



## Short communication

## Controlled molecular reorientation enables strong cellulose fibers regenerated from ionic liquid solutions



Johan Sundberg<sup>a, b</sup>, Valentina Guccini<sup>a, c</sup>, Karl M.O. Håkansson<sup>a, b</sup>, German Salazar-Alvarez<sup>a, c</sup>, Guillermo Toriz<sup>a, d</sup>, Paul Gatenholm<sup>a, b, \*</sup>

<sup>a</sup> Wallenberg Wood Science Center, Sweden

<sup>b</sup> Department of Chemistry and Chemical Engineering, Biopolymer Technology, Chalmers University of Technology, 412 96 Gothenburg, Sweden

<sup>c</sup> Department of Materials and Environmental Chemistry, Stockholm University, 106 91 Stockholm, Sweden

<sup>d</sup> Department of Wood, Cellulose and Paper Research, University of Guadalajara, Guadalajara, Jalisco, Mexico

## ARTICLE INFO

## Article history:

Received 12 June 2015

Received in revised form

17 August 2015

Accepted 18 August 2015

Available online 20 August 2015

## Keywords:

Regenerated cellulose fibers

Ionic liquid

Mechanical properties

Reorientation

## ABSTRACT

Cellulose is difficult to solubilize and undergoes thermal decomposition prior to melting. In recent years ionic liquids have been evaluated as solvents of cellulose. In the regeneration process the non-solvent governs the resulting material's crystallinity. Water adsorbs to amorphous cellulose, acts as plasticizer and lowers the  $T_g$ , hence the degree of crystallinity will affect the potential strain induced reorientation. We prepared regenerated cellulose fibers from ionic liquid using different non-solvents. The influence of shear forces upon cellulose chain alignment during extrusion was simulated *in silico* based upon rheological measurements. The regenerated fibers had different physical, morphological and mechanical properties. Molecular re-orientation in fibers induced by mechanical strain, at humidities above the  $T_g$ , resulted in much improved mechanical properties with the Young's modulus reaching  $23.4 \pm 0.8$  GPa and the stress at break  $504.6 \pm 51.9$  MPa, which is comparable to commercially available cellulose fibers.

© 2015 Elsevier Ltd. All rights reserved.

## 1. Introduction

There is a dire need to transform our petrochemical based economy into a sustainable bioeconomy in order to minimize our environmental impact. The forest constitutes a vast renewable resource for different wood biopolymers, which could be utilized as substitutes to polymers from fossil fuels. Cellulose is the most abundant wood biopolymer, and provides the structural strength in plants. Different approaches to utilize nanofibrillated cellulose (CNF) inherent strength to reassembly mechanically strong materials have been evaluated [1–3]. However, in order to fully utilize the innate potential mechanical properties of cellulose a fundamental understanding of the molecular assembly and regeneration processes is necessary. By controlling the reassembly/regeneration of cellulose, bottom-up fabrication of ultra-strong materials could be possible. There is, however, a lack in understanding of the intermolecular interactions in cellulose and the subsequent effects on structure and properties caused by these interactions. Due to strong

hydrogen bonds in conjunction with its amphiphilic nature [4–7], cellulose is difficult to solubilize and undergoes thermal decomposition prior to melting [8]. Current, industrially applied, cellulose solvent systems are coupled to different environmental sustainability issues as well as difficulties in processing. In recent years ionic liquids (ILs) have been evaluated as non-derivatizing solvents of cellulose [9,10], and several reports describing the preparation of materials by regeneration of lignocellulosics from ILs have been recently published [11–18]. It has been observed that crystallinity of the regenerated materials is dependent upon the dissolution time, the regeneration process [19–22] and the choice of non-solvent [21–23]. The use of non-polar non-solvents prevents molecular stacking by hydrophobic interactions resulting in less crystalline cellulose [21,23,24]. Water plasticizes cellulose and lowers the glass transition temperature ( $T_g$ ) [25–27]. We have previously found that cellulose undergoes a phase transition at approximately 70% relative humidity (RH) [16] analogous to  $T_g$ , which allows the cellulose chains to move more freely [28,29]. Since water only absorbs into the amorphous regions of cellulose [30,31], the degree of crystallinity will directly affect the possible reorientation induced by mechanical strain. In this work, we present evidence to support re-orientation of regenerated cellulose

\* Corresponding author.

E-mail address: [paul.gatenholm@chalmers.se](mailto:paul.gatenholm@chalmers.se) (P. Gatenholm).

induced by mechanical strain, especially at 90% RH. The reoriented materials show much improved mechanical properties compared to the unstrained controls with absolute values higher than previously reported flow focused CNF fibers [3], and comparable to commercially available cellulose fibers [32–34].

## 2. Materials and methods

### 2.1. Cellulose extraction from spruce wood

Spruce cellulose was isolated by chlorite delignification according to the Wise and Timell methods [35,36]. Briefly, 150 g of wood meal was delignified with sodium chlorite at 70–80 °C, by adding glacial CH<sub>3</sub>COOH and NaClO<sub>2</sub> (15 cm<sup>3</sup>: 45 g respectively) to a 1:25 wood to liquor ratio in a three-necked round flask every 12 h four times. The obtained holocellulose (about 100 g) was then treated with 24 wt% KOH in a ratio 1:7 wt/vol for 24 h at room temperature in order to extract 4-O-methyl-glucuronarabinoxylan and galactoglucomannans. The non-soluble material was treated with a mixture of sodium hydroxide (17.5 wt%) and boric acid (4 wt%) at room temperature for 24 h to extract glucomannans. The obtained cellulose was washed with diluted acetic acid until neutral pH and air-dried on the lab bench.

### 2.2. Rheology of solutions

The rheological properties of the cellulose solution were analyzed using a Discovery HR-2 (TA instruments) at 25 °C and 70 °C. A cone plate configuration was used with a diameter of 40 mm and a cone angle of 1.99°. The shear rate was ramped from  $1 \times 10^{-2}$ –1500 s<sup>-1</sup>.

The Carreau viscosity model, defined as:

$$\eta_{eff}(\dot{\gamma}) = \eta_{inf} + (\eta_0 - \eta_{inf}) \left(1 + (\tau\dot{\gamma})^2\right)^{\frac{n-1}{2}},$$

where  $\eta_{eff}$  is the viscosity,  $\dot{\gamma}$  is the shear rate,  $\eta_0$  is the viscosity at zero shear rate,  $\eta_{inf}$  is the viscosity at infinite shear rate,  $\tau$  is the relaxation time and  $n$  is the power index was used to describe the solutions. The best fit parameters at 25 °C are  $\eta_0 = 25$ ,  $\eta_{inf} = 0.001$ ,  $\tau = 0.16$  and  $n = 0.54$ , while for 70 °C the following values were used:  $\eta_0 = 2$ ,  $\eta_{inf} = 0.001$ ,  $\tau = 0.015$  and  $n = 0.63$ .

### 2.3. Numerical velocity simulation

The incompressible Navier–Stokes equations for momentum and mass conservation were solved numerically with COMSOL Multiphysics 5. A built-in Carreau fluid model was used to take into account the shear thinning behavior of the solutions, with the best-fit parameters stated in the rheology section above. A 2d-axisymmetric geometry with no-slip boundary conditions, laminar inflow and zero pressure at the exit was used. Moreover, the resolution of the grid was seen to be converged and the error less than 1%.

### 2.4. Fiber preparation

Fibers were prepared from Spruce cellulose (DP 300–1700) [37]. A total dry weight of 0.5 g of cellulose were solubilized in 12.5 g of EmimAc (BASF, Sigma Aldrich) at 70 °C for 96 h until the solution became clear and homogeneous. The clear solutions were extruded using a 1 cm<sup>3</sup> syringe with a 0.25 mm flat tip needle into a coagulation bath of either 99.8% ethanol (Scharlau, Fisher Scientific) or MilliQ water at an approximate rate of 0.03 cm<sup>3</sup>/s. The gelled fibers were left to in the non-solvent, which was exchanged until all the

EmimAc was removed in accordance with washing protocols previously employed for similar materials [16]. The fibers were dried on Teflon sheets and dried at 105 °C for 10 min.

### 2.5. Tensile testing

The tensile tests were conducted in a DMA Q800 (TA Instruments) with an attached RH control unit to allow for controlled relative humidity during the tests. The fiber thickness (average of three measurements) was obtained using a digital caliper. The samples were mounted in the testing chamber with an approximate distance between the clamps of 1.0 cm. The samples were then allowed to equilibrate to the desired humidity before testing commenced. Two different conditions were used 30% RH at 25 °C (DCS) and 90% RH at 80 °C (WWS). A preload of 0.001 N was used and the stress was ramped with 0.15 N/min (DCS) or 0.1 N/min (WWS). A minimum of 3 replicates were tested for each fiber at each humidity.

### 2.6. Scanning electron microscopy (SEM)

Samples for scanning electron microscopy (SEM) were mounted onto aluminum stubs and sputter with gold (Edwards Sputter Coater S150B) prior to observation with a Leo Ultra 55 FEG SEM.

### 2.7. X-ray diffraction (XRD)

The x-ray diffraction patterns were acquired with a Bruker D8 Venture Single crystal diffractometer equipped with a 2D detector PHOTON-100 (1024 × 1024 px<sup>2</sup> with a pixel size of 96 × 96 μm<sup>2</sup>), using molybdenum radiation with wavelength of 0.71073 Å. The fibers were mounted with modeling clay on a brass pin orthogonal to the beam direction using a sample to detector distance of 100 mm. Still images were then obtained using an integration time of 999 s. Azimuthal plots of the most intense reflection (at ca. 9.3°) were obtained from the 2D images of the fibers using *ImageJ* v1.48 [38] and the plugin Azimuthal Average [39]. A Gaussian fitting of the profile was used to calculate the full width at half maximum (FWHM). The degree of orientation (DO) was then calculated as  $DO = FWHM - 180/180$ . Note that no significant dependency of the DO was detected after scanning the fiber radially in steps of 10°. In order to calculate the crystallinity index (CI) of the samples, images were taken rotating the sample radially using an acquisition time of 999 s. The 2D images were calibrated and corrected for detector distortion using the software Fit2D [40] with silicon powder as calibrant. The integrated powder patterns were analyzed with the software Maud [41] using the cellulose II structure [42] and fitting the background with a polynomial of 5th order and a Gaussian peak which was assumed to correspond to the amorphous content. The CI was calculated using a height ratio similar to “Method A” described by Park et al. (2010) [43], i.e., the CI was calculated as the height ratio of the most intense peak,  $I_{110}$ , normalized by the sum of heights of the crystalline and the amorphous parts, e.g.,  $CI = I_{110}/I_{110} + I_{Gauss}$ .

## 3. Result and discussion

Cellulose isolated from Norwegian Spruce was dissolved in 1-ethyl-3-methylimidazolium acetate (EmimAc) at 70 °C. The rheological properties of the cellulose solution were analyzed at 25 °C and 70 °C and the solutions showed a shear-thinning behavior due to polymer chain alignment (vide infra). The rheological properties correspond well to similar solutions under similar conditions reported in the literature [44–46]. The viscosity of cellulose IL solutions is dependent on concentration, temperature and degree of

Download English Version:

<https://daneshyari.com/en/article/5179998>

Download Persian Version:

<https://daneshyari.com/article/5179998>

[Daneshyari.com](https://daneshyari.com)