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CONDUCITVITY OF COPPER FILLED COMPOSITES WITH DIFFERENT POLYMER MATRICES

PROVODNOST KOMPOZITA SA RAZLIČITIM MATRICAMA PUNJENIH BAKROM

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IZVOD

U ovom radu su prikazani eksperimentalni rezultati ispitivanja kompozitnih materijala na bazi lignoceluloznih (LC) I polimetilmetakrilatnih (PMMA) matrica punjenih bakarnim prahom. Zapreminski udeli metalnog punioca su varirani u opsegu od 0.5-29.8% (v/v), a uzorci su pripremljeni hladnim presovanjm I izlivanjem u kalup. Karakterizacija je uključivala ispitivanje uticaja veličine čestica I morfologije na provodnost I perkolacioni prag kompozita koristeći različite tehnike ispitivanja: SEM, TGA, AFM. Termalna analiza pripremljenih kompozita je pokazala poboljšanje termičkih svojstava kompozita u odnosu na čiste polimere. Ovo poboljšanje se javlja usled prisustva metalnog punioca, koji je jako dobar termički provodnik, te se toplota emitovana tokom TGA merenja prvenstveno akumulira u puniocu, pa tek onda u polimernoj matrici, bila ona LC ili PMMA. Prisustvo trodimenzionalnih provodnih puteva je takođe potvrđeno.

ABSTRACT

In this manuscript the results of experimental studies of the properties of composite materials based on lignocellulosic (LC) and poly(methylmetacrylate) matrces filled with electrolytic copper powder are presented. Volume fractions of metal fillers in composite materials and tested samples were varied in the range of 0.5-29.8% (v/v), and the samples were prepared by compression and molding. Characterization included examination of the influence of particle size and morphology on the conductivity and percolation threshold of the composites using a variety of testing techniques: SEM, TGA, AFM. Thermal analysis of the prepared composites showed the improvement of the thermal characteristics of the composites. This was due to the presence of the metallic fillers, which are very good thermal conductors, hence accumulating the heat

emitted during TGA measurements primary to matrix, whether it was lignocellulosic or PMMA. Presence of three dimensional conductive pathways was confirmed.

INTRODUCTION

In recent years, scientists and engineers have focused on reducing carbon dioxide emissions of all existing products, either by mixing bio-plastics and synthetic plastics and/or reinforcing it with synthetic fibers and fillers [1].

All biocomposites obtained from natural fibers and biodegradable plastics derived from natural origin (biopolymers and bioplastics) are highly environmentally friendly [2]. These environmentally friendly green composites have the potential to become new materials XXI century and can be a partial solution to many global problems. Consequently, renewable polymer materials provide an answer to the question of sustainable development of economically and environmentally attractive and acceptable technology [2].

Lignocellulose is a term used to describe the three-dimensional polymer composite formed by plants as their structural material. It consists of a variable amount of cellulose, hemicellulose and lignin [1,2]. Lignocellulosic raw materials are mainly composed of carbohydrate polymers (cellulose and hemicellulose) and phenolic polymers (lignin). Minor concentrations of various other compounds, such as proteins, acids, salts and various minerals are also present.

Research in the field of electro-conducting polymer composites filled with metal powders have experienced great development in the last two decades. Adding metal filler polymer matrix allows the preservation of the mechanical properties of polymers while, at the same time, exploiting the electric conductive properties of metal [3]. The conductivity of composites with conductive fillers depends on the nature of contacts between the conductive filler particles and filler volume fraction, which is well explained by the percolation theory [3-5].

Composites with metal fillers have found application as self-regulating heaters, photothermal optical recorders, chemical sensors and electronic noses, chemical and electrochemical catalysts and adsorbents [3-5].

EXPERIMENTAL

In the experimental part of the work, lignocellulose and poly(methylmethacrylate) (PMMA) were used as matrices. Lignocellulose was produced in *Maize Research Institute "Zemun Polje"* was used for synthesis of tested composites [6]. Celgran® C fraction was used, which was milled in a ball mill, and then dry sieved through mesh with openings of 45 μm. PMMA used 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.

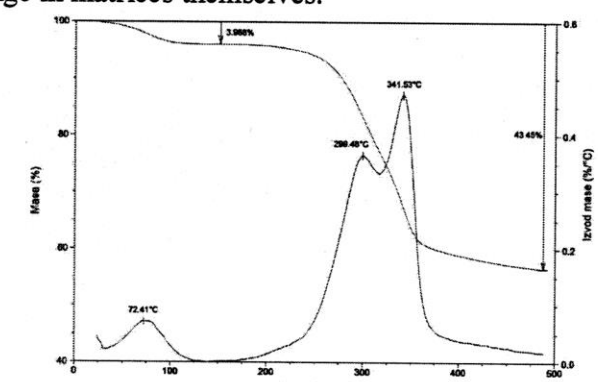
The electrolytic copper powder used in this study was galvanostatically produced as described in [5].

Polymer composites of lignocellulose and PMMA filled with copper powder were prepared with the filler volume fraction from 0.5% (v/v) - 29.8% (v/v). All the samples were produced from thoroughly homogenized mixtures of powders. SEM, EDS, TGA and AFM analysis of lignocellulose and PMMA composites were examined in more detail.

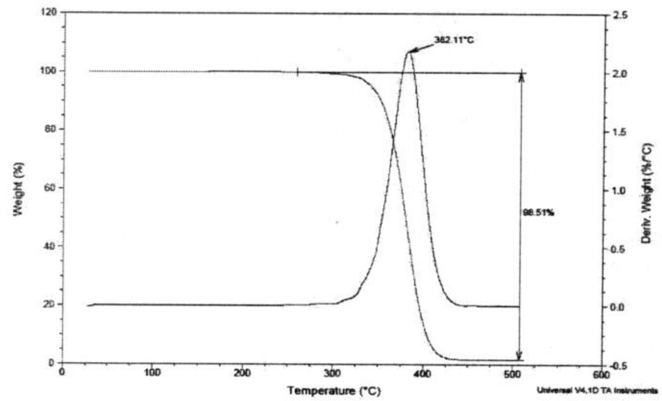
RESULTS AND DISCUSSION

The conductivity of the conductive polymer composites is highly dependent on the nature of contacts between the conductive filler elements. In order to achieve better electrical fillers with highly developed free surfaces were 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 [5, 7].

TGA curves shown in Figure 1 illustrate the thermal behavior (stability) of lignocellulose and PMMA composites filled with electrochemically deposited copper powder at percolation threshold. Characteristic temperatures of the observed thermal events in Figure 1 confirm presence of the main constituents (cellulose, hemicellulose, PMMA and lignin) [7]. All presented results showed 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 matrices themselves.



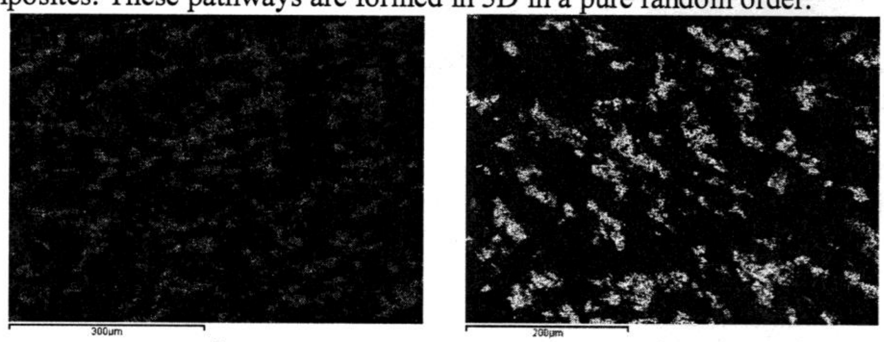
a)



b)

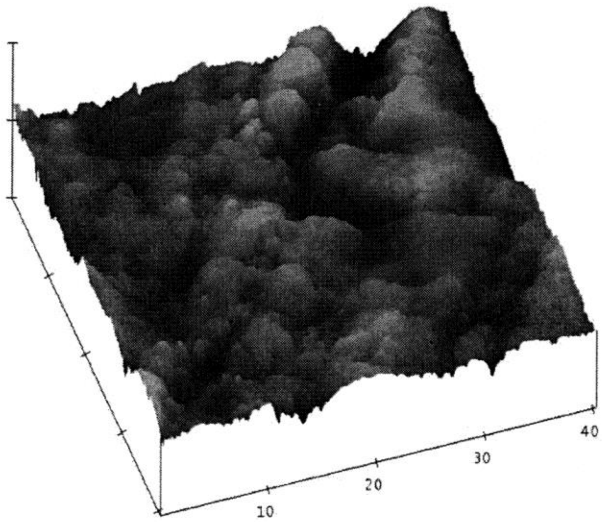
Figure 1. The results of thermogravimetric analysis of composites a) lignocellulose matrix filled with copper powder, treatment pressure of 20 MPa; b) PMMA matrix filled with copper powder.

EDS measurements (Figure 2) show the existence of copper conductive pathways throughout the composites volumes. Due to the packaging effect and more pronounced interparticle contact with smaller, highly porous, highly dendritic particles with high values of specific area lead to "movement" of percolation threshold towards lower filler content. This feature can be observed on both on Figure 2 and Figure 3. Figure 3 presents AFM image of the lignocellulose and PMMA composite surfaces after breaking. Conductive pathways were confirmed by EDS measurements, and the conductivity of the composite is obtained through conductive pathways of the filler that form in the composites. These pathways are formed in 3D in a pure random order.



a) b)

Figure 2. EDS images of the LC (a) and PMMA composites (b) prepared at percolation threshold. White dots represent Cu.



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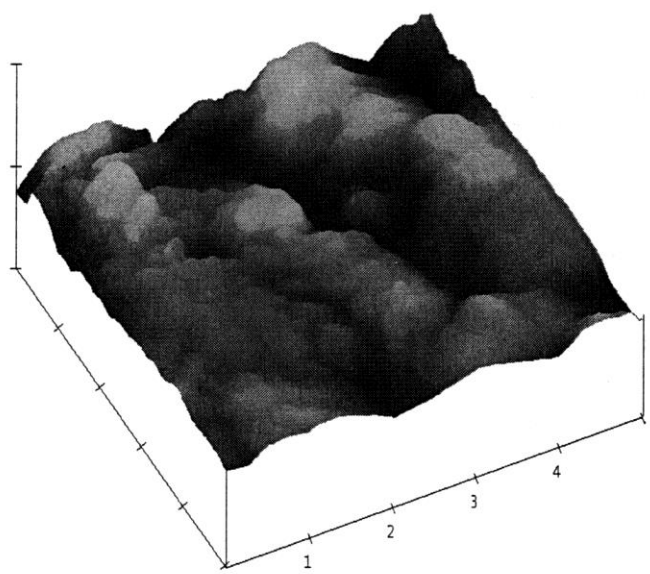

b)

Figure 3. 3D AFM images of the PMMA (left) and LC (right) composite filled with copper powder at percolation threshold

Greater roughness that can be seen on Figure 3 is assigned to copper powder, since it has greater hardness and greater free surface area than the matrix, which was confirmed by EDS measurements.

CONCLUSION

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.

Acknowledgements

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