

Dielectric behaviour and functionality of polymer matrix – ceramic BaTiO₃ composites

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Abstract. Dielectric properties of polymer matrix – ceramic BaTiO₃ composites were examined by means of Broadband Dielectric Spectroscopy (BDS) in the frequency range of 10⁻¹–10⁷ Hz and over the temperature range of 30–160°C, varying the content of ferroelectric particles. Experimental results provide evidence that the recorded relaxation phenomena include contributions from both the polymeric matrix and the presence of the reinforcing phase. Obtained results are analysed via the electric modulus formalism. Polymer matrix exhibits two distinct relaxation processes attributed, with ascending relaxation rate, to glass/rubber transition, and local motions of polar side groups. Interfacial polarization or Maxwell-Wagner-Sillars process is present in the low frequency range and at high temperatures. Finally, in the vicinity of the characteristic Curie temperature (*T_c*) an abrupt variation of the real part of dielectric permittivity with temperature is recorded. This peak is probably related to the ferroelectric to paraelectric phase transition of the employed ceramic inclusions.

Keywords: *polymer composites, dielectric spectroscopy, smart materials, ceramic BaTiO₃, ferroelectrics*

1. Introduction

Ceramic-polymer composites consisting of ferroelectric crystal particles, homogeneously distributed, in an amorphous host represent a novel class of materials, with several interesting properties [1–4]. High tech electronic devices require new high dielectric permittivity materials (known as high-K materials), which combine at the same time, suitable dielectric properties, mechanical strength and ease processing. Recently, ceramic-polymer composites have been studied in various applications including integrated capacitors, acoustic emission sensors and for the reduction of leakage currents [5–10].

Many polymers have been proved suitable matrices in the development of composite structures due to their ease production and processing, good adhesion with reinforcing elements, resistance to corro-

sive environment, light weight and in some cases ductile mechanical performance. Further, polymers are basically electrical insulators with low dielectric permittivity and often high dielectric strength. On the other hand, ceramic particles are brittle materials, with high dielectric permittivity and thermal strength. Combining two materials with deviating properties in a new composite structure, could lead in a materials system with superior performance. Furthermore, if the embedded ceramic particles are ferroelectric, functional or self-tunable properties can be disclosed to the composite structure. Ferroelectric materials exhibit spontaneous polarization and are characterized by a temperature dependent disorder to order transition. The electrical response of polymer matrix particulate composites depends on various factors such as the permittivity and conductivity of the constituent

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phases, the size, shape and volume fraction of the filler and the type of distribution of the inclusions. In the present study composite systems of epoxy resin and ceramic BaTiO₃ particles have been prepared, varying the volume fraction of the inclusions. The dielectric response of the composites was studied in a wide frequency and temperature range by means of Broadband Dielectric Spectroscopy (BDS). Experimental data were analyzed by means of dielectric permittivity and electric modulus formalisms [11–13]. From the conducted analysis arises, that the recorded dielectric relaxations are related to both the polymer matrix and the presence of the reinforcing phase. Finally, the electrical response of ferroelectric particles – polymer matrix composites is influenced by the ferroelectric to paraelectric transition of the inclusions.

2. Experimental

2.1. Samples preparation

Commercially available low viscosity epoxy resin (Epoxol 2004A, Neotex S.A., Athens, Greece) was used as a prepolymer. The employed curing agent (Epoxol 2004B) operating at a slow rate was supplied by the same company also. Barium titanate was purchased from Sigma-Aldrich. The mean particle diameter was less than 2 μm . The followed procedure includes mixing of the resin with the curing agent in a 2:1 (w/w) ratio. While the above systems were still in the liquid state, various amounts of the ceramic powder were added for the production of the composite samples. Stirring at a low rate and degassing the mixture in vacuum-oven were

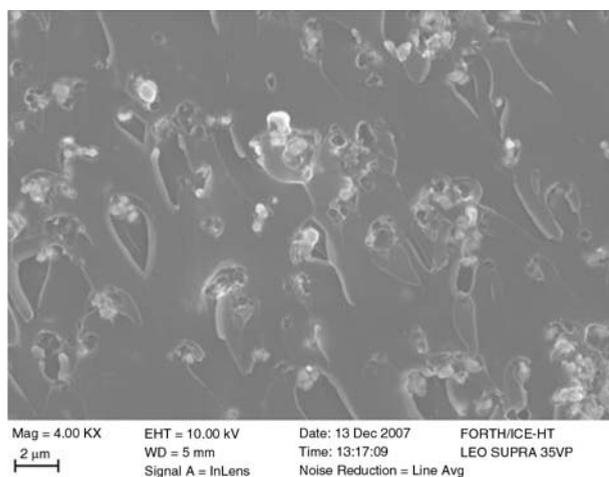


Figure 1. Scanning Electron Microscopy image of fractured surface of the specimen with 20 phr in BaTiO₃ content

also included in the preparation process. The initial curing took place at ambient for a week, followed by post-curing at 100°C for 4 hours. Finally, specimens' morphology was checked for voids and extensive clusters by means of Scanning Electron Microscopy (Leo Supra 35VP). In all samples the distribution of the filler is characterized as satisfactorily and more or less homogeneous, Figure 1.

2.2. Thermal characterisation

A Diamond (Perkin Elmer, Shelton, USA) differential scanning calorimeter operating at a scan rate of 10°C/min was used to characterise thermal transitions of the employed epoxy resin and the produced composites. Samples were placed in an aluminum crucible and an empty aluminum crucible was serving as reference. Temperature was varied from ambient to 200°C.

2.3. Dielectric measurements

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, supplied by Novocontrol Technologies (Hundsagen, Germany). The dielectric cell was a three terminal guarded system constructed according to the ASTM D150 specifications. Samples were placed between metal electrodes and problems arising from possible electrode polarisation were excluded by employing the electric modulus formalism [11–13]. Isothermal frequency scans were conducted, for each of examined specimens, from ambient to 160°C with a temperature step of 10°C. The amplitude of the applied voltage was 1000 mV.

3. Results and discussion

The DSC thermographs for all the tested specimens were analyzed by employing suitable software supplied by Perkin Elmer. Glass transition temperature (T_g) was determined via the point of inflection of the transition. The determined values are listed in Table 1. Electrical relaxation effects in polymer matrix composites arise from interfacial effects, phase transitions and polarization or conductivity mechanisms. The recorded dielectric data, of all the

Table 1. Concentration of BaTiO₃ particles in all the examined systems and the corresponding glass transition temperatures

Sample	Volume fraction of BaTiO ₃ [%]	Glass transition temperature, T _g [°C]
Epoxy	0	56.6
Epoxy + 10 phr BaTiO ₃	2.71	58.9
Epoxy + 20 phr BaTiO ₃	4.81	59.3
Epoxy + 40 phr BaTiO ₃	11.46	62.3
Epoxy + 50 phr BaTiO ₃	13.62	64.0

examined specimens, were first expressed in terms of real and imaginary part of permittivity and then transformed, via Equation (1), to the electric modulus formalism. Arguments for the resulting benefits of the electric modulus presentation have been exhibited and discussed elsewhere [11–13]. Electric modulus is defined as the inverse quantity of complex permittivity by the Equation (1):

$$M^* = \frac{1}{\epsilon^*} = \frac{1}{\epsilon' - j\epsilon''} = \frac{\epsilon'}{\epsilon'^2 + \epsilon''^2} + j \frac{\epsilon''}{\epsilon'^2 + \epsilon''^2} = M' + jM'' \quad (1)$$

where ϵ' , M' are the real and ϵ'' , M'' the imaginary parts of dielectric permittivity and electric modulus respectively. The frequency dependence of the real part of electric modulus (M') for the composites with 10, 20 and 50 phr in BaTiO₃ particles, at temperatures varying from 30 to 160°C, is shown in Figures 2a, 3a and 4a. The existence of a step-like transition from low to high values of (M') is evident in all specimens, at temperatures higher than 50°C. The recorded transitions imply the presence of a relaxation process, which should be accompanied by a loss peak in the diagrams of the imaginary part of electric modulus (M'') versus frequency. As it

can be seen in Figures 2b, 3b and 4b loss peaks are clearly formed in the frequency range where transitions occur. Relaxation peaks shift to higher frequencies with the increase of temperature. The shape and magnitude of the formed peaks remain more or less constant in the range of 50 to 100°C. At temperatures higher than 100°C a reduction of the peak shift rate is observed, which is accompanied with an increment of the (M'') maxima. Above 120°C and in the low frequency region an additional peak is recorded. Finally, in the high frequency edge a tendency for the formation of a third relaxation peak is present. In order of increasing frequency, at constant temperature, the recorded loss peaks can be assigned to Interfacial Polarization (IP) known also as Maxwell-Wagner-Sillars (MWS) effect, glass/rubber transition (α -mode) and to local rearrangement of polar side groups of the polymer chain (β -mode). Attributing dielectric peaks to specific relaxation mechanisms is not an easy procedure, which cannot be carried out by simple observing the isothermal plots of Figures 2–4. In Figure 5 comparative plots of the real and imaginary part of electric modulus versus frequency, for all the examined composites, at constant temperature ($T = 150^\circ\text{C}$) are shown. Two relaxation processes, located in the low and inter-

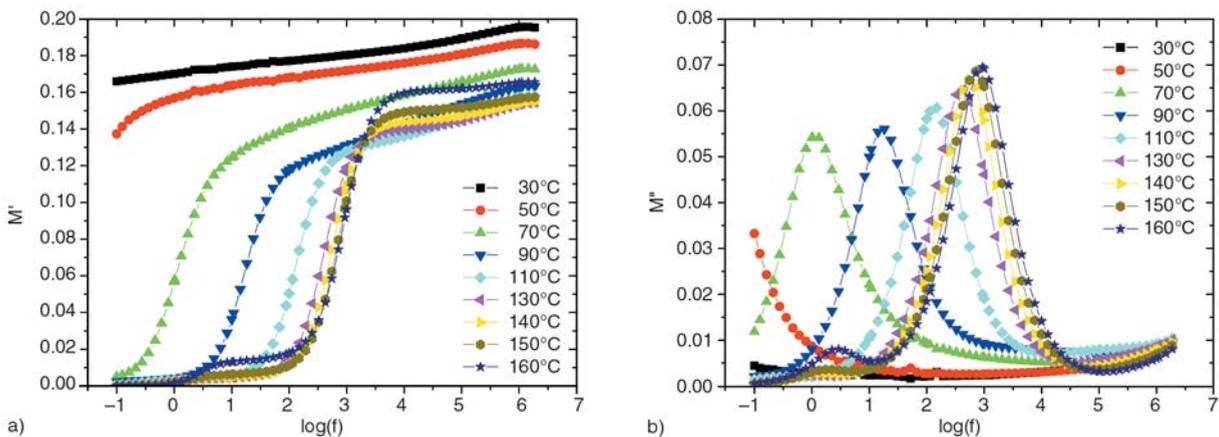


Figure 2. Real (a) and imaginary (b) part of electric modulus vs. frequency for the specimen with 10 phr in BaTiO₃ content

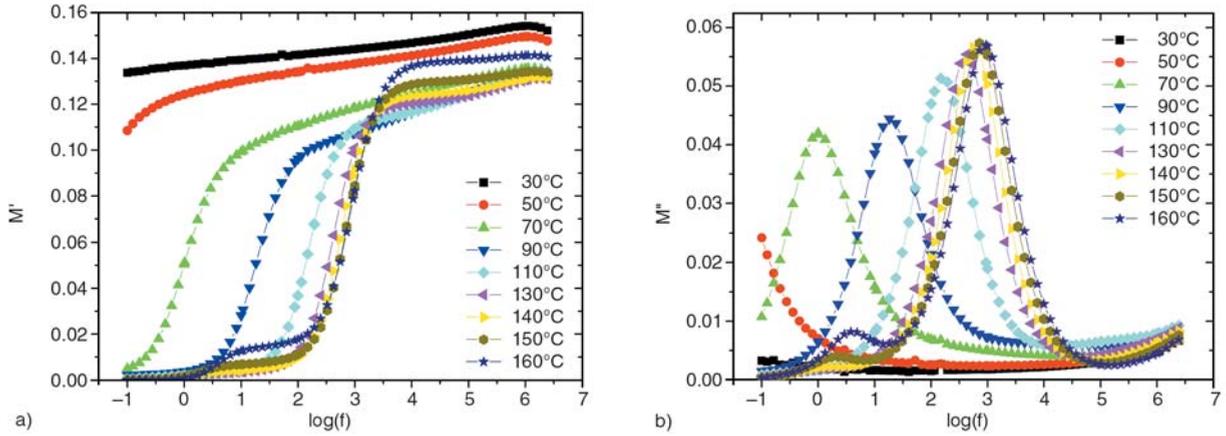


Figure 3. Real (a) and imaginary (b) part of electric modulus vs. frequency for the specimen with 20 phr in BaTiO₃ content

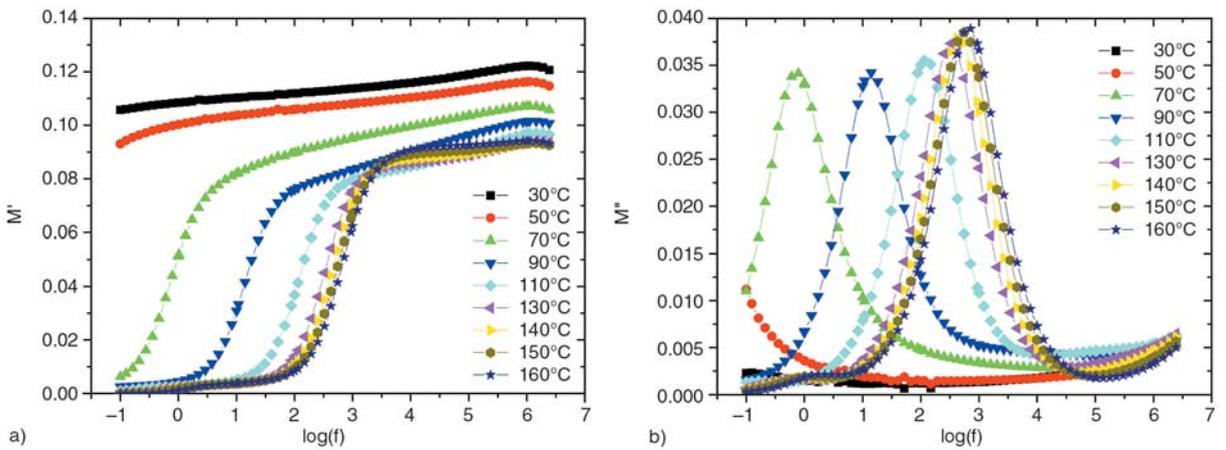


Figure 4. Real (a) and imaginary (b) part of electric modulus vs. frequency for the specimen with 50 phr in BaTiO₃ content

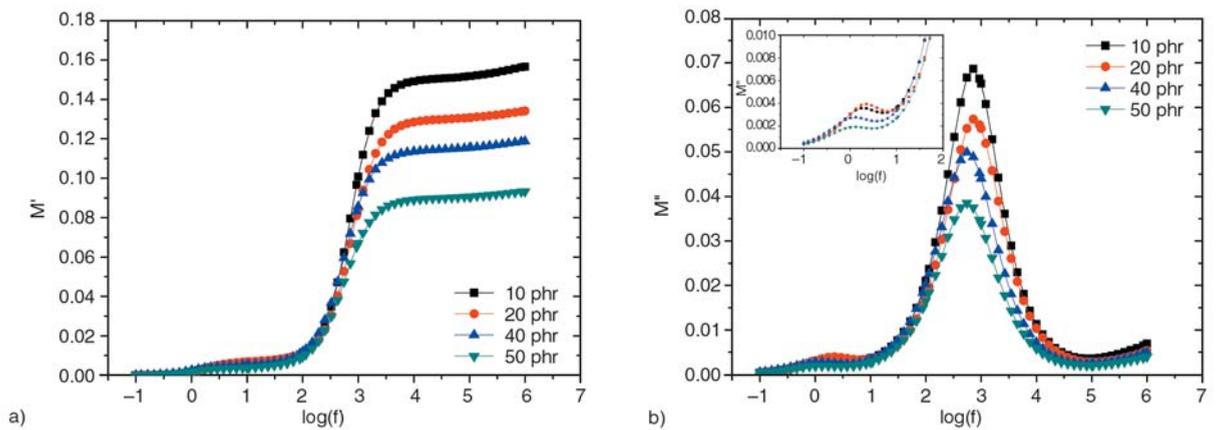


Figure 5. Real (a) and imaginary (b) part of electric modulus vs. frequency for all tested specimens at 150°C

mediate frequency range, are clearly recorded. Increase of the BaTiO₃ content results in lower values of M' , implying that the real part of dielectric permittivity increases with ceramic filler. It is interesting to note that the more intense relaxation peak, occurring in the intermediate frequency region,

appears to be dependent on the BaTiO₃ content. Its loss maxima diminish monotonically with filler concentration. In Figure 6, Cole-Cole plots of all composite specimens, at $T = 150^\circ\text{C}$, are depicted. In the Cole-Cole presentation relaxation mechanisms become evident via the formation of com-

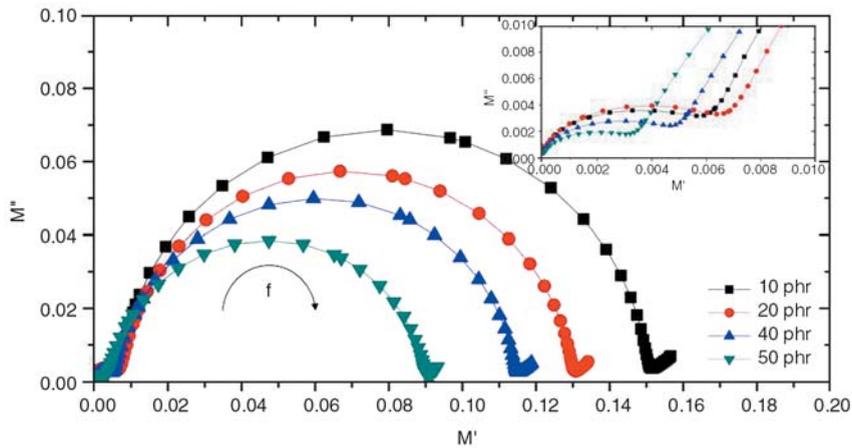


Figure 6. Cole-Cole plots for all tested specimens at 150°C

pleted or even uncompleted semicircles. In our case two distinct semicircles are clearly formed, while in the high frequency edge a tendency for the formation of a third semicircle is present. In the low frequency range the trace of dielectric data forms a small semicircle, the beginning of which coincides with the origin of the graph. So, it can be concluded that no other process, slower than this, is present in the examined composite systems.

It is well known [14–16] that MWS effect appears in complex systems exhibiting electrical heterogeneity, due to the accumulation of charges at the interfaces of the system. Dielectric permittivity of BaTiO₃ is remarkably higher than that of epoxy resin. Thus unbounded charges, arising from the stage of specimens’ preparation, form large dipoles at the polymer matrix – ceramic inclusions interface. The induced dipoles encounter difficulties to follow the alternation of the electric field and thus the resulting relaxation process occurs in the low

frequency region and at high temperatures, being the slowest from all the recorded processes.

α -relaxation process is associated with glass to rubber transition. If sufficient thermal energy is provided to the polymer, then large parts of amorphous macromolecular chains can relax simultaneously in a cooperative motion. The whole process is characterized by glass transition temperature (T_g), which is considered as the temperature where transition occurs. In polymer matrix composite systems, glass transition is related to the chemical structure of the polymer chains and in many cases to the type of the employed filler. As a rule of thumb, glass transition temperature is taken as the temperature at which the α -relaxation loss peak is recorded in the dielectric spectrum at constant frequency equal to 0.1 Hz [15, 17–19]. In Figure 7 loss modulus index (M'') as a function of temperature, at constant frequency, for all the examined systems is presented. It is interesting to note that the intensive peak which is present

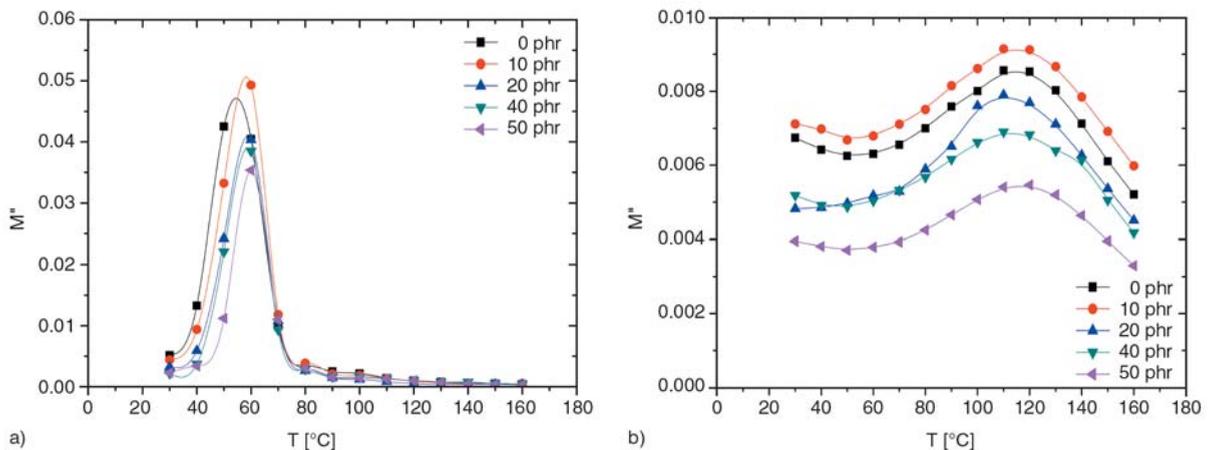


Figure 7. Imaginary part of electric modulus as a function of temperature, for all the tested specimens, at (a) $f = 0.1$ Hz and (b) $f = 1$ MHz

in all specimens and is recorded in the intermediate frequency range (Figures 2–4) is now located at 60°C, when $f = 0.1$ Hz, Figure 7a. This value is very close to the glass transition temperature of the polymer matrix, as determined via DSC measurements, Table 1. Thus it is reasonable to suggest that the relatively slow dielectric relaxation process recorded in the medium frequency range of dielectric spectra corresponds to glass/rubber transition. The evolution of the α -mode peak with temperature becomes evident with the shift of loss maxima to higher frequencies, Figures 2–4. Recalling Figure 5b, the concentration of BaTiO₃ particles influences a systematic variation of the α -mode loss maximum. The intensity of the peak diminishes with the increase of BaTiO₃ particles and at the same time slightly shifts to lower frequencies at the higher concentrations. From the definition of electric modulus, Equation (1), decreasing values of (M'') correspond to enhanced values of dielectric loss index (ϵ'') and thus, to more pronounced relaxation phenomena. Increased values of dielectric loss signify that the relative effect consumes more energy. In addition the peak shift rate of the same process, in the loss modulus vs. frequency graphs (Figures 2–4), reduces at temperatures higher than 100°C. The above remarks indicate that the kinetics of α -relaxation process is modified by the amount of ceramic particles and in particular the whole process becomes slower as the amount of ceramic filler increases. Glass transition temperature is expected to increase slightly with BaTiO₃ content. Variations between glass transition temperature (T_g) of bulk polymer and thin polymer films on a ceramic substrate or polymer nanocomposites with ceramic inclusions have already been observed and reported [20–22]. These variations have been attributed to interactions occurring between the polymer and the nanoinclusions or substrate. The length scale of the ceramic constituent (from substrate to nanoinclusions) is highly diverging, starting from nanometers and reaching millimeters or even centimeters. If polymer/ceramic interactions are able to appear in these two diverging edges of length scale, then it is reasonable to suggest that the same type interactions could occur at the intermediate level of micrometers. However, these initial indications should be further confirmed by additional experimental work, which should be carried out in the near future.

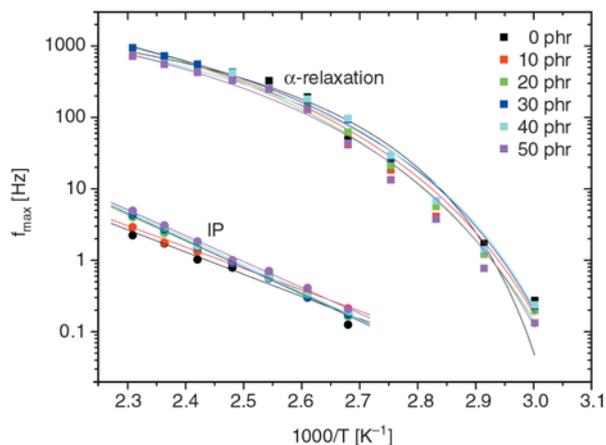


Figure 8. Loss peak position as a function of the reciprocal temperature for the MWS and α -relaxation processes, for all the examined systems

In the high frequency edge all specimens exhibit a tendency for the formation of an extra loss peak, Figures 2–6. This process, which is the faster from all the recorded mechanisms, can be seen only at high frequencies. In Figure 7b, at constant frequency of 1 MHz, a broad peak can be observed, which is attributed to local motions of polymer’s polar side groups (β -mode).

The temperature dependence of the loss peaks positions, for both IP and α process is depicted in Figure 8. As it can be seen interfacial polarization follows the Arrhenius type temperature dependence, which is described by Equation (2):

$$f_{\max} = f_0 \exp\left(-\frac{E_A}{k_B T}\right) \quad (2)$$

where E_A is the activation energy, f_0 pre-exponential factor and k_B the Boltzmann constant.

On the other hand α -mode can be described by means of Vogel-Fulcher-Tamann equation, which considers that relaxation rate increases rapidly at lower temperatures because of the reduction of free volume, as expressed by Equation (3):

$$f_{\max} = f_0 \exp\left(-\frac{AT_0}{T-T_0}\right) \quad (3)$$

where f_0 is a pre-exponential factor, A a constant (being a measure of the activation energy), and T_0 Vogel temperature or ideal glass transition temperature. Activation energy calculated via linear regression of Equation (2), as well as all fitted parameters of Equation (3), for each of the tested

Table 2. Values of activation energy, calculated via Equation (2), for the IP process, and fitting parameters of Equation (3) for α -mode

Sample	α -mode		IP/ E_A [eV]
	T_0 [K]	A [K ⁻¹]	
Epoxy	284	293	0.612
Epoxy + 10 phr BaTiO ₃	285	518	0.592
Epoxy + 20 phr BaTiO ₃	287	600	0.727
Epoxy + 40 phr BaTiO ₃	298	390	0.750
Epoxy + 50 phr BaTiO ₃	302	478	0.753

samples are listed in Table 2. Activation energy of the IP (MWS) process increases with the content of BaTiO₃ denoting the increase of heterogeneity. The parameter T_0 increases also with the filler content, being in accordance with the experimentally determined values of glass transition temperature.

The real part of dielectric permittivity (ϵ') vs. temperature, at constant frequency $f = 10$ Hz, is depicted in Figure 9. The variation of permittivity with temperature becomes significant in the range of 110–140°C. At lower temperatures (ϵ') attains rather constant values, while at temperatures higher than 100°C increases rapidly (up to 18 times) with temperature and composition showing a maximum at ~140°C and then vanishes. Pure epoxy and the composite system with the maximum employed content in BaTiO₃ (50 phr) do not exhibit a peak. The relatively high values of pure epoxy sample in the high temperature region could be attributed to a weak MWS effect (since Interfacial Polarization is almost always present in polymers due to additives, plasticizers etc) and to the possible occurrence of electrode polarization. It is well known [23] from

dielectric theory that polarization is proportional to the real part of dielectric permittivity (ϵ'). Thus any variations occurring in (ϵ') spectrum, reflects changes in the polarization of the composite system. At this temperature range the increase of (ϵ') is attributed to the enhanced mobility of large parts of the polymer chains and to the co-operating contribution of IP effect in the composite systems. However, the superposition of these two effects cannot explain the formation of the peaks.

On the other hand BaTiO₃ is a typical ferroelectric material, exhibiting a ferroelectric to paraelectric phase transition at the characteristic temperature of ~140°C [24], which is known as Curie temperature (T_C). Below T_C , BaTiO₃ is consisted by domains showing spontaneous polarization, due to the lower symmetry of the crystal unit cell (tetragonal) in comparison to the unit cell in the paraelectric phase (cubic). In the present study the employed filler is polycrystalline BaTiO₃ and is composed by a large number of grains and domains with different orientation. Under the influence of the electric field the dipole moment, at least of a part, of these domains will be able to follow the applied field contributing to the overall polarization of the system. However, as the temperature is approaching T_C a disorder to order transition takes place in the crystal structure of ceramic filler, which becomes evident through the formed peaks in Figure 9. In the paraelectric phase BaTiO₃ does not exhibit spontaneous polarization and thus a decrease in the real part of dielectric permittivity occurs. This transition is referred as first order phase transition [24, 25] and characterized by the appearance of local maxima in some physical properties, as a function of temperature, in ferroelectric materials.

Since the applied electric field is low, it is reasonable to expect [26] a linear relation between the achieved polarization (P) and the intensity of the field (E), which under the assumption of quasi-

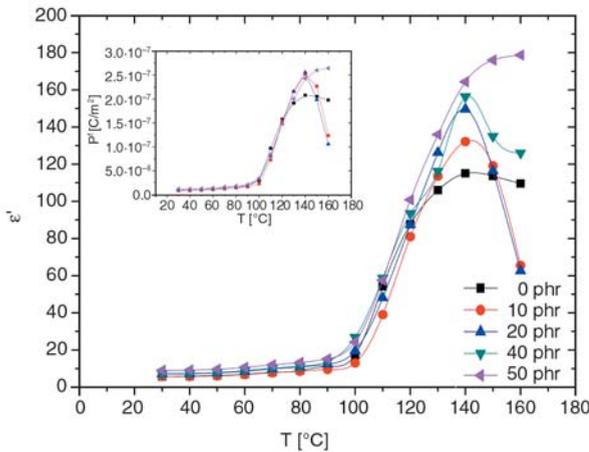


Figure 9. The real part of dielectric permittivity as a function of temperature, for all the tested specimens, at $f = 10$ Hz. Inset depicts the corresponding variation of polarization.

static conditions takes the form [27] given by Equation (4):

$$P^f = \epsilon_0(\epsilon' - 1)E \quad (4)$$

where P^f is polarization at constant frequency and ϵ_0 is the permittivity of free space. The inset of Figure 9 depicts the variation of polarization with temperature for all the tested systems, at constant frequency.

The ‘switch’ type performance of the, embedded in the polymer matrix, ceramic particles of BaTiO₃ lend functional behaviour to the whole composite structure. Optimum functional behaviour is achieved for the 20 phr in BaTiO₃ composite, since at higher BaTiO₃ concentrations IP (MWS) effect dominates in the dielectric spectra of the composites, diminishing thus their functionality. The latter becomes evident by the absence of the relative peak in the spectrum of the composite with 50 phr in BaTiO₃. As adaptive or smart materials are considered composite systems, which are able to vary some of their properties (such as shape, natural vibration frequency, damping coefficient, polarization etc.) in a controllable fashion, under the influence of an external stimulus [27–30]. In accordance with the previous definition, polymer matrix composites incorporating ferroelectric elements can be considered as a suitable base for the development of smart systems, conditioning that critical temperature (T_C) lies within the operational temperature range of the composites.

4. Conclusions

The dielectric response of polymer matrix – ceramic BaTiO₃ composites, in a wide frequency and temperature range, was investigated in the present study. Relaxation phenomena were found to be present in all the examined systems. From the slower to the faster one, the recorded processes were attributed to interfacial polarization or MWS effect, glass to rubber transition of the amorphous polymer matrix and local motions of polar side groups of the macromolecular chains. Finally, the functionality of the filler, arising from the thermally activated disorder to order transition, offers a ‘switch’ type polarization response to the composites with low or moderate BaTiO₃ content in the vicinity of the critical temperature (T_C).

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