass-transition temperature at least equal to 167°C. Several isothermal kinetic experiments were performed at 120°C, 140°C, 160°C, and 180°C in order to simulate the cure experimental conditions in the heating press. It is important to note that temper-

atures above 180°C led to the thermo-oxidation of the epoxy resin.

With the method used for the manufacture of the cured sample, the temperature of polymerization obviously was not obtained immediately in the core of the sample because of the limited thermal-specific conductivity of the resin within an important mass of resin.

During the curing process temperature was recorded by a K-type thermocouple set in a first-sample core close to a ceramic tablet in another sample to register the temperature profile. For example, for a 160°C isotherm, the step temperature was just reached after 30 min between two heating plates.

Then, in a first approximation, the sample controlled by DSC underwent an average temperature scanning rate close to 4.5°C/min, going from room temperature to 160°C, followed by the 160°C temperature step. So the next results stemmed from trials performed in the following conditions: four scanning rates, estimated by a proportional rule to be 2.5°C/min, 3°C/min, 4.5°C/min, and 6.5°C/min, followed by temperature steps of 120°C, 140°C, 160°C, and 180°C, respectively, all maintained for 75 minutes.

The cure process was carried out in either a nitrogen or an air atmosphere. For each temperature step, two T_g' values were determined. The first value, T_{g1}' , was measured after the cured sample was cooled slowly to room temperature and then warmed at 10°C/min to 200°C. After another cooling, the samples were submitted to a postcure for 1000 min at 120°C, and a T_{g2}' was measured. Table III summarizes the T_{g1}' and T_{g2}' values in both atmospheres at the four temperature steps. It can be clearly seen that the T_g values were better for samples subjected to a nitrogen flow than for these submitted to an air flow for step temperatures 120°C, 140°C, and 160°C. In contrast, whatever the atmosphere, the maximum T_g obtained for a cure temperature of 180°C was 166°C. Moreover, we noticed that the postcure did not influence the transition temperature for the 180°C-step temperature.

On the one hand, a polymerization cycle for the manufacture of the samples was defined by thermo-mechanical analysis. The optimization of the different parameters gave a temperature of 110°C for 10 min in

TABLE III
 T_{g1}' and T_{g2}' Values for air and Nitrogen Atmospheres and for Temperature Steps 120°C, 140°C, 160°C, and 180°C

Scanning rate (°C/min)	Step temperature (°C)	T_{g1} (°C) air	T_{g2} (°C) air	T_{g1} (°C) nitrogen	T_{g2} (°C) nitrogen
2.5	120	132 ± 1	161 ± 1	131 ± 1	158 ± 1
3	140	152 ± 1	157 ± 1	148 ± 1	158 ± 1
4.5	160	164 ± 1	165 ± 1	163 ± 1	164 ± 1
6.5	180	165 ± 1	166 ± 1	167 ± 1	169 ± 1

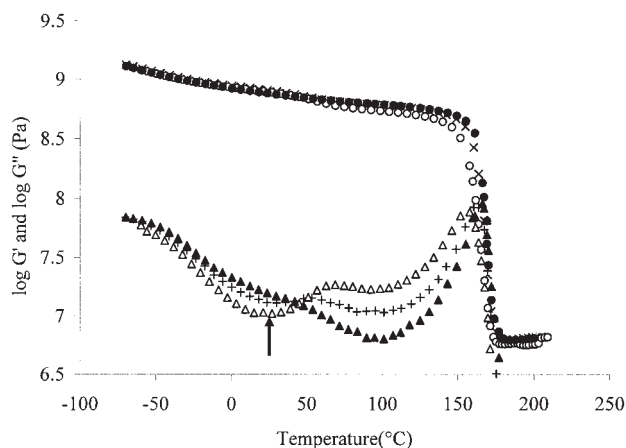


Figure 7 Effect of the cooling process on the thermomechanical behavior of the neat DGEBA-mPDA: normal G' (●), G'' (▲); air G' (×), G'' (+); water G' (○), G'' (△).

the first step, followed by the crosslinking stage of 75 min at 180°C.

On the other hand, the higher the glass-transition temperature was, the more important were the residual stresses during the thermal cycle, particularly the cooling phase.⁸ So, rheometry was used to analyze these residual stresses.

Thermomechanical study of crosslinked DER 331

The thermomechanical behavior of the epoxy-amine is presented in Figure 7 from -70°C to 200°C for the three cooling processes. On the G'' curve, an α peak centered at 170°C can be observed. This phenomenon is the rheological characteristic of the glass transition of the polymer. Its temperature, T_{α} , was slightly higher than the T_g determined by DSC studies. This small difference occurred because the T_{α} depended on the angular frequency, ω , used in the rheological test: the higher ω , the greater the difference, $T_{\alpha} - T_g$.

For experimental reasons, thermorheological studies did not allow a study of the behavior for temperatures below -70°C . However, it is clear that the β transition peak, attributed to the cooperative motion of glycerol groups and the diphenylpropane units in the network structure,^{17,19,21,25} occurred over a broad temperature range adjusted on -70°C .

For the water- and air-cooling processes a broad relaxation, called the α' peak, appeared in the 40°C – 80°C temperature range between the two relaxations previously referred to as α and β on the G'' representation. For the water-cooling process, the α' peak was shifted to higher temperatures, so it appeared as a shoulder on the alpha peak. But, in all cases, the β was slightly modified. The shift of the α' peak to high temperature induced the formation of a hollow, indi-

cated by the arrow in Figure 7. In contrast, G' seemed almost independent of the cooling process.

There have been numerous articles that reported the observation of such an intermediate relaxation mode^{7,20,22} on the viscoelastic spectra of epoxy resin-based systems. Unfortunately, assessment of α' relaxation remains obscure. A first mechanism was reported that implied unreacted molecular segments and inhomogeneities in the network arising from regions of dissimilar density of the crosslink points.²⁰ Some authors also associated the α' relaxation with *p*-phenylene groups.²² Other researchers observed that for a DGEBA-mPDA system, the intensity of this relaxation was reduced or disappeared on annealing.⁷ So, this phenomenon was attributed to the presence of nonequilibrium stresses frozen in the sample during preparation. Gupta et al. supported their hypothesis by measuring the polymer internal stresses by removal layer. Indeed, the achieved values were close to 11 MPa before annealing and 7.5 MPa after.

The first mechanism is unlikely to have occurred in our study because all the samples were cured in the same experimental conditions. The correlation between the α' relaxation and *p*-phenylene groups, as suggested by the second approach, was, in our sense, inconsistent with the same mechanism being proposed to explain the β relaxation. On the contrary, the change in the loss modulus, G'' , reported by Gupta for the α' relaxation because of the presence of nonequilibrium stresses can be understood as follows. The elastic properties changed during cooling. In the DGEBA-mPDA, the shear and Young's moduli at the initial temperature of 180°C (polymerization temperature) were 100 times smaller than those at room temperature. The required temperature was obviously not obtained immediately in the core of a sample because of the limited thermal-specific conductivity of the resin with respect to the equations of heat conduction. It is well known that the cooling process can create thermal discrepancies between the shell and the core of a sample. Consequently, these discrepancies will be enhanced by the cooling rate. Though the outside layers were contracted first during cooling, the stiffness of the counteracted core was so small that no stresses could build up. On the contrary, when the core became rigid, stresses appeared between the different layers of the samples because of their shifted stiffness: the shell was under compression, whereas the core was in a state of tension.

To further examine the effect of the first thermal history, the polymer was heated to its glass temperature so that molecular mobility became sufficient. So these chains would relax to a lower-energy state.

A cured epoxy-mPDA sample with the water-cooling process was subjected to three consecutive thermomechanical scans from -70°C ($< T_g$) to 200°C ($> T_g$). Each heating was followed by a cooling process,

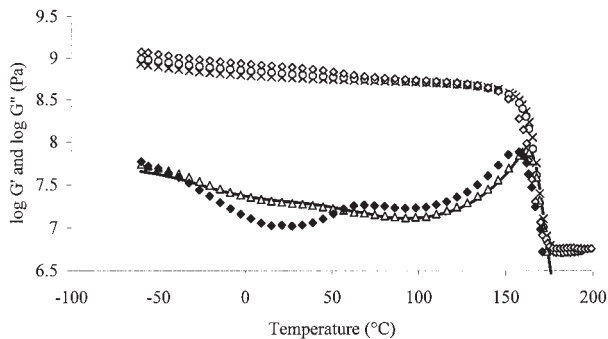


Figure 8 Effect of sub- T_g aging on the thermomechanical behavior of a sample subjected to the “water”-cooling process: first scan G' (\blacklozenge), G'' (\blacklozenge); second scan G' (\circ), G'' (\triangle); third scan G' (\times), G'' ($-$).

obtained by switching off the heating of the plates (Fig. 8).

After the second and third scans, the amplitude of the α' peak initially observed on the G'' curve was strongly attenuated. As a consequence, the α' temperature was difficult to measure precisely. In other words, these results demonstrated that the level of residual thermal stresses drastically influenced the shape of G'' in the intermediate zone between the β and α relaxations. This information agrees with the results obtained by Vadil²⁹ on DGEBA–mPDA mixtures.

We noticed that along the three scans, the elastic modulus, G' , decreased at a constant temperature. This reduction was interpreted as another consequence of the stress relaxation. This phenomenon was described in several studies as the physical aging form.^{10,16,23–25}

In filled polymers, the fillers and the polymer matrix have different thermal expansion coefficients, creating additional stresses. To ensure the continuity of strains and stresses at the ceramic/polymer interface, samples are submitted to strain sweeps at different temperatures to check the linearity between the imposed strains and the measured stresses. Therefore, thermomechanical studies of tablet-form crosslinked samples with the ceramic filler in the central part of the tablet (Fig. 3) were performed in the thermal range of -70°C and 190°C . These experiments provided the following information.

First, the intermediate region between the α and β relaxations was strongly dependent on the cooling process, as described previously with neat polymer (Fig. 9).

Second, a comparison of the thermomechanical responses between the composite and the neat polymer samples showed that the introduction of ceramic in the polymer matrix induced a similar vertical shift of the storage, G' , and the loss, G'' , moduli (Fig. 10). This evolution was simply a result of a reinforcement ef-

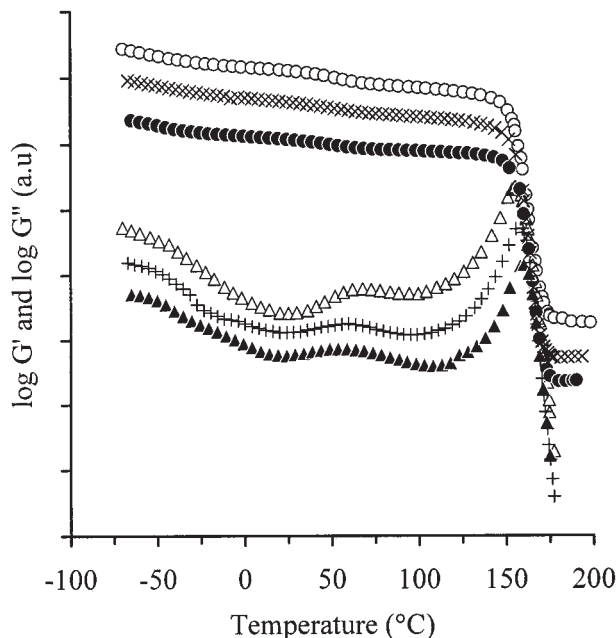


Figure 9 Influence of the cooling process on the thermomechanical behavior of the composite: normal G' (\bullet), G'' (\blacktriangle); air G' (\times), G'' ($+$); water G' (\circ), G'' (\triangle). The different curves have been arbitrarily shifted along the y axis.

fect. To break free from this translation, the rheological behavior between unfilled and filled samples at a given cooling process were observed from the $\tan \delta$ curves [Fig. 11(a–c)]. It was clearly shown that whatever the cooling process, T_α in a filled sample was

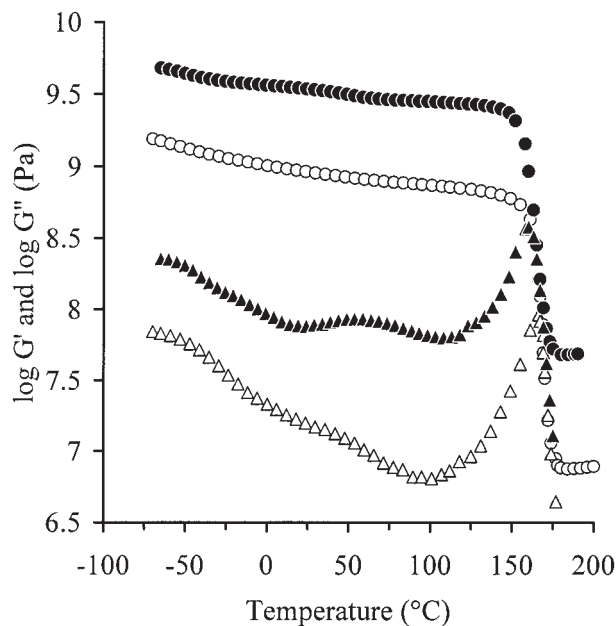


Figure 10 Comparison of the thermomechanical response between a neat polymer and a composite for a “normal” cooling process: neat polymer G' (\circ), G'' (\triangle); composite G' (\bullet), G'' (\blacktriangle).

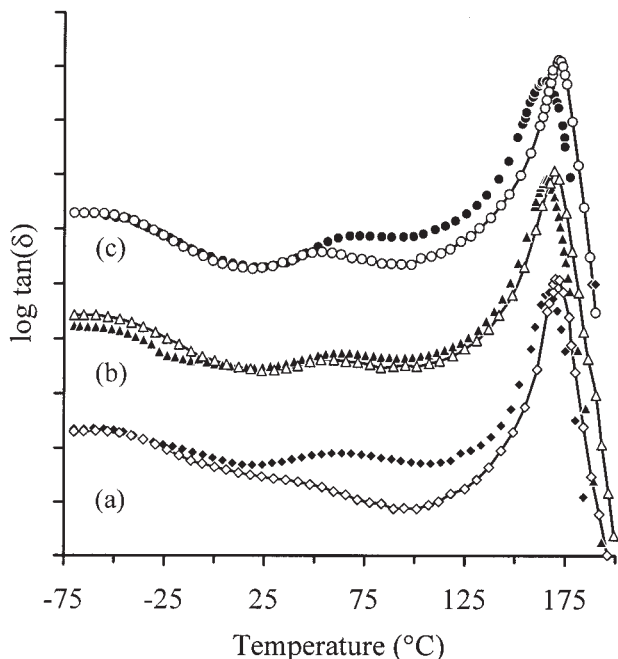


Figure 11 Evolution of $\tan \delta$ according to temperature in composite (solid symbol) and neat polymer (open symbol) samples for: (a) "normal" cooling, (b) "air" cooling, (c) "water" cooling (the different curves have been arbitrarily shifted along the y axis).

lowered by 5 $^{\circ}\text{C}$. The apparent peak shift to lower temperatures was merely a result of the better thermal-specific conductivity of the ceramic compared to the resin. Indeed, this peculiarity reduced the thermal gradient between the shell and the core of the polymer sample. Moreover, as observed in the G'' curves, the α' peak was more pronounced in the composite thermo-mechanical behavior compared to the neat polymer. This demonstrated the occurrence of additional stresses because of the difference between the ceramic and polymer thermal expansion coefficients. Thermal stresses also have been seen by photoelastometry.

Figure 12(a,b) illustrates two composite samples subjected to the normal- and water-cooling processes, respectively. In the polymer, dark fringes can be seen, signifying stresses in the matrix. Whatever the cooling process, these internal stresses increased in the neighborhood of the ceramic-polymer interface, particularly at the corner of the filler, supporting stress creation because of the difference between the ceramic and the polymer thermal expansion coefficients.

Theoretical description

As evidence, thermomechanical characterization is a powerful experimental technique for the classification of the severity of the cooling process. Although quantitative measurement of stress was not carried out, we

propose a simplified calculation to compare the different rheological responses.

The classical thermoelastic model usually applied to composite material or thermoset resin-coated metal strip or neat polymer suggests that residual stresses can be estimated from the elastic modulus by the formula

$$\sigma_r = A \int_{RT}^{T_\alpha} E \times dT = A' \int_{RT}^{T_\alpha} G \times dT \quad (5)$$

where A is a constant depending on the nature and shape of the sample. For example, A is equal to $(\alpha_m - \alpha_f)$ for a composite structure³⁰ with $\alpha_{m,f}$ as the thermal expansion coefficient of each component of the system. It is proportional to $\alpha E / (1 - \nu)$ for a polymer infinite flat sheet with ν as the poisson ratio.³¹ The lower limit of integration is room temperature (RT), whereas the upper limit is taken down at the α transition temperature.

In a dynamic shearing experiment at low imposed strain, γ_0 , the resulting stress is given by:

$$\sigma^* = \sigma' + j\sigma'' = \gamma_0 G^* = \gamma_0 G' + j\gamma_0 G'' = G_0 \cos \delta + jG_0 \sin \delta \quad (6)$$

with

$$\tan \delta = \frac{G''}{G'} = \frac{\sin \delta}{\cos \delta} \quad (7)$$

So the temperature dependence of the mechanical behavior is represented by the complex modulus, G^* , given at an angular frequency of 1 rad/s. To take into account the viscoelastic behavior of the material in the complex residual stress (σ^*) response, we suggest generalizing eq. (5) by eq. (8)

$$\sigma_r^* = A' \int_{RT}^{T_\alpha} G^* \times dT \quad (8)$$

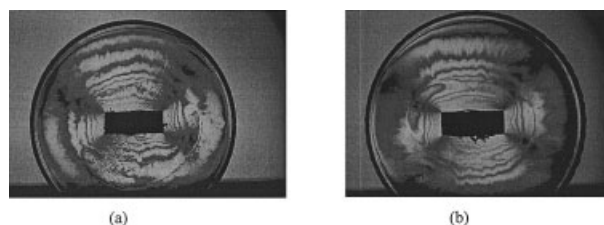


Figure 12 Effect of the cooling process on the stress level detected by photoelastometry in two composite samples: (a) "normal" cooling, (b) "water" cooling.

TABLE IV
The Solutions of eq. (10) between Two Thermal Processes

	$\frac{\int_{RT}^{T_\alpha} \tan \delta_j \times dT - \int_{RT}^{T_\alpha} \tan \delta_{\text{normal}} \times dT}{\int_{RT}^{T_\alpha} \tan \delta_{\text{normal}} \times dT}$	$\frac{\int_{RT}^{T_\alpha} \tan \delta_j \times dT - \int_{RT}^{T_\alpha} \tan \delta_{\text{normal}} \times dT}{\int_{RT}^{T_\alpha} \tan \delta_{\text{normal}} \times dT}$
Polymer sample	376%	158%
Composite sample	70%	42%

In our case, we previously showed that the formation of residual stresses mainly influences the dissipative property (G'' modulus) of the polymer, shown in Figure 7 [or the composite (Fig. 9)]. Then, starting from this crude assumption, that is, that only the G'' modulus is affected by the cooling effect, the Z function can be defined as proportional to the imaginary part of the complex residual stress response (σ^*) depending only on the loss modulus, G'' .

Z is defined by:

$$Z = A' \int_{RT}^{T_\alpha} G'' \times dT = B \int_{RT}^{T_\alpha} \sin \delta \times dT \approx C \int_{RT}^{T_\alpha} \tan \delta \times dT \quad (9)$$

because, in the glassy state, the values of the loss angle, δ , are quite small ($\sin \delta = \tan \delta$).

As evidence, the previous relation was used to compare qualitatively the effect of the cooling process on the production of residual stresses for a given material (polymer or composite) because a comparison between the neat polymer and the composite would be impossible because of two different A' values. In each case, the reference designates the less stressed sample, that is, the component cooled by the normal process.

In the first step, for a given sample we measured the area of curve Z between the room temperature and the glass temperature. Second, we calculated the ratio of two different thermal processes in order to break free from pre-factor C according to

$$\frac{\int_{RT}^{T_\alpha} \tan \delta_j \times dT - \int_{RT}^{T_\alpha} \tan \delta_{\text{normal}} \times dT}{\int_{RT}^{T_\alpha} \tan \delta_{\text{normal}} \times dT} / j = \{\text{air, water}\} \quad (10)$$

Table IV shows the different ratios calculated with

eq. (10). These values were clearly representative of the severity of the cooling processes for a sample of a given form (neat polymer or composite). Moreover, they allowed us to classify them in the same way we classified thermal relaxation time, τ , previously described in Table I.

On the one hand, the stresses created in a composite [Fig. 11(a–c)] came from the superposition of the non-equilibrium cooling stresses and the cooling stresses supported by a more pronounced α' relaxation because of reduced shrinkage during cool-down of the filler compared with the polymer matrix. On the other hand, according to eq. (10), the ratio for a composite was weaker at a given cooling process.

In the first interpretation, both results seem inconsistent. This wrong contradiction is explained by eq. (9). Indeed, the introduction of ceramic in the polymer matrix induced a similar vertical shift of the storage and loss moduli, G' and G'' , respectively (Fig. 10). So, to work with the $\tan \delta$ variations instead of the G'' variation enabled breaking free from the effect of the reinforcement on the moduli values. Thus, both stress sources in a composite sample are separated by order to simulate the cooling effect alone. In the present study, 70% and 42%, respectively, compared to 376% and 158%, respectively, were explained by the ceramic having better thermal-specific conductivity (25 W/m/°C) than the resin (0.5 W/m/°C). The effects of cooling rate and thermal gradients were smoothed in composite.

In conclusion, the use of dynamic rheometry in association with the proposed calculation [eq. (10)] was an easy and reliable technique for classifying the effects of the thermal treatments on the mechanical behavior of filled or unfilled polymer.

CONCLUSIONS

The first results concerned the optimization of the cure cycle of the DGEBA/mPDA system. This step was achieved by kinetic viscosimetry to determine the minimal viscosity before curing. Moreover, dynamic rheological kinetic studies also were useful

for determining the critical gelation temperature, T_{gel} . In addition, calorimetric experiments were carried out to measure the influence of the thermal scan rate and the curing temperature on the glass-transition temperature (T_g) of the cured polymer. As a result, the best cure conditions were achieved with a first step at 110°C for 10 min followed by a crosslinking stage lasting 75 min at 180°C. The samples manufactured according this process were subjected to thermomechanical analysis to estimate the effects of different cooling steps. Our results showed the existence of three relaxations on the loss modulus curve, $G''(T)$. The α peak, observed at 170°C, was the rheological characteristic of the glass transition of the polymer. The β relaxation, centered at -70°C, could clearly be attributed to the cooperative motions of the glycerol and diphenylpropane units in the network structure. For the water- and air-cooling processes, a broad relaxation called α' appeared between the β and α peaks. Our results clearly showed that the position and amplitude of the α' peak increased with cooling rate: as a sample was cooled from its surface inward, inherent heterogeneity involved thermal stresses. These frozen-in internal stresses were able to relax when molecular mobility was high enough ($T > T_g$). Indeed, peak intensity was reduced by successive thermomechanical scans up to 200°C. Similar results were observed with epoxy-alumina composites. Nevertheless, their thermomechanical responses displayed an increasing amplitude of the α' relaxation. We interpreted this particularity as being a consequence of additional stresses because of the difference between the ceramic and polymer thermal expansion coefficients. Finally, the rate of residual stresses in the sample was evaluated using the classical thermoelastic model modified to take into account the viscoelastic behavior of the material.

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