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Cellulose Nanocrystals from Forest Residues as Reinforcing Agents for Composites: A Study from Macro- to Nano-Dimensions

Rosana Moriana[a,*], Francisco Vilaplana[b,c], Monica Ek[a]

[a] School of Chemical Science and Engineering Department of Fibre and Polymer Technology, Royal Institute of Technology- KTH, SE-100 44, Stockholm, Sweden
[b] School of Biotechnology, Division of Glycoscience, Royal Institute of Technology, AlbaNova University Centre, SE-10691, Stockholm Sweden
[c] Wallenberg Wood Science Centre (WWSC), Teknikringen 56-58, SE-10044, Stockholm Sweden

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ABSTRACT

This study investigates for the first time the feasibility of extracting cellulose nanocrystals (CNCs) from softwood forestry logging residues (woody chips, branches and pine needles), with an obtained gravimetric yield of over 13%. Compared with the other residues, woody chips rendered a higher yield of bleached cellulosic fibers with higher hemicellulose, pectin and lignin content, longer diameter, and lower crystallinity and thermal stability. The isolation of CNCs from these bleached cellulosic fibers was verified by the removal of most of their amorphous components, the increase in the crystallinity index, and the nano-dimensions of the individual crystals. The differences in the physico-chemical properties of the fibers extracted from the three logging residues resulted in CNCs with specific physico-chemical properties. The potential of using the resulting CNCs as reinforcements in nanocomposites was discussed in terms of aspect ratio, crystallinity and thermal stability.

1. Introduction

Rapid developments in nanotechnology and material sciences provide new knowledge and many opportunities for the application of reinforced composites to a wide variety of fields ranging from packaging to construction and biomedicine (Abdul Khalil, Bhat, & Yusra Ireana, 2012). To improve the competitiveness of the pulp and paper sector, the Association American Forest and Paper Association (2005) recommended the development of novel or improved products based on polymer composites and nano-reinforced materials (Hubbe, Orlando, Lucia, & Sain, 2008). Therefore, nanosized cellulosic particles have received increased interest as reinforcing agents in composites (Wegner, 2011). Depending on their preparation methods, the nanosized cellulosic particles can be divided in two main families: cellulose nanofibrils (CNFs) and cellulose nanocrystals (CNCs) (TAPPI, 2011). Wood pulp suspensions were disintegrated into CNFs for the first time through a homogenizer in a study by Turbak, Snyder, & Sandberg (1983). Later, other mechanical alternatives were employed to isolate CNFs, including microfluidization (Siqueira, Bras, & Dufresne, 2009; Spence, Venditti, Rojas, Habibi, & Pawlak, 2011), high-intensity ultrasonication (Chen et al., 2011), high-speed counter collision (Kondo, 2005) and grinding (Dufresne, 2012). The resulting CNFs were several microns in length and displayed amorphous regions intercalated between crystalline regions. On the other hand, the extraction of elongated rod-like crystalline cellulosic regions (CNCs), also called nanowhiskers, was performed for the first time by Rånby (1951) who produced colloidal suspensions of CNCs by sulfuric acid hydrolysis. Later developments on the preparation of CNCs included the optimization of different production parameters, such as the use of sulfuric acid or hydrochloric acid, the acid concentration, the ratio of acid:cellulose, the duration and temperature of hydrolysis, and the duration of sonication to disperse the CNC suspensions (Araki, Wada, Kuga, & Okano, 1998; Bondeson, Mathew, & Oksman, 2006; Kargarzadeh et al., 2012). CNCs have a highly crystalline nature, with low density (around 1.566 g cm^{-3}), large specific surface area (estimated to be several hundred of $m^2 \cdot g^{-1}$) and a very high Young's modulus (approximately 150 GPa) (Dufresne, 2003; Dufresne, 2012; Silvério, Flauzino Neto, Dantas, & Pasquini, 2013). These properties defined the CNCs as a preferred reinforcing agent over the CNFs to improve toughness, strength and stiffness through the interaction between the reinforcement and the matrix in composites (Lu & Hsieh, 2010; Ng et al., 2015).

* Corresponding author. Division of Wood Chemistry and Pulp Technology, School of Chemical Science and Engineering, KTH Royal Institute of Technology, Teknikringen 56, SE-10044 Stockholm, Sweden Tel.: +467075 95434; fax: +46 8 790 6166.
E-mail address: rosana@kth.se (R. Moriana).

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The different properties of the nanosized cellulosic particles depend not only on the disintegration method itself but also on the cellulose raw materials and their pretreatments (Abdul Khalil, Bhat, & Yusra Ireana, 2012; Spence et al., 2011). Nanosized cellulosic particles can be obtained from a variety of sources; however, most research efforts used partially or nearly completely purified versions of wood, such as microcrystalline cellulose (MCC) (Bondeson et al., 2006; Marcovich, Auad, Bellesi, Nutt, & Aranguren, 2006), bleached softwood pulp (Araki et al., 1998; Beck-Candanedo, Roman, & Gray, 2005; Revol, Godbout, & Gray, 1998) and bleached hardwood pulp (Beck-Candanedo et al., 2005). The cost of these raw materials and the low extraction yields of nanosized cellulose could be considered major economic disadvantages for their use as reinforcing agents in large-scale nanocomposite production. Therefore, different inexpensive agricultural biomass residues have been considered as raw materials to isolate CNCs, such as branch-barks of mulberry (Li et al., 2009), coconut husk fibers (Rosa et al., 2010), pea hull fibers (Chen, Liu, Chang, Cao, & Anderson, 2009), pineapple leaf fibers (Bibin et al., 2010), and empty-fruit bunches of oil palm (Fhama, Iwamoto, Hori, Iwata, & Takemura, 2010). This interest in using biomass residues is aligned with the sustainability concept defined by Abdul (Abdul Khalil, Bhat, & Yusra Ireana, 2012) as an alternative to optimize the exploitation of natural resources to sustainably fulfill the requirement for developing advanced materials. Forest residues from final fellings (i.e., logging residues, such as pine needles, branches and chips) constitute the largest waste share in forestlands; however, to our knowledge, no studies considering them as raw material to produce CNCs have been reported. The chemical composition, structure and thermal properties of these logging residues have recently been reported to evaluate their potential to produce new added-value cellulosic products and to introduce new opportunities for material applications (Moriana, Vilaplana, & Ek, 2015). In this study, we propose for the first time the use of forest logging biomass as an inexpensive raw material to produce CNCs to study their potential as reinforcing agents for nanocomposites. It is known that the morphology and properties of the CNCs influence their performance as reinforcing agents and influence the composite end-properties (Silvério et al., 2013). The morphology of the CNCs is determined by the aspect ratio (length/diameter); a higher CNC aspect ratio results in larger surface specific area and may enhance the thermo-mechanical properties for composites (Kargarzadeh et al., 2012). Silvério et al. (2013), however, reported that crystallinity in the CNCs could have a greater influence on the reinforcing mechanical capabilities than the aspect ratio. In addition, it is known that the use of sulfuric acid to hydrolyze cellulose significantly decreases its thermal stability. Because typical processing temperatures for polymeric composites reach approximately 200 °C, the thermal behavior of the CNC is another key factor to be considered to evaluate their potential as reinforcing agents of polymer composites (Rosa et al., 2010). The goals of this study include the following: (i) to study the feasibility of extracting cellulose fibers and cellulose nanocrystals from logging residues; (ii) to evaluate the changes in chemical composition, morphology, structure and thermal properties of this residual biomass during conversion from macro- to nano-dimensions; and (iii) to evaluate the physico-chemical properties of the CNCs and their possible use as reinforcing agents in composites in terms of aspect ratio, crystallinity and thermal stability.

2. Experimental

2.1. Materials

The logging residues were kindly provided by the SCA R&D Centre (Sundsvall, Sweden), and they were collected from a Swedish forest primarily composed of Scots pines (*Pinus sylvestris*) and Norway spruce (*Picea abies*). These forest residues from final fellings were composed of branches and chips of different sizes, along with needles. A detailed description of their physical aspects related to their amounts was described in a previous study (Moriana et al., 2015). Among these different types of forest residues, three lignocellulosic raw materials, namely, large woody chips (W), medium branches (B) and pine needles (PN), were selected to evaluate the feasibility of the isolation of CNCs. The selected forest residues were dried at room temperature for one week and successively milled to 20 mesh as previously reported (Moriana et al., 2015).

Sodium hydroxide (NaOH), methyl iodide (CH_3I), dimethyl sulfoxide (DMSO), dichloromethane, trifluoroacetic acid (TFA), sodium borohydride ($NaBH_4$), ammonia (NH_3), pyridine, acetic anhydride, ethyl acetate, sodium chlorite, sulfuric acid (96 wt %), ethanol (99%), acetone, acetic acid, and sodium acetate from Sigma-Aldrich, Germany, were used without further purification. The water used was purified using a Millipore Milli-Q system. Monosaccharide standards were purchased from Sigma-Aldrich (Germany). Polysaccharide standards (cellulose, starch, galactomannan, glucomannan, arabinoxylan, arabinogalactan, arabinan) were purchased from Sigma-Aldrich or Megazyme (Ireland).

2.2. Experimental Procedures

2.2.1. Cellulose Isolation

The cellulose extraction was performed following the methodology previously described by Kargarzadeh et al. (2012), Siqueira et al. (2009) and Siqueira, Abdillahi, Bras, & Dufresne, (2010a). An alkaline and bleaching treatment was proposed to remove the hemicellulose and lignin from the raw materials. At least three different batches were considered for each forest residue. During the alkaline treatment, 4 wt% milled samples were treated three times with a 4.5 wt% NaOH solution at 80 °C for 2 h under mechanical stirring. Then, the alkaline samples were subjected to five bleaching treatments under 80 °C for 4 h under mechanical stirring. The solution used in the bleaching treatment consisted of equal parts of acetate buffer (2 M, pH 4.8), aqueous chlorite (1.7% w/v in water), and water. After each treatment (alkaline and bleaching), the material was filtered and washed with water until the chemicals were removed, and dried at room temperature.

2.2.2. Cellulose Nanocrystal Isolation and Preparation

The bleached materials were subjected to acid hydrolysis to obtain a 4 wt% of colloidal suspensions of CNCs. This hydrolysis was achieved at 45 °C with 65 wt% sulfuric acid (preheated) under mechanical stirring for 40 min. These preparation parameters were selected because they were identified as the optimum sulfuric hydrolysis parameters for the production of CNCs with a high aspect ratio (> 10) (Kargarzadeh et al., 2012). The suspensions were diluted with ice cubes to stop the reaction. They were washed with purified water by successive centrifugations at 25000 g (Rotofix 32A Hettich Zentrifugen, Germany) at 10 °C for 20 min for each step until supernatant reached constant pH. The precipitate of the CNCs suspensions were resuspended in purified water and dialyzed for a week against purified water until the water pH remained constant. The suspensions were further sonicated for 10 min at 7,125 W/ml of power density using an ultrasonic homogenizer (Model 500 W, Cole Parmer Instrument Co, CH, USA) while cooling in an ice bath, centrifuged to remove the higher particles and to obtain the CNCs in suspension. The CNC suspensions were stored at 4 °C and dried at room temperature for further characterization.