

Comparison two types of nanowires on the dielectric properties of epoxy resin with SiO₂ nanoparticles

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Abstract — In this study, the effect of 0.75 weight percent filler silica (SiO₂) with PI or PA nanowires for dielectric properties of epoxy resin EPOXYLITE 3750 LV (ER) was studied. For this purpose, direct unidirectional conductivity measurements and broadband dielectric spectroscopy measurements were used to describe changes in the dielectric responses of ER / SiO₂ nanocomposites with nanowires in the frequency and temperature range. The presence of nanowires and nanoparticles in the epoxy resin affected the segmental dynamics of the polymer chain and altered the charge distribution in the system. These changes caused a change in permittivity values and a shift in local relaxation peaks in the imaginary permittivity and dissipation factor spectra of nanocomposites. Experiments have shown that temperature-dependent transitions of electrical properties in nanocomposites are associated with to relaxation processes.

Keywords— Nanoparticles, epoxy resin, nanocomposites, dielectric properties

I. INTRODUCTION

Polymer materials have been widely used in various fields of our production and life in recent years and have become an indispensable part of our lives [1]. From available data it is clear, 75% of all produced polymers are thermosetting and thermoplastic used in electro-energy sector [2, 3].

Efforts to improve dielectric characteristics, including reducing space charge accumulation and improving internal potential distribution, have focused on high-voltage electrical insulation with mixed polymer nanofiber applications [4].

As outlined in current scientific articles, nanocomposite systems with three components are used to form dielectric barriers in high-voltage engineering. Electro-insulations are typically made with glass cloth, PET (polyethylene terephthalate), or PI (polyimide) films. Mica paper is the second component - also called the dielectric barrier.

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An epoxy resin, polyester resin or silicone resin constitutes the third component - the matrix [5].

Direct application research on nanocomposites is focused on nanocomposite systems composed of polymer matrices, where e.g. epoxy resin matrices are often used as base materials for nanocomposite dielectrics. The mechanical and thermal properties of epoxy resins are highly advantageous [6], as well as their resistance to aggressive environments. In the case of nanocomponents, layer silicates, organic oxides, and other fillers [7 - 13] are examined closely.

Polyamides are high-performance thermoplastic elastomers that are characterized by high operating temperature, good thermal aging and resistance to solvents. In addition, polyamides have high modulus and impact properties, low coefficient of friction and high abrasion resistance. Although polyamides are designed to have a wide range of properties, they all consist of amide (-CONH-) bonds in their polymer chain. An amide group is a polar group that allows polyamides to form hydrogen bonds between chains, thereby improving the attractiveness between chains. This increases the mechanical properties of the polyamide. Strength and stiffness can be reduced by increasing the number of carbon atoms between the amide bonds. Therefore, the length of the hydrocarbon backbone is a key property that determines the performance of the polyamide material. Due to the polarity of the amide group, polar solvents, especially water, can act on polyamides. The main difference between polyamide and polyimide is in their chemical structures; the polyamide has amide (-CONH-) bonds in its polymer backbone, while the polyimide has an imide group (-CO-N-OC-) in its polymer backbone.

A commercial epoxy resin matrix is used as a matrix for the fabrication of nanocomposite dielectric materials. In this contribution the properties of the epoxy resin bisphenol A – epichlorohydrin (EpoxyLite 3750LV, product of ELANTAS Italia) was modified by adding fillers. Effects of nanofibers are monitored to see if they influence dielectric properties of nanocomposite materials. The dielectric properties of prepared nanocomposites were modified by 0.75 wt. % of

SiO₂ (hydrophobic silica AEROSIL R 972) + polyimide (PI) (NANOPHARMA a.s. from Czech Republic) for the first investigated sample (tag as Sample PI). Second investigated sample was on the base of the same epoxy resin (3750LV) and was modified by 0.75 wt. % of SiO₂ + polyamide (PA) (tag as Sample PA).

Summarized results indicate that the designed material exhibits corresponding electrical characteristics, and that the nature of the nanoparticles affects the critical characteristics of the monitored nanocomposite systems.

II. EXPERIMENTAL RESULTS AND DISCUSSION

The measurement of surface and volume resistivity was implemented on DC voltage of 500 V, power frequency 50 Hz and temperature 20 °C. The measurement of volume resistivity was carried out according to IEC 62631-3-1 [14]. Measured data are shown in Table I. From the results is evident an increase of volume resistivity due to inclusion of hydrophobic nanosilica with polyimid nanowires in the matrix, from $6.8 \cdot 10^{12}$ to $12.4 \cdot 10^{12} \Omega \cdot m$ while for mixture with polyamid nanowires there is decrease to $3.7 \cdot 10^{12} \Omega \cdot m$. In case of surface resistivity it was similar.

TABLE I. ELECTRICAL PARAMETERS AND THEIR STANDART DEVIATION OF THE STUDIED NANOCOMPOSITED.

Sample	$\rho_v (\Omega \cdot m)$	$\rho_s (\Omega \cdot m)$	$\epsilon_r (50 \text{ Hz})$
Pure ER	$6.28 \cdot 10^{12}$	$52.6 \cdot 10^{12}$	2.95
Stand. dev.	$1.08 \cdot 10^{12}$	$12.8 \cdot 10^{12}$	
Sample PI	$12.4 \cdot 10^{12}$	$97.3 \cdot 10^{12}$	4.58
Stand. dev.	$1.28 \cdot 10^{12}$	$30.1 \cdot 10^{12}$	
Sample PA	$3.71 \cdot 10^{12}$	$52.3 \cdot 10^{12}$	4.1
Stand. dev.	$1.19 \cdot 10^{12}$	$10.1 \cdot 10^{12}$	

Figure 1 depicts the real and imaginary parts of the complex permittivity of a sample PI measured at various temperatures. Very high real relative permittivity (ϵ_r , Fig. 1a) was characterized at low frequencies (nanowires), whereas higher frequencies had almost stable value. Temperature had a significant effect on the development of ϵ_r . Fig. 1b shows that the imaginary part of permittivity (ϵ_i) extremely increased for sub-frequencies. For frequencies higher than 10 kHz and 60 °C is almost constant again. At temperature 100 °C and higher can be observed a local maximum around 100 Hz. For the second sample the development of complex relative permittivity was similar.

The Cole-Cole fits of experimental data only for temperatures 80 °C, 100 °C and 120 °C are represented by the thick full lines in Fig. 1. The thin lines connect the measured points. Cole-Cole equation describes dielectric relaxations as a relaxation model and has the following form:

$$\epsilon^* = \epsilon_\infty + \frac{\Delta\epsilon}{1+(j\omega\tau)^{1-a}} + j \frac{\sigma}{\epsilon_0 \omega} \quad (1)$$

where ϵ^* is the complex dielectric constant, ϵ_∞ is the "infinite frequency" dielectric constants, $\omega = 2\pi f$, τ is a time constant of the relaxation process, σ is the DC conductivity and a is the distribution parameter. For the fit of experimental data was used software Origin 7.0. Obtained parameters from the fit by the Cole-Cole equation are listed in Tab. II. The ϵ_i component had a local maximum at the eigenfrequency $f_c = 1/(2\pi\tau)$, which corresponds to the α -relaxation process (the result of micro-scaled Brownian motion of the whole chain) with relaxation time τ . The relaxation time could be affected by the presence of nanowires and captured charges. The given

relaxation times with others parameters are listed in Table. II. Cole-Cole fit was made only for temperatures of 80 °C and higher, because only in this temperature range did the relaxation process associated with micro-scaled Brownian motion appear.

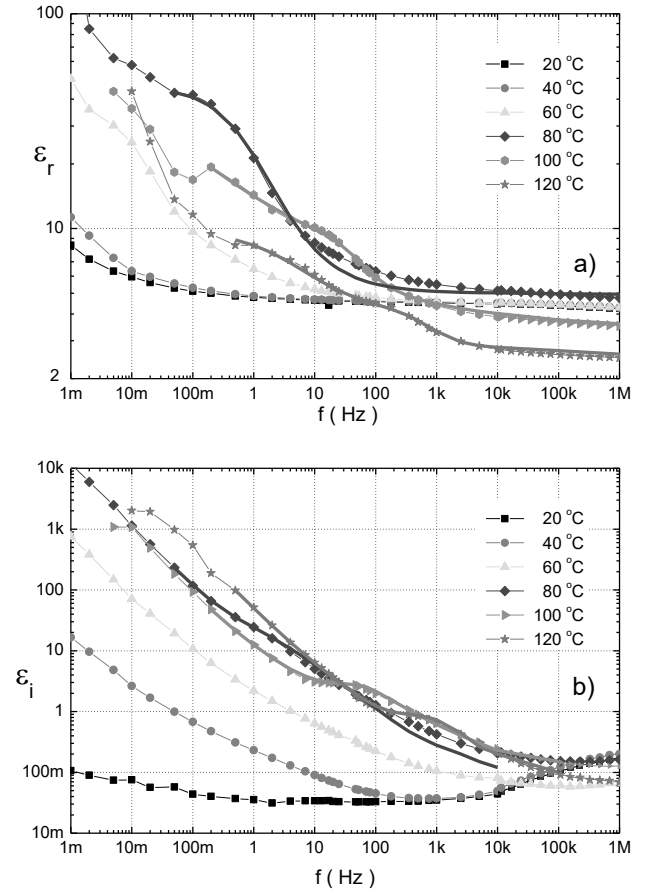


Fig. 1. The dependence of the a) real and b) imaginary part of relative complex permittivity of sample PI on the frequency for temperatures in the range from 20 °C to 120 °C. (Thick full lines for temperatures 80 °C - 120 °C correspond to the Cole-Cole fit of measured data.)

Fig. 2 shows the frequency dependence of dissipation factor at different temperatures for sample PA. We can see several important characteristics of the development of dissipation factor as high values at sub-hertz frequencies, local maxima and slow increase at frequencies over 100 kHz. The most important parameter is the eigenfrequency f_c of the local maximum. It is associated with the relaxation process of polarization [15, 16] and the local peaks of the imaginary part of complex permittivity (Fig. 1a). There is a shift of the local maxima of dissipation factor with temperature.

TABLE II. PARAMETERS FROM COLE-COLE FIT OF THE COMPLEX PERMITTIVITY AT VARIOUS TEMPERATURES.

Temperature	Sample	τ (ms)	f_c (Hz)	σ (μS)
80 °C	Pure ER	22	7.3	0,35
	Sample PI	227	0.7	630
	Sample PA	153	1.0	611
100 °C	Pure ER	1.4	111	0,62
	Sample PI	3.1	51	1550
	Sample PA	4.5	35	620
120 °C	Pure ER	0.27	590	0,88
	Sample PI	0.23	690	2700
	Sample PA	0.55	289	640

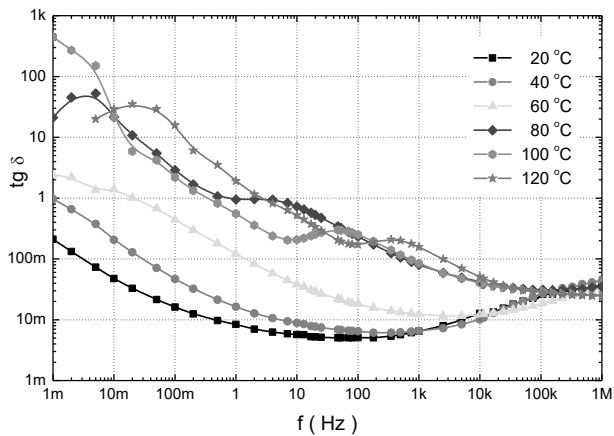


Fig. 2. The frequency dependence of dissipation factor of sample PA at various temperatures.

The influence of various types of nanowires on ϵ_r and $\text{tg } \delta$ of pure ER at temperature 100 °C in the wide frequency range are shown in Fig 3. In this case both nanowires cause increase of ϵ_r to pure ER in whole frequency range. This was caused by several effects. The first one is influence of nanoparticles and their higher relative permittivity as pure ER. Next is the interfacial polarization [3, 4], which is caused by the difference in conductivities and permittivity's of the constituents at the macroscopic interfaces causing space-charges to accumulate. A local electric field (charge multiplication) appears at the interface of the NP and ER matrix (bound and released layers) caused by these trapped charges (electrons and ions). This multiplication has a big effect on the increase of relative permittivity at low frequencies. The last factor is the presence of nanowires, which around which nanoparticles are captured and help charge multiplication and further increase in permittivity and dissipation factor at sub-Hertz frequencies.

The dissipation factor for both nanowires has higher values than for pure ER. The next important factor is the shift of local maxima f_e to lower values as in UP. This shift at 100 °C is very well observed in Fig. 3b, where is comparison of the development of dissipation factor for pure ER and its nanocomposites with nanoparticles and various nanowires. For temperatures 80 °C, 100 °C and 120 °C the comparison of eigenfrequency and corresponding α -relaxation times are listed in Table II. Charge multiplication causes a higher electric field than Laplacian or geometric electric fields, so it influences the reorientation of the electric dipoles of ER chains bound in layers around the NP. By increasing the electric field, dipole charges can be transferred faster. This is due to the shift of the local maximum caused by the α -relaxation process to higher frequencies, and ϵ_r increases more dramatically at low frequencies.

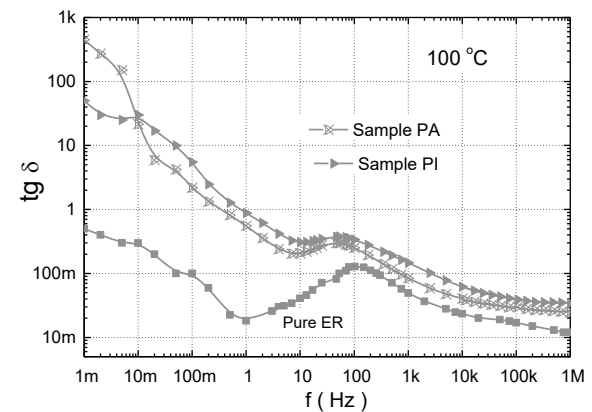
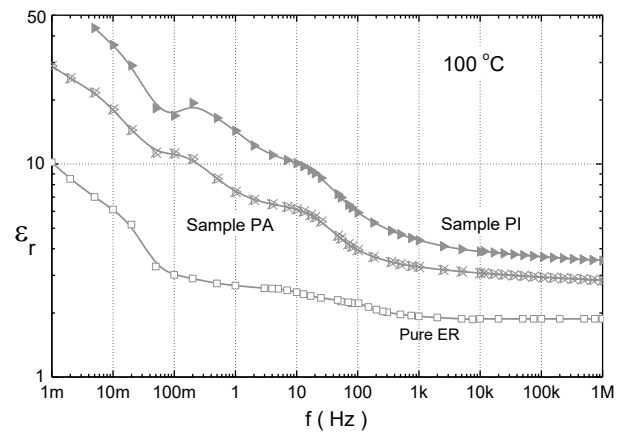


Fig. 3. The comparison of a) real part of relative complex permittivity and b) the dissipation factor on the frequency at temperature 100 °C.

III. CONCLUSION

We studied the dielectric properties of epoxy resin EPOXYLITE 3750 LV with SiO_2 nanoparticles and PI or PA nanofibers. Measurements of the conductivity and broadband dielectric spectroscopy were used to investigate the dielectric responses of nanocomposites in the frequency and temperature range. By containing both nanoparticles and nanofibers, the epoxy resin affected the dynamics of polymer chains and altered charge distribution. As a result, the permittivity values in nanocomposites changed with big increases and local relaxation peaks shifted in the imaginary spectrum of permittivity and dissipation factor. It has been shown that polyimide fibers cause a larger change in dielectric parameters than polyamide nanofibers, which is due to the weaker combination of nanofibers with polymer chains.

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