

# The Influence of ZnO Nanoparticles on the Dielectric Properties of Epoxy Resin

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**Abstract.** Interesting electrical properties represent the epoxy nanocomposites, because the addition of nanofillers to a pure epoxy resin demonstrate several advantages opposite to pure epoxy resin without nanofillers. In the last 20 years, the dielectric properties (the complex permittivity and dissipation factor) of epoxy nanocomposites had been evaluated and the results clearly show that they are lower than that of base epoxy and microcomposites when insulating oxides were used as the fillers. Nowadays the epoxy and epoxy based composites are preferred insulating materials for many electrical applications. The influence of the various concentrations of ZnO nanoparticles in epoxy resin Vukol 022 on the changes of the complex permittivity and dissipation factor has been measured at the temperature range from 20 °C to 120 °C by a capacitance method in the frequency ranges from 1 mHz to 1 MHz. In this contribution, we present a study of the influence of 1,0 wt.% and 5,0 wt. % concentrations of ZnO nanofillers on the dielectric properties of the epoxy resin. From the frequency dependence of dissipation factor,  $\alpha$ -relaxation process and its shift to lower frequencies with ZnO fillers were observed.

## 1. INTRODUCTION

At use of insulating materials in electrical equipment for safe and reliable operation, the condition must be met, the great dielectric and thermo- mechanical properties of insulation [1]. In recent years, it is interesting mainly of the materials with ease of production, light weight, and often ductile nature. These role polymers they took over, due to their unique characteristics and 70% of all produced polymers represent thermosetting resins and thermoplastics [2]. In recent years, mainly during the last two decades studies into organic-inorganic nanocomposites have gained importance in order to improve the electrical, thermal and mechanical properties of polymers as insulating materials [2, 3]. The term “epoxy resin” refers to both the prepolymer and its cured resin/hardener system. Interesting electrical properties represent the epoxy-based nanodielectric systems because the introduction of nanofillers to the pure epoxy resin demonstrate several advantages opposite to pure epoxy resin without nanofillers [4]. Studies carried out in recent years clearly shows that the nanocomposites have exhibited markedly improved mechanical, thermal, optical and physic-chemical properties, owing to the nanometer-size particles obtained by dispersion, when compared with the pure polymers [2, 4].

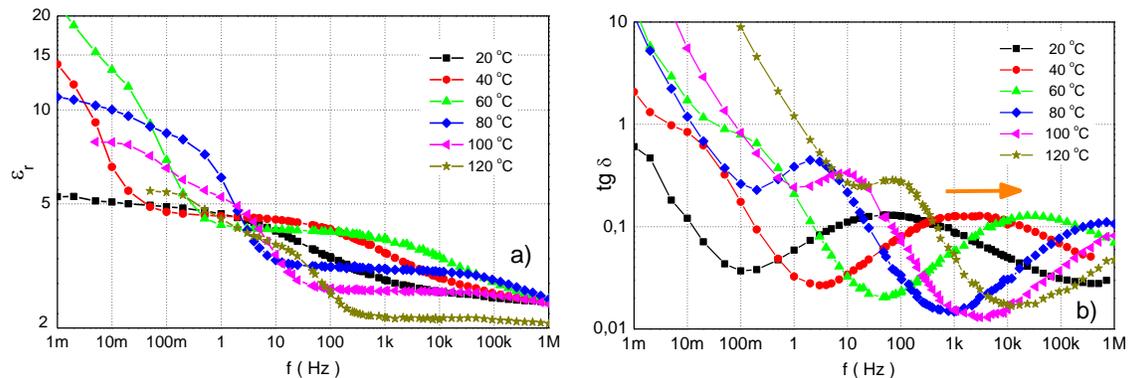
Level of breakdown voltage is very important insulating capability for dielectric materials, which is a measure of the insulating capability to withstand at high electric field stress without breaking down. A very important property for determining the quality of dielectric material is electrical breakdown voltage because it is a combination of a series of complex phenomena in solid dielectrics and it depends on the waveform of applied voltage, the growth rate of applied voltage, the shape of electrodes and the thickness of the sample [3]. The defects (voids and cavities) which are formed in solid insulating materials (within the medium or at the interfaces dielectric and metal (electrodes) have generally a lower dielectric strength that may promote the formation of electrical discharge under

normal operating conditions followed by the erosion of solid dielectric and its ultimate failure [5]. In HV electrical insulation system the polymeric composites with fillers of the size of nanometers had been which is the proof of many articles about the influence of nanofillers on the dielectric properties of the nanocomposites. In the last 20 years, the dielectric properties (the permittivity  $\epsilon_r$  and dissipation factor  $\text{tg } \delta$ ) of epoxy nanocomposites had been evaluated and the results clearly show that they are lower than that of base epoxy and microcomposites when insulating oxides were used as the nanofillers [1-7]. For the epoxy resin, the chain molecular structure is characteristic. The epoxy chains are connected to nanoparticles so interfacial regions are formed around them, which has a significant influence on the dielectric properties of the final nanocomposites. The mixing of conductive nanofillers in the polymer matrix can significantly improve the dielectric constant of composites when the nanofiller content approaches the percolation threshold [8, 9].

## 2. PREPARATION OF SAMPLES

In the laboratory conditions, the preparation of epoxy nanocomposites was done by the method of direct dispersion. In a laboratory furnace at 80 °C the nanoparticles are drying for 24 hours to lose their surface moisture. Next, the epoxy resin (VUKOL 022) was heated to obtain a better viscosity for mixing. This was followed by high shear mechanical mixing nanoparticles with epoxy resin at 700 rpm / 1 min at the time 5 hours. To achieve the desired concentration (1,0 wt.% and 5,0 wt. %) the right weight of the ZnO fillers has been added. The vacuuming process followed for 5 hours and was used to remove bubbles from the mixture. The hardener (VUKIT M) was added to the decanted mixture to cure the epoxy resin (ER) in ratio 100: 37. The resulting mixture was poured into a pre-prepared container with the option of check a sample thickness. From each prepared concentration, the five pieces of samples were made for repeated measurement and confirmation of measured results.

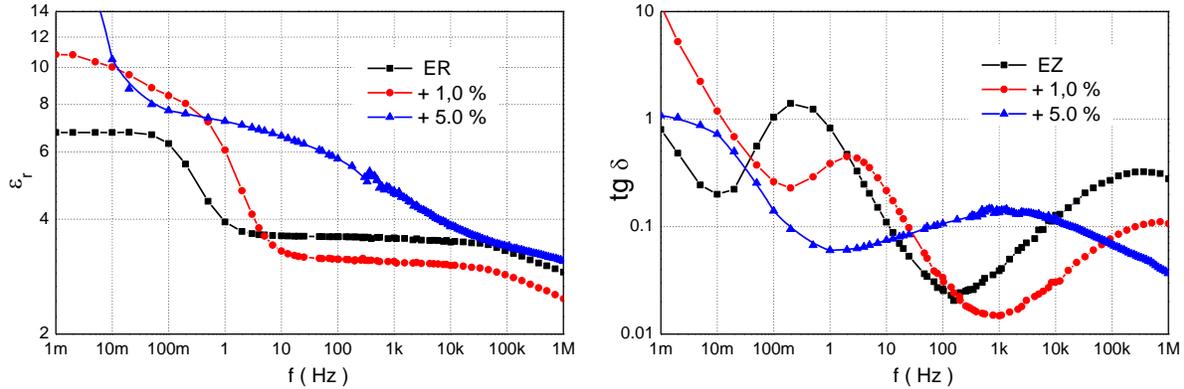
## 3. EXPERIMENTAL RESULTS



**FIGURE 1.** The frequency dependence of the real part of the complex relative permittivity (a) and dissipation factor (b) for the epoxy resin with 1 wt. % of ZnO filler at various temperatures.

The frequency dependences of the real part of the complex relative permittivity ( $\epsilon_r$ ) and dissipation factor of the ER with 1,0 wt. % ZnO is shown in Fig. 1. At the temperature 20 °C  $\epsilon_r$  was almost constant for frequencies below 1 Hz (can be named as plato) and for higher frequencies it slightly decreases to the second constant value ( $f > 300$  kHz) 2,4. With increasing temperature, the whole development of  $\epsilon_r$  moved to higher frequencies and its large increase can be observed for sub-Hertz frequencies. Frequency developments of dissipation factor at various temperatures were more interesting. At the temperature 20 °C we can observe only one local maximum around 50 Hz, which on the base of literature [2, 10] is caused by the  $\beta$ -relaxation process (the orientation or rotation of polar side groups about C-C bond). With increasing of temperature, it moves to higher frequencies as is shown by the arrow in Fig. 1b). Its position for temperatures higher than 100 °C was more than 1 MHz. The next local maximum of  $\text{tg } \delta$  appeared at 9 mHz at the temperature of 40 °C. This local maximum caused by the  $\alpha$ -relaxation

process (micro-Brownian motion of the whole chain, formally this motion is designated as glass transition) [11] was also observed in various works [11-13] and it also moves to higher frequencies.



**FIGURE 2.** The frequency dependence of the real part of the complex relative permittivity (a) and dissipation factor (b) at the temperature 80°C for the epoxy resin and its mixtures with 1 wt. % and 5 wt. % ZnO fillers.

In Fig. 2a are showed the frequencies dependences of  $\epsilon_r$  and dissipation factor of pure ER and its mixture with two different concentrations of ZnO fillers at 80 °C. At higher temperatures the developments of the dissipation factor were similar, but maxima's were shifted to higher frequencies. Within the given frequency range, we observe a significant change in  $\epsilon_r$  of nanocomposites with the concentration of nanoparticles. 1 wt. % of ZnO filler caused a decrease of  $\epsilon_r$  relative to pure epoxy resin only for frequencies higher than 5 Hz. 5 wt. % of ZnO filler caused a big increase of the real relative permittivity in consideration of the pure epoxy resin. In the case of dissipation factor (Fig. 2b), we notice a significant shift of the local maximum due to  $\alpha$ -relaxation to the higher frequency of 2 Hz and to lower frequency around 9 mHz. The position of the second local maximum is shifted from 350 kHz to 785 kHz for 1 wt. % of ZnO fillers. At higher concentration, we see a completely different development of the dissipation factor for whole frequencies range and the position of the second peak is shifted to 1 kHz.

#### 4. DISCUSSION

The results on Fig. 2 showed that various concentration of nanoparticles in the epoxy resin have different influence on its dielectric properties [12]. These changes are caused mainly by two factors: the interfacial region around the NPs and their relative permittivity. The decrease in  $\epsilon_r$  for frequency higher than 5 Hz at 1 wt% ZnO filler in the ER (Fig. 2a) is the effect the interfacial region (bonded and bond layers) around the NP. In this region, the immobility of epoxy chains decreases, which reduces the effect of polarization and it is associated with a decrease of  $\epsilon_r$ . At higher concentration of the filler,  $\epsilon_r$  increased due to the dominance of the NPs permittivity.

Dissipation factor frequency dependence for two concentrations of ZnO filler at the temperature of 80 °C (Fig. 2b) has two local maximums. The  $\alpha$ -relaxation process observed at low frequencies is mainly influence by the local electric field. At NPs with their interfacial region are captured charges – electrons or ions, which generate a high local electric field. Due to this field changes the reorientation of electric dipoles of epoxy chains bounded in layers around NP is much quicker (shift of local maximum to higher frequencies). At high concentration, the inter-particle distances between NPs are smaller and dimer or oligomers from NPs are created. These structures with the overlapping layers led to increased interfacial polarization and there is a better transfer of charges within the structure. These effects cause a rapid increase in relaxation time with concentration. These big structures also cause big shift of the position of the second local maximums, the  $\beta$ -relaxation process, to lower frequencies. A more detailed explanation of such a significant change would require numerical simulation.

## 5. CONCLUSION

The dielectric spectroscopy for the study of the epoxy nanocomposite systems with ZnO nanoparticles as fillers was used. The multi-layer model for the description of the changes of nanocomposites dielectric properties was applied. The real part of the complex relative permittivity and dissipation factor of nanocomposites measured within the frequency range from 1 mHz to 1 MHz were dependent on the concentration of nanoparticles. Decrease of the relative permittivity for frequencies higher than 5 Hz was observed for 1 wt. % ZnO filler. This decrease was caused by the presence of highly immobile epoxy chains in the interfacial regions around nanoparticles. The observed local maxima's of dissipation factor at various temperatures revealed the presence of the  $\alpha$ - and  $\beta$ -relaxation processes. The shift of peak related to the  $\alpha$ -relaxation process by high local electric field was observed.

## ACKNOWLEDGMENTS

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