



WATER AND THERMAL AGING INFLUENCE ON DIELECTRIC RESPONSE OF LOW DENSITY POLYETHYLENE- Al_2O_3 NANOCOMPOSITES

FLORIN CIUPRINA¹, LAURA ANDREI¹

Key words: Nanodielectrics, Dielectric spectroscopy, Temperature variation, Thermal aging, Water exposure.

Water and thermal aging influence on the dielectric response of low density polyethylene (LDPE)- Al_2O_3 nanocomposites with 2 wt% filler content was discussed in this paper. The dielectric response, consisting in frequency variation in the range 10 mHz – 1 MHz and for temperatures from 30 to 70 °C of the real and imaginary parts of the complex permittivity, measured before any treatment, after one week immersion in deionized water and after three stages of thermal aging at 90 °C are presented and discussed in this paper, with a focus on the stability of the dielectric properties to the applied stresses.

1. INTRODUCTION

The interest in nanodielectrics is relatively recent, the first experimental results for nanometric dielectrics being reported in 2002 [1, 2]. The nanometric dielectrics are obtained as a combination between a polymer matrix and filler consisting of a small amount of nanoparticles of various types. Their mechanical, electrical or thermal properties are defined by the huge polymer-nanoparticles interface, having a surface of tens of square kilometers per cubic meter of nanocomposite containing 10% nanoparticles with average sizes of 10 nm [3–6].

In order to improve their properties versus microcomposites or polymers without particles, a lot of effort was involved in research that either focused on the nanocomposite formulation, or on developing theories and models for the phenomena involved [7–11].

The recent studies are more oriented towards large scale applications that use nanodielectrics. In this context, another issue that has to be considered when new nanocomposite formulations are proposed for applications is that, besides the improved dielectric properties, a high stability is ensured when the material is exposed to water and thermal stress. This is necessary because such materials are very often used in devices that are exposed to such conditions. The studies carried out in [12–15] referred to the influence of water absorption on the dielectric response, for various combinations of polymer matrix – filler. Lau et al. obtained higher values of permittivity and loss tangent under a higher water absorption in the case of polyethylene/nanosilica formulation versus the polyethylene without filler [12]. Despite the reduced water absorption, Ayoob et al. obtained a dielectric response of water exposed polyethylene hexagonal boron nitride nanocomposites extremely different from the samples not exposed to water [15].

A lot of papers reported studies on the effect of temperature on the dielectric spectra of nanodielectrics, many of them mentioning a thermal activated dielectric response, but unusual behavior was reported sometimes [13, 16, 17]. However, according to our knowledge, the information published on the effect of the thermal aging on the dielectric behavior of polymer nanocomposites is quite scarce.

The dielectric responses presented in this paper are

obtained from experiments in which the samples were first measured unexposed to any stress, and then exposed to water during a week, followed by a thermal stress exposure that lasted one month.

The samples we used, namely low density polyethylene (LDPE)/nano- Al_2O_3 nanodielectrics, with 2 wt% filler content (where wt% means weight percent), have improved electrical and mechanical properties with respect to LDPE or other LDPE based nanocomposites, as we emphasized in [16]. We show and discuss the dielectric spectra in the frequency range 10 mHz – 1 MHz and for temperature range 30 to 70 °C, obtained in the following cases: before any stress, after immersion in deionized water for a week and after three thermal aging stages, summing up to a month. The stability of the dielectric properties after the applied stresses is also discussed in this paper, which is a development of [18].

2. EXPERIMENTAL

Sample preparation

Low density polyethylene (LDPE) with a density of 0.916 g/cm³ and a melt flow index (190 °C) of 0.3 g/10 min, supplied by Arpechim, Romania, was used as polymer matrix. Alumina (Al_2O_3) nanopowder, with nearly spherical particles, having an average particle diameter of 45 nm, was used as filler with 2 wt% concentration. The polymer-filler compatibilization was enhanced with maleic anhydride grafted polypropylene (MA-PE) from Sigma-Aldrich Co., with the density 0.925 g/cm³ and having 3 % grafted maleic anhydride. The polypropylene nanocomposite was prepared by direct mixing method in a Brabender LabStation having the speed of the rotors of 75 rpm. The mixing temperature was 160 °C and the mixing time was 10 min. Finally, square sheets (10 x 10 cm²) with the thickness of 0.5 – 0.6 mm were prepared by hot melt pressing at 170 °C, for 5 min. This preparation procedure leads to a uniform distribution of Al_2O_3 nanoparticles inside LDPE matrix as revealed by scanning electron microscopy analysis [19].

Dielectric spectroscopy

The frequency variations of the real and imaginary parts (ϵ_r' and ϵ_r'') of the complex permittivity of LDPE- Al_2O_3 nanodielectrics were determined at different temperatures with a Novocontrol ALPHA-A Analyzer in combination with an Active Sample Cell ZGS. Three samples (disks of

¹ ELMAT Laboratory, Faculty of Electrical Engineering, University Politehnica of Bucharest, Bucharest, Romania, florin@elmat.pub.ro

30 mm diameter) were tested by dielectric spectroscopy (DS) measurements over the frequency range $10^{-2} - 10^6$ Hz, at step-like increasing temperatures from 30 °C to 70 °C with a temperature step of 20 °C. At each step, the samples were kept 10 minutes for temperature stabilization, before the start of measurements.

The DS tests were performed on nanocomposite samples in different conditions:

- “initial” - before any conditioning procedure;
- “wet” – after immersion in deionized water for 163 hours, at ambient temperature.
- “heated” – after thermally aging at 90 ± 2 °C in a Caloris-ECV-100 oven with forced air circulation for different periods of time: “heated I” (for 163 hours), “heated II” (for 493 hours) and “heated III” (for 680 hours).

3. RESULTS AND DISCUSSION

The dielectric spectroscopy results in terms of frequency variations of real and imaginary permittivities (ϵ_r' and ϵ_r'') of LDPE - Al₂O₃ (2 wt %) nanocomposite tested are shown in Fig. 1 for “initial” state, in Fig. 3 for “wet” samples and in Fig. 4 for the three stages of thermally aged samples.

Real permittivity ϵ_r' values for the nanocomposites decrease with respect to the increasing temperature in the entire frequency range for all conditions tested (initial, wet and the three thermally aged stages). The main responsible for this behavior is the thermal agitation, which hinders the dipole orientation in the different regions of nanodielectrics.

On the other hand, for all conditions and at all temperatures tested, ϵ_r' variation with frequency decrease quite sharply at low frequencies and show a slighter decrease at higher frequencies. A possible explanation for this behavior can be a combination between electrode polarization in the low frequency range and other types of relaxations, as resulting by analyzing also the frequency variation of the imaginary permittivity ϵ_r'' .

The analysis of the frequency variation of the imaginary permittivity ϵ_r'' mainly emphasizes the appearance of three loss peaks corresponding to three relaxation mechanisms, for all conditions (initial, wet and thermal aging). To better highlight these peaks, the DS data for “heated I” state are fitted in Fig. 5 with Havriliak-Negami (HN) equation [20]:

$$\epsilon^*(\omega) = \epsilon'(\omega) - j\epsilon''(\omega) = \sum_k \left[\frac{\Delta\epsilon_k}{(1 + (j\omega\tau_{HN})^\alpha)^\beta} + \epsilon_\infty \right], \quad (1)$$

where ϵ^* is the complex permittivity, $\omega = 2\pi f$ the angular frequency, $\Delta\epsilon_k$ is the strength of the k relaxation, τ_{HN} is the HN relaxation time, α and β are parameters that quantify the slope and the asymmetry of a given relaxation peak, respectively. The actual relaxation time is $\tau_{\max} = 1/2\pi f_{\max}$, where f_{\max} is the frequency where the relaxation occurs, calculated using the equation:

$$\tau_{\max} = \tau_{HN} \left[\frac{\sin\left(\frac{\pi\alpha\beta}{2(\beta+1)}\right)}{\sin\left(\frac{\pi\alpha}{2(\beta+1)}\right)} \right]^{1/\alpha} \quad (2)$$

The HN parameters for the three relaxation processes emphasized in Fig. 5 are shown in Table 1.

Table 1
HN parameters for fitting heated I DS data

	α	β	τ_{\max} [s]
LF peak	1	0.48	16.46
MF peak	0.29	0.84	$5.793 \cdot 10^{-2}$
HF peak	0.26	1	$2.855 \cdot 10^{-5}$

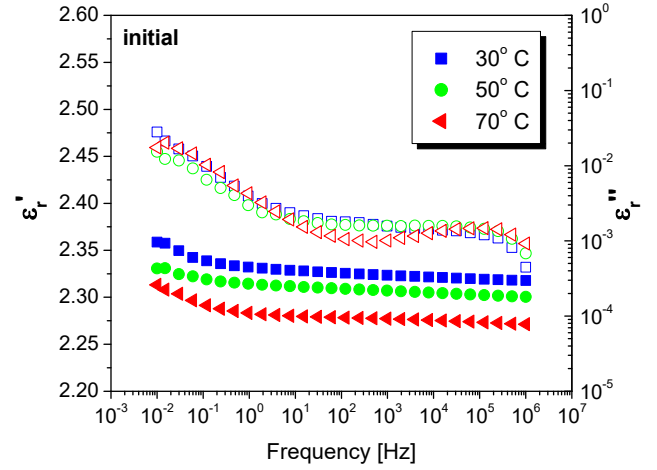


Fig. 1 – Frequency variation of ϵ_r' (full symbols) and ϵ_r'' (empty symbols) for PE-Al₂O₃ nanocomposite - initial measurements.

The low frequency (LF) loss peak, remarked in the range $10^{-2} - 10^{-1}$ Hz, can be associated with localized space charge movements in the polymer matrix [21–23] and/or to twists of chains in the crystal lamellae favored by the disorder of the lamella-amorphous interface caused by an increase of the free volume during nanostructuration. Besides, the electrode polarization (EP), due to the charge accumulation at the electrode/nanodielectric interface, is highlighted by a sharp increase in ϵ_r' with decreasing frequency corroborated with ϵ_r'' peak in the LF range, which is the signature of EP relaxation at the lowest frequencies [24, 25]. As frequently the molecular relaxations at low frequencies are masked by the significantly large ϵ_r'' values due to the dc conduction contributions, complex electric modulus spectrum can be used to resolve this inconvenient by suppressing the conduction effects, thus emphasizing the relaxations at low frequencies.

Complex electric modulus (M^*) is the inverse of relative complex permittivity, which is expressed by the following equation:

$$\begin{aligned} M^*(\omega) &= \frac{1}{\epsilon^*(\omega)} = \frac{1}{\epsilon' - j\epsilon''} = \\ &= \frac{\epsilon'}{\epsilon'^2 + j\epsilon''^2} + j \frac{\epsilon''}{\epsilon'^2 + j\epsilon''^2} = M' + jM'' \end{aligned} \quad (3)$$

Since both ϵ_r' and ϵ_r'' appear at the denominator, M' and M'' are small for large permittivity values, and therefore the overwhelming of relaxation peaks by dc conduction contribution is eliminated.

The low frequency relaxation is sustained in Fig. 2 by the representation of the imaginary part of electrical modulus. The representation of modulus is necessary to show if the influence of dc conductivity is important. [26, 27] The electric modulus is the inverse of the electric permittivity and shows for a dielectric relaxation process, a relaxation peak in both representations. Physically, the electric modulus corresponds to the relaxation of the electric field in the material when the electric displacement remains

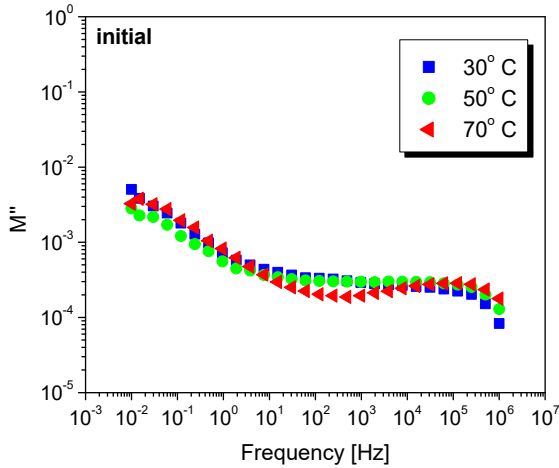


Fig. 2 – Frequency variation of imaginary part of electrical modulus for PE- Al_2O_3 nanocomposite at different increasing temperatures - initial measurement.

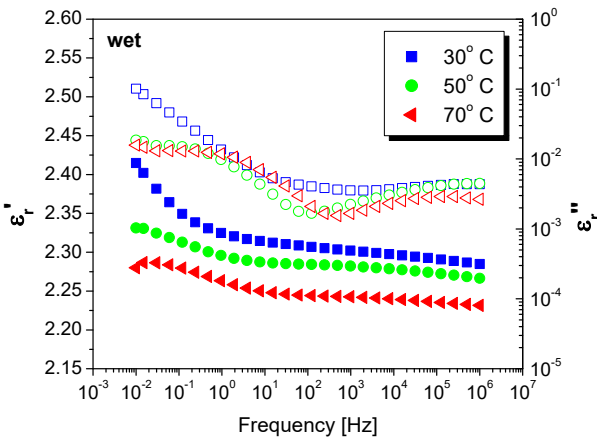


Fig. 3 – Frequency variation of ϵ'_r (full symbols) and ϵ''_r (empty symbols) for **wet** PE- Al_2O_3 nanocomposite at different increasing temperatures.

constant, so that the electric modulus represents the real dielectric relaxation process.

The medium frequency (MF) peak can be seen around 10^2 Hz, and this can be assigned to a Maxwell–Wagner–Sillars (MWS) relaxation, due to charge accumulation on the different layers of the nanoparticle – polymer matrix interface. The high frequency peak (HF) noticed at 10^4 – 10^5 Hz may possibly emphasize a relaxation due to clustered water containing ions introduced during polymer nanocomposite preparation or water exposure.

The dielectric spectra from Figs. 1–4 show an important influence of temperature on the relaxation processes. The LF and HF relaxation peaks move to higher frequencies with increasing temperature, which suggests a thermal activation of the polarization mechanisms, *e.g.* dipole orientation. The MF loss peak, visible at 30 °C for all three conditions tested (initial, wet and heated), can be seen at 50 °C only in the “initial” DS loss spectrum, but it is not visible in any ϵ_r variation for 70 °C. This behavior indicates that thermal agitation, which is more intense when the temperature increases, prevents the charge carriers to accumulate on the nanoparticle-matrix interface, thus reducing the interfacial polarization.

The results from Figs. 1–4 show small differences in ϵ_r values both between “wet” and “initial” states and between

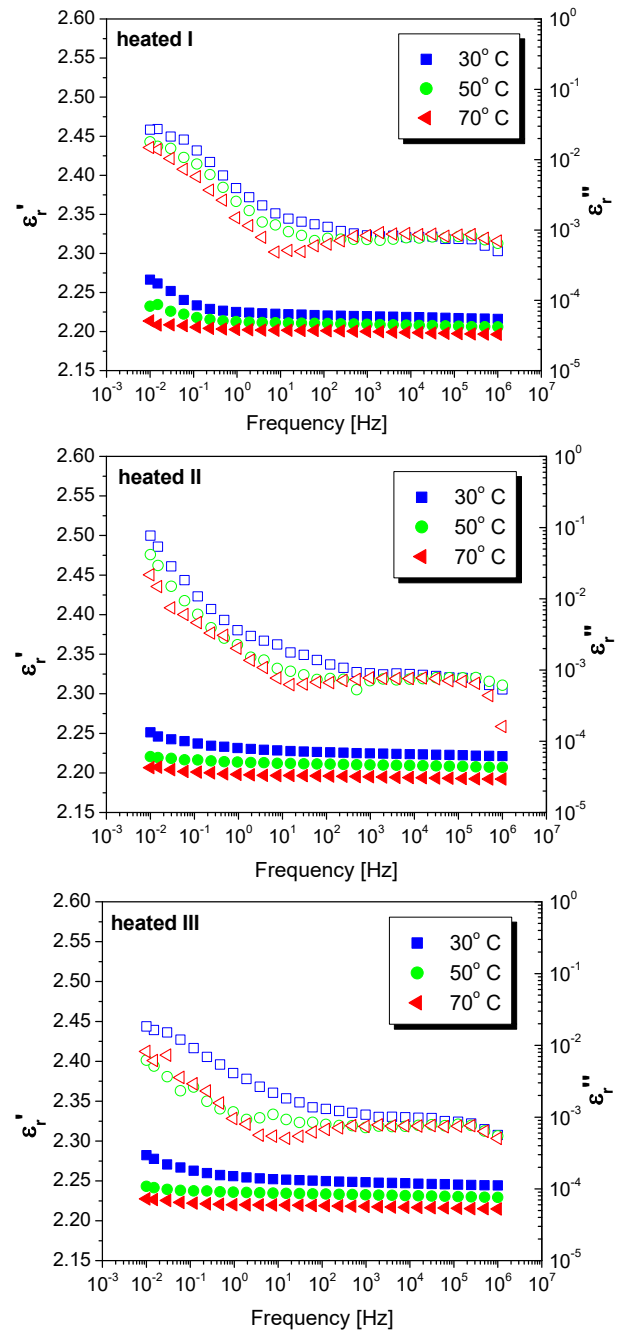


Fig. 4 – Frequency variation of ϵ'_r (full symbols) and ϵ''_r (empty symbols) for the three stages of thermally aged PE- Al_2O_3 nanocomposite at different increasing temperatures.

all three thermally aged states and “initial” state. These small differences are emphasized in Table 2, which shows the Euclidean distance over the entire DS frequency range between “wet” ϵ_r values and those in “initial” condition, as well as between thermally aged vs. “initial” ϵ_r values. The values in Table 1 indicate a reduced influence of both water exposure (1 %) and thermal aging (less than 5 %) on the real permittivity of the LDPE- Al_2O_3 nanocomposite with 2 wt % filler content tested in the present work. Moreover, for the longest time of thermal aging (680 hours, “heated III”) the influence of aging on ϵ_r values becomes even smaller.

The water exposure and thermal aging influence on dielectric losses consists mainly in some changes in peak position and height remarked in the ϵ_r variations, but

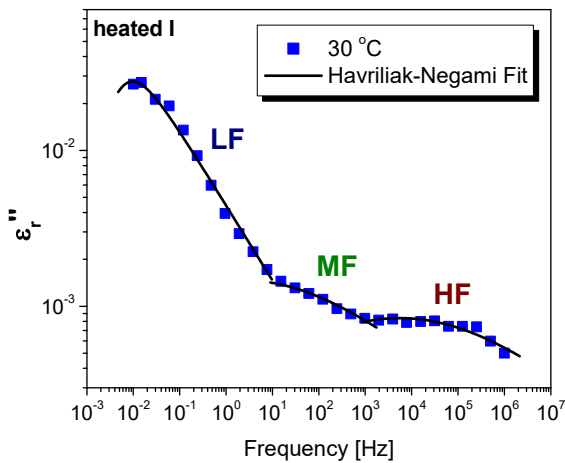


Fig. 5 – Frequency variation of ϵ_r' for heated I PE- Al_2O_3 nanocomposite at 30°C and the fitting of experimental data using Havriliak-Negami function.

Table 2

Water and thermal aging effects on real permittivity

	wet vs initial [%]	heated I vs initial [%]	heated II vs initial [%]	heated III vs initial [%]
30 °C	1.0627	4.4325	4.3019	3.2477
50 °C	1.0013	4.253	4.2881	3.3319
70 °C	1.3618	3.5462	3.7479	2.7797

without changing the order of magnitude of ϵ_r'' for any of the three frequency regions (LF, MF and HF). The DS spectra of ϵ_r'' in “wet” condition (Fig. 3) show a shift of LF peak to higher frequency and a broader HF peak than in “initial” condition. Such a behavior, also remarked also for polypropylene/nanosilica nanocomposites, is thought to be due to the presence of water in nanodielectric, which behaves as a plasticizer, thus leading to the increase of the free volume and enhancing the mobility of different dipoles [17]. Beside the three relaxation peaks described above, another relaxation peak can be noticed in the HF region for thermally aged samples, at 10^3 – 10^4 Hz. This slight relaxation can emphasize some thermal aging of the samples leading to oxidation, during which carboxylic groups (-COOH) can appear and contribute to the polar groups. The DS results of the thermally aged samples, explored for higher aging times (heated II and heated III) show also this oxidation peak at 10^3 – 10^4 Hz, which seems to become broader with aging, suggesting changes of the charge dynamics due to oxidation in nanodielectric with aging.

The small differences in ϵ_r' values, around 1 % after water exposure and less than 5 % after heat exposure, together with small differences in loss behavior after water and thermal aging, emphasize a high dielectric stability of the LDPE - Al_2O_3 (2 %) nanodielectric. As we previously found, this nanodielectric possess improved dielectric and mechanical properties with respect to those of the unfilled polymer [19]. These previous results, and the fact that its dielectric behavior is quite stable to water and thermal aging, recommend it for application in the electrical insulation industry.

4. CONCLUSIONS

The water and thermal aging have a slight influence on

the dielectric behavior of LDPE - Al_2O_3 nanodielectric with 2 wt % filler content, for the experimental conditions tested in this work. The ϵ_r' values are modified with 1 % after water exposure and less than 5% after thermal aging. Small differences in loss behavior after water and thermal aging, without changing the order of magnitude of ϵ_r'' values, emphasize a high dielectric stability of the tested LDPE- Al_2O_3 nanodielectric. These dielectric spectroscopy results, together with previous ones that showed improved mechanical and dielectric properties of this nanodielectric as compared to unfilled LDPE, strongly recommend this material for applications as electrical insulation.

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