Hydrophobic Treatment for Jute Fibers Based on Zinc Oxide Nanoparticles

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ABSTRACT

This work aims at developing a hydrophobic treatment for jute fibers based on the grafting and growth of zinc oxide (ZnO) nanorods on the fiber surface. The first step consists in removing impurities from the fiber surface by a scouring treatment. In the second step, the jute fibers are coated with a layer of ZnO nanoseeds. A hydrothermal process is carried out as the third step to ensure a uniform growth of ZnO nanorods on the surface of the jute fibers. Finally, a hydrophobic treatment is performed on the ZnO nanorod-covered jute fibers using stearic acid (SA), a typical fatty acid. A large improvement in the fiber hydrophobicity was obtained without any negative effect on strength and thermal stability. Complementary measurement by scanning electron microscopy and X-ray diffraction were also performed and reveal a hexagonal system for the ZnO nanorods.

Keywords: jute fiber, zinc oxide, nanorods, stearic acid, hydrophobic treatment

1 INTRODUCTION

The use of ZnO nanoparticles in the textile sector was the subject of several studies aimed at making fibrous materials multifunctional and more resistant [1]. For example, applying ZnO nanoparticles to natural fibers could make them superhydrophobic. This can be done by combining the nanoscale surface roughness created with ZnO nanoparticles with a hydrophobic treatment [2].

With its low cost, low density, large availability, and interesting specific mechanical performance, jute is a natural fiber largely used in the fields of goods packaging and civil engineering [3]. However, it is hydrophilic and biodegradable. These characteristics make it incompatible with hydrophobic matrices generally used in composite manufacturing, resulting in delamination and cracks [4]. Making it hydrophobic can help improve its compatibility with organic matrices as well as its resistance to biological degradation, which would open a wide range of new opportunities for jute fibers.

Nanoparticle immobilization on the fiber surface can be done by a hydrothermal treatment [5], by application of a synthetic binder [6] or by electroless deposition [7] for instance. The shape and size of the nanoparticles are directly related to the operational conditions. They can exist as nanorods, nanoflowers, nano-discs, nanospheres, etc. Their geometrical characteristics may affect the properties of the treated fiber, including its wettability. Trials were made using a hydrothermal process to grow ZnO nanorods on the surface of jute fibers. This type of process was favoured because of its low cost and ease of implementation. The effect of each step of the treatment was assessed in terms of coating uniformity, fiber morphology, water contact angle, thermal stability, and fiber mechanical properties.

2 EXPERIMENTAL

2.1 Materials

Recycled jute fibers were graciously provided by Leigh Textile Inc. (Canada). Sodium hydroxide (pellets) (NaOH), nonwetting agent Triton X-100, and SA (97%) were purchased from Fisher Scientfic. Zinc nitrate hexahydrate (Reagent Grade, 98%) (ZnNi), zinc acetate dihydrate (ACS Reagent, ≥98%) (ZnAc) and hexamethylenetetramine, (ACS Reagent, ≥99.0%) (HMTA) were purchased from Sigma-Aldrich. Anhydrous ethanol (EthOH) was purchased from the Societé des Alcools du Québec.

2.2 Treatment Method

The treatment proceeds with four steps (Figure 1). A scouring treatment is initially applied to the jute fibers by immersing them into 8 $g.L^{-1}$ of NaOH water solution and a 1.5 $mL.L^{-1}$ of Triton X-100 (step 1). The mixture is maintained under stirring conditions at 95°C for 60 min. The fibers are then rinsed with cold water, dried at room temperature, and stored in a desiccator.

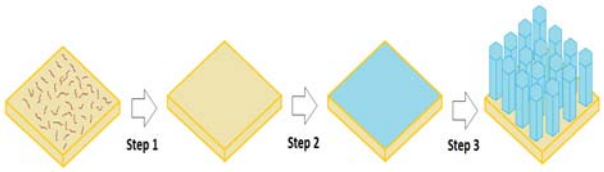

Figure 1: Schematic representation of the three initial steps of the hydrophobic treatment.

For step 2, a ZnO nanoseed solution was prepared according to [8-9] with the following modifications: 25 mM of NaOH and ZnAc were dissolved separately in EthOH and kept at 60°C under vigorous stirring until their

complete dissolution. The NaOH solution was then added drop by drop into the ZnAc solution under stirring at 60°C. The resulting solution was then heated in a water bath at 60°C until it became clear.

The scoured jute fibers were impregnated with the ZnO nanoseed solution for 15 min and dried at 120°C for 15 min. This treatment was repeated 4 times to ensure an optimal fixation of the ZnO nanoseeds onto the fiber surface.

The ZnO seeded fibers were then immersed in a solution composed of 50mM of hexamethylenetetramine and zinc nitrate hexahydrate and left at 95°C for 5 h to promote the growth of the ZnO nanorods (step 3). They were then rinsed with distilled water and dried at room temperature.

Step 4 involved a final dip of the fibers into a 20 mM SA-EthOH solution for 3h to make them hydrophobic followed by a 15 min drying period at 100°C.

2.3 Characterization Methods

The surface morphology of the untreated and treated jute fibers was observed at 5 kV with a field emission scanning electron microscope (FE-SEM) Hitachi SU-70. Each sample was previously coated with a very thin gold layer using an Emitech K550X metallizer in order to ensure sufficient electrical conductivity.

The crystalline characteristics of the ZnO nanoparticles grafted on jute fiber surface were determined with a PANalytical diffractometer using the Cu-Kα radiation generated at 45 kV. Samples were scanned between 2θ = 4-100° at 1.2°.min^{-1} with a step of 0.033°.

The wettability of the treated and untreated jute fibers was evaluated by dynamic water contact angle (θ) measurement using a DCAT-11 tensiometer. θ was computed using the following formula:

$$\theta = \cos^{-1}\left(\frac{F.g}{2\pi\rho.\sigma_{lv}}\right) \quad (1)$$

With: -F: force of interaction between water and the jute fiber at zero buoyancy (mN)
- g: gravitational acceleration (9.805 m.s^{-2})
- ρ: jute fiber average diameter (50 µm)
- σ_{lv}: water surface tension (72.75 mN.m^{-1})

The effect of the hydrophobic treatment on the mechanical properties of the jute fibers was assessed with a Zwick Z050 dynamometer according to the standard test method ASTM D 3822-07. The mechanical performance was evaluated in terms of breaking force and elongation at break on individual fibers conditioned at 21°C and 65% RH for 48 hours.

The thermal properties of the treated and untreated jute fibers were characterized by thermogravimetry using a TGA Q500. 10 mg fiber samples were heated at 10°C.min^{-1} rate in nitrogen up to 800°C. Then the atmosphere was switched to air to reach full combustion.

3 RESULTS

3.1 Surface Morphology

Figure 2 shows the effect of each step of the treatment on the jute fiber surface morphology. The fiber surface remained smooth during the first two steps of the treatment, i.e. scouring and ZnO seeding. However, Figure 2-b shows the existence of small particles fixed on jute surface which indicate the deposition of a very thin layer of ZnO seeds on the fiber surface. From the third step onwards, the surface became rough due to the growth of the ZnO nanorods (Figure 2-c).

Despite corrugations on the surface of jute fibers and the use of recycled fibers, the nanorod growth appears to be uniform. This indicates that the scouring treatment applied initially is efficient at cleaning the fiber and activating the grafting sites on its surface. The ZnO nanorods display a hexagonal shape and an average diameter of 150 nm (Figure 2-d).

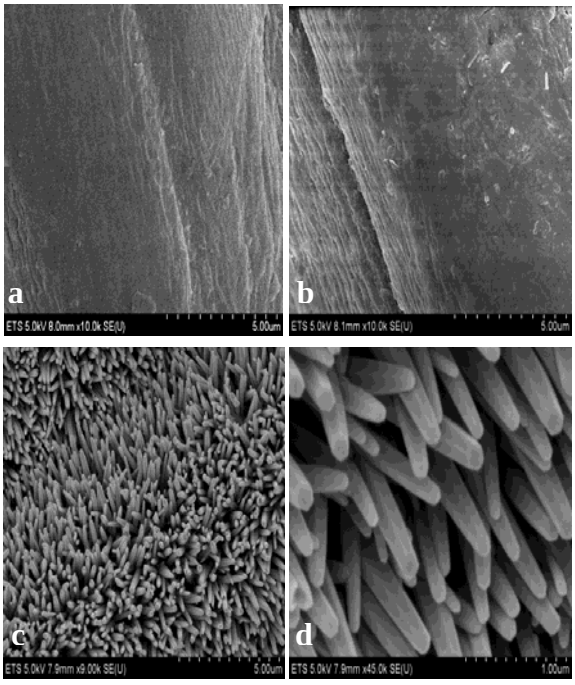

Figure 2: SEM pictures: a) scoured jute; b) ZnO seeded jute; c) and d) jute fiber coated with ZnO nanorods.

3.2 Crystal Structure

X-ray diffraction results in Figure 3 show that treated and untreated jute fibers have two common peaks located at 14.6° and 22.3°. They can be attributed to cellulose I and lignin respectively [10]. Higher peak intensity was observed with seeded jute fibers. This possible increase in crystallinity may be explained by the reaction between ZnO seeds and lignin and cellulose reactive groups.

ZnO coated jute fibers present three additional peaks located at 31.8°, 34.4°, and 36.3°. These peaks can be attributed to (100), (002) and (101) ZnO crystal planes. This indicates that ZnO grows along its c-axis on the jute fiber surface [11]. This confirms the formation of a hexagonal system for the ZnO nanorods.

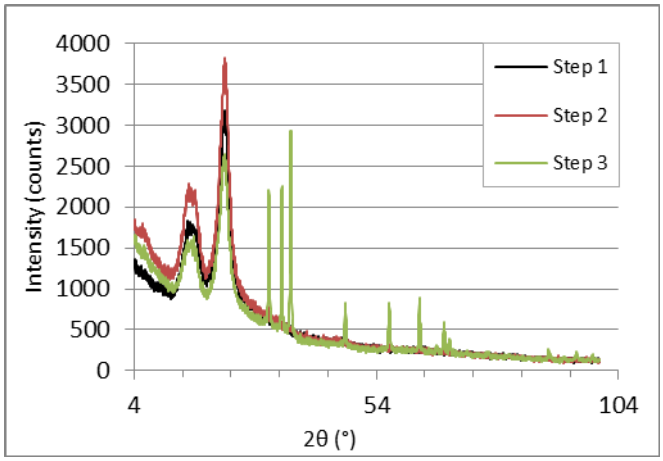

Figure 3: XRD results for each step of the jute fiber ZnO treatment.

The ZnO nanorods growing directions are controlled during the hydrothermal treatment. ZnNi is a generator of Zn^{2+} ions which react with the OH^- ions produced by HMTA. HMTA also acts as an apolar chelating agent [12]. It binds to the side surfaces of the nanorods in the a and b directions, cutting access to Zn^{2+} and leaving only epitaxial growth of ZnO in the c direction.

It may also be noted that an equimolar ratio of HMTA and ZnNi is required to obtain a hexagonal nanorod shape [12]. A higher HMTA concentration leads to tapered nanorods system formation.

3.3 Hydrophobicity

The result of the measurement of the dynamic water contact angle is shown in Figure 4 for the scoured jute fibers as well as fibers treated with ZnO, SA, and a succession of both treatments. Scoured jute fibers display a hydrophilic behavior with a contact angle of 33°. The fiber becomes more hydrophobic when it is covered by polar ZnO nanorods but it still in the hydrophilic range ($\theta<90°$).

A significant change was observed with SA treated jute fiber; the contact angle reached 115° for the treated scoured fiber, indicating that it had become hydrophobic. With the addition of a nanoscale surface roughness underneath the fatty acid coating, the jute fiber became superhydrophobic with a contact angle of 148°.

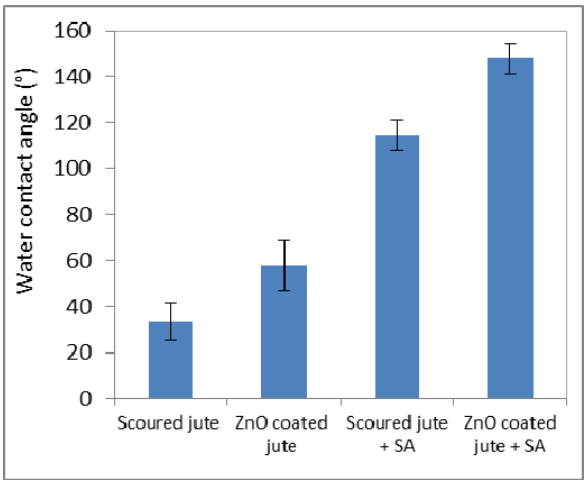

Figure 4: Wettabilty results for untreated and treated jute fiber.

3.4 Mechanical Properties

Figure 5 shows the fiber breaking force after each step of the hydrothermal process as well as for the as-received recycled jute fibers. A 16% reduction in breaking force is observed after the scouring treatment. After the ZnO nanoseeding step, the jute fiber mechanical performance is further decreased by 9%. This may be attributed to the sensitivity of jute fiber to the basic pH of the scouring and ZnO nanoseed solutions as well as an enventual partial hydrolysis of cellulose in the ZnO nanoseed solution.

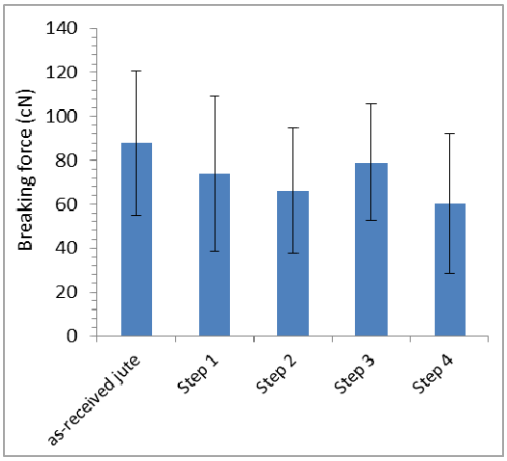

Figure 5: Mechanical performance results for each step of the hydrothermal treatment.

This reduction is mostly offset as a result of ZnO nanorod growth. Such increase in strength with nanoparticle coating has already been reported with other natural fibers [13] and may be attributed to a stiffening effect of the rigid nanorod coating on the fiber surface.

Finally, the mechanical performance of jute fiber is once again reduced after the fatty acid treatment in step 4, with a

32% loss in breaking force. This may be attributed to the sensibility of jute fibers to acids.

3.5 Thermal Analysis

A slight reduction in the jute fiber degradation temperature may be observed in Figure 6 after the ZnO nano seeding step compared to the scoured fiber. This may be attributed to the sensitivity of jute fiber to the basic pH of the nanoseed solution.

On the other hand, the ZnO nanorods grafted on the surface of the jute fibers improve slightly their thermal resistance; an increase in the cellulose degradation temperature 276 ± 5°C at the end of step 2 to 315 ± 7°C at the end of step 3 is observed. This may be associated with the thermally protective nature of the ZnO nanorod layer around the jute fiber [14].

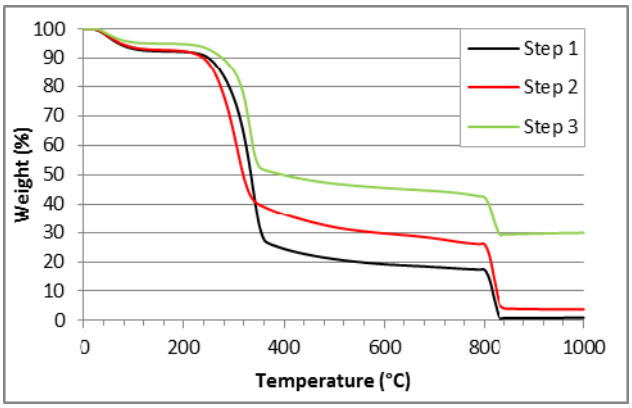

Figure 6: TGA results for each step of the jute fiber ZnO treatment.

TGA measurement also provided the quantity of ZnO deposited on the jute fiber surface. Results indicate that the nanoseed step add 3% of ZnO while the percentage reaches 26% at the end of nanorods growth.

4 DISCUSSION

In addition to the superhydrophobicity provided to jute fibers by the ZnO nanorod coating developed in this study, other functionalities may be obtained. For example, ZnO nanoparticles have been shown to display antibacterial and antifungal activity [15]. They could limit the natural sensitivity of jute fibers to biological degradation. ZnO nanoparticles are also strong UV-blockers [2] and could help protect jute fibers against photodegradation. With such a multifunctional coating, jute fibers may find new applications as reinforcement for composites, for example in the aerospace industry where weight is the main issue.

5 CONCLUSION

This study demonstrates the potential of ZnO nanorods grown on jute fibers to made them superhydrophobic after further treatment by a fatty acid. The water contact angle increased from 33° for the scoured fiber to 148° after the ZnO nanorod/stearic acid hydrothermal treatment. The ZnO coating obtained is uniform and consists in a forrest of the hexagonal nanorods. The effect of the treatment on the jute fiber thermal and mechanical properties remains limited.

This low cost, fast, and ecological treatment could be applied industrially, for example to promote the adhesion between matrix and reinforcement in jute fiber reinforced composite parts.

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