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PRELIMINARY INVESTIGATION OF BAMBOO FIBRE METALLIZATION VIA CHEMICAL/ELECTROCHEMICAL METHODS

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Abstract: *In this study, the multifunctional potential of conductive textile fibres based on natural bamboo metalized with chemical/electrochemical deposits and copper particles/layers was investigated. The synthesis was done in three steps: pre-treatment of nonconductive textiles; chemical deposition of Cu particles by the cyclic dipping method; and obtaining conductive bamboo fibres using the electroplating method. The Cu layer was electrodeposited galvanostatically on bamboo from the sulphate electrolytes without wetting agents. To tighten the textile bamboo cloth, a frame designed using 3D printing was used because immersing the textile in the electrolyte and during drying causes wrinkles and creases, which affect the non-uniform distribution of both conductive particles and the thickness of the copper metallization layer. Characterized by SEM and optical microscopy, the chemical and electrochemical depositions of Cu around the bamboo fibres were confirmed. The particles filled the micro spaces between the bamboo fibres and on the surface of the fibres and made the network. This network between nonconductive fibre-conductive nano particles and a conductive Cu layer contributes to increasing the electrical conductivity of the synthesized multifunctional composite. The electroplating of Cu in the form of a compact layer as shells contributed to the trapping of Cu particles on the bamboo fibres themselves, so they are not removed after washing.*

Keywords: *copper, natural bamboo fibres, electroplating, flexible conductive textile, additive technology, microstructure.*

1. INTRODUCTION

One of the eco-friendly building materials that have been used for various engineering fields around for millennia is bamboo. Bamboo will acquire new properties when combined with metal elements, including conductivity, weather resistance, anti-corrosion, and electromagnetic shielding [1]. Bamboo fibres and metal coatings are separated by a natural barrier. This research suggests employing an effective and sustainable electrodeposition technology with chemical activation of non-conductive natural bamboo fibres to fabricate new bamboo-based

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metal composites (BMC), which are made of copper coating and bamboo substrate without the need for adhesive. Using a low-temperature process, the copper coatings is synthesized via electrochemically way on the activated bamboo fibres after chemical reaction and then characterized.

One of the plants that grow very fast is bamboo three, which may reach a maximum growth rate of 100 cm per day and can be exploited and cut every 5-6 years, unlike standard trees like oak, pine or hybrid varieties where you must wait several decades for yield [2]. From a material point of view, this natural source of fibres has environmental advantages such as moisture resistance, climate tolerance, and structural rigidity. Modern material technologies enable raw bamboo to be transformed into a variety of industrial goods that are seen to be perfect replacements for lumber in the construction sector.

The latest research points to a responsible and environmentally conscious use of natural resources. So, bamboo as a material becomes interesting in the textile industry as well [3]. The textile industry used more advantages of these kind natural fibres, such as: environmentally friendly characteristics, softness, breathability, antibacterial features, but textile engineering deals with solving a few disadvantages of this class of materials such as: very low capacity to absorb dyes, limits of various pre-treatment methods, ability to absorb liquids (sweat), eliminate unsuitable compounds like lignin and hemicellulose.

Zhang at all used chemical and non-electric technique, named electroless plating, in the metallization of natural materials (bamboo fibres) to investigate the effects of electroless process on the thermal stability, electrical and magnetic conductivity, and moisture absorption of bamboo fibres with variation the metal type deposits [4].

Wang at all described a hierarchically porous hybrid filter membrane based on FeOOH (iron(hydr)oxides) / bamboo fibre composite for very effective As(III)-ions removal [5]. The authors applied electrodeposition technique for synthesized nano sheets of FeOOH, directly on carbonized bamboo substrate. This paper illustrates highly applicable research of the hybrid membrane composite in treating arsenic-contaminated water.

Textiles like as bamboo or cotton can be employed in military applications that require electromagnetic shielding and medical sanitary if military members are injured, as well as in environmentally friendly applications like as electrodes for machines [6].

The chemical composition of bamboo fibre varies depending on the age of the plant, the location, i.e. the natural habitat and the type of bamboo. According to research conducted by a group of authors, bamboo fibre consists of the following compounds: 73.83% of cellulose, 12.49% of hemicellulose, 10.15% lignin, 3.16% an aqueous extract and 0.37% pectin [7].

Metallization process or surfaces-metal coating is produced by electrochemically depositing technique (old name “electroplating”) a thin layer of reduced metal ions using electric current on electrically conductive substrates [8]. In order to ensure that the metal particles adhere to the surface effectively, the substrate needs to be cleaned before electroplating. Numerous factors, including the interface between the coating and substrate, the coating and environment, and the coating material itself, have an impact on the process [9]. Galvanostatically electrodeposition technique generally involves three primary steps on cathode: (i) ion migration, (ii) electron transfer, and (iii) intercalation of adsorbed metal ions [10].

The electrochemical deposition (ED) technique of the thin metallic films or coatings on a flexible non-conductive fibre-substrate has several advantages and disadvantages over other techniques. The advantages are as follows: 1. easy controlling the morphology, deposition rate and thickness; 2. technique that is reasonably priced; 3. simple and eco-friendly process with a high deposition rate, 4. industrially scalable technique, 5. compatible technique with other metallization techniques such as chemical – electroless and spray deposition techniques, and 6. large selection of materials or alloys that can be deposited in this way. The biggest disadvantage of this technique is that it requires a conductive substrate for the current to flow between the electrodes through the electrolyte and that during deposition there may be contamination of the electrolyte and incorporation of impurities from the cathode material.

When it comes to textile materials or polymers, they are generally natural insulators and it is necessary to make the surfaces conductive, before electroplating process.

2. EXPERIMENTAL

2.1. Chemical pre-treatment of bamboo fibre textile

A piece of bamboo cloths is pre-treated with citric acid to increase the functional groups over the cellulose structure before the metal particles are deposited on the bamboo substrate. First, 0.5 l of distilled water was used to dissolve 7.5 g of citric acid, and the mixture was well-stirred. For 2h, the bamboo substrates were submerged in the solution at 100 °C. After that, the submerged fibres were dried for 30 minutes at 90 °C and rinsed with distilled water.

2.2. Chemical deposition of Cu particles on bamboo fibre textile by the cyclic dipping and reduction methods

The process of chemical reduction method was used to deposit the copper particles to achieve the conductivity of the bamboo fibres for the further electrodeposition process. Textile samples were immersed in solution of dissolved copper-sulphate (5 g) in deionized water (0.5 l) for approximately 15-20 minutes and dried in the oven at 90 °C for 10 minutes [6]. The procedure of dipping bamboo samples and drying in oven were continuously carried out up to 10 cycles.

The modified bamboo substrate was then added to the sodium hydrosulfite ($Na_2S_2O_4$) solution (10 g/l) [6]. Among all reducing agents, sodium hydrosulfite is the most consistent and produces the tiniest particles, which is it's an advantage. For almost 40-50 minutes, the reduction process was carried out. During the reduction, the colour of the bamboo fabric changes from light yellow to brown, which is proof that the reduction has been done successfully. In this way, the activation of non-conductive fibres and reduction of copper were successfully performed, and an excellent foundation was created for the further step of electrochemical deposition of copper.

2.3. Electrodeposition method of copper films on bamboo fibre textile

Galvanostatic regime – DC (direct current) with electrolyte magnetic mixing (DC/MS regime) applied and used to generate copper films on modified bamboo substrate at constant current density (j = 100 mA·cm^{-2}). The following electrolyte was utilized in the electrodeposition processes: 240 g/l $CuSO_4 \cdot 5\,H_2O$ + 60 g/l H_2SO_4 + 1 l H_2O. Copper particle-coated activated bamboo cloth served as the cathode of the source, and copper metal bars served as the anode. The electroplating bath solution was constantly agitated (100 rpm). The temperature and pH-values were maintained at 25 ± 0.5 °C and 0.30, respectively. The copper thickness is controlled by an optical microscope. The surface of the deposition is 1 cm × 1 cm, and the surface of the entire frame on which the bamboo fabric was stretched was 4 cm × 4 cm. The design of the frame using the 3D printing method for fabric tensioning will be shown in the results section.

2.4. Characterization of bamboo fibres

2.4.1. Optical microscopy

An optical microscope with the lowest magnification was used to observe pure bamboo fibres, then bamboo fibres with deposited copper particles, and to observe the thickness of the copper films deposited by the electrodeposition method with variations deposition times (30, 60, 90, and 120 minutes).

2.4.2. Field Emission Scanning Electron Microscope

The microstructure of the raw bamboo fibres; activated bamboo fibres with copper particles, and electrodeposited copper films on textile were investigated using a 20 kV emission scanning electron microscope (FE-SEM Mira3 Tescan XMU). This FE-SEM was also utilised to investigate the structural characteristics of pure copper coatings electrodeposited on modified bamboo fibres. Sample of raw bamboo fibres have been sputtered with a thin layer of Au prior to imaging to achieving conductivity. The other samples (bamboo + Cu particles and bamboo + Cu particles + Cu films) did not require sputtered with a conductive Au layer.

The image analysis software named Image Pro Plus [11] was applied in order to processing FE-SEM pictures. This program is very suitable for determining copper particle size, fibre's diameter and distribution of individual particles on bamboo fibre.

2.4.3. Water absorption test

Before water absorption test, all the bamboo-fibres samples were placed in an oven for at least 12 h to reduce the moisture. Then, raw bamboo sample, bamboo + Cu particles, and bamboo + Cu particles + Cu film (4 cm × 4 cm) were immersed in deionized water. To evaluate the effect of absorption water during the experiment, the content of water absorbed in the bamboo-materials were calculated by the weight difference. The mass of dry samples and samples after immersion in water was measured. Weights of samples were measured with an analytical balance. The amount of absorbed water (Q) at the time (t) was defined as [12]:

$$Q = \frac{m - m_0}{m_0} \cdot 100 \qquad (1)$$

where m (g) was the bamboo-based samples mass after immersion in water at the time t (min), and m_0 was the dry specimen mass (g). The amount of absorbed water - Q values, was plotted vs. time to give the water absorption curve. Before weight detection (wet samples), the samples were first centrifuged.

3. RESULTS

3.1. 3D-printing-PLA frame design

The production of the bamboo textile tensioning frame was carried out using additive technology. An acid-resistant and environmentally friendly filament was chosen. In the enclosure realization, polylactic acid (PLA) thermoplastic and biodegradable polymer [13] with a diameter of 1.75 mm was used.

The diameter of the nozzle of 3D printer was 0.4 mm. The nozzle's maximum temperature is usually defined by software, and according to the material characteristics. Also, PLA is environmentally acceptable and is a non-toxic thermoplastic material. It is known to be derived from renewable sources such as cornstarch. The following parameters should be considered in printing process: infill density, wall line contours, infill orientation, and number of shells.

The selected printing parameters are shown in Table 1. The realized PLA filament frame with woven bamboo fabric is shown in Figure 1.

The production of auxiliary tools facilitates the work in the deposition of copper particles and the uniform deposition of the copper film. On the other hand, it allows us to fix the textile electrode in the solution and adjust the height as well as the distance from the copper electrode. An opening is left in the middle of the holder, which allows connecting the contacts without them getting wet, which is another advantage of the holder designed in this way.

Table 1. Printing parameters

Printing parameters	Values
Layer Height	0.15
Wall Line Contour	2
Top Layers	2
Bottom Layers	2
Printing Temperature	210°C
Build Plate Temperature	65°C
Printing Speed	50 mm/s
Travel Speed	80 mm/s
Infill Density	100%
Infill Orientation	-45°/+45°

Figure 1. Designed holder with a frame made of PLA filaments for the needs of tensioning bamboo textiles during metallization process.

3.2. Optical microscopy of bamboo samples, before and after metallization

The photographs taken on the optical microscope are shown in Figure 2. Figure 2a shows bamboo fibres in their original form before modification and reduction. Figure 2b shows bamboo fibres after deposition of copper particles, while Figures 2c-f represent photographs after an electroplating of copper film with variation of plating times. In Figure 2b, the fine deposited copper particles cannot be observed, but will be confirmed using FE-SEM microscopy.

The diameter of the metallized fibres ranges from 60 to 300 μm (depending on the deposition time), indicating that the deposition rate is 2 μm / min, approximately. The extension of the deposition time affects the joining of the metallized fibres and the bending of the fibres inward (Figures 2d and 2e), due to the increase in the mass of the metal layer. Further extension of the deposition time (120 min) leads to the formation of a copper powder structure, see Figure 2f. It is interesting that the adhesion strength of the copper film to the modified bamboo fibres is very good, without falling off the metallized layer.

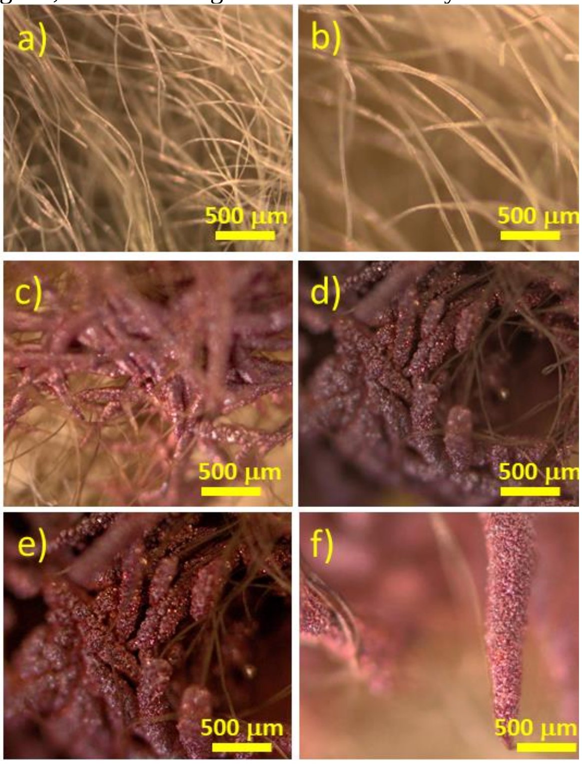

Figure 2. The photos from optical microscope of a) raw bamboo fibres (non-treated), b) bamboo fibres with Cu particles (chemically activated). The electrodeposited copper films with variation deposition times on activated bamboo fibres were given, also: c) t = 30 min, d) t = 60 min, e) t = 90 min, and f) t = 120 min. The galvanostatically mode was used and constant current density (j = 100 mA·cm^{-2}).

3.3. Water absorption test

In Figure 3 the water absorption curves for three samples: raw bamboo fibres, bamboo + Cu particles (after 10 cycles of dipping method), and bamboo + Cu particles + copper film (electrodeposited sample obtained using current density – j = 100 mA·cm^{-2} and deposition time t = 30 min) are presented. Comparing metalized and non-metalized bamboo fibres, the improvement of water hostility can be recorded.

The maximum amount of absorbed water, Q, (Figure 3) is 225 % (for raw bamboo), 161 % (for bamboo + deposited Cu particles) and 155 % for bamboo coated with Cu films. From the apparent absorbed water curves, bamboo fibres with Cu particles and Cu films show comparable weaker wetting properties than raw bamboo fibres.

The copper particles deposited on the bamboo fabric have the function of hindering the penetration of water into the bamboo fabric and cellulose chain [14, 12]. As such, they act as a super moisture barrier and increase the hydrophobicity of the fabric. The high concentration of lignin on surface of bamboo fibres and specific microstructure of these natural fibres seems to be responsible for their water absorbed properties.

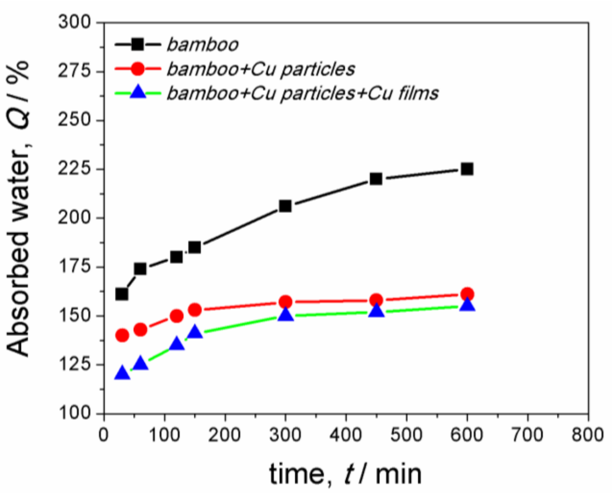

Figure 3. Water absorption curves for bamboo (black line), bamboo with Cu particles deposited chemically (red line), and bamboo fibres with Cu particles and electrodeposited Cu films (green line).

3.4. Microstructural analysis of uncoated/coated bamboo fibres

The FE-SEM micrographs with different magnifications of uncoated (Figures 4a and 4c), and copper coated bamboo fibres with Cu particles before reduction process (Figures 4b and 4d) are presented. The structure with well-developed micro-bubbles and the striped structure are confirmed by FE-SEM analysis.

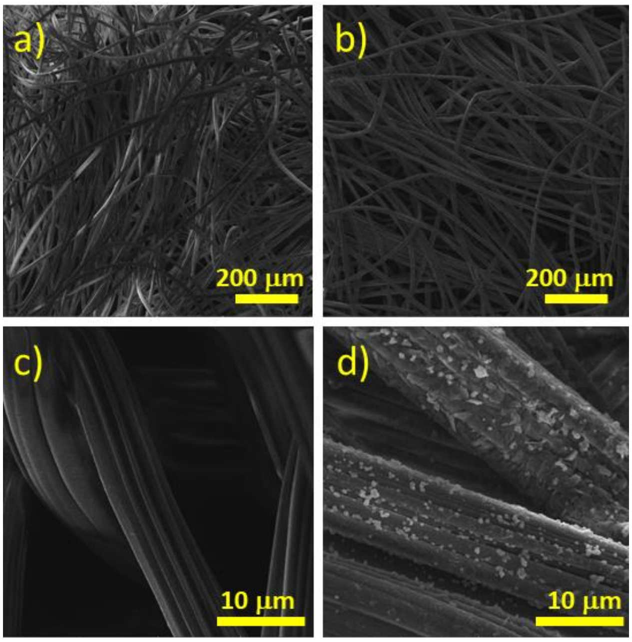

Figure 4. The FE-SEM micrographs of a) raw bamboo fibres (uncoated sample), and b) bamboo fibres with Cu particles activated on chemically ways. The magnifications were: × 200 (a, b), and × 5 000 (c, d).

The uncoated bamboo fibres have a very smooth and compact surface (Figure 4c), and some vertical holes are observable. These vertical grooves are very suitable places for copper crystallites after metallization, because these grooves prevent the precipitation of nano particles from falling off (Figure 4d). The bamboo + Cu particles sample is uniformly covered with Cu nano particles and very well dispersed on bamboo surface (Figure 4d). We can see that the surface of bamboo + Cu particles sample is rougher than that of raw bamboo sample if compared Figures 4c and 4d.

The average diameter of the measured bamboo fibres is 11 µm, and the distribution of diameters are from 5.5 for smaller fibres to 16.5 µm for larger ones (Figure 5a). The formation of different shapes of Cu particles can be seen with variations of particle's diameters in the range of 155 to 550 nm (see Figure 5b). The average diameter of the deposited copper nanoparticles on the bamboo fibres is 325 nm.

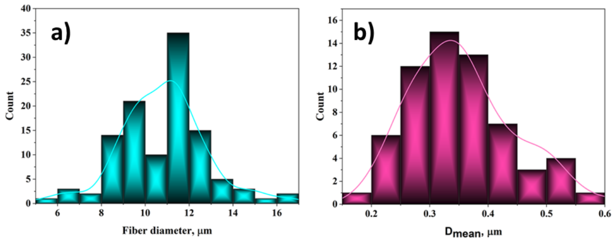

Figure 5. The distribution of a) bamboo fibre diameter and b) copper particles size deposited on bamboo fibre before reduction process.

The FE-SEM micrographs of copper films electrodeposited on activated bamboo fibres with Cu particles (Figures 6a and 6b) are presented.

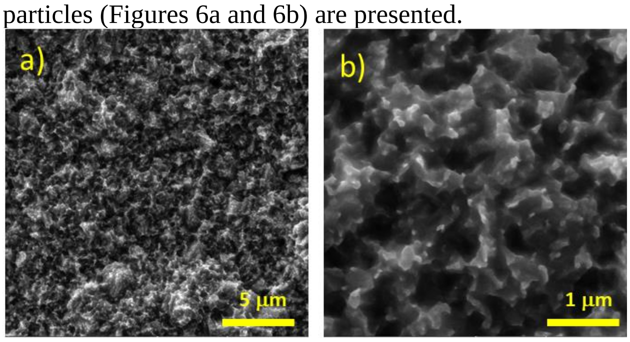

Figure 6. The FE-SEM micrographs of electrodeposited copper films on activated bamboo fibres after 30 minutes of electrodeposition process: a) magnification is × 5000, and b) × 50 000.

Two different magnifications were applied: × 5000 and × 50 000. The electroplating time was fixed at 30 minutes. As seen from these figures, the fine-grained Cu films were formed at the modified bamboo fibres. The honeycomb-like structure that turns into a copper powder form is noted at higher magnification (Figure 6b). Copper nano sized grains tend to form micro agglomerates and holes between them. There is a possibility that these cavities retain air, and by their very nature represent a gaseous barrier for the penetration of water during absorption measurements [14]. The reduction of water penetration into Cu films such as obtained nanostructured films can also be explained by the increase in surface roughness [15].

4. CONCLUSION

Copper film was deposited on modified bamboo-fibre substrate by dipping/reduction processes to prepare bamboo + Cu particles + Cu film composite. The copper particles were distributed on the bamboo fibre very good, with diameter size about 325 nm. By chemical reduction of copper particles on bamboo fibres, it is obtained a conductive substrate for further electrochemical deposition of copper films.

Using additive technology, a fabric tensioning frame was designed. An environmentally friendly material (PLA) was used.

The water absorption curves showed a higher resistance to water penetration in the composite than in pure bamboo fibres. The water resistance of the textile was achieved by simple metallization, and thus the electrical conductivity is expected to increase of the textile. Further research will be focused on characterization electrical properties of the composite.

Similarly, the conductive bamboo-based textiles composites showed washing stability, and without observed loss of copper film after intense washing in the washing machine.

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