

ELECTROMAGNETIC PROPERTIES OF POLYETHYLENE-NEODYMIUM COMPOSITES

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Abstract

In this paper a study regarding the influence of Neodymium (Nd) powder content on the electric and magnetic properties of low density polyethylene composites is presented. The distribution of the particles in the polymeric matrix was determined by Scanning Electron Microscopy (SEM) and optical microscopy (OM). A relative uniform dispersion of the particles in LDPE was observed.

The variations of the electrical conductivity and real and imaginary complex permittivity parts with the electric field frequency, the temperature and the filler content were studied. Neodymium filler determines important increases of real ϵ_r' and imaginary ϵ_r'' permittivity but also the conductivity components of samples, and their magnetic properties i.e. remnant magnetization, maximum magnetization and magnetic susceptibility.

The increase of temperature determines, generally, a decrease of the real part of permittivity but a frequency range for each sample when an increase of ϵ_r' with temperature was observed.

Key words: electromagnetic properties, magnetic composites, percolation

1. INTRODUCTION

The use of multifunctional composite materials allowed lately, getting remarkable results in several industrial domains (electronics, electrical engineering, aviation, transportation etc.), they presenting special electrical, magnetical, thermal and mechanical properties, easy processability and low cost (Ramajo 2009). Properties of the composites depend on the one hand, on the chemical nature of the two essential components, the matrix and filler and, on the other hand, the characteristics of their manufacturing processes.

For electronics and electrical engineering materials with high or low electrical conductivity, low dielectric loss, high magnetic permeability and low magnetic loss, coercive field and high magnetic energy density etc. are needed. For their manufacture thermoplastic and thermoset polymer matrix such as natural rubber (Lertsurawat 2009 & Kong 2010), low density polyethylene (Borah 2010, Huang 2007, Zois 2003), high-density polyethylene (Foulger 1999), block copolymer of [styrene-butylene/butylene-b-styrene] (SEBS) (Yang 2008), acrylonitril-butadiene-styrene (ABS) (Panaitescu 2001, Notingher 2004), polyvinylchloride (Jasem 2012, Trojanowska-Tomczak 2014, Mamunya 2002), polystyrene (PS) (Yacubowicz 1990), polypropylene (Tang 2009), Ethylene Vinyl Acetate (Wang 2012), PMMA (Trojanowska-Tomczak 2014), polyamide (PA) (Zois 2003), polyoxymethylene (POM) (Zois 2003), triblock copolymer with polystyrene end blocks and a rubbery poly(ethylene-butylene) mid block (Gokturk 1993), polycarbonate, epoxy resin (Ramajo 2007, Ramajo 2009, Ramajo 2014, Mamunya 2002, Singh 2003), nylon 6,6 etc were used.

As filler, aluminum (Huang 2007, Singh 2003), copper (Panaitescu 2002, Mamunya 2002), nickel-iron powder (Gokturk 1993, Mamunya 2002), $\text{Ni}_8\text{Fe}_{22}$ (permalloy) fine flakes (Shirakata 2008), iron oxide (Fe_3O_4) (Yacubowicz 1990, Yang 2008), steel (Notingher 2004), nickel or silver particles (Tang 2009, Clingerman 2002, Mamunya 2002), cobalt ferrite nanoparticles (Borah 2010), barium ferrites (Yacubowicz 1990), neodymium (Stancu 2013, Stancu 2015), rare-earth ions (Akamatsu 2011), Nd-Fe-B (Grujic 2010, Dobrzański 2006), carbon and graphite (Foulger 1999, Jasem 2012, Tang 2009), Single-Walled Carbon Nanotubes (Choi 2012), Wood's metal ($\text{Bi}_{50}\text{Pb}_{25}\text{Sn}_{12.5}\text{Cd}_{12.5}$) (Trojanowska-Tomczak 2014), $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) polycrystalline ceramics (Ramajo 2007), aluminum nitrides (Salaneck 1991), barium titanate (Ramajo 2007) etc. were used. These new materials are used for

encapsulating, thin film coating, packing of electronic circuits (Jasem 2012), electromagnetic and radio-frequency interference (EMI/RFI) shielding for electronic devices and electrostatic dissipation (ESD) (Clingerman 2002, Chung 2000).

The properties of polymer composites depends, on the one hand, on the characteristics of the matrix and fillers, and, on the other hand, the parameters of technological processes and environmental action (Panaiteescu 2002 Dyre 2000). In a number of papers the influence of nature, contents and filler size on the electrical properties of polymer composites with conductive (Jasem 2012, Huang 2007, Foulger 1999, Tsangaris 1999) or magnetic filler (Stancu 2013, Zois 2003, Yacubowicz 1990) is presented. In other papers (Stancu 2013, Efros 1976, Doyle 1995) the existence of a critical concentration for that the percolation phenomenon occurs is highlighted. This phenomenon leads to significant variations in both the electrical conductivity, permittivity and dielectric loss factor.

Due to the many possible applications of polymer composite materials with magnetic fillers (hard disc components, electric appliances, automobile industry, sensing elements, electronic, small motors in video recorders, camcorders, printers, communication and micro-electro-mechanical system (MEMS) applications, actuators, magnetic buffers etc.), in recent decades a series of multidisciplinary research to achieve both of bonded magnetic materials (based on Nd-Fe-B magnetic and epoxy resins powders) and the of rubber magnets (magnetic particle of the same, but with thermoplastic polymers) have been conducted. These research are directed into four directions: (a) increase of magnetic energy density, (b) improving corrosion resistance, (c) optimization production process of process parameters and (d) reduction of the subtle rare earth content (Nd), targeting decreasing the price of the magnetic material (Grujić 2011).

In (Stancu 2013, Stancu 2015) a study of the electrical conductivity (measured both in DC and AC), and (Stancu 2014) - a study of the magnetic properties of the polyethylene samples with magnetic fillers are presented. This paper presents the results of an experimental study conducted on samples of low density polyethylene filled with particles of micron sized neodymium regarding their behavior in steady-state and time variables electric and magnetic fields. Variations of the complex permittivity and conductivity components and loss factor for different frequencies of the electric field are determined. Their dependencies on the filler content, temperature and frequency of the electric field are analyzed. It also analyzes the structural characteristics (optical and electron microscopy) and the magnetic properties of the samples. The results are analyzed in terms of using these materials in electrical engineering (electromagnetic shielding etc.).

2. ELECTRICAL CONDUCTIVITY

The electrical conductivity of the polymer composites with conductive filler significantly depend on the filler volume fraction c_v (Stancu 2013). For small values of c_v , the composites conductivity values are still close to those of the matrix polymers (Clingerman 2002). For a certain amount of filler concentration, called percolation volume fraction (c_{vp}), the conductivity increases (almost suddenly) by several orders of magnitude for very low concentration increases. For concentration values higher than c_v , conductivity further increases, approaching that of the filler. The percolation concentration is the value of the concentration for that the filler content is enough high to give rise to a conductive network inside the composite (Dyre 2000).

There are several models that estimate the conductivity values based on the concentration of filler, the physical properties of the matrix and fillers, structural properties of composites, matrix-filler interface characteristics, particle shapes and sizes, etc. These can be grouped into four classes, namely statistical, thermodynamic and geometric structure-oriented. A critical qualitative analysis of the 4 types of models is shown in (Clingerman 2002).

The models used in the analysis of polymer composites conductivity with conductive fillers are part of the statistical models percolation type. Among them stands Kirkpatrick's model (Kirkpatrick 1973), (Zallen 1983) Bueche (Bueche 1972) and McLachlan (McLachlan 1990), but they take into account only the filler concentration and electrical conductivity of the components.

A more advanced model is the thermodynamic model of Mamunya et al. (Mamunya 2002), the conductivity depends on other factors such as polymer surface energies, polymer melt viscosity etc. (McGeary 1961).

For concentration values lower than percolation one c_{vp} , the following variation law of the conductivity σ with the filler content c_v is considered:

$$\sigma = \frac{b}{(c_{vp} - c_v)^s} \quad (1)$$

where b is a material parameter that depends on the filler conductivity and s is known to be the critical exponent for percolation transition of electrical conductivity. The exponent s is 2 for three-dimensional and 1.3 for two-dimensional randomly distributed objects, respectively, in the percolation model (Clingerman 2002, Psarras 2006, Stauffer 1991).

Regarding the conduction mechanisms, in the case of steady-state electric fields and for filler content values lower than percolation one it is considered that the composite materials show no metal particles in contact and no percolation paths. As a result, composites behave as insulator, charge carriers moving through thermally activated jumps (Clingerman 2002) (Psarras 2006).

If alternating electric fields, the conduction of composites can be described by random free-energy barrier model developed by Dyre (Dyre 2000). Dyre's model considers that AC conductivity is less dependent on temperature and the electrical conduction is dominated by processes with activation energies E_{Ad} lower than in continuous electrical fields E_{Ac} .

On the other hand, knowing the complex relative permittivity components ϵ_r^* ($\epsilon_r^* = \epsilon_r' + j\epsilon_r''$) the complex conductivity components $\sigma'(\omega)$ and $\sigma''(\omega)$ may be calculated with the following equations:

$$\begin{aligned} \sigma'(\omega) &= \sigma_{AC}(\omega) = \epsilon_0 \omega \epsilon_r'' \\ \sigma''(\omega) &= \epsilon_0 \omega \epsilon_r' \end{aligned} \quad (2)$$

where $\epsilon_0 = 8.85 \cdot 10^{-12}$ F/m is the vacuum permittivity (method used in this work).

3. ELECTRICAL PERMITTIVITY

If a DC voltage U_0 is suddenly applied to the test object, a current $i_a(t)$ occurs through the test object:

$$i_a(t) = C_0 U_0 \left[\frac{\sigma_t}{\epsilon_0} + \epsilon_\infty \delta(t) + f(t) \right] \quad (3)$$

where C_0 is the geometric capacitance of the test object, $\delta(t)$ is the delta function from the suddenly applied step voltage at $t = t_0$ and $f(t)$ is the so-called dielectric response function in time domain (Stancu 2011, Zaengl 2003, Joncher 1996).

If the test object is short-circuited at $t = t_c$, the resorption current $i_r(t)$ can be measured. The sudden reduction of the voltage U_0 is regarded as a negative voltage step at time $t = t_c$ and, neglecting the second term in equation (2) (which is again a very short current pulse), we obtain for $t \geq t_0 + T_c$ (Stancu 2011):

$$i_r(t) = -C_0 U_0 [f(t) - f(t + T_c)]. \quad (4)$$

Supposing that T_c is high enough so that $f(t + T_c) \approx 0$, it results from (4):

$$f(t) \approx -\frac{i_r(t)}{C_0 U_0}. \quad (5)$$

Considering that an AC voltage of pulsation ω is applied to a capacitor, that the polarization processes are instantaneous, and $\underline{F}(\omega)$ is the Fourier transform of the dielectric response function $f(t)$, respectively the complex susceptibility $\underline{\chi}(\omega)$, it results:

$$\underline{F}(\omega) = \underline{\chi}(\omega) = \int_0^{\infty} f(t) \exp(-i\omega t) dt = \chi'(\omega) - i\chi''(\omega), \quad (6)$$

$$\chi'(\omega) = \varepsilon_r'(\omega) - 1 = \int_0^{+\infty} f(t) \cos(\omega t) dt, \quad (7)$$

$$\chi''(\omega) = \varepsilon_r''(\omega) = \int_0^{+\infty} f(t) \sin(\omega t) dt, \quad (8)$$

where $\chi'(\omega)$ and $\chi''(\omega)$ represent the real and imaginary parts of complex susceptibility $\underline{\chi}(\omega)$, $\varepsilon_r'(\omega)$ and $\varepsilon_r''(\omega)$ - real, respectively imaginary part of complex permittivity $\varepsilon_r^*(\omega)$ ($\varepsilon_r^*(\omega) = \varepsilon_r'(\omega) + j\varepsilon_r''(\omega)$).

4. MAGNETIC PERMEABILITY

Relative magnetic permeability μ_r of polymer composites increase with filler content c , an estimation of this growth can be achieved with the linear relation:

$$\mu_r(c) = 1 + Cc_v, \quad (9)$$

where c_v represents the volume filler content, and C is a coefficient which depends of the magnetic properties, the shape and the volume fraction of the filler (Fiske 1997, Fiske 1996).

If the filler concentration is high ($c > 0.25$), magnetic permeability values significantly deviate from linear variation, in some papers a parabolic variation is presented (Fiske 1996).

$$\mu_r(c) = 1 + C'c^2. \quad (10)$$

On the other hand, the mechanical properties (the tensile strength etc.) of the composites are lower comparative to those without magnetic fillers (Dobrzański 2006, Sun 2008). An improvement of the properties of these materials is obtained with the use of nano-sized fillers (Kong 2010 Nowosielski 2005 Kokab 2005 Shimba 2011).

In a previous paper (Stancu 2011) the authors present the calculation of the dielectric response function for inhomogeneous samples of polyethylene (containing water trees), and (Stancu 2013) a study of the electrical conductivity - measured both in dc and ac - of polyethylene samples with magnetic fillers.

This paper presents the results of an experimental study conducted on samples of low density polyethylene with fillers of micron sized particles of neodymium regarding their behavior in steady-state and time-varying electric fields. Variations of complex permittivity and conductivity components are determined and their dependencies on the filler content, temperature and frequency of the electric field are analyzed. The dependency of some magnetic properties on the magnetic field strength and neodymium filler is studied.

5. EXPERIMENTS

Experiments were performed on flat samples of composites prepared from low density polyethylene LDPE with a melt flow index (190 °C, 2.16 kg) of 0.3 g/10 min, a density of 0.920 g/cm³ at 23 °C and an electrical conductivity of 5·10⁻¹⁷ S/m. The particles of Neodymium have the length of 75-100 µm and the width of 30-50 µm (Fig. 1), the density of 7 kg/dm³ and the electrical conductivity of 1.56·10⁶ S/m. Maleic anhydride-grafted polyethylene (MA-PE), with a density of 0.925 g/cm³ and a melting point of 105 °C, was used as compatibility agent. A 50 cm³ mixing chamber of a Brabender Plasti-Corder LabStation was used for mixing and homogenizing Neodymium powder with the polymer matrix and the compatibility agent (5 wt % MA-PE). Metal powders (concentration of 5, 10 and 15 wt %) were slowly added (~ 2 minutes) to the mixture of PE and MA-PE and mixed at 160 °C, for 8 min (the speed of the rotors of 100 rpm).

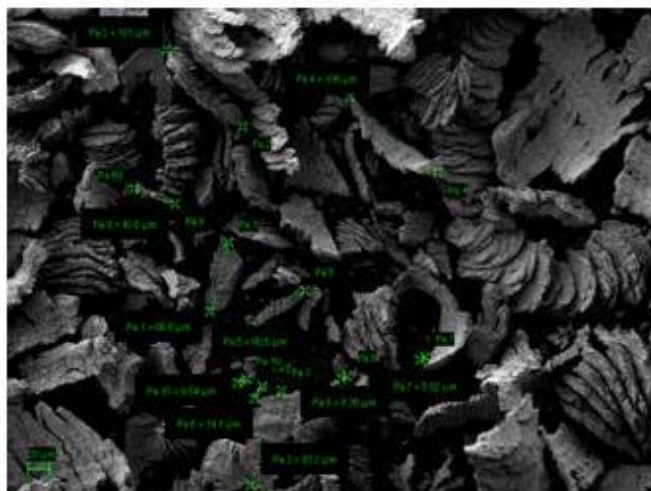


Fig.1. Neodymium particles (Optical microscopy, 200 X).

Square plates 100x100x0.5 mm³ have been realized by hot pressing at 170 °C for 5 min., with a force of 50 kN. After pressing, the samples were cooled to room temperature under a pressure of 5 bars.

The structure of samples and the dispersion of neodymium particles in polyethylene matrix were analyzed using the optical microscopy (with a NIKOV TI-e microscope) and Scanning Electron Microscopy SEM (with a workstation Karl Zeiss SMT-model AURIGA and detector type EVERHART-THORNLEY).

The absorption and resorption currents were measured on square plates (of side $a = 100$ mm) with a Keithley 6517 electrometer. The applied voltage U_0 was from 100 to 1000 V and the temperatures

between $25 \div 70$ °C. The components of the complex permittivity were measured on square plates (of side $b = 40$ mm) with a Novocontrol Impedance Analyzer. The applied voltage was 1 V and the frequency between 1 mHz and 1 MHz (Stancu 2011).

For each type of material (E0, E1, E2 and E3, see Table 1), 6 samples (3 with $a = 100$ mm and 3 with $b = 40$ mm) were manufactured. All measurements (currents, permittivity components) were performed 3 times on each sample and the average values were calculated.

6. RESULTS AND DISCUSSIONS

Structure, electrical (conductivity, complex permittivity components) and magnetically (permeability, magnetization cycles, remanence magnetization, coercive field) characteristics were determined for all samples type. Their dependence on the filler content was analyzed.

6.1. Microscopic investigation

SEM analysis reveals a small (almost negligible) porosity in both surface and volume of the samples (P, Fig. 2). LDPE shows a lamellar structure and neodymium particles form clusters (metal “islands” (Stancu 2014) (Fig. 3) of variable dimensions (Fig. 3, Table 1). These clusters are cvasiuniform distributed in the samples and the distance d between them decreases with the increase of the filler content (Fig. 4). Thus, for samples E1 the distance d varies between $99.5 \div 275$ μm and for E3 varies between $67.5 \div 211$ μm . On the other hand, the dimensions of the clusters increase with the filler content (Table 1).

Table 1. Dimensions and distances between clusters

Sample	Nd volumic concentration c_v (%)	Average clusters dimension (μm)	Average distance between clusters (μm)
E0	0	0	0
E1	0.688	95.92	117.81
E2	1.377	100.95	94.04
E3	2.064	103.6	67.5

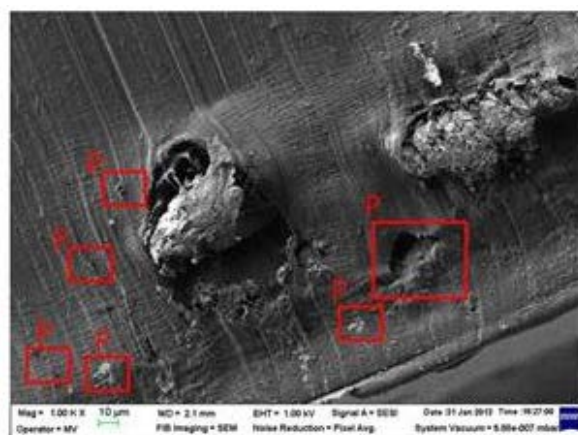


Fig. 2. Neodymium particles clusters and pores in LDPE matrix (SEM, 1000 X).

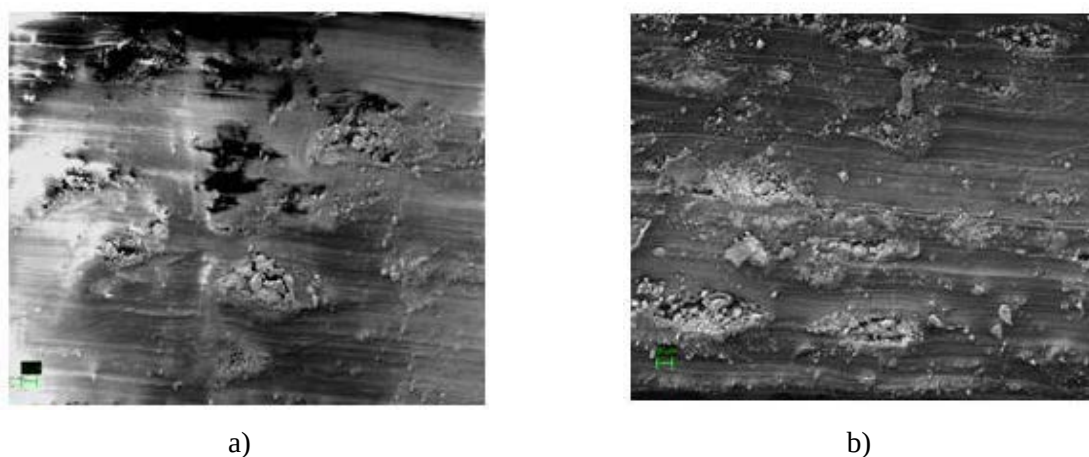


Fig. 3. Neodymium particles clusters (metal “island”) in A2 (a) and A3 (b) samples (Optical microscopy, 200 X).

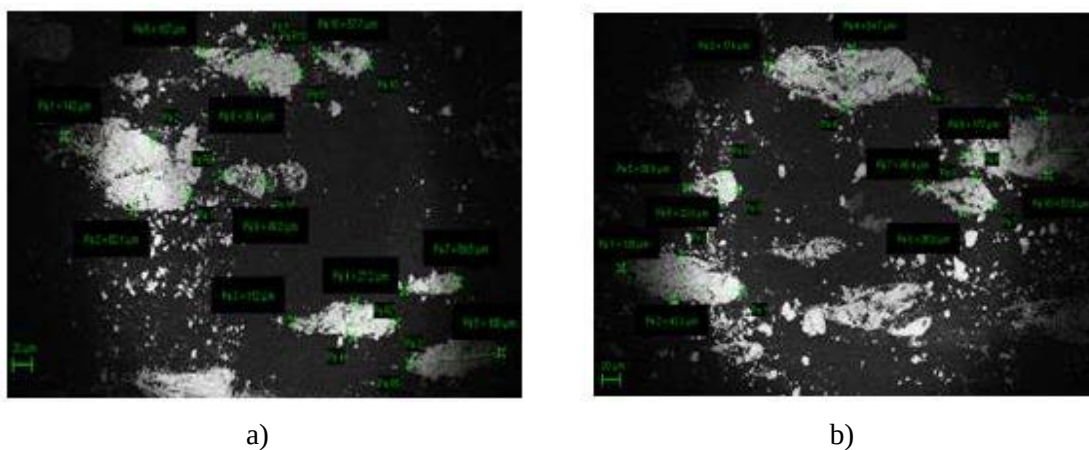


Fig. 4. Dimensions (a) and distances between neodymium particles clusters (b) in A3 samples (Optical Microscopy, 200X).

6.2. DC Conductivity

The values of the dc conductivity ($\sigma_{DC}(t)$) were calculated with the relation :

$$\sigma_{DC}(t) = \frac{i_a(t) - i_r(t)}{U_0} \cdot \frac{g}{S}, \quad (11)$$

where $i_a(t)$ and $i_r(t)$ are the absorption, respectively resorption currents, U_0 – the value of the DC voltage applied to the tested sample, g – the sample thickness and S – the area of the electrodes' active surface of the measuring cell (Stancu 2013).

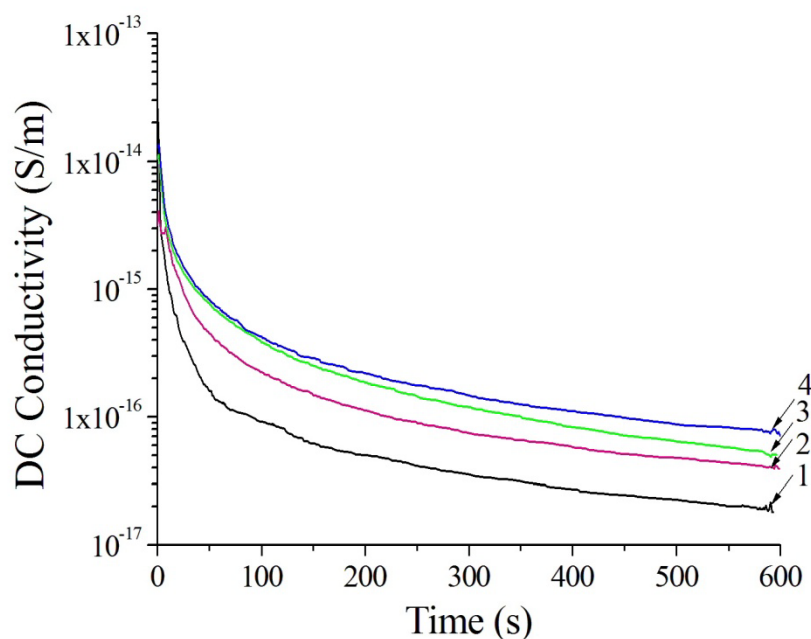


Fig. 5. Variation with time of the DC conductivity for samples E0 (1), E1 (2), E2 (3) and E3 (4) ($T = 25\text{ }^{\circ}\text{C}$).

Figure 5 presents the time variation of dc conductivity determined by measuring the absorption and resorption currents at voltage $U_0 = 500\text{ V}$ and temperature $T = 25\text{ }^{\circ}\text{C}$ on samples without filler (curve 1) and with different filler concentrations (curves 2, 3 and 4). It is found that increasing concentrations of filler causes an increase in DC electrical conductivity values but this not a spectacular growth (Table 2). This shows that the values of the filler volume concentrations (C_{vi}) are not too close to the percolation concentration value (c_{vp}) for that the conductivity values increase significantly (approaching the recommended value for electromagnetic shielding (i.e. $\sigma_c = 10^{-2}\text{ S / m}$ (Chung 2000)).

Table 2. Values of DC conductivity experimentally determined (at 600 s) and calculated

Sample	Volume concentration c_{vi} (%)	Experimental conductivity (S/m)	Calculated conductivity (S/m)
E0	0	2.8×10^{-17}	2.85×10^{-17}
E1	0.688	3.92×10^{-17}	3.93×10^{-17}
E2	1.377	5.02×10^{-17}	5.10×10^{-17}
E3	2.064	7.13×10^{-17}	6.88×10^{-17}

Table 3. Estimated values of DC conductivity for $c_v < c_{vp}$

c_v (%)	2.064	6.2	6.3	6.315	6.319	6.319995
σ_{DC} (S/m)	$6.88 \cdot 10^{-17}$	$8.66 \cdot 10^{-16}$	$3.11 \cdot 10^{-12}$	$4.99 \cdot 10^{-11}$	$1.25 \cdot 10^{-9}$	$1.247 \cdot 10^{-5}$

Using the conductivity values experimentally determined on samples E1, E2 and E3 (at 600 s from the voltage application), the percolation concentration $c_{vp} = 6.32 \cdot 10^{-2}$ was calculated (with equation (1) and considering $s = 2$). Then, using the equation (2) and considering $c_{vp} = 6.32 \cdot 10^{-2}$ the DC conductivity values for different filler content c_v (Table2) (Stancu 2013) were calculated. It is found that if the volume concentration takes values close to c_{vp} , the calculated values of conductivity increases by 12 orders of magnitude (Table 3), approaching the value $\sigma_c = 10^{-2}$ S / m. This is due, obviously, to the percolation and conductive network between metallic particles occurrence.

6.3. AC Conductivity

To study the influence of the filler on AC conductivity, measurements were performed on groups of three samples of each type of composite, at constant voltage and variables frequency and temperature.

Figure 6 shows the variation of the real part of the complex conductivity σ' (i.e. AC conductivity $\sigma_{AC} = \sigma'$) with frequency for polyethylene samples without (curve 1) and 2.064% filler (curve 2). It is found that the values of σ' increase with increasing frequency. This variation can be explained by using symmetric hopping model for solids with microscopic disorder. Increased frequency causes an increase of attempt-frequency potential crossing barriers and thus ac conductivity. Also, the values of σ' increase with filler content.

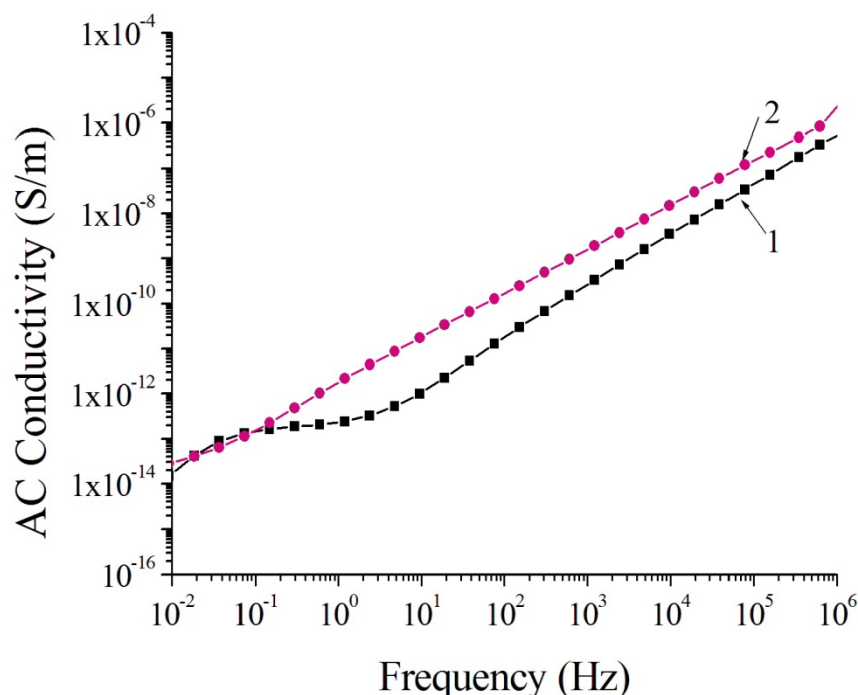


Fig. 6. Variation of the real part of the complex conductivity with frequency for samples E0 (1) and E3 (2) ($T = 30^\circ \text{C}$).

On the other hand, the existence of a critical frequency f_c , dependent on the temperature and filler content, from which the conductivity is proportional with f^n is verified. Thus, for $c_v = 2.06\%$, $f_c = 1$ Hz for $T = 30^\circ \text{C}$, $f_c = 10$ Hz for $T = 50^\circ \text{C}$ and $f_c = 50$ Hz for $T = 70^\circ \text{C}$. Also, "the ac universality law" is verified and the relation $\sigma'(\omega) = \sigma'(0) + a\omega^n$, in which a and n ($0.6 \leq n \leq 1$, (Dyre 2000)) are expressed according to temperature and the nature and concentration of the filler (characterizing the hopping conduction (Psarras 2006)). As can be seen in Figure 7, for higher frequencies (above 1 kHz), the slopes of the curves $\sigma_{AC}(f)$ and the values of n increases with temperature.

Curves $\sigma'(f)$ (i.e. $\sigma_{AC}(f)$) has two peaks: one at low frequency f_{pl} (range 0.01 ... 1 Hz) and one at high frequency f_{ph} (1.3 - 1.4 MHz). It is found that if the values of f_{pl} increase long enough with temperature, those of f_{ph} not depend practically on the temperature (Fig. 7).

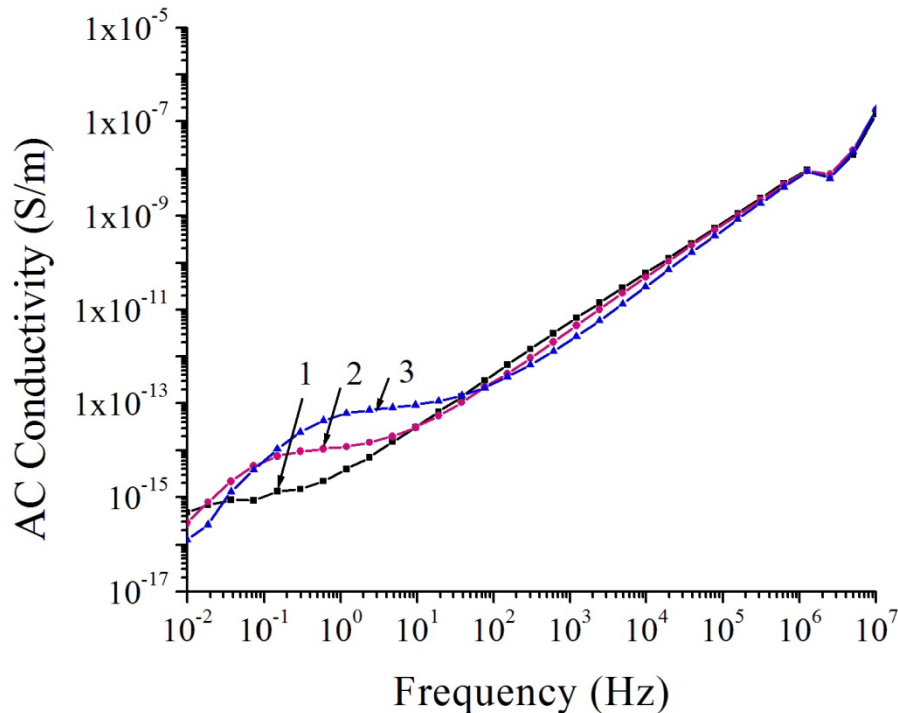


Fig. 7. Variation of the conductivity (σ') with frequency for samples E1 at 30 °C (1), 50 °C (2) and 70 °C (3).

6.4. Electrical permittivity

Values of the complex permittivity components (ϵ_r' and ϵ_r'') for frequencies between 1 mHz and 1 MHz and temperatures between 30 and 80 °C, for all type of samples (E0...E3) were determined.

6.4.1. Real part of permittivity

In Figure 8 the variations of the real part of permittivity ϵ_r' with frequency is presented. It comes out that ϵ_r' increases with the frequency decrease for all samples, similar variation being observed by other authors (Foulger 1999), (Tsangaris 1999, Huang 2007, Zois 2003, Yacubowicz 1990, McGeary 1961). This is due, on one hand, to the space charge separation at the polyethylene/filler interfaces at lower frequencies and thus to the interfacial polarization increase, and on the other hand to larger movements (at low frequencies) of afferent entities polar dipoles with higher molecular weight (longer branches in low density polyethylene, hexyl laterale, aldehyda maleica groups etc.) contained by the samples.

Analyzing the curves $\epsilon_r'(f)$ drawn for different temperatures (Fig. 9) is comes out that for each sample type, there are two critical frequencies (f_{c1} and f_{c2}), dependent on the temperature and filler content, where changes in the variation mode with frequency of the ϵ_r' occur.

Thus, for frequencies within the range interval (f_{c1} , f_{c2}), the values of ϵ_r' increase with the temperature, and for values of f outside this range, the values of ϵ_r' decrease with increasing temperature. An

explanation of these variations can be given based on the structure of the samples and the component weights of ϵ_r associated with different polarization mechanisms (Stancu 2015).

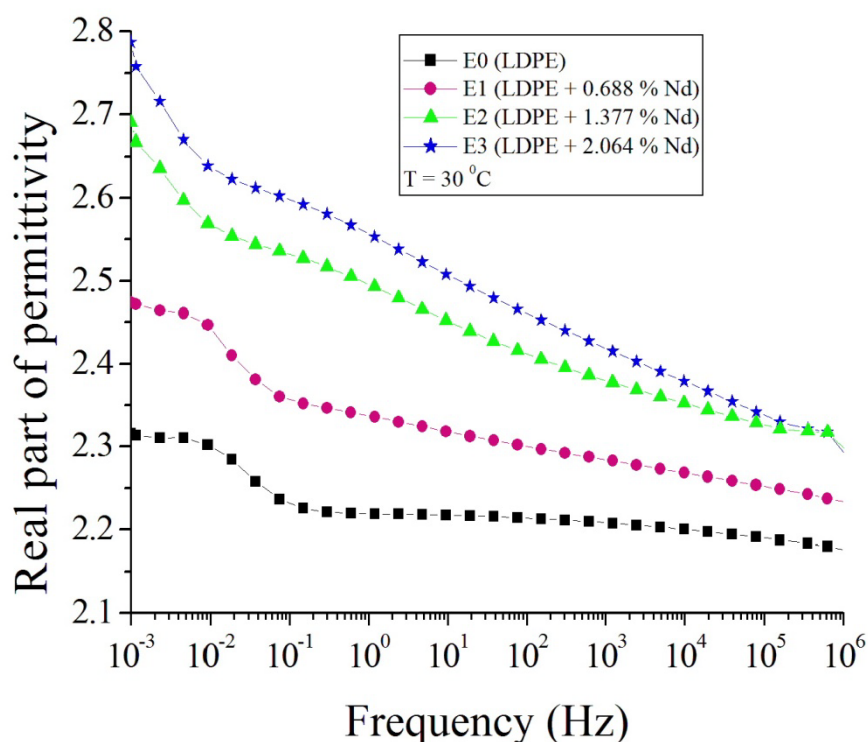
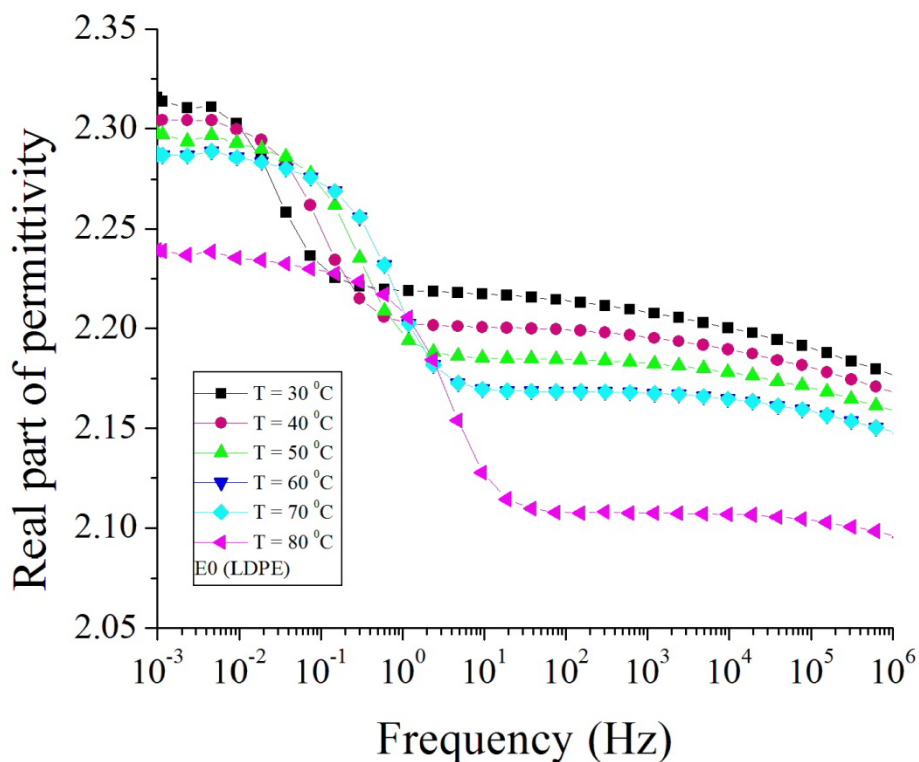
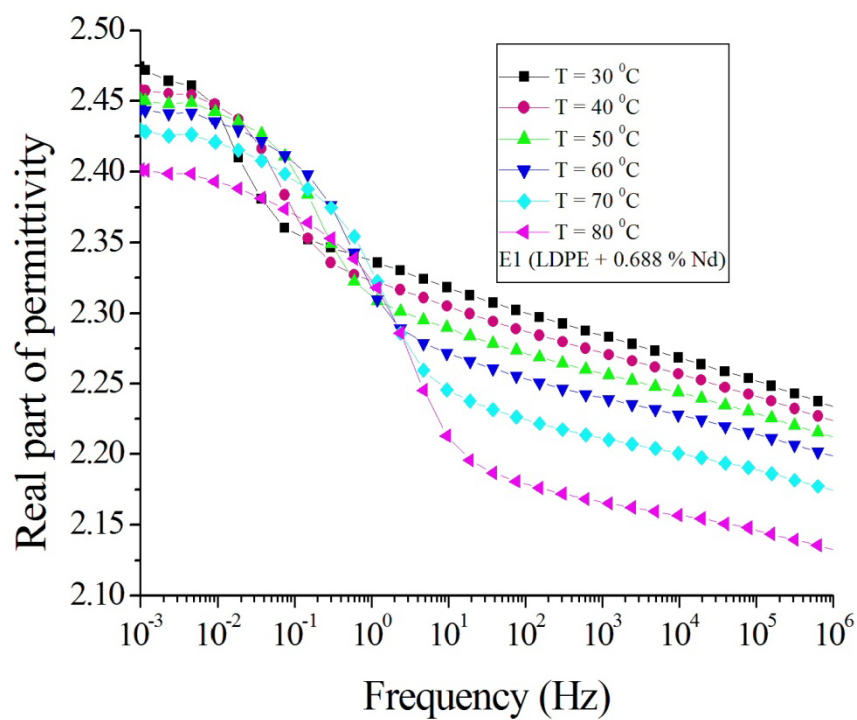


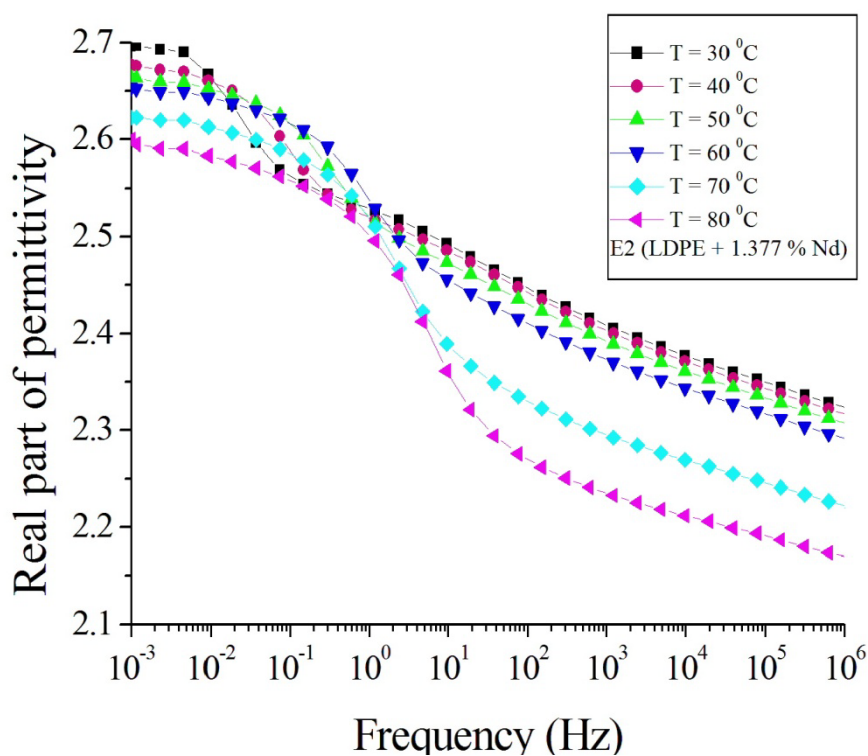
Fig. 8. Variation with frequency of real part of complex permittivity samples E0, E1, E2 and E3 ($T = 30^\circ\text{C}$).



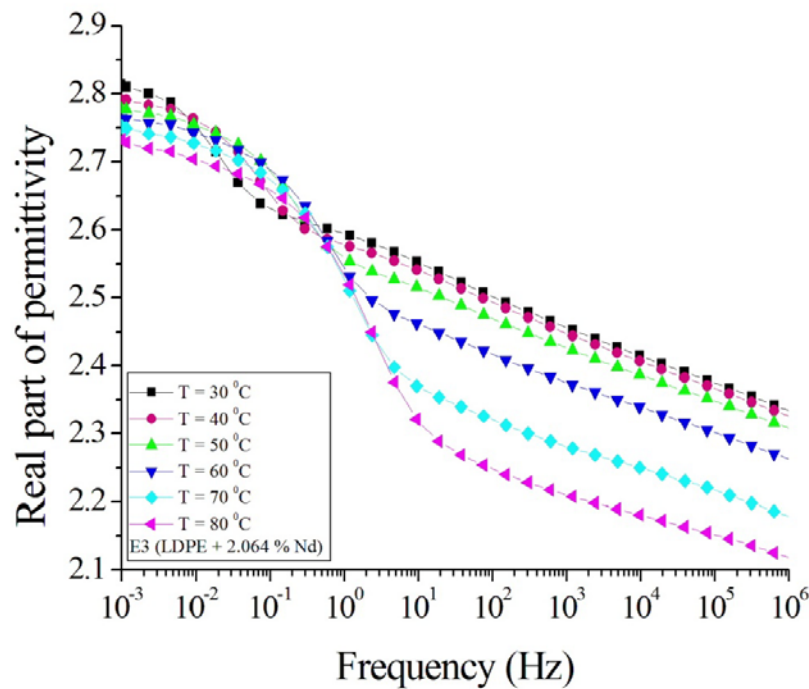
a)



b)



c)



d)

Figure 9. Variation with frequency of the real part of complex permittivity ϵ'_r for samples E0 (a), E1 (b), E2 (c) and E3 (d).

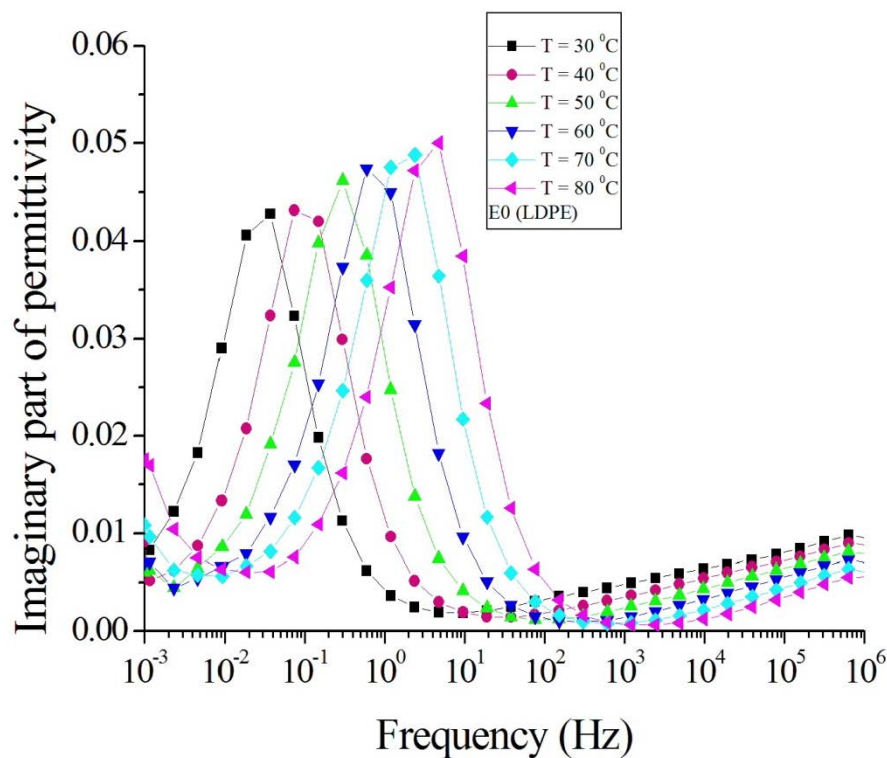
6.4.2. Imaginary part of permittivity

Figure 10 shows variations of the imaginary part of the complex permittivity ϵ''_r with frequency of the electric field for the samples E0...E3 at different temperatures. It is found that the curves show a first maximum (peak) at relatively low frequencies, i.e. in the range (0.02, 0.4) Hz. This maximum (indicated in (Yacubowicz 1990) for polystyrene / barium ferrite) composites is probably due to α -relaxation polyethylene branches, maleic anhydride and charge carriers forming space charge (and which led to the interfacial polarization) (Morshuis 2013). On the other hand, increasing the filler content causes an increase in size and a shift of their peaks towards lower values of frequency (Fig. 10). It is probably due to the increase of the interfaces area LPDE/Nd and thus of the space charge separated at these interfaces and to number of maleic anhydride molecules and molecular chains fixed on neodymium particles (which leads to the increase of the required energy to rotate the electric dipoles with the change of the electric field direction) (Panaitescu 2013).

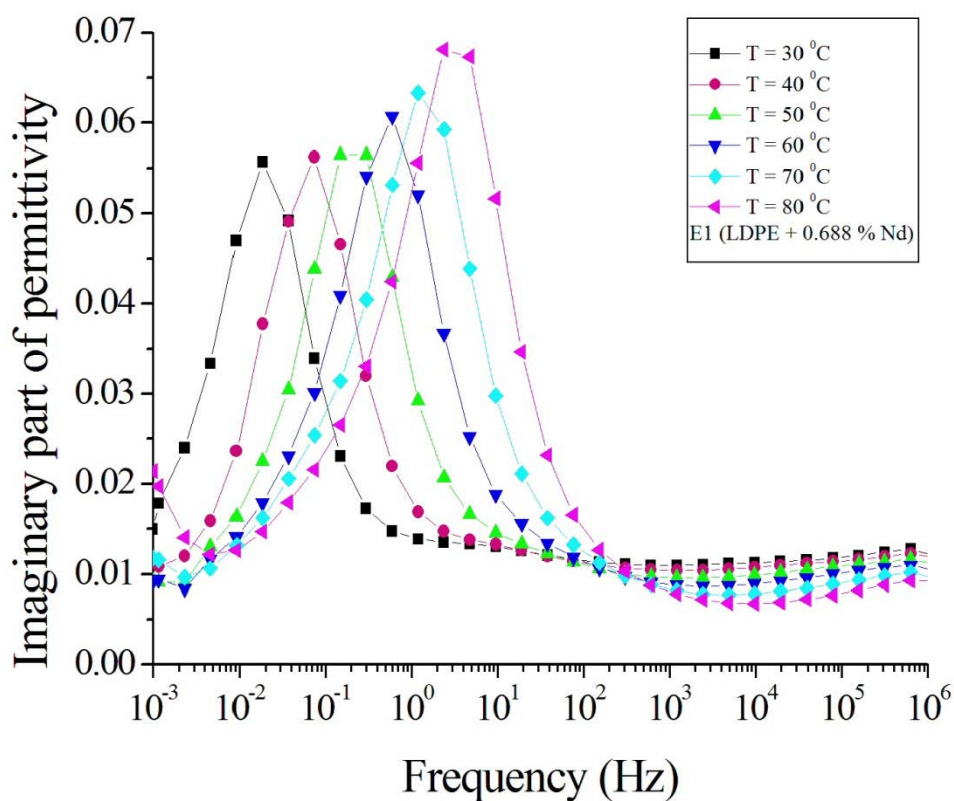
For all test temperatures, the curves have approximately the same shape, but with increasing temperature (especially in the case of samples with higher concentrations of Nd and higher temperatures), both heights and widths peaks grow and shift to higher values of frequency, a phenomenon reported in (Gefle 2005). This is probably due to the increase of the weight (number, amplitude oscillations) dipolar species with greater molecular weight during the polarization orientation process. On the other hand, at temperatures below 60 °C, the curves stands (especially for E2 and E3 samples, Fig. 10c and d) the appearance of a second peak whose height decreases with increasing temperature and whose frequency is in the range of 40 ... 100 Hz. This may be probably due to the separated charge and end chains fixed on LDPE/Nd interfaces, whose values and number increase with filler content, i.e. by the increase of the interfacial component.

At frequencies above 100 Hz, ϵ''_r decreases with increasing temperature (Fig 10), variation also observed in LDPE composites / NiFe_2O_4 (Borah 2012). This decrease of ϵ''_r may be explained by the

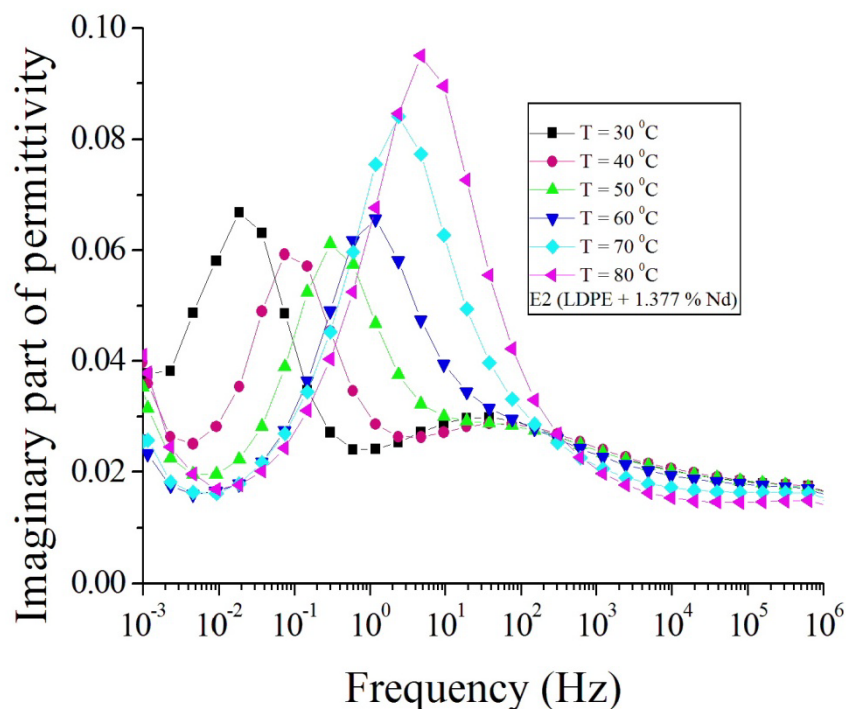
increase of own energy of electric dipoles (with increasing temperature) and, thus, reduction of received energy from the electric field to their rotation under it action.



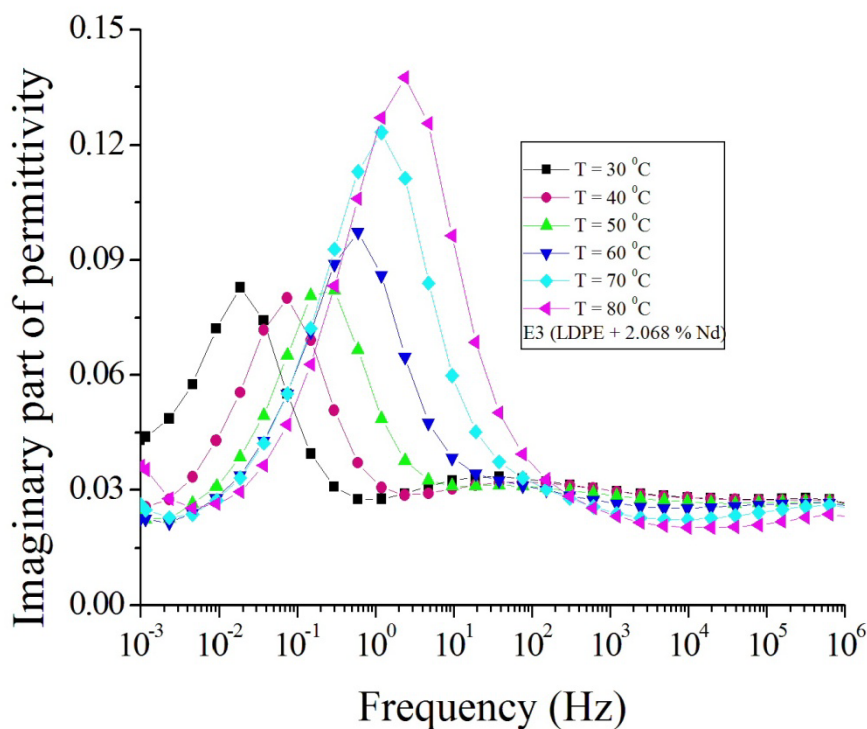
a)



b)



c)



d)

Fig. 10. Variation with frequency of the imaginary part of complex permittivity E0 for the samples (a), E1 (b), E2 (c) and E3 (d).

6.5. Magnetic Properties

In Figure 11 the magnetization cycle of the sample A3 for values of the magnetic field between 0 and 955 kA/m is presented. It was found that their shapes depend essentially on the filler content. On the other hand, the cycles are very thin and unsaturated (Fig. 11), while in the case of NdFeB are larger and present magnetic saturation phenomenon (Stancu 2014). It results that composite materials based on polyethylene with neodymium filler have the characteristics of soft magnetic materials.

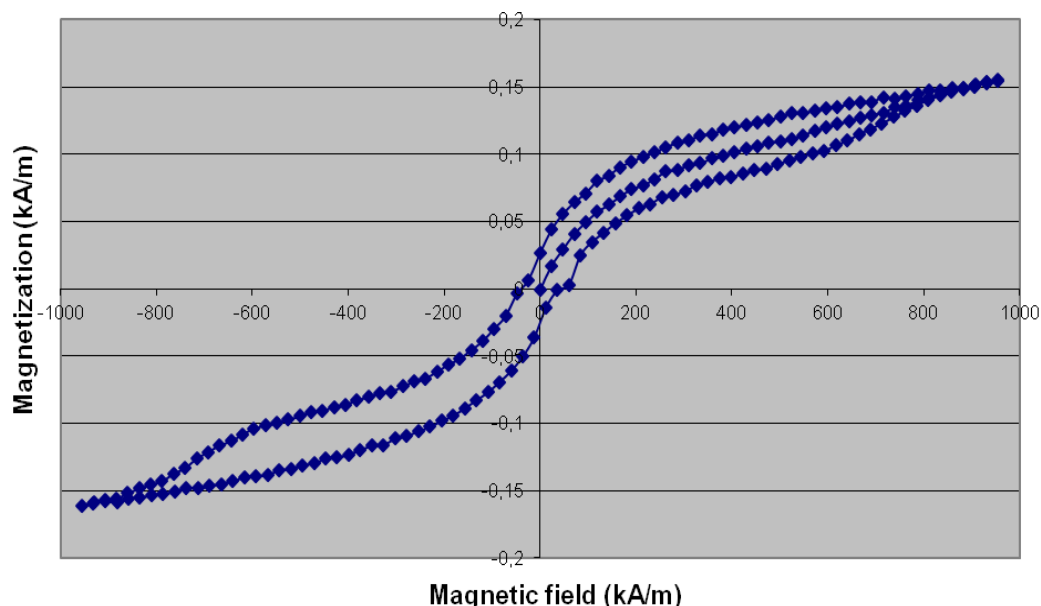


Fig. 11. Magnetization cycle for samples A3.

The values of the coercive field (H_c), remnance (M_r) and maximum magnetization ($M_{\max}$) are relative small (Table 4). This is due to reduced interactions between the unpaired electron moments of type Nd-Nd for samples A. On the other hand, the values of the ratio $k = M_r/M_{\max}$ are small too ($k < 0.2$) for these samples. It comes out that Nd composite materials may be used for magnetic circuits, electromagnetic shields (Stancu 2013) etc.

Table 4. Values of coercive field (H_c), magnetization remnant (M_r), maximum magnetization ($M_{\max}$), maximum magnetic susceptibility $\chi_{m,\max}$ and ratio $k = M_r/M_{\max}$

Samples	H_c (kA/m)	M_r (kA/m)	$M_{\max}$ (kA/m)	$\chi_{m,\max}$	k
A1	38.42	0.00565	0.0309	0.013	0.178
A2	1.68	0.01369	0.0697	0.338	0.196
A3	0.35	0.02532	0.1680	0.580	0.151

Increasing the filler content, the remanence and maximum magnetization increase also (Table 3). The coercive field values decrease slightly (due to reduction of the distances between the magnetic particles and interactions intensification between them (Gokturk 1993)).

Variations of magnetic susceptibility χ_m with magnetic field strength H that correspond to the first magnetization curves (quadrant I) are presented in Figure 12. It comes out that the values of χ_m

increase with H . Curves $\chi_m(H)$ present maxima for values of H that increase with the neodymium content of the samples (Fig. 12). For higher values of H , the values of χ_m are relative low.

Generally, the values of χ_m are relatively small (below 0.0031), due to the low volume filler content (below 2.1 %) (Gokturk 1993, Kong 2010). Therefore, to use of such materials for the magnetic circuits, the content of Nd should be increased.

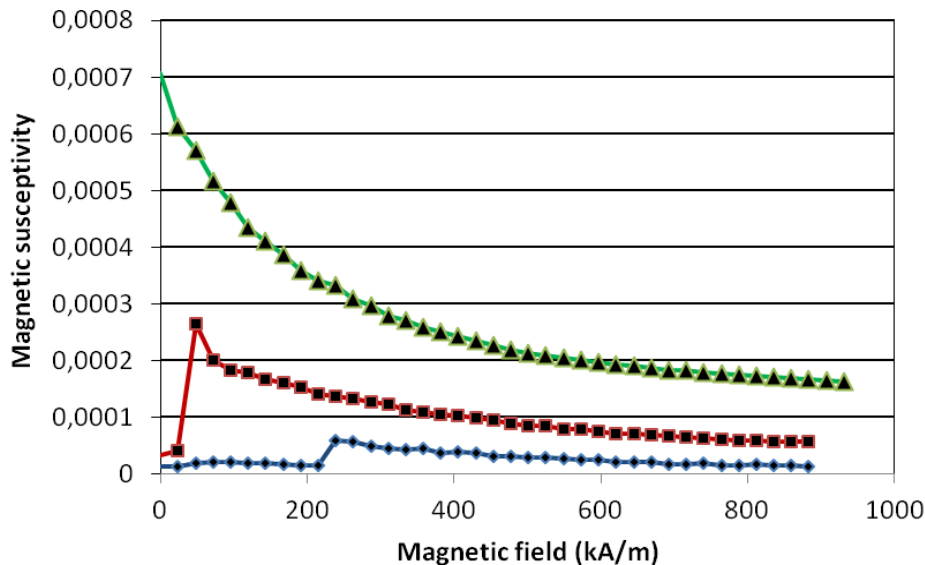


Fig. 12. Variation of magnetic susceptibility with magnetic field strength for samples E1(♦), E2 (■) si E3 (▲).

7. CONCLUSIONS

Tests performed on samples with low concentrations of neodymium allowed to determine, based on a relatively simple model of electrical conductivity variation with volume concentration of filler, the percolation concentration determination for LDPE - neodymium composites ($c_{vp} = 6.32\%$).

DC conductivity values increase with the content of impurities and temperature, while the DC activation energy decreases with temperature.

The AC conductivity values increase with frequency and has two peaks of concentration and temperature dependent, one for low frequencies (0.1 ... 5. Hz) and one for high frequencies (1.2 ... 1.3 MHz). Reducing the frequency of the electric field to 10^{-4} Hz leads to an important increase of ϵ_r' values for all samples type. In the case of ϵ_r'' the increase of the frequency from 1 mHz to 1 MHz causes two peaks: one of great value in the range (0.02, 0.4) Hz that corresponds to α -relaxation in LDPE and the other one in the range (40, 100) Hz.

The increase of temperature determines, generally, a decrease of the real part of permittivity. There are, for each type of sample, a range of frequencies (f_{c1}, f_{c2}), so that, for $f \in (f_{c1}, f_{c2})$ ϵ_r' increases with temperature. f_{c1} and f_{c2} critical frequency values depend on the values of neodymium concentration and temperature.

Increase of the filler content leads to the increase of the magnetization, magnetic susceptibility and hysteresis losses, due to the ferromagnetic interactions between the electrons.

The values of the volume filler content used in this paper being lower (below 2.1 %), the magnetization is relative low and the hysteresis cycles area and magnetic susceptibility have also low values. Therefore, the magnets obtained from such composites have weak characteristics (comparing to the ferrites ones).

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