Carbohydrate Polymers 154 (2016) 151–166

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Review

Nanofibrillated cellulose as an additive in papermaking process: A review

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ARTICLE INFO

Article history:
Received 1 July 2016
Received in revised form 28 July 2016
Accepted 28 July 2016
Available online 30 July 2016

Keywords:
Nanofibrillated cellulose
Paper
Mechanical properties
CNF
Wet-end
Physical properties

ABSTRACT

During the last two decades, cellulose nanofibres (CNF) have emerged as a promising, sustainable reinforcement with outstanding potential in material sciences. Though application of CNF in papermaking is recent, it is expected to find implementation in the near future to give a broader commercial market to this type of cellulose. The present review highlights recent progress in the field of the application of cellulose nanofibres as additives in papermaking. The effect of CNF addition on the wet end process is analysed according to the type of pulp used for papermaking. According to the literature consulted, improvement in paper's overall properties after CNF addition depended not only on the type and amount of CNF applied, but also in the pulp's origin and treatment. Bulk and surface application of CNF also presented significant differences regarding paper's final properties. This review also revises the mechanisms behind CNF reinforcing effect on paper and the effect of chemically modified CNF as additives.

Contents

1. Introduction

The increasing interest in nanomaterials from renewable origins and their unique properties have led to intensive research in the area of nanocelluloses produced from resources available worldwide (Kalia, Boufi, Celli, & Kango, 2014; Zhang, Batchelor, Varanasi, Tsuzuki, & Wang, 2012). More specifically, nanofibrillar cellulose, nanosized cellulose fibrils produced by the fibrillation of the cell wall of cellulose fibres through intensive mechanical action, have gained increasing attention in papermaking as a wet-end additive,

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http://dx.doi.org/10.1016/j.carbpol.2016.07.117
0144-8617/

with potential applications as a dry and wet strength agent but also as a coating to improve the barrier properties of paper (Lavoine, Bras, & Desloges, 2012; Lindström & Aulin, 2014; Shatkin, Wegner, & Bilek, 2014).

Different reasons motivated the interest of CNF as a new family of paper component: (i) The nanoscale lateral dimension of CNF expands the specific surface, (ii) their lengths in the micrometer, (iii) their semi-crystalline structure composed of extended cellulose chains, (iv) their high intrinsic mechanical strength along with good flexibility, (v) their high potential to interact with cellulosic fibres through hydrogen bonding, and (vi) their inherent tendency to form strong entangled network accounted. Although the application of CNFs as additives in papermaking is quite recent, it is promising in the near future and is likely to give a broader commercial market to sustainable reinforcement.

Several reviews on topics about cellulose nanofibres have been already published. Most of them deal with properties and application of cellulose nanofibres in composite materials based on polymeric matrices (Eichorn et al., 2010; Khalil, Bhat, & Yusra, 2012; Moon, Martini, Nairn, Simonsen, & Youngblood, 2011; Siró & Plackett, 2010). Other reviews analysed the current techniques used for CNF production and characterization (Kangas et al., 2014; Khalil et al., 2014), barrier properties (Lavoine, Desloges, Dufresne, & Bras, 2012) or general properties and possible applications of CNFs (Klemm et al., 2011). To the best of the authors' knowledge, there are only two publications (Brodin, Gregersen, & Syverud, 2014; Osong, Norgren, & Engstrand, 2015) that present advances of CNF application into papermaking slurries. The present review further highlights recent progress in the field of the usefulness of CNF as an additive for papermaking including wood pulps, agricultural wastes and recycled paper. This review also includes a brief introduction to nanocellulose, the application of CNFs as additives in pulps according to their origin, their reinforcing effect mechanism, and their application as a coating material.

2. From cellulose to nanocellulose

Cellulose is a semi-crystalline polysaccharide appearing in nature in the form of fibres with 0.5 to up several mm in length and is organized in four hierarchical levels (Klemm et al., 2011). At the molecular level (∼Å), cellulose is composed of β-D-glucopyranose units linked by 1-4-β glycosidic bonds with alternately rotated glucose units. At the supramolecular level, cellulose chains aggregate together in the form of elementary fibrils, each one about 3 nm in diameter, formed by alternated crystalline and amorphous domains. These elementary fibrils are aligned and further aggregate into larger microfibrils or macrofibrils with diameter of 10–25 nm. At the structural level the microfibrils stick together in a spiral manner within a three layer cell wall structure to form the cellulose fibres (Fengel & Wegener, 1984).

Given the hierarchical structure of cellulose, it is possible to break down the cell wall into nanoscale cellulose known as nanocellulose with different morphology according to the extraction mode. Cellulose nanocrystals (CNC) and cellulose nanofibres (CNF) constituted the two main families of nanocelluloses. The terms microfibrillated cellulose (MFC) and nanofibrillated cellulose (NFC) are still frequently found in literature to describe cellulose nanofibres suspensions. However, the present review will only use the term CNF to describe suspensions containing cellulose fibres of nanometric size. Cellulose nanocrystals are extracted from fibres after a complete dissolution of the non-crystalline fractions, while the cellulose nanofibres are produced mainly through an intensive mechanical shearing action to break out the cell wall of fibres and release the cellulose fibrils in the form of bundles of elementary fibrils. CNF is the main type of nanocellulose that has attracted attention for papermaking applications.

Since the introduction of CNF in 1983 by Turbak, Snyder, and Sandberg (1983), the high pressure homogenization and the microfluidization are still the main methods currently used to effectively produce CNF (Davoudpour et al., 2015). Nevertheless, in the last years the use of grinders and refiners has increased as preferred methods for CNF fabrication because they can operate at higher CNF concentrations, fibre pre-treatment is optional and clogging problems are non-existent.

Albeit the promising potential uses of CNFs in multitude applications, their scale-up production is still limited and below expectation. One major obstacle to this development is the high energy consumption involved during the mechanical disintegration of the fibres into nanofibres (Josset et al., 2014; Naderi, Lindström, & Sundström, 2015). Another challenge is the capacity to produce CNF with uniform size. The energy consumption is strongly dependent on the fibres pre-treatment method. Values ranging from 10 up to 100 kW h per Kg of dry CNF have been reported (Chaker, Mutjé, Rei Vilar, & Boufi, 2014; Klemm et al., 2011). This high energy demand results from the necessity to operate under high pressure ranging from 200 to 800 bar with multiple passes until a high fibrillation degree is reached. The fibres pre-treatment prior to the disintegration process is another approach currently adopted to strongly decrease the energy demand. Chemical pre-treatment has emerged as one of the most efficient and popular pre-treatment strategies to facilitate the break-up of the fibres network by generating ionic or ionisable groups within the internal structure of the fibres. This can be achieved via a TEMPO-mediated oxidation (Saito, Nishiyama, Putaux, Vignon, & Isogai, 2006), carboxymethylation (Siró and Plackett, 2010; Wågberg et al., 2008) via sulfonation with sodium bisulphate (Buzała, Przybysz, Rosicka-Kaczmarek, & Kalinowska, 2015), periodate oxidation (Liimatainen, Visanko, Sirviö, Hormi, & Niinimäki, 2013), or quaternization (Chaker & Boufi, 2015; Ho, Zimmermann, Hauert, & Caseri, 2011). However a critical content in ionic groups is needed to effectively facilitate the release of the cellulose nanofibres and break down the cell wall of the fibres (Besbes, Alila, & Boufi, 2011; Besbes, Rei Vilar, & Boufi, 2011). These surface charges will have a key role in papermaking wet-end chemistry. Another merit of the pre-treatment is the reduction of the risk of clogging during the homogenization or microfluidization processes. In addition to the fibres pre-treatment approach, the delignification mode was recently shown to affect the fibrillation efficiency of the bleached cellulose fibres (Chaker, Alila, Mutjé, Rei Vilar, & Boufi, 2013). Though chemical pre-treatment can drastically reduce the energy consumption of CNF fabrication, in many cases the price of some chemicals clearly surpasses the energy costs saved (Delgado-Aguilar, González et al., 2015).

3. Application of CNF into papermaking pulps

3.1. Chemical pulps

Table 1 resumes some results reported by several authors on the effect that CNF produce when used as additives in papermaking suspensions. The columns indicate, from left to right, the author and year of publication of the consulted work, type of CNF in reference to the type of pretreatment used before homogenization/microfluidization, pulp used for paper sheet production, maximum amount of CNF added, type of retention agent used (if any) and the maximum increase in strength produced by the maximum CNF content. According to literature consulted, most of the published works on CNF applied to fibrous slurries were based on experiments performed on chemical pulps. Chemical pulps are made by cooking (digesting) the raw materials, using the kraft