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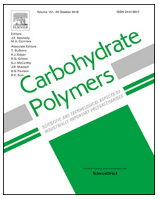

CNFs from twin screw extrusion and high pressure homogenization: A comparative study

Rim Baati[a], Ayman Ben Mabrouk[a,b,c], Albert Magnin[b,c], Sami Boufi[a,*]

[a] *University of Sfax, Faculty of Science, LMSE, BP 802, 3018 Sfax, Tunisia*
[b] *Univ. Grenoble Alpes, CNRS, Grenoble INP, LRP, 38000 Grenoble, France*
[c] *CNRS, LRP, F-38000 Grenoble, France*

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ABSTRACT

Cellulose nanofibrils (CNFs) from oxidized never dried Eucalyptus pulps have been produced by using twin screw extrusion (TSE) and high pressure homogenizer (HPH), and their properties were compared. CNFs from TSE are produced at 10% solid content and then diluted to 1% for purpose of comparison against HPH. The nanosized fraction (NF) was around 90% for CNFs from HPH compared to 70% when TSE was used. Difference in the fibrillation extent has led to a higher transparency degree for CNFs gel from HPH. However, the rheological properties of two CNFs gels are quite similar with a solid-like aspect. The elastic modulus is one order of magnitude higher than viscous modulus and nearly frequency-independent. Analysis of the nanosized fraction with AFM has revealed long nanosized fibrils 3–4 nm in width for both CNFs types. When mixed with waterborne polymer dispersion, transparent to translucide nanocomposite films were obtained. However, the reinforcing potential of CNFs from HPH has been shown to be stronger than that from TSE.

1. Introduction

CNFs has emerged as one of the most promising sustainable nanosized reinforcement from renewable resource combining specific attribute such as high aspect ratio, high strength and stiffness, light weightiness, safety with large possibility of functionalization which is expected to further expand the area of potential applications of CNFs (Dufresne, 2013).

CNFs are produced by breaking down the cell wall of cellulose fibers into their elementary fibrils using different physical disintegration actions. In addition to the most popular high pressure homogenizer and microfluidizer (Kalia, Boufi, Celli, & Kango, 2014; Nechyporchuk, Belgacem, & Bras, 2016) used to produce CNFs, several technological strategies have been reported to break down cellulose fibers into their nanosized building blocks, including ultra-fine friction grinding (Chen et al., 2013; Taniguchi & Okamura, 1998), ultrasonication and high speed-disintegration (Boufi & Chaker, 2016). CNF-based products are at their beginning. Substantial potential for economic growth is expected in the near future, especially in paper coating and papermaking (Boufi, González, Delgado-Aguilar, Quim, & Mutjé, 2016; Gonzalez et al., 2013), nanofiller for coating and waterborne dispersion, and cement (Galao, Baeza, Zornoza, & Garcés, 2014). Increasing number of companies have been launched to produce CNFs at commercial/pilot scale, including Paperlogic, Forest Products Laboratory (cooperating with the University of Maine), American Process (USA), Borregaard (Norway), Innventia (Sweden), Nippon Paper, Oji Paper (both Japan), CTP/FCBA (France).

The large-scale commercializations of CNFs are impeded by three main obstacles. The high energy consumption involved in the production of CNFs is the first issue, especially when a high pressure homogenizer or a microfluidizer are used (Desmaisons, Boutonnet, Rueff, Dufresne, & Bras, 2017). Thought, the chemical pretreatment was shown to notably decrease the energy input to less than 20 kWh kg^{-1}, still too high for industrial scale up production at the present time. The second obstacle relates to the high cost of the equipment when a high-pressure homogenizer or the microfluidizer are used as disintegration mode. The third issue is the low solid content of the CNFs produced, which in the best of cases not exceed 2.5%, when one of the above method was used. This low consistency engenders increasing transport cost and has led to a huge dilution effect when CNFs is used as additive. For instance with a CNFs suspension with 2% solid content, the addition of CNFs at a content of 5% brings about 250% dilution effect, which is likely to strongly affect the physical properties of the mixture.

Twin screw extrusion (TSE) which is commonly used for nanocomposites and composites processing, might be an interesting alternative for the production of CNFs with high solid content ranging from

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[*] Corresponding author at: Faculty of Science, LMSE, University of Sfax, BP 1171, 3000 Sfax, Tunisia.
E-mail address: sami.boufi@fss.rnu.tn (S. Boufi).

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10 up to 25%. Although, this approach is not as popular as HPH, grinding or microfluidization, it is promising for the high consistency production of CNFs with low energy demand. Referring to the literature data, only three papers have focused on the production of CNFs *via* TSE. The first one was reported by Ho et al. (Ho, Abe, Zimmermann, & Yano, 2015) who used a twin-screw extruder for the disintegration of fibers at 28% consistency. The TSE screw was a combination of kneading and feeding screws and such that after 10–15 passes through the TSE, the fibrillated material was obtained as a humid powder form at 33–45% solid content. Although, a successful fibrillation of the fibers was observed after several passes through the extruder, the ensuing fibrils were quite large with a size exceeding 100 nm, and the aqueous suspensions of 0.2 wt% fibrillated cellulose looks opaque with high fraction of sedimented material after standing for several hours. The second work was published by our research group (Baati, Magnin, & Boufi, 2017) in 2017 where nanofibrillated cellulose with a high solid content of 10% were produced from TEMPO-mediated oxidized pulps with a carboxyl content from 300 to 900 μmol g^{-1} using a twin-screw mini-compounder. A strong gel with high yield in nanofibrillated material exceeding 80% was obtained after 30 min of recirculation through the extruder. CNFs with a lateral dimension lower than 5 nm and a length within the micron-scale was produced through this simple approach. No evolution in crystallinity in terms of crystalline indexes was observed after prolonged extrusion up to 30 min. The third publication was recently reported by Rol et al. in 2017 (Rol et al., 2017), successfully reports produced nanofibrillated cellulose at high solid contents (20%) from enzymatic pretreatment or TEMPO oxidated eucalyptus pulp followed by seven passes through a lab scale TSE with L/D of 45. After 7 passes through TSE, the nanosized fraction was about 65 ± 7%, and 37 ± 12% for the refined enzymaticaland TEMPO-oxidized fibers respectively. Without any pretreatment of the fibers, TSE failed to produce CNFs with measurable extent. The size of the prepared CNFs measured by AFM was found to be around 25–35 nm.

In the present work, we pursue our investigation concerning the production of CNFs by TSE by comparing the properties of the ensuing CNFs with respect to that produced by HPH. The properties of CNFs produced through the two disintegration routes in terms of, the effectiveness of fibrillation process, the morphology of the CNFs, their crystallinity and their rehological properties are discussed. The reinforcing potential of the CNFs when included into a polymer matrix is also studied by preparing nanocomposites films by mixing CNFs suspension with latex dispersion followed by film-formation process.

2. Experimental section

2.1. Materials

Wood chips (approximately 1 × 0.5 × 0.2 cm of size) were prepared from Eucalyptus Grandis wood. They were air-dried to a final humidity of 8–10% and then stored for later use. Before lignin extraction, woodchips were ground to pass a screen of 2 mm aperture. Sodium chlorite ($NaClO_2$), acetic acid (AA) 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) and sodium bromide (NaBr) are from Aldrich and used as received. Sodium hypochlorite solution (NaClO) was a commercial product.

The pulping procedure has been carried out as detailed below.

2.2. Delignification processes

The $NaClO_2$/Acetic acid (AA) pulping process was carried out as follows: 5 g of dry biomass are added to water and mixed to form a suspension with a solid content 10 wt%. Then, 0.5 g of sodium chlorite ($NaClO_2$) and 0.5 mL of acetic acid per gram of dry biomass are added to the suspension and the suspension was kept under mechanical stirring at 70 °C for 6 h without removal of any liquor. Each hour, a fresh dose of $NaClO_2$ (0.5 g) and acetic acid (0.5 g) was added until complete release of fibers. After filtration and water washing white cellulose fibers were obtained without any need to perform a bleaching treatment. The effective removal of lignin was checked by acid-insoluble lignin and acid-soluble lignin according to TAPPI method T222 om-98.

2.3. TEMPO-mediated oxidation

The TEMPO-mediated oxidation has been carried out at pH 10 following the method reported in our previous work (Besbes, Alila, & Boufi, 2011). In brief, 30 mg of TEMPO and 250 mg of NaBr were added to 2 g of pulp in water at 2% consistency. Then, 50 mL of a NaClO solution (4 wt.%) was added dropwise to the suspension kept at a temperature around 5 °C. NaOH solution (0.1 M) was added intermittently to maintain the pH around 10. The oxidized fibers were recovered by filtration and washing with water until the conductivity of the suspension became lower than 200 μs m^{-1}.

2.4. Carboxyl content

The carboxyl content of the oxidized cellulose has been determined using a conductimetric titration, as described in our previous work (Besbes et al., 2011).

2.5. Production of CNFs via twin screw extrusion

The extrusion of oxidized pulp was carried out with a laboratory scale co-rotating conical twin-screw mini extruder (TSE) DSM-Xplore 15cc Micro-extruder. Pulps with a solid content of 10% have been fed into the barrel and continuously extruded at a constant screw-speed of 240 rpm *via* recirculation for 30 min. The continuous recirculation through the channel allows continuous disintegration of the fibers without the need to keep out the extruded pulps (Fig. 1).

2.6. Production of CNFs via high pressure homogenizer

The oxidized fibers were disintegrated within a high pressure

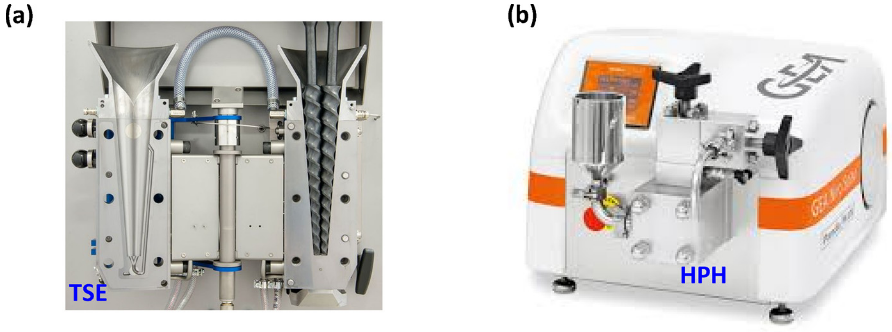

Fig. 1. The (a) twin-screw mini extruder (TSE) and (b) the high pressure homogenizer (HPH) used for the disintegration of fibers.