Composites Part B 95 (2016) 9–17

Contents lists available at ScienceDirect

Composites Part B

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

Reinforcement of ozone pre-treated and enzyme hydrolyzed longer jute micro crystals in poly lactic acid composite films

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ARTICLE INFO

Article history:
Received 2 March 2016
Received in revised form
25 March 2016
Accepted 30 March 2016
Available online 7 April 2016

Keywords:
A. Particle-reinforcement
A. Recycling
B. Mechanical properties
E. Surface treatments

ABSTRACT

In present study, jute fibers were pre-treated with ozone gas to remove the lignin. The effect of ozone treatment on change in single fiber strength, fiber surface morphology, whiteness, moisture absorbency, etc was studied. For comparison purpose, chemical pre-treatment of jute fibers was also carried out. In subsequent step, untreated, chemical and ozone pre-treated jute fibers were hydrolyzed by cellulase enzymes for separation of longer jute micro crystals. The influence of non-cellulosic contents on the enzyme hydrolysis and morphology of obtained micro crystals was presented. Later, 3 wt% of these jute micro crystals were incorporated into poly (lactic acid) matrix to prepare composite films by solvent casting. The reinforcement behavior was evaluated from tensile tests, dynamic mechanical analysis, and differential scanning calorimetry.

1. Introduction

In recent years, renewable materials have gained significant importance due to limited availability of petroleum resources and increased awareness of environmental concerns. The natural fibers are increasingly replacing glass, carbon and other synthetic fibers in composite applications [1]. Jute is commonly used as reinforcement in composites due to its higher strength and higher aspect ratio. In addition, jute has another important inherent properties such as biodegradability, moderate moisture regain, good thermal and acoustic insulation and low price [2]. Nevertheless, for further growth of jute fiber based composites, it is necessary to overcome certain drawbacks. Jute fibers have few disadvantages such as high moisture absorption, swelling, low toughness, limited compatibility with some matrices, low processing temperature, low thermal stability, high biodegradability, and low dimensional stability [3]. To overcome these drawbacks, considerable efforts have been made by the researchers such as surface modification of jute fibers, isolation of elementary cellulose fibrils/crystals, etc.

Jute fibers consist of lignin (12–14%), hemicellulose (21–24%), cellulose (58–63%), fats and waxes (0.4–0.8%), inorganic matter (0.6–1.2%), nitrogenous matter (0.8–1.5%) and traces of pigments [4,5]. However, the presence of non-cellulosic substances found to hinder the reaction between hydroxyl groups of fibers and polymer matrices, which consequently deteriorated the mechanical properties of composites [6]. In order to have better bonding between fibers and matrix, the non-cellulosic contents should be removed. The various surface treatments such as sodium hydroxide, peroxide, organic and inorganic acids, silane, anhydrides and acrylic monomers have been attempted by researchers in previous works to improve the compatibility between fibers and matrix [6]. However, such chemical treatments are not environment friendly and require more energy, time and water. The motivation of present work was to search for alternative techniques for surface modification of jute fibers.

The oxidation of jute fibers using ozone gas is one of the alternatives over chemical treatments for removal of lignin. Ozone is an oxidizing agent with a strong oxidation potential of 2.07 V [7]. It is an unstable allotrope of oxygen containing three atoms. Ozone is highly reactive towards compounds incorporated with conjugated double bonds and functional groups of high electron densities [8]. Due to high content of C=C bonds in lignin, ozone treatment of jute fibers is likely to remove lignin by release of soluble compounds of less molecular weight such as organic acids. Therefore, the ozone treatment is environment friendly, causes minimal degradation of cellulose and hemicelluloses, and requires less energy, time and water [9]. The effectiveness of ozone treatments in the textile wet processing has already been demonstrated. The ozone treatment was found suitable for bleaching of cotton [8]. In another study, the effect of ozone was found to improve the whiteness degree and dye

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http://dx.doi.org/10.1016/j.compositesb.2016.03.093
1359-8368/

ability of Angora rabbit fibers [10]. The study of ozone treatment on silk reported it to turn into yellowish, harsh and without luster [7].

More recently separation of individual cellulose fibrils or crystals is reported in many research works for achieving extremely higher mechanical properties suitable in high performance composites [11]. In order to disintegrate fibers to the level of mechanically strong cellulose elementary fibrils without complete dissolution, it is necessary to work on chemically less aggressive hydrolysis concepts. The ozone pre-treatment of jute fibers before the action of enzyme hydrolysis is considered to be advantageous in this aspect. Due to removal of lignin by ozone pre-treatment, the jute fibers are expected to have less strength and more open structure. In this way, even a less concentration of cellulase enzyme or less hydrolysis time is likely to provide extensively entangled networks, higher strength and higher aspect ratio of the cellulose elementary fibrils. Cellulases are a group of multi component enzyme systems produced by microorganisms that help in the degradation of cellulose. The filamentous fungus *Trichoderma reesei* is one of the most efficient producers of extra cellular cellulase enzyme [12]. There are further two sub-groups of cellulase that affect crystalline and amorphous regions of cellulose separately. Cellobiohydrolase attacks the crystalline structure of cellulose, whereas endogluconase catalyzes the hydrolysis of amorphous cellulose [13].

In present study, jute fibers were pre-treated with ozone gas for removal of lignin. The change in single fiber strength, fiber surface morphology, whiteness, moisture absorbency, etc of jute fibers due to ozone pre-treatment is discussed in detail. For comparison purpose, chemical pre-treatment of jute fibers was also carried out. In subsequent step, untreated, chemical and ozone pre-treated jute fibers were hydrolyzed by cellulase enzymes for separation of longer jute micro crystals. The influence of non-cellulosic contents on the enzyme hydrolysis and morphology of obtained micro crystals was investigated. Later, 3 wt% of jute micro crystals were incorporated into poly (lactic acid) (PLA) matrix to prepare composite films by solvent casting. The reinforcement behavior was evaluated from tensile tests, dynamic mechanical analysis, and differential scanning calorimetry.

2. Materials and methods

2.1. Materials

Short waste jute fibers were obtained from India. The fibers were measured to have a density of 1.58 g/cm^3, modulus of 20 GPa, tensile strength of 440 MPa and elongation of 2%. PLA was purchased from NatureWorks LLC, USA through local supplier Resinex, Czech Republic. The PLA had a density of 1.25 g/cm^3 and the average molecular weight (Mw) of 200,000. The chloroform, which was used as solvent, purchased from Thermofisher Czech Republic. The TEXAZYM AP cellulase enzyme was provided by the company INOTEX in Czech Republic. The optimal pH in range of 4.5–5.5 and temperature in range of 50–60 °C was selected for enzyme activity.

2.2. Pre-treatment of short jute fibers

In order to remove the non-cellulosic contents in jute fibers, chemical and ozone pre-treatment was carried out before the enzyme hydrolysis.

2.2.1. Chemical pre-treatment

It was carried out sequentially with 4% sodium hydroxide (NaOH) at 80 °C for 1 h and with 7 g/L sodium hypochlorite (NaOCl) at room temperature for 2 h under pH 10–11. Subsequently, the fibers were antichlor treated with 0.1% sodium sulphite at 50 °C for 20 min.

2.2.2. Ozone pre-treatment

Jute fibers were treated with ozone gas for the duration of 4 h. For effective ozone treatment, one humidification system was introduced between Oxygen Concentrator Krober MEDIZINTECHNIK and Ozone Generator TRIOTECH GO 5LAB-K as shown in Fig. 1. The jute fibers were pre-humidified by spraying 50% water (w/w) and then placed inside the container for ozone treatment of 4 h. The ozone concentration 4.5 mg/L with charging time of 1.5 min was used. The oxygen production setting of 5.0 L/min was used as an input source for the Ozone Generator. After ozone treatment, the jute fibers were washed with 1 g/L nonionic surfactant for 1 h in order to remove residual ozone. The fibers were then rinsed by distilled water and dried at 105 °C in an oven for 3 h.

2.3. Characterization of pre-treated jute fibers

2.3.1. Fiber morphology

The surface morphology of untreated jute fibers (UTJF), chemical treated jute fibers (CTJF) and ozone treated jute fibers (OTJF) was observed using scanning electron microscope. SEM images were taken on TS5130-Tescan SEM at 20 kV accelerated voltage.

2.3.2. FTIR analysis

The removal of lignin and modification of internal physical microstructure of the jute fibers after ozone treatments was evaluated by FTIR analysis. It was performed on Nicolet iZ10 reflection ATR technique on an adapter with a crystal of ZnSe.

2.3.3. Single fiber strength

The single fiber strength of untreated, chemical and ozone treated jute fiber was evaluated from VIBRODYNE Lenzing Instruments in order to know the change in mechanical properties. The single fiber strength was performed with a gauge length of 10 mm at a crosshead speed of 10 mm/min and at pre-tension of 2000 mg. Total 50 readings were taken and then average was calculated. In the end, the additional properties like moisture absorption, whiteness index, etc. were also determined.

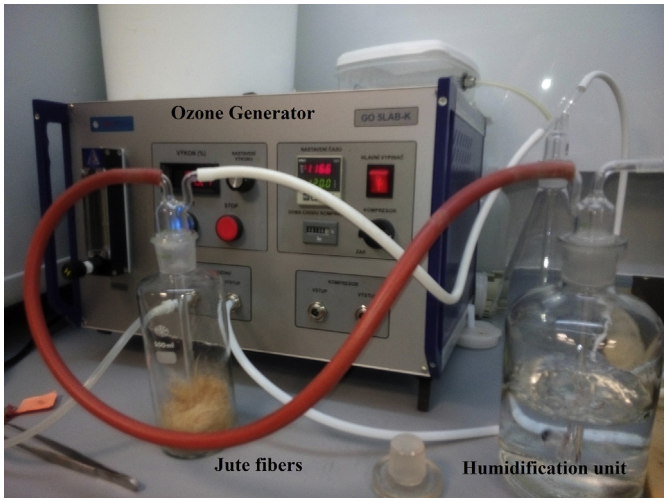

Fig. 1. Set up for ozone treatment of jute fibers.