

Influence of the Processing on the Completion of Curing in Epoxy-Based Composites

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Received 10 May 2004; accepted 13 October 2004

DOI 10.1002/app.21564

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Differential scanning calorimetry analysis was used to investigate interrelationships between several thermal parameters and the processing conditions of particle-filled thermosetting resins. On the same piece, obtained by injection molding, epoxy-based composites exhibited sensible differences within a set of measurements of the glass-transition temperature, the width of the transition, the difference in the heat capacity, and the conversion degree. Statistical analysis showed a strong intercorrelation between these thermal parameters, but it could not provide any explanation for the disparities. The dispersion of the measured properties could, in a second step, be directly related to a sample's position with respect to the injection point in

the mold. Moreover, even the postcuring stage could not erase this topological effect. As a result, a phenomenological model is proposed that fairly describes the experimental trends. This simple polynomial approach can subsequently be used either to determine the thermal parameters of any point of a molded piece or to shed some light on phenomena responsible for the large variations of the measured quantities. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1368–1376, 2005

Key words: composites; curing of polymers; differential scanning calorimetry (DSC); processing

INTRODUCTION

The electric industry commonly employs epoxy-based composites as insulators because of their ability to withstand large electric fields and mechanical stresses over long periods of time. Besides imparting better mechanical properties and reducing the price of the final product, the addition of mineral fillers to thermosetting resins is an old but efficient way of preventing thermal degradation. Common inorganic fillers reduce epoxy overheating during curing because of a dilution effect and because of the larger heat capacity and thermal conductivity of the fillers in comparison with those of the neat resin.¹

According to the literature, the performances of these materials seem to strongly vary with the nature of the constituents² and even within a given class of composites. The nature of the second phase (often a mineral filler)³ and its topological arrangement are often invoked to explain variations in macroscopic physical properties.^{4,5} It is furthermore well known and understood that the thermal history,⁶ water ad-

sorption,⁷ and interface quality^{8,9} strongly alter the glass-transition temperatures (T_g 's) of these composites. The reason for the large variations within the thermal parameters, which can even affect apparently very similar samples, remains, however, an open question. Because it induces huge variations within a material's structure, the process could plausibly be held responsible for at least a part of this phenomenon. More specifically, the curing stage in the hot mold, characterized by the irreversible formation of a three-dimensional dense molecular network by means of an exothermic reaction that promotes extensive crosslinks,¹⁰ could induce variations from sample to sample. In particular, the large temperature rise produced during the curing stage might induce uneven thermal degradation.¹¹ This degradation is a well-known phenomenon¹⁰ naturally attributed to the low thermal conductivity of the material, which induces significant temperature gradients in thick parts.

This study was carried out on composites based on epoxy anhydride matrices reinforced by mineral particles. It seemed interesting to characterize the structural variations of the matrices originating from samples taken from industrial pieces. These samples were obtained by pseudorandom withdrawal all over the pieces. Despite considerable care in operation to ensure the reliability of the results, surprisingly broad distributions within measured thermal quantities (e.g.,

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Contract grant sponsor: Région Rhône-Alpes (through Thématiques Prioritaires grants).
Contract grant sponsor: Areva T&D.

T_g) were obtained, and this shows that the composites possessed intrinsically inhomogeneous properties on a centimeter scale. The literature on the relationship between the process and thermal parameters of this kind of particulate composite is, however, not abundant.¹⁰ It was then interesting to determine why some zones appeared to achieve a higher degree of completion in the reticulation process than others. A representation of the thermal parameters as a function of a sample's distance from the injection point in the mold clearly revealed that the topological characteristics were the relevant parameters. The overall thermal parameters appeared to be much less noisy when they were depicted versus the z coordinate of the withdrawal position within the vertical mold. The new representation led to a phenomenological model of the thermal properties that fairly fit the whole set of measured data. Considering the topological position of the samples could thus, by interpolation, lead to the values of the thermal quantities at any point of the global part with excellent statistical confidence. More interestingly, the phenomenological model proposed could, in return, serve as a tool for giving hints on the mechanisms occurring during the process of this type of complex composite. A difference in the thermal history during the very first stage of the process was believed to be the ground reason for the final scatter in the experimental data. It is furthermore demonstrated that the postcuring stage reduced the breadth of the distribution but did not erase the topological effect.

EXPERIMENTAL

Materials and curing procedures

Two systems of particle-filled composites were studied that differed in the chemical nature of the hardener but had similar diglycidyl ethers of bisphenol A as the prepolymer. The so-called C2 material was obtained with an anhydride hardener that, once reticulated, was aliphatic. The second one, called C3, was also obtained with an anhydride hardener, but it was aromatic. Despite this slight difference in the chemical natures of the hardeners, both systems were basically processed in the same way. The inorganic fillers (the nature of which could not be determined) were dried by being placed into an oven at 60°C for 48 h to reduce as much as possible the influence of water. The resin, the hardener, and the filler were then mixed and stirred at 56°C and degasified *in vacuo*. The mixtures were then injected under pressure at the bottom of a vertical mold and underwent the cure process at 150°C for 15 min. The composites were postcured for 8 h at 140°C and for 12 h at 60°C to complete the reticulation process.

In addition, a third material, called C3' was also investigated. This material corresponded to the C3

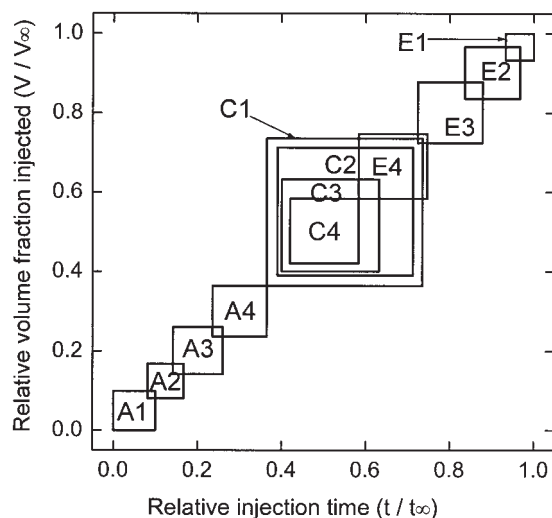


Figure 1 Representation of the relative volume fraction as a function of t_{rel} for the 12 analyzed zones.

formulation, being processed in the same way but not postcured. The decision to investigate this material was guided by color differences visible to the naked eye on millimeter-to-centimeter scales, especially after the postcuring of C3.

The thermal analyses were carried out at several positions of the piece according to their topological situation with respect to the injection point. For each material, 12 zones were analyzed, which actually solely differed by the injection time of the corresponding sample within the mold. The different sizes of the squares in Figure 1 represent the results of calculations with computer aided design software with the help of the exact shape of the piece (not shown). These 12 zones permitted us to explore every time domain associated with the process.

All the studied samples were conditioned *in vacuo* at 60°C for a week before testing to prevent possible moisture differences.

For both systems, the amount of the filler was verified by thermogravimetric analysis (TGA) as a function of the previously defined zones (Fig. 2). The volume fraction of the filler was rather homogeneous overall. A minor decantation process (<0.5 wt %) could nevertheless be detected that induced a slightly larger amount of filler in the bottom parts of the pieces, that is, close to the injection point. Similar results were obtained with a loss-on-ignition technique.

Differential scanning calorimetry (DSC) analysis

DSC analysis was carried out in a DSC 7 PerkinElmer device. The calorimeter had previously been calibrated with an indium standard. The baseline was accepted when, after several iterations, the amplitude

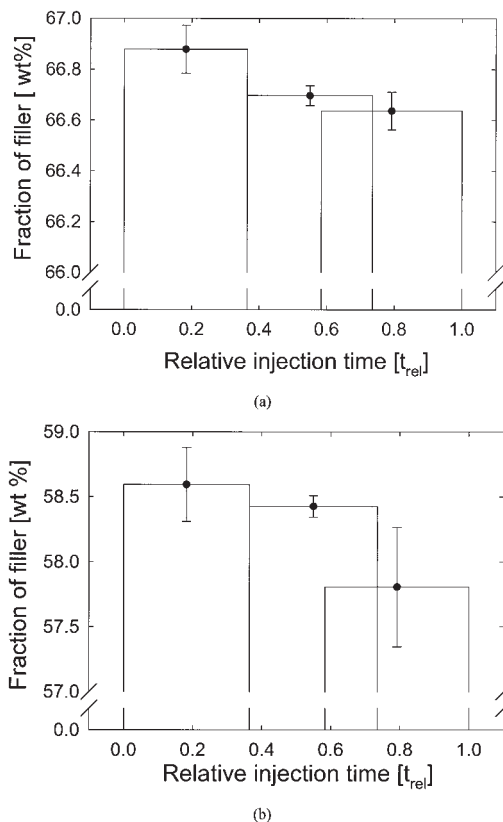


Figure 2 Weight fraction of mineral fillers (as determined with TGA) as a function of t_{rel} for (a) C2 and (b) C3 and C3'.

of the heat flow without samples and the reference was below 0.5 mW in the considered range of temperatures. The analysis was then carried out with samples containing 10 ± 1 mg of the polymer. DSC thermograms were recorded under a nitrogen atmosphere from 40 to 170°C. Measurements of the heat flow were taken at a heating rate of $10^\circ\text{C min}^{-1}$. For each sample, two successive temperature increases with a 5-min hold stage at 170°C between each ramp were carried out to impart to each sample a similar thermal history. The data presented in this article correspond to rejuvenated samples (second heating ramp) to prevent aging effects.

Definition of the extracted parameters

T_g is usually defined in three different ways¹² (Fig. 3). For this article, a fourth definition was chosen that corresponded to the actual onset of the glass transition. It was accordingly defined as the temperature at which the DSC thermogram split from the baseline. The endset T_g was similarly defined as the temperature at which the thermogram returned to the thermodynamic equilibrium state. These definitions were chosen because they brought robust parameters with evident physical meanings. To further improve the

stability and reproducibility of the parameters, a numerical method was developed that was based on the calculation of the first derivative of the thermograms. Overall, three independent parameters were eventually extracted from each thermogram that clearly characterized the structural state of the polymer within the composite:

- T_g : The actual beginning of molecular mobility induced by the glass transition (the temperature corresponding to the takeoff from the baseline).
- ΔT_g : Width of the glass transition (endset T_g – T_g).
- ΔC_p : Difference in the heat capacity between the rubbery and glassy states.

An example of such a determination is proposed in Figure 3(b), corresponding to the raw data of a C2 composite for three zones.

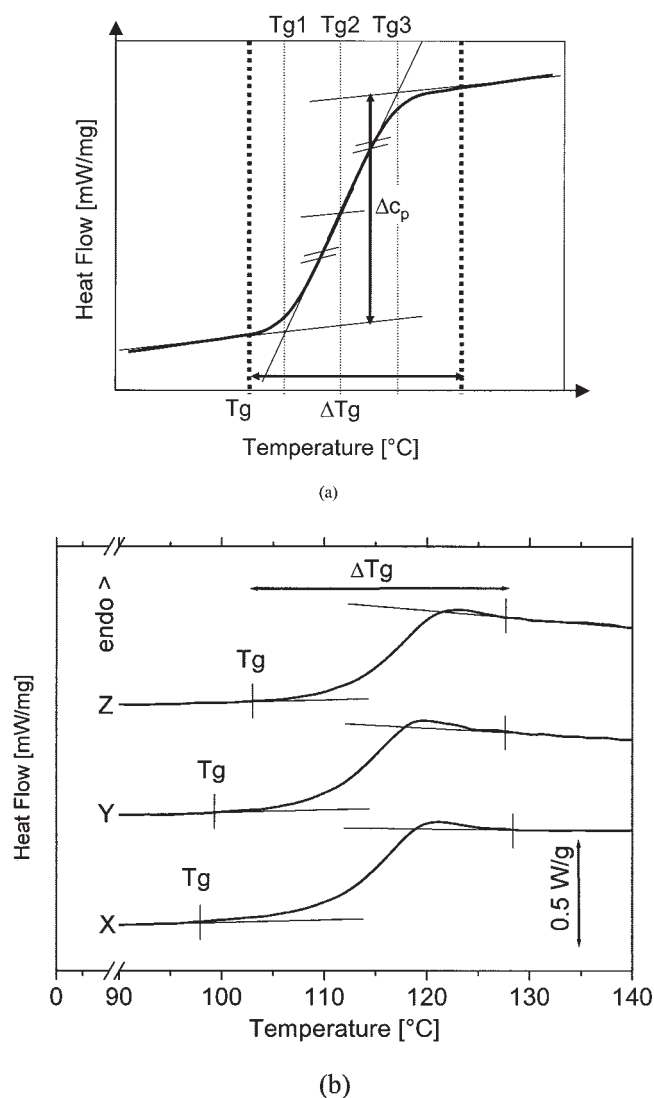


Figure 3 Definition of the three independent parameters: T_g , ΔT_g , and ΔC_p .

For a stoichiometric blend, a low T_g generally results from an incomplete reaction; it thus seemed pertinent to employ a fourth dependent parameter with a clear physical meaning: the extent of cure (α). The DiBenedetto equation, as modified by Pascault and Williams,¹³ is a well-accepted equation for interrelating T_g and α :

$$\frac{T_g - T_{g0}}{T_{g\infty} - T_{g0}} = \frac{\lambda\alpha}{1 - [1 - \lambda]\alpha} \quad (1)$$

where T_{g0} is the glass-transition temperature of the initial unreacted mixture, $T_{g\infty}$ is the maximum glass-transition temperature reached with isothermal curing, and λ is an adjustable parameter between 0 and 1 that represents the ratio of the segmental mobility for the crosslinked and uncrosslinked polymers. Montserrat¹⁴⁻¹⁷ determined the different parameters ($T_{g\infty} = 109^\circ\text{C}$, $T_{g0} = -23.2^\circ\text{C}$, $\lambda = 0.69$) for a system chemically similar to C2. Although these parameters were determined experimentally for the neat resin, it seemed reasonable to assume that they were not much altered by the presence of the filler (the heat capacity was indeed not involved in the formula). A fit of the $T_{g\infty}$ parameter was nevertheless necessary to adapt the numerical values to the different definition of T_g . α in this article was hence determined through eq. (1) with $T_{g\infty} = 104^\circ\text{C}$, $T_{g0} = -23.2^\circ\text{C}$, and $\lambda = 0.69$.

RESULTS AND DISCUSSION

Although random sample withdrawal has shortcomings, it is commonly and successfully used for the characterization of the properties of massive composite parts, and so it was the starting point of this study. The three independent parameters were first analyzed for all materials with a pseudorandom sample withdrawal method; this means that the positions of the samples in the mold were not considered. Figure 3(b) depicts, as an example, three raw thermograms for C2, showing the magnitude of the measured differences in the T_g values.

Dispersion of the thermal parameters

The histograms displaying T_g , ΔT_g , and ΔC_p populations could not be fitted to Gaussian curves because the sampling was not totally random, each zone of each material being represented (Fig. 4). The experimental values for ΔT_g and ΔC_p were not quantified for the nonpostcured material (C3') because of the presence of a postcuring peak, which greatly altered ΔT_g and ΔC_p .

T_g

As expected, both the thermal history and the chemical nature of the matrix primarily influenced the T_g

values. The C2 and C3 composites, with similar thermal histories, exhibited differences due to the chemical nature of the hardener. The aromatic hardener led to higher T_g values than the aliphatic one. The C3' composite (not postcured), which most likely had a lack of curing, exhibited a much lower T_g than C3. A comparison of C3' and C3 also revealed that the width of the distribution in T_g was reduced by postcuring. For C3, the postcuring process thus improved the properties for two reasons: an increase in T_g and a decrease in the width of the T_g distribution. Overall, T_g 's for the entire piece followed broad bell-shaped distributions [$10 < \text{maximum } T_g - \text{minimum } T_g < 18$; Fig. 4(a)].

ΔT_g and ΔC_p

Figure 4(b,c) displays the ΔT_g and ΔC_p dispersions, respectively, for all the studied composites. The T_g transition appears systematically broader for the C3 formulation. The C3 composites indeed exhibited up to 40°C between the starting of the molecular mobility and the return to the equilibrium state. This fact is related to the visible heterogeneities in C3, which most likely corresponded to different reticulation states. These heterogeneities took the form of darker and lighter areas. A comparison of the measurements of darker ($T_g = 110^\circ\text{C}$) and lighter ($T_g = 119^\circ\text{C}$) samples from zone X1, in which the colored areas were separated enough to be cut off distinctively, supported this hypothesis. ΔC_p also presented a rather dispersed behavior, but it did not seem to change significantly between darker and lighter areas.

This short analysis suggests that the random sample withdrawal method used to determine the thermal parameters failed to give a reasonable characterization of the measured properties of the composites. In fact, the dispersion in the measured data was so broad that the uncertainty of the thermal parameters could not faithfully express the material properties. It was then assumed that this dispersion in the measured data was due to bad data points that should be removed by statistical analysis. Such an approach was then undertaken by the removal of points too far from the mean value (with the jackknife technique¹⁸), but it appeared that most of the physical information was lost. In particular, the very good correlation between T_g and ΔT_g seemed to reveal that the entire set of data had to be considered and that the apparent noise within the experimental points was actually related to the fact that an important parameter was missing in the representation. This is treated in the next section.

Representation of the thermal parameters as a function of the sample locations within the mold

An exploratory analysis was undertaken to reduce the apparent noise in these broad distributions. Regarding

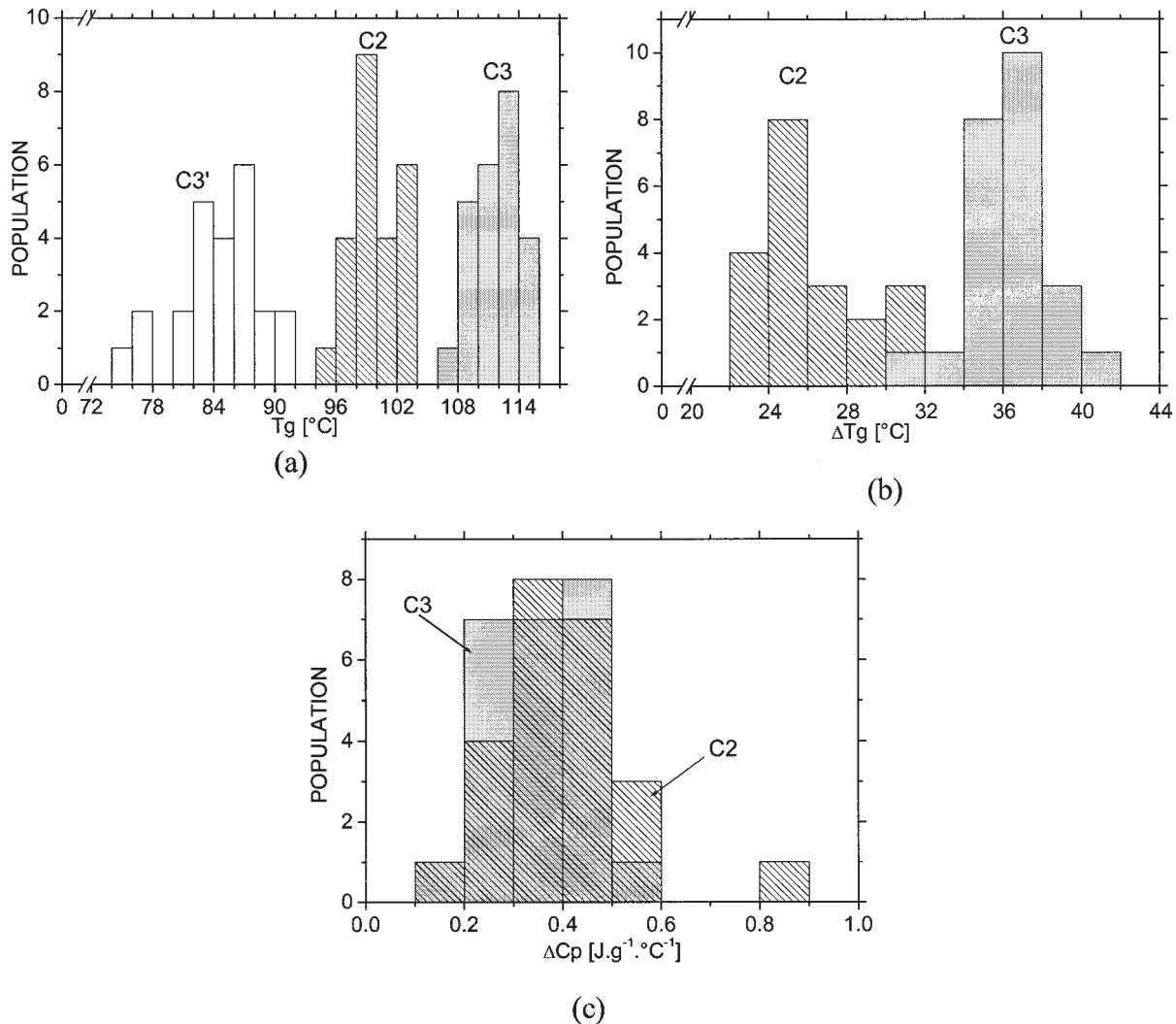


Figure 4 Histograms of populations of the three independent parameters: (a) T_g , (b) ΔT_g , and (c) ΔC_p (the experimental data are presented without an accounting of the withdrawal position).

the rather straightforward processing conditions, the sole issue that differentiated the samples appeared to be their position in the mold. It was first assumed that the thermal quantities should, to some extent, follow a regular variation within the global piece. To better reveal this continuity, we labeled T_g , ΔT_g and ΔC_p as a function of the topological location of the corresponding samples in the mold. More precisely, the 12 zones were differentiated by the relative time of injection of the resin during the injection process ($t_{rel} =$ relative injection time (t)/maximum time of injection (t_x)). Under the assumption that gravity was the leading parameter, the zones close to the injection point received fresh resin until the end of the injection process and thus came up with the shortest curing times (zone X, Fig. 1). On the contrary, the top of the mold was eventually filled with the material that first came into the mold and thus had the longest curing time. Figure 5(a–c) depicts the same experimental T_g values as

Figure 4, but as a function of t_{rel} . The parabolic behavior that this new representation brought out emerged with much less apparent noise in the experimental data. A statistical analysis with the entire set of data confirmed the dependence, with an excellent correlation between these two variables (T_g and t_{rel}). The heterogeneous material (C3) also followed a similar tendency, even if T_g kept, to some extent, a fluctuating behavior (Table I). A comparison of C3 and C3' showed that, even if the overall distribution were reduced, the heterogeneities were actually accentuated during the postcuring process (Fig. 5).

The representation of T_g as a function of t_{rel} hence appeared to be fruitful. The same method was thus applied to ΔT_g and ΔC_p . ΔT_g , when represented versus t_{rel} , also fairly followed a parabolic law, as shown in Figure 6(a,b). For the two materials for which this parameter could be determined (C2 and C3), ΔT_g and

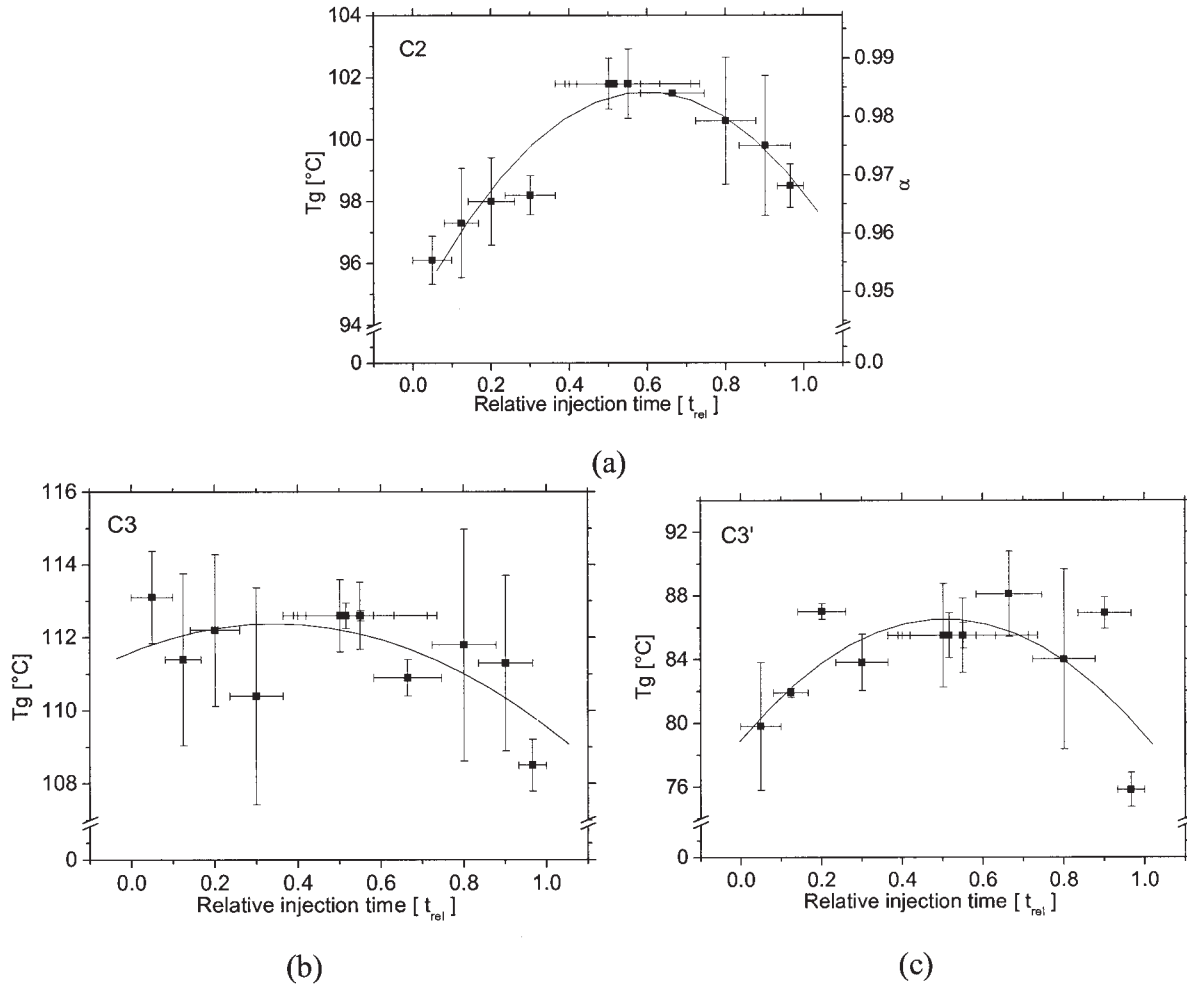


Figure 5 T_g 's for (a) C2, (b) C3, and (c) C3' as a function of t_{rel} .

t_{rel} were significantly correlated with a confidence interval of 97% (Table I).

The last determined parameter, ΔC_p , also tended to follow a parabolic behavior in the new representation [Fig. 7(a,b)]. Only for the heterogeneous material was the statistical correlation relatively poor (Table I).

According to these results, although they both followed a parabolic tendency, T_g (or α) and ΔT_g exhibited inversed behaviors. In other words, the coefficients corresponding to t_{rel}^2 had opposite signs. A statistical anal-

ysis confirmed that ΔT_g was significantly correlated to α , as shown in Table II and Figure 8. Moreover, ΔT_g could thus be considered a pertinent parameter for estimating the homogeneity of a cured epoxy system. The relationship between ΔT_g and T_g takes a linear form:

$$\Delta T_g = a - bT_g \quad (2)$$

where $a = 258^\circ\text{C}$ and $b = 2.36$ represent experimentally estimated constants. Equation (2) actually pro-

TABLE I
Coefficients of Determination and p Values Between T_g , ΔT_g , ΔC_p , and t_{rel} for the composites C2, C3, and C3'

	C2		C3		C3'	
	Coefficient of determination	p	Coefficient of determination	p	Coefficient of determination	p
T_g/t_{rel}	0.8198	9.51×10^{-7}	0.3630	3.63×10^{-1}	0.5783	3.07×10^{-3}
$\Delta T_g/t_{rel}$	0.8036	2.26×10^{-6}	0.4491	2.77×10^{-2}	^a	^a
$\Delta C_p/t_{rel}$	0.5160	9.84×10^{-3}	0.3535	9.02×10^{-2}	^a	^a

^a The postcuring process occurring in the C3' composites prevented the accurate determination of these parameters.

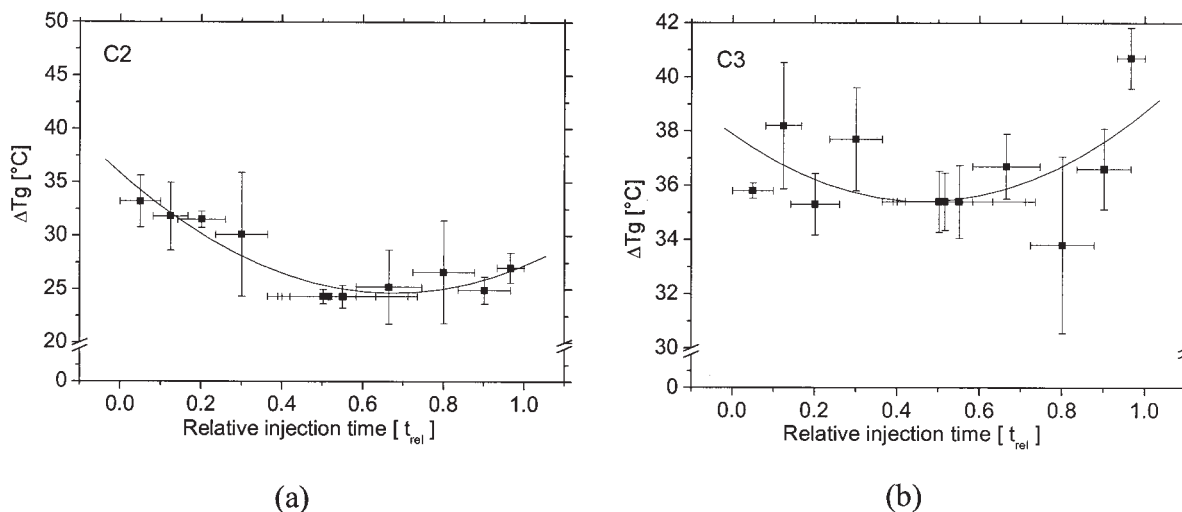


Figure 6 ΔT_g for (a) C2 and (b) C3 as a function of t_{rel} .

vides a rationalization of the fact that the studied polymer (a thermosetting matrix in a composite with an incomplete reticulation) contains heterogeneities that increase ΔT_g and reduce its absolute value.

Finally, Montserrat¹⁶ showed that α could also be significantly correlated to ΔC_p . It was thus interesting to attempt to confirm this tendency with this set of data. ΔC_p did not appear to be significantly correlated, in the statistical sense, to α , as shown in Table II and Figure 9. This result seems to have arisen from the large uncertainty always affecting measurements of ΔC_p ¹⁶ and the relatively narrow variations in the α values. The use of the Boyer equation,¹⁹ as derived by Montserrat,¹⁶

$$\Delta C_p = c + \frac{d}{T_g} \quad (3)$$

with the same parameters ($c = 8.9 \times 10^{-2} \text{ J g}^{-1} \text{ °C}^{-1}$ and $d = 1.1 \times 10^2 \text{ J g}^{-1}$) gave nevertheless a curve compatible with the measured variations of ΔC_p (Fig. 9).

OVERVIEW

The thermal parameters of the composites appeared, at first glance, to present a stochastic distribution. With a new representation of the experimental data versus t_{rel} , the entire set of data could, however, be defined with a much better resolution. A parabolic behavior was systematically obtained for the three independent parameters— T_g , ΔT_g , and ΔC_p —without the elimination of any data, even those statistically considered not significant.

An explanation of the bell shape of the curves of T_g as a function of t_{rel} can be proposed (Fig. 10). For the

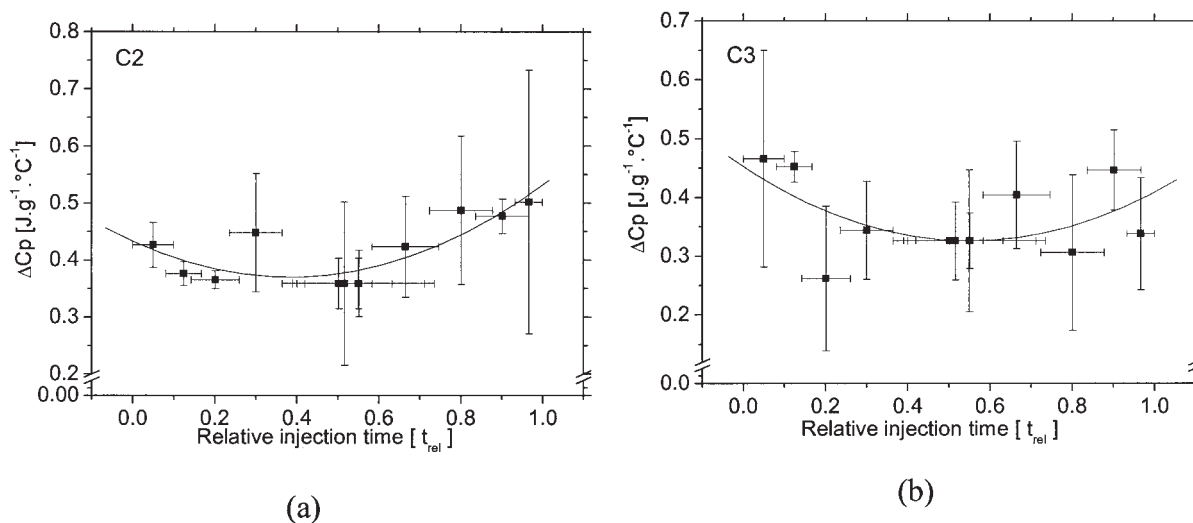


Figure 7 ΔC_p for (a) C2 and (b) C3 as a function of t_{rel} .

TABLE II
Coefficients of Determination and p values Between ΔT_g , ΔC_p , and α for the C2 Composite

	Coefficient of determination	P
$\Delta T_g/\alpha$	0.7573	1.80×10^{-5}
$\Delta C_p/\alpha$	0.1045	6.27×10^{-1}

zones far away from the injection point (the bottom of the mold), a lower value of T_g can be interpreted as follows:

1. A stoichiometric defect resulting from the slight decantation of the filler during the process, as observed by TGA (Fig. 2). The decantation process could indeed induce a decantation of the prepolymer, which had a better affinity to the mineral filler, and thereby modify the stoichiometry and decrease T_g .²⁰
2. An overheating of the composite that caused chemical degradation of the polymer.²¹ The overheating could obviously be a direct result of the longer curing time. This hypothesis is, however, also supported by the fact that the top zones were eventually filled with the materials that went through the hot mold all the way (corresponding to the hot front). In addition, overheating could be magnified by the lower amounts of fillers measured in the top zones of the mold. The fillers indeed acted as heat dissipaters because of their high heat conductivity and specific heat, in comparison with those of the polymer. The later interpretation is, however, not likely because of the very low decantation observed (Fig. 2).

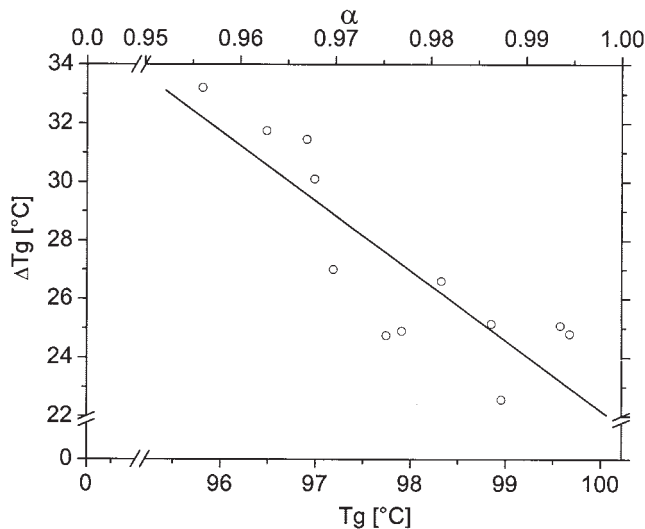


Figure 8 ΔT_g versus α for the C2 composites.

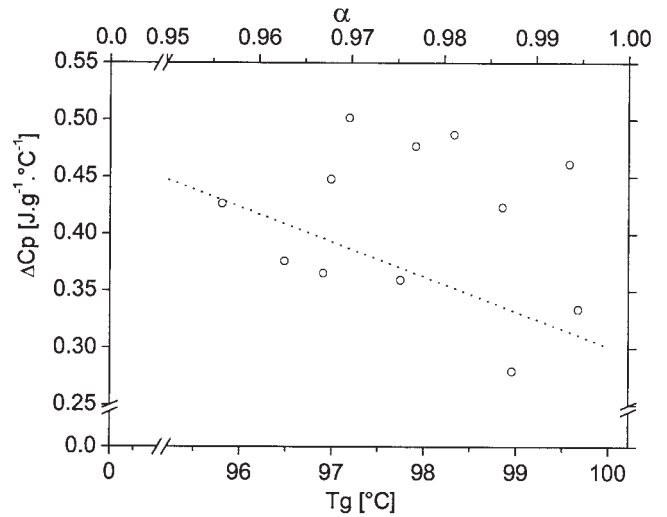


Figure 9 ΔC_p as a function of α or T_g for the C2 composites. The dotted line was calculated with eqs. (1) and (2) according to Montserrat.

For the zones close to the injection point, a symmetric thought process can be applied to describe the relatively lower T_g values:

1. A stoichiometric effect²⁰ similar to the one described previously and induced by filler decantation during the process.
2. A thermal effect²² induced by a shorter curing time,²³ a lower temperature (compared with that of the top zone), and a slightly lower amount of reinforcing particles.

The first explanation, which would require at least a partial phase separation and diffusion between the two very compatible components of the polymer, does not seem to be likely. The second possibility could, on

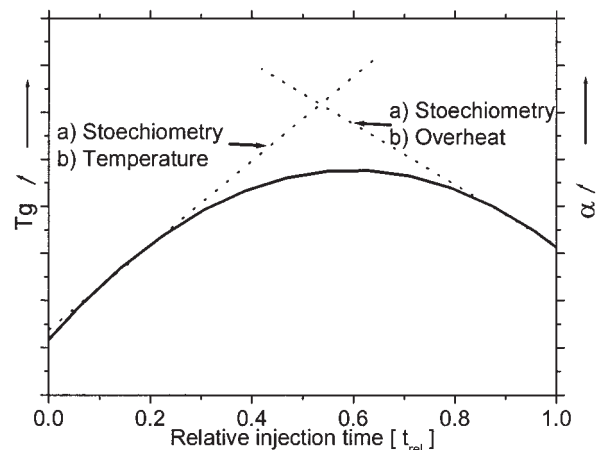


Figure 10 Schematic representation of T_g as a function of t_{rel} .

the contrary, arise from realistic events and accordingly seems reasonable for these composites.

CONCLUSIONS

The processing of epoxy-based composites induced a broad dispersion in DSC-measured independent thermal parameters (T_g , ΔT_g , and ΔC_p) on the scale of a molded piece. These distributions, which first appeared to be stochastic, could actually be directly related to the withdrawal zone of the analyzed sample. A new parameter was defined, t_{rel} , that enabled us to describe the entire set of data by parabolic curves. This method produced fairly good agreement with materials homogeneous on the millimeter scale. For formulations that led to composites with heterogeneity visible to the naked eye, similar behavior was observed, even if the resolution was rather poor in the latter case.

These parabolic behaviors revealed that T_g (or α , as linked by the DiBenedetto equation) possessed lower values in the vicinity of the injection point and at the top of the vertical mold.

ΔT_g and ΔC_p also exhibited parabolic behavior when displayed against t_{rel} , but the extreme zones (close and far from the injection point) led to the highest values. This inversed behavior was confirmed by the statistical study. Because ΔT_g was defined as the temperature difference between the very beginning of the molecular mobility associated with T_g and the temperature at which the system went back to the thermodynamic equilibrium, it seemed to be the pertinent parameter for assessing the network heterogeneity. This work thus indicates that epoxy anhydrides in an under-reticulation state possess a rather heterogeneous network. In particular, the postcuring step not only contributes to higher absolute values of T_g but also favors network homogenization.

Even with a very well controlled process, some variability remained. Having taken precautions and using a large set of data, we could extract physico-chemical information because of this variability, without any intervention of the process itself.

Although no definitive interpretation can be given for this topological dependence of the thermal parameters, a difference in the thermal history during the very first step of the process is believed to be the ground reason for the final scatter in the experimental data. It was additionally observed that even a postcuring stage performed much above T_g could not erase this topological effect. It could now be interesting to confirm the correlation with samples presenting a

wider range of reticulation states to obtain even more sensitive data. The linear relationship in the studied domain between α and T_g limited the study of the new relationship linking T_g (or α) to ΔT_g . It would consequently be of particular interest to reveal whether α or T_g could be related to ΔT_g over a broader range of variations.

The authors gratefully thank G. Verhaghe of the Areva Aix-Les-Bains Center for providing the samples for this study. The authors also acknowledge A. B eroual for discussions.

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