



## Research paper

# Fabrication and evaluation of regenerated cellulose/nanoparticle fibers from lignocellulosic biomass



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## ABSTRACT

This paper presents a new approach for converting lignocellulosic biomass into regenerated cellulose fibers. A major research objective is to examine the effectiveness of nanoparticles as cellulose fillers on improving thermal and mechanical properties of the regenerated cellulose fibers. Pure wood and bagasse cellulose solutions and cellulose/nanoparticle composite solutions were prepared using N-methylmorpholine-N-oxide (NMMO) solvent, and were spun into filament fiber through an extruding device. The thermal analysis methods of TGA and DSC were used for characterizing the solution properties. The regenerated bagasse cellulose fiber was also compared with regenerated wood cellulose fiber and nanoparticle/cellulose fibers in terms of mechanical strength and elongation. Distribution of nanoparticles in the cellulose matrix was evaluated using a method of image analysis for fiber photomicrographs. Tested results indicated that the tensile strength of the regenerated bagasse cellulose fiber was considerably lower than that of the regenerated wood cellulose fiber but the elongation was consistent between these two fibers. The research also revealed that adding a small amount of nanoparticles to fill in the wood cellulose matrix resulted in an increase of the cellulose fiber tensile strength and modulus by 14% and 6% respectively, and a decrease of cellulose glass transition temperature. The nanoparticle distribution in the cellulose matrix was correctly detected by a computing image technique based on a mean shift method.

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## 1. Introduction

In the U.S., almost all biomass feedstocks are used for bioenergy production. Cellulose biomass, often divided into wood and non-wood biomass, is a natural resource for cellulose polymer. Wood pulp is a major commodity product of cellulose polymer from wood biomass. In contrast, sugarcane is one of the nation's primary agricultural crops. It not only is a major feedstock supply for the production of sugar and bioethanol, but also produces a large quantity of bagasse, the residue from sugarcane refinery. The U.S. sugarcane production varies around 32 billion kilograms per year [1]. Considering the fact that water content in sugarcane is in the range of 50–60%, it could be estimated that about 16 million tons of dry bagasse would be produced annually after sugar refinery.

Traditionally, the bagasse residue is utilized as an in-house combustion fuel to generate electricity for energy compensation,

because bagasse has an average cellulose content of 40%. However, this traditional method is unable to use up all bagasse biomass produced annually. Other approaches for making use of the bagasse biomass economically and environmentally are needed, among which a conversion of bagasse into cellulose polymers is worth investigating. A primary application of cellulose polymers is the manufacture of cellulosic man-made fiber, such as Rayon, a regenerated cellulose fiber commercially produced in the 1900s [2–4]. The production of rayon fiber uses a chemical approach that generates a cellulose derivative called sodium cellulose xanthate. Because this chemical method requires a heavy use of sodium hydroxide and sulfuric acid, environmental pollution by manufacturing effluents becomes a serious concern. The production of rayon fiber has been decreased dramatically in the U.S. and EU countries since the 1980s. However, to date, rayon is still a favorite fashion fiber dominating the global use of cellulose fibers because of high production capacity and price competitiveness [5].

For fashion marketing and environmental protection, an eco-friendly approach for manufacturing regenerated cellulose fiber became an industrial need. It was found that N-methylmorpholine-

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N-oxide (NMMO) is one of the non-derivative solvents to directly dissolve cellulose pulp [6]. With a series of R&D efforts, a new type of regenerated cellulose fiber using the NMMO technology was commercially produced in the 1990s with the trade name Tencel<sup>®</sup>. Now the name lyocell is recognized by the Federal Trade Commission as a generic subclass of rayon. It is known that the regenerated cellulose fiber using the NMMO technology can be produced with higher dry and wet strength [7–12]. The NMMO-spun cellulose fiber also renders good fiber thermal stability, chemical stability, fabric dimensional stability, and dye ability [13–16]. In the meantime, the NMMO from the washing unit can be recycled through a solvent recovery system where the dilute NMMO solvent can be concentrated to a desired concentration for dissolving new pulp [17].

The purpose of this research was to study the feasibility of using NMMO solvent to produce regenerated cellulose fiber from bagasse biomass. Compared to commercial wood pulp, bagasse pulp usually has a low quality given a lower molecular weight, lower polymerization degree, and lower cellulose purity. This would inevitably make bagasse cellulose behave differently when dissolved in NMMO solvent and coagulated in spin bath. As a result, tensile properties of regenerated cellulose fiber from bagasse would likely be unable to compete with that of Tencel<sup>®</sup> fiber from wood. To address this challenge, we decided to add nano fillers into the cellulose to improve fiber mechanical properties [18–21]. By adding nano fillers, polymer materials change their structures and physical properties while still keeping same chemical properties. For instance, silicon nanoparticles have been added into polyethylene to produce nano-silicon/polyethylene composite fibers during the melting spinning process. Test data indicated that the tenacity of the nano-silicon/polyethylene fibers was increased by 11–30% [22–25]. The objectives of this study were to explore a practical way to convert lignocelluloses biomass into regenerated cellulose fibers using the NMMO solvent and solvent spinning process; to improve tensile strength of the regenerated bagasse cellulose fiber by adding nano particles into the NMMO cellulose solution; and to examine the distribution of nanoparticles inside the regenerated cellulose fiber and cellulose crystalline orientation using a computerized image analysis technique.

## 2. Experiment

### 2.1. Raw materials

The cellulose powder used in this study was from Buckeye Technology Inc., with 1720 of degree of polymerization. The cleaned bagasse residue fiber was soaked with 1 N sodium hydroxide solution using a weight ratio of 10:1 (liquid: fiber). The liquid was then heated to 100 °C and cooked for 3 h. The alkalinized fiber was separated from the black liquid and thoroughly rinsed with tap water. The rinsed fiber was soaked in a 6% chlorine liquor for bleaching, followed by cold water rinse and conventional oven drying. The dried bagasse pulp was cut and ground into powder before dissolving.

The solvent of 4.8 M NMMO water solution (50% in water, density 1.13 g/mL) was purchased from Aldrich and was used to dissolve cellulose powder. The nano materials were supplied by Nanostructured & Amorphous Materials Inc. They included multi-wall carbon nano-tube (purity of 95%, outside diameter of 3–20 nm, and length of 0.1–10 μm), carbon nano-fiber (purity of 95%, outside diameter of 80–200 nm, and length of 0.5–20 μm), and amorphous nano silicon oxide particles with 99% of purity and 80 nm of average spherical particle size.

### 2.2. Preparations of nano materials and cellulose-NMMO-water solutions

The method to prepare cellulose/nanoparticle NMMO solution in a lab scale is as follows. The finely powdered wood pulp was put into a spherical flask. Then an amount of 50% aqueous NMMO solution was added to the pulp powder. A nanoparticle material such as carbon nano-tubes or nano silicon oxide particles was added into the solution and dispersed by an ultrasonic device (VWR Model 50T) for 1 h. The ratio of nanoparticle to cellulose was 0.1/99.9 by weight. Cellulose solution of about 0.2 mM (wood pulp mass fraction of 4%) was prepared by a Rotavaporator under the vacuum condition and maximum heating temperature of 100 °C controlled by a water heating bath. The molar solution concentration for bagasse pulp is not known as the molecular weight of cellulose from bagasse pulp is not known, but the ratio of bagasse pulp to NMMO was the same as that of wood pulp. By removing excess water under continuous vacuum and rotation, a viscose cellulose solution was formed when the NMMO/H<sub>2</sub>O balance approached 87/13. Studies showed that NMMO was thermally stable when temperature was below 120 °C. The prolonged processing time at higher temperatures resulted in an increased NMMO decomposition [26,27]. Therefore, the temperature was held between 75 °C and 100 °C during the preparation of cellulose solution and the solvent spinning of the cellulose/nano-filler composite fibers.

The cellulose/nanoparticle composites were spun into cellulose fibers by an advanced capillary extrusion rheometer ACER 2000 from Rheometric Scientific Inc. (Fig. 1). Before the start, the cellulose/nanoparticle solutions were equilibrated in the barrel at a predetermined temperature (75 °C) to reach a steady state. Under the mechanical force, the solution was forced out through the capillary die of 1-mm diameter at a shear rate of 800 s<sup>-1</sup> into a spin water bath. The NMMO solvent in the cellulose solution system was dissolved in the water bath, resulting in a coagulation of the cellulose/nanoparticle composite fiber in the water bath. The produced composite fibers were dried at 100 °C for 2 h and then were conditioned at 25 °C for 48 h before the fiber mechanical properties were tested.

### 2.3. Testing procedures

Test of tensile strength for the composites fibers was referred to the ASTM D 3822-01 for the single textile fiber break strength and tested using an Instron tester Model 4301. The gauge length was set to 25 mm for all the tensile tests. The crosshead speed was set to 15 mm/min. The sampling rate was 6 points per second. A range of 25–30 fiber specimens were randomly selected to test tensile properties for each type of fibers from pure cellulose and nano filler composite cellulose fibers. The thermal stability of the fibers was measured from 30 to 600 °C at a heating rate of 5 °C/min by a thermogravimetry analyzer 2950 TGA HR (TA Instruments). The glass transition temperature was determined by an MDSC 2920 (TA Instruments). A scanning electron microscope Cambridge 260 Stereoscan was used to observe the microstructures of the cellulose fibers. The obtained fiber SEM images were imported into a PC-based image analysis program for evaluating the nanoparticle distribution. This image analysis technique was based on a mean shift method (MS). MS is a nonparametric clustering technique for image segmentation and edge detection. In the MS procedure, each data point is moved in the feature space towards the weighted average of its neighboring points. The procedure is repeated until convergence is reached, and then clusters can be detected. In this application, the feature space is a 3D space which spans the image lattice and intensity, and each cluster corresponds to a homogeneous region. After the MS analysis, the background is smoothed and

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