

## THERMAL ANALYSIS OF LIGNOCELLULOSE COMPOSITES FILLED WITH METAL POWDERS

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**Abstract:** Composite materials are gaining increasing industrial applications worldwide. Composites based on polymers with conductive fillers have been recently in the focus of extensive research primarily because of their growing importance from the point of view of application. Natural polymers based on renewable materials with selected fillers can be used directly as contemporary materials in: electronics, medicine, industry, as contact conductive materials, electromagnetic and radio wave shields, photothermal optical recorders, electronic noses sensitive to certain chemicals, as well as economically acceptable catalysts. In this paper the results of experimental studies of the properties of composite materials based on lignocellulosic matrix (LC) filled with electrolytic copper powder and chemically obtained silver powder are presented. Volume fractions of metal fillers in the composite materials in tested samples were varied in the range of 1.6-30% (v/v), and the samples were prepared by compression – cold pressing. 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, DSC, particle size distribution and conductivity measurements. The 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 emitted heat during TGA measurements primary to lignocellulosic matrix. On the other hand, there is no difference in the response with different metallic fillers and particles with different morphologies. Glass transition temperature is improved by 20 °C for all the composites

**Keywords:** thermal analysis, composite materials, lignocellulose, DSC, TGA.

### 1. INTRODUCTION

Research in the field of electroconducting polymer composites filled with metal powder has seen a great development in the last two decades. The addition of metal fillers to polymer matrix preserves the mechanical properties of the polymer while simultaneously exploiting the electric conductive properties of the metal [1]. The conductivity of composites with conductive fillers depends on the nature of contacts between the conductive filler particles and the volume fraction of filler, which is well explained and discussed by the percolation theory [2-4].

In recent years there has been a great deal of information in the literature about the possibilities of application of polymers containing dispersed conductive fillers, and various methods for producing such materials can be found [5-12]. One-component epoxy thermosets are extremely favorable for obtaining the blends of polymer with metal fillers. In addition to these, the most commonly used epoxy polymers, phenolic resins, polyesters and elastomeric polymers are used. Extruders with stirrers are extremely effective in dry blends preparation, but they can cause problems when it comes to temperature control, which is the most important for thermosets. When preparing the blends of polymers and metal fillers, it

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is always necessary to take into account the difference between the density of the polymer matrix and metal filler. As the viscosity of the mixture reduces during processing, heavier metal particles tend to segregate [13].

In commercially available apertures and mixtures of polymers iron, copper, aluminum and silver powders and flakes can be commonly encountered. Specific volume fractions of metal powders or flakes are commercially mixed in liquid polymers, aqueous dispersions of polymeric systems, or they are prepared for incorporating at an elevated temperature and/or pressure, or in extrusion equipment, crushers and mills.

The combination of metal particles, carbon or graphite fibers, metal fibers, metal-coated fibers or films cut to the required size, metal coated films etc. give an unlimited variety of techniques for use of metals and conductive fillers in polymer mixtures. Commercially available apertures meet the requirements for the use of these mixtures, only if they do not require large amounts of metal/polymer blends for everyday use [13].

Fine metal particles dispersed in polymer matrices have contributed to numerous industrial applications. When the volume fraction of the polymer matrix is greater than the volume fraction of the metal filler, a given composite has the mechanical properties such as tensile strength and elongation as the polymer itself, whereas it has electrical properties, such as conductivity and dielectric constants, enhanced by the presence of a conductive metal, and the thermal conductivity is increased as well [13]. Composites with metallic fillers have found application as electromagnetic protection of computers and electronic equipment, conductive adhesives for electronic equipment, cold solders, circuit breakers, materials for spreading static electricity and protection of the devices against power surges [1,13–16]. They have also found numerous technological applications as self-regulating heaters, photothermal optical recorders, chemical sensors and electronic noses, chemical and electrochemical catalysts and adsorbents [17–22].

The most important feature of the composites with metal fillers is increase in the electrical conductivity and the transition from insulator to conductor. These 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 [1].

Biocomposites are essential for the material world because they have unique properties that do not

occur independently in nature. Also, their properties can be tailored to the design of their composition and processing. This feature allows biocomposites to be used in different industry sectors, from aviation industry and space exploration, through automotive, construction, maritime, consumer products to electronic components [23].

In recent years, scientists and engineers have focused on reducing carbon dioxide emissions of all existing products either by mixing bioplastics with synthetic plastics and/or by strengthening the synthetic plastics with natural or synthetic fibers and fillers. Essentially, biocomposites are obtained by any combination of biodegradable polymers as matrices and/or fillers [24]. Thus, the term biocomposites refers to composites which are made of synthetic plastics and bioplastics impregnated with natural or synthetic fibers or both.

Biocomposites obtained from natural vegetable fibers and biodegradable plastics derived from natural sources (biopolymers and bioplastics) are highly environmentally friendly, and they are also called „green composites“ [25]. These environmentally friendly green composites have a potential to become new materials of XXI century and could be a partial solution to many global problems. Consequently, renewable polymer materials provide an answer to the question of sustainable development of economical and environmentally friendly and attractive technology [25].

Lignocellulose is a term used to describe the three-dimensional polymer composite produced by plants as their structural material. It consists of a variable amount of cellulose, hemicellulose and lignin [26]. Lignocellulosic feedstocks are primarily composed of carbohydrate polymers (cellulose and hemicelluloses) and phenolic polymers (lignin). A smaller concentration of a variety of other compounds, such as proteins, acids, salts, and various minerals is also found in lignocellulose.

Corn cob is a very important by-product in the production of corn grain. Each ton of corn grain yields 180 to 200 kg of corncob. Serbia annually produces 1.2–1.5 million tones of this secondary raw material. The traditional use of corncobs in agriculture for heating or cellulosic food for livestock, has been significantly expanded in the industry.

In the world, most of industrially used corncob is used in chemical industry for the production of furfural, and the rest of it, after furfural separation found use as specific food or for the production of carbon black. An attempt was made to obtain acetic acid, methanol, charcoal, xylitol, furfural, etc. by industrial processing of corncob [27,28]. Neither in Serbia, nor in Bosnia and Herzegovina there is a

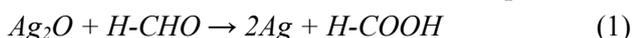
facility for commercial cob processing, and most of attention is mainly devoted to direct combustion of corncob for heating and warm air production for drying grains.

## 2. EXPERIMENTAL

Lignocellulose used in the experimental part of the work for the synthesis of the composites was produced by *Maize Research Institute „Zemun Polje“* [28]. Celgran® C fraction was used, milled in a ball mill, and then dry-sieved through sieves with the openings smaller than 88 µm and 45 µm before performing the experiments.

Electrolytic copper powder used in this study was galvanostatically produced under the following conditions: current density,  $j = 3600 \text{ A/m}^2$ , time of powder removal  $\tau_r = 15 \text{ min}$ , electrolyte flow  $Q = 1 \text{ cell volume/h}$ , temperature of the electrolyte  $t = (50 \pm 2)^\circ\text{C}$ , concentration  $C(\text{Cu}^{+2}) = 15 \text{ g/m}^3$  and the concentration of sulfuric acid  $C(\text{H}_2\text{SO}_4) = 140 \text{ g/dm}^3$ . 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 acid promotes rapid oxidation of powder during the drying process. This copper powder was subsequently washed with aqueous solution of sodium soap SAP G-30 in order to protect the powder from subsequent oxidation, which has been prepared and used as described in the previous work [29]. After drying in a tunnel furnace at 110–120°C in a controlled nitrogen atmosphere, the copper powder was sieved through a sieve with openings of 88 µm and 45 µm.

Silver nitrate solution, having a concentration of  $230 \text{ g/dm}^3$  was prepared in distilled water. Silver powder was chemically precipitated from this solution. 10% sodium hydroxide was used in excess in order to deposit silver oxide. The resulting solution with precipitated silver oxide at the bottom was well mixed, and then slowly, with vigorous stirring, formaldehyde was added in small amounts, which led to reduction of the silver oxide into silver powder.



The end of reduction reaction was indicated by color change from black (silver oxide) to metallic silver-gray color of pure silver powder.

Chemically precipitated silver powder was rinsed by demineralized water at room temperature. Rinsing was carried out until traces of methane acid were completely removed. pH-value of leached silver powder was not higher than 5.0. Thereafter, the obtained silver powder was dried in a tunnel furnace in nitrogen atmosphere for 24 h. The nitrogen flow was  $30 \text{ cm}^3/\text{h}$ , and drying temperature was 135°C. After completion of drying, the powder was cooled

in a stream of nitrogen to a temperature of 35–40 °C and stored in a desiccator. Silver powder was sieved through a mesh with 45 µm openings.

The morphology of electrodeposited copper powder, chemically obtained silver powder and lignocellulose was examined by scanning electron microscopy using a JEOL JSM – 6610LV microscope. Detailed morphological analysis of the obtained electrodeposited copper powder is given in [30].

The particle size distribution of used lignocellulose, copper and silver powders was analyzed using a Malvern Instruments Mastersizer 2000 laser diffractometer with Scirocco 2000 module with measuring range from 0.02 µm to 2000 µm. Measurements were conducted five times for each test sample at room temperature. For data analysis, Mie's theory was used. Double-distilled water having a RI of 1.33 was used for dispersing powder particles.

Lignocellulosic composites filled with copper and silver powder were prepared with filler volume fractions in the range 1.7% (v/v) – 29.8% (v/v), and pure lignocellulose, copper and silver samples were prepared as reference materials. Samples were prepared from thoroughly homogenized powder mixtures which were pressed in tablets having 16 mm in diameter at room temperature ( $t = 25^\circ\text{C}$ ) and pressures of 10, 20 and 27 MPa.

Thermogravimetric analysis was performed on used lignocellulose and lignocellulose composites filled with copper and silver powder in order to illustrate thermal behavior (stability). Thermal stability was investigated using TA Instruments Q600 thermal analyzer with the heating rate of 10 °C/min in the dynamic atmosphere of nitrogen.

TA Instruments Q100 instrument was used for differential scanning calorimetry (DSC analysis) experiments. The analysis was performed from 50 °C to 200 °C with a heating rate of 10 °C/min.

## 3. RESULTS AND DISCUSSION

Conductivity of the conductive polymer composite is very dependent on the nature of the contacts between the conductive filler elements. In order to achieve better electrical conductivity of the conductive polymer composites, and hence saving in material, the use of different types of fillers, particularly those with highly developed surfaces is preferable. Theoretical and experimental considerations have shown that the use of these fillers leads to the formation of conductive network throughout the entire sample volume at much lower filler volume fractions [31,32]. However, percolation threshold,

electrical conductivity, electrical behavior of composite systems with the fillers with highly developed surface area, and primarily thermal behavior of these materials have not been explored in details. Therefore, there is a need for more detailed study of real synergetic effects of different fillers dimensionalities suitable for construction of conductive networks in conductive polymer composites. For this reason, copper powder was galvanostatically produced with distinct dendritic morphology and large surface area, and silver powder was chemically produced.

The results of morphological analysis of the obtained copper powder showed that this powder has a very large surface area.  $f_R$  value [30] or roundness of the particles, which has the lowest value for the

circle, shows very specific characteristics typical of highly dendritic particles with well-developed primary and secondary dendritic arms with angles between them typical for the cubic lattice.

$f_L$  and  $f_R$  values [30] show that copper powder particles are not compact and round, but have dendritic branches. Therefore, these powders are a good prerequisite for the formation of a larger number of interparticle contacts between the conductive powder particles and lowering of percolation threshold.

Particle size distribution curve of the produced electrolytic copper powder, with particle size  $\leq 88\mu\text{m}$  is shown in Figure 1a, and with particle size  $\leq 45\mu\text{m}$  in Figure 1b.

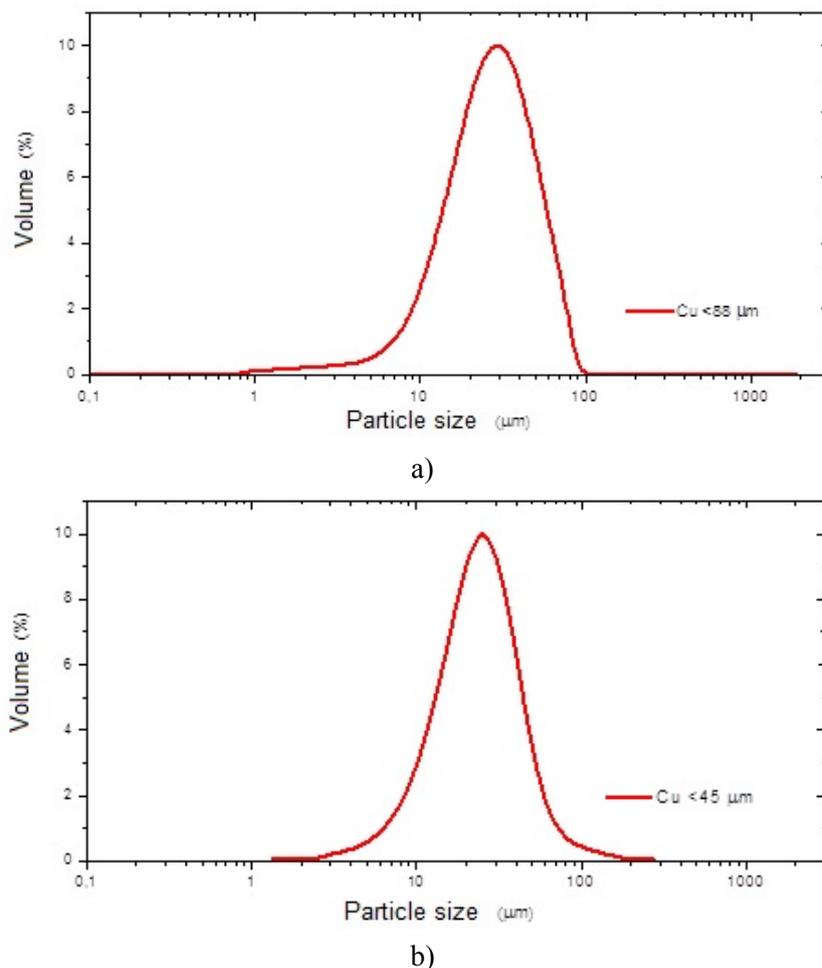


Figure 1. Particle size distribution curve for copper powder a) particles sieved through a mesh with  $\leq 88\mu\text{m}$  openings and b) particles sieved through a mesh with  $\leq 45\mu\text{m}$  openings.

Particle size distribution is monomodal, the diameter of the largest particle did not exceed  $92\mu\text{m}$ . The particles exhibit a uniform size distribution, with a simple Gaussian distribution with a mean copper powder particle size having the following values:  $d(0.1) = 11.329\mu\text{m}$ ,  $d(0.5) = 27.219\mu\text{m}$  and  $d(0.9) = 55.074\mu\text{m}$  for particles  $\leq 88\mu\text{m}$ , and  $d(0.15) = 12.5\mu\text{m}$ ,  $d(0.5) = 23.6\mu\text{m}$  and

$d(0.9) = 46.6\mu\text{m}$  for particles  $\leq 45\mu\text{m}$ . Aggregation degree was low ( $\leq 1\%$ ), because all measured particle diameters, both for  $\leq 88\mu\text{m}$  and  $\leq 45\mu\text{m}$  are in accordance with mesh openings through which these particles were sieved.

Lignocellulosic powder used to prepare the composite has a particle size distribution shown in Figure 2. Lignocellulosic particles exhibit broader

particle size distribution than copper and silver powders, with lower uniformity and greater proportion of larger particles fractions. The mean particle size determined by laser diffractometry have the following values:  $d(0.1) = 16.833 \mu\text{m}$ ,

$d(0.5) = 60.544 \mu\text{m}$  and  $d(0.9) = 127.909 \mu\text{m}$  for particles  $\leq 88\mu\text{m}$ , and  $d(0.15) = 7.05 \mu\text{m}$ ,  $d(0.5) = 24.0 \mu\text{m}$  and  $d(0.9) = 62.1 \mu\text{m}$  for particles  $\leq 45\mu\text{m}$ .

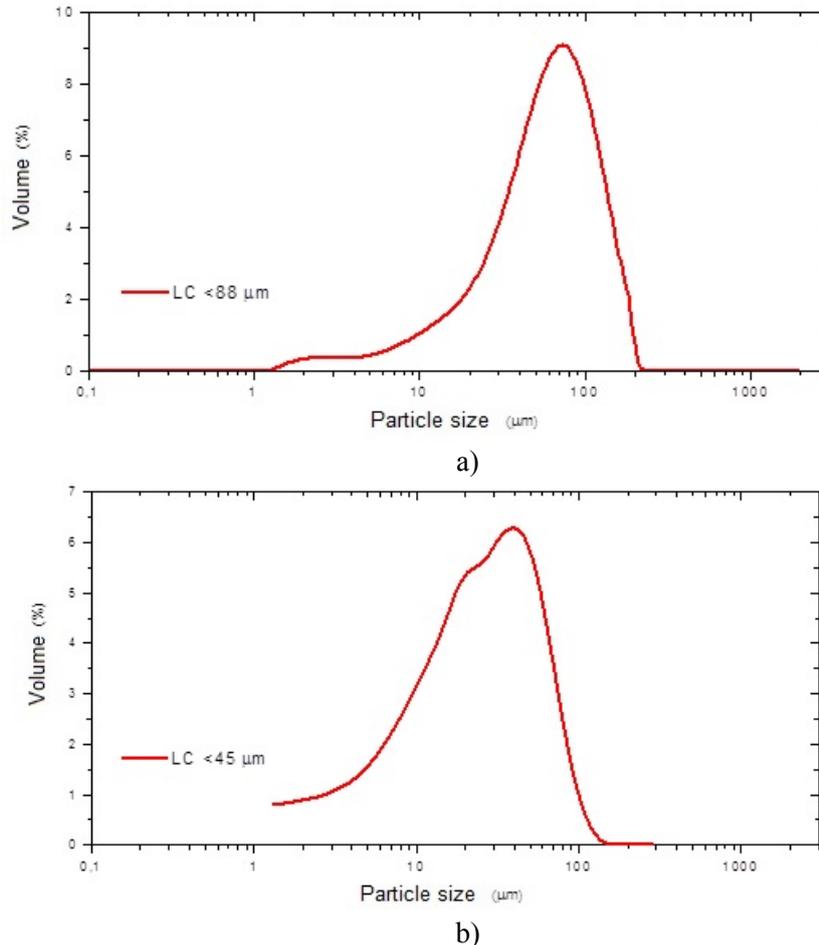


Figure 2. Particle size distribution curve for lignocellulose powder a) particles sieved through a mesh with  $\leq 88\mu\text{m}$  openings and b) particles sieved through a mesh with  $\leq 45\mu\text{m}$  openings.

As it can be noticed, both copper and lignocellulose powder particle size distribution gives similar results for the same powder, as expected. The only difference is in the average size of the particles in fractions after sieving through  $2 \leq 88\mu\text{m}$  and  $\leq 45\mu\text{m}$  sieves.

Due to the ease of obtaining silver powder by chemical reduction, as well as by well developed surface, silver powder was produced by this method as described in the Experimental part. Morphological analysis of the obtained silver powder shows that produced silver powder has a very large surface area. The resulting powder has cauliflower shape, with well developed surface area, but less developed than copper powder. Like the copper powder, chemically obtained silver powder is a good precondition for the formation of a large number of interparticulate contacts between the conductive silver particles and lowering of percolation threshold.

Particle size distribution curve for the silver powder sieved through a mesh with  $\leq 45\mu\text{m}$  openings is shown in Figure 3.

Chemically obtained silver powder particles show very narrow monomodal distribution, which was expected from powder obtained by this method. The mean particle size of the silver powder had the following values:  $d(0.1) = 1.299 \mu\text{m}$ ,  $d(0.5) = 1.666 \mu\text{m}$  and  $d(0.9) = 4.605 \mu\text{m}$ . As opposed to the copper and lignocellulose powders, particle size distribution of silver powder was much more uniform and narrow, with much smaller mean particle size. Difference is not only in the mean size of particles in single fractions, but also in particle size distribution.

The resulting TGA curve, shown in Figure 4, illustrates the thermal behavior (stability) of used lignocellulose. The characteristic temperatures of the observed thermal events confirm the presence of the main constituents (cellulose, hemicellulose and lignin) [28].

The weight loss gradually increases with the increase in temperature to about 200 °C, while in the range between 200 and 400 °C there is a significant mass loss. The obtained TGA curve (Figure 4) shows two different peaks in the measured temperature range, which suggest the existence of two separate thermal events. According to the literature data [33–35], the first event, which occurs at 210–300 °C, can be linked to hemicellulose and slow lignin degradation, while the

other event (275–350 °C) can be attributed to the degradation of cellulose. Possible differences between the data in the literature and the results obtained by TGA measurements can be assigned to the amount of cellulose and lignin in the lignocellulosic material, given that Shebani et al. [33] and D'Almeida et al. [36] showed that higher content of cellulose and lignin in lignocellulosic materials leads to a higher thermal stability.

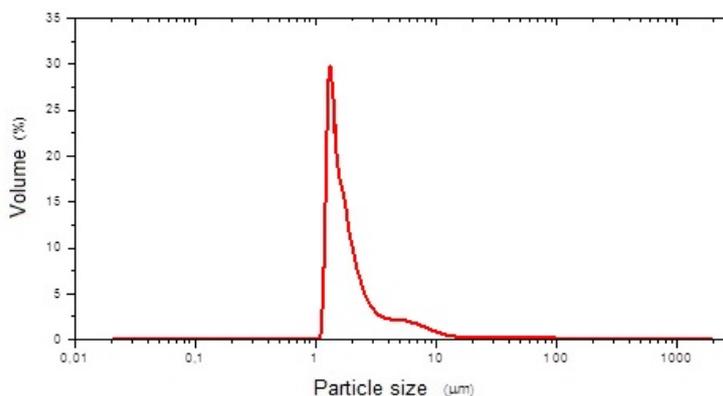


Figure 3. Particle size distribution curve of the silver powder. The particles were sieved through a mesh with  $\leq 45\mu\text{m}$  openings.

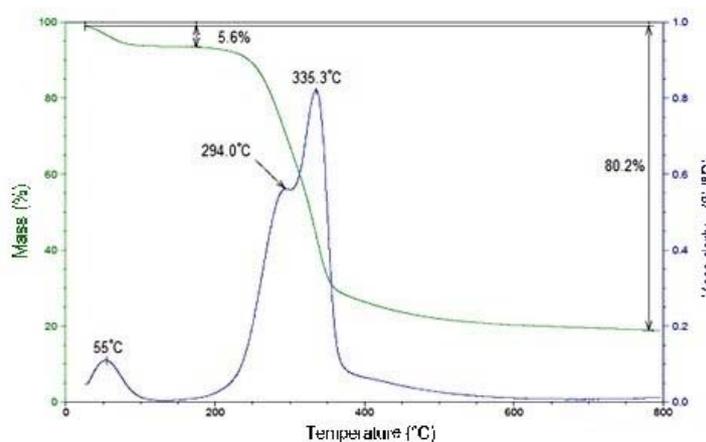


Figure 4. The results of thermogravimetric analysis of lignocellulose - Fraction Celgran<sup>®</sup> C.

Smaller peak, which occurs at 55 °C in the TGA curve can be associated with an endothermic event (55.8 °C) observed in the DSC curve of used lignocellulose – fraction Celgran<sup>®</sup> C, which is shown in Figure 8. This event is likely to correspond to the glass transition temperature of hemicellulose or lignin, given that, according to Furuta et al. [37], the glass transition temperature for hemicellulose is about 40 °C and 50 °C to 100 °C for lignin. Many authors have reported vitrification of wood and its chemical components under different conditions that can considerably vary, especially bearing in mind that reducing the moisture content in the wood increases the glass transition temperature [38]. Generally, for lignin in green grass and plants, glass transition temperature (the temperature of the glass transition) is about 60 °C [39].

The curve shown in Figure 5 illustrates more pronounced endothermic event in the temperature range from 70 °C to 200 °C with the peak at about 129.7 °C. According to Monteiro et al. [40], it can be assumed that this event is associated with the release of water, in connection with the hydration of lignocellulosic structures, before macromolecular chains degradation.

The TGA curves shown in Figure 6 illustrate thermal behavior (stability) of lignocellulose composites filled with electrochemically prepared copper powder and chemically obtained silver powder at the percolation threshold. The peaks characteristic for presence of cellulose, hemicellulose and lignin have previously been explained, as well as the events that occur at 210–300 °C and 275–350 °C.

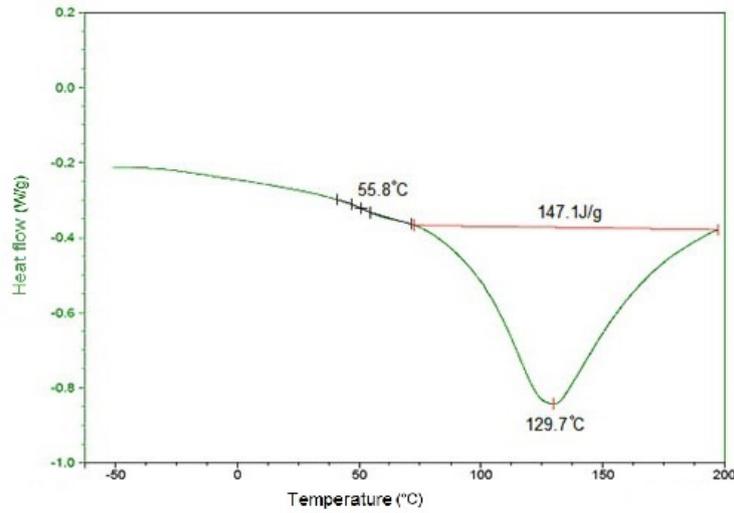


Figure 5. DSC curve of used lignocellulose - Fraction Celgran® C.

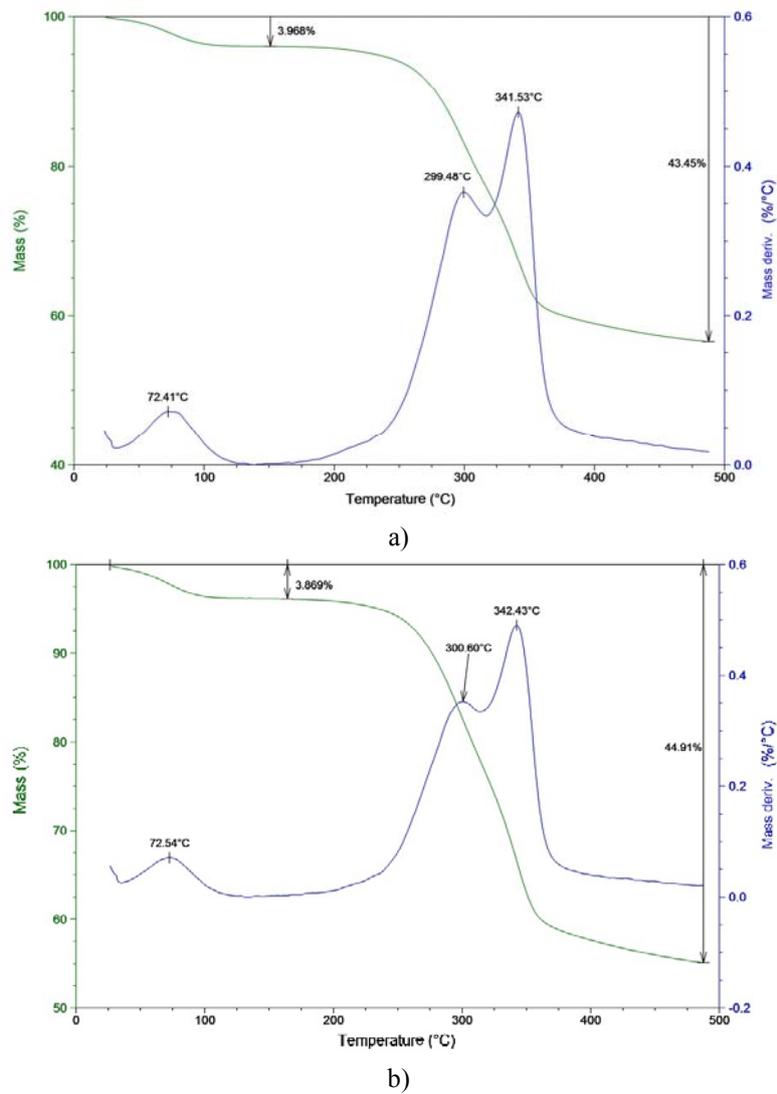


Figure 6. The results of thermogravimetric analysis of lignocellulose and a) copper powder with particle size  $\leq 45\mu\text{m}$ , treatment pressure of 20 MPa; b) silver powder particle size  $\leq 45\mu\text{m}$ , the pressure treatment of 20 MPa.

The results, on the other hand, show a slight improvement in the thermal characteristics of the composite due to the presence of copper and silver powder, which are very good heat conductors, so that the amount of heat emitted during the TGA measurements initially accumulates in copper and silver powder particles, and the change in the lignocellulose occurs only later. It was also shown that

there is no difference in the response of composites with different particle sizes.

DSC curves of lignocellulose composite filled with copper and silver powder at percolation threshold are shown in Figure 7. The smaller peaks that occur at 72 °C on TGA curve may be associated with endothermic event (73.4 °C and 71.8 °C) observed in the DSC curve of used composites.

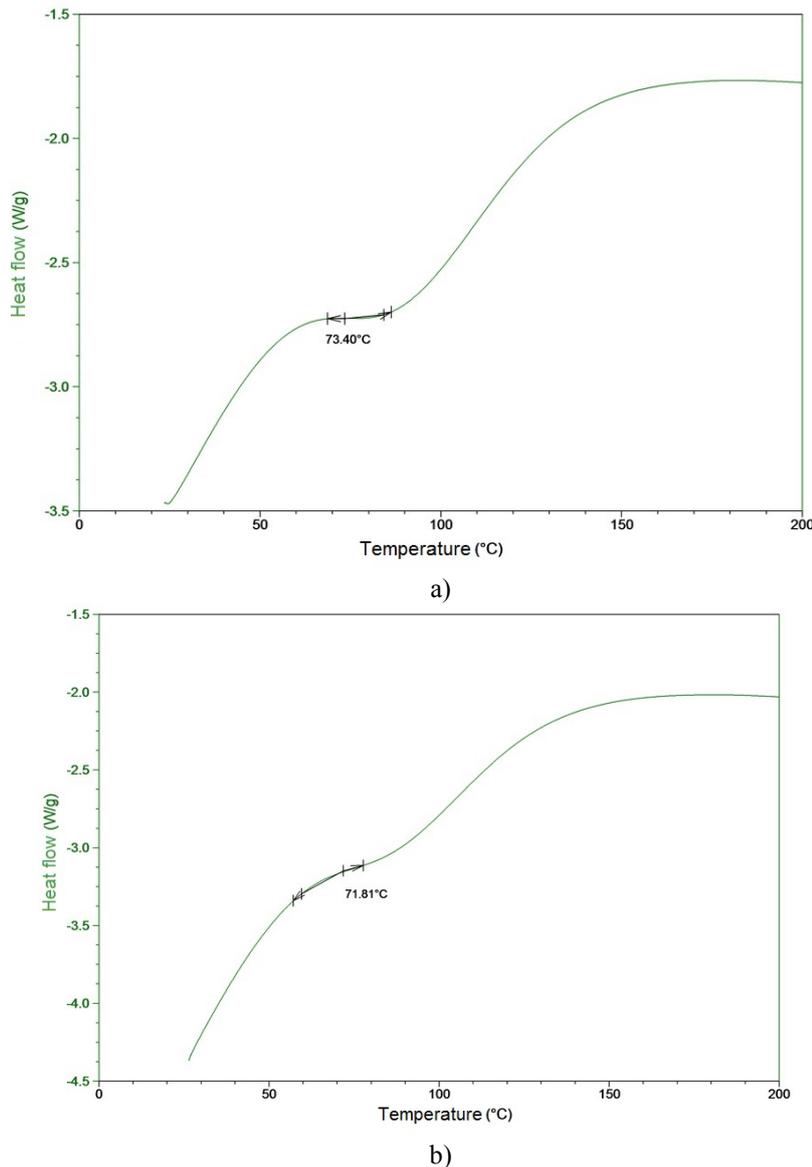


Figure 7. DSC curves of lignocellulose and a) copper powder with particle size  $\leq 45\mu\text{m}$ , treatment pressure of 20 MPa; b) silver powder particle size  $\leq 45\mu\text{m}$ , the pressure treatment of 20 MPa.

#### 4. CONCLUSIONS

The results showed that the shape and morphology of copper and silver powder, and fillers in general, play an important role in electrical conductivity and appearance of percolation threshold. Particles with a highly developed surface area and extremely dendritic and branched structure, such as

particles of galvanostatically obtained copper powder, easily and more often form interparticle contacts at lower volume fractions of powders as fillers than particles with a more regular surface.

The results of thermal analysis of prepared composites show slight improvement in thermal characteristics of the composite due to the presence of metallic fillers that are extremely good thermal

conductors, so the amount of heat emitted during the TGA measurements initially accumulates in filler particles, and only after there is a change in the lignocellulose. On the other hand, there is no difference in the response of composites with different sizes and types of particles. The glass transition temperature of lignocellulose in all prepared composites was increased by about 20 °C. This is due to improvements of thermal characteristics of the composite materials obtained by blending polymer with low heat transfer coefficient and metal fillers with high values of the heat transfer coefficient. Radiated heat is primarily locally accumulated in filler particles and conductive paths, and afterwards it is absorbed by lignocellulose. DSC analysis results support the conclusion that copper and silver powders, due to their good thermal conductivity, improved thermal characteristics of composites filled with this powder. The absence of peak at about 129.7 °C, which was present in the DSC measurement of lignocellulose sample is notable. This can be explained by the very pretreatment of the starting materials, where samples were dried in a tunnel furnace in nitrogen atmosphere. The absence of peaks indicates the absence of water in the material that is normally present in lignocellulose.

## 5. ACKNOWLEDGEMENT

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## ТЕРМИЈСКА АНАЛИЗА КОМПОЗИТА ЛИГНОЦЕЛУЛОЗЕ ПУЊЕНЕ МЕТАЛНИМ ПРАХОВИМА

**Сажетак:** Композитни материјали добијају све већу индустријску примену у свету. Композити базирани на полимерима са проводним пуниоцима су у новије време у ширем истраживачком фокусу пре свега због њиховог растућег значаја са гледишта примене. Природни полимери на бази обновљивих материјала, са додатком одабраних пунилаца могу се директно користити као савремени материјали у електроници, медицини, индустрији, као контактни проводни материјали, електромагнетни и радиоталасни штитови, фототермални оптички снимачи, електронски носеви осетљиви на одређене хемикалије, али и као економски прихватљивији катализатори. У овом раду су приказани експериментални резултати истраживања термијских својстава композитних материјала на бази лигноцелулозне матрице (LC) пуњених електролитичким бакарним прахом и хемијски добијеним сребрним прахом. Удео металних пунилаца у композитним материјалима у испитним узорцима вариран је у опсегу 1.6–30% (v/v), а узорци су припремљени хладним пресовањем – компактирањем при различитим притисцима. Карактеризација и испитивање утицаја величине и морфологије честица на термијске карактеристике добијених композита укључивала је различите технике испитивања: SEM, TGA, DSC, расподелу величина честица и мерења проводности. Резултати термијске анализе припремљених композита показују побољшање термалних карактеристика самих композита услед присуства металних пунилаца који су изразито добари термички проводници, тако да се емитована количина топлоте током TGA мерења првобитно акумулира у честицама пунилаца, па тек потом долази до промене у самој лигноцелулози. Са друге стране, нема разлике у одговору композита са различитим величинама и врстама честица. Температура преласка у стакласто стање лигноцелулозе код свих припремљених композита повећана је за око 20 °C.

**Кључне речи:** термијска анализа, композитни материјали, лигноцелулоза, DSC, TGA.

