

# Preparation of cross-linked cellulose nanofibril aerogel with water absorbency and shape recovery

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**Abstract** Cellulose nanofibril (CNF) aerogels are promising materials for various applications because of their highly porous and ultralight characteristics. The fiber network of CNF aerogels held together by hydrogen bonding and mechanical entanglement of adjacent fibers is easily destroyed when it is exposed to water. In this study, cross-linked CNF aerogels were prepared using maleic acid and sodium hypophosphite as cross-linking agents. In the first step of treatment, CNF dispersed in water was reacted with maleic acid to form an ester linkage. Sodium hypophosphite was then added to the maleic acid-functionalized CNF suspension and the suspension was rapidly frozen using liquid nitrogen. CNF aerogel was obtained after freeze drying. The cross-linking of the cellulose was formed by the reaction between the carbon–carbon double bond of maleic acid-functionalized CNF and hypophosphite. The cross-linked CNF aerogel exhibited good network stability in water and springiness after compression.

**Keywords** Cellulose nanofibril · Aerogel · Cross-linking · Water absorbency · Shape recovery

## Introduction

Cellulose nanofibril (CNF) is a nano-scale fibrous material which can be obtained from the cellulose fiber using various types of mechanical shearing treatments. The preparation of CNF was reported in early 80s by Turbak et al. (1983) and Herrick et al. (1983). It has been shown that cellulose fibrils with nanometer width can be produced by the high pressure shearing action during the homogenizing process. Besides the high pressure homogenizer (Nakagaito and Yano 2004; Iwamoto et al. 2005), grinder (Iwamoto et al. 2007; Sim et al. 2015), microfluidizer (Zimmermann et al. 2010; Siqueira et al. 2010), cryo-crushing equipment (Dufresne et al. 1997; Alemdar and Sain 2007), refiner (Heiskanen et al. 2012), and high speed blender (Uetani and Yano 2011) have been employed to produce CNF. Producing CNF by means of mechanical disintegration of cellulose fiber inevitably requires a great deal of energy. To reduce the energy consumption several pretreatment techniques including oxidation (Saito et al. 2006, 2007; Isogai et al. 2011), carboxymethylation (Aulin et al. 2010; Taipale et al. 2010), and enzymatic hydrolysis (Pääkkö et al. 2007; Henriksson et al. 2007; Siqueira et al. 2010) of cellulose fiber have been suggested.

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The morphological characteristics of CNF may vary depending upon the type of mechanical treatment, degree of applied shear forces and pre-treatment. In general, CNF is an aggregation of 10–50 cellulose elementary fibrils with a complex web-like network structure. Its diameter and length range 5–50 nm and several  $\mu\text{m}$ , respectively (Missoum et al. 2013).

CNF has a range of possible applications because of its high specific surface area and strong mechanical properties. For example, CNF can be used as a reinforcing agent for biocomposite materials (Shibata and Nakai 2010) or building material for translucent sheets (Yano and Nakahara 2004). Another promising application of CNF is to prepare cellulose aerogel (Pääkkö et al. 2008).

Aerogels are highly porous and ultra-lightweight materials formed by removing the liquid dispersion medium from the gel without collapsing the network structure (Hüsing and Schubert 1998). Since aerogels were first introduced by Kistler (1931), most aerogels have been prepared by the sol–gel process or by the supercritical fluid drying of inorganic metal-oxide materials or polymers (Pierre and Pajonk 2002). These processes, however, require multiple solvent-exchange steps and use of the considerable amount of energy, which brings both environmental and economic issues that should be resolved for their wider acceptance.

Because of the morphological characteristics of CNF, they entangle mechanically in aqueous suspension and form a homogenous gel structure at a very low concentration (Missoum et al. 2013). The capability of CNF to form interfiber hydrogen bonds allows the preparation of aerogel by removing the water. In particular, rapid freezing and freeze-drying of the CNF hydrogel makes the preparation of the highly porous and ultra-lightweight CNF aerogel possible. Unlike conventional aerogels, there is no need for a cross-linking treatment for the CNF aerogel. Solvent exchange or supercritical drying processes are also unnecessary in preparing CNF hydrogel (Cervin et al. 2012; Chen et al. 2011; Aulin et al. 2010).

Mechanical flexibility of CNF aerogels and the possibility of adapting various functionalities by utilizing the abundant hydroxyl groups for chemical modifications allow a number of potential applications of the CNF aerogels. Potential applications of CNF aerogels include kinetic energy absorbers, thermal and

acoustic insulating materials, reinforcing platforms, drug carrier, tissue engineering scaffolds and others (Sehaqui et al. 2010).

CNF aerogels, however, show poor structural stability in aqueous condition. This is because the network structure of the CNF aerogel relies on the interfiber hydrogen bonding and mechanical entanglement that is partly destroyed in aqueous condition. Structural stability of CNF aerogels in aqueous condition can be improved by covalent cross-linking. Zhang et al. (2012) have reported cross-linked CNF aerogels which showed significantly improved network stability in wet state using polyamide-epichlorohydrin resin. Syverud et al. (2015) have shown that the stability of CNF hydrogel can be improved using aldehyde groups as a cross-linking agent. It is worthwhile, however, to find a new approach to improve the stability of the CNF aerogel in aqueous conditions to have more possibilities to control the properties of aerogels.

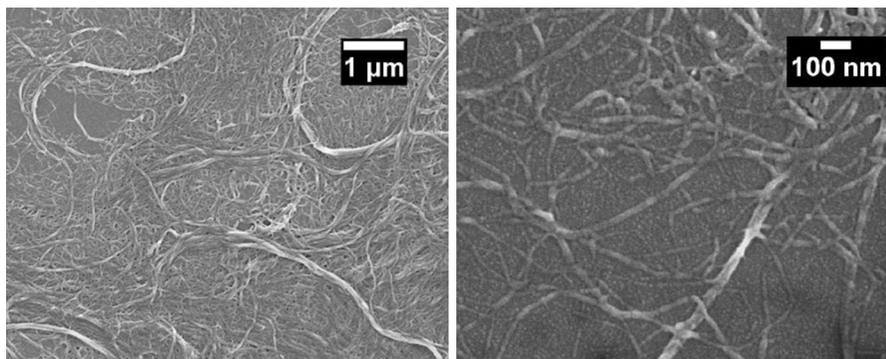
In this study, a covalently cross-linked CNF aerogel was prepared using maleic acid and sodium hypophosphite in aqueous media. Maleic acid was grafted onto cellulose fiber, and covalent cross-linking of CNF was formed by the reaction between maleic acid and hypophosphite. The network stability of the cross-linked CNF aerogel in a wet state as well as their physical and structural characteristics were investigated.

## Experimental

### Preparation of CNF

CNF was prepared using a grinding method according to Sim et al. (2015). Once-dried, commercial bleached eucalyptus kraft pulp was used as a raw material for the preparation of the CNF. Dried pulp sheets were dispersed in deionized water and refined using a laboratory Valley beater to a freeness value of 450 mL CSF. The consistency of the beaten pulp suspension was adjusted to 2 %, after which the suspension was subjected to a mechanical treatment using a grinder (Super Masscollider MKCA6-3, Masuko Sanguo Co.). The rotation speed and gap of the grinding stone were 1500 rpm and  $-60 \mu\text{m}$ , respectively. After 40 cycles of the grinding treatments, CNF hydrogel was obtained. Scanning electron microscope (SEM) images of the prepared CNF were shown in Fig. 1.

**Fig. 1** SEM images of prepared CNF



The chemical composition of the CNF was determined by the NREL (National Renewable Energy Laboratory, USA) method (NREL/TP-510-42618). The contents of  $\alpha$ -cellulose, hemicellulose, lignin and ash were found to be 79.4, 18.7, 1.5, and 0.5 %, respectively. To confirm esterification of cellulose with maleic acid, filter paper CNF was also prepared from pure cellulose. Advantac 5C grade filter paper and the same procedure described above was used in preparing filter paper based CNF for FT-IR spectroscopy.

#### Preparation of maleic acid-functionalized CNF

For the cross-linking reaction of the CNF aerogel, analytical-grade maleic acid and sodium hypophosphite, supplied by Sigma-Aldrich, were used. Maleic acid and sodium hypophosphite were added to the CNF suspension. The dosage of maleic acid based on the weight of anhydroglucose unit (AGU) of cellulose was 10. To determine this dosage ratio, it was assumed that CNF was composed of cellulose only. Sodium hypophosphite was added as a catalyst for the esterification reaction of cellulose and maleic acid. The dosage of sodium hypophosphite was 5 wt% of the maleic acid. After mixing for 30 min, the CNF suspension containing maleic acid and sodium hypophosphite was heated to 120 °C and kept at that temperature for 30 min in an autoclave for esterification. Unreacted chemicals after the esterification reaction were removed by centrifugal washing at 3000g for 10 min. After which the maleic acid-functionalized CNF (CNF-MA) was settled down and the clear supernatant containing unreacted maleic acid and sodium hypophosphite was removed. The CNF-MA pad was re-dispersed in deionized water and successive washing steps were carried out. After six

times of centrifugal washings, CNF-MA was collected and used for cross-linking reaction. Maleic acid-functionalized filter paper CNF (filter paper CNF-MA) was also prepared with same procedure to verify the esterification of cellulose using FT-IR spectroscopy analysis.

#### Preparation of the cross-linked CNF aerogel

Twenty wt% of sodium hypophosphite based on the oven dried weight of CNF-MA was added to the CNF-MA suspension. The CNF-MA hydrogel mixed with sodium hypophosphite of which solids content was adjusted to 1.0–3.0 wt% was poured into polystyrene cuvette molds. The CNF hydrogels in the cuvette were precooled by placing in a refrigerator at 4 °C for overnight to minimize the fracture of the frozen CNF suspension during the subsequent rapid freezing step (Zheng et al. 2014). The precooled CNF hydrogels were rapidly frozen at  $-196$  °C using liquid nitrogen. These frozen samples were subjected to freeze-drying at  $-80$  °C and 5 mmHg using a freeze-dryer (FD8518, Ilshin Lab) for 3 days, and CNF aerogels were obtained. For cross-linking of CNF, the CNF aerogels were placed in a convection oven and cured for 10 min at 170 °C. Cross-linked CNF aerogels were cut into cubic shapes with a dimension of  $10 \times 10 \times 10$  mm<sup>3</sup> and conditioned in a control room at 23 °C and 50 % RH.

#### Characterization of cross-linked CNF aerogel

Maleic acid-functionalized filter paper CNF (filter paper CNF-MA) was used for FT-IR spectroscopy to identify the ester linkage between the maleic acid and cellulose. After the esterification process, the filter

paper CNF-MA suspensions were treated with a 0.1 M NaOH solution at room temperature for 1 h to convert carboxylic acid to carboxylate anion. Then it was vacuum-filtered to obtain a filter paper CNF-MA film and dried in a convection oven for 2 days at 40 °C. FT-IR spectra of the filter paper CNF-MA film were obtained using a FT-IR spectrometer (Cary 660, Agilent) in ATR mode. For each spectrum, 32 scans were collected with a range of 600–4000  $\text{cm}^{-1}$  at a resolution of 4  $\text{cm}^{-1}$ .

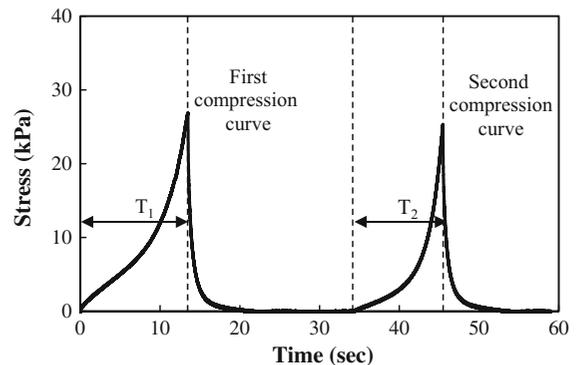
A scanning electron microscope (SEM, Auriga, Carl Zeiss) was used for the observation of the cross-linked CNF aerogels. Cross-linked CNF aerogel samples were frozen at  $-196$  °C using liquid nitrogen, and its cross-section was prepared by fracturing the frozen sample. Then sample was attached to a sample stub with a double-sided adhesive conductive carbon tape and sputter-coated with platinum.

The specific surface area of the aerogel was determined using nitrogen adsorption/desorption measurements (ASAP 2020, Micromeritics Instruments Co.) at  $-196$  °C. Before the adsorption measurement, the samples, dried at 105 °C for 24 h to remove moisture, were degassed at 120 °C for 4 h for the complete elimination of moisture. Both the adsorption and desorption isotherms were measured, and the surface area was determined from the adsorption curve by the Brunauer–Emmett–Teller (BET) method.

To measure the moisture uptake of the cross-linked CNF aerogel, saturated lithium chloride, calcium chloride, and sodium chloride solutions were used to control the relative humidity of air to 15, 37, and 75 % RH at 23 °C, respectively. These saturated salt solutions were placed in a humidity chamber and the weight changes of the fully dried cross-linked aerogels were measured to determine the moisture contents.

To evaluate the compressive strength and shape-recovery performance of the cross-linked CNF aerogel, a texture analyzer (TA XT Plus, Stable Micro Systems, Ltd.) with a 50 mm cylindrical probe and a 50 kg load cell was used. During the compression of cross-linked CNF aerogel, no fracture point or inflection point was observed on the stress–strain curve until 90 % of its original dimension. The compressive stress at a strain level of 90 % was determined as the compress strength. In this test, the probe speed was adjusted to 1 mm/sec.

To evaluate the shape-recovery performance of the cross-linked CNF aerogel in the wet state, a texture



**Fig. 2** Time–stress curve in TPA test

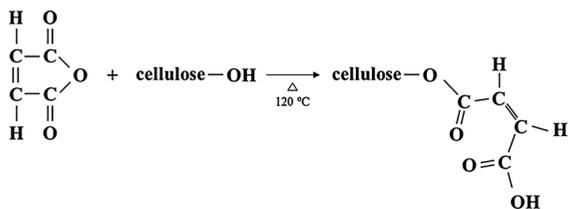
profile analysis (TPA) was carried out. This test consists of two successive 70 % strain compressions of the cross-linked CNF aerogel, as shown in Fig. 2. Springiness, the recovery ratio of the deformed material after the removal of a deforming force, was obtained as in Eq. (1).  $T_1$  and  $T_2$  represent the time required for 70 % compression of the cross-linked CNF aerogel in the first and second compression cycles, respectively. When the springiness value is closer to one, the cross-linked CNF aerogel easily recovers to its original shape after compression. For the TPA test, the probe speed was adjusted to 0.5 mm/s. The time interval between the first and second compression was 5 s.

$$\text{Springiness} = \frac{T_2}{T_1} \quad (1)$$

## Results and discussion

### Esterification of maleic acid onto CNF

The cross-linking of CNF takes place in two separate reactions when maleic acid and hypophosphite were used. The first step is an esterification reaction between maleic acid and hydroxyl group of cellulose. In an aqueous solution, maleic acid forms a five-member cyclic anhydride by the dehydration of two carboxylic groups. This intermediate reacts with the hydroxyl group of cellulose to form an ester linkage (Fig. 3). In this esterification process, sodium hypophosphite was used as a catalyst. When the reaction temperature is below 140 °C, the reaction rate



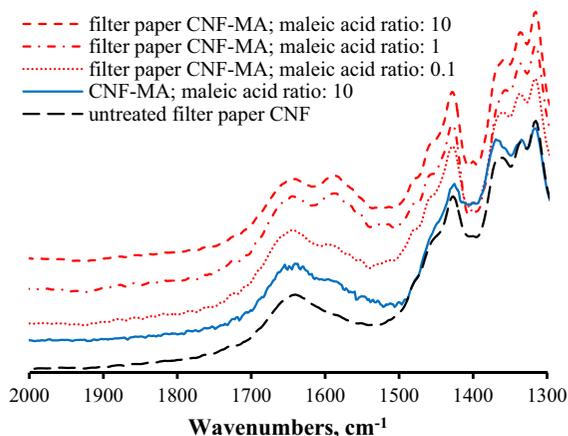
**Fig. 3** Esterification between cellulose and maleic acid anhydride

of esterification is drastically increased by the presence of sodium hypophosphite (Yang et al. 2010).

The FT-IR spectra of the filter paper CNF-MA are shown in Fig. 4. As more maleic acid was added to the filter paper CNF suspension, the peak at  $1570\text{ cm}^{-1}$ , assigned to the C–O stretching vibration of the ester linkage, increased. When the CNF made of hardwood kraft pulp was used, the FT-IR spectra of the CNF-MA did not show any significant difference compared to that of untreated CNF. This is because the bleached hardwood kraft pulp contains nearly 20 % of hemicellulose and lignin, which gave absorption peaks at  $1570\text{ cm}^{-1}$ .

#### Cross-linking of cellulose

Polycarboxylic acids such as 1,2,3,4,-butanetetracarboxylic acid (BTCA) are used as cross-linking agents for the durable press finishes of cotton fabric because they form multiple ester linkages with cellulose (Yang et al. 2010; Yao et al. 2013). Maleic acid does not crosslink cellulose. The presence of hypophosphite ion, however, allows the cross-linking of maleic acid-



**Fig. 4** FT-IR spectra of CNF-MA and filter paper CNF-MA

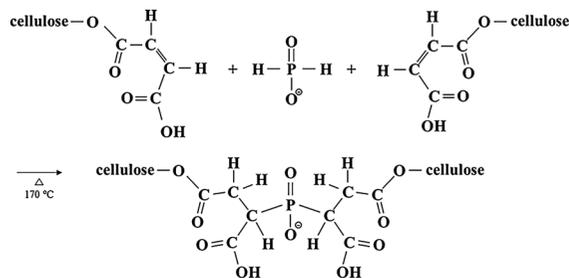
functionalized CNF. When the reaction temperature was  $120\text{ }^{\circ}\text{C}$  as in esterification process, sodium hypophosphite acts as a catalyst. Whereas hypophosphite ions react with carbon–carbon double bonds of maleic acid-functionalized CNF as shown in Fig. 5 (Yang et al. 2010), when the reaction temperature is higher than  $140\text{ }^{\circ}\text{C}$ .

#### Cross-linking of CNF aerogel

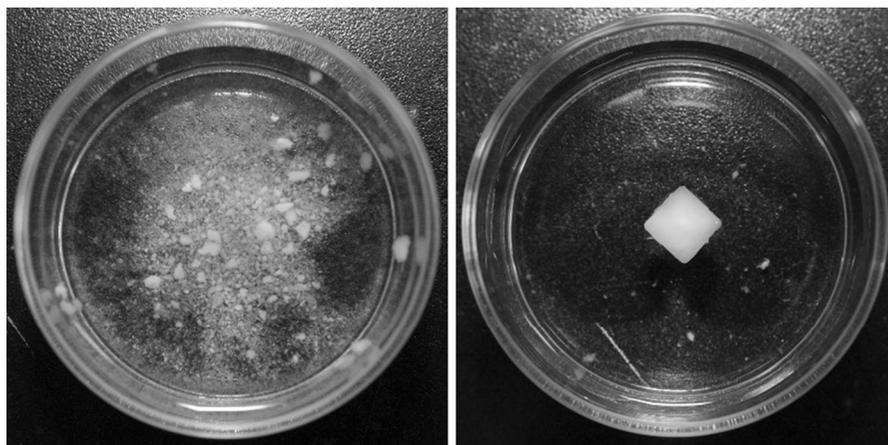
In the case of typical CNF aerogels, the network structure is built by hydrogen bonds and physical entanglements between adjacent CNFs. When the typical CNF aerogels are exposed to moisture, inter-fiber hydrogen bonds are replaced with cellulose-water hydrogen bonds. As a result, the entire network structure of aerogels loses its strength.

The cross-linked and untreated CNF aerogels in cubic shapes ( $10 \times 10 \times 10\text{ mm}^3$ ) were immersed in deionized water and stirred for 1 min with a magnetic stirrer at 300 rpm. The density of aerogel was  $31.5\text{ kg/m}^3$ . As shown in Fig. 6, the CNF aerogel which had not undergone a cross-linking treatment disintegrated and dispersed in the water, while the cross-linked CNF aerogel maintained its original structure. This shows that the covalent cross-linking of CNF was formed through the treatment with maleic acid and hypophosphite.

In Table 1, the compressive strengths of the cross-linked and untreated CNF aerogel with density of  $31.5\text{ kg/m}^3$  were compared. The cross-linked CNF aerogel exhibited greater compressive strength in both dry and wet state; this indicates that the covalent cross-linking of CNF was formed via the reaction between the cellulose-grafted maleic acid and hypophosphite. The compressive strength of the untreated aerogels, however, was around 70 % of that of the cross-linked



**Fig. 5** Cross-linking of cellulose by the reaction between maleic acid and hypophosphite



**Fig. 6** Pictures of untreated CNF aerogel (*left*) and cross-lined CNF aerogel (*right*) after magnetic stirring for 1 min in water

**Table 1** Compressive strength of cross-linked and untreated CNF aerogel in dry and wet state

	Compressive strength (kPa)	
	Dry state	Wet state
Cross-linked CNF aerogel	411 (44) <sup>S.D.</sup>	180 (16)
Untreated CNF aerogel	317 (35)	120 (13)

*S.D.* standard deviation

samples, which indicates that significant parts of the CNF networks are still formed via hydrogen bonding.

#### Internal structure of the cross-linked CNF aerogel

The water present in the CNF hydrogel was replaced with air by rapid freezing and freeze-drying, which gave CNF aerogels without a collapse or shrink (Aulin et al. 2010). In other words, the apparent volume of the CNF aerogels is equal to the original volume of the CNF suspension in the mold. Therefore, the density of aerogel is proportional to the solids content of CNF suspension (Table 2). The specific surface area of the CNF aerogel with a density of 26.7 kg/m<sup>3</sup> was 19.5 m<sup>2</sup>/g, which was quite lower than that of organic or inorganic aerogels. For instance, Cai et al. (2012) reported that the specific surface area of aerogels

prepared with sol–gel processes were 400–654 m<sup>2</sup>/g. Our result, however, is in good agreement with previously reported values for freeze-dried CNF aerogels. Sehaqui et al. (2010) have shown that specific surface areas of 15–45 m<sup>2</sup>/g could be obtained for CNF aerogels with densities ranging from 7 to 103 kg/m<sup>3</sup>.

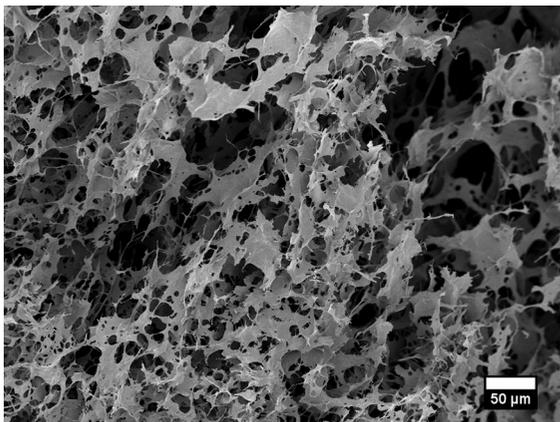
Cross-sectional images of a CNF aerogel with a density of 26.7 kg/m<sup>3</sup> are shown in Fig. 7. This CNF aerogel exhibits a highly porous internal structure with open pores. It was noted that the network structure of the CNF aerogel was built with very thin nanopapers. Svagan et al. (2008) and Chen et al. (2011) have shown that randomly distributed nanofibers are forced out by the growing ice crystals and develop film-like cellulose nanopaperlets during the freeze-drying process. This nanopaper structure is commonly found in cellulose aerogels prepared by the freeze-drying of a CNF suspension (Cervin et al. 2012; Aulin et al. 2010; Sehaqui et al. 2010; Syverud et al. 2011).

#### Water absorption performance of the cross-linked CNF aerogel

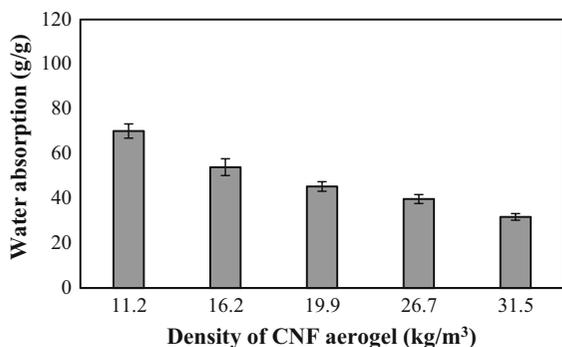
A water-absorption test was carried out by immersing the CNF aerogels into deionized water. The CNF aerogels absorbed water instantly by wetting and

**Table 2** Density of CNF aerogel and specific surface area

Solids content of CNF hydrogel (wt%)	1.0	1.5	2.0	2.5	3.0
Density of CNF aerogel (kg/m <sup>3</sup> )	11.2	16.2	19.9	26.7	31.5



**Fig. 7** SEM image of internal structure of the cross-linked CNF aerogel

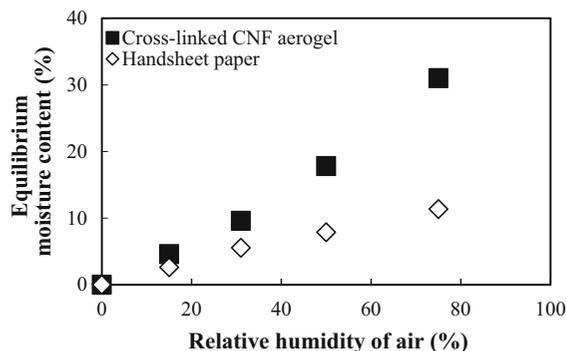


**Fig. 8** Water absorbency of cross-linked CNF aerogel

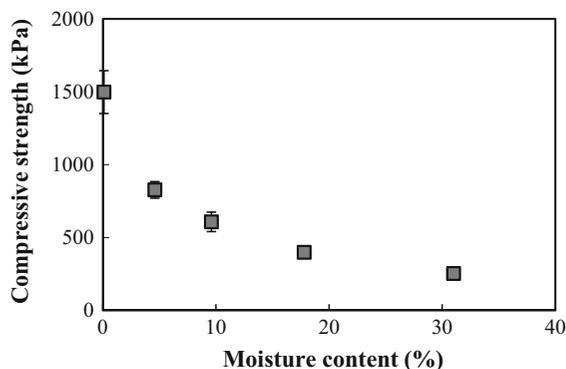
capillary action due to the hydrophilic and porous nature of CNF aerogels. Because hydrogen bonding and mechanical entanglement of fibers are the main source of structural rigidity of the CNF aerogel, its network structure is destroyed and irreversibly collapsed upon the absorption of water. On the other hand, the cross-linked CNF aerogel retained its original shape and volume, and its water-absorbing capacity corresponded to its internal pore volume (Fig. 8).

#### Moisture uptake and its effect on the mechanical strength

As shown in Fig. 9, the equilibrium moisture content of cross-linked CNF aerogel was drastically increased with the relative humidity of air, and it was significantly greater for the typical handsheets prepared with



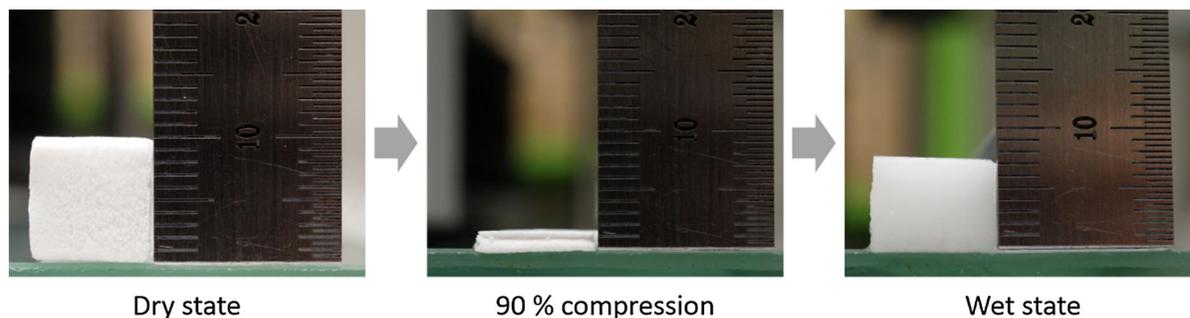
**Fig. 9** Equilibrium moisture contents of cross-linked CNF aerogel and typical handsheet paper with a basis weight of 150 g/m<sup>2</sup> as a function of relative humidity of air



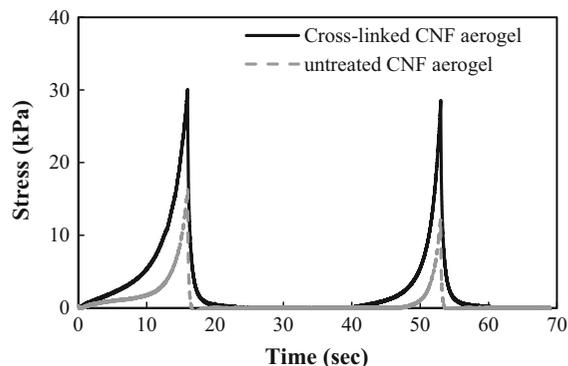
**Fig. 10** Compressive strength of cross-linked CNF aerogel versus moisture content

the same bleached eucalyptus kraft pulp. At 75 % RH condition, the moisture contents of the cross-linked CNF aerogel was 31 %, while that of the handsheet was 11 %. The large specific surface area of the cross-linked CNF aerogel resulted in greater adsorption of water and gave higher equilibrium moisture content.

In Fig. 10, the compressive strength of cross-linked CNF aerogel was plotted as a function of the moisture content. The density of the cross-linked CNF aerogel was 31.5 kg/m<sup>3</sup>. The compressive strength was drastically decreased as the moisture content was increased. The adsorption of water reduces the inter-fiber hydrogen bond of adjacent celluloses (Kang and Kim 2012; Kim et al. 2006). The reduction of compressive strength indicated that a considerable portion of the CNF network structure is still consisted of hydrogen bond even after the cross-linking treatment.



**Fig. 11** Shape recovery of cross-linked CNF aerogel by absorbing water



**Fig. 12** Time–stress curve in TPA test of cross-linked and untreated CNF aerogel in wet state

### Shape recovery of the cross-linked CNF aerogel

Cross-linking of CNF aerogel caused difference in the shape-recovery behavior after compressive deformation. Compressed CNF aerogels remained in compressed shape in dry state irrespective of the cross-linking treatment (Fig. 11). After wetting, the compressed cross-linked CNF aerogels showed substantially greater shape recovery characteristics. The cross-linked CNF aerogel recovered nearly 70 % of the original shape within a few seconds after wetting. On the other hand, untreated CNF aerogel remained compressed even after wetting with water. The shape recovery property of cross-linked CNF aerogel in the wet state was examined with the use of TPA test (Fig. 12). The cross-linked CNF aerogel recovered its original volume after wet compression and the springiness value was 0.78. On the other hand, the untreated CNF aerogel gave the springiness of 0.33.

Zhang et al. (2012) described that the shape-recovery of the cross-linked CNF aerogels stems from the interaction between the absorbed water and CNF. Compression of the fiber network of CNF aerogel takes place by bending of individual fibers or breaking of interfiber bonds, and by the loss of both friction between adjacent fibers and physical entanglement of the fibers. Since the longitudinal compression of cellulose fibrils can be neglected, only the bending of the fiber can be taken into account during the compressive deformation of CNF aerogels. The elastic modulus of the crystal region of cellulose ranges from 130 to 250 GPa (Zimmermann et al. 2004; Sakurada et al. 1962), while that of the amorphous region is reported to be 12.2 (Wang et al. 2014) or 10.4 GPa (Chen et al. 2004). Due to this substantial difference in the elastic moduli in the crystalline and amorphous regions of cellulose, the bending of CNFs under compression is confined to the amorphous region. When the compressed cross-linked CNF aerogel absorb water, the amorphous region swells partially, causing the CNF to expand to a more stretched form and recovers its original shape. And the presence of connecting points in the cross-linked CNF aerogels caused the stretching of CNF transforms into structural expansion. In other words, the network structure of cross-linked CNF provides improved mechanical stability both in dry and wet states. As a result, the cross-linked CNF aerogel maintains its original interfiber network structure during the compression and recovery processes. When the external force is removed, the deformed individual fibers recover their original shape, and this expanding force allows the entire network return back closer to its original shape.

## Conclusions

Cross-linked CNF aerogels were prepared using maleic acid and sodium hypophosphite. The cross-linking reaction was composed of two steps; (1) grafting of maleic acid onto CNF via an esterification process, and (2) formation of cellulose cross-linking by a reaction between the grafted maleic acid and hypophosphite. The prepared cross-linked CNF aerogel showed improved network stability in a wet state indicating that the cross-linking reactions between CNF were obtained. The water absorbency of the cross-linked CNF decreased from 70.2 to 31.9 g/g when the density of the cross-linked CNF aerogel was 11.2–31.5 kg/m<sup>3</sup>. The moisture uptake of the cross-linked CNF aerogel at a given relative humidity increased significantly compared to a typical filter paper because of its high specific surface area. The cross-linked CNF aerogel showed typical plastic deformation behavior in dry state. When the cross-linked CNF aerogel absorbs water, it recovered its original shape. The cross-linked CNF aerogel showed higher springiness value than uncross-linked one.

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