Dielectric Properties of Nanodielectrics with Inorganic Fillers

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Abstract- One of the main targets of the research in the field of polymer nanocomposite dielectrics is to obtain new materials with improved dielectric properties (resistivity, dielectric strength, permittivity and dielectric losses). In this paper the variation of the real part of the permittivity and of the loss tangent with the frequency are investigated for three formulations of nanocomposites obtained from polyethylene filled with nanoparticles of SiO$_2$, TiO$_2$ and Al$_2$O$_3$, respectively. The influence of the filler concentration (between 2 and 10 wt%) on the dielectric behavior of the nanocomposite is analyzed as well. To simulate the electrical behavior of the polymer-filler interface which might explain the experimental results a 3D electrostatic model proposed on the basis of Tanaka’s multi-core model is discussed. This model allows one to study the influence of several parameters such as the nanoparticle diameter, thickness of the interface layers, concentration and permittivity of the nanoparticles or the permittivities of the interface layers, on the effective permittivity of a plane nanodielectric sample.

I. INTRODUCTION

In the last five years many research groups in the field of dielectrics have been focusing their energies and resources towards a new topic called nanodielectrics [1-3]. These newly born materials are polymer nanocomposites with dielectric and electrical insulating properties which are increasingly becoming popular due to significantly improved behaviour compared to the traditional polymer microcomposites. The nanofillers are usually 1 to 100 nm in size, 1 to 10 wt% in content, and should be homogeneously dispersed in the polymer matrix. Until now several methods for processing and characterization have been tested, and some theories and models have been proposed to explain the behaviour of these materials having a huge nanofiller-polymer interface area which seems to be the main responsible for their unique properties [4, 5]. Despite the encouraging advances in this field we are still far from a complete understanding and controlling of phenomena in these materials.

In our previous studies we analyzed the influence of the inorganic nanofillers (SiO$_2$, TiO$_2$ and Al$_2$O$_3$) on the absorption-resorption currents in LDPE nanocomposites [6], the response of LDPE-Al$_2$O$_3$ nanocomposites at dielectric spectroscopy, alternate polarization currents, chemiluminescence and mechanical tests [7,8] and we have proposed a 3D electrostatic model, based on Tanaka’s multi-core model [9], in order to study the electric field distribution inside a nanodielectric containing spherical particles with uniform distribution in a homogeneous matrix [10]. In the present work the dielectric behaviour of plane samples made of low density polyethylene (LDPE) filled with nanoparticles of SiO$_2$, TiO$_2$ and Al$_2$O$_3$ is analysed by using the permittivity and tan delta values determined by dielectric spectroscopy (DS) over a frequency range of 1 mHz – 1 MHz. The dielectric properties are discussed in connection with modelling results regarding the electric field distribution obtained with the above mentioned 3D electrostatic model.

II. EXPERIMENTAL

A. Systems investigated

Three types of polyethylene nanocomposites were prepared with nanofillers of SiO$_2$, TiO$_2$ and Al$_2$O$_3$. The content of nanoparticles of the tested formulations was 2, 5 and 10 wt%. The average nanoparticle diameter was 40 nm for Al$_2$O$_3$ and 15 nm for SiO$_2$ and TiO$_2$. The surface of the nanoparticles was treated with maleinized polyethylene (MP) for a better compatibility between the nanofiller and the polymer matrix, and for a better dispersion of the nanoparticles. The polymer matrix was a low density polyethylene (LDPE) commercially available at Arpechim Pitesti (Romania). The polyethylene nanocomposites were manufactured by direct mixing method at 160 °C for 10 min [11]. Finally, plane samples of square shape (10 x 10 cm$^2$) having the thickness of 0.5-0.6 mm were prepared by hot melt pressing at 170 °C, for 3 min (after pre-heating for 2 min).

B. Dielectric spectroscopy

The real part of the permittivity ($\varepsilon'_r$) and the loss tangent (tan $\delta$) were determined by dielectric spectroscopy (DS) using a Novocontrol ALPHA-A Analyzer in combination with an Active Sample Cell ZGS, over the frequency range $10^3$ – $10^6$ Hz, at ambient temperature (25 °C). Four disks of 40 mm diameter were cut from one plaque of each formulation and tested by dielectric spectroscopy.
III. NUMERICAL MODEL

A plane sample with a thickness of 1 mm of a nanodielectric consisting of a polymer matrix containing identical spherical nanoparticles, uniformly distributed inside the sample volume was numerically modeled (Fig. 1). Each nanoparticle of radius \( r \) is surrounded by a multi-layered interface \( i \) of thickness \( \Delta r \), placed in-between the particle \( p \) and the polymer matrix \( m \). Different concentrations of nanoparticles (1-10\%) were analyzed, and different sphere diameters (15-100 nm) were considered. The analysis of the electrostatic field in this domain which includes a composite material was carried out by using a computational model based on finite elements. The electrostatic field computation model expressed in electric scalar potential \( V \), is based on Poisson differential equation

\[
\text{div}(\varepsilon \text{ grad } V) = \rho,
\]

where \( \varepsilon \) is the electric permittivity and \( \rho \), the volume charge density. The computational domain of the simplified 3D model is reduced to an elementary fraction of the whole geometry of the material sample (Fig. 2), by taking into account the existing physical symmetries imposed by appropriate boundary conditions \[10\]. The simulations were carried out using the software package FLUX3D \[12\].

The above model allows one to study the influence of several parameters, such as the diameter of the nanoparticle \( d = 2r \), thickness of each of the interface layers \( \Delta r_k \), where \( \Sigma \Delta r_k = \Delta r \), concentration of nanoparticles, permittivity of the nanoparticle and the permittivity of each interface layer, nanoparticle surface charge density, and volume charge density of each interface layer.

In our software implementation, all these parameters are included in a dedicated so-called spy file, which allows the automatic generation, solving and post-processing of each numerical model that corresponds to a given set of parameters.

IV. RESULTS AND DISCUSSION

A. Dielectric spectroscopy

The DS results revealed, on the one hand, the influence of the filler content and, on the other hand, the effect of the filler type on the dielectric properties analyzed \( (\varepsilon_r', \tan \delta) \).

The influence of the filler content on the dielectric behavior can be seen in the Fig. 3 and 4, which show the variations of the real part of the complex relative permittivity \( \varepsilon_r' \) and of the loss tangent \( (\tan \delta) \) respectively with the filler concentration for different frequencies.

The effects of filler type on the dielectric behavior of the LDPE nanocomposites is given in Fig. 5 and 6 which show the variations with the frequency of the real part of the permittivity and of the loss tangent, respectively, for different filler types: SiO2, TiO2 and Al2O3 nanoparticles, for the same concentration 2 wt%.

It is well known that the dielectric behavior over a broad range of frequencies for polymer based insulating materials (including nanocomposites) is governed by different polarization mechanisms and relaxation effects. As for the loss tangent, besides the polarization, the electrical conduction due to different types of carriers determines the \( \tan \delta \) variations with the increasing frequency as resulting from the relation

\[
\tan \delta = \tan \delta_d + \tan \delta_c,
\]

where \( \tan \delta_d = \varepsilon''/\varepsilon' \) is the dielectric loss component and \( \tan \delta_c = \sigma/(\omega \varepsilon') \) is the conduction loss component, \( \sigma \) is the conductivity, \( \omega \) is the angular frequency, \( \varepsilon' \) and \( \varepsilon'' \) are, respectively, the real and imaginary parts of the complex permittivity \( \varepsilon^* \) \( (\varepsilon^* = \varepsilon' - j \varepsilon'' = \varepsilon_0(\varepsilon_r' - j \varepsilon_r''), \) where \( \varepsilon_0 \) is the vacuum permittivity).

The \( \varepsilon_r' \) decreases with the frequency both for LDPE without fillers and for all the tested nanocomposites, as shown in Fig. 3 and 5. The decrease of \( \varepsilon_r' \) with the frequency was also reported for other types of polymer nanocomposites \[2, 5, 13\] and this was mainly ascribed to the reduction of the polarizations caused by dipolar groups both in polyethylene and in nanoparticles.
In the case of LDPE-Al₂O₃ nanocomposites (Fig. 3), for very low frequencies (10⁻³-10⁻² Hz) the ε'_r values for 2 and 5 % filler content are smaller than for the unfilled polymer. This is thought to arise from a reduced chain movement of the polymer in the nanocomposite with respect to the unfilled polyethylene [5, 13]. The ε'_r values for 10 wt% filler content are higher than both unfilled polymer and with 2 and 5 wt% filler content, probably due to a more important contribution of the interfacial polarization.

As for the effect of the filler type on the ε'_r variation with frequency, one can remark from Fig. 5 that for 2 % filler loading the values of the permittivity in the case of LDPE-TiO₂ as in the case of LDPE-Al₂O₃ nanocomposites are smaller than for the unfilled polymer. In the case of LDPE-SiO₂ nanocomposites the permittivity is higher than for the unfilled polymer only up to 5 kHz. Another observation is the occurrence of a perturbation in the frequency variation of the ε'_r for TiO₂ and for SiO₂ fillers, showing a dielectric relaxation due to presence of the nanoparticles.

The variation of tan δ with the frequency for all tested filler concentrations and types is a classical one, with the distinct separation of the parts ascribed mainly to polarization (tan δ_p) and conduction (tan δ_c). It can be remarked that for LDPE-Al₂O₃ nanocomposites (Fig. 4) the tan δ values are smaller than in the unfilled polymer for all the filler concentrations, especially at very low frequencies where the conduction component is important. The same observation for LDPE-TiO₂ nanocomposites (Fig. 6), whereas for LDPE-SiO₂ nanocomposites the tan δ values are higher than in the unfilled polymer for all the frequency range analyzed. Similar results of a lower tan δ in polymer nanocomposites have been also reported in other studies [13, 14]. In nanocomposites the huge area of the filler polymer interfaces and the polymer chain entanglements may hinder the movement of charges in the material and, consequently, may cause a reduction of the electrical conductivity and consequently of the component tan δ_c. Another remark is a peak appearing in the tan δ variation for TiO₂ and for SiO₂ fillers. In the case of TiO₂ filler the peak is located at about 100 Hz and is higher than in
the case of the SiO₂ filler, which is located at about 10 Hz. These peaks correspond to the perturbations of ε′ variation noticed in the case of these fillers.

B. Electric field distribution

The chart of the electric field strength in a nanocomposite containing 5 % nanoparticles of 40 nm diameter is shown in Fig. 7.

![Electric field strength in a cut passing through the nanoparticle](Image)

The permittivity values considered were ε₀ = 2.2 (corresponding to polyethylene) for the polymer matrix, εᵣᵣ = 6 for the interface and εᵣₚ = 10 (corresponding to Al₂O₃) for the nanoparticle.

It can be remarked that the field is strongly perturbed by the presence of the nanoparticle. On the one hand, the electric field inside the nanoparticle is significantly lower than in the polymer matrix, whereas on the other hand, the electric field is amplified outside, just near the nanoparticle. This field distribution could influence significantly the dielectric behavior and consequently the effective permittivity of the nanocomposite, together with the above discussed chain immobilization and interfacial polarization.

V. CONCLUSIONS

The preliminary results obtained at room temperature emphasize different dielectric behaviours of the nanocomposites, depending on the frequency and on the filler concentration and type. In the case of the permittivity, values smaller than those for the base polymer are noticed for the LDPE nanocomposites with a low content of Al₂O₃ and of TiO₂ fillers at very low frequencies. The tan δ values are smaller than for the unfilled polymer only in the case of TiO₂ and Al₂O₃ fillers at very low frequencies. A reduced chain movement is thought to be responsible for the lowering of the nanocomposites’ permittivity and loss tangent with respect to the unfilled polymer, but further analysis is required. A peak is remarked in the frequency variation of tan δ for TiO₂ and for SiO₂ fillers, showing a dielectric relaxation due to polymer nanodielectrification. The numerical results obtained with the proposed 3D model show a strong perturbation of the electric field distribution due to the nanoparticles, which can play an important role on the dielectric behaviour of the nanodielectric. Further, this parametric model will be included in a procedure for the optimization of the content and dimensions of inorganic nanoparticles to be added in a polymer in order to obtain a polymer nanocomposite dielectric with an imposed relative permittivity.

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REFERENCES