

# Dynamic Mechanical Analysis of Particulate-Filled Epoxy Resin

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**ABSTRACT:** The dynamic mechanical properties of epoxy composites filled with different amounts of quartz powder were investigated. The storage modulus and loss tangent were measured at frequencies between 7.8 and 323 Hz from room temperature up to 460 K. The influence of the filler content on the temperature and frequency behavior of the dynamic mechanical properties is discussed and explained in terms of models presented in the literature. In particular,

the dependence of the composite damping with the quartz content is explained with regard to damping due to particle-particle and polymer-particle interaction. Also, the glass-transition temperature as a function of filler content was obtained and was related to the results obtained for the apparent activation energies of the  $\alpha$  relaxation, which were estimated with the Williams, Landel, and Ferry equation. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 883–892, 2003

## INTRODUCTION

Fillers are additives that usually modify the mechanical performance of a polymeric composite. An example of this type of system is the addition of silica to an epoxy matrix to lower the material's coefficient of thermal expansion (CTE). However, adding silica will not only decrease the CTE, but it will also increase its modulus and modify other mechanical properties.

The mechanical properties are affected by the filler concentration, particle shape and packing, and relative modulus of the components. All these factors also affect another important mechanical property, the loss tangent ( $\tan \delta$ ), which is a measurement of damping, the relation between the elastic energy stored and the energy dissipated per cycle of vibration.<sup>1–4</sup>

When two or more materials are combined together to form a composite, the properties of the composite are governed not only by the properties of individual components but also by the interface between them. Then, when the composite undergoes vibration damping, additional mechanisms will be introduced. The interface effects and adhesion degree are not very important factors in obtaining the elastic modulus, but they are very important for determining the damping behavior of composites.

Dynamic mechanical measurements are very useful for analyzing the correlation between the structure and properties of polymeric materials. Dynamic mechanical tests can give information about the modifications induced by the introduction of a filler. For example, changes in the main mechanical relaxation of reinforced polymers could result both from changes in the molecular mobility of polymer matrix due to interactions at the polymer-filler interfaces and from a mechanical coupling effect between phases.<sup>1,3,5–10</sup> Also, previous studies have shown that these filler effects are temperature dependent.

In this work, we studied the dynamic mechanical behavior of epoxy resins filled with varying contents of quartz powder. The dependence of the composites ( $\tan \delta_c$  and the Young's storage modulus of the composites ( $E'_c$ ) with the volume fraction of the filler ( $\phi$ ) are discussed for temperatures between 290 and 460 K and at excitation frequencies ( $\nu$ 's) in the range of 7.8–323 Hz. The activation energy of  $\alpha$  relaxation ( $E_a$ ) was computed and analyzed in connection with  $\phi$  with the superposition principle due to Williams, Landel, and Ferry (WLF).<sup>11</sup>

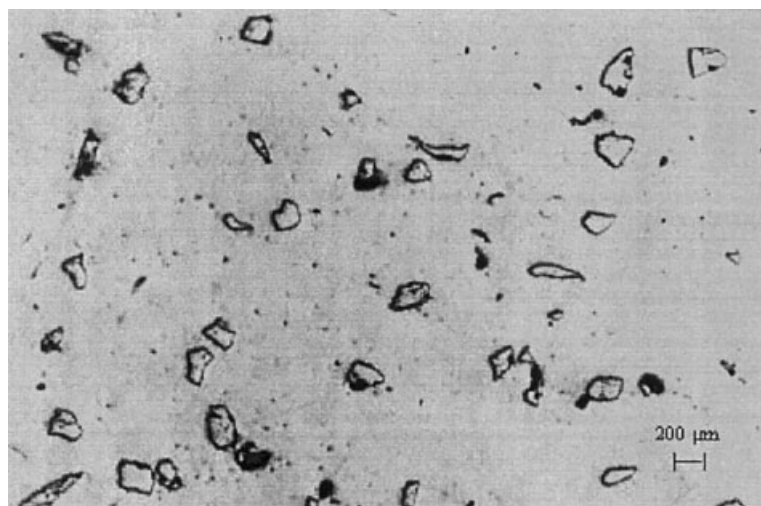
## EXPERIMENTAL

The material used in this study was an epoxy resin reinforced with different amounts of quartz powder. The epoxy resin, the curing agent, and the accelerator used were a diglycidyl ether of bisphenol A, a methyl tetrahydrophthalic anhydride, and heterocyclic amine (*N*-metil imidazol), respectively. All of them were provided by Ciba Co. (Argentina).

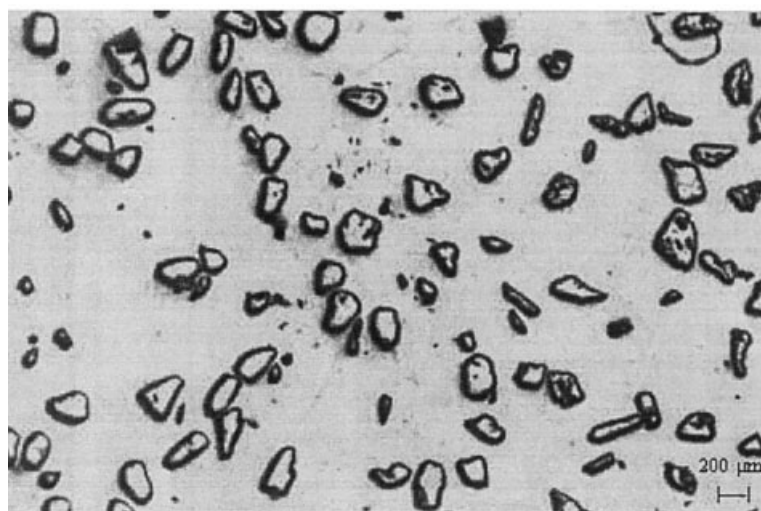
Correspondence to: S. N. Goyanes (goyanes@df.uba.ar).

Contract grant sponsor: Fundación Antorchas.

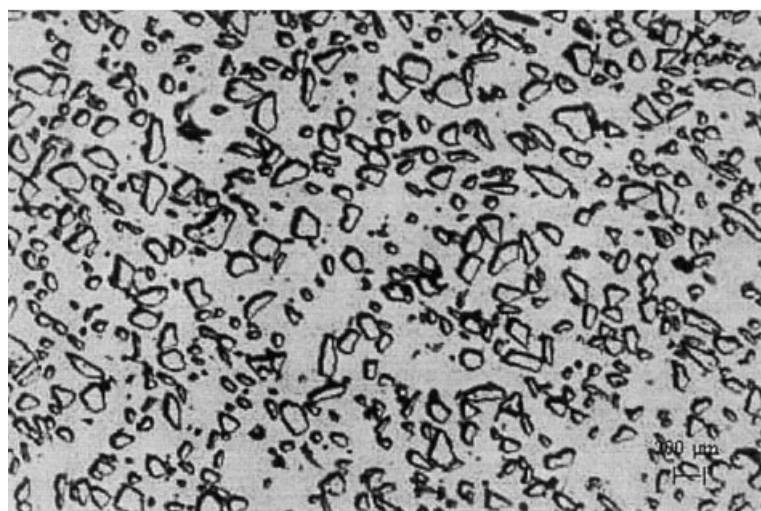
Contract grant sponsor: Universidad de Buenos Aires (Investigation Project X182).



(a)

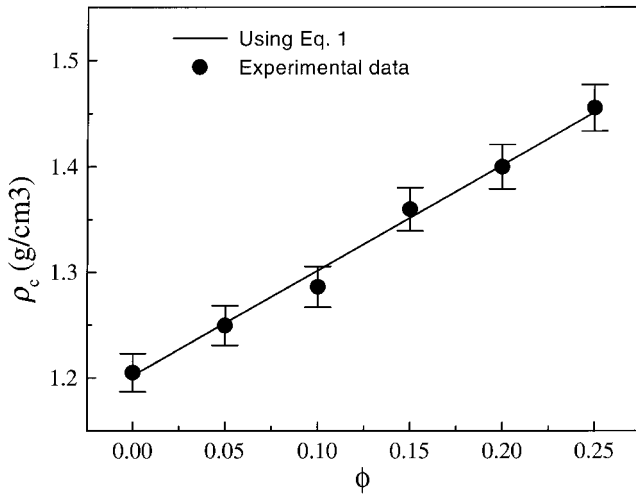


(b)



(c)

**Figure 1** Optical microscope photographs of quartz filler composites for three different  $\phi$ 's: (a) 0.05, (b) 0.15, and (c) 0.25 (scale = 200  $\mu\text{m}$ ).



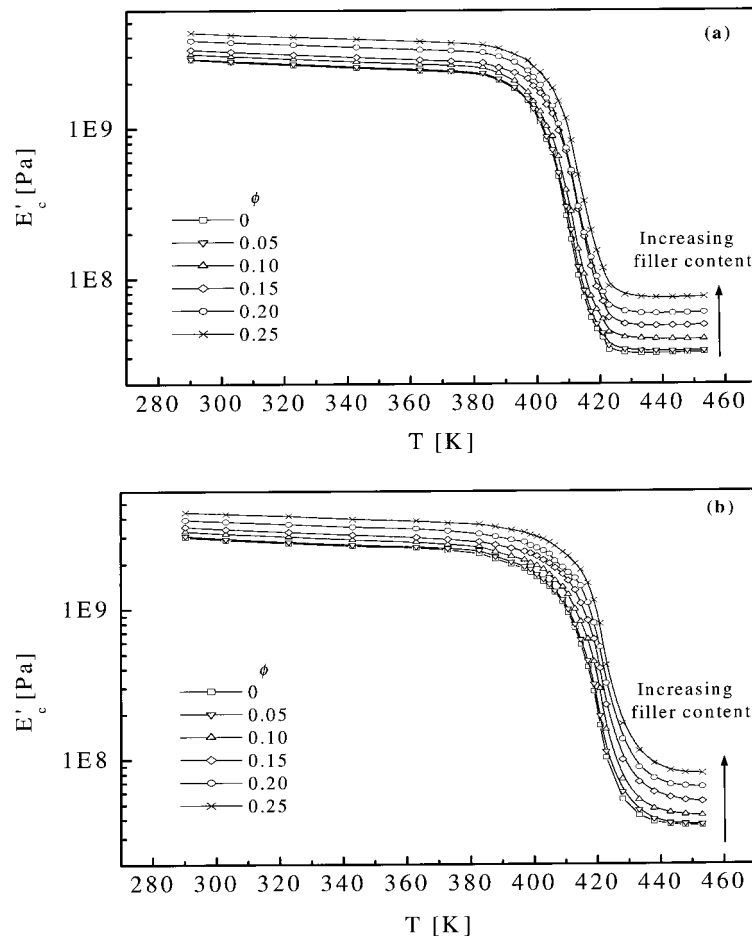
**Figure 2** Density of the fabricated composites as a function of filler content.

A sieve was used to obtain quartz particles between 106 and 125  $\mu\text{m}$ . The appropriate amounts of quartz particles, dried at 383 K, were mixed with epoxy resin [100 parts by weight (pbw)] and hardener (90 pbw) by

stirring at room temperature for 30 min under vacuum. The accelerator (0.7 pbw) was added to the compound and stirred for 2 min under vacuum. The degassed compound was poured in a Pyrex tubular mold 4 mm in diameter and 100 mm in length. Seven molds were placed in a horizontal position in a device orientated along the axis of a tubular oven. To prevent the settling down of the quartz filler, the device imposed a rotation to the Pyrex molds at a frequency of 0.08 Hz during the whole curing process, which consisted of the following steps: first, there was a heating phase at a rate of 0.8 K/min up to 393 K. Then, the temperature was kept at this level for 14 h. Finally, the samples were cooled inside the oven until they reached room temperature.

Samples with  $\phi$ 's of 0, 0.05, 0.10, 0.15, 0.20, and 0.25 were molded.

Particle distribution and the presence of agglomerates and holes were determined in all samples by photographs obtained with an optical microscope. Figure 1 shows the photographs of the samples with  $\phi$ 's of 0.05, 0.15, and 0.25. A homogeneous particle distribution, with no signs of agglomerates or holes, was observed in all samples. The black stains shown in



**Figure 3** Dependence of  $E'_c$  with temperature for samples with different filler contents: (a) 7.8 and (b) 323 Hz.

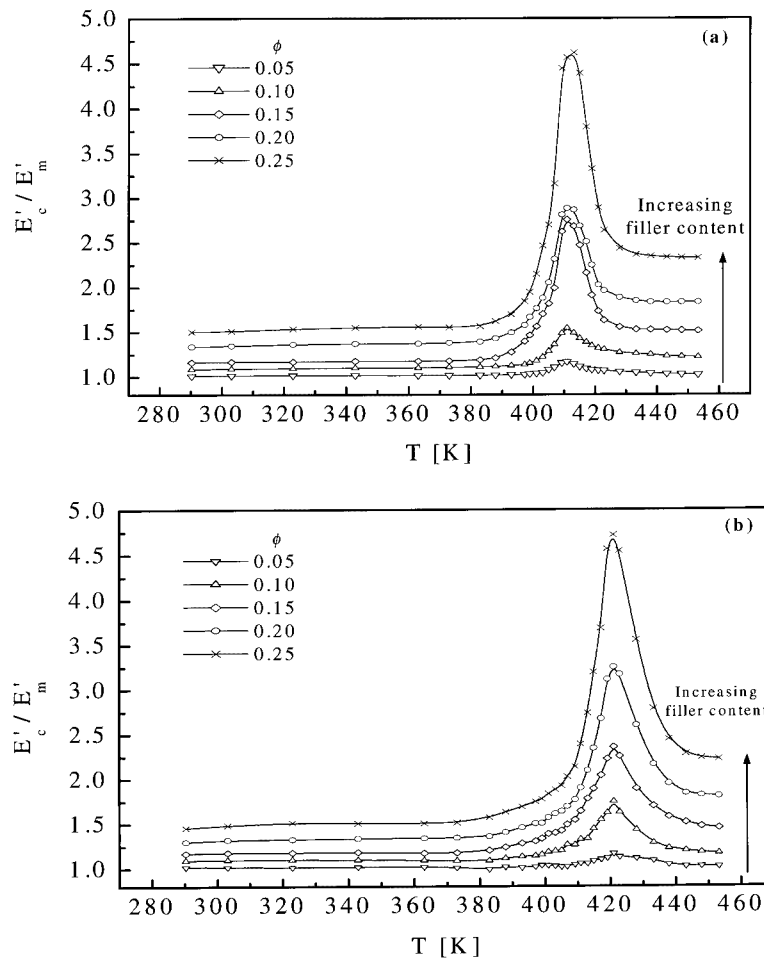


Figure 4  $E'_c$  as a function of temperature for all composites: (a) 7.8 and (b) 323 Hz.

Figure 1 are particles that were torn out during the sample preparation for the photographs.

Density ( $\rho$ ) measurements of the composites were carried out to verify that there were not holes in the samples. The  $\rho$ 's were obtained by application of the Archimedeian principle, by measurement of the weight of the sample in air and in water. Figure 2 shows  $\rho$  at room temperature as a function of the volume fraction of quartz powder in the composites. The values of  $\rho$  associated to each  $\phi$  value were the mathematical average of five measurements.

Usually,  $\rho$  of a two-phase compound is expressed by

$$\rho_c = (1 - \phi)\rho_m + \phi\rho_f \quad (1)$$

where the subscripts  $c$ ,  $m$ , and  $f$  refer to the compound, matrix, and filler, respectively.

The fitting of eq. (1) to the experimental data is drawn as a full line in Figure 2, with a value of  $\rho_f = 2.2 \text{ g/cm}^3$  for the quartz powder<sup>12</sup> and  $\rho_m = 1.20 \text{ g/cm}^3$  for the matrix, according to the supplier's specifications. Although the same dispersion could be observed, the good fit of experimental data to eq. (1), together with the evidence of the microscopic obser-

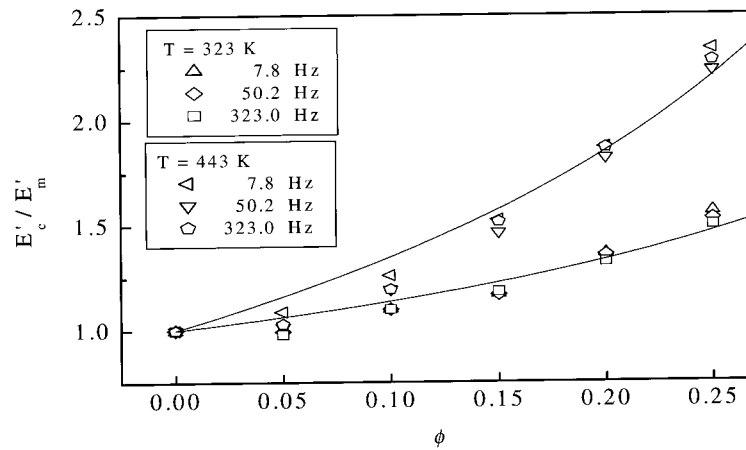
vations, confirmed the absence of macroscopic holes in the samples.

Dynamic mechanical spectrometry was performed on unfilled epoxy and composite materials with a Metravib viscoanalyzer. Composite samples were tested at frequencies between 7.8 and 323 Hz, within a temperature range between 290 and 460 K in the tension-compression mode with a fixed displacement amplitude of  $4 \mu\text{m}$ . These tests allowed us to obtain, for each  $\nu$ ,  $E'$  and  $\tan \delta$  dependence with  $\phi$ , and therefore, the effect of the frequency on  $E'_c$  and  $\tan \delta_c$  for each  $\phi$  value.

## RESULTS AND DISCUSSION

### Storage modulus

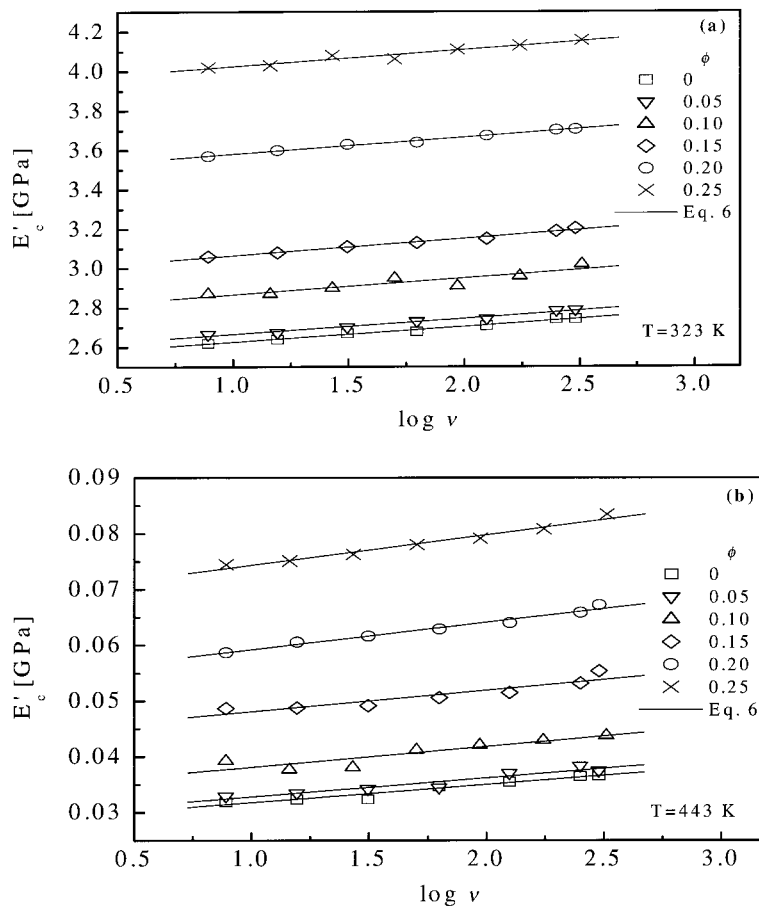
Figure 3(a,b) shows the temperature dependence of  $E'_c$  for all of the composites studied at the two extreme values of  $\nu$  (7.8 and 323 Hz). Both graphs show the well-known effect of the storage modulus fall of nearly two orders of magnitude in the temperature region associated to the glass-transition temperature ( $T_g$ ). It is interesting to note two other effects, which



**Figure 5** Dependence of  $E'_c$  as a function of  $\phi$  for different frequencies and temperatures. The solids lines represents the Lewis-Nielsen model.

seemed to be independent of  $\nu$ . On one hand,  $E'_c$  increases strongly with increasing  $\phi$ . On the other hand, this increase was more important at the rubbery zone ( $T > T_g$ ) than at the glassy region ( $T < T_g$ ). This last effect, already observed by other authors,<sup>1,13-15</sup> can be seen more clearly in Figure 4(a,b), where the

relative modulus ( $E'_r = E'_c/E'_m$ ) is plotted as a function of temperature for all  $\phi$  values.  $E'_r$  changed dramatically with temperature. After Lee and Nielsen,<sup>13</sup> this effect can be explained by the fact that filled systems are never perfectly dispersed. There are always some particles in contact with each other, called *agglomer-*



**Figure 6** Dependence of  $E'_c$  with  $\nu$  for all  $\phi$  values at two values of temperature: (a) 323 K (glassy zone) and (b) 443 K (rubbery zone). The solid lines indicate the experimental data fitting by eq. (6).

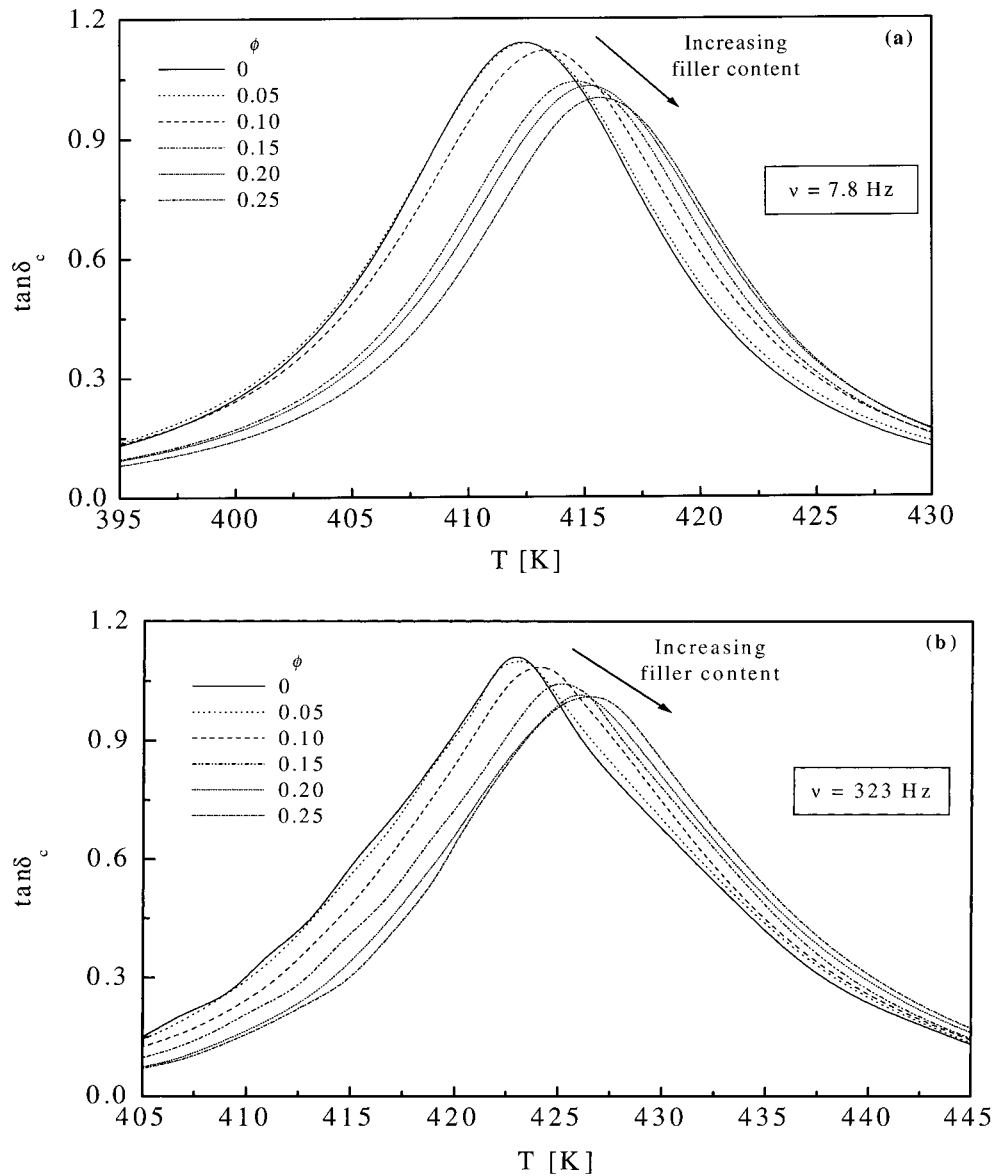


Figure 7  $\tan \delta_c$  as a function of temperature for two frequency values: (a) 7.8 and (b) 323 Hz.

ates. Rigid agglomerates, in which no motion occurs at particle–particle contact points, increase the modulus more than is found in perfectly dispersed systems. If the forces on the agglomerates during the deformation of the composite are great enough to produce motion at the contact points, the modulus decreases. Below  $T_{gr}$  the polymer can exert large forces on the agglomerates because of its high modulus, so a great deal of particle–particle motion should take place. However, above  $T_{gr}$ , where the polymer modulus decreases strongly, the forces created in deforming the material may not be great enough to overcome the friction at the contact point and may break up the agglomerate. On the basis of this idea, it may be expected that this effect would increase with particle content, which agrees with our experimental results, as shown in Figure 4(a,b).

According to the literature, the dependence of  $E'_c$  with  $\phi$  for each frequency and temperature value can be described with the model proposed by Lewis and Nielsen:<sup>1</sup>

$$\frac{E'_c}{E'_m} = \frac{1 + AB\phi}{1 - B\psi\phi} \quad (2)$$

where  $A = k_E - 1$  ( $k_E$  is the Einstein's coefficient) and  $B$  and  $\psi$  are given by

$$B = \frac{E'_f/E'_m - 1}{E'_f/E'_m + A} \quad (3)$$

$$\psi = 1 + \frac{1 - \phi_{\max}}{\phi_{\max}^2} \phi \quad (4)$$

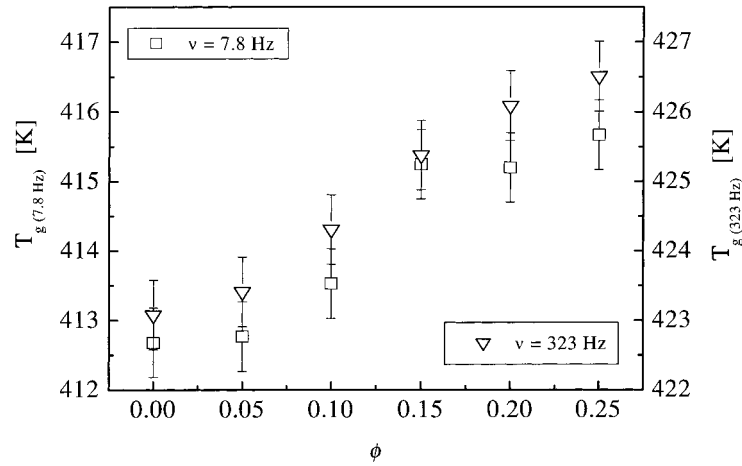


Figure 8 Dependence of  $T_g$  as a function of  $\phi$  for two extreme frequency values.

where  $\phi_{\max}$  is the maximum packing fraction of the filler.

Points in Figure 5 show the dependence of the experimental data with  $\phi$  for three different excitation frequencies and two temperatures, one corresponding to the glassy zone and the other one to the rubbery zone. Solid lines represent data fitted by the Lewis–Nielsen model. From fitting, it turned out that  $k_E = 1.21$  and  $\phi_{\max} = 0.655$  at the glassy zone and  $k_E = 2.98$  and  $\phi_{\max} = 0.59$  at the rubbery zone.

When we considered that a high Einstein's coefficient is associated with a strong adhesion between particles and matrix, the values obtained for  $k_E$  agree with the idea of possible polymer slippage through the particle agglomerates at the glassy zone.<sup>8–13</sup> In the data fitting of Figure 5, no  $\phi_{\max}$  value was proposed, contrary to that found in the literature.<sup>13</sup> Instead it was obtained from the fitting parameters of the experimental data. The two different values of  $\phi_{\max}$  could be explained again, within the Lewis–Nielsen<sup>13</sup> hypothesis. A decrease in the amount of immobilized polymer between particles (which occurred at  $T < T_g$ ) indicated less apparent volume occupied by the the filler; when the following was considered.

$$\phi_{\max} = \frac{\text{True volumen of the filler}}{\text{Apparent volume occupied by the filler}} \quad (5)$$

the value of  $\phi_{\max}$  had to increase at  $T < T_g$ . Also, the results in Figure 5 seem to indicate that the dependence of the storage modulus with filler content was independent of  $\nu$ . However, analyzing this effect from relative modulus data may lead to the wrong conclusions. According to Lagakos et al.,<sup>16</sup> in rigid polymers, the  $\nu$  dependence of the storage modulus follows this equation:

$$E'_c = A \log \nu + B \quad (6)$$

where  $A$  and  $B$  are constant for a given polymer. In the case of composites with different amounts of  $\phi$ , it is obvious that parameter  $B$  is a function of  $\phi$  and  $A$  shows the influence of filler content on the frequency dependence of the storage modulus.

Figure 6(a,b) displays the dependence of  $E'_c$  with  $\nu$  for all  $\phi$  values at two values of temperature: 323 K (glassy zone) and 443 K (rubbery zone). In this figure, one can see that for a fixed value of  $\phi$ , the storage modulus of a composite increased with  $\nu$  according to eq. (6). The solid lines indicate the experimental data fitting by eq. (6). It turned out that at the glassy zone, parameter  $A$  was not dependent on  $\phi$  and took a value of  $A = (8.3 \pm 0.3) \times 10^7$ , whereas at the rubbery zone, the value increased from  $(0.33 \pm 0.03) \times 10^7$  to  $(0.55 \pm 0.04) \times 10^7$ , when the filler content increased from 0 to 0.25. This means that at the rubbery zone, the filler content slightly modified the frequency dependence of the storage modulus, which was more noticeable from  $\phi = 0.2$ .

### Tan $\delta_c$

Figure 7(a,b) shows  $\tan \delta_c$  as a function of temperature for two extreme  $\nu$ 's values, 7.8 and 323 Hz, for all of the studied  $\phi$ 's. A shift to higher temperatures of the  $\tan \delta_c$  peak corresponding to  $\alpha$  relaxation was observed with increasing filler content. Also, the amplitude was reduced proportionally to  $\phi$ , whereas the peak width apparently did not change.

With the data shown in Figure 7,  $T_g$  was obtained as the maximum of the  $\tan \delta_c$  peaks. Figure 8 shows the values obtained as a function of  $\phi$  at the two extreme  $\nu$ 's. For each frequency, an increase of  $T_g$  with the filler content was observed, but for a fixed  $\phi$  value,  $T_g$  increased with  $\nu$ . Both results agree with the data usually reported in the literature.<sup>1,5–8</sup> A new and in-

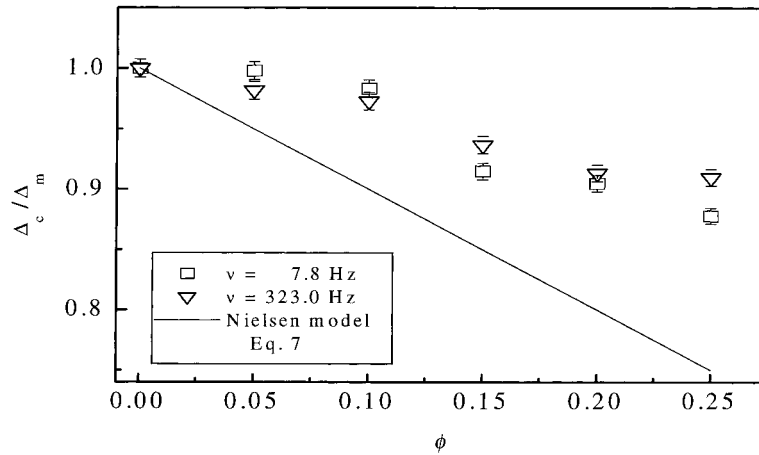


Figure 9 Dependence of  $\Delta_c/\Delta_m$  for two extreme frequency values. The solid line corresponds to eq. (7).

interesting result was that the  $T_g$  dependence with  $\phi$  seemed not to depend on  $\nu$ .

From Figure 7, besides the information about  $T_g$ , it is possible to determine how  $\phi$  affected the composite's damping. Figure 9 shows the dependence of relative damping ( $\Delta_c/\Delta_m$ ) with filler content, for both extreme  $\nu$ 's.

Nielsen<sup>17,18</sup> noticed that if damping in the filled polymer originates only from the same mechanisms that produce the damping in the unfilled matrix, the following relationship holds:

$$\frac{\Delta_c}{\Delta_m} = (1 - \phi) \quad (7)$$

The solid line in Figure 9 represents the damping dependence with  $\phi$  according to the Nielsen model. The fact that eq. (7) does not explain the experimental results could be understood if one considers that this model neglects the damping due to particle-particle and polymer-particle interactions.

Zorowski and Murayama<sup>19,20</sup> proposed a model that considers damping effects originated in polymer-particle interactions, such as interface damping ( $\Delta_{\text{int}}$ ), which can be estimated by the following equation:

$$\Delta_{\text{int}} = \Delta_c - \Delta_c^c \quad (8)$$

$$\Delta_c^c = \frac{\Delta_f E_f' \phi + \Delta_m E_m' (1 - \phi)}{E_c'} \quad (9)$$

where  $\Delta_c^c$  is the damping calculated when the friction originated in the polymer-particle interface is not considered and the subscripts  $m, f$ , and  $c$  correspond to the magnitudes of the matrix, filler, and composite, respectively.

When this model was applied to the experimental data, the dependence with the fraction filler content of the damping component due to the internal friction in the matrix-particle interface was obtained (see Fig. 10).

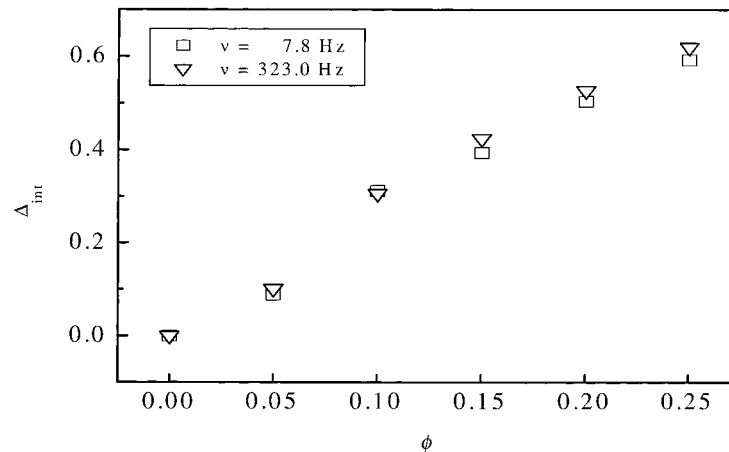


Figure 10 Dependence of the internal friction originated in the polymer-particle interface as a function of  $\phi$ .



It is interesting to note that  $\Delta_{\text{int}}$  increased with  $\phi$  independently of  $\nu$ , at least in the frequency range studied in this work.

### Activation energy

A correct estimation  $E_\alpha$  must be done with the superposition principle due to WLF.<sup>11</sup> The master curves for  $E'$  and  $E''$  were built for all composites at a reference temperature of  $T_0 = 403$  K. In Figure 11, for example, the master curves for the unfilled sample and samples with  $\phi = 0.15$  and  $0.25$  are shown. The apparent activation energy was determined from fitting the temperature dependence of the shift factor ( $\log a_T$ ) in the WLF model according to:<sup>11</sup>

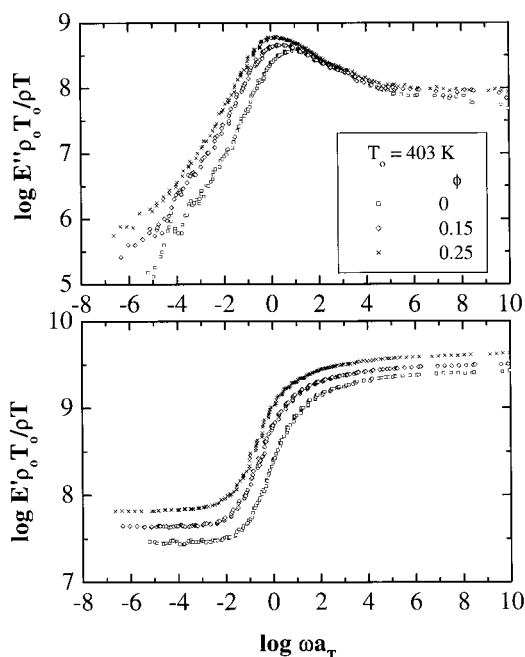
$$\log a_T = -c_1^0(T - T_0)/(c_2^0 + T - T_0) \quad (10)$$

$$E_\alpha = 2.303 R c_1^0 T_g^2 / c_2^0 \quad (11)$$

where  $R$  is the gas constant and  $c_1^0$  and  $c_2^0$  are the coefficients  $c_1$  and  $c_2$  evaluated at  $T_g$ .<sup>11</sup>

The shift factors  $c_1$  and  $c_2$  at two different reference temperatures (403 K and  $T_g$ ) and the apparent activation energies are given in Table I for each composite.

As could be expected,  $E_\alpha$  increased with filler content in the composite due to the reduction in the mobility of the macromolecular chains close to the quartz particles.<sup>5,8</sup> This result agrees with the observed reduction in the loss tangent peak at higher  $\phi$ 's (Fig. 7) and with the increment of  $T_g$  with  $\phi$  (Fig. 8).



**Figure 11** Master curves for quartz powder-epoxy composites at three  $\phi$  values.

**TABLE I**  
Dependence of WLF Parameters with  $\phi$  and  $E_\alpha$

$\phi$	$T_0 = 403$ K		$T_0 = T_g$		$E_\alpha$ (KJ/mol)
	$c_1$ (K)	$c_2$ (K)	$c_1$ (K)	$c_2$ (K)	
0	22.8	39	21.4	153.7	659
0.05	23.0	35	21.5	149.8	678
0.15	27.0	59	25.4	174.5	689
0.20	31.0	84	29.1	201.2	691
0.25	32.0	90	30.0	207.7	693

### CONCLUSIONS

In this study, dynamic mechanical properties of epoxy resin filled with quartz powder were examined.

The storage modulus increased strongly with increasing  $\phi$ , but this increase was more important at the rubbery zone than at the glassy region. When these data were fitted by the Lewis-Nielsen model, two couples of values for  $k_E$  and  $\phi_{\text{max}}$  were found, one for  $T < T_g$  and another for  $T > T_g$ . This effect was explained by the fact that filled systems are never perfectly dispersed. It was also shown that at the glassy zone, the filler content did not modify the dependence of the storage modulus with frequency, whereas in the rubbery zone, a slight dependence was observed, but this became important at  $\phi = 0.2$  or higher.

The loss tangent peak corresponding to  $\alpha$  relaxation shifted to higher temperatures with increasing filler content. Its amplitude was reduced proportionally to  $\phi$ , whereas the peak width apparently did not change. The composite damping dependence with  $\phi$  was explained by damping mechanisms due to particle-particle and polymer-particle interaction.

Master curves of the dynamic modulus were obtained at a reference temperature with the time-temperature principle and the WLF relationship for all of the composites studied.  $E_\alpha$  was estimated, showing an increase with the filler content, and this result was linked to the glass-transition behavior.

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