DIELECTRIC, THERMOMECHANICAL AND FUNCTIONAL BEHAVIOR OF EPOXY RESIN-BARIUM TITANATE AND/OR GRAPHITE NANOPLATELES NANOCOMPOSITES

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Abstract
Ceramic barium titanate nanoparticles and different forms of carbon are used as epoxy reinforcements, resulting in composites with improved dielectric and thermo-mechanical properties. The carbon fillers used are carbon black, vapor grown carbon fibers and exfoliated graphite nanoplatelets. Electrical characterization of the composites was conducted by means of broadband dielectric spectroscopy, while viscoelastic properties were determined using a dynamic mechanical analyzer and the morphology was investigated by means of scanning electron microscopy. Composite systems exhibit relaxations arising from both the polymer and the reinforcing phases. The incorporation of exfoliated graphite nanoplatelets appears to be beneficial to both dielectric and mechanical performance. Finally, the energy storing efficiency of the composites is examined as a function of the temperature, the frequency of the field, the type and the amount of the employed filler.

1 Introduction

Polymer matrix nanocomposites receive increased attention, mostly, due to their enhanced mechanical and electrical performance [1,2]. Incorporating ferroelectric or piezoelectric nanoparticles within a polymer matrix results in the formation of novel engineering materials, because in addition to enhancing their electrical and mechanical properties it provides functionality. Ferroelectric materials undergo a "disorder-to-order" transition at a critical characteristic temperature, known as Curie temperature (T_C) [3]. Below the critical temperature, ferroelectrics exhibit spontaneous polarization in the absence of electric field, because of their low symmetry level. Above T_C, at the paraelectric phase, ferroelectrics' structure is characterized by high symmetry level and no spontaneous polarization occurs. This externally controlled phase transition can be exploited in polymer matrix/ferroelectric particles composites in order to add functionality to the systems. Further, the distribution of semiconducting and/or conductive nanoinclusions within the polymer matrix produces a network of nanocapacitors. The embedded nanocapacitors could act as energy storing devices, introducing a new type of nanodevices.

In this study micro- or nano-BaTiO$_3$/epoxy composites, as well as carbon/epoxy composites were prepared and tested, varying the amount and the type of the filler. Dielectric response, mechanical properties and viscoelastic behaviour of BaTiO$_3$/epoxy composites are compared to the corresponding performance of carbon reinforced epoxy systems. The carbon fillers used are carbon black (CB), vapor grown carbon fibers (VGCF) and exfoliated graphite nanoplatelets (xGnP). Controlling the type and amount of inclusions is expected to address the engineering demands for suitable dielectric and mechanical properties for various applications.

2 Materials and testing methods

2.1 Materials

The polymers used in this research is a low viscosity epoxy resin with the trade name Araldite LY 564 and curing agent Aradur-HY2954 provided by Huntsman Advanced Materials. In addition two types of reinforcements were used ceramic BaTiO$_3$ and carbon fillers. BaTiO$_3$ was in the form of powder varying the mean particle diameter, in order to study the effect of the filler size on the dielectric properties of the BaTiO$_3$ composites. The first one has mean particle diameter less than 2 μm and the second one has mean particle diameter in the range of 30-50 nm. Both powders were supplied by Sigma Aldrich. The carbon fillers used are: i) nano-size high structure carbon black (CB) with mean particle diameter in the range of 40-50 nm (KETJENBLACK EC-600 JD), provided by Akzo Novel Polymer Chemicals LLC, ii) vapor grown carbon fibers (VGCF) with mean particle diameter less than 150 nm (Pyrograf III, PR-19 PS grade), supplied by Pyrograf Products, Inc., and iii) exfoliated graphite nanoplatelets (xGnP-1) with mean particle diameter less than 1 μm and an average thickness of 10-20 nm supplied by XG Sciences (East Lansing, MI).

2.2 Fabrication of composites

The solution method was used to fabricate the composites. Nano-filler inclusions (ceramic or carbon) were mixed for 30 minutes at ambient temperature with isopropyl alcohol (IPA) using a sonication probe (1/2" probe size, 40% amplitude for 40 min, Misonix 4000) in order to break down the filler agglomerates. The powder was collected after filtering the IPA and mixed with the epoxy at 800 rpm and T=60 ^{o}C for 1 hour using a magnetic stirring plate. The curing agent was then added to the filler/monomer solution and mixing at 800 rpm and ambient temperature continued for 30 min. The mixture was degassed in a vacuum oven, casted in a mold and cured at T=80 ^{o}C for 1 hour followed by post curing at T=100 ^{o}C for 4 hours.

2.3 Testing methods

The electrical characterization of the composites was conducted by means of Broadband Dielectric Spectroscopy (BDS) in the frequency range of 0.1 Hz to 10MHz, using Alpha-N Frequency Response Analyser and a 1200 BDS dielectric cell provided by Novocontrol. Isothermal frequency scans were conducted, for each specimen, from ambient temperature to 160 ^{o}C with a step of 5 ^{o}C. Novotherm system supplied by Novocontrol was used to control the temperature. The viscoelastic properties, including storage and loss modulus and tan delta, of the composites were determined using a Dynamic Mechanical Analyzer (DMA, Q800, TA Instruments). The specimens were characterized using single-cantilever mode as a function of temperature (30 to 160 ^{o}C, heating rate 5 ^{o}C/min). A constant force of 100 mN was applied at frequency of 1 Hz. Finally the composites morphology was investigated using scanning electron microscopy (SEM, Zeiss Ultra 60) for presence of voids and agglomerates, and the state of filler dispersion within the polymer matrix. Flexural properties, strength and modulus, were measured according to the ASTM D790 standard.

3. Results and discussion

Barium titanate is a technologically important ferroelectric material, especially in the electroceramics industry. $BaTiO_3$ undergoes structural change at T_C (~130°C) by switching its lattice from the polar tetragonal phase to the non-polar cubic phase. The former is known as ferroelectric phase, while the latter is called paraelectric phase. The thermally induced change from the low symmetry-polar structure to the high symmetry-non polar structure, provides to $BaTiO_3$ functional behaviour, and thus is also characterized as active dielectric. Transition between ferroelectric to paraelectric phase can be detected via X-ray diffraction (XRD) spectra. Functional behaviour of polymer matrix barium titanate composites is based on this transition. Figure 1 depicts XRD spectra from micro- and nano-sized $BaTiO_3$ particles at temperatures below and above the T_C. A significant change is apparent in the spectra of the micro-particles, below and above T_C, reflecting clearly the transition from tetragonal to cubic lattice [4,5,6]. On the other hand in the spectra of nano-particles, at the same temperatures, ferroelectric to paraelectric transition is only partially present [4,5,7]. It is still an open issue in the literature, if nano-sized $BaTiO_3$ crystallizes in cubic, tetragonal, or both lattices below T_C. Data presented in this study support the co-existence of both phases, and thus the extent of transition is much limited compared to the one of micro-sized $BaTiO_3$.
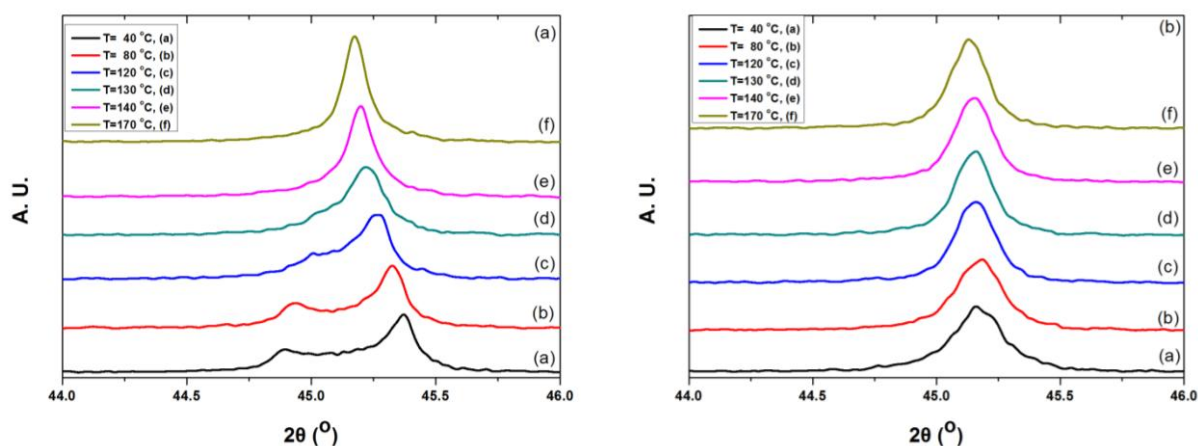

Figure 1. XRD spectra of (a) micro and (b) nano-$BaTiO_3$ particles at various temperatures.
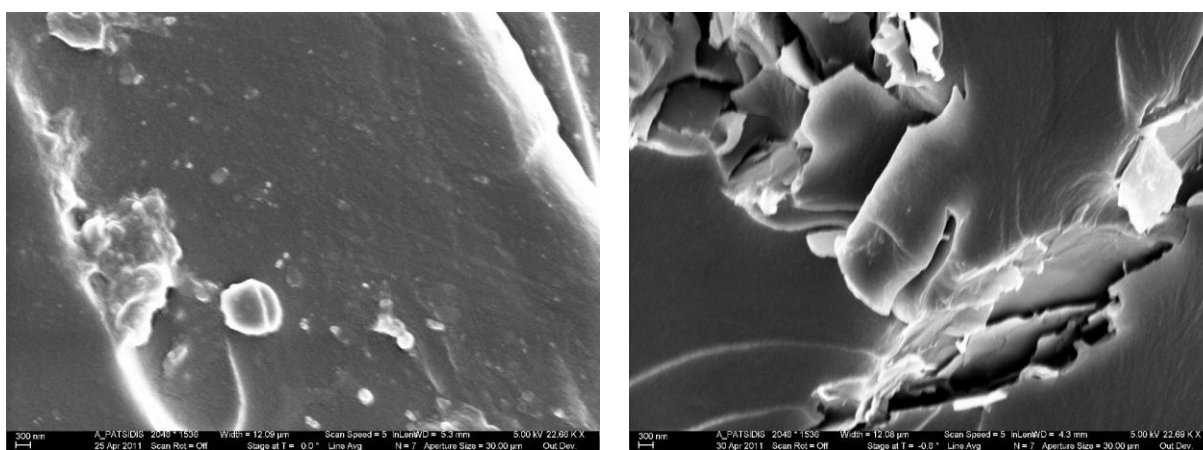

Figure 2. SEM images from the specimens with (a) 5phr nano-$BaTiO_3$ particles and (b) 5phr xGnP.

The specimens' morphology is illustrated in Figure 2. SEM images reveal that $BaTiO_3$ particles and xGnP inclusions are homogeneously distributed within the polymer matrix, although, nanodispersions co-exist with agglomerates.

Dielectric permittivity as a function of frequency and filler content, at two temperatures, is shown in Figure 3. Permittivity decreases with frequency reflecting the reduction of the achieved polarization, since permanent and induced dipoles fail to follow the alternation of the field as the frequency becomes higher. Moreover, permittivity increases in general with filler content. This is more evident in the case of xGnP, because of their high conductivity. Increased heterogeneity in xGnP/epoxy systems gives rise to Interfacial Polarization (IP). IP should play a crucial role in their electrical response, contributing to permittivity values. On the other side BaTiO$_3$ is a wide band semiconductor, with low conductivity. Although, its permittivity value is much higher than the one of the polymer matrix, the electrical heterogeneity of the BaTiO$_3$/epoxy systems is moderate and the resulting IP not pronounced.
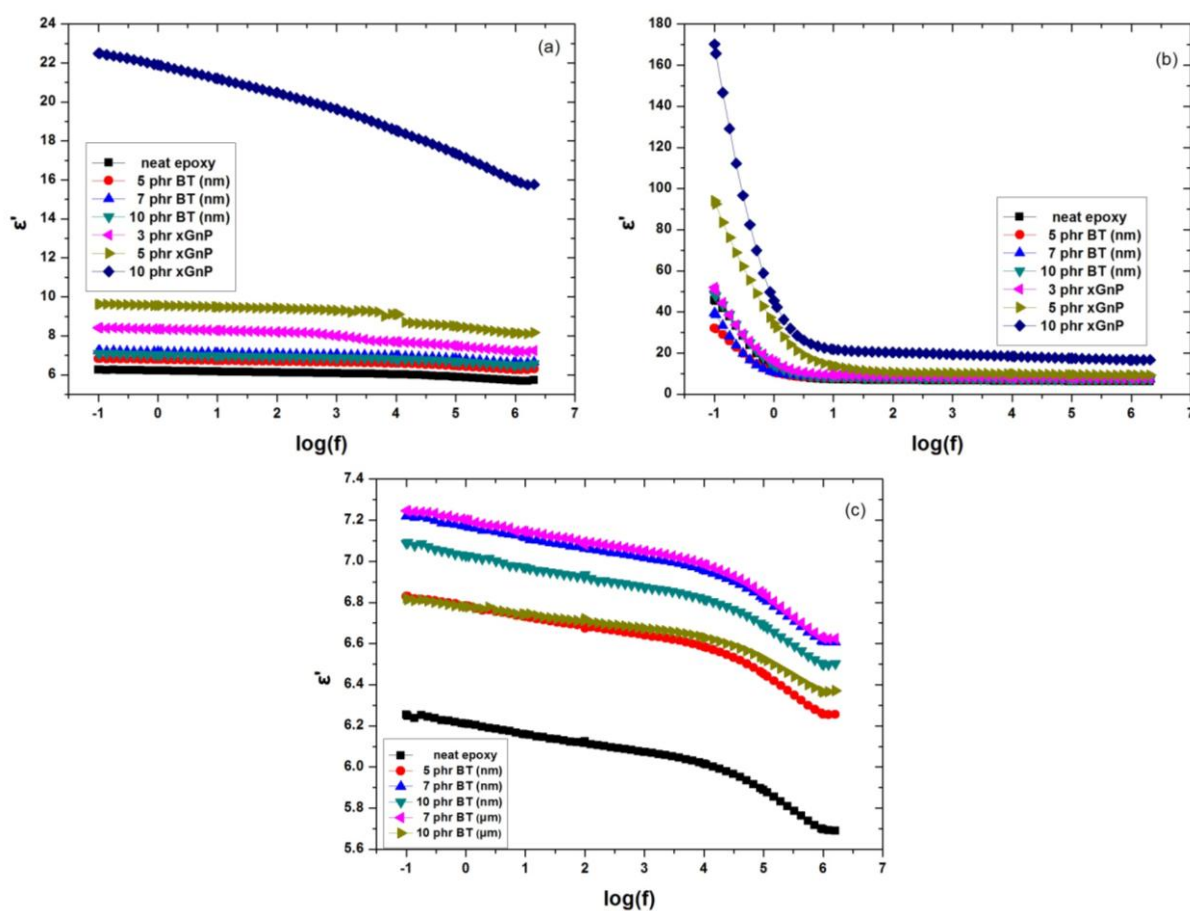

Figure 3. Variation of the real part of dielectric permittivity for the BaTiO$_3$/epoxy and xGnP/epoxy nanocomposites (a) at 40°C, (b) at 160°C, and (c) for the BaTiO$_3$/ epoxy systems at 40°C.

IP appears in heterogeneous systems via the accumulation of unbounded charges at the interfaces of the systems' components, where they form large dipoles. Induced dipoles are rather large compared to other kind of induced or permanent dipoles and thus are characterized by increased inertia in responding to the applied field. IP is a slow relaxation process, occurring in the low frequency range and at high temperatures, resulting in enhanced permittivity values. In the case of the xGnP/epoxy composites there is a systematic increase of (ε') with filler content. In Figure 3a the effect of BaTiO$_3$ size on the real part of the dielectric permittivity is depicted. For the same filler content and at the same temperature the micro-composites exhibit higher permittivity than the nano-composites, indicating a higher level of polarization. The latter most probably is related to the higher polar nature (pure tetragonal

lattice) of the micro-particles. As already mentioned, ferroelectric materials undergo a "disorder to order" transition at the critical characteristic temperature (T_C). Below that temperature, ferroelectrics exhibit spontaneous polarization in the absence of electric field, because of their low symmetry level. Above T_C, at the paraelectric phase, ferroelectrics' structure is characterized by high symmetry level and no spontaneous polarization occurs.
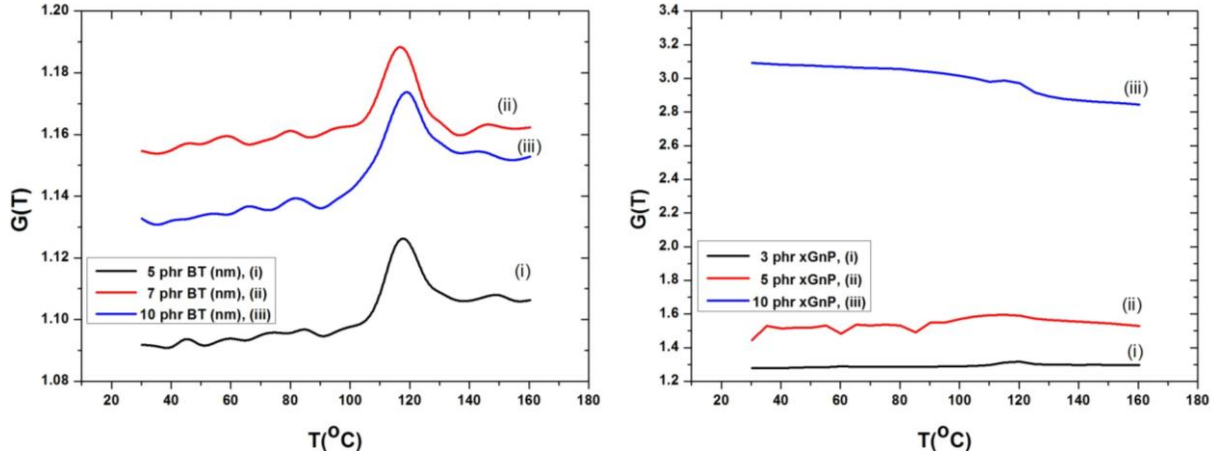

Figure 4. DRF versus temperature for the (a) BaTiO$_3$/epoxy and (b) xGnP/epoxy nanocomposites at 100Hz.
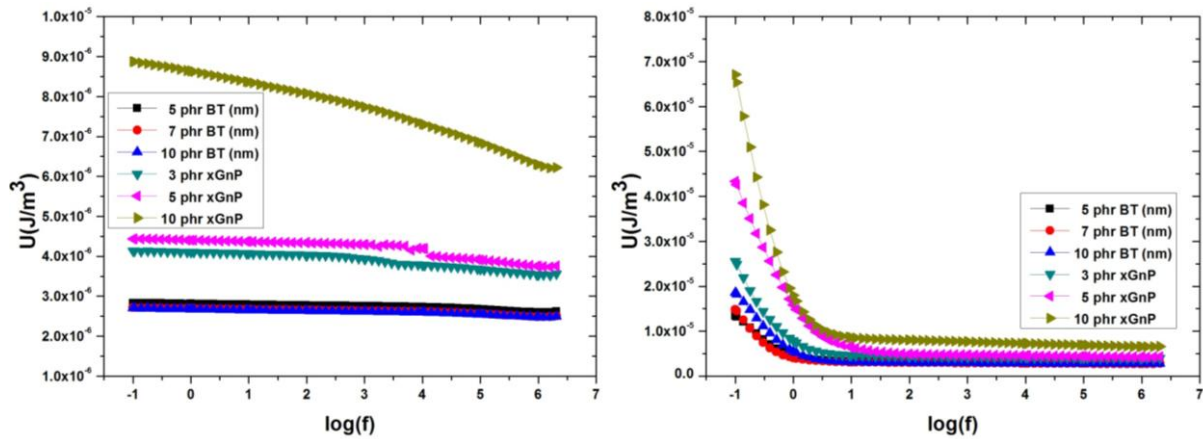

Figure 5. Energy density versus frequency, for the BaTiO$_3$ and xGnP nanocomposites, at (a) 40°C, and (b) 160°C.

Composites functional behavior can be examined by means of Dielectric Reinforcing Function (DRF). DRF removes the influence of geometrical characteristics upon the produced polarization and relates functional behavior with materials properties. DRF is defined as follows [8]:

$$G(\omega,T) = \frac{\varepsilon'_{comp}(\omega,T)}{\varepsilon'_{mat}(\omega,T)} \qquad (1)$$

where $\varepsilon'_{comp}(\omega,T)$ and $\varepsilon'_{mat}(\omega,T)$ are the real part of dielectric permittivity of the composite and the matrix respectively, while ω is the angular frequency of the field and T the sample's temperature.

DRF reflects the dielectric strengthening by being the measure of the normalized polarization. Further, DRF express the level of the energy storing efficiency [8]. Figure 4a and b presents the variation of DRF with temperature at constant frequency $f = 100Hz$ for the BaTiO$_3$ and xGnP reinforced nanocomposites, respectively. The xGnP/epoxy systems attain much higher values than the systems with BaTiO$_3$. This difference denotes the variation in the energy storing efficiency of the systems. DRF curves of the BaTiO$_3$/epoxy systems, exhibit peaks and "humps", which can be assigned to relaxation processes. In the low frequency region and at temperatures higher than 100°C, three dynamic polarization mechanisms are present. Glass to rubber transition, recorded in the vicinity of the glass transition temperature of the polymer matrix (*Tg*) is the first one. *Tg* of the polymer matrix found to be close to 130°C. The formed peaks in Figure 4a, which lie close to 130°C, are attributed to α-relaxation process. The second mechanism is IP, which is an even slower process occurring at high temperatures and low frequencies. Finally, the third dynamic polarization mechanism reflects the structural transition of the BaTiO$_3$ particles from the ferroelectric to the paraelectric phase at *Tc*. The "hump" next to the peak, in the spectra of *G*(*T*) in Figure 4a, is attributed to ferroelectric to paraelectric transition of BaTiO$_3$, while the weak peak at higher temperatures to IP. The DRF spectra of xGnP/epoxy samples, Figure 4b, attain rather constant values, and only close to glass transition temperature some variations are notable. The energy storing efficiency of the examined systems can also be expressed via the energy density function, depicted in Figure 5. The enhanced ability of the xGnP/epoxy systems is obvious, and should be related with their high conductivity.

The thermomechanical behavior of the composites, in terms of transition temperatures and relaxation mechanisms has also been examined, in order to understand any synergy between the thermal relaxations of the matrix and the dielectric relaxations of caused by the reinforcements. The viscoelastic properties of the BaTiO$_3$ nano-composites were studied and compared with the properties of the composites incorporating carbon fillers, in order to investigate the effect of the filler size, concentration and geometry. The variation of storage modulus as a function of temperature for carbon and barium titanate epoxy reinforced systems, at constant loading 3phr, is given in Figure 6. Nanocomposites exhibit higher values of storage modulus than neat epoxy from ambient temperature up to 100°C. Adding VGCF or CB gives composites with increased storage modulus in comparison to BaTiO$_3$/epoxy system, at ambient. However, this difference is reversed, in favor of BaTiO$_3$, above 50°C. System incorporating xGnP demonstrates the highest storage modulus from all the examined composites up to 110°C. High stiffness of xGnP and their homogeneous distribution within the polymer matrix can be the reason for this behaviour. At temperatures above 120°C, storage modulus of all composites becomes lower than that of pure epoxy signifying that energy is dissipated faster in the composite. Glass transition temperature (*Tg*), defined as the temperature corresponding to the tan delta peak, of BaTiO$_3$ (nm) and carbon reinforced epoxy composites at 3 phr content are presented in Table 1. The *Tg* values and the corresponding standard deviation are reported. It should be noted that CB significantly increases *Tg* of the epoxy while xGnP reduces it. The variation of glass transition temperature with the filler type could be related to strong or weak interactions between filler's surface and polymer chains [9].
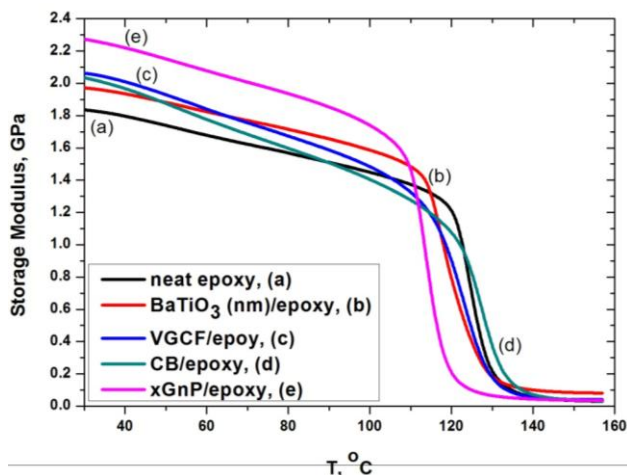
Figure 6. Storage modulus of nanocomposites at 3 phr filler content as a function of temperature.

Composites	Tg (^{o}C)
Epoxy	132.0 ± 0.3
BaTiO$_3$ (nm)	132.0 ± 0.2
VGCF	133.0 ± 0.1
CB	137.0 ± 0.6
xGnP-1	125.0 ± 2.0

Table 1. Glass transition temperature, *Tg* of BaTiO$_3$ and carbon reinforced epoxy composites at 3phr filler content.

	Flexural strength (MPa)			
phr	(nm) BaTiO$_3$	(μm) BaTiO$_3$	xGnP	CB
0	99.0 ± 2.0	99.0 ± 2.0	99.0 ± 2.0	99.0 ± 2.0
3	51.0 ± 2.0		57.7 ± 0.9	92.0 ± 2.0
5	45.0 ± 2.0		51.0 ± 1.0	*
7	35.0 ± 0.8	65.0 ± 2.0	47.0 ± 1.0	*
10	32.0 ± 0.7	41.0 ± 1.0	45.3 ± 0.7	*

Table 2. Flexural strength, of BaTiO$_3$ and carbon reinforced epoxy composites in MPa.

	Flexural modulus (GPa)			
phr	(nm) BaTiO$_3$	(μm) BaTiO$_3$	xGnP	CB
0	1.60 ± 0.06	1.60 ± 0.06	1.60 ± 0.06	1.60 ± 0.06
3	2.20 ± 0.08		2.20 ± 0.02	2.30 ± 0.03
5	2.20 ± 0.03		2.50 ± 0.09	*
7	2.40 ± 0.03	2.20 ± 0.02	2.50 ± 0.05	*
10	2.50 ± 0.08	2.70 ± 0.06	$2.6 0\pm 0.01$	*

Table 3. Flexural modulus, of BaTiO$_3$ and carbon reinforced epoxy composites in GPa.

The mechanical performance of composites, in particular flexural strength and flexural modulus are listed in Tables 2 and 3. Flexural strength decreases with increasing the concentration of the inclusions [10]. The composite with the highest value of the flexural strength is the 3 phr CB, followed by the 7 phr (μm) BaTiO$_3$ and the 3 phr xGnP. Note that it was not possible to prepare composite samples with higher concentration of CB inclusions. The size and weight of the inclusions in those cases led to very high solution viscosity of the mixture, so it was impossible to cast it in the mold without the presence of air bubbles and defects. Further, higher values of flexural modulus by increasing the amount of inclusions are

observed. The composite system with the highest flexural modulus is the 10 phr (μm) $BaTiO_3$ followed by the 10 phr xGnP respectively.

Conclusions

The dielectric response of $BaTiO_3$/epoxy micro- and nano-composites, as well as of xGnP/epoxy nanocompsoitesc was studied in this work. It was found that dielectric permittivity increases with filler content and diminishes rapidly with frequency. It was also observed that the dielectric permittivity increases with temperature. Functional performance of $BaTiO_3$/epoxy systems is related to the ferroelectric to paraelectric transition of the employed ceramic inclusions, which occurs at T_C close to 130^oC. Comparison of $BaTiO_3$ –to xGnP-/epoxy composites showed that the presence of xGnP increases further the dielectric permittivity, enhances the energy storing ability of the systems, and improves the mechanical properties of the systems.

Acknowledgements

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