

Metamaterials based on polymer dispersions of nanoparticles and particles of copper obtained by cathodic current pulse electrolysis*

PRZEMYSŁAW ŁOŚ^{1†}, ANETA ŁUKOMSKA¹, SYLWIA KOWALSKA¹, REGINA JEZIÓRSKA¹,
PRZEMYSŁAW ZAPRZALSKI², JERZY KRUPKA³,

¹ Industrial Chemistry Research Institute, ul. Rydygiera 8, 01-793 Warsaw, Poland,

² Nano Jackets Ltd, ul. Klecińska 125, 54-413, Wrocław, Poland,

³ Department of Electronics and Information Technology, Warsaw University of Technology,
Nowowiejska 15/19, 00-665 Warsaw, Poland.

In the present paper a novel group of electromagnetic metamaterials as well as the method of their fabrication is presented. The studied metamaterials are polymer composites and nanocomposites made of polymer matrix/host (ethylene-vinyl acetate (EVA), polyethylene, polypropylene etc.) filled with copper flakes, of micrometer and/or nanometer size, as the conducting inclusions. The copper filler flakes were obtained by cathodic current pulse electrolysis from copper sulfate electrolytes at the stainless steel electrodes. SEM analysis showed that the morphology and structure of the copper deposit can be precisely controlled by applying different kind of current pulse and reversed current pulsed electrolysis. The polymer composite metamaterials formed by extrusion of small beads of polymer mixed with the copper flakes consisted of polymer matrix and copper flakes, ranging in length from 1 to 500 micrometers, and ranging in thickness from 80 nm to 2000 nm. The concentration of the copper flakes ranged from 0.5 wt% to 40 wt%, depending on the applications and required electromagnetic and mechanical properties. The studied materials were found to exhibit effective magnetic permeability that was smaller than unity, which is indicative of the typical properties of metamaterials. Present development solves technological and economical problems related to modern microelectronics methods which are currently mainly used for metamaterial fabrication.

Keywords: *metamaterials, composite polymers, nano-copper, current pulse reverse electrolysis, EMI shielding*

© Wrocław University of Technology.

1. Introduction

The present paper is concerned with metamaterials and a method of producing such materials. Interest in metamaterials has been growing rapidly and the number of publications related to this topic has recently increased to a few thousand per year [1, 2]. As is pointed out in the paper [3], metamaterials are materials that gain their prop-

erties from their structure rather than from their composition. Metamaterials exhibit unusual electromagnetic properties and may find applications in devices exploiting microwave frequencies through terahertz up to optical frequencies. One important class of metamaterials is a metal-dielectric structure. Materials of this kind exhibit diamagnetic (smaller than unity) effective permeability and very large in-plane effective permittivity. The first attribute is related to the eddy currents induced in conductive inclusions and the second attribute, an enhancement of the dielectric constant, is related to the large capacitances between adjacent

*The paper was presented during the 6th International Conference on Microwave Materials and their Applications MMA-2010, September 1–3, 2010, Warszawa

[†]E-mail: Przemyslaw.Los@ichp.pl

conductive clusters. There are a few major methods for fabricating metamaterials that exhibit diamagnetic (smaller than unity) effective permeability and very large in-plane effective permittivity. One of the most important methods of manufacturing artificial metamaterials is based on the placement of a plurality of resonant circuits on the dielectric substrate. In some examples the voltage-tunable capacitor includes a MEMS (micro electro-mechanical systems) structure, as is shown in the patent applications [4–6]. It is therefore clear that the main methods for the production of metamaterials are classical methods of modern microelectronics. They are characterized by quite high costs and capital investment in the equipment. Additionally, there are physical limitations to such methods as classical lithography for the resonators below 1 micrometer. In such cases, electronic lithography should be used. The main disadvantage of the last method is its low speed. The metamaterials discussed in the present paper are polymer composites and nanocomposites made of polymer matrix/host (ethylene-vinyl acetate (EVA), polyethylene, polypropylene etc.) filled with copper flakes of micrometer and/or nanometer size, as conducting inclusions. The copper fillers were obtained by cathodic current pulse electrolysis from copper sulfate electrolytes at the stainless steel electrodes. In our previous papers [7, 8] we have developed a novel approach to control the size and shape of deposited copper particles and nanoparticles from industrial electrolytes at the ultramicroelectrodes (UME). The copper nanopowders were electrodeposited by potentiostatic pulse electrolysis on different metallic substrates from copper electrorefinery electrolytes. On the basis of these studies a current pulse, with and without changing the direction of current, was applied to obtain the copper coatings and nano-flakes on the stainless steel base. The polymer composites were formed by extrusion of small beads of polymer mixed with the copper flakes. Surprisingly, the obtained composites exhibit properties typical for metamaterials.

2. Experimental

The copper coatings were obtained using an AUTOLAB GSTST30 system.

The measurements were conducted in a two-electrode configuration. 304L stainless steel plates, having an area of approximately 8 cm², were employed as the cathode/working electrodes. The counter/reference electrode was a large surface area copper plate. The electrolyte contained from 40 000 g/m³ to 46 000 g/m³ of Cu and 180 000 g/m³ H₂SO₄. After electrochemical deposition of copper on the electrode, the structure and dimensions of the deposited copper foil were analysed by scanning electron microscopy (SEM), using a JOEL 64–90 LV equipped with an energy dispersive spectrometer (EDS). Analysis of the energy dispersion spectrum (EDS) of the deposited copper confirmed the purity of the product obtained; only the spectral lines characteristic of copper were present. The applied pulse current densities ranged from –100 A/m² to –1000 A/m² for cathodic pulses, and +10 A/m² to +500 A/m² for anodic pulses.

All experiments were performed at room temperature.

The polymer composites based on halogen free flame retardant ethylene-vinyl acetate (HFFR/EVA) matrix containing from 0.1 wt% to 40 wt% copper flakes were obtained in laboratory conditions in the extruder Plasti-Corder, Brabender. The extruder was equipped with a mixing container of volume $V = 0.00005 \text{ m}^3$. The extrusion/mixing process was carried out at a temperature of 165 °C and under a rotation speed of 60 rpm. The processing time was 10 minutes for approximately 100 g of the obtained composite polymer sample. The plates of the polymer samples of the thickness of approximately 1 mm (used to study mechanical properties of the polymer composites) and plates of the thickness ranging from 0.5 mm to 0.6 mm (used for electromagnetic properties studies) were obtained by pressing the composite polymer beads at a temperature of 165 °C.

The electromagnetic properties (the complex permittivity ϵ and the complex permeability μ) of the obtained sample plates were measured using

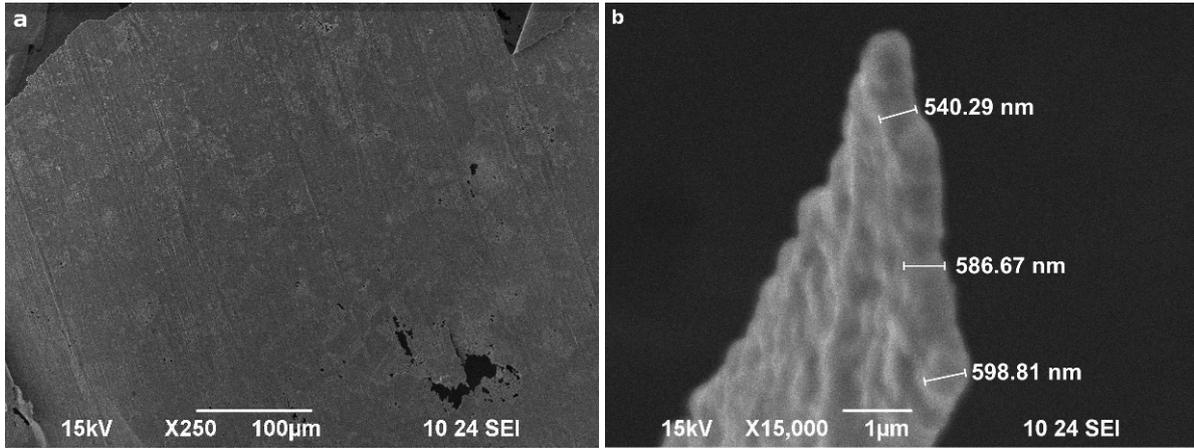


Fig. 1. The exemplary SEM image of copper foil of thickness approximately of 550–600 nm obtained by current pulse with a reverse of the current direction at stainless cathode; a) general view of the foil b) selected part of the foil showing its thickness. Electrolysis conditions (six pulses): $i_1 = -250 \text{ A/m}^2$ ($t_1 = 45 \text{ s}$); $i_2 = +250 \text{ A/m}^2$ ($t_2 = 3 \text{ s}$); $i_3 = -187.5 \text{ A/m}^2$ ($t_3 = 15 \text{ s}$); $i_4 = +250 \text{ A/m}^2$ ($t_4 = 3 \text{ s}$); $i_5 = -187.5 \text{ A/cm}^2$ ($t_5 = 15 \text{ s}$); $i_6 = +250 \text{ A/m}^2$ ($t_6 = 3 \text{ s}$); where: i – pulse current; t – pulse time; indexes 1, 2... 6 – number of consecutive cathodic and anodic pulses, negative values for cathodic current pulses and positive values for anodic current pulses.

the split post dielectric resonator [3] method at frequencies 4.8 GHz (both μ and ϵ) and 1.9 GHz (only effective ϵ).

3. Results and discussions

The electromagnetic properties of the polymer composites depend on many factors, such as electrical conductivity, permittivity as well as the composition, structure and size of the conductive component [9, 10]. In order for a conductive filler to be highly effective, it should preferably have a high so called “aspect ratio”, which is the ratio of the length, l and thickness, d of the metallic/conductive particles and nanoparticles. Generally, the larger the aspect ratio, the larger the effective permittivity of the polymer composite for a given concentration of conducting inclusions. That is why precise control of the size and structure of the conductive filler material is very important.

The first step in the fabrication of the metamaterials under study here, namely electromagnetic polymer composites, was to produce the conductive component – copper flakes. Copper or nanocopper foil was electrodeposited on a stainless steel electrode from aqueous copper sulfate solu-

tion by cathodic current pulse electrolysis. After electrochemical deposition of copper on the electrode, the structure and dimensions of deposited copper foil were analysed with a scanning electron microscope. Depending on the duration of the pulse, copper foil of different thickness can be obtained. The quality of the foil is improved when current reversal electrolysis is used.

An example of a deposited copper layer, as a function of electrolysis conditions, is presented in Fig. 1. The details regarding the dependence of the structure and thickness of deposited Cu layers on the kind of current electrolysis are given in [6].

In the next step, the copper foil is mechanically removed from the stainless steel electrode, which is quite easy due to the weak interaction between the copper and stainless steel base, and then it is fragmented into the form of flakes.

The next stage is mechanical mixing of copper flakes and polymer beads, with the desired weight % concentration of components, and finally the extrusion of polymer composite metamaterial is performed. A proper mixing of the polymer and added electrically conductive component of the polymer composite is very important for EM metamaterial to be obtained.

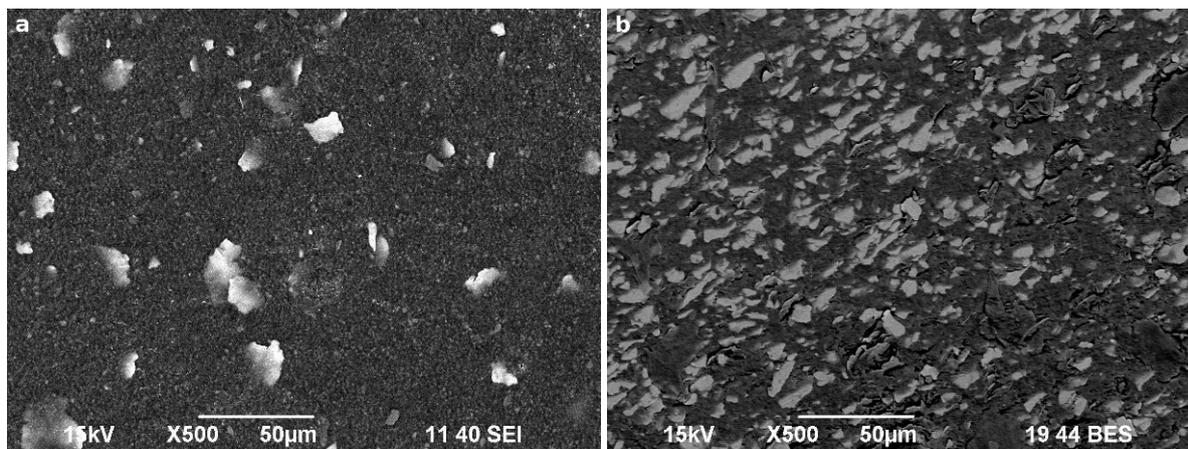


Fig. 2. The SEM images of cross section of polymer composites plates; a) HFFR/5 % Cu flakes; b) HFFR/40 % Cu flakes.

Exemplary SEM images of a cross-section of EVA polymer/Cu flakes plate for 5 and 40 %wt of Cu fillers are presented in Fig. 2. The micrographs show the heterogeneous structure of the polymer composite, with good interfacial adhesion between the polymer matrix and copper flakes fillers.

Test measurements for the permittivities and permeabilities of HFFR/EVA type polymer samples, for concentration levels of copper flakes ranging from 0 wt% to 40 wt%, are presented in Table 1 and Fig. 3. The average length of the copper flakes is approximately 20 μm and the average thickness is approximately 400 nm, which gives an aspect ratio of 50. One may observe that the value of the real part of the magnetic permeability, $\text{real}(\mu)$, is lower than 1 at 4.8 GHz, for the studied polymer composites of Cu concentrations ≥ 1 wt% Cu concentrations. It is inversely proportional to the concentration of Cu filler in the polymer composites. The lowest value of $\text{real}(\mu)$, equal to 0.952, is obtained for a copper concentration of 40 wt%. On the basis of this data, it is concluded that the polymer composites based on the HFFR/EVA matrix containing from 1 wt% to 40 wt% copper flakes exhibit properties that are typical of metamaterials.

It is also interesting to note that, at a frequency of 4.8 GHz, the imaginary part of dielectric permittivity always stays relatively small (ranging between 0.00883 and 0.01720, for all Cu concentrations under consideration), whereas the real part

of the dielectric permittivity changes substantially, from 3.52 (Cu concentration = 0 wt%) to 24.4 (Cu concentration = 40 wt%). A linear dependence of $\log[\text{real}(\epsilon)]$ on the concentration of copper flakes, expressed in wt%, is observed. The results show that the composite polymer studied in this paper exhibits low electrical conductivity when dielectric permittivity is relatively high. This might have relevance for electromagnetic interference (EMI) shielding applications.

4. Conclusions

In the present paper a novel group of electromagnetic metamaterials and a method for their fabrication are presented. The studied metamaterials are polymer composites and nanocomposites made of polymer matrix/host (ethylene-vinyl acetate (EVA), polyethylene, polypropylene etc.) filled with copper flakes, of micrometer and/or nanometer size, as the conducting inclusions. The copper filler is produced from copper foil deposited from aqueous sulfate solution at the stainless steel electrode. Precise control of the thickness and structure of the copper foil is achieved by the application of the current pulse and reversed current pulsed electrolysis. The permittivities and permeabilities of the composite polymers obtained by extrusion show monotonic variation, as functions of the copper concentration. The real part of per-

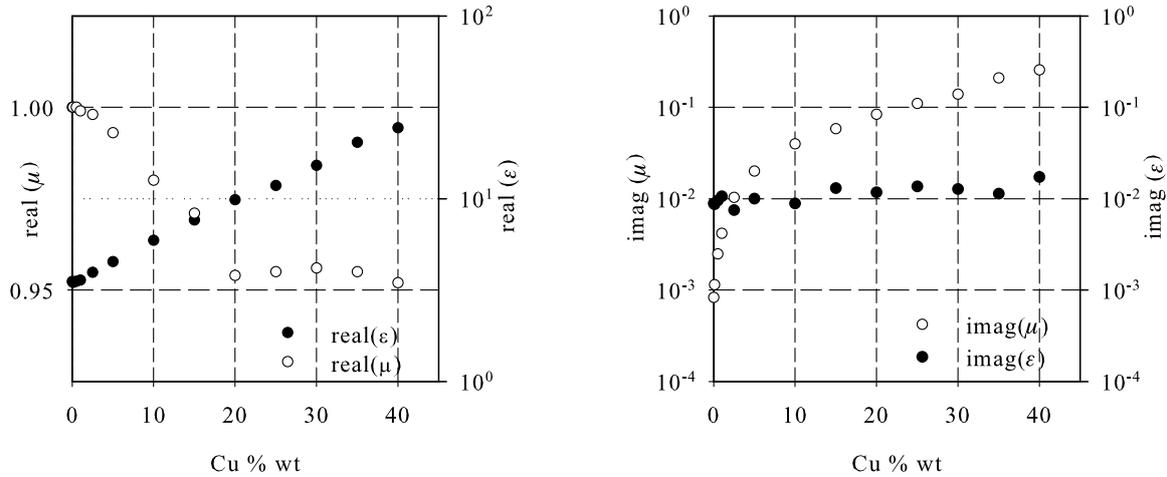


Fig. 3. Complex permittivity (ϵ) and permeability (μ) of copper flakes loaded polymers at the frequency 4.8 GHz.

Table 1. Complex permittivity (ϵ) and permeability (μ) of copper flakes loaded polymers using split post dielectric resonator [3] method at the frequency 4.8 GHz.

Copper content, wt% in polymer composite	4.8 GHz			
	real(ϵ)	real(μ)	imag(ϵ)	imag(μ)
0.0	3.52	1.000	0.00883	0.000829
0.1	3.48	1.000	0.00869	0.001140
0.5	3.53	1.000	0.00954	0.002480
1.0	3.58	0.999	0.01060	0.004160
2.5	3.95	0.998	0.00747	0.010300
5.0	4.52	0.993	0.01000	0.020000
10	5.91	0.980	0.00885	0.039700
15	7.64	0.971	0.01300	0.058200
20	9.86	0.954	0.01170	0.083700
25	11.8	0.955	0.01360	0.110000
30	15.2	0.956	0.01270	0.139000
35	20.3	0.955	0.01130	0.209000
40	24.4	0.952	0.01720	0.256000

mittivity is proportional to the copper concentration, whereas the real part of permeability is inversely proportional to the copper concentration. The real part of permeability varies in the range from 1.0 (for pure dielectric matrix) to 0.952 (for a copper concentration of 40 wt%), while the real part of permittivity varies from 3.52 (for a pure dielectric matrix) to 24.4 (for a copper concentration of 40 wt%). For large copper concentrations, the dominant loss mechanism in our metal-dielectric metamaterial is associated with the magnetic field, which is described quantitatively by the imaginary

part of permeability. Physically, these losses are associated with eddy current losses induced in the metal particles by the magnetic field. The obtained material can be used in electromagnetic interference (EMI) shielding.

References

- [1] HOFFMAN A.J., ALEKSEYEV L., HOWARD S.S., FRANZ K.J., WASSERMAN D., PODOLSKIY V.A., NARIMANOV E.E., SIVCO D.L., GMACHL C., *Nature Materials* 6 (2007), 946.

- [2] FANG N., XI D., XU J., AMBATI M., SRITURAVANICH W., SUN C, ZHANG X., *Nature Materials* 5 (2006), 452.
- [3] KRUPKA J., DERZAKOWSKI K., HARTNETT J.G., *Meas. Sci. Technol.*, 20 (2009), 105702.
- [4] NGUYEN V.N., YONAK S.H., SMITH D.R., KIM J., *Patent application*, US 2009/0206963 A1.
- [5] MOSALLAEI H., *Patent application*, US 2009/0040131 A1.
- [6] LOS P., LUKOMSKA A., JEZIORSKA R., KOWALSKA S., *Patent Application*, UP RP Poland 2010.
- [7] LUKOMSKA A., PLEWKA A., LOS. P., *J. Electroanal. Chem.*, 637 (2009), 50.
- [8] LUKOMSKA A., PLEWKA A., LOS. P., *J. Electroanal. Chem.*, 633 (2009), 92.
- [9] KOLEDINTSEVA M.Y., DREWNIAK J., DUBRO R., *Progress In Electromagnetics Research B*, 15 (2009), 197.
- [10] LIU Z., BAI G., HUANG Y., MA Y., DU F., LI F., GUO T., CHEN Y., *Carbon* 45 (2007), 821.

Received 13.09.2010

Accepted 13.09.2010