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EFFECTS OF TEMPERATURE AND NANOPARTICLES ON DIELECTRIC PROPERTIES OF PVC

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In this paper, the influence of the temperature, in the range 310 – 340 K, on the dielectric behaviour of plane samples of polyvinyl chloride (PVC) without and with inorganic nanofillers of SiO_2, TiO_2 and Al_2O_3, is analyzed by dielectric spectroscopy over a frequency range of 10^{-2} – 10^6 Hz. Differences are observed in dielectric behaviour of the tested samples, depending on the presence and the type of the tested inorganic nanofillers, as well as on the temperature at which the measurements were performed. The obtained results emphasize low frequency dispersion for both unfilled and nanoparticle filled PVC, having the characteristic frequency increasing with the temperature. The presence of TiO_2 nanoparticles in PVC leads to lower loss tangent values at all tested temperatures.

Keywords: PVC, nanodielectrics, dielectric spectroscopy

1. Introduction

PVC is one of the most used polymer in an extremely broad range of applications, including windows frames, medical containers for blood, heart bypass sets, wire harnesses and modules for auto vehicles, consumer goods as bags, bottles, toys, televisions, as well as many electrical applications from cable insulations to computers and household electrical appliances [1]. The features which recommend PVC as general purpose plastic mainly reside from its amorphous structure with polar chlorine atoms in the molecular composition, which determines different performances with respect to other polymers such as polyethylene (PE) or polypropylene (PP), which have only carbon and hydrogen atoms in their molecular structures. Among the remarkable physical properties of PVC due to its structure are fire retarding properties, durability (high resistance to oxidation), oil/chemical resistance, mechanical stability, and good ability to mix with various other substances. Besides, PVC has excellent electrical insulation characteristics as high resistivity and high dielectric strength. However, the dielectric losses of PVC are quite high and they become even higher due to the

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use of plasicizers needed to enhance its softness diminishes the electrical resistivity and increase the permittivity.

In the last decade, nanostructured polymer dielectrics have known an increased attention from the researchers working in the field of dielectrics all over the world [2-9], aiming to improvement the polymer properties (electrical, thermal, mechanical, etc). The main reason for this huge interest are the promising results reported in literature, which recommend these new materials for industrial applications ranging from dielectrics for high energy storage capacitors up to electrical insulations with low losses and high breakdown resistance [7, 8]. These nanodielectrics are obtained by mixing polymers with nano-fillers, having at least on dimension up to 100 nm and a concentration usually lower than 10 wt%. PVC was one of the main polymers which were mixed with nanoparticles to create improved dielectric materials [2]. Thus, among the PVC nanocomposites for which improved properties were reported are nanoclay PVC composites [10], PVC with multi-walled carbon nanotubes (MWCNT) [11], or ZnO/PVCnanocomposites [12].

In our previous research on PVC nanocomposites we studied the influence of γ radiations on the dielectric behaviour and on the thermal stability of PVC with inorganic nanofillers as SiO_2, TiO_2 and Al_2O_3 [13], while the influence of water, electric field and ionizing radiation on electrical properties of PVC insulations was studied in [14].

In this paper, the influence of the temperature, in the range 310 – 340 K, on the dielectric behaviour of PVC with and without inorganic nanofillers is analyzed by dielectric spectroscopy over a frequency range of 10^{-2} – 10^{6} Hz.

2. Experimental

Plane samples made of unfilled PVC and of PVC filled with nanoparticles of SiO_2, TiO_2 and Al_2O_3, having the filler concentration of 5 wt%, were tested in this study. The polymer matrix was flexible PVC, containing 25% plasticizer. The average diameter of the SiO_2 and of the TiO_2 nano-particles was 15 nm while the average diameter of the Al_2O_3 nano-particles was 40 nm. The nanocomposite samples for electrical tests performed in this study were plaques of square shape (10 x 10 cm^2) having the thickness of 0.5 mm.

The real and the imaginary parts of the permittivity (ε_r' and ε_r'', respectively) and the loss tangent (tan δ) were determined by dielectric spectroscopy (DS) using a Novocontrol ALPHA-A Analyzer in combination with an Active Sample Cell ZGS, over the frequency range 10^{-2} – 10^{6} Hz. The measurements were performed at three temperatures (310 K, 320 K □i 340 K) in two ways: by increasing the temperature from 310 K to 340 K, and by decreasing the temperature from 340 K to 310 K. In both cases, the samples were maintained

30 minutes at each temperature, under air flow, before being measured. Two disks of 40 mm diameter were cut from one plaque of each formulation and tested by dielectric spectroscopy.

3. Results and discussion

The frequency variations of ε_r' and ε_r'', at 310 K and at 340 K, on samples of neat PVC and of PVC nanocomposites with alumina (Al_2O_3), silica (SiO_2) and titania (TiO_2) nanoparticles are shown in Fig. 1-4 respectively. The results in all these figures do not show a typical frequency dependence of of ε_r' and ε_r'', i.e. an increment of the real component together with a peak in the frequency dependence of the imaginary component, which would reveal a relaxation process. Instead, both components of the complex permittivity show rather an almost inverse proportionality with frequency, this being characterized by a higher slope (having the modulus in the range 0.7 - 1) at low frequencies and by a lower slope (< 0.3) at high frequencies, a cross-over occurring at a characteristic frequency f_c. This behaviour was already reported for a number of polymer nanocomposites and is known as “low frequency dispersion” (LFD) or quasi-dc (QDC) behaviour, [15, 16]. A model to explain LFD for partial crystalline polymers was proposed by Dissado and Hill, and uses the concept of cluster, i.e. a region with partial structural regularity where there are hopping movements of quasi-mobile charges (especially ions) to unoccupied sites. Besides the intracluster motions, some intercluster movements of charges could arise when the access to sites is restricted. Schonhals and Schlosser have extended the cluster approach for amorphous polymers, as it is the case of PVC, by considering that only intramolecular motions (along a few chain units) could be possible for short times (high frequency), while intermolecular (large scale) motions of charges, along many chain units can be presents in polymer for long times (low frequency) [17].

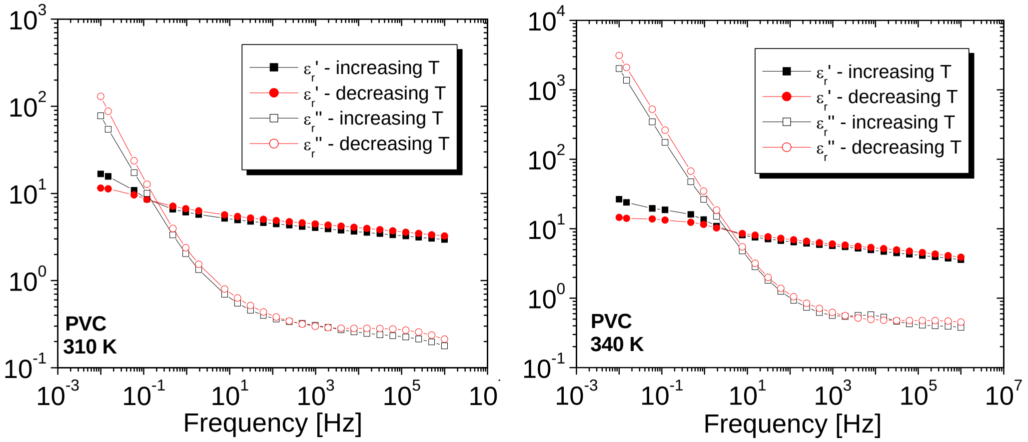

(a) (b)

Fig. 1. Frequency variation of ε_r' and of ε_r'' (b), for unfilled PVC, at 310 K (a) and at 340 K (b)

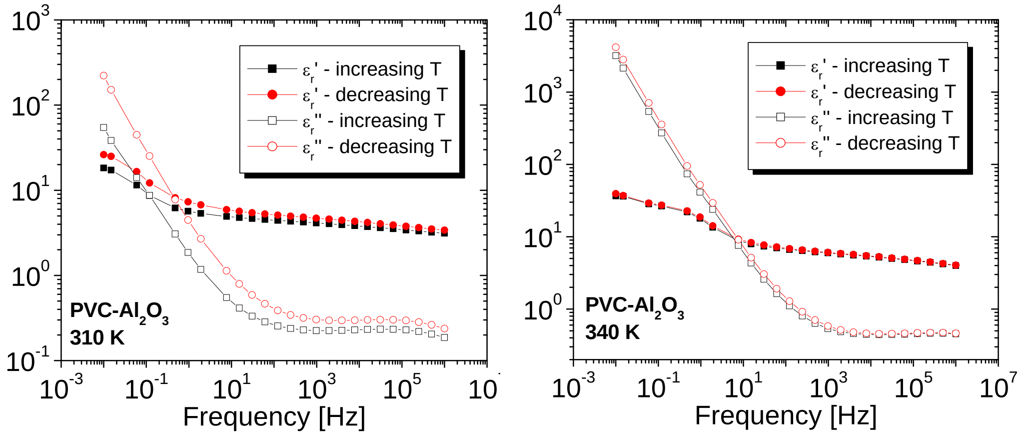

(a) (b)

Fig. 2. Frequency variation of ε_r' and of ε_r'' (b), for PVC-Al_2O_3 nanocomposites, at 310 K (a) and at 340 K (b).

The results in Figs. 1-4 show that the characteristic frequency increases with the temperature, from $\approx 10^{-1}$ Hz at 310 K to 1-10 Hz at 340 K

Another remark related to the results from Figs. 1-4, is the differences between the dielectric spectra determined at the increasing temperature with respect to those at the decreasing temperature. Different dielectric spectra at the increasing temperature with respect to the decreasing temperature would emphasize the influence of the material “history” on the dielectric behaviour. However, these differences are quite small for all the cases shown here, and they depend on the temperature and on filler type. Thus, the highest differences are observed for PVC-Al_2O_3 and for PVC-TiO_2 nanocomposites, but only at 310 K, while for higher temperature the differences become insignificant. For neat PVC there are small differences which do not seem to be affected by temperature, while for PVC-SiO_2 nanocomposites the differences are insignificant regardless the temperature.

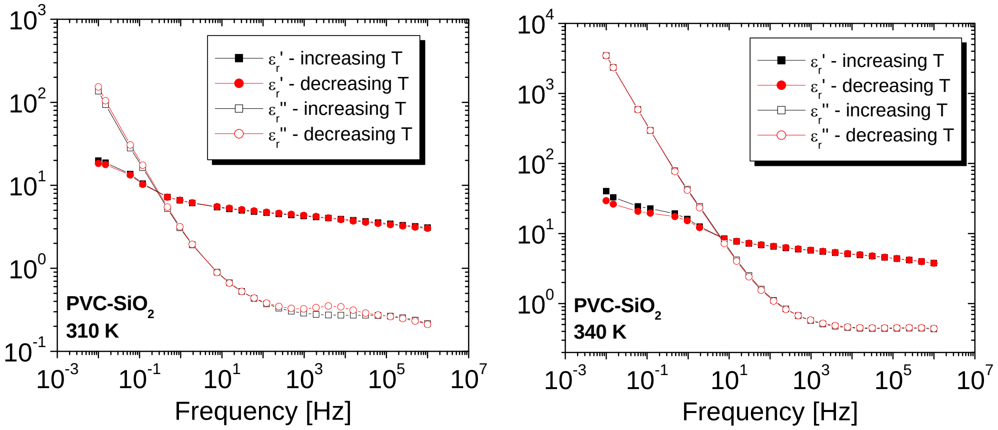

(a) (b)

Fig. 3. Frequency variation of ε_r' and of ε_r'' (b), for PVC-SiO_2 nanocomposites, at 310 K (a) and at 340 K (b)

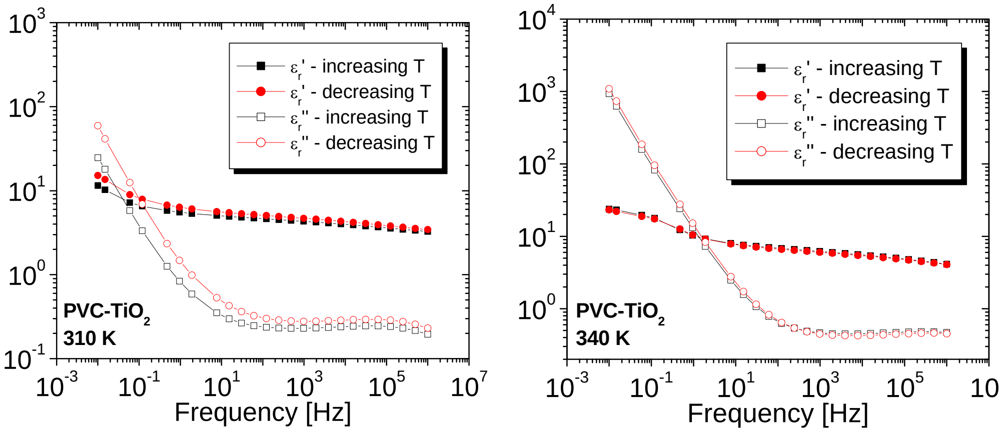

(a) (b)

Fig. 4. Frequency variation of ε_r' and of ε_r'' (b), for PVC-TiO_2 nanocomposites, at 310 K (a) and at 340 K (b)

The influence of the different nanoparticles on the dielectric response of PVC is shown in Fig. 5, where the frequency variation of ε_r' and of loss tangent (tan δ) is given for neat PVC and for PVC nanocomposites at 320 K. First, an increase of ε_r' values in all three PVC nanocomposites compared to neat PVC, can be noticed, especially at low frequencies, up to 1 Hz. This increase in permittivity was also found for other nanocompostites and it can be due to the new dipoles introduced in PVC by nanostructuration and to the interfacial polarization induced by the charge at the nanoparticle-polymer interface [13]. It can be seen that the highest values for ε_r' were obtained in the case of PVC-Al_2O_3 nanocomposites, while the lowest in the case of PVC-TiO_2 nanocomposites. This could be explained by the fact that when the filler has a much greater permittiviy than the polymer matrix, as in the case of PVC-TiO_2 nanocomposites, a very low electric field acts on the high permittivity nanoparticle and on its nearest interface region. On the contrary, when the filler permittivity is not very different from the polymer permittivity, as in the case of Al_2O_3 nanoparticles, a much lower inhomogeneous electric filed is present in nanocomposites and hence, the increase in nanocomposite effective permittivity is mainly due to the increase of the number of quasi-mobile charges and of dipolar movements in the filler-matrix interface. A similar behaviour was observed in one of our previous study on epoxy nanocomposites [18].

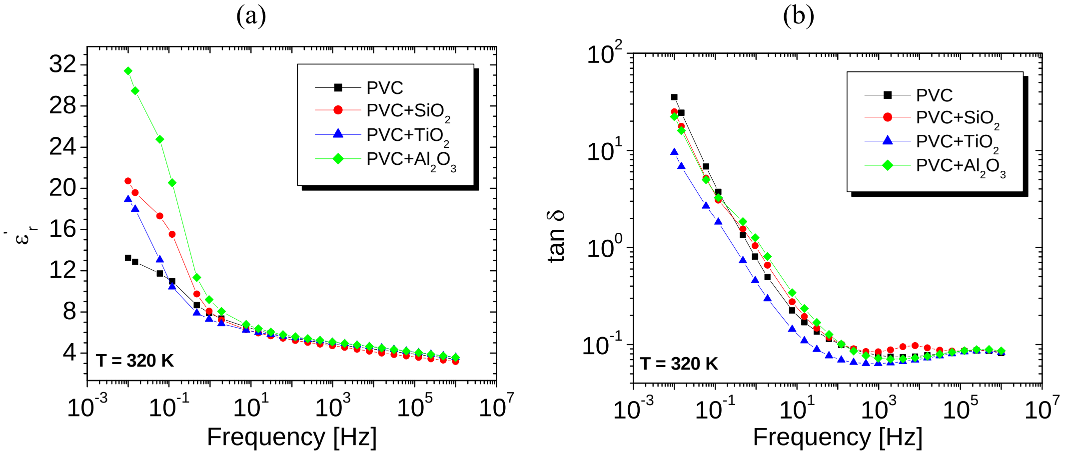
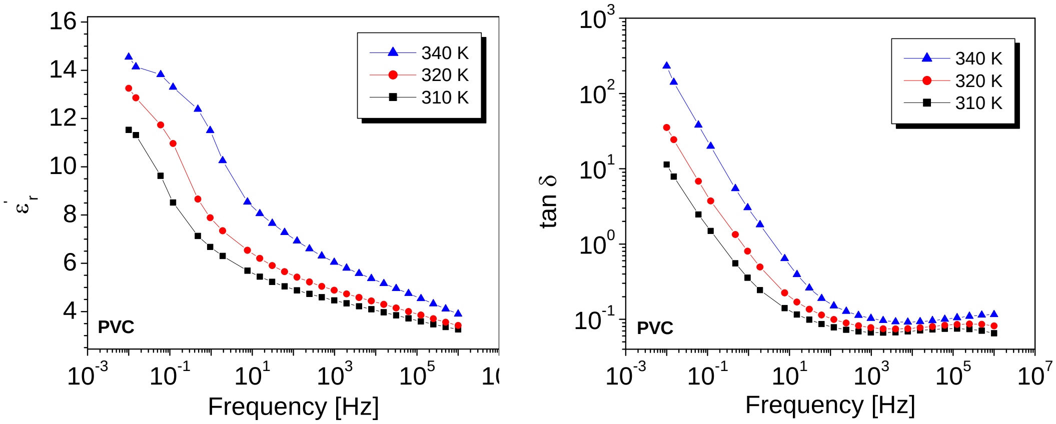

(a) (b)

Fig. 5. Frequency variation of ε_r' (a) and of tan δ (b), for neat PVC and for PVC nanocomposites at 320 K

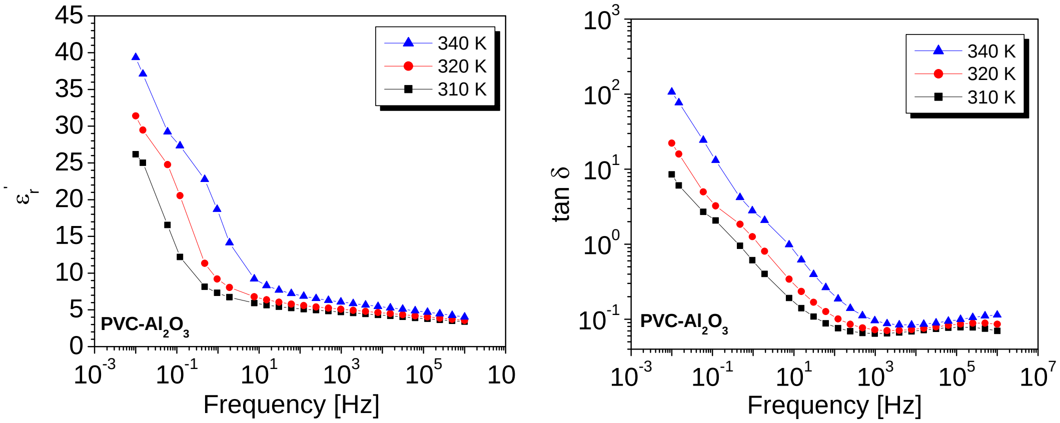
As for the loss tangent, significant lower tan δ values can be seen in Fig 5b for PVC-TiO_2 nanocomposites with respect to the neat PVC and to the other two nanocomposites, for a large range of frequencies. A similar behaviour was also noticed at 310 K and at 340 K. This behaviour suggests that the structure alteration produced in PVC by TiO_2 nanoparticles would hinder the intermolecular, and even the intramolecular charge transport inside the nanocomposite.

The influence of temperature between 310 K and 340 K on the dielectric behaviour of neat PVC and of PVC nanocomposites is shown in Figs. 6-9. The dielectric spectra given in these figures were determined at the decreasing temperature.



(a) (b)

Fig. 6. Frequency variation of ε_r' (a) and of tan δ (b), for neat PVC at different temperatures



(a) (b)

Fig. 7. Frequency variation of ε_r' (a) and of tan δ (b), for PVC-Al_2O_3 nanocomposites at different temperatures

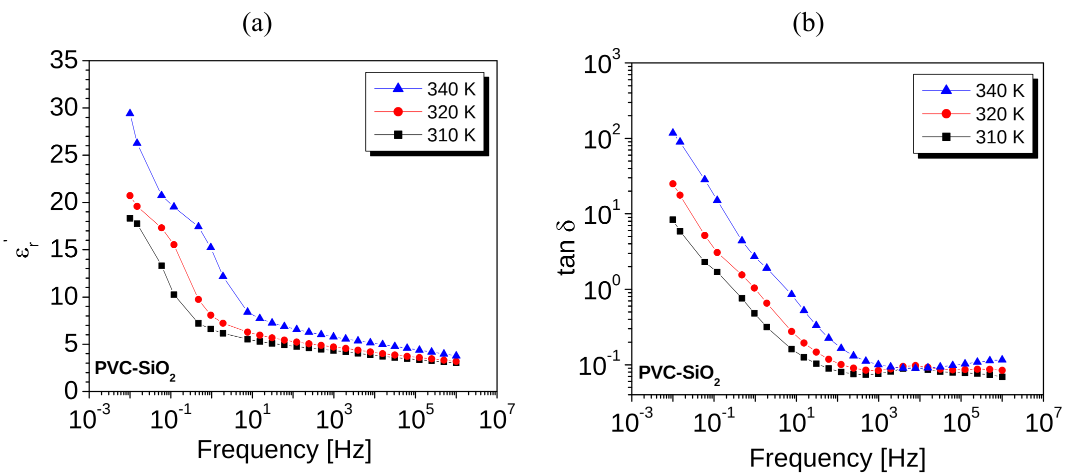


Fig. 8. Frequency variation of ε_r' (a) and of tan δ (b), for PVC-SiO$_2$ nanocomposites at different temperatures

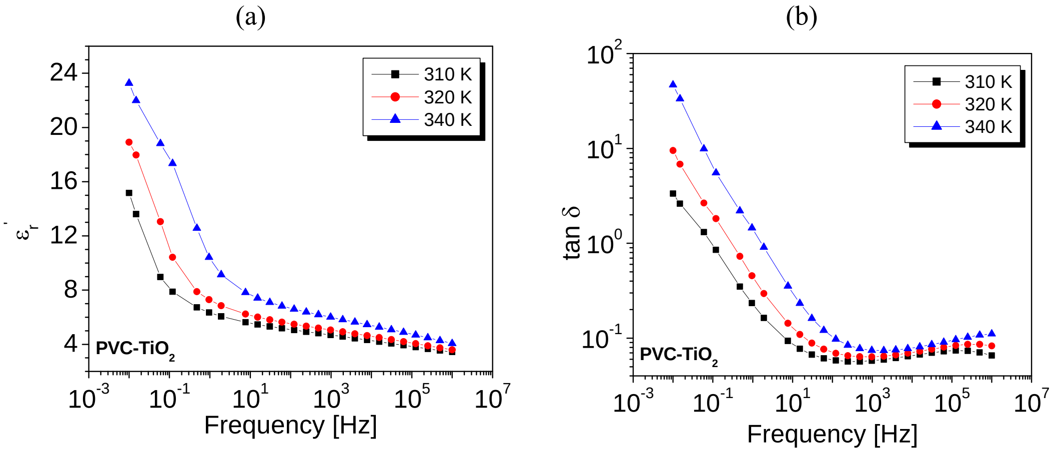


Fig. 9. Frequency variation of ε_r' (a) and of tan δ (b), for PVC-TiO$_2$ nanocomposites at different temperatures

It can be noticed that the increase of temperature leads to an increase of real relative permittivity and loss tangent at all frequencies and for both neat PVC and all tested PVC nanocomposites. This level of this increase depends on the presence and type of nanoparticles and it is more important at low frequencies, where the intermolecular charge motion is prevailing. The presence of different types of nanoparticles in PVC matrix does not seem to influence significantly the temperature influence on the tan δ values and variation, but the increase of the ε_r'

values at low frequencies with the temperature is strongly influenced by the type of filler. Thus, at 10^{-2} Hz, ε_r' increases from 310 K to 340 K, with 26% for neat PVC, 50% for PVC-Al_2O_3 nanocomposites, 61% for PVC-SiO_2 nanocomposites, and 53% for PVC-TiO_2 nanocomposites.

4. Conclusions

Differences are observed in dielectric behaviour of the tested samples, depending on the presence and the type of the tested inorganic nanofillers, as well as on the temperature at which the measurements were performed.

The results emphasize, for both unfilled and nanoparticle filled PVC, a quasi-dc behaviour. The temperature increase leads to an increase of the quasi-dc characteristic frequency.

An increase of ε_r' values in all three PVC nanocomposites compared to neat PVC, can be noticed, especially at low frequencies.

The loss tangent values for PVC-TiO_2 nanocomposites are lower than those for neat PVC and for the other tested PVC nanocomposites, at all tested temperatures.

The increase of temperature leads to an increase of ε_r' and tan δ at all frequencies and for both neat PVC and all tested PVC nanocomposites. The increase of permittivity with temperature is strongly influenced by the type of the filler.

Acknowledgement

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R E F E R E N C E S

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