The Study on Nanocellulose and Their Biocomposites

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ABSTRACT

Nanocellulose fibers (CNFs) with the average diameter below 100nm were successfully obtained by a high shear fluid processor, viz. a microfluidizer. Their large surface area and nano-scale dimensions can lead to the emerging materials for reinforcements in polymer composites, differentiating from common polymer composites and providing the opportunity for nano-engineered materials that could have not achieved from conventional materials. CNF nanopapers with synthetic fibers such as polylactic acid (PLA) were fabricated by a wet-laid sheet forming process, and then molded by high pressure calendering to manufacture CNF/PLA nanocomposites. The wet-laid process was found a good way to make CNF/PLA nanopapers and nanocomposites. Their mechanical performances were increased by the incorporation of CNFs due to the reinforcing effects of CNFs.

Keywords: Microfibrllated cellulose, Poly lactic acid fibers, Homogenizer, Composites, Wet-laid sheet forming process

1 INTRODUCTION

Over the last decades, there has been an emerging interest in the development of novel composite materials based on biodegradable and renewable materials. Therefore, it is advantageous to utilize different types of cellulosic fibers as reinforcements in such biocomposites, since cellulose is an abundant, renewable and biodegradable resource. Furthermore, the mechanical properties of cellulose fibers are desirable in the utilization as reinforcements in novel low-density and high strength materials [1].

Wood pulp fibers are presently a major area of research for several end-use applications. Celluloses can be utilised as reinforcements in biodegradable composites and as a source of raw materials for bioenergy and biochemical production. Wood pulp fibers have been applied as the raw material for the production of fibrillated materials, which were introduced and defined as microfibrillated cellulose (MFC) by Turbak et al. [1] and Herrick et al. [2]. Several modern and hightech nano-applications have been envisaged for MFC [1]. Although cellulose fibers have

constituted the main source for MFC production, the utilisation of other pulp fibers, agricultural crops and by-products have also been explored [3-5]. With the years, various subjective definitions have been given to the fibrillated materials, e.g. nanofibrillated cellulose, nanofibers, nanofibrils, microfibrils and nanocellulose [6-10].

In the context of nanocomposites, cellulose nanofibers are also of interest. Due to the high modulus and strength of 134 GPa and 4 GPa, respectively, CNFs are suitable as reinforcements in polymer nanocomposites [11]. Cellulose exists as a load-bearing component in plant cell walls on land, but is also found in algae and tunicate sea animals or can be produced by bacteria. Cellulose is a linear polysaccharide, poly-ß(1,4)-D-glucan. The molecules aggregate and are present as microfibrils. These microfibrils consist of aligned extended molecules, laterally stabilized by hydrogen bonds [12] and contain both ordered and less ordered regions [13]. The cross-sectional dimension of these microfibrils varies due to the origin of the cellulose, but is about 4 nm for wood cellulose. Wood microfibrils form aggregates and are present as 15-18 nm thick microfibril aggregates in wood pulp fibers. In nanocomposites, wood based cellulose nanofibrils are used either in the form of microcrystalline cellulose or microfibrillated cellulose.

In the present study, the effects of the processing conditions of the microfluidizer were systematically investigated on the morphology and properties of the resultant CNFs. The CNF/PLA nanopapers and nanocomposites were fibricated by wet-laid paper-making method and hot calendering at high pressure in order to fully realizes the potential of CNFs and identify opportunities regarding the future directions of CNFs and their nanocomposites.

2 EXPERIMENTAL

2.1 Preparation of Cellulose Nanofibers

Microcrystalline celluloses (VIVAPUR® 102, JRS, Germany) were used to prepare celliulose nanofibers (CNFs). The celluloses were dispersed in distilled water at a

solid weight content of 0.5% using an overhead mixer for 30 minutes.

The resulting slurry was subject to high pressure homogenization to fibrillize the cellulose fibers. The homogenization of the slurry was performed by a microfluidizer (MinideBee, Bee International, USA) with a parallel flow nozzle setup configuration for the fabrication of CNFs. The slurry was totally passed 30 times through the microfluidizer with various nozzles sizes and various operating pressures.

The first ten passes were carried out a operation pressure of 10,000 psi with a nozzle of 10/1000" diameter, and then the second ten passes at a operation pressure of 30,000 psi with a nozzle of 8/1000" diameter and the last ten passes at a operation pressure of 45,000 psi with a nozzle of 5/1000" diameter.

2.2 Preparation of CNF/PLA composite sheet

The 240ml of CNFs was diluted to 2000 mL with water (CNF content of 1.2g). The CNF slurry and 2.8g of polylactic acid fibers were mixed and sheet-formed with a weight ratio of 3:7 using 400 grade stainless steel mesh. The composite sheet was dried at 80°C for 24 hours in a convection oven at ambient pressure. The resulting sheets were calendered under the pressure of 800 psi at 180°C for CNF/PLA nanopaper or 5 times at 196°C for fully melting of PLA fibers to manufacture CNF/PLA nanocomposites.

2.3 Characterization

The specific surface area of the CNFs was determined using Congo red dye absorption method [14]. A 5mg of CNFs in a phosphate solution (pH 6) was dyed with various concentration of Congo red ranging from 0.01mg/ml to 0.16mg/ml at 30°C for 90 minutes by a shaker. The suspension was filtered and the final dye solution was used to determine the dye concentration by its UV-VIS absorbance at 500nm with a spectrophotometer (Cary 500, Varian, Australia). The absorbed amount of Congo red on the nanopaper surface was calculated by the Langmuir equation (Eq. 1) and a plot of 1/A versus 1/C [15]:

$$\frac{1}{A} = (\frac{1}{K_{ads}[A]_{max}})(\frac{1}{C}) + (\frac{1}{[A]_{max}})$$ (1)

where A is the amount of dye absorbed by substrate [mg dye/mg substrate], C is the amount of dye not absorbed [mg/mL], $[A]_{max}$ is the maximum amount of dye absorbed by substrate [mg/g], and K_{ads} is the equilibrium constant. The specific surface area (SSA) of the cellulose sample was determined by the following equation [15]:

$$SSA_{substrate} = [A]_{max} \times N_A \times SA_{CR} / CR$$ (2)

where N_A is the Avogadro constant (6.022×10^{23} mol^{-1}), SA_{CR} is the surface area of a molecule of Congo red (1.73 nm^2), and CR is the molecular weight (696.7 g/mol) of Congo red.

3 RESULTS AND DISCUSSION

Table 1 shows a significant increase in specific surface area (SSA) of CNFs, indicating the increased extent of fibrillation during homogenization progress. The final cellulose nanofiber increases to the values of 282.2 m^2/g. Compared with Vivapur (as received), the increase in SSA for CNFs is in agreement to the results of the microscopic study, showing that the fiber diameter was reduced by a few orders of magnitude as shown in Figure 1. The reduction in the fiber diameter can contribute to the higher SSA in the nanopaper. The higher SSA is an essential prerequisite for the reinforcements in nanocomposites. The nanoscale fibers with high SSA create one to three orders of magnitude more internal interfacial area per the fiber than the conventional microscale fibers [16]. The larger interfacial area with matrix materials improves the reinforcement efficiency by increasing the interfacial area to transfer stresses from the matrix materials to or between fibers.

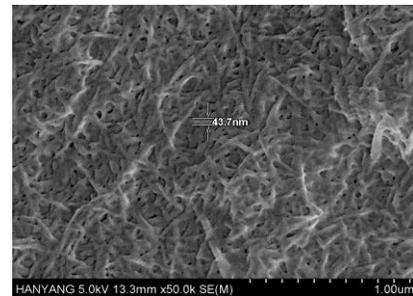| Sample code	[A]max [mg/g]	SSA [m2/g]
VIVAPUR (as received)	142.9	213.6
CNFs	188.7	282.2

Table 1: Specific surface area of CNFs

Figure 1: FE-SEM micrographs of CNFs

Figure 2 shows the tensile strength and modulus of CNF/PLA nanopapers and nanocomposites as a function of the CNF content. The tensile strength and modulus for CNF/PLA nanopapers are increased with increasing the CNF content due to reinforcing effects of CNF. However, the CNF/PLA nanocomposite has the lower strength than the PLA film but highest modulus among the other cellulosic materials.

The scanning elecrtron microscopic (SEM) study was conducted to characaterize the mophology of CNF/PLA nanocomposites. Figure 3 shows the FE-SEM micrographs of surface and tensile fracure surfaces of PLA films and CNF/PLA nanocomposites. It is demonstrated that the spaces between the PLA fibers are filled with CNFs and the surfaces are largely covered with CNFs. However, the pores and debonding between CNF and PLA fibers can be still observed, and that may result in the detrimental effects on the mechanical properties of the nanocomposites, i.e. lower strength of CNF/PLA nanocomposites than PLA films.

Figure 3: FE-SEM micrographs of surfaces and tensile fracture surfaces of PLA films and CNF/PLA nanocomposites.
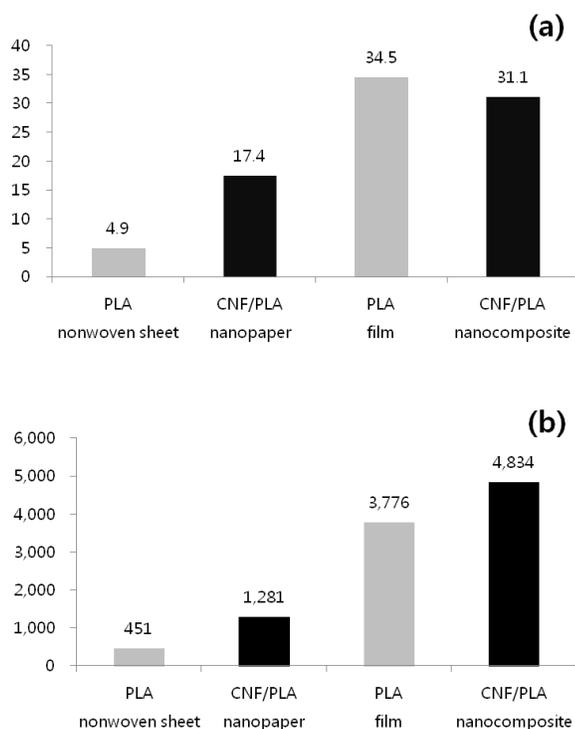
(a)

(b)

Figure 2: Tensile strength and modulus of CNF/PLA nanopapers and nanocomposites as a function of the CNF content; (a) tensile strength, (b) tensile modulus.
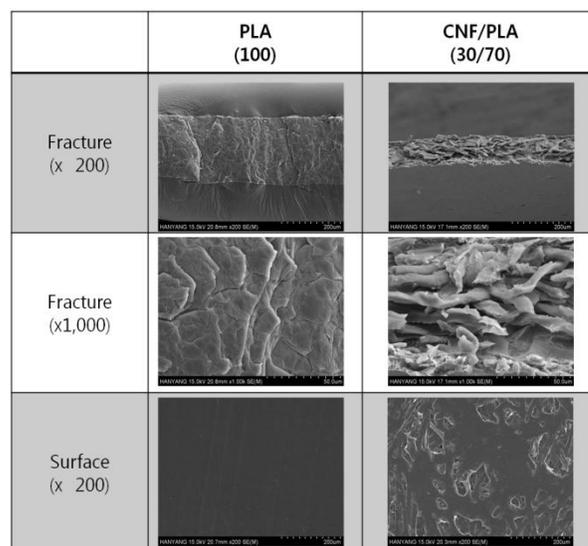
4 CONCLUSION

Cellulose nanofibers and their nanopapers were successfully prepared using high pressure homogenization processes with a microfluidizer and vacuum filtration paper-making processes, respectively. The nanocomposite with the ratio of 3:7 of CNF and PLA has the highest tensile modulus among the other cellulose materials due to reinforcing effects of CNF. However, the lower strength in CNF/PLA nanocomposites may be due to the pores and debonding between CNF and PLA fibers. The increase in the tensile modulus and specific surface area of the nanopapers successfully demonstrated the potential use of cellulose nanofibers in the reinforcement for polymer nanocomposites. However, the further study is needed to increase interfacial bonding beteen CNFs and PLA fibers, and to reduce the voids through the development of efficient composite manufacturing processes.

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