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Električna provodnost PMMA kompozita punjenih bakarnim prahom

Electrical conductivity of PMMA composites filled with copper powder

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Izvod

Ovaj članak se bavi sintezom i karakterizacijom elektroprovodnih kompozitnih materijala toplim moldovanjem mešavina polimetilmetakrilata (PMMA) i elektrohemijski dobijenog bakarnog praha, kao i ispitivanjem uticaja morfologije čestica na provodnost i perkolacioni prag dobijenih kompozita i termijske karakteristike dobijenih kompozita. Udeo elektrohemijski dobijenog bakarnog praha je variran od 0.5 – 8.8 vol%. Analiza najznačajnijih osobina kako pojedinačnih komponenti tako i dobijenih kompozita je uključivala strukturnu analizu i merenja električne provodljivosti. Značajan porast električne provodljivosti može se primetiti kad sadržaj bakarnog praha u kompozitima dostigne perkolacioni prag što je iznosilo na 2.98 vol%. U ispitivanom opsegu koncentracija elektrohemijski dobijenog bakarnog praha u kompozitima i pritiscima prerade porast električne provodljivosti je iznosio čak šesnaest redova veličine. Primećeno je da se ovaj prelaz javlja pri nižim vrednostima udela punioca nego što je navedeno u literaturi, što može biti posledica upotrebe punioca sa velikim vrednostima specifične površine.

Ključne reči: *provodni polimerni kompoziti, elektrolitički bakarni prag, PMMA, termijska analiza, električna provodljivost, perkolacioni prag*

Abstract

This article is concerned with synthesis and characterization of electroconductive composite materials prepared by hot molding of mixtures of PMMA and electrochemically deposited copper powder and investigation of the influence of particle morphology on conductivity and percolation threshold of obtained composites and thermal characteristics. Electrodeposited copper powder content was varied from 0.5-8.8 vol%. Analysis of the most significant properties of individual components and prepared composites included structural analysis and measurements of electrical conductivity. The significant increase of the electrical conductivity can be observed as the copper powder content reaches the percolation threshold at 2.98 vol%. In the investigated range of electrodeposited copper powder concentrations and applied pressures the increase of the electrical conductivity of composites is as much as sixteen orders of magnitude. It was found that this transition occurs at lower volume fractions than stated in the literature which can be due to the filler with high specific area.

Keywords: *Conducting polymer composites, electrolytic copper powder, PMMA, thermal analysis, electrical conductivity, percolation threshold*

Introduction

Word composite means that the material consists of two or more different parts which are combined in a controlled manner in order to achieve a mixture which has more useful properties than any of the starting ingredients alone [1]. In the engineering design, composites comprise of one or more discontinuous phases embedded within the continuous phase. Depending on the purpose of the

composite, discontinuous phase, which is typically more rigid and stronger than the continuous phase, is referred to as a filler or reinforcement, and the continuous phase is called the matrix. The term "reinforcement" is often used when the objective of the discontinuous phase is to improve the mechanical properties of the composite, while the term "filler" is used when the main objective is cost reduction or modification of other, mainly non-mechanical properties. Composite materials reinforced with fibers consist of fibers of high shear strength and modulus that are embedded in or bonded to a matrix with a variety of interactions between them. In this embodiment, the fibers and the matrix maintain their physical and chemical identities and properties, but they add to the final product a combination of properties that cannot be achieved with any of the ingredients individually. Properties of the composites are heavily influenced by properties of the starting constituent materials, their distribution, processing method and the interaction between them. The properties of the composite do not depend only on the concentration of filler, but also on size, shape (geometric ratio), interstitial interaction between filler and matrix and filler orientation [2,3].

Attempts to improve material properties by adding fillers, either inorganic or organic, are not new. For a long time synthetic polymer composites are used in various industrial fields, equipment, automotive industry, and even in the aviation industry.

Conductive or semiconductive polymer composites are widely studied because of their numerous high-tech, electrical and electronic applications in various fields, such as self-regulating heaters, electric and temperature regulators for device protection and materials for removal of electromagnetic/radio frequency interferences (EMI / RFI) in electronic devices [4-14]. Conductive polymer composites can be prepared by different techniques and with different materials [15-24].

It is well known that the electrical resistance of polymer composites do not increase linearly with the increase of electrically conducting filler, but there is a critical volume fraction of filler (percolation concentration) at which the resistance of material sharply decreases from insulating range to the values of semiconductors or metallic conductors [8,22]. For efficiency, but also in order to improve the processability and to reduce costs of processing, as well as other economic parameters, the amount of conductive phase needed to obtain materials with high conductivity should be as small as possible. A variety of statistical, geometrical and thermodynamic models are proposed in order to estimate the conductivity (or inverse resistivity) [6,26,29]. An interesting overview of the different theories gave Lux et al. [29].

In this paper, the effect of filler concentration on the electrical conductivity of composites produced by warm molding of polymethylmethacrylate (PMMA) matrix and galvanostatically obtained copper powder. The data can be helpful in development of theoretical models for better understanding of the electrical properties of such materials.

Experimental part

Electrolytically obtained copper powder that was used in this study was galvanostatically produced under the following conditions: current density, j=3600 A/m^2, powder brush-up time was τ_r=15 min, electrolyte flow Q=1 changes of the cell volume/h, the temperature of the electrolyte t=(50±2) $^{\circ}$C, copper concentration C(Cu^{+2})=15 g/dm^3 and the concentration of sulfuric acid C(H_2SO_4)=140 g/dm^3. The wet powder was washed several times with plenty of demineralised water until there were no traces of acid, at room temperature, since the acid promotes rapid oxidation of the powder during drying process. The resulting copper powder was subsequently washed by the solution of sodium soap SAP G-30 in order to protect it from subsequent oxidation. After drying in a tunnel furnace at 110 - 120 °C in a controlled nitrogen atmosphere, copper powder was sieved through a mesh with 45 μm openings.

The polymer matrix used in the experiments was commercial PMMA in form of beads, supplied by Sigma-Aldrich, having average molecular weight of M_w ~350000, with a density of 1.20 g / cm^3, and the electrical conductivity of about 10^{-12} S / cm. Before use, the polymer was dried in a tunnel furnace at 60 ° C in a controlled nitrogen atmosphere.

The morphology of obtained electrodeposited copper powder was examined in details by means of scanning electron microscopy using a JEOL JSM - 6610LV microscope.
PMMA composites filled with copper powder were prepared with the copper powder volume fraction ranging 0.5 % (v/v) - 8.8% (v/v), while pure PMMA and the copper samples were prepared as reference materials. Samples were prepared by mixing and homogenizing the PMMA matrix and the copper powder in molder while heating at t=180 ^{o}C for 30 min. After preparation, the samples were cooled at room temperature for about 30 min. In order to obtain flat surface for conductivity measurements, samples were polished with sandpaper. The thickness of samples (necessary for the conductivity calculation) was determined using micrometer with accuracy of 0.01 mm. The thickness was measured several times per sample, and then averaged.
The measurement of electrical conductivity was derived from measuring the DC I/O characteristics of the samples using Simpson Electric Company digital multimeter, model 464. The geometry of used instrument contacts (rings) was such that it minimizes the edge effects, hence it can be assumed that these effects did not exist.
Thermogravimetric analysis was performed on PMMA and PMMA composites filled with copper powder in order to illustrate the thermal behavior (stability) and the possible temperature range use. Thermal stability of PMMA was investigated using TA Instruments Q600 thermal analyzer with a heating rate of 20°C/ min in a dynamic nitrogen atmosphere.
TA Instruments Q100 instrument was used for differential scanning calorimetry (DSC analysis) experiments. The analysis was performed from 30 ° C to 200 ° C with a heating rate of 20^{o}C / min.

Results and discussion

Conductivity of the conductive polymer composites strongly depends on nature of contacts between the conductive filler elements. In order to achieve better electrical conductivity of the conductive polymer composites with the same or similar characteristics, and hence saving in material usage, different types of fillers, particularly those with highly developed free surfaces, are used. Theoretical and experimental considerations have shown that their use leads to the formation of conductive network through the entire volume of the sample at much lower filler volume fraction [30, 31]. However, there is need for more detailed study of real synergetic effects of different fillers having different dimensionalities that are suitable for formation of conductive networks in conductive polymer composites. For this reason the copper powder was galvanostatically produced with distinct dendritic morphology, having high specific surface area, as shown in Figure 1.

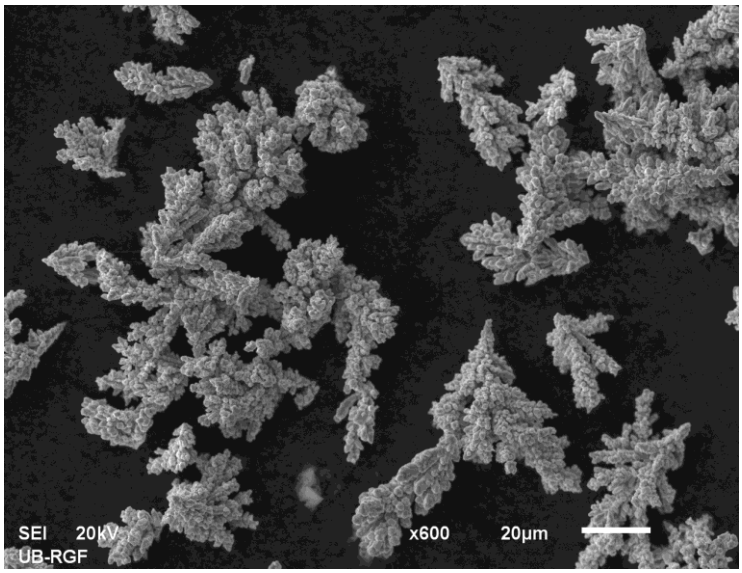

Figure 1. *SEM photograph of copper powder particles obtained by constant current deposition and sieved through mesh <45 µm.*

Presented results of copper powder morphological analysis showed that the powder has very large free surface. The powder shows specific characteristics typical of highly dendritic particles with distinctly developed primary and secondary dendritic arms with angles between them typical for centered cubic lattice. Therefore, this powder is a good prerequisite for the formation of great number of interpartical contacts between the conductive copper powder particles, hence decreasing percolation threshold.

The electrical conductivity was determined according to the relationship:

$$\sigma = \frac{I}{U} \cdot \frac{l}{S} \qquad (1)$$

where σ - electrical conductivity, *and* - the current through the sample, *In* - potential difference l - equivalent length of the sample through which the current and S - cross-sectional area of the sample.

Electrical conductivity of the composites, as a function of filler volume fraction, for all samples, was measured as mentioned in the Experimental part. DC I/O characteristics conductivity measurements for samples with a particle size ≤45 μm is shown in Figure 2. Typical S shaped dependence, with three different regions (insulating, transitional and conductive) can be observed. Percolation threshold value was obtained from the maximum of conductivity derivative as a function of volume fraction of filler.

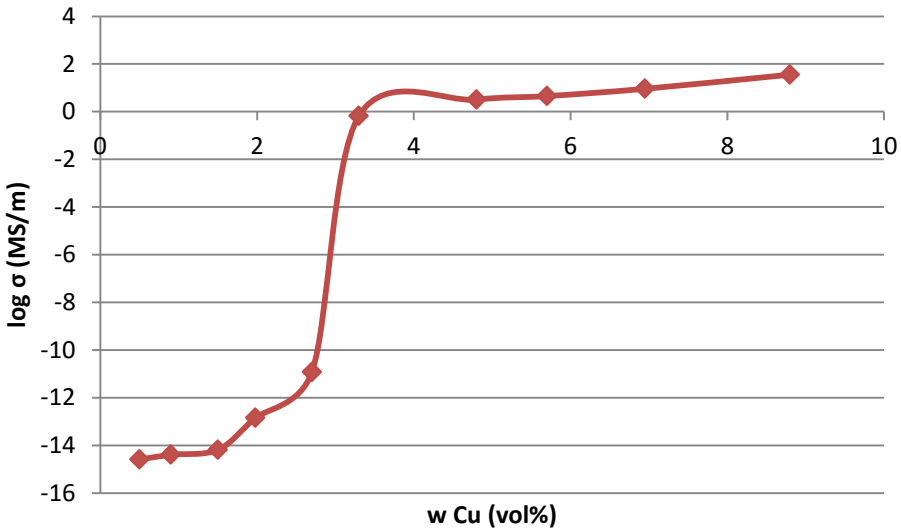

Figure 2. *Change in electrical conductivity as a function of filler volume fraction for PMMA composites filled with copper powder*

Experiments have shown that the morphology of the particles plays a significant role for the percolation threshold appearance. Due expressed interparticle contact with small particles having a high specific surface area, and the impact of packaging phenomenom, the percolation threshold occurs at lower value of filler volume fraction for particles ≤45μm than stated in the literature [32]. As it can be seen in Figure 2, the percolation threshold was 2.98% (v/v), which is an improvement of over 10 times than stated in literature [32].

TGA curves shown in Figure 3 illustrate thermal behavior (stability) of both polymer matrix and PMMA composite filled with electrochemically prepared copper powder on the percolation threshold. A characteristic peak that can be observed corresponds to degradation of the matrix (an event that occurs at 279-382 °C). Presented results, on the other hand, showed slight improvement in the thermal characteristics of the composites due to the presence of copper powder, which is extremely good thermal conductor, so that the amount of heat emitted during the TGA

measurements was originally accumulated in the copper powder particles, and only after this accumulation there is a change in PMMA itself.

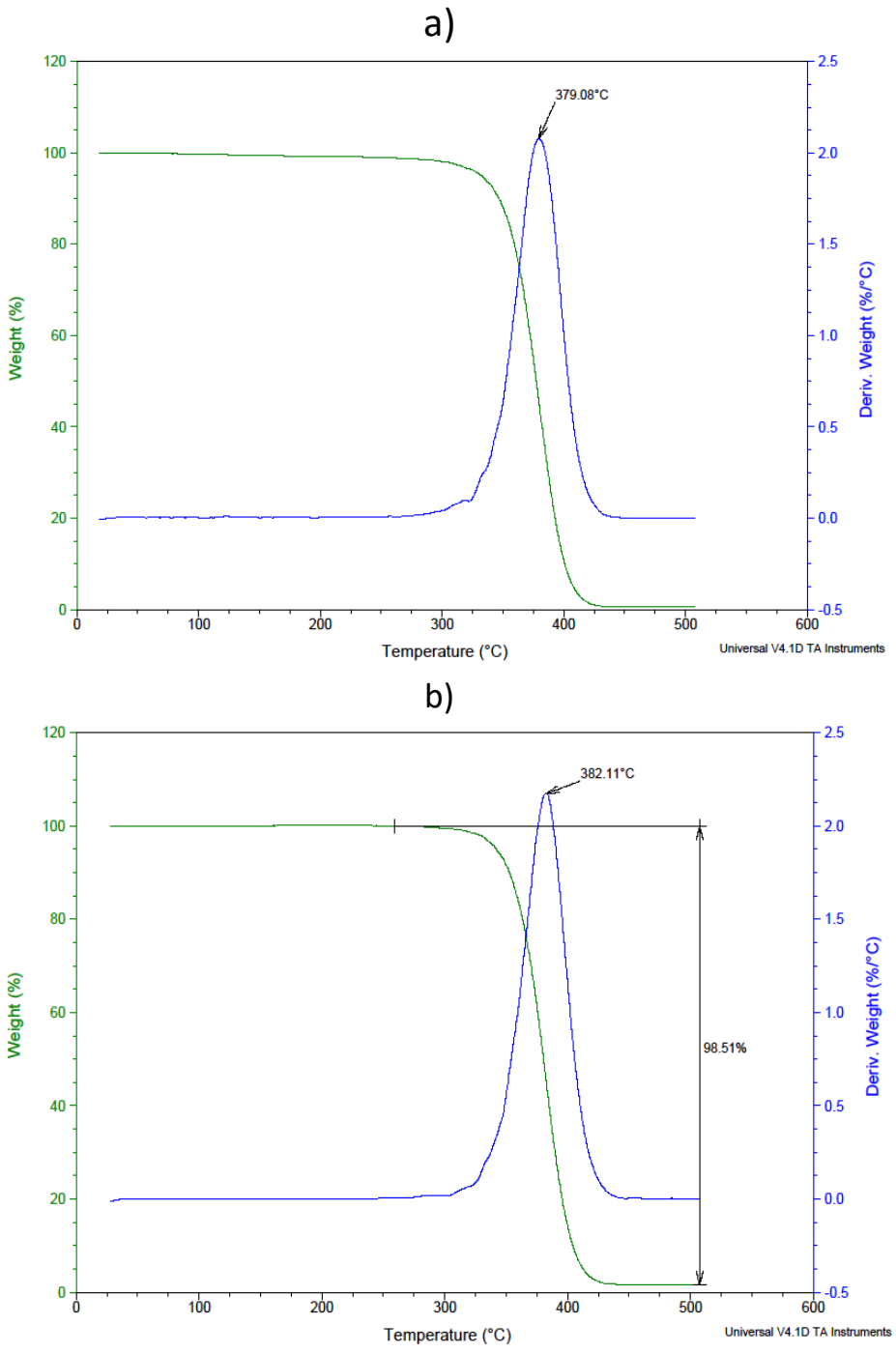

Figure 3. *The results of thermogravimetric analysis of PMMA matrix and PMMA composite filled with copper powder having particle size ≤45μm. a) PMMA matrix, b) PMMA and Cu*

DSC curves of the PMMA matrix, as well as PMMA composite filled with copper powder on the percolation threshold for particle size ≤45μm are shown in Figure 4. The smaller peak that occurs at 201 °C corresponds to the temperature of the beginning of melting for both the matrix and composite.

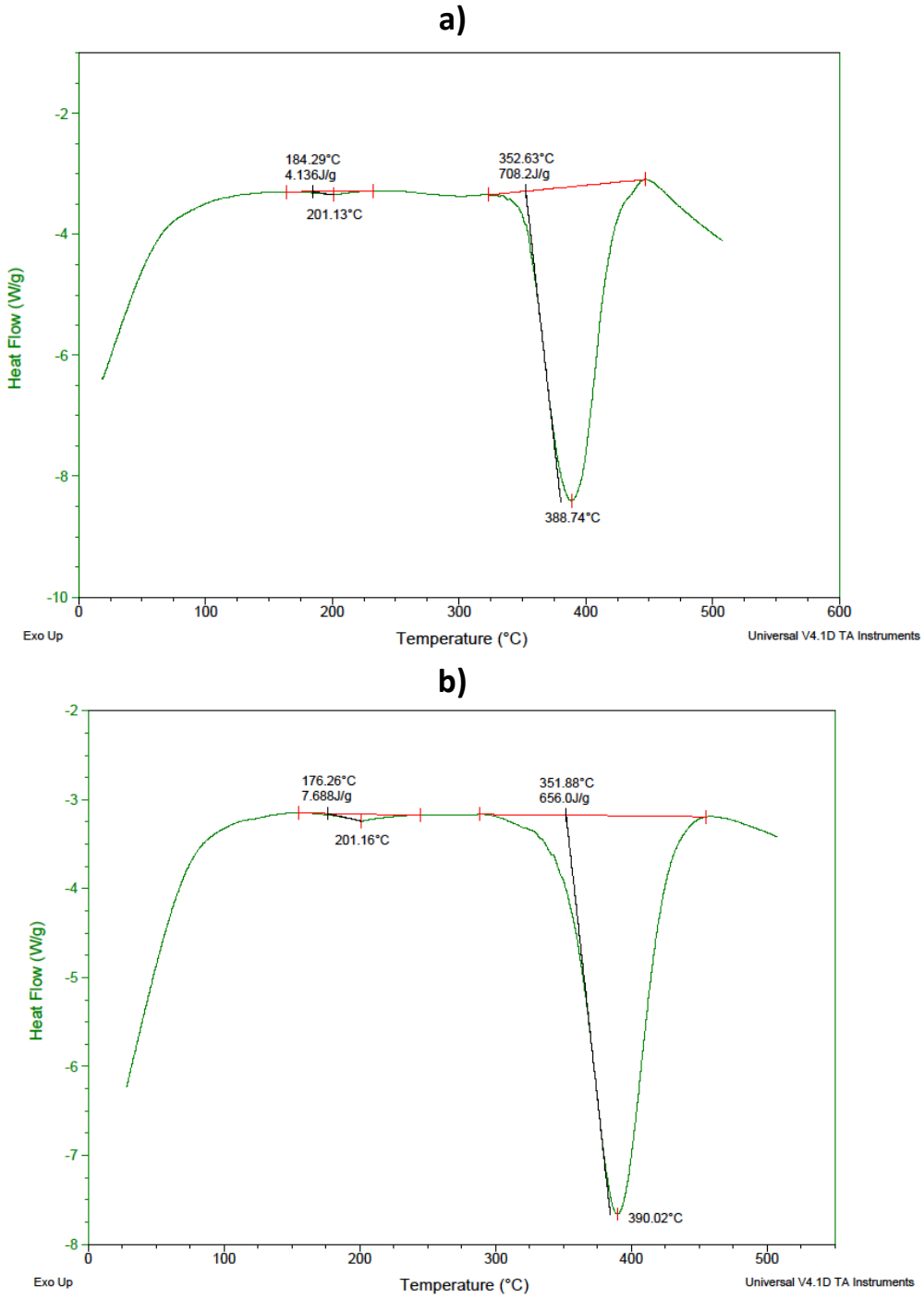

Figure 4. *The results of DSC analysis of PMMA matrix and PMMA composite filled with copper powder having particle size ≤45μm. a) PMMA matrix, b) PMMA and Cu*

Conclusions

This article has shown the experimental study of deposited copper powder particles morphology effects on the electrical conductivity of the PMMA matrix composites filled with powder of this metal. The results showed that the morphology of the powder with a large specific surface area and a distinct dendritic features play an important role in the electrical conductivity of the prepared samples. Conductivity measurements have shown typical S shape dependence, with the percolation transition from non-conductive to conductive region. The effect of packaging and pronounced interpartical contact with smaller, highly porous, highly dendritic particles with a large specific

surface area values has led to a "shift" of percolation threshold towards lower filler volume fraction values. For given range of filler volume fractions the increase in composites electrical conductivity was as much as 16 orders of magnitude.

The results of thermal analysis of prepared composites have shown slight improvement in thermal characteristics of the composites due to presence of metal filler, which is outstanding thermal conductor. The amount of heat emitted during the TGA measurements originally accumulates in filler particles, and only afterwards there is a change in PMMA matrix.

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