BULETINUL INSTITUTULUI POLITEHNIC DIN IAŞI
Publicat de
Universitatea Tehnică „Gheorghe Asachi" din Iaşi
Tomul LVII (LXI), Fasc. 3, 2011
Secţia
ELECTROTEHNICĂ. ENERGETICĂ. ELECTRONICĂ

DIELECTRIC TESTING OF NOVEL NANO-CONDUCTIVE-POLYMER COMPOSITES

BY

MARIA URSAN[*], ROMEO-CRISTIAN CIOBANU and GEORGE-ANDREI URSAN

"Gheorghe Asachi" Technical University of Iaşi,
Faculty of Electrical Engineering, Energetics
and Applied Informatics

Received, June 12, 2011
Accepted for publication: August 16, 2011

Abstract. This paper presents the testing results of overall dielectric and electromagnetic compatibility (EMC) properties of composite materials consisting of novel block copolymers having metal binding functionalities combined with rare metals and metal oxides and promotes the novel concept of nano-conductive-polymer composites for microelectronic applications at GHz (microwave) domain.

Key words: dielectric properties; nano-conductive-polymer composites.

1. Introduction

Two families of well-defined block copolymers having metal binding functionalities were prepared employing a controlled radical polymerization method namely Reversible Addition-Fragmentation Chain Transfer (RAFT) polymerization. The RAFT process represents a versatile polymerization technique, which allows the preparation of well-defined polymers of various architectures. The metal binding block segment was combined with (i) a

[*] Corresponding author: *e-mail*: mursan@ee.tuiasi.ro

hydrophobic block in the first polymer family and (ii) a hydrophilic block in the second polymer family.

Due to their amphiphilic character, the proposed block copolymers are expected to self-assemble in selective organic or aqueous solvents creating micellar nanomorphologies. These micelles, consisting of a ligating core containing metal-binding moieties and either a hydrophobic (in a selective organic solvent) or a hydrophilic (in a selective aqueous solvent) corona was serve as a nano-containers for the encapsulation and stabilization of metal and metal oxide nanoparticles in solution. More precisely, micelles of the proposed copolymers generated in selective solvents were evaluated towards their ability to act as effective steric stabilizers for: (i) palladium nanoparticles in organic solvents and (ii) magnetic iron oxide nanoparticles in aqueous solutions. Two samples in the form of films (LauMA$_{50}$-*b*-AEMA$_9$/Pd and LauMA$_{277}$-*b*-AEMA$_{81}$/Au) on glass substrates were prepared.

2. Synthesis of LauMA$_x$-*b*-AEMA$_y$/Pd Micellar Nanohybrids in Organic Solvents

A schematic presentation of the two-step synthetic methodology followed for the fabrication of the LauMA$_x$-*b*-AEMA$_y$/Pd micellar nanohybrids in *n*-hexane is presented in Fig. 1.

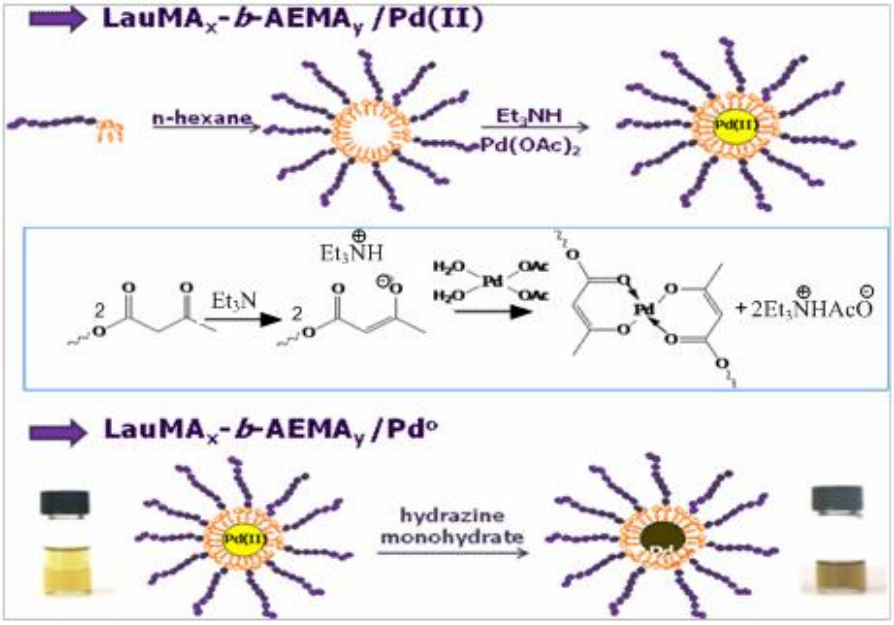

Fig. 1 – Two-step synthetic methodology followed for the preparation of the LauMA$_x$-*b*-AEMA$_y$/Pd micellar nanohybrids in *n*-hexane.

The methodology followed for the preparation of LauMA$_x$-*b*-AEMA$_y$/Pd micellar hybrids in *n*-hexane is described as follows: 20 mg of LauMA$_{50}$-*b*-AEMA$_9$ (1.84×10^{-2} mmol of AEMA units) was dissolved in *n*-hexane (5 mL). After complete dissolution of the polymer, four droplets of triethylamine were added to the solution. Subsequently, the resulting solution was mixed with $Pd(CH_3COO)_2$ (4 mg, 0.006 mmol) and left to stir at room temperature until complete solubilization of the salt. In the process of complexation and solubilization the colour of the solution changed from white to yellow transparent. Finally, two droplets of hydrazine monohydrate were added to the solution upon stirring. The reduction of Pd(II) ions to noble palladium was accompanied by a colour change of the solution from yellow to dark brown.

3. Synthesis of LauMA$_x$-*b*-AEMA$_y$/Au Micellar Nanohybrids in Organic Solvents

A schematic presentation of the single-step synthetic methodology followed for the fabrication of the LauMA$_x$-*b*-AEMA$_y$/Au micellar nanohybrids in *n*-hexane is presented in Fig. 2.

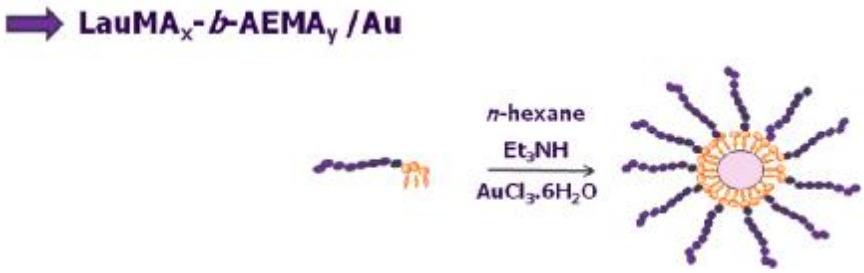

Fig. 2 – Synthetic methodology followed for the preparation of the LauMA$_x$-*b*-AEMA$_y$/Au micellar nanohybrids in *n*-hexane.

The procedure followed for the preparation of LauMA$_x$-*b*-AEMA$_y$/Au hybrid systems as follows: LauMA$_{277}$-*b*-AEMA$_{81}$ (179 mg) was dissolved in *n*-hexane (10 ml). After complete dissolution of the polymer, triethylamine (80 μL) were added to the solution. Subsequently, the resulting solution was mixed with $HAuCl_4.3H_2O$ (6.5 mg, 0.017 mmol) and left to stir at room temperature until solubilization of the salt. The complexation and reduction of gold ions was accompanied by a colour change from white to pink-purple transparent. The solution was then filtered for the removal of uncomplexed Au and the triethylamine hydrochloride salt which is a side-product in this reaction.

4. Dielectric Testing

The dielectric measurements were carried out using a Broadband Dielectric Spectrometer (Novocontrol GMBH) encompassing an Alpha

frequency response analyser 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, $\underline{\varepsilon}^*(f) = \varepsilon'(f) + j\varepsilon''(f)$, has been determined in the frequency (f) range from 1 Hz to 10^9 Hz and at temperature range from 25°C to 60°C The temperature was increased gradually with a step of 5°C (the temperature stabilization time – 3 min). 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 the temperature dependence of dielectric constant (ε'), dielectric losses (ε''), as well as the complex conductivities (σ' and σ'') are provided. For each sample the dependence *vs.* temperature of its dielectric properties can be observed, thus ε', ε'' and σ', σ'' are increasing personalized on composition while increasing the temperature (Figs. 3 and 4).

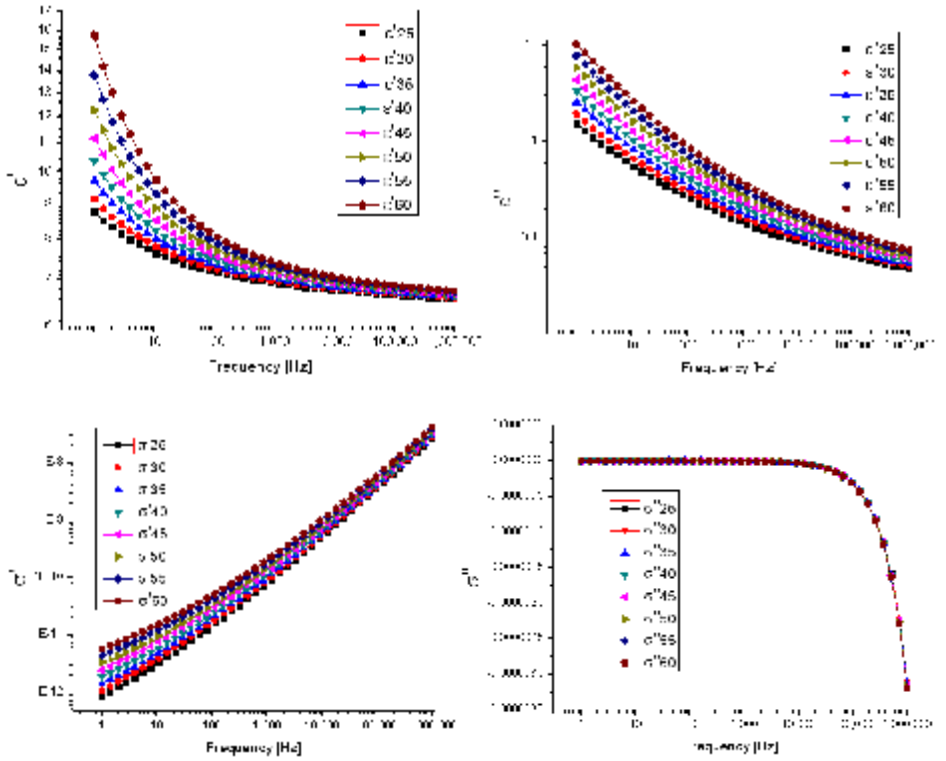

Fig. 3 – Temperature dependence of dielectric constant (ε'), dielectric losses (ε''), as well as the complex components conductivities (σ' and σ'') corresponding to sample LauMA$_{50}$-*b*-AEMA$_9$/Pd prepared by spin-coating on a glass substrate.

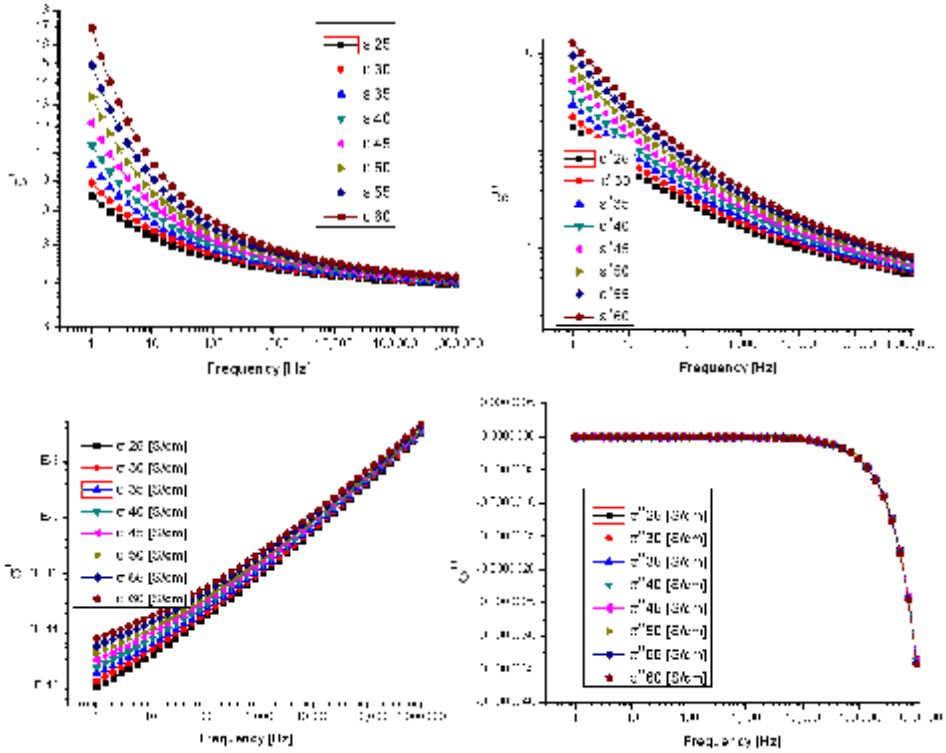

Fig. 4 – Temperature dependence of dielectric constant (ε'), dielectric losses (ε''), as well as the complex components conductivities (σ' and σ'') corresponding to sample LauMA$_{277}$-*b*-AEMA$_{81}$/Au prepared by spin-coating on a glass substrate.

5. Conclusions

1. The association of hybrid composites with glass substrate envisaged the potential applications for solar cells or dedicated sensors, but also related to the concepts of self-cleaning and self-healing of such components.

2. The spin-coating deposition offers an obviously more uniform, adherent and resilient thin layer associated to the glass substrate.

3. At a first view, the absolute figures seem to be very close in all experiments, aspect due to the much higher thickness of glass comparing to the hybrid composites, and to the peculiar behavior of glass polarization, with dielectric constant equal to 7.

4. In reality, by analysing the relative figures, LauMA$_{50}$-*b*-AEMA$_9$/Pd is obviously more electromagnetically active than LauMA$_{277}$-*b*-AEMA$_{81}$/Au.

5. All composites provided a high thermal stability of their electromagnetic behavior at MHz…GHz domain, so they can be recommended for applications in this range.

6. The electromagnetic shielding efficiency is obvious from 10 MHz and increases in GHz domain.

Acknowledgments. This work was developed in the framework of the Project "BRAIN" (PhD Scholarships ID 6681, OI POS DRU Ministry of Education, Research and Innovation). The authors gratefully acknowledge the support from the Romanian – Cyprus Bilateral Project no.436/18.06.2010.

REFERENCES

Avdeev M.V., Bica D., Vekas L. *et al., Comparative Structure Analysis of Non-Polar Organic Ferrofluids Stabilized by Saturated Mono-Carboxylic Acids*. J. of Coll. a. Interface Sci., **334**, *1*, 37-41 (2009).

Demetriou M., Papaphilippou P., Vekas L., Taculescu A., Savva I., Ciobanu R., *Development of Novel Hybrid Materials Consisting of Functional Block Copolymers and Metals or Metal Oxide Nanoparticles in Order to Investigate their Electromagnetic Features*. EPE 2010, Iaşi, Romania, **1**, 361-362 (2010).

Demetriou M., Krasia-Christoforou T., *Synthesis and Characterization of Well-Defined Block and Statistical Copolymers Based on Lauryl Methacrylate and 2-(acetoacetoxy)ethyl Methacrylate Using RAFT-controlled Radical Polymerization*. J. of Polymer Sci. Part A: Polymer Chem., **46**, *16*, 5442-5451 (2008).

* * www.novocontrol.de.

TESTAREA DIELECTRICĂ A UNOR NOI STRUCTURI COMPOZITE NANO-CONDUCTIVE POLIMERICE

(Rezumat)

Se efectuează sinteza unor structuri compozite nano-conductive sub formă de film, formate din copolimeri bloc şi nanoparticule de Au şi Pd. Acestor materiale i-au fost analizate proprietăţile dielectrice cu ajutorul spectrometrului dielectric de la Novocontrol, evidenţiindu-se că $LauMA_{50}$-*b*-$AEMA_9$/Pd este mult mai activ electromagnetic decât $LauMA_{277}$-*b*-$AEMA_{81}$/Au. Ambele materiale compozite prezintă o stabilitate termică ridicată a comportamentului electromagnetic în domeniul de frecvenţă MHz…GHz, astfel încât ele pot fi recomandate pentru aplicaţii destinate acestui domeniu de frecvenţă.