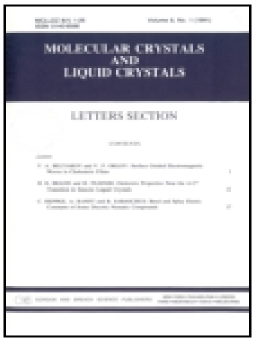

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Dielectric characterization of lead zirconate-titane(PZT) /polyurethane(PU) thin film composite: Volume fraction, frequency and temperature dependence

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ABSTRACT
The Lead Zirconate-titane(PZT) ceramic is known by its piezoelectric characteristic, but also by its stiffness. The use of a composite based on a polyurethane (PU) matrix charged by a piezoelectric material, enable to generate a large deformation of the material, therefore harvesting more energy. This new material will provide a competitive alternative and low cost manufacturing technology of autonomous systems (smart clothes, car seat, boat sail, flag …). A thin film of the PZT/PU composite was prepared using up to 80 vol. % of ceramic. Due to the dielectric nature of the PZT,inclusions of this one in a PU matrix raise the permittivity of the composite. For the most of industrial applications, the composite will not be used at room temperature, and as the energy harvested from this new materials have a direct relation with their permittivity we have made a study about the variation of the permittivity at different temperature and frequencies.

KEYWORDS
Piezoelectric; dielectric; composite; PZT; PU

1. Introduction

Nowadays there has been an increasing number of research about new materials used for multifunctional device, sensor and actuator applications [1], especially, piezoelectric ceramics procuring high mechanical coupling coefficients[2], high piezoelectric coefficients and low dielectric losses [3], although, the polymers have an attractive properties too, with their flexibility, ease to fabricate and high breakdown strength [4].

For those reasons, the researchers thought of the use of a new material, a composite ceramic/polymer. This type of composite has high capability of energy storage and can be used in capacitors and energy storage devices [5].

The connection between the composite phases controls the properties of the composite and also the process employed in the manufacture [6, 7]. In other words the distribution and the grain size of the fillers should be controlled.

The piezoelectric ceramic particles most used in ceramic/polymer composites is lead zirconate-titanate, $\mathrm{Pb(ZrxTi1-x)O_3}$ or PZT [8]. The use of an electrostrictive polymer had successfully demonstrated to be useful in piezoelectric, and during the last years many

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researchers have been interested into this material especially the Polyurethane (PU), which have very important properties such as: excellent mechanical properties, good biocompatibility, design flexibility, light weight and low cost, the variation of the hard and soft segment of this elastomer endows the mechanical and dielectric properties and due to which the dielectric constant could reach high values as a function of the electric field and temperature, furthermore the PU have many application especially medical devices and automotive sensors and this makes the material very attractive for a lot of electromechanical applications.Many researcher works are interested on the enhancement of the energy harvested from this electrostrictive polymer [9, 10] the combination of the PolyurethanePU and the Lead Zirconate-titane PZT appears as a good compromise between the two material's properties. This composites exhibit a high flexibility, a low density but also a high piezoelectric coefficient.

The need of using sensors and actuators in conditions with high temperature requires a large study of the temperature dependence of the composite characterization. In this work, composites with different percentage volume fraction of PZT were prepared. Indeed dielectric behavior was investigated at different temperature in order to build a mathematical model which can predict the dielectric constant at any temperature.

2. Experimental procedure

2.1 *Fabrication of the PZT/PU composite films*

Composites with different percentage volume fraction of PZT were prepared asthefollowing: Initially the PU pellets were dissolved in 15 mL of THF (tetrahydrofuran) under magnetic stirring at the room temperature. After the complete dissolution of the PU, the powder of PZT was added to the mixed under magnetic then ultrasound stirring. Finally the mixture was tape casted by Ductor Bade process and dried at room temperature. Samples were then metalized by gold evaporation. The electrode thickness is about 100nm.

2.2 *Polarization process*

The sample is heated in silicone oiluntil 60°C, in the same time a bias voltage applied increases up to saturation. At this stage the external field is fixed at about 2000V/cm during the heating and then we maintain the same field during the cooling too until room temperature. In one hand high temperature helps to easily orient diploes and by the other hand, the cooling allows them to maintain their position fixed into the matrix. More the matrix contains dipoles oriented in the same direction the more we harvest energy from it.

The polarization is a dipole moment which is created when a dielectric material is placed in an electric field, there are many types of polarization that could be occur during the application of the field, this latest change with frequency and temperature [11].

2.3 *Scanning electron microscopy (SEM)*

In order to behold the PZT dispersion into the polymer matrix which was prepared at first section, we used the SEM technique (scanning electron microscopy); this one produces images of sample's sectional and surface views with very high resolution. The sample they should be conductive and must also be of an appropriate size to fit in the specimen chamber

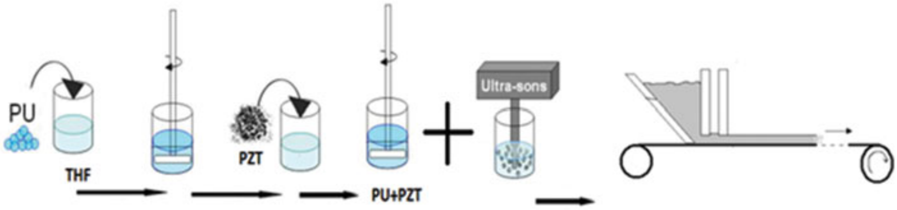


Figure 1. Procedure of preparation of the composite.

2.4 *The dielectric constant measurement*

A perfect dielectric material is a non-conductive which can bepolarizedunder a biasing effect of an external electric field. These phenomena result macroscopically by the occurrence of charges at the surface of the material. It results from the movement of the different entities in the sample considered (electrons, ions, dipole …). However, it is not easy to predict the response of certain materials to an external applied field.The permittivity is the parameter that relates polarization to the applied field and it has a direct relationship with the recovered energy of the piezoelectric material as shown by the following equation:

$$W = 1/2\varepsilon_0\varepsilon_r E^2 \tag{1}$$

Where E is the voltage between electrodes, the effective dielectric constant is obtained out eventually [12], εr is the relative permittivity and ε0 is the permittivity of free space. The magnitude of ε' (or the dielectric constant εr) indicates the ability of thematerial to store energy from the applied electric field. A parallel plate capacitor with area S andthickness e has a capacitance given by

$$\varepsilon_r = C_p * e/(S * \varepsilon_0) \tag{2}$$

The capacity is measured rresponds to the measuring tape to the meter. The sample is a rectangular active areaof 400 mm.

3. Results and discussion

3.1 *Scanning electron microscopy (SEM)*

Figure 2 (a to d) illustrate the scanning electron microscopy (SEM) images of sectional view of ceramic/polymer composite with 50, 60, 70 and 80% respectively of PZT fillers bended in PU. The microstructure of PZT/PU composite illustrated by SEM images indicates clearly the presences of PZT grains in light region which are more dense and compacted while the dark regions are related to PU polymer with a smooth surface. Therefore more the PZT fraction increases the light region becomes more present. Besides the PZT/PU composite structure indicatesan uniformity of the white dots for which are homogenously dispersed within the PU matrix into the four compositions.

4. Mathematical models of dielectric constants

There are many theoretical studies on dielectric constant of composites which describe the dependence on the volume fraction of the filler particles, the dielectric constant of polymer and filler and the possible interaction between both constituents.In the present work, the theoretical dielectric constant was calculated according to various models and compared to the

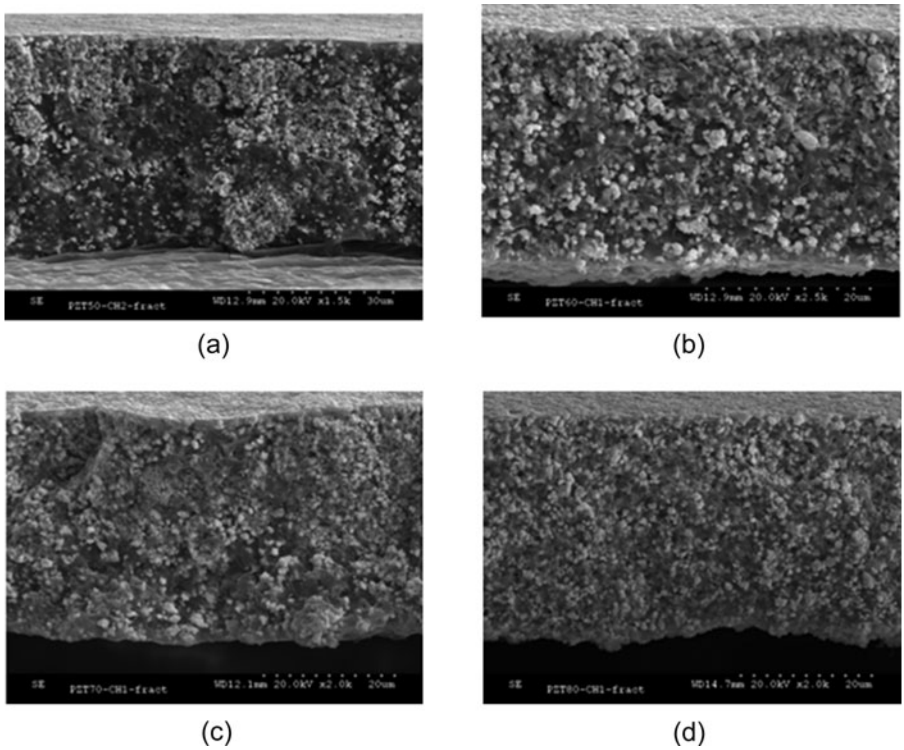


Figure 2. Scanning electron microscopy images of samples with different volume fraction of PZT (a): Dispersion of 50% ofP PZT into the matrix (b): Dispersion of 60% of PZT into the matrix (c): Dispersion of 70% of PZT into the matrix (d): Dispersion of 80% of PZT into the matrix.

experimental resultswhich were made by an HP Agilent 4194A Impedance/Gain-Phase Analyzer and the basic measurement accuracy is about 0.17% (all the dielectric measurements in this work were made as the same way); Fig. 6 depicts the variation of experimental and theoretical dielectric constant for different volume fractions of PZT at room temperature and at 1KH. In this study the following equations were used to calculate the effective relative permittivity of the PZT/PU composites. In1892, Rayleigh developed an equation which describes the dispersion of homogeneous spheres in a continuum medium [13], This model consider the composite systems as polymer matrix where spherical conclusions are embedded, but it doesn't take into account the interactions between particles neither the size of the inclusions. Furukawa et al. [14] have concluded another model when the dielectric constant of the matrix is much low compared to that of the fillers, but not the morphology, the effective medium theory (EMT), include a ceramic morphology fitting factor"n." The small value of n indicates the filler particles to be in near-spherically shape, while a high value of indicates largely non-spherically shaped particles. In our case we have taken $n = 0.45$. Yamada et al. [15] have described the theoretical effective dielectric constant also, by a model that contains a morphology form factor and the volume fraction of the PZT.

Based on Fig. 3 we can conclude that the model which describes the best the behavior of the composite's constant dielectric is the EMT model, in other hand there are many other parameters that influence the behavior of the composite dielectric constant, one of this parameters is temperature.

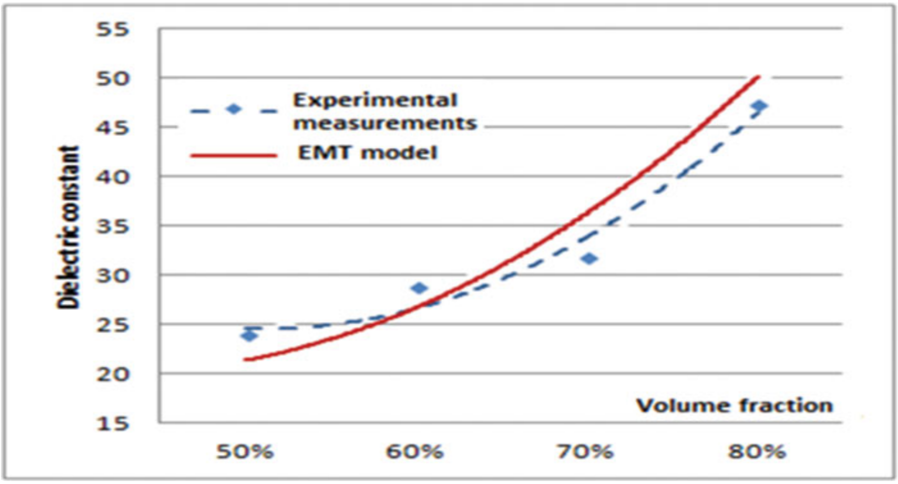


Figure 3. Concentration dependent dielectric constant of PZT/PU

We have made the same measurements as the last one for the composite which contain 80%Vol. of PZT the dielectric constant for different frequency but at different temperature, we have observed that this last parameter influence the dielectric constant behavior.

As seen before dielectric parameters were measured for each composition and it was fined that the high ones correspond to the composite which contain 80% of PZT fillers (Fig. 3). Therefore this study will be focused on the composition with 80 vol. % of PZT. Dielectric spectroscopy measurements were carried in 1 KHz at room temperature.The poling process was conducted at a field between 100 and 500 KV/cm, in 20Hz and at a room temperature.

The composite is a heterogeneous material, the determination of the apparent dielectric constant of this type of material is a little bit complicated, and so to simplify it, the system can be described by an apparent dielectric constant, which is based on the composite components, the volume fraction of the added particles and their spatial distribution on the matrix. According to Hashin and Shtrikman[16], the apparent permittivity is an essential property which characterizes the physical situation of the dielectric composite, generally we don't have any information about the material expect that it is homogenous and isotropic, so the randomness and the connectedness properties of the structure inside the material should be extremely studied. In our case the material is made of monodisperse inhomogeneities of a permittivity $\epsilon 1$ which are randomly dispersed on a matrix of a permittivity $\varepsilon 2$ with a volume V.

The dielectric constant increases by increasing the added PZTvolume fraction but according to Figure 4, the disadvantage of adding PZT grains is that the composite becomes more and more stiff, the Young modulus increases, and the elastic domain of the composite is reduced, measurements were made by a Lhomargy DY 30 machine having an uncertainty about 0.5. Figure 6 describes the behavior of the two phases of the composite according to the frequency; the relative permittivity of the two components decreases with the increase frequency, thus we can explain the dependence of the composite with frequency (Figure 6).

Figure 6 shows the variation of the apparent dielectric constant of the composite according to frequency for compositions for different volume fraction of PZT particles from 50% up to 80%, based on this figure, we can note that the dispersion increase with the increasing volume fraction of the fillers, this could be caused by the space charge effects, indeed we remark that the dielectric constant increase with the increase of the particles percentage, but it decrease with the increasing frequency. Obviously in this effective medium the correlation between the

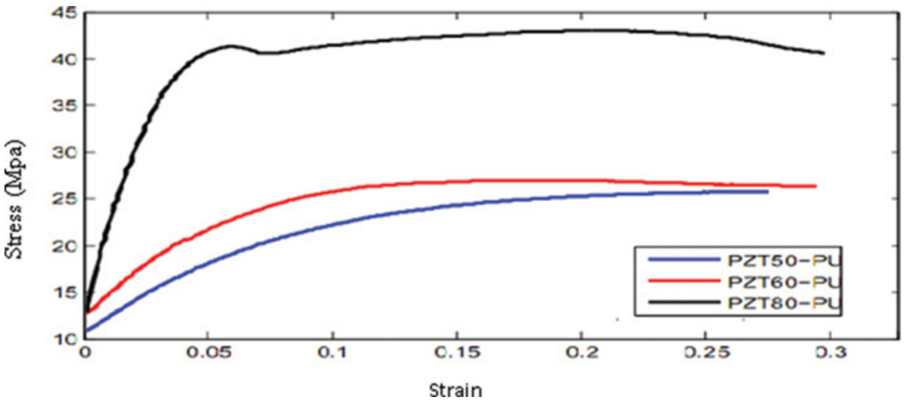


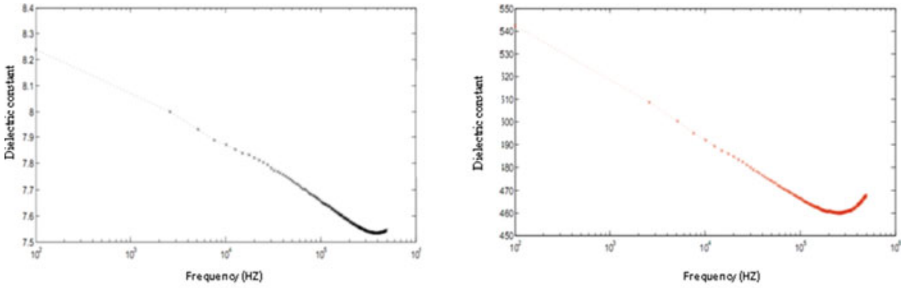
Figure 4. Young modulus for different compositions.

particles increases with the increase of their percentage, also we can note that the permittivity and the losses dependence with frequency is more important when their volume fraction increases, this is because of the increase of the two types of polarization, the interfacial charges polarization and the intrinsic dipoles polarization on the composite. This phenomenon generally happens on the heterogeneous systems like PZT/PU composite, this is because of the accumulation of the electric charges on the interface boundaries and the formation of large dipoles or cluster of ceramics, in this case the polarization degree increase with the increasing percentage of PZT into the composite, and by the way the dielectric constant increases as well.

Based on the same figure wecan note thatthe dielectric constant decreases with the increasing frequency and it is the same for the tow components also (Figure 5),this phenomenon could be originate from the dielectric relaxation of ceramic (PZT), and the interfaces in the composite. Concerningthe polymer matrix, the alternation of the elastic andthe movement of the domains walls[17, 18, 19], at high frequency region could be a reasonof the decrease of its dielectric constant with frequency, another reason is the relaxation process in the PU networks, its sensitivity is given by the chemical structure of the polyurethane chains and by the chemical cross-linking structure of the hard domain, the dependence of the dielectric constant on frequency can be obtained from the Maxwell–Wagner model:

$$\varepsilon' = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty)/\left(1 + \omega^2\tau^2\right) \tag{3}$$

where ε' is the dielectric constant, ε_∞ is the dielectric constant at infinitely high ε_s frequency,is the dielectric constant at low frequency, ω is the frequency. τ is the relaxation time, it describes



(a) (b)

Figure 5. The variation of the dielectric constant of the PZT (a) and PU (b) according to the frequency.

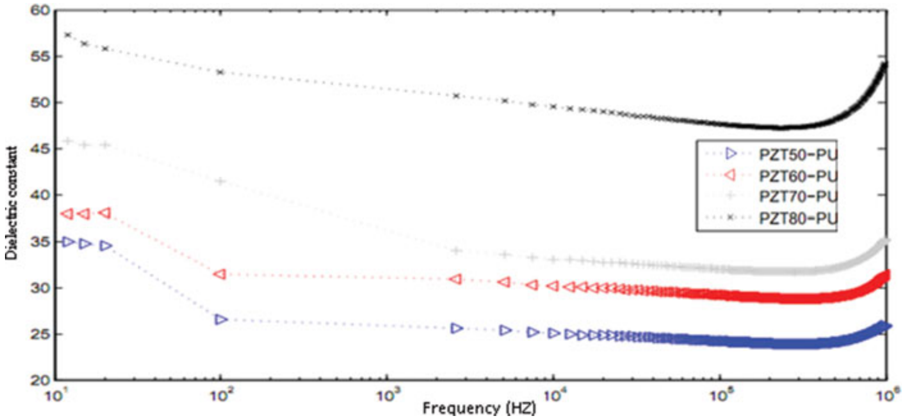


Figure 6. The variation of the dielectric constant of the PZT/PU composite according to frequency.

the time needed for dipoles to have the same orientation as the applied field, Or the time required for dipoles to be disoriented after removing the electric field.Studies showed that the relaxation time is temperature dependent because the movements become faster as the temperature increase.

As mentioned above, the relaxation time is temperature dependent, thus the permittivity is too; therefore it is more appropriate to writeequation (4) as Debye's model does:

$$\varepsilon_r(\omega, \theta) = \varepsilon_\infty(\theta) + (\varepsilon_s(\theta) - \varepsilon_\infty(\theta))/(1 + j\omega\tau(\theta)) \tag{4}$$

Figures 6 and 7 depict the variation of the real and imaginarily (loss) permittivity, according to the temperature, from the ambient temperature up to 250°C at a frequency of 10KHz, it is clearly remarkable that the losses increase gradually with the increasing temperature, that can be explained by the increase of the interfacial polarization, because of the accumulation of the charges in the interfacial electrodes of the composite and/or amorphous crystalline interfaces of the polymer[20]. On other hand the mobility of molecules increases with temperature, so

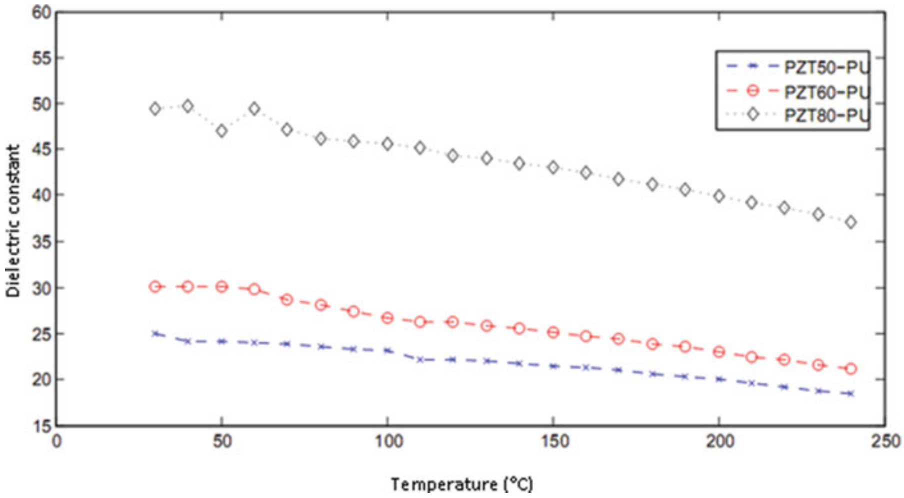


Figure 7. The variation of the dielectric constant of the PZT/PU composite according to temperature.

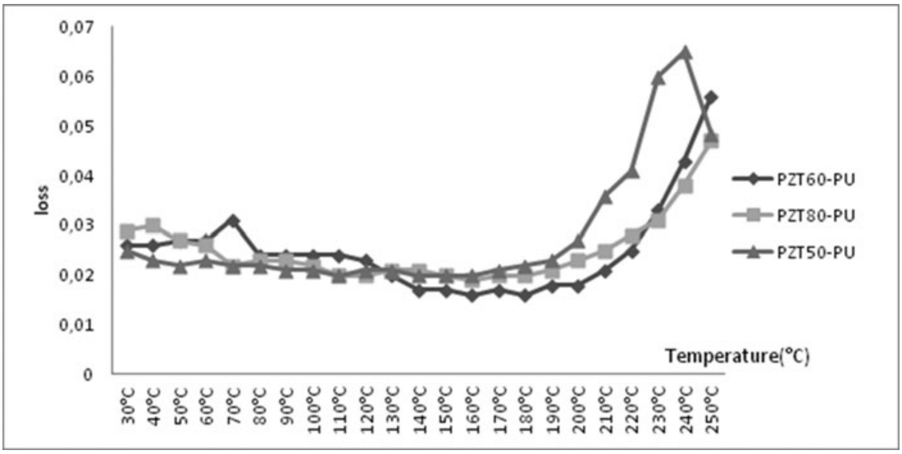


Figure 8. The variation of the dielectric loss of the PZT/PU composite according to temperature.

at high frequency the maximum loss is at high temperature because the time required for the molecules align in the direction of the electric field is not sufficient.

It is clear that the temperature affect the dielectric properties, concerning the polymer matrix, at high temperature where the thermal agitation is enhanced, the intermolecular forces between the polymer chains is broken thus the polar groups (PZT particles and clusters) are more free to move and change their orientation, so they lose their polarization, on the other hand at low temperature, the polar groups are fixed inside the polymer matrix. During the permittivity measurements, the electronic and atomic polarizations are spontaneous, whereas the dipole polarization is directly affected by temperature; in fact the relaxation time (τ) decreases with the increasing temperature, this is because the polymer segment couldfollow the oscillating electric field [21, 22].

As a result of what we have explained before, figure 6 depicts the variation of the dielectric constant of the whole composite according to temperature, we note that the relative permittivity decreases with the increasing temperature; this could be explained by the fact that the molecules have more thermal energy and then the thermal motion is greater. This cause a deviation of the dipoles from the perfect alignment with the field to a random direction otherwise the molecules are less closely aligned with each other. Furthermore, at high temperature, the PZT grains could be changed, this fact can also be the origin of the modification

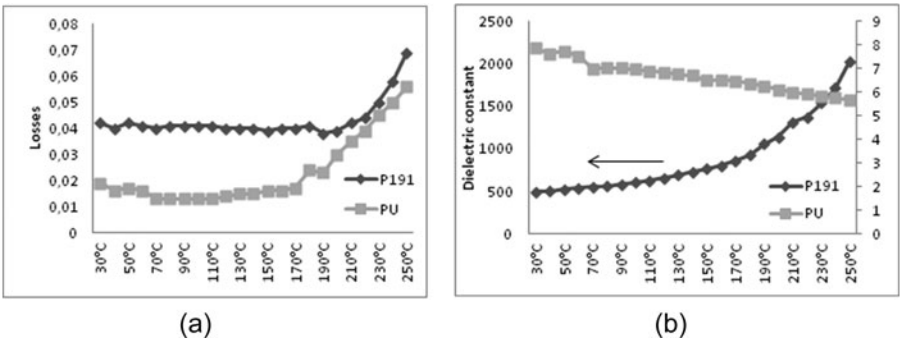


Figure 9. The variation of the dielectric constant of the PZT (a) and PU (b) according to temperature

of the dielectric response of the composite. However, this does not mean that, at low temperature, the permittivity will necessarily increases, because the permittivity change especially with structure changes, that why it depends on the phase boundaries which change with temperature also [23].The relative permittivity of the composite has the same behavior as the host material (polyurethane) (Figure 8), but it is enhanced by the added ceramic particles. In other words, the behavior of the relative permittivity of the composite depends on the behavior of the two phases; the matrix and the fillers

5. Conclusions

A composite based on a polymer (PU) matrix charged by 50, 60, 70 and 80 vol. % of ceramic fillers (PZT) was prepared. The dielectric properties were examined, experimental results were compared to several theoretical predictions among various models, and they were comparable with the EMT model. It was demonstrated that the permittivity depends on many factors especially the volume fraction of the fillers, the frequency which have a direct effect on the polarization of the dipoles and the temperature which could change the macroscopic structure of the composite and thus the resulting permittivity. We have found that the effective dielectric constant of the composite decreases with frequency, because the degree of polarization decreases at high frequencies. The effective permittivity decreases also with the increasing temperature because the structure of the composite changes especially the polymer matrix.

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