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Dynamics of *In Situ* Synthetized Silver-Epoxy Nanocomposites as Studied by Dielectric Relaxation Spectroscopy

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ABSTRACT: *In situ* synthetized silver-photocurable epoxy resin nanocomposites were analyzed by dielectric spectroscopy to study the local dynamics at temperatures well below the glass-transition temperature and the effect of silver nanoparticles on them. Two secondary processes, β and γ, were detected both for the neat matrix and nanocomposites. Relaxation times of the β secondary relaxation, obtained by fitting to Havriliak-Negami equation, were lower in the nanocomposites, as well as the activation energies calculated from the Arrhenius temperature dependence of relaxation times, due to the plasticization effect of the trapped solvent. The electric modulus formalism was used to detect the interfacial or MWS polarization, present both in the neat matrix and in the nanocomposites due to heterogeneities and interfaces. The activation energy of this relaxation increased with nanoparticle content, thus indicating an increase of the heterogeneities due to the nanoparticles. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 2361–2367, 2011

Key words: epoxy; nanoparticles; nanocomposites; molecular dynamics; dielectric

INTRODUCTION

Nanocomposites based on polymers and nanoparticles continue to receive tremendous attention for application such as microelectronics, organic batteries, optics, and catalysis and also for conventional engineering purposes.[1] Irrespective of the type of base polymer material (thermoplastic or thermoset), significant enhancements in several physical properties, like thermal conductivity (with conducting fillers) or dielectric properties like resistivity, permittivity, dielectric strength, tracking, and partial discharge resistant characteristics (with insulating fillers), tensile properties, thermal stability, flame retardance, etc., are observed when compared with similar properties in traditional polymer microcomposites.[2–7] These observations are mainly attributed to the unique properties of nanoparticles and the large interfacial area in polymer nanocomposites.[8–10]

Epoxy resins have been widely used as matrices in advanced composites for aerospace applications, and also in insulation such as electrical machinery, in power electronic devices, and packing of integrated circuits. They have also been employed as coatings and adhesives. For some interesting applications, the improvement of their electrical conductivity is needed; so, the dispersion of conductive metallic nanoparticles allows to reach higher electrical conductivity, forming consequently conductive or semiconductive nanocomposites. Their performances depend on many factors such as electrical properties of constituents, volume fraction of the filler, and its spatial distribution within the polymeric matrix.[11–15] Among several conductive metallic nanoparticles, silver ones have been found to be very important for their excellent electrical conductivity,[16] antimicrobial effect,[17] and optical properties.[18]

The main challenge in this area is to overcome nanoparticle agglomeration; because of their high surface area, metal nanoparticles have a strong tendency to agglomerate. Many different approaches have been successfully reported in literature.[19–22] In particular, Sangermano et al.[23] proposed an elegant *in situ* synthesis of silver-epoxy nanocomposite,

Cured sample	Experimental char content (wt %)	Approximate NP content (wt %)	T_g (°C)
Neat epoxy	0.7	0	185
5 wt % AgSbF$_6$	1.8	1.1	180
10 wt % AgSbF$_6$	3.2	2.5	170
15 wt % AgSbF$_6$	4.8	4.1	164

Nanoparticle content has been calculated from thermogravimetric analysis while T_g values have been obtained by the maximum of tanδ peak from dynamic mechanical thermal analysis.

which was achieved by simultaneous photoinduced electron transfer and cationic polymerization processes. The results established a novel approach for the preparation of nanocomposites by which nanoparticle formation and crosslinking processes can be accomplished in one pot by simply irradiating appropriate formulations.

In the other hand, dielectric spectroscopy has been found to be a suitable technique for the study of the relaxational behavior and dielectric properties of thermosetting matrices and nanocomposites based on them. Several authors have used dielectric spectroscopy to study dielectric properties of nanocomposites based on metallic nanoparticles.[24–29] Dielectric and conductivity relaxations that are present in these nanocomposites can be investigated. However, due to the presence of conductive nanoparticles, dielectric or conductivity relaxations may be obscured, as for example in the case of interfacial polarization.[30] It is then more convenient to use the formalism "electric modulus" first introduced by McGram et al.[31] to monitor the evolution of all the relaxation processes and the effect of the filler amount on them.

In our previous paper,[32] in situ synthetized silver-epoxy nanocomposites were characterized in terms of thermal and dielectric properties. The T_g of the nanocomposites was found to be lower as the silver precursor salt amount increased (as it can be seen in Table I, where T_g values for all the systems studied are presented) due to the plasticization effect of the solvent. On the other hand, all the nanocomposites analyzed were found to be below the percolation threshold, as indicated by the evolution of dielectric properties with nanoparticle amount.

In this article, local dynamics of those silver-epoxy nanocomposites has been characterized in terms of dielectric spectroscopy at low temperatures, below their T_g. Both permittivity and modulus formalisms have been used to follow the evolution of sencondary, interfacial and conductivity relaxations, analyzing the effect on the filler and its amount on them.

EXPERIMENTAL

Materials

Epoxy resin, 3,4-epoxycyclohexylmethyl-3′,4′-epoxy-cyclohexanecarboxylate (CE, Cytec, Brussels, Belgium), silver hexafluoroantimonate (AgSbF$_6$, Aldrich, Milan, Italy), propylene carbonate (Aldrich), and the radical photoiniatitor, 2-2 dimethoxy-2-phenyl acetophenone (DMPA, Irgacur 651, Ciba, Marcon (Venezia), Italy were used as received.

Sample preparation

The silver precursor was dissolved in propylene carbonate (1 : 1 weight ratio). The CE resin formulations containing actual AgSbF$_6$ content ranging from 5 to 15 wt % (the nanoparticle content for each sample, as calculated from thermogravimetric analysis, is presented in Table I), and DMPA (2 wt %) were spread onto glass substrates using a wire-wound applicator, and then, the films were exposed to UV light by using a Fusion Lamp with a light intensity on the surface of the sample of about 150 mW/cm^2 (measured by EIT photometer) and a belt speed of 6 m/min. Cured tack-free films of about 100 μm were obtained. Further details of the sample preparation can be found in previous publications.[20,32]

Instrumentation

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

RESULTS AND DISCUSSION

Figure 1 shows the loss factor (ε″) versus frequency curves at several temperatures between −60 and 70°C for the neat epoxy matrix. Data have been fitted to Havriliak-Negami (HN), by using a HN term for each dipolar relaxation. The Havriliak-Negami formalism is based on an analytical expression for the complex dielectric permittivity:

$$\varepsilon^*(\omega) - \varepsilon_\infty = \frac{\varepsilon_0 - \varepsilon_\infty}{\left[1 + (i\omega\tau_0)^b\right]^c} \tag{1}$$

where $\varepsilon_0 - \varepsilon_\infty = \Delta\varepsilon$ is the dielectric strength, τ_0 is the central relaxation time, and b and c are parameters which describe the shape of the relaxation time distribution function (symmetric and asymmetric
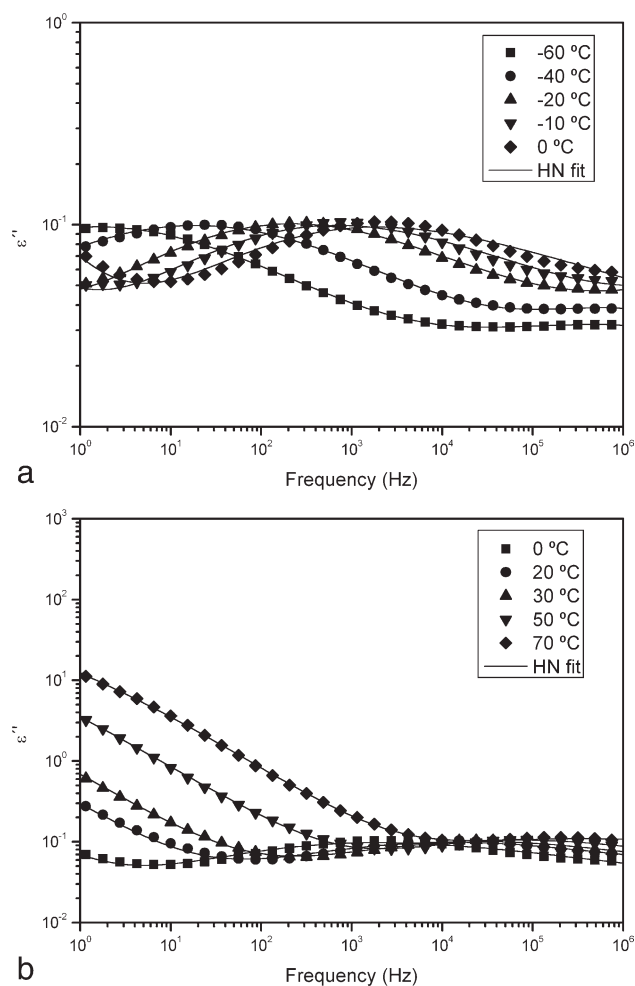
a

b

Figure 1 Evolution of dielectric loss with frequency at two temperature ranges: (a) from −60 to 0°C and (b) from 0 to 70°C for the neat epoxy matrix. Solid lines indicate fitting to Havriliak-Negami equation.

broadening). The following conductivity term (which takes into account the polarization of ions or charge carriers) has been added to HN terms for the temperatures at which the conductivity contributes to the spectra:

$$\varepsilon_c'' = \left(\frac{\sigma}{\varepsilon_0 \omega}\right) \qquad (2)$$

As it was pointed out in our previous work, temperatures at which measurements were carried out are well below the calorimetric T_g^{32} of the samples, so the main α process related with segmental dynamics is not observed. Two local dipolar relaxation processes are observed as follows: β and γ, in the order of increasing frequency at a constant temperature. γ relaxation is observed only at low temperatures and high frequencies, moving out of the analyzed frequency window, thus making a further analysis impossible. The analysis of relaxation times

and activation energies of β relaxation will be commented below, compared with those corresponding to nanocomposites. The origin of the β process in epoxy matrices has been a matter of discussion in the literature[33–37] and was analyzed in our previous work.[25] First studies[36,37] related β and γ relaxations in epoxy networks to motions of hydroxyl groups and ether linkage of the glycidyl moiety, respectively. Other authors have associate β relaxation with the motion of hydroxypropylether group or other groups formed during the curing reaction.[38,39] For fotocurable epoxy resins like these used in this study, Uragawa et al.[40] related the β relaxation with motions of the cyclohexyl rings. Several authors have related the γ relaxation with motions of unreacted epoxide rings.[38,39,41]

Figures 2–4 show the loss factor (ε″) versus frequency curves at several temperatures between −60 and 70°C for the nanocomposites with 1.1, 2.5, and
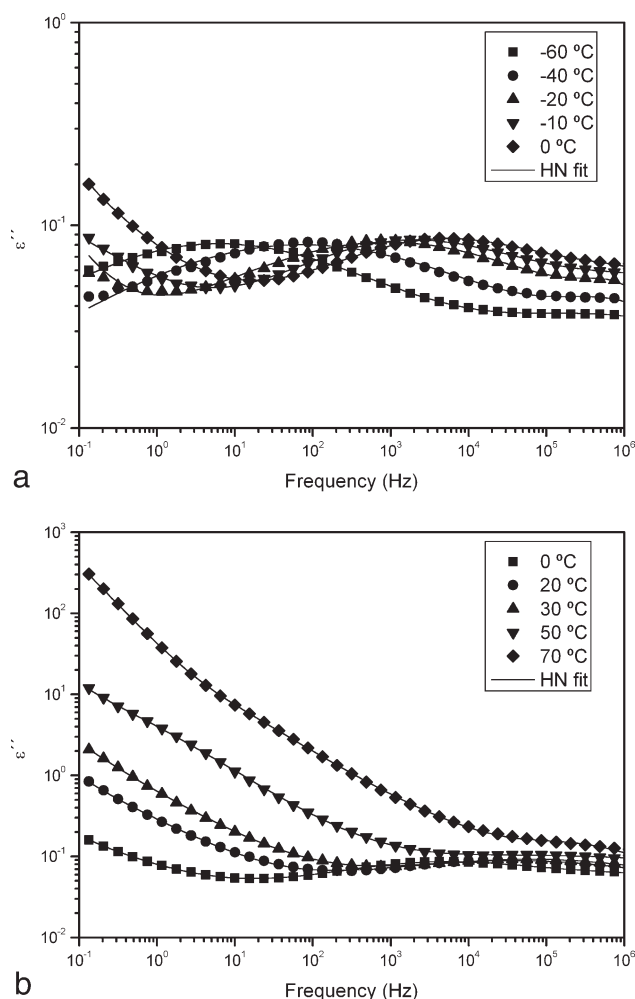

a

b

Figure 2 Evolution of dielectric loss with frequency at two temperature ranges: (a) from −60 to 0°C and (b) from 0 to 70°C for the nanocomposites with 1.1 wt % of nanoparticles. Solid lines indicate fitting to Havriliak-Negami equation.
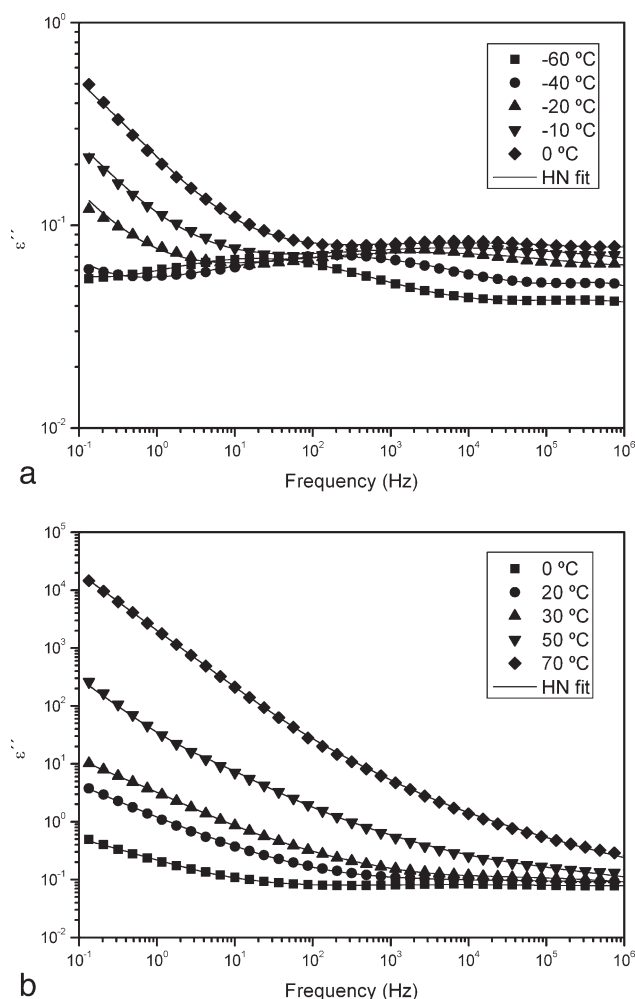
Figure 3 Evolution of dielectric loss with frequency at two temperature ranges: (a) from −60 to 0°C and (b) from 0 to 70°C for the nanocomposites with 2.5 wt % of nanoparticles. Solid lines indicate fitting to Havriliak-Negami equation.

4.1 wt % of nanoparticles, respectively. ε'' values increase with nanoparticle content, probably due to an increase in the a.c. conductivity that is produced as the proximity between nanoparticles increases.[42] In spite of the conductivity increase, it has to be pointed out that the nanocomposites were below the percolation threshold.[32] If the percolation threshold was achieved, there would be a much higher conductivity increase (several orders of magnitude), due to the formation of a continuous electrical path throughout the matrix. In our previous work, we demonstrated by morphological analysis that this pathway was not formed for these nanoparticle content.[32] Moreover, Gonon and Boudefel[43] calculated a theoretical threshold of around 15 wt %, at higher concentrations than those used in this work. β and γ secondary relaxations are detected for nanocomposites. γ appears in the high frequency tail of the spectra only at the lower temperatures, moving then

out of the frequency range. Regarding β relaxation, one can see that it is displaced toward higher frequencies with the nanoparticle content, probably due to the plasticization effect induced by the presence of the propylene carbonate solvent which remains trapped into the glassy polymer network (the boiling point of propylene carbonate is 240°C).[32] This plasticization effect was probed by preparing the neat epoxy system with the same solvent content than the nanocomposite with the highest nanoparticle amount. The T_g of the so prepared system was found to decrease, reaching a value of around 165°C, very similar to that of the nanocomposite with the highest nanoparticle amount. Relaxation times obtained from Havriliak-Negami fitting for several temperatures are presented in Figure 5. Relaxation times are lower for the nanocomposites, decreasing with the nanoparticle content as was explained above. The process shows an Arrhenius
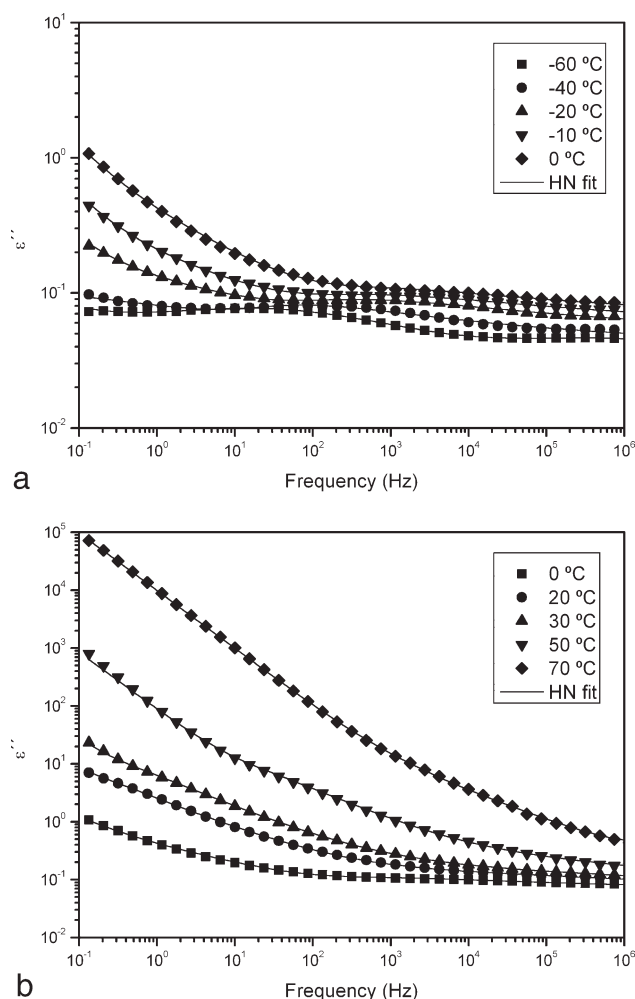

Figure 4 Evolution of dielectric loss with frequency at two temperature ranges: (a) from −60 to 0°C and (b) from 0 to 70°C for the nanocomposites with 4.1 wt % of nanoparticles. Solid lines indicate fitting to Havriliak-Negami equation.
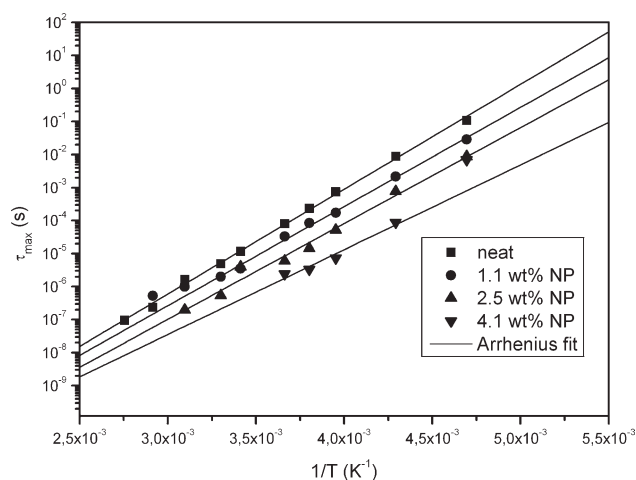
Figure 5 Evolution of relaxation times obtained from HN fit with the reciprocal of temperature for all the systems studied. Solid lines indicate fitting to Arrhenius equation.

temperature dependence for all the systems. Obtained activation energies were 61 kJ/mol for the matrix (value that agree with those found in the lit-

erature for the β process of epoxy resins[25,34,36]), 58 kJ/mol for the nanocomposite with 1.1 wt % of nanoparticles, 56 kJ/mol for the nanocomposite with 2.5 wt % of nanoparticles, and 50 kJ/mol for the nanocomposite with 4.1 wt %. There is a decrease of the activation energy with the nanoparticle content, that could be related with the plasticization effect of the solvent commented above.

In the case of the nanocomposites, when the deconvolution and the fitting to Havriliak-Negami were carried out, the presence of some other relaxation processes was noticed. Because of the presence of conductive nanoparticles, dielectric relaxations may be obscured, as for example in the case of interfacial polarization observed in heterogeneous systems.[24,30] It is then more convenient to use the electric modulus formalism, which shifts the loss peaks to the region of frequencies where the most measuring equipments operate and at the same time diminishes the values of abscissa because of the definition of electric modulus ($M^* = 1/\varepsilon^*$, where ε^* is the complex permittivity)[24,30]:
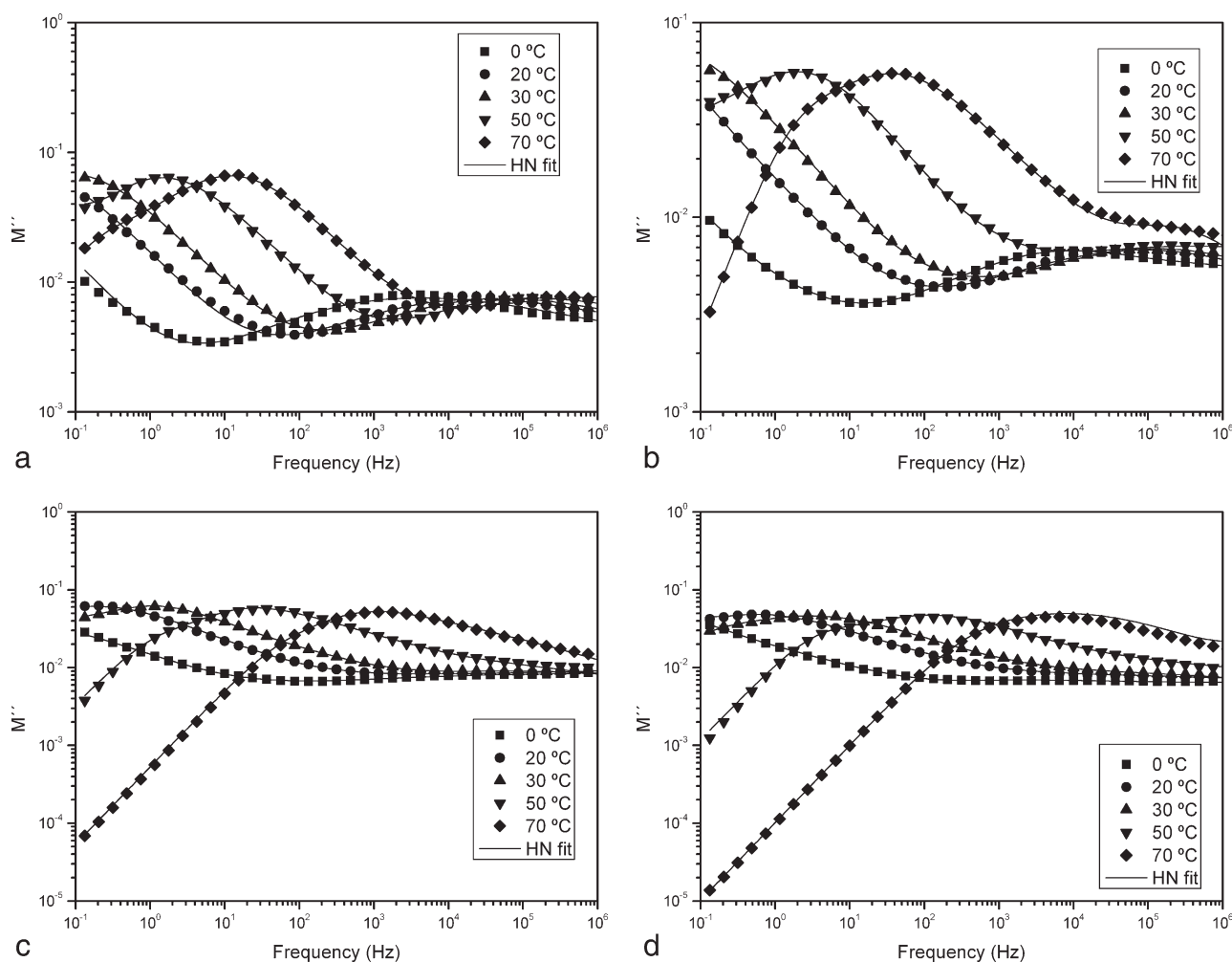

Figure 6 Evolution of the imaginary part of electric modulus, M'', with frequency for all the systems analyzed in the temperature range from 0 to 70°C. Solid lines indicate fitting to Havriliak-Negami equation.
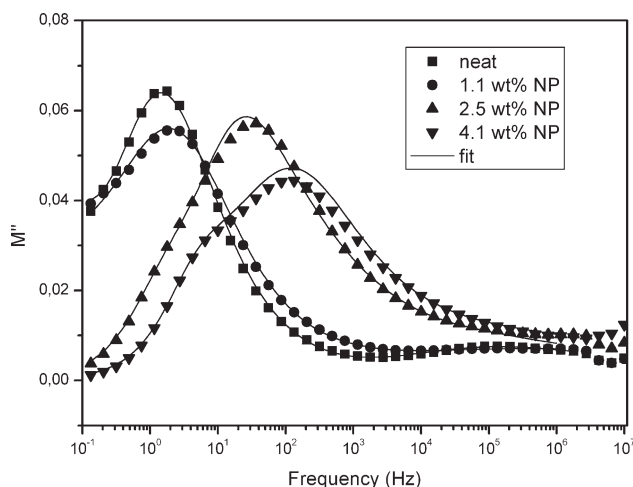
Figure 7 Evolution of the imaginary part of the modulus M'' with frequency for all the systems analyzed at 50°C.

$$M^* = \frac{1}{\varepsilon' - j\varepsilon''} = M' + jM'' \qquad (3)$$

Figure 6 shows the evolution of the imaginary part of the modulus, M'', with frequency for all the systems studied in the temperature range at which new relaxations appear. Solid lines indicate fitting to Havriliak-Negami equation. Data for the fitting have been obtained by fitting permittivity values to Havriliak-Negami equation and obtaining from them values for the modulus by using eq. (3). As it can be seen, there is a new process present in all the systems at low frequencies, that is displaced toward higher frequencies with temperature. The process starts to appear in our frequency range at around 50°C for the neat matrix and the nanocomposite with 1.1 wt %, but the temperature of appearance decreases with the nanoparticle content, being the process in our frequency range even at 20°C for the nanocomposite with 4.1 wt %. So, increasing the nanoparticle amount the process is displaced toward higher frequencies. This is the typical behavior of the process related to the interfacial polarization known as Maxwell-Wagner-Sillars effect.[44,45] The origin of the MWS relaxation in heterogeneous media exhibits the presence of free charges (impurities, ions, etc.) in the interfaces, because of the discrepancies of dielectric properties (conductivity, permittivity) of these two media, producing an interfacial polarization. Interfacial polarization in neat epoxy systems has been found by several authors[46–48] and could be due to the presence of microspherical voids produced during mixing process. In our case, as the curing process is very fast, the voids produced during mixing process could remain in the sample. In the case of the nanocomposites, the heterogeneity is much higher, because besides possible voids, the trapped solvent and the presence of nanoparticles

increases considerably the interfaces and heterogeneity of the system. Figure 7 compares the evolution of M'' for all the systems at 50°C, to analyze the effect of filler amount. Besides the aforementioned displacement toward higher frequencies, the magnitude of the peak decreases with the nanoparticle amount, as expected because of the MWS type of relaxation, due to the higher permittivity values of those systems.[24,45] On the other hand, and specially for the nanocomposite with the highest nanoparticle amount and high temperatures, another relaxation can be seen at the low frequency part, as a shoulder of the previous. This relaxation has been defined as a conductivity relaxation[24,49,50] occurring because of the field-based diffusion of charge carriers. The fact that appears only for the highest nanoparticle amount at high temperatures makes impossible a more complete study of this process.

The evolution of the frequency of the maximum in M'' with temperature is shown in Figure 8 for all the nanocomposites. The relaxation shows an Arrhenius-type temperature dependence, with activation energies of 58 kJ/mol for the neat matrix (very close to the value found by Patsidis and Psarras[51] for the MWS process in neat epoxy) and 119, 144, and 159 kJ/mol for the nanocomposites with 1.1, 2.5, and 4.1 wt % of nanoparticles, respectively. The increase in the activation energy with nanoparticle content indicates the increase in heterogeneity.[51] In fact, the big increase among the neat matrix and the nanocomposites could be due to the increase of interfaces and heterogeneity produced by the nanoparticles. Among the nanocomposites, the heterogeneity and number of interfaces increases with nanoparticle content, thus increasing the activation energy values.
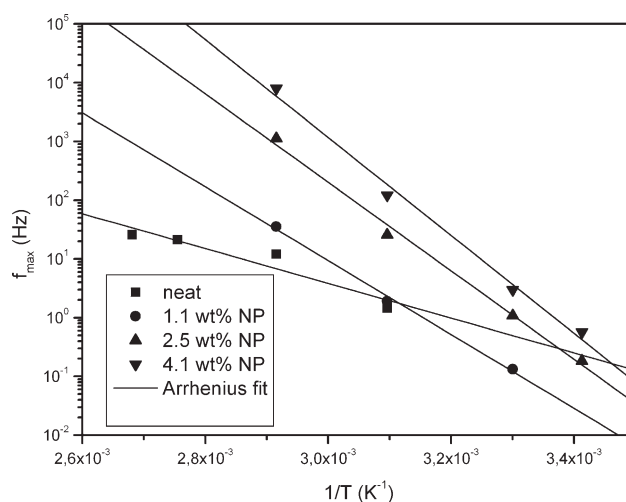

Figure 8 Evolution of the frequency of the maximum in M'' with the reciprocal of temperature for all the systems studied. Solid lines indicate fitting to Arrhenius equation.

CONCLUSIONS

The following conclusions were made with regard to the local dynamics of photocured silver-epoxy nanocomposites. There was an increase in ε'' values with nanoparticle content because of the increase in a.c. conductivity produced by the increase in the proximity among the nanoparticles. Two secondary relaxations were detected, β and γ. β relaxation appeared at higher frequencies for the nanocomposites when compared with neat matrix, with lower activation energy values. This could be due to the plasticization effect of the solvent, trapped in the glassy matrix. With the use of the electric modulus formalism, another two relaxations were detected. The first one, related with the interfacial polarization due to heterogeneities in the systems (voids created during mixing or trapped solvent in the case of the matrix and besides those the effect of interfaces created by the nanoparticles in the nanocomposites). This relaxation followed an Arrhenius-type temperature dependence and activation energy values increased with nanoparticles content, indicating an increase in the heterogeneities. The other relaxation, related to conductivity, is detected only for the nanocomposites with the higher nanoparticle content at high temperatures.

References

1. Ishida, H.; Campbell, S.; Blackwell, J. Chem Mater 2000, 12, 1260.
2. Tanaka, T. IEEE Trans Dielectr Electr Insul 2005, 12, 914.
3. Cao, Y.; Irwin, P. C.; Younsi, K. IEEE Trans Dielectr Electr Insul 2004, 11, 797.
4. Imai, T.; Sawa, F.; Ozaki, T.; Inoue, Y.; Shimizu, T.; Tanaka, T. Comparison of insulation breakdown properties of epoxy nanocomposites under homogeneous and divergent electric fields. IEEE Conference on Electrical Insulation and Dielectric Phenomena (CEIDP), Kansas City, USA, October 15–18, pp. 306–309, 2006.
5. Bryning, M. B.; Islam, M. F.; Kikkawa, J. M.; Yodh, A. G. Adv Mater 2005, 17, 1186.
6. Kashiwagi, T.; Du, F.; Douglas, J. F.; Winey, K. Y.; Harris, R. H.; Shields, J. R. Nat Mater 2005, 4, 928.
7. Zhang, S. H.; Zhang, N. Y.; Huang, C.; Ren, K. L.; Zhang, Q. M. Adv Mater 2005, 17, 1897.
8. Lewis, T. J. IEEE Trans Dielectr Electr Insul 2004, 11, 739.
9. Roy, M.; Nelson, J. K.; MacCrone, R. K.; Schadler, L. S. IEEE Trans Dielectr Electr Insul 2005, 12, 629.
10. Ajayan, P. M.; Schadler, L. S.; Braun, P. V. Nanocomposite Science and Technology; Wiley: London, 2003.
11. Carmona, F.; Mouney, C. J Mater Sci 1992, 27, 1322.
12. Chen, I. G.; Johnson, W. B. J Mater Sci 1991, 26, 1565.
13. Boiteux, G.; Fournier, J.; Issotier, D.; Seytre, G. Synth Met 1999, 102, 1234.
14. Fournier, J.; Boiteux, G.; Seytre, G. J Mater Sci Lett 1997, 16, 1677.
15. Mamunya, Y. P.; Davidenko, V. V.; Pissis, P. Eur Polym J 2002, 38, 1887.
16. Chang, L. T.; Yen, C. C. J Appl Polym Sci 1995, 55, 371.
17. Shanmugam, S.; Viswanathan, B.; Varadorojan, T. K. Mater Chem Phys 2005, 95, 51.
18. Lin, W. C.; Yang, M. C. Macromol Rapid Commun 2005, 26, 1942.
19. Jana, N. R.; Gearheart, L.; Murphy, C. J. J Phys Chem 2001, 105, 4065.
20. Yagci, Y.; Sangermano, M.; Rizza, G. Chem Commun 2004, 2771.
21. Gadubert, V. J.; Lennox, R. B. Langmuir 2005, 21, 6532.
22. Majima, T.; Sakamoto, M.; Tachikawa, T.; Fujitsuka, M. Chem Phys Lett 2006, 420, 90.
23. Sangermano, M.; Yagci, Y.; Rizza, G. Macromolecules 2007, 40, 8827.
24. Psarras, G. C.; Manolaki, E.; Tsangaris, G. M. Compos A 2002, 33, 375.
25. Kortaberria, G.; Arruti, P.; Jimeno, A.; Mondragon, I.; Sangermano, M. J Appl Polym Sci 2008, 109, 3224.
26. Pissis, P.; Fragiadakis, D. J Macromol Sci Phys 2007, 46, 119.
27. Ramajo, L.; Castro, M. S.; Reboredo, M. J Mater Sci 2010, 45, 106.
28. Dang, Z. M.; Lin, Y. H.; Nan, C. W. Adv Mater 2003, 15, 1625.
29. Huang, X. Y.; Jiang, P. K.; Kim, C. U. J Appl Phys 2007, 102, 124103.
30. Tsangaris, G. M.; Psarras, G. C.; Kouloumbi, N. J Mater Sci 1998, 33, 2027.
31. McGram, N. G.; Read, B. E.; Williams, G. In Anelastic and Dielectric Effects in Polymeric Solids; Wiley: London, 1967.
32. Vescovo, L.; Sangermano, M.; Scarazzini, R.; Kortaberria, G.; Mondragon, I. Macromol Chem Phys 2010, 211, 1933.
33. Schroter, K.; Unger, R.; Reissig, S.; Garwe, F.; Kahle, S.; Beiner, M.; Donth, E. Macromolecules 1998, 31, 8966.
34. Correia, N.; Ramos, J. J. Phys Chem Chem Phys 2000, 2, 5712.
35. Doss, A.; Paluch, M.; Sillescu, H.; Hinze, G. Phys Rev Lett 2002, 88, 095701.
36. Pochan, J. M.; Gruber, R. J.; Pochan, D. F. J Polym Sci Polym Phys Ed 1981, 19, 143.
37. Butta, E.; Livi, A.; Levita, G.; Rolla, P. A. J Polym Sci Part B: Polym Phys 1995, 33, 2253.
38. Boye, J.; Demont, P.; Lacabanne, C. J Polym Sci Part B: Polym Phys 1994, 32, 1359.
39. Mangion, M. B.; Johari, G. P. J Polym Sci Part B: Polym Phys 1990, 28, 71.
40. Uragawa, A.; Yamamoto, Y.; Inoue, Y.; Chujo, R. Polymer 1991, 32, 2779.
41. Mijovic, J.; Zhang, H. Macromolecules 2003, 36, 1279.
42. Costa, L. C.; Valente, M.; Sa, M. A.; Henry, F. Polym Bull 2006, 57, 881.
43. Gonon, P.; Boudefel, A. J Appl Phys 2006, 99, 024308.
44. Tsangaris, G. M.; Kouloumbi, N.; Kyvelidis, S. Mater Chem Phys 1996, 44, 245.
45. Hammami, M.; Arous, M.; Lagache, M.; Kallel, A. J Alloys Compd 2007, 430, 1.
46. Smaoui, H.; Mir, L. E.; Guermazi, H.; Agnel, S.; Toureille, A. J Alloys Compd 2009, 477, 316.
47. Baziard, Y.; Breton, S.; Toutain, S.; Gourdenne, A. Eur Polym J 1988, 24, 521.
48. Ramajo, L.; Reboredo, M.; Castro, M. Compos A 2005, 36, 1267.
49. Hodge, I. M.; Angell, C. A. J Chem Phys 1977, 67, 1647.
50. Kalogeras, I. M.; Roussos, M.; Vassilikou, A.; Spanoudaki, A.; Pissis, P.; Savelyev, Y.; Shtompel, V. I.; Robota, L. P. Eur Phys J 2005, E18, 467.
51. Patsidis, A.; Psarras, G. C. Express Polym Lett 2008, 10, 718.