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A novel, cost-effective and eco-friendly method for preparation of textile fibers from cellulosic pulps

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ABSTRACT

Although cellulosic fibers are increasingly used in textile products, current methods for production of cellulose-based textiles suffer certain economic and/or environmental drawbacks. We have developed a new, cost-effective and environmentally-friendly (CS_2-free) process that overcomes some of the shortcomings of existing technologies. The process is based on a modified method for periodate oxidation of cellulose that is then cross-linked with chitosan and extruded to obtain cellulosic fibers in the form of textile fibers. The produced fibers have low content of aldehyde groups (~2 mmol/g cellulose) and water retention values of 1.5–2.0 g/g fibers. The new process makes use of both hardwood and softwood pulps, and offers significant yield advantages over the use of dissolving pulp as a raw material. The mechanical, water absorbency and morphological properties of the new textile fibers and their potential applications are discussed. The potential techno-economic and environmental benefits of the process are summarized.

1. Introduction

Natural fibers such as cotton and wool have always dominated the textile markets, however, in recent years due to rise in production costs associated with the use of arable land and growing demand for fibers from newly emerged economic powers in Asia, regenerated cellulose fibers have begun to experience renaissance. For example, in 2015 the market for cellulosic fibers was 5.2 million tons which is projected to grow to 10 million tons in 2030 (Carmichael, 2015).

Fibers from regenerated cellulose, such as viscose rayon and Lyocell are increasingly used to enhance the comfort and softness of woven products (Woodings, 2001, 1995). Rayon, the main commercial product made from regenerated cellulose, is currently produced at an annual rate of 3.7 million metric tons and valued at over 10 billion dollars per year (Global Rayon Fibers Market, 2014). Viscose rayon is a wet-spun fiber produced by xanthation of dissolving pulp using carbon disulfide (CS_2), a highly toxic chemical banned in North America and Europe (Fushimi, Watanabe, & Hiyoshi, 1996). Other disadvantages related to the use of CS_2 include limited dissolving capability, high cost of solvent recovery, uncontrollable side reactions, and instability during cellulose processing and/or derivatization (Chen et al., 2007). As cellulose xanthate is soluble in sodium hydroxide (5–10% NaOH), the resultant viscose dope can be regenerated at 8–15% consistency in a coagulation bath in the form of cellulose filaments with a water holding capacity of 1 mL/g fiber (Thomas & Denning, 1978). In contrast, the Lyocell process is based on direct dissolution of cellulose in an environmentally friendly polar solvent, *N*-methylmorpholine-*N*-oxide (NMMO). However, the Lyocell production process is more expensive than rayon due to the high cost of NMMO and the use of high temperatures used for dissolving cellulose (Ingildeev, Effenberger, Bredereck, & Hermanutz, 2013; Liu, Wang, & Li, 2011). Cuprammonium rayon is another type of regenerated cellulose filament that is produced with the use of hazardous chemicals (ammonium) and accompanied by the generation of heavy metal salts that are difficult to dispose of (Philipp, 1993). In recent years, a green process for regenerated cellulose textile fibers was developed via direct dissolution of cellulose in a NaOH/thiourea solution at sub-zero temperatures (Cai and Zhang, 2005; Chen et al., 2007). The NaOH/thiourea solvent however has two major limitations: 1) limited abilities to dissolve cellulose with a high degree of polymerization (DP); and 2) the cellulose concentrations in this solvent cannot exceed 10 wt%. Furthermore, the process is energy-intensive and produced fibers have poor mechanical properties that are not suitable for textile applications. More recently, ionic liquids (ILs) have attracted much attention due to their high electrochemical and thermal stability, nonflammability, and outstanding dissolving capacity for cellulose (Rogers & Seddon, 2003; El Seoud, Koschella, Fidale, Dorn, & Heinze, 2007). ILs have

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been used to prepare cellulose or cellulose blend fibers (Hummel et al., 2016; Mundsinger, Muller, Beyer, & Hermanutz, 2015), however, there are a few hurdles that need to be overcome for the establishment of a large-scale, multi-filament, IL-based wet spinning process such as cost, toxicity and reusability of ILs.

The above-described methods for production of cellulose-based textile fibers all suffer certain techno-economic and/or environmental drawbacks. In an attempt to address these challenges we have developed a new, cost-effective and environmentally-friendly (CS_2-free) process that overcomes some of the shortcomings of existing technologies. The process is based on a modified method for periodate oxidation of cellulose that is cross-linked with chitosan and extruded to obtain cellulosic fibers in the form of textile fibers. We used chitosan as a green cross-linker by taking advantage of the functionality of its amine groups to assist in forming covalent bonds. Here we describe the new process and its advantages, and report on properties of the new textile fibers and their potential applications.

2. Experimental

2.1. Materials

Bleached softwood kraft pulp (BSWK) was obtained from a pulp mill in Canada. Sodium (meta) periodate, sodium chloride, ethylene glycol, hydroxylamine hydrochloride, chitosan (310–375 KDa, viscosity 800–2000 cP), sodium sulfate, sulfuric acid and hydrochloric acid were purchased from Sigma-Aldrich (Mississauga, Ontario, Canada). Sodium hydroxide and ethanol were supplied by Fisher Scientific (Whitby, Ontario, Canada). All chemicals were used as received.

2.2. Periodate oxidation of cellulosic fibers

Periodate oxidation was carried out in an aqueous medium under following reaction conditions: BSWK (10.0 g), sodium metaperiodate (13.6 g; 100 mol% based on moles of anhydroglucose units “AGU” (a dehydrated glucose unit) and sodium chloride (29 g; 0.5 N final concentration) were dissolved in 500 mL deionised water using a glass beaker with overhead stirrer (Caframo, Georgian Bluffs, Ontario, Canada). The reaction mixture was gently stirred at room temperature in the dark for 12 h. Thereafter, the modified pulp was filtered out and washed three times with deionized water (approximately 1L each time). The aldehyde content of the modified cellulose was 1.6 mmol/g cellulose.

2.3. Cellulose-chitosan gels

Five (5) g of modified cellulose following periodate oxidation was first dispersed in 50 g of 6 wt% NaOH solution in a stainless steel vessel that was precooled to <0 °C, and then stirred vigorously at 500 rpm and room temperature for 10 min. One (1) g of chitosan powder was dispersed in 24 g of 10 wt% NaOH solution and stirred at room temperature and 500 rpm for 20 min. Thereafter, 6.25 g of the chitosan dispersion was added to the cellulose dispersion (described above), and the mixture was stirred at room temperature and 300 rpm for 30 min. The formed dope (gel) was filtered through a 400 mesh (pore size ~40 μm) and degassed under vacuum at room temperature for 5 min.

2.4. Fiber extrusion

The dope was transferred into a syringe equipped with a needle and extruded in the form of fibers (as shown in Fig. 1) into a 12.5 wt% H_2SO_4/10 wt% Na_2SO_4 solution (selected as a coagulation bath) at room temperature and constant flow rate of 1 mL/min. The dope solidified on contact with the acid in the coagulation bath and was drawn into a wash water bath where the excess of NaOH, H_2SO_4 and/or their salt was removed. After washing, the fibers were gradually dried in air at room temperature under controlled tension using a fixed wooden frame (Fig. 1).

2.5. Characterization

The aldehyde content of the modified cellulose was determined as described by Alam, Antal, Tejado, and van de Ven (2012). The hydroxylamine-hydrochloride ($NH_2OH\bullet HCl$) standard titration method was used to calculate the amount of aldehyde groups (Marte & Owens, 1956). According to this method, the HCl released from the reaction of aldehydes and $NH_2OH\bullet HCl$ is determined by titration with NaOH solution of known normality. The aldehyde content of cellulose was calculated using Eq.

$$A_c = (V_{NaOH} x N_{NaOH)}/DW_c \quad (1)$$

where A_c is aldehyde content of cellulose (mmol/g cellulose)
V_{NaOH} is volume of NaOH (mL) required for titration
N_{NaOH} is normality of NaOH (eq/L)
DW_c is weight of dry cellulose initially dissolved (g)

The water uptake value was measured by dispersing 0.5 g of fibers in deionized water, soaking for 12 h, and then centrifuging the fibers at 1000 g for 10 min in a tube with a porous screen at the bottom for fiber-water separation. The centrifuged fibers were weighed to obtain the wet weight Y_W. After drying in oven at 105 °C, the dry fibers weight Y_d was reweighed and the water uptake value was calculated as:

$$\text{Wateruptake} = \frac{Y_w - Y_d}{Y_d} \quad (2)$$

Fourier Transform Infrared Spectroscopy (FT-IR) measurements of the samples were performed on a FTIR spectrometer using a Bruker Tensor 37 (Bruker, Ettlingen, Germany) with PIKE MIRacle diamond Attenuated Total Reflectance (ATR) accessory. Solid samples were placed directly on the ATR crystal and maximum pressure was applied by lowering the tip of the pressure clamp using a ratchet-type clutch mechanism. All spectra of measured samples from 32 scans were averaged from 550 to 4000 cm^{-1} with a resolution of 4 cm^{-1}.

The effect of crystalline properties of cross-linked cellulose with chitosan were examined by X-ray diffraction (XRD). The measurements were performed on a X′Pert Pro Diffractometer (PANalytical B.V., Netherlands) with Pixcel detector and Kα radiation (λ = 1.54 Å). The X-ray diffractograms were acquired with a 2θ (Bragg angle) range of 10–30° at a scan rate of 0.005° s^{-1}.

A TMI LabMaster tensile machine (John Chatillon & Sons, New York, USA) was used for tensile testing. The span length of the sample was 50 mm and strain rate (crosshead rate) of 5 mm/min. It is important to note that the temperature and humidity within the room were not controlled. Results obtained were presented as the average value of four independent measurements.

The morphology of the textile fibers was investigated with Hitachi Su-70 Field Emission Scanning Electron Microscope (Hitachi, Chiyoda, Tokyo, Japan). Samples were prepared on double-sided carbon adhesive discs attached to aluminium specimen stubs and then sputter-coated with carbon to improve specimen conductivity. The images were taken at an accelerating voltage of 5 kV.

3. Results and discussion

3.1. Chemical crosslinking of cellulose

Modified pulp fibers (after periodate oxidation reaction of pulp cellulose) were cross-linked with different amounts of chitosan