Preparation of Ultralong Cellulose Nanofibers and Optically Transparent Nanopapers Derived from Waste Corrugated Paper Pulp

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Ultralong cellulose nanofibers with extremely high aspect ratio were successfully manufactured from waste corrugated paper pulp through a series of chemical treatments combined with grinding, ultrasonication, and centrifugation. SEM images revealed that the prepared cellulose nanofibers exhibited a uniform width ranging from 30 to 100 nm and a web-like network structure. The nanopaper was produced by filtration and oven drying using the obtained cellulose nanofibrils suspension. An interesting phenomenon occurred, namely that the nanopaper formed in multilayered nanofibrous flakes, which can be seen in the SEM image of the nanopaper cross section. The nanopaper derived from waste corrugated paper presented high tensile properties, with a tensile strength of 135 MPa and a tensile modulus of 6.67 GPa, which was approximately 10 times higher than the untreated waste corrugated paper. The obtained nanopaper also exhibited high transmittance of 85.2% at 600 nm wavelength and low thermal expansion of 16.2 ppm/K. The high performance nanopaper seems to be a strong candidate for fabricating optical electronics, solar cells, and panel sensors.

Keywords: Ultralong cellulose nanofibers; Nanopaper; Tensile strength; Light transmittance; Thermal expansion

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INTRODUCTION

The production of nano-scale cellulose fibers and their application in composite materials has gained increasing attention due to their high strength and stiffness combined with low weight, biodegradability, and renewability (Siró and Plackett 2010). The abundantly available and relatively low-cost nanofiber material can be used to produce films, sometimes called "nanopapers" in the literature (Kulachenko *et al.* 2012). It has potential as a strong sheet-like material or as a lightweight reinforcement phase in biocomposites (Sehaqui *et al.* 2011). Ultrastrength nanopaper with foldable, high strength, low-CTE (Coefficient of Thermal Expansion), and optically transparent properties appears to be an ideal candidate for substrates for transparent conductive films, metal wiring, e-papers, solar cells (Eichhorn *et al.* 2010; Nogi *et al.* 2009; Iwamoto *et al.* 2007), and gas barrier films (Fukuzumi *et al.* 2009; Syverud and Stenius 2009).

Cellulose microfibrils and related nanofibers can be isolated from various plant fibers (wood, cotton, hemp, flax, *etc.*), marine animals (tunicate), or algae, fungi, invertebrates, and bacteria (Lavoine *et al.* 2012). Chemical treatment is a relatively popular method for surface modification of natural fibers. Alkaline treatment, for instance with the use of sodium hydroxide (NaOH), eliminates natural products such as

hemicellulose, lignin, extractives, and waxes, presenting a rough surface and causing fibrillation of cellulose in the natural fibers (Chun *et al.* 2011).

The manufacture of MFC (microfibrillated cellulose) can be achieved by means of pretreatment, TEMPO-mediated oxidation, enzymatic pre-treatment, electrospinning methods, and mechanical methods consisting of grinding, high-pressure homogenization, ultrasonication, and cryocrushing (Hubbe *et al.* 2008; Siró and Plackett 2010). Among the various cellulose nanofiber (CNF) preparation routes, ultrasonication seems to be a well-suited method for isolating CNFs with relatively long lengths (Cheng *et al.* 2007; Cheng *et al.* 2009; Tischer *et al.* 2010; Zhao *et al.* 2007). Ultralong CNFs have a high aspect ratio and surface area, as well as a web-like entangled structure that could improve the toughness of the composites, all of which may provide new opportunities for many applications (Chen *et al.* 2011). However, few references are currently available that detail the manufacturing method of transparent nanopaper prepared by chemical modification combined with ultrasonication using waste paper pulp as the raw material.

Utilizing waste paper as the raw material for papermaking has long been essential for environmental and economic reasons. Among waste papers, corrugated paper is a major class of recycled paper for fiber reutilization. The manufacture of cellulose nano-fibers from renewable sources has gained more attention in recent years because of their exceptional properties (Nishino *et al.* 2004; Orts *et al.* 2005). Hrabalova *et al.* produced nano-fibrillated cellulose from flax and wheat straw pulps by high pressure disintegration and evaluated the reinforcing potential of nanocelluloses in a polyvinyl-alcohol matrix (2011). Pandey *et al.* extracted the cellulose nanofibers by using newspaper waste as the cellulosic source (2012). Considering that corrugated carton is the most widely used packaging product and waste corrugated paper is renewable, abundant, and cheap, the principal objective of this study was to prepare ultralong cellulose nanofibers from it and to examine the effects of chemical and mechanical treatment on the morphology, tensile performance, light transmittance, and thermal expansion of the cellulose nanopaper.

EXPERIMENTAL

Materials

Waste paper pulp was prepared from waste corrugated carton. The waste corrugated paper pulp was first soaked in water for several hours, and then it was cut into pieces with a high-speed blender, as is shown in Fig. 1a. Sodium hydroxide, acidified sodium chlorite, potassium hydroxide, and hydrochloric acid solution were of laboratory grade and used without further purification.

Methods

Chemical modification

In order to extract cellulose fibers from waste corrugated paper pulp, the prepared sample was subjected to a series of chemical treatments. To leach ink, hemicelluloses, extractives, and glue, the sample was treated in a 2 wt% sodium hydroxide (NaOH) solution at 90 °C for 2 h (Fig. 1b). Next, to leach lignin, the sample was cyclically treated three times using an acidified sodium chlorite ($NaClO_2$) solution at 75 °C for an hour according to the method of Okahisa *et al.* (2011), as is shown in Fig. 1c. Afterwards, the sample was treated in 2 wt% potassium hydroxide (KOH) at 90 °C for 2 h to remove residual ink and hemicelluloses. In order to obtain highly purified cellulose, the sample

was further treated with an acidified sodium chlorite solution at 75 °C for 1 h, and then was treated with 5 wt% potassium hydroxide at 90 °C for 2 h (Fig. 1d). Lastly, highly purified cellulose fibers were treated with 1 wt% hydrochloric acid solution at 80 °C for 2 h (Fig. 1e). The samples were washed with deionized water until a neutral pH was reached throughout the process, after which they were kept in a water-swollen state at all times.

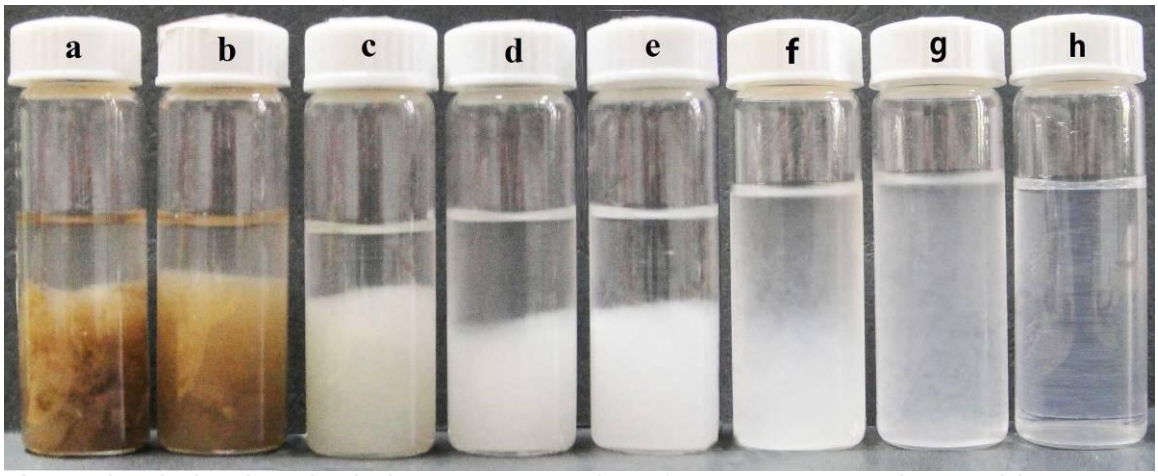

Fig. 1. Chemical and mechanical treatment procedures for waste corrugated paper: (a) raw material, (b) cellulose fibers with 2 wt% NaOH solution at 90 °C for 2 h, (c) cellulose fibers of b with $NaClO_2$ solution at 75 °C for 1 h three times, (d) cellulose fibers of c with further KOH and $NaClO_2$ treatment, (e) cellulose fibers of d with 1 wt% HCl at 80 °C for 2 h, (f) dispersion state of the chemically purified cellulose fiber after grinding 20 times, (g) suspension of f with ultrasonic output power of 1000 W, (h) supernatant of suspension g after centrifugation

Preparation of cellulose nanofibrils

The slurry of 1 wt% undried, purified sample was passed 20 times through the grinder (MKCA6-2, Masuko Corp., Japan) at 1600 rpm with the grinding stones pressed closely together (Fig. 1f). After grinder treatment, the cellulose fibers were soaked in distilled water at approximately 0.2 wt% solids content.

About 250 mL of a solution containing cellulose fibers was then placed in a common ultrasonic generator (XO-1200, Nanjing Xianou Bio Technology Co. Ltd., China) with a frequency of 20 to 25 kHz. Subsequent ultrasonication was conducted for 40 min at an output power of 1000 W, resulting in a sufficiently dispersed cellulose nanofibrils suspension (Fig. 1g). The sonicated suspension was then subjected to centrifugation, and slender nanofibrils were obtained from the supernatant fraction (Fig. 1h).

Preparation of nanopapers

After centrifugation, the water suspension of well-dispersed cellulose nanofibrils was slowly filtered with a membrane filter (pore size 200 nm; 40 mm in diameter) with a glass filter support. A wet film was formed by removing water from suspensions by vacuum filtration. The obtained film was sandwiched between two filter membranes, which were loaded between two smooth metal plates, then dried at 55 °C for 48 h under a weight of 5 kg. Finally, the dried nanopaper with high optical transparency was obtained.

Morphology of cellulose nanofibers

The suspension of cellulose nanofibrils after the centrifugation process was subjected to freeze-drying. Morphological studies on the freeze-dried cellulose nanofibers and examination of the cross-section of the nanopaper were performed using a scanning electron microscope (SEM) (Quanta 200, FEI, Ltd.). The morphology of the surface of the nanopaper was observed by a field emission scanning electron microscope (FE-SEM) (HITACHI S-4800, HITACHI, Japan).

Tensile properties

The tensile properties of the nanopaper sheets were measured using a universal materials testing machine (Shenzhen SANS Tensile Machine Co. Ltd., China) for samples 20 mm long, 3 mm wide, and 50 to 60 µm thick at a crosshead speed of 1 mm/min with a specimen gage length of 10 mm. The load cell capacity was 100 N. The average values of the tensile strength and the Young's modulus were calculated from at least five specimens.

Light transmittance

The regular luminous transmittance of the nanopaper was measured at wave-lengths from 200 to 1000 nm using a UV-visible spectrometer with an integrating sphere 60 mm in diameter (U-4100, HITACHI). Three replicate tests were conducted for each sample.

Coefficient of thermal expansion (CTE)

The CTE of the nanopaper derived from waste corrugated paper was obtained with a thermomechanical analyzer (TMA 402-F1, NETZSCH Inc.). The specimens were 20 mm long and 3 mm wide with a 15 mm span. The measurements were carried out with a heating rate of 5 °C min^{-1} in a nitrogen atmosphere under a load of 30 mN in tensile mode.

RESULTS AND DISCUSSION

Morphology

Figure 2 exhibits the SEM images of the resulting nanofibers made from waste corrugated paper pulp that were recovered by freeze-drying. The low magnification SEM images (Fig. 2a and 2b) revealed that the length of individual cellulose nanofibers (CNFs) were greater than one millimeter. Observed by SEM, there was cellulose nanofiber with a length at or exceeding 3 mm, but crimpy fibers were identified in some parts. Space between the CNFs was observed, owing to the sublimation of frozen water during freeze-drying. Chen *et al.* extracted CNFs with a high aspect ratio from bamboo, wheat straw, and softwood fibers, and it was reported that the obtained CNFs were assembled from slender cellulose nanofibrils during freeze-drying, due to the high specific area and strong hydrogen bonds established between the nanofibrils (2011). Thus, the uniform nanofibers isolated in this study are so-called microfibril aggregates (Donaldson 2007). The ultralong CNFs exhibited straight and smooth surfaces. The diameter range of the isolated CNFs from waste corrugated paper was 30 to 100 nm (Fig. 2c and 2d), showing relatively uniform particle size distribution. The aspect ratio of single CNFs was over

10,000, indicating that ultralong CNFs were individualized from waste corrugated paper pulp using this method.

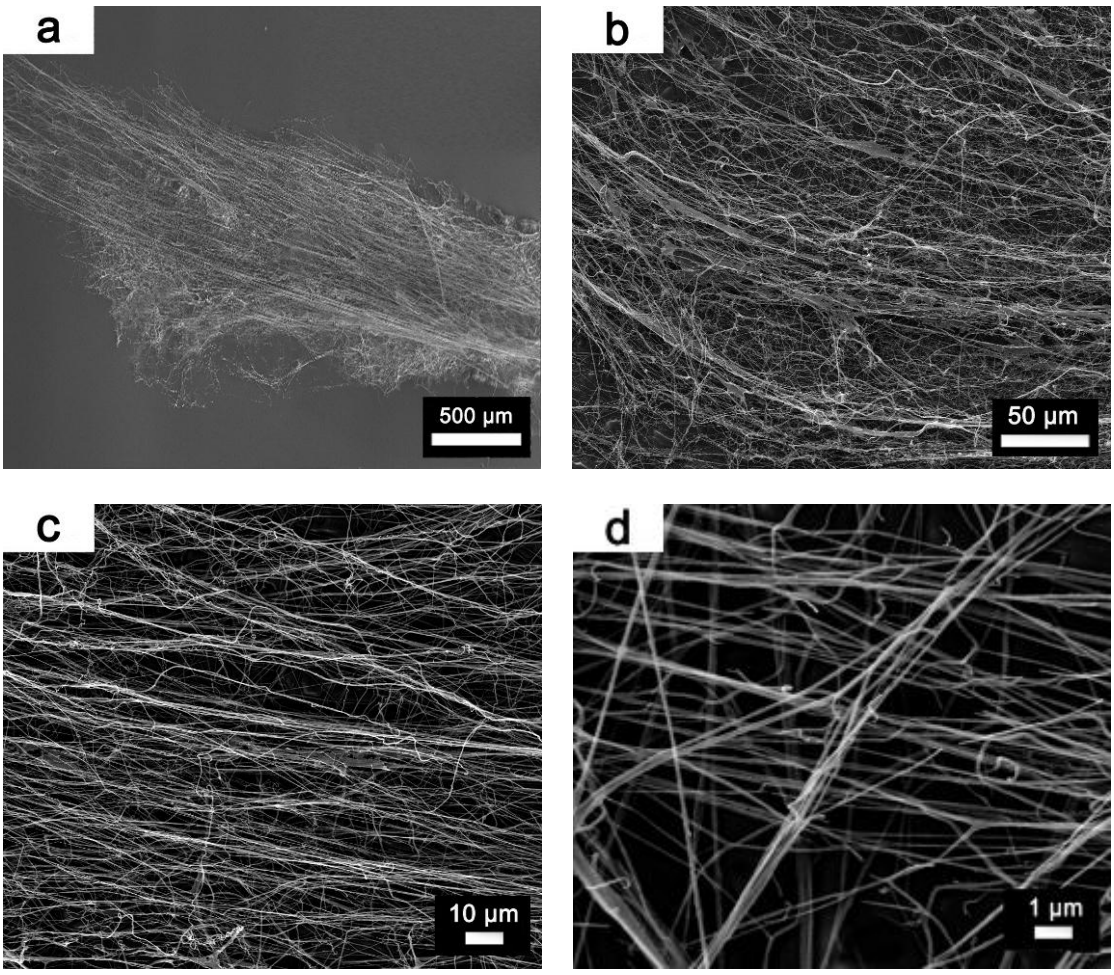

Fig. 2. SEM observation of ultralong CNFs assembled from slender cellulose nanofibrils

Figure 3a shows an SEM image of the cross section of a cellulose nanopaper made from waste corrugated paper, in which a homogeneous structure of nanofibers was observed. It was revealed that nanofibers isolated from waste corrugated paper pulp were quite smooth and uniform. The cross-sectional width of the nanopaper was about 50 μm. Apparently, a layered structure can be seen in the image of the nanopaper cross section. Figure 3b exhibits the fracture surface of the nanopaper with a 3-dimensional structure and a large number of CNFs. This view represented an interesting phenomenon – that nanopaper was formed by multilayered nanofibrous flakes – which may be attributed to the filtration process. The well-dispersed nanofibrils suspension was slowly filtered so that nanofibrils were piled uniformly in a wet sheet. In other words, cellulose nanofibrils have a tendency to self-assemble into layers.

Figure 4a shows an FE-SEM image of the undamaged and smooth surface of the nanopaper. It was revealed that the cellulose fibers were nano-fibrillated uniformly, with diameters between 30 and 100 nm, and assembled nanofibers were identified in some parts. Figure 4b shows the interior morphology of the nanopaper in a location where its surface layer had been pierced and torn by a needle; from this image it can be seen that

parts of slender nanofibers were torn out, indicating that the nanofibrous bundles may be strongly and tightly combined together to provide excellent mechanical properties for the nanopaper.

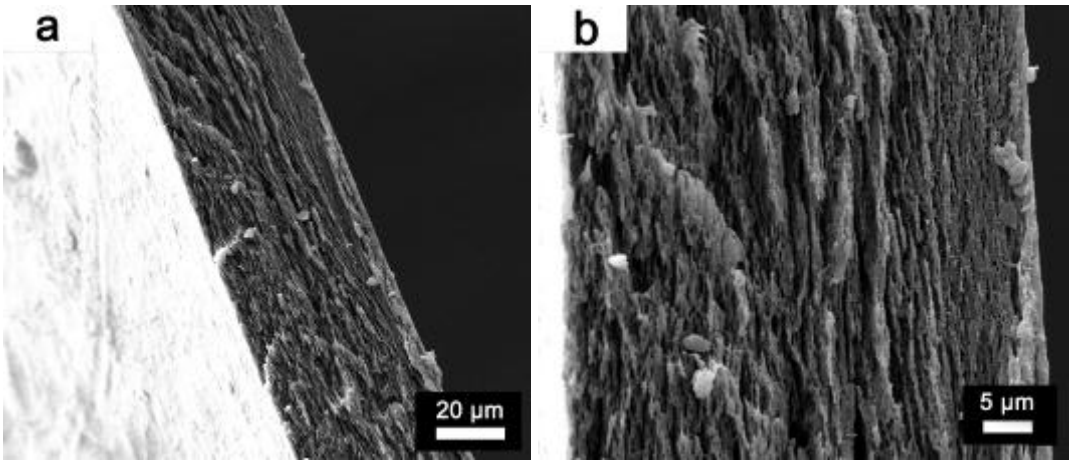

Fig. 3. SEM micrographs of the fracture surface of the cellulose nanopaper

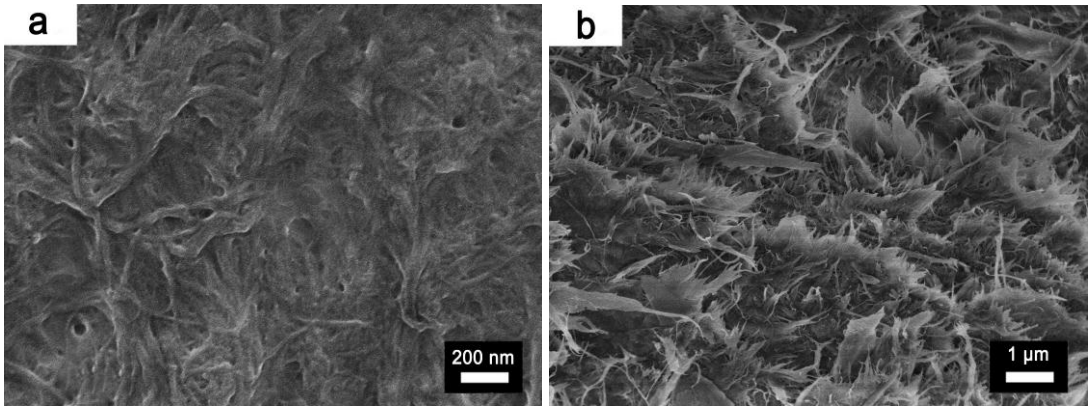

Fig. 4. FE-SEM image of (a) undamaged surface of nanopaper and (b) nanopaper surface pierced and torn by a needle

Tensile Properties

In addition to their morphology, nanopapers derived from waste corrugated paper exhibited good mechanical properties. Three sample types were prepared. The first was the untreated waste corrugated paper prepared as a control sample (with a density of 1.20 g/cm^3 and thickness of 0.15 mm). The second was nanopaper prepared by the oven-dried method previously described; the material was then kept in air-dry conditions at room temperature (25 °C) for 24 h (with density of 1.29 g/cm^3, and thickness of 0.078 mm). Finally, the third was the nanopaper, oven-dried as previously described, hot-pressed at 180 °C under 10 MPa for 15 min, then cooled down to room temperature (with a density of 1.30 g/cm^3, and thickness of 0.072 mm).

At a pressing temperature of 180 °C, the nanopaper became yellowish, and its tensile strength (152 MPa) and tensile modulus (9.26 GPa) were increased greatly, compared to the nanopaper prepared at room temperature, which may be attributed to the tight adhesion produced by the plasticization of residual lignin in nanopaper, although the lignin content was very small (Abe *et al.* 2009). And the higher density also contributes to the high mechanical properties of nanopapers.

The present results can be compared with the results of earlier studies involving nanopaper. Nogi *et al.* developed an optically transparent paper with a Young's modulus of 13 GPa and tensile strength of 223 MPa (2009). Abe *et al.* (2009) applied a one-time grinder treatment to disintegrate chemi-thermomechanical pulp (CTMP) and obtained micro- to nanometer-sized fibrous fragments and produced compression-molded products without any resin or adhesives by plasticizing lignin on CTMP fragment surfaces.

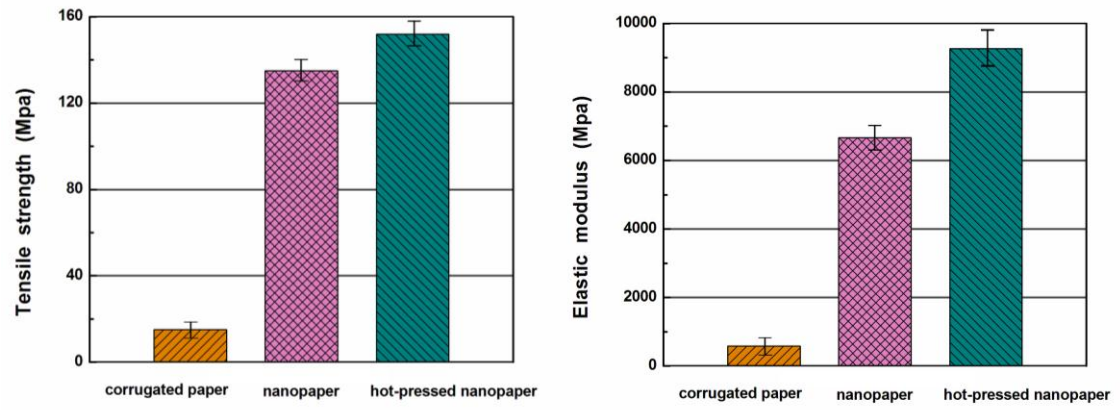

Fig. 5. Tensile properties of untreated waste corrugated paper, nanopaper at room temperature, and nanopaper hot-pressed at 180 °C

Regular Light Transmittance

Another remarkable feature of nanopaper is its high transparency. Fukuzumi *et al.* reported that 20 μm-thick TEMPO-oxidized MFC films prepared from hardwood and softwood cellulose transmit 78% and 90% of the light at 600 nm, respectively (2009). Nogi *et al.* evaluated the influence of film surface roughness on film transparency and found that when film surfaces were polished or impregnated with an optically transparent polymer layer (*e.g.*, using an acrylic resin), the total light transmittance could be increased up to 89.7% (Nogi *et al.* 2009; Nogi and Yano 2009).

The regular light transmittances of nanopaper derived from waste corrugated paper were evaluated in this paper. The appearance of the nanopaper at room temperature and nanopaper hot-pressed at 180 °C are shown in Fig. 6. Nanopaper at room temperature exhibited high optical transparency, while the hot-pressed nanopaper was yellowish and not as transparent.

At the 600 nm wavelength, nanopaper at room temperature transmitted 85.2% of the light (with density of 1.29 g/cm^3, and thickness of 0.078 mm), whereas the nanopaper hot-pressed at 180 °C transmitted 79% of the light (with a density of 1.30 g/cm^3, and thickness of 0.072 mm). As is shown in the FE-SEM observation, the individual cellulose nanofibers from the waste corrugated paper had relatively uniform dimension. The high transparency of the nanopaper may depend on uniform nano-sized fibrillation of pulp fibers.

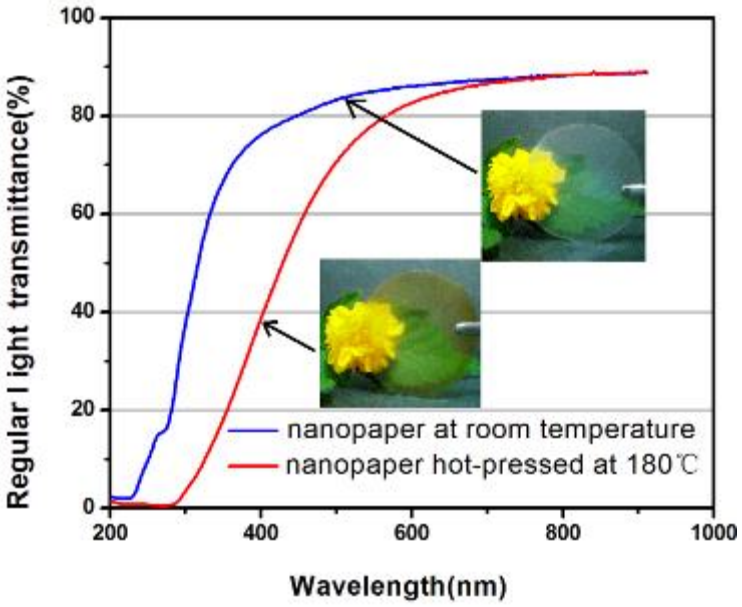

Fig. 6. Regular light transmittances of nanopaper at room temperature and nanopaper that was hot-pressed at 180 °C

Coefficient of Thermal Expansion (CTE)

One of the extraordinary properties of cellulose nanofibers is their extremely low thermal expansion. Nogi and Yano reported that transparent cellulose nanofiber sheets prepared from MFC and coated with acrylic resin have low CTEs of 8.5 to 14.9 ppm/K and a modulus of 7.2 to 13 GPa (Nogi *et al.* 2009; Nogi and Yano 2009). Iwamoto *et al.* (2007) investigated the effect of fibrillation on the physical properties of nanocomposites based on fibrillated pulp fibers and acrylic resin. Okahisa *et al.* (2011) reported that the CTEs of nanofiber sheets from immature bamboo and mature bamboo were found to be 10.4 ppm/K and 12.3 ppm/K, respectively.

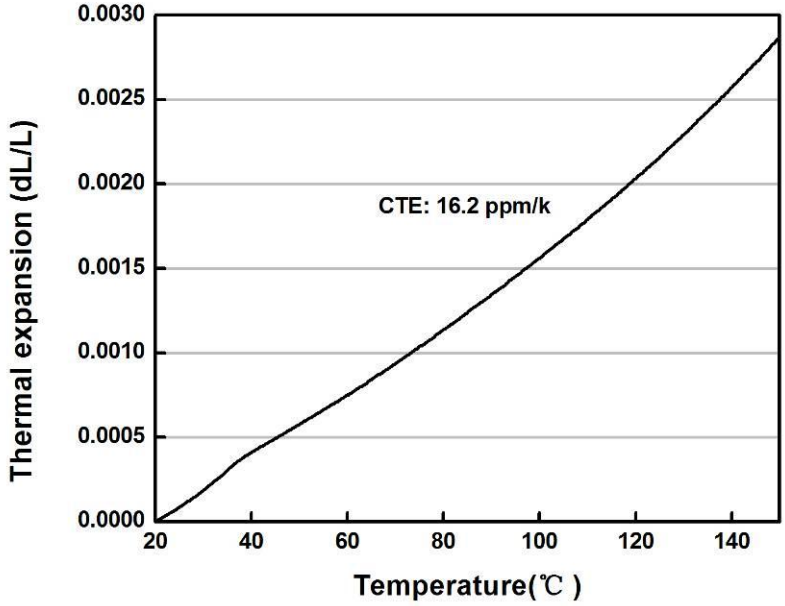

Fig. 7. Coefficient of thermal expansion (CTE) of the nanopaper made with CNFs from waste corrugated paper

The thermal expansion of the nanopaper derived from waste corrugated paper was studied in this work. The CTE values were determined in the temperature range of 20 to 150 °C in the second run. The CTE (α_T, 1/ °C) value was calculated as,

$$\alpha_T = \frac{1}{L}\frac{dL}{dT} \quad (1)$$

where L is the linear dimension of the test sample and dL/dT is the rate of change in the linear dimension per unit temperature. Figure 7 indicates that the coefficient of thermal expansion (CTE) of the nanopaper derived from waste corrugated paper was 16.2 ppm/K in the temperature range of 20 to 150 °C. This low CTE combined with high strength and modulus could make cellulose nanofiber a potential reinforcing material in roll-to-roll technologies, *e.g.*, for fabricating flexible displays, solar cells, electronic paper, panel sensors, and actuators (Siró and Plackett 2010).

CONCLUSIONS

1. Cellulose nanofibers having a uniform width and a web-like network structure were successfully individualized from waste corrugated paper by a combination of chemical treatment (involving alkali, sodium chlorite, and acid steps), grinding, ultrasonication, and centrifugation treatments. A morphological study showed that the average diameter range of the isolated CNFs from waste corrugated paper was 30 to 100 nm and the aspect ratio of the CNFs was over 10,000.
2. The nanopaper derived from waste corrugated paper pulp was produced by filtration and oven dying using the obtained cellulose nanofibrils suspension. The SEM image of the nanopaper cross-section presented a layered structure, indicating that cellulose nanofibrils have a tendency to self-assemble into layers during the filtration process.
3. The nanopaper obtained exhibited high tensile properties, high optical transparency, and low thermal expansion properties. It was mechanically strong and stiff, with a tensile strength and modulus approximately 9 and 11 times higher than the untreated waste corrugated paper.
4. The obtained nanopaper (with density of 1.29 g/cm^3, and thickness of 0.078 mm) also exhibited high transmittance of 85.2% at a 600 nm wavelength and low thermal expansion property of 16.2 ppm/K, which makes it a potential reinforcing material in optical electronic technologies.

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