Composites Science and Technology 72 (2012) 828–834

Contents lists available at SciVerse ScienceDirect

Composites Science and Technology

journal homepage: www.elsevier.com/locate/compscitech

Electromagnetic interference shielding, mechanical properties and water absorption of copper/bamboo fabric (Cu/BF) composites

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A R T I C L E I N F O

Article history:
Received 28 July 2011
Received in revised form 1 February 2012
Accepted 11 February 2012
Available online 19 February 2012

Keywords:
A. Textile composites
B. Electrical properties
B. Mechanical properties
Electromagnetic shielding interference

A B S T R A C T

Copper/bamboo fabric (Cu/BF) composites were prepared by electroless deposition via a tin-free process. The process involved 3-aminopropyltrimethoxysilane modification, noble metal (Au or Pd) activation and electroless copper planting of BF. The copper deposition rate via Pd catalytic process was 1.01 mg/cm^2 h, higher than that by Au catalytic process (0.85 mg/cm^2 h). The microstructure of Cu/BF composites was analyzed by scanning electron microscopy (SEM), and the copper coatings were composed of ball-shaped copper particles. The composition and chemical state of copper layers were measured by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) spectra, Cu^0 was detected but copper dioxide was not found in both spectra. The electromagnetic interference, water absorption, mechanical tension, conductivity and adhesion properties of Cu/BF samples (weight ratio of Cu/BF: 0.36 ± 0.01) were measured to obtain the qualities of the composites.

1. Introduction

Bamboo fabric (BF) is made from the raw material of bamboo. It is produced by an eco-friendly process without chemical additives. BF is also a unique biodegradable textile material. As a natural cellulose fabric, BF can be 100% biodegraded in soil by microorganisms and sunshine [1,2]. Scientists have found that BF owns an unusual anti-bacteria and bacteriostatic bio-agent. BF is praised as "the natural, green and eco-friendly textile material of 21st century" [3,4]. However, BF is an insulator, a serious problem with electromagnetic interference (EMI), which can cause noise signals and even malfunction of the electronic appliances, is encountered [5]. One effective technique to overcome the EMI problem is to improve the electrical conductivity of BF by incorporation of conductive fillers in the insulate matrix. Generally, insulator can be made electrically conductive composites by either coating or compounding with conductive materials. Among these investigations, copper coated fabrics provide the composites with good EMI shielding, high strength and elasticity modulus, light weight, and high aspect ratio of fabrics [6–9].

Since electroless copper deposition takes place only on conductors, it is necessary to use a catalyst to seed the insulator's (BF's) surface with catalytic metal particles. Traditionally, a two-step treatment is used in which a $SnCl_2$ solution acts as a sensitizer and a $PdCl_2$ solution as an activator to provide catalytic metallic Pd sites. The method uses tin which is known to be toxic and therefore it is not suitable for medical implants and human-bodies [10,11]. From the economic and environmental points of view, as well as the simplicity in process operation, it is of importance to develop a tin-free, one-step activation process for the industry [12,13].

In the present work, electroless copper planting on natural bamboo fabrics by a tin-free process was reported. Firstly, the bamboo textile was modified by 3-aminopropyltrimethoxysilane (hereafter abbreviated as silane), and NH_2 groups was grafted to the surface of the substrate [14]. Secondly, the grafted bamboo fabrics (BFs) were activated by Au or Pd particles in solution via Au–N or Pd–N chemical bonds [15]. Finally, the activated BFs were covered by copper layer by electroless deposition. Various characterization techniques were utilized to obtain information on the sample morphology, and the quantity of Cu/BF composite. Moreover, the mechanical properties and wetting behavior of the copper coated BF samples were investigated, and compared them with the original natural bamboo textiles.

2. Methods

2.1. Copper coating on BF

Plain weave 100% natural bamboo fabrics (BFs) (108 × 58 counts/cm^2, 220 g/m^2) with a thickness of 100 μm in white color were used as the substrate. The surface area of each specimen is

Abbreviations: BF(s), bamboo fabric(s); Cu/BF, copper/bamboo fabric; SE, shielding effectiveness; EMI, electromagnetic interference; Silane, 3-aminopropyltrimethoxysilane; PVP, polyvinylpyrrolidone; Au-process, Au catalytic process; Pd-process, Pd catalytic process; Au-process sample, samples from Au catalytic process; Pd-process sample, samples from Pd catalytic process.

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doi:10.1016/j.compscitech.2012.02.012

200 (20×10) cm^2. 3-Aminopropyltrimethoxysilane was purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). Other reagents were of analytical grade and were used without further purification unless otherwise mentioned.

2.1.1. Silane modified BF

BFs were ultrasonically cleaned in acetone and ethanol, respectively, for 5 min and dried at 60 °C for 24 h. The treatment of fabrics with 3-aminopropyltrimethoxysilane (0.05 M) modification was carried out in 80/20 v/v ethanol/water (100 ml) for 24 h under nitrogen atmosphere and heated at 100 °C for 4 h in order to promote the actual chemical coupling [16,17]. After the treatment, the BF samples were washed in an ethanol/water (80/20v/v) solution at room temperature.

2.1.2. Preparation of metal colloids

Au and Pd colloids were synthesized by the reduction of a metal salt by $NaBH_4$ in the presence of polyvinylpyrrolidone (PVP) at 0–5 °C for one day, which gave a stable aqueous suspension containing metal nanoparticles [18]. A 0.05 mmol of noble metal salt ($HAuCl_4 \cdot 4H_2O$, or $PdCl_2$) was dissolved in 90 ml water. In the case of $PdCl_2$, NaCl (0.25 mmol) was added to dissolve it. For the preparation of the Au colloids, an aqueous solution (5 ml) of 10 mg of PVP was added to the solution, and then, an aqueous solution (1 ml) of $NaBH_4$ (0.2 mmol) was poured into the mixture with vigorous stirring. For the Pd colloid preparation, the amount of PVP was reduced to 1 mg to enhance the catalytic activity. After stirring for 1 h, the solution was kept at 0–5 °C for one day.

2.1.3. Activation of modified BF

The activation of the silane modified BFs by Au or Pd colloid was made by immersion of the BF samples in the aqueous metal colloid solution for 24 h at room temperature. Then the BF samples were taken off from the solution and rinsed with deionized water for 5 min to remove physical absorption particles.

2.1.4. Copper deposition

Electroless deposition of Cu onto the activated surface (area: 20×10 cm^2) was performed at room temperature from tartrate/formaldehyde bath containing (g/l): $CuSO_4 \cdot 5H_2O$-20, KNa-tartrate-100, NaOH-20, Na_2CO_3-15 and formalin (38%) as reducing agent-20 ml/l, at pH 12.0–12.5 [19]. In the post-treatment stage, all the Cu coated BFs were rinsed with deionized water at room temperature for 20 min immediately after electroless copper plating and then dried in an oven at 60 °C. The Cu coated BFs were conditioned according to the standard practice for conditioning and testing textiles ASTM D1776-04 before measurement [20]. Copper deposition rate was calculated from the weight gain of the specimen before and after the electroless plating procedure and plating time, and the unit was expressed as mg/cm^2 h.

2.2. Characterizations of copper coating

Scanning electron micrographs (SEM) were obtained using an electron microscope (XL 30, Philips, Eindhoven, Netherlands). X-ray diffraction (XRD) patterns of bamboo composites (2θ ranges from 5° to 94°) were recorded at room temperature with scanning speed of 0.15°/min using Cu Kα radiation (λ = 0.154 nm) from a 40 kV X-ray source and diffracted beam monochromator (Rigaku D/max-γB, Tokyo, Japan), operated at 100 mA. X-ray photoelectron spectroscopy (XPS) measurements were performed on a 5000C ESCA system (PHI, Minnesota, USA) with Mg Kα source at 14.0 kV and 25 mA. Spectrum analyzer (AT5011, ATTEN, Shenzhen, China) was used to measure the shielding effectiveness (SE) of Cu/BF composites (sample area: 20×10 cm^2). The coaxial transmission line method as described in ASTM D 4935-99 was used to test the electromagnetic interference shielding effectiveness of the conductive fabrics. For SE reported here, at least ten sample measurements were performed and averaged.

2.3. Bonding test

For the qualitative evaluation of adhesion, a standard Scotch®-tape test (ASTM D 3359 cross-cut tape test performed with a Scotch®-Ruban Magic Tape$^{TM/MC}$ (3 M, Minnesota, USA)) was used. The adhesion strength was checked by pulling the tape to assure any film did not get peeled off from the substrate or not [21].

2.4. Tensile test

All samples were conditioned at 65 ± 2% relative humidity and room temperature for 24 h before measuring to relieve any localized stresses caused by handling during preparation. Measurements were performed on ten samples (150×50 mm^2) which were prepared according the standard ISO 13934-1:1999 (65 ± 2% relative humidity, room temperature) [22,23]. Tensile properties (Young's modulus E, breaking force F and failure strain ε) of BF samples were obtained at room temperature by using a tensile testing machine (CMT6104, Shenzhen, China) with a gauge length of 100 mm, the machine was equipped with a 10 KN capacity load cell. The BF samples (one set in the warp direction and the other in the weft direction) were loaded at a constant crosshead displacement rate of 100 mm/min until rupture. For mechanical data reported here, ten sample measurements were averaged. It should be noted that, for copper coated samples, the weight ratio of Cu/BF was 0.36 ± 0.01, since most of the textiles for commercial EMI protection had metal/fabric weight ratio of 0.3–0.4 [24]. And this kind of sample was also used for the following measurements in the text.

2.5. Water absorption test

Before water absorption measurements, all the BF samples were placed in a desiccator under vacuum with P_2O_5 for at least 24 h to reduce the moisture content to the maximum at room temperature. In that way, initially, the moisture content of all the treated fabrics was highly reduced and was below 1% [25,26].

The above treated BF samples (5×5 cm^2) were immersed in deionized water, or kept in an environmental condition of 65 ± 2% relative humidity and room temperature. To evaluate the effect of absorption phenomena during the experiment, the content of water absorbed by the BF sample was calculated by the weight difference between the weight of the textile before and after water absorption. Weight was measured with an electronic microbalance (FA1104, Shunyu, Shanghai, China) to a resolution of 1 μg. The amount of absorbed water (Q) at the time (t) was defined as:

$$Q = [(M - M_0)/M_0] \times 100 \quad (1)$$

where M was the specimen mass (g) at the time (t) and M_0 was the dry specimen mass (g). Q values were plotted vs. time (in hours) to give the water absorption curve [27,28]. For water immersion process, the samples were performed on a centrifuge (80-1, Jintan, Changzhou, China) for 30 s (speed: 1000 rpm) before weight detection [29].

3. Results and discussion

3.1. Characterization of Cu/BF

3.1.1. SEM analysis

The surface morphology of thin metallic films may affect their electrical, mechanical, and optical properties. SEM micrographs with different magnifications of uncoated and copper coated