



Strength and modulus improvement of wet-spun cellulose I filaments by sequential physical and chemical cross-linking



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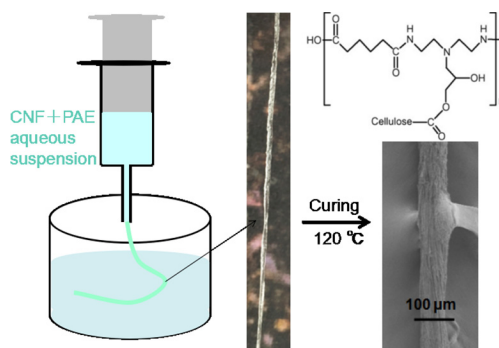
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HIGHLIGHTS

- Cellulose nanofibres with high aspect ratio were produced from raw jute fibers and the dimension was also characterized.
- The cellulose nanofibre suspension was successfully wet-spun into filaments with high strength and modulus.
- Strength and modulus of the filaments was improved by physical and chemical cross-linking using polyamide-epichlorohydrin.

GRAPHICAL ABSTRACT



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ABSTRACT

Cellulose nanofibres (CNFs) were characterized by microscopy (transmission electron microscopy (TEM) and atomic force microscopy (AFM)) and small-angle neutron scattering (SANS); they were observed to be 5.4 nm wide and 1.8 nm thick while their length was >400 nm. The CNF suspension was successfully wet-spun into highly oriented filaments owing to flow-induced and contact-induced alignment. The mechanical properties of the filaments increased with an increase in the spinning rate due to the higher degree of orientation along the axial direction of the filaments. It is noted that the strength and modulus of the filaments increased from 268.7 MPa and 22.8 GPa to 369.8 MPa and 28.9 GPa, respectively, after physical and chemical cross-linking using a polyamide-epichlorohydrin (PAE) resin. This phenomenon might be attributed to the fact that the tensile fracture of the dense CNF/PAE filaments involved the breakage of both CNFs and interfibre bonds. The resulting filaments show potential as an excellent replacement for naturally and industrially produced fibres.

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1. Introduction

The processing and production of high-performance cellulose-based materials are currently the focus of the materials research community, owing to their specific renewability, low density, low cost, and good

mechanical properties [1]. More recently, there have been quite a few advances in the development of nanocellulose [2–7], the smallest constituent of a cellulose fibre. Nanocellulose was applied as an effective reinforcing filler in nanocomposites [8], biological scaffolds [9], gas barrier films [10], and water purification membranes [11,12], on the basis of its high aspect ratio and surface area.

It has been reported that single cellulose nanocrystals possessed an ultra-high Young's modulus, which was estimated to be in the range of 100 GPa to 160 GPa [13]. However, such high mechanical properties

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can never be obtained with cellulose-based materials, even natural fibres consisting of highly oriented cellulose nanofibres. Even so, many efforts have been made to achieve the theoretical modulus value of cellulose nanocrystals by aligning cellulose nanofibres (CNFs). Iwamoto et al. [14] were the first to develop wet-spun cellulose filaments from TEMPO-oxidized cellulose nanofibres. It was found that the mechanical properties of the produced filaments were strongly dependent on the spinning rates and the cellulose sources; the highest tensile strength and Young's modulus of cellulose fibres spun from wood are 321 MPa and 23.6 GPa, respectively. The influence of CNF hydrogel quality on the properties of the spun filaments, including mechanical strength and stability in water, were further investigated by Lundahl et al. [15]. The hydrogel properties were affected by the CNF solid fraction and surface charge. Hooshmand et al. [16] successfully produced CNF filaments by dry spinning without the use of any organic solvents. However, highly concentrated CNF suspensions were needed for dry spinning, as a result, the voids in the spun filaments caused by the air entrapped in the suspension (due to the low fluidity of concentrated CNF suspensions) lowered the mechanical properties. In order to improve the mechanical properties of CNF filaments so that they can be used as replacements for cotton and industrially produced polymer fibres, Hakansson et al. [17] combined hydrodynamic alignment and dispersion-gel transition to achieve a tensile strength of 490 MPa using a self-designed flow-focusing channel system.

It should be noticed that the above efforts to enhance the strength of CNF filaments were based on the adjustment of the spinning process or the spinning technology. As an alternative, the strength of the material itself can be improved by processes such as cross-linking. Different ions of different valence states have been used to achieve high-modulus negatively charged cellulose nanofibre hydrogels by physical cross-linking [18–21]. High-strength CNF filaments were also fabricated when NaCl solution was transferred to the flow channel to inhibit electrostatic repulsion between the CNFs [17]. Moreover, in order to obtain a stable structure and low swelling rate, cellulose-based materials with three dimensional networks were prepared by chemical cross-linking [22–24]. To the best of our knowledge, the strengthening of CNF filaments by sequential physical and chemical cross-linking has not been investigated thus far.

Polyamide-epichlorohydrin (PAE) resin is usually used as a wet-strength agent in the papermaking industry to improve the strength of paper in water [25]. It has also been incorporated into a cellulose matrix to strengthen dry cellulose membranes and aerogels via chemical cross-linking [26,27]. The cross-linking mechanism is attributed to the formation of covalent ester bonds between the carboxyl groups of cellulose and the azetidinium groups of PAE during the curing process [28, 29]. In addition, positively charged PAE would screen the electrostatic repulsion between the negatively charged CNFs. Therefore, it is worthwhile to investigate the improvement in the strength of wet-spun cellulose filaments produced from highly charged CNFs by sequential physical and chemical cross-linking with PAE.

In this study, cellulose nanofibres were first prepared by 2,2,6,6-tetramethylpiperidinyl-1-oxyl (TEMPO)-mediated oxidation followed by mechanical disintegration. The produced CNFs were then characterized by transmission electron microscopy (TEM), atomic force microscopy (AFM), and solution small-angle neutron scattering (SANS). Subsequently, the CNFs were wet-spun into filaments at different spinning rates. Prior to spinning, various amounts of PAE were incorporated into the CNF dispersions to enhance the mechanical properties of the filaments by physical and chemical cross-linking.

2. Experimental

2.1. Materials

Raw jute fibres were purchased from Toptrans Bangladesh Ltd. (Bangladesh). Sodium bromide (NaBr, ACS grade), sodium chlorite

(NaClO₂, ACS grade), acetic acid, sodium acetate, uranyl acetate, and hydrochloric acid (36.5 wt%) were obtained from Sigma-Aldrich. TEMPO and sodium hypochlorite (NaClO, solution, 12 wt%) were purchased from Acros and Spectrum, respectively. Sodium hydroxide (NaOH) was procured from Fisher Scientific while PAE was purchased from Alibaba. De-ionized (DI) water was used throughout the study.

2.2. Preparation of cellulose nanofibres

Cellulose nanofibres (CNFs) were defibrillated from raw jute fibres by TEMPO-mediated oxidation [30]. The raw materials were first bleached using a NaClO₂ buffer solution (pH 5) at 70 °C [31]. The bleaching process was repeated several times until the colour of the jute fibres turned white. Subsequently, the bleached fibres were isolated by TEMPO oxidation and homogenized. Firstly, 10 g of the bleached jute fibres were suspended in 960 mL of DI water containing 1 g of NaBr and 0.2 g of TEMPO. The oxidation reaction started when 75 g of NaClO (12% aqueous solution) was added to the suspension. The reaction was carried out for 24 h under stirring to ensure its completion. Meanwhile, the pH value of the slurry was maintained in the range of 10.0 to 10.5. The obtained slurry was then dialyzed against DI water until the conductivity of the DI water (environment) was below 5 µS (equilibration for 12 h). CNFs were obtained after defibrillating the slurry using a homogenizer (GEA Niro Soavi, Panda PLUS 2000) for five passes. The concentration of the CNF suspension was subsequently determined by gravimetric analysis.

2.3. Wet-spinning of the cellulose nanofibres

CNF suspensions (1.0 wt% concentration) were spun into an acetone coagulation bath using a syringe with a needle of 0.9 mm diameter and 90 mm length [14,15]. The spinning rates were maintained at 5 mL/min (7.9 m/min), 10 mL/min (15.8 m/min), and 25 mL/min (39.5 m/min) by controlling the syringe pump pushing the syringe (16 mm diameter). Later, the two ends of the wet-spun fibres were held on a glass sheet under weak tension to eliminate any twist in the fibres and fibre shrinkage due to the relaxation of the oriented filaments (see Fig. 1). Subsequently, they were dried in an oven for 24 h at 60 °C.

The highly viscous 1.0 wt% CNF suspension was diluted to 0.3 wt% for easy mixing. Different amounts of PAE were added to the diluted CNF suspensions while stirring. After evaporation into 1.0 wt% hydrogel at 40 °C, the CNF suspensions containing PAE were also spun at the same conditions as neat CNF suspensions. The ratios between CNF and PAE were set at 10:0.5 and 10:1. After drying, the CNF/PAE filaments were cured at 120 °C for 3 h.

2.4. TEM and AFM measurements

The sample for TEM measurement was prepared by depositing a drop of 0.01% CNF suspension on a carbon film-coated copper grid.



Fig. 1. Drying of wet-spun CNF filaments.

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