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Dielectric response of $Ag/BaTiO_3$/epoxy nanocomposites

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Abstract Dielectric properties and relaxation phenomena of hybrid material (functionalized nanosilver/$BaTiO_3$/epoxy) were studied as a function of ceramic content. Nanoparticles were obtained through chemical reduction in ethanol and triethylenetetramine. Epoxy resin, functionalized Ag and $BaTiO_3$ were mixed and composites were prepared onto glass substrates by dipping technique. Samples containing various amounts of ceramic filler were examined by thermal and SEM analysis. Dielectric measurements were performed at different frequencies and temperatures. It was found that hybrid materials had high permittivities and their relaxation processes were influenced by the epoxy resin near its T_g, while metallic and ceramic content modified the real permittivity values.

Introduction

In recent years, there has been an increasing interest on high dielectric constant flexible particulate composites made up from a mixture of ferroelectric ceramic and polymer for high energy storage and capacitor applications related to microelectronic packaging [1–6]. Thus, $BaTiO_3$ has demonstrated to have good performance as filler because of its high dielectric permittivity and low cost. Nevertheless, there is a new generation of conductive nanofillers which can be incorporated to $BaTiO_3$/epoxy composites in order to obtain a better material performance [7].

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The dielectric properties of the composites with metallic fillers are attributed to the formation of infinite number of tiny capacitors with many conducting particles separated by thin insulating layers. Thus, a heterogeneous system of this kind can result in a capacitor with excellent characteristics for charge storage [7].

In these systems, the dielectric constant is influenced by metal and ceramic particles concentrations [8, 9], but also by the metallic particle area. Generally, samples prepared with micrometric metal particles have lower properties than samples made using lower nanoparticles amount, due to the former lower specific area.

In this work, hybrid materials made incorporating 1 wt% of functionalized nanosilver was studied and compared with $BaTiO_3$/epoxy composites. They were all obtained by the dipping technique. Nanoparticles were prepared through a chemical reduction in ethanol and triethylenetetramine was used to stabilize and functionalize the particles. Dielectric measurements were performed as a function of frequency and temperature in order to understand the relaxation process.

Experimental

Silver nanoparticles were obtained through $AgNO_3$ chemical reduction in ethanol and D.E.H. 24 (triethylenetetramine, Dow Chemical) was used to stabilize and functionalize the particles in a 1:10 relation (Ag/D.E.H 24) [10]. Three-hundred milligram of $AgNO_3$ was added to 200 mL of ethanol in a glass container at 70 °C, under constant stirring. The triethilenetetramine, previously dissolved in ethanol, was dispersed into the $AgNO_3$ alcoholic solution in order to obtain a 1:10 $AgNO_3$:Amine ratio. The particles were precipitated by alcohol evaporation at 90 °C for 2 h. As a result, a solution of amine with precipitated silver nanoparticles was achieved. Shape and size of nanoparticles were determined by Transmission Electron Microscopy (TEM), Philips CM200 with an acceleration voltage of 200 KV.

A commercial epoxy resin, DER 325 (Dow Chemical) and a curing agent, triethylenetetramine (D.E.H. 24, Dow Chemical), were employed. Also, 75 wt% of tetrahydrofuran (THF, Dorwil Chemical) was added to reduce resin viscosity.

The respective amount of curing agent (D.E.H. 24) in the resin formulation was adjusted by Differential Scanning Calorimeter analysis (DSC) using a Shimadzu DSC-50 (nitrogen atmosphere and a heating rate of 10 °C/min from room temperature to 200 °C).

Commercial barium titanate, $BaTiO_3$ (TAM, Ceramics Inc.) was doped with 0.6 wt% of Nb_2O_5 to modify its dielectrical properties. Powders were mixed in isopropilic alcohol by agitation at 6000 rpm during 5 min. Afterwards, alcohol was eliminated by heating at 65 °C until constant weight. The powder was thermally treated at 1350 °C for 180 min using a heating and a cooling rate of 3 °C/min. The powder was milled using a planetary mill with ZrO_2 balls (Fritsch, Pulverisette 7) for 90 min, in isopropilic medium until an average particle size of 1.4 μm was obtained.

The ceramic powder was added to the epoxy resin mixture (epoxy + functionalized Ag + curing agent) at two different volume fractions (35–40 vol%) and then suitably blended using an ultrasonic mixer (Sonic vibra-cell 150 W) during 4 min. THF was introduced, after $BaTiO_3$ incorporation, to reduce the viscosity of the mixture.

Films were obtained using the dipping technique. First, a suspension containing $BaTiO_3$ powder, solvent (THF), epoxy and curing agent with nanosilver were prepared in a glass container. The suspension was placed on a glass substrate with gold electrodes previously deposited by dc-sputtering, using a dipping rate of 3 cm/min. The films were cured at 100 °C for 2 h. Top electrodes were deposited by dc-sputtering through a shadow mask.

Ag and $BaTiO_3$ weight fractions were determined by thermogravimetry (TGA, Shimadzu TGA-50) under nitrogen atmosphere with a heating rate of 10 °C/min from room temperature to 800 °C. Dispersion of $BaTiO_3$ particles into the composites was analyzed through Scanning Electron Microscopy (SEM, JEOL 6460LV). Thicknesses were measured employing a micrometer (Mitutoyo), subtracting the substrate thickness at to the substrate and film thickness.

Dielectric measurements were performed using a Hewlett Packard 4284A Impedance Analyser in the frequency range from 20 Hz to 1 MHz. Temperature was varied from room temperature to 120 °C.

Results and discussion

Transmission Electron Microscopy (TEM)

A representative TEM image of silver nanoparticles is shown in Fig. 1. Aggregates of particles with irregular size and not spherical shape can be seen. The agglomerate average size is around 150–170 nm (after five observations). An average particle size of 25 is observed. The agglomeration effect can be ascribed to the adsorption of a molecule of triethylenetetramine at different Ag nanoparticles simultaneously.

Thermal analysis

The concentration of curing agent was determined by analyzing the curing behavior by DSC (Table 1). To achieve a cost-effective processing, the reaction temperature (T_r) and glass transition temperature (T_g) should be similar to the ratio recommend by Dow Chemical for the resin without nanoparticles (12.5 phr%). Based on this criterion, the system with 17.5 phr% amine–Ag was similar

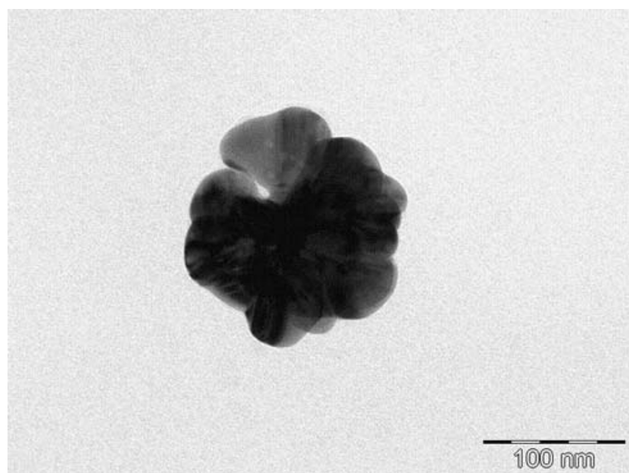

Fig. 1 TEM of silver nanoparticles

Table 1 List of epoxy formulations and the results of DSC analysis

Ratio (phr %)	T_g (°C)	T_r (°C)
Amine (optimum ratio)[a]		
12.5	94	100
Amine/Ag		
12.5	70	96
15.0	90	97
17.5	95	99
21.5	90	95

[a] Recommended by Dow Chemical

Table 2 Real $BaTiO_3$ volume fraction for composites and hybrids with two different ceramic filler concentrations

Ag (wt%)	Initial $BaTiO_3$ (vol%)	Real $BaTiO_3$[a] (vol%)
0	45	38
1	40	34
	45	39

[a] Determined through TGA

to the ratio recommended (12.5 phr%—without Ag). In addition, systems cured with lower or higher concentrations than 17.5% showed lower T_g and T_r temperatures due to differences in the cross linking density.

Finally, the real $BaTiO_3$ volume fractions, determined by TGA analysis for all the materials are shown in Table 2. It can be observed that the composites show similar accuracy in their preparation (around 1%).

Scanning Electron Microscopy (SEM)

Transversal areas of hybrid materials with different $BaTiO_3$ amount are shown in Fig. 2a and b. Both figures show areas without filler and some trails of micro-porosity. It can be clearly observed that the particle distribution is not homogeneous and some agglomeration of particles appears in both composites. On the other hand, the film thickness ranged from 90 to 100 μm with a scattering of 5%. The measurements were verified by SEM (figures not reported).

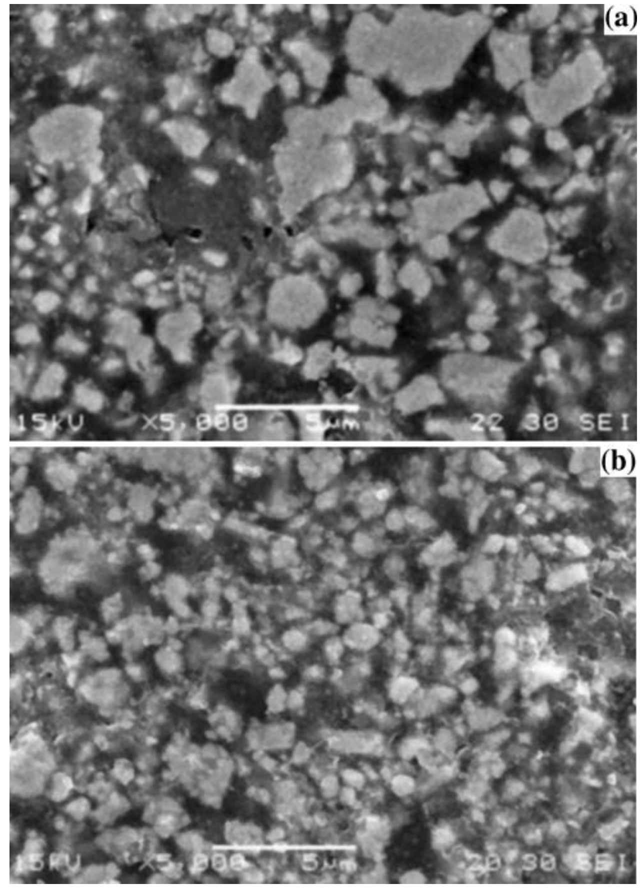

Fig. 2 SEM of composites with 34 (**a**) and 39 vol% (**b**) of $BaTiO_3$ and 1 wt% of Ag. Bar 5 μm

Dielectric properties

Real and imaginary permittivities of epoxy (with and without nanoparticles) as a function of frequencies (at 30 °C) are plotted in Fig. 3. It can be seen that real and imaginary permittivity are up to 15% higher than pure epoxy. It suggests that metallic particles (with higher area/volume ratio) increase the electric charge transference and behave as tiny capacitors disperse in the matrix.

Real (ε') and imaginary (ε'') permittivity values for composites and hybrid materials as a function of frequency and percentage of ceramic particles at 30 °C are plotted in Fig. 4a and b. It can be seen that real and imaginary parts of the permittivity are influenced by filler amount and frequency. In all samples, imaginary part of permittivity decreases with frequency due to dc conductivity effect. Systems containing nanosilver particles showed higher dielectric properties than $BaTiO_3$/epoxy composites. Permittivity as high as 65 at 1000 Hz is obtained by adding only 39 vol% of $BaTiO_3$ and 1 wt% of Ag. It represents a rise of 100% on the dielectric constant in contrast to the classic composite systems. In all cases, real and imaginary parts rise with the ceramic amount and decrease with the frequency. However, dielectric properties of hybrids are strongly influenced by frequency due to metal nanoparticles increase the dc conductivity because of rise electronic hopping transport [11].

Finally, Fig. 5 shows real and imaginary permittivity parts as a function of temperature. As it can be seen, in composites without nanoparticles, real and imaginary permittivities increase softly when temperature rises, due to the higher polymeric chains mobility. This segmental mobility corresponds to the α-relaxation associated to T_g and which appears around 90 °C [12]. These changes are stronger in systems prepared with nanoparticles, both real and imaginary permittivities increase abruptly around 90 °C.

Relaxation process

In order to study the frequency and temperature dependence over the relaxation processes, the electrical modulus (M′) was analyzed. Figure 6 shows the real and imaginary parts of the electrical modulus [13] as a function of frequency. As it can be seen, M′ values for $BaTiO_3$ composite

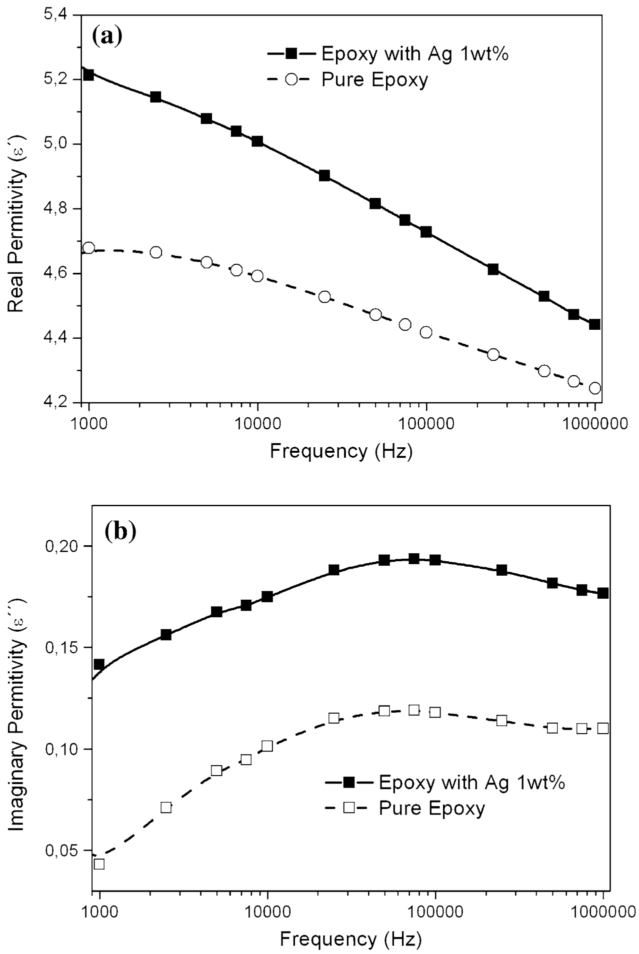

Fig. 3 Real (**a**) and imaginary (**b**) permittivity versus frequency of pure epoxy and epoxy with 1 wt% of nanoparticles (Temp. 30 °C)

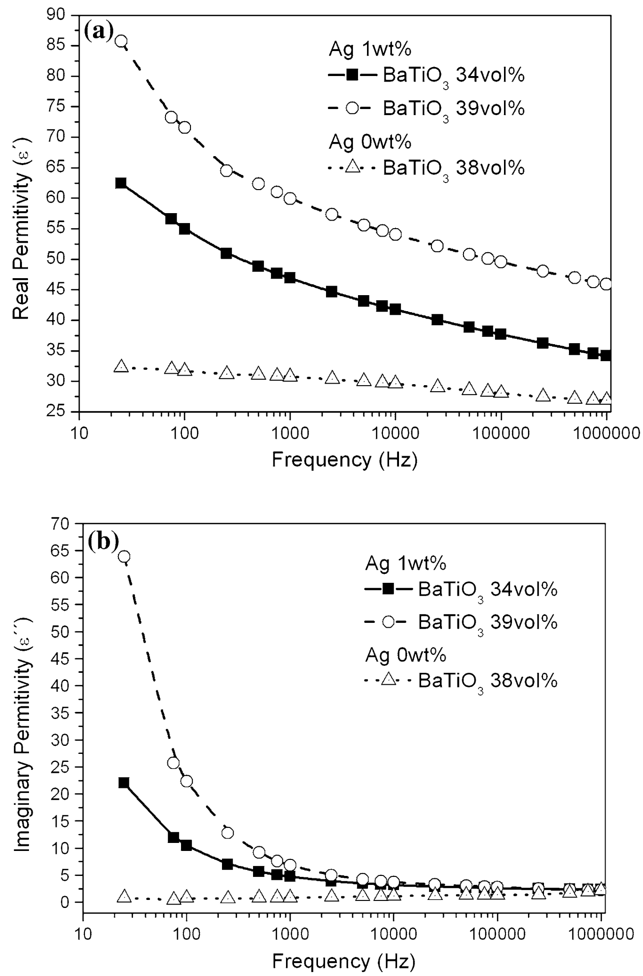

Fig. 4 Real (**a**) and imaginary (**b**) permittivity versus frequency and $BaTiO_3$ volume fraction (Temp. 30 °C)

increase quickly with frequency until they reach a less pronouncing slope. The temperature increment produces a diminution of M′ at low frequencies, although it has negligible effects at high frequencies. Moreover, a peak in M″ values at 120 °C is observed, indicating a relaxation process, which is not evident by analyzing the loss-tangent curve. This peak corresponds to α-relaxation and starts to be formed at high temperatures near epoxy T_g, as mobility of polymer molecules is enhanced [14].

In systems containing nanosilver particles, it can also be observed that M′ values increase with the frequency and tend to asymptotic values. However, this behavior cannot be completely verified in the frequency range analyzed. On the other hand, α-relaxation peaks on M″ spectra are observed at relaxation frequencies higher than those corresponding to $BaTiO_3$ composites. A decrease in the dipolar polarization in the composite matrix can be responsible for this behavior because of the higher amine ratio. Also, the interfacial polarization Maxwell–Wagner–Sillar (MWS) process due to the heterogeneity of the systems can take place [9]. In this process, the piling of charges at the interface causes large-scale field distortion or orientation of bound charge carriers, in contrast to the others types of polarizations (atomic, electronic, and dipolar) [13].

ac conductivity

From the ε'' values at different frequencies, the ac conductivity (σ_{ac}) data can be calculated according to the following equation:

$$\sigma_{ac} = \varepsilon'' \cdot \varepsilon_0 \cdot \omega \quad (1)$$

being $\varepsilon_0 = 8.85 \times 10^{-12}$ F/m and $\omega = 2 \cdot \pi f$.

The ac conductivity of the hybrid materials clearly depends on the temperature and frequency, increasing σ_{ac} as both rise (as showed in Fig. 7). At high frequencies, the dependence of the conductivity with the temperature can be neglected. Nevertheless, at low frequencies the relaxation processes are influenced by both the temperature and the dc

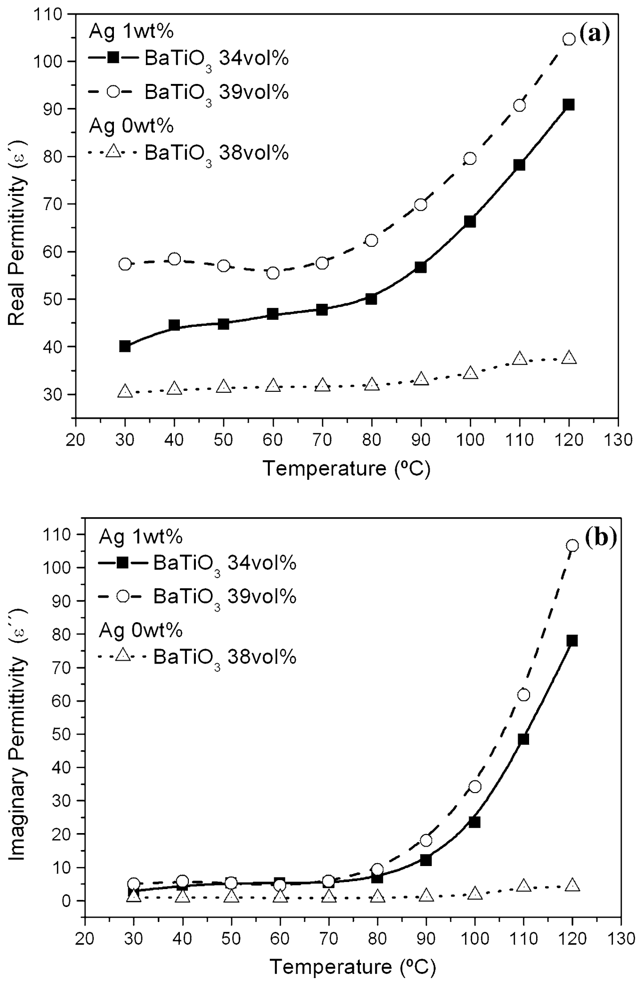

Fig. 5 Real (**a**) and imaginary (**b**) permittivity versus temperature and $BaTiO_3$ volume fraction (Freq. 2500 Hz)

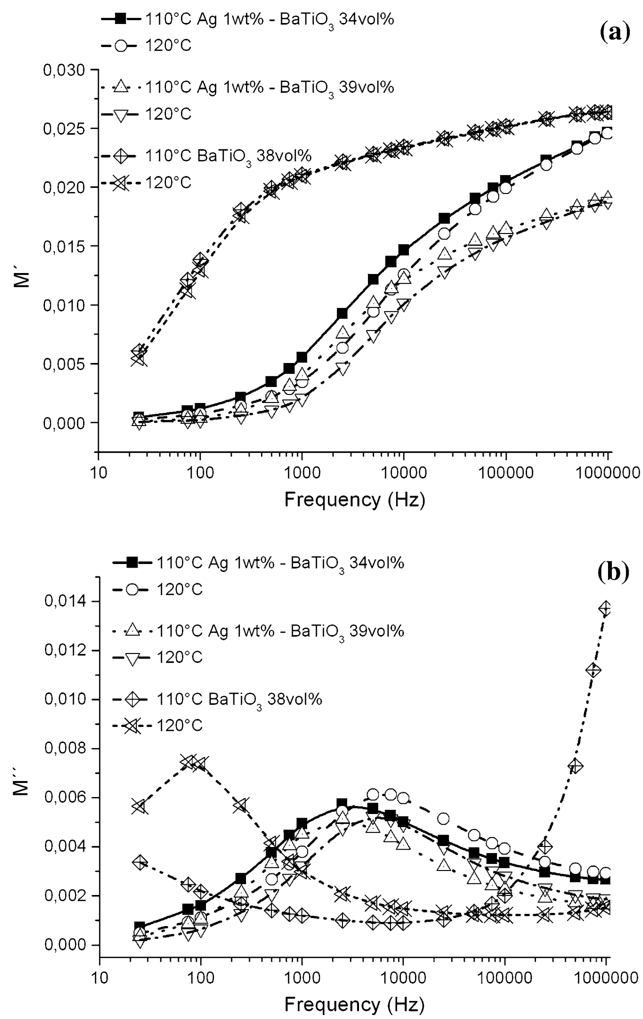

Fig. 6 Real part (M′) (**a**) and imaginary part (M″) (**b**) of electrical modulus versus frequency (at 120 °C)

conductivity. The relationship between σ_{ac} and the frequency can be expressed according to a power law $\sigma_{ac} \sim \omega^s$ $(0 \leq s \leq 1)$ [9]. In general, the conductivity is higher in hybrid samples, suggesting that metal helps to increase the electric charge transference at the interfaces.

Conclusions

Electric properties of epoxy/$BaTiO_3$/nano Ag hybrids materials obtained by dipping process have been investigated. The following conclusions were reached.

1- Lower concentration of silver nanoparticles can increase up to 15% the dielectric permittivity of pure epoxy resin due to electric charge transference between metal particles and resin.
2- Hybrids prepared using $BaTiO_3$ and silver nanoparticles have higher dielectric properties (up to 100%) than epoxy/$BaTiO_3$ composites. Also, these materials

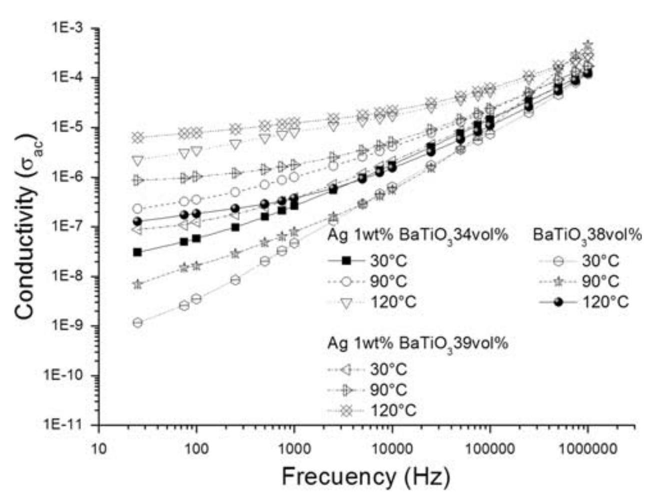

Fig. 7 The ac conductivity (σ_{ac}) versus frequency of composites at 30, 90 and 120 °C

were more affected by temperature and frequency than systems prepared without silver nanoparticles.

3- Dielectric relaxation phenomena were attributed to the resin. They were influenced by Ag nanoparticles and $BaTiO_3$ concentration because of MWS effects.

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