Rapid preparation of all-cellulose composites by solvent welding based on the use of aqueous solvent

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A B S T R A C T

In the present study, the dissolution of softwood fibers and fabrication of all-cellulose composites was investigated using aqueous tetraethylammonium hydroxide solution (TEAOH, 35 wt%) at room temperature. The bulk of the cellulose fibers were instantly dissolved when mixed with the solvent, and suspensions up to 3 wt% were fabricated with ease. During the dissolution, a few remaining larger fiber flocks were fully dissolved within 3 h of mixing at room temperature. TEAOH was further studied in the production of all-cellulose composites by solvent welding (partial dissolution) of cellulose fiber sheets. Tensile strength of the original cellulose sheet increased from 3.3 to 55.0 MPa only after 30 s of room-temperature solvent welding, and an increase of over 23-fold (up to 76.7 MPa) was obtained by high-pressure-aided hot-pressing of the partially dissolved sheets before drying. The demonstrated fabrication of all-cellulose composites yielded many benefits in comparison to the current dissolution systems, such as short treatment time, ambient operation conditions, and readily applicable processing solutions, which makes it a potential methodology applicable even at an industrial scale.

1. Introduction

Cellulose is the most abundant organic polymer on earth, and its broad availability makes it a promising raw material for novel applications [1]. Chemical modification or solvent-based shaping (including dissolution) of cellulose can broaden its properties, as required by various applications [2,3]. However, owing to its hydrogen bonding interaction and high crystallinity, cellulose has poor solubility in most common solvents [4]. Therefore, novel dissolution methods of cellulose have high importance in the field of sustainable chemistry and materials fabrication.

Cellulose can be dissolved using chemical derivatization (e.g., esterification [5] or carbamation [6,7]). However, these systems change the chemical and physical properties of cellulose. Cellulose can also be dissolved in various non-derivatizing solvent systems, including N-methylmorpholine-N-oxide (NMMO) [8], dimethylacedamide/LiCl [9], and molten salt hydrates [10]. However, these systems exhibit certain disadvantages, such as solvent instability, degradation of cellulose, and high toxicity. Ionic liquids are currently one of the most utilized solvents for cellulose dissolution [11,12]. Some novel ionic liquids and organic solvent mixtures (termed as organic electrolyte solutions) have been shown to rapidly dissolve cellulose [13]. With respect to sustainability, aqueous alkaline (sodium or lithium) hydroxides together

with urea or thiourea are some of the most promising cellulose solvents [14–16]. Minor disadvantages of these systems include the requisite for dissolution at a chilled temperature of −12 °C [17] and limited capacity to dissolve high-molecular-weight cellulose [18]. Recently, tetra-alkylammonium hydroxides were shown to efficiently dissolve cellulose even at room temperature (however, the dissolution of high-molecular-weight cellulose generally requires elevated temperatures) [19–21]. Despite the apparent toxicity of alkylammonium cations, the recyclability makes tetra-alkylammonium hydroxides a suitable solvent for isolation of cellulose originating from different sources [20,22].

All-cellulose composites (ACCs) are a relatively new class of cellulosic material, in which dissolved cellulose is utilized as a matrix to bond together natural cellulose fibers [2]. ACCs can be produced by mixing together dissolved cellulose and cellulose fibers (supposing that fibers do not dissolve during the processing) followed by casting and regeneration. Another way is solvent-based modification of cellulose sheets by partial dissolution and regeneration (referred as surface selective dissolution [23], partial fiber dissolution [24], or solvent welding [25]). Several different solvent systems have been studied for solvent welding of cellulose fibers, including dimethyl acetamide/LiCl [24], NMMO [26], ionic liquids [27], or NaOH-urea [28,29]. With these systems, ACCs were successfully produced with good properties, but they all pose some shortcomings, including long dissolution times and

requirement of either high (e.g., 80 °C) or low temperatures (< 0 °C). Use of high or low temperature can be environmentally desirable due to the high energy consumption, in addition to increase of the product cost. Especially from an industrial point of view, the dilatory dissolution of cellulose can be challenging to implement if a continuous process operation is desired.

In this study, the dissolution of high-molecular-weight cellulose fibers from dissolving pulp was studied using aqueous tetra-ethylammonium hydroxide (TEAOH, 35 wt% in water). The effect of dissolution and regeneration on the degree of polymerization (DP) and crystallinity of cellulose were studied using limiting viscosity and wide-angle X-ray diffraction (WAXD), respectively. ACCs were produced based on the rapid dissolution efficiency of TEAOH by solvent welding cellulose sheets. The effect of the dissolution time and hot-pressing on the surface morphology and mechanical properties of ACCs were investigated by scanning electron microscopy (SEM) and tensile testing, respectively.

2. Material and methods

2.1. Materials

Cellulose dissolving pulp (softwood) was obtained as dry sheets, whose properties are presented elsewhere [30]. TEAOH (35% in water) was obtained from Sigma Aldrich (Germany). Ethanol and HCl (0.1 M) were acquired from VWR (Finland).

2.2. Dissolution of cellulose

Dissolving pulp sheets were disintegrated in water using standard procedure [31] followed by filtration, washing with technical ethanol for 30 min, and filtration again before drying in an oven (60 °C). Fibers were then dissolved in 35 wt% TEAOH in water by mixing the fibers directly in the solvent using magnetic stirrer or by adding the solvent to the fibers (0.5–3 wt% cellulose solutions) while simultaneously mixing at room temperature. After solvent addition, the suspensions were mixed for 3 h until all the fibers were dissolved, and the solubility was verified using an optical microscope. Cellulose was regenerated by pouring the solution into ethanol while mixing. Regenerated cellulose was filtered and washed using ethanol until the washing liquid was neutral (checked using pH paper).

2.3. Fabrication of all-cellulose composites

Laboratory hand sheets (80 g/m^2) were prepared from the dissolving pulp, according to a standard procedure to produce sheet with thickness around 180 μm [32]. Around 5 cm × 7 cm pieces were cut from the laboratory sheets and immersed in excess of TEAOH for 30, 60, 120, or 180 s for solvent welding of the fibers. No mixing of the solvent applied. The sheets were then carefully lifted from the solvent and placed in 0.1 M HCl solution for 120 s. After acid coagulation, ACCs were first washed in a beaker containing deionized water (500 ml) for 30 min and then rinsed under running deionized water until the surfaces were neutral (checked using pH paper). Two different drying procedures were applied in the finalization of ACCs fabrication. The ACCs were placed between a filter paper and hand sheet on both sides and dried either in a drying grill (temperature of plates was around 125 °C) for 5 min or under high-pressure and heat (high-pressure aided hot-pressing, hp) using the Fontune Press (the Netherlands). In the latter, two consecutive steps were applied: (1) the sample was dried using a force of 45 kN together with the filter papers. (2) The dried ACC without filter papers was placed between the hot metal plates and pressed with a force of 300 kN to remove possible residual moisture. The temperature in both steps was 150 °C.

2.4. Attenuated total reflection infrared spectroscopy

The chemical characterization of raw, regenerated, and ACCs was performed using an ATR-IR. The spectra were collected from dried samples using a Bruker Tensor II FT-IR Spectrometer with a Hyperion 3000 FT-IR Microscope (USA). Spectra were obtained in the 600–4000 cm^{-1} range, and 40 scans were taken at a resolution of 4 cm^{-1} for each sample.

2.5. Degree of polymerization

The average degree of polymerization (DP) of the dissolving cellulose pulp and regenerated cellulose were evaluated using the limiting viscosity number, as measured in the CED solution according to the ISO 5351 standard. The samples were freeze-dried prior to the measurement. The limiting viscosity numbers were converted to DP using Eq. (1),

$$DP = \left(\frac{(1.65[\eta] - 116H)}{C} \right)^{1.111} \tag{1}$$

where [η] is the limiting viscosity number, C is the mass fraction of the cellulose, and H is the mass fraction of the hemicelluloses. This calculation corrects for the contribution of the hemicelluloses to the limiting viscosity number and DP of the cellulose, assuming that the average DP of the hemicelluloses is 140.

2.6. Mechanical properties

The tensile tests were performed using a universal material testing machine (Instron 5544, USA) equipped with a 100 N load cell. The laboratory sheet from the dissolving pulp and ACCs were cut into thin strips with a specimen width of 5 mm, and their thicknesses were measured using a precision thickness gauge (Hanatek FT3, UK). For the tensile testing, a 40 mm gauge length was set under a strain rate of 4 mm/min and six specimens were measured. The tests were conducted in 50% RH at a temperature of 23 °C and under a pre-load of 0.05–0.1 N. Prior to testing, the specimens were conditioned for at least one day in the same environment. The elastic modulus was calculated from the initial linear portion of the stress–strain curve, and the ultimate tensile strength was defined as the stress at the specimen breakage. At least five specimens from each samples were measured and specimens flailed at the clamps were excluded.

2.7. X-ray diffraction

The crystalline structures of the dissolving pulp, regenerated cellulose, and ACCs were investigated using WAXD. Measurements were conducted on a Rigaku SmartLab 9 kW rotating anode diffractometer (Japan) using a Co Kα radiation (40 kV, 135 mA) (λ = 1.79030 nm). Samples from the dissolving pulp and regenerated cellulose were prepared by pressing tablets of freeze-dried celluloses to a thickness of 1 mm. ACCs were measured similarly. Scans were taken over a 2θ (Bragg angle) range from 5° to 50° at a scanning speed of 10°/min, using a step width of 0.5°. The degree of crystallinity was determined by the method of Nam et al. [33] with the modifications suggested by Piltonen et al. [29] Since it is known from the literature that regenerated cellulose tends to have a preferred orientation, the March–Dollase parameter for the (1 1̄ 0)-plane in cellulose II was adjusted in the simulated patterns for each sample to find the best matching fit [34]. The March–Dollase parameter was then converted to the degree of preferred orientation of cellulose II using Eq. (2), [35].

$$\eta_{po} = 100\% \sqrt{\frac{(1-r)^3}{1-r^3}} \tag{2}$$

where η_{PO} is the degree of the preferred orientation, and r is the