

DEVELOPMENT AND CHARACTERIZATION OF EPOXY RESIN/ SILICON CARBIDE COMPOSITE NANODIELECTRICS

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Abstract

Polymer matrix composite nanodielectrics represent a novel class of engineering materials which attract enhanced interest from the scientific community, since they combine the high dielectric strength of polymers and the high dielectric constant of the ceramic filler nanoparticles [1-4]. In the present study, three series with a total of seventeen specimens were manufactured varying the filler's concentration and size. The samples were characterized by means of Scanning Electron Microscopy, Broadband Dielectric Spectroscopy (0,1 Hz – 1 MHz and 30 °C – 200 °C range) and Dynamic Mechanical Analysis (1 Hz and 30 °C – 140 °C range). SEM pictures are provided, and properties such as dielectric permittivity, loss tangent and ac conductivity are measured via BDS. In addition, energy density and relative energy density for all samples was calculated, as well as the relaxations dynamics and the associated parameters. Finally, storage modulus and loss tangent are examined via DMA and information about the specimens' T_g is derived.

1. Introduction

Polymer matrix composite nanodielectric materials exhibit significant dielectric properties due to the combination of the high dielectric permittivity of the included phase and the high dielectric strength of the polymer matrix. The final products are materials exhibiting significant properties that represent a field of current research focus for scientists worldwide and are useful for a wide range of applications. In addition, the use of polymeric materials as matrices provides to this type of composites ease of molding, while at the same time keeps the overall cost of the manufactured material low [1].

In nanodielectric materials, inclusions have at least one of their dimensions smaller than 100 nanometers. The presence of nanoparticles dictates the dielectric and mechanical properties of the composites and in many cases enhances the properties of the matrix by a significant amount. The surface area of the nanoparticles, called the interface, is more extend than the corresponding in microparticles, and although is related to the enhanced properties of nanocomposites its properties remain largely unexplored to date [2, 3].

In this study, nanocomposites with epoxy resin acting as polymer matrix and nanoparticles of silicon carbide acting as reinforcing phase were manufactured varying the concentration of the filler content, and then characterized by various techniques. Scanning Electron Microscopy was conducted to study the morphology of the fabricated composites and examine the fine dispersion of nano inclusions. Dynamic Mechanical Analysis was used to study the mechanical properties of the composite materials, and specifically properties such as storage modulus, loss modulus and loss tangent. Lastly, Broadband Dielectric Spectroscopy was a huge part of this study, providing information about a large amount of the composites' properties including real and imaginary part of dielectric permittivity,

electric modulus, ac conductivity, $\tan\delta$, energy density and relaxation dynamics of the epoxy resin/silicon carbide composites.

2. Experimental

During the manufacturing process commercially available materials were used, including the Ren Lam LY 5138-2 type resin and the Ren HY 5138 type hardener from Huntsman Corporation and silicon carbide nanopowder with different particles' size, purchased from Plasma Chem Corporation. According to the supplier's data sheet the particles' size was 20 ± 7 nm, 25-50 nm, and finally 150-200 nm.

A set of 17 specimens were manufactured, specifically 1-2-4-8 phr (parts per hundred resin per weight) for the particle size of 20 ± 7 nm, 1-2-4-8-10-12 phr for the particle size of 25-50 nm, 1-2-4-8-12-16 phr for the particle size of 150-200 nm and lastly a pure epoxy resin sample. The actual process included slow stirring of the resin and the hardener until the mixture became homogeneous, followed by the addition of the correct amount of nanoparticles for each specific sample, which was then stirred inside an ultrasonicator to avoid the formation of agglomerates within the polymer matrix as well as pockets of air. Agglomerations and trapped air are both defects, affecting the properties of the produced materials. Afterwards, the mixture was poured into molds where it remained for 7 days for the curing process. Finally, a post curing process which included heating at 120° C for 4 hours took place.

Morphology and proper nanoparticle dispersion was examined via Scanning Electron Microscopy (SEM), by means of a Carl Zeiss EVO MA 10 apparatus.

The dielectric response of the specimens was tested via Broadband Dielectric Spectroscopy (BDS), using the Alpha-N analyzer and a BDS 1200 dielectric cell. Experiments were conducted in the range of 30° C to 200° C for temperature and 1 MHz to 0,1 Hz for frequency. Data acquisition was handled by the WinDeta software. Dielectric setup was purchased from Novocontrol.

The mechanical properties of the nanocomposites were studied with Dynamic Mechanical Analysis (DMA) and specifically with the 3-point bending clamps, using a Q800 DMA of TA Corporation device. The frequency in which the tests were conducted was 1 Hz, and the temperature ranged from 30 °C to 140 °C.

3. Results and Discussion

Scanning electron microscopy proved the high quality of the manufactured specimens. As shown in Fig. 1, the dispersion of nanoparticles within the polymer matrix is fine, and the formation of agglomerates has been avoided. The density of the SiC granules in specimens with higher filler concentration is increased, as expected, although the dispersion remains adequate.

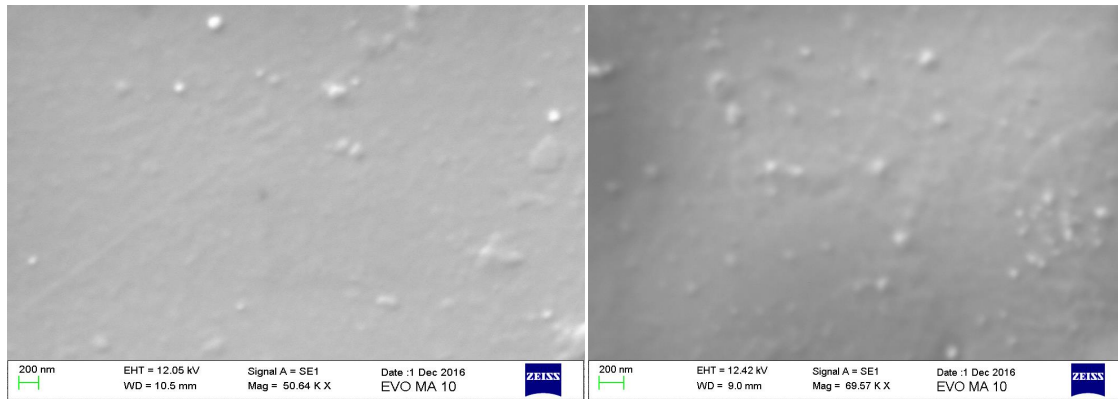


Figure 1. SEM pictures for the 1 phr SiC specimen with 20 nm particle size (left) and the 8 phr SiC specimen with 25-50 nm particle size (right).

In Fig. 2 (left), a 3-D plot of the loss tangent as a function of temperature and frequency for the 4 phr specimen can be observed. Three relaxation mechanisms become evident in it, namely interfacial polarization, α -relaxation and β -relaxation. Interfacial polarization, also known as Maxwell- Wagner-Sillars phenomenon, is attributed to the concentration of charges on the interface between the matrix and the inclusions, and can be observed in the low frequency range (10^{-1} - 10^1 Hz). Next, at medium (10^2 - 10^4 Hz) frequencies, α -relaxation can be observed, which is caused by the glass to rubber transition of the polymer matrix. The last relaxation which can be observed at high frequencies (10^4 - 10^6 Hz) is called β -relaxation and is caused by the reorientation of polar side groups of the main polymeric chain [4].

The next plot (Fig. 2 right) depicts ac conductivity as a function of frequency for the 4 phr specimen. Two distinct regions are detected, at low frequencies, conductivity values tend to reach a constant value, which increases with temperature, while at high frequencies a rapid increase of conductivity can be observed. The latter is attributed to charge carriers moving between adjacent conducting points, without covering large distances. The recorded behaviour, indicates that hopping conductivity mechanism [5] is present in the examined specimens. This behaviour common in disordered solids, such as the materials used in this project, can be described via the ac universality law [6].

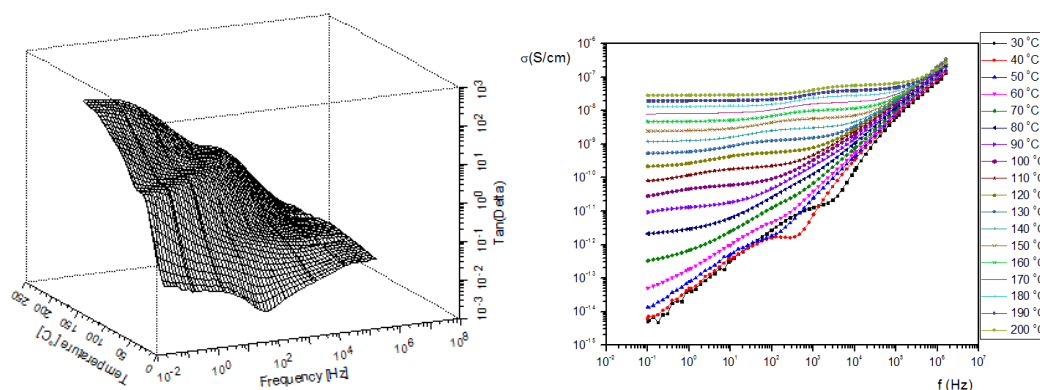


Figure 2. Loss tangent as a function of temperature and frequency for the 4 phr specimen with 25-50 nm particle size (left) and ac conductivity as a function of frequency for the 4 phr specimen with 25-50 nm particle size (right).

Fig. 3 (left) depicts the real part of dielectric permittivity, as a function of frequency at 30^o C, for all specimens with 25-50 nm particle size. The filler's contribution to the permittivity increase is evident,

since the composite specimens exhibit higher permittivity values in comparison to the epoxy sample. Moreover, permittivity values increase further at higher temperatures and lower frequencies (not shown in the graphs). This is due to the fact that dipoles have enhanced time to be polarized according to the rotation of the electric field at lower frequencies, and acquire more energy to follow the rotation of the field at higher temperatures.

Two distinct relaxation mechanisms are depicted in the relative energy plots, Figure 3 (right). The first one, at low frequency range, is associated with the interfacial polarization mechanism, while the relaxation at medium frequencies is attributed to the glass to rubber transition of the polymer matrix. Furthermore, the nanocomposites are able to store more energy compared to the neat polymer matrix specimen, with the highest concentration specimen reaching the value of 5 more [7].

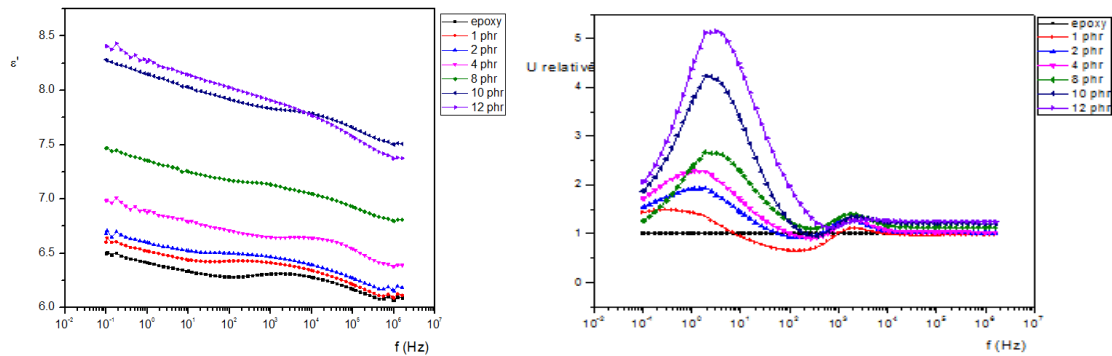


Figure 3. Real part of dielectric permittivity as a function of frequency at 30° C for all specimens with 25-50 nm particle size (left) and $U_{relative}$ as a function of frequency at 200 °C for all specimens with 25-50 nm particle size (right).

Figure 4 shows the Arrhenius plot, for all specimens with 20 nm particle size. The interfacial polarization follows Eq. (1), while α -relaxation follows Eq. (2).

$$f_{max} = f_0 \exp(-E_A/k_B T) \quad (1)$$

$$f_{max} = f_0 \exp(-B/(T_V - T)) \quad (2)$$

where f_0 , E_A , k_B , B , T_V are a pre-exponential factor, the activation energy of the relaxation mechanism, the Boltzmann constant, a parameter of the activation energy of the system and the ideal glass transition temperature (Vogel temperature) respectively.

Data deduced from the dynamic analysis indicate that activation energy decreases at low filler content, facilitating thus the Maxwell-Wagner-Sillars phenomenon, while at medium filler concentrations requires more energy to be activated. The α -relaxation analysis indicates a significant decrease in Vogel temperature for the 1 phr specimen, while the rest of the examined ones show a smaller decrease compared to the epoxy sample. Variation of relaxation dynamics with filler content reflects the dominant type of interactions, i.e. between particle-particle or macromolecule-particle [8].

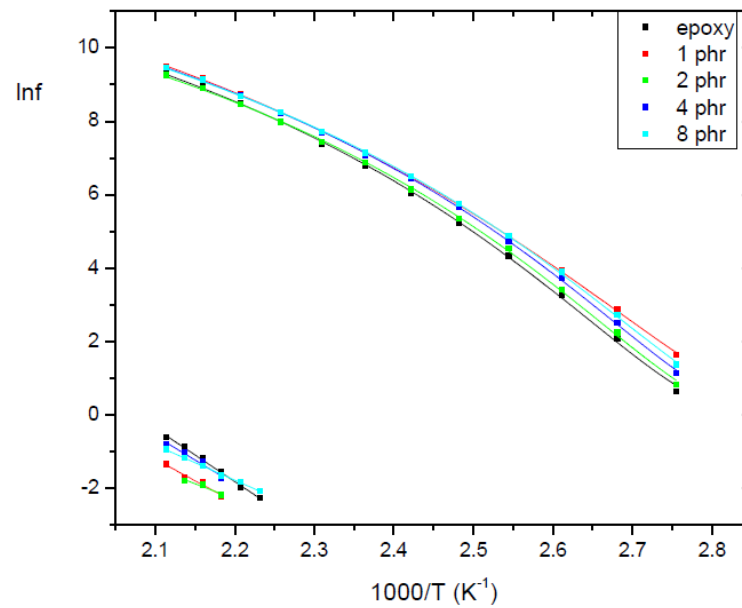


Figure 4. Loss peak position as a function of reciprocal temperature for all specimens with 20 nm particle size.

Table 1. Activation energy and parameters derived via studying the relaxation mechanisms for all specimens with 20 nm particle size.

Specimens	MWS	α - relaxation	α - relaxation
	E_a (eV)	T_v (K)	B (K)
Epoxy	1.25	340.06	29.44
1 phr	1.01	328.54	33.85
2 phr	0.72	339.67	28.03
4 phr	1.13	336.99	28.62
8 phr	0.82	334.70	29.01

Fig. 5 (left) depicts loss tangent as a function of temperature at 1 Hz for all samples with 25-50 nm particle size. The peak corresponds to the glass to rubber transition temperature of each specimen, and its shift to lower temperatures is an indicator for the transition's facilitation. On the contrary, shifting of the peak at higher temperatures indicates transition's obstruction and strong interactions between macromolecules and filler's particles.

Storage modulus is clearly increased with the addition of silicon carbide nanoparticles, as shown in Fig. 5 (right). Specifically, the neat epoxy resin sample reaches the max value of 4 GPa, while the 10 phr sample shows an increase of approximately 1,5 GPa. Near the glass to rubber transition, the samples' ability to bear mechanical load is significantly reduced and thus the storage modulus values decrease rapidly.

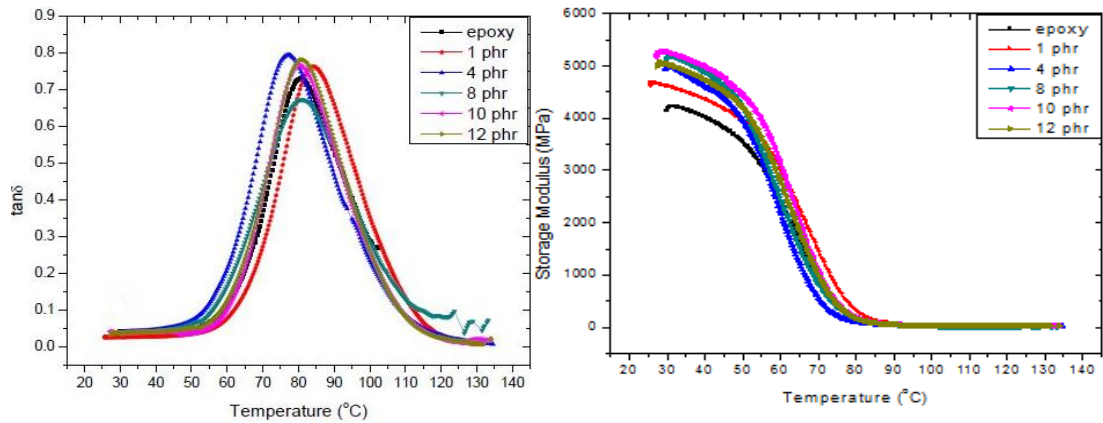


Figure 5. Loss tangent at 1 Hz as a function of temperature for all specimens with 25-50 nm particle size (left) and storage modulus at 1 Hz as a function of temperature for all specimens with 25-50 nm particle size (right).

4. Conclusion

In the present study nanocomposites with epoxy resin as matrix and silicon carbide as reinforcing phase were manufactured, and tested via Scanning Electron Microscopy, Broadband Dielectric Spectroscopy and Dynamic Mechanical Analysis. All specimens had adequate nanoparticle dispersion, as proved via SEM. The nanoparticles enhance the properties of the matrix, as shown by both BDS and DMA characterization techniques, in permittivity values and subsequently U_{relative} values, as well as storage modulus values. Three relaxation mechanisms were observed, namely interfacial polarization (which is attributed to a high concentration of charges on the interface between the matrix and the inclusions, observed around 10^{-1} - 10^1 Hz), α -relaxation (caused by the glass to rubber transition of the polymer matrix, observed at about 10^2 - 10^4 Hz) and β -relaxation (caused by reorientation of polar side groups of the main polymeric chain, seen at approximately 10^4 - 10^6 Hz). The dynamics of the relaxation processes were also examined, and information about activation energies and Vogel temperatures were deduced.

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