EFFECTS OF IONIZING RADIATION ON THE DIELECTRIC PROPERTIES OF LDPE-AL_2O_3 NANOCOMPOSITES

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Scopul acestei lucrări este de a studia efectele iradierii asupra comportamentului dielectric al nanocompozitelor polimerice pe bază de polietilenă de joasă densitate (PEJD) şi nanoparticule de alumină (Al_2O_3). Atât partea reală a permitivităţii electrice cât şi factorul de pierderi au fost determinate prin spectroscopie dielectrică în gama de frecvenţe 1 mHz – 10 MHz, pe eşantioane plane realizate din nanodielectricii testaţi. În această lucrare a fost discutată dependenţa dintre concentraţia de umplutură cuprinsă între 2 şi 10 % şi efectele iradierii asupra proprietăţilor dielectrice.

The goal of this paper is to study the irradiation effects on the dielectric behaviour of a polymer nanocomposite dielectric made of low density polyethylene filled with nanoparticles of Al_2O_3. The permittivity and tan delta values were determined by dielectric spectroscopy over a frequency range of 1 mHz – 10 MHz on plane samples of the tested nanodielectrics. The dependance between the filler concentration, between 2 and 10 wt.%, and the irradiation effects on the dielectric properties is also discussed in the paper.

Keywords: dielectric properties, ionizing radiation, nanodielectrics

1. Introduction

In the last five years many groups of research in the field of dielectrics from all over the world have been focused their energies and resources toward 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

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to the traditional polymer microcomposites. The nano-fillers are usually 1 to 100 nm in size, 1 to 10 wt.% in content, and should be homogeneously dispersed in the polymer matrix. These materials can be manufactured by the direct mixing method, the intercalation method, and the sol-gel method that focus the separation of cohesive nano-fillers from each other. Such separation can be obtained by imposing shear force between neighboring nano-fillers or by increasing chemical and or physical intimacy between nano-fillers and their contacting polymer matrix [1]. Until now several methods for processing and characterization have been tested, and some theories and models have been proposed for these materials having a huge nanofiller-polymer interface area which seems to be the main responsible for their unique properties [4-6]. Despite the encouraging advances in this field we are still far from understanding and controlling the phenomena in these materials. The accelerated testing by irradiation of LDPE has been extensively studied in order to reach optimized formulation [7,8]. The formation of free radicals as precursors for the generation of radiolysis product causes the structural modification of polymer matrix. The presence of nanophase in LDPE under γ exposure provides new information on the changes in dielectric properties, as well as in durability.

In the present work the influence of the γ-radiation on the dielectric behaviour of low density polyethylene (LDPE) filled with nanoparticles of Al_2O_3 is analysed. Thus, the permittivity and tan delta values were determined by dielectric spectroscopy (DS) over a frequency range of 1 mHz – 1 MHz on plane samples of the tested nanodielectrics, before and after irradiation with γ-rays.

2. Experimental

Systems Investigated

In the paper, there will be no apparatus or installation descriptions. The materials tested in this study were polyethylene-Al_2O_3 nanocomposites. The content of nanofillers of the tested formulations was 2, 5 and 10 wt.%. For all the formulations the nanoparticles of Al_2O_3 had the average diameter of 40 nm. The polymer matrix was a low density polyethylene (LDPE) commercially available at Arpechim Pitesti. The nanocomposites were manufactured by direct mixing method, using the installation shown in Figure 1.

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 nanocomposite samples for electrical tests performed in this study were plaques of square shape (10 x 10 cm^2) having the thickness of 0.5-0.6 mm.

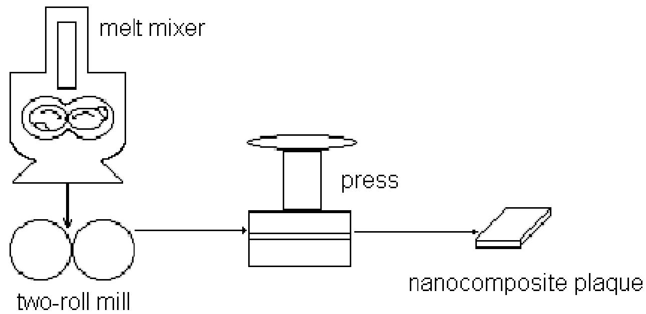

Fig. 1. Installation used for nanocomposite manufacturing [9]

Sample Irradiation

The samples were subjected to the action of γ-rays provided by ^{137}Cs source, incorporated in GAMMATOR M-38-2 irradiator, at a dose rate of 0.4 kGy/h, in air, at room temperature. The absorbed dose for all samples was 10 kGy. Irradiation/measurement cycles were applied for the dose accumulation.

Dielectric Spectroscopy

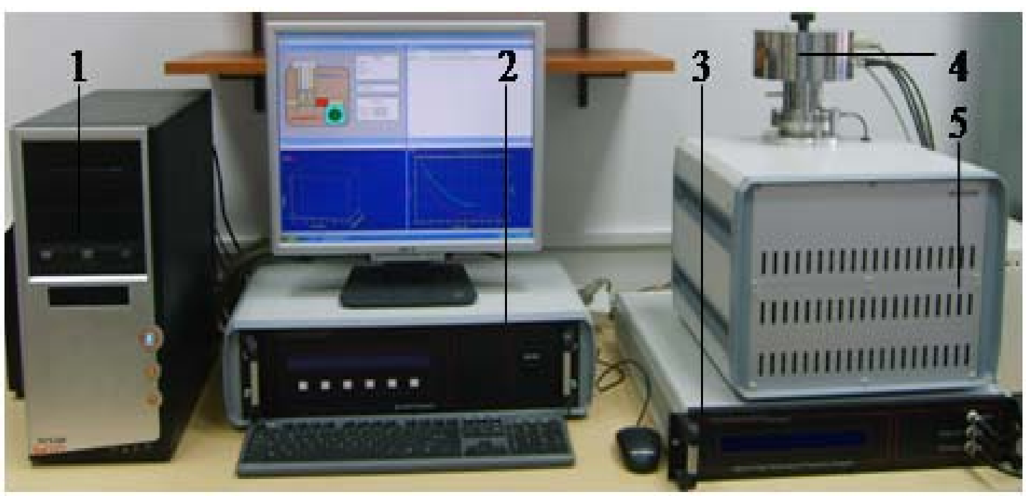

Fig. 2. Setup for dielectric spectroscopy measurements (1 – PC; 2 – Control System; 3 – Modular Measurement System; 4 – Measurement Cell; 5 – Temperature Control System)

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 (Figure 2), over the frequency range 10^{-3} – 10^{7} 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.

3. Results and Discussion

The DS results revealed, on the one hand, the influence of the filler content and, on the other hand, the effect of the γ-rays on the dielectric properties analyzed ($\varepsilon_r^{'}$, $\tan\delta$).

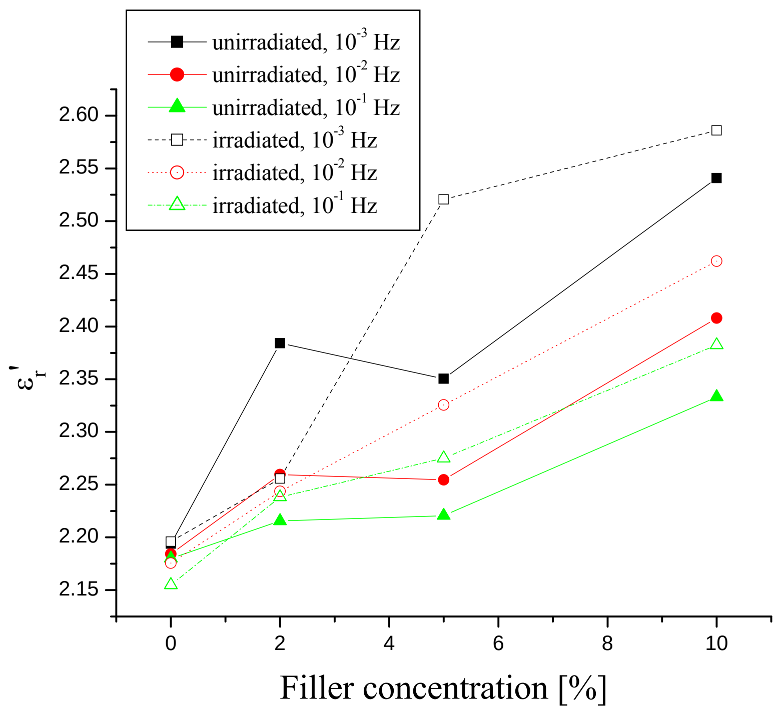

Fig. 3. Variation of $\varepsilon_r^{'}$ vs. filler concentration for 10^{-3}-10^{-1} Hz

The influence of the filler content on the real part of the complex relative permittivity ($\varepsilon_r^{'}$) of the irradiated and unirradiated samples can be seen in the Figure 3 for low frequencies and in Figure 4 for higher frequencies.

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:

$$\tan\delta = \tan\delta_d + \tan\delta_c \tag{1}$$

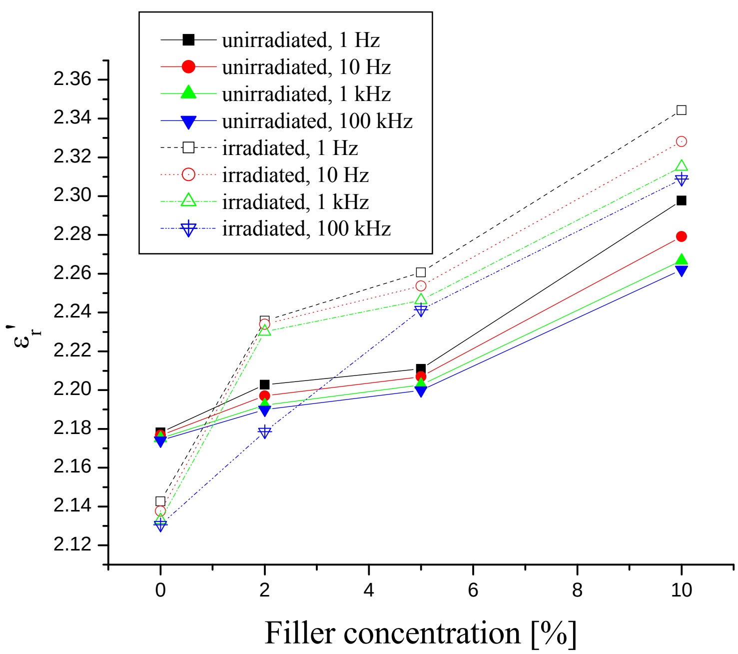

Fig. 4. Variation of $\varepsilon_r^{'}$ vs. filler concentration for 1-10^5 Hz

where $\tan\delta_d = \varepsilon^{"}/\varepsilon^{'}$ is the dielectric loss component and $\tan\delta_c = \sigma/(\omega\,\varepsilon^{'})$ is the conduction loss component, σ is the conductivity, ω is the angular frequency, $\varepsilon^{'}$

and ε'' are, respectively, the real and imaginary parts of the complex permittivity $\varepsilon^* = \varepsilon' - \varepsilon'' = \varepsilon_0\left(\varepsilon_r' - j\,\varepsilon_r''\right)$, and ε_0 is the vacuum permittivity.

From the results presented in Figures 3 and 4 it can be observed that, at low frequencies (10^{-3}-10^{-1} Hz), for both unirradiated and irradiated samples the ε_r' values in the nanocomposite samples are higher than those for the unfilled polymer, and they mainly increase with filler content. This increase is probably due to a more important contribution of the interfacial polarization with the increase of the filler content. However, a slow decrease of the permittivity values can by noticed at low frequencies (10^{-3}-10^{-1} Hz) for unirradiated samples between 2 and 5 wt.% filler content. This is thought to arise from a reduced chain movement of the polymer in the nanocomposite due to the increasing presence of the nanoparticles [5, 11].

The irradiation effect on ε_r' depends on the nanofiller concentration and on the electric field frequency.

For low content of nanofiller (2 wt.%), the presence of free radicals appeared in low quantity, during irradiation at 10 kGy, do not provide a noticeable modification in the material polarisation. Higher nanofiller concentration leads to an intensification of the interaction processes between filler and polymer matrix, where radicals were formed as a consequence of high energy exposure. Thus, in the case of 5 wt.% filler level, ε_r' values for the irradiated samples record a significant increase with respect to those for unirradiated samples, especially at low frequency (10^{-3} Hz) where this increase is of 7 %. For 10 wt.% filler concentration, this increase of ε_r' values in the case of irradiated samples has practically the same level (of about 2 %) for all the analysed frequencies. This aspect can be explained by the polarisation intensification due to the oxigenated radiolysis products.

One of the main polarization mechanisms in Al_2O_3 filled polyethylene is due to the orientation of the different dipolar groups attached to polymer chains. The orientation process depends on the chain mobility which seems to be reduced due to a strong bonding of the polymer chains and the particle surface inside the nanosized layers of the polymer-particle interface [12]. Thus, the higher the filler content, the more the immobile are the polymer chains, and consequently the permittivity should reduce with the increase of the filler concentration. But, on the other hand in the nanocomposite material there are several dipolar groups (inside polymer matrix or inside nanoparticles) which are not affected by the chain immobilizations and which would be free to orient with the applied field and with increasing filler content the permittivity will tend to go up. Besides, an increase of the nanofiller concentration results in an increase of the filler-polymer interface area where interfacial polarization may occur especially at low frequencies. This is due to the accumulation of space charges at interface boundaries, as emphasized by the increase of the absorption current [13]. All these processes take place simultaneously and the understanding of their complex dynamics remains to be elucidated by other studies, but the balance between the rate of permittivity lowering due to chain immobilization and the rate of permittivity enhancement due to filler loading determines which way the permittivity of the nanocomposite will change. The nanodielectric irradiation affects this balance by introducing, in the polymer matrix, of the free radicals which react with the nanoparticles resulting modifications of the dipolar groups. As a consequence, the polarisation is modified with respect to the unirradiated material, the irradiated material responding differently at the electric field action depending on the frequency and an the filler concentration.

The influence of the filler content on the loss tangent ($\tan\delta$) of the irradiated and unirradiated samples can be seen in the Figure 5 for low frequencies and in Figure 6 for higher frequencies.

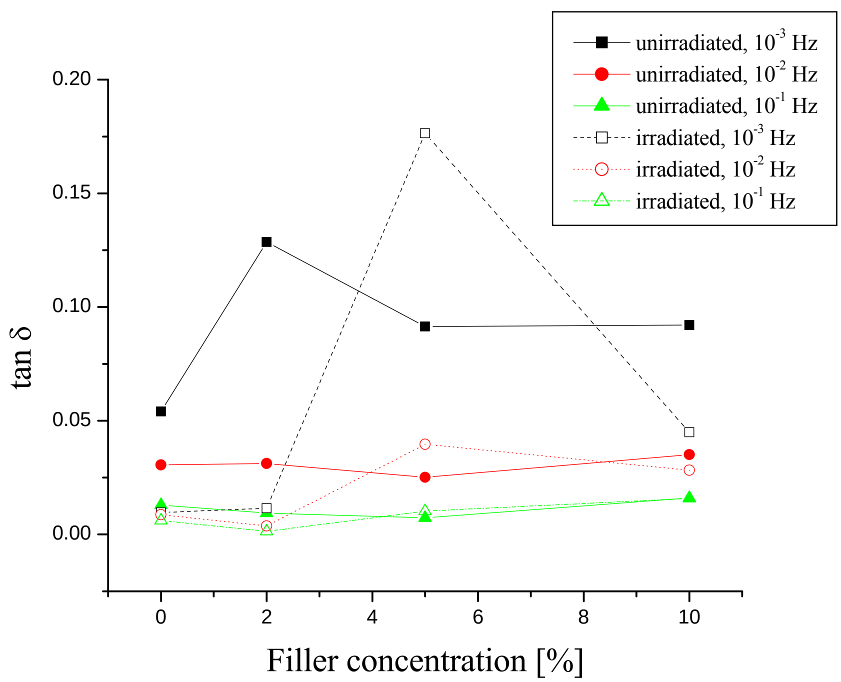

Fig. 5. Variation of $\tan\delta$ vs. filler concentration for 10^{-3}-10^{-1} Hz

As for the irradiation effect on the loss factor in the studied samples, it is similar to that of the permittivity. Thus can be remarked, as for the $\varepsilon_r^{'}$ values, an important increase of the $\tan\delta$ values in the irradiated samples with respect to the unirradiated ones for the 5 wt.% filler concentration, especially for the lower frequencies of the electric field. This result show that the polarisation is more affected by γ radiation exposure than the conduction process.Another observation is that even if there are differences between the $\tan\delta$ values in the irradiated samples with respect to the unirradiated ones, the irradiation process does not affect the order of magnitude of the loss tangent for any the tested frequencies.

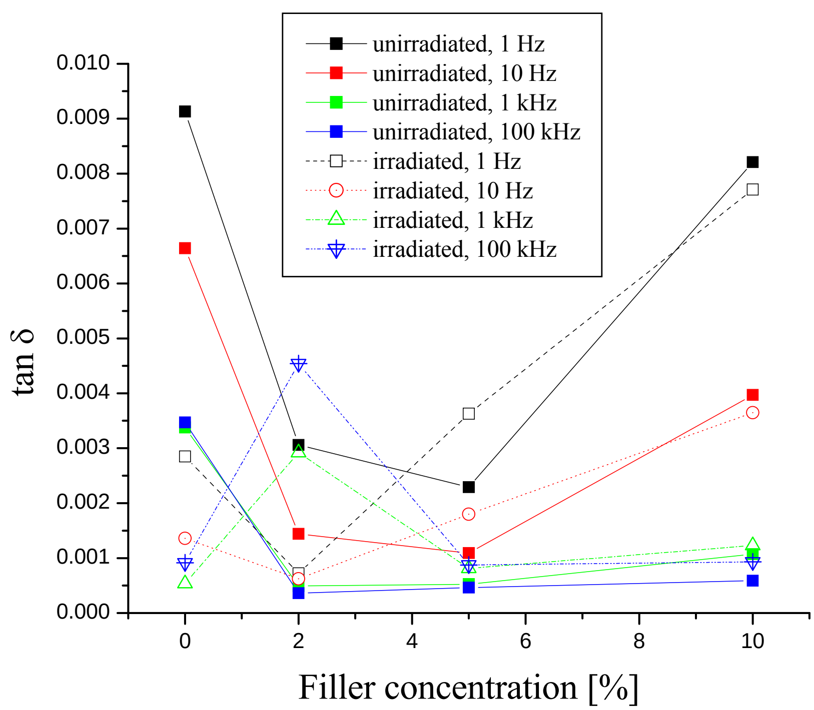

Fig. 6. Variation of $\tan\delta$ vs. filler concentration for 1-10^5 Hz

6. Conclusions

Ionizing radiation induces modifications in dielectric properties related to the formation of free radicals, which subsequently are oxidized. The polar groups that appear during exposure interact with filler nanoparticles and the permittivity and tan delta are direct related to the received dose for each concentration of Al_2O_3. The concentration of free radicals that appears in nanocomposites during irradiation represents an important factor that affect the variation of the $\varepsilon_r^{'}$ and $\tan\delta$ values with the electric field frequency.

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