Dielectric response, functionality and energy storage in epoxy nanocomposites: Barium titanate vs exfoliated graphite nanoplatelets

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HIGHLIGHTS

► Relaxation phenomena were found to be present in all studied systems.
► Two processes emanate from the polymer matrix (α-mode and β-mode).
► Systems' electrical heterogeneity gives rise to interfacial polarization.
► BaTiO$_3$/epoxy composites exhibit functional behavior due to structural changes.
► xGnP/epoxy composites exhibit increased energy storing efficiency.

GRAPHICAL ABSTRACT
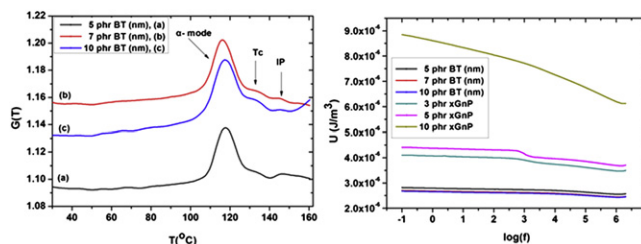
ABSTRACT

Barium titanate/epoxy and exfoliated graphite nanoplatelets/epoxy nanocomposites were prepared and studied varying the filler content. Morphological characteristics were examined via scanning electron microscopy, while structural changes occurring in barium titanate as a function of temperature were investigated by means of X-ray diffraction. Broadband dielectric spectroscopy was employed for determining the dielectric response of the prepared systems. Based on the conducted analysis it was found that three relaxation processes are present in the spectra of the examined materials. From the slower to the faster one, these are interfacial polarization, glass to rubber transition of the polymer matrix, and rearrangement of polar side groups of the polymer chain. Systems' functionality and energy storing efficiency were assessed in terms of dielectric reinforcing function. Finally, the energy density of all systems was evaluated. Composite systems with embedded graphite nanoplatelets exhibit higher energy storing efficiency, while thermally induced structural changes in ferroelectric particles provide functional behavior to barium titanate composites.

1. Introduction

Polymer matrix nanoreinforced composites attract significant scientific and technological attention because of both the versatility of improved properties and their current or potential applications [1–10]. Nanodispersions within a polymer matrix offer the possibility to exploit the filler's pronounced surface area to volume ratio, achieving thus improved thermomechanical, rheological, electrical and optical behavior. The employed nanoinclusions can be divided with respect to their electrical nature in to two main categories: conductive, including metals and various allotropic types of carbon and non-conductive such as layered silicates, piezoelectric and ferroelectric ceramics which exhibit dielectric behavior, that is are able to be polarized under the influence of an external electric field.

Current applications of inorganic-polymer nanocomposites, include packaging, electromagnetic radiation shielding, circuit board, interlayer dielectrics, leakage current controllers, self-

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current regulators, passive protection etc [4,5,11–14]. Nowadays a lot of research is carried out in developing compact systems with integrated nanocapacitors, which could act as electrical energy storing devices [3,15–17]. The latter could be used in emerging technological applications such as cellular phones, wireless personal digital assistants, acoustic emission sensors, stationary power systems and hybrid electric vehicles [3,5,18,19].

Materials used in the above applications should exhibit high electric energy storing capability, which requires high electric field and/or high dielectric permittivity. Dielectric strength, defined as the upper limit of the applied field, above which dielectric breakdown occurs and the material stops being operational, estimates the maximum applied field. Optimum behavior is achieved by employing materials that demonstrate both high dielectric strength and permittivity. Such materials are polymer nanocomposites reinforced with ceramic polar oxides or ceramic ferroelectrics that in addition to the above they exhibit flexibility, processability, light weight, resistance to corrosion, good mechanical behavior, high dielectric breakdown strength, low cost, and high dielectric permittivity. Further, embedding ferroelectric elements within the polymer matrix adds functionality to the composite system because of the change from ferroelectric to paraelectric phase of the inclusions, at a critical temperature known as Curie temperature (T_C) [20,21]. This structural change from the low to the high symmetry lattice is a first order transition and affects the electrical performance of the system. In addition to ceramic filled polymer systems, polymer composites containing conductive fillers at concentrations around the percolation threshold are also of main technological importance because of their high dielectric permittivity values [22–24].

The focus of this study is to characterize the dielectric response, functionality and energy storing efficiency of epoxy based nanocomposites reinforced with either barium titanate ($BaTiO_3$) nanoparticles or exfoliated graphite nanoplatelets (xGnP). The effect of the filler type, concentration and size on the dielectric response and functionality of the nanocomposites was determined by means of broadband dielectric spectroscopy (BDS) in a wide frequency and temperature range by employing dielectric permittivity and electric modulus formalisms and by means of dielectric reinforcing function. The energy storing efficiency of the nanocomposites was assessed by calculating the electric energy density. The morphology of the prepared systems was examined via scanning electron microscopy (SEM) and X-ray diffraction (XRD).

2. Experimental

2.1. Materials

Nanocomposite specimens were prepared by employing commercially available materials. In particular, a low viscosity epoxy resin with the trade name Araldite LY 1564 and curing agent Aradur-HY2954 provided by Huntsman Advanced Materials were used as matrix. In addition two types of reinforcements were used, ceramic $BaTiO_3$, supplied by Sigma Aldrich, and xGnP supplied by XG Sciences (East Lansing, MI). Aiming to study the effect of the filler's size upon the dielectric properties two different powder sizes of $BaTiO_3$ were used. One with a mean particle diameter less than 2 μm and another that has mean particle diameter in the range of 30–50 nm. xGnP have mean diameter less than 1 μm and an average thickness of 10–20 nm.

2.2. Fabrication of composites

The solution method was used to fabricate the composites. Nano-filler inclusions (ceramic or carbon) were mixed for 30 min 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 breakdown the filler agglomerates. The powder was collected after filtering the IPA and mixed with the epoxy at 800 rpm and $T = 60$ °C for 1 h 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 $T = 80$ °C for 1 h followed by post curing at $T = 100$ °C for 4 h. The employed filler contents expressed in wt% of particles per hundred parts of resin (phr) are listed in Table 1.

2.3. Characterization techniques

The morphology of the composites including the presence of voids and agglomerates and the quality of the filler dispersion within the polymer matrix was assessed by SEM (Zeiss SEM Ultra 60). The crystalline structure of the ceramic powders was investigated via X-ray diffraction, using a D8 Advance (Bruker AXS) with a CuKa source (1.54 Å, 1.6 kW power), in order to detect the transition from the non-symmetrical, polar structure (ferroelectric phase) to the symmetrical, non-polar structure (paraelectric phase) of $BaTiO_3$. The electrical characterization of the composites was conducted by means of Broadband Dielectric Spectroscopy (BDS) in the frequency range of 0.1 Hz to 10 MHz, 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 °C with a step of 5 °C. Novotherm system supplied also by Novocontrol was used to control the temperature.

3. Results and discussion

Representative SEM micrographs of the fracture surface of the examined systems are shown in Fig. 1. Fig. 1(a) refers to neat epoxy, while Fig. 1(b) and (c) to the 5 phr nano-$BaTiO_3$/epoxy system at low and high magnification, and Fig. 1(d) and (e) to the 5 phr xGnP/epoxy system at low and high magnification respectively. As depicted the $BaTiO_3$ powder is homogeneously distributed but as agglomerates not as single particles considering that individual particles have a diameter in the range of 30–50 nm. The same trend is observed in case of xGnP/epoxy composites. The diameter of the graphite platelets depicted in Fig. 1(c) is less than 1 μm however, their thickness is significantly larger than 10–20 nm indicating presence of agglomerates due to strong van der Waals forces among adjacent graphite platelets. It is also noted that there are voids at the xGnP/epoxy interface as a result of weak interfacial interactions.

XRD patterns of $BaTiO_3$ nano- and micro-size particles at $T = 40$ °C and $T = 170$ °C, shown in Fig. 2 reveal the structural

Table 1
Type and concentration of the reinforcing phase, for all the examined systems. Values of activation energy, for each system, as resulted by fitting data via equation (5).

Sample	E_A (eV)
Neat epoxy	0.503
5 (nm) $BaTiO_3$/epoxy	1.225
7 (nm) $BaTiO_3$/epoxy	1.225
10 (nm) $BaTiO_3$/epoxy	1.270
7 (μm) $BaTiO_3$/epoxy	1.240
10 (μm) $BaTiO_3$/epoxy	1.188
3 xGnP/epoxy	1.747
5 xGnP/epoxy	1.914
10 xGnP/epoxy	1.603