

Int. J. Electrochem. Sci., 7 (2012) 8883 - 8893

**International Journal of
ELECTROCHEMICAL
SCIENCE**

www.electrochemsci.org

Electrical Conductivity of Lignocellulose Composites Loaded with Electrodeposited Copper Powders. Part II. Influence of Particle Size on Percolation Threshold

M.M. Pavlović^{1,}, V. Čosović¹, M.G. Pavlović², V. Bojanić³, N. D. Nikolić², R. Aleksic⁴*

¹University of Belgrade, ICTM-CMM, 11000 Belgrade, Njegoševa 12, Serbia

²University of Belgrade, ICTM-CEH, 11000 Belgrade, Njegoševa 12, Serbia

³University of Banja Luka, Agrifaculty, Banja Luka, Republic of Srpska, Bosnia and Herzegovina

⁴University of Belgrade, Faculty of Technology and Metallurgy, 11000 Belgrade, Karnegijeva 4, Serbia

*E-mail: mpavlovic@tmf.bg.ac.rs

Received: 3 August 2012 / *Accepted:* 24 August 2012 / *Published:* 1 September 2012

This article is concerned with synthesis and characterization of electroconductive composite materials prepared by the compression molding of mixtures of lignocellulose and electrochemically deposited copper powder under different pressures, and investigation of the influence of particle size on conductivity and percolation threshold of obtained composites. Electrodeposited copper powder content was varied from 2.0-29.8 vol%. Analysis of the most significant properties of individual components and prepared composites included structural and morphological analysis and measurements of hardness and electrical conductivity. Hardness of the investigated composites, as expected, increased with the increase of the processing pressure, as well as lowering the particle size compared to previous work. The significant increase of the electrical conductivity can be observed as the copper powder content reaches the percolation threshold. The packaging effect and more pronounced interparticulate contact with smaller, highly porous, highly dendritic particles with high values of specific area lead to “movement” of percolation threshold towards lower filler content, which for the particles <45 μm and highest processing pressure of 27 MPa was 7.2% (v/v). In the investigated range of electrodeposited copper powder concentrations and applied pressures the increase of the electrical conductivity of composites is as much as fourteen 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, constant current, lignocellulose, particle size, electrical conductivity, percolation threshold

1. INTRODUCTION

Due to growing environmental awareness, increased crude oil price and anxiety about global warming, there have been intensive attempts and interests to develop environmentally friendly and biodegradable products both in academic and industrial fields [1-3]. Cellulose microfibril in the cell wall is the basic structural unit generated during plant photosynthesis. It has very high strength and potential reinforcement for polymer materials. The high strength and elasticity of wood come from the composite structure of its cell walls [4-6]. Biopolymers, like lignocellulose (LC), are a good alternative to polymers based on petrochemical industry due to their environmental benefits like biodegradability and renewability [6]. Biocomposites based on raw materials derived from natural resources are of great interests and have been a major subject in a large number of publications. Produced by wooden plants and having a large range of properties, lignocellulose can be used for applications like packaging, agriculture, hygiene, and automotive industry [1-9].

Lignocelulose can be obtained by physical treatment such as high pressure homogenizer and grinder treatment, using high mechanical shear force to generate bundles of microfibrils called cellulose microfibril or microfibrillated cellulose with diameters from tens of nm to μm [6].

The research area of electrically conducting polymer composites filled with metallic powders has had a great development in the last two decades. The addition of metals fillers into a polymer matrix enables the preservation of the mechanical properties of the polymer while exploiting the electrical conduction properties of the metal [10,11]. The conductivity of filled polymers is usually strongly dependent on the nature of the contact between the conductive filler elements and depends critically on the volume fraction of the conducting filler particles. Therefore composites filled with conducting particles with high surface area will conduct electricity at lower volume fractions of the filler than the ones with smoother surface, which is explained by Pavlović et al [6].

Lower cost, ease of manufacture, high flexibility, reduced weight, mechanical shock absorption ability, corrosion resistance, and conductivity control are just some of the advantages that polymer-based electrically conducting composites have several over their pure metal counterparts [10].

The method most often employed to alter the electrical properties of a polymer is the approach where the insulating polymer is combined with a conductive additive. The conducting additive is incorporated into polymers at levels that allow the composite to maintain its electrically insulative qualities, hence allowing the composite to become both electrically semiconductive and conductive. As the volume fraction of the conducting filler particles increases, the particles come into contact with one another to form the conduction paths through the composite [10,11].

In the previous research, the influence of the particle shape on the percolation threshold was investigated, which was explained in the Part one [6]. The aim of this work was to compare electrical properties of copper powder filled lignocellulose matrix composites produced under different pressures with previous results, where the influence of particle size and pressure on percolation threshold is observed.

2. EXPERIMENTAL PART

Electrolytic copper powder used in this research was deposited galvanostatically in the same manner as stated by Pavlović et al. [6], with all the same parameters of electrolysis and deposition times. The wet powder was washed several times with a large amount of demineralized water until the powder was free from traces of acid, at room temperature, because the acid promotes rapid oxidation of the powder during drying. Obtained copper powder was washed afterwards with sodium soap SAP G-30 solution to protect the powder against subsequent oxidation, which was prepared and used as in previous work [6]. After drying in the tunnel furnaces at 110 – 120 °C in a controlled nitrogen atmosphere, the copper powder was sieved through a mesh with 45µm openings.

As a source of lignocellulose the same corn cob produced by Maize Research Institute "Zemun Polje" was used as in [6]. Celgran[®] C fraction was used in experiments [6], milled and then sieved, with particle size below 45 µm as natural polymer matrix.

Particle size distribution of obtained copper powder and lignocellulose was analysed using Nauchnye Pribory Co., St. Petersburg laser diffractometer MicroSizer 201.

Quantitative microstructural analysis of the copper powder was recorded by Leica Q500 MC ("Reichert-Jung") [12,13].

The morphology of the electrochemically deposited copper powder and lignocellulose was further investigated by means of scanning electron microscopy using a JEOL JSM-6610LV microscope.

Investigated lignocellulose and copper powder composites were prepared with filler contents in the range 2.0% (v/v) – 29.8% (v/v), while pure lignocellulose and copper samples were prepared as reference materials. The samples were produced from thoroughly homogenized powder mixtures that were pressed into 16 mm diameter tablets at ambient temperature ($t = 25\text{ }^{\circ}\text{C}$) under pressures of 10, 20 and 27 MPa.

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

Electrical conductivity measurements were carried out by DC U/I-characteristic measurements of the samples using Digital Multimeter, Model 464, Simpson Electric Company. Geometry of the instrument contacts (rings) used is such that it minimizes edge effects thus it can be assumed that they do not exist.

Hardness of the samples was determined at ambient temperature using Shore D hardness testing method in accordance with ASTM D 2240-68 standard using Omnitron OMGE003 hardness tester. Five data points were taken for each sample and no difference was found between values obtained for both faces of each sample.

3. RESULTS AND DISCUSSION

Electrical properties of a polymer are oftenly altered by addition of conductive filler in the insulating polymer. The conducting additive is incorporated into polymers at levels that allow the

composite to maintain its electrically insulative qualities, as well as at higher levels, which allow the composite to become electrically semiconductive. In this manner, the electrical conductivity of polymer composites does not increase continuously with increasing electroconductive filler content, but rather has rapid increase in conductivity when the percolation threshold of the conductive filler content is reached. This is observed as an increase of several (sometimes up to 14 [6]) orders of magnitude on the conductivity vs. filler content curve, which has typical S shape. This phenomenon occurs at critical composition (percolation threshold) when insulating polymer composite becomes semiconductive or metallic conductive [6,11,14-16].

As previously mentioned, the conductivity of filled polymers is strongly dependent on the nature of the contact between the conductive filler elements. This was shown in [6] where highly dendritic copper powder was used, and the percolation threshold was moved to lower filler content. Therefore, the same copper powder was galvanostatically produced with distinct dendritic morphology and large specific area [17-19]. This feature can be seen in Figure 1b, which shows typical copper powder particle obtained by constant current deposition, while Figure 1a shows general view of the powder particles. Copper powder particles have pronounced dendrite branching and, hence, this powder is good prerequisite for formation of more interparticle contacts between conductive copper particles and lowering the percolation threshold.

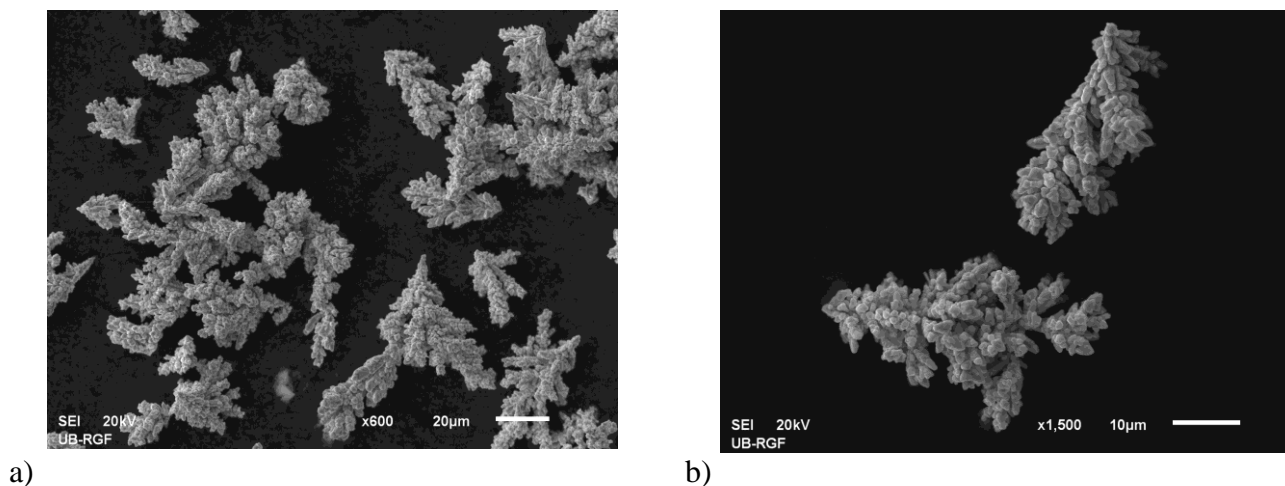


Figure 1. SEM photomicrographs of copper powder particles obtained in constant current deposition and sieved through mesh <math><45 \mu\text{m}</math>. a) general view b) typical powder particle

This powder was then dry-sieved through a mesh of 45 μm opening, hence being almost twice smaller in size than the one used in [6]. Particle size distribution curve of produced and sieved electrolytic copper powder is presented in Figure 2.

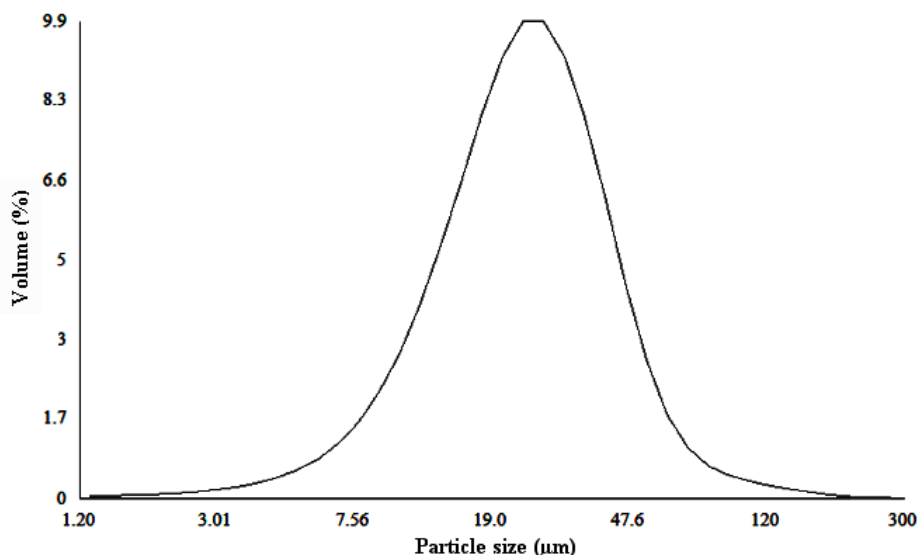
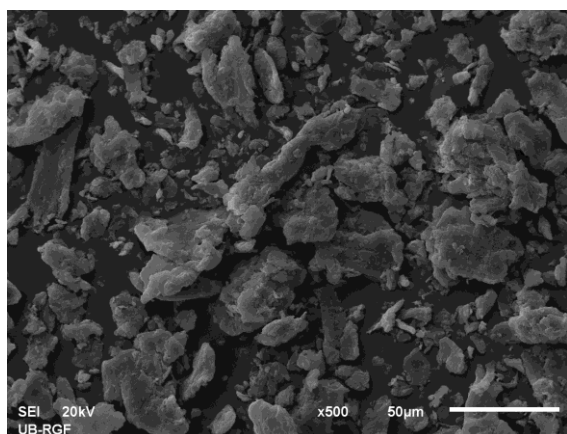


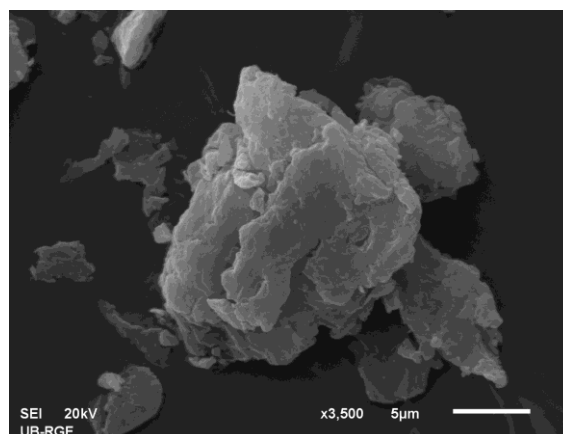
Figure 2. Copper powder particle size distribution curve

The particles show uniform size distribution, with uniform Gaussian distribution and with the mean particle size of copper powder determined by laser diffractometry having following values: $d(0.15) = 12.5 \mu\text{m}$, $d(0.5) = 23.6 \mu\text{m}$ and $d(0.9) = 46.6 \mu\text{m}$. The apparent density of electrodeposited copper powder was the same as in previous research, with the value of 0.557 g/cm^3 [6].

Figure 3a shows SEM photomicrographs of the used lignocellulose. Distinct layered structure of the lignocellulose bionanocomposite used as matrix can be observed in Figure 3b.



a)



b)

Figure 3. SEM photomicrographs lignocellulose matrix used in composite preparation. a) General view b) single particle view (layered structure)

Lignocellulose powder used for composite preparation has particle size distribution presented in Figure 4. Lignocellulose particles show wider size distribution than the copper powder particles, with less uniformity and with higher volume fractions of larger particles. The mean particle size of

lignocellulose powder determined by laser diffractometry has following values: $d(0.15) = 7.05 \mu\text{m}$, $d(0.5) = 24.0 \mu\text{m}$ and $d(0.9) = 62.1 \mu\text{m}$.

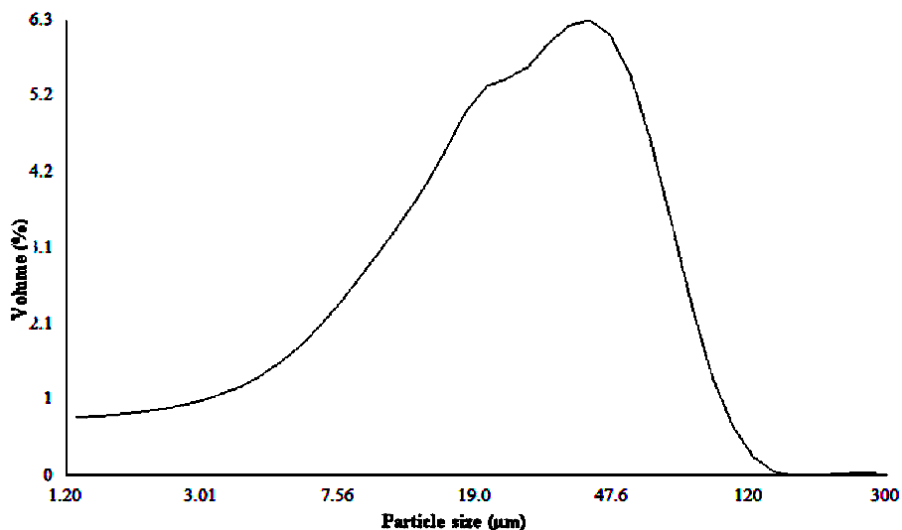


Figure 4. Particle size distribution curve of used lignocellulose matrix

Theoretical density of composites, ρ_t , was calculated according to relation [6]:

$$\rho_t = (1 - V_f)\rho_m + V_f\rho_f \tag{1}$$

where V is volume fraction, ρ – density while f and m indexes correspond to filler (copper powder) and matrix (lignocellulose), respectively.

Porosity of the investigated composites, τ , was determined by comparison of experimental and theoretical densities of the samples according to relation:

$$\tau = \left(\frac{\rho_t - \rho_e}{\rho_t} \right) \times 100 \tag{2}$$

where ρ_e – is experimentally obtained value of composite density.

Electrical conductivity was determined according to relation:

$$\sigma = \frac{I}{U} \cdot \frac{l}{S} \tag{3}$$

where σ is electrical conductivity, I – current through sample, U – potential difference, l – length and S – cross-section area of the sample.

Figure 5 represents the porosity rate of different composites as function of the filler volume fraction at various processing pressures. It can be seen that, as shown in previous work, the porosity

decreases with the increase of pressure, due to higher packaging effect. However, as the volume fraction of the very porous natural matrix decreases, the porosity does not change, i.e. it is rather constant for the given pressure. This is due to smaller particle size, where the maximum packing is obtained. Comparing to the particle size of $<88 \mu\text{m}$ where the porosity was between 24% and 30%, in the case where particle size was $<45 \mu\text{m}$ the porosity was between 14% and 20%, which is quite smaller. These results show that the quality of the obtained composites was good, and that lowering the particle size leads to decrease in porosity.

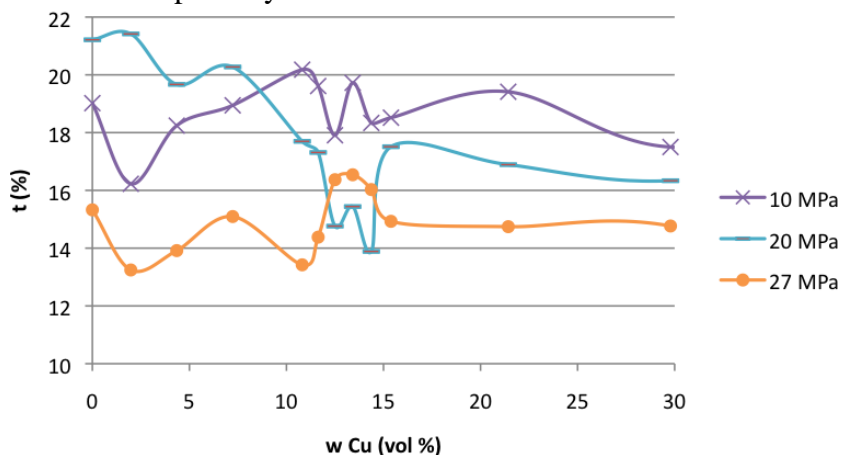


Figure 5. Porosity of the copper powder filled lignocellulose matrix composites at various pressures

Figure 6 shows the dependence of hardness measured as shore D values, in various composites of lignocelluloses matrix and copper powder filler prepared under various pressures. Hardness of the investigated composites, as expected and shown in the previous work [6], increases with the increase of the molding pressure. On the other hand the increase of the filler fraction has less significant influence on the hardness values, resulting in approximately constant values, nearly independent of the filler fraction. However, it can be concluded that lowering the particle size leads to increase of hardness for the same pressure, which is the consequence of better packaging effect that smaller particles have.

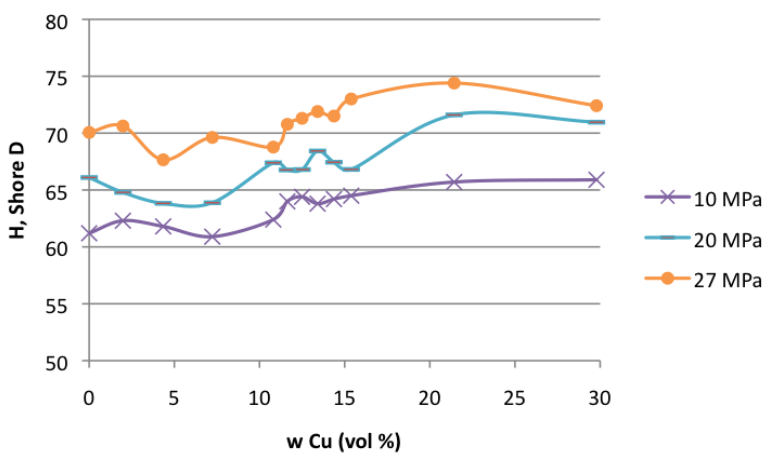


Figure 6. Hardness of lignocelluloses matrix and copper powder filler composites prepared under various pressures. Measurements are shown as Shore D values

The electrical conductivity of all the particle size composites as a function of filler content for all the samples was measured as stated in Experimental part. In previous research [6] it was shown that pressure does not play significant role for the percolation threshold for particles <88 μm, however more precise measurements are made around percolation threshold, and there is slight impact of pressure on it. As it can be seen in Figure 7, percolation threshold for the lowest pressure of 10 MPa was 14.4% (v/v), then 13.4% (v/v) for 20 MPa and 13.0% (v/v) for 27 MPa. The value of the percolation threshold was obtained from of the maximum of the derivative of the conductivity as a function of filler volume fraction.

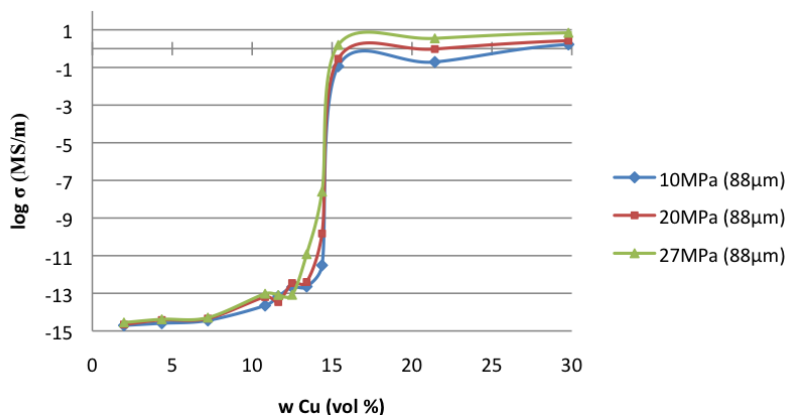


Figure 7. Variation of electrical conductivity, as a function of filler content, of lignocelluloses composites filled with copper powder under different processing pressures for particle sizes <88 μm

The conductivity measurements for these samples are shown in Figure 8, and typical S-shaped dependency with three distinct regions: dielectric, transition and conductive can be observed. As in the previous case the value of the percolation threshold was obtained from of the maximum of the derivative of the conductivity as a function of filler volume fraction.

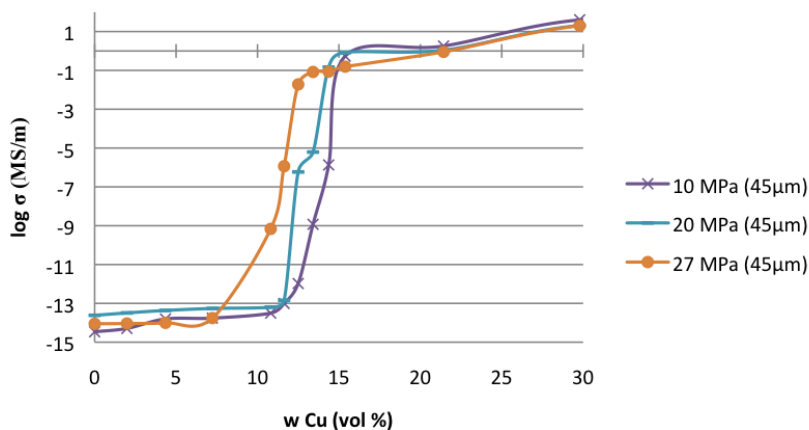
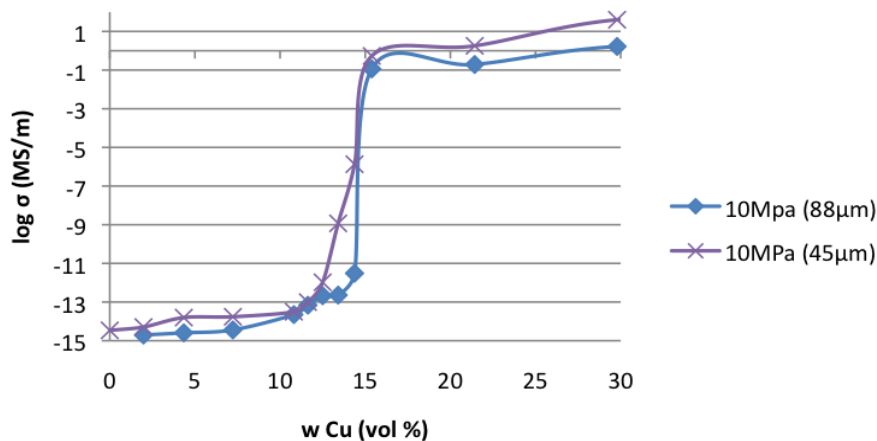


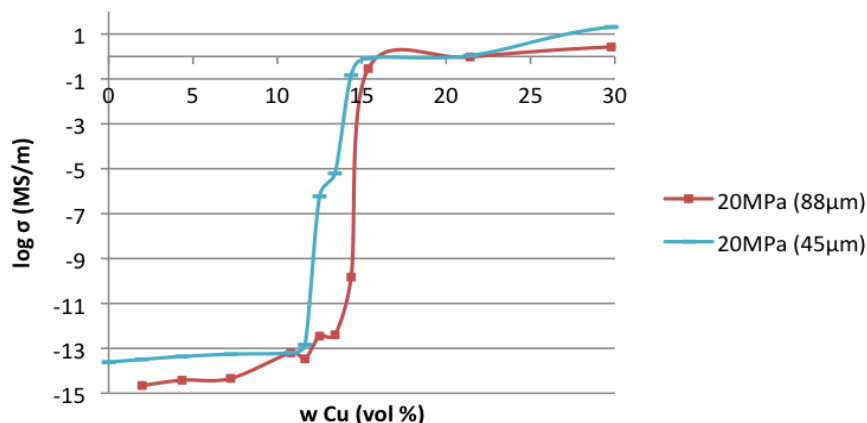
Figure 8. Variation of electrical conductivity, as a function of filler content, of lignocellulose composites filled with copper powder under different processing pressures for particle sizes <45 μm

In both cases the samples with low filler content are nonconductive, where the electrical conductivity of the composites increases with the increase of the conductive filler content.

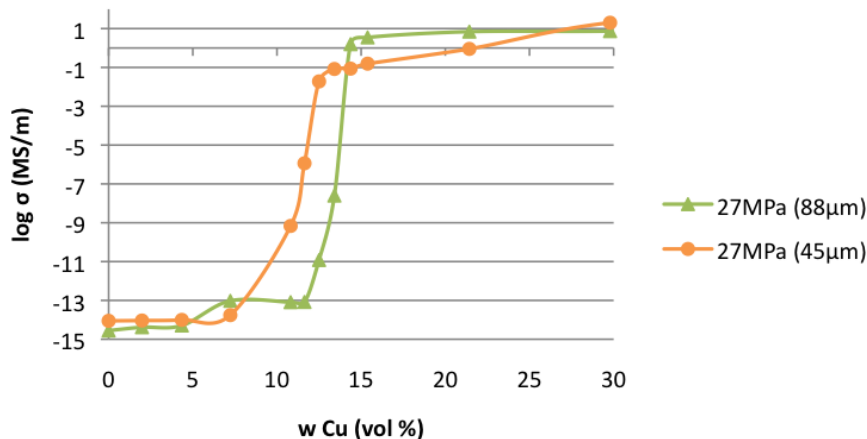
Figure 9 shows the impact of the particle size on percolation threshold for equivalent processing pressures.



a)



b)



c)

Figure 9. Electrical conductivity, as a function of filler content, of lignocellulose composites filled with copper powder with different particle sizes under different processing pressures. a) 10 MPa, b) 20 MPa, c) 27 MPa

For all the pressures, percolation threshold for smaller particle sizes is lower than for larger ones. As the processing pressure increases this difference enlarges which is best seen at highest processing pressure. 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. For the pressure of 10 MPa the percolation threshold was lowered to 12.5% (v/v) for particles <45 μm , for 20 MPa it was 11.6% (v.v), and for 27 MPa was 7.2% (v/v) which is the difference of 5.8% (v/v) in filler content. As Flandin et al. [20] state that typical values of 20–40% (v/v) for percolation threshold for spherical filler particles, highly dendritic, high surface area electrodeposited copper powder particles represent excellent choice as conductive composite fillers.

It can be observed from Figure 9 that even the lowest processing pressure for smaller particle size has lower percolation threshold than the highest processing pressure for larger particle size. As the particle size lowers, smaller volume fraction of filler is needed to obtain the clusters of connected particles that give rise to the so-called conducting infinite cluster above the threshold, which is explained by statistical percolation theory [21,22]. Being highly dendritic, electrolytic copper powder particles lower threshold even more.

Above the percolation threshold, the conductivity of composite increased by much as fourteen orders of magnitude for all the investigated samples, which is in accordance with previous research [6].

4. CONCLUSIONS

In this article, experimental study about the effects of particle size of electrodeposited copper powder on the electrical conductivity of composites of lignocellulose matrix filled with powder of that metal has been described. Results have shown that particle size of this powder with very high surface area and pronounced dendrite branching plays significant role on electrical conductivity of the prepared samples. The conductivity measurements showed S-shaped dependency with percolation transition from non-conductive to conductive region. For all the processing pressures, percolation threshold for smaller particle sizes was lower than for larger ones. As the processing pressure increased, this difference enlarged. Packaging effect and more pronounced interpartical contact with smaller, highly porous, highly dendritic particles with high values of specific area lead to “movement” of percolation threshold towards lower filler content. For 27 MPa and particle size <45 μm this value was 7.2% (v/v), which is 7.2% (v/v) lower than for composite prepared under 10 MPa and with particle size of <88 μm . For a given range of filler concentration and pressures the increase of the electrical conductivity of composites is as much as 14 orders of magnitude, which is in accordance with previous research [6]. Smaller particle size also led to smaller porosity, as expected due to packaging effect, and the same was eligible for the Shore D hardness.

This research has undoubtedly shown that particle size of galvanostatically obtained copper powder and lignocellulose matrix play significant role in electrical conductivity and some of the mechanical properties. The value of percolation threshold is lowered even more than in previous

research. Surely it would be interesting to investigate identical system, but with other electrochemically obtained metal powders.

ACKNOWLEDGEMENT

This work was financially supported by Ministry of Education and Science of the Republic of Serbia under the research projects: ON172046 and ON172037.

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