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Ecological Truth

Editors
Radoje V. Pantovic
Zoran S. Marković

EcoIst '16

12 – 15 June 2016
Hotel "BREZA" Vrnjacka Banja,
SERBIA

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BIODEGRADABLE POLYMERS AS MATRICES
FOR ELECTROCONDUCTIVE COMPOSITES

Miroslav M. Pavlovic[*], M. Pantovic, V. Pavelkic,
J. Stevanovic, M. G. Pavlovic

University of Belgrade, ICTM-CEH, Njegoseva 12, Belgrade, SERBIA

[*]*mpavlovic@tmf.bg.ac.rs*

ABSTRACT

In this manuscript the results of experimental studies of the properties of composite materials based on lignocellulosic (LC) and poly(methylmetacrylate) matrices 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 - cold pressing 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.

Key words: thermal analysis, composite materials, lignocellulose, PMMA, AFM, TGA.

INTRODUCTION

Composites are multiphase materials with a clear phase boundaries, in which two or more materials with different chemical composition (ceramics, polymers) and/or forms (granules, fibers, flakes, lamellas) form a single structure with clearly marked borders. Specific properties are achieved by combining the components in the composite (hardness, density, stiffness, thermal and electrical conductivity). Properties of composites depend on the properties of the components themselves, their chemical and constitutional composition. Basic constitutional components of the composite are: matrix and the additive (filler/ reinforcement), the material that achieves needed combination of properties in composite. Composites can be made of ceramic, polymer and metal matrix. In recent years, from the ecological aspect, special place has been occupied by biocomposites and green composites [1]. Green composites are fully made out from renewable natural materials (both matrix and reinforcement). Biocomposites are composites in which at least one segment, the matrix or reinforcement, is made out from renewable material, including wood, agricultural wastes, grasses and natural fibers consisting of carbohydrates (sugars and starches, cellulose and lignin), as well as

vegetable oils and proteins. Biocomposites can be made of: a) natural fibers (plant or animal origin) and biologically non-degradable polymers: thermosets (epoxy resins, phenolic resins) and plastomers (PE, PP, PVC, PS); b) synthetic fibers and biopolymers (incurred from plant processing) and c) from natural fibers and biopolymers, which are the most ecological composites and they are often called green composites. Biocomposites are essential for material world because they have unique properties that do not occur independently in nature. Also, their properties can be tailored in relation to the design of their composition and processing. This feature gives space for use of biocomposites in various sectors, like aviation industry and space exploration, automotive industry, construction, maritime, consumer products and electronic components [2].

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 [3].

All biocomposites obtained from natural fibers and biodegradable plastics derived from natural origin (biopolymers and bioplastics) are highly environmentally [4]. 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 [4].

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 [5]. 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.

Corncob is a very important by-product of the production of corn grain. Every ton of corn grain yields 180-200 kg of corncob. About 1.2-1.5 million tons of corncob is produced every year in Serbia as secondary raw materials. In the world, traditional use of corncob in agriculture, as heating material, material burnt for warming air in grain drying processes or coarse cellulosic food for feedstock, has been significantly expanded to the industry. An attempt has been made to produce acetic acid, methanol, charcoal, xylitol, furfurol etc. out from corncob [6, 7].

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 [8]. 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 [9-11].

In recent years, in literature, numerous information on the possibilities of application of polymers containing dispersed conductive fillers, as well as various methods for producing such materials, can be found [12-19]. The fine metal particles dispersed in polymer matrices have contributed to a number of industrial applications.

Composites with metal fillers have found application as electromagnetic protection of computers and electronic equipment, conductive adhesives for electronic equipment, cold solders, switches, materials for dissipation of static electricity in devices for protection against power surges [8, 20-23]. They also found numerous technological applications as self-regulating heaters, photothermal optical recorders, chemical sensors and electronic noses, chemical and electrochemical catalysts and adsorbents [24]. Electrically conductive polymer composites have several advantages over their constituents, which include lower cost and ease of production, high flexibility, reduced weight, greater ability to absorb mechanical shocks, corrosion resistance and conductivity control [8].

EXPERIMENTAL PART

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 [7]. 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 / cm³, 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 under following conditions: current density, j=3600 A/m², 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/dm³ and concentration of sulfuric acid $C(H_2SO_4)$=140 g/dm³. Wet powder was washed several times with a large amount of demineralized water until the powder was left without traces of acid at room temperature, because the acid promotes rapid oxidation of the powder during drying process. Obtained copper powder was subsequently washed with aqueous solution of sodium soap SAP G-30 to protect the powder from succeeding oxidation, which was prepared and used as explained by Pavlović et al. [25]. After drying in a tunnel furnace at 110 - 120 ° C in controlled nitrogen atmosphere, copper powder was sieved through mesh with openings of 45 μm.

Polymer composites of lignocellulose filled with copper powder were prepared with the filler volume fraction from 2.0% (v/v) - 29.8% (v/v), while PMMA composites filled with same powder were prepared with the filler volume fraction ranging 0.5 % (v/v) - 8.8% (v/v). Pure lignocellulose, PMMA and copper samples were prepared as reference materials. All the samples were produced from thoroughly homogenized mixtures of powders, where lignocellulosic composites were cold pressed into tablets 16 mm in diameter at room temperature (T = 25 °C) at pressures of 10, 20 and 27 MPa, and PMMA composites were molded while heated at t=180 °C for 30 min. After preparation of PMMA composites, samples were cooled at room temperature for about 30 min. In order to obtain flat surface for conductivity measurements, samples were polished with sandpaper.

EDS analysis of lignocellulose and PMMA composites was examined in more detail using scanning electron microscopy VEGA TS 5130MM microscope (Tescan).

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For the illustration of thermal behavior (stability), thermogravimetric analysis was performed on all the samples. Thermogravimeter TA Instruments Q600 thermal analyzer with a heating rate of 20 °C/min in a dynamic nitrogen atmosphere was used.

Topography of obtained PMMA composites was examined by Atomic Forces Microscope, type "Nanosnope III" AFM "Multi Mode Scanning Probe Microscope", produced by "Digital Instruments".

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 conductivity of the conductive polymer composites with the same or similar characteristics, and hence saving in material, different types of fillers are used, particularly those with highly developed free surfaces. Theoretical and experimental considerations have shown that their use leads to the formation of conductive network through the entire volume of the sample at a much lower filler volume fraction [26] However, the percolation threshold, the electrical conductivity and the electrical behavior of the composite systems with fillers with highly developed surface area, primarily thermal behavior of these materials, have not been fully explored. Therefore there is a need for more detailed study of real synergetic effects of different fillers dimensionality suitable for construction of conductive networks in conductive polymer composites.

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

The mass loss increases with temperature gradually up to approximately 200 °C, while in the region between 200 and 400 °C more significant mass loss occurs. On the obtained TGA curve (Figure 1) two distinct peaks can be observed within this temperature interval, suggesting the existence of two separate thermal events. According to the literature data [27,28], the first event that occurs at 210-300 °C can be associated with the decomposition of hemicellulose and the slow degradation of lignin, while the second event (275-350 °C) can be attributed to the degradation of cellulose. Possible discrepancies between literature data and the TGA results may be associated with the amount of cellulose and lignin in the lignocellulose material, given that Shebani et al. [27] demonstrated that higher cellulose and lignin content in lignocellulosic materials leads to a greater thermal stability.

A characteristic peak that can be observed in Figure 1b corresponds to degradation of the matrix (an event that occurs at 279-382 °C). All 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 matrices themselves.
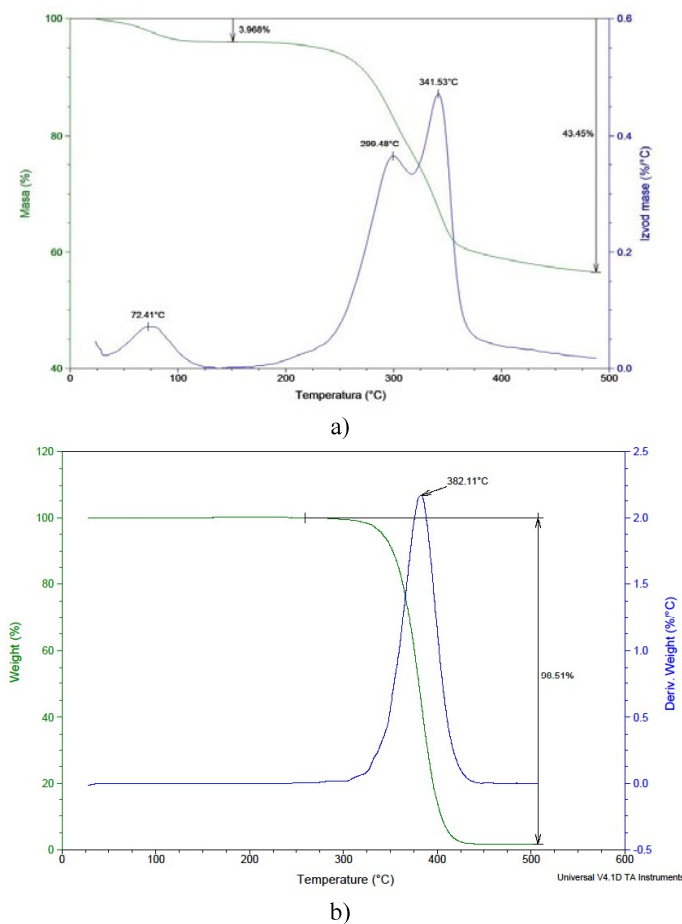
a)

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 PMMA composite surface 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.
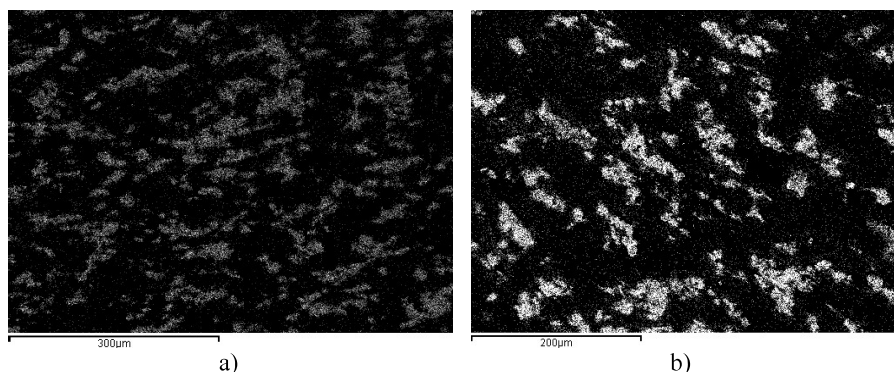
a)   b)

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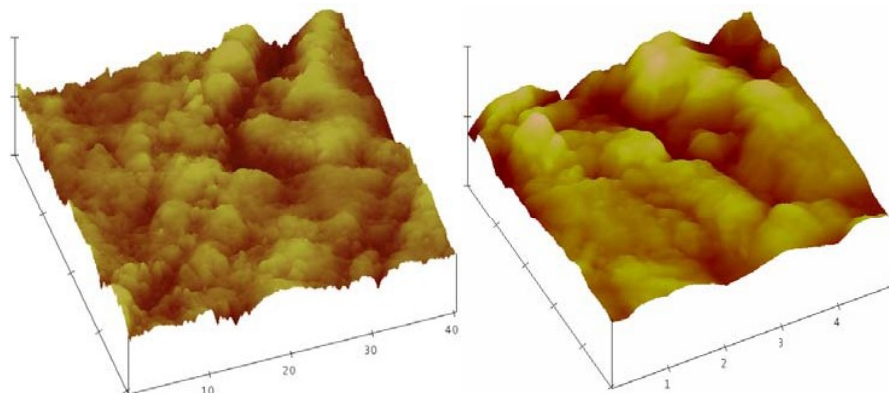

Figure 3. 3D AFM images of the PMMA (left) and LC (right) composite filled with copper powder at percolation threshold

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.

CONCLUSIONS

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. The particles with highly developed free surface and dendritic and highly branched structure, such as

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galvanostatically obtained copper powder particles can easier form interparticle contacts at lower filler volume fractions than particles with more regular surface.

The results of thermal analysis of prepared composites show a slight improvement thermal characteristics of the composites due to the presence of metal fillers which are outstanding thermal conductors, so that the amount of heat emitted during the TGA measurements is initially accumulated in the filler, and only then there is change in the matrix.

When two different matrices are compared, slight advantage can be given to PMMA since the percolation threshold is at lower value. Both matrices have improved thermal characteristics when filler is added. However, lignocellulose is biodegradable, green matrix, and it comes from abundant, sustainable resource, and it can be used for green composite production.

Acknowledgements

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