# DEVELOPMENT AND CHARACTERIZATION OF TITANIUM BORIDE/BORON CARBIDE/ POLYMER MATRIX HYBRID NANODIELECTRICS

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**Keywords:** Composite Materials, Nanodielectrics, Polymer matrix, Boron Carbide, Titanium Boride.

## Abstract

Polymer matrix composites constitute a novel type of materials with considerable scientific and technological interest, due to their properties and the wide range of potential applications. In the present study a series of composite specimens were manufactured using commercially available materials. Epoxy resin was used as matrix and boron carbide/titanium boride hybrid nanogranules as the reinforcing material. The composites were characterized by means of Broadband Dielectric Spectroscopy in a wide frequency (0.1 Hz- $10^6$ Hz) and temperature ($30^o$ C- $160^o$ C) range. The results of the dielectric characterization suggest the existence of three distinct relaxation processes, which can be attributed to the interfacial polarization, known as Maxwell-Wagner-Sillars effect, glass to rubber transition and reorientation of polar side groups of the polymer matrix.

## 1. Introduction

Composites are materials are produced by the combination of two or more materials, which are mechanically separable exhibiting properties superior to those of their individual components [1,2]. Composite materials are classified in different types depending on the inclusion and the matrix. The particle size and morphology of the inclusion heavily influence the properties of the composite. Smaller particles result in an increase of the interfacial surface area, which in turn increases the real part of dielectric permittivity of the composite material. Dielectrics are materials which can store energy through the polarization of their molecules. Dielectric materials can be used to store electrical energy in the form of charge separation when dipoles and charge distributions are polarized by an external electric field [3].

## 2. Experimental

The investigated specimens were manufactured by employing the following constituents: Commercially available low viscosity epoxy resin (Epoxol 2004A) and hardener (Epoxol 2004B) from Neotex SA Athens, Greece, along with Boron Carbide ($B_4C$) / Titanium boride ($TiB_2$) hybrid nanopowder (PlasmaChem, Berlin, Germany) which was used as the reinforcing phase.

Seven specimens were manufactured varying the concentration of the inclusions. Filler content is expressed in parts per hundred resin per weight (phr). The produces specimens were: epoxy resin, 1 phr, 3 phr, 5 phr, 7 phr, 10 phr and 12 phr specimen. The weight fraction of $B_4C/TiB_2$ in all composites was 80/20. A total of 5 gr of resin-hardener was used, at a 2:1 w/w ratio. During the manufacturing process of the specimens gentle

stirring of the resin and hardener was employed. Then the appropriate amount of nanoparticles was added to the mixture, with continuous stirring. The goal was to create a homogeneous mixture while simultaneously avoiding the formation of agglomerates or air pockets within the polymer matrix. It is important to avoid the existence of agglomerates inside the specimens as they severely degrade the quality of the composites, resulting in systems exhibiting inferior properties than expected. The stirring process was carried out in an ultrasonic bath. Upon the completion of the stirring process, specimens were poured into round-shaped moulds and left for 7 days at room temperature for the curing process. Curing was followed by the post-curing process which was conducted in an oven at 100° C for 4 hours.

The dielectric characterization of the prepared samples was conducted by means of broadband dielectric spectroscopy (BDS), using an Alpha-N frequency response analyzer and the BDS 1200 dielectric cell. Temperature was controlled by a Novotherm system and data acquisition was handled via the Windeta software. All devices and software were purchased from Novocontrol (Germany). This experimental method allows studying the temperature and electric field's frequency dependence of the real ($\varepsilon'$) and the imaginary ($\varepsilon''$) part of the dielectric permittivity. Using this method one can study the mechanisms governing the relaxation processes exhibited by the specimens. In addition, broadband dielectric spectroscopy can provide information with respect to a large number of the specimen's properties, such as the ac conductivity, the electric modulus and the loss tangent (tan$\delta$) [4].

## 3. Results and Discussion

The results of Broadband Dielectric Spectroscopy suggest the existence of three distinct relaxation processes, namely α- relaxation (glass to rubber transition), β- relaxation (reorientation of polar side groups of the polymer matrix) and lastly interfacial polarization, known as Maxwell-Wagner-Sillars phenomenon. These relaxations can easily be observed in Fig. 1a. Specifically β-relaxation is recorded at high frequencies ($10^4$-$10^6$ Hz), α-relaxation at medium frequencies ($10^2$-$10^4$ Hz) and interfacial polarization in the low frequency range ($10^{-1}$-$10^1$ Hz) [5,6].

Fig. 1b depicts the real part of the dielectric permittivity ($\varepsilon'$) as a function of temperature and frequency in a 3-D plot. In this diagram an increase in permittivity values is observed with decreasing frequencies and increasing temperatures. As the frequency increases the permanent and induced dipoles inside the composite do not have the time needed to be polarized due to the rapid rotation of the electrical field, and thus their values decline quickly. On the contrary, with increasing temperature, the dipoles have adequate time and energy to follow the rotation of the electrical field, and for this reason an increase in permittivity values is observed. Also, the values of the real part of dielectric permittivity at high temperatures and low frequencies suggest the presence of Maxwell-Wagner-Sillars phenomenon. The step-like transition in the intermediate frequency range is associated with the glass to rubber transition of the polymeric matrix (namely α-relaxation).
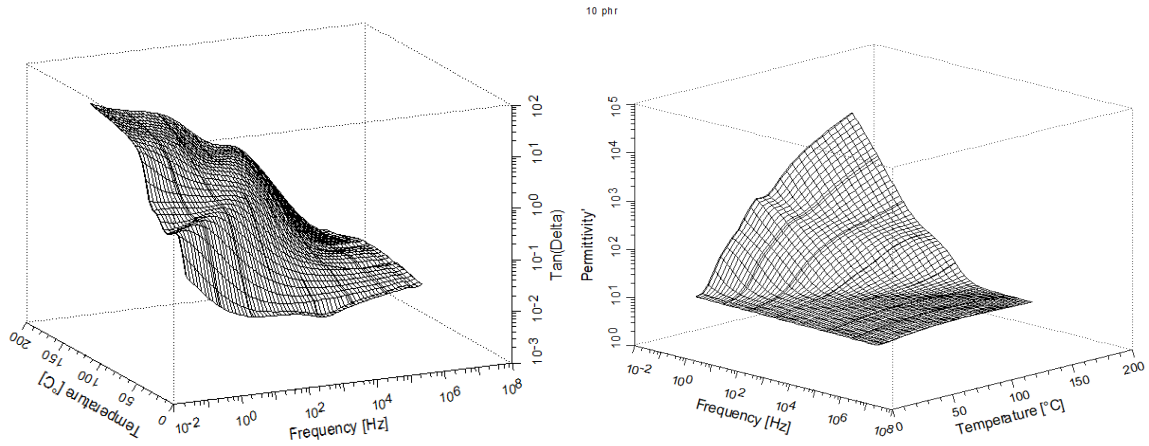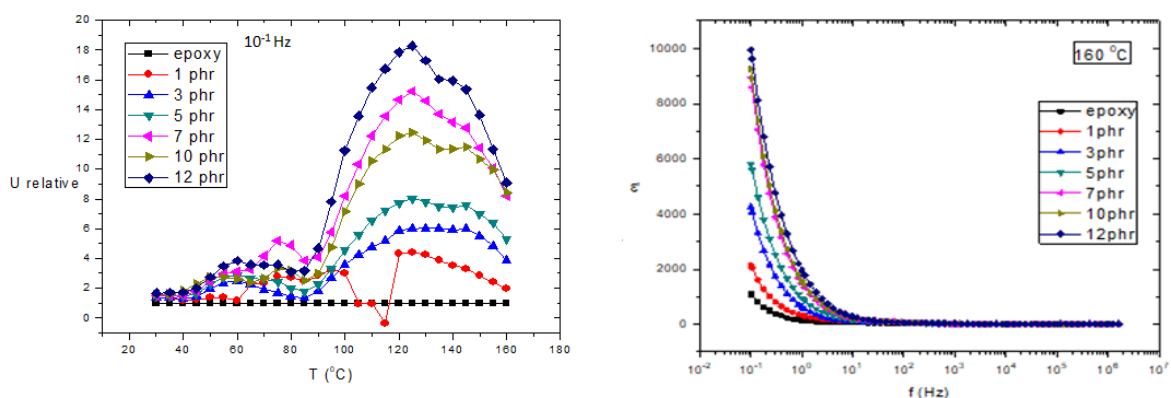
**Figure 1.** (a) tanδ (left) and (b) real part of dielectric permittivity (ε′) (right), as a function of temperature and frequency for the specimen with 10 phr filler content.

In Fig. 2a the specimens' energy storage ability is determined via the relative energy density plots. Relative energy density is defined according to Eq. (1):

$$U_{relative} = \frac{U_{composite}}{U_{matrix}}$$

(1)

where $U_{composite}$ and $U_{matrix}$ are the energy density of the composite material and the neat matrix at a given temperature and frequency. This figure represents the variation of relative energy density as a function of temperature, at constant frequency of 0.1 Hz, for all studied specimens. As it can be seen, at elevated temperatures and low frequencies, the highest observed value of Urelative is 19, which is considered as quite high [2] and indicates an enhanced ability of the nanocomposites to store energy.

In Fig. 2b the real part of dielectric permittivity as a function of frequency at 160° C, for all studied composites, is depicted. It is clearly shown that the increase of filler concentration (titanium boride/boron carbide hybrid nanopowder) heavily influences the permittivity values of the composite materials, since the permittivity of the filler is significantly higher than that of the epoxy resin. Composite specimens exhibit higher permittivity with increasing filler content, reflecting the enhancement of heterogeneity.



**Figure 2.** (a) $U_{relative}$ as a function of temperature at $10^{-1}$ Hz (left) and (b) real part of dielectric permittivity (ε′) as a function of frequency at 160° C (right) for all studied systems.

In the ac conductivity plot, shown in Fig. 3a, two distinct conductivity mechanisms are shown. At low frequencies values tend to reach a fixed value, which increases with temperature. This value corresponds to

the dc conductivity of the composites. However at high frequencies a steep exponential increase is depicted, ac conductivity increases over four orders of magnitude, from $10^{-10}$ S/cm to $10^{-6}$ S/cm, while the influence of temperature becomes negligible. This phenomenon is attributed to charges and dipoles rapidly moving between nearby conductive points, thus increasing conductivity values without moving long distances within the polymer matrix. This is type of conductive mechanism is called hopping conductivity in the relative literature [7].

Fig. 3b, shows the imaginary part of electric modulus at $10^3$ Hz as a function of temperature, for all studied systems. The observed peak in this plot is associated with α-relaxation. The peak position slightly moves to lower temperatures according to the boron carbide and titanium boride concentration. This behaviour indicates that the glass transition temperature ($T_g$) depends on the type of interactions between the nanoparticles and the polymer matrix. In the examined specimens, with increasing filler concentration the peak associated with the glass to rubber transition moves to lower temperatures, suggesting that the nanoparticles facilitate the transition.
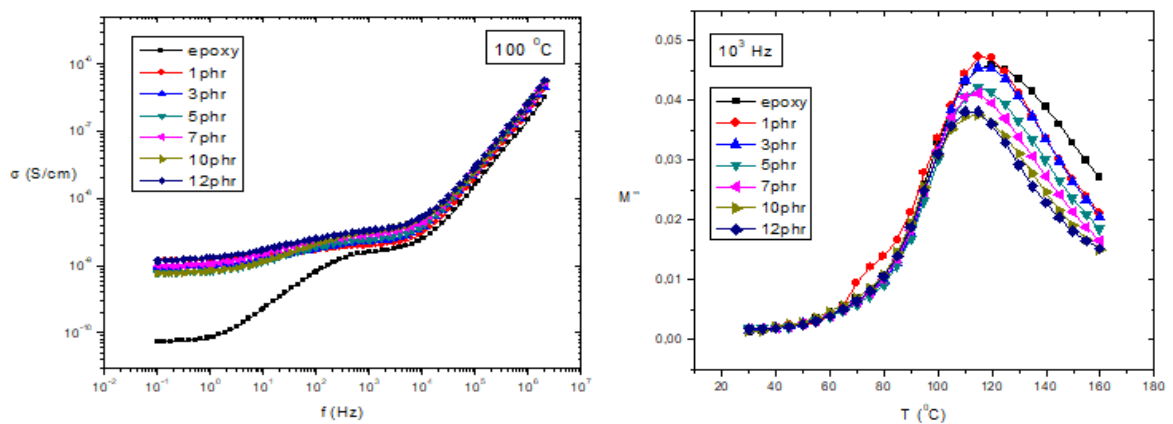


**Figure 3.** (a) AC conductivity as a function of frequency at $100^0$ C (left) and (b) imaginary part of electric modulus at $10^3$ Hz (right), for all studied systems.

## 4. Conclusion

A set of seven specimens consisted of epoxy resin and boron carbide/titanium boride particles, were successfully manufactured and studied. An increase in ε´ was observed with decreasing frequency and increasing temperature. Moreover, the increase of the filler content results in higher permittivity values, with the 12 phr sample to exhibit the highest permittivity values. Ac conductivity tends to reach constant values for low frequencies, while at high frequencies an exponential increase was observed, associated with a phenomenon referred to as hopping conductivity. Three relaxation mechanisms were observed, namely interfacial polarization, α-relaxation and β-relaxation. Furthermore, the filler content was proven to affect the glass to rubber transition temperature, allowing for fine tuning of the composites' properties. Finally, the $U_{relative}$ plots indicated a significant increase in the composites' energy storage capabilities since the 12 phr specimen appear able to store 19 times more energy than the epoxy specimen. This value is considered quite high.

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**References**

[1] G. Ioannou, A. Patsidis, and G.C. Psarras. Dielectric and functional properties of polymer matrix/ZnO/BaTiO$_3$ hybrid composites. *Composites Part A: applied science and manufacturing*, 42:104-110, 2011.

[2] A. Sanida, S.G. Stavropoulos, Th. Speliotis, and G.C. Psarras. Development, characterization, energy storage and interface dielectric properties in SrFe$_{12}$O$_{19}$ /epoxy nanocomposites. *Polymer*, 120:73-81, 2017.

[3] M.F. Fréchette, M.L. Trudeau, H.D. Alamdari and S. Boily. Introductory remarks on nanodielectrics. *IEEE Trans. Dielectr. Electr. Insul.*, 11,5:808–818, 2004.

[4] A. Schonhals and F. Kremer. *Broadband dielectric spectroscopy.* Springer, 2003.

[5] G.C. Psarras. *Polymer nanocomposites: Physical properties and applications: Conductivity and dielectric characterization of polymer nanocomposites*, edited by S.C. Tjong, and Y.M. Mai. Woodhead Publishing Limited, Cambridge, 2010.

[6] G.A. Kontos, A.L. Soulintzis, P.K. Karahaliou, G.C. Psarras, S.N. Georga, C.A. Krontiras and M.N. Pisanias. Electrical relaxation dynamics in TiO2 – polymer matrix composites, *Express Polymer Letters*, 12:781–789, 2007.

[7] R. Zallen. *The Physics of Amorphous Solids*. Wiley-VCH Verlag GmbH, 1998.