JUBILEE

Synthesis : : Materials : : Corrosion : : Environment : : Energy

XXYuCorr

Analyse : : Discover : : Coat : : Green : : Protect : : Save : : Sustain

MEĐUNARODNA KONFERENCIJA

INTERNATIONAL CONFERENCE

STECIŠTE NAUKE I PRAKSE U OBLASTIMA KOROZIJE, ZAŠTITE MATERIJALA I ŽIVOTNE SREDINE

MEETING POINT OF THE SCIENCE AND PRACTICE IN THE FIELDS OF CORROSION, MATERIALS AND ENVIRONMENTAL PROTECTION

PROCEEDINGS

KNJIGA RADOVA

Pod pokroviteljstvom

Under the auspicies of the

MINISTARSTVO PROSVETE, NAUKE I TEHNOLOŠKOG RAZVOJA REPUBLIKE SRBIJE

MINISTRY OF EDUCATION, SCIENCE AND TECHNOLOGICAL DEVELOPMENT OF THE REPUBLIC OF SERBIA

May 21-24, 2018 : : Tara Mountain, Serbia

CIP - Каталогизација у публикацији - Народна библиотека Србије, Београд

620.193/.197(082)(0.034.2)
621.793/.795(082)(0.034.2)
667.6(082)(0.034.2)
502/504(082)(0.034.2)
66.017/.018(082)(0.034.2)

МЕЂУНАРОДНА конференција ЈУКОР (20 ; 2018 ; Тара)
Stecište nauke i prakse u oblastima korozije, zaštite materijala i životne sredine [Elektronski izvor] : knjiga radova = Meeting Point of the Science and Practice in the Fields of Corrosion, Materials and Environmental Protection : proceedings / XX YuCorr [Jugoslovenska korozija] Međunarodna konferencija = XX YuCorr International Conference, May 21-24, 2018, Tara Mountain, Serbia ; [organizatori Udruženje inženjera Srbije za koroziju i zaštitu materijala ... [et al.] = [organized by] Serbian Society of Corrosion and Materials Protection ... [et al.] ; urednici, editors Miomir Pavlović, Miroslav Pavlović]. - Beograd : Udruženje inženjera Srbije za koroziju i zaštitu materijala UISKOZAM, 2018 (Beograd : Udruženje inženjera Srbije). - 1 elektronski optički disk (CD-ROM) ; 12 cm

Sistemski zahtevi: Nisu navedeni. - Nasl. sa naslovne strane dokumenta. - Tiraž 200. - Bibliografija uz većinu radova. - Abstracts. - Registar.

ISBN 978-86-82343-26-4
1. Удружење инжењера Србије за корозију и заштиту материјала (Београд)
a) Премази, антикорозиони - Зборници b) Превлаке, антикорозионе - Зборници c) Антикорозиона заштита - Зборници d) Животна средина - Заштита - Зборници e) Наука о материјалима - Зборници
COBISS.SR-ID 263766284

XX YUCORR – Međunarodna konferencija | *International Conference*

IZDAVAČ |PUBLISHED BY
UDRUŽENJE INŽENJERA SRBIJE ZA KORZIJU I ZAŠTITU MATERIJALA (UISKOZAM),
SERBIAN SOCIETY OF CORROSION AND MATERIALS PROTECTION (UISKOZAM)
Kneza Miloša 7a/II, 11000 Beograd, Srebija, tel/fax: +381 11 3230 028, office@sitzam.org.rs; www.sitzam.org.rs

ZA IZDAVAČA | FOR PUBLISHER: *Prof. dr MIOMIR PAVLOVIĆ, predsednik UISKOZAM*

UREDNICI | *EDITORS:* *Prof. dr Miomir Pavlović, Dr Miroslav Pavlović*

OBLAST | *SCIENTIFIC AREA:* KOROZIJA I ZAŠTITA MATERIJALA / *CORROSION AND MATERIALS PROTECTION*

KOMPJUTERSKA OBRADA I SLOG | *PAGE LAYOUT:* *Dr Miroslav Pavlović*

TIRAŽ | *CIRCULATION:* *200 primeraka* **/** *copies*

ISBN 978-86-82343-26-4

Influence of biodegradable matrix on electrical conductivity of copper filled composites

Zoran Janković[1], Miroslav M. Pavlović[2], Anto Gajić[3], Marijana R. Pantović Pavlović[2], Nebojša D. Nikolić[2], Jasmina S. Stevanović[2], Miomir G. Pavlović[2]

[1]*V&Z Zaštita, d.o.o., Banja Luka, Republic of Srpska, Bosnia and Herzegovina*

[2]*University of Belgrade, ICTM-Department of Electrochemistry, Belgrade, Serbia*

[3]*Rudnik i termoelektrana Ugljevik, Republic of Srpska, Bosnia and Herzegovina*

Abstract

The results of experimental studies of the properties of composite materials based on Poly (lactic acid) (PLA) and Poly (3-hydroxybutyrate) (PHB) matrices 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 %(v/v). The samples were prepared by hot molding injection at 170°C. Influence of particle size and morphology, as well as influence of matrix type on the conductivity and percolation threshold of the composites were examined and characterization included: Electrical conductivity measurements using Impedance Spectroscopy (IS), Scanning Electron Microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDS) and Fourier-transform Infrared Spectroscopy (FTIR). Presence of three dimensional conductive pathways was confirmed. The obtained percolation threshold of 2.83 %(v/v) for PLA and 3.13 %(v/v) for PHB 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, PLA, PHB, electrolytic copper powder*

Introduction

During the past century, many synthetic polymers made from non-renewable fossil fuels such as polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polyethylene terephthalate (PET), polyamide (PA) and polystyrene (PS) have been used due to their extraordinary properties. These properties include high availability at relatively low cost, good mechanical performance, such as tensile and impact strength, good barrier properties, etc. [1]. However, the production of these synthetic polymers must be limited as it leads to the depletion of oil resources. 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 [2]. 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 (lactic acid) (PLA) 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 [3]. It can be transformed by spinning into filaments for subsequent fabrication of preferred textile structures. The medical application of this polymer arises from its biocompatibility, since the degradation product of PLA, which is lactic acid, is metabolically harmless. These fibres can be produced in various shapes and can be used for implants and other surgical applications. Tissue

engineering is the newest domain in which poly (lactic acid) is used and is one of the most favourable matrix materials. [4]

The production of PLA has numerous advantages including: production of the lactide monomer from lactic acid, significant energy savings, the ability to recycle back to lactic acid by hydrolysis or alcoholysis; the capability of producing packaging that is compostable, improvement of the agricultural economy and the ability to tailor physical properties through material modifications [5]. There were many PLA applications, but they were not widely used due to the relatively high price, high stiffness and poor properties of moisture barriers [6-9].

On the other hand, poly (3-hydroxybutyrate) (PHB) is fully biodegradable and biocompatible polyester synthesized by bacterial fermentation from renewable sources such as sugar cane, which recently attracted much attention as an alternative to oil-based polymer materials [10]. PHB is an isotactic linear thermoplastic made of 3-hydroxy butyric acid. This biopolymer has already been used in smaller disposable products and packaging materials [11]. However, it possesses several imperfections for commercial use, such as high crystallinity, resulting in inherent brittleness and poor impact resistance, relatively high water vapour permeability, and low resistance to thermal degradation. These properties impact PHB in a way that it can be easily decomposed, and relatively high melting point (about 175 ° C) results in a narrow processing window. In order to expand a number of practical applications, new approaches for practical use of PHB included mixing with other polymers [11, 12] or filling with nano-fillers such as coffee waste [13], multilayer carbon nanotubes [14], hydroxyapatite (HA) [15, 16], lignocellulose [17], pulp fibres [18] or layered silicates [19]. Improved mechanical performance and higher thermal and barrier properties were obtained by adding small amounts of nanoparticles into this biopolymer matrix, although improvements are still insufficient for industrial applications.

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 [20]. Today, various combinations of fillers and bioplastics have been successfully made in ecocomposites with improved mechanical properties, as well as achieving low cost products [20, 21].

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 [22]. 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 [23-26].

Data on a numerous existing capabilities of polymers that contain dispersed conductive fillers and various methods for the production of such materials are published in the literature in the last few years. Metal filled polymer composites have found the use in electromagnetic protective shielding and electronic devices, as adhesives, in electronic packaging, switches and overvoltage protection devices [22, 27, 28]. They also found numerous applications as self-regulating heaters, chemical and electrochemical catalysts and adsorbents [29, 30]. These polymer based polymer based composites have some advantages over pure metals, including incredibly low price, ease of production, high flexibility, reduced weight, corrosion resistance and conductivity control [22].

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 PLA and PHB, 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 (lactic acid) (PLA) and poly (3-hydroxybutyrate) (PHB) 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 PLA and PHB 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 (lactic acid) (PLA) and poly (3-hydroxybutyrate) (PHB) were used as matrices. Both polymers were used as commercially available powders supplied by Sigma-Aldrich. PLA had average molecular weight of Mw ~10000, with a density of 1.25 g/cm^3, and the electrical conductivity of about 10^{-12} S/cm. PHB had average molecular weight of Mw ~100000, with a density of 1.25 g/cm^3, and the electrical conductivity of about 10^{-12} S/cm.

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, 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. In the process of electrolysis, the both cathode and anode were of copper. All electrolytes were prepared from p.a. chemicals obtained from Merck and demineralized water.

At the end of the precipitation, the powder was removed from the electrode by shaking it. The powder was then washed, protected from oxidation, and the stabilization and drying processes were performed.

Because the acid promotes a rapid oxidation of powder during drying process, the produced copper powder was washed with distilled water at the room temperature until the powder was left without traces of acid. After this phase, the copper powder was washed with aqueous solution of a sodium soap SAP G-30 (Henkel Merima) with the aim to protect the powder from succeeding oxidation [34, 35]. After drying in a tunnel furnace at 110 – 120 °C in controlled nitrogen atmosphere, 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 % (v/v) – 8.8% (v/v). Pure PLA, PHB and copper samples were prepared as reference materials. Both PLA and PHB 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 PLA and PHB 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.

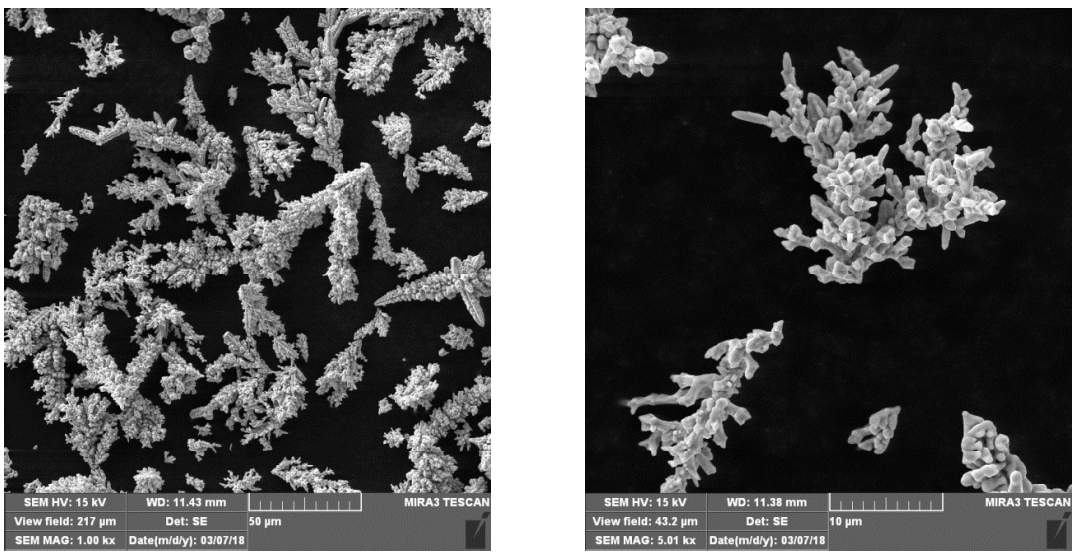
Electrical conductivity was measured by impedance spectroscopy (IS). Experiments were performed in potentiostatic mode on all prepared composites. Instrumentation involved Bio-Logic® SAS Instrument, model SP-200, guided by EC-Lab® software. Samples were put between two metal plates and they responded to the potential input sinusoidal signal of ±10mV (rms) amplitude. Geometry of the instrument contacts used is such that it minimizes edge effects thus it can be assumed that they do not exist. 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 PLA and PHB 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).
Fourier transform infrared spectroscopy (FTIR) was recorded on stabilized copper powder, PLA, PHB and composites. Michelson MB Series Bomen FTIR was used (Hartmann Braun), scanning from 500 to 4000 cm^{-1}

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.



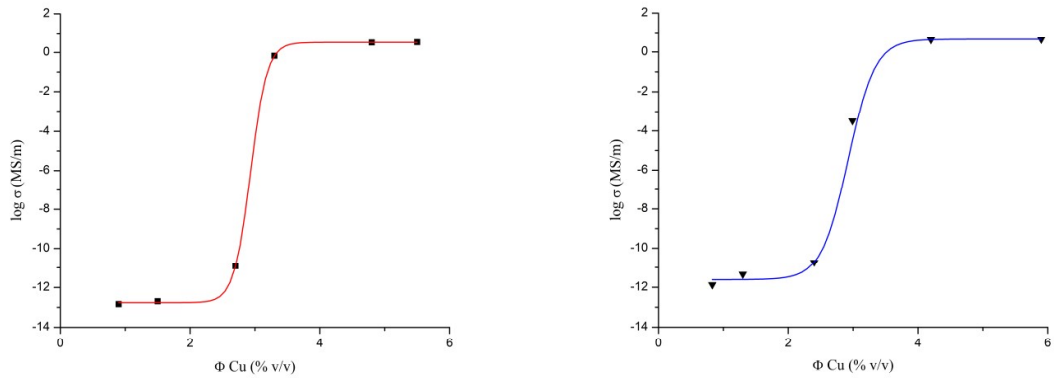
a) *b)*

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 PMMA composites as a function of filler content for all prepared samples was measured as stated in Experimental part. The electrical conductivity of composites as a function of filler content for all the samples was measured and calculated from impedance characteristics of a composite using Equation (1):

$$\sigma = \frac{1}{\sum_{1}^{7} R_i} \cdot \frac{l}{S} \qquad (1)$$

where σ is electrical conductivity, R_i – resistivity of a layer in equivalent circuit, l – length and S – *cross-section area* of the sample. The conductivity of PMMA composites, showing typical S-shaped dependency with three distinct regions: dielectric, transition and conductive, as expected, is shown on Figure 2.

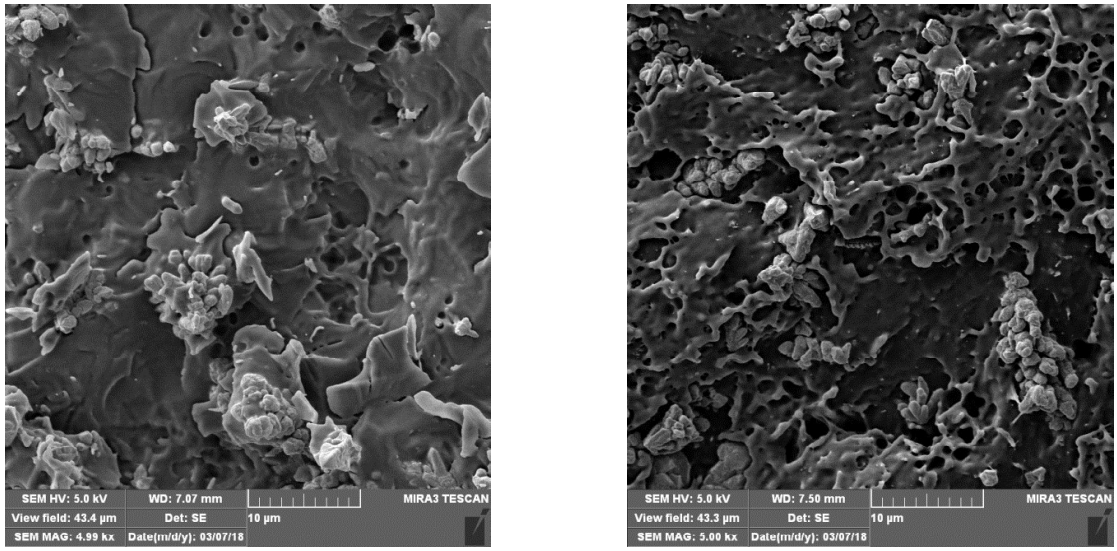


a) *b)*

Figure 2. *Change in electrical conductivity as a function of filler volume fraction for a) PLA composites and b) PHB composites filled with copper powder*

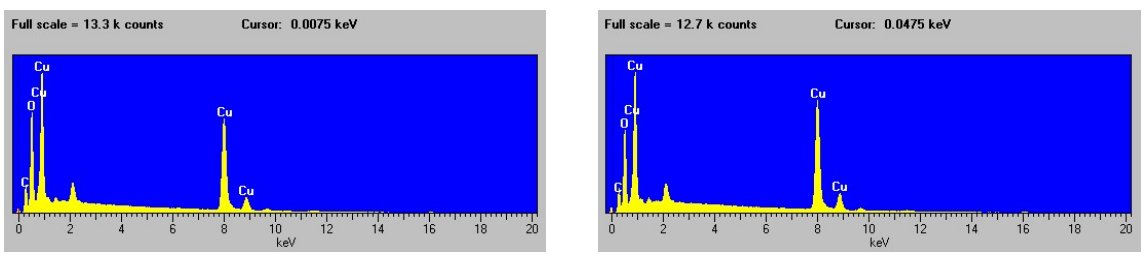
Percolation threshold value was obtained from the maximum of conductivity derivative as a function of volume fraction of filler. As it can be seen from Figure 2, as well as from calculated value, the percolation threshold was at 2.83 % (v/v) for PLA composites and 3.13 % (v/v) for PHB composites. These low values that occur are 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. Besides the filler morphology, polymer matrix type, as well as preparation method influences the percolation threshold, which further moves towards lower values.

For investigation of electrical conductivity, as well as for morphology examination of PLA and PHB composites, cross sections of the samples at percolation threshold perpendicular to the surfaces at which the electrical conductivity was measured, were 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 PLA and PHB composites 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 PMMA-Cu composites. These results are shown in Figure 4.



a) *b)*

Figure 3. *SEM image of cross section of a) PLA composite and b) PHB composite filled with galvanostatically produced copper powder at percolation threshold. Cu powder particle size <45 µm.*



a) *b)*

Figure 4. *EDS spectrums of cross section of a) PLA-Cu composite surface and b) PLA-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 are shown in Table 1.

Table 1. Elemental analysis of cross sections of a) PLA composite and b) PHB composite filled with Cu powder at percolation threshold

Element type	Atomic %
C	47.03
O	45.00
Cu	7.97
Total	100

a)

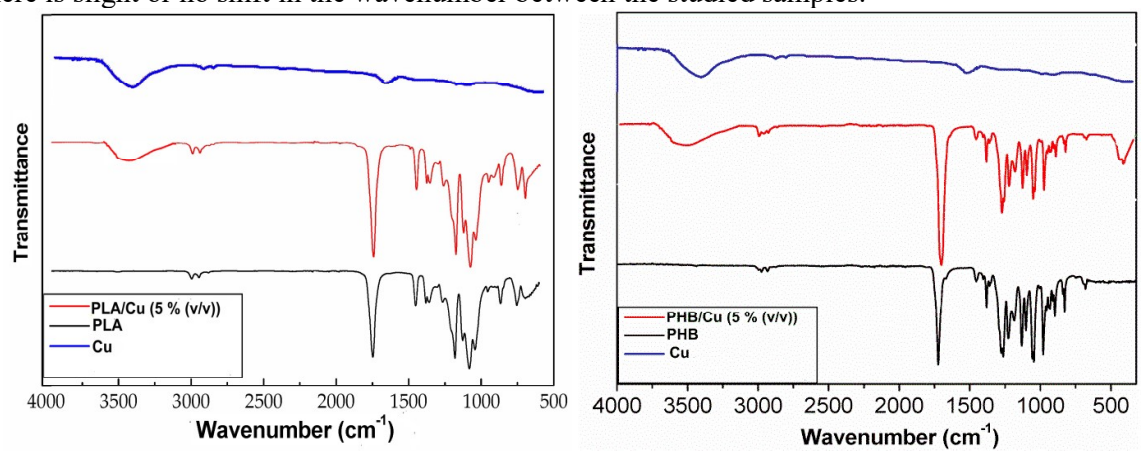
Element type	Atomic %
C	47.16
O	44.56
Cu	8.28
Total	100

b)

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, since the size of copper phase present in the figures (> 200 µm) is much larger than size of copper powder particles (< 45 µm from Figure 1) used for composite

preparation. Clearly, composites conduct electricity through conductive pathways that are formed in 3D in pure random order.

Figure 5 shows results of the FTIR spectra of the experiments performed on stabilized copper powder, PLA, PHB and their composites with 5.0% (v/v) copper powder content. FTIR spectrum of the Cu powder shows three distinct peaks at 3423 cm^{-1} characteristic for O-H alcohol groups, 2921.9 cm^{-1} characteristic for C-H methyl and methylene groups and 1623.2 cm^{-1} characteristic for C=C alkene bonds. This is in good agreement with statement that copper powder was stabilized with sodium soap SAP G-30, which contains 78% of total fatty acids, in order to protect the powder against subsequent oxidation. It can be concluded that there is no chemical reaction occurring between PLA, PHB and copper powder, and that the influence of the O-H, C-H and C=C groups on the spectra is amplified. There is slight or no shift in the wavenumber between the studied samples.



a) *b)*

Figure 5. *FTIR spectra of the a) pure stabilized copper powder, PLA and its composite at 5 % (v/v) Cu content and b) pure stabilized copper powder, PHB and its composite at 5 % (v/v) Cu content.*

Conclusion

In this article, experimental study about the effects of electrodeposited copper powder content on the electrical conductivity of composites of PLA and PHB matrices 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 2.83 % Cu (v/v) for PLA and at 3.13 % Cu (v/v) for PHB composites. The results showed that conductivities of PLA and PHB 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. FTIR measurements have shown that there is no chemical reaction occurring between PLA, PHB and copper powder.

References

1. V. Siracusa, P. Rocculi, S. Romani and M.D. Rosa, *Trends Food Sci. Tech.,* 2008, **19**, 634.
2. C.S. Wu, *Polym. Degrad. Stab.*, 2009, **94**, 1076.
3. K.S. Chun, S. Husseinsyah and H. Osman, *J. Polym. Res.*, 2012, **19**, 1.
4. B. Gupta, N. Revagade and J. Hilborn, *Prog. Polym. Sci.,* 2007, **32**, 455.
5. J.R. Dorgan, H. Lehermeier and M. Mang, *J. Polym. Environ.,* 2000, **8**, 1.
6. L. Yu, K. Dean and L. Li, *Prog. Polym. Sci.*, 2006, **31**, 576.
7. F. Carroso, P. Pages, P.J. Gamez, O.O. Satana and M.L. Maspoch, *Polym. Degrad. Stab.*, 2010, **95**, 116.
8. F. Schwark, C.A.S. Hill, Z. Xiao, H. Militz and C. Mai, *J. Clean. Prod.*, 2009, **17**, 644.
9. K.M. Nampoothiri, N.R. Nair and R.P. John, Bioresour.Technol., 2010, **101**, 8493.
10. T. Keshavarz and I. Roy, *Curr. Opin. Microbiol.,* 2010, **13**, 321.
11. K. Sudesh, H. Abe and Y. Doi, *Prog. Polym. Sci*., 2000, **25**, 1503.
12. C. Vogel, E. Wessel and H.W. Siester, *Biomacromolecules,* 2008, **9**, 523.
13. K. Reis, L. Pereira, I. Melo, J. Marconcini, P. Trugilho and G. Tonoli, *Mat. Res.* 2015, **18(3)**, 546.
14. C. Xu and Z. Qiu, *Polym. Adv. Technol*. 2011, **22**, 538.
15. N. Ramesh, S.C. Moratti and G.J. Dias, *J. Biomed. Mater. Res. B,* 2015, **00B**, 000. doi:10.1002/jbm.b.33950.
16. M. Sadat-Shojai, M.-T. Khorasani, A. Jamshidi and S. Irani, *Mater. Sci. Eng. C,* 2013, **33**, 2776.
17. A. Dufresne, D. Dupeyre and M. Paillet, *J. Appl. Polym. Sci.,* 2003, **87**, 1302.
18. H. Ren, Y. Zhang, H. Zhai and J. Chen, *Cellulose Chem. Technol.,* 2015, **49 (7-8)**, 641.
19. P. Maiti, C.A. Batt and P. Giannelis, *Biomacromolecules,* 2007, **11**, 3393.
20. J. Sarki, S.B. Hassan, V.S. Aigbodion and J.E. Oghenevweta, *J. Ally. Compd.,* 2011, **509**, 2381.
21. Q. Zhao, J. Tao, C.M.R. Yam, C.K.A. Mok, K.Y.R. Li, and C.J. Song, *Polym. Degrad. Stab.,* 2008, **93**, 1571.
22. V.H. Poblete, M.P. Alvarez and V.M. Fuenzalida, *Polym. Compos.*, 2009, **30**, 328.
23. E.P. Mamunya, V.V. Davidenko and E.V. Lebedev, *Compos. Interfaces*, 1997, **4**, 169.
24. E.P. Mamunya, V.V. Davydenko, P. Pissis and E.V. Lebedev, *Euro. Polym. J.*, 2002, **38**, 1887.
25. M.M. Pavlović, M.G. Pavlović, V. Ćosović, V. Bojanić, N.D. Nikolić, R. Aleksić, *Int. J. Electrochem. Sci.,* 2014, **9(12)**, 8355.
26. Z. Janković, M.M. Pavlović, M.R. Pantović Pavlović, M.G. Pavlović, N.D. Nikolić, J.S. Stevanović, S. Pršić, *Int. J. Electrochem. Sci.,* 2018, **13(1)**, 45.
27. L. Xiangcheng and D.D.L. Chung, *Compos. B: Eng.,* 1999, **30**, 227.
28. M.L. Sham and J.K. Kim, *Compos. Part A: Appl. Sci. Manuf.,* 2004, **35**, 537.
29. P. Lafuente, A. Fontecha, J.M. Diaz and A.E. Munoz, *Rev. Plast. Mod.,* 1993, **447**, 257.
30. B.C. Munoz, G. Steinthal and S. Sunshine, *Sens. Rev.,* 1999, **19**, 300.