RESEARCH ARTICLE

Ceramic/Polymer Nanodielectrics: Towards a Multifunctional or Smart Performance

Georgios C. Psarras

ABSTRACT: Ceramic nanoparticles/polymer composite nanodielectrics constitute a novel class of engineering materials, which exhibit tunable mechanical, thermal, electrical and magnetic properties, energy storing/recovering ability in tandem with processability and corrosion resistance. By these means the produced nanocomposites are characterized by multifunctionality since structural components are able to perform a wide range of desirable functions. When the embedded nanoparticles are polar oxides and/or piezo/ferro-electrics, or any kind of stimuli responsive materials additional functional performance is induced in the nanocomposites, providing a suitable basis for the development of smart materials.

Keywords: Polymer Nanocomposites, Nanodielectrics, Multifunctionality, Energy Storage, Smart Materials

1. INTRODUCTION

Polymer matrix composites incorporating ceramic nanoinclusions receive enhanced scientific and technological interest, because of their advanced performance [1-7]. This type of materials, also referred as nanodielectrics, appears as a promising one for current emerging technologies, such as stationary power systems, cellular phones, wireless personal digital assistants and hybrid electric vehicles. The term nanodielectrics refers to: (a) polycrystalline semiconducting or insulating materials, with grain diameter at the nanoscale level and (b) polymer composites incorporating nanoinclusions. Polar oxides/polymer nanodielectrics exhibit tunable polarization, related to the piezoelectric and/or ferroelectric behavior of the filler [3, 8-11]. Furthermore, nanoinclusions could be able to service as inherent nanocapacitors, where energy could be stored [1, 8-11].

Functional materials constitute a class of materials having the ability to execute certain functions (operations) under the influence of an external (environmental) stimulus or sign control. Functional materials retain their

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ability to execute an operation even if their volume is subdivided [12] and could be classified as passive and active. Passive functional materials are characterized by the occurrence of local maxima, minima, or point of inflexions, in at least one of their physical quantities. Materials able to convert energy from one kind to another one are considered as active functional materials. This materials' category could provide high responses in external stimuli, without any irregularities in their performance. Types of mutually transformed energies could be thermal, electric, magnetic, and mechanical energy. Moreover, the converted energy could be static, like the electrostatic energy stored in a capacitor, or dynamic like electromagnetic waves [12].

Until recently, the choice of engineering materials for a specific application was solely based on the values of their mechanical and physical properties, such as Young's modulus, tensile strength, refractive index, electrical conductivity etc. All these values compose the material's behavior at service. Nowadays, requirements/expectations of engineering materials are enhanced, and they should be able to respond in real time to a rapidly varying environment or control signals. For this reason, besides the nominal values of various materials' properties, their functionality and their controllable behavior under different conditions and stimuli is of great importance and constitutes the main goal of novel materials. However, monolithic materials do not exhibit the

required set of responses in their performance and new composite materials or materials' systems should be designed and developed [13-15].

Multifunctionality is the combination of various desirable properties in a material or materials' system, aiming to develop a single material/system exhibiting all necessary responses under various loading conditions at service. Mechanical sustainability, suitable thermal response, tunable electric conductivity, variable electric polarization and dielectric permittivity, magnetic properties, thermally induced phase changes could be parts of the overall multifunctional behavior, Figure 1. Moreover, materials exhibiting smart performance are expected to be able to tune their behavior responding to an external or internal stimulus. Certain properties of these systems can be varied in a controllable way, such as stiffness, shape, damping capacity, natural vibration frequency, polarization, conductivity, energy storing efficiency etc. Smart structures are usually material systems incorporating functional constituents that are able to perform the operations of sensing, actuation and control [12, 16-18].

By these means "smart performance" should be chased out in composite materials and composites based on a polymer matrix appear to be adequate systems for adapting it. Thermosetting, thermoplastic or elastomeric polymer matrices exhibit thermomechanical stability, are easily mechanically reinforced, their electrical behavior can be tuned by controlling the type and amount of the filler content, interactions between macromolecules and reinforcing phase are adjustable, can be processed easily and their cost is relatively low [19], thus are considered as suitable base for the development of smart systems. The schematic presentation shown in Figure 2, summarizes the functions/operations which should be executed by the constituent materials in composite system in order to be considered as a "smart" one.

Figure 3 provides a schematic representation of the hierarchy of materials. Starting at the first level, "structural materials" which could be contemporary or well known for centuries, the materials properties define the possible applications and service performance. At the second level, materials' properties matter in tandem with the functions which can be executed. Finally, at the higher level, properties, functions and autonomous response constitute smart performance [12].

Dielectrics are non-conductive materials being able to be polarized under the influence of an external electric field. Active or functional dielectrics are dielectric materials which have the ability to be polarized even in the absence of an applied electric field. Active dielectrics are typically semi-conductive materials with noncentrosymmetric structure. Noncentrosymmetric crystals are polar with unit cells exhibiting dipole moment. Piezoelectrics, ferroelectrics and pyroelectrics are classified as active dielectrics.

In the present study ceramic piezo/ferro-electric polar oxides, and carbides nanoparticles are embedded in a polymer matrix. However, ferromagnetic and carbon allotropes nanoparticles have also been studued [14, 15]. Morphology, thermal properties, static and dynamic mechanical behavior, dielectric response, conductivity, magnetic properties and induced multifunctionality are investigated by means of several experimental techniques. Considering the importance of interface in all nanocomposite systems, obtained data are also used targeting to the quantification of the inter-facial/phacial area and the investigation its properties [20, 21]. Optimum type or types and amount of reinforcing phase leading to the synergy of the occurring physical mechanisms in the under test systems are analyzed and discussed.
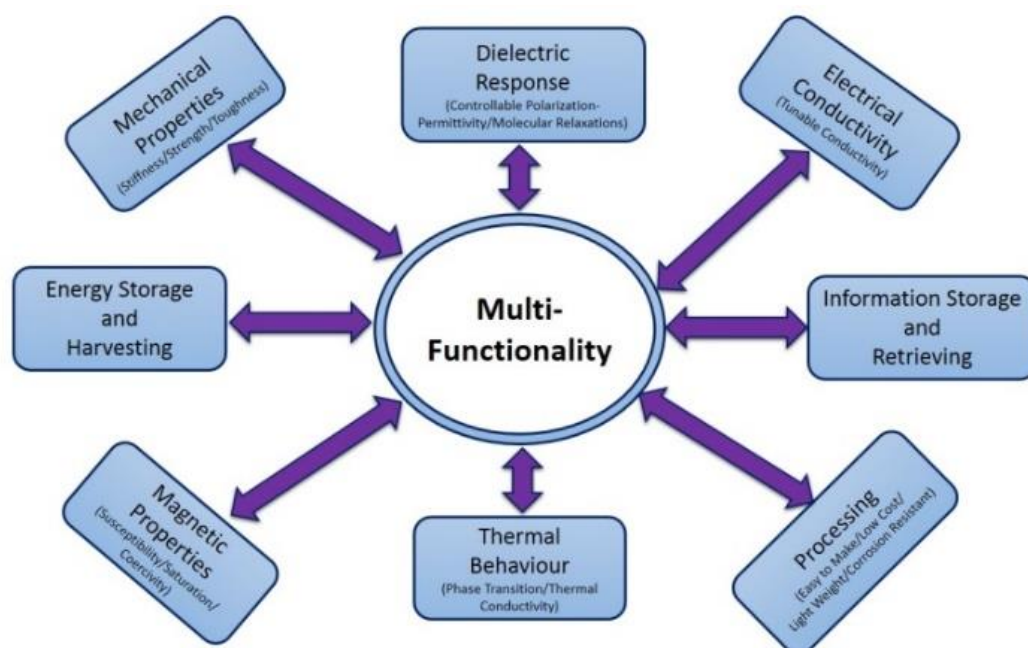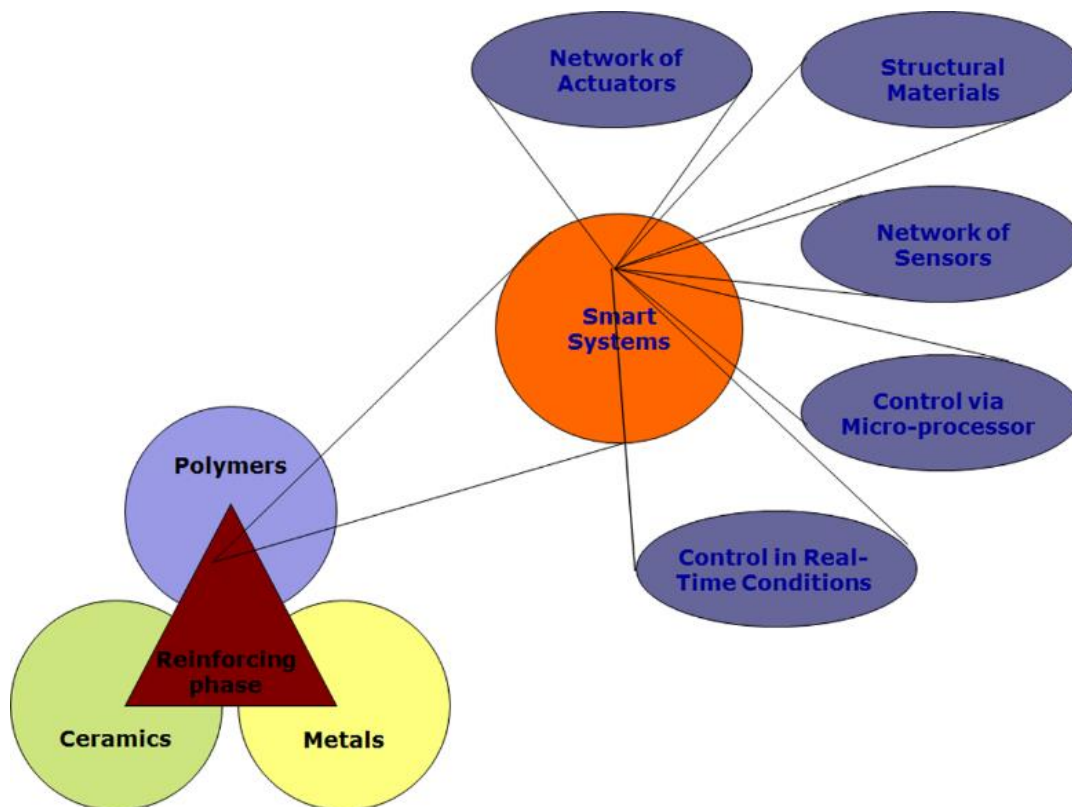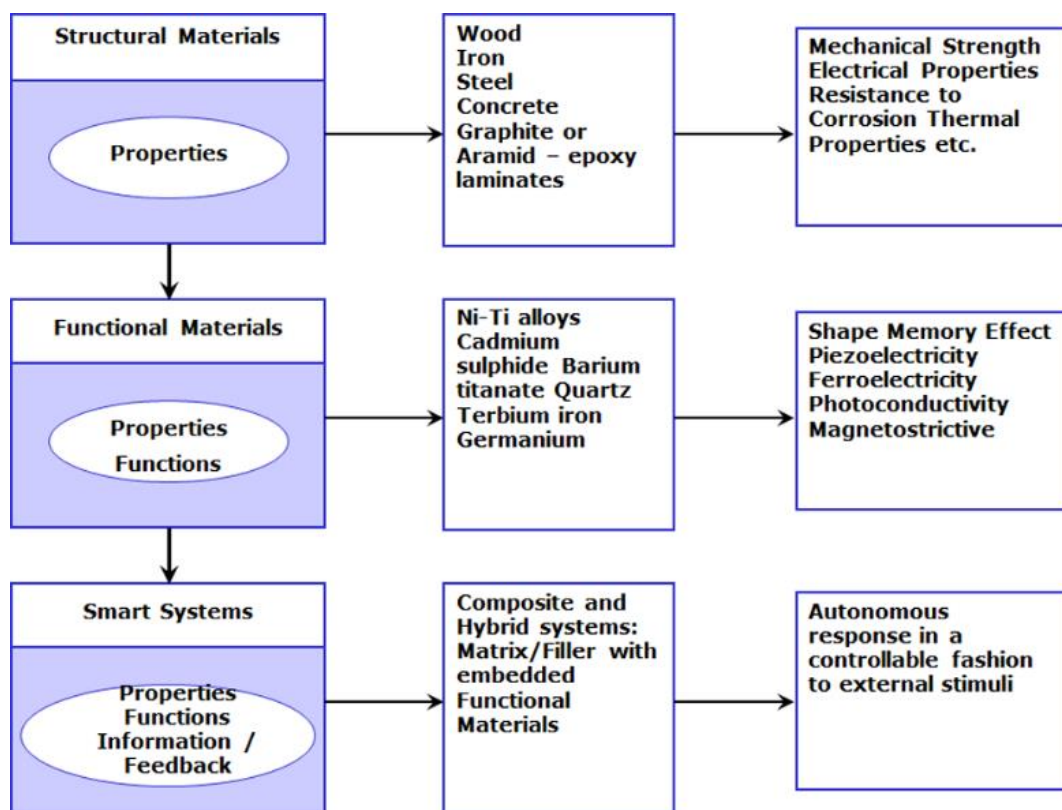

Fig. 1. Schematic representation of materials' multifunctionality.

Fig. 2. Schematic representation of the functions/operations executed by the constituent materials in a smart system. Reprinted with permission from ref. [12], G. C. Psarras, Smart Materials. Patras University Press, Patras 2004. Copyright © University of Patras.

Fig. 3. Schematic representation of materials' hierarchy. Reprinted with permission from ref. [12], G. C. Psarras, Smart Materials. Patras University Press, Patras 2004. Copyright © University of Patras.

2. MATERIALS AND METHODS

Commercially available materials were used for the manufacturing of nanocomposite systems. Ceramic fillers were purchased from Sigma-Aldrich or PlasmaChem, while epoxy resin and hardener were purchased from Neotex SA (Epoxol 2004A, 2004B) and Huntsman Advanced Materials (Araldite LY 1564, Aradur-HY2954). The employed method for preparation is given analytically elsewhere [10].

Specimens' morphology was assessed via scanning electron microscopy (SEM) and X-ray diffraction pattern (XRD) by employing a Carl Zeiss EVO MA 10 device and a Philips PW 1050/25 goniometer with Cu Ka X-ray radiation, 1 ¼ 1.5418 Å apparatus, respectively. Thermomechanical response was studied by means of differential scanning calorimetry (DSC) via Q200 and dynamic mechanical analysis (DMA) Q800, Thermal Analysis Instruments, respectively. The dielectric characterization was conducted by means of broadband dielectric spectroscopy (BDS), using an Alpha-N Frequency Response Analyzer, a BDS1200 dielectric cell and Windeta software. Temperature was controlled by a Novotherm system with ± 0.1°C accuracy. Software and all dielectric devices were provided by Novocontrol Technologies.

3. RESULTS AND DISCUSSION

Barium titanate is a typical ferroelectric material, which undergoes a structural transition from the polar ferroelectric phase (tetragonal crystal structure) to the non-polar paraelectric phase (cubic crystal structure) at a critical temperature (T_C), known as Curie temperature [10, 11, 22, 23]. Critical temperature for $BaTiO_3$ is close to 130°C. XRD pattern of micro- and nano-$BaTiO_3$ particles are shown in Figure 4(a) and (b) respectively, at two temperatures, i.e. below and above T_C. It is obvious that in the case of micro-$BaTiO_3$ particles a clear transition from the tetragonal to the cubic phase takes place, while in the case of nano-$BaTiO_3$ particles both phases appear to co-exist below T_C. As the dimensions of $BaTiO_3$ nanoparticles are diminishing the a/c

ratio tends to one and thus the unit cell's tetragonality vanishes. At temperatures above T_C (Figure 4(b)) both micro- and nano-$BaTiO_3$ particles are in the cubic phase. Transition from polar to non-polar crystal structure induces variable polarization, which is reflected to the real part of dielectric permittivity. Variable polarization can also be induced by polar oxides, such as ZnO and TiO_2, because of their anisotropy and piezoelectric properties [10, 24, 25]. Embedding ferroelectric or polar oxides in the form of ceramic nanoparticles in a polymer matrix leads to the development of functional or sometimes multifunctional nanocomposite systems. In such cases, nanocomposites can also be termed as nanodielectrics and in their functionalities are included, the variation of conductivity with temperature or the applied field and the ability to store energy at the dispersed nanocapacitors [1, 8, 10]. Further enhancement in their multifunctional behavior refers to suitable thermo-mechanical response, environmental stability and magnetic properties [21, 26].

Figure 5 presents the variation of ε' with temperature at constant frequency 0.1 Hz for micro-$BaTiO_3$ particles. Between 130 and 140°C a peak is formed denoting the transition from the polar ferroelectric to the non-polar paraelectric phase (tetragonal to cubic structure). In the low temperature region, a tendency for the formation of another peak is recorded, which should be assigned to the transition to orthorhombic structure.

Figures 6 (a) and (b) provide characteristic examples of the variation of the real part of dielectric permittivity with temperature, at 0.1 Hz, for the hybrid epoxy/ZnO/TiO_2 nanocomposite system. The recorded peaks are related to variations of polarization due to relaxation phenomena. The latter are ascribed to polarization processes of the polymeric matrix, to interfacial effects between matrix and filler particles, to intrinsic interfacial polarization effects in the ceramic phase, and to structural transitions of the ceramic filler [10, 25]. Relaxation processes are more easily detected in dielectric loss spectra in the form of imaginary part of permittivity (ε''), loss tangent (tanδ), and loss modulus index (M''), via the formed loss peaks [19].
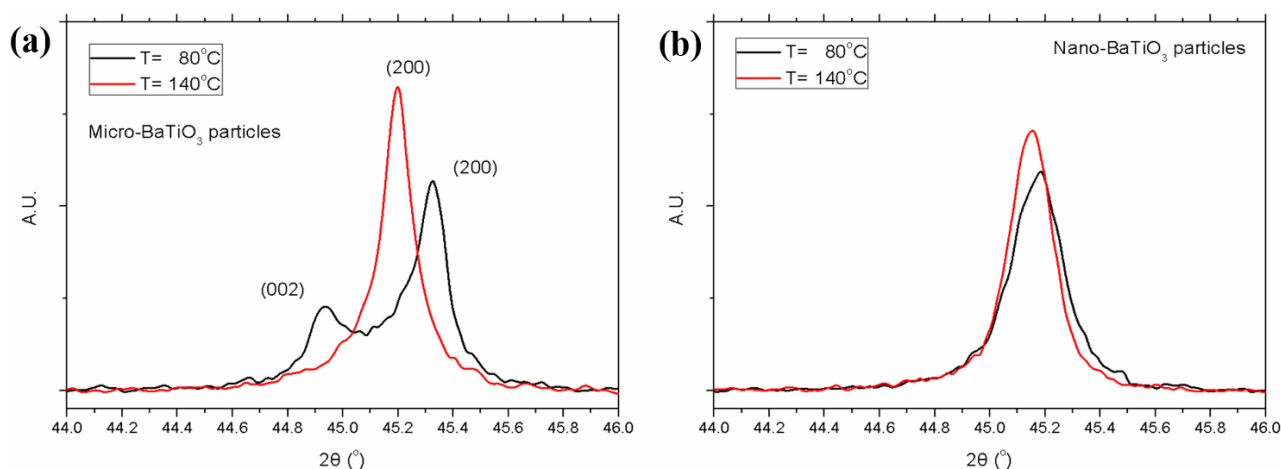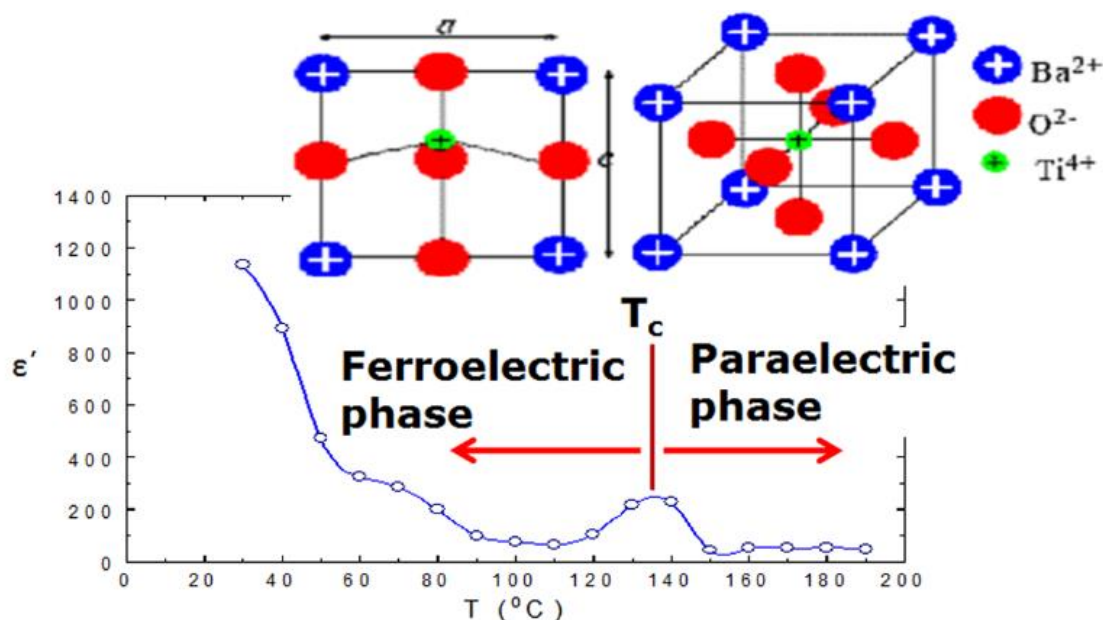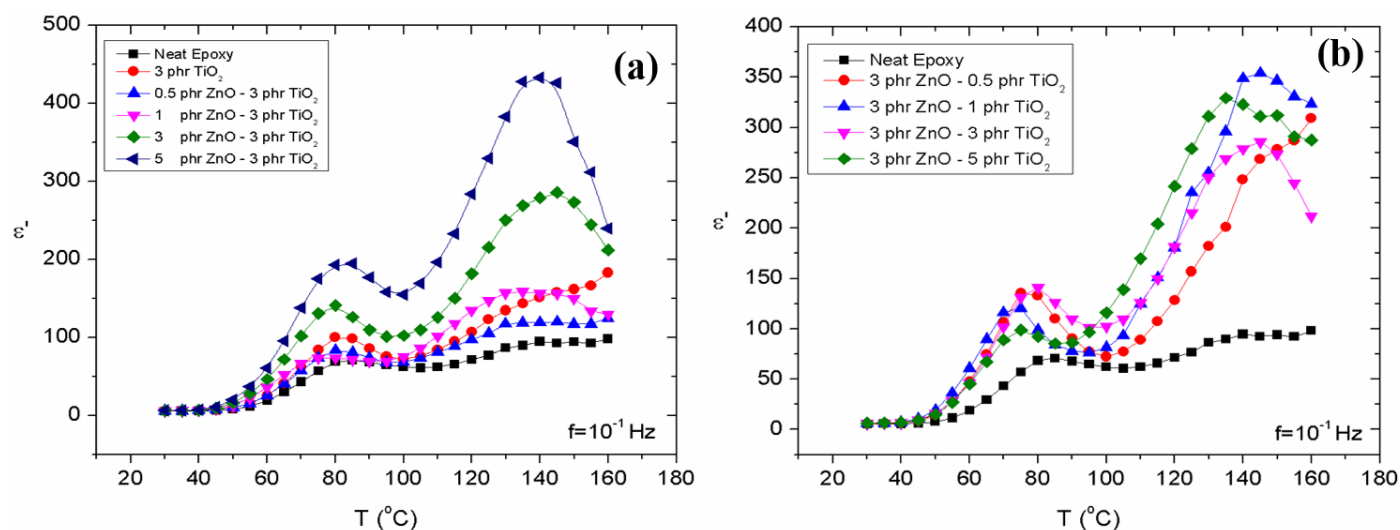

Fig. 4. XRD spectra of (a) micro-, and (b) nano-$BaTiO_3$ particles, at 80 and 140°C.

Fig. 5. The real part of dielectric permittivity as a function of temperature at f = 0.1 Hz for micro-BaTiO$_3$ particles, indicating the ferroelectric to paraelectric transition.

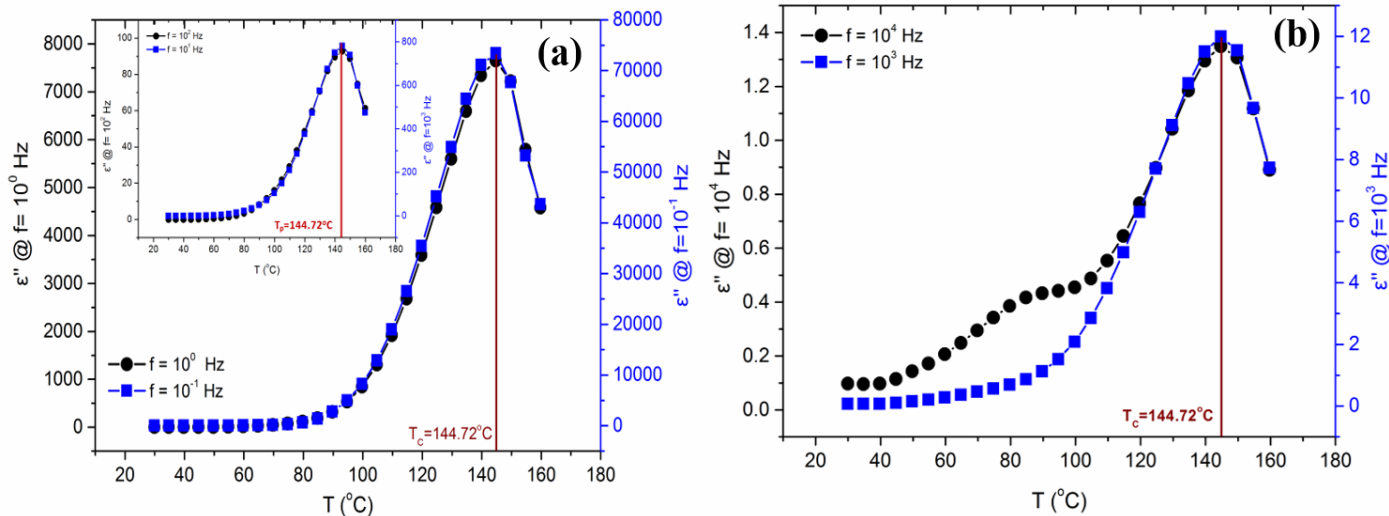**Fig. 6.** The real part of dielectric permittivity as a function of temperature at f = 0.1 Hz for hybrid epoxy/ZnO/TiO$_2$ nanocomposites, varying filler content.

The dielectric loss index (ε'') as a function of temperature at various frequencies is depicted in the plots of Figures 7 (a) and (b), for the hybrid nanocomposite epoxy/5 phr ZnO/3 phr TiO$_2$. It can be observed that the variation of ε'', in all cases, follows the same pattern forming a peak at the high temperature range. Although the maximum value of the peak increases with lowering the frequency of the applied field, since the achieved polarization level diminishes with frequency, the peak's position remains unchanged with frequency. Such a behavior implies the presence of a phase transition, which until its completion undergoes at constant

temperature. Considering the amorphous nature of the employed polymer matrix and that the used ceramic particles melt at very high temperatures, this "phase transition-type" peak cannot be attributed to crystallization/melting procedures. ZnO and TiO$_2$ are polar ceramic materials exhibiting anisotropy in their unit cells. The occurring dipole moments is the result of this anisotropy. Zinc oxide, because of its structure, is characterized by higher anisotropy and its augmented influence on the dielectric response of the nanocomposites can be easily observed in the plots of Figure 6. The c/a ratio of the lattice parameters in the hexagonal

wurtzite structure of ZnO is responsible for its piezoelectric properties [27]. Moreover, with increasing temperature and in a temperature range roughly between -50 to 180ºC, the value of the c/a ratio decreases approaching one [27].

Thermal expansion coefficients in the two directions are not only different, but also vary with temperature dissimilarly, leading to a relative arsis of anisotropy or to a weak ferroelectric response [27].

Fig. 7. Imaginary part of dielectric permittivity as a function of temperature at various frequencies for the hybrid nanocomposite epoxy/5 phr ZnO/3 phr TiO$_2$.
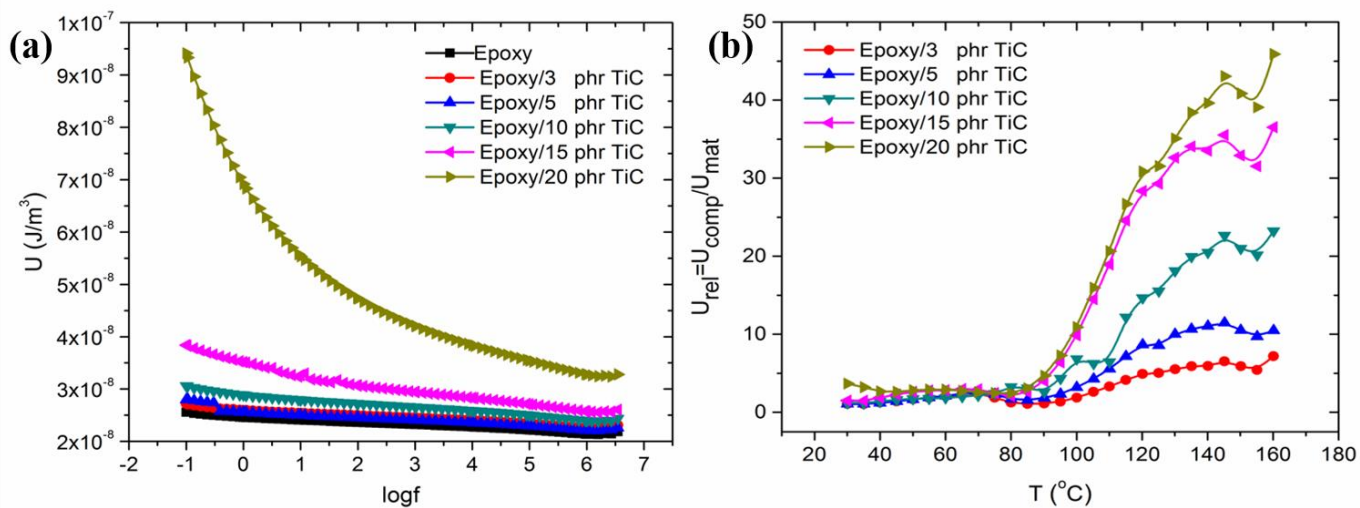
Fig. 8. (a) Energy density as a function of frequency at 30ºC, and (b) relative energy density as a function of temperature at f = 0.1 Hz, for the TiC/epoxy nanocomposite system.

Dispersed nanoparticles within a polymer matrix can act as a distributed network of nano-capacitors, where energy can be stored and harvested [9, 10, 28]. Energy density or energy per unit volume for a dielectric material is defined according to Equation 1 [28, 29]:

$$U = \int_{D_{max}}^{0} E \cdot dD \qquad (1)$$

where E is the electric field, D the electric displacement, and D_{max} the maximum value of electric displacement

corresponding to the highest value of the electric field. In the case of linear dielectrics, i.e. for low or relatively low fields, Equation (1) takes the form:

$$U = \frac{1}{2}\varepsilon_0 \varepsilon' E^2 \qquad (2)$$

where ε_0 is the permittivity of free space and ε' the real part of dielectric permittivity. From Equation (2) is apparent that energy density depends strongly on the applied field. Values of energy density increase rapidly with E. Failure of a

dielectric, at the breakdown strength, defines the upper limit of the stored energy density for a specific material. However, applied field is related to the working conditions of the dielectric material and does not express any material property. In Equation (2) the only quantity expressing a material property is ε', so under the same working conditions, that is applied field, the dielectric with the higher ability to store energy is the one with the larger value of ε'.

Plots in Figure 8 provide characteristic examples for the variation of energy density in polymer matrix composite nanodielectrics. The dependence of energy density upon the frequency of the field at 30°C is shown in Figure 8(a) for a TiC/epoxy set of nanocomposites, while Figure 8(b) presents the dependence of relative energy density upon temperature at 0.1 Hz, for the same system. Relative energy density (U_{rel}) is defined according to Equation (3):

$$U_{rel}\Big|_{E,T,f=cons\tan t} = \frac{U_{comp}}{U_{mat}}\Big|_{E,T,f=cons\tan t} \qquad (3)$$

where U_{comp} and U_{mat} are the energy densities of the composite and the matrix respectively, at constant applied field, temperature and frequency.

It is obvious that the presence of nanoparticles increases drastically the ability for energy storing in nanocomposites and the maximum augment of energy density exceeds 40 times the corresponding value of the unreinforced matrix.

4. CONCLUSION

Ceramic particles/polymer matrix composites constitute an interesting novel class of engineering materials with tunable properties. Filler content can be used in order to adjust thermo-mechanical response, electric and magnetic properties, inducing multifunctionality to the composites' behavior. In the case that the employed filler is a polar oxide, or a piezo/ferroelectric material additional functional performance is induced in the nanocomposites, providing a suitable basis for the development of smart materials.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests.

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