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Short communication

Using carboxylated nanocrystalline cellulose as an additive in cellulosic paper and poly (vinyl alcohol) fiber paper

Ruitao Cha[a,c,*,1], Chengyu Wang[c,1], Shaoling Cheng[c], Zhibin He[b], Xingyu Jiang[a]

[a] CAS Key Lab for Biological Effects of Nanomaterials and Nanosafety, National Center for Nanoscience and Technology, Beijing 100190, China
[b] Limerick Pulp and Paper Centre, Department of Chemical Engineering, University of New Brunswick, Fredericton, New Brunswick E3B 5A3, Canada
[c] Tianjin Key Laboratory of Pulp and Paper, Tianjin University of Science and Technology, Tianjin 300457, China

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ABSTRACT

Specialty paper (e.g. cigarette paper and battery diaphragm paper) requires extremely high strength properties. The addition of strength agents plays an important role in increasing strength properties of paper. Nanocrystalline cellulose (NCC), or cellulose whiskers, has the potential to enhance the strength properties of paper via improving inter-fibers bonding. This paper was to determine the potential of using carboxylated nanocrystalline cellulose (CNCC) to improve the strength properties of paper made of cellulosic fiber or poly (vinyl alcohol) (PVA) fiber. The results indicated that the addition of CNCC can effectively improve the strength properties. At a CNCC dosage of 0.7%, the tear index and tensile index of the cellulosic paper reached the maximum of 12.8 mN m^2/g and 100.7 N m/g, respectively. More importantly, when increasing the CNCC dosage from 0.1 to 1.0%, the tear index and tensile index of PVA fiber paper were increased by 67.29%, 22.55%, respectively.

1. Introduction

Nanocrystalline cellulose (NCC), also known as cellulose whiskers, appeared as important bio-based products, therefore has received great attention in recent years (Brinchi, Cotana, Fortunati, & Kenny, 2013; Fan & Li, 2012; Huq et al., 2012; Idström, Brelid, Nydén, & Nordstierna, 2013; Khan et al., 2012). Due to its unique characteristics and bio-degradability, NCC holds promise in many different applications e.g. in papermaking industry, regenerative medicine and nanocomposite materials (Cha, He, & Ni, 2012; Zaman, Liu, Xiao, Chibante, & Ni, 2012; Zaman, Liu, Xiao, Chibante, & Ni, 2013; Zoppe et al., 2010). In 2008, Henriksson, Berglund, Isaksson, Lindstrom, and Nishino (2008) successfully achieved an eye-catching cellulosic nanopaper with remarkably high toughness using wood nanofibrils. It was found that cellulose nanopaper was a network composed of intertwined nanofibrils, with an aspect ratio exceeding 100 and with a tensile index of 214 MPa, quite close to that of industrial steel (250 MPa). Similar finding was shown in a recent work (Peresin, Habibi, Zoppe, Pawlak, & Rojas, 2010) in which NCC was used as an additive to effectively improve the mechanical properties of PVA fibers.

In general, over the past decade, NCC was widely used to improve the mechanical properties of PVA-based thin films and nanocomposites. For instance, research result showed that effective stress delivered to the oriented NCC led to the remarkable enhancement in mechanical properties of PVA-based nanocomposites (Uddin, Araki, Gotoh, & Takatera, 2011a; Uddin, Araki, & Gotoh, 2011b). In another study, the oriented NCC were assumed to be embedded in the inter-fibrillar regions and formed lateral interlinks between fibrils by hydrogen bonding that resist the PVA fibrils from being pushed apart (Uddin et al., 2011a; Uddin et al., 2011b). In addition, much effort was made to the tailored carboxylate surface modification of NCC and its potential application. Montanari et al. developed carboxylated nanocrystalline cellulose (CNCC) based on TEMPO (1-oxo-2,2,6,6-tétraméthylpipyridine 1-oxyle) mediated oxidation (Montanari, Rountani, Heux, & Vignon, 2005). In our recent work, a copolymer of CNCC was synthesized using N-Isopropyl acrylamide (NIPAAm) by free radical polymerization and subsequently used to prepare a pH/thermal-sensitive hydrogel with high mechanical properties (Cha et al., 2012).

Specialty paper sheet (e.g. battery diaphragm paper) requires extremely high tensile strength and tearing resistance in machine direction, as well as air permeability (Venter, Zhao, Breden, Linton, & Heaton, 2001). Traditional methods mainly focus on either increasing beating degree or using strength additives,

* Corresponding author at: CAS Key Lab for Biological Effects of Nanomaterials and Nanosafety, National Center for Nanoscience and Technology, Beijing 100190, China. Tel.: +86 10 82545631; fax: +86 10 82545631.
E-mail address: chart@nanoctr.cn (R. Cha).
[1] These authors contributed equally to this work.

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i.e. polyacrylamide, both of which exert limited effects on the improvement in paper strength (Sakaemura & Yamauchi, 2011; Shen, Song, & Qian, 2011). Alternatively, using NCC to improve the mechanical properties of PVA solution instead of PVA fiber is another practical approach. In the present work, we focused the effect of CNCC on the mechanical properties of paper made of cellulosic fiber or PVA fiber, providing a newly unique window of functional application of CNCC with the objective of potentially enhancing the mechanical properties of specialty paper.

2. Experimental

2.1. Materials

CNCC was obtained from Biovision Technology Inc., Canada. It has the physicochemical characteristics as follows: average length of 130–150 nm, average width of 3–4 nm, pH (1% dispersion in deionized water) of 7.2, conductivity (1% dispersion in deionized water) of 405 μS, viscosity (1% dispersion in deionized water) of 1.3 mPa S, crystallinity index of 80%, moisture content of less than 8%, and carboxylate substitution degree at C_6 of 0.1–0.2.

Bleached Kraft softwood pulp with a beating degree of 17 °SR was received from Canfor Co., Canada. Commercially available precipitated calcium carbonate was provided by the Nanjing GuanYe Chemical Co., Ltd., China. It possesses the whiteness of more than 95%, deionized water content of less than 0.60%, and particle size of 4000 mesh, PVA fibers (Model GH-20) were purchased from Nippon Synthetic Chemical Industry Co., Ltd., Japan. All other reagents were of analytical grades and used without further purification.

2.2. Preparation of CNCC dispersion and pulp

(1) 2 ml CNCC of 3.0% was stirred vigorously in an electromagnetic stirrer (DZ-1, Shanghai) for a few minutes until dispersion was homogeneous (time required depends on the stirring speed). Subsequently, 0.1 g/ml CNCC dispersion was prepared with a 100 ml volumetric flask at room temperature.
(2) 32.6 g market pulp sample (in dry sheet form with moisture of 92%, 30.0 g O.D. pulp) was initially cut into pieces with lengths of 2–3 cm, and then immersed in water for 4 h. Subsequently, the pulp suspension was treated in a Valley beater (deionized water added was totally 270 mL) for 30 min, followed by centrifugation to remove the surplus water. Eventually, the resulting pulp was cut into pieces with lengths of 0.5–1 cm and then put inside the volumetric flask.
(3) 300.0 g prepared pulp was put into a pulp disintegrator (total number of revolution is 15,000 r) for latency removal, in which 2000 ml deionized water was added. Disintegrated pulp was poured into the bucket with a supply of 700 ml deionized water. Then 1.2 g precipitated calcium carbonate was added to form a well mixed mixture (precipitated calcium carbonate: dry pulp = 1:25).

2.3. Preparation of cellulosic paper reinforced with CNCC

Cellulosic paper with a basic weight of 60 g/m^2, containing added filler of 25% (O.D.), was prepared in laboratory procedure. In order to evaluate the effect of CNCC addition on the mechanical properties, various amounts of CNCC at 0, 1.1, 3.0, 5.2, 6.9 and 9.2%, respectively were incorporated into the resulting paper. Wet paper sheet was front pressured for 5 min and back pressured for 2 min at a press pressure of 1.06 MPa, followed by drying process at 93 °C for 3 min.

Afterwards, resulting paper was kept under a constant temperature of (23 ± 1)° C and humidity of (50 ± 2)% for 4 h according to Standard of GB/T 2679.13-1996 GB/T455, ISO1974 and GB/T 12914-2008. The air permeability, tear index and tensile index were measured as standards required as well.

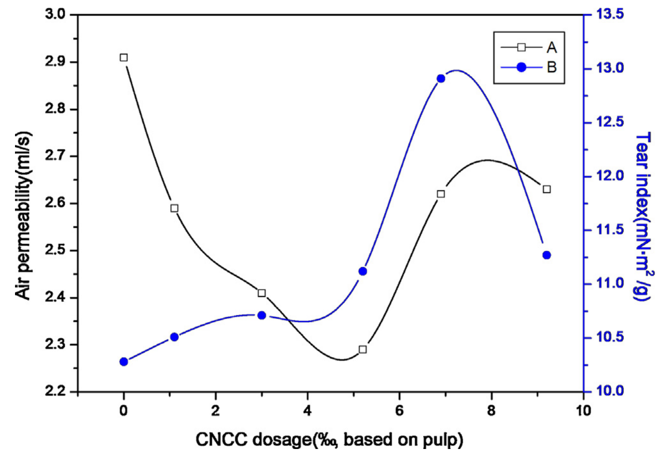

Fig. 1. Effect of CNCC dosage on the air permeability and tear index of cellulosic paper.

2.4. Preparation of PVA fiber paper reinforced with CNCC

2 g of PVA fibers was formulated into 1000 ml PVA suspensions, then were beat and dispersed in a disintegrator (total number of revolution is 15,000 r).

The remaining experimental procedures were the same as those of the preparation of cellulosic paper.

3. Results and discussion

3.1. Effect of CNCC on the mechanical properties of cellulosic paper

Curve A in Fig. 1 presents the air permeability of the cellulosic paper as a function of various dosage of CNCC. It can be observed that the air permeability decreased first and then increased. Specifically, when the CNCC dosage increased from 0 to 0.5%, there was a significant decrease in the air permeability. The air permeability reached the minimum of 2.34 mL/s at a CNCC dosage of 0.5%. When further increasing the CNCC dosage from 0.5 to 0.8%, the air permeability had a significant increase up to 2.61 mL/s at 0.7% CNCC and then reached a plateau. The significant change in air permeability can be mainly ascribed to the distribution state of CNCC. Overall, CNCC can fill in the gap between fibers and/or locate on the surface of fibers. At a low dosage of CNCC (0–0.5%), the gap between fibers can provide enough space for the filling of CNCC, therefore the air permeability sharply decreased with the increased CNCC dosage. However, excessive CNCC addition (0.7–0.8%) led to the increased air permeability presumably due to the distribution of part of CNCC on the surface of fibers.

Effect of CNCC addition on the tear index of cellulosic paper was investigated, and the result is shown in Curve B in Fig. 1. It can be found that the tear index consistently increased to 12.9 mN m^2/g as the CNCC addition increased from 0 to 0.7%, implying that the presence of CNCC exerted a significant effect on the enhancement of tear index. When the CNCC dosage was over 0.7%, the tear index declined rapidly. The visible improvement in tear index can be attributed to the chemical structure of the added CNCC. Lots of hydroxyl groups on the surface of CNCC offer opportunity to form hydrogen bonding and improve the bonding between fibers, thus leading to the improved tightness and tear index of paper. At a given NCC dosage over 0.7%, the tear index showed a downward trend,

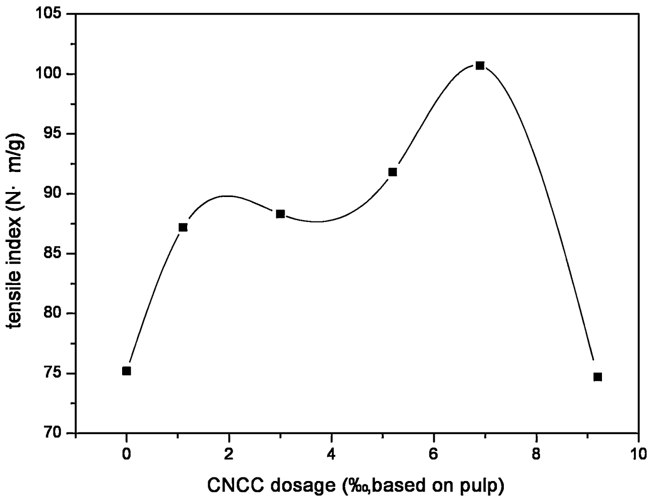

Fig. 2. Effect of CNCC dosage on the tensile index of cellulosic paper.

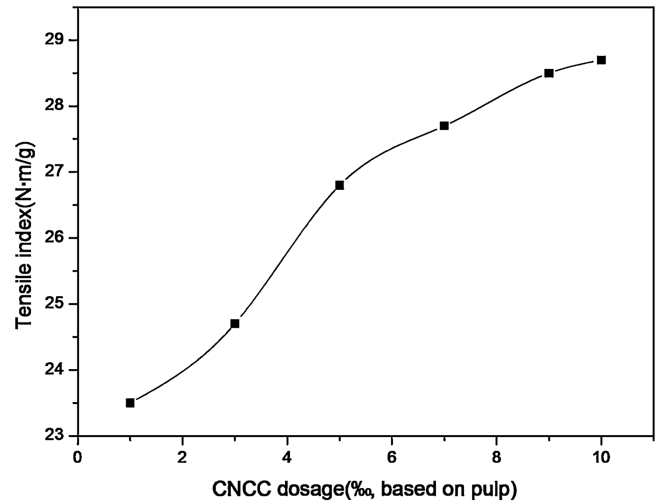

Fig. 4. Effect of CNCC dosage on the tensile index of PVA fiber paper.

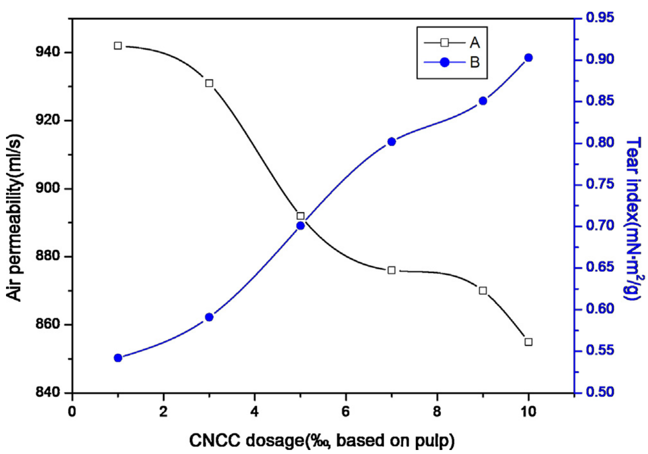

Fig. 3. Effect of CNCC dosage on the air permeability and tear index of PVA fiber paper.

which might be associated with the aggregation issue of part of CNCC.

Fig. 2 gives an indication of the change in tensile index with the increase of CNCC dosage from 0 to 0.8%. Similar to the tear index variation in Fig. 1, in the absence of CNCC, the tensile index was 10.4 mN m^2/g, which increased to 12.8 mN m^2/g at a CNCC dosage of 0.7%. Similarly, the tensile index reached the maximum of 100.7 N m/g at a CNCC dosage of 0.7%.

3.2. Effects of CNCC on the mechanical properties of PVA fiber paper

As can be seen from Curve A in Fig. 3, with the increase of CNCC dosage from 0.1% to 1.0%, the air permeability of PVA fiber paper sheet decreased continuously from 940 mL/s to 845 mL/s, showing a different change tendency from that of cellulosic paper sheet discussed above. One can assume that there were more sufficient gap between PVA fibers than cellulosic fibers, therefore allowed for the filling of higher dosage of CNCC, which might be responsible for the continuously decreased air permeability with the increased dosage of CNCC.

For Curve B in Fig. 3, increasing the CNCC dosage led to the increased tear index of PVA fiber paper. In the absence of CNCC, the tear index was 0.54 mN m^2/g, then increased to 0.9 mN m^2/g at a CNCC dosage of 1.0%, showing a percentage increase of 67.29%. This result provided direct evidence that CNCC addition was effective in reinforcing the mechanical properties of PVA fiber paper. The reason for that can be mainly attributed to the abundant carboxyl groups on the surface of CNCC, which facilitates the combining of its own hydrogen bonding or the hydroxyl groups of PVA fiber to form hydrogen-densely reticular structure, thereby resulting in the significantly improved tear index of PVA fiber paper (Li, Renneckar, & Barone, 2010). Similar result was presented in the literature (Uddin et al., 2011a; Uddin et al., 2011b). In the previous study, NCC was used for reducing fibrillation of PVA fibers, where oriented NCC was put inside in the inter-fibrillar areas and found to automatically form lateral interlinks between fibrils by hydrogen bonding which made fibrils a relatively complete unit and improved the tear index of PVA fibers.

Fig. 4 gives a clear indication that the tensile index of PVA fiber paper increased dramatically from 23.5 to 28.8 N m/g with increasing the CNCC dosage from 0.1 to 1.0%. The formation of hydrogen-gathered reticular structure was assumed to contribute to improving the tensile index of PVA fiber paper, which agreed well with the proposed result that the elastic modulus of the nanocomposite mats increased tremendously as a result of the reinforcing effect of NCC via the reticular network held by hydrogen bonds (Peresin et al., 2010).

In contrast, the tear index and tensile index, important parameters representing the mechanical properties, of PVA fiber paper were far lower than those of cellulosic paper. The discrepancy can be explained by the fact that the PVA fiber paper obtained here was made from the PVA fiber instead of PVA solution, the latter of which can be indeed used to make paper sheet with the tear index and tensile index similar to those of cellulosic paper. As a matter of fact, PVA fiber possesses inherently poor mechanical properties, which makes it inferior to cellulosic paper when applied to make paper. However, in our present work, significant improvement in the mechanical properties of PVA fiber paper using CNCC as strength agent was successfully achieved, which would set an attractive base for an eco-friendly and cost-effective manufacturing potential for the production of PVA fiber paper sheet with desired mechanical properties.

4. Conclusions

(1) Carboxylated nanocrystalline cellulose (CNCC) can be applied to improve the mechanical properties of both cellulosic paper and PVA fiber paper.

(2) For the cellulosic paper, the addition of CNCC can dramatically improve the mechanical properties. At its dosage of 0.7%, the tear index and tensile index reached the maximum of 12.9 mN m^2/g and 100.7 N m/g respectively.
(3) For the PVA fiber paper, with CNCC dosage increasing from 0.1% to 1.0%, the tensile index and tear index increased continuously, while the air permeability decreased.

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