Electrical Conductivity of Lignocellulose Composites Loaded with Electrodeposited Copper Powders. Part III. Influence of Particle Morphology on Appearance of Electrical Conductive Layers

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The electrical conductivity of the system based on lignocellulose (LC) biopolymer matrix filled with electrodeposited copper powder has been studied. Galvanostatically produced copper powder, having highly porous, highly dendritic particles with high values of specific area was used as filler. Volume fraction of the electrodeposited copper powder was varied from 2.0-29.8 vol%. Analysis of the most significant properties of prepared composites and its components included measurements of electrical conductivity, impedance spectroscopy (IS) behavior, structural and morphological analysis. The composite preparation conditions allowed the formation of a random distribution of metallic particles in the polymer matrix volume. It was shown that percolation threshold depends on both particle shape and type of spatial distribution. IS measurements have shown that particle morphology having pronounced grain boundaries has great effect on appearance of electric conductive layers, i.e. "movement" of percolation threshold towards lower filler volume fractions. IS response of the composites showed existence of electrical conductive layers, each having different resistivity which increases towards interior of the composite.

1. INTRODUCTION

Impedance spectroscopy (IS) is gaining more important role in fundamental and applied electrochemistry and materials science in the last years. In a number of respects it is the method of choice for characterizing the electrical behavior of systems in which the overall system behavior is

determined by a number of strongly coupled processes, each proceeding at a different rate [1]. Impedance spectroscopy is a relatively new and powerful method of characterizing many of the electrical properties of materials and their interfaces with electronically conducting materials. It may be used to investigate the dynamics of bound or mobile charge in the bulk or interfacial regions of any kind of solid or liquid material: ionic, semiconducting, mixed electronic–ionic, and even insulators (dielectrics). It can be used for measurements in wide range of materials from solid electrolyte materials (amorphous, polycrystalline and single crystal), solid metallic electrodes, fused salts, aqueous electrolytes and composite materials [1].

On the other hand composite materials are of fundamental importance in view of their unique properties and possibilities for applications, and they represent one of the milestones of material science. Polymer composites filled with metals and other conductive particles are of interest for many fields of engineering [2–10]. Lower cost, ease of manufacture, reduced weight, high flexibility, corrosion resistance, mechanical shock absorption ability and conductivity control are just some of the advantages that electroconducting polymer composites have over pure metals [10]. Electrical characteristics of such composites are close to the properties of metals, whereas the mechanical properties and processing methods are typical for nonconductive polymers [2,10]. The achievement of metallic properties in such composites depends on many factors, and it is just the possibility of controlling the electrical and physical characteristics, which determines the variety of ranges of their application. The influence of the type of polymer matrix and filler on the electrical characteristics of the composite has been studied in many works [10–14]. It was observed experimentally that the conductivity of filled polymers is strongly dependant on particle size and shape, the nature of the contact between the conductive filler elements, the volume fraction and the spatial arrangement of the conducting filler particles [10,14-16].

The method most often used for changing the electrical properties of a polymer is mixing and combining the insulating polymer with a conductive additive. The conducting filler 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 reaches a critical value (so-called percolation threshold), an infinite conductive cluster (IC) is formed and, consequently, the composite becomes conductive [10,14-19].

In the previous research, the influence of the particle size and shape on the percolation threshold was investigated, which was explained in the Part one [10] and Part two [14]. The aim of this work was to compare results of electrical conductivity of copper powder filled lignocellulose matrix composites produced under different pressures obtained by different measuring techniques, and to explain the influence of particle shape (i.e. particle morphology) on percolation threshold by impedance spectroscopy.

2. EXPERIMENTAL PART

Copper powder was galvanostatically produced with distinct dendritic morphology and large specific area [20-22] in the same manner as stated by Pavlović et al. [10] and Pavlović et al. [14]. Electrolytic copper powder has been produced from electrolyte containing 140 g/dm^3 sulfuric acid and

15 g/dm^3 copper ions, using an electrolyte temperature (50±2) ºC. The powder was deposited galvanostatically at current density of 3600 A/m^2 and the deposition time (time of powder removal by brush) was 15 min, where the experimental setup was the same as in [10,14]. 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. The later promotes rapid oxidation of the powder during drying. Sodium soap SAP G-30 solution was used for stabilizing the obtained copper powder, since it protects the powder against subsequent oxidation. Stabilizing SAP G-30 solution was prepared and used as in previous work [10,14]. After drying in the tunnel furnaces at 110 – 120 ºC in a controlled nitrogen atmosphere, two different particle sizes copper powders were obtained by sieving it through meshes with 88μm and 45μm openings.

Celgran® C fraction of the corn cob produced by Maize Research Institute "Zemun Polje" was used as a source of lignocellulose. It is the same lignocellulose used in experiments [10,14], which was milled and then sieved, with two different particle sizes: below 88 μm and below 45 μm. Lignocellulose prepared and obtained in this manner was used 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.

The morphology of the electrochemically deposited copper powder and lignocellulose was investigated by scanning electron microscopy using a JEOL JSM-6610LV microscope, while qunatitative microstructural analysis of the copper powder was performed by Reichert-Jung Leica Q500 MC.

Investigated composites of lignocellulose matrix filled with copper powder were prepared with filler contents in the range 2.0% (v/v) – 29.8% (v/v), while pure lignocellulose samples were prepared as reference materials. Thoroughly homogenized composite powder mixtures were pressed into 16 mm diameter pellets under pressures of 10, 20 and 27 MPa. at ambient temperature (t = 25 ºC)

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 [23].

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

3. RESULTS AND DISCUSSION

Electrical properties of lignocellulose polymer matrix are altered by addition of conductive copper powder as filler. The electrical conductivity of polymer composites does not increase continuously with increasing electroconductive filler content. Instead it has rapid increase in

conductivity when the percolation threshold of the conductive filler content is reached. As previously shown [10,14], the conductivity of filled polymers is strongly dependent on the particle size, shape of the conductive particle filler and nature of the contact between the conductive filler elements. Therefore, the copper powder was galvanostatically produced since it should have distinct dendritic morphology and large specific area [20-22].

The apparent density of electrodeposited copper powder was 0.548 g/cm^3, and the results of quantitative microstructural analysis for the sieved powders are shown in Table 1 and Table 2. The symbols used have the following meanings:

– A (area) – Feature area (the total number of detected pixels within the feature).

– D_{max} – Diameter (length) of the largest (longest) particle.

– D_{min} – Diameter (length) of the smallest (shortest) particle.

– L_p (perimeter) – The total length of the boundary of the feature. This is calculated from the horizontal and vertical projections, with an allowance for the number of corners.

– f_A (form area) – A shape factor of area. This is calculated from the ratio:

$$f_A = \frac{4A}{\pi \cdot D_{max} \cdot D_{min}}$$ (1)

and for a circle and ellipse is equal to 1.

– f_L (form perimeter)–A shape factor of perimeter. This is calculated from the ratio:

$$f_L = \frac{4\pi A}{L_p^2}$$ (2)

and for a circle and ellipse is equal to 1.

– f_R (roundness) –A shape factor which gives a minimum value of unity for a circle. This is calculated from the ratio of perimeter squared to area:

$$f_R = \frac{L_p^2}{4\pi \cdot A \cdot 1.064}$$ (3)

The adjustment factor of 1.064 corrects the perimeter for the effect of the corners produced by the digitization of the image.

– f_w – This is the ratio of the length of the polygon circumscribing the feature formed by tangents to its boundary (very similar to the length of a piece of string stretched around the feature) to perimeter.

Table 1. Parameters which characterize sieved fraction ($\leq 88\mu m$) of electrolytic copper powder deposited galvanostatically at current density of 3600 A/m^2

	Max	Min	Mean
A (area) (μm^2)	1137.48	8.64	187.42
L_p (perimeter) (μm)	349.27	1.89	117.96
D_{max} (μm)	103.82	4.12	57.21
D_{min} (μm)	25.69	1.08	12.08
f_A (form area)	1.00	0.37	0.75
f_L (form perimeter)	0.87	0.12	0.51
f_W	1.00	0.75	0.90
f_R	4.00	1.21	2.11

Table 2. Parameters which characterize sieved fraction ($\leq 45\mu m$) of electrolytic copper powder deposited galvanostatically at current density of 3600 A/m^2

	Max	Min	Mean
A (area) (μm^2)	589.71	5.32	93.18
L_p (perimeter) (μm)	176.25	0.99	58.98
D_{max} (μm)	51.62	2.87	28.61
D_{min} (μm)	12.97	0.98	6.34
f_A (form area)	1.00	0.37	0.75
f_L (form perimeter)	0.87	0.12	0.51
f_W	1.00	0.75	0.90
f_R	4.00	1.21	2.11

The obtained results of the used copper powder show that the powder has very high surface area. The shape factor for roundness of the particles, f_R, which has the smallest values for circle, shows very distinct features for highly porous, highly dendritic particles with high values of specific area with well developed primary and secondary dendrite arms.
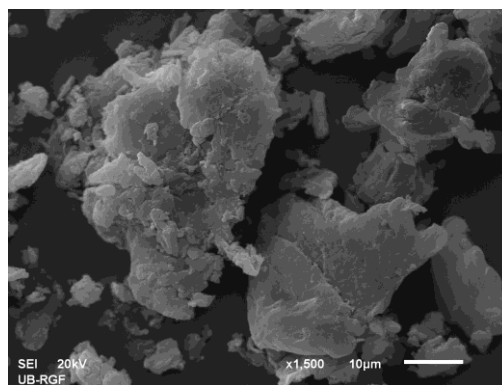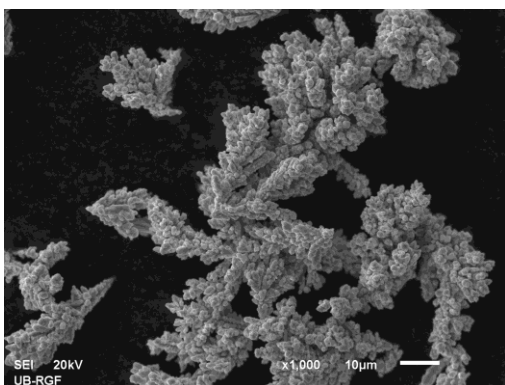
Figure 1. SEM photomicrographs of a) copper powder particles obtained in constant current deposition and b) lignocellulose matrix used in composite preparation.

This feature can be observed in Figure 1a, which shows typical copper powder particle obtained as stated in Experimental part. Figure 1b shows SEM photomicrograph of the used lignocellulose. Distinct layered structure of the lignocellulose bionanocomposite used as matrix can be observed.

The electrical conductivity of all the particle size composites as a function of filler content for all the samples was measured from impedance characteristics of a composite having the filler of characteristic morphology. Electrical conductivity was determined according to relation:

$$\sigma = \frac{1}{\sum_{1}^{7} R_i} \cdot \frac{l}{S} \tag{4}$$

where σ is electrical conductivity, R_i – resistivity of a layer in equivalent circuit, l – length and S – cross-section area of the sample. Measurements of electrical conductivity as a function of filler content for all the samples are presented in Figure 2.
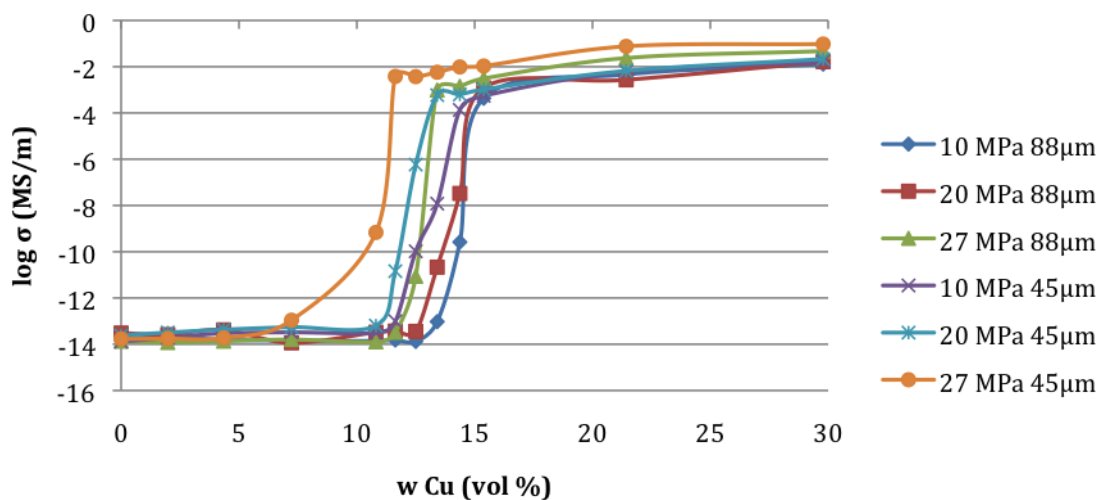

Figure 2. Comparison of electrical conductivities, as a function of filler content, of lignocellulose composites filled with copper powder with different particle sizes under different processing pressures.

Results of the percolation threshold (obtained from of the maximum of the derivative of the conductivity as a function of filler volume fraction) measured from the experimental data of impedance spectroscopy are in good agreement with previous results [10,14]. It can be noticed that for all the pressures, percolation threshold for smaller particle sizes is lower than for larger ones.

At an interface between two phases in the composite, physical properties like crystallographic, mechanical, compositional, and, particularly, electrical change precipitously and heterogeneous charge distributions (polarizations) reduce the overall electrical conductivity of a system. Proliferation of interfaces is a distinguishing feature of solid state systems, where this system is commonly

polycrystalline. Each interface will polarize in its unique way when the system is subjected to an applied potential difference. The rate at which a polarized region will change when the applied voltage is reversed is characteristic of the type of interface: slow for processes at the triple phase contacts between atmosphere, matrix and filler, appreciably faster across grain boundaries in the polycrystalline composite. The electrical response of a heterogeneous composite can vary substantially depending on the species of charge present, the microstructure of the composite itself and the texture and nature of the composite components. Flandin et al. [9] state that typical values of 20–40% (v/v) for percolation threshold for spherical filler particles. The morphology of used copper powder (Figure 1) shows that greater interpartical contact of smaller, highly porous, highly dendritic particles with high values of specific area move percolation threshold towards lower filler content.

　　　　Simulation of registered impedance data by equivalent electrical circuits based on transmission line model [24] has been done. The equivalent electrical circuits which gave the best fitting results (chi-squared based on modulus calculated was below 0.001, while relative error of the parameter values of the elements did not exceed 20%) are schematically presented in Figure 4, while their IS responses are given by lines in Figure 3. A transmission line circuit of the seventh order (i.e., circuit consists of seven transmission branches, Figure 4) best describes the IS behavior. Measurements for all the samples and pressures showed exact behavior as presented in Figure 3.
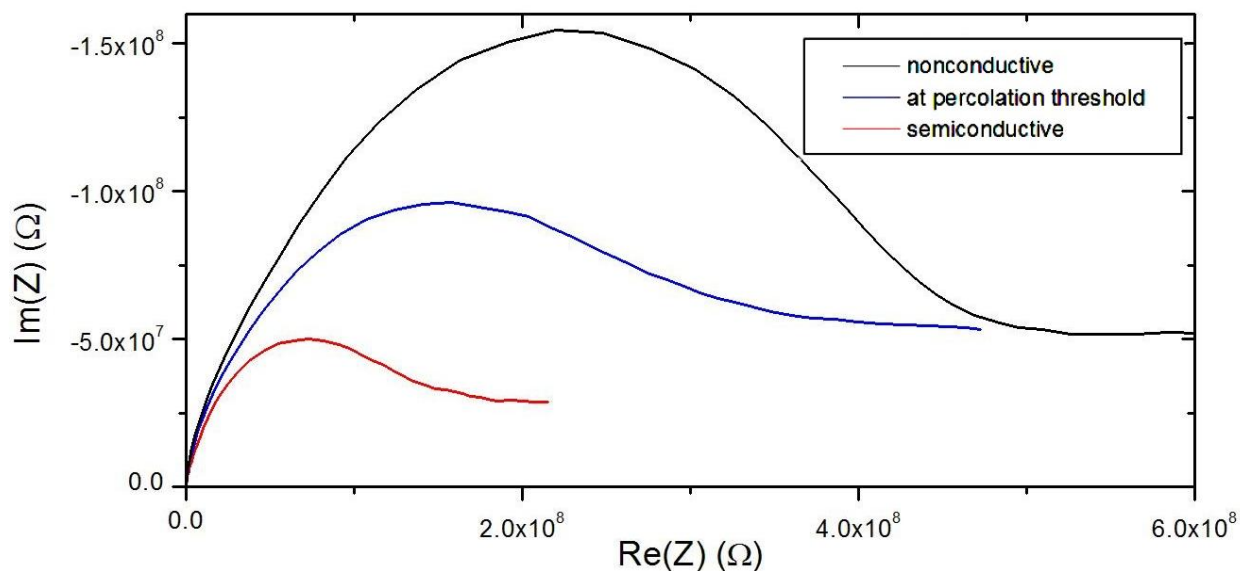

Figure 3. Impedance measurements results showing electric resistance distribution throughout the composite layer in the complex plane. Typical behavior for nonconductive, at percolation threshold and semiconductive for all the composites. Samples shown: p=20 MPa, <45μm w(Cu)=2.0 vol% (black); w(Cu)=10.8 vol% and w(Cu)=12.5 vol%

　　　　These transmission line circuits of the composites represent distributed *RC* time constants as a measure of accessibility of different parts of internal surface of a layer. Circuits from Figure 3 include electrolyte ohmic resistance in the outer layer, R_1, and subsequent resistances, R_n (*n*=2-7), related to conductivity in the inner layers. Number of resistors related to layer resistance, R_n, in *n* transmission

branches depends on a morphology of filler and matrix, paricle size and porosity. Capacitance of the overall composite surface, available through the layer resistances, are represented by a network of capacitors of the capacitances C_n.
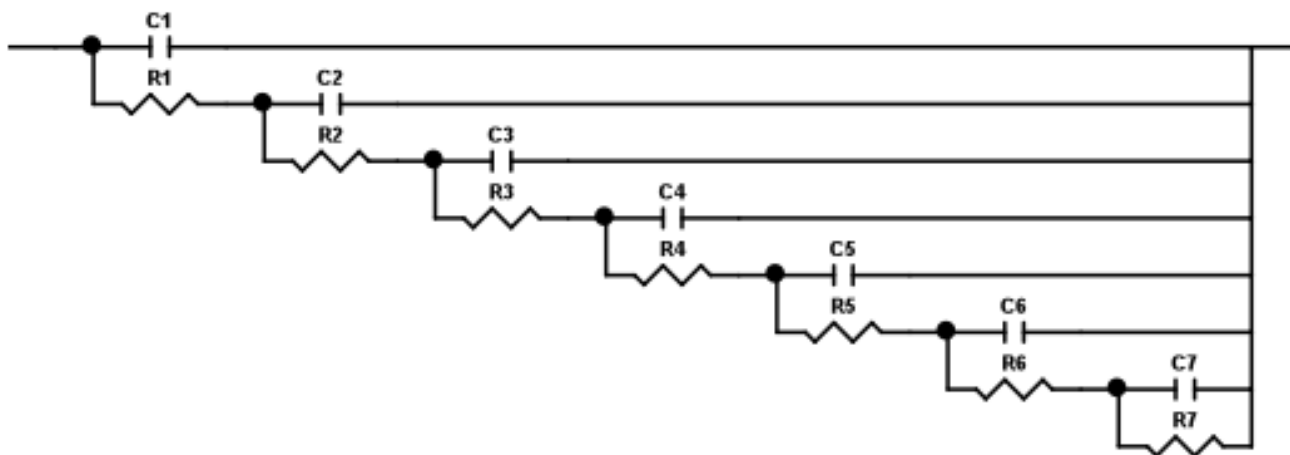

Figure 4. The most suitable equivalent electrical circuits used to simulate IS data of LC-Cu composites from Figure 3.

Figure 5 shows typical impedance response of the lignocellulose-copper powder composites. Measurement results are presented in dots, while fitting results are given by line. It is noticeable that suggested transmission circuits best describe the IS behavior of the measured composites.
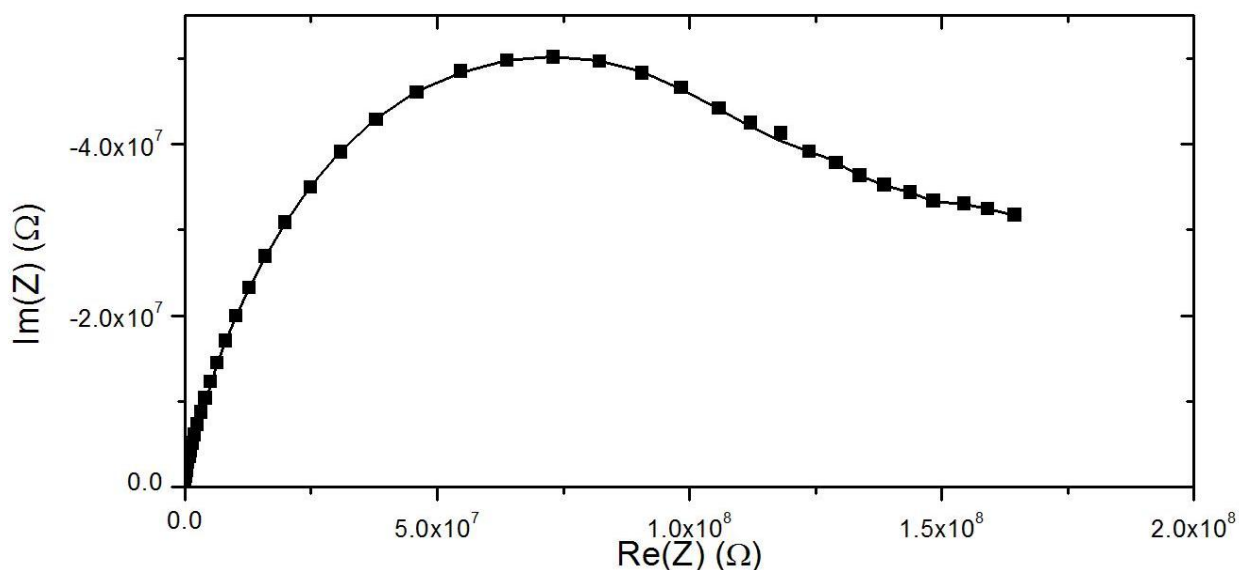

Figure 5. Typical impedance complex plane plots of LC-Cu composites recorded in potentiostatic mode with potential input sinusoidal signal of ±10mV (rms) amplitude. Fitting results are given by lines. Sample shown: p=20 MPa, <45μm, w(Cu)=12.5 vol%

Starting from the external surface, (1ˢᵗ branch, $n = 1$) towards interior of the composite, the

increase in resistance for a three order of magnitude is obtained, which is associated with increase in the capacitance of the same magnitude (down to 7th branch, $n = 7$). It should be noted that resistance of the inner layers is guiding process of the overall resistance of the composite. Considering composite layered morphology, and morphology of the electrodeposited copper powder used as filler (Table 1 and 2) it can be envisaged that resistance increases due to the increasing contribution of the part of internal surface of polymer matrix as frequency decreases. In the certain frequency range, which corresponds to time constants of 4th to 7th transmission branches, capacitance and resistance values are similar. Since capacitors are connected in parallel (Figure 3), the layer capacitance in this frequency range can be calculated as the sum of capacitances in all preceding circuit branches. The same is eligible for resistance, since resistors are connected in series.

In the simplest case, these effects would lead to purely geometric reductions in the conductivity with respect to the single crystal. In addition, impurities may be present as a second phase at the grain boundaries. It was found in [25] that the presence of a second phase at the grain boundaries in dense material led to the introduction of a second time constant in the equivalent circuit. This additional impedance was absent in the very-high-purity material. Bauerle [25] envisaged the ionically insulating second phase as introducing a constriction in the area of contact between the grains of the highly conducting phase. A distribution of time constants for the grain boundary behavior was appropriate, rather than the single RC—time constant. Grain boundary (intergrain) conductivity had greater activation energy than single grain materials. Polycrystallinity introduces anomalous frequency dispersion into the bulk impedance behavior before a second and separate contribution from an intergrain impedance appears.

Bruce and West [26] attributed the constriction to the smaller area of contact between grains rather than to the presence of an ionically insulating second phase. Close to a grain boundary, the transport properties of the crystal are controlled by imperfections, and are expected to be present there in higher concentration that in the center of a grain, leading to an additional contribution to the intergrain impedance. This means that conducting phase is introduced into nonconducting solid as finely dispersed particles. The internal space charge created at the phase boundaries may lead to a significant increase in the concentration of mobile defects. Further, the circuit response is purely geometric reductions in the conductivity with respect to the single crystal, the elongated coupled resistances with constant impedance "tail" towards lower frequencies (Figure 3). In addition, impurities may be present as a second phase at the grain boundaries.

4. CONCLUSIONS

Experimental study about the effects of particle morphology of electrodeposited copper powder on the electrical conductivity of lignocellulose composites filled with this powder has been described in this article. Results have shown that particle shape of copper powder with very high surface area and pronounced dendrite branching plays significant role on electrical conductivity of the prepared samples. Electrical conductivity was calculated from the results of impedance spectroscopy measurements and it is in agreement with previously published results [10,14]. Layered electrical

conductivity through the samples was found, where the resistance of the inner layers is guiding process of the overall resistance of the composite. It can be envisaged that resistance increases due to the increasing contribution of the part of internal surface of polymer matrix as frequency decreases. Also, grain boundary plays significant effect. The internal space charge that is created at the phase boundaries leads to a significant increase in the concentration of mobile defects, hence giving the circuit response with purely geometric reductions in the conductivity with respect to the single crystal. This response is elongated coupled resistance with constant impedance "tail" towards lower frequencies. Polycristallinity, high surface area, greater number of interparticle contacts and grain boundary effect of the copper powder are key factors influencing percolation threshold in the LC-Cu composites. This research has undeniably shown that particle morphology of galvanostatically obtained copper powder and lignocellulose matrix plays significant role in electrical conductivity of the composites.

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