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Fundamental Properties of Nanofibrillated Cellulose in Suspension and Mat States

Advisor Professor: Dr. Hye Jung Youn

By Jaeho Ryu
Abstract

Fundamental Properties of Nanofibrillated Cellulose in Suspension and Mat States

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Nanofibrillated cellulose has great potential as a new material in cosmetics, automobiles, pharmaceutical and medical science, electrical devices, papermaking industry, and other applications. Nanofibrillated cellulose has a high aspect ratio and hydrophilic characteristics that lead to unique rheological properties and network forming ability from even low consistency. Nanofibrillated cellulose suspension may have several processes such as transferring, dewatering and drying to use as the shape of sheet or foam. Therefore, the network properties and mechanical properties of nanofibrillated cellulose need investigation and better understanding. To achieve these objectives, the effect of nanofibrillation process, solidification of nanofibrillated cellulose, and the addition of polyelectrolyte on network properties are investigated.

Nanofibrillated cellulose is prepared by mechanical treatment using a grinder. The morphological change of the pulp fiber with mechanical treatment, water retention value, sedimentation concentration, and viscosity are evaluated through a number of passes. In this study, nanofibrillated cellulose can be prepared through 15 - 20 passes. However, it is important that the number of passes could be improved by changing the method of pretreatment or operation condition in the grinding process.

Network properties are evaluated as the state of suspension and mat through dynamic and tensile measurements. The network strength of
nanofibrillated cellulose increased rapidly as a function of solids content, and showed a power law relationship. This result is similar to pulp fiber suspension. Thus, the network forming phenomenon is similar, even though the aspect ratio of nanofibrillated cellulose is much higher and the dimension is much smaller than pulp fiber. However, network formation of nanofibrillated cellulose occurred at a lower consistency of 0.2%, and the network strength is 5 - 20 times higher than pulp fiber with solids content.

Previous studies on network properties of nanofibrillated cellulose are limited to a low consistency. However, nanofibrillated cellulose of high solids content can be prepared using pressurized dewatering equipment, which is developed in this study. The yield stress had a power law relationship with the solids content over a wide range from 0.5% to 99% independent of the measurement method. Elastic modulus, tensile breaking stress and strain at break are evaluated. The elastic modulus and tensile breaking stress increased exponentially as a function of solids content. The wet strain at break of pulp fiber decreased gradually. However, the nanofibrillated cellulose increased until 50% of the solids content. When the degree of nanofibrillation is high, the strain at break increased more rapidly. Over 50% of the solids content, and strain at break decreased greatly. Therefore, the increase in the ability of maintaining the network structure even at higher deformation of nanofibrillated cellulose mat may be the reason. However, the solids content affected the ability of standing from deformation. Above 50% of the solids content, the rigidity increased significantly, which may be due the increase of hydrogen bonded areas.

The network properties of nanofibrillated cellulose can be changed by the addition of polyelectrolytes. Different types of polyelectrolytes are applied in this study. In particular, polyethyleneimine with a branched structure showed an increase in yield stress with increasing addition amount. However, the yield stress of nanofibrillated cellulose suspension with a linear structure
polyelectrolyte such as poly-diallyldimethyl ammonium chloride and cationic polyacrylamide decreased above a certain addition amount. The structure type and molecular weight of polyelectrolyte influenced the viscosity and the reformation of the network structure of nanofibrillated cellulose. Furthermore, polyelectrolytes affected the dewatering ability even though nanofibrillated cellulose is highly associated with each other. The results indicate that polyelectrolyte can change the network structure of nanofibrillated cellulose. The tensile properties of nanofibrillated cellulose are evaluated through a wet and dry state. In particular, the tensile breaking stress increased more than three times in the case of wet mat as to the type of polyelectrolyte and the addition amount. In the case of branched polyelectrolyte, the rapid change of tensile breaking stress is observed at the isoelectric point. From this result, it was found that the modification of surface charge of nanofibrillated cellulose is an important factor that determines the network or mechanical properties of the nanofibrillated cellulose mat. In the case of dry mat, the effect of the polyelectrolyte is not shown. For this reason, the effect of the hydrogen bond may be much higher than the polyelectrolyte.

This study provides a foundation for utilizing nanofibrillated cellulose. The network properties of nanofibrillated cellulose with solids content are traced and the possibility of controlling network properties by adding polyelectrolyte is investigated. It was expected that utilization of nanofibrillated cellulose for various fields of applications can increased.

Keywords : nanofibrillated cellulose, network strength, rheological properties, solids content, tensile breaking stress, strain at break, polyelectrolytes

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Chapter 1.

Introduction
1. Introduction

The meaning of nanotechnology was first introduced by Dexler (1992) during the manufacturing of a material at the atomic or molecular level. Presently, nanotechnology is generally accepted for the handling of nano-scale material, dealing with a device, equipment, and analysis method or the dimension of material ranging within 1 nm - 100 nm. Since the 1990’s, spreading of the “Nano” concept has had a strong impact on the world of science in general and “Forest products” in particular. Nanocellulose is an example of the forest products.

Turbak et al. (1983) and Herrick et al. (1983) introduced microfibrillated cellulose (MFC), using a high-pressure homogenizer from wood pulp. After MFC was introduced, a few studies have been reported, which covers two decades. Fig. 1-1 shows these studies. However, research on nanocellulose has rapidly increased since the mid 2000’s. The potential of nanocellulose is widely recognized with the development of analysis techniques and the increase in interest by many interested player people including this country (Lee et al. 2009; Chun et al. 2012).

Nanocellulose is classified into several groups that depend on the manufacturing method. These groups include nanofibrillated cellulose (NFC), cellulose nanocrystals (CNCs), and bacterial cellulose. Characteristics such as size, aspect ratio, and crystallinity are considered important factors for selecting an appropriate application field. The size of CNC is 5 nm - 20 nm in width and 100 nm - 300 nm in length depending on the source of cellulose.
NFC is 5 nm - 50 nm in width and several micrometers in length. The suspension looks like a cream. Because the viscosity of NFC suspension is high, it is usually produced at a low consistency of less than 3%. On the other hand, bacterial cellulose is produced as a “pellicle”, which is a matrix of fibrils and is 2 nm - 4 nm in width. Fig. 1-2 shows the images of nanocellulose observed using a Transmission Electron Microscope (TEM) or a Field Emission-Scanning Electron Microscope (FE-SEM).

Cellulose nanocrystals have high crystallinity, elastic modulus, and unique optical properties. Recently, CelluForce attempted to produce cellulose nanocrystals at a commercial scale. CelluForce is a joint venture of Domtar and FPInnovation. Eichhorn et al. (2010) reported the application of NFC as a filler material in composites and coatings, and in the use of security elements. Nanofibrillated cellulose is produced by a relatively simple process and has an advantage in productivity. Bacterial cellulose is a good material for research on characterization. However, bacterial cellulose has a limitation in massive production.

NFC has unique characteristics. Because the size of NFC is much smaller than pulp fiber, the specific surface area is very high. NFC also has hydrophilicity, which is attributed to many hydroxyl groups on the surface, high crystallinity, mechanical strength, thermal stability, and other characteristics. Moreover, NFC is a sustainable and biodegradable material because of natural origin. Therefore, NFC is recognized as valuable, potential and a promising material in food, cosmetics, paints, lubricants and within the
medical and pharmaceutical industries (Turbak et al. 1983, Lee et al. 2009). When NFC was dispersed well in plastic matrix, the elastic modulus increased with a small addition. Studies on surface modifying and increasing compatibility with solvent have also been performed (Andresen et al. 2006; Ifuku et al. 2007).

Transparent film with high mechanical properties and thermal stability can be produced by using NFC. The existing display film is used with cellulose acetate. However, NFC film has higher mechanical properties and similar transparency (Iwamoto et al. 2005).

Aulin et al. (2010) reported that the crystallinity of NFC is 63%, and the densification of film occurs highly by hydrogen bonding and packing. These results led to the high barrier properties of gas and liquid. The existing barrier coating agent is polyethylene or latex. However, latex is hard to bio-degrade because it is manufactured from fossil fuels. Cellulose is not a conductive or heat transfer material by itself. However, polyethylene oxide or lithium imide salt addition can endow ionic character of NFC. These two compounds can concurrently improve the mechanical properties and conductivity of NFC (Azizi Samir et al. 2004; Azizi Samir et al. 2005). A higher value-added product such as display film, barrier film, filter or membrane, and other various films or membranes has been proposed for NFC. Particularly, the use of NFC hydrogel on tissue engineering can promote the regeneration of a wound (Michailova et al. 2005) by controlling of the emission rate in drug-delivery systems.
In spite of the great potentials of NFC, there are still some limitations of utilization. Dealing with very small size materials and heterogeneity characteristics still remains a challenge (Miller et al. 1983). Mechanical treatment necessarily demands high energy costs. To reduce the costs, enzymatic or chemical pretreatment has been reported (Pääkkö et al. 2007; Saito et al. 2006). Above all, understanding nanofibrillation procedure is important for proper utilization because the dimension determines mainly the characteristic of the fiber. Therefore, the properties of the fiber during nanofibrillation by mechanical treatment need to be traced.

NFC is prepared in a suspension state with low consistency. A lot of water is contained in the suspension, and should be removed by a proper method. However, NFC has a tremendously large surface area and hydrophilic characteristics, which makes it difficult to remove water. For utilization as a filter or membrane, NFC suspension should be converted to a sheet or foam. Therefore, it is important to understand the consolidation and drying behavior of NFC.
Fig. 1-1. Research on nanocellulose. Data analysis from the web of science in 2013.

Fig. 1-2. Morphology of nanocellulose, (a) cellulose nanocrystal (Ryu and Youn 2011), (b) nanofibrillated cellulose (Ryu et al. 2012), (c) bacterial cellulose (Nakagaito et al. 2005).
2. Objectives

The intrinsic characteristics of NFC enable NFC to be easily shaped into a sheet or film. However, the removal of water from NFC suspension is still challenging and should be resolved. Because the difficulty to remove water is attributed to the nature of NFC, change of NFC characteristics may be one option. However, the behavior of NFC network with an increase in the solids content should be first understood.

The primary intent of this study is to investigate the fundamental properties of NFC in suspension and mat states.

- Preparation of NFC and investigation of the nanofibrillation of pulp fiber from the aspects of morphology, water retention value and rheological properties

- Investigation of the effect of morphological changes by nanofibrillation on the mechanical properties of fiber suspension. Investigation of network properties of NFC mat

- Investigation of the effect of polyelectrolyte addition on network properties of NFC.
3. Literature review

3.1 Preparation of nanocellulose

Rånby (1951) produced colloidal particles of 70 Å in width and 460 Å in length by hydrolysis of wood pulp with sulfuric acid. Because the concept of “nano” was not generally used at that time, the colloidal particle produced was called “cellulose micelle”. The reactivity with sulfuric acid is different depending on the crystallinity of the cellulose fiber. The amorphous region had a higher reactivity by two orders of magnitude compared to the crystalline region (Seaman 1945). Therefore, the crystalline region was preserved and the amorphous region was decomposed by sulfuric acid under controlled hydrolysis conditions. The yield and size distribution of products can be controlled by hydrolysis conditions such as the concentration of acid, reaction time and temperature. (Ryu and Youn 2011). Presently, this type of rod-like particles is expressed in various terms such as “cellulose nanocrystals” (CNCs) or “nanocellulose crystals” (NCC). The expression of cellulose whisker is also used in northern Europe (de Rodriguez et al. 2006; Oksman et al. 2006).

Nanocellulose can be prepared through mechanical treatment. Mechanical treatment was first introduced by Turbak et al. (1983) and Herrick et al. (1983). When cellulose fibers pass through a narrow gap under a high pressure of 1000 bar, cellulose fibers are deconstructed into nanofibril. Cellulose nanofiber produced by this process is called “cellulose nanofibril” or “nanofibrillated cellulose”. The equipment for producing nanofibrillated cellulose was a high pressure homogenizer and microfluidizer (Zimmermann
et al. 2004; López-Rubio et al. 2007). A grinder was also used as the equipment for mechanical treatment (Taniguchi and Okamura 1998). Nano-scaled cellulose fiber that is prepared by mechanical treatment is called as many terms such as microfibrillated cellulose (Barton 1984), nanofibrillar cellulose (Syverud and Stenius 2009), cellulose nanofibril (Ahola et al. 2008), cellulose nanofiber (Abe and Yano 2012), and other various terms. The different terms for nano-scaled cellulose fiber were due to the different perceptions about the material (Chinga-Carrasco 2011). Wood pulp fibers have been used as the raw material for the production of fibrillated materials (Turbak et al. 1983; Herrick et al. 1983). They treated wood fiber mechanically using a high pressure homogenizer and announced it as microfibrillated cellulose (MFC).

As expected, there are many applications such as food, cosmetics, paints, drilling mud, and carrier for medicine for NFC fiber. Other various other applications for NFC such as biocomposites, packaging, coating, and absorbent have also been recently proposed. Many studies (Henriksson et al. 2007; Vartiainen et al. 2011) were reported that NFC is promising and environmental friendly material. Understanding and characterization of NFC have been performed. Nonetheless, there are still unsolved problems in producing large quantity of NFC. Energy consumption and production rates may be major limitations for expanding the application and commercialization of NFC. Pretreatment prior to mechanical treatment could reduce the energy consumption. Diverse combinations of pretreatment and mechanical treatment have also been investigated (Siró and Plackett 2010). For example, refining and high pressure homogenization for manufacturing MFC was performed
(Nakagaito et al. 2005; Stenstad et al. 2008). When diluted pulp slurry was passed repeatedly through a disk refiner, internal and external fibrillation was promoted. External fibrillation peeled the primary wall and S1 layer in the secondary wall and the internal fibrillation loose cell walls (Nakagaito and Yano 2004). However, severe refining damaged the crystallinity and molecular weight of cellulose (Henriksson et al. 2008).

Taniguchi and Okamura (1998) produced NFC by using a grinder. The width of NFC was between 20 nm and 90 nm. A grinder can pulverize or separate fibers into nanofibrils by a specially designed rough-faced stone. The fibers are subjected by intensive shear while passing through the gap between a rotating stone and static stone. After repeated treatment, structural decomposition of fiber occurs. By mechanical treatment, pulp fiber separates into nanofibril and nanofibril aggregates. The distribution in width is typically extensive (Abe et al. 2007). The manufacturing method of NFC using a microfluidizer was investigated (Zimmermann et al. 2004; López-Rubio et al. 2007). The size of NFC was determined as 20 nm - 100 nm in width and tens of micrometers in length. NFC is produced through several passing treatments. Iwamoto et al. (2005) reported that fourteen mechanical treatments were sufficient. This result was supported by Malainine et al.( 2005).
3.2 Network properties of pulp fiber and nanofibrillated cellulose

Mason et al. (1954) investigated the effect of consistency on the elastic properties of pulp fiber suspension. Thalén and Wahren (1964a; 1964b; 1968) studied the effects of shear force and shear rate on a fiber network. The relationship between network strength and consistency was evaluated using elasto-viscometer. They found that the aspect ratio and elasticity of pulp fiber affected network strength. Meyer and Wahren (1964) theoretically studied fiber networks in a 3-D plane which is the aspect ratio affected sedimentation concentration. The results of Meyer and Wahren (1964) supported experimental results of Thalén and Wahren (1964a; 1964b).

Kurath (1959) reported that storage modulus was logarithmically proportional to the consistency with the order of 3.1. This relationship was generalized by Meyer and Wahren (1964). Kerekes and Schell (1992) explained the degree of contact between fibers in flowing suspension using the concept of “crowding factor”. The degree of contact that is enough to make a network under shear is 60 - 130. This number means that a “floc” can be formed with at least three contact points within one fiber and another fiber. Parker (1972) also reported similar results. Kerekes et al. (1985) investigated three mechanisms that determined by three mechanism: colloidal aggregation, mechanical entanglement and elastic bending. The yield stress increased with increasing consistency following the power function. Bennington et al. (1990) suggested that the volume concentration was well matched with network
Uniform dispersion of fibers is very important in papermaking wet-end process. Therefore, the understanding of rheology of pulp slurry is important. The flocs can be considered as the areas of higher fiber density within a network (Björkman 2000; Kerekes 2006). The increase in consistency in a headbox has led to degrading uniformity and has caused some problems with mechanical properties. However, the low consistency in a headbox leads to dewatering problem and high drying energy. Youn and Lee (2002) found network strength with diverse pulp fibers and the effect of mechanical treatment and crill content on the network strength.

Tatsumi and Matsumoto (2007) explained the relationship between the storage modulus and consistency of diversely treated cellulose fiber by measuring rheological properties. The effect of the aspect ratio and flexibility was investigated. The exponent in the power function was 2.25 with the mass consistency. It matched with the theoretical calculation. The exponent was 3 and volume consistency, which has a good agreement or similar results of Bennington et al. (1990).

Pääkkö et al. (2007) explained the rheological properties of NFC according to the theory by Jones and Marquès (1990). The relationship between physical networking and concentration very important. The storage modulus of NFC was 100 times larger than that of cellulose nanocrystals.
NFC forms an entangled, three-dimensional network (Pääkkö et al. 2007).

Saarikoski et al. (2012) reported that the floc structure of NFC is similar to that of pulp suspensions, even though the dimension of NFC was much smaller than pulp fibers. Saarikoski et al. (2012) studied the flocculated structure of NFC by image analysis. The flocculated structure of pulp suspension was also studied by image analysis (Beghello 1998; Wågberg and Nordqvist 1999; Chen et al. 2002; Björkman 2003a; Björkman 2003b; Karppinen et al. 2012).
3.3 Mechanical properties of the sheet made of cellulose fibers

The strength of the wet web is an important factor that affects runnability in papermaking (Stevens and Pearson 1970). The strength of wet web is determined by the parameters. The first one is fiber-to-fiber interaction (Seth 1995). The second one is related to the mechanism of the stretch of the web, which is controlled by the extent of curl and microcompression of the fibers (Seth 1995).

A wet web at low solids is mainly held together by the forces of surface tension acting between the fibers (Lyne and Gallay 1954). However, the fiber-to-fiber interaction is dominant compared to forces acting between fibers at a molecular level above 40% of the solids content.

Nordman et al. (1972) investigated the effects of fiber length and coarseness on wet web strength. Because fibers do not break during the failure of a wet web, only fiber length and coarseness are expected to influence wet web strength. Seth (1990) also studied the effect of fiber length and coarseness on wet webs. The tensile strength of wet webs at 30% solids made from softwood kraft pulps was found to be proportional to fiber length and inversely proportional to the square of fiber coarseness (Seth 1995).

Page (1993) derived the theoretical wet-web strength of pulp fiber as demonstrated in Eq. [1-1]. The zero-span tensile strength and fiber cross-section area that support dry strength of paper are not presented here. The friction between fibers and surface tension is important in a wet web.
\[ T = \frac{\mu \gamma P L RBA}{12cr} \ldots \text{Eq. [1-1]} \]

Where, \( T \) is the wet web tensile strength, \( \mu \) is the friction coefficient between two wet fibers, \( \gamma \) is the surface tension of water, and \( P, L \) and \( C \) are their fiber perimeter, length and coarseness, respectively. \( RBA \) is the proportion of the fiber surface contained within a water meniscus of radius of curvature \( r \), holding adjacent fiber together.

The mechanical properties of NFC with the state of film were reported by many studies (Siró and placket 2010; Zimmermann et al. 2004; Bruce et al. 2005; Leitner et al. 2007). The tensile breaking stress of NFC film was 100 MPa - 300 MPa and the strain at break was 2.5% - 17.5%. The difference of mechanical properties was due to the cellulose sources, preparation method of NFC, and the preparation method of film. Zimmermann et al. (2004) reported that the tensile strength of NFC film was 80 MPa - 100 MPa and a modulus of elasticity was about 6 GPa. The result was similar to that of Bruce et al. (2005) and Leitner et al. (2007).

The mechanical properties of NFC films decreased when it was immersed in water. However, the structure retained (Henriksson et al. 2007). The relationship between structure and mechanical property for NFC films was represented differently with degree of polymerization of cellulose (Henriksson et al. 2008). It was found that the NFC films had high mechanical properties with the elastic modulus of 13.2±0.6 GPa and the tensile strength of 214±3.8 MPa despite of a relatively high porosity up to 28% (Henriksson et al. 2008).
Assuming that NFC film has an ideal distribution (straight and random) of nanofibrils, Page et al. (1977) suggested that the maximum theoretical elastic modulus of cellulose fiber at zero fibril angle was 80 GPa. According to Cox (1952), the elastic modulus of a film which was randomly oriented and straight fiber might be about 27 GPa which was one-third that of individual fibers. However, NFC network deviated from the ideal, and significantly lower values were reported.

Yano and Nakahara (2004) estimated the strength of nanofibril at least 2 GPa based on the strength of kraft pulp fiber. 70% - 80% of the cellulose nanofibrils (microfibrils) were arranged parallel to the fiber direction. This was quite a low value considering that the estimated elastic modulus of a perfect crystal of native cellulose is between 130 GPa and 250 GPa (Zimmermann et al. 2004; Sakurada et al., 1962). The large discrepancy in results can be explained by the cellulose source and crystal structure. The use of different methods to measure the elastic modulus may be another reason.
3.4 Water removal from the cellulose fiber suspension

Kozeny (1927) reported that the water flow passing through the layer structure with small particles is related to the pore size and pore number. Carman (1938; 1939) expanded the Kozeny’s theory and derived the Kozeny-Carman equation. According to the theory, viscosity of fluid, surface area, and void volume are also considered in the Kozeny-Carman equation.

Ingmanson (1952; 1953) reported that the materials that can be compressed by pressure could be applied to the Kozeny-Carman equation, even though several modifications were required. Many studies modified the theory of Kozeny-Carman. Chan et al. (1996) suggested that the Kozeny-Carman equation is valid, even though the particle size or distribution is different if the surface area is the same.

Hubbe and Heitmann (2007) reviewed the strategy of practical dewatering in papermaking. The key points are to decrease surface area and to secure the dewatering channel.
3.5. Degree of polymerization and crystallinity of cellulose nanofibril

The degree of polymerization (DP) is strongly correlated with the aspect ratio and length of the nanofibers (Iwamoto et al., 2007; Zimmermann et al., 2010). Cupri-ethylene diamine solution was generally used to measure the viscosity and DP was estimated using the viscosity of the cellulose solution. Nanofibrillation of pulp fiber clearly reduced the DP of cellulose. NFC produced from softwood sulfite pulp had a DP of 825 whereas the DP of the initial pulp was 2249 (Zimmermann et al., 2010).

The degree of crystallinity could explain the behavior and mechanical properties of the material. The crystallinity of cellulose sources is generally evaluated by X-ray diffraction method and a peak area approach (Garvey et al., 2005; He et al., 2008) and a peak intensity approach (Segal et al., 1959). A high degree of crystallinity of NFC was reported as about 78% for wheat straw and 70% for soy hull (Alemdar and Sain 2008). Even higher values of about 90% were obtained by Siqueira et al. (2010a; 2010b). Iwamoto et al. (2007) reported that the crystallinity of NFC decreased with an increase in number of passes.
3.6 Rheological properties of NFC

NFC has specific rheological properties that can be described in terms of “pseudoplastic behavior” or “shear thinning behavior” (Herrick et al., 1983; Pääkkö et al., 2007). Pääkkö et al. (2007) reported that the NFC suspension formed network from a low consistency of 0.125 wt%. The storage modulus was 10 times higher than the loss modulus regardless of consistency. According to Pääkkö et al. (2007), it is due to the high aspect ratio which forms an inherently entangled network structure. It is difficult to explain the shear thinning phenomenon. However, shear thinning maybe due to the aggregation of NFC, which means a limitation of continuous network formation at a high shear rate might be a reason. This hypothesis was confirmed by a recent study (Missoum et al. 2010). Karppinen et al. (2012) visualized the flocculation behavior of NFC with increasing shear strain. A “shoulder” represented in shear thinning behavior may be due to the structure change. Iotti et al. (2011) performed a detailed study of NFC suspension at consistencies ranging from 1% to 4% and temperatures between 25°C and 60°C. Hysteresis loop between viscosity and shear rate was emphasized to understand the behavior of NFC under the induced shear force. Interacting forces between nanofibrils and flocculation phenomenon can be changed by various means. Salt addition (One et al. 2004; Saarikoski et al. 2012), and polyelectrolyte addition (Wågberg and Nordqvist 1999; Hubbe 2007; Karppinen et al. 2011), change of pH (Beghello 1998) were reported. The structural changes affected the rheological properties, which are important to industrial process, such as pumping, storage, and other applications.
Chapter 2.
Preparation and characterization of nanofibrillated cellulose
1. Introduction

NFC is a unique material that is prepared through deconstructing cellulosic fibers into nanofibrils. It was introduced by Turbak et al. (1983) and Herrick et al. (1983) in 1980s. Homogenizer was used for the disintegration at first. However, the suspension should maintain with low consistency of 0.5% in manufacturing. It seems that the deconstructing by homogenizer has a weak point in productivity. Cooling is another problem of homogenizer because very high pressure is required. Taniguchi and Okamura (1998) was produced NFC using grinder. Grinder leaves a room for scale-up because the rotor and the stator could become big if it is intended.

Although the manufacturing method of NFC was already introduced with many studies, there should be more attention to the procedure of nanofibrillation. Besides, once-dried pulp fiber which is generally used in a papermaking industry was not used much in research because it is hard to deconstruct.

Refining is an essential process in developing desired quality level of fibers in the papermaking. Internal fibrillation, external fibrillation, fines formation, fiber shortening or cutting, and fiber curling or straightening (Giertz 1957; Higgins and Yong 1961; Giertz 1980; Ebeling 1980; Page 1989) are representative effects by refining. In this study, pulp fibers were prepared before grinding process with three level of beating degree. Then, they were ground by different number of passes.
This chapter focused on the preparation and characterization of NFC. Morphology of nanofibrillated cellulose was investigated with grinding number using Field Emission-Scanning Electron Microscope (FE-SEM) and Atomic Force Microscope (AFM). Water Retention Value (WRV) was evaluated to determine the degree of nanofibrillation. Low shear viscosity and rotational viscosity were measured. The network properties of the NFC suspension with the consistency were also investigated.
2. Materials and methods

2.1 Pulp

Bleached Eucalyptus kraft pulp was used as a raw material. Length weighted average fiber length was 0.51 mm which was measured by Kajaani FiberLab analyzer (KajaaniFiberLab V.3, Metso). Chemical composition of pulp fiber was measured by TAPPI method (T 203 om-93). The content of α-Cellulose in pulp fiber was 88.1% ± 1.1%. Hemicellulose content was 11.9% ± 1.1%. The brightness was 86.57% (ISO 2470). Specific surface area of beaten fiber (450 mL CSF) was 23.4 m²/g by BET method. The pulp fiber was pretreated before BET measurement by solvent exchange using ethanol, aceton and hexane to minimize hydrogen bonding between fibers.

2.2 Preparation of nanofibrillated cellulose

NFC was prepared with two steps of mechanical pretreatment and grinding. The mechanical pretreatment was performed with a laboratory Valley beater. Unbeaten, slightly beaten and fully beaten fibers were prepared by controlling beating time (Table 2-1). Mechanically pretreated fibers were processed using a grinder (Super Masscolloider, Masuko Co.). The picture of a grinder used was shown in Fig. 2-1. The pictures of a rotor and a stator were shown in Fig. 2-2.
Table 2-1. Mechanical pretreatment of Hw-BKP prior to grinding

<table>
<thead>
<tr>
<th></th>
<th>Unbeaten</th>
<th>Slightly beaten</th>
<th>Fully beaten</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freeness, mL CSF</td>
<td>600</td>
<td>450</td>
<td>N.D*</td>
</tr>
<tr>
<td>Beating time, min</td>
<td>0 (disintegrated only)</td>
<td>12</td>
<td>120</td>
</tr>
</tbody>
</table>

* Not determined using Canadian freeness tester.
Fig. 2-1. Picture of a grinder.

Fig. 2-2. Rotor (left) and stator (right) in a grinder.
2.3 Characterization of nanofibrillated cellulose

2.3.1 Morphology

NFC suspension of 0.03% was dried on silicon wafer at room temperature. The sample was coated with platinum by an ion sputter and observed with FE-SEM (SUPRA 55VP, Carl Zeiss).

AFM (XE-100, Parksystem, Korea) was also used for the investigation of morphology of NFC. Transmission Electron Microscope (TEM, JEM1010, JEOL, Japan) was used to determine the length of NFC.
2.3.2 Sedimentation concentration

0.05 w/v% NFC slurry was prepared in 1 L-graduated cylinder. The suspension was settled for 24 h as shown in Fig. 2-3. Then, the sedimented volume of fiber was measured. The sedimentation concentration was calculated using Eq. [2-1].

\[
\text{Sediment concentration, } \% = \frac{\text{Solid weight per volume}}{\text{Volume of slurry}} \times 100 \ldots [2-1]
\]

Fig. 2-3. Sedimentation volume.
2.3.3 Water retention value

Water retention value was evaluated for the degree of nanofibrillation in accordance with TAPPI Useful method UM 256. WRV is calculated as Eq. [2-2].

\[
WRV, \frac{g}{g} = \frac{B-A}{A} \quad [2-2]
\]

where, A is the weight of oven-dried weight of NFC and B is the weight of NFC after centrifuging 900 G for 30 min.

2.3.4 Dewatering ability

The dewatering ability of NFC suspension was evaluated by measuring drainage time under vacuum and pressurized conditions. In vacuum dewatering, the NFC suspension was diluted to 0.02%. The time to drain 80% of water from the suspension of 100 mL under vacuum was measured (Fig 2-4). The vacuum of -75 kPa was applied. For pressurized dewatering, NFC suspension was prepared with 2% concentration. The suspension was drained using Pressurized Dewatering Equipment (PDE) as shown in Fig 2-5. It was designed to remove water by increasing pressure on NFC suspension above filter medium. The pressure was adjusted at 7 bar. Drained water was measured continuously by balance (CUX4200H, CAS Co., Korea). The diameter of vessel was 70 mm and maximum capacity was 250 mL. Dewatering time was evaluated when 67% of water drained. From the results of dewatering, specific resistance to filtration (SRF) was calculated based on Darcy’s law (Rafael and Letterman 1976). Simply, Darcy’s law is a
relationship that flow rate passing porous medium is proportional to the viscosity of fluid, pressure drop, flow distance and area as shown in Eq. [2-3].

\[ Q = \frac{k \Delta P A}{\eta L} \quad \text{[2-3]} \]

where, \( Q \) is flow rate (m\(^3\)/s), \( k \) is permeability (m/s), \( \Delta P \) is pressure drop (Pa), \( A \) is area (m\(^2\)), and \( \eta = \) viscosity (kg/m·s).

Eq. [2-3] could be modified as below.

\[ \frac{1}{Q} \cdot \frac{t}{V} = \frac{\eta \gamma C}{2 \Delta P A^2} V \quad \text{[2-4]} \]

where, \( V \) is volume of filtrate, \( \gamma \) is average specific resistance to filtration (m/kg), and \( C \) is solids content (mg/L).

Eq. [2-4] could be changed to Eq. [2-5].

\[ \frac{t}{V} = a V \quad \text{[2-5]} \]

where, \( a = \frac{\eta \gamma C}{2 \Delta P A^2} \)

In this study, dewatering time and drained water obtained from the dewatering experiment in pressurized and vacuum condition. \( t/V \) and \( V \) has linear relationship and \( a \) is the slope of the plotted graph. Therefore, specific resistance to filtrate could be calculated with Eq. [2-6].

\[ \gamma = 2PA^2a/\eta C \quad \text{[2-6]} \]
Fig 2-4. Dewatering of the NFC suspension in vacuum condition.
Fig. 2-5. Pressurized dewatering equipment. (a) scheme of apparatus, (b) main part, and (c) picture of vessel.
2.4 Rheological properties

Low shear viscosity was measured using a Brookfield viscometer (LVDV-II+pro) to evaluate flow resistance of NFC. Rotation speed was 100 rpm and the temperature was 23°C. The 0.5% and 1.5% of NFC slurries were used for viscosity measurement. No. 4 spindle was used.

Rheological properties were studied using Bohlin rheometer (CVO, Malvern instrument, USA) shown in Fig. 2-6. The Geometry was cone and plate type (cone angle : 4°, Diameter : 4 cm). Rotational viscosity with an increase in shear rate was measured.

Oscillatory rheometer was also used. Two modes were selected to study the rheological properties. Amplitude sweep mode was performed in mode of stress controlled ranged from 0.16 Pa to 100 Pa at a constant frequency of 1 Hz (=6.28 rad/s). Frequency sweep mode was carried out over the range of 1 Hz - 50 Hz at constant stress of 5 Pa. 30 passed NFC slurry was used for dynamic rheology.
Fig. 2-6. Picture of Bohlin rheometer
2.5 Specific surface area

Solvent exchange was performed with pulp fiber and NFC to measure specific surface area. The fibers were immersed in 20, 50, 80, and 99 wt% of ethanol for 1 hr, successively. Then, they were immersed in acetone and hexane for 1 day.

The specific surface area was determined by nitrogen gas (N\textsubscript{2}) adsorption and desorption measurements using a TriStar II 3020 (Micromeritics Instrument Co., USA). The samples dried at 100°C for 72 hours to remove the extra moisture thoroughly before measurement and followed by nitrogen gas adsorption at -196°C. The specific surface area of pulp fiber and NFC were determined from the Brunauer-Emmett-Teller (BET) method.
3. Results and discussion

3.1 Morphology of pulp fiber

Mechanical pretreatment using a Valley beater was performed prior to grinding process. The beating degree was controlled by three levels. The morphological changes which was observed using FE-SEM were shown in Fig. 2-7. The width of pulp fiber (Fig. 2-7 (a)) is about 20 μm. The external fibrillation is clearly shown with an increase in a beating time (Fig. 2-7 (b) and (c)).

The shrinkage of pulp fiber was represented differently. Considering that the images were taken after drying, it was because of the structural changes of cell wall. The arrows indicated the shrinkages of pulp fiber which was attributed to the collapses of cell wall by internal fibrillation of cell wall. Beating promoted not only external fibrillation but also the internal fibrillation (Giertz 1957; Higgins and Yong 1961; Giertz 1980; Ebeling 1980; Page 1989).
Fig. 2-7 Morphological changes with beating degrees; (a) unbeaten fiber (b) slightly beaten fiber, (c) extremely beaten fiber. The arrows indicate shrinkage attributed to the collapses of cell wall.
3.2 Nanofibrillation of pulp fiber with an increase in number of passes

3.2.1 Morphology changes

Morphological changes of unbeaten fibers with number of passes in a grinder were shown in Fig. 2-8. The stock consistency during grinding process was 1.5%. A very intensive mechanical energy was loaded on pulp fiber during grinding. External fibrillation occurred dominantly on unbeaten fiber by grinding. However, the preserved part of pulp fiber remained although pulp fibers were subjected by high mechanical energy. The shape of pulp fiber was almost preserved even with 20 passes in a grinder. Partial collapses happened at 30 passes.

When the consistency of a suspension was increased to 3%, external fibrillation was promoted as shown in Fig. 2-9. The increase in fibrillation at high consistency might be due to the increase in fiber-to fiber friction (Smook, G. A. 2002). The “peeling off” of pulp fiber was observed in Fig. 2-9. The pulp fiber with preserving cell wall structure was shown and it was fibrillized externally rather than internally.
Fig. 2-8. Morphological changes of unbeaten fiber with an increase in pass number by grinder, (a) 1 pass, (b) 5 passes, (c) 10 passes, (d) 15 passes, (e) 20 passes, and (f) 30 passes. The consistency of the suspension during grinding was 1.5%.
Fig. 2-9. Morphology of unbeaten fiber with 15 pass by grinder. The stock consistency during grinding was 3%.
The morphological changes of slightly beaten fiber by grinding were presented in Fig. 2-10. Fibrillation on the fiber surface was observed at 1 pass. The arranged fiber angle was observed until 5 passes. However, the orientation of fiber disappeared with an increase in number of passes. Randomly dispersed nanofibrils without any orientation was observed after 15 - 20 passes. Removal of primary wall exposes the secondary wall and allows water to be absorbed into the molecular structure and fiber swelling (Smook 1982).

In the case of extremely beaten pulp fiber, it was hard to find the shape of pulp fiber preserved. However, the orientation still observed with arranged one direction. The partial nanofibrillation appeared, however the orientation still appeared up to 10 passes. The randomly oriented nanofibrils were observed after 15 passes. Therefore it was enough mechanical treatment to produced NFC.

Mechanical pretreatment using a Valley beater facilitated nanofibrillation of pulp fiber in the aspect of number of passes. However, it appeared that a slight beating pretreatment (450 mL CSF) was enough to producing NFC, which means that a proper level of beating degree helped nanofibrillation by grinder.
Fig. 2-10. Morphological changes of slightly beaten fiber with an increase in number of passes by grinder, (a) 1 pass, (b) 5 passes, (c) 10 passes, (d) 15 passes, (e) 20 passes, (f) 30 passes.
Fig. 2-11. Morphological changes of extremely beaten fiber with an increase in number of passes by grinder, (a) 1 pass, (b) 5 passes, (c) 10 passes, (d) 15 passes, (e) 20 passes, and (f) 30 passes.
Once-dried pulp fiber is considered to require more energy to be separated into individual nanofibrils. Therefore, if never dried pulp fiber is used, fully treated NFC could be achieved with weak pretreatment or small number of passes in a grinder.

It was found that the pulp fiber is separated into nanofibrils with width of 10 nm - 50 nm and their aggregates with width of over than 50 nm (Fig. 2-12). Other research reported that similar size of NFC. Taniguchi and Okamura (1998) reported the width of nanofibrils produced by grinder was in the range from 20 nm to 90 nm. Iwamoto et al. (2005) reported that 30 times of passing through a high pressure homogenizer and 10 times of grinding treatment from kraft pulp produced NFC with the range from 50 nm to 100 nm in width and several micrometer in length.
Fig. 2-12. Nanofibrillated cellulose.
It is hard to measure the exact width of nanofibril using FE-SEM because coating process with Pt is needed to observe by FE-SEM. Therefore, AFM was used to measure the exact width of nanofibrils prepared from pulp fiber.

AFM images on nanofibrils and nanofibril aggregate were shown in Fig. 2-11. The nanofibrils were placed on silicon wafer which was extremely smooth surface (root mean square < 1 nm). Because the tip on cantilever in AFM probe has radius of 10 nm, the width of NFC can be overestimated. In this case, the height of a sample generally considered as the width. The average width of a single nanofibril was 6.7 nm. The width of aggregate was measured as about 50 nm.

The “peels” presented during grinding was also measured shown in Fig. 2-13. The width appeared from 0.7 μm to 1 μm and the height was presented from 70 nm to 130 nm. Considering from the information of the dimensions of peels, the “peels” was consisted of 1-2 layers of nanofibril aggregate in height and 14 to 20 of nanofibril aggregates in width. Because it was observed only from the unbeaten fiber stock with high consistency, internal fibrillation is suggested to increase the grinding efficiency.

The phase images from the measurement using AFM were represented in Fig. 2-14. Since phase images are composed by the feed-back signals, they show more clear images in 2-D plane. The roughness of NFC in phase images were below 1 or 2 nm.
Fig. 2-13. Dimension measurement for nanofibrils and nanofibril aggregates (up) and “peels” (bottom) by AFM.

Fig. 2-14. Phase images of nanofibrils and nanofibril aggregates (left) and “peels” (right).
Determination of the width of nanofibrils or nanofibril aggregates was possible using AFM. However, it is difficult to measure the width and the length of nanofibrils concurrently because the proper magnification to satisfy both purpose doesn’t exist. For example, the proper magnification to distinguish the width of nanofibrils is over than $\times$ 50,000, but the length of nanofibril is bigger than the size of image. Through the observation by FE-SEM, the length of nanofibrils are more than at least 5 $\mu$m.

The images of nanofibrils and nanofibril aggregates using TEM was shown in Fig. 2-15. The nanofibrils and the nanofibril aggregates could be observed by TEM. The length was from 4 $\mu$m to 11 $\mu$m according to TEM image.

The aspect ratio of nanofibrils was not determined clearly. Many studies reported that the length of nanofibril was several micrometers (Siró and Plackett 2010). It was majorly dependent on the cellulose source. According to the result of this study, the aspect ratio of nanofibril was present from 100 to 1000. It is high value compared to pulp fiber which is 50 -100 in general. The aspect ratio of NFC is 2-20 times longer than pulp fiber.
Fig. 2-15. TEM images of nanofibrils and nanofibril aggregates.
3.2.2 Viscosity

NFC was prepared from slightly beaten fiber. The Brookfield viscosity of NFC suspension with increasing number of passes was shown in Fig. 2-16. The viscosity increased both for 0.5% and 1.5% stock with nanofibrillation until 20 passes, which showed a linear relationship between number of passes and viscosity. However, the viscosity of NFC didn’t show any more increase above 20 passes. Because the increase in the viscosity is likely to be due to the nanofibrillation of pulp fiber, 20 passes might be enough for making fully mechanically treated NFC, which is supported by morphological changes with nanofibrillation (Fig. 2-10). Nanofibrillation with increasing number of passes showed that the pulp fiber was separated into nanofibrils involving increase in aspect ratio and surface area due to the result from morphological changes. It indicates the network structure in the NFC suspension turns more complex than pulp fiber suspension with an increase in the number of contacts and flexibility.

Low shear viscosity with consistency was depicted in Fig. 2-17. The relationship between viscosity and consistency followed a power law. Therefore, it seemed that the physical complexity induced by an increase in number of nanofibrils induced an increase in viscosity because higher consistency led to increase in the contacts between nanofibrils and physical entanglements.
Fig. 2-16. Low shear viscosity of NFC with an increase in number of passes.

\[ y = 94.14x + 539.59 \quad \text{R}^2 = 0.9989 \]

\[ y = 9.1325x + 19.286 \quad \text{R}^2 = 0.9936 \]

Fig. 2-17. Low shear viscosity of NFC with an increase in consistency.

\[ y = 757.45x^{2.556} \quad \text{R}^2 = 0.9995 \]
3.2.3 Sedimentation concentration

Because of the effect of both Van der Waals forces and zeta potentials, different behavior of sedimentation is observed depending on the fiber concentration and the tendency of the particles to cohere (Fitch 1979). Sedimentation concentration is calculated from sedimentation volume. It is known as a starting point of forming network. In other words, a suspension is formed network structure over the sedimentation concentration. The sedimentation concentration with increasing number of passes was shown in Fig. 2-18. Sedimentation concentration of pulp fiber (450 mL CSF) was 0.43%. It decreased with increasing number of passes until 20 passes and maintained. Sedimentation concentration of fully treated NFC was about 0.18% - 0.2%.
Fig. 2-18. Sedimentation concentration of NFC with an increase in number of passes.
3.2.4 Water retention value

The WRV was shown in Fig. 2-19 with beating degree and consistency of pulp fiber. The WRV is considered as the amount of bound water on fiber surface. Therefore, it could be an index of surface area or degree of nanofibrillation. The increase in surface area as a result of nanofibrillation by grinding increased the amount of bound water as shown in Fig. 2-19.

Before grinding, the fibers showed different water retention values depending on pretreated condition. When the pretreatment was conducted severely, it made water retention value almost double by only one pass of grinding compared to the initial pulp fiber. The difference in between extremely pretreated fibers and slightly one was the biggest the first pass in grinder. However the difference was gradually reduced until 10 times of grinding and they had similar values above that pass number. The WRVs after 15 passes were 7.1 g/g - 7.6 g/g. The WRV of unbeaten fibers gradually increased but the increase was rather small compared to pretreated fibers. However, the high consistency during grinding promoted nanofibrillation of fiber. That is because of the increase in the friction force between fibers.

Both of the internal fibrillation and the external fibrillation were promoted by mechanical pretreatment. Internal fibrillation can be considered as a destruction of internal bonding between fibrils. Therefore, a proper pretreatment before grinding seemed to be important to produce NFC by low energy consumption.
Fig. 2-19. Water retention value with an increase in number of passes of NFC at different pretreatment condition.
3.2.5 Dewatering ability

Two methods were used to evaluate dewatering properties of NFC suspension. Vacuum filtration was performed with diluted suspension of 0.02%. Pressurized dewatering was carried out with suspension of 2%.

The dewatering ability of diluted suspension with an increase in number of passes was shown in Fig. 2-20. The slope of the plotted graph means dewatering rate. The dewatering rate decreased with an increase in number of passes because the degree of nanofibrillation was increased. According to Kozeny (1927) and Carman (1938;1953), surface area and void volume are important variables. Because nanofibrillation increased surface area and decreased void volume, the structure of NFC mat became compact and the dewatering channel became narrow. Consequently, the dewatering rate decreased.

At the consistency of 2% which formed network of NFC, the drained water from the suspension with an increase in number of passes was shown in Fig. 2-21. The dewatering rate of NFC suspension decreased with increasing number of passes showing the similar tendency to diluted suspension. In the case of pulp fiber suspension, more than 65% of water was drained within 1 min. However, NFC suspension of 20 passes showed that it took 20 min during 60% of water was drained.
Fig. 2-20. Dewatering amount of diluted NFC suspension with an increase in dewatering time.

Fig. 2-21. Drain water with an increase in dewatering time using PDE.
The specific resistance to filtration (SRF) with increasing number of passes was shown in Fig. 2-22. The SRF from 0.02% suspension showed almost a linear relationship with increasing number of passes. Finally, the SRF of NFC which was treated 20 times was $1.11 \times 10^8$ m/kg.

The SRF from 2% suspension was dramatically increased with increasing number of passes. The increasing tendency of SRF was represented more rapid. It meant that the consistency at beginning of dewatering was important in dewatering process when the pulp fiber is changed to NFC, especially. The SRF of NFC which was treated 20 times was $1.15 \times 10^9$ m/kg when the consistency at beginning was 2%.
Fig. 2-22. Specific resistance to filtration with an increase in the number of passes from 0.02% and 2% suspension.
3.3 Rheological properties with the number of passes and the consistency

3.3.1 Rotational viscosity

NFC was prepared with 30 passes at 2%. Fig. 2-23 shows the flow curves of NFC suspensions with shear rate at different consistency. NFC suspension showed a typical shear thinning behavior. Although the NFC suspension has high viscosity due to the characteristics of forming network, shear force can reduce the viscosity. When the consistency of NFC suspension was higher, the viscosity increased. It is due to the increase in friction between nanofibrils.

Vistogram showed shear thinning. It might imply that the NFC suspension of higher consistency would have certain orientation in an associated state. The shoulder region was presented around the middle of flow curve with the range of the shear rate from 2 s\(^{-1}\) to 4 s\(^{-1}\). It was dominant in the range of 0.5\% -1.5\%. It might be because the network structure was fractured with this range of shear rates. Previous studies reported similar phenomenon (Pääkkö et al. 2007; Lowys et al. 2001; Agoda-Tandjawa et al. 2010). As the viscosity is the ratio of shear stress and shear rate, the existence of a shoulder implied the rapid increase in shear stress. Randomly dispersed individual nanofibrils without certain orientation turned into having orientation along flow direction during an increase in shear rate. It was attributed to the breakdown of network. However, 2\% of NFC suspension didn’t show the shoulder because of its highly associated state. The viscosity decreased when shear rate increased.
Fig. 2-23 Rotational viscosity of NFC suspensions with the consistency.
Viscosity of NFC suspensions with increasing number of passes was represented in Fig. 2-24. The viscosity was increased slightly with an increase in number of passes. It could be divided into two groups depending on number of passes at 100 s\(^{-1}\). The viscosity had similar value over than 15 passes. It showed a similar tendency to the result of WRV. Because the friction between nanofibrils is related to the contact area, the tendency between WRV and viscosity correlated. Consequently, The viscosity could be an index for nanofibrillation.
Fig. 2-24. Rotational viscosity of NFC suspensions with the number of passes.
3.3.2 Dynamic rheology

Stress sweep was performed to find out the network properties using Bohlin rheometer. The storage modulus with increasing shear stress was shown in Fig. 2-25. The storage modulus had a plateau region within a low level of shear stress. Because the storage modulus is independent on increasing stress, this is called “linear viscoelastic region”. When the shear stress was increased further, however, the storage modulus was decreased significantly over certain point. This point was regarded as yield point. After yield point, the storage modulus showed non-linear viscoelastic behavior meaning that it is dependent on stress changes.

The storage modulus and the loss modulus of NFC suspension with increasing frequency at a different consistency were shown in Fig. 2-26. Generally, frequency sweep is evaluated at a constant stress. NFC suspension at a low consistency of 0.5% or 1% showed a crossover point of G’ and G’’ while increasing frequency. It indicates weakly associated state of NFC network. When the consistency increased, however, the storage modulus (G’) and loss modulus (G’’) were separated clearly, indicating highly associated state of NFC network. It was suggested that the network structure hardened by increasing contact number between nanofibrils.
Fig. 2-25. The storage modulus as a function of stress with NFC consistency.

Fig. 2-26. The storage modulus ($G'$) and the loss modulus ($G''$) for NFC suspension with frequency sweep.
The storage modulus at plateau region with increasing consistency was shown in Fig. 2-27. A power law relationship appeared between the consistency and the storage modulus. The critical stress (yield point) was represented in Fig. 2-28. It also showed a power law relationship with consistency. The relationship was described in Eq. [2-3].

\[ G' = \alpha \times C^\beta \quad \text{[2-3]} \]

Where \( G' \) is storage modulus, \( C \) is consistency of suspension, \( \alpha \) is proportional to the aspect ratio (Tatsumi 2007), and \( \beta \) represents flocculation tendency.

In this study, empirical results was provided as \( G' = 50.7 \times C^{3.37} \) and \( \tau = 7.89 \times C^{1.94} \). The power law relationship was reported also with many studies (Pääkkö et al. 2007; Agoda-Tandjawa et al. 2010; Tatsumi 2007). The exponent is related to the flocculation tendency (Saarikoski et al. 2012). Previous studies about NFC suspension including pulp fiber reported that the exponent was close to 3 (Bennington 1999; Tatsumi 2007; Pääkkö et al. 2007). The stress-controlled rheometer was used in this chapter. The result using strain-controlled rheometer would be discussed in next chapter, additionally.

The storage modulus and the critical stress below 0.2% of NFC suspension did not follow a power law equation. This is because that the diluted suspensions did not form the network structure yet. As the sedimentation concentration was below than 0.2%, the percolation limit must be above 0.2%.
There are two network models those are percolation and fibrillar model (Guenet 2000). Fibrillar model relies on experimental results. With the aspect of fibrillar model, it is important that the mesh size of the structure should be above certain consistency that is enough to stand out any flocculation or deformation of that structure. The exponent was 3.37 with the plateau storage modulus. This value suggests a fractal dimension ($D_F$) is 1.61 according to Eq. [2-4] from Jones and Marquès (1990). This result was closed to Pääkkö et al. (2007) ($(D_F = 1.5)$).

\[ G' \propto C^{(3+D_F)/(3-D_F)} \]  

[2-4]

where $G'$ is storage modulus, $C$ is consistency of suspension and $D_F$ is fractal dimension.

High aspect ratio of NFC which made it attractive in many application fields is a unique characteristics. When it is used as a filler materials in composites, however, the dispersion of NFC uniformly is limited due to the entanglement inherence and hydrophilic surface. Post treatment such as grafting, silylation, endowing hydrophobicity would be a solution to this issue.
Fig. 2-27. The storage modulus of NFC as a function of consistency.
Fig. 2-28. Critical stress of NFC as a function of consistency.
3.4 Specific surface area and chemical composition of pulp fiber and NFC

Surface area is one of the key properties of NFC. However, because of the hydrophilic characteristics of cellulose surface, it is quite difficult to measure this property due to the strong aggregation of NFC during drying. The estimated value of specific area by modeling tools which use the length and diameter is about 600 m$^2$/g. According to Siqueira et al. (2010c), the specific area of sisal NFC was around 50 m$^2$/g, which was about 10 times greater than that of the fiber through BET method. Berlioz (2007) also attempted a BET method to measure specific area of NFC. However, it showed still underestimated showing 23.4 m$^2$/g. In this study, the bonding between nanofibrils was restricted as much as possible through solvent exchanges. Then, the specific area was measured by BET method. The specific area of pulp fiber which was at the state of slightly beaten was 22.4 m$^2$/g. NFC of fully treated was represented 174 m$^2$/g. Spence et al. (2010) reported the specific surface area of pulp fiber by using the method of Congo red molecules adsorption at the surface. It ranged from 100 m$^2$/g to 200 m$^2$/g. The specific surface area of hardwood pulp fiber was 174 m$^2$/g, which was very close to the result in this study.

The content of α-Cellulose in pulp fiber and NFC was evaluated using TAPPI method (T 203 om-93). The content of pulp fiber was 88.1% ± 1.1% and that of NFC was 83.5% ± 1.4%. It was slightly decreased during grinding process. It might be due to the increase of surface area and more hemicellulose was extracted due to the nano-size fibrillation from pulp fiber.
4. Summary

NFC was prepared and characterized. The morphology, water retention value, sedimentation concentration, dewatering property and rheological properties were investigated. The degree of nanofibrillation from pulp fiber can be determined by an evaluation of those characteristics. No further change by a mechanical treatment with pulp fiber was noted after than 15 - 20 passes. However, it may be more important that the characteristics of NFC should be considered depending on the level of demand for further applications. The low shear viscosity of the NFC suspension was 200 cPs at 0.5% and 2400 cPs at 1.5% with above 20 passes. WRV increased more than six times, and sedimentation concentration decreased more than twice. The nanofibrillation of pulp fiber could be determined with those indexes, especially viscosity. The dewatering abilities of pulp fiber and NFC were compared. It was found that the initial consistency of NFC was significantly affected by its specific resistance to filtration. NFC showed a higher specific resistance to filtration by tenfold compared to pulp fiber at a consistency of 2%. This indicates that a conventional dewatering process during papermaking is highly limited in the case of NFC. Rheological properties were investigated with dynamic mode. The cross-over between the storage modulus and loss modulus showed the degree of association state between nanofibrils. More than 1.5% consistency showed highly associated state. The storage modulus and the critical stress showed rapid increase with increasing consistency. Specific surface area of NFC was evaluated with BET method (174 m²/g). The value was underestimated compared to theoretical value due to the aggregation in sample preparation for measurement.
Chapter 3.

Effect of nanofibrillation and solids content on mechanical properties of NFC
1. Introduction

Nanofibrillated cellulose has a larger surface area (more than 100 times) and higher aspect ratio (20-100 times) compared to pulp fiber. Not only the rheological properties of pulp fiber suspension but also the mechanical properties of wet sheet by pulp fibers were studied (Seth et al. 1984; Page 1993; Seth 1995). However, a wet mat composed of NFC with the solids content has not been investigated to date. As the dimension of NFC is too small and the specific resistance to filtration is too high, removal of water using a conventional dewatering system is difficult. Pressurized dewatering equipment was designed to remove water from nanofibrillated suspension in this study.

Based on by Page’s (1969) well-known theories of tensile strength of dry sheet, Williams’s (1983) and Page’s (1993) theories of wet sheet strength have been developed. Fiber dimension, relative bonding area, and shear strength of fiber to fiber bond determined tensile strength of wet sheet. A wet sheet with low solids content maintains the structure mainly by surface tension which acts between the fibers (Lyne and Gallay 1954). As the water contained between the fibers is displaced with air, more fiber-air-water interfaces are created where the surface tension could act. However, at higher solids content level, generally above 40%, interaction between the fibers was more dominant than the effect of surface tension (Seth 1984).

The rheology of NFC suspension at a low consistency has been extensively studied (Pääkkö et al. 2007; Agoda-Tandjawa et al. 2010; Tatsumi
2007). The mechanical properties of NFC film which was made through casting or vacuum filtering were also reported (Siró and Plackett 2010). However, research on the rheological and mechanical properties of NFC at high solids content levels is rare to find. The research has a limit to a low consistency after preparation of NFC yet. However, dewatering from NFC suspension is necessary for the use of NFC. Moreover, the network properties of wide range of solids content should be investigated when production in the state of “web” in the process is taken into account. It is expected that the causes affecting the difference can be understood through the evaluation of mechanical properties during changes of solids content.

In this chapter, the effect of morphological changes with a number of passes on mechanical properties was investigated. Furthermore, the effect of solids content of the NFC mat on mechanical properties was investigated to identify the relationship between NFC and water.
2. Materials and methods

2.1 Pulp

Bleached Eucalyptus kraft pulp was used as a raw material. Mechanical pretreatment was conducted using a laboratory Valley beater. The beating degree was 450 mL CSF.

2.2 Preparation of NFC

NFC was prepared from pulp fiber using a grinder (Super Masscolloider, Masuko Co.). The number of passes was adjusted to 5, 10, 15 passes.

2.3 Preparation of NFC suspension and mat with different solids content

1.5% of NFC suspension was drained under pressure using Pressurized Dewatering Equipment. The solids content of the NFC mat was controlled with dewatering time. The solids content of the mat was measured by the oven drying method at 105°C after pressurized dewatering. Fig. 3-1 shows the solids content of NFC mat with dewatering time. The solids content did not increase after 30 minutes of dewatering. Solids content higher than 18% was adjusted by drying NFC mat at room temperature after 30 minutes of pressurized dewatering. The solids content had a linear relationship with drying time as shown in Fig. 3-2. The grammage of NFC mat was 200 g/m².
Fig. 3-1. The solids content of NFC with dewatering time.

Fig. 3-2. The solids content of NFC with drying at room temperature.
2.4 Evaluation of tensile properties

Tensile properties of NFC mat were evaluated using UTM (Universal Testing Machine, Instron, USA) (Fig. 3-3). The strain rate was kept constant at 10%/min. A NFC mat with different solids content was prepared for measurement. The width of NFC mat specimen was 15 mm. The length of the NFC mat specimen was 20 mm. The thickness was 0.3 mm - 1.3 mm in the case of wet mat and 0.2 mm in the case of dry mat.

2.5 Evaluation of rheological properties

The rheological properties of the NFC suspension and mat were measured using the Advanced Rheometric Expansion System (ARES, TA instrument, USA) using parallel plate geometry ($\phi = 25$ mm). ARES is a strain-controlled rheometer which is sensitive to deformation of a sample. The gap between the plates was controlled in the range of 1 mm - 3 mm. The samples were allowed to rest for 5 minutes in the geometry before each testing. Critical stress was determined as the stress at the critical strain from strain sweep mode where a constant frequency of 1 Hz (=6.28 rad/s) was allowed. The typical result of strain sweep for NFC suspension is represented in Fig. 3-4. Frequency sweep in the range from 1 Hz to 100 Hz was performed with a constant strain of 1%, where the network structure remained intact. Storage modulus and loss modulus could be obtained as well as viscosity.
Fig. 3-3. Universal testing machine (left) and fractured specimen (right).

Fig. 3-4. A typical result of strain sweep test. Yield stress is obtained from the stress at the critical strain.
3. Results and discussion

3.1 Effect of nanofibrillation of pulp fiber on tensile properties

The mat was prepared with a different number of passes so that the morphology of fiber was changed with the increase in the treated times using a grinder. The fibrillation increased as the pass number increased. In that situation, the increase in fibrillation might affect the mechanical properties. The NFC mats with different solids content and the number of passes were prepared and their tensile properties were measured.

Stress-strain curves obtained from the tensile measurement of mat with the increasing number of passes is shown in Fig. 3-5. The solids content of mat was 99%. The tensile breaking stress of pulp fiber increased approximately exponentially with increasing solids content (Jantunen 1985). In this study, tensile breaking stress of the NFC mat and pulp fiber mat were represented with solids content as shown in Fig. 3-6. The deviation compared to the ideal exponential function ($R^2$ is close to 1) reduced as the number of passes increased because the density of the NFC mat increased by nanofibrillation from pulp fiber with size minimization. In other words, the water distributed in the NFC mat became uniform. 15 passes of treatment showed almost perfect exponential relationship between tensile breaking stress and solids content.

The wet strength of wet paper is important in papermaking, which has open draw in process, especially the “speed” and “breaking frequency” (Seth
Generally, the solids content of wet paper after pressing process is between 45% and 50%. The tensile breaking stress of “0 pass” which means pulp fiber at 50% of solids content had a similar value to the tensile breaking stress of fully grinded NFC at 25% of solids content.

Strain at break of pulp fiber (0 pass) decreased as increasing solids content, however the process of nanofibrillation by grinding made the breaking strain increased with increasing solids content until it reached about 50%, as shown in Fig. 3-7. The increase in the number of passes showed a steeper increase in strain at break because the effective area of an inter-fibrillar contact increased as the number of passes increased. More than 50% of solids content, however, the breaking stain decreased rapidly. It might be due to the decrease of plasticity which was attributed to the hydrogen bonding between nanofibrils.

Elastic modulus with an increasing number of passes is shown in Fig. 3-8. The increasing number of passes caused an increase in the elastic modulus. The NFC mat at 99% of solids content showed 100 - 150 times greater elastic modulus than that at 50% of solids content. It was due to the increase of hydrogen bonding following solidification. The water may play a role of “plastisizer”.
Fig. 3-5. Stress-strain curves of mats with increasing number of passes. The solids content of the mat was 99%.
Fig. 3-6. Tensile breaking stress of mats with increasing solids content. Each legend represents the number of passes.

Fig. 3-7. Strain at break of mats with increasing solids content. Each legend represents the number of passes.
Fig. 3-8. Elastic modulus of NFC mat with an increase in number of passes.
3.2 Effect of mixing ratio between pulp fiber and NFC on tensile properties

Wet and dry state mats with different NFC content were prepared to find out more precisely about the effect of the fiber morphology. The ratio between NFC and pulp fiber was controlled to 1:9, 3:7, 5:5, 7:3 and 9:1. The solids content of wet mat was 23% and of dry mat was 99%.

Stress-strain curves obtained from the tensile measurement of mat with the mixing ratio (increasing NFC content) is shown in Fig. 3-9. The solids content of mat was 23%. The tensile breaking stress with NFC content was shown in Fig. 3-10. In the case of a dry mat, the tensile breaking stress increased gradually with an increase in NFC content. NFC had much smaller dimension than pulp fiber, therefore, the increase of NFC content created more bonding sites after mat formation. Relative bonding area (RBA) is one of the factors which affect tensile strength both of wet and dry sheet (Page 1969; 1993). In the case of a wet mat, the tensile breaking stress was maximized at 70% of NFC content in wet mat. The length of fiber as well as RBA had a positive effect on tensile breaking stress.

The strain at break of wet and dry mats with NFC content was represented in Fig. 3-11. The strain at break with NFC content showed a little difference up to 50% between wet and dry mat. In other words, the extension was almost the same between wet and dry mat until the break point. However, the extension of wet mat was higher than that of dry mat above 50% of NFC content. The different of strain at break between wet and dry mat might be
attributed to the existence of water between nanofibrils. That would be possible for acting capillary force if the distance is close enough to make meniscus. In this case, the capillary force might be effective from the NFC content was 50% (the ratio between NFC and pulp fiber was 5:5).

These two results remind us that the role of hydrogen bond between nanofibrils and capillary force. Because hydrogen bond occurs when two surfaces are closer than 5 Å, the increase in NFC content made the mat denser as the tensile elastic modulus was represented much higher in the dry mat (Fig. 3-12). Increasing NFC content represents the creation of more effective contact area.
Fig. 3-9. Stress-strain curves of mats with increasing NFC content. The solids content of the mat was 23%.
Fig. 3-10. Effect of mixing ratio of pulp fiber and NFC on tensile breaking stress.

Fig. 3-11. Effect of mixing ratio of pulp fiber and NFC on tensile strain.
Fig. 3-12. Elastic modulus of wet and dry mat as increase in NFC content.
3.3 Network properties with solids content

Rheological properties, especially elastic modulus and yield stress, were reported in many studies. Power law relationship was shown between those properties and consistency although the slopes had a little difference depending on the studies. Storage modulus or yield stress is known as proportional to the consistency to about the three orders of magnitude. However, testing consistency has been limited to 7%, in most cases. Therefore, when the consistency of NFC suspension is high, it could not be determined by a dynamic experiment due to the limitation of testing method. To achieve high solids content, specially designed pressurized dewatering equipment was used to adjust the consistency in this study.

Yield stress and critical strain of NFC with increasing solids content are represented in Fig. 3-13. Yield stress is generally accepted as network strength (Kurath 1959; Bennington et al. 1990; Kerekes and Schell 1992; Tatsumi and Matsumoto 2007). The network associated by nanofibrils began to break down from a certain point as the increase in shear strain. This point is referred to critical strain and it is a criterion which distinguishes the linear viscoelastic region and non-linear viscoelastic region (see, Fig. 3-3). In this experiment, the solids content was plotted up to 10.2%.

The network strength increased with an increase in solids content. On the contrary, critical strain decreased with an increase in solids content. This means that the rigidity of the network increased with increasing solids content.
Fig. 3-13. Yield stress and critical strain of NFC at lower consistency region (<10%).
The frequency sweep was also performed to find out the network properties of NFC suspension with increasing solids content. In the frequency sweep, a strain is generally fixed. From the result of the strain sweep, a strain of 1% was selected because it was below the critical strain as shown in Fig. 3-14.

The storage modulus of NFC suspension with frequency change was represented in Fig. 3-15. It was constant within the measured frequency range. The storage modulus was increased with an increase in solids content. Storage modulus means a restoring force per unit area. Therefore, the network of NFC was highly associated with an increase in solids content. Tan δ within this range of solids content was 0.3. This means the storage modulus was measured within the intact structure of NFC.

From the frequency sweep measurement, the viscosity could be obtained because the frequency is considered as a strain rate. The viscosity showed thixotropic behavior. This means that the viscosity was very high when it is high solids content, however it could be lowered by increase in shear rate at the level of NFC suspension at least 10% of solids content. The viscosity with change in solids content at the frequency of 10 Hz was compared as shown in Fig. 3-16. A power law relationship was presented, however it didn’t show any more increase over 10% of solids content. The storage modulus and the yield stress showed in Fig. 3-17. A power laws relationship was also presented. The exponent of each relationship was 2.87 and 2.52.
Fig. 3-14. Storage modulus of NFC suspension with change in frequency. The legend represents solids content.

Fig. 3-15. Viscosity of NFC suspension with change in frequency. The legend represents solids content.
Fig. 3-16. Viscosity of NFC suspension at the frequency of 10 Hz as the function of solids content.

Fig. 3-17. Storage modulus and yield stress of NFC mat as the function of solids content.
3.4 Tensile properties of NFC mat with an increase in solids content

It was found that the rheological properties measured by ARES for viscoelasticity was valid for up to 10% of solids content. It might be unsuitable for measuring the rheological properties because the NFC in mat-like state was too stiff to be measured by rheometer with dynamic mode. The ‘slip’ between plates might happen.

NFC mat in high solids content could be evaluated by tensile measurement using UTM. Stress-strain curves of the NFC mat with increasing solids content is shown in Fig. 3-18. The yield stress is shown in Fig. 3-19. The relationship between the yield stress and the solids content followed a power law relation. The exponent was 2.99.
Fig. 3-18. Stress-strain curves of the NFC mat with increasing solids content.

Fig. 3-19. The yield stress of the NFC mat by tensile measurement as a function of solids content.
The power law relationship between solids content and yield stress was still consistent at all measured range of solids content regardless of the methods of dynamic measurement and tensile measurement. Because the yield stress is the beginning of the breaking network, it is considered as network strength. Over the range of the all solids content, all data located in one line in log-log scale coordinates as shown in Fig. 3-20. The coefficient in the power law relationship was determined by the characteristics of fiber itself, such as aspect ratio, flexibility, and length etc. (Tatsumi and Matsumoto 2007). The exponent depends on the fiber volume fraction (Hill 2008). This means that the exponent is determined by the flocculation as a substructure in the network. In this study, the exponent was 2.74. Theoretically, the exponent is 3 with the assumption of fibers as a cylinder shape. Because the exponent in this experiment was 2.74, fractal dimension ($D_f$) was calculated as 1.4. This result was similar to Pääkkö et al. (2007).

The solids content was investigated over the wider range than previous studies. From this result, it was found that the flocculation behavior of nanofibillated cellulose is similar to pulp fiber although NFC has much higher aspect ratio and much smaller in dimension.
Fig. 3-20. Yield stress of NFC mat with increasing solids content. NFC mat with solids content of 1% - 10% was measured with ARES and NFC mat with solids content over 10% was measured using UTM.
The elastic modulus of NFC mat with solids content was obtained from the strain-stress curve. The elastic modulus increased exponentially with an increase in solids content as shown in Fig. 3-21. The elastic modulus was fitted well with solids content. The elastic modulus of wet paper also showed exponential relationship with solids content, approximately. (Jantunen 1985). The equation of elastic modulus was represented in Eq. 3-1 (Page 1993; Seth 1995).

\[
\frac{\sigma}{(d\epsilon/dt)} \propto \eta A_c N_c \quad [3-1]
\]

where, \(\eta\) is viscosity, \(A_c\) is effective contact area, and \(N_c\) is number of contact.

There is “water” between nanofibrils in wet mat because the surface of nanofibrils has a lot of hydroxyl groups. The increase in solids content made the water layers thin. The rigidity or stiffness of a wet mat is attributed to the surface tension, mechanical contacts, and maybe fibrillar entanglements that holds fibers together and contributes to the effective “friction” or “viscosity” of the inter-fiber contacts (Seth et al. 1984; Page 1993; Seth 1995). Therefore, it resulted in the increase in elastic modulus.
Fig. 3-21. Elastic modulus of NFC mat with solids content.

\[ y = 1.2195e^{0.0611x} \]

\[ R^2 = 0.993 \]
Fig. 3-22 shows the tensile strength and elongation of the NFC mat with an increase in solids content. The tensile strength was increased with increasing solids content. It showed a rapid increase from around 50%. Elongation increased with increasing solids content up to around 50% and decreased above that level of solids content.

The strain rate was kept at constant in UTM testing. The increase in tensile strength with solids content might be related to the interaction between nanofibrils. The contact number increased with increasing solids content because the decrease of water content resulted in getting nanofibrils closer. Campbell (1933) considered the Laplace pressure between two plates with water between them. Because of the negative curvature of the meniscus, these two plates attract each other. However, the attractive force becomes zero when the water reaches the edges of the plates. Evaporation of water results in the plates moving closer together without changing this force. Considering of a matrix which is a network composed of NFC, capillary force exists among nanofibrils. A modified Lucas-Washburn equation was represented in Eq. 3-2. The capillary force \( F = \Delta PA_{SL} \) might be increased as the distance between nanofibrils becomes closer.

\[
\Delta p = \frac{2\gamma \cos \theta}{r} \quad \ldots [3-2]
\]

Where, \( \Delta p \) is the driving pressure difference, \( \gamma \) is surface tension of water, and \( r \) is radius of curvature.
The increase in tensile strength of NFC mat can be explained by Eq. 3-1 as the same with pulp fiber because the flocculation structure of NFC might be similar to pulp fiber. The flocculation of NFC was similar to pulp fiber although the dimension is very small compared to pulp fiber. In this study, the exponent in power law relationship between yield stress and solids content was close to 3 over the solids content from 0.5% to 99%. Tatsumi et al. (2002) demonstrated that the network strength of cellulose fiber in the state of suspension was logarithmically proportional to aspect ratio. Seth (1995) reported that the wet strength was proportional to the fiber length and inversely proportional to the fiber coarseness. Because the coarseness of the fiber is related to the thickness of the fiber, the result may be also related to the aspect ratio.

The elongation showed an inflection point at around 50%. The increase in tensile strength might be attributed to the increase in strain until around 50% of solids content. It seemed that the dissipation of stress occurred before failure during deformation. The study about solids content and mechanical properties with pulp fiber showed that the phase lag (tanδ) between stress and strain was maximized at around 45% - 50% in dynamic measurement (Hanson et al. 1989). Tensile stiffness increased rapidly from around 45% of solids content (Hanson et al. 1989). These results meant the hydrogen bonding between fibers and fibers occurred from the solids content of around 45%. In this study, the elastic modulus showed exponential function with increasing solids content. The increasing tendency changed from around 40% as shown in Fig. 3-21.
One more interesting possibility that could be found from this result is that the water exists after pressing. The existence of water between nanofibrils means that there is a volume occupied by water until around 50% of solids content. There would be a possibility, if that volume by water displaced with air. It would be a method to control pore size and distribution by controlling solids content.
Fig. 3-22. Elongation and tensile strength of the NFC mat with increasing solids content.
4. Summary

In this study, the effect of nanofibrillation was evaluated by controlling the number of passes and mixing ratio. It was found that the nanofibrillation increased in tensile breaking stress. Tensile breaking stress of NFC increased by a fold difference of 5 - 20 compared to pulp fiber. The effect of solids content of the NFC mat on network properties was evaluated. The solids content of NFC mat was controlled from 0.5% to 99%. The rheological properties were evaluated by an ARES with strain sweep mode and frequency sweep mode. The yield stress of NFC suspension had a power law relationship with solids content up to about 10%. A UTM was used to evaluate tensile properties of NFC mat at high solids content, more than 10%. The yield stress showed also the power law relationship. The exponent (2.74) indicated that the flocculation of nanofibrils were similar with pulp fiber, although the aspect ratio is much higher and the dimension is much smaller than pulp fiber. However, NFC forms network from a lower consistency (0.2%) and the network strength is much higher than pulp fiber. The tensile breaking strength also followed the power law relationship. Nanofibrillation increased tensile breaking stress and strain at break at all solids content measured. NFC mat of 25% has a similar tensile breaking stress to pulp fiber mat of 50%.
Chapter 4.

Effect of polyelectrolyte addition on fundamental properties of NFC
1. Introduction

Polyelectrolytes are used in the papermaking process to enhance diverse performance such as retention, air removal, increase in paper properties. A lot of polyelectrolytes are generally used in the papermaking process.

In the previous chapter, it was found that the network strength of nanofibrillated cellulose reflected a power law relationship and the exponent indicated that NFC flocculated a similar structure to pulp fiber, even if high solids content of more than 10% was evaluated, although the aspect ratio was much higher and the dimension was much smaller than pulp fiber.

Wahren (1964) suggested that fiber flocs could be considered as the fragment of the fiber network which was formed by mechanical entanglement. It is often considered that network strength depends on floc strength. The influence of the ions on the fiber flocculation was studied by Bjellfors et al (1965). They suggested that the flocculation by the different ionic form had a different effect on shear modulus.

Hubbe (2007) reported a review article about flocculation and redispersion of cellulose fiber suspensions. He defined the flocculation phenomenon of cellulose fiber as a matter of size. Two size regimes were considered. At a molecular scale, it was determined by surface interaction such as electrostatic, dispersion, and polymer bridging forces. At a macroscopic scale, fiber content and relationship between length and
thickness of fiber determined the flocculation phenomenon.

Two attraction mechanisms are typical of pulp fiber with polyelectrolyte in papermaking process. One is bridging attraction (La Mer and Healy 1963; Gregory 1976) and the other is charged-patch attraction (Pfau et al. 1999; Horn 2001). The polyelectrolyte which has the molecular weight of 4 - 20 million was used for bridging attraction for pulp fiber. High charge density and low molecular weight polyelectrolyte showed charged-patch attraction. The difference of the two attraction mechanisms can be determined by the strength of flocculation under shear condition. The flocculation by bridging attraction is irreversible, however, that by charged-patch attraction is reversible.

In the case of chemical treatment, the meaning of flocculation is generally accepted when using high molecular-mass polyelectrolyte. There are some words representing the state of flocculation. The words “agglomeration” and “deposition” means solid objects remaining in contact and “coagulation” means charge neutralization or localized electrostatic effects. Even if there is a repulsive force by surface charge in the suspension, the formation of clumps or plugs of fibers would occur by mechanical and hydrodynamic reasons Hubbe (2007).

Most research of pulp fibers about rheological properties focused on the low consistency because it was proper consistency for transportation, storage, and dewatering in the use in papermaking process, generally. However, the
network strength of NFC is much higher than pulp fiber because of the high aspect ratio and large surface area, meaning high contact number between nanofibrils at the same solids content.

Swerin (1992) reported that the critical strain of pulp fiber suspension above 4% with cationic polyelectrolytes was independent on the polyelectrolyte additions. Those experiments were performed with a low strain, a low addition amount of cationic polyelectrolytes, and high molecular weight of polyelectrolytes. Even though the effect of polyelectrolyte was not observed with pulp fiber, there would be brought about different results with the NFC suspension. Supposing that the polyelectrolytes cover about 100 nm of gyration radius at best, the dimension between pulp fiber and NFC differs significantly, especially in the case of molecular scale flocculation.

The flocculation is a matter of the volume fraction and it was found that the flocculation of macroscopic scale, such as solids content, which was confirmed in the previous chapter, followed the phenomenon of pulp fiber. However, there would be still the possibility of changing network properties of NFC by polyelectrolyte.

In this chapter, the effect of polyelectrolyte on network properties of NFC was investigated. Shear modulus and yield stress were evaluated by strain controlled rheometer. Dewatering of NFC suspensions was evaluated with the consistency of the network formed (1.5%) and with the consistency of non-associated state (0.02%). At high solids content, more than 20% which was
achieved by the pressing process, mechanical properties were evaluated to find out the effect of polyelectrolytes on the NFC mat.
2. Materials and methods

2.1 Pulp

Bleached Eucalyptus kraft pulp was used as raw material.

2.2 Polyelectrolytes

Polyethyleneimine, poly(diallyldimethyl ammonium chloride), Cationic polyacrylamide, poly(sodium 4-styrene sulfonate) were used. They had different molecular weight, charge density and structure. The properties of the polyelectrolytes used were shown in Table 4-1.

2.3 Preparation of nanofibrillated cellulose

Preparation of NFC was performed in two steps, mechanical pretreatment and grinding. The mechanical pretreatment was performed with a laboratory Valley beater. Beating degree was 450 mL CSF. NFC was prepared at 2% using a grinder (Super Masscolloider, Masuko Co.).

2.4 Addition of polyelectrolytes to NFC suspension

Polyelectrolyte solution with 1% concentration (1 wt %) was added to a NFC suspension under a shear condition of 1300 rpm. After adding polyelectrolyte, the final consistency of suspension was adjusted to 1.5%. Because PEI is affected by pH condition, NFC suspension with PEI was
adjusted to pH 6. Other polyelectrolytes which are independent on pH condition were added to NFC suspension at pH 7. The addition amount was 1%, 3%, 5%, 7% and 10% on oven dried weight of NFC.

1.5% of the NFC suspension with polyelectrolyte was diluted to 0.01% suspension with deionized water for the measurement of zeta potential. Zetasizer (Nano-ZS, Malvern instrument, USA) was used for the zeta potential measurement.
Table 4-1. Properties of polymers

<table>
<thead>
<tr>
<th>Structure</th>
<th>Polyelectrolyte</th>
<th>ID</th>
<th>Molecular weight, g/mol</th>
<th>Charge density, meq/g</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Branched</td>
<td>Polymethyleneimine</td>
<td>LmPEI</td>
<td>-2,000</td>
<td>+6.4~6.5</td>
<td></td>
</tr>
<tr>
<td>Cationic</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Sigma-aldrich</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HmPEI</td>
<td>-750,000</td>
<td>@ pH 6(^a)</td>
<td></td>
</tr>
<tr>
<td>Linear</td>
<td>poly(diallyldimethyl ammonium chloride)</td>
<td>LmPD</td>
<td>100,000 -200,000</td>
<td>+6.1(^b)</td>
<td></td>
</tr>
<tr>
<td>Cationic</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Songkang</td>
</tr>
<tr>
<td></td>
<td>Cationic-polyacrylamide</td>
<td>CPAM</td>
<td>2,000,000</td>
<td>+2.5(^a)</td>
<td></td>
</tr>
<tr>
<td>Linear</td>
<td>poly(sodium 4-styrene sulfonate)</td>
<td>LmPSS</td>
<td>200,000</td>
<td>-4.7(^a)</td>
<td>Sigma-aldrich</td>
</tr>
<tr>
<td>Anionic</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>HmPSS</td>
<td>1,000,000</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Measured by PCD-02

\(^b\) According to the supplier
2.5 Dewatering ability

The dewatering ability of NFC suspension was evaluated by measuring drainage time under vacuum and pressurized condition. In vacuum condition, the NFC suspension which was polyelectrolyte added was diluted to 0.02% and 80% of water that was drained from the suspension of 100 mL was measured. The vacuum condition was -75 kPa. In pressurized condition, NFC suspension was prepared with 1.5% as the state of polyelectrolyte added. The suspension was drained using Pressurized Dewatering Equipment. The pressure was controlled at 7 bar. Drained water was measured continuously by balance (CUX4200H, CAS Co., Korea). The diameter of vessel was 70 mm and maximum capacity was 250 mL. Dewatering time was evaluated for 68% of water drained.
2.6 Rheological properties

Rotational viscosity at steady state flow was measured with stress-controlled Bohlin rheometer using parallel plate geometry \((\phi = 40 \text{ mm})\). The gap size was 1 mm. A shear rate from 0.07 s\(^{-1}\) to 100 s\(^{-1}\) was controlled. At the mid-point (1 s\(^{-1}\)) within the performed shear rate range, “Hysteresis index” was evaluated as shown in Eq. 4-1 and Fig. 4-1

\[
\text{Hysteresis index} = A - B \quad [4-1]
\]

where, A is the viscosity at 1 s\(^{-1}\) while shear rate increases and B is the viscosity at 1 s\(^{-1}\) while shear rate decreases.

The rheological properties of NFC suspension were measured by ARES using parallel plate geometry \((\phi = 50 \text{ mm})\). The gap between the plates was controlled to 1 mm. The samples were allowed to rest five minutes in the geometry before each test. Yield stress was the stress at critical strain at strain sweep mode while constant frequency of 1 Hz (\(=6.28 \text{ rad/s}\)) was allowed. Frequency sweep was performed with a constant strain of 10% between 0.5 Hz and 500 Hz.
Fig. 4-1. Thixotropic behavior of NFC suspension.
2.7 Flocculation of nanofibrillated with polyelectrolytes by automated imaging system

A size analysis of the NFC flocs affected by polyelectrolyte was performed using automated imaging system (FlowCAM, Fluid Imaging Technologies, USA). Polyelectrolyte added NFC suspension was diluted to 0.1%. The flow rate was controlled to 0.5 mL/min. The suspension passed through rectangular channel of 100 μm in depth. The floc size below 5 μm in diameter did not include for calculation of NFC. The measurement was continued until 50,000 images were taken. The area of each image was calculated and the average area was compared with the polyelectrolyte and its addition amount. Typical images obtained by FlowCAM during measurement is shown in Fig. 4-2.
Fig. 4-2. The images obtained from FlowCAM.
2.8 Mechanical properties

Mechanical properties of the NFC mat were evaluated by UTM (Universal Testing Machine, Instron, USA) as the state of wet and dry. The strain rate was kept constant at 10%/min. The width of the NFC mat was 15 mm. The length of the NFC mat was 20 mm. The thickness was around 1 mm in the case of the wet mat and 0.2 mm in the case of the dry mat.

2.9 Measurement of shrinkage after freeze drying of the nanofibrillated cellulose suspension

Prepared NFC suspension with polyelectrolyte was poured in the petri-dish of 49 mm in diameter and 7 mm in depth. The shrinkage of the NFC mat after freeze drying was calculated as described in Eq. 4-2.

\[ Shrinkage = \frac{\Delta \phi}{\phi} \times 100 \quad \cdots \quad [4-2] \]

where, \( \phi \) is the diameter of NFC mat before freeze drying, \( \Delta \phi \) is the diameter change of NFC mat after freeze drying.

The procedure of measurement was represented in Fig 4-3.
Fig 4-3. The procedure of shrinkage measurement with the NFC mat.

Freezing (-20°C)

Freeze drying
(-79°C, 5 mTorr)
3. Results and discussion

3.1 Zeta potential of NFC with polyelectrolytes

The zeta potential of NFC was -44 mV. The zeta potential of NFC which was changed by the addition of the polyelectrolyte was represented in Figs. 4-4 - 4-6. The zeta potential of NFC was changed from the negative charge to the positive one by the adsorption of the cationic polyelectrolyte. The adsorption of polyelectrolyte on NFC was dominated by electrostatic attraction (Elimelech et al. 1994).

The addition amount to achieve the isoelectric point (ISP) of NFC by PEI was approximately 0.7% - 0.8%. The effect of the molecular weight on the change of the zeta potential differed depending on the addition amount below and above around isoelectric point. A higher molecular weight increased the zeta potential of NFC higher at the same addition amount above the ISP. There may have been more of an opportunity for free-bonding ions to remain after the adsorption on the NFC surfaces. However, the effect of the molecular weight on the zeta potential was opposite below the isoelectric point. Because the increase in the zeta potential is determined by overcompensation, a higher molecular weight increased the zeta potential more than a lower molecular weight. In terms of site-bonding theory (Yates et al., 1974), the site of a positively charged NFC surface encounters another site of a negatively charged NFC surface. This indicates that the coagulation of NFCs (by charge neutralization) is easier when a polyelectrolyte with a higher molecular weight
is used. Consequently, the net charge of the NFC suspension with a high molecular weight was lower below the isoelectric point.

The addition amount to achieve the ISP of NFC by poly-DADMAC was around 0.6%. The difference between the molecular weights was not clear. The difference in the zeta potential between PEI and poly-DADMAC with a 1% addition was 20 mV - 30 mV. The maximum zeta potential toward the positive side was greater than 60 mV. In the case of PEI, it was below 60 mV. Compared to the branched type PEI, poly-DADMAC has the potential for free-bonding ions to remain after the polyelectrolyte was adsorbed on the NFC surface is greater because the configuration of the linear type of polyelectrolyte adsorbed on the NFC surface tends occur in the form of loops and tails (Rojas et al., 1998). The charge density level of the PEI and poly-DADMAC were similar in this study.

CPAM, a polyelectrolyte with a relatively low charge density and high molecular weight required a much greater addition amount for NFC to be neutralized. In the case of CPAM_H which had a slightly higher charge density than CPAM, the isoelectric point was reached with an addition amount of 1.3%. The rapid increase in the zeta potential by CPAM_H was attributed to the higher charge density compared to CPAM.
Fig. 4-4. Zeta potential of NFC with addition amount of PEI.
Fig. 4-5. Zeta potential of NFC with addition amount of poly-DADMAC.
Fig. 4-6. Zeta potential of NFC with addition amount of CPAM.
3.2 Effect of polyelectrolytes on the dewatering ability

The dewatering time to take to drain 68% of water from 1.5% NFC suspension (60 g) was shown in Figs 4-7 - 4-9. A shorter dewatering time indicates a better dewatering ability.

The NFC suspension with LmPEI added showed that the dewatering ability increased up to 1% with addition amount and maintained over 1% of addition amount. However, NFC suspension with addition of HmPEI showed that the dewatering ability was increased up to 0.5% and it was deteriorated again when the addition amount increased more than 1% (Fig.4 -7). The dewatering time with addition of poly-DADMAC is shown in Fig. 4-8. The dewatering ability was maximized at 1% of addition amount. The difference in the molecular weight was not shown clearly. However, an excessive addition of poly-DADMAC with a high molecular weight decreased the dewatering ability. CPAM showed that the dewatering ability was maximized at 5% of addition amount. However, CPAM_H showed that 1% was enough to maximize the dewatering ability (Fig. 4-9). The addition of PSS to the NFC suspension decreased the dewatering ability, as shown in Fig. 4-10. The consistency of NFC suspension was 1.5% which was highly associated state. The anionic polyelectrolyte acted as a dispersant, which prevented nanofibril flocculating. Therefore, the network structure of NFC developed did not have efficient dewatering channel.

The increase in the dewatering ability was due to securing the dewatering
channel which was attributed to the flocculation. The increase in electrostatic attraction between nanofibrils by addition of cationic polyelectrolyte increased dewatering channels. For the PEI and poly-DADMAC, the maximized addition amount was close to the isoelectric point.

LmPEI showed superior dewatering ability, even with a large addition amount, as shown in Fig 4-7. This indicates that the flocculation phenomenon was different depending on the molecular weight of the PEI. Polyelectrolyte with high charge density gave the better dewatering ability of NFC suspension because the floc strength was attributed to the bonding strength as induced by electrostatic attraction.
Fig. 4-7. Dewatering time of the NFC suspension with addition of PEI.
Fig. 4-8. Dewatering time of the NFC suspension with addition of polye-DADMAC.
Fig. 4-9. Dewatering time of the NFC suspension with addition of CPAM.
Fig. 4-10. Dewatering time of the NFC suspension with addition of PSS.
Vacuum dewatering was performed with a diluted suspension state of 0.02% and the dewatering ability was evaluated with an addition of PEI, as shown in Fig. 4-11. The dewatering ability increased was compared to the NFC suspension without polyelectrolyte. The dewatering ability was maximized with a 1% of addition amount which was close to the isoelectric point by PEI. This indicates that the dewatering channels were maximized with the addition amount to reach the isoelectric point. This result is similar to the pressurized dewatering result, as shown in Fig. 4-7.

The relative effect of the molecular weight around the isoelectric point on the dewatering ability showed different result. Because the flocculation phenomenon is strongly related to the dewatering ability, the results attributed to the difference in the molecular weight are important. A cationic polyelectrolyte with a higher molecular weight has more charged ions in its functional group. Therefore, the flocculation below the isoelectric point and deflocculation above the isoelectric point proceeded more quickly.
Fig. 4-11. Vacuum dewatering time of diluted NFC suspension with addition of PEI.
3.3 Rheological properties of NFC with polyelectrolytes

3.3.1 Effect of polyelectrolytes addition on the viscosity and the hysteresis of the NFC suspension

The viscosity flow curves of the NFC suspension with the LmPD was added with increasing addition amount is shown in Fig 4-12. When 1% of LmPD added NFC suspension showed noticeable difference in viscosity. It showed great difference in viscosity compared to other addition amount condition. The addition amount of 1% turned the surface charge of NFC close to isoelectric point. This indicates that the change of viscosity flow curve may be attributed to the flocculation behavior of NFC

The changes in the viscosity of the NFC suspension with the addition of polyelectrolyte were evaluated. The viscosity at the shear rate of 1 s\(^{-1}\) of NFC suspension with polyelectrolyte was shown in Figs. 4-13 and 4-14. It appeared that the viscosity of the NFC suspension was mostly independent of the addition amount of polyelectrolyte significantly although small differences were observed. Karppiene et al. (2011) reported that a cationic and amphiphilic polyelectrolyte increased the flow viscosity with increasing addition amount although the behavior on shear rate was different.

This discrepancy might be because of the higher consistency of the suspension tested compared to the previous studies. The increase of consistency might reduce the effect of flocculation by polyelectrolyte because
the flocculation structure would be tightened much more with increasing consistency. In this study, the consistency of NFC was 1.5% which was highly associated. However, Karppiene et al. (2011) tested with 0.5% suspension.

The viscosity was nearly maintained with an addition of LmPEI. The molecular weight of LmPEI was 2,000 g/mol, suggesting a very small size. There may be little possibility flocculating due to a bridging attraction. However, the friction force between the nanofibrils may be increased due to patch attraction. Considering that the LmPEI was effective for enhancing the dewatering ability, the floc strength induced by LmPEI may also increase, maintaining the size of “NFC flocs” as a fragment of the network (Saarikoski et al. 2012). The viscosity was decreased by HmPEI, despite the fact that it was a cationic polyelectrolyte. The friction between the nanofibrils may have been decreased by steric force rather than electrostatic attraction. The value was rather odd at 1% of added amount because the net surface charge of the NFC was neutralized, which promote the flocculation by reducing electrostatic repulsion. However, the repulsive force was dominant above the isoelectric point. The steric force and electrostatic repulsion by polyelectrolyte also had an effect. Anionic polyelectrolytes decreased the viscosity of the NFC suspension. The polyelectrolyte with a higher molecular weight was added to NFC suspension, a greater decrease in the viscosity was noted. Peterson (1994) and Beghello (1998) reported the presence of debris acting as a lubricant during flocculation. In a state with no electrostatic attraction, polyelectrolyte can act as a lubricant. Therefore, further effect was not noted
on the viscosity after the additions. Considering that the width of the NFC was 5 nm - 50 nm, the distance between the nanofibrils was very close enough to affect the viscosity change due to the polyelectrolytes.

A linear type of cationic polyelectrolyte was added to the NFC suspension and the viscosity was shown to increase with addition amount, as shown in Fig. 4-13. HmPD and CPAM had little effect on the viscosity. However, LmPD showed a different result compared to others. Once a small amount of LmPD was added (1%), the viscosity decreased significantly. However, the viscosity increased with increasing addition amount of LmPD. Patch-like attraction may appear in NFC because LmPD has linear structure and a low molecular weight.

The heterogeneity of the network structure of the NFC suspension, which was caused by the flocculation was due to the charge neutralizing. However, the increasing addition amount of LmPD decreased the heterogeneity of the network structure of the NFC suspension. From the results above, it was found that the viscosity of the NFC suspension as changed by the polyelectrolyte was majorly affected by the molecular weight.
Fig. 4-12. Viscosity of NFC suspension with LmPD was added to NFC suspension.
Fig. 4-13. Viscosity at the shear rate of 1 s$^{-1}$ of NFC suspension by addition of PEI and PSS.

Fig. 4-14. Viscosity at the shear rate of 1 s$^{-1}$ of NFC suspension by addition of poly-DADMAC and CPAM.
The NFC suspension in the steady state flow shows shear thinning behavior. This result was also reported in previous studies (Ono et al. 2004; Iotti et al. 2011; Lasseguette et al. 2008). However, the viscosity hysteresis between increasing shear rate (up-curve) and decreasing shear rate (down-curve) was rarely reported (Iotti et al. 2011). It can help to understand deformation and reformation of NFC structure. NFC suspension of 1.5% consistency was evaluated. The viscosity showed a logarithmic decrease with an increase in the shear rate. Compared to other studies which used a consistency of 0.5%, the “shoulder” at the shear rates of 0 s\(^{-1}\) - 50 s\(^{-1}\) and 2 s\(^{-1}\) - 20 s\(^{-1}\) did not appeared clearly which might be because of a higher consistency of NFC suspension in this experiment (Iotti et al. 2011; Lasseguette et al. 2008; Karppinen et al. 2011).

The hysteresis index was determined the difference in viscosities by increasing and decreasing shear rate. It is because of energy loss while shear rate increased that the down-curve falls below the up-curve. The flow curves of NFC suspension with 5% of PEI were shown in Fig 4-15.

The gap between up and down flow curves at 1 s\(^{-1}\) was different depending on addition amount and polyelectrolyte type. In the case of NFC without polyelectrolyte, the hysteresis index was 12.5 Pa\(\cdot\)s. When LmPEI was added to the NFC suspension by 5%, the hysteresis index increased to 20.6 Pa\(\cdot\)s. However, it decreased down to 2.5 Pa\(\cdot\)s when HmPEI was added to the NFC suspension by 5%. In that the up curve viscosity for each condition had similar located value as shown in Fig 4-15, the hysteresis index was
determined by the value of the down flow curve. The hysteresis is related to the reformation of the NFC structure. When the hysteresis index is small, the reformation of the structure may occur more rapidly after it is aligned, following the flow direction at a high shear rate.
Fig. 4-15. Thixotropy of NFC suspension with PEI by 5%.
The effect of polyelectrolyte type and addition amount on hysteresis indices were depicted in Figs. 4-16 - 4-18. The effect of the molecular weight of PEI was shown in Fig. 4-16. For the hysteresis index, a large difference was shown with the molecular weight of PEI.

The effect of the linear cationic polyelectrolyte is shown in Fig. 4-17. LmPD showed gradually increase in the hysteresis index with an increase in the addition amount. On the other hand, HmPD showed decrease of hysteresis index. CPAM with a higher molecular weight and a lower charge density than poly-DADMAC also showed a greater decrease in the hysteresis index.

It was suggested that polyelectrolyte with high molecular weight had a great impact on the reformation of the structure of NFC suspension. Because the reversion of the surface charge of NFC occurred over than 1% of addition amount for most polyelectrolytes, electrostatic repulsion might act between nanofibrils. A higher molecular weight had a greater effect in this situation.
Fig. 4-16. Hysteresis index of NFC suspension with PEI with different molecular weights (M<sub>w</sub> 1,800 vs. M<sub>w</sub> 750,000).

Fig. 4-17. Hysteresis indices of NFC suspensions with poly-DADMAC and CPAM.
The addition of PSS decreased the hysteresis index of the NFC suspension (Fig. 4-18). This also occurred on account of the electrostatic repulsion between the NFC and the PSS. Although PSS was not absorbed on the NFC surface, it affected the hysteresis of the NFC suspension. This implies that the PSS in the NFC suspension can be understood through the concept of colloidal particles, considering that the dimension of the polyelectrolyte and the width of the NFC are comparable.
Fig. 4-18. Hysteresis index of NFC suspension with PSS with different molecular weights ($M_w$ 200,000 vs. $M_w$ 1,000,000).
3.3.2 Effect of polyelectrolytes addition on the network strength of the NFC suspension

When the strain increased during a strain sweep test, the network of the nanofibrils reached the yield point, at which the network begins to break down. The yield stress was shown to be a function of the addition amount depending on the different types of polyelectrolyte in Figs. 4-19 - 4-21.

A break of the network occurred after the expansion of the NFC network. The characteristics of polyelectrolytes can affect the behavior of the extension and break down the NFC network. The network strength of NFC mainly depended upon the interlocking of elastically bent fibers, which indicated floc strength (Bennington et al. 1990). Therefore, the role of the polyelectrolyte can be determined in terms of how much it changed the network strength.

The effect of the molecular weight of polyelectrolyte on the network strength showed opposite results according to the structure of the polyelectrolyte. The branched type polymer with a higher molecular weight showed higher network strength, as shown in Fig. 4-19 However, in the case of the linear type polymer showed a lower molecular weight one increased the network strength, as shown in Fig. 4-20. Considering that electrostatic attraction between nanofibrils as caused by a cationic polyelectrolyte may not appear with the added amount exceeds 1%, the increase in the network strength is attributed to the structural changes of the NFC. HmPEI induced stronger flocculation of nanofibrils. On the contrary, polymer with higher molecular
weight and low charge density like CPAM made weaker floc, as shown in Fig. 4-21.

Swerin (1998) reported the rheological properties of cellulosic fiber suspensions flocculated by cationic polyacrylamides. There existed the optimum addition amount and charge density to increase the elastic shear modulus. Similarly, this phenomenon appeared in NFC with the linear type polyelectrolyte, as shown in Fig. 4-21.

Comparing the network strength depending on the structure of the polyelectrolyte, branched type showed higher yield stress. The network strength is attributed to the floc strength and the floc density. The flocculation of NFC by the polyelectrolytes with patch or bridging attraction determined the density of floc. When the polyelectrolyte was adsorbed on the surface of nanofibril in flat, the floc density would be greater than by bridging attraction. Because the dimension of NFC is much smaller than pulp fiber, the adsorption mechanism of polyelectrolyte on the surface of nanofibrils was different depending on the type, such as the structure and charge density. Swerin (1993) reported that the fibre flocculation is influenced both by the added amount and the charge density.

The PSS of an anionic polyelectrolyte cannot be flocculated with NFC by electrostatic attraction. Nevertheless, HmPSS decreased the network strength. This result is related to the result of the viscosity, as shown in Fig. 4-21.
Fig. 4-19. Yield stress of NFC suspension with addition of PEI.
Fig. 4-20. Yield stress of NFC suspension with addition of poly-DADMAC and CPAM.
Fig. 4-21. Yield stress of NFC suspension with addition of PSS.
3.4 Effect of polyelectrolytes on the flocculation of NFC

The size distribution of spherical material can be determined rather easily by dynamic light scattering method. However, NFC flocs is not easy to be determined because of the shape. In this study, automated imaging system was used to determine the flocculation degree of NFC by polyelectrolyte. 50,000 images were taken automatically by camera and the area of flocs was evaluated. Flocculation of NFC by polyelectrolyte could be compared using this result.

The area of the NFC flocs as changed by addition of PEI is shown in Fig. 4-22. The area increased rapidly up to an added amount of 1%. LmPEI caused the area to increase slowly and then level out with 1% of added amount. However, HmPEI caused the area to decrese. In the case of poly-DADMAC, the area was largest at and added amount of 0.5% which was close to isoelectric point. However, CPAM showed a gradual increasing trend with an increase in added amount (Fig. 4-23). In the cases of HmPEI and poly-DADMAC, the results were feasible considering the zeta potential. However, the added amount to maximize the area showed only a slight difference from the expected amount in this cases of LmPEI and CPAM. However, if the relationship between the size of flocculation and dewatering ability is considered, the larger size of NFC flocs is related to the better dewatering ability. This is not a perfect match because the flocculation density could not be determined by the automated imaging technique.
Fig. 4-22. The size of NFC flocs with addition of PEI.

Fig. 4-23. The size of NFC flocs with addition of poly-DADMAC and CPAM.
3.5 Effect of polyelectrolytes on the mechanical properties

The mechanical properties of NFC mats were evaluated using UTM. The effect of type and addition amount of polyelectrolyte on the tensile properties of wet and dry mats were evaluated. There would be two possible aspects which affected tensile properties. One is the electrostatic attraction between the nanofibrils, and the other is the floc as a substructure consisting network. The rheological properties of pulp fiber were not affected by the cationic polyelectrolyte above 3% of consistency (Swerin 1992). This needs to be evaluated at high solids content of NFC with the polyelectrolyte.

The tensile breaking stress and strain at break of the NFC mat with PEI are shown in Figs. 4-24 - 4-25. For a wet mat (the solids content was 23%), the addition of PEI increased the tensile breaking stress. LmPEI showed a much greater increase than HmPEI, especially at the small addition amount. However, it did not show any significant change by PEI for a dry mat. It was noted that as the strength between the nanofibril was very strong in the case of a dry mat, the PEI had no effect.

The effect of the molecular weight of PEI differed between a wet mat and a dry mat. A higher molecular weight showed superior network strength compared to a lower molecular weight, when it was added to the NFC suspension. However, a lower molecular weight showed a greater tensile breaking stress with a wet mat. The network strength was logarithmically proportional to the solids content due to the denser floc of NFC with
increasing solids content. When a cationic polyelectrolyte added, larger floc induced by a higher molecular weight of the PEI showed a higher network strength in the suspension. However, the tensile breaking stress showed opposite behavior because a less dense floc was induced by the higher molecular weight. When the mat was oven-dried, the steric force between the nanofibrils caused by the polyelectrolyte mostly disappeared due to the strong force of hydrogen bonding.
Fig. 4-24. Tensile breaking stress of NFC wet and dry mats with PEI.

Fig. 4-25. Strain at break of NFC wet and dry mats with PEI.
The cationic linear type polyelectrolytes did not show a meaningful difference in terms of their molecular weights (Figs. 4-26 - 4-29). However, the tensile breaking stress of the NFC wet mat increased with an increase in addition amount of the cationic polyelectrolyte. This can be attributed to the increase of strain. When poly-DADMAC and CPAM were compared, CPAM showed a lower strain at break and tensile breaking stress of wet mat. A higher molecular weight polyelectrolyte prevented the nanofibrils approached. When the addition amount was increased, the strain at break and the tensile breaking stress was decreased.

The mechanical properties of the NFC dry mats with poly-DADMAC are shown in Figs. 4-26 - 4-27. The effect of the molecular weight of the polyelectrolyte was not noticeable in general. Only 10% of addition amount which was excessive amount slightly showed the difference both PEI and poly-DADMAC. The distance between the nanofibrils of the dry mat was very close regardless of the existence of a polyelectrolyte. Therefore, if there were any differences caused by the polyelectrolyte, they would stem from the flocculation of the NFC rather than from electrostatic interaction.

The strain at break and the tensile breaking stress were evaluated when PSS and CPAM were added on NFC, as shown in Figs. 4-27 and 4-28. A difference was not noted in the strain at break between the wet and dry mat. On the other hand, a difference was noted in the tensile stress in the case of the wet NFC mat.
Fig. 4-26. Tensile breaking stress of NFC wet and dry mats with poly-DADMAC.

Fig. 4-27. Strain at break of NFC wet and dry mats with poly-DADMAC.
Fig. 4-28. Tensile breaking stress of NFC wet and dry mats with CPAM and PSS.

Fig. 4-29. Strain at break of NFC wet and dry mats with CPAM and PSS.
3.6 **Effect of polyelectrolytes addition on shrinkage of the NFC gel**

The shrinkage of the NFC gel in terms of its diameter after freeze drying is shown in Figs. 4-30 and 4-31. The addition polyelectrolyte by 1% shrunk the NFC more compared to NFC without a polyelectrolyte. From the aspect of addition amount, the shrinkage of NFC gel was increased up to around 1% and then decreased over this dosage. Because freeze drying minimized the effect of the meniscus of the water, the shrinkage have resulted due to a change of a substructure, which is flocculation of NFC. Flocculation of NFC increased the shrinkage because the attraction of each nanofibrils caused the decrease from the volume of the NFC gel. However a higher addition amount reduced the shrinkage of the NFC mat because of electrostatic repulsion. Excessive addition amount decreased the shrinkage below that of an untreated NFC suspension.
Fig. 4-30. Drying shrinkage of NFC suspension with addition of PEI.

Fig. 4-31. Drying shrinkage of NFC suspension with addition of poly-DADMAC and CPAM.
4. Summary

The effects of a polyelectrolyte on the mechanical properties of NFC were evaluated. The zeta potential of NFC with a polyelectrolyte and addition amount was measured and the electrostatic interaction between nanofibrils was determined from the results. The viscosity and the hysteresis index indicated that structure type and the molecular weight of the polyelectrolytes determined the reformation of the network structure after it was deformed by an increase in the shear rate. The dewatering ability of the NFC suspensions in a diluted state (0.02%) and in a highly associated state (1.5%) was evaluated. The flocculation behavior of NFC with polyelectrolyte influenced the dewatering ability. A higher molecular weight of a polyelectrolyte showed mostly better dewatering with a proper addition amount which was close to the isoelectric point. However, over dosages of the NFC suspension decreased the dewatering ability. Polyelectrolyte with a high molecular weight and high charge density promoted the decrease of dewatering ability. The PSS decreased the dewatering ability. Not only the electrostatic interaction, but also steric forces acted between the polyelectrolyte and NFC. The mechanical properties, including rheological properties of NFC were affected by polyelectrolytes. The addition amount and the molecular weight of polyelectrolyte were both important in the mechanical properties of NFC in suspension and mat state. This indicates that the flocculation of NFC affected by the polyelectrolyte at the molecular level. The NFC suspension was influenced by the polyelectrolyte in terms of the network strength, the strain at break, and the tensile breaking stress.
Chapter 5.

Overall conclusions and future work
NFC has great potential as a new material in cosmetics, automobiles, pharmaceutical and medical science, electrical devices, papermaking industry, and other applications. NFC has a high aspect ratio and hydrophilic characteristics that leads to unique rheological properties and network forming ability from even low consistency. NFC suspension may have several processes such as transferring, dewatering and drying to use as the shape of sheet or foam. Therefore, the network properties and mechanical properties of NFC need investigation and better understanding. This study was carried out to investigate the fundamental properties of nanofibrillated cellulose and the possibility of changing the network properties by polyelectrolyte. Diverse evaluations in nanofibrillation of cellulose pulp fiber were performed. The network properties were evaluated by dynamic and tensile measurements. The effects of nanofibillation, increase in solids content of NFC, and polyelectrolyte on the network properties were investigated.

NFC was prepared and characterized. The morphology, water retention value, sedimentation concentration, dewatering property and rheological properties were investigated. The degree of nanofibrillation from pulp fiber can be determined by an evaluation of those characteristics. In this study, no further change by a mechanical treatment (grinding) of pulp fiber was noted after than 15 - 20 passes. However, it may be more important that the characteristics of NFC should be considered depending on the level of demand for further applications. The dewatering abilities of pulp fiber and NFC were compared. It was found that the initial consistency of NFC was significantly affected by its specific resistance to filtration. NFC showed a higher specific resistance to filtration by tenfold compared to pulp fiber at a consistency of 2%. This indicates that a conventional dewatering process
during papermaking is highly limited in the case of NFC.

The effects of the solids content of a NFC mat on the network properties were investigated with the rheological and tensile properties. It was difficult to adjust the solids content of NFC. In this study, however, the solids content of NFC could be adjusted up to 20% by controlling the dewatering time using pressurized dewatering equipment. The solids content more than 20% could be gained by controlling the drying time at room temperature. The rheological properties were evaluated in strain sweep mode and frequency sweep mode. In the case of NFC suspension, the yield stress had a power law relationship with the solids content up to 10%. In the case of NFC mat, the tensile properties were evaluated at high solids content, more than 10%.

The yield stress had a power law relationship with the solids content over a wide range from 0.5% to 99% independent of the measurement method. Elastic modulus, tensile breaking stress and strain at break are evaluated. A power law relationship with a wide range of solids content was evaluated. The exponent was close to 3 that indicated the flocculation behavior of nanofibrils were similar to pulp fiber, although the aspect ratio is much higher and the dimension is much smaller than pulp fiber. However, NFC formed the network structure from 0.2% which was 2 times lower than that of pulp fiber, and the network strength is 5 - 20 times higher than pulp fiber with solids content. The elastic modulus and tensile breaking stress increased exponentially as a function of solids content. The wet strain at break of pulp fiber decreased gradually. However, the NFC increased until 50% of the solids content. The nanofibrillation of pulp fiber increased the tensile breaking
stress and strain at break within all solids content tested. NFC mat of 25% has a similar tensile breaking stress to pulp fiber mat of 50%. When the degree of nanofibrillation is high, the strain at break increased more rapidly. Over 50% of the solids content, and strain at break decreased greatly. Therefore, the increase in the ability of maintaining the network structure even at higher deformation of NFC mat may be the reason. However, the solids content affected the ability of standing from deformation. Above 50% of the solids content, the rigidity increased significantly, which may be due the increase of hydrogen bonded areas.

The effects of a polyelectrolyte on the network properties of NFC were evaluated. An addition of polyelectrolyte changed the surface charge of NFC and determined the flocculation behavior. The viscosity and the hysteresis index indicated that the structure and the molecular weight of the polyelectrolytes determined the reformation of the network structure after it was deformed by the increase in the shear strain rate. The dewatering ability of the NFC suspensions in a non-associated state and in a highly associated state was evaluated. A higher molecular weight of polyelectrolyte commonly showed a better dewatering ability at proper addition amount which was closed to isoelectric point. However, overdosage on the NFC suspension decreased the dewatering ability and a high molecular weight and a high charge density promoted the decrease of the dewatering ability. An anionic polyelectrolyte decreased the dewatering ability. Not only the electrostatic interaction, but also steric forces acted between polyelectrolyte and NFC. The mechanical properties, including the rheological properties of NFC, were
affected by polyelectrolytes. The addition amount and the molecular weight were both important in mechanical properties. The flocculation of NFC influenced the network strength by polyelectrolyte, even though the molecular weight was not great. The tensile breaking stress was more distinguishable with addition of polyelectrolyte in a wet mat.

The network properties of NFC were determined by the substructure of the network. The substructure could be controlled with the type of polyelectrolyte. Because NFC also has colloidal characteristics, not only electrostatic interaction but also steric forces influenced the network properties, in particular, the NFC suspension was already flocculated at a consistency of 1.5% when the polyelectrolyte added. Therefore, controlling the substructure of NFC can be a method for controlling whole network properties of NFC. To utilize NFC requires an understanding of the relationship between NFC and water. Due to the NFC network which forms in the water from the preparation process, the removal of the water needs to be performed strategically. Not only by controlling network properties of NFC, but also the effective dewatering process such as continuous operation is required. It was expected that this study would be a fundamental research for utilization of NFC.
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초 록

나노피브릴화 셀룰로오스 현탁액 및 매트의 주요 특성 연구

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나노피브릴화 셀룰로오스는 제지 산업을 포함하여 화장품, 자동차, 의약품, 디스플레이용 필름, 전자 소재 등 다양한 분야에서 잠재적 신소재로서 인정받고 있다. 종합적으로 크고 친수성을 가지는 표면 특성으로 인하여 독특한 전화학적 성질을 나타내며 저농도에서부터 네트워크를 형성한다. 현탁액으로 제조되는 나노피브릴화 셀룰로오스를 시트 및 폼 형태로 활용하기 위해서는 이송, 탈수, 건조 등의 공정을 거쳐야 한다. 따라서 나노피브릴화 셀룰로오스의 탈수 특성, 네트워크 특성 및 기계적 물성에 대한 이해가 반드시 필요하다. 이를 위하여 본 연구에서는 나노피브릴화의 과정과 고형분 함량에 따른 네트워크 특성을 구명하고, 고분자전해질이 네트워크 특성에 미치는 영향을 구명하고자 하였다.

그라인더를 이용한 기계적 처리를 통하여 나노피브릴화 셀룰로오스를 제조하였다. 형태적 특성, 보수도, 침전 농도, 점도 분석을 통해 처리 횟수에 따른 나노피브릴화 정도를 평가하였다. 이를 통해 밀프 섬유로부터 나노피브릴화가 진행되는 정도를 판단할 수 있는
근거를 마련하였다. 본 연구에서는 15회-20회 처리로 나노피브릴화 셀룰로오스를 제조할 수 있는 것으로 나타났으나, 이는 전체 처리 조건 및 그라인더의 운전조건 변화 다양한 요인에 의해 더욱 개선될 수 있을 것으로 판단된다.

고형분 함량에 따른 나노피브릴화 셀룰로오스의 네트워크 특성은 현탁액상과 매트상으로 구분하여 평가하였다. 저농도 현탁액 수준에서는 유연특성 평가에 무관한 기존 연구의 한계를 벗어나 고농도 및 건조되기까지의 고형분 함량에 따른 네트워크 특성을 구명하기 위해 가압 탈수 장치를 이용한 압착 및 건조를 통해 고형분 함량을 조절하였다. 나노피브릴화 셀룰로오스는 현탁액 상태(0.5%–10%)로부터 매트 상태(10%–99%)에 이르기까지 네트워크 강도는 농도에 대한 하나의 핵심주 관계를 나타냈다. 이는 나노피브릴화 셀룰로오스가 펄프 섬유에 비해 매우 큰 종합비를 가지고 그 크기가 매우 작은 수준에서도 불구하고 고형분 함량 증가에 따른 네트워크의 형성은 유사하게 진행됨을 의미하였다. 그러나 나노피브릴화 셀룰로오스는 펄프 섬유에 비해 2배 이상 더 낮은 농도인 0.2%에서부터 네트워크가 형성되었으며 형성된 네트워크 강도는 펄프 섬유에 비해 5-20배 더 크게 나타났다.

매트상의 나노피브릴화 셀룰로오스의 인장 특성을 평가한 결과, 탄성계수는 고형분 함량의 증가에 대해 지수 합수적인 경향을 따랐다. 인장 응력은 네트워크 강도와 마찬가지로 고형분 함량에 따라 역합수적인 관계를 따르는 것으로 나타났다. 그러나 변형률은 고형분 함량 약 50%까지 증가하였다. 이는 나노피브릴화 셀룰로오스 매트의 경우 변형에 의해 파괴되는 시점까지 네트워크 구조가 유지되었기 때문으로 판단된다. 고형분 함량 약 50% 이상에서 변형률의
급격한 감소는 나노피브릴간의 수소 결합이 형성되면서 가소성이 감소했기 때문으로 판단된다. 또한 나노피브릴화가 많이 진행된 섬유일수록 변형률은 크게 나타났다. 펄프 섬유 매트의 변형률은 고형분 함량의 증가에 따라 지속적으로 감소하였다.

다양한 고분자전해질을 이용하여 나노피브릴화 셀룰로오스 현탁액의 네트워크 특성을 변화시키킬 수 있었다. 특히 양이온성 분지상 고분자전해질인 polyethyleneimine은 양이온성 선형 고분자전해질 (polydiallyldimethyl ammonium chloride, cationic polyacrylamide)과는 다르게 투입량의 증가에 따라 현탁액의 네트워크 강도를 지속적으로 증가시켰다. 또한 고분자전해질의 전하 특성, 구조 및 분자량에 따라 점도와 이력 현상을 변화시킬 수 있었다. 고도로 네트워크를 이루고 있는 나노피브릴화 셀룰로오스 현탁액은 탈수성이 매우 낮지만, 고분자전해질의 투입에 의해 탈수성이 조절될 수 있었고 최대 3배까지 증가시킬 수 있었다. 매트의 인장 특성을 고분자전해질의 종류 및 투입량에 따라 습윤 매트와 건조 매트로 구분하여 평가하였다. 특히 습윤 매트의 경우 고분자전해질의 종류 및 투입량에 따라 인장 응력이 최대 325%까지 증가하였다. 특히 분지상 고분자전해질의 경우 등전점을 나타내는 투입량에서 인장 응력의 급격한 변화가 나타났고 이를 통해 표면 전하 특성을 변화시키는 것이 고고형률 함량에서의 네트워크 특성 및 기계적 물성을 좌우하는 중요한 요소로 판단되었다. 그러나 완전히 건조된 매트의 인장 응력은 건조 과정에서 수소 결합에 의한 영향이 고분자전해질에 비하여 훨씬 더 컸기 때문에 그 영향은 미미하였다.

본 연구를 통해 향후 나노피브릴화 셀룰로오스의 활용성을 높일 수 있는 기초를 마련하였다. 특히 물의 제거 과정에서 네트워크 특
성이 변화하는 바를 연속적으로 추적하였고, 고분자전해질을 이용해 네트워크 특성 변화의 가능성을 살펴보았다. 본 연구는 향후 나노피브릴화 셜룰로오스의 활용성을 높일 수 있을 것으로 기대된다.

주요어: 나노피브릴화 셜룰로오스, 네트워크 강도, 유변 특성, 고형분 함량, 인장 응력, 파괴 시 변형률, 고분자전해질

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