DIELECTRIC CHARACTERISTICS OF NOVEL HYBRID MATERIALS CONSISTING OF FUNCTIONAL BLOCK COPOLYMERS AND METAL OXIDE NANOPARTICLES AT TEMPERATURE AND FREQUENCY VARIATION

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Abstract – **Most polymeric materials are characterized by low surface energies; therefore, in order for a polymer to be able to adhere efficiently onto a metallic/metal-oxide surface, the development of specific polymer-metal interactions is required. Such interactions include among others hydrogen- or covalent bonding, dipolar and electrostatic interactions, and require the presence of specific functional sites on the polymer backbone. The resulting organic-inorganic hybrid materials are particularly interesting, since they inherit properties of the polymer (such as good mechanical performance, formation of well-defined nano-morphologies) and of the metals (electro-magnetic, thermal, and optical properties). To further understand the dielectric behavior of nano- conductive–polymer composites, this experimental work reports the trends of dielectric permittivities and tan delta (loss tangent) of polymer/metal hybrid nanomaterials: LauMA-b-AEMA/Pd and LauMA-b-AEMA/Au and OA.Fe3O4 at temperature and frequency variation using a system for automated dielectric spectroscopy, given by Novocontrol GmbH, Germany. The dielectric properties were measured in the frequency range from 1 to 10^6 Hz and a temperature range of 35°C - 70°C for all samples.**

Keywords: *block copolymers, polymer/metal hybrid nanomaterials, dielectric properties.*

1. INTRODUCTION

Electromagnetic Interference (EMI) and Electromagnetic compatibility (EMC) are becoming important issues in the design of novel high-speed transmission networks and producing safe and sure equipment, with fast growing market at more than 5-7% per year. The need for novel electromagnetic active materials and technological solutions - mainly starting from nano/micro-scale concepts is related to urgent and large scale implementation of Council Recommendation 1999/519/EC on the limitation of exposure of the general public to electromagnetic fields and also Directive 2004/40/EC on the minimum health and safety requirements regarding the exposure of workers to the risks arising from physical agents (EMFs), which will determine an explosion in the next 3-5 years of the actual EMC/EMI market. [1]

The present situation of European industry in the EM field consists in the transition from intensive use of resources to high added value material production, by implementing new materials with improved properties, new functionalities, and new applications according to new environmental requirements. [2]

Some actual technical solutions developed in the last 5 years, but still unsuccessfully promoted on market are as follows:

- composites with carbon nanotubes, blended with epoxy resin for e.g. composite radar absorbing materials (RAM). The polymer composite paste technology is available, i.e. to be put into dedicated metal plates to form a prototype. Carbon nanotubes may be characterized by TEM, and radar absorbing properties may be detected by a RAM measuring system of arch method reflectivity. The double absorbing peaks of the sample with mm thickness may be obtained when the carbon nanotubes and epoxy resin are in a ratio of e.g. 1:100. The material has unfortunately low features reproducibility.
- nanocomposites of magnetic materials using e.g. α-Fe/C, Fe_2B/C or $Fe_{1.4}Co_{0.6}B/C$, nowadays used for other purposes, but intended to be adaptable for EM applications. They may be made as complex composites prepared by mechanically grinding α-Fe, Fe_2B, or $Fe_{1.4}Co_{0.6}B$ with amorphous carbon [C(a)] powders. Complex permittivity, permeability, and electromagnetic wave absorption properties of such resin compacts containing e.g. 40-vol % composite powders of α-Fe/C(a), Fe_2B/C(a), and $Fe_{1.4}Co_{0.6}B$/C(a) may be adapted for conventional reflection/transmission technique, for dedicated applications in ranges of 4.3-8.2 GHz (G band), 7.5-16.0 GHz (X band), and 26.5-40 GHz. The material has unfortunately low reliability.
- conductive polyaniline/iron carbonyl powder composite material, prepared based on conductive

polymer and soft magnetic metals, which have very good characteristics of electromagnetic wave absorbing. Implemented on the market, but with low frequency domain, under 0.1 GHz.

- composite metal-backed single layered electromagnetic wave absorber of (spinel-type Ni-Zn ferrite, SiO_2) composite materials, which operates in the frequency region from 1 to 8 GHz. The material has unfortunately low features reproducibility.
- composite systems based on polymeric matrices (polystyrene, polyethylene) containing conductive (Pd, Ag, Ag alloys) and dielectric (ferroelectric) components such as $BaTiO_3$ or piezo-sonic powder, to be developed and investigated in bulk and coating films as complementary barriers for Salisbury absorbers. The material has unfortunately low features reproducibility.
- electromagnetic shielding coatings for better performance of mobile telephones - Magnetron sputtering - the last trend in high frequency EM shielding starting with 2006 - is represented by a vacuum technology for depositing metal coatings onto plastics (mainly high conductive copper films to protect electronic devices from electromagnetic interference). Until now, process problems have limited magnetron sputtering of plastic substrates to small coating areas, aspect that casted a final doubt on the direct use of metal for GHz applications.

This paper aims to test, assess and benchmark the overall dielectric properties of the new concept of nano-conductive-polymer composites with predefined architecture and customized dielectric properties, based on block copolymers having b-ketoester functionalities used as stabilizers for nanoparticles of rare metals and metal oxides developed in order to provide important information about the overall engineering feasibility of the novel concep.

2. EXPERIMENTAL DETAILS

2.1. Nano- conductive– polymer composites samples preparation

Most polymeric materials [3] are characterized by low surface energies; therefore, in order for a polymer to be able to adhere efficiently onto a metallic/metal-oxide surface, the development of specific polymer-metal interactions is required. Such interactions include among others hydrogen- or covalent bonding, dipolar and electrostatic interactions, and require the presence of specific functional sites on the polymer backbone. [4] The resulting organic-inorganic hybrid materials are particularly interesting, since they inherit properties of the polymer (such as good mechanical performance, formation of well-defined nano-morphologies) and of the metals (electro-magnetic, thermal, and optical properties).

Hybrid materials based on block copolymers and nanoparticles are a promising class of nanocomposites. Tailoring the block copolymer properties by using supramolecular chemistry allows control of the particle spatial organization and resulting composite properties. Hybrid materials based on a polymeric matrix and inorganic nanoparticles hold great promise for obtaining materials with optical, electronic or magnetic properties — generally limited to metals, oxides and ceramic materials — while preserving the easy processability of polymers.

The novel hybrid materials consisting of functional block copolymers and metal oxide nanoparticles have been developed aiming towards the investigation of their dielectric properties and applications. [5] More precisely, methacrylate-based amphiphilic block copolymers were fabricated employing RAFT controlled radical polymerization. So far a family of diblock copolymers was synthesized consisting of a ligating block segment based on 2-(acetoacetoxy ethyl methacrylate) (AEMA) and a hydrophobic block constituted of either lauryl methacrylate (LauMA, hydrophobic) repeating units. [6] The chemical structure of the diblock copolymer is illustrated in figure 1.

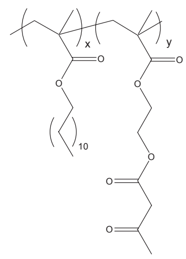


Figure1: Chemical structures of the LauMA-b-AEMA diblock copolymers.

Hybrid micellar solutions were generated in organic solvents consisting of LauMA-b-AEMA/Pd and LauMA-b-AEMA/Au in n-hexane. Moreover, oleic acid-coated magnetite nanoparticles (OA.Fe3O4) were synthesised by the chemical co-precipitation of Fe(III) and Fe(II) cations in a 1:2 molar ratio under weak basic conditions (NH_4OH).[6] It were employed different methods for the characterization of the OA.Fe_3O_4 and the polymer/metal hybrid nanomaterials, including UV-Vis spectroscopy, dynamic light scattering, scanning force microscopy, vibrational sample magnetometry.

2.2. Technologies for the investigations of dielectric properties based on broadband spectroscopy

2.2.1. Principles

The dielectric tests of the materials used are a prerequisite for every analytical and numerical analysis of the problem. In order to perform simulations which will have at least a chance to be in concordance with the measurements, detailed characterization of the material, in a wide frequency range must be performed. [7]

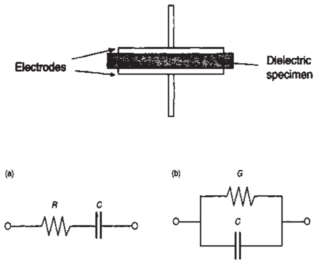


Figure 2: A dielectric specimen in a plane-parallel-electrode admittance cell.

Typical measurement setup consists in implementation of an admittance cell for which the series (a) or parallel (b) equivalent circuit is determined (figure 2).

2.2.2 Measurement setup

Our laboratory benefits from the presence of a system for automated dielectric spectroscopy, in a wide frequency range (10 μHz ÷ 8 GHz) and wide temperature range (-160 °C ÷ +400 °C) given by Novocontrol GmbH, Germany.
This Novocontrol measurement setup includes [8]:

- Novocontrol AlphaN mainframe dielectric analyser
- Novocontrol BDS 1200 sample cell (maximum frequency 8GHz)
- QUATRO-Cryosystem: cooling and heating system (liquid nitrogen: -160 °C ÷ +400 °C)
- WinDETA/WinFIT software package, for automated control, measurement and calibration, and data analysis
- Rhode-Schwartz NVR Network Analyser, frequency range 20 kHz ÷ 8 GHz, impedance range 0.1 Ω .. 10 k Ω, tan(d) accuracy > $3 * 10^{-2}$ or > 10^{-2}.

The samples must be as thin as possible (under 5-7 mm) and about 4-5 cm diameter.

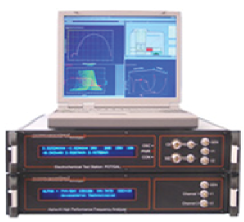


Figure 3: Novocontrol dielectric analyser.

3. RESULTS AND DISCUSSIONS

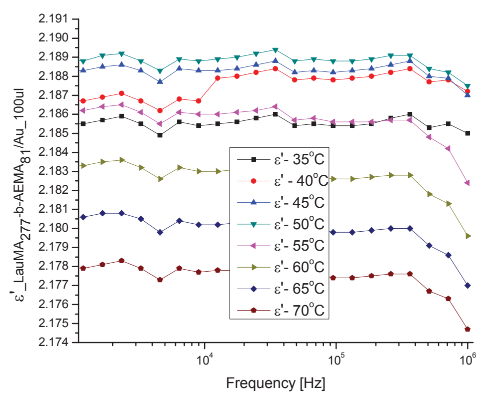
Functional hybrid films were prepared upon spin-coating to ensure uniformity (4500 rpm, spinning time 40 sec.) of the above-mentioned hybrid solutions (LauMA-b-AEMA/Pd, LauMA-b-AEMA/Au and OA.Fe_3O_4) on low density polyethylene (LDPE) substrates.

	Sample Description
1	$LauMA_{277}$-b-$AEMA_{81}$/Au, 100 ul (LDPE)
	$LauMA_{277}$-b-$AEMA_{81}$/Au, 200 ul (LDPE)
2	$LauMA_{277}$-b-$AEMA_{81}$/Pd, 100 ul (LDPE)
	$LauMA_{277}$-b-$AEMA_{81}$/Pd, 200 ul (LDPE)
3	OA.Fe_3O_4, 100 ul (LDPE)
	OA.Fe_3O_4, 200 ul (LDPE)

Table 1: Sample Description.

The dielectric measurements were carried out using a Broadband Dielectric Spectrometer (Novocontrol GMBH) encompassing an Alpha frequency response analyzer and Quattro temperature controller. The samples where sandwiched between two copper electrodes of diameter 20 mm and placed inside temperature controlled sample cell. The complex permittivity: $\varepsilon^*(f) = \varepsilon'(f) + i\varepsilon''(f)$ has been determined in the frequency (f) range from 1 Hz to 10^6 Hz and at temperature range from 35°C to 70°C. The temperature was increased gradually with a step of 5 Celsius degrees (the temperature stabilization time = 3 minutes). The AC voltage applied to the capacitor was equal to 1 V. Temperature was controlled using a nitrogen gas cryostat and the temperature stability of the sample was better than 0.1°C. Below we are providing the temperature dependences of dielectric constant (ε') and loss tangent (tgδ) of composites on thin LDPE substrate.

a) <u>$LauMA_{277}$-b-$AEMA_{81}$/Au, 100 ul (LDPE) and $LauMA_{277}$-b-$AEMA_{81}$/Au, 200 ul (LDPE)</u>



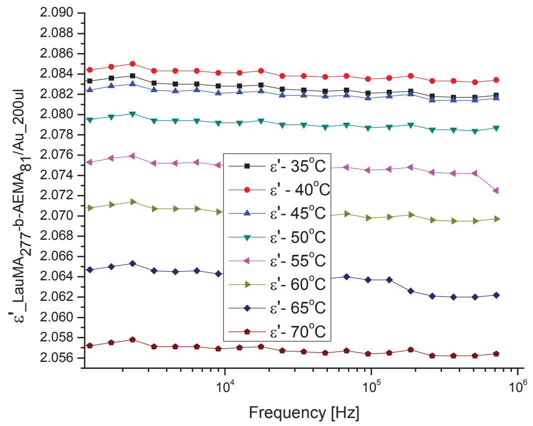
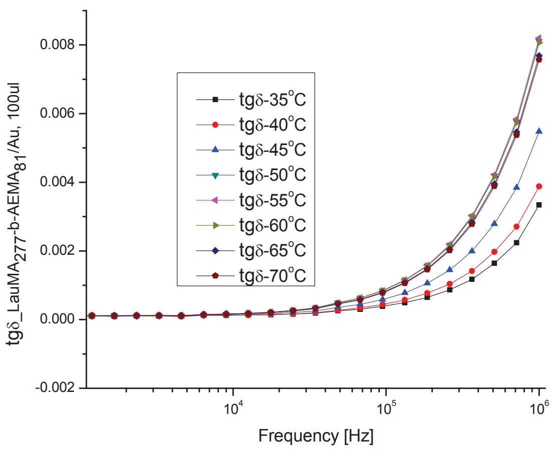


Figure 4: Temperature dependencies of dielectric constant (ε'), corresponding to samples $LauMA_{277}$-b-$AEMA_{81}$/Au, 100 ul and 200 ul, prepared by spin-coating on thin LDPE substrate.

Regarding the dielectric constant of $LauMA_{277}$-b-$AEMA_{81}$/Au_100ul composite, it can be observe a remarkable stability in the frequency range 1 Hz - 1 MHz for all temperatures investigated 35 °C - 70 °C. At concentration of 200 ul Au, the dielectric constant is less with 5% than at concentration of 100 ul Au in the frequency and temperature range considered, a phenomenon expected because the inclusion of more nano-conductive material reduces the polar effect of the composite. Regarding the dielectric constant evolution with temperature, it can be observe small variations (less than 1%) in the temperature range.

It is considered that the composite with 100 ul Au behaves optimally at 50 °C while the composite with 200ul Au has an optimal behavior at 40 °C.



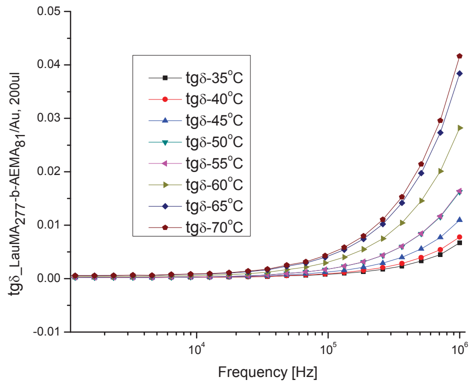


Figure 5: Temperature dependencies of loss tangent (tgδ), corresponding to samples $LauMA_{277}$-b-$AEMA_{81}$/Au, 100 ul and $LauMA_{277}$-b-$AEMA_{81}$/Au, 200 ul, prepared by spin-coating on thin LDPE substrate.

For both composites there is a significant increase of the loss tangent at frequencies over 1 MHz, which determines their application to selective EMC for frequency higher than 1 MHz.

b) <u>$LauMA_{277}$-b-$AEMA_{81}$/Pd, 100 ul (LDPE) and $LauMA_{277}$-b-$AEMA_{81}$/Pd, 200 ul (LDPE)</u>

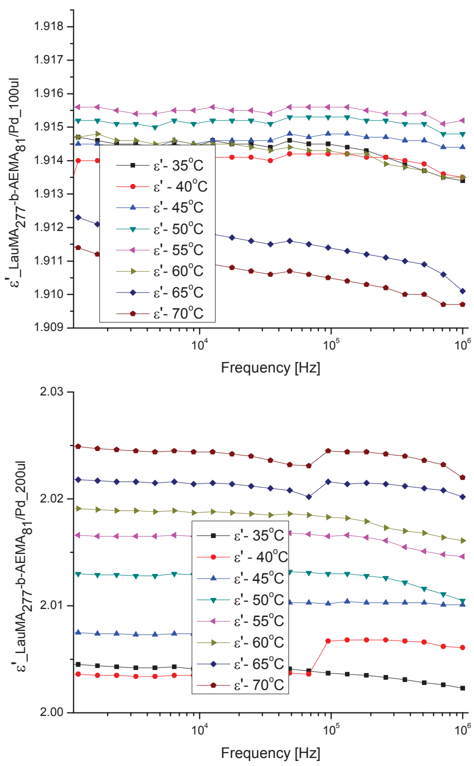


Figure 6: Temperature dependencies of dielectric constant (ε'), corresponding to samples $LauMA_{277}$-b-$AEMA_{81}$/Pd, 100 ul and $LauMA_{277}$-b-$AEMA_{81}$/Pd, 200 ul, prepared by spin-coating on thin LDPE substrate.

Regarding the dielectric constant evolution of $LauMA_{277}$-b-$AEMA_{81}$/Pd composite, indicates that the material with 100ul Pd has the similar effect with $LauMA_{277}$-b-$AEMA_{81}$/Au at same concentration. There is a stability of characteristics for all frequency range and a very low temperature decreasing (only 0.5 %) among 35 °C - 70 °C, the optimum temperature being around 55 °C.

If we compare the $LauMA_{277}$-b- $AEMA_{81}$ composite with 100ul Pd concentration, with $LauMA_{277}$-b-$AEMA_{81}$ composite with 200ul Pd concentration, there is a significant change in dielectric behavior, an increase of dielectric constant by about 10% across the range frequency for the $LauMA_{277}$-b-$AEMA_{81}$ composite with 200ul Pd. The difference is obvious if we compare with $LauMA_{277}$-b-$AEMA_{81}$ composite with 200ul Au, and explanation would be that Pd is an ingredient with higher affinity to the polymeric support, making new polar connections and interfacial nanopolarizations. For $LauMA_{277}$-b-$AEMA_{81}$ composite with 200ul Pd, the thermal stability is remarkable only up to 60 °C temperatures, for higher temperatures at frequencies greater than 1 MHz finding a significant diminution of the polar effect.

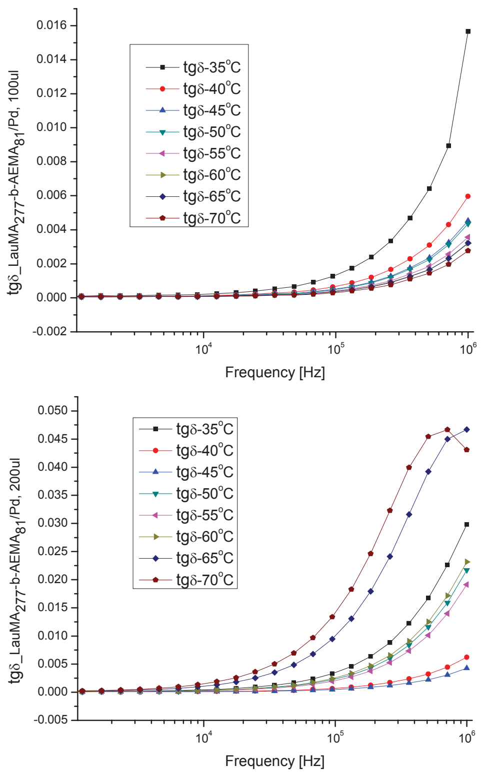


Figure 7: Temperature dependencies of loss tangent (tgδ), corresponding to samples $LauMA_{277}$-b-$AEMA_{81}$/Pd, 100 ul and $LauMA_{277}$-b-$AEMA_{81}$/Pd, 200 ul, prepared by spin-coating on thin LDPE substrate.

Analyzing the graphs for $LauMA_{277}$-b-$AEMA_{81}$/Pd_200ul and $LauMA_{277}$-b-$AEMA_{81}$/Pd_100ul, we can say that the introduction of Pd has the same effect of increasing for frequencies over 1 MHz like in case of $LauMA_{277}$-b-$AEMA_{81}$ with Au. Moreover, the dipolar activity of the complex polymeric Pd connections is enhanced by higher concentration of the Pd; the increase of the characteristic becomes significant for $LauMA_{277}$-b-$AEMA_{81}$/Pd_200ul since from the 10 kHz. Thus, the composites with concentration of Pd are suitable for a wider frequency, with a greater efficiency for electromagnetic shielding, with condition to not exceed the operation temperature (60°C).

<u>c) $OA.Fe_3O_4$, 100 ul (LDPE) and $OA.Fe_3O_4$, 200 ul (LDPE)</u>

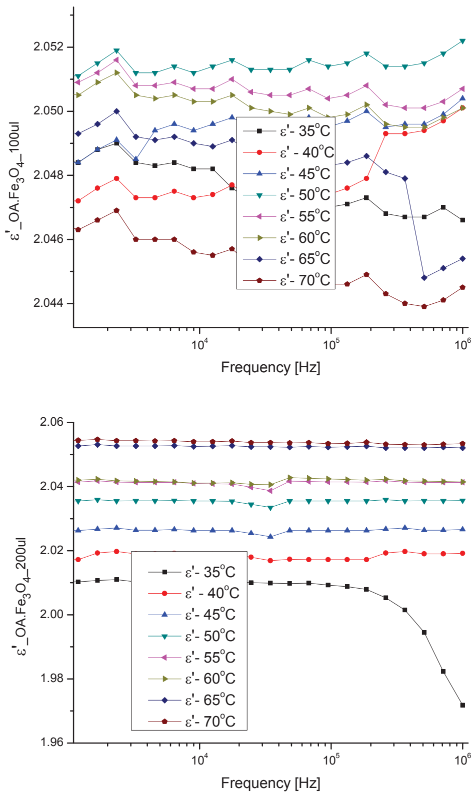


Figure 8 Temperature dependencies of dielectric constant (ε'), corresponding to samples $OA.Fe_3O_4$, 100 ul (LDPE) and $OA.Fe_3O_4$, 200 ul, prepared by spin-coating on thin LDPE substrate.

$OA.Fe_3O_4$_100ul composite has a high stability with temperature and frequency range only up to 55 °C, then dielectric constant decreases with the frequency about 2% for temperatures above 55 °C. Optimum temperature $OA.Fe_3O_4$_100ul composite is 50 °C. For $OA.Fe_3O_4$_200ul, the value of dielectric constant is greater due to higher concentration of ferrites and a better stability at high temperatures; the optimum temperature being 65 °C.

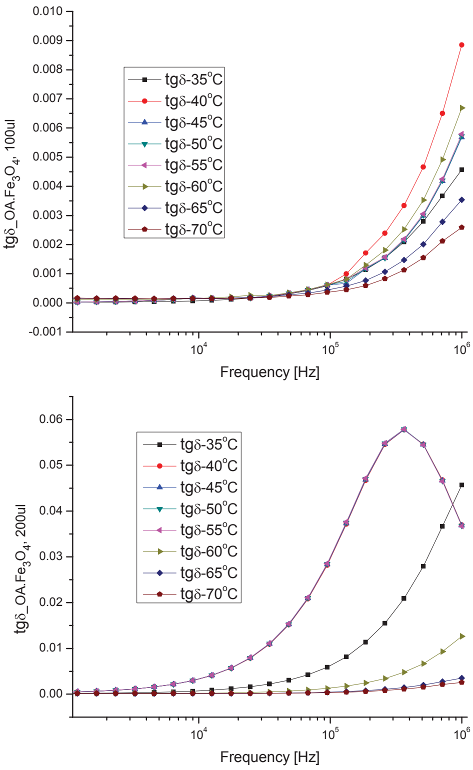


Figure 9: Temperature dependencie of loss tangent (tgδ), corresponding to samples . $OA.Fe_3O_4$, 100 ul (LDPE) and $OA.Fe_3O_4$, 200 ul, prepared by spin-coating on thin LDPE substrate.

A remarkable behavior we have for $OA.Fe_3O_4$_200ul, for which can be observed an increase with frequency from 10 kHz, the effect being influenced by temperature variation.

Comparing the dielectric loss tangent characteristic of the $LauMA_{277}$-b- $AEMA_{81}$_200ul Pd and $OA.Fe_3O_4$_200ul, there is a similar behavior, significant values of 0.04 for all temperature range. At frequencies above 1 MHz, for $OA.Fe_3O_4$_200ul, the characteristic is more sensitive to temperature.

It is noted that at 70 °C temperature occurs the characteristic frequency of the polarization dipole, around 300 kHz for $OA.Fe_3O_4$ and 500 kHz for $LauMA_{277}$-b-$AEMA_{81}$ with Pd.

Thus, in these cases the maximum efficiency of electromagnetic shielding is limited at high frequencies over 1 MHz, only applications up to 70 °C temperature.

4. CONCLUSIONS

Functional hybrid films were prepared upon spin-coating to ensure uniformity (4500 rpm, spinning time 40 sec.) of the above-mentioned hybrid solutions (LauMA-b-AEMA/Pd, LauMA-b-AEMA/Au and $OA.Fe_3O_4$) on plastic substrates aiming to investigate for the first time the dielectric properties of these materials, thus widening their application window. $OA.Fe_3O_4$_200ul composite is suitable for lower frequency applications, respectively $LauMA_{277}$-b-$AEMA_{81}$ with 200ul Pd and both $LauMA_{277}$-b-$AEMA_{81}$ with 100ul Au and Pd are recommended for high frequencies applications.

The new advanced materials developed are from the class of polymer composites capable of providing stability at the interfaces of materials with different chemical structures, polarities and cohesion energies (i.e. metallic or metal-oxide interfaces). The proposed work constitutes the first systematic work including the synthesis, characterization of electro-magnetic features of block copolymers having metal binding functionalities.

Acknowledgements

This paper was supported by the Romanian – Cyprus Bilateral Project no.436/18.06.2010, MANUNET ERANET MAGBOND 7-042/2011 project financed by UEFISCDI and the project PERFORM-ERA "Postdoctoral Performance for Integration in the European Research Area" (ID-57649), financed by the European Social Fund and the Romanian Government.

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