

Local Dynamics in Epoxy Coatings Containing Iron Oxide Nanoparticles by Dielectric Relaxation Spectroscopy

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ABSTRACT: Nanocomposites of photocurable epoxy resin and epoxy-modified iron oxide magnetic nanoparticles were analyzed by dielectric relaxation spectroscopy to study the local dynamics at temperatures well below the glass-transition temperature. Two secondary processes were detected, β and γ processes, but the second one was just detected at lower temperatures in the high-frequency part of the spectra and moved out of the frequency range at higher temperatures. Data were fitted to the Havriliak–Negami and Arrhenius models, and the obtained parameters were analyzed. Relaxation times of the β secondary relaxation did not change with the nano-

particle content, but the relaxation strength increased. The increase could not be explained when we took into account the molecular origin of the relaxation. The presence of ferromagnetic nanoparticles enhanced the internal field and increased the relaxation strengths. Transmission electron microscopy images showed that the nanoparticles were well dispersed in the matrix, without magnetic agglomerates. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 3224–3229, 2008

Key words: dielectric properties; nanocomposites; photopolymerization; relaxation

INTRODUCTION

Polymer nanocomposites have drawn considerable attention in recent years because of improvements in various properties, such as scratch resistance, abrasion resistance, heat stability, and other mechanical properties.^{1–3} Specifically, polymeric nanocomposites containing metal oxides have attracted a great deal of interest from researchers because they frequently exhibit unexpected hybrid properties synergistically derived from both components.^{4,5} Different metal oxide nanoparticles have been used as fillers; in particular, SiO₂, TiO₂, and ZnO have been deeply investigated in the literature.⁶ Polymeric iron oxide nanocomposites have been investigated for their potential application in electrochromic devices, gas and vapor sensors, nonlinear optic systems, and photovoltaic solar cells.⁷ Furthermore, the magnetic properties of iron oxide can be used in potential applications,

including magnetic filters and future generations of electronic, magnetic, and photonic devices used for information storage or magnetic imaging.⁸ Several good review articles have been published on the synthesis, characterization, and applications of these polymeric nanocomposites.^{9,10} Nevertheless, to the best of our knowledge, there have not been any investigations on the dispersion of iron oxide nanoparticles in photocurable formulations. The UV curing technique is gaining increasing importance in the field of coatings because of its peculiar characteristics, including fast transformation of the liquid monomer into the solid film and environmental behavior without the use of solvents and heating processes, which assures the saving of energy.

Among several experimental techniques, including nuclear magnetic resonance,^{11,12} rheology^{13,14} and gas permeation chromatography,¹⁵ dielectric relaxation spectroscopy (DRS) is a suitable technique for the study of nanocomposites. When placed in an electric field, for example, nanocomposites are subject to ionic, interfacial, and dipole polarizations. Those polarization mechanisms have considerably different timescales and length scales, which makes dielectric spectroscopy, with its unparalleled range of frequency and temperature, uniquely suited for the study of nanocomposite dynamics through the analysis of the effect of nanofillers on the dynamics and relaxations of polymeric chains.^{16–20} In this way, Majszczyk et al.²¹ carried out an investigation on the

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influence of iron oxide magnetic nanoparticles in the dielectric spectra of a poly(ether-*b*-ester) copolymer matrix. They found that the main relaxation process of the matrix was shifted toward lower temperatures as the nanoparticle content increased, whereas the secondary relaxations were not affected. They also observed an interfacial polarization effect in the samples with nanoparticles. Costa et al.,²² working with polystyrene doped with iron nanoparticles, found that the dielectric loss (ϵ'') and dielectric permittivity (ϵ') values rose with the nanoparticle content. The increase in ϵ'' related to the increase in conductivity may have been due to the proximity between the nanoparticles, whereas the increase in ϵ' was related to the increase in the volume fraction of the electric dipoles. Dey et al.²³ studied dielectric relaxation in Fe₃O₄-polypyrrole nanocomposites, concluding that the magnitude and the frequency dependence of ϵ' were dependent on the nanoparticle content. Their obtained nanocomposites presented high dielectric constants compared with the neat matrix.

In this study, iron oxide nanoparticles modified with a silane containing an epoxy group for increasing the compatibility with the epoxy matrix were used to prepare nanocomposites with the epoxy matrix. Films of the nanocomposites were obtained by photocuring and were characterized in terms of DRS. Frequency sweeps were carried out over a wide frequency range at several temperatures, and we analyzed the main relaxation processes. The behavior was modeled with the Havriliak–Negami and Arrhenius equations, and we obtained the corresponding fitting parameters and the effect of the nanoparticles on them. Together with the effect of the nanoparticles on the dielectric properties, the obtained morphologies were analyzed by transmission electronic microscopy (TEM).

EXPERIMENTAL

Materials

Maghemite (Fe₃O₄) magnetic nanoparticles with a nominal size of 9 nm and a polydispersity of 1.08 were purchased from Integran Technologies, Inc. (Toronto, Canada) and were used as received. 3,4-Epoxy-cyclohexylmethyl-3',4'-epoxy-cyclohexanecarboxylate by Dow Chemical (Iberica, Bilbao, Spain) was used as the epoxy matrix. A commercially available mixture of antimonate sulfonium salts (UVI 6976) was supplied by Dow as solution in propylene carbonate (50% w/w) and was added to the curable mixtures at a concentration of 2% w/w as well.

The functionalization on the iron oxide surfaces was carried out according to a similar procedure that was previously reported.^{24–26} The modification of nanoparticles in their surfaces was proven by Fou-

rier transform infrared spectroscopy, with the appearance of bands related to the silane in the modified nanoparticles.²⁶ The grafting density was found to be about 3.8 $\mu\text{mol}/\text{m}^2$, which corresponded to 1.5 molecules/nm², as determined by thermogravimetric analysis.^{26,27}

The functionalized iron oxide nanoparticles were dispersed in the liquid resin in the range between 0 and 10 wt %, with the aid of an ultrasonic bath. The cationic photoinitiator (2 wt %) was then added to the mixtures. Liquid formulations were coated onto a different substrate (PP or glass) with a wire-wound applicator, and then, the liquid films were exposed to UV light, with a radiation intensity on the surface of the sample of 30 mW/cm². We obtained films of about 100 μm , as previously reported.²⁸

Instrumentation

DRS measurements were carried out in a Novocontrol Alpha high-resolution dielectric analyzer (Hundsangen, Germany) over a frequency range between 0.1 Hz and 10 MHz at several temperatures above and below the glass-transition temperature. The instrument was interfaced to a computer and equipped with a Novocontrol Novocool cryogenic system for temperature control. The circular sheets obtained by photopolymerization were placed between the gold-plated electrodes in a sandwich configuration.

Samples were prepared for TEM observation by an argon ion polishing system (Gatan Pips, Warrendale, PA) working at 3.5 keV at an angle of 7°. They were examined in a Philips CM30 300-keV transmission electron microscope. Micrographs were processed with a slow-scan charged coupling device camera and analyzed with the Digital Micrograph program (Philips, Eindhoven, The Netherlands).

RESULTS AND DISCUSSION

The relaxation spectra of the neat epoxy matrix were analyzed first. Figure 1 shows the ϵ'' -frequency curves at several temperatures between -20 and 80°C . The low frequency parts of data were cut for a clear understanding of the relaxations. Data were fitted to the Havriliak–Negami equation with a Havriliak–Negami term for each dipolar relaxation. The Havriliak–Negami formalism proposes an analytical expression for the complex dielectric permittivity [$\epsilon^*(\omega)$]:

$$\epsilon^*(\omega) - \epsilon_\infty = \frac{\epsilon_0 - \epsilon_\infty}{\left[1 + (i\omega\tau_0)^b\right]^c} \quad (1)$$

where ω is angular frequency, ϵ_∞ is the permittivity at the high frequency limit, $\epsilon_0 - \epsilon_\infty = \Delta\epsilon$ is the dielectric strength, ϵ_0 is the vacuum permittivity, τ_0

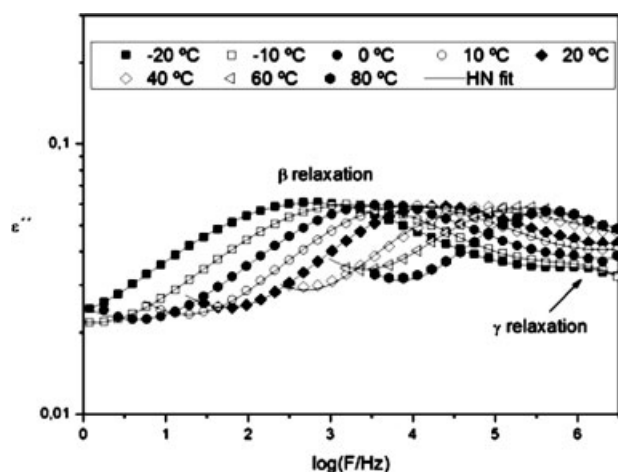


Figure 1 ϵ'' versus the frequency (F) at several temperatures between -20 and 80°C for the neat epoxy matrix. Solid lines indicate fitting to the Havriliak–Negami (HN) equation.

is the central relaxation time, and b and c are parameters that describe the shape of the relaxation time distribution function (symmetric and asymmetric broadening). To describe the whole spectrum, the Havriliak–Negami equation must be combined with the following conductivity term (which takes into account the polarization of ions or charge carriers) for the temperatures at which it contributes:

$$\epsilon_c'' = \left(\frac{\sigma}{\epsilon_0 \omega} \right) \quad (2)$$

where ϵ_c' is the conductive contribution of the loss factor.

As an example, the deconvoluted spectrum at -20°C is shown in Figure 2 for the neat matrix. Analyzed temperatures were well below the calorimetric glass-transition temperature,²⁶ and the segmental α

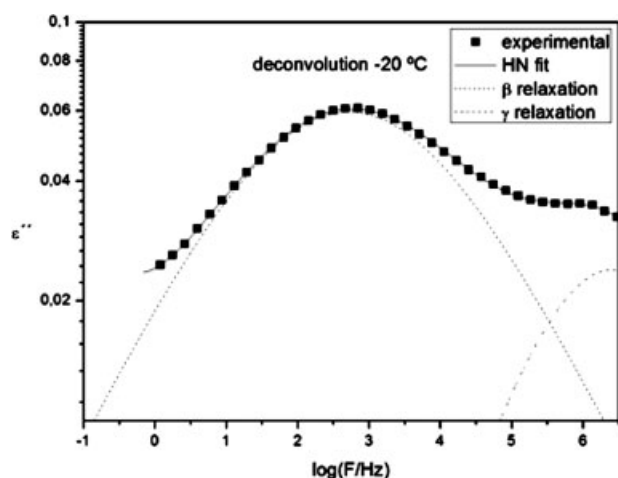


Figure 2 Deconvoluted ϵ'' versus the frequency (F) for the neat epoxy matrix at -20°C (HN = Havriliak–Negami).

process was not observed. Two local dipolar relaxation processes were observed and termed β and γ in the order of increasing frequency at a constant temperature. γ relaxation was observed only for the lower temperatures at the high-frequency edge of the spectra, so data about relaxation time evolution with temperature and activation energies were not obtained. Those for β relaxation are discussed later, compared with the corresponding to nanocomposites. We acknowledge the ongoing debate in the literature about the nature of the β process in glass formers.^{29–31} Earlier studies^{32,33} have suggested that β and γ relaxations in epoxy networks are related to the localized motions of hydroxyl groups and ether linkages of the glycidyl moiety, respectively. In other systems, β relaxation has been associated with the motion of hydroxypropylether groups or other groups formed during the curing reaction.^{34,35} Udagawa et al.³⁶ studied the dynamic mechanical properties of photocurable cycloaliphatic epoxy resins like those analyzed in this study, and the β relaxation was related with the molecular motions of the cyclohexyl rings. The γ relaxation has been mainly attributed to the motions of unreacted epoxide rings.^{34,35,37}

Figures 3 and 4 show the ϵ'' –frequency curves for nanocomposites with 5 and 10 wt % Fe_3O_4 , respectively, in the same temperature range. ϵ'' values increased with ferromagnetic particle content, probably because of an increase in the alternating-current conductivity that was produced as the proximity between nanoparticles increased.²² The increase was not so pronounced as in those systems in which at higher concentrations than the percolation threshold, the contact among particles formed a continuous electrical path throughout the matrix and strongly increased conductivity and, consequently, ϵ'' . On the

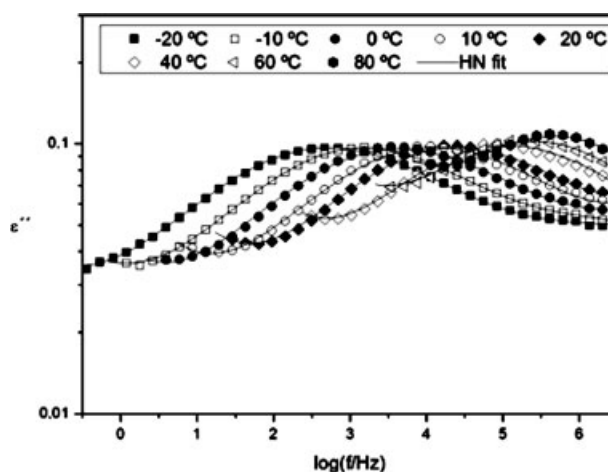


Figure 3 ϵ'' versus the frequency (f) at several temperatures between -20 and 80°C for the epoxy matrix modified with 5 wt % nanoparticles. Solid lines indicate fitting to the Havriliak–Negami (HN) equation.

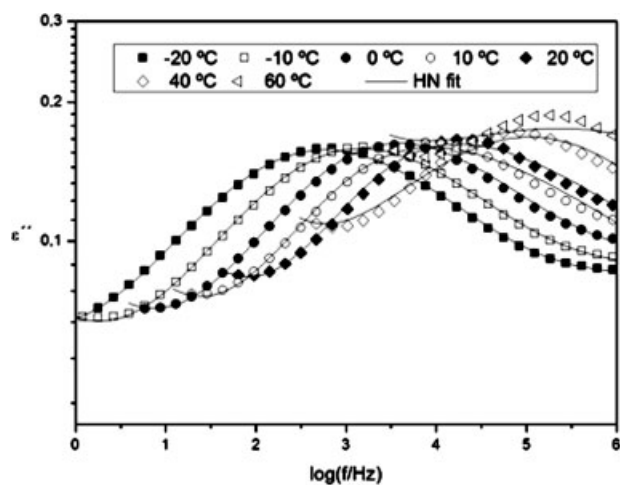


Figure 4 ϵ'' versus the frequency (f) at several temperatures between -20 and 60°C for the epoxy matrix modified with 10 wt % nanoparticles. Solid lines indicate fitting to the Havriliak–Negami (HN) equation.

other hand, both secondary relaxations were detected for the nanocomposites. The frequencies at which the relaxations appeared were very similar to those in the neat matrix. As shown, γ relaxation was not so clear as for the neat epoxy, but deconvolution of the spectra allowed us to detect it at lower temperatures in the high-frequency tail of the spectra. For higher temperatures, it moved out of the analyzed frequency range.

From the Havriliak–Negami fitting of the data, relaxation times and other fitting parameters such as $\Delta\epsilon$ were obtained at several temperatures for β relaxation. The peak corresponding to γ relaxation was present only at lower temperatures and then disappeared from the analyzed frequency range.

Figure 5 shows the evolution of $\Delta\epsilon$ for β relaxation with temperature for the neat matrix and nanocom-

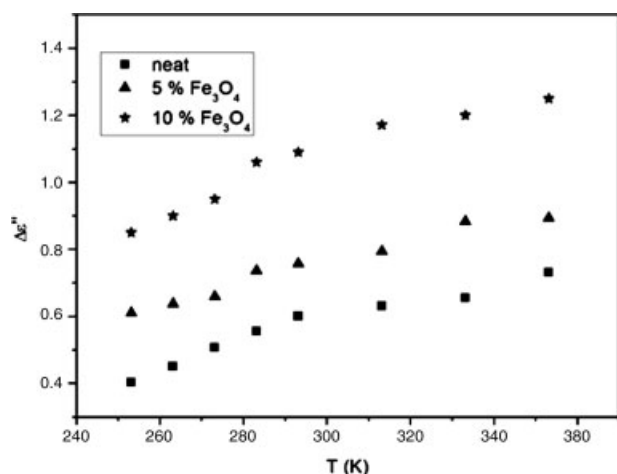


Figure 5 Evolution of $\Delta\epsilon''$ values obtained from Havriliak–Negami fitting with the temperature (T) for all of the analyzed systems.

posites. As expected, $\Delta\epsilon$ increased with temperature for all of the systems. Surprisingly, the strength of β relaxation increased with nanoparticle content. This fact could not be explained when we took into account the origin of the relaxation discussed previously. If the relaxation was related to hydroxyl groups (formed during the cure reaction), the strength should have been higher in the case of the matrix because the reaction extent (epoxy conversion) was higher (0.72 for the neat matrix and 0.62 and 0.59 for the nanocomposites).²⁸ If the relaxation was related to the motions of cyclohexyl rings, the strength should also have been higher for the matrix because the amount of epoxy resin was higher. The explanation could be the electromagnetic induction effect created by the ferromagnetic material incorporated into the matrix: the origination of a strong magnetic field in the ferromagnetic phase, variable with time, could have promoted the reduction of the electric field on it. Consequently, the electric field in the matrix must have increased, with the subsequent enhancement of the intensity and relaxation strength. Page and Adachi¹⁷ found something similar for poly(isoprene) and poly(buthylene oxide) matrices modified with montmorillonite, with higher relaxation strengths for nanocomposites than in pure polymers because of the enhancement of the internal field by the presence of montmorillonite.

Relaxation times of β relaxation obtained from Havriliak–Negami fitting for several temperatures are presented in Figure 6 for the neat matrix and nanocomposites. The β process showed an Arrhenius temperature dependence. There was no almost variation in the relaxation times between the matrix and nanocomposites. The obtained activation energies were 58 kJ/mol for the matrix, 60 kJ/mol for the nanocomposite with 5 wt % nanoparticles

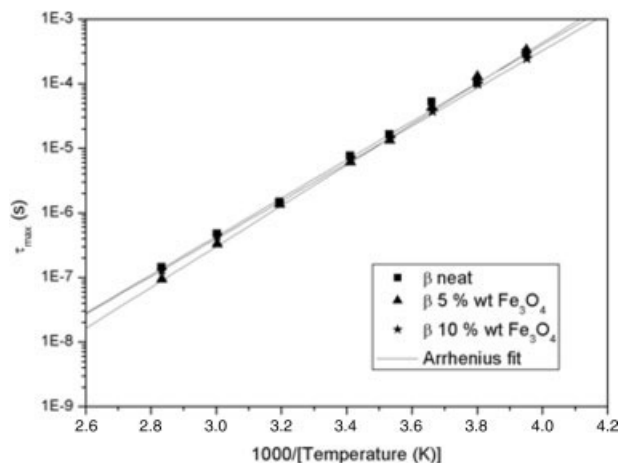


Figure 6 Temperature dependence of the maximum relaxation time (τ_{\max}) obtained from Havriliak–Negami fitting for all of the analyzed systems. Solid lines indicate fitting to the Arrhenius equation.

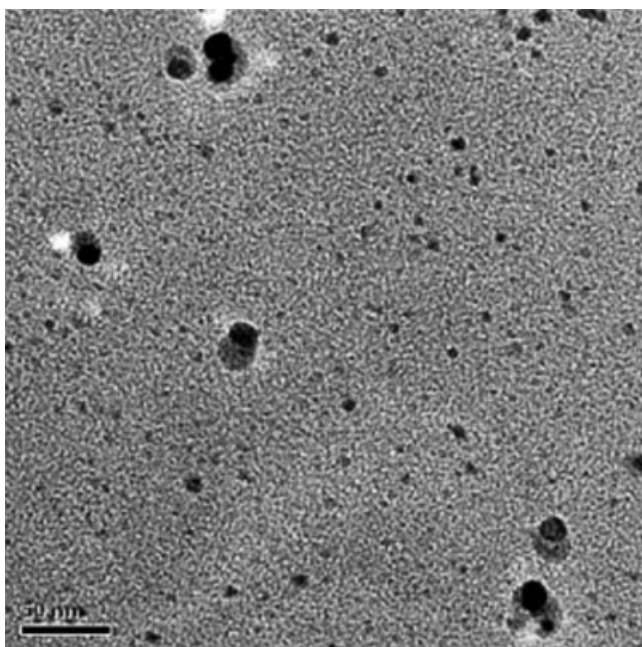


Figure 7 Bright-field TEM micrograph for the epoxy matrix modified with 10 wt % nanoparticles.

and 57 kJ/mol for the 10 wt % one. The values were very similar to those found in the literature^{35,37} for β relaxations in epoxy systems.

As an example of obtained morphologies, the bright-field TEM micrograph for the cured film containing 10 wt % of nanoparticles is shown in Figure 7. All of the particles were well dispersed with no significant macroscopic agglomerations; the observed features had a size distribution ranging between 5 and 20 nm. All of the samples were transparent. This was evidence that the organic–inorganic phase separation, if any, was on nanometric length scale. The absence of agglomerations could explain the fact that the interfacial polarization (Maxwell–Wagner–Sillars polarization) was not observed in our dielectric spectra of the nanocomposites. The polarization should have been very weak because of the absence of magnetic agglomerates because it was strongly dependent on their size, the concentration, and the existence of phase separation.^{21,38}

CONCLUSIONS

The following conclusions were made with regard to the local dynamics of the photocured epoxy/Fe₃O₄ nanocomposites. There was an increase in ϵ'' values with nanoparticle content because of the increase in alternating-current conductivity, which was produced as the proximity between the nanoparticles increased. Two secondary relaxations were detected, β and γ . Surprisingly, the strength of β relaxation increased with the nanoparticle content. This behav-

ior could not be explained when we took into account the molecular origin of the process. The incorporation of a ferromagnetic material into the matrix increased the internal electric field in the sample as a consequence of the electromagnetic induction, which led to an increase in the relaxation strengths.

Morphologies obtained by TEM revealed that the nanoparticles were well dispersed in the epoxy matrix, without the formation of agglomerates. This could explain the fact that interfacial polarization was not detected by dielectric spectroscopy.

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