Carbohydrate Polymers 186 (2018) 73–81

Contents lists available at ScienceDirect

Carbohydrate Polymers

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

Effect of retention rate of fluorescent cellulose nanofibrils on paper properties and structure

Qijun Ding, Jinsong Zeng*, Bin Wang*, Wenhua Gao, Kefu Chen, Zhe Yuan, Jun Xu, Darong Tang

State Key Laboratory of Pulp and Paper Engineering, Plant Micro/Nano Fiber Research Center, School of Light Industry and Engineering, South China University of Technology, Guangzhou, 516640, China

ARTICLE INFO

Keywords:
Cellulose nanofibrils (CNF)
Fluorescent labeling
Retention rate
Loss rate
Distribution of CNF
Structure of paper

ABSTRACT

In this work, we report a new characterization method using fluorescent cellulose nanofibrils to analyze retention and loss rates in the papermaking process. Cellulose nanofibrils (CNF) were isolated from chemical pulp by enzymatic pretreatment and used as a strengthening additive in sheet forming. The aim of this paper was to investigate its effects on flocculation, retention and loss rate and the physical and mechanical properties. CNF was subjected to fluorescent labeling with RBITC (Rhodamine B isothiocyanate), and the retention of fluorescent cellulose nanofibrils (FCNF) was analyzed by elemental analysis and fluorescence intensity. The retention and loss rate of the FCNF decreased with increasing the addition of FCNF. Laser Confocal Scanning Microscopy (LCSM) and Scanning Electron Microscope (SEM) images confirmed that FCNF can be evenly distributed in the paper. A thorough investigation of the relation between the retention rate and papersheet performance was conducted.

1. Introduction

Developing nanocomposite materials with light-weight and high-strength is now a promising area (Madani, Kiiskinen, Olson, & Martinez, 2011). Cellulose nanofibrils (CNF) has the advantageous properties such as high availability, mechanical strength, aspect ratios, barrier properties and large specific surface area, as well as their dimensional stability, biodegradability and biocompatibility. Therefore it is attracting widespread scientific and commercial interest (Eichhorn et al., 2010; Fredrik, Øyvind, & Kristin, 2014). CNF reinforced polymer composites had recently found applications in foods, cosmetics, pharmaceuticals, paints, drilling muds, paper additives and paperboard barriers, hygiene products, automotive, aerospace and construction industries due to their strength as well as their active or “smart” properties (Azeredo, 2009; Brodin & Theliander, 2013; Feldman, 2015; Klemm et al., 2011; Qiu, Zhao, & Mcclements, 2015). CNF can be added directly into the pulp furnish or with suitable retention aids. The retention rate of CNF in the paper has an important effect on the structure and properties of paper. However, until now, there are few reports about the retention efficiency of CNF on paper sheet, and it is unclear whether the CNF can be effectively retained.

As a reinforced additive, CNF applied in papermaking has attracted much industrial interest due to it is a non-petroleum based material with large production potential. CNF separated from most pulping operations has an inherent length distribution (Azizi Samir, Alloin, & Dufresne, 2005). It is generally known that enhancing the length and aspect ratio distribution of CNF significantly influences the strength properties of the resulting composite (Dubief, Samain, & Dufresne, 1999; Saito & Isogai, 2005; Tom, Christian, Magnus, & Torgny, 2015). The addition of CNF to the pulp fibers may result in a hierarchical structure due to the presence of fibrous materials at different length scales. CNF at fiber–fiber bonds may give a more favorable type of failure process so that the material becomes tougher (Balea, Merayo, De La Fuente, Negro, & Blanco, 2017; Delgado-Aguilar et al., 2015; Delgado-Aguilar et al., 2016; Osong, Norgren, & Engstrand, 2016; Sehaqui, Allais, Zhou, & Berglund, 2011; Siró & Plackett, 2010). In addition, the chemical structure similarity of CNF and pulp fibers can promote their good filler-matrix interaction. Hence, there are many different strategies for CNF to add into papermaking process. In one case, CNF can be directly mixed into the paper pulp without consideration of retention aid (Ahola, Österberg, & Laine, 2008; Eriksen, Syverud, & Gregersen, 2008; Hii, Gregersen, Chinga-Carrasco, & Eriksen, 2012; Taipale, Österberg, Nykänen, Ruokolainen, & Laine, 2010). In another case, CNF may be premixed with a certain furnish component such as the filler or long fiber fraction and deposited on the surfaces of this furnish component by retention aids (Guimond, Chabot, Law, & Daneault, 2010; Lin, Yin, Retulainen, & Nazhad, 2007).

The mechanism of interaction occurring between CNF and retention

* Corresponding authors.
E-mail addresses: fezengjs@scut.edu.cn (J. Zeng), febwang@scut.edu.cn (B. Wang).

https://doi.org/10.1016/j.carbpol.2018.01.040
Received 2 November 2017; Received in revised form 6 January 2018; Accepted 11 January 2018

aids had been also systematically studied (Merayo, Balea, Fuente, Blanco, & Negro, 2016). Generally, the addition of CNF can improve the stability of floc and minimize the overdosing effects. Marjo et al. were the first to discuss the retention rate of CNF and the effect of CNF on the structure of the paper sheet (Manninen, Kajanto, & Paltakari, 2009), while they did not measure the amount of additive in the final sheet. They considered the percentage of additives to be quite constant because the sheet grammages did not change significantly. However, pulp fibers loss may affect the accuracy of the additives retention. To solve the above problems, quantitatively measure on the retention and loss rate of fluorescent labeling CNF should be developed.

In this work, rhodamine B isothiocyanate (RBITC) labeled CNF was used in papermaking process to analyze the retention and loss rates by elemental analysis and fluorescence intensity. Furthermore, the distribution of FCNF in paper was studied by Laser Scanning Confocal Microscopy (LSCM) and Scanning Electron Microscopy (SEM). CNF retention, strength properties and formation properties were also investigated in our work. The study will promote the application of CNF as strengthening additive used in cellulose-based nanocomposites.

2. Experimental

2.1. Material

The cellulose source was never-dried masson pine chemical pulp and eucalyptus mechanical pulp from Guangxi Golden Paper Company. Commercial cellulase (*Celluclast* 1.5 l, activity 84.5 FPU/g) from *Trichoderma reesei* was purchased from Novozymes (Beijing, China). Sodium hydroxide, epichlorohydrin (> 99.0%, GC), polyquaternium-11 ($C_{42}H_{72}N_6O_9X_2$, molecular weight 805.06 g/mol), poly (N-isopropylacrylamide) (PAM, molecular weight > 8000000 g/mol), cationic starch (Cs) (degree of substitution of 0.04), amine hydroxide (AR) and rhodamine B isothiocyanate (RBITC) ($C_{29}H_{30}N_3O_3S{\cdot}Cl$, molecular weight 536.09 g/mol) were obtained from commercial sources and used as received. Organic solvents were purchased and used without further purification.

2.2. Preparation of CNF

The procedure was carried out according to the previously published enzymatic pretreatment (Henriksson, Henriksson, Berglund, & Lindström, 2007). It had been suggested that the use of enzymatic techniques was superior to chemical methods due to low cost, high selectivity, and environmental characteristics (Hassan, Hassan, & Oksman, 2011). Briefly, 10.0 g pulp was suspended in 500 ml of a 50 mM citrate acid-sodium citrate buffer (pH 4.8) with enzyme loading of 20 FPU/g substrates. And the mixture was kept in a boiling bath for 10 min to inactive the enzyme. Then the mixture of pulp, buffer, and enzyme was centrifuged to separate the solid and liquid phases. The concentration of the pulp after pretreatment was adjusted to about 2.0%. The suspension of pulp was subjected to the homogenizing action of a microfluidics for 5 times at 30000 PSI. A detailed description of the fibrillated material applied in this study was given by Siqueira et al (Siqueira, Bras, & Dufresne, 2010).

2.3. Preparation of fluorescent CNF (FCNF)

The experiment was conducted according to the previously reported method by Mahmoud et al. and Ding et al. (Ding et al., 2017; Mahmoud et al., 2010). In order to introduce the epoxy group on the OH groups of CNF, firstly, CNF was firstly activated with epichlorohydrin (5 ml/g CNF) in alkaline conditions (pH 12.0) at 60 °C under stirring for 2 h. Then the suspensions were centrifuged and filtered with deionized water to remove unreacted reagents until neutral. Secondly, ammonium hydroxide (5 ml/g CNF) was added to the activated CNF suspensions at 60 °C under mechanical stirring for 2 h. Then the suspensions were centrifuged, washed repeatedly with deionized water. Finally, RBITC (0.01 g/ g CNF) was added to the CNF suspensions at room temperature for 24 h in the dark. Then the fluorescent CNF were washed to remove unreacted reagents by centrifuging and filtering with deionized water. Until fluorescence signals had not been detected in the filtrate by fluorescence and UV/vis spectroscopy.

2.4. Preparation of retention aid

Retention aids are single- or multi-components systems involving natural or synthetic polymers based on previous studies (Hubbe, Nanko, & Mcneal, 2009). In our work, the retention system were used in two different ways: (1) A dual-component retention system (DRS) composed of a low-molecular-weight component (polyquaternium-11) and a high-molecular-weight component (PAM). The cationic charge density of polyquaternium-11 and PAM were 0.052 meq/g and 1.032 meq/g which are measured as anionic demand by Particle Charge Detector (PCD) with 0.001N sodium poly (ethene sulfonate), respectively. The DRS was prepared by dilution of commercial solution in ultrapure water. PAM was prepared by dissolving 0.01 g solid PAM in 100 ml ultrapure water. (2) Cationic starch (Cs) with a cationic charge density (anionic demand) of 0.30 meq/g was prepared by the following procedure. 1.0 g of starch powder was added into 100 ml ultrapure water and was cooked at 85–90 °C for 15 min with continuous stirring. Then cationic starch was obtained after cooling to room temperature. To avoid the effect of aging, flocculants were matured for 90 min.

2.5. Paper sheet preparation and characterization

Unbleached eucalyptus pulp and FCNF were dispersed using a laboratory disintegrator at 10000 revolutions. The target basis weight of handsheets were kept at 60 g/m^2 by adding with 0, 2, 4, 6, 8, 10, 20 and 30 wt.% of FCNF. Then loaded retention aid (Cs 1 wt% or PAM 0.05 wt % and polyquaternium-11 0.7 wt% or no retention aid) and kept the slurry stirring for 20 min. FCNF should dilute in the same multiple in each process of papermaking. The paper sheets were prepared according to ISO 5289/2, using the model Rapid Köthen sheet former (PTI, Vorchdorf, Austria). The wire was washed properly after papersheets finished by running water. Finally the paper sheet were conditioned in a weather chamber at 25 °C and 50% RH for 24 h. The white water was also collected for the detection of fluorescence intensity.

2.6. Characterization

Tensile strength and elongation were performed with L&W tensile strength tester (L&W CE062, Swedish) following the ISO 1924-2:1994 standard. Thickness and density were determined on a L&W thickness gauge (L&W 251, Swedish) following the ISO 534:1988 standard. Light scattering (ISO 9416:1998) and opacity (ISO 2471:1998) were measured using Residual ink whiteness tester (technidyne Color Touch PC CTP-ISO, America). The internal bond strength and the formation index were measured with the interlayer bonding strength tester (TMI 80-01-01-0002, America) and the formation tester (2D LAB F/SENSOR, Germany), respectively. All the above experimental data was obtained from the average of five measurements.

The porosity was determined from the density of the paper by applying Eq. (1).

$$\text{Porosity}(\%) = \left(1 - \frac{\rho_{sample}}{\rho_{cellulose}}\right)*100\% \quad (1)$$

where ρ_{sample} is the density of the paper sheet and $\rho_{cellulose}$ is the density of the cellulose (1.6 g/cm^3).

The morphology and size of CNF and FCNF were characterized by atomic force microscopy (AFM) using a Nanoscope IIIa (VeccoInc., USA). CNF and FCNF solution (0.001 wt.%) was deposited onto a