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ČETVRTI MEĐUNARODNI SIMPOZIJUM O KOROZIJI I ZAŠTITI MATERIJALA, ŽIVOTNOJ SREDINI I ZAŠTITI OD POŽARA

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Electrical Conductivity of Poly(D,L-Lactide-co-Glycolide) Composites Filled With Galvanostatically Produced Copper Powder

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Abstract

The results of experimental studies of the properties of composite materials based on poly(D,L-lactide-co-glycolide) (PLG) matrix filled with electrolytic copper powder, having very high dendritic structure, are presented in this manuscript. Copper powder volume fractions used as filler in all prepared composites were varied in the range of 0.5-6.0 vol. %. The samples were prepared by hot moulding injection at 170°C. Influence of particle morphology on the conductivity and percolation threshold of the composites were examined and characterization included: Electrical conductivity measurements using AC Impedance Spectroscopy (IS), Scanning Electron Microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDS). Presence of three dimensional conductive pathways was confirmed. The obtained percolation threshold of 2.97 vol. % for PLG composites was measured, which is about three times lower than the one stated in the literature for similar composites. This property is ascribed to different morphology of filler used in investigation.

Keywords: *electrical conductivity, composite materials, PLG, electrolytic copper powder*

Introduction

The production rate of plastic waste is growing annually. Although plastic material can be recycled, only a small number of plastic materials can actually be completely recycled [1]. Therefore, biodegradable bioplastics become important and replaces some of the conventional plastic products in the short life cycle. Biodegradable plastic materials have significantly increased the interest of researchers and industry due to environmental problems including the accumulation of plastic waste. Therefore, biodegradable alternatives are highly desirable. Poly(D,L-lactide-co-glycolide) (PLG) is a biodegradable bioplastic, which is very suitable for the application of a short life cycle, such as a packing container, a food container and cutlery.[2] The copolymer poly(D,L-lactide-co-glycolide) is one of the most interesting polymers for medical applications. This interest is justified by the fact that it is bioreabsorbable, biocompatible and non-toxic, while its degradation kinetics can be modified by the copolymerization ratio of the monomers. It can be transformed by spinning into filaments for subsequent fabrication of preferred textile structures. These fibres can be produced in various shapes and can be used for implants and other surgical applications. [2].

Biocomposites are made from bioplastics that are environmentally friendly and biodegradable, and they can be filled with different materials. These ecocomposites develop rapidly, mainly due to improvements in process technologies and economic factors [3]. Today, various combinations of fillers and bioplastics have been successfully made in ecocomposites with improved mechanical properties, as well as achieving low cost products [3, 4].

The research effort on electroconductive polymers filled with metal powder has had a good development in the last few decades. The addition of a metal base in a polymer matrix allows the mechanical properties of the polymer to be retained while exploiting the electrical properties of the metal [5]. Conductivity of these polymer composites is largely dependent on the nature of the contact between the filler particles and is critically dependent on the volume fraction of the conductive filler particles. This is well explained by the percolation theory [6-9].

However, percolation threshold, electrical conductivity and electrical behaviour of composite systems with fillers which have highly developed surface area have not been explored in details. Also, systems with biodegradable polymers matrices, such as PLG, have not been studied in the literature. Therefore there is need for more detailed study of real synergetic effects of different fillers dimensionalities suitable for construction of conductive networks in conductive polymer composites with biodegradable matrices. For this reason, the copper powder was galvanostatically produced with distinct dendritic morphology and large surface area.

The need for highly conductive polymer-based materials has been the motivation to develop poly(D,L-lactide-co-glycolide) (PLG) composites filled with electrodeposited copper powder particles which would retain desirable polymer characteristics, including biodegradability, ease of processing, and that would obtain high conductivity at low cost. The strategy consisted in manipulating the morphology of the filler so that high conductivity could be achieved at a low percolation threshold.

This work shows the results of electrical conductivity of PLG composites filled with galvanostatically produced copper powder particles, and the influence of polymer matrix on electrical conductivity of the composites.

Experimental

In the experimental part of the work, poly(D,L-lactide-co-glycolide) (PLG) was used as matrix. Polymer used was commercially available powder supplied by Sigma-Aldrich with average molecular weight of ~100000 g mol^{-1} and having density of 1.15 g cm^{-3}.

Copper powder was produced by the galvanostatic regime of electrolysis under following conditions: current density: j = 3600 A m^{-2}, time of powder growth: τ_r=15 min, electrolyte flow: Q = 1 change of the cell volume h^{-1}, temperature of the electrolyte: t = (50 ± 2)° C, concentration of copper: $c(Cu^{+2})$ = 15 g dm^{-3} and concentration of sulfuric acid: $c(H_2SO_4)$ = 140 g dm^{-3}.

The produced powder was washed, protected from oxidation, and the stabilization with aqueous solution of a sodium soap SAP G-30 (Henkel Merima) and drying processes were performed. The produced copper powder was sieved through mesh with openings of 45 μm.

Polymer composites filled with galvanostatically produced copper powder were prepared with the filler volume fraction ranging from 0.5 vol. % – 6.0 vol. %. Pure PLG and copper samples were prepared as reference materials. PLG was preheated and melted at t = 170 °C for 30 min. Previously measured amount of copper powder was added afterwards and mixed until the mixture was fully homogenized. Samples were produced from this homogenized mixture in the molder, Atlas Polymer Evaluation Products LMM Model H30, having size 3.9×10.3×13.3 mm. After preparation of PLG composites, samples were cooled at the room temperature for about 30 min. In order to obtain flat surface for conductivity measurements, samples were polished with sandpaper.

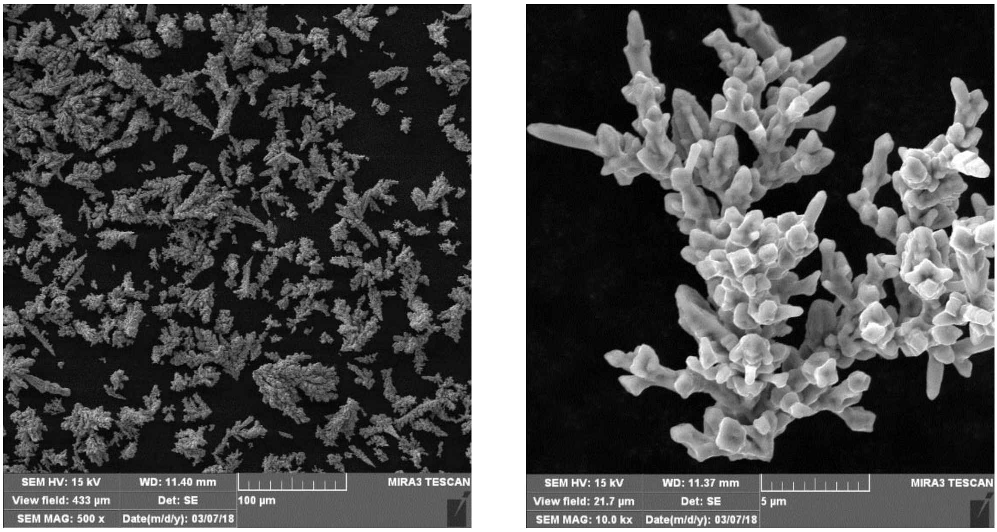
Electrical conductivity was measured by AC impedance spectroscopy (IS). Experiments were performed in potentiostatic mode on all prepared composites. Instrumentation involved Bio-Logic® SAS Instrument, model SP-200, guided by EC-Lab® software. Experimental IS data were fitted by ZView® software.

Sample thickness (necessary for the calculation of conductivity) was determined using micrometre, to an accuracy of 0.01 mm. Several thickness measurements were taken per sample and then averaged.

Scanning Electron Microscopy (SEM) analysis of PLG composites and constituents was performed on Tescan Mira 3 XMU FEG-SEM. Energy-dispersive X-ray spectroscopy (EDS) of the compacts was performed on a Jeol JSM 5800 SEM with a SiLi X-Ray detector (Oxford Link Isis series 300, UK).

Results and discussion

Figure 1 shows morphology of galvanostatically produced copper powder particles, from which can be noticed very dendritic 3D (three-dimensional) structure of the obtained powder.



a) b)

Figure 1. SEM microphotographs of Cu powder particles obtained by the galvanostatic regime of electrolysis and sieved through mesh < 45 μm: a) general view and b) single particle view.

It can be seen from image scales on Figure 1 that typical copper powder particle is < 45 μm in size. The high dendritic character of the obtained particles is a good prerequisite for the formation of a larger number of interparticle contacts between the conductive powder particles and lowering of percolation threshold. Also, this very branchy structure of the particles enables formation of multiple contacts with neighbouring particles at lower filler volume fractions.

The electrical conductivity of the PLG composites as a function of filler content for all prepared samples was measured as stated in Experimental part. The conductivity of PLG composites, showing typical S-shaped dependency with three distinct regions: dielectric, transition and conductive, as expected, is shown on Figure 2.

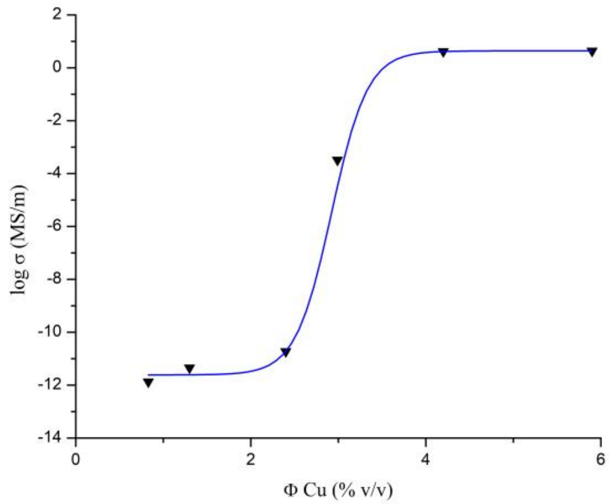


Figure 2. Change in electrical conductivity as a function of filler volume fraction for PLG composites

Percolation threshold value was obtained from the maximum of conductivity derivative as a function of volume fraction of filler. As it can be seen from Figure 2, as well as from calculated value, the percolation threshold was at 2.97 vol. %. This low value that occur is most likely due to filler shape, *i.e.* powder particles, which were very dendritic with high-developed free surface area, and hence less filler was needed to form conductive network throughout the composite volume. Namely, more regular, rounded shapes of copper powder filler, obtain higher values of percolation threshold. Experiments have shown that the morphology of the particles plays a crucial role for the percolation threshold appearance. This value of percolation threshold is about three times lower than the one stated in literature, but for composites of the same filler and different (PMMA) matrix [5]. Authors use this data as comparison since the system is the closest to ones presented in this manuscript, and it is the first time that PLG composites are used as matrix.

For investigation of electrical conductivity, as well as for morphology examination of PLG composites, cross sections of the sample at percolation threshold perpendicular to the surface at which the electrical conductivity was measured, was made. This cross section was 3.9 × 13.3 mm in size, and it was polished before further investigation. Figure 3 shows SEM image of the cross section of PLG composite filled with copper powder at percolation threshold. Two different phases can be seen on Figure 3. However, mechanism of the electrical conductivity, as well as interparticle contacts could not be clearly concluded from the Figure 3. For this reason EDS measurements were performed on same cross section of the composites. This result is shown in Figure 4.

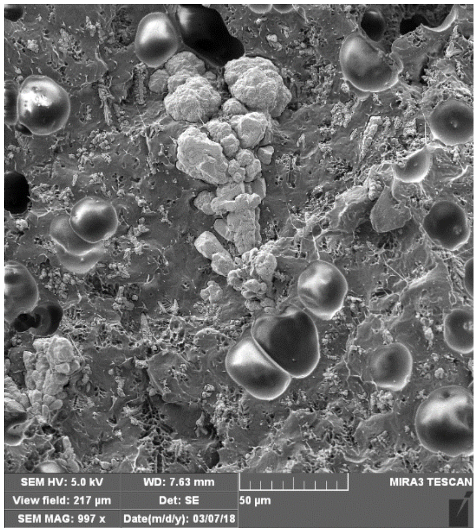


Figure 3. SEM image of cross section of PLG composite filled with galvanostatically produced copper powder at percolation threshold. Cu powder particle size <45 μm.

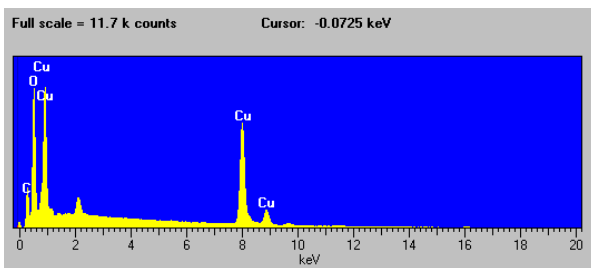


Figure 4. EDS spectrums of cross section of PLG-Cu composite surface with analyses of different phases.

Full surface EDS analysis was performed on the samples cross section. Results of surface area EDS analysis show presence of all major components of the composites on the cross section surface, where Cu powder forms interpartical connections throughout the surface in PLG composite. From the measurements of electric conductivity, and knowing that presented sample is conductive and that it is at percolation threshold, it can be concluded that conductive pathways are formed throughout the surface of the composite. Clearly, composites conduct electricity through conductive pathways that are formed in 3D in pure random order.

Conclusions

In this article, experimental study about the effects of electrodeposited copper powder content on the electrical conductivity of PLG composites filled with that powder has been described. Results have shown that the powder has very high surface area and it has pronounced dendrite branching with well-developed primary and secondary dendrite arms. The conductivity measurements showed S-shaped dependency with percolation transition from non-conductive to conductive region, typical for such polymer composite materials. The results showed that the shape and morphology of the copper powder, and filler at all, play a significant role in the phenomenon of electrical conductivity of the prepared samples and the appearance percolation threshold. Conductivity measurements have shown that percolation threshold is at 2.97 vol. % Cu. The results showed that conductivity of PLG composites are much improved comparing to similar composites filled with more regular structure fillers that can be find in the literature. Morphology of the samples showed presence of conductive pathways throughout the sample, which was proven by EDS measurements. Clearly, it was shown that composites conduct electricity throughout conductive pathways that are formed in 3D in pure random order.

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References

1. Wu CS. Renewable resource-based composites of recycled natural fibers and maleated polylactide bioplastic: characterization and biodegradability. *Polym Degrad Stab.* 2009; 94: 1076-1084.
2. Carvalho Erbetta CA, Alves RJ, Resende JM, Souza Freitas RF, Sousa RG. Synthesis and Characterization of Poly(D,L-Lactide-co-Glycolide) Copolymer. *J Biomat Nanobiotechn*. 2012; 3: 208-225.
3. Sarki J, Hassan SB, Aigbodion VS, Oghenevweta JE. Potential of using coconut shell particle fllers in eco-composite materials. *J Ally Compd.* 2011; 509: 2381-2385.
4. Zhao Q, Tao J, Yam RCM, Mok ACK, Li RKY, Song C. Biodegradation behavior of polycaprolactone/rice husk ecocomposites in simulated soil medium. *Polym Degrad Stab.* 2008; 93: 1571-1576.
5. Poblete VH, Alvarez MP, Fuenzalida VM. Conductive copper-PMMA nanocomposites: Microstructure, electrical behavior, and percolation

threshold as a function of metal filler concentration. *Polym Compos*. 2009; 30: 328-333.
6. Mamunya EP, Davidenko VV, Lebedev EV. Effect of polymer-filler interface interactions on percolation conductivity of thermoplastics filled with carbon black, *Compos Interfaces*. 1997; 4: 169-176.
7. Mamunya EP, Davydenko VV, Pissis P, Lebedev EV. Electrical and thermal conductivity of polymers filled with metal powders. *Euro Polym J*. 2002; 38: 1887-1897.
8. Pavlović MM, Pavlović MG, Ćosović V, Bojanić V, Nikolić ND, Aleksić R. Influence of electrolytic copper powder particle morphology on electrical conductivity of lignocellulose composites and formation of conductive pathways. *Int J Electrochem Sci*. 2014; 9: 8355-8366.
9. Janković Z, Pavlović MM, Pantović Pavlović MR, Pavlović MG, Nikolić ND, Stevanović JS, Pršić S. Electrical and thermal properties of poly(methylmetacrylate) composites filled with electrolytic copper powder. *Int J Electrochem Sci*. 2018; 13: 45-57.