Dielectric Properties and Electromagnetic Behaviour of Pan/Nmpy Conductive Composites

S. Ursache, R. C. Ciobanu, M. Olariu, and Alina Neamtu

***Abstract*—Nowadays, because the synthesis of new materials is a very active field of research and industrial development, the different types of materials available for electromagnetic shielding structures is always increasing. Conducting polymers exhibit excellent electrical, electrochemical and optical properties; however the common usage of these materials has been restricted due to their poor processability and stability. Polyacrylonitrile (PAN) is an outstanding engineering material used in many applications owing to its good mechanical and thermal properties and its low cost [1].**

This paper investigates the dielectric and electromagnetic behavior of polyacrilonitrile composites thin films. Polyacrylonitrile/N-Methyl-Pyrrole composite thin films were prepared by polymerization of pyrrole on polyacrylonitrile matrix. Different concentrations of n-methyl-pyrrole were added to the polyacrylonitrile/dimethylformamide solution to achieve polymerization of pyrrole. The amount of n-methyl pyrrole was varied in order to investigate the influence of the concentration on the dielectric and also on electromagnetic properties in special electromagnetic shielding of the composite polymer.

***Index Terms*—Conductive polymers, dielectric spectroscopy, electromagnetic interference, shielding effectiveness.**

I. Introduction

Electromagnetic pollution is a term given to all the electromagnetic fields of various frequencies caused by existing artificial sources. The introduction in the 1990s of mobile phones using the digital Global System for Mobile Communications (GSM) with bandwidths of 900 and 1800 MHz and the further introduction of the Universal Mobile Telecommunications System (UMTS) have led to widespread use of this technology and to a substantial increase in the number of mobile phone base stations all over the world. This development has raised public concerns and substantial controversy about the potential health effects of the radiofrequency electromagnetic field emissions of this technology. A small part of the population attributes some strange symptoms of ill-health, such as sleep disturbances or headache to exposure to electromagnetic fields. This phenomenon is described as electromagnetic hypersensitivity or “environmental intolerance with attribution to electromagnetic fields” [2]. Additionally, individuals who are hypersensitive to electromagnetic fields often claim to be able to perceive radiofrequency electromagnetic fields in their daily life. People are generally exposed to mobile phone base stations radiation under far-field conditions, i.e. radiation from a source located at a distance of more than one wavelength. This results in relatively homogenous whole-body exposure. Mobile phone base stations exposure can occur continuously but the levels are considerably lower than the local maximum levels that occur when someone uses a mobile phone handset. A recent study [3] that measured personal exposure to radiofrequency electromagnetic fields in a Europe population sample demonstrated that the average exposure contribution from mobile phone base stations is relevant for cumulative long-term whole-body exposure to radiofrequency electromagnetic fields. In the scope to reduce human exposure to this type of radiations there are used electromagnetic screens.

Electromagnetic shielding is the process of reducing the electromagnetic field in a space by blocking the radiation with barriers made of special materials. Polyacrylonitrile (PAN) is a resinous, fibrous, or rubbery organic polymer. Almost all polyacrylonitrile resins are copolymers made from mixtures of monomers with acrylonitrile as the main component. PAN fibers are the chemical precursor of high-quality carbon fiber. It is chemically modified to make the carbon fibers found in plenty of both high-tech and common daily applications. Dimethylformamide (DMF) is a suitable solvent for PAN which has a plasticizing effect and is capable of forming complexes with PAN. The presence of DMF provides increased mobility of individual segments of polymer molecules [4]. Polypyrrole is one of the new generations of polymeric materials. In the last years it has been the main focus of researchers due to the advantage such as environmentally stable, ease to synthesis and relatively high conductivity as compared to other derivatives [4].

II. Materials

Now, because the synthesis of new materials is well represented in research and in industrial development, the arsenal of materials available for the realization of shielding structures is always increasing. Most shielding structures are fabricated by means of standard (i.e., nonmagnetic), conductive materials or by means of ferromagnetic materials, which are often preferred for their mechanical properties rather than their ferromagnetic behavior. Generally, the materials used for this type of shielding are not pure and any variation in their chemical composition is able to modify their conductivity [6]. Some materials whose main function is not that of shielding EMC fields have also been modified in their chemical composition or structure in order to provide them some EM performance while maintaining their original features.

The materials under test were obtained with the kind support of Istanbul Technical University [4], [5].

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S. Ursache, R. C. Ciobanu, M. Olariu, and Alina Neamtu are with the National Institute of Standards and Technology, Boulder, CO 80305 USA (e-mail: ursi_stefan@yahoo.com).

Polymerization was carried out in a flat-bottomed flask equipped with a stirrer and a condenser by the addition of cerium (IV) dissolved in HNO_3-water to an aqueous solution of monomer and oxalic acid. All operations were conducted in water at 25 ^{o}C. Polymerization started with addition of cerium (IV) solution at 25 ^{o}C water bath temperature and reaction concentrations of oxidant, monomer, and acid as following: $[Ce(IV)]=2\times10^{-2}$ M, $[HNO_3]=0.1$ M, $[OA]=2\times10^{-2}$ M, [AN]= 2.4 M. After 1 hour, the temperature was increased up to 60 ^{o}C and was kept at this temperature for 1 hour. After 2 hours of polymerization, the resulting polymer was precipitated, filtered and washed with distilled water. The filtered polymer was dried at room temperature. The polymerization chain is presented below: 0.375 g of polymerized polyacrylonitrile (PAN) was dissolved in 10 ml dimethylformamide (DMF) and then 50 µl of N-methyl-Pyrrole was added to the solution. This solution was mixed for about one hour at room temperature. After one hour, to the solution was added ceric ammonium nitrate (CAN) to achieve polymerization of N-Methyl-Pyrrole. Temperature was increased up to 80˚C for about 15 minutes to evaporate the solvent and to obtain a viscous solution. This viscous solution was casted as a film on a glass substrate area. The homogeneity of viscous solution was acquired by using four-sided film applicator (figure 1). In the final the casted solutions were dried in a 600 mmHg vacuum stove for 24 hours at 60˚C to evaporate the solvent. The whole procedure was repeated for 100, 150 and 200 µl N-methyl-pyrrole added to the initial solution.

III. Methods

Dielectric measurements were performed by Novocontrol Broadband Dielectric Spectrometer - schematic represented in Fig. 1 (Alpha-A High Performance Frequency Analyzer) at room temperature in frequency range between 10^6 and $3\text{x}10^9$ Hz.

The calibration of spectrometer was performed using WINDETA software which is a complete package of programs that can control with high precision the measurements of components, samples and interfaces with powerful electric and electronic equipment [6].

Fig. 1. Dielectric Novocontrol System Concept

Electromagnetic simulations that prove the electromagnetic performances of the material have been performed. The software used for simulations was CST Microwave Studio. The solver of CST package is based on a rectangular meshing scheme, which has been shown in many studies to be the most efficient time domain method available. In the scheme field values are distributed around the edges and face centers of mesh cells, but the software has always had the ability to arbitrarily slice a cell into two regions — one dielectric field region and one metal region through the method PBA® - Perfect Boundary Approximation ™. PBA allows the modelling of arbitrary curved surfaces, thus reducing the need for finer meshing and eliminating all staircase approximation errors. PBA also takes into account the thickness of metallic sheets or strip lines within one grid cell, without explicitly meshing it [8].

IV. Dielectric Results

The dielectric parameter as a function of frequency is described by the complex permittivity in the form [7]:

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - \varepsilon''(\omega) \quad (1)$$

where the real part $\varepsilon'(\omega)$ and imaginary part $\varepsilon''(\omega)$ are the components for the energy storage and energy loss, respectively, in each cycle of the electric field.

For the dielectric characteristics of irradiated and unirradiated composite samples, the measured capacitance, $C(\omega)$ was used to calculate the dielectric constant, $\varepsilon'(\omega)$ using the following expression:

$$\varepsilon'(\omega) = C(\omega)\frac{d}{A} \quad (2)$$

where d is sample thickness and A is surface area of the sample.

For dielectric loss, $\varepsilon''(\omega)$ is:

$$\varepsilon''(\omega) = \varepsilon'(\omega) \cdot \tan\delta(\omega) \quad (3)$$

where tan δ is tangent delta.

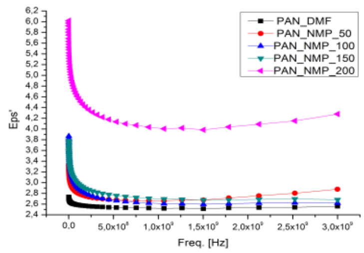

Fig. 2. Relative permittivity for composite films of PAN with different concentrations of NMPy

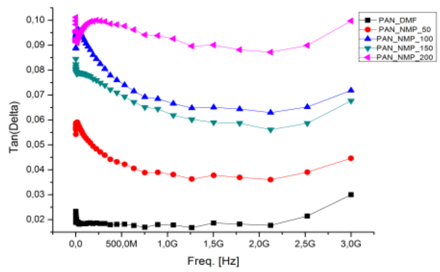

Fig. 3. Tan delta for composite films of PAN with different concentrations of NMPy

The dielectric permittivity as it showed in Fig. 2 decrease with the increasing of frequency. It also can be observed that relative permittivity increases with the concentration of NMPy. Therefore this fact can be attributed to the tendency of dipoles in polymeric samples to orient themselves in the direction of the applied field.

The tangent loss parameter is related to the ability of the material to be penetrated by an electric field and dissipate energy as heat. As depicted in figure 5 by increasing the concentration of initially added n-methyl-pyrrole the tangent loss increases.

V. Numerical Electromagnetic Results

Electromagnetic solvers simulate the Maxwell's equations [8] and their variations on a computer depending on electromagnetic field and material properties. The results were obtained in transient solver, which can cover the entire broadband frequency behavior of the simulated device from only one calculation run (in contrast to the frequency stepping approach of many other simulators). This solver is very efficient for most kinds of high frequency applications such as connectors, transmission lines, filters, antennas and many more. This simulator is equipped with the new Multilevel Subgridding Scheme (MSS™) which helps to improve the meshing efficiency and thus can significantly speed up simulations especially for complex devices [9].

Electromagnetic simulation results show the S (scattering) parameters for the structure. In the shielding theory the typical macroscopic parameters that define the reflectance, transmittance and absorption are defined relative to the electromagnetic power and are related to the S parameters [10] as shown in equations (4), (5), (6):

$$R = |S_{11}|^2 \tag{4}$$

$$T = |S_{21}|^2 \tag{5}$$

$$A = 1 - R - T = 1 - |S_{11}|^2 - |S_{21}|^2 \tag{6}$$

The structure designed under numeric tests is a material sample with defining dimensions 45 mm x 20 mm x 4 mm and the materials properties, electric permittivity and loss angle tangent, were parametric varied with the values from dielectric measurements previously performed corresponding of different percentages of N-methyl-pyrrole (NMP) in the base matrix of Polyacrylonitrile (PAN). The discretization was made in tetrahedral meshing for better accuracy - Fig. 4.

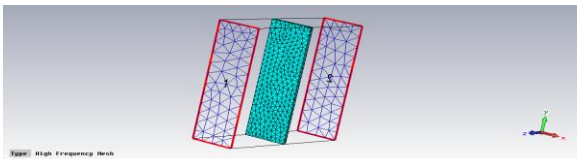

Fig. 4. Tetrahedral meshing of the structure

We have investigated the interaction between a plane wave and an infinitely large sheet of conductive polymer with material's parameters obtained in the dielectric measurements, at normal incidence. The boundary conditions are set to electric wall (both walls on x directions) and magnetic wall (y direction walls) Fig. 5. An input wave port is placed at some space from the structure; the second (exit) wave port is added only when losses inside the structure are taken into account.

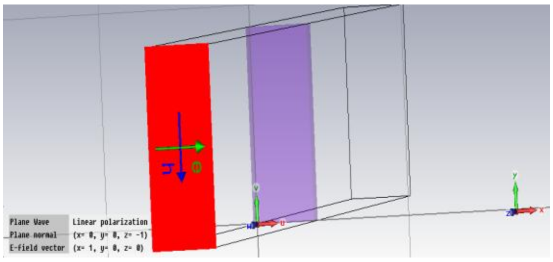

Fig. 5. Boundary conditions and plane wave

The simulations of the electromagnetic behaviour for the structure was made using parametric sweep simulations tool of the CST software for different values of dielectric permittivity (ε) and loss tangent (tg δ) obtained previously with dielectric spectroscopy.

The frequency range for de solver was set in the range 0.1 to 3 Ghz because it cover the frequencies most used in the domestic mobile communications (GSM, UMTS, Wi-Fi, Bluetooth), the target application of the structure propose.

Typical results are those from Fig. 6. and Fig. 7. Fig. 6 shows the S_{11} parameter, defining the electromagnetic reflective properties of the material. In Fig.7, S_{21}, the electromagnetic transmission through the structure is plotted.

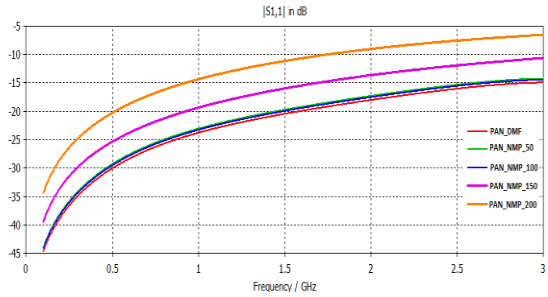

Fig. 6. Reflectance vs. frequency

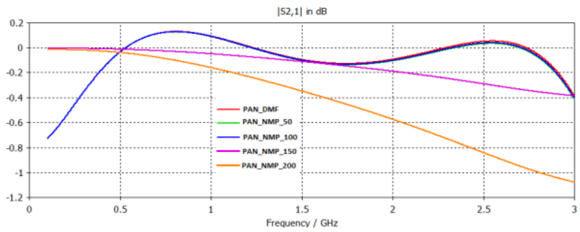

Fig. 7. Transmission of radiation through screen depending on dielectric losses

VI. Conclusions

The present communication shows that the different amounts of n-methyl-pyrrole have a great influence on the trend and magnitude of dielectric properties and accordingly to these, the electromagnetic characteristics. Regarding dielectric behavior we can observe that the dielectric permittivity decrease with the increasing of frequency and also with the concentration of NMPy and the tangent loss increasing together with the concentration of initially added n-methyl-pyrrole.

Electromagnetic predictions show that the transmittance is influenced mainly by the losses in the dielectric that means that the growing percent of NMPy provide better results. We observe a good enough attenuation ranging from 10 ÷ 25 dB in the 0.1 ÷ 2.5 GHz bandwidth (which cover GSM band, wireless communications and power line transmitters) which indicates that these kind of materials are suitable for use in shielding applications [11].

Because of the high complexity of electromagnetic phenomena, it is used numerical techniques to simulate the EMC behavior. For validation, we use another types of measurements like dielectric spectroscopy which is a very complex method for materials and fields characterization. The adoption of any numerical technique always requires knowing its basic formulation and certainly the input variables in order to apply it correctly and be aware of its accuracy, efficiency, and utility for specific problem under analysis.

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REFERENCES

[1] Y. Xia and Y. Lu, “Conductive polymers/polyacrylonitrile composite fibers: Fabrication and properties,” *Polymer Composites*, vol. 31, no. 2, pp. 340–346, February 2010.

[2] G. J. Rubin, R. Nieto-Hernandez, and S. Wessely, “Idiopathic environmental intolerance attributed to electromagnetic fields (formerly ‘electromagnetic hypersensitivity’): An updated systematic review of provocation studies,” *Bioelectromagnetics*, no. 31, pp 1–11, August 2009.

[3] W. Joseph, P. Frei, M. Roösli, *et. al*, “Comparison of personal radio frequency electromagnetic field exposure in different urban areas across Europe,” *Environmental Research*, vol. 110, no. 7, October 2010, pp. 658-663.

[4] A. S. Saraç, S. Özkara, B. Ustamehmetoğlu, and G. Özgür, “Electroinduced Polymerization of Acrylonitrile in the Presence of Ce(IV),” *Polymer Science: Part A: Polymer Chemistry*, vol. 37, pp. 2319–2327.

[5] A. S. Saraç, B. Ustamehmetoğlu, and H. Yıldırım, “Electroinduced Dispersion Polymerization of Acrylonitrile in the Presence of Poly(acrylic acid) and Catalytic Amount of Ce(IV),” *Applied Polymer Science*, vol. 84, pp. 723-728, 2002.

[6] Novocontrol. [Online]. Available: http:// www.novocontrol.de

[7] F. Kremer and A. Schonhals, *Broadband Dielectric Spectroscopy, Springer*, 2003.

[8] S. Ursache, S. Aradoaei, and R. Ciobanu, “Numerical Techniques for Electromagnetic Problems in Screening Applications”, in *Proc. 4th International Conference* on *Electrical* and *Power Engineering*, Iai, Tomul LII (LVI), Fasc. 5, 2006, pp. 689-694.

[9] CST. [Online]. Available: http://www.cst.de.

[10] R. F. Damian, R. Ciobanu, and C. Schreiner, “EMC tests and properties vs. microstructure for auxetic materials”, in *Proc. 15th IMEKO TC4 Symposium* on *Novelties* in *Electrical Measurements* and *Instrumentation*, Iasi, Romania, Sept. 19-21 2007, pp. 105-109, 2007.

[11] H. M. Hamzah, E. Saion, N. Yahya, A. Kassim, and M. Ekramul, “The Study of Conductivity of Polypyrrole Conducting Polymer, ”in *Proc. 5th Putra Physics Seminar Proceedings*, pp. 73-76, 2004.

S. Ursache is (Ph. D. Postdoc) a researcher at Technical University ‘Gheorghe Asachi’ of Iasi, Faculty of Electrical Engineering, Development and support of multidisciplinary postdoctoral programmes in major technical areas of national strategy of Research - Development - Innovation" 4D-POSTDOC program. He obtained the Ph.D. Degree in Electrical Engineering in 2009. Professional skills: use of data acquisition systems, virtual instrumentation,electrical measurements, advanced dielectric measurements (mainly dielectric spectroscopy), electromagnetic modeling and simulations, CST (Computer Simulation Technology) Software.