Wet Strength Improvement of Nanofibrillated Cellulose Film Using Polyamideamine-Epichlorohydrin (PAE) Resin: The Role of Carboxyl Contents

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An approach to improve water resistance and wet strength of films from nanofibrillated cellulose (NFC) was investigated using polyamideamine-epichlorohydrin (PAE) as a cross-linker. To increase the cross-linking reaction, carboxymethylation of pulp fiber was conducted as a chemical pretreatment. NFC was prepared by grinding, and the pass number required in the grinding process differed depending on the carboxyl contents introduced by the carboxymethylation process. First, PAE was added to the NFC suspension, and then NFC films were prepared by casting the suspension followed by heat treatment. The covalent bond formation between the azetidium groups of PAE and carboxyl groups of NFC was confirmed by Fourier transform infrared (FT-IR) spectroscopy analysis. The water contact angle indicated that hydrophobicity of PAE/NFC films remarkably increased by the carboxyl content of NFC indicating that the carboxyl groups interacted with the cationic PAE to give higher water contact angles. While the dry tensile strength of NFC films was not influenced by PAE, wet tensile strength was clearly improved with PAE.

INTRODUCTION

Petroleum-derived polymers have been used widely because of their simple processing steps, low manufacturing costs, and excellent physical properties. Despite the performance and economic advantages of petroleum-based polymers, the use of renewable and sustainable materials is attracting attention due to increased environmental concerns. In response, nanofibrillated cellulose (NFC) has been widely researched in diverse scientific and commercial application fields. An alternative term for NFC is cellulose nanofibril. NFC products have unique chemical and physical characteristics. For instance, they contain abundant hydroxyl groups, and they have a nano-sized diameter and high aspect ratio (Ahola *et al*. 2008; Österberg *et al*. 2013). These characteristics make NFC an attractive material for fabricating transparent films, porous sheets, aerogels, and many other products (Fukuzumi *et al*. 2013; Sim and Youn 2016; Tang *et al*. 2019). The

transparent films prepared from NFC have good strength and optical transparency. However, these excellent performances of NFC films decrease under moist environments or in water due to the hydrophilic characteristics of NFC, which causes the cleavage of the interfibrillar hydrogen bonding (Pelton *et al*. 2019). Thus, improving the water-resistance of NFC-based substrates is an important challenge to meet in many practical applications.

Hill (2000) has shown that chemical modifications provide the means of permanently altering the nature of cellulose to have hydrophobic characteristics. However, large amounts of chemicals and organic solvents are required to introduce sufficient amounts of hydrophobic groups onto cellulose. Moreover, a decrease in the crystallinity of NFC accompanying the chemical modification often results in a decrease of mechanical properties (Sassi and Chanzy 1995; Rodionova *et al*. 2011). Therefore, it would be very useful if the hydrophobization of NFC could be achieved in an easy, non-toxic, and environmentally friendly way.

Saito and Isogai (2006) introduced aldehyde groups onto cellulose fibers by TEMPO-mediated oxidation and found that the surface aldehyde groups that form hemiacetal linkages with hydroxyl groups of cellulose increased the wet strength of the paper sheet. The addition of reactive water-soluble polymers such as polyamideamine-epichlorohydrin (PAE) in the cellulose suspension has been found to increase the wet strength of paper (Su *et al*. 2012). NFC films and aerogels with excellent dry and wet strengths were achieved by adding PAE as a cross-linker (Sharma and Deng 2016; Zhang *et al*. 2012). Zhang *et al.* (2012) reported that NFC aerogels containing PAE as a cross-linker showed an excellent shape recovery property in water.

Polyamideamine-epichlorohydrin has abundant active groups including azetidinium and alkyl functional groups. Even though the functional groups of PAE may self-crosslink, the main mechanism of improving the wet-strength by PAE is the covalent ester bond formation between the carboxyl groups of cellulose and cationic azetidinium groups of PAE. Thus, the cross-linking reactivity between cellulose and PAE depends on the amount of carboxyl groups of cellulose (Obokata and Isogai 2007).

Carboxymethylation, which is a process to introduce the carboxyl groups onto the pulp fiber, can be conducted by the etherification of the hydroxyl groups with monochloroacetic acid (MCA) in the presence of sodium hydroxide (Chen *et al.* 2013). Recently, Im *et al*. (2018a) investigated the reaction condition of carboxymethylation for optimization as a pretreatment method for carboxymethylated NFC preparation, and they reported that the carboxymethylated pulp can be deconstructed to NFC having 12 to 14 nm of width at a remarkably lower energy consumption compared to untreated pulp. They also showed that the carboxyl group content of NFC can be controlled by adjusting the reaction sequence and the amount of MCA and water content in the reaction medium. Yang *et al*. (2017) reported that TEMPO-oxidized NFC with abundant carboxyl groups has a high adsorbing capacity for PAE, which improves the wet strength and thermal-stability of PAE/TEMPO-oxidized NFC films.

The mechanical performance of NFC film after it has been rewetted by water is necessary to fully use the intrinsic functionalities of NFC film. In this study, NFC films with stable wet-strength were prepared by adding PAE as a cross-linker. In addition, the effects of the carboxyl group content of NFC on the cross-linking with PAE were investigated because the carboxyl content of NFC is an important factor for the cross-linking between PAE and NFC. To produce NFCs with different carboxyl group contents, the amount of MCA was controlled in the carboxymethylation process. PAE/NFC films were prepared by solution-casting with different levels of PAE addition. To confirm the

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covalent bond formation between azetidinium groups of PAE and carboxyl groups of NFC, Fourier transform infrared (FT-IR) spectroscopy analysis was employed. The surface hydrophobicity of PAE/NFC films was evaluated by measuring the water contact angle. In addition, dry and wet tensile strengths of PAE/NFC films were examined.

EXPERIMENTAL

Materials

Never-dried bleached eucalyptus kraft pulp provided by Moorim P & P (Ulsan, Korea) was used as a raw material. The chemical components of the pulp were comprised of $79.4 \pm 0.6\%$ cellulose, $18.8 \pm 0.2\%$ hemicellulose, and small amounts of lignin and ash, whose contents were determined in accordance with a TAPPI method (T 203 om-93). The pulp was washed with deionized water and filtrated using a vacuum filtration system to a consistency of 24% before the carboxymethylation process. Monochloroacetic acid (MCA, Sigma-Aldrich, St. Louis, USA, 99.0%) and sodium hydroxide (NaOH, Samchun Chemicals, Seoul, Korea, 98.0%) were used for carboxymethylation. Isopropanol (IPA, Duksan Reagents, Ansan, Korea, 99.5%) was used as a solvent medium without further purification. A commercial PAE solution with 2.6 meq/g of charge density (solid content of 12.5%) was provided by a supplier (EPtech, Ansung, Korea), which was diluted 1% with deionized water prior to use in the experiment.

Methods

Carboxymethylation of pulp fiber and preparation of NFC

Carboxymethylation (CM) was carried out to introduce carboxyl groups onto the pulp fiber. The introduction of carboxyl groups generates electrostatic repulsion between fibrils, which reduces the energy consumption for NFC production (Saito and Isogai 2006). Briefly, 20 g of pulp fiber was impregnated with 4 mmol/g of NaOH dissolved in 2 L of IPA for 30 min at 35 °C for alkalization. In this reaction chamber, 0.8 mmol/g and 1 mmol/g of MCA were added for etherification, which was carried out for 60 min at 65 °C. After the carboxymethylation reaction, the reacted pulp fiber was washed with deionized water until the pH and conductivity reached 6.5 ± 0.5 and ≤50 μS/cm, respectively. The carboxyl group content introduced by CM was evaluated by the conductometric titration method in accordance with SCAN-CM 65:02. From the calculated carboxyl content of CM pulp and the molecular weight of anhydroglucose unit, 162 g/mol, the degree of substitution (DS) can easily be calculated (Sahin 2018), following Eq. 1.

$$DS = CM \text{ content mmol/100 g} \times 162 \text{ g/mol} / (1000 \text{ mmol/mol} \times 100 \text{ g}) \qquad (1)$$

To prepare NFC, untreated and CM pulps with different carboxyl contents were diluted with deionized water to 1 wt%, and then NFC was prepared using a grinder (Super Masscolloider, Masuko Sangyo Co., Ltd, Kawaguchi, Japan). The operation speed and gap distance of the grinder were adjusted to 1,500 rpm and -80 μm, respectively.

Table 1. Carboxyl Group Contents and Average Degree of Substitution of CM Pulps Depending on the Amount of MCA Used in Carboxymethylation and the Number of Grinding Pass to Complete Nano-Fibrillation

Classification	MCA (µmol/g)	Carboxyl Contents (µmol/g)	Average Degree of Substitution	Number of Grinding Pass
Untreated pulp	-	50	-	30
CM NFC (Low)	0.8	296 ± 8	0.049	10
CM NFC (High)	1.0	513 ± 11	0.081	7

Table 1 shows the carboxyl contents and degree of substitution of untreated pulp and CM pulps prepared at two different MCA levels. The carboxyl content of the untreated NFC was 50 µmol/g because of the hemicellulose contained in the pulp fiber. The carboxyl contents of two CM pulps were around 300 and 500 µmol/g, respectively. The number of the grinding passes required for complete nanofibrillation of the pulp fiber was determined from the low shear viscosity data according to Im *et al.* (2018a). The CM pulp with a higher amount of carboxyl groups required a smaller number of grinding passes because of the greater electrostatic repulsion force generated by the carboxyl groups. The CM NFCs were classified as CM NFC (Low) and CM NFC (High) depending on their carboxyl contents.

Characterization of NFC

The morphologies of NFC were investigated using a field emission scanning electron microscope (FE-SEM, Carl Zeiss, Oberkochen, Germany). To prepare the fibril specimen for FE-SEM measurement, the NFC suspension was diluted with deionized water to 0.003 wt%, and the suspension was deposited on the glow-discharged carbon grid. Then, the specimen was sputtered with platinum for 100 s at 20 mA using a sputter coater. The average and distribution of fibril widths were calculated using an Image-J software. The average width of NFC was obtained from the measurements of at least 100 fibrils.

Electrostatic properties of NFC suspension depending on PAE addition level

To confirm the electrostatic interaction between NFC and PAE, the zeta potentials of the NFC suspensions at different PAE addition levels were evaluated using a Zetasizer (Nano ZS, Malvern Instruments, Ltd., Malvern, UK) at 25 °C. PAE solution and NFC suspension were diluted with deionized water to 0.1 wt%, respectively. The diluted PAE solution was then added to the NFC suspension from 0 to 10 wt% based on the oven dried weight of NFC. After gentle shaking using a stirrer for 10 min, the suspension was injected into a folded capillary cell. The zeta potential was calculated by measuring the electrophoretic mobility.

Preparation and characterization of PAE crosslinked NFC films

To prepare NFC films, PAE solution, diluted with deionized water to 1%, was added to the NFC suspension from 0 wt% to 8 wt% based on the oven dried weight of NFC. The NFC suspension was degassed under 0.1 MPa vacuum for 1 h. The suspension was poured into circular polystyrene Petri dishes (15 mm in diameter) and dried at 25 °C and 55% relative humidity for 5 days. After completely drying, the film was cured at 120 °C for 3 h to induce chemical crosslinking.

After preparation, FT-IR spectrometric analysis was conducted using a FT-IR spectrometer (Nicolet 6700, Thermo Scientific, Waltham, MA, USA) equipped with an attenuated total reflectance mode (ATR, ATR Acc.) to determine the chemical structure

and bond type of the NFC films. The initial static water contact angle of the NFC films was measured with a drop shape analyzer (DSA 100, KRÜSS, GmbH, Hamburg, Germany). A water droplet of 5 µL was deposited on the film and imaged immediately, and the contact angle was obtained from the image. The mechanical properties of the NFC films with different PAE addition levels were evaluated using a universal testing machine (Instron Co., Norwood, USA). The width of the specimen and the measurement span were 15 mm and 30 mm, respectively. The strain rate for the measurement was adjusted to 3 mm/min. In the case of the wet tensile strength measurement, the NFC film was impregnated in deionized water for 30 min before the measurement.

RESULTS AND DISCUSSION

Characterization of CM NFC

Fourier transform infrared spectroscopy was used to confirm the carboxymethyla-tion reaction and to determine the influence of the MCA amount. Figure 1 shows the FT-IR spectra in the wavelength range from 1400 to 1800 cm^{-1}. A new absorption band around 1500 to 1700 cm^{-1} was observed after the carboxymethylation of pulp, which was attributed to the asymmetric stretching vibration of the carboxyl groups (Eyholzer *et al*. 2010; Mohkami and Talaeipour 2011). This clearly showed that the carboxymethylation was successfully performed. In addition, the absorption band intensity increased as the amount of MCA used in the carboxymethylation increased. This is consistent with the carboxyl contents calculated by the conductometric titration method (Table 1).

Figure 2 shows the morphological properties of NFC prepared by mechanical treatment, *i.e*., grinding, after the carboxymethylation pretreatment. In the case of untreated pulp, large fibril bundles remained even after forty grinding passes. However, CM pulp was completely fibrillated to NFC after seven or ten grinding passes depending on the carboxyl content of the pulp. The CM NFC with different carboxyl contents showed similar average widths ranging from 9.3 to 12.5 nm regardless of the surface charge.
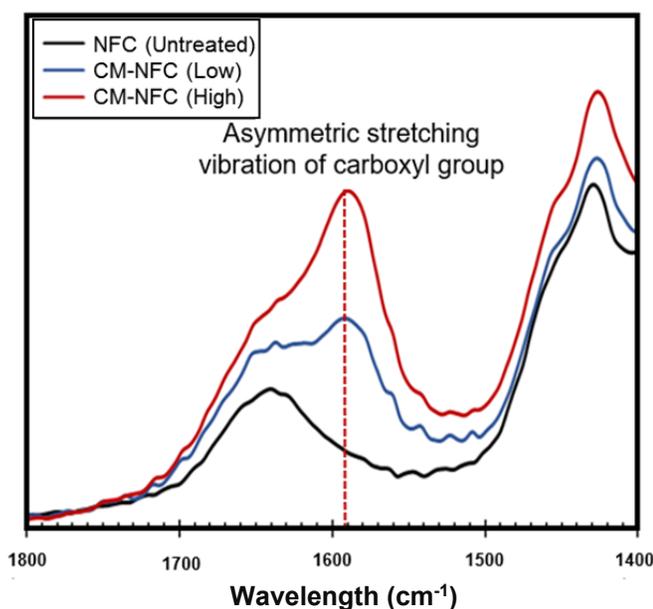
Fig. 1. FT-IR spectra of untreated and CM NFC films

(a) Morphology of NFCs

NFC (Untreated)   CM NFC (Low)   CM NFC (High)
100 nm   100 nm   100 nm
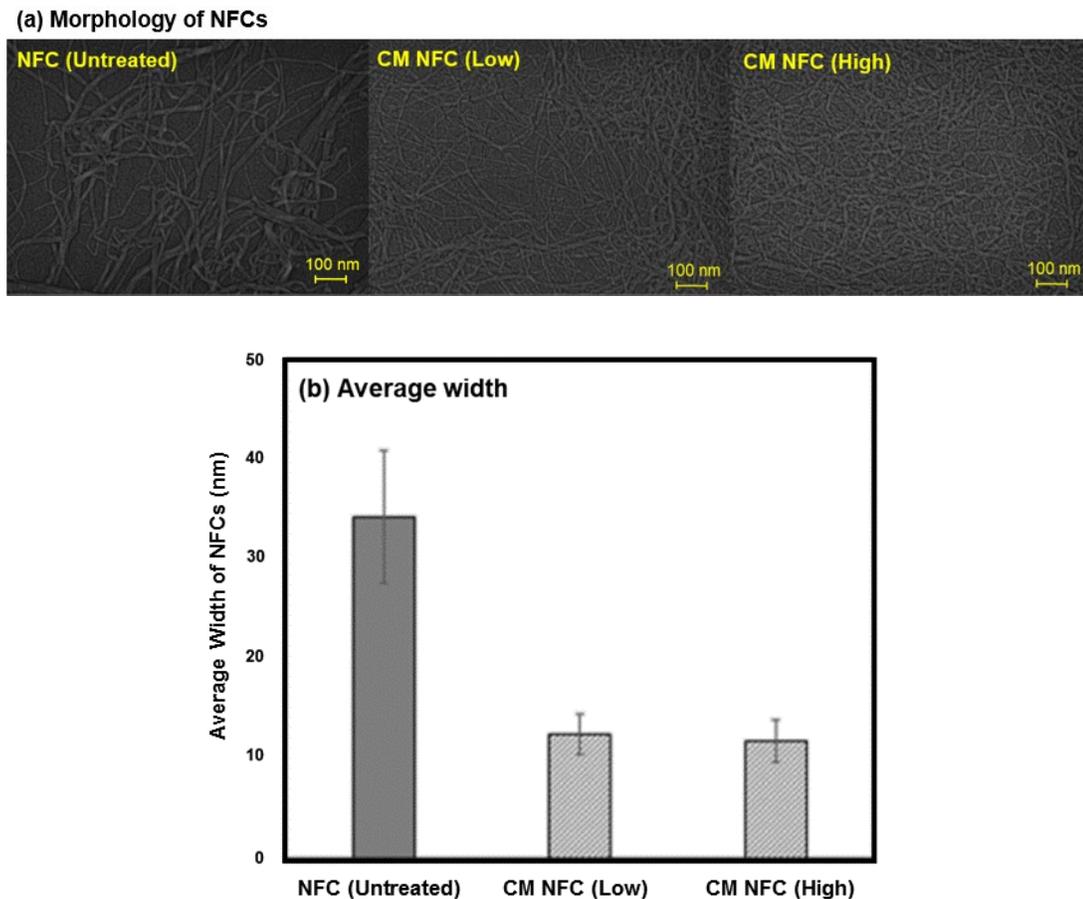
(b) Average width

Fig. 2. Morphological property (a) and an average width of untreated and CM NFCs (b)

Electrostatic Interaction between NFC and PAE

Figure 3 shows the zeta potential of the NFC suspensions at 0.1% depending on the PAE addition level. Cationic PAE adsorbed and retained in the cellulose fibrils by electrostatic interaction or ionic bond formation with the anionic fibril surfaces (Obokata and Isogai 2007). The CM NFC (High) showed the highest negative zeta potential in deionized water because it contained more carboxyl groups than other NFCs. The zeta potentials of all NFC suspensions increased with the increase of the PAE addition level. The amount of PAE required to neutralize the zeta potential of NFC suspension is strongly associated with the carboxyl contents of NFC. In the case of untreated NFC, which had 50 µmol/g of carboxyl groups, the amount of PAE needed to neutralize the zeta potential was approximately 0.3 wt%. However, the amounts of PAE required for charge neutralization increased to 2.7 wt% and 5.5 wt% for CM NFC (Low) and CM NFC (High), respectively, because the carboxyl group contents increased to around 300 and 500 µmol/g, respectively, for these two NFCs.
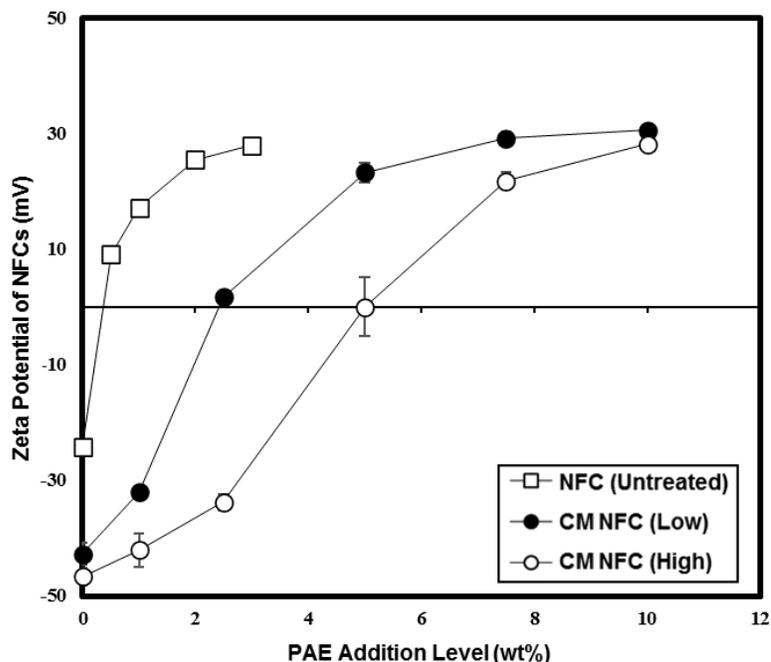
Fig. 3. Zeta potential of NFC depending on the addition level of PAE

Chemical Bonds between NFC and PAE

To investigate the cross-linking between NFC and PAE, FT-IR analysis of PAE containing NFC films were performed (Fig. 4). In the case of CM NFC films, the ester bonds formed between the carboxyl groups of cellulose and azetidinium groups of PAE were observed around 1,740 cm^{-1}, which was attributed to the C=O stretching vibration of aliphatic carboxylic ester groups (Yang *et al*. 2017). The presence of the ester bond in the NFC films showed the covalent bond formation between PAE and NFC. However, this signal was remarkably weaker for untreated NFC because it contained much less carboxyl groups compared to the CM NFC.

Effect of Carboxyl Contents and PAE Additions on Hydrophobicity and Tensile Strength of NFC Films

Water contact angle measurements were conducted to demonstrate the change of the surface hydrophobicity of NFC films depending on PAE addition level. As shown in Fig. 5, untreated NFC film showed hydrophilic characteristics, and its initial water contact angle was 42°. The water contact angle of untreated NFC film increased as the PAE addition level increased because a small amount of aliphatic functional groups was introduced through the esterification with PAE. The cross-linking between PAE and untreated NFC reduced the water absorption and increased the hydrophobicity of the film. Similar results have been reported by Sharma and Deng (2016), and they attributed the densification of NFC film to the PAE cross-linking. It is worth noting that the water contact angle of CM NFC film was much higher than untreated NFC film although PAE was not added.

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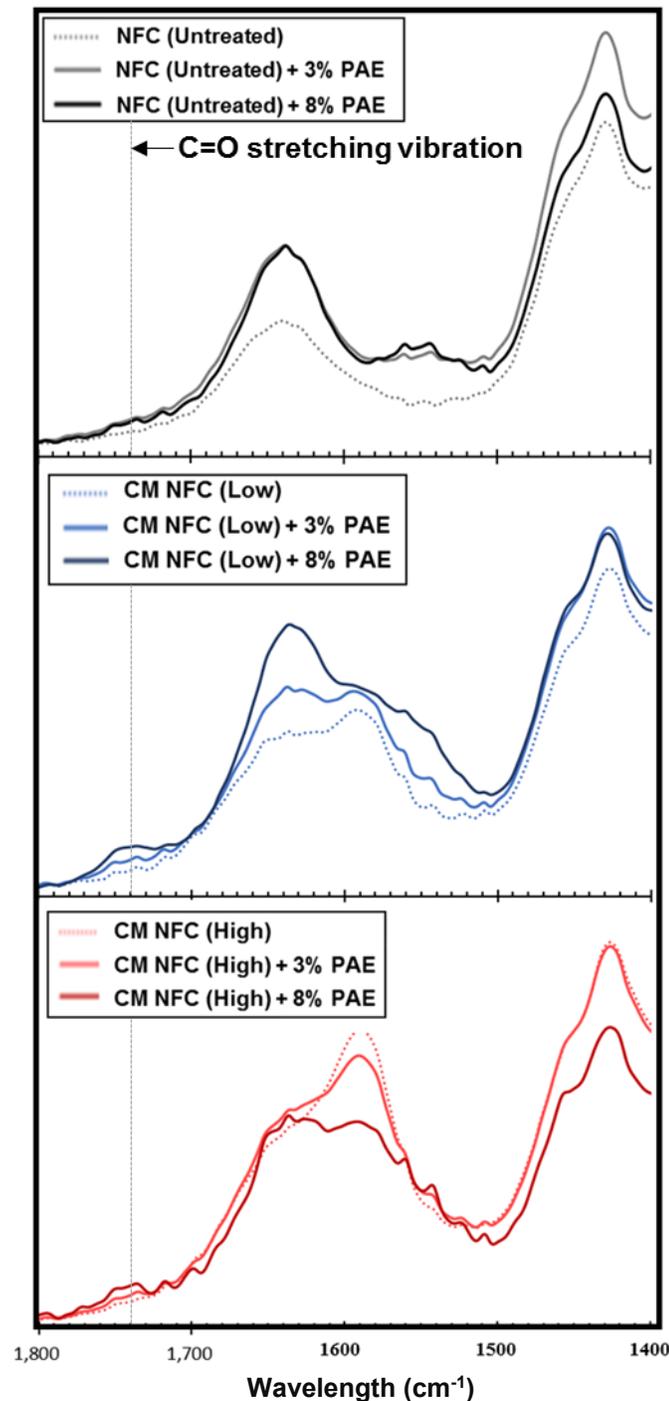
Fig. 4. FT-IR spectra of PAE added untreated and CM NFC films

Water contact angle of cellulosic materials is affected by various factors, such as chemical property, roughness, and porosity (Hubbe *et al*. 2015). In general, carboxy-methylation increased the hydrophilic nature of pulp fiber (Wilpiszewska *et al*. 2020). Nevertheless, higher water contact angle of the CM NFC film in this study might be attributed to the smooth and very dense structure of CM NFC film. Furthermore, as the PAE addition level increased, the water contact angle increased further up to 110°. These results are confirmed in Fig. 6. In conclusion, the hydrophilic surface of the untreated NFC

film can be changed to a hydrophobic one through the cross-linking reaction with PAE, and the hydrophobicity of NFC films can be increased further by using CM NFC.
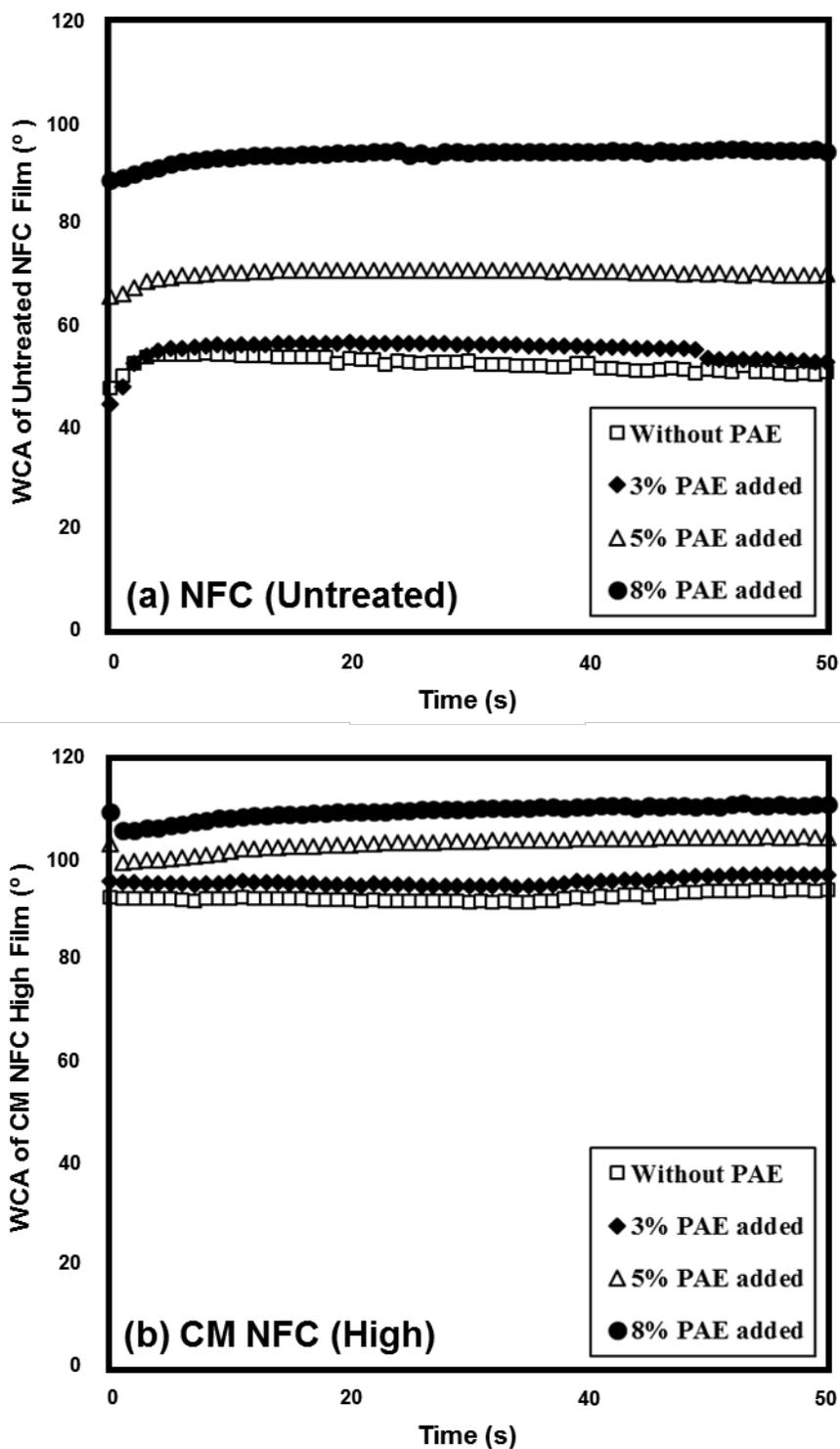
Fig. 5. Water contact angle of PAE cross-linked NFC films as a function of time; (a) Untreated NFC, and (b) CM NFC (high)

(a) NFC (Untreated)
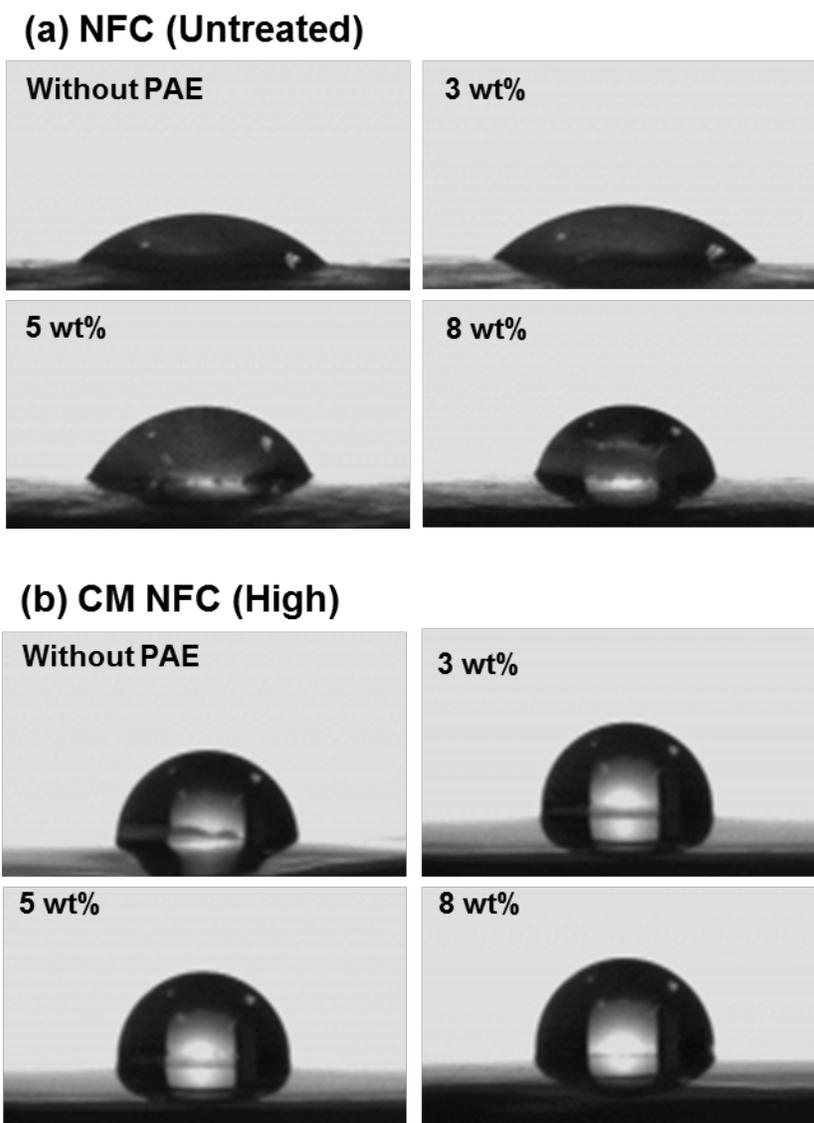
(b) CM NFC (High)

Fig. 6. Shape of water drop depending on PAE addition level; (a) untreated NFC, and (b) CM NFC (High)

Figure 7 shows the dry and wet strength of the NFC film depending on the PAE addition level. Saito and Isogai (2007) compared the dry strength of paper prepared by TEMPO-oxidized fibers with cationic polymers including PAE. They reported that dry tensile strength increased slightly with the addition of cationic polymers, irrespective of the cationic polymer types. In this experiment, however, there was no continuous increase in dry strength as the PAE content increased (Fig. 7(a)). On the other hand, much greater and continuous improvement in wet tensile strength was obtained as the addition level of PAE increased as shown in Fig. 7(b), which agreed very well with the result by Saito and Isogai (2007).
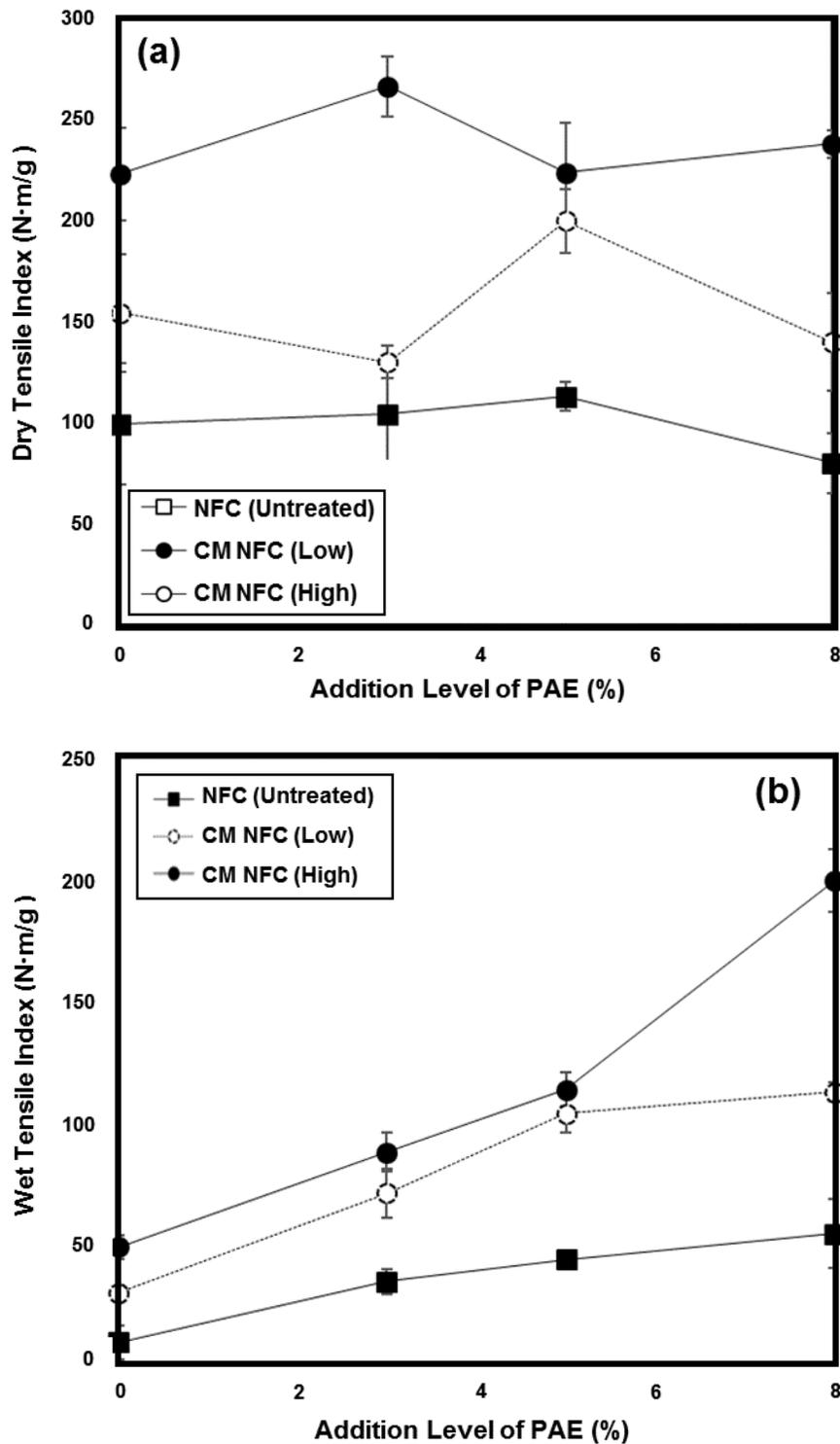
Fig. 7. Dry tensile index (a) and wet tensile index (b) of NFC films depending on PAE addition level.

It appeared that the improvement of dry strength by PAE addition was marginal because the density of the NFC film prepared with nano-sized fibrils was much higher than that of paper, which made it difficult for further interfiber bonding to occur. The film prepared with the CM NFC (High) exhibited much higher dry strength than the film

prepared with the CM NFC (Low). Im *et al.* (2018b) reported the effect of carboxyl contents of pulp fiber on the mechanical treatment intensity required to produce NFC and the aspect ratio of the product. They showed that the CM NFC that required less mechanical energy, *i.e.*, a smaller number of grinding passes, had the high aspect ratio. The morphological properties of NFC appeared to influence the dry strength of CM NFC films. The addition of PAE clearly increased the wet strength irrespective of the type of NFC. Particularly, CM NFC (High) showed the highest improvement in wet strength due to its high cross-linking capability with the cationic azetidinium groups of PAE.

CONCLUSIONS

1. Nanofibrillated cellulose (NFC) films with stable wet-strength were prepared by adding polyamide-amine-epichlorohydrin (PAE) as a cross-linker, and the effects of the carboxyl group content of NFC on the cross-linking with PAE were investigated.

2. The carboxyl contents of NFC were adjusted by a carboxymethylation reaction, which substituted the hydroxyl groups of cellulose with carboxyl groups. The Fourier transform infrared (FT-IR) spectra and conductometric titration analysis indicated that successful carboxymethylation of the pulp was achieved, and the amount of carboxyl groups could be controlled by adjusting the amount of monochloroacetic acid (MCA) in the carboxymethylation reaction.

3. Adsorption of PAE onto NFC and covalent bond formation between NFC and PAE were evaluated using zeta potential and FT-IR analysis, respectively. The results indicated that the efficiency of PAE can be increased by carboxymethylation of NFC and the interaction of NFC and PAE relied on the carboxyl content of NFC at the same PAE addition level.

4. The PAE/NFC films prepared using carboxymethylated (CM) NFC with higher carboxyl contents showed higher water contact angle, indicating that the surface hydrophobicity of the films was improved. There was no substantial improvement in the dry strength of NFC films depending on PAE addition level because the dense structure of NFC films excluded the further interfiber bond formation. However, as the PAE addition level increased, the wet strength of the films clearly increased.

ACKNOWLEDGMENTS

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