

Improvement of Mechanical Performance of Epoxy Resins Filled with Cobalt and Chromium Powders

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ABSTRACT: Epoxy/ powder metal composites have interesting electrical properties, becoming conductors above the percolation threshold. To complete this study, mechanical investigations have been carried out to show the influence of the fillers on the mechanical performance of these composites. In this framework, different epoxy/metallic powders (Cobalt, Chromium) composites were prepared. Scanning Electron Microscopy showed that the dispersion of the metallic fillers in the matrix is almost homogeneous. The dynamic mechanical thermal analysis (DMTA) measurements showed the dependence of the viscoelastic param-

eters with the frequency, temperature, nature, and content of fillers. The main relaxations observed are the primary α relaxation (associated to the glass transition, T_g) and a secondary β relaxation. A second DMTA run on the same samples showed a slight increase of the T_g . It clearly showed that the used metallic fillers improve the mechanical properties of the obtained composites. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 3701–3706, 2010

Key words: composites; resins; fillers; aging; viscoelastic properties

INTRODUCTION

Electroconductive polymeric composites are materials, which induced strong research efforts and obtained important industrial applications: shielding of electromagnetic fields of devices, conductive adhesives, cold seals, over-current protection devices, underfill for flip chips, static charges dissipating materials, self regulating heaters, aeronautic, aerospace technology, photothermal optical recording, encapsulation of electronic devices that protect them from adverse environment and increases their long-term reliability, flame retardancy, direction finding antennas, chemical detecting sensors used in electronic noses, and more. This development is generally because of their various advantages over other conductive materials owing to their processability,

flexibility, ability to absorb mechanical shock, corrosion resistance, lightweight, and the possibility of electrical conductivity control.^{1–4}

Among these materials, epoxy resins are widely used in various applications, particularly as adhesives for bonding and as matrix with conducting or nonconducting fillers, to obtain materials for high-performance composites.^{5–16}

In our previous research, we have elaborated and studied the electrical properties of epoxy filled with metallic fillers.^{9,17} These materials showed a good electrical performance above the percolation threshold. Modulus of elasticity and its thermal evolution are other important properties that become critical for practice applications. Indeed, the dynamic mechanical analysis is related to the mobility of the polymer chains, and it has been widely used in studies of inter-phase properties of composites materials.^{18–20}

The present research deals with the study of visco-thermo-mechanical properties by dynamic mechanical thermal analysis (DMTA) and structural morphology by Scanning Electron Microscopy (SEM) of the same composites studied by electrical characterization¹⁷ of epoxy loaded with cobalt and chromium powders. The percolation thresholds were around 16 and 11 vol % for cobalt and chromium filled epoxy, respectively. Thus, the mechanical properties of different composites with filler content under and upper the threshold will be compared.

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TABLE I
Comparison of T_g Values of the Epoxy/Cr and Epoxy/Co Composites, Respectively, Determined at 3 Hz by DMTA Measurements

Neat Epoxy	Glass transition temperature (°C)				
	92				
	1 vol %	10 vol %	16 vol %	24 vol %	30 vol %
Epoxy/Chromium	94	96	92	—	91
Epoxy/Cobalt	99	96	97	100	—

EXPERIMENTAL

Material and preparation

The matrix used was a bisphenol A epoxy resin (Araldite F) with a hardener (HY956) (Ciba-Geigy). The polymer obtained had a density of 1.14 (g/cm³) at 22°C. The fillers were commercial powders of chromium and cobalt from Sigma-Aldrich 1 (Tres Cantos, Madrid, Spain). Their purity is 99.9% and their mean size is 100 mesh (149 μm) for cobalt and 325 mesh (44 μm) for chromium.

A series of composites were prepared by adding the metallic filler powders, with filler contents ranging from 1 to around 30 vol %, into the matrix. Because of the difference in the density between the fillers and the matrix, the mixtures were introduced into a

prism-shaped mold and rotated (at around 80 rpm) during the polymerization in an oven maintained at 40°C during around 2 h, to prevent the precipitation of the metallic fillers in the bottom of the mold.

Equipment and procedures

The morphology of the particles and their dispersion inside the composites were observed by using SEM. The SEM images were obtained with a Philips XL 30 ESEM, with an accelerating voltage of 25 kV. The samples were fractured into liquid nitrogen.

For the DMTA, the specimens were polished with sandpaper to form bars with prism geometry of nominal dimensions 10 × 11 × 3 mm³. The tests were performed on a Rheometric Scientific DMTA V instrument

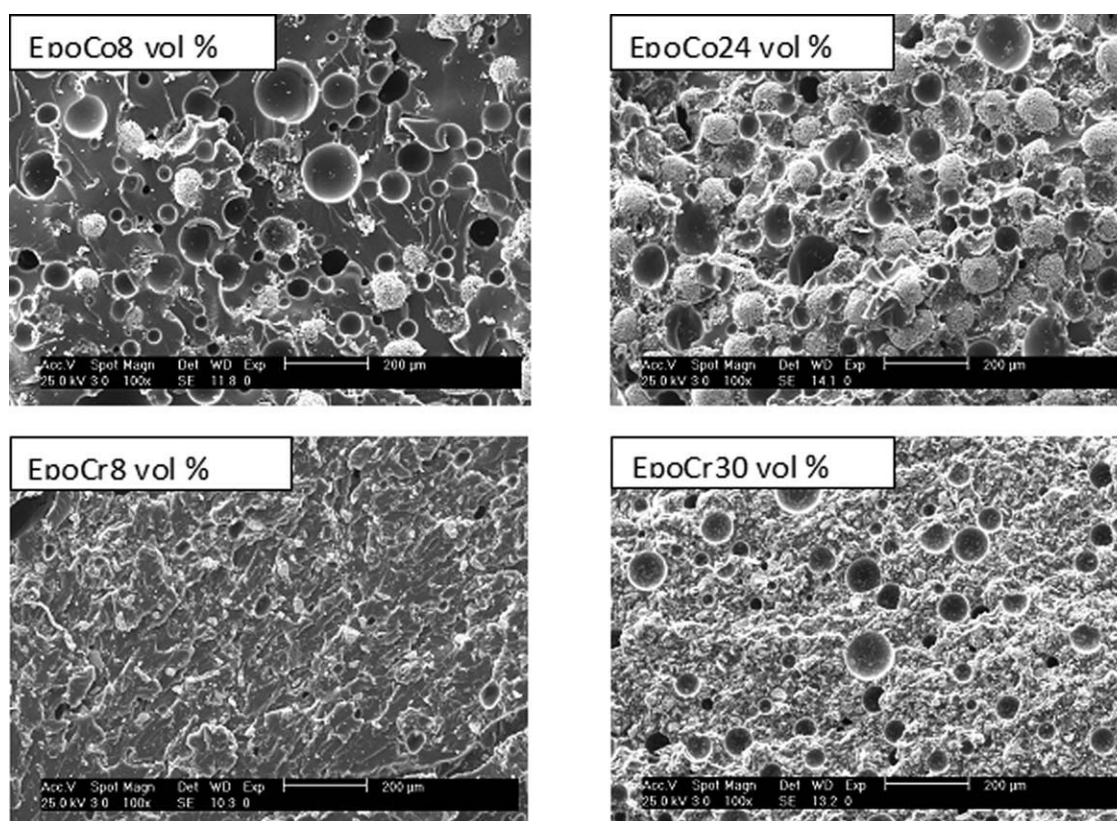


Figure 1 Upper part: Electron images of cobalt (8 and 24 vol %); Lower part: Electron images of chromium (8 and 30 vol %) in epoxy, taken at 25 kV and 100x.

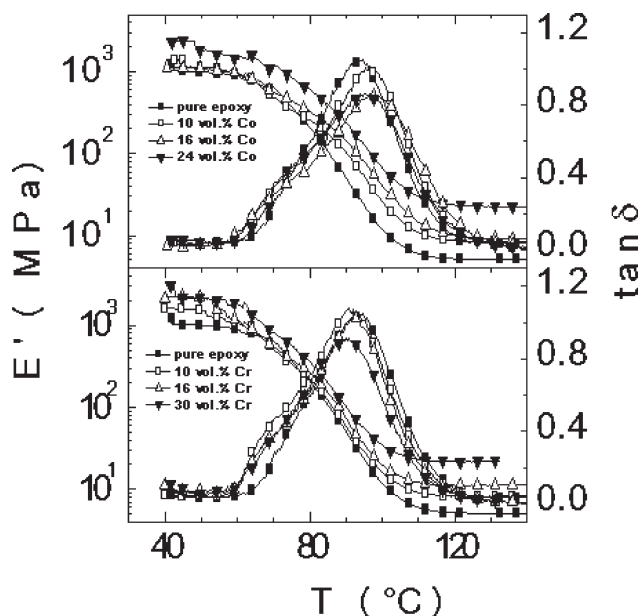


Figure 2 Plots of storage modulus and $\tan \delta$ vs temperature at 3 Hz of epoxy filled with different cobalt and chromium contents.

operating in the dual cantilever mode at oscillation frequencies of 1, 3, 10, and 30 Hz. Data were collected from 40 to 150°C at a scanning rate of 1.5°C/min.

RESULTS AND DISCUSSION

Morphology of samples

Figure 1 shows the SEM micrographs of Co and Cr composites with two compositions for both, under and upper percolation threshold, proving that the dispersion of the metallic particles is almost homogeneous inside the polymeric matrix. The observed cavities are produced by some vacuum bulbs and the extortion of fillers at the time of the treatment of the sample for the observation to the microscope. Moreover, the difference in size between cobalt (149 μm) and chromium (44 μm) fillers is clearly observed. The noteworthy result is the geometrical aspect. Indeed, the SEM pictures show quite plainly rough and almost spherical-like shape in the case of cobalt particles and rough - irregular shape in the case of chromium particles. This morphological difference may influence the interfacial forces interactions between filler and matrix and induce a difference in the thermomechanical behavior; as already observed in the electrical one.⁹

DMTA data

Influence of the filler content on DMTA parameters

Figure 2 shows the DMTA plots of storage modulus, E' and loss tangent $\tan \delta$ (ratio of energy dissipated

to energy stored per cycle of deformation) at 3 Hz, vs temperature, as a function of cobalt and chromium contents, respectively. It can be observed that for the all composites, the storage modulus decreases when the temperature increases. However, it increases as the filler content increases in all ranges of temperature. This increasing is more important at high-temperature ($T \geq 100^\circ\text{C}$) for epoxy loaded either with chromium or cobalt. For example, the storage modulus of the composite of epoxy with 30 vol % of chromium and 24 vol % of cobalt, respectively, showed almost four orders of magnitude improvement from the pure epoxy at 135°C. Whereas, only two orders were observed at 45°C for the epoxy loaded with chromium and less for epoxy/cobalt composites. Moreover, the increase becomes important when the content of filler is higher than the value of percolation threshold. Therefore, the thermomechanical properties are increased by the addition of metallic fillers, even though this increase in mechanical performance seems slightly more important in the case of epoxy/chromium composites.

The nature, size, and shape of filler are important physical properties of composites.⁹ Indeed, the SEM pictures illustrated in Figure 1 show clearly a rough and almost spherical-like shape in the case of cobalt particles and rough and irregular shape in the case of chromium particles. The rough surface of filler yields a higher storage modulus of the composites than the materials containing the filler with smooth surface. This rough character induces a better adhesion between filler and epoxy interface. A good interfacial adhesion between the resin and the filler results in better reinforcement and hence, a higher modulus is obtained.⁶

The observed difference in storage modulus at low-temperature between composites with cobalt and chromium fillers might be related to the difference in nature, size, and shape. In our case, the mean size of cobalt is 149 μm , whereas that of chromium is only 44 μm . In a previous study,⁹ it was shown that there is some analogy between electrical and mechanical behaviors. Indeed, when the volume fraction of filler increased up to the critical threshold, both electrical conductivity and Young's modulus started to increase. After the percolation, the electrical conductivity reaches a saturation value by an additional increase of filler, whereas Young's modulus continues to increase.⁷ In other respects, it was shown that the electrical percolation threshold decreases when the size of copper fillers in nylon 6 decreases.²¹ Thus, because the electrical percolation threshold of chromium occurs below 16 vol % (percent used in this experiment), the modulus of epoxy/Cr composites starts to increase quickly before than the modulus of epoxy/Co composite, with higher percolation

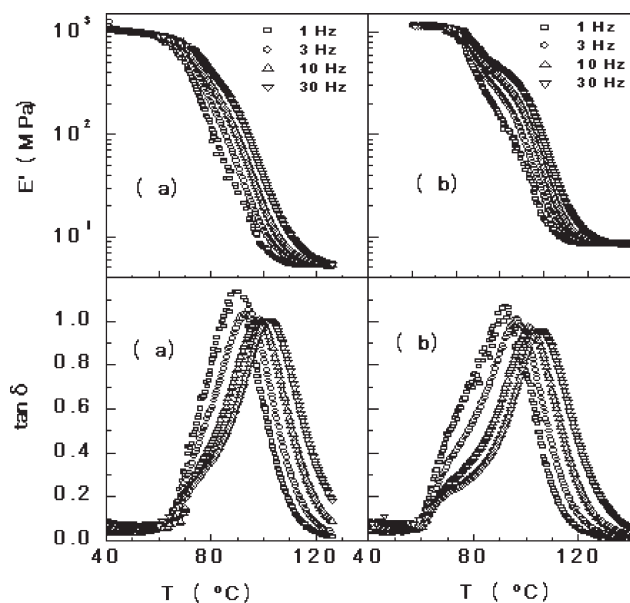


Figure 3 Storage modulus and $\tan \delta$ vs temperature at different frequencies of (a) pure epoxy first melting and (b) epoxy/Co,10 vol % composite first melting.

threshold.^{9,17} It is also believed that other parameters like the shape, the surface energy of the particles, and the polymer surface tension might be at origin of this difference. It has been indicated that the surface tension of inorganic fillers, such as alumina, copper dioxide, silica or titanium dioxide, can be affected by the addition of a polymer, inducing changes in the particle surface energy.^{22,23}

The DMTA data allows the determination of the glass transition temperature T_g . It can be determined from the peak position of $\tan \delta$. As shown in Figure 2, the addition of metallic fillers does not significantly change the T_g values. Only in the epoxy filled with cobalt (upper part of Fig. 2) a slight increase of T_g with the metallic content can be seen, indicating that the mobility of polymer molecules are restricted by their partial adsorption onto the filler. This phenomenon is the consequence of attractive interfacial interactions between metallic fillers and the epoxy matrix and leads to the observed increase in thermal stability around and above T_g . Thus, a strong increase of the storage modulus and a small shift in T_g are observed, as reported by Nielsen and Landel.²⁴ Moreover, the observed decrease of the peak of $\tan \delta$ for higher filler contents of both cobalt and chromium can be related to the increasing of agglomeration of fillers, leading to less energy dissipating in the system under viscoelastic deformation, as pointed out by Gojny and Schulte.¹⁰ Therefore, the nature of fillers seems to have some influence on the thermomechanical properties of composites, because those loaded with cobalt present T_g values somewhat higher than the values obtained with chromium fillers at 3 Hz (Table I).

The full width at half maximum of the $\tan \delta$ peak divided by its height was used to define the peak factor, which allows assessing the homogeneity of epoxy network.¹² This factor is almost the same in the neat epoxy and its metallic composites indicating that the homogeneity of materials is good, in good agreement with microscopic observations.

Temperature and frequency dependences

Figure 3 illustrates, the temperature and frequency dependences of DMTA parameters (storage modulus and $\tan \delta$) respectively, for the pure epoxy and the epoxy filled with cobalt (10 vol %). A similar behavior was obtained with epoxy loaded with chromium.

The shape of all curves is similar and the E' values show a dependence on frequency at all temperatures from the beginning of the glass transition up to the complete loss in stiffness. The E' values increase as the frequency of deformation does. Moreover, $\tan \delta$ peak values are shifted to higher temperatures with frequency, as it is expected, and the maximum in the intensity of $\tan \delta$ decreases when the frequency increases.

It can be seen that at the high-temperature region, the largest loss peak corresponds to the α relaxation, and it is associated with the glass transition temperature. This transition occurs with the beginning of segmental motions of the molecular chains. The apparent activation energy is high (as commented below), 320 kJ/mol, as corresponds to a glass transition. In the low-temperature region, below the α -peak, a small peak (shoulder) appears, which is related to the β -relaxation. The activation energy of this secondary relaxation is generally lower than that of the α transition, as it corresponds to motions of moieties of a size smaller than those related to the segmental motions of the main chain.²⁵ This relaxation appears not only in pure epoxy but rather also in the composites. The origin of this small relaxation is probably related to the aging process associated to the metastable states observed in glass phases. This assumption seems to be confirmed by DSC measurements.²⁶

The $\tan \delta$ peak dependence on frequency can be used to estimate the apparent activation energy of the glass transition process. This apparent activation energy determines the amount of energy required to develop molecular mobility in the polymer chains, which includes segmental chain bonds motion.²⁷ The injection of metallic fillers in epoxy has an important effect on the apparent activation energy. Even though the frequency shift of the T_g values obeys to the Williams-Landel-Ferry equation, for the low-frequencies range the glass transition temperature can be related to the frequency by the Arrhenius equation:

$$f = f_0 \exp(-\Delta H/RT)$$

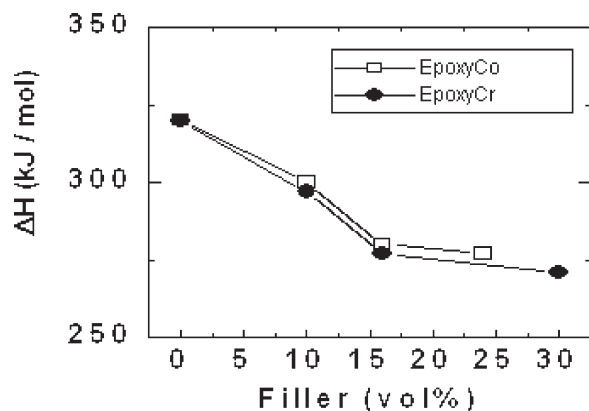


Figure 4 Apparent activation energies of the epoxy/Co (□) and epoxy/Cr (●) composites vs the volume fraction of the cobalt and chromium fillers.

Where ΔH is the apparent activation energy, R is the gas constant and T is the glass transition temperature corresponding to the frequency f . The different values of T_g vs frequency are obtained from the maximum of $\tan \delta$ vs temperature measured at different frequencies (Fig. 3). Then, the plot of $\ln(f/f_0)$ vs reciprocal temperature (glass transition) is used to estimate the activation energy ΔH . Figure 4 gives the variation of the obtained activation energy of the composites epoxy/Cr and epoxy/Co with different amounts of chromium and cobalt. It can be seen that the activation energy decreases with the content of metallic filler, and the values obtained for epoxy loaded with cobalt are always slightly higher than the ones corresponding to the epoxy filled with chromium. A change of trend is clearly observed around 16 vol %. Then, the value of the activation energy begins to vary slowly with the increasing of volume fraction of filler. As indicated before, when the critical value of filler is reached, the system becomes electrically conductor leading to more absorption of significant heat; hence, it is more stable and the mechanical performances are better. It seems such situation was happened in this case. The activation energy is considered as energy of system, and when it decreases, the system goes to equilibrium state. The activation energy of composites is lowered by about 50 kJ/mol compared with the pure epoxy. It is clear that the inclusion of metallic fillers inside epoxy gives good thermomechanical performances.

Influence of the DMTA behavior history

The second DMTA run carried out on each sample has an important influence on the thermomechanical properties of composites (Fig. 5). It was carried out at 3 Hz from 40 to 150°C. The overall behavior obtained in this second run is almost the same

observed in first run. Nevertheless, as it can be seen, the heating improves the thermomechanical properties of the composites, as measured during the first run (Fig. 5). Indeed, a particular increase in the magnitude of the storage modulus was observed in the second run, between 70 to 100°C, after the disappear of β -relaxation and before the glass phase transition occurrence. The magnitude of storage modulus of both the composites and pure epoxy increased continuously to reach 300% from first run around to 80°C and decreased then to reach the values of the first run from 100°C. This effect seems more important for the composites case than the pure epoxy.

It is also interesting to note that the β -relaxation disappears, taking place only a single and almost symmetric α relaxation at higher temperature, as can be seen in Figure 5. The disappearance of the shoulder at around 60–70°C and the small step in storage modulus are related to the elimination of the aging, which is a quasi-thermoreversible process that takes place in all glassy materials and affects their properties by changing the relaxation time of the macromolecules. When a glassy material is stored at a temperature below its T_g , as it is the case of the epoxy resins and composites studied in this work, the material remains in a metastable state and evolves toward equilibrium. This aging process is erased when the sample is heated above the glass transition, as occurs in the samples studied in the second DMTA run.

Moreover, this second run changes an important parameter, the glass transition temperature that increased in a variable percentage from 1 to 8.6%, with the content of metallic fillers (Fig. 5). The

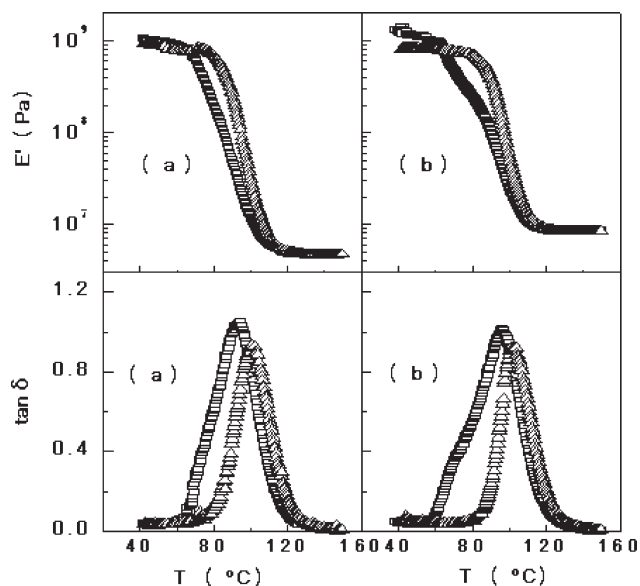


Figure 5 Storage modulus and $\tan \delta$ as function of temperature of (a) pure epoxy and (b) epoxy/Co, 10 vol % composite, first (□) and second (▽) melting at 3Hz.

magnitude of this increase is higher for the low-volume fraction of the fillers than for the high one. This behavior can be related to the polymeric chains motions; in the low-volume concentration the polymeric chains are free to move, as they are organized by the first test. Whereas, for the samples with higher filler contents, the motions of polymeric chains are restricted by the metallic fillers.

CONCLUSIONS

Composite epoxy/metallic powders were prepared. They have showed good electrically performances. In the aim to check if they have the same performances in thermomechanical properties, their study with SEM and DMTA were undertaken. The main conclusions are: – The metallic powder fillers were well dispersed in epoxy matrix, indicating a good affinity and leading to attractive interactions.– These attractive interactions restrict the mobility of polymer molecules and lead to a good interfacial adhesion between the resin and the filler inducing an increase in elastic modulus.– The size and shape of fillers seem to have an effect on thermomechanical properties.– The metallic fillers improve mechanical performances, and stabilize thermally the epoxy matrix.– The aging process of polymer was evidenced in these types of materials and it played an important role in improvement of elastic modulus and slight shift in T_g .

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