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Obtaining and properties of polyolefin composites metamaterials with copper micro- and nanoflakes

RAPID COMMUNICATION

Summary — In the paper a novel preparation method of polyolefin composites of metamaterial properties is presented. The studied composites were obtained by melt mixing of polyolefins and copper flakes of micrometer and/or nanometer-size, as conducting inclusions. The precise control of thickness and structure of the copper layer was achieved by the application of the current pulse and reversed current pulse electrolysis. The structure of the deposited layer on a stainless steel plate and size of copper flakes in polymer composites were studied using a scanning electron microscope (SEM). The electromagnetic properties of prepared metamaterials were measured by split dielectric resonator methods.
Keywords: metamaterials, polyolefin composites, copper nanoflakes, current pulse reverse electrolysis.

OTRZYMYWANIE I WŁAŚCIWOŚCI METAMATERIAŁÓW KOMPOZYTOWYCH NA BAZIE POLIOLEFIN Z MIKRO- I NANOPŁATKAMI MIEDZI

Streszczenie — W artykule przedstawiono nową metodę otrzymywania kompozytów poliolefinowych o właściwościach metamateriałów. Kompozyty wytwarzano metodą mieszania w stanie stopionym poliolefin oraz mikro- i nanopłatków miedzi za pomocą mieszalnika typu PlastiCorder firmy Brabender. Płatki miedzi o wymiarach mikro/nanometrycznych otrzymywano usuwając mechanicznie z płytki stalowej warstwę miedzi osadzoną tam podczas procesu pulsowej elektrolizy prądowej ze zmianą kierunku prądu. Do badań struktury osadzonej warstwy miedzi jak i wymiarów płatków miedzi w matrycy polimerowej użyto skaningowego mikroskopu elektronowego (SEM) (rys. 1 i 2). Właściwości elektromagnetyczne otrzymanych metamateriałów badano za pomocą metody rezonatorów dielektrycznych (tabela 1).
Słowa kluczowe: metamateriały, kompozyty poliolefinowe, nanopłatki miedzi, impulsowa elektroliza prądowa ze zmianą kierunku prądu.

Electromagnetic properties of materials are an important topic due to their commercial, military, communication and environmental protection applications [1—4]. For instance, in electromagnetic interference (EMI) shielding applications mostly metal based screening materials were used in the past. In comparison to metals, polymer composite based EMI shields are advantageous because they are characterized by low specific weight, high corrosion resistance, plasticity and simple, low cost processing methods.

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The examples of materials, which are characterized by internal reflection of electromagnetic fields, are high surface filler polymer composites. They might be polymer composites filled with electrically conductive fillers such as particles of metals, carbon or carbon fibers. Their shielding effectiveness is higher when filler concentration is higher and when there is higher aspect ratio parameter of filler (ratio of fiber length to thickness/diameter) [2, 3]. Internal reflections are especially common for composites filled with small dimensions fillers *e.g.* nanoparticles. According to the percolation theory there is a threshold concentration of the filler when its particles are close enough to establish a continuous electric current pathway and above this concentration electrical conductivity of the composite polymer increases substantially.

In our previous papers [5—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 pulse deposited on different metallic substrates from copper electrorefinery electrolytes. It was shown that using ultramicroelectrodes in the diffusion control regime (potentials of voltametric plateau) it is possible to control the shape and size of copper crystals electrodeposited in potentiostatic pulse electrolysis. On the basis of these studies a current pulse electrolysis method with and without changing the direction of current was developed to obtain the copper coatings and nanoflakes on the stainless steel base. Surprisingly, the obtained composites exhibit metamaterial properties.

In this paper a novel preparation method of metamaterials such as polyolefin composites, containing micrometer and/or nanometer-size copper flakes, as conducting inclusions, obtained by current reverse pulse electrolysis is described.

EXPERIMENTAL

Materials

The low-density polyethylene (PE-LD, Malen E FGNX 23D022) with a melt mass-flow rate *MFR* = 2.2 g/10 min (ISO 1133) from Basell Orlen Polyolefins (Poland), linear low density polyethylene (PE-LLD, Stamylex FFH 02945) with *MFR* = 2.2 g/10 min (ISO 1133) supplied by Dex Plastomers and polypropylene (PP, Moplen EP440G) with *MFR* = 1.3 g/10 min (ISO 1133) from Lyondellbasell were used as polymer matrices.

Copper micro- and nanoflakes obtained according to the procedure described in patent application [5] were used as a filler.

Composites and nanocomposites preparation

The method of preparation of copper based polymer composite metamaterial consists of the following steps:

— cathodic pulse deposition of a copper or nanocopper layer from aqueous sulfate solutions of copper ions on a stainless steel base,

— mechanical removal of the copper layer from stainless steel base and fragmentation of the layer into the form of flakes,

— mechanical mixing of copper flakes and polymer at the desired concentration of components,

— melt mixing of polyolefin composites which can be formed into the desired shape by further processing *e.g.* compression molding.

Preparation of copper micro- and nanoflakes

The electrocrystallization of cupric(II) ions was carried out using Autolab GSTST30 system. All experiments were performed at room temperature.

The electrolyses were conducted in the two-electrode configuration. A 304L stainless steel plate of approximately 8 cm^2 size was employed as the cathode/working electrode. The counter/reference electrode was a large surface copper plate. The electrolyte contained 40—46 g/dm^3 Cu^{2+} and 180 g/dm^3 H_2SO_4. All experiments were carried out at the cathodic pulse current densities of copper electrodeposition ranging from 0.010 to 0.100 A/cm^2.

Preparation of polymer composites with copper

PE-LD, PE-LLD and PP composites, containing from 1 to 30 wt. % of copper flakes, were prepared by melt mixing using an internal mixer (Brabender Plasti-Corder), equipped with a mixing chamber 50 cm^3 in volume. Processing of an approximately 100 g sample was carried out using a screw speed of 60 rpm, at temperature 210 °C, 240 °C and 216 °C for PE-LD, PE-LLD and PP, respectively. The mixing time was 10 min.

Samples suitable for electromagnetic testing were prepared by compression molding of 0.5—0.6 mm thick sheets at temperature listed above, then slowly cooled at the rate approximately 2 °C/min, down to the room temperature.

Methods of testing

After electrochemical deposition of copper on the electrode the structure and dimensions of the deposited copper layer have been studied using a scanning electron microscope (SEM) images obtained with JOEL 64-90 LV system. On the basis of the analysis of the energy dispersion spectrum (EDS) of deposited copper it has been stated that only the lines characteristic of copper are present, which shows the purity of the obtained product. The SEM method was also used to study the size of copper flakes in polymer composites.

The electromagnetic properties [the complex permittivity (ε) and the complex permeability (μ)] of the obtained sample sheets have been measured using the split post dielectric resonator [9] method at the frequency 4.8 GHz (both ε and μ).

RESULTS AND DISCUSSIONS

It is generally accepted [2, 3] that the electromagnetic properties of polymer composites depend on the composition, structure and size of the conductive component. Especially, the ratio of the length (l) and thickness (d) of the metallic, conductive particles and nanoparticles, called aspect ratio [2] is important to predict the electromagnetic properties of the polymer composites. In general, the higher the aspect ratio, the higher is the dielectric constant of the polymer composites for a given conducting inclusions concentration. Additionally, a proper mixing of the polymer and added electrically conductive component of the polymer composites is important to

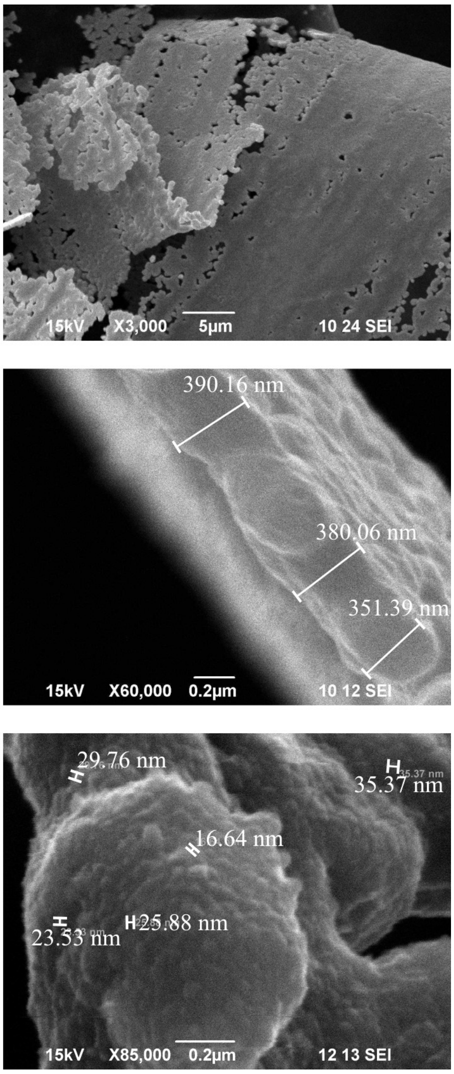
a)
b)
c)


Fig. 1. The SEM image of the copper layer of thickness approximately 200—400 nm obtained by current pulse electrolysis with a reverse of the current direction at stainless cathode; SEM magnifications: a) 3000, b) 60 000, c) 85 000

obtain metamaterial. Consequently, it is very important to control the size and structure of the deposited copper layer. In the present study precise control of the thickness and structure of the copper layer deposited on a stainless steel base is achieved by application of the current pulse and reversed current pulse electrolysis. The best quality of the copper layer is obtained when current reversed electrolysis is used. Preliminary experiments showed that optimal dimensions of flakes was ensured by the following conditions of current densities and times: i_1 = -0.025 A/cm^2, t_1 = 30 s; i_2 = +0.025 A/cm^2, t_2 = 3 s; i_3 = -0.01875 A/cm^2, t_3 = 10 s; i_4 = +0.025 A/cm^2, t_4 = 3 s; i_5 = -0.015 A/cm^2, t_5 = 10 s; i_6 = +0.025 A/cm^2, t_6 = 3 s. The SEM images of the obtained copper layer are presented in Figure 1. The stainless steel base is used because of the ease of mechanical removal of the copper layer from the cathode after electrolysis [6—8].

At the initial stage of the galvanostatic electrolysis, spherical copper nuclei are created at the stainless steel cathode according to the 3D progressive nucleation model [7]. The growth of the copper layers is a result of the copper ions diffusion fluxes overlapping at longer times of electrolysis. Consequently, the layer consists of spherical crystallites of copper. The mechanism of the copper layer growth is always the same and whatever is the size of the spherical crystallites and the thickness of the electrodeposited copper layer, the obtained material is built of nanocrystallites of the size between 15 and 50 nm as it is shown in Figure 1c. Taking into account the structure of the copper substrate used as a filler, one should consider it as the nanomaterial.

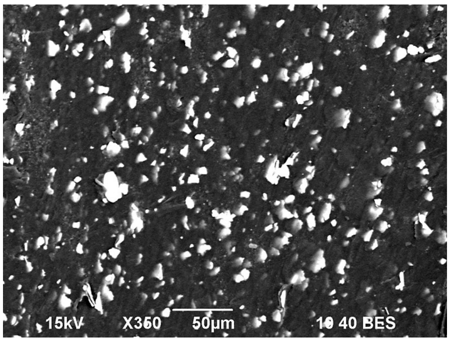


Fig. 2. The SEM image of a cross section of a PE-LD polymer composite with 30 wt. % of Cu flakes

The exemplary SEM image of a cross-section of polymer composite with Cu flakes is presented in Figure 2.

T a b l e 1. The real and imaginary part of complex permittivity and permeability [*real*(ε), *imag*(ε), *real*(μ) and *imag*(μ), respectively] of copper flakes loaded polymers

Copper content in the polymer composite wt. %	Type of the polymer matrix	*real*(ε)	*imag*(ε)	*real*(μ)	*imag*(μ)
1	PE-LD	2.4700	0.0040	1.0000	0.0055
1	PE-LLD	2.3800	0.0021	1.0000	0.0033
1	PP	2.3800	0.0116	1.0000	0.0025
10	PP	3.4200	0.0131	0.9860	0.0266
15	PE-LLD	4.0700	0.0192	0.9830	0.0365
20	PE-LD	5.1900	0.0161	0.9690	0.0567
20	PE-LLD	5.0600	0.0192	0.9730	0.0515
20	PP	5.0100	0.0042	0.9750	0.0555
30	PE-LD	7.1900	0.0090	0.9620	0.0783

The average length of the copper flakes is approximately 10 μm and the average thickness is approximately 200—400 nm (established from SEM images of the prepared polymer composites) which give the aspect ratio between 25 and 50. The results of the electromagnetic properties measurements as a function of the copper flakes concentration in the polymer ranging between 1 and 30 wt. % are presented in Table 1. The value of the real part of magnetic permeability *real*(μ) is lower than 1 at 4.8 GHz for studied polymer composites whereas Cu concentrations are higher than 1 wt. % Cu. It decreases with the increase of the content of Cu fillers in polymer composites. The lowest value of *real*(μ) equal to 0.962 is obtained for PE-LD and copper concentration of 30 wt. %.

For copper concentrations higher than 1 wt. % dominant loss mechanism in the studied metal-dielectric metamaterial is associated with the magnetic field which is described quantitatively by the imaginary part of permeability [*imag*(ε)]. Physically these losses are associated with eddy current losses induced in the metal particles by the magnetic field.

From the results of electromagnetic polymer composites properties *i.e.* real and imaginary parts of permittivity, *real*(ε) and *imag*(ε), respectively, it can be concluded that the composites obtained exhibit low electrical conductivity and relatively high dielectric permittivity what indicates very good EMI shielding properties of the materials studied. The EMI properties discussion is beyond the scope of this paper and will be presented in the future [10].

On the basis of these studies it is stated that the PE-LD, PE-LLD and PP composites containing from 1 to 30 wt. % of copper flakes exhibit properties typical of metamaterials.

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