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Application of Cellulose Nanofibrils to PVA Impregnation for the Improvement of Durability of Papers

종이의 내구성 향상을 위한 폴리비닐알코올 함침의 첨가제로서 셀룰로오스 나노피브릴의 활용

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Abstract

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High durable papers are required to the specific area where their shape or properties have to be conserved for a long time. Banknote, poster, and passport are representative papers which need durability. In order to develop the durability of papers, long service life, high mechanical strength and anti-soiling property should be considered. Anti-soiling property means resistance against moisture and contaminants. The conventional method of manufacturing durable papers is the impregnation of polyvinyl alcohol (PVA). However, the durability of papers should be improved for a long circulation use. This study focuses on the use of another additive in PVA solution, cellulose nanofibrils (CNF).

The application of CNF to PVA impregnation was analyzed in terms of mechanical strength and anti-soiling property. The addition level of CNF was controlled when prepared CNF-PVA suspension and the miscibility of the suspension was good enough to apply PVA-CNF suspension to the impregnation. 5% CNF content improved tensile strength and folding

endurance despite of lower pickup weight of impregnated papers. It points out the impregnated papers by PVA-CNF suspension could be made use of lightweight papers with good mechanical strength. However, the anti-soiling properties under dry and wet condition were not improved, which PAE was introduced as another additive of impregnating agent. . As PVA-CNF suspension including PAE showed high low shear viscosity, impregnated papers by the suspension presented lower pickup weight and folding endurance than impregnated papers by PVA solution. However, anti-soiling property of impregnated papers dramatically increased. While the paper impregnated by PVA-CNF(5%) suspension was destroyed after 20 min-soiling, the paper by PVA-CNF(5%)+PAE suspension was well preserved. Lastly, silylated CNF suspension (SCNF) was applied as an additive of PVA solution instead of CNF. SCNF suspension was obtained by the silylation of CNF suspension using methyltrimethoxysilane (MTMS) under an aqueous system. The miscibility of PVA-SCNF suspension was good but anti-soiling of this part did not show any significant increase. The water contact angle of impregnated papers by PVA-SCNF suspension was higher than PVA-CNF suspension, which can have the possibility to increase the anti-soiling by using other silane agents instead of using MTMS.

Key words: Cellulose nanofibrils, polyvinyl alcohol, silylation, impregnation, durability, anti-soiling property, mechanical strength

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1. Introduction

Durable papers such as map, book and banknote have been used in the special area where needs high mechanical strength and long service life. Durability requires the maintenance of shape even under harsh environment and circulation of uses. Durability is defined to ‘a characteristic of paper and paperboard relating to its ability to stand up and retain its original properties under constant use over extended periods of time’ (Lavigne 1986). In order to meet durability, papers should have high mechanical strength as well as the resistance against soiling. In addition, long service life and high printability are demanded. The anti-soiling property is one of important considerations to evaluate the durability, which means the ability to resist against contaminants. The conventional method for producing durable papers is an impregnation using polyvinyl alcohol and borax (Kim 2007).

Polyvinyl alcohol (PVA), water soluble polymer, has been utilized to form bio-composite or environmentally friendly film due to its good film formation (Hentzschel 2007). For the application to paper industry, PVA was used as the impregnating agent or surface sizing agent in order to enhance the smoothness and dimensional stability of paper as well as the mechanical strength. As PVA also has high resistance toward oxygen permeability, PVA was applied to a papermaking area such as the manufacture of specialty paper (Hentzschel 2007).

Even though the paper impregnated by polyvinyl alcohol shows good performance, the durability of paper still needs to be enhanced when longer circulation of use is needed. Considering tensile strength and folding endurance of papers, which are typical requisite for durable papers (Kim 2007), Cellulose nanofibirils (CNF) can be introduced in this field.

Cellulose nanofibrils (CNF) is nano-sized cellulose isolated from mainly wood fiber by mechanical treatment. CNF has a high aspect ratio, large specific surface area, high mechanical strength, biodegradability, a number of hydroxyl groups on the surface and good network formation at low consistency. These characteristics of CNF lead to be introduced in papermaking applications (Rantanen and Maloney 2013, Gonzalez et al. 2012), cosmetics (Brodin and Theliander 2013), nanocomposites (Seydibeyoğlu and Oksman 2008, Benhamou et al. 2015), and other applications. As CNF was applied as a strengthening additive of pulp suspension, not only the density increased but the strength of paper enhanced (Brodin et al. 2014). CNF has also been utilized as a coating material, which showed high strength and good oxygen permeation resistance for barrier coating (Hubbe et al. 2017). Syverud and Stenius (2009) revealed that the application of thin MFC film onto the paper improved the strength properties of paper[13)].

It has been reported that CNF could be a reinforcing element of biocomposite. The biocomposite of PVA-CNF has been also attracted due to a good network formation of CNF at a low consistency and large

specific surface area (Qu et al. 2010, Moon et al. 2011). Lu et al. (2008) showed that the transparent film could be made PVA reinforced by CNF. Liu et al. (2013) revealed that the tensile strength of PVA-CNF film increased because the hydrogen bonding occurred between the hydroxyl of PVA and the chain of CNF.

CNF has abundant hydroxyl groups on the surface, which enables the chemical modification easy. Through the surface chemical modification to increase the hydrophobicity of the CNF surface, the miscibility of CNF in hydrophobic matrix can be improved. Several studies have suggested the method of the modification such as surface adsorption or grafting (Missoum et al. 2013). Acetylation and silylation of CNF are representative ways to increase the hydrophobicity of CNF. However, most of these methods are based on organic solvents. Zhang et al. (2014) tried to silylated CNF suspension without using organic solvent to produce aerogels for oil-removal sponges.

Polyamideamine-epichlorohydrin (PAE) is synthesized from polyamideamine chains by reacting with epichlorohydrin. PAE has been used as a wet-strength agent in a papermaking. Obokata and Isogai (2017) reported that wet-tensile strength of sheets increased with increasing PAE content. In addition, heating treatment improved the wet strength of sheets more (Obokata and Isogai 2017). These results were due to a covalent bond between an azetidinium group of PAE and carboxyl group on the pulp fibers.

In this study, CNF is applied to impregnation as an additive of PVA solution in order to develop the durability of papers (Fig. 1). The additional level of CNF into PVA was optimized in terms of mechanical strength and anti-soiling property of papers. PAE was added in PVA-CNF suspension in order to increase wet-strength of papers. Lastly, hydrophobization of CNF suspension was applied to reveal if it could improve anti-soiling. The aim of this study was to utilize CNF as an additive of PVA impregnation (1), to analyze the distribution of CNF in a paper for figuring out the impact of CNF when applied to impregnation (2), and to find out the method of improving the anti-soiling properties of papers using hydrophobizied CNF and another additive (3).

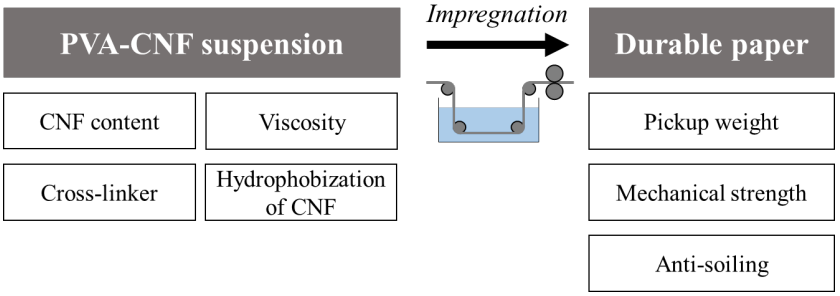

Fig. 1. Experimental scheme of the application of CNF to PVA impregnating solution.

2. Literature Review

2.1 Manufacture of durable papers

Durable papers are required to papers which need long service life and high mechanical strength as well as high anti-soiling. The efficient impregnation of papers using polyvinyl alcohol was introduced by Kim (2007). Comparing to size pressing, impregnation is effective for polyvinyl alcohol to penetrate into the inside of paper. In addition, the process of impregnation is a simple and cost-inexpensive process. In order to improve the wet strength of papers, hardener, borax, was applied to the PVA impregnation. Kim (2007) suggested that the appropriate of concentration of PVA was 4 – 6% and the one of borax was 2 – 3%. Also, it is presented that the critical factor of durability of paper would be the wet strength and bulk of paper.

Other ways to improve the durability of papers have been introduced. Post-print coating or pre-print coating with vanish on paper were also effective for soiling-resistance and abrasion resistance properties. Starch has been also used as the size pressing agent as well as internal sizing agent at an addition rate of between 2 – 5 % (Gurnagul et al. 1993). No standard methods for evaluating the durability of papers are exist. Jung et al. (2007) classified methods of durability measurement. Strength properties, folding endurance, tearing resistance and crumpled porosity, and artificial soiling test were done as well as soap resistance.

2.2 Application of cellulose nanofibrils (CNF) as a reinforcing element

The influence of nanocellulose as a reinforcing element was first reported by Favier et al. (1995). Cellulose nanofibrils, cellulose nanocrystals and bacterial cellulose are representatives of nanocellulose. CNF especially has a high aspect ratio, high surface area, and good network formation at low consistency which could contribute to the reinforcement of the composites. The stress transfer occurs from the matrix to the reinforcing phase owing to the high aspect ratio of CNF (Eichhorn, et al. 2010). Isogai (2013) argued that CNF without chemical pretreatment would be utilized for making lightweight nanocomposite with high mechanical strength such as films or aerogels.

Nanocomposites reinforced by CNF have been introduced over 10 years. Iwamoto et al. (2005) prepared the CNF composite impregnated by resin. They emphasized that the composite had low thermal expansion coefficient, which was comparable to that of glass. They mentioned the CNF-reinforced composite is not compromised even at high fiber content. Iwamoto et al. (2007) investigated the effect of fibrillation of CNF on nanocomposite. They also revealed that the fiber hydrolyzed by sulfuric acid enabled the thermal expansion of the composites decreased owing to the increase of the degree of crystallinity.

Srithep et al. (2012) investigated the properties of two types of PVA-CNF composites, films and foams. The desorption degree of CO_2

increased PVA-CNF foam, which implied potential material for light weight foams. Liu et al. (2013) proposed the use of CNF as an additive of PVA film, of which thermal stability and tensile strength increased. Liu et al. (2014) also applied this CNF to a foam and revealed that the dimensional stability of foam increased and the rate of absorbance of water decreased. They emphasized that the application of CNF could be one of promising packaging materials with biodegradability.

Composites of PVA-CNF have been developed by the combination of crosslinking materials or the modification of CNF. Zheng et al. (2013) and Javadi et al. (2013) prepared PVA-CNF hybrid organic aerogels with multi-walled carbon nanotube or graphene oxide. They used an environmentally friendly, cost-effective method and the result showed the mechanical properties were remarkable. Zheng et al. (2014) also treated silane on PVA-CNF hybrid aerogels to obtain superior elasticity and mechanical durability.

CNF has also been utilized in papermaking process as a strengthening additive in wet-end, coating material, and etc. Syverud and Stenius (2009) argued that MFC deposited on the top of the wet base paper increased the strength of base paper. They also investigated that less than 10% MFC was effective for strength of paper. Dimic-Misic et al. (2013) utilized CNF as a cobinder in the coating formulation, which showed the improvement of the strength properties on paper surface.

2.3 Hydrophobization of cellulose nanofibrils

Cellulose nanofibrils has some limitation to its use, such as aggregation, low compatibility with hydrophobic polymer matrix, and low concentration suspension. In order to overcome these drawbacks of CNF, researchers have been tried to modify the surface energy of CNF, by two representative approaches. One is by adsorption of molecules onto the surface of CNF, the other is by a chemical grafting of covalent bonds between cellulosic substrates and the hydrophobic agent. Zhao et al. (2015), for example, tried to modify CNF suspension by MTMS sol and fabricate the silica aerogels with silylated-CNF scaffolds biotemplete. The compatibility between silica and silylated-CNF increased compared to unmodified CNF.

Rodionova et al. (2011) carried out the acetylation of CNF suspension using acetic anhydride. They compared films prepared from unmodified CNF and modified CNF. The dynamic contact angle showed hydrophobic surface of modified CNF and the oxygen transmission rate of modified CNF was comparable to usual packaging materials. Acetylation of the surface of CNF enables to the application of CNF on barrier coating materials.

Andresen et al. (2006) tried to prepare CNF silylated with chlorodimethylisopropylsilane (CDMIPS). The water contact angle of films prepared from silylated CNF implied super hydrophobic (146 º) because of decreased surface energy and increased surface roughness

(Andresen et al. 2006). Andresen et al. (2007) also determined antibacterial activity of CNF silylated with CDMIPS. The films from surface-modified cellulose nanofibrils showed antibacterial activity. They argued that the MFC films would be possible to apply food packaging, medical applications, or antimicrobial separation filters.

Unlike the Andresen's study, Zhang et al. (2014) performed silylation of CNF without using organic or toxic compounds. The CNF suspension adjusted to pH 4 was reacted with hydrolyzed methyltrimethoxysilane (MTMS). They obtained flexible, ultralight, and hydrophobic CNF sponges, which efficiently removed dodecane. Most silylated CNF aerogels showed water contact angle above 105º and the surface of the aerogel was almost entirely covered by polysiloxane sol with increase in silane level, which reached maximum value of water contact angle of 136 º.

3. Materials and Methods

3.1 Raw materials

Paper made of linter cotton supplied from KOMSCO Co. (Korea) was used as base paper for impregnation. For the production of cellulose nanofibrils (CNF), hardwood bleached kraft pulp (Hw-BKP) fibers was beaten before grinding. Polyvinyl alcohol (PVA, Fig. 2) was selected as an impregnation agent. The properties of PVA were presented in Table 1. Borax ($Na_2B_4O_7 \cdot 10H_2O$) was used as a hardner for PVA. Polyamideamine-epichlorohydrin (PAE, solids content: 2.5%) was used as a wet-strength agent. Methyltrimethoxysilane (MTMS) was purchased from Sigma-aldrich to hydrophobize CNF.

Table 1. Properties of a base paper

Item	Value
Basis weight	88.7±1.0 g/m^2
Thickness	144 μm
Tensile strength/ folding endurance	46 N·m/g / 46 double folds

Table 2. Properties of PVA

Item	Value
Degree of polymerization	1700 – 1800
Degree of hydrolysis	98.0 mol%
Ash	~ 1.0%

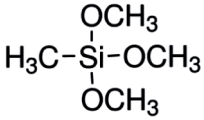

Fig. 2. Chemical structure of MTMS.

3.2 Preparation of an impregnating agent

3.2.1 Preparation of PVA solution

PVA was dissolved to the desired consistency in deionized water at 100℃, and then cooled down to room temperature. The consistency of PVA was adjusted to 2% solution for the evaluation of the miscibility of PVA and CNF suspension and was adjusted to 4% for the impregnation.

3.2.2 Preparation of CNF suspension

CNF was prepared from Hw-BKP suspension (2%) by mechanical treatment. Mechanical treatment was conduct by grinder (Supermasscolloider, Masuko Sangyo Co. Ltd., Japan). The operation gap size between grinder stones was -80 μm and the rotating speed was 1,500 rpm.

3.2.3 Preparation of PVA-CNF suspension

CNF was prepared to 2% and PVA was dissolved to the same consistency, 2%, for the measurement of the miscibility of the mixed suspension. The CNF suspension was mixed with PVA solution depending on the mixing ratio of PVA and CNF based on oven-dried weight (100:0 – 0:100 wt%). The mixed suspension of PVA-CNF was stirred for half an hour at about 1,000 rpm. On the contrary, PVA-CNF

suspension for the impregnation was prepared with different addition level of CNF suspension (0 – 20%) based on the oven-dried weight of PVA. The consistency of PVA solution was 4% for the impregnation.

3.2.4 Addition of PAE to PVA-CNF suspension

When PVA-CNF suspension was prepared, polyamideamine-epichlorohydrin (PAE) could be applied to the suspension in need. In order to examine the effect of PAE on the durability of papers, PAE was added into the PVA-CNF suspension by 0.4 w/v%.

3.2.5 Hydrophobization of CNF

The surface modification of CNF was conducted to evaluate the effect on anti-soiling properties of papers. Silylation was chosen for the hydrophobization of CNF, especially performed in an aqueous system. Reaction of silylation in an aqueous system was selected due to an environmentally friendliness and the miscibility with PVA. According to Zhang et al. (2014), MTMS was added dropwise to distilled water which was adjusted to pH 4. After 5 min stirring, polysiloxane sol was prepared after 5 min. CNF suspension was also adjusted to pH 4, and then the polysiloxane sol was added dropwise to the CNF suspension. The suspension was stirred for 2 h to complete the reaction. The addition level of methyltrimethoxysilane (MTMS) based on oven-dried weight of CNF was controlled (CNF:MTMS=1:0.5, 1:1, 1:2). Hydrophobizied

CNF was called SCNF. The hydrophobicity of modified CNF was measured by water contact angle of the film made of the modified CNF suspension.

3.3 Evaluation of properties of PVA-CNF suspension

The miscibility between PVA and CNF needs to be evaluated prior to the application of impregnation. The property of the suspension was evaluated in terms of dispersion stability and rheological properties.

3.3.1 Dispersion stability

The change of suspension status over time was evaluated by Turbiscan instrument (Formulaction Ltd., France), which indicated the dispersion stability of suspension. This instrument is composed of detection devices of transmission and back scattering infrared light. If the back scattering (%) of the bottom of a vial increases, it indicates that the suspension has a sedimentation. If the back scattering (%) of the upper part of a vial increases, the suspension has a creamy bubble. If the back scattering (%) of all part of vial is unchanged by passing time, the suspension seems stable. (Fig. 3)

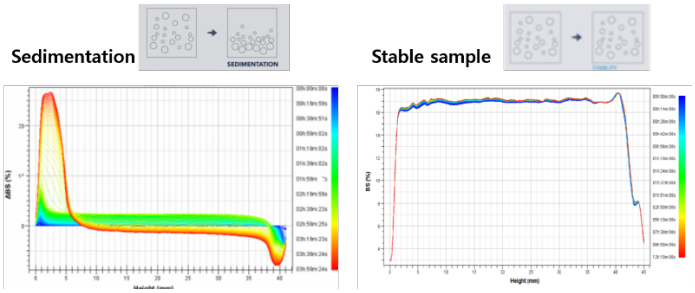

Fig. 3. Examples of back scattering profile of Turbiscan.

Turbiscan stability index (TSI) is also calculated to express the stability of the suspension over time using Eq. [1]. The lower TSI index is, the more stable the suspension is.

$$\mathrm{TSI} = \sqrt{\frac{\sum_{i=1}^{n}(x_i - x_{BS})^2}{n-1}} \qquad \text{Eq. [1]}$$

where, x_i means the average of scattering light measured per minute, x_{BS} is the mean value of x_i, and n shows the number of measured scans.

3.3.2. Sedimentation behavior

The dispersion stability of PVA-CNF suspension was further analyzed in terms of sedimentation behavior. PVA-CNF suspensions from five different mixing ratios were kept at the room temperature. The consistency of PVA-CNF suspensions was also controlled (0.2-2.0%). After 24 h, the sedimentation height was measured.

3.3.3 Rheological properties

The low shear viscosity of suspension was measured using Brookfield viscometer (Brookfield DV2T-LV, USA). The viscosity was evaluated at 100 rpm for 30 seconds at 25℃. The oscillatory rheological properties of the PVA-CNF suspension were evaluated by Bohlin viscometer depending on the mixing ratio of PVA-CNF. The stress was varied from 0.1 to 100 Pa and parallel plates with 1 mm gap size was used. The storage modulus and yield stress were obtained. The rotational viscosity was also measured varying shear rate from 0.1 to 100 s^{-1} in order to analyze visco-elastic properties of the PVA-CNF suspension.

3.4 Impregnation of PVA-CNF suspension into base paper

3.4.1 Process of impregnation

PVA was prepared at 4% consistency. Impregnating suspension was prepared by adding CNF suspension to PVA solution with different addition levels of CNF. The addition level of CNF was controlled from 0 to 20 wt% based on oven-dried weight of PVA. Base paper was impregnated in a bath containing PVA-CNF suspension which was kept constant at 50℃. After impregnating, the paper was removed from the bath and couched with filter paper to eliminate excess suspension from the paper. The same process was conducted after the paper was impregnated into bath containing borax. Finally, the paper was dried

using drum dryer at 120℃ (Fig. 4). Pickup weight of papers was calculated by the difference between basis weight of base paper and impregnated paper.

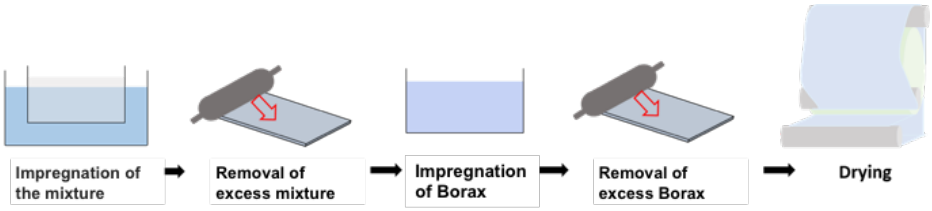

Fig. 4. Scheme of impregnation procedure.

3.4.2 Evaluation of properties of the impregnated paper

Properties of paper impregnated by the suspension were evaluated. The properties of durable paper are mechanical strength, surface properties of paper, water resistance, and anti-soiling property. The properties of impregnated papers were compared between using unmodified CNF and modified CNF.

3.4.2.1 Mechanical strength

Tensile strength of paper was measured in the machine direction in accordance with ISO Test method ISO 1924-2 and folding endurance of paper was evaluated in the cross direction by ISO Test method ISO 5626 (MIT tester for folding endurance). The load for the folding endurance was 1 kgf.

3.4.2.2 Surface properties

The water contact angle of the surface of paper relates to hydrophobicity, which was evaluated using DSA (KRÜSS, Germany). The angle was measured at sessile mode for 60 seconds. The surface coverage of impregnated papers by PVA-CNF suspension was analyzed by FE-SEM (Field Emission Scanning Electron Microscope, SUPRA 55VP, Sweden).

3.4.2.3 Penetration behavior of the suspension into paper by impregnation

In order to reveal the influence of CNF on PVA impregnation, the penetration behavior of the suspension into paper should be analyzed. PVA and CNF were stained with different fluorescent dyes respectively and cross section images of impregnated papers were measured by CLSM (Confocal laser scanning microscopy, LSM 710, Carl Zeiss, Germany) to analyze the distribution of PVA-CNF in Z-direction of paper. The base paper which was used for the penetration test was porous filter paper from Adventec® (Toyo Roshi Kaisha, Ltd., Japan). Acridine orange and calcofluor white were used as fluorescent dyes. PVA was dyed by acridine orange and CNF was identified by calcofluor white stain. Excitation and emission wavelength used for acridine orange were 488 nm and 490-545 nm and for Calcofluor white were 405nm and 410-483 nm.

3.4.2.4 Anti-soiling performance

Soiling-resistance test was performed under a dry and wet condition. In a dry condition, contaminants were prepared with 2,000 g glass bead, 0.4 mL oil, 0.3 g clay and 0.4 mL ethanol. After shaking 2,000 g of glass beads and contaminants in a box, impregnated papers were put in the soiling tester and rotated for 30 min. After swiping out samples with wet towel, the brightness was compared and could be quantified by using grayscale specified from ISO.

In a wet condition, the bottle contained ceramic bead, color powder, artificial sweat and lanolin as contaminants. In a turbular mixer, prepared contaminants and impregnated papers were put together and shaken for each 5 min to 20 min. After washing samples with water and drying, brightness and remained shape were compared.

4. Results and Discussion

4.1 Properties of PVA-CNF suspension

Before the application of CNF to PVA impregnation, compatibility of PVA-CNF suspension was analyzed in terms of dispersion stability and rheological properties. PVA-CNF suspension was prepared by mixing with different weight ratio (PVA:CNF=100:0, 75:25, 50:50, 25:75, 0:100 wt%). The consistency of the PVA-CNF mixed suspension was adjusted to 0.2 and 2 wt%.

4.1.1 Dispersion stability

The delta transmission (ΔT) profile of PVA solution and delta backscattering (ΔBS) profiles of each PVA-CNF suspension for 12 h were shown in Fig. 5. According to Fig. 5, the profiles did not change during the measuring time and kept almost constant in all parts of a vial. TSI value was also low over all CNF content. It suggested that all suspension at 2% was stable regardless of CNF content. In order to examine the interaction between PVA solution and CNF suspension further, the suspension was diluted at 0.2%, results of which were shown in Fig. 6. Unlike the suspension at 2%, samples including 25, 50, 75% of CNF content presented sedimentation at the bottom of a vial. In other words, while phase separation or aggregation were not occurred over a certain concentration of the suspension, CNF tended to present flocculation behavior by gravity in a low concentration of the suspension.

Sedimentation behavior was further examined depending on various concentration and mixing ratio of the suspension, which is shown in Figs. 7 and 8. The sedimentation height was measured after 24 h till samples stored at the room temperature. The sedimentation height was not proportional to CNF content. CNF content over than 0.1 g/40 mL (0.25 g/100 mL) formed a percolated network. In other words, when PVA-CNF suspension is applied to the impregnation process, the consistency of the suspension and CNF content would be a crucial consideration for stable process.

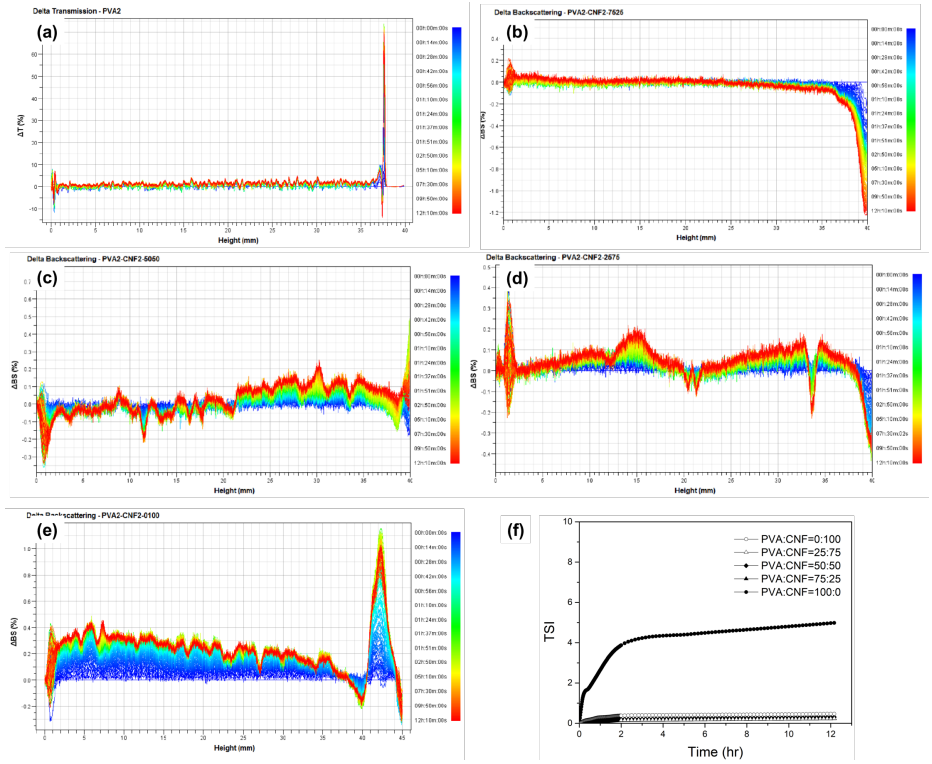

Fig. 5. Profile of ΔT (%): PVA:CNF=100:0 (a), profile of ΔBS: PVA:CNF=75:25 (b), 50:50 (c), 25:75 (d), 0:100 (e), and TSI value (f).

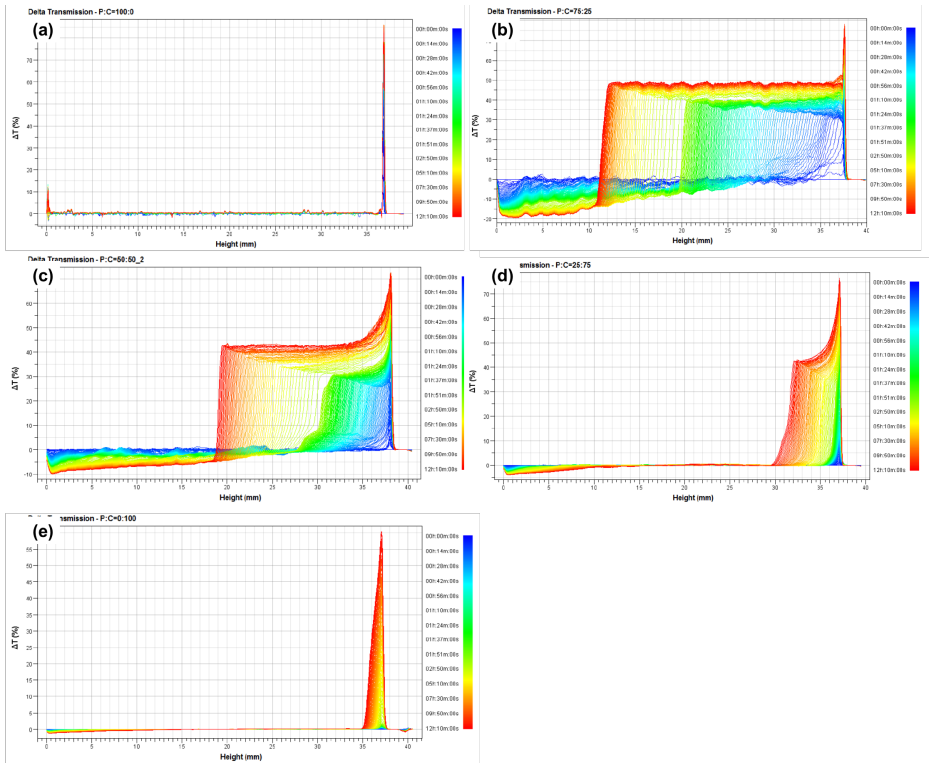

Fig. 6. Profile of ΔT (%): PVA:CNF=100:0 (a), 75:25 (b), 50:50 (c), 25:75 (d), and 0:100 (e).

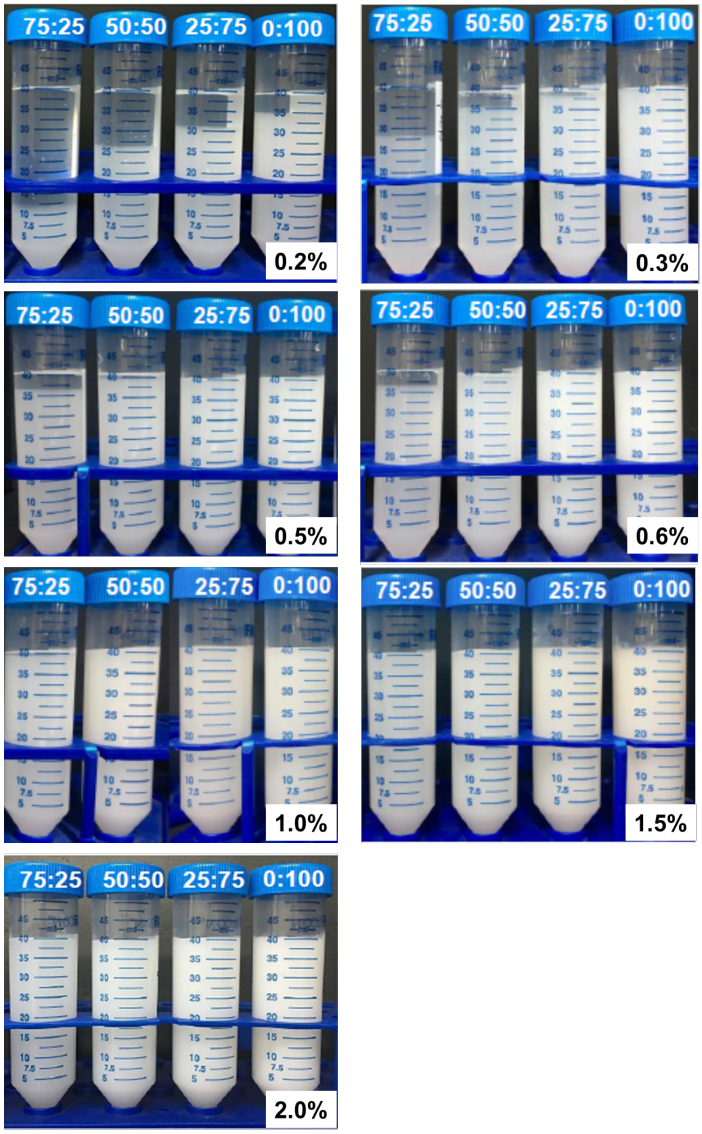

Fig. 7. Sedimentation behavior of PVA-CNF suspension (PVA:CNF) depending on the concentration of the suspension (0.2 – 2.0 %).

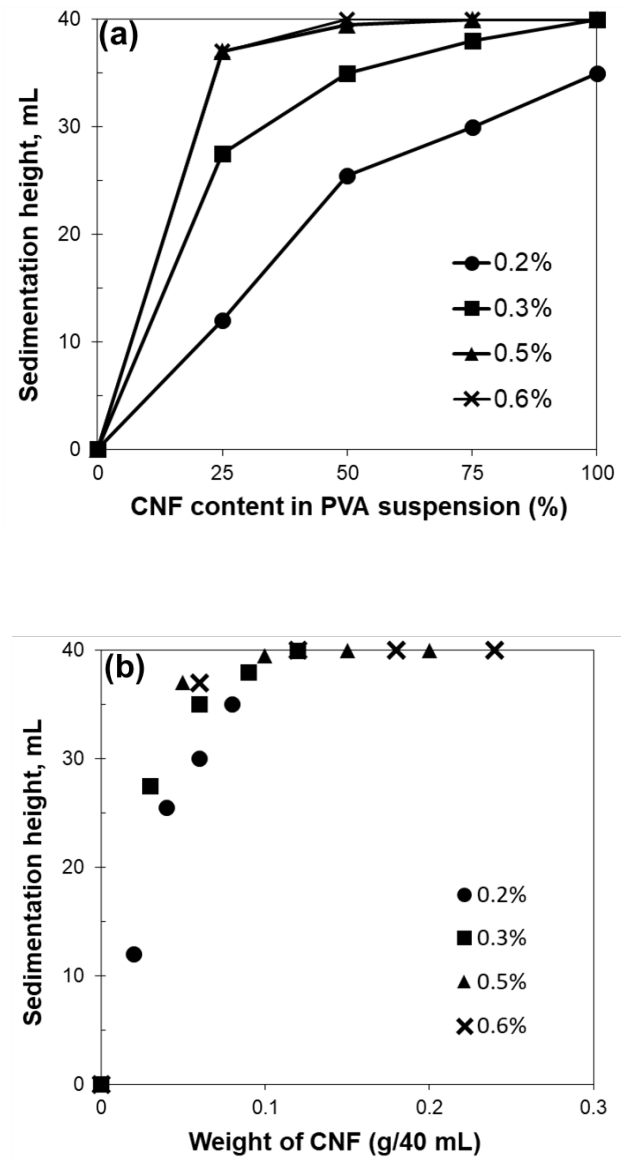

Fig. 8. Sedimentation height depending on CNF content (a) and weight of CNF (b).

4.1.2 Rheological properties of PVA-CNF suspension

Fig. 9 shows the low shear viscosity of PVA-CNF suspension depending on the CNF content in the suspension. Low shear viscosity increased with an increase in CNF content and did not increase linearly. The viscosity sharply increased over 25% CNF content. The rotational viscosity showed a similar trend to low shear viscosity (Fig. 10). Fig. 10 shows the viscosity of PVA-CNF suspension depending on the shear rate and the mixing ratio from the rotational viscometer. Viscosity increased with increase in CNF content and a significant increase in viscosity was observed at 25% CNF content. The PVA-CNF suspension showed pseudoplastic behavior, which can be applied to the impregnation process. Therefore, two viscosity results implied that there is a limited content of CNF when CNF was applied to PVA impregnation.

Stress sweep was performed in order to investigate on the network property of PVA-CNF suspension, shown in Fig. 11. While viscosity of PVA-CNF suspension increased sharply at 25% CNF content, the storage modulus at the same content showed linear depending on the shear stress. It means the suspension containing 25% CNF had a liquid-like behavior. On the contrary, in PVA-CNF suspension containing over 50% CNF, the suspension seemed solid-like behavior at low shear stress. The yield point is where the storage modulus begins to decrease significantly as the shear stress increased. The obtained yield point of each suspension are presented in Fig. 11(b). Consequently, when PVA-CNF suspension is prepared, CNF content should be considered.

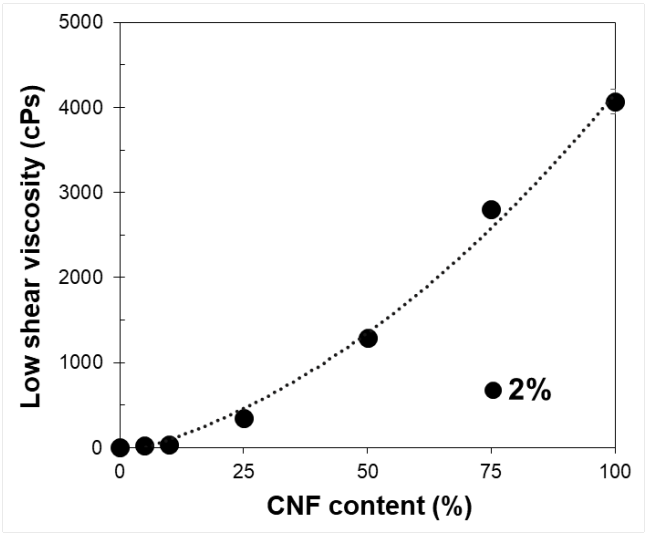

Fig. 9. Low shear viscosity of PVA-CNF suspension.

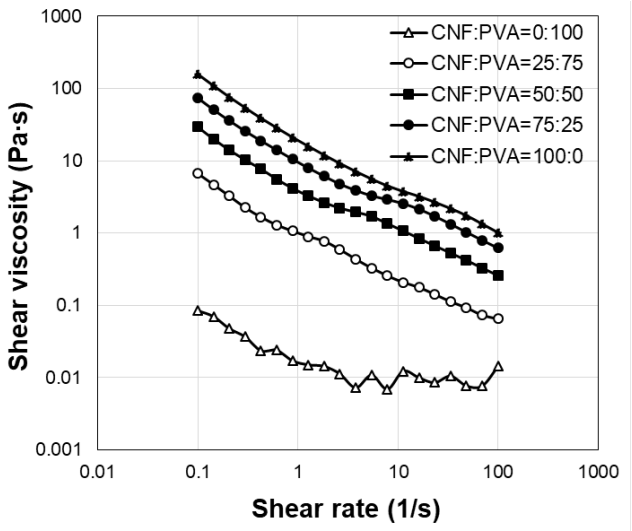

Fig. 10. Rotational viscosity of PVA-CNF suspension with shear rate.

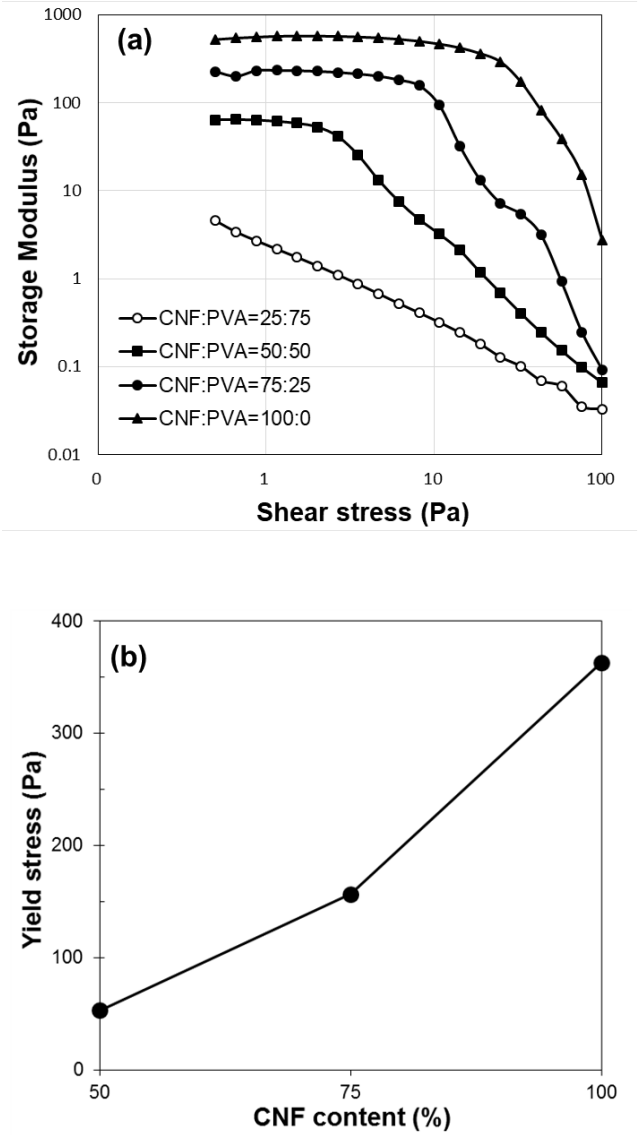

Fig. 11. Storage modulus of PVA-CNF suspension with shear stress (a) and yield stress depending on CNF content (b).

4.2 Application of CNF to PVA impregnation

4.2.1 Mechanical strength of impregnated papers

Tensile strengths of impregnated papers (MD) with different addition levels of CNF (0, 5, 10, 20 %) were shown in Fig. 12. Pickup weights of the impregnated papers by PVA solution (4%) were about 5 g/m^2, while those of papers impregnated by the suspension containing CNF ranged from 2.3 to 3.0 g/m^2. The pickup weight of the papers by PVA-CNF suspension was two times lower than neat PVA solution. This result may be explained by the fact that viscosity of PVA-CNF suspension was higher than PVA solution. On the contrary, tensile index of impregnated papers by the suspension containing 5% CNF content was similar to impregnated papers by only PVA solution at the same consistency of total impregnating agent. It indicates that CNF has a possibility to produce light weight papers with good mechanical strength. However, when using CNF as an additive into PVA impregnation, pickup weight should be increased for better durability.

Folding endurance of impregnated papers (CD) by different level of CNF in PVA solution same as above was shown in Fig. 13. Folding endurance of the impregnated papers by PVA solution was over 1700 double folds. Unlike PVA solution, that of impregnated papers by the suspension containing 5% CNF was around 1000 double folds, which was similar to the papers by PVA solution (3%). There was no big increase in folding endurance associated with using PVA-CNF suspension.

The effect of CNF was studied as a reinforcement of PVA complex in many works (Srithep et al. 2012, Liu et al. 2013). Contrary to previous results, CNF did not show any significant increase in mechanical strength of papers when applied to impregnation. This may be because of low pickup weights of papers, which should be improved by controlling porosity of base paper, viscosity of impregnated solution, or pressure application.

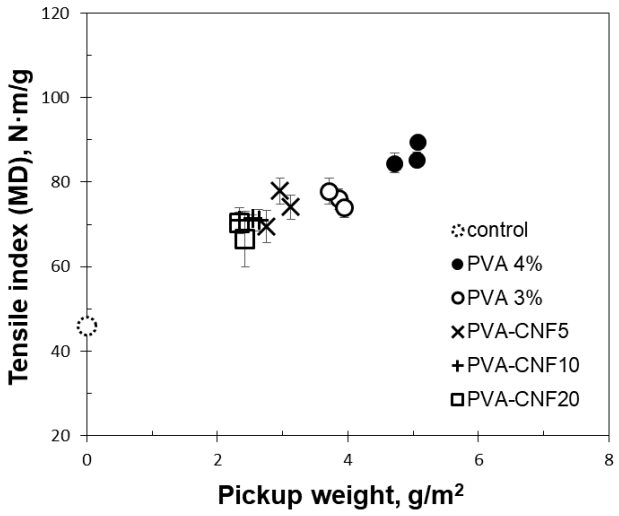

Fig. 12. Tensile index of impregnated papers (MD) depending on CNF content.

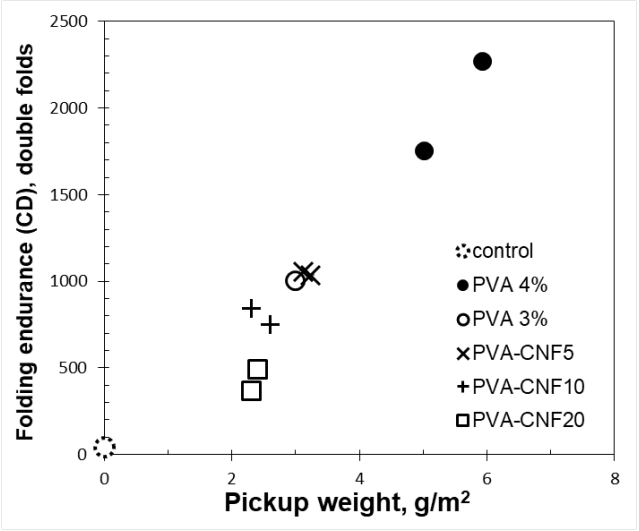

Fig. 13. Folding endurance of impregnated papers (CD) depending on CNF content.

4.2.2 Surface property of impregnated papers.

Fig. 14 shows FE-SEM images of the surfaces of the impregnated papers. In the Figure, (a) is the surface of base paper, (b) is of the impregnated paper of only PVA solution, and (c)-(g) is of PVA-CNF suspension containing different addition level of CNF. As pickup weight of impregnated papers were all different, each pickup weight is provided in Fig. 14. Despite of lower pickup weight, the surface images of the impregnated papers by PVA-CNF suspension looked similar to the case of PVA solution.

Water contact angle was measured to analyze the effect of addition level of CNF on the surface property of impregnated paper. The results at 1 and 30 seconds after the water drop contacts on the surface of the paper are shown in Fig. 15. The water contact angle of a base paper was 27.7° at 1 second. The water contact angle of impregnated papers by PVA solution was 80° at 1 second. From the data in Fig. 15, the water contact angle of the papers increased slightly as the addition level of CNF increased. In addition, it can clearly be seen that the changes of the water contact angle over measuring time was a few among all samples. This result could be attributed to the covered pores of the paper by the PVA-CNF suspension.

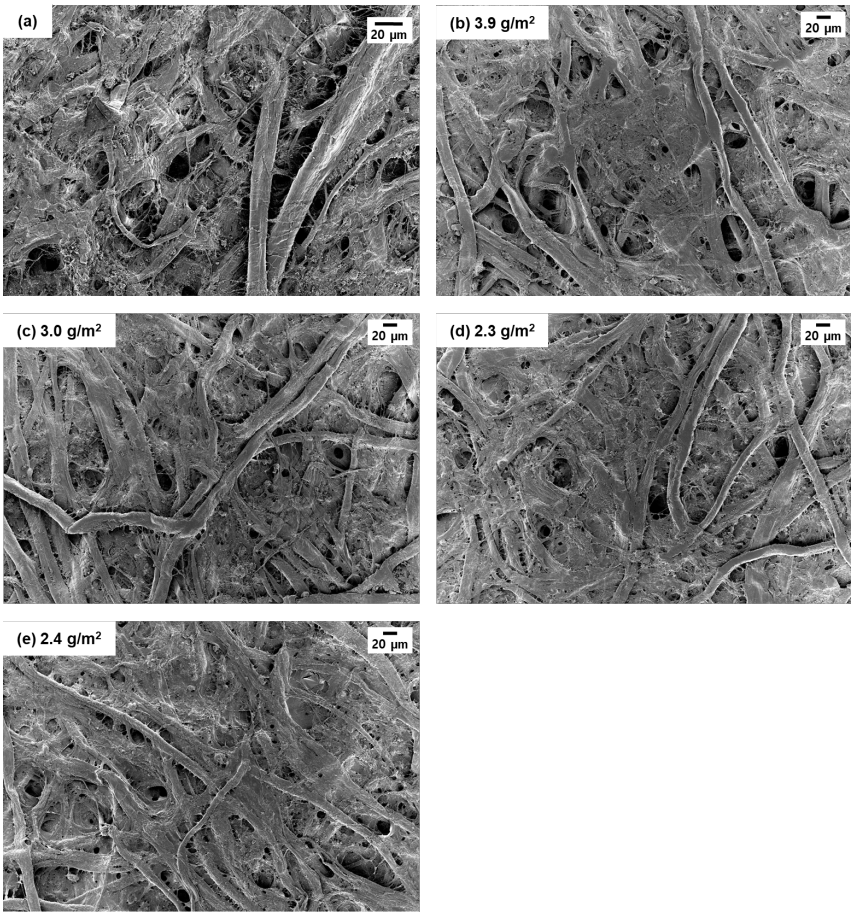

Fig. 14. FE-SEM images of base paper (a) and impregnated paper in PVA-CNF suspension without CNF (b) and with 5% CNF (c), 10% CNF (d), and 20% CNF (e).

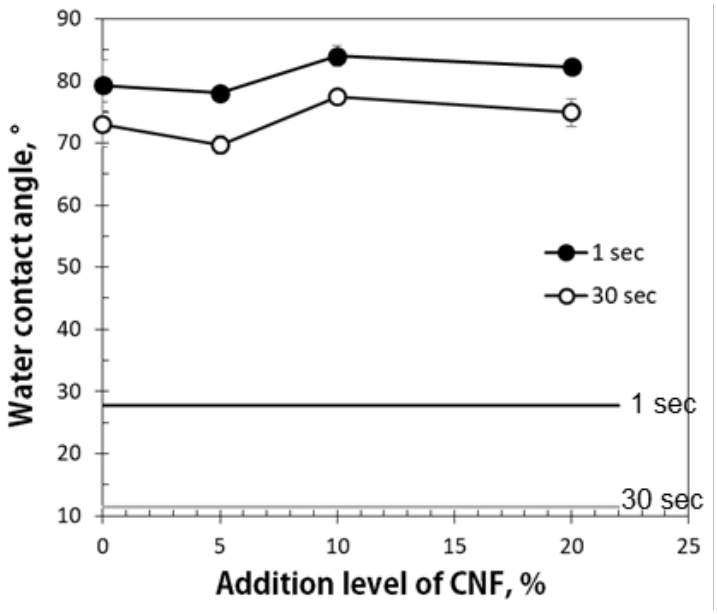

Fig. 15. Water contact angle of impregnated papers with the addition of CNF.

4.2.3 Soiling-resistance of impregnated papers

Fig. 16 represents the soiling-resistance of impregnated papers under wet condition. Fig. 16(a) presented bill papers used in one of South-east Asia countries, (b) was impregnated papers by the suspension containing 5% CNF content, (c) 10% CNF content and (d) 20% CNF. Test was carried out until samples were destroyed or became dark. The brightness of specimens which were impregnated by PVA-CNF suspension seemed similar to the standard sample after soiling. On the contrary, (b) and (c) were destroyed after 20 min from soiling. This result suggests that the application of untreated CNF to PVA impregnation had a limitation to the durability of papers in aspects of anti-soiling performance.

Fig. 17 shows the soiling-resistance of impregnated papers under dry condition. The condition of (a) was the impregnated paper by the suspension containing 5% CNF content, that of (b) was by the suspension containing 10% CNF content and (c) was containing 20% CNF content. The soiling-resistance can be presented by comparing grayscale and the grayscale of all samples was similar. There was no significant enhancement of soiling-resistance under dry condition applying CNF to the impregnation.

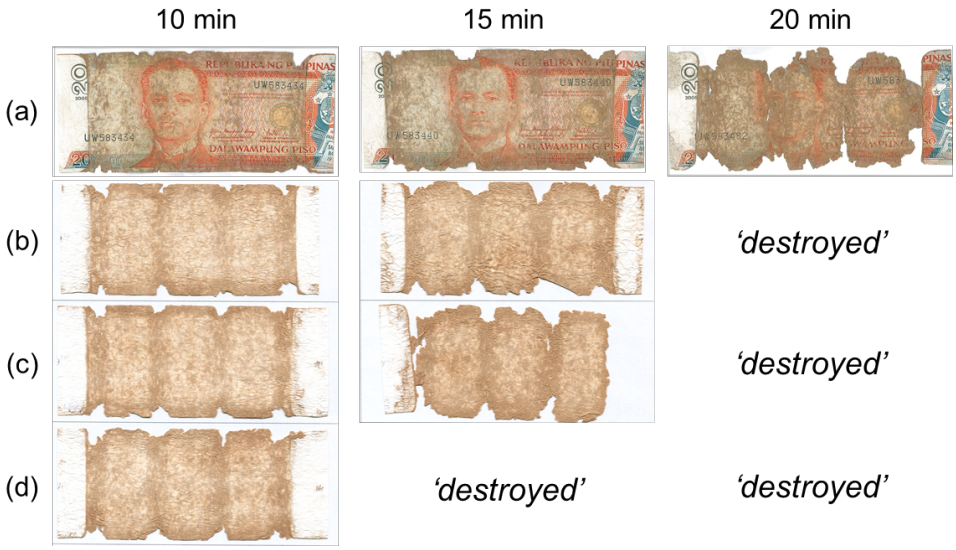

Fig. 16. Soiling-resistance of reference samples from South-east Asia (a) and impregnated papers under wet condition: 5% CNF (b), 10% CNF (c), 20% CNF content (d).

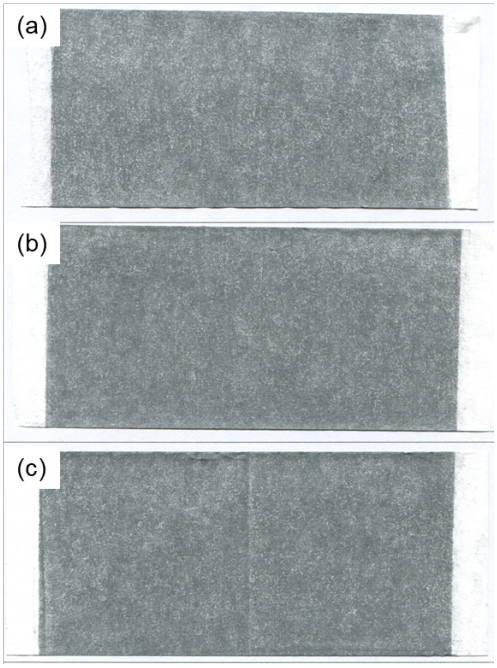

Fig. 17. Soil-resistance of impregnated papers under dry condition: 5% CNF (a), 10% CNF (b), and 20% CNF content (c).

4.2.4 Penetration of PVA-CNF suspension into paper

In order to figure out the reason of low pickup weight of impregnated papers by PVA-CNF suspension, penetration depth of PVA and CNF into a paper was analyzed. In Fig. 18, upper one is the cross section image of paper impregnated by PVA solution and bottom ones are the papers impregnated by PVA-CNF suspension containing 5% CNF using CLSM analyzation. Pickup weight of the impregnated paper by PVA solution was 5.9 g/m^2 but that by PVA-CNF suspension was 4.1 g/m^2. Green light exhibits acridine orange which indicates PVA and blue light presents calcofluor white which indicates CNF. As seen in Fig. 18, CNF also penetrated into a certain depth of a paper but mostly existed near the surface of a paper. The depth of the penetration of PVA was different from two samples. Distribution of PVA in the cross section of the paper by PVA-CNF suspension was not deep compared to only PVA solution due to the presence of CNF. This means the velocity of each PVA and CNF into a paper is different. If pore size of base paper and external pressure in an impregnating process could be adjusted, CNF could penetrate deeper into a paper.

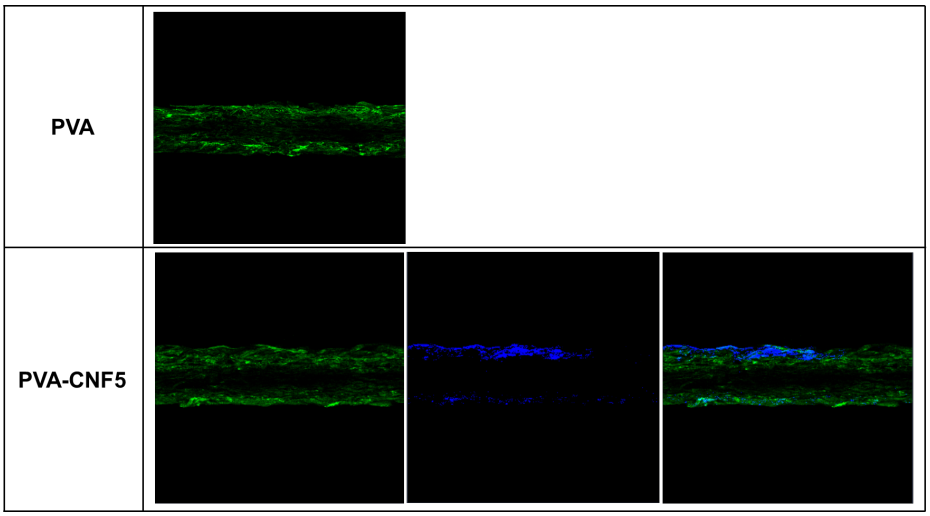

Fig. 18. CLSM results of the cross section of impregnated papers by PVA solution and PVA-CNF suspension.

4.3 Effect of PAE as an additive of PVA-CNF suspension

In order to increase anti-soiling properties of papers, in particular under wet condition, PAE was applied to PVA-CNF suspension as another additive. PAE was known as wet strength agent in papermaking industry (Obokata et al. 2007).

4.3.1 Low shear viscosity of the PVA-CNF suspension adding PAE

Fig. 19 compares low shear viscosity between PVA-CNF suspension and the suspension adding PAE. The addition of PAE increased the viscosity of the suspension. A possible explanation for this is that strong electrostatic interaction occurred between cationic PAE and anionic CNF (Zhang et al. 2012, Sharama et al. 2016).

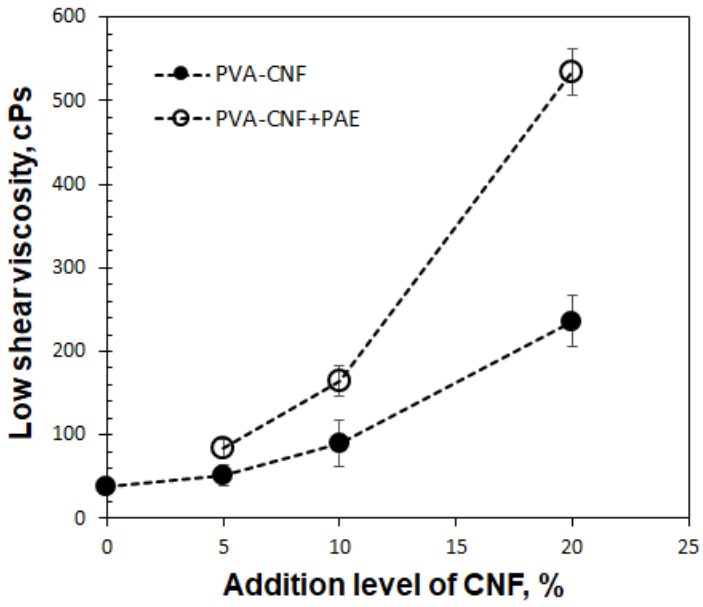

Fig. 19. Low shear viscosity of PVA-CNF suspension and the suspension containing PAE.

4.3.2 Impregnation of PVA-CNF suspension containing PAE

4.3.2.1 Mechanical strength of impregnated papers

Tensile strength and folding endurance of impregnated papers are shown in Figs. 20 and 21. Tensile index of the base paper was 46 N·m/g and folding endurance was 46 double folds. Pickup weight of impregnated papers by PVA+PAE solution was about 4.2 g/m^2, tensile index was 84 N·m/g and folding endurance was 1,660 double folds. Pickup weight of impregnated papers by PVA-CNF+PAE suspension containing 1% CNF was 3.5 g/m^2 and pickup weights for the rest of CNF content (5, 10, 20%) were all about 3 g/m^2. Tensile index of impregnated papers by PVA-CNF+PAE suspension ranged from 71 to 76 N·m/g. Folding endurance of impregnated papers by PVA-CNF+PAE suspension ranged from 480 to 790 double folds. Typically 1 and 5% CNF content showed higher folding endurance rather than other CNF content, of which folding endurance was over 700 double folds.

Tensile index and folding endurance as well as pickup weight of impregnated papers by the PVA-CNF+PAE suspension was lower than those by only PVA+PAE solution. The results of mechanical strength did not show any significant effect of PAE on the impregnation compared to PVA-CNF suspension. These results were contrary to the effect of PAE as known in previous study. Obokata et al. (2007) reported that the PAE formation of inter and intra-crosslinking with fiber crosslinks in paper improved the tensile strength of paper re-wetted in water. Still high viscosity of the suspension affected lower pickup weight, which might be resulted in poor mechanical strength. However, the result implies that

1-5% CNF content showed higher mechanical strength among CNF content.

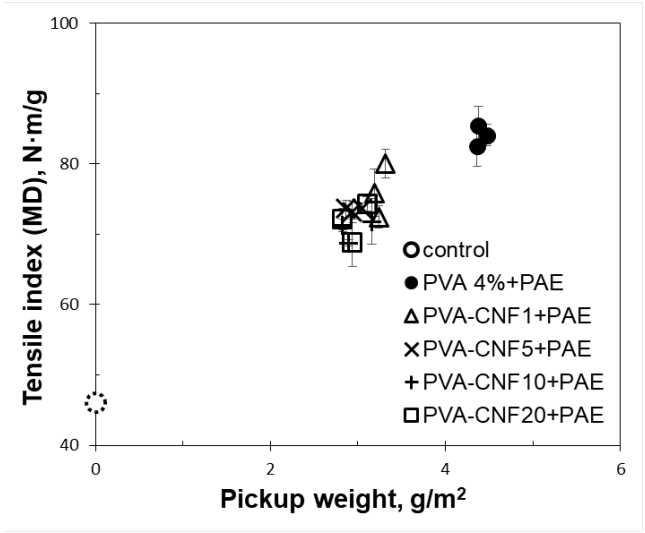

Fig. 20. Tensile index of impregnated papers (MD) by PVA-CNF suspension containing PAE.

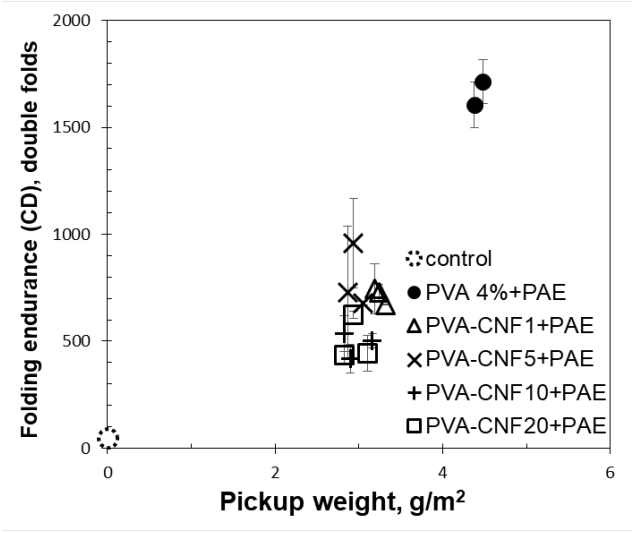

Fig. 21. Folding endurance of impregnated papers (CD) by PVA-CNF suspension containing PAE.

4.3.2.2 Surface property of impregnated papers

The FE-SEM images of the surface of the papers impregnated by PVA-CNF+PAE are shown in Fig. 22. Fig. 22(a) is for the base paper, (b) is for the paper treated by only PVA+PAE solution, (c) by the PVA-CNF+PAE suspension containing 5% CNF, and (d) by the suspension containing 10% CNF. Surface images of impregnated papers by all samples seemed similar and CNF could be found in the surface of the papers according to the magnified image of Fig. 22(d).

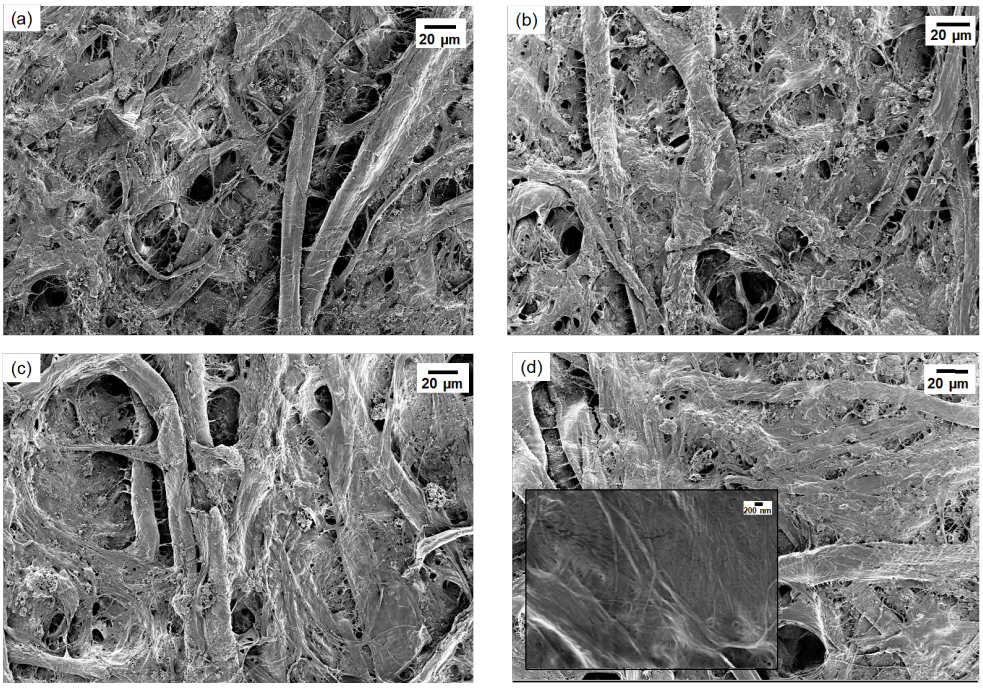

Fig. 22. FE-SEM images of the surface of a base paper (a), the paper impregnated by PVA+PAE (b), PVA-CNF5+PAE (c), and PVA-CNF10+PAE (d). The insert image of (d) is the magnified image of the surface.

4.3.2.3 Soiling-resistance of impregnated papers

The impact of PAE on anti-soiling properties under wet condition was investigated. Fig. 23 presents the tested specimens, one from using PVA-CNF suspension containing 5% CNF suspension and the other from the suspension adding PAE at the same CNF content. Comparing two results, (b) is seen to maintain its shape after 20 min soiling. The addition of PAE into the suspension improved anti-soiling properties of papers under wet condition. This results have an accordance with previous studies about the effect of PAE on increasing wet-strength of papers (Obokata et al. 2007, sharma et al. 2016).

Fig. 24 indicates the effect of CNF content on wet anti-soiling property when PAE was added into PVA-CNF suspension. All samples was not broken even after 20 min soiling, which revealed the effect of PAE in PVA-CNF. In addition, there were no big differences among different CNF content.

Fig. 25 shows the anti-soiling property under dry condition depending on different CNF content in PVA-CNF suspension adding PAE. The gray scale of all samples was similar. The addition of PAE shows that CNF content did not cause the difference of anti-soiling property under dry condition.

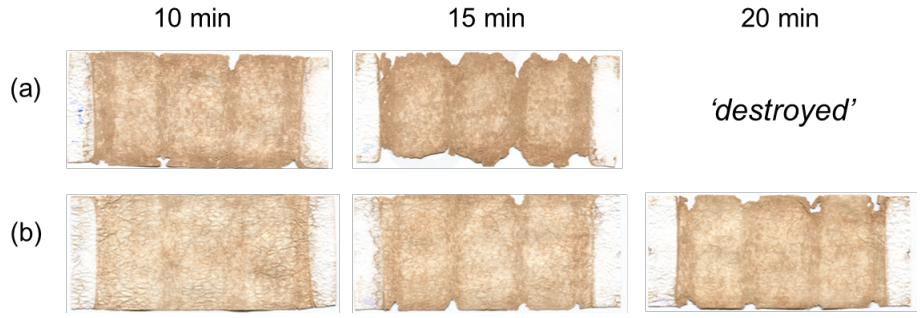

Fig. 23. Anti-soiling of impregnated papers under wet condition: PVA-CNF (5%) (a) and PVA-CNF+PAE (5%) (b).

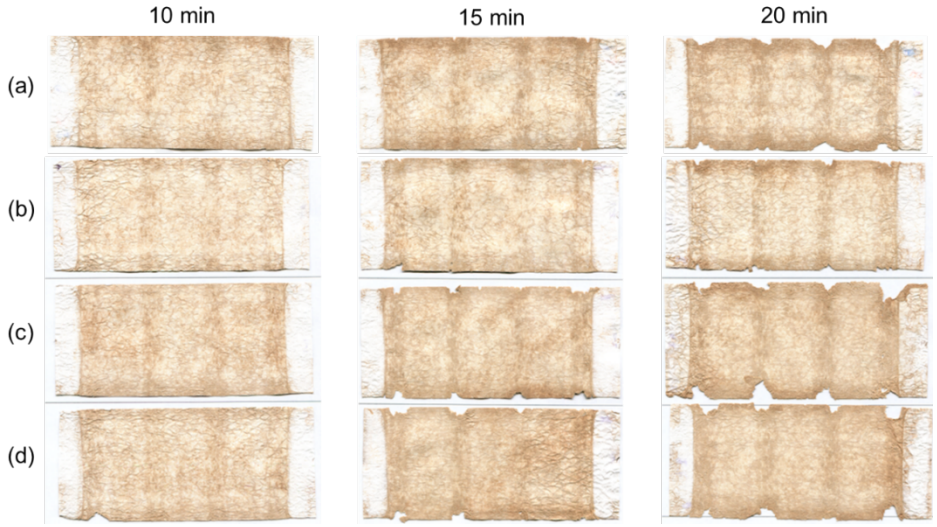

Fig. 24. Anti-soiling of impregnated papers under wet condition by PVA-CNF suspension containing PAE: PVA (a), 1% CNF (b), 10% CNF (c), and 20% CNF (d).

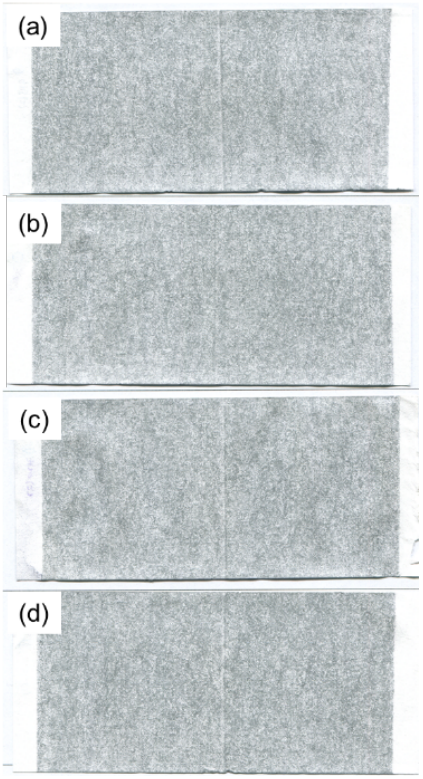

Fig. 25. Anti-soiling of impregnated papers under dry condition by PVA-CNF suspension including PAE: 1% CNF (a), 5% CNF (b), 10% CNF (c), and 20% CNF (d)

4.4 Effects of the hydrophobization of cellulose nanofibrils

4.4.1 Evaluation of silylation of CNF

4.4.1.1 Water contact angle of SCNF film

To assess the hydrophobicity of silylated CNF suspension, film was casted and the water contact angle of the film was analyzed. The water contact of angle of SCNF film depending on the ratio of CNF and MTMS is presented in Fig. 26. The water contact of angle of SCNF film increased until the mixing ratio of 'CNF:MTMS=1:1'. The water contact angle of SCNF film at 'CNF:MTMS=1:2' rather decreased, which might be related to uneven distribution of polysiloxane sol on CNF matrix. In other words, the excessive amount of MTMS reduced the reactivity between CNF and polysiloxane sol.

Fig. 27 shows the water contact of SCNF film (CNF:MTMS=1:1) depending on curing time, which was conduct at 105℃. The initial water contact angle of CNF film was 70°, but that of SCNF film after 4 hours of curing increased to 104°. 4 hours of curing was enough to increase the water contact angle of SCNF film. The observed increase in the hydrophobicity could be attributed to the presence of the bonding between CNF and polysiloxane by curing (Salon et al. 2007). As a result, CNF can be successfully hydrophobized by MTMS under an aqueous system.

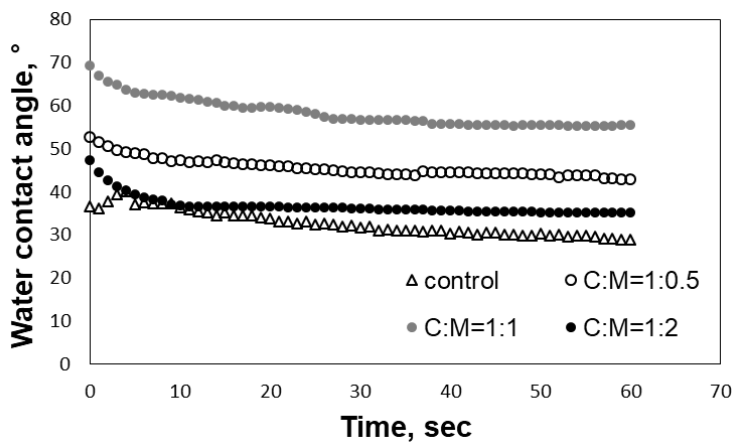

Fig. 26. Water contact angle of SCNF film depending on the ratio of CNF and MTMS (Park et al. 2018).

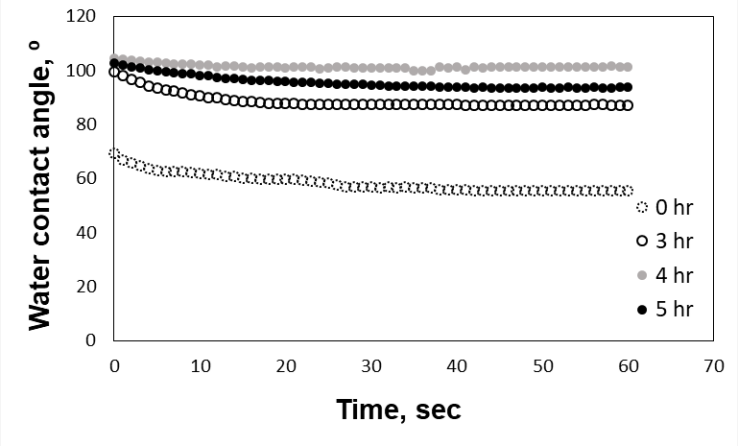

Fig. 27. Water contact angle of SCNF film (CNF:MTMS=1:1) depending on curing time (Park et al. 2018).

4.4.1.2 FTIR analysis of silylated CNF

In order to confirm the silylation of CNF using MTMS, FITR spectroscope analysis was conducted. FTIR spectra of the film in the 1500-600 cm^{-1} region, by unmodified CNF and silylated CNF (CNF:MTMS=1:0.5, 1:1), are shown in Fig. 28. The changes in the peak of 1270 cm^{-1} at C-H of methyl group, 1137 cm^{-1} at Si-O-Si, 925 cm^{-1} at Si-OH and 800-720 cm^{-1} at Si-C and Si-O-Si of polysiloxane sol were identified. The peak of Si-O-Cellulose also was classified in 1200-1150 cm^{-1}.

As the addition level of MTMS increased, the height of peak in 1270 cm^{-1} and 800-720 cm^{-1} of polysiloxane sol. This result was also observed by several studies (Zhang et al. 2014, Sai et al. 2015, Zanini et al. 2017). The effect of curing the film was also clarified in FTIR spectroscopy. As uncured and cured SCNF film at 'CNF:MTMS=1:1' were compared, the peak of Si-OH decreased and Si-O-Cellulose increased with the peak of polysiloxane sol unchanged. This poses polysiloxane sol exists by the silylation of CNF using MTMS and the chemical reaction of CNF and polysiloxane sol occurs especially through curing.

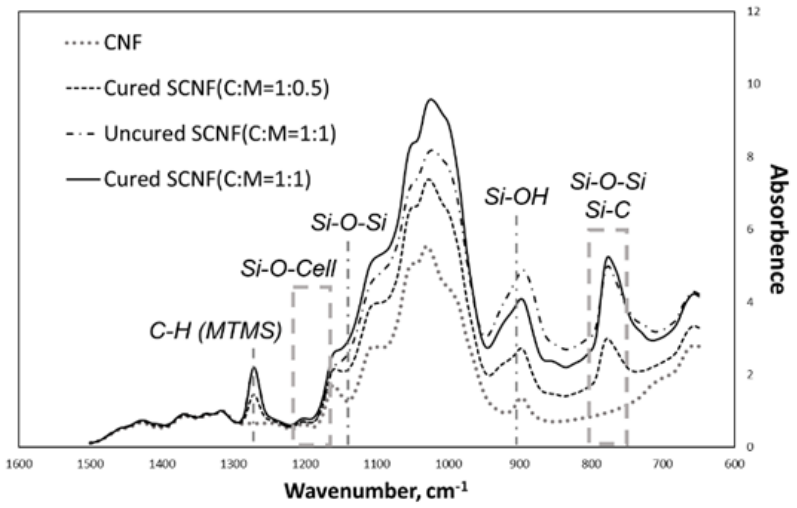

Fig. 28. FTIR spectra of film made of unmodified CNF and silylated CNF (CNF:MTMS=1:0.5, 1:1) (Park et al. 2018).

4.4.2. Characterization of PVA-SCNF suspension

Compatibility of PVA-SCNF suspension is an important consideration on applying to the impregnation. Fig. 29 presents backscattering profiles of the PVA-SCNF suspension (CNF:MTMS=1:0.5, 1:1) for an hour. The addition level of SCNF into PVA solution was same between samples to 7.5%. Dispersion stability of the suspension was good enough to be applied, which each sample did not show any variation of profiles during measuring time.

The low shear viscosity of PVA-SCNF suspension is shown in Fig. 30. While low shear viscosity of PVA-CNF suspension was 52 cPs, that of PVA-SCNF suspensions was 64 cPs. Low shear viscosity of PVA-SCNF suspension increased a little by the addition of SCNF, but it was not dependent on the amount of MTMS.

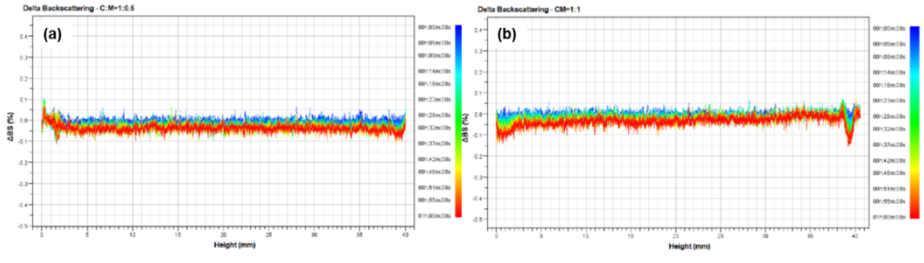

Fig. 29. Profile of ΔBS of PVA-SCNF suspension: CNF:MTMS=1:0.5 (a) and CNF:MTMS=1:1 (b).

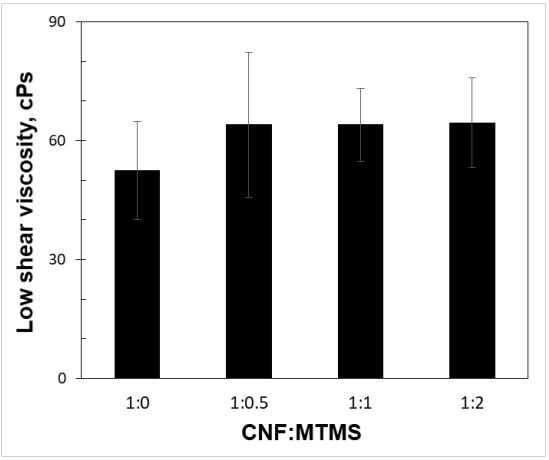

Fig. 30. Low shear viscosity of PVA-SCNF suspension.

4.4.3. Impregnation of PVA-SNCF suspension

Impregnation was performed as the same way as mentioned before. For the PVA-SCNF suspension, the addition level of SCNF suspension into PVA solution was fixed to 7.5%, which the CNF content was 5%. This addition level of SCNF is decided according to the result from the effect of CNF on PVA impregnation. 5% CNF content showed good mechanical strength of impregnated papers. SCNF suspension was prepared by controlling the mixing ratio of CNF and MTMS (CNF:MTMS=1:0.5, 1:1, 1:2).

4.4.3.1. Properties of impregnated papers by PVA-SCNF suspension

In order to analyze the effect of using SCNF on the hydrophobicity of the surface of papers, water contact angle was measured in advance. Fig. 31 shows the change of water contact angle for 60 sec depending on CNF type. SCNF was prepared at 1:1 weight ratio condition. The water contact angle of base paper was 30° and the base paper completely absorbed water before the measurement finished. The water contact angle of the impregnated paper by only PVA solution was around 80°. The water contact angle of the impregnated paper by the PVA-CNF suspension was around 70°, while that by the PVA-SCNF suspension was around 90°. Silylated CNF gave higher water contact angle, which enhanced to nearly the same result of PVA one. This result implies that the surface of papers was given hydrophobicity by PVA-SCNF suspension.

Fig. 32 suggests tensile index of the paper impregnated by silylated CNF. The pickup weight and tensile strength of impregnated papers by PVA-SCNF suspension was lower than PVA-CNF suspension. This result indicates that the silylation of CNF had an adverse influence on mechanical strength of papers.

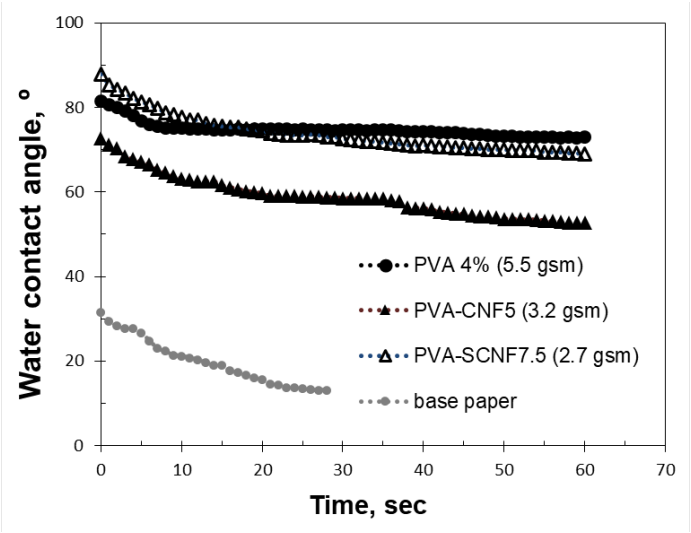

Fig. 31. Water contact angle of impregnated papers by PVA-SCNF suspension.

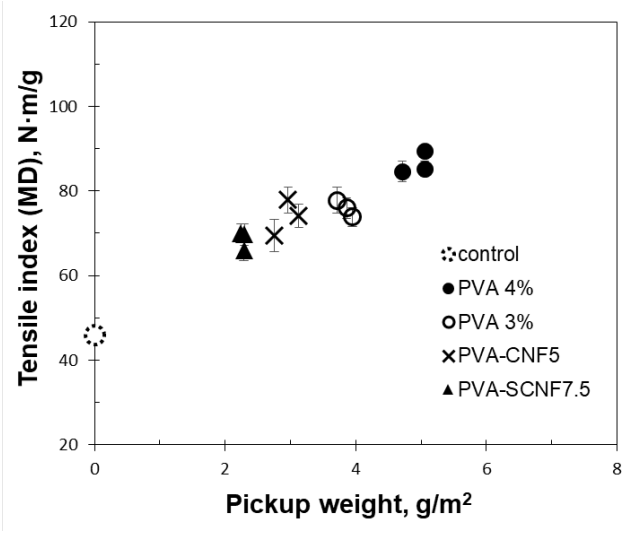

Fig. 32. Tensile index of papers (MD) impregnated by PVA-CNF and PVA-SCNF suspension.

4.4.3.2. Soiling-resistance of impregnated papers

The results of anti-soiling properties of impregnated papers under wet condition are shown in Fig. 33. They compares the differences between using unmodified CNF and silyalted CNF. The application of SCNF brought a positive result in the durability of impregnated papers. Even though the brightness of impregnated papers by PVA-SCNF suspension was similar to PVA-CNF suspension, a specimen from PVA-SCNF suspension (CNF:MTMS=1:0.5) was preserved after 20 min soiling like the result of PVA solution. It implied the SCNF can be adjusted as an additive of PVA impregnation to improve anti-soiling properties of papers.

The results of anti-soiling properties under dry condition are shown in Fig. 34. However, the difference between impregnated papers by PVA-CNF suspension and by PVA-SCNF suspension was not significant. The results may be because the hydrophobicity of CNF is not enough high. Consequently, if SCNF is applied to PVA impregnation, modification of CNF with higher hydrophobicity under an aqueous system has to be developed.

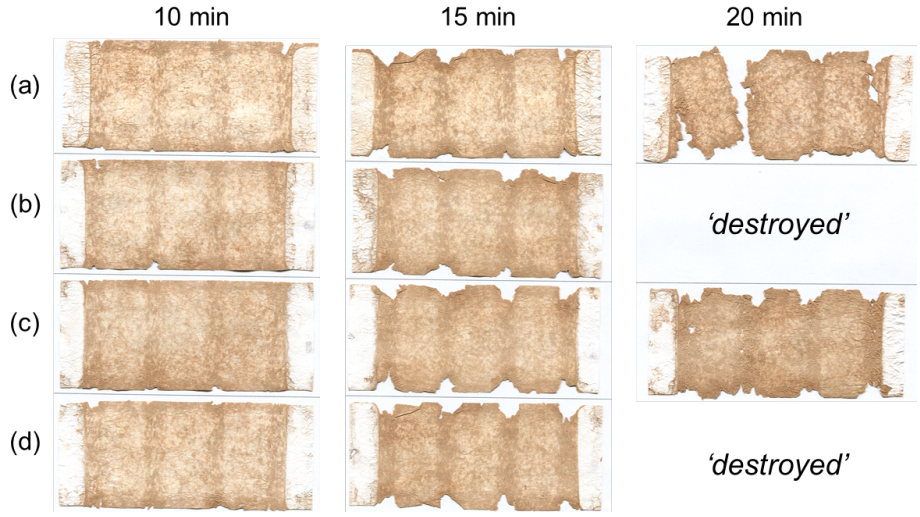

Fig. 33. Anti-soiling of impregnated papers under wet condition: PVA solution (a), PVA-CNF suspension (b), PVA-SCNF suspension (CNF:MTMS=1:0.5) (c), and PVA-SCNF suspension (CNF:MTMS=1:1) (d).

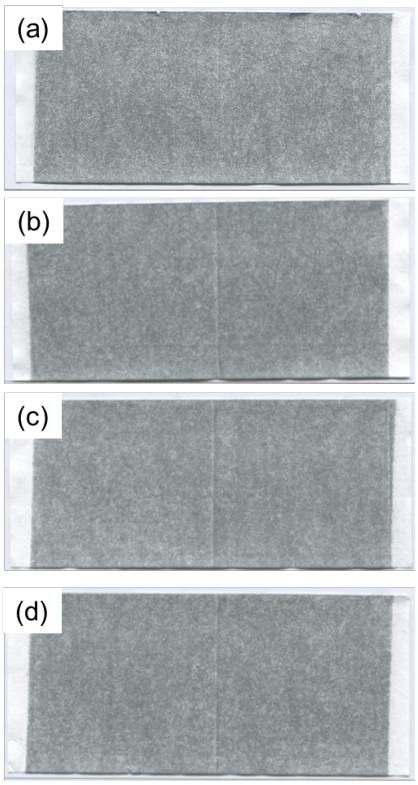

Fig. 34. Anti-soiling of impregnated papers under dry condition: PVA solution (a), PVA-CNF suspension (b), PVA-SCNF suspension (CNF:MTMS=1:0.5) (c), and PVA-SCNF suspension (CNF:MTMS=1:1) (d).

5. Conclusions

CNF was introduced as an additive of PVA impregnation for the durability of papers in this study and the developed way of the application of CNF to PVA impregnation was suggested. First, the effect of CNF on the durability of papers was investigated in terms of mechanical strength and anti-soiling property and the addition level of CNF based on oven-dried weight of PVA was optimized. The dispersion stability of PVA-CNF suspension was enough good to apply to the impregnation. However, the PVA-CNF suspension showed high viscosity compared to PVA solution, which lowered pickup weight of impregnated papers. In the hope that, when PVA-CNF suspension containing 5% CNF content was applied, tensile strength and folding endurance of impregnated papers were similar to the same consistency of PVA solution. This result implied CNF would have a possibility to produce light-weight papers with good mechanical strengths. In order to figure out the penetration of PVA and CNF into a paper, CLSM was analyzed using the cross section image of impregnated papers. CNF also penetrated into a certain depth of a paper and existed near the surface of a paper.

In the second part of this study, PAE was added in PVA-CNF suspension in order to improve the anti-soiling property of papers. Since CNF and PAE had a strong electrostatic interaction, the viscosity of PVA-CNF suspension including PAE was still high, which lowers pickup weights of papers. The addition of PAE pointed out that the anti-

soiling property of impregnated papers was significantly enhanced and improved property was shown on all CNF content. Lastly, hydrophobization of CNF was also suggested as an additive of PVA impregnation for the durability of papers. The silylation under an aqueous system was performed because of the environmental issue and the compatibility of PVA. Silyalted CNF suspension (SCNF) was obtained by the silylation with methyltrimethoxysilane (MTMS). Mixing ratio of CNF and MTMS was controlled and the miscibility of PVA-SCNF suspension under all mixing ratio showed stable dispersion stability. The water contact angle of the surface of impregnated papers by PVA-SCNF suspension was higher than PVA-CNF suspension. However, the results of anti-soiling property under dry condition did not show any big enhancement.

As a result, the impact of CNF as an additive of PVA impregnation was investigated on mechanical strength and anti-soiling property of papers. CNF can be highly possible to be applied to PVA impregnation for the durability of papers. The results of the penetration of PVA-CNF suspension indicate the pickup weight can be increased by controlling the viscosity of the suspension, pore size of a base paper and adding an external pressure in an impregnating process. In addition, the way of increasing hydrophobicity of the surface of papers was suggested by the silylation under an aqueous system. In order to improve the anti-soiling property under dry condition, the use of silane agent with longer alkyl than MTMS can be adjusted.

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초 록

내구성은 지폐, 포스터, 옥외 포스터 등에 요구되는 종이의 특성으로 주로 폴리비닐알코올(PVA) 용액을 함침하여 제조되어 왔다. 그러나 종이의 내구성을 더욱 향상시키기 위해서는 PVA 용액의 단독 사용으로는 한계가 있으며 새로운 첨가제가 필요하다. 본 연구에서는 새로운 첨가제로서 셀룰로오스 나노피브릴(CNF)를 선정하여 PVA 전건무게에 따른 CNF 투입비를 달리하여 혼합액을 제조하고 분산 안정성과 유변성 특징으로 혼합액의 특성을 평가하였다. 또한 이 혼합액을 함침한 종이의 기계적 강도 및 내오염성을 평가함으로써 CNF 가 종이의 내구성에 미치는 영향을 파악하고 함침 공정 첨가제로서의 가능성을 제시하고자 하였다.

CNF 의 투입량에 관계 없이 PVA-CNF 혼합액은 분산 안정성을 보였으나 CNF 의 투입량이 증가할수록 혼합액의 점도는 증가하였다. 이로 인해 혼합액이 함침된 종이의 픽업량은 PVA 용액만 함침된 종이보다 감소하였다. 그러나 같은 농도에서의 PVA 용액만 함침된 종이와 5% CNF 가 투입된 PVA-CNF 혼합액이 함침된 종이의 인장강도나 내절도가 비슷하게 나타났기 때문에 CNF 우수한 강도를 지니며 저평량 용지를 제조하는 데 이용할 수 있는 첨가제로서의 가능을 보였다. CNF 를 첨가제로 사용 시 함침지의 내오염성을 향상시키기 위하여 PVA-CNF 혼합액에 polyamideamine-epichlorohydrin(PAE)를 투입하였다. 5% CNF 가 투입된 PVA-CNF 함침지는 습식 조건에서 20 분 오염 후 파괴되는 양상을 보였으나, PAE 를 투입한 PVA-CNF 함침지는 20 분 오염

실시 후에도 시편이 보존되었다. 또한 높은 CNF 의 투입비에서도 PAE 를 투입한 결과 오염 후 시편의 밝기가 향상되었다. 반면 PAE 투입은 건식 조건에서 내오염성이 크게 향상되지 않았으며 이를 해결하기 위해 실란화를 통해 소수성이 부여된 CNF 를 PAE 용액의 첨가제로 사용하였다. 실란화는 PVA 의 상용성과 친환경적인 공정을 고려하여 수계에서 사용 가능한 methyltrimethoxysilane(MTMS)를 선정하여 진행하였다. 소수화된 CNF 를 함침 첨가제로 사용 시 함침지의 표면 접촉각은 CNF 사용 시보다 더 증가함에 따라 종이의 표면의 소수성을 부여시킬 수 있었다. 그러나 종이의 건식 내오염성은 크게 향상되지 않았으며, 이는 수계에서 일어나는 실란화 반응은 함침으로 종이의 소수성을 발현시키는데 한계를 지니고 있다고 판단되었다.

주요어 : 셀룰로오스 나노피브릴, 폴리비닐알코올, 실란화, 함침, 내구성, 내오염성, 기계적 강도

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연구실에 입학할 때 세 명의 후배를 이끄느라 고생한 제곤오빠, 오빠는 가끔 말하면서 꼰대가 아닐까라고 하지만 전혀 꼰대가 아니었고 저에게 멋진 선배님입니다. 도움이 필요한 순간마다

연구실에 나타나서 도움을 주신 규정오빠, 오빠 힘이 아니었으면 제가 새로운 주제를 맡아서 연구할 때 고생 많이 했을 것 같습니다. 같이 연구실 생활은 하지 않았지만 매번 학회에서 정말 제가 듣고 싶은 말을 해주신 재호오빠에게도 감사드립니다. 저랑 같이 입학하여 이년을 보낸 희태오빠와 석호오빠, 고생 많이 했고 고마워요. 오빠들이 먼저 제 곁을 떠나는데 울고 싶은데 눈물이 안 나오는 이유는 모르지만 진짜로 오빠들 아니었으면 혼자 외로워서 늙어갔을 거에요. 그리고 신영이 저 멀리서 이곳으로 들어와 연구실에 적응하느라 힘들었을 텐데 많이 도와줘서 정말 고마워. 도와준 게 너무 많아 여기에 다 열거할 수 없지만 앞으로도 그 은혜 잊지 않을게. 내 첫 후배인 심엽이, 들어오자마자 나 많이 도와주고 신경 써줘서 고마워. 내가 첫 후배라서 서툰게 많았지만 많이 가르쳐주고 싶고 잘 대해주고 싶어서 그랬는데 이제 혼자서도 잘해서 졸업 잘 할 것이라고 믿어.

환경재료과학 전공인 다른 연구실의 대학원생 분들께도 감사드립니다. 저희 연구실만큼이나 많은 도움이 된 제지과학실, 가끔 제가 횡설수설해도 얘기 잘 들어주시면서 지도해주신 규덕오빠, 장난기 가득한 모습으로 지치지 않게 웃음을 주신 완희오빠, 젠틀한 모습으로 대해준 Araz 오빠, 내가 놀려도 다 받아주는 지홍이, 편하게 수다를 떨 수 있는 마음의 의지가 된 수진이, 항상 먼저 다가와 얘기를 걸어주는 Zhenghui 오빠, 다 잊지 못할 거에요. 같이 학위논문을 준비하면서 제게 큰 힘이 되었던 세영언니와 세심한 마음으로 챙겨주신 용건오빠에게도 감사드립니다. 또한 제 학위논문 연구를 같이 진행하면서 도와주신 조폐공사 분들께도 감사드립니다.

내가 제일 사랑하는 우리 아빠, 엄마 그리고 하규, 이번에도 뒤에서 묵묵히 힘이 되어줘서 감사합니다. 내가 학위 논문을 준비한다고 집에서 칭얼칭얼거려도 다 받아주고 좋은 말로 다독여줘서 너무 고맙고 앞으로 더 자랑스러운 딸이자 누나가 되어 더 큰 사랑으로 보답할게요. 공부하느라 힘들까봐 걱정해주시는 우리 할머니와 가족분들께도 감사드립니다. 특히 삼촌, 대학원에 필요한 조언 주셔서 감사드립니다.

언제나 내가 필요할 때 한 걸음에 달려와주는 사랑하는 우리 준호와 연주에게도 너무 고마워. 같은 대학원생의 길을 밟아 서로에게 의지가 되고 내가 필요한 것이 무엇인지 가장 잘 아는 너희 둘은 이제 친구 이상으로 나에게 소중한 존재야. 우리 신그모 친구들, 다름, 수린, 지은, 양신, 지현, 예진이 매번 모일 때마다 나의 몰골을 걱정해주고 10 년이나 같이한 만큼 나를 진심으로 걱정해주는 너희 덕분에 잘 마칠 수 있었던 것 같아. 항상 사랑한다, 영원하자 신그모. 우리 민수언니 나를 생각해주는 마음 너무 고맙고 나도 언니에게 큰 힘이 될게. 나를 놀리느라고 바쁜 윤하와 준형이에게 고마워해야 할지 모르겠지만 고맙고, 내 또 다른 동생인 우리 지원이 나의 활력소, 너무 고마워. 제가 가는 길에 멋지다고 항상 응원해주는 우리 소연언니에게도 고마운 말을 전합니다.

수상 소감인 것처럼 많은 사람들의 이름을 적으면서 감사의 인사를 드린 것 같은데 제가 미처 언급하지 못한 분들이 있더라도 이해해주시고 제 석사학위논문을 완성할 수 있게 도움을 주셔서 감사드립니다.