Reinforcement of Cellulose Nanofibers On the Stiffness and Strength of Composite Sheets Under Dry and Wet Conditions

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Research Article

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Abstract

The objective of this study was to evaluate how a wide range (0–100%) of cellulose nanofiber (CNF) addition affects the mechanical properties of composite sheets made of bleached pulp fibers and CNFs. It was found that adding CNFs could reduce the porosity of the sheets, thus increasing the dry Young's modulus within the CNF addition range of 0–100%, whereas the dry specific Young's modulus of all the sheets was constant. The dry tensile strength of the sheets increased as the CNF addition increased to 70% because of the increased hydrogen bond density between the pulp fibers. However, there was no further improvement in the dry tensile strength when the CNF addition was more than 70%. Although the wet Young's modulus decreased when the CNF addition was more than 20% owing to the increase in the thickness of the sheets, the wet tensile strength of the sheets increased almost linearly as more CNFs were added up to 70%, and the maximum wet strength retention reached nearly 10% at 40% CNF addition.

Introduction

Cellulosic paper, bulk and lightweight sheets based on the type of plant fibers, and nanopaper, thin and dense sheets made from nanocelluloses, have served as promising biomaterials for a wide range of applications, including biomedical devices (Deka et al. 2020), flexible substrates (Siegel et al. 2010), food packaging (Khwaldia et al. 2014), storage (Nyholm et al. 2011), and sensors (Dungchai et al. 2009; Liana et al. 2012). The manufacturing of paper is facile, and the raw material for paper, cellulose fiber, is the most abundant renewable biopolymer on the earth, which is sourced from wood (Boufi et al. 2016), grass (Obi Reddy et al. 2014), cotton (Shi et al. 2010), and even bacteria (Sözen et al. 2021). Although paper has numerous advantages, such as cost-effectiveness, sustainability, renewability, and high potential to replace plastic in some fields, the mechanical and physical property requirements limit its diverse applications in composites. In particular, at high relative humidity, overcoming the water absorption characteristics of paper and protecting hydrogen bonding between fibers has always been a challenge.

Traditional methods such as refining and beating can enhance the strength of paper by improving the fiber strength and fibrillation degree (Ang et al. 2019; Motamedian et al. 2019); however, they have a negative effect on the bending stiffness of paper. Thus, more chemical additives were chosen instead of beating or refining, such as dry strength agent (cationic polyacrylamide, CPAM) (Djafari Petroudy et al. 2014) and wet strength agent (polyamide amine-epichlorohydrin, PAE) (Obokata et al. 2005; Obokata and Isogai 2007; Su et al. 2012). Although the use of chemical additives has greatly improved the strength, it is not environmentally friendly, owing to the production of by-products in the manufacture and use process, and it is also not conducive to the recycling of paper (Hagiopol and Johnston 2011; Onur et al. 2019). In addition, chemicals could induce an increase in wastewater load. These serious problems have stimulated the papermaking industry and researchers to seek green, biodegradable substitutions for these chemical additives and traditional methods. So far, natural materials such as starch (Ghasemian et al. 2012; Hamzeh et al. 2013), guar gum (Xie et al. 2016), chitosan (Chen et al. 2013; Rahmaninia et al. 2018), carboxymethyl cellulose (CMC) (Uematsu et al. 2011; Siqueira et al. 2015), and nanocelluloses (nanocrystals (CNCs), and nanofibers (CNFs)) (Sun et al. 2015; Vallejos et al. 2016) have been used in

papermaking to improve paper strength. Additionally, in recent years, ionic liquids, such as 1-butyl-3-methyl-imidazollium chloride ([BMIM]Cl), have been explored as a wet strength agent for paper sheets by partially dissolving the cellulose to form a thin cellulose film on the paper surface and increasing the wet strength (Ichiura et al. 2017). The use of phosphoric acid-urea solution to treat cellulose paper to increase the wet strength was also investigated (Yamamoto et al. 2019). However, there are temperature requirements (80–140 ℃) for the pretreatment of paper using these two methods.

An ideal reinforcing material for paper may (i) be sourced from natural and green processing, (ii) require no damage to pulp fibers, (iii) be easily mixed with fibers, fillers, and other additives to improve paper properties, and (iv) extend paper lifetime for recycling. Compared with other natural reinforcing materials, CNFs have attracted great attention as an alternative to traditional methods and chemical agents because they not only meet these requirements but also have excellent performance. CNFs have extremely good mechanical properties, including a high Young's modulus of up to 150 GPa (Iwamoto et al. 2009) and excellent tensile strength up to 6 GPa (Saito et al. 2013). These unique inherent properties of CNFs can play a key role in the reinforcement of composites. Furthermore, they have diameters in the range of 5–50 nm and several micrometres in length, leading to a large specific surface area and a high aspect ratio (Moon et al. 2011; Zhu et al. 2015), which also plays an important role in improving the hydrogen bonding between fibers. The inherent tendency to form strong entangled networks also promotes interfacial contact with the fibers (Boufi et al. 2016).

CNFs as an additive for paper with and without other polymetric strength additives, including wood pulp (Kumar et al. 2016; Mocchiutti et al. 2016; Ottesen et al. 2016; Tozluoglu and Poyraz 2016), agricultural waste pulp (Balea et al. 2017), and recycled pulp (Delgado-Aguilar et al. 2015), have been studied. Generally, adding a small number of CNFs to the pulp suspensions reinforces the physical and mechanical properties of paper, resulting in reduced porosity, increased density, and the improvement of overall strength (Jonoobi et al. 2012; Boufi et al. 2016). Sehaqui et al. (2011) added 2% CNF to bleached pulp, which induced a more compact and hierarchical structure that was formed by the nanoscale CNF networks embedded into microscale pulp fiber networks. They found that all the sheets containing CNFs had a higher dry tensile strength and dry Young's modulus compared to that of the pulp sheet without CNFs. Adding 20 wt% CNF to aramid pulp gave the composite sheet good tensile index and tear index in dry conditions, which were 2.04 times and 2.36 times that of the control sample, respectively (Lu et al. 2017). Adding 10 wt% CNF to unbeaten pulp improved the wet strength of the composite sheet by one order of magnitude, and the wet strength was further improved by approximately two orders of magnitude for the pure CNF sheet compared to non-beaten sheet (Sehaqui et al. 2013).

Although the reinforcement of CNFs on composite sheets has been studied and reported, there are few detailed reports on how a wide range (0–100%) of CNF addition affects the stiffness and strength of composite sheets. Whether the stiffness and strength of the composite sheets increase with an increase in the CNF content and whether the pure CNF sheet can have the maximum tensile strength and Young's modulus under dry and wet conditions are unknown. To better understand these questions, we designed an experiment. In particular, composite sheets made of bleached pulp fibers and CNFs were produced by

vacuum filtration. The effect of 0–100% CNF on the Young's modulus and tensile strength under dry and wet conditions was investigated by tensile testing and scanning electric microscope (SEM) observations.

Experimental

Materials

Wood powder from Hinoki cypress (Chamaecyparis obtusa) was used for the preparation of CNFs. Kraft bleached softwood pulp fibers and CNFs from Hinoki powder were used as raw materials for the composite sheets. Sodium chlorite ($NaClO_2$) and potassium hydroxide (KOH) were obtained from Nacalai Tesque (Kyoto, Japan). Acetic acid was obtained from Wako Pure Chemicals (Osaka, Japan). An ADVANTEC hydrophilic PTFE membrane with a pore size of 0.1 μm was used for vacuum filtration to obtain a wet sheet.

Preparation of CNFs

CNFs were prepared following our laboratory methods (Abe et al. 2007; Abe and Yano 2011; Abe and Utsumi 2020) and other studies (Wise et al. 1946). In particular, 30 g of Hinoki wood powder was dispersed in 1800 mL of distilled water and heated in a water bath at 80°C. Then, 18 g of $NaClO_2$ and 2.4 mL of acetic acid were added to the above suspension hourly, which was repeated four times to remove lignin. The resultant residues were washed until the pH reached approximately 7. The washed sample was heated at 90°C for 2 h in a 6 wt% KOH solution to remove hemicellulose. The resulting residues were filtered, collected, and then delignificated again according to the mentioned methods for another 5 h. Finally, the purified pulp was obtained and adjusted to a concentration of around 0.8 wt%. Consequently, the purified pulp was passed through a grinder (MKCA6-2; Masuko Sangyo Co., Ltd. Saitamaken, Japan) to obtain CNF dispersion.

Manufacture of composite sheets

A mixed suspension (240 g) consisting of CNFs and pulp fibers was vacuum filtrated to form a wet sheet on the PTFE membrane. The mixing ratio of CNFs varied from 0–100%. Stirring was manually used to ensure that the CNFs and pulp fibers were fully mixed. The wet sheets were dried at 120°C under 2 MPa for 15 min using a hot press. All the sheets were conditioned at 23 ± 1°C and a relative humidity of 50 ± 2% for at least 24 h prior to all measurements.

Thickness and density

All the measured specimens cut from the sheets were 30 mm long and 6 mm wide. The thickness of the specimens measured using a digital micrometre was taken as the average of six points. The density was calculated by measuring the average dimensions and weights of the specimens. The porosity was calculated from the density of the composite sheets according to the following formula, assuming the density of the cellulose to be 1.5 g/cm^3 (Henriksson et al. 2011).

$$porosity(\%) = (1 - \rho_{sheet}/\rho_{cellulose}) \times 100$$

1

Tensile test

The specimens prepared for density measurement were subjected to a tensile test using a universal testing machine (Model 3365; Instron Crop., Canton, MA) equipped with a 2-KN load cell at a crosshead speed of 1 mm/min. The tensile strength and Young's modulus were recorded for the six specimens for each sample. The specific Young's modulus and specific tensile strength were calculated by dividing the Young's modulus and the tensile strength by the density.

Before the wet tensile test, all the specimens were soaked in distilled water for 30 min and then gently wiped using filter paper to remove free water. The width and thickness of all the specimens before and after soaking were measured and taken as the average of six points.

Wet strength retention (WSR) (Ichiura et al. 2017) was determined using the following formula (2).

$$WSR(\%) = (WTS/DTS) \times 100$$

2

Here, DTS is the tensile strength of the dry specimens, and WTS is the tensile strength of the wet specimens.

Water uptake and swelling degree

Water uptake was determined by measuring the weight before and after soaking in distilled water for 30 min, based on three specimens for each condition, using the following formula (3).

$$Wateruptake(\%) = (M_w - M_d)/M_d \times 100$$

3

Here, M_w is the weight of the specimens after soaking in distilled water, and M_d is the weight of the oven-dried specimens.

The swelling degree was calculated using formula (4).

$$Swellingrateinthickness(\%) = (T_w - T_d)/T_d \times 100$$

4

Here, T_d is the thickness of the dry specimens, and T_w is the thickness of the wet specimens.

SEM analysis

The morphologies of the pulp fibers and sheets were observed by SEM (JSM-7800F Prime JEOL, Tokyo) at an acceleration voltage of 2.0 kV. The wet pulp fibers were air-dried for SEM observations. All the sheets and pulp fibers were coated directly with a layer of platinum by sputtering for 90 s before observation. Although the coating thickness was approximately 4 nm, we believe that the coating did not have an influence on the lateral dimensions of the pulp fibers and CNFs.

X-ray diffraction analysis

The dried pure pulp sheet and pure CNF sheet were subjected to X-ray diffraction measurement in reflection mode. The diffraction patterns were carried out with a MAXimaXRD-7000 using Cu-Kα radiation (Shimadzu, Japan) at 40 kV and 30 mA with a scanning rate of 2º/min in the angle range of 5º to 40º.

The crystallinity CI was determined using the following formula (5) (Segal et al. 1959) after removing the background by subtracting the intensity at 2θ in 40 °.

$$CI(\%) = (I_{200} - I_{am}) / I_{200} \times 100$$

5

Here, I_{200} is the maximum intensity of the 200 lattice diffraction, and I_{am} is the intensity of diffraction at 2θ = 18º.

Results And Discussion

The width of the pulp fibers was approximately 25–30 μm, as shown in Fig. 1a. The diameter of CNFs prepared in this study was tens of nanometres, as shown in Fig. 1b, which is consistent with our previous report (Abe and Yano 2009). All the sheets were prepared by filtrating the mixture of CNFs and pulp fibers on the fine membrane with a pore size of 0.1 μm to prevent CNFs from going through the filter.

Structure analysis of dry sheets

To better understand the mechanical behaviour of the composite sheets, the basic characteristics, thickness, density, and porosity were measured and calculated, as shown in Fig. 2. It is well known that the density of a sheet is the ratio of the basis weight to the thickness of the sheet. In the present work, the quality and concentration of the mixed suspensions consisting of CNFs and pulp fibers were controlled to be about 240 g and 0.2 wt%, regardless of the CNF ratios. It can be clearly seen from Fig. 2a that adding CNFs could decrease the thickness of the sheets, thus increasing the density. The density of sheets increased gradually with the increase of CNF addition from 0–100%, and the highest density (1.30 g/cm^3) was obtained at CNF addition of 100%, which increased by 59% compared to that of pure pulp sheet. Correspondingly, the porosity gradually decreased with an increase in CNF addition from 0–100%. The minimum porosity (13%) was obtained with 100% CNF addition, which was 71% lower than that of the pure pulp sheet. These results suggest that adding CNFs could effectively reduce the number of voids and compact the sheet structure. One possible reason is that the nano size and high specific area of

CNFs make it easier to form denser structure than long pulp fibers. The other is that CNFs fill the micropores formed by pulp fibers (Sehaqui et al. 2011). In addition, considering that there were lumens in the pulp fibers, reducing the addition of pulp fibers could reduce the thickness and increase the density of the sheets (Cai et al. 2015).

The surface morphologies of the sheets are presented in Fig. 3. There was an obvious difference in the surface smoothness of the composite sheets compared to that of the pure pulp sheet. The surface of the pure pulp sheet was rough, and micropores were apparent, which would not be desirable for sheets with a good load transition. However, with the increase in CNF addition, these micropores disappeared, which was mainly because CNFs coated on the surface of the pulp fibers or filling the micropores between the pulp fibers, and the surface smoothness improved significantly; in particular, the surface of the pure CNF sheet looked like a film. These results are in agreement with the results shown in Fig. 2b. These changes in the structure of the sheets were desirable for providing good load-carrying and transfer ability to the composite sheets.

Young’s modulus of dry sheets

Figure 4a shows the dry Young’s modulus and specific Young’s modulus of the composite sheets. In the present work, the dry Young’s modulus (7.80 ± 0.83 GPa) of the pure CNF sheet was in accordance with the reported value range of nanopaper (6–18 GPa) made of fully bleached fibers (Rojo et al. 2015). Because the density has a certain impact on the mechanical properties of composite sheets, the specific Young's modulus was also calculated to compare the effect of CNF addition on the Young's modulus more accurately. The dry Young’s modulus gradually increased as the CNF addition increased form 0–100%, and the maximum value was reached at 100% CNF, which was 68% higher than that of the pure pulp sheet. It was confirmed that adding CNFs made the sheets stiffer. Although the dry Young’s modulus increased, the dry specific Young’s modulus did not change significantly with the addition of CNFs. These results suggest that the increase in the dry Young’s modulus was mainly due to the increased density. As shown in Figs. 1 and 2, adding more CNFs could significantly reduce the porosity, leading to a denser sheet structure, which contributed to substantial load-carrying and transfer to sheets, leading to an increased dry Young’s modulus.

The specific Young’s modulus was constant with increasing CNF content. This result seems to indicate that the pure CNF sheet and pure pulp sheet are essentially the same for Young’s modulus. Therefore, we carried out X-ray diffraction on the pure pulp sheet and pure CNF sheet. Figure 4b shows the XRD patterns of pure pulp sheet and pure CNF sheet. The CI of pure pulp sheet and pure CNF sheet were 77% and 76%, respectively, which supported our speculation to some extent. In other words, a pure pulp sheet made of bleached pulp fibers could be regarded as aggregates of countless CNFs in randomly distributed conditions. This is because CNFs have been isolated from bleached pulp fibers (Sehaqui et al. 2011; Wang et al. 2012; Alcalá et al. 2013). Sehaqui et al. (2011) also found similar results; that is, the specific Young’s modulus of composite sheets did not increase when a small amount of CNFs (2–10%) was added to bleached softwood pulp. However, it must be mentioned that, according to Alcala et al., the

specific Young's modulus almost linearly increased as CNFs (0–12%) was added to unbleached eucalyptus pulp, which disagrees with our results. This is because the unbleached pulp fibers have lower stiffness than the bleached pulp fibers and CNFs due to the presence of residual amorphous lignin and other chemical compositions (Jonoobi et al. 2009). As a result, adding CNFs to the unbleached pulp improved the specific Young's modulus of the sheets.

Tensile strength of dry sheets

Figure 5 presents the results of the dry tensile strength and dry specific tensile strength of the composite sheets. In the present work, the dry tensile strength (107.9 ± 9.7 MPa) of the pure CNF sheet was in accordance with the reported value range of nanopaper (75–250 MPa) made of fully bleached fibers in the literature (Rojo et al. 2015). The dry tensile strength gradually increased for CNF addition in the range of 0–70% while there was no further increase when the CNF content was higher than 70%. The specific tensile strength also gradually increased for the CNF addition in the range of 0–70%, followed by a slight decrease. When CNFs were added to the pulp suspension, CNFs percolated into the pulp fiber networks (matrix) to link adjacent pulp fibers, which increases the hydrogen bond density between pulp fibers, resulting in reinforced dry tensile strength and specific tensile strength. Similar changes in dry tensile strength were also found by Hassan et al. (2011). In particular, the dry tensile index of composite sheets made of microfibrillated cellulose (MFCs) and pulp fibers gradually improved with increasing MFC addition up to 50%, but there were no significant changes when the MFC addition was greater than 50% and up to 80%. Compared with Hassan's results, the better reinforcement in this work was likely due to the higher specific area and fibrillation of CNFs than that of MFCs.

The constant dry tensile strength when CNFs were added was more than 70%. This was possibly due to the difference between the structures of the composite sheets with different CNF additions. Therefore, we analysed the fracture surface of the composite sheets before and after the tensile tests. As shown in Fig. 6, both composite sheets with 70% CNF and pure CNF sheet had obvious layers, but the difference was that the layers of composite sheets with 70% CNF were thicker, probably due to the presence of pulp fibers. In addition, there were no other significant differences between the fracture morphologies according to the SEM images. In contrast, the fracture surfaces with different CNF contents after the tensile test showed obvious differences. In the pure pulp sheet (Fig. 6c), tens of microns of pulp fibers were pulled out, and the fracture surface was highly rough, which suggested that the fracture of the sheet was governed by the pulled-out pulp fibers. With an increase in the CNF content, the fracture surface became much flatter and more regular (Fig. 6d, e, and f), which proved that stronger interfiber interaction occurred because of the presence of CNFs. In the composite sheet with 50% CNF addition, traces of tens of microns of pulp fibers could still be found (yellow box), whereas as the CNF content increased to 70%, there was almost no trace of tens of microns of pulp fibers on the fracture surfaces. These irregular thin fragments of several microns in Fig. 6e should be CNF aggregates (orange box). The pure CNF sheet had the most regular and flat fracture surface with some CNF aggregates, and the gaps between CNF layers were collapsed when compared to those of other composites owing to the disappearance of microscale pulp fibers, which suggested that the fracture of the pure CNF sheet was governed by the pulled-out CNFs.

Based on these SEM observations, we propose the following reinforcement mechanism of CNF additon on the tensile strength of the composite sheets. When CNF addition was less than 70%, the fracture of the sheets was determined by pulling out the pulp fibers. At this point, CNFs, as a reinforcing filler, percolated in the pulp fiber networks (Fig. 7a). With an increase in the CNF content, the hydrogen bond density between the pulp fibers increased, which dissipated more energy under loading when the pulp fiber networks were damaged and the pulp fibers were pulled out, thus increasing the dry tensile strength. However, when pulp fiber addition was reduced (< 30%), pulp fibers could not form continuous networks owing to the low aspect ratio and volume fraction. Therefore, the fracture of the sheets was determined by the pulling out of the CNFs. At this point, the composite sheets were formed by the stacked CNF layers (Fig. 7b), and the pulp fibers were probably sandwiched into the stacked CNF layers. The hydrogen bond density between CNFs in the plane of each CNF layer might not change with increasing CNF content. As a result, the dry tensile strength of the sheets no longer improved.

Mechanical properties of wet sheets

We also explored the effect of CNF addition on the wet strength of the composite sheets under different CNF ratios. Before the wet tensile strength test, the swelling width and thickness were measured. The maximum swelling rates in width and thickness were approximately 3.4% and 112%, respectively. Figure 8 presents the relationship between CNF addition and the water uptake and swelling rate in the thickness of the sheets. The water uptake sharply decreased from 143–108% with the addition of CNFs in the range of 0–50%, followed by a gradual increase. A slight decline was observed in the thickness swelling rate with CNF addition of less than 20%, followed by a gradually accelerating rise as the CNF content increased from 20–100%. The pure pulp sheet had a fluffy structure with the highest porosity, which facilitated the capillary effect of the sheet when soaked in water, thus leading to the maximum water uptake. When CNFs were added, the porosity of the sheet decreased because CNFs filled the micropores between the pulp fibers, which weakened the capillary effect of the sheet, resulting in reduced water uptake. The gradually increased water uptake was mainly due to the water absorption of CNFs, owing to the rich surface hydroxyl groups of CNFs when CNF addition was higher than 50%. The increase in the thickness of the swelling rate was mainly due to the swelling of CNFs after water absorption. The water uptake of the pure CNF sheet reached 140%, which was almost the same as that of the pure pulp sheet. This also makes CNFs a promising green moisture additive and recyclable adsorbent.

The wet Young's modulus, wet tensile strength, and WSR of the composite sheets were characterised and are presented in Fig. 9. The wet Young's modulus slightly increased at CNF additions of less than 20% and then decreased. In contrast, the wet tensile strength linearly increased for CNF addition in the range of 0–70% and the maximum value of 9.89 ± 1.33 MPa was reached at 50% of CNF addition, which was improved by one order of magnitude compared to that of the pure pulp sheet. It was confirmed that adding CNFs had a remarkable reinforcement effect on the wet tensile strength of the sheets. Thereafter, no further increase in the wet tensile strength was observed with an increase in CNF addition, but there was a gradual decline. WSR behaved similarly, increasing almost linearly as more CNFs were added in the range of 0–50%, followed by a slight decline. A similar tendency of wet tensile strength was also

observed for bagasse pulp sheets reinforced by MFCs (Hassan et al. 2011). Specifically, the wet tensile load linearly increased with increasing CNF addition up to 40%; thereafter, no further improvement occurred with increasing MFCs continually, but there was a slight decline. In the present work, the highest wet strength and WSR reached 9.89 MPa and 10%, respectively, which were higher than that of Hassan et al., who reported a maximum wet tensile load less than 0.14 N (Hassan et al. 2011), and comparable to that of Ichiura et al. (2017), who reported that WSR reached 10% when filter paper was treated with [BMIM]Cl for 10 s.

Similar to the reinforcing effect of CNF addition on the dry sheets, the increase in the wet tensile strength and WSR for CNF addition in the range of 0–70% was due to the increase in the hydrogen bond density between the pulp fibers upon the introduction of CNFs. CNFs existing between pulp fibers (Fig. 10) could dissipate more energy between pulp fibers under loading, giving rise to increased wet tensile strength and WSR. Although there was a slight decrease in the wet tensile strength when the CNF content was more than 70%, the wet tensile strength and WSR were at least 6 MPa and 6%, respectively, owing to the higher density of CNF-CNF bonds. The slight decrease in the wet tensile strength and WSR was derived from the increase in thickness. The increased thickness also caused a dramatic decline in the wet Young's modulus after adding 20% of CNF. It should be noted that although the pure CNF sheet had the same water uptake as the pure pulp sheet, its wet tensile strength was 8.3 times that of the pure pulp sheet, owing to the high hydrogen bond density between the CNFs, which was attributed to the high specific surface area and high fibrillation of CNFs. This revealed that CNFs could be as a potential material for reinforcing the wet strength of composite sheets. The advantage of CNFs as a reinforcing material is that it can improve the wet tensile strength without reducing the water absorption, although the wet Young's modulus was reduced. This is a great challenge and limitation for applications requiring both high strength and high Young's modulus. However, for some applications that high stiffness is not required such as skincare, cosmetics, and healthcare, it is an ideal high-moisturizing material.

Conclusions

In this study, the effects of reinforcement with CNF addition (0–100%) on the Young's modulus and tensile strength of composite sheets under dry and wet conditions were explored. It was found that CNFs could effectively improve the Young's modulus and tensile strength of composite sheets. The addition of CNFs reduced the porosity of the sheets, which could increase the dry Young's modulus, and the hydrogen bond density between pulp fibers could also increase, thus improving the dry and wet tensile strength. The results showed that the dry Young's modulus increased as the CNF addition increased from 0–100%, and the dry tensile strength increased as the CNF content increased to 70%. Furthermore, the wet tensile strength increased almost linearly with 0–70% CNF addition, and the WSR reached approximately 10% at 40% CNF addition.

Some interesting results in this work were that 1) the pure CNF sheet obtained almost the same specific Young's modulus as the pure pulp sheet under random conditions, which was confirmed to be the same substance as the bleached pulp fibers essentially, because CNFs were isolated from the bleached pulp;

and 2) excessive CNFs (> 70%) did not improve the dry and wet tensile strength of the sheets. When CNF addition was low (< 70%), CNFs as a reinforcing filler percolated in the pulp fiber networks, which could increase the hydrogen bond density between the pulp fibers, thus improving the tensile strength of the composite sheets. However, when CNF addition increased (> 70%), the pulp fiber networks disappeared, and the CNF layers were replaced. In this state, the continuous increase in CNF addition would not improve the hydrogen bond density between the CNFs, resulting in unchanged dry tensile strength. This means that the formation of pulp fiber networks is the basis for achieving the reinforcement effect of CNF addition on the composite sheets. Additionally, the pure CNF sheet obtained almost the same water uptake as the pure pulp sheet which suggested that CNFs can be a promising moisture additive and recycle adsorbent. Furthermore, the wet strength of the pure CNF sheet was 8.3 times that of pure pulp sheet, which indicated that the advantage of CNFs as a reinforcement additive is that it can improve the wet tensile strength without reducing the water absorption of sheets. For some applications, such as skincare, cosmetics, and healthcare, it is an ideal high-moisturizing material.

Declarations

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Conflicts of interest

The authors declare that they have no conflict of interest.

Human and animal rights

This research does not contain any experiments with human participants or animals.

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Figures

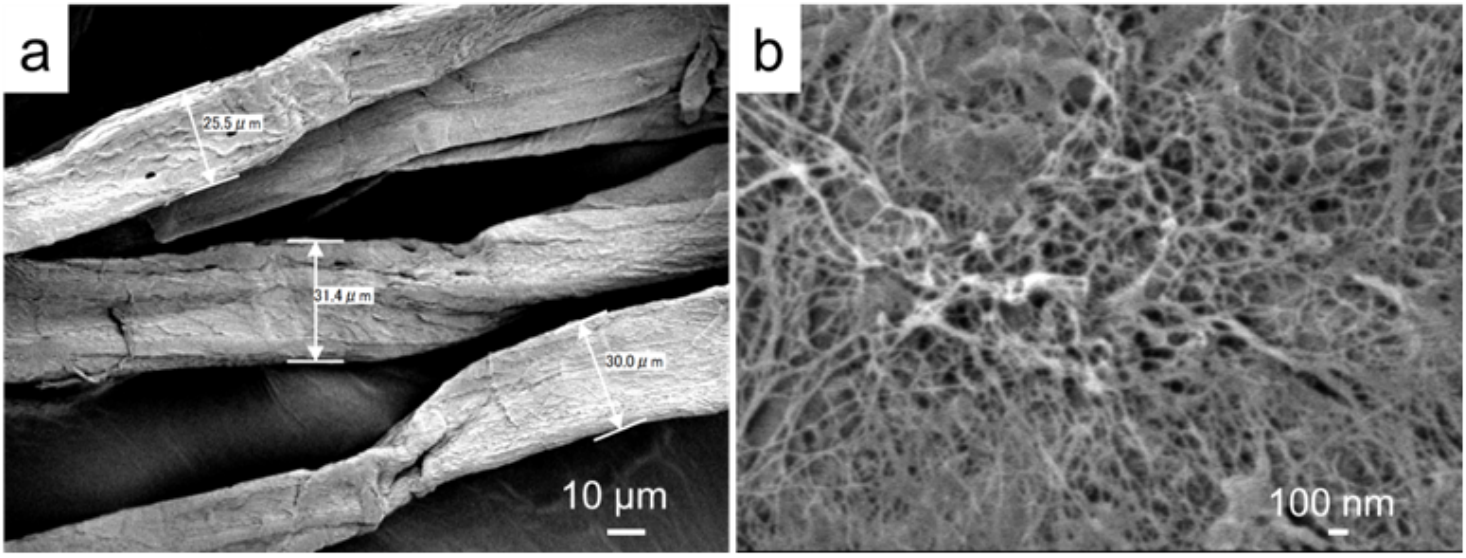

Figure 1

SEM images of (a) air-dried pulp fibersand (b) freeze-dried pure CNF sheet.

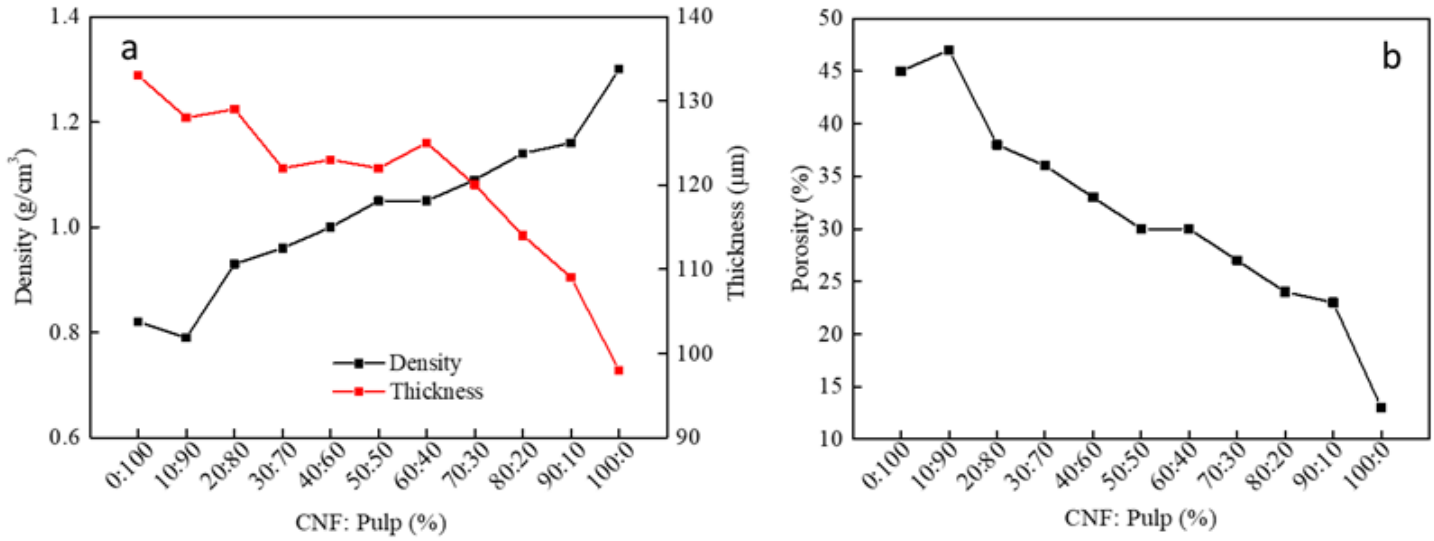

Figure 2

Measured thickness and density (a) and porosity (b) of sheets.

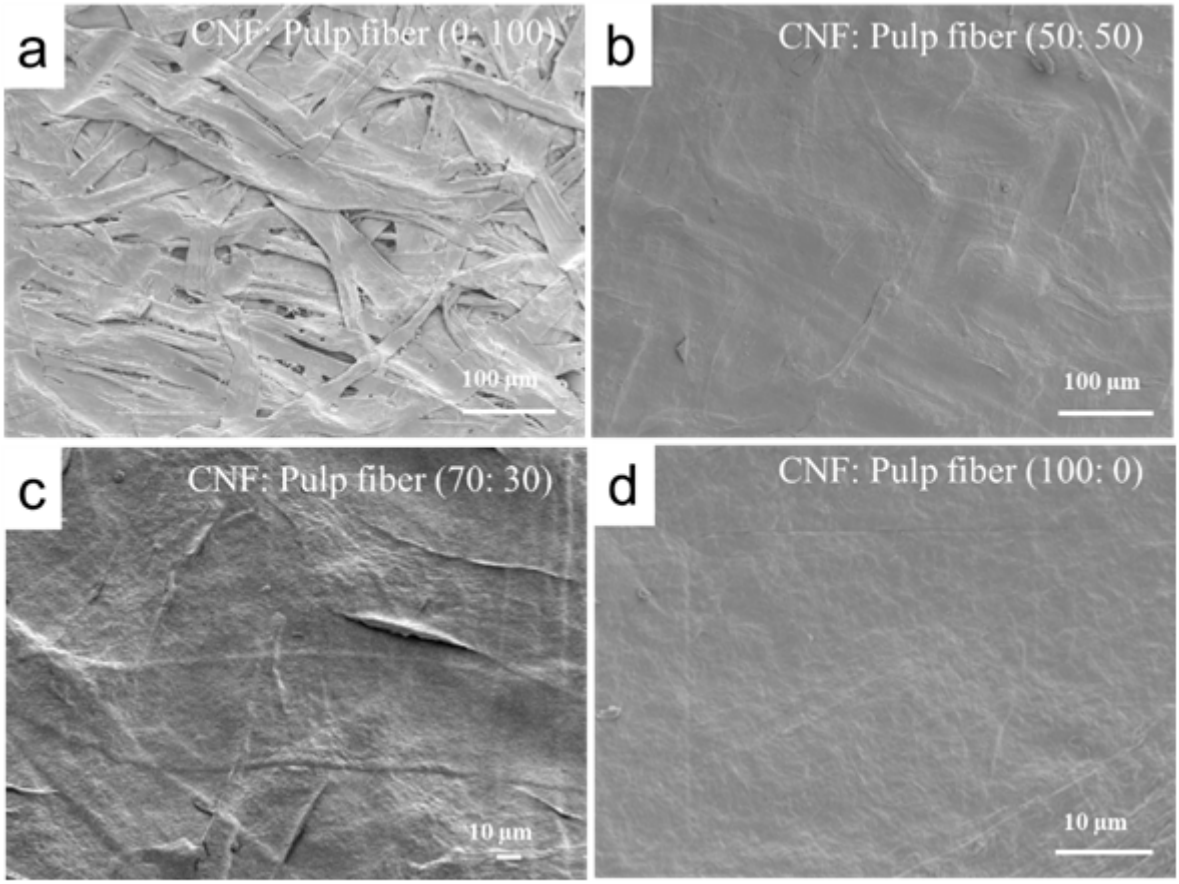

Figure 3

SEM images of surface of sheets with out CNF (a), and with 50% (b), 70% (c), and 100% (d)CNF addition.

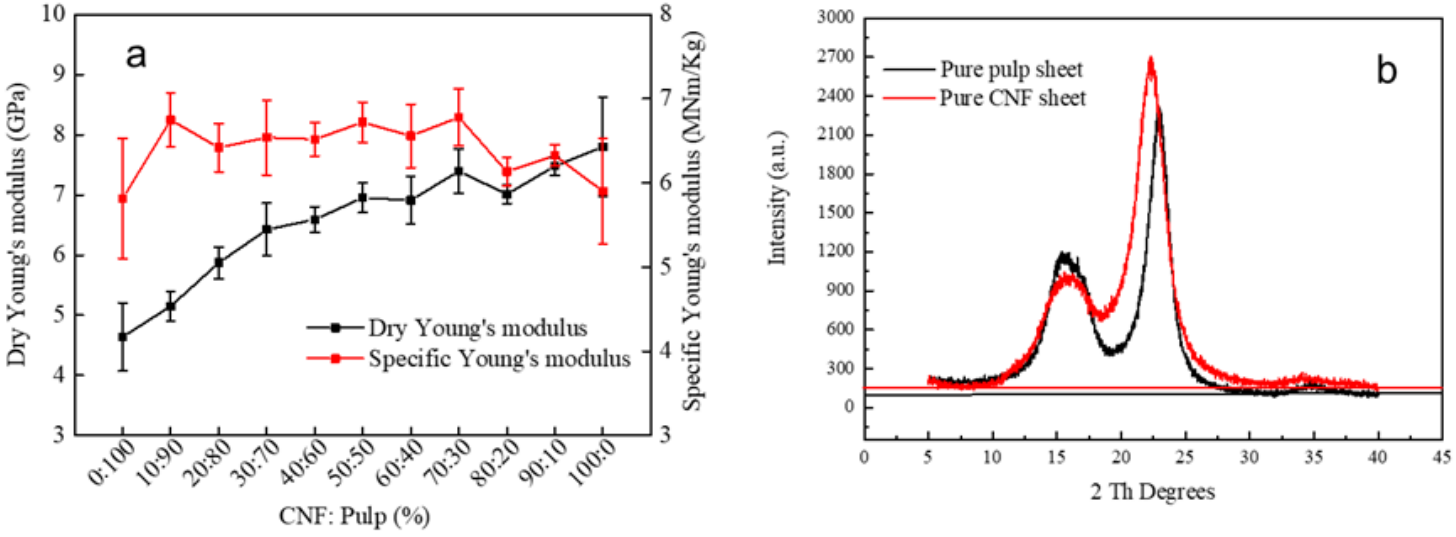

Figure 4

Dry Young's modulus and specific Young's modulusof composite sheets; (b)XRD patterns of pure pulp sheet and CNF sheet.

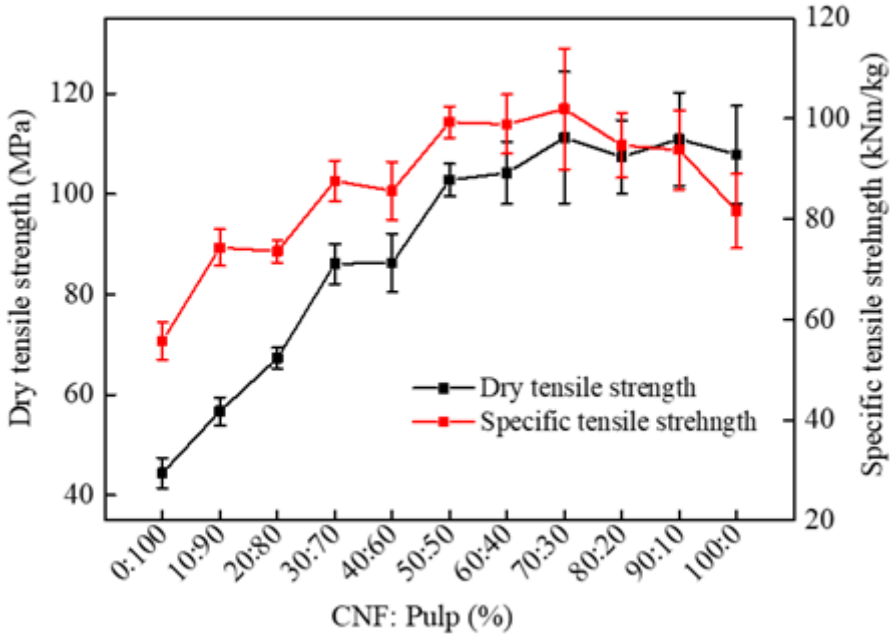

Figure 5

Dry tensile strength and specific tensile strength of sheets.

Figure 6

SEM images of the fracture surfaces of sheets with (a) 70% CNFand (b) 100% CNF before tensile tests. SEM images of fracture surfaces of sheets from tensile tests with (c) 0% CNF, (d) 50% CNF, (e) 70% CNF, and (f) 100% CNF.

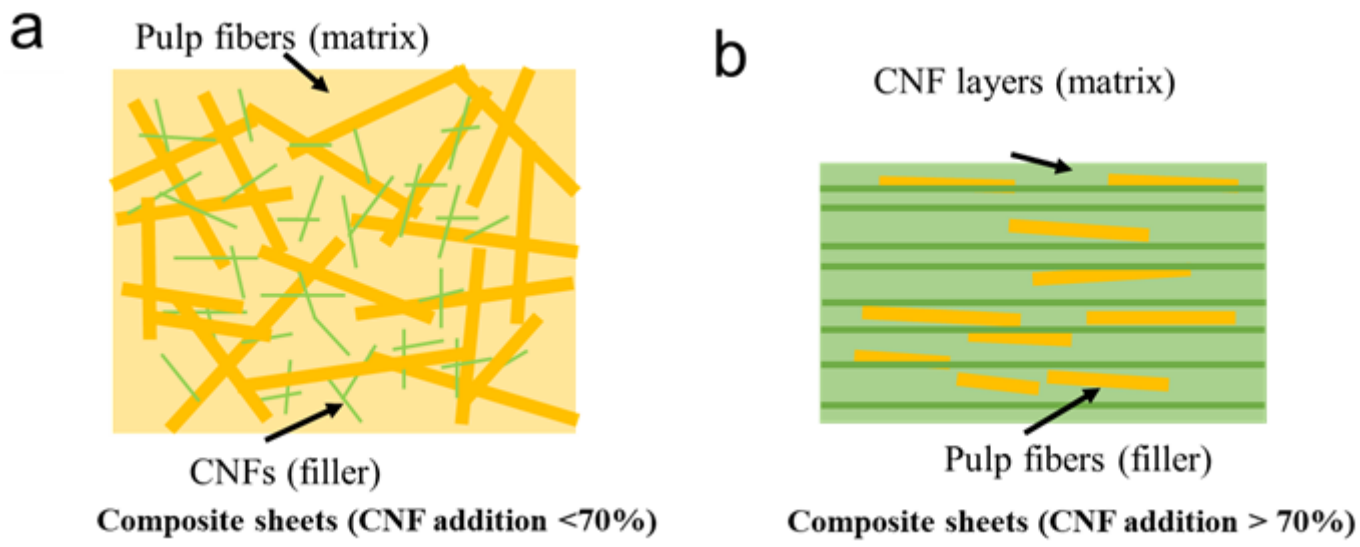

Figure 7

Schematic illustration of composite sheet structure with different CNF additions (a) and (b).

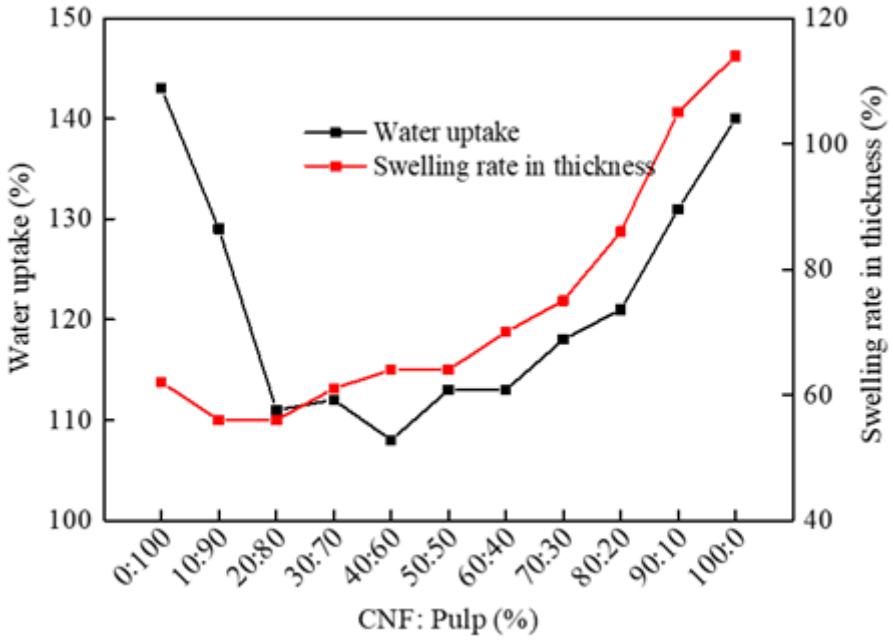

Figure 8

Water uptake and swelling rate in thickness of sheets.

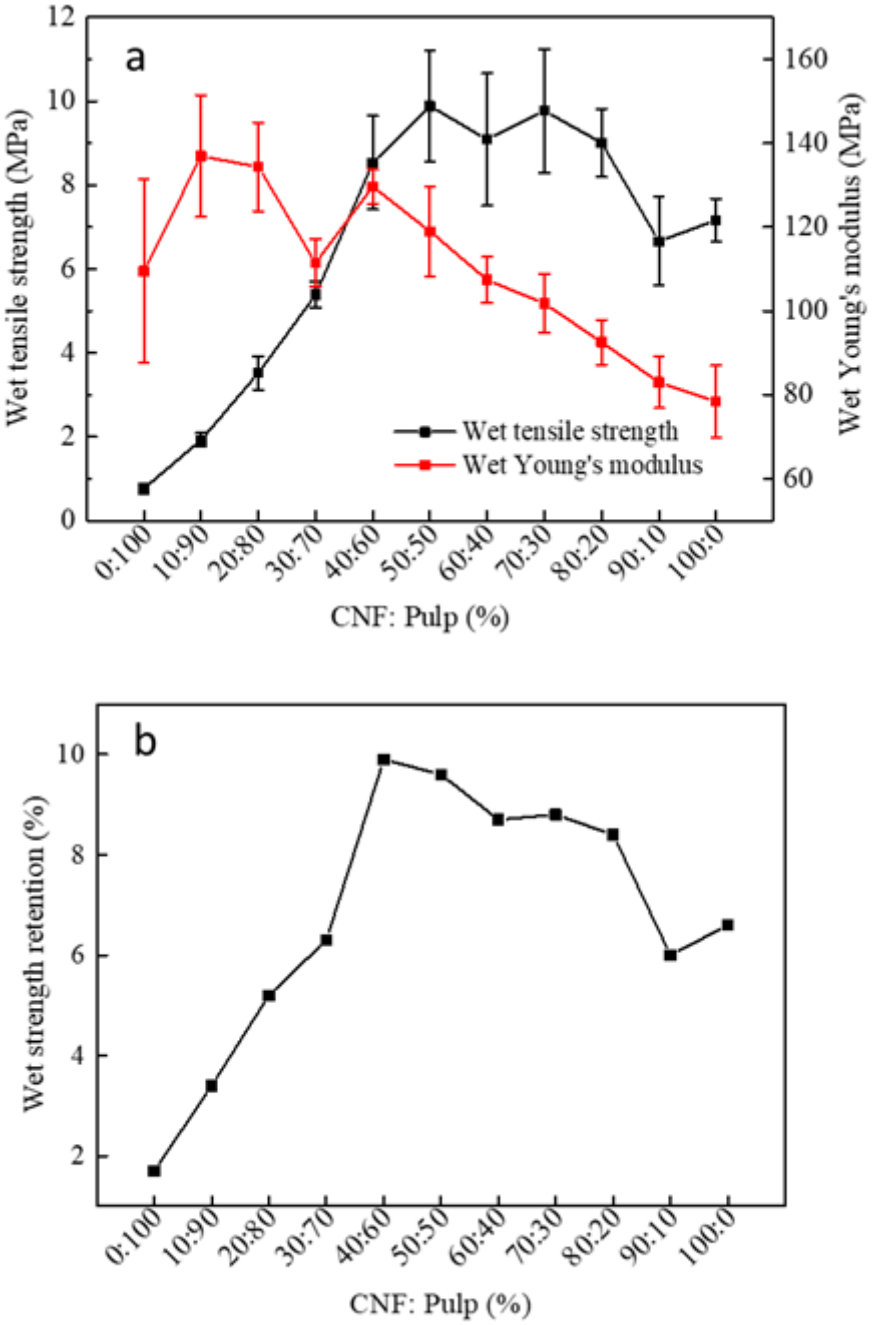

Figure 9

(a) Wet Young's modulus and wet tensile strength and (b) WSR of sheets.

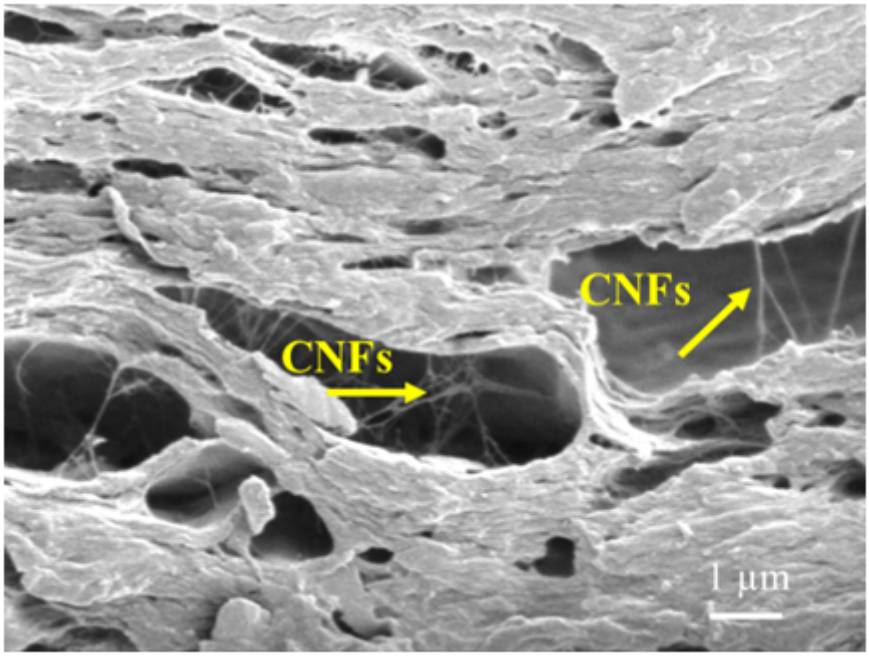

Figure 10

SEM image of the freeze-dried composite sheet with 50% CNF addition after soaking in distilled water for 30 min.