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In Situ Synthetized Silver/Epoxy Nanocomposites: Electrical Characterization in Terms of Dielectric Relaxation Spectroscopy

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Summary: In situ synthesis of silver/epoxy nanocomposites was achieved by UV-induced polymerization through a simultaneous photoinduced electron transfer and cationic polymerization processes. The evolution of dielectric properties with frequency and NP content seem to indicate that the nanocomposites of this study remain below the percolation threshold.

Keywords: dielectric properties; epoxy; nanocomposites; nanoparticles

Introduction

The fabrication of metallic nanoparticles (NP) is a topic of extreme interest in material science because of the wide range of optical and electronic properties that are accessible in the nanometer size-range. The good dispersion of metallic nanoparticles within a polymeric matrix is a tough goal of increasing importance since these hybrid materials could have high potentiality for applications in many technologies such as catalysis,[1] electron or energy storage[2] and sensors.[3] In particular silver nanoparticles are very important for their excellent electrical conductivity,[4] antimicrobial effect[5] and optical properties.[6] 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. The main challenge is to overcome NPs agglomeration; because of their high surface area, metal nanoparticles have a strong tendency to agglomerate. Many different approaches have been successfully reported in literature. In particular Sangermano and Yagci[7] proposed an elegant *in situ* synthesis of silver-epoxy nanocomposite, which was achieved by simultaneous photoinduced electron transfer and cationic polymerization processes.

In this paper, we have prepared silver/epoxy nanostructured films by following the aforementioned approach. Obtained coatings were characterized by dielectric spectroscopy, which offers the possibility to characterize nanocomposites over an unparalleled range of frequency and temperature, being uniquely suited for the study of nanocomposites in general and of metallic NP-based nanocomposites in particular. Nanocomposite dynamics (by analyzing the effect of nanofillers on the dynamics and relaxations of the polymeric chains) as well as electrical properties can be analyzed in a very wide range of frequency and/or temperature.

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Experimental Part

Epoxy resin, 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexanecarboxylate (CE, Cytec, Belgium), silver hexafluoroantimonate ($AgSbF_6$, Aldrich), propylene carbonate (Aldrich) and the radical photoiniatitor, 2-2 dimethoxy-2-phenyl acetophenone (DMPA, Irgacur 651, Ciba) were used as received. The silver precursor was dissolved in propylene carbonate 1:1 weight ration. The CE resin formulations containing actual $AgSbF_6$ content ranging from 3 to 20 wt%, and DMPA (2 wt%) were coated onto glass substrates using a wire-wound applicator, and then the films were exposed to UV light.

The kinetics of the photopolymerization was determined by real time Fourier-transform infrared (FT-IR) spectroscopy, employing a Thermo-Nicolet 5700. The formulations were coated onto a silicon wafer with a thickness of 50 μm. The sample was exposed simultaneously to the UV beam,which induces the polymerization, and to the IR beam, which analyzes the extent of the reaction in situ. Because the IR absorbance is proportional to the monomer concentration, conversion versus irradiation time profiles can be obtained. Epoxy group conversion was followed by monitoring the decrease in the absorbance due to epoxy groups in the region of 780 cm^{-1}. As an internal reference, in order to normalize differences in thickness, the absorption band of carbonyl group (centered at 1700 cm^{-1}) was taken into account.

Dielectric relaxation spectroscopy (DRS) was carried out in a Novocontrol Alpha high-resolution dielectric analyzer over a frequency range between 1 Hz and 1 MHz at room 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

The complex dielectric permittivity ($\varepsilon^* = \varepsilon' + i\varepsilon''$) and AC conductivity ($\sigma_{AC}$) values have been measured for all the nanocomposites by frequency sweeps (from 1 Hz to 10 MHz) at room temperature, in order to analyze the effect of silver NPs and their amount on the electrical properties of the nanocomposites. The approximate weight percentage of silver NPs of each nanocomposite has been calculated from thermogravimetric analysis (not shown here). Table 1 shows the approximate silver NP amount for each nanocomposite, depending on the precursor content, calculated by extracting the experimental char amount of the neat epoxy sample from the experimental char amount of each nanocomposite.

Figure 1 shows, the evolution of the dielectric constant (ε'), dielectric loss (expressed as tan δ, the ratio between ε' and ε'') and AC conductivity (σ_{AC}) with frequency as measured at room temperature, for all the nanocomposites studied. Comparing the spectrum of the neat epoxy matrix with those of the nanocomposites, it

Table 1.
Nanoparticle content and T_g values for each nanocomposite. Nanoparticle content has been calculated from thermogravimetric analysis while T_g values have been obtained by from the maximum of tan δ peak from dynamic mechanical thermal analysis.

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

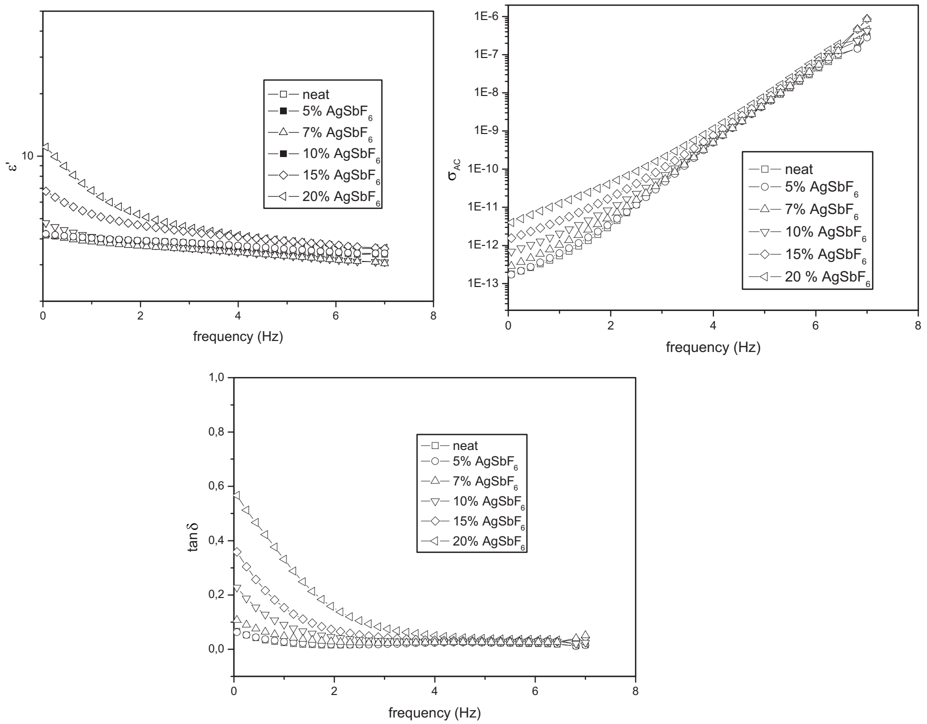

Figure 1.

Evolution of dielectric constant, tan δ and AC conductivity with frequency for all the nanocomposites studied, as measured at room temperature.

can be seen that there is an increase of ε′ at low frequencies, which may be due to the piling of charges at the extended interface of the nanocomposites and/or in presence of more conducting particles.[25] Moreover, except for the lower frequencies (where interfacial charge piling due to the generation of NP/polymer interfaces increases the dielectric constant with NP content), dielectric constant values and behavior with frequency is very similar in the neat matrix and the nanocomposites, being almost nearly frequency independent. Several authors have pointed out that this fact corresponds to nanocomposites based on conductive nanofillers below the percolation threshold,[8–10] while for nanocomposites above the percolation threshold there is a big frequency dependence of the dielectric constant. As can also be seen, compared with the epoxy matrix, the dielectric loss of the nanocomposites increases slightly, which maybe owing to the interfacial loss due to the newly introduced interface. Regarding the evolution of AC conductivity, it can be seen that there are no significant differences between the neat matrix and nanocomposites. AC conductivity increases almost linearly with frequency, thus indicating that the nanocomposites studied are below the percolation threshold, behaving as dielectrics. Several authors have found that once the percolation is reached, the AC conductivity of nanocomposites with conductive fillers becomes frequency independent, the nanocomposite acting like a conductor.[11–15]

The evolution of the parameters seems to indicate that the percolation threshold has not been reached, even for the nanocomposite with 20 wt% of precursor (approximately 5 wt% of NP). Gonon and Boudefel[16] calculated a theoretical threshold of 15 wt% (which would agree with our results), but found an experimental one of around 1 wt%. They related this low threshold to the very segregated distribution of the fillers in the epoxy matrix. In the present study, threshold seems to be higher. It seems that the in situ generated metal NP are well distributed within the polymeric network but too distant one from the other. We should probably increase the precursor content in the epoxy photocurable formulation in order to achieve percolation, but this is a difficult task because of solubility limit of the silver salt.

Figure 2 shows the evolution of dielectric constant, tan δ and AC conductivity with nanoparticle content at room temperature and several frequencies ranging from 1 kHz to 1 MHz. For all the systems studied, values are very similar to those found for the neat matrix, without any rapid climbing of the properties with NP content, thus indicating that the nanocomposites are below the percolation threshold. Several authors have related the rapid climbing of those properties as indicative of percolation in nanocomposites based on polymer matrices and conductive fillers such as metallic NPs or carbon nanotubes.[17–21]

Epoxy group conversion as a function of irradiation time for the investigated formulations is reported in Figure 3. While the slope of the curves gives an indication of the rate of polymerization, the plateau value gives the final epoxy group conversion. From the curves reported in Figure 3, it is evident that silver hexafluoroantimonate is quite efficient at converting UV-generated free radicals into propagating carbocations, which start cationic epoxy ring-opening polymerization with high reactivity. The polymerization rate is very similar for all the investigated formulations, with just a

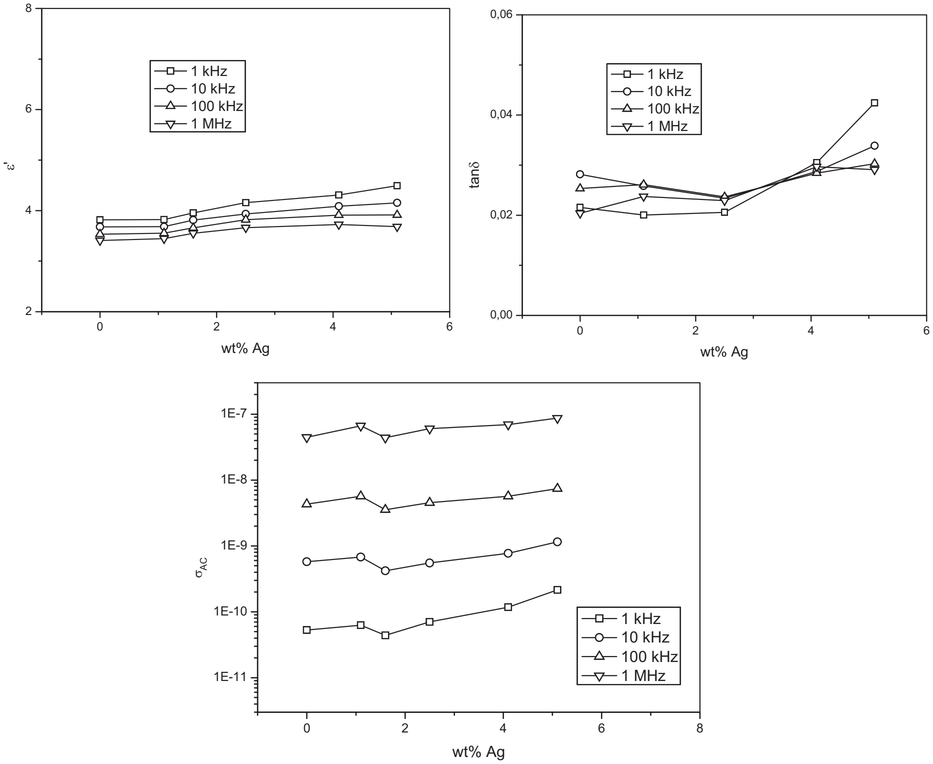

Figure 2.

Evolution of dielectric constant, tan δ and AC conductivity with nanoparticle content at room temperature and several frequencies from 1 kHz to 1 MHz.

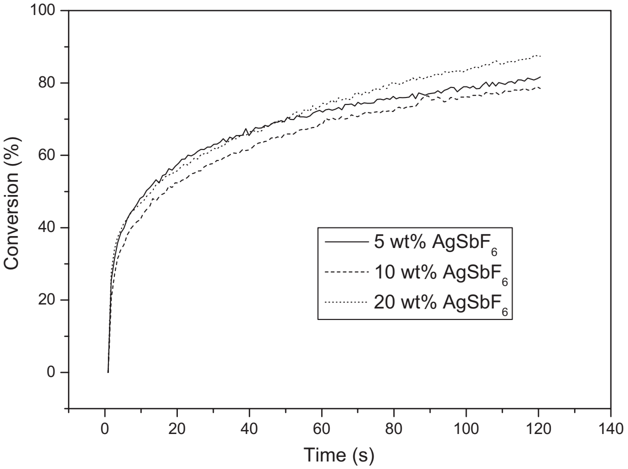

Figure 3.
Real-time FTIR epoxy group conversion as a function of irradiation time for epoxy-based nanocomposites containing different $AgSbF_6$ contents.

slight increase of epoxy group conversion in the presence of 20 wt% of the silver precursor. This result could be due to the fact that the silver salt is introduced in the photocurable formulation using propylene carbonate solution (1:1 wt% ratio). By increasing the actual content of the silver precursor up to 20 wt% it means to add an important amount of solvent in the photocurable formulation which decrease the viscosity of the medium and allows a higher mobility of the reactive species and therefore a higher final epoxy group conversion.

Conclusion

In situ synthesis of silver/epoxy nanocomposites were achieved by UV-induced polymerization through a simultaneous photoinduced electron transfer and cationic polymerization processes. The overall process was investigated by means of real-time FT-IR analysis showing that silver hexafluoroantimonate is quite efficient at converting light-generated free radicals into propagating carbocations. A slight decrease on T_g values was observed by increasing the silver precursor content in the photocurable formulations probably due to a higher solvent content, which could act as plasticizing agent for the coating. The evolution of dielectric properties with frequency and NP content seem to indicate that the nanocomposites of this study remain below the percolation threshold. Dielectric constant is almost frequency independent (while for nanocomposites above threshold it should be dependent), while AC conductivity increases linearly with frequency, thus indicating that percolation has not been reached, because AC conductivity above threshold should be frequency independent. Also the evolution of those properties with NP content show a very slight difference with the matrix, without any sharp increase of several orders of magnitude, as pointed out by several authors at the percolation threshold.

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