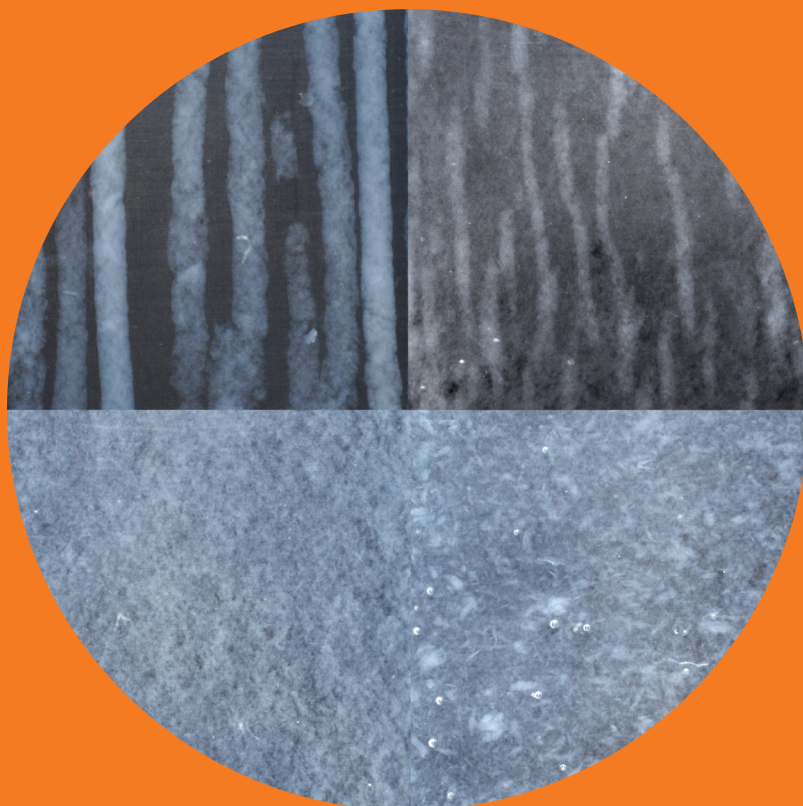


Department of Biotechnology and Chemical Technology

Rheology and flocculation of polymer-modified microfibrillated cellulose suspensions

Anni Karppinen



Rheology and flocculation of polymer- modified microfibrillated cellulose suspensions

Anni Karppinen

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Abstract

In this thesis, the rheology and flocculation of microfibrillated cellulose (MFC) suspensions was modified using different cationic and anionic polymers and surface modification. For this purpose, MFC suspensions were studied simultaneously with a dynamic rotational rheometer and two imaging methods. The flocculation tendency of the suspensions was mainly evaluated using photographing through a transparent rheometer cup, and for some suspensions, optical coherence tomography (OCT), which gives information of the structure and flow of the suspension inside the gap.

Three cationic polymers were studied as flocculants: two small molecular weight, high charge density polymethacrylates and high molecular weight, low charge density cationic polyacrylamide (CPAM). Polymethacrylates changed the gel strength of the MFC suspensions but did not have a significant effect on the flocculation even at a high polymer concentration. Instead, CPAM affected the gel strength and flocculation drastically at low concentrations. CPAM formed bridges between the MFC fibers, thus making the flocs very strong.

Carboxymethylcellulose (CMC), xanthan gum and three different anionic polyacrylamides (APAM) were tested as dispersants for the MFC suspensions. They all reduced the gel strength of the suspensions at optimized concentration and prevented shear-induced flocculation. The dispersion mechanism was probably a combination of increased viscosity of the suspending medium and the entrapment of the polymer chains between the approaching MFC fibers. CMC and xanthan gum were more effective at preventing shear-induced flocculation than APAMs. Oxidation of pulp with TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl radical) before grinding it to MFC gives the fibers negative surface charge and enhances the fibrillation upon grinding. The dimensions of the resulting fibers were smaller than without any pretreatment. Its water suspension was transparent and therefore the flocculation of the fibers could not be directly studied with the imaging methods. The gel strength was close to that of native MFC, although TEMPO-oxidized fibers have a higher surface charge.

The combination of rheometry and imaging proved to be a useful tool to study the effect of flocculants and deflocculants on the MFC suspensions. The direct observation of the suspension structure aided the interpretation of the rheological results. The measurement of the gel strength is an easy way to optimize the flocculant or deflocculant concentration for MFC suspensions in processing or different applications.

Keywords microfibrillated cellulose, rheology, image analysis, flocculation, polyelectrolyte, gel strength

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Tekijä

Anni Karppinen

Väitöskirjan nimi

Polymeereillä muokattujen nanoselluloosasuspensioiden reologia ja flokkautuminen

Julkaisija Kemian tekniikan korkeakoulu**Yksikkö** Biotekniikan ja kemian tekniikan laitos**Sarja** Aalto University publication series DOCTORAL DISSERTATIONS 129/2014**Tutkimusala** Polymeeritekniologia**Käsikirjoituksen pvm** 31.08.2014**Väitöspäivä** 17.10.2014**Julkaisuluvan myöntämispäivä** 19.08.2014**Kieli** Englanti **Monografia** **Yhdistelmäväitöskirja (yhteenvedo-osa + erillisartikkelit)****Tiivistelmä**

Tässä työssä tutkittiin mikrofibrilloidun selluloosan (MFC) reologiaa samanaikaisesti flokkautumisen kanssa sekä näiden ominaisuuksien muokkausta polymeereillä tai pintavaruksella. Tutkimiseen käytettiin reometriä sekä kahdenlaista kuvantamismenetelmää. Analyysi perustui pääosin valokuviin, joita otettiin läpinäkyvän näyttekupin läpi flokkirakenteesta. Lisäksi joitakin näytteitä tutkittiin optisella koherenssitomografialla (OCT), jonka avulla voidaan tutkia rakennetta syvemmällä suspensiossa.

Työssä tutkittiin kolmea kationista polymeeriä: kahta pienimoolimassaista ja korkeavaruksista polymetakrylaattia sekä suurimoolimassaista kationista polyakryyliamidia (CPAM). Polymetakrylaatit nostivat MFC:n geelilujuutta optimoidulla konsentraatiolla mutta eivät merkittävästi vaikuttaneet MFC:n flokkirakenteeseen. CPAM puolestaan flokkuloi MFC:tä voimakkaasti ja aiheutti suurilla polymeeripitoisuuksilla jopa pysyviä flokkeja suspensioon sekä nosti geelilujuutta alhaisilla polymeeripitoisuuksilla.

Karboksymetyyliselluloosaa (CMC), ksantaanikumia ja kolmea anionista polyakryyliamidia (APAM) tutkittiin dispergointiaineina MFC:lle. Kaikki anioniset polymeerit laskivat MFC-suspension geelilujuutta optimoidussa konsentraatiossa ja estivät leikkauksesta johtuvaa flokkuloitumista. CMC ja ksantaanikumi olivat tehokkaampia dispergoimissa kuin APAM:t. Eri APAM:ja tutkittaessa huomattiin, että korkeampi varaus ja moolimassa vähensivät polymeerimäärää, joka tarvittiin optimaaliseen dispergointiin. Dispergointi oli luultavasti seurausta useammasta tekijästä: väliaineen korkeammasta viskositeetista ja toisaalta polymeeriketjuista lähestyvien MFC-kuitujen välissä.

Hapettamalla sellukuituja ennen jauhamista TEMPO-radikaalilla (2,2,6,6-tetrametyylipiperidiini-1-oksyyli) mahdollistaa pienempien kuitujen tuottamisen, joilla on lisäksi negatiivinen pintavarauks. TEMPO-hapettamalla esikäsitellyt nanokuidut muodostivat läpinäkyvän suspension, jonka flokkuloitumista ei voitu luotettavasti seurata käytetyillä kuvantamismenetelmillä. TEMPO-hapettettujen nanokuitujen geelilujuus oli samaa luokkaa kuin käsittelemättömän MFC:n, mikä oli hieman yllättävää ottaen huomioon niiden suuremman pintavaruksen.

Yhdistämällä reometri tämän kaltaisiin kuvantamismenetelmiin voidaan kattavasti tutkia flokkulanttien ja dispergointiaineiden vaikutusta MFC-suspensioiden ominaisuuksiin, sillä kuvantamismenetelmät ohjaavat reologisten tulosten tulkintaa. Tällainen mittaus on myös helppo tapa optimoida polymeerilisiä aineiden määrä MFC:n prosessoinnissa tai erilaisissa sovelluksissa.

Avainsanat mikrofibrilloitu selluloosa, reologia, kuva-analyysi, flokkuloituminen, polyelektrolyytti, geelilujuus

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Preface

This work was carried out in the Department of Biotechnology and Chemical Technology, Aalto University School of Chemical Technology during the years 2010-2014. The work was started within the Nanosellu I and III projects established by the Finnish Centre for Nanocellulosic Technology and funded by the Finnish Funding Agency for Technology and Innovation (Tekes). Later, it was continued within the EffNet project by Finnish Forest Cluster Ltd and within the Graduate School in Chemical Engineering. All of the funding sources are gratefully acknowledged for their contribution to this thesis.

I would like to express my gratitude to Prof. Jukka Seppälä for offering me the opportunity to do my doctoral studies in his group. Apart from the interesting research topic, I am also grateful to him for encouraging me to participate in the Nordic collaboration in the field of polymers and rheology.

I want to thank Dr. Pirjo Pietikäinen, my thesis advisor, for all the time and support. My scientific career and interest in nanocellulose started when Pirjo offered me the possibility to work as a summer trainee in the Polymer Technology research group. Dr. Arja-Helena Vesterinen is thanked for the help she gave when I was preparing my first article.

Special thanks go to Tapio Saarinen, who helped me get a flying start to my research and who has always been there commenting on my work and encouraging me to go forward.

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Kuisma Littunen, Arto Salminen, Dr. Steven Spoljaric, and all the other colleagues in the Polymer Technology research group are thanked for their help and the fun coffee breaks. Our coffee room is a place where you always get answers to your questions, no matter what they are about!

Finally, I want to thank my family and friends who have supported me all these years. Your help has been invaluable.

Espoo, 8 August 2014

Anni Karppinen

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List of Abbreviations and Symbols

AFM	atomic force microscopy
APAM	anionic polyacrylamide
CMC	carboxymethylcellulose
CNC	cellulose nanocrystals
CPAM	cationic polyacrylamide
cryo-TEM	cryogenic transmission electron microscopy
CS	cationic starch
C_v	volumetric concentration
d	diameter
DP	degree of polymerization
DS	degree of substitution
e	elementary charge
FESEM	field emission scanning electron microscopy
G'	storage modulus
G''	loss modulus
HCD	high charge density
HMW	high molecular weight
k_T	Boltzmann's constant
L	fiber length
LCD	low charge density
LMW	low molecular weight
METAI	2-(methacryloyloxy)ethyl trimethyl ammonium iodide
MFC	microfibrillated cellulose
N	crowding factor

NCC	nanocrystalline cellulose
NFC	nanofibrillated cellulose
n_i	concentration of the ion “i” in consistent units
OCT	optical coherence tomography
PDADMAC	poly(diallyldimethylammonium chloride)
PDMQ	poly([2-(methacryloyloxy)ethyl] trimethyl ammonium iodide)
PEI	polyethyleneimine
PEO	poly(ethylene oxide)
PSMA13Q	cationized statistical copolymer of METAI and SMA
QCM-D	quartz crystal microbalance with dissipation
SMA	stearyl methacrylate
T	absolute temperature
TEMPO	2,2,6,6-tetramethylpiperidine-1-oxyl radical
z_i	valence of the ion “i”
ε	dielectric constant
ε_0	permittivity of vacuum
κ^{-1}	Debye length

List of Publications

This doctoral dissertation consists of a summary and of the following publications which are referred to in the text by their numerals

- I. Karppinen, Anni; Saarinen, Tapio; Salmela, Juha; Laukkanen, Antti; Nuopponen, Markus; Seppälä, Jukka; Flocculation of microfibrillated cellulose in shear flow, *Cellulose* **19** (2012) 1807–1819.
- II. Saarinen, Tapio; Haavisto, Sanna; Sorvari, Anni; Salmela, Juha; Seppälä Jukka; The effect of wall depletion on the rheology of microfibrillated cellulose water suspensions by optical coherence tomography, *Cellulose* (2014) DOI 10.1007/s10570-014-0187-5.
- III. Karppinen, Anni; Vesterinen, Arja-Helena; Saarinen, Tapio; Pietikäinen, Pirjo; Seppälä, Jukka; Effect of cationic polymethacrylates on the rheology and flocculation of microfibrillated cellulose, *Cellulose* **18** (2011) 1381-1390.
- IV. Sorvari, Anni; Saarinen, Tapio; Haavisto, Sanna; Salmela, Juha; Vuoriluoto, Maija; Seppälä, Jukka; Modifying the flocculation of microfibrillated cellulose suspensions by soluble polysaccharides under conditions unfavorable to adsorption, *Carbohydrate Polymers*, **106** (2014) 283-292.
- V. Korhonen, Markus H.J.; Sorvari, Anni; Saarinen, Tapio; Seppälä, Jukka; Laine, Janne; Deflocculation of cellulosic suspensions with anionic high molecular weight polyelectrolytes, *BioResources*, **9**(2) (2014) 3550-3570.
- VI. Mohtaschemi, Mikael; Sorvari, Anni; Puisto, Antti; Nuopponen, Markus; Seppälä, Jukka; Alava, Mikko J.; The vane method and kinetic modeling: Shear rheology of nanofibrillated cellulose suspensions, *Cellulose* (2014) DOI: 10.1007/s10570-014-0409-x.

Author's Contribution

Publication I: Flocculation of microfibrillated cellulose in shear flow

Anni Karppinen planned and carried out the experiments together with the co-authors, and wrote the manuscript with the assistance of the co-authors.

Publication II: The effect of wall depletion on the rheology of microfibrillated cellulose water suspensions by optical coherence tomography

Anni Karppinen (former Sorvari) participated in defining the research plan, carrying out the rheological experiments, analyzing the results and writing the manuscript with the co-authors.

Publication III: Effect of cationic polymethacrylates on the rheology and flocculation of microfibrillated cellulose

Anni Karppinen planned and carried out the rheological experiments together with co-authors, and wrote the manuscript with the assistance of the co-authors.

Publication IV: Modifying the flocculation of microfibrillated cellulose suspensions by soluble polysaccharides under conditions unfavorable to adsorption

Anni Karppinen (former Sorvari) planned and carried out the rheological experiments together with co-authors, and wrote the manuscript with the assistance of the co-authors.

Publication V: Deflocculation of cellulosic suspensions with anionic high molecular weight polyelectrolytes

Anni Karppinen (former Sorvari) planned and carried out the rheological experiments and participated in writing the manuscript with the co-authors.

Publication VI: The vane method and kinetic modeling: Shear rheology of nanofibrillated cellulose suspensions

Anni Karppinen (former Sorvari) planned and carried out the rheological experiments and participated in writing the manuscript with the co-authors.

1. Introduction

Fibers with at least one dimension between 1-100 nm and prepared from cellulose raw materials can be called nanocellulose. Nanocellulose has raised growing interest since its discovery in the 1980's, because it is a renewable, lightweight, and strong material. The term 'nanocellulose' covers very different types of materials considering the size, shape and physical properties of the fibers and various terms are used for the different grades. Mechanically prepared nanocellulose, which has long and entangled fibers, is normally called micro-/nanofibrillated cellulose (M/NFC) or cellulose nanofibers (CNF). Acid hydrolysis can be used to produce shorter, rod-like fibers which are called nanocrystalline cellulose (NCC), cellulose whiskers, cellulose microcrystallites, microcrystals, or cellulose nanocrystals (CNC). This thesis concentrates on cellulose microfibrils obtained by mechanical treatment of pulp fibers. In this thesis, the following nomenclature is used: microfibrillated cellulose (MFC) is used for mechanically prepared fibers without any pre- or post-treatments. Fibers with pretreatment or removal of larger fiber fractions are called nanofibrillated cellulose (NFC), since their dimensions are smaller compared to the purely mechanically prepared fibers.

MFC suspensions show interesting rheological properties due to the flocculated fiber network structure. Rheological characterization of the suspensions is important when planning handling, storage, processing, and transport of fiber suspensions. For example, high yield stress is related to the ability to stabilize solid particles in dispersion. Flocculation of the MFC suspension can be a desired or undesired property. For instance in nanocomposites, fibers must be well dispersed in order to show transparency and good mechanical performance. On the other hand, for pumping or drying of the suspension, flocculation can be beneficial.

In this thesis, the following themes were studied: 1) What is a reliable way of measuring the rheology of MFC suspensions? How can we measure flocculation of MFC suspensions and how is it related to the rheology? 2) How can we flocculate or deflocculate MFC suspensions? 3) How are these reflected in rheological properties? First, MFC suspensions were studied without additives and at different concentrations to characterize the material and to determine suitable methods for studying its rheology and flocculation (paper I and II). Imaging methods were used in combination with the rheometer. Then, different polymers were added to MFC suspension to modify the rheological behavior and to disperse or flocculate the suspension. Small molecular weight, high-

ly cationic polymers poly([2-(methacryloyloxy)ethyl] trimethyl ammonium iodide) (PDMQ) and amphiphilic statistical copolymer of 2-(methacryloyloxy)ethyl trimethyl ammonium iodide and stearyl methacrylate (PSMA13Q) were studied in paper III. These polymers adsorb onto the cellulose surface, thus bringing a cationic surface charge. In addition, PSMA13Q carry hydrophobic segments, which causes a coiled conformation of the polymer and a thicker adsorption layer. To complement the picture of the effect of the cationic polymers, unpublished data on high molecular weight, low charge density cationic polyacrylamide (CPAM) is presented here. CPAM is able to form bridges between fibers and thus induce flocculation.

Anionic carboxymethylcellulose (CMC) and xanthan gum were investigated in paper IV. They are both polysaccharides like cellulose having similar backbones. However, in this study, the conditions were such that neither of them adsorbed on the MFC surface. Paper V concentrated on the effect of molecular weight and charge density of anionic polyacrylamides (APAM) on their efficiency to disperse cellulosic fibers. Finally, in paper VI, the rheology of TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl radical) oxidized NFC fibers was studied using a vane method which overcomes some problems of the rheological measurements observed in papers I and II. In addition, some unpublished data is presented to show the effect of fiber length to gel strength of NFC suspension.

The main method used in this thesis was dynamic rotational rheometry combined with imaging of the suspension. Rheology gives information about the interactions between cellulose fibers and how they can be modified with polymers. It is a complementary method to surface analysis methods like atomic force microscopy (AFM) or quartz crystal microbalance with dissipation (QCM-D). Studies have shown good correlation between rheological properties, such as yield stress and viscosity, and the surface forces measured by techniques like AFM^{1,2}. An advantage of rheological measurements is that real suspensions can be used instead of model systems, and measurements are rather easy to conduct. The imaging brings additional information and help for interpreting the rheological data.

In this thesis, we have used a dynamic rotational rheometer combined with imaging methods to observe the rheology and flocculation of nanocellulose suspensions simultaneously. Other types of rheometers exist as well but rotational dynamic rheometers have some advantages compared to others: small sample volumes can be used, it is easy to operate, it is a compact device, and in principle the data is easy to analyze.

2. Background

2.1 Microfibrillated cellulose

Microfibrillated cellulose (MFC) is a nanomaterial which is prepared by disintegration of wood or other cellulosic fibers to fibrils. It was first introduced by Turbak et al.³ and Herrick et al.⁴ in the 1980s. They prepared it purely by mechanical disintegration. Today, oxidation⁵ or enzymatic^{6, 7} pretreatments can be used prior mechanical processing to lower the energy demand in the disintegration step and to modify the fiber surface. Due to its high aspect ratio and nanoscale dimensions, it has been widely studied as a reinforcing material for nanocomposites^{8, 9, 10, 11}. Further benefits of MFC in nanocomposites are low coefficient of thermal expansion¹², the possibility to produce transparent and flexible composite¹³ and renewable raw materials. Other possible applications include rheological modifiers in food, cosmetics, and paints⁴ and as additives to enhance strength^{14, 15, 16} and barrier additive^{3, 17} of paper and board.

2.1.1 Preparation of microfibrillated cellulose

Different methods have been used for the mechanical disintegration of cellulosic raw material to MFC: including homogenizers, microfluidizers, and grinders¹⁷. A relatively high amount of energy is needed to individualize the fibrils in all of these methods and this has been one of the main hindrances preventing greater commercialization of the material. In the homogenizer, the pulp is passed several times through a small orifice with a spring-loaded valve^{3, 4, 18}. This causes a large pressure drop and exerts high shear forces on the material, enabling the disintegration. In the microfluidizer, the material is forced through a Z-shaped channel under very high pressure and this is repeated with chambers of different sizes, until the desired fibrillation level is achieved. The diameter of the chambers is normally between 200-400 μm . With a microfluidizer, it is possible to produce MFC with rather uniform diameters. However, up to 30 passes through the microfluidizer may be needed to achieve the desired size¹⁹. A third commonly used method to produce MFC is grinding with stone plates. The pulp is passed between static and rotating grinding stone with rotating speed of 1500 rpm. Normally, 3 to 5 passes are employed to produce MFC. After 5 passes, no significant changes were observed in the fiber morphology²⁰.

Wood pulp is the most commonly used raw material for MFC but other cellulosic resources have also been utilized, such as agricultural crops and their by-products¹⁷. For instance, sugar beet pulp^{21, 22}, tunicin⁵, cotton⁵, and potato starch^{23, 24} have been studied. Pulp is a popular raw material, since it is commercially available in industrial scale. However, other raw materials can be appealing, since the fibrils are more easily separated than in wood cells¹⁷.

2.1.2 Microfibrillated cellulose morphology

MFC is prepared by breaking the wood cell structure and disintegrating the pulp fibers into fibrils or fibril aggregates. Cellulose is a polymer, and the chains consist of repeating units called cellobiose which is shown in Figure 1. In cellobiose, there are two anhydro-D-glucose rings that are linked to each other by β -1,4-linkages. In wood cells, these chains are packed in elementary fibrils, containing crystalline and amorphous regions. These elementary fibrils build up fibril bundles, which are located in the secondary wall of a wood cell²⁵. The purpose of the mechanical treatment is to separate these fibril bundles and fibrils apart without destroying the amorphous regions.

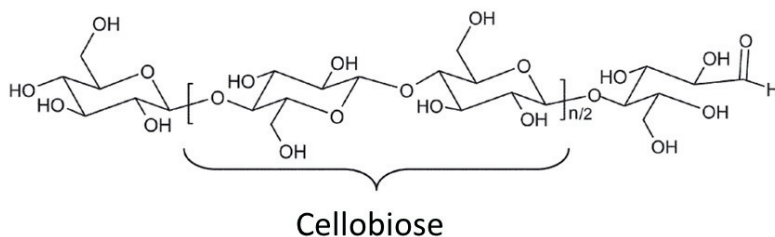


Figure 1. Structure of cellulose chain.

MFC fibers have a high aspect ratio and diameter mainly between 5 and 100 nm depending on the raw materials^{5, 12} and manufacturing procedure^{26, 27}. MFC consists of fibers and fibrils with a broad range of diameters, and if the larger fibers are not separated, some fibers can even be visible with optical microscopy. Therefore, the water suspension of MFC is normally opaque and not transparent. The fibers form a network structure which is shown in a cryo-TEM image and SEM image in Figure 2. The diameters of the fibers in this network vary from micrometer scale to nanometer scale.

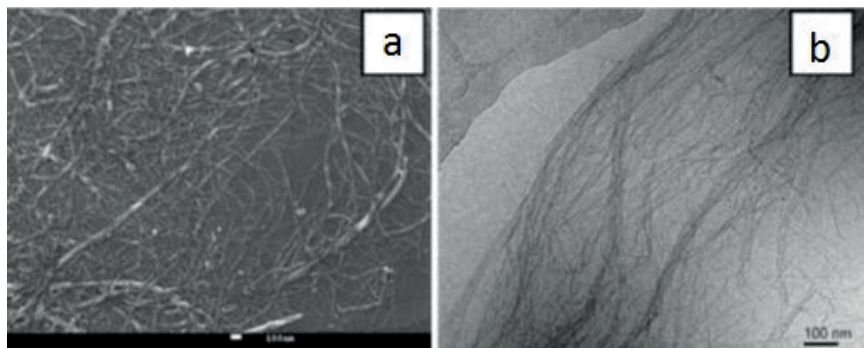


Figure 2. MFC suspension measured by SEM (a) and cryo-TEM (b). Modified from ref²⁸.

Since the dimensions of MFC fibers differ many decades from nanosized to micron sized fibers, the statistical reliability in size evaluation is challenging to achieve. It is important to note that the observed diameters are dependent on the method and magnification used for size determination. Without separation of the largest fraction, there are fibril aggregates which are not visible under larger magnification²⁹. To prepare NFC containing only nanoscale fibers by mechanical treatment, larger fiber fractions must be separated. The separation can be done by ultracentrifugation^{16, 30}, where the nanosized fibers stay in the supernatant and larger fibers settle at the bottom. The fibrils form an entangled, three-dimensional fiber network in water⁶ which gives rise to interesting rheological properties including a very high viscosity already at low concentrations. The junction points in this network are partially disintegrated fibers and mechanical entanglements^{6, 29}. The morphology is very similar between MFC from different raw materials and by different manufacturing methods, whereas the dimensions of the fibers are dependent on both of those aforementioned parameters. The amount of lignin and hemicellulose within the raw material affect the fibrillation; lignin hinders the fibrillation³¹, whereas hemicellulose makes it easier¹².

The diameter of MFC fibers can be measured with microscopic methods, like atomic force microscopy (AFM), scanning electron microscopy (SEM) or transmission electron microscopy (TEM). However, the length of the fibers is normally too large to be observed entirely within one microscope image. If the area of the image is enlarged, the magnification becomes too low to see individual MFC fibers¹⁷, which makes the length very hard to measure. Normally, the length is estimated to be several microns. Ishii et al.³² used an indirect method to measure the length of TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl radical) oxidized NFC when they measured the viscoelastic moduli of the suspension and estimated the length from the crossover point of the loss and storage modulus. Light transmittance through a suspension⁵ or composite film^{12, 20} of MFC can also be used to estimate the length and diameter although it does not give exact values. Light transmittance is more sensitive towards larger particles, and therefore, it can be used to supplement microscopic methods which emphasize the smaller particles.

Compared to pulp fibers, MFC fibers have significantly larger specific area which gives rise to new properties. However, the specific surface area is challenging to measure accurately, since the MFC fibers tend to aggregate upon drying. Siqueira et al.³³ calculated the specific surface area based on the diameters measured with field emission SEM (FESEM) and obtained $51 \text{ m}^2\text{g}^{-1}$ when the diameter of the fibers was 52 nm. Spence et al.³¹ measured the specific surface area for MFC using the Congo red adsorption method. Depending on the raw material, they obtained specific surface areas of $29\text{-}202 \text{ m}^2\text{g}^{-1}$ for different MFCs. Fibers diameters between 62 and 1006 nm were observed with FESEM.

The chemical composition of MFC depends on the properties of the raw material. The surface chemical composition of pulp is determined by the pulping process. For example, thermomechanical pulp (TMP) fiber surfaces contain large amounts of lignin, whereas chemical pulping processes, such as the kraft process, removes the most of the lignin, but the pulp still contains hemicelluloses³⁴. MFC has a slightly negative surface charge, which is mainly due to carboxylic groups on hemicellulose present within the fibers. Pääkkö et al.⁶ reported a surface charge of $44 \text{ } \mu\text{eqg}^{-1}$ for enzymatically pretreated pulp while Eronen et al.³⁵ recorded $65 \text{ } \mu\text{eqg}^{-1}$ for native pulp. The slightly negative surface causes repulsion between the fibers, reducing aggregation of the fibers. Although cellulose chains contain three OH groups per one anhydroglucose unit, they are mostly involved in inter- and intramolecular hydrogen bonds and therefore the surface is not as hydrophilic as might be expected based on the number of OH groups³⁴.

2.1.3 Pretreatments prior to fibrillation

Pretreatments of pulp fibers before fibrillation have two aims: i) to reduce the energy consumption during the disintegration of fibers and ii) to modify the surface properties of the resulting MFC fibers. Surface properties of the fibers affect, for instance, the aggregation of the fibers in the suspension and compatibility of the fibers with the matrix in composite materials. According to Lavoine et al.¹⁷, TEMPO oxidation, enzymatic treatment and carboxymethylation are the most used pretreatments. Enzymatic pretreatment with endoglucanase before mechanical disintegration reduces the energy consumption of the process but does not essentially affect the surface properties of the fibers⁶ or degree of polymerization (DP)⁷. Carboxymethylation is a chemical treatment used prior to mechanical disintegration. It introduces a negative charge onto the fiber surface and reduces the energy consumption of the mechanical process^{16, 36}.

TEMPO-mediated oxidation of pulp^{5, 26} also lowers the energy consumption of the disintegration process and produces a high negative surface charge on the fibers. The resulting fibers have a smaller diameter than MFC, and thus, they can be called nanofibrillated cellulose (NFC). TEMPO-mediated oxidation is regioselective towards primary hydroxyl groups on the C6 carbon atom in the cellulose chain. TEMPO and NaClO are used in catalytic amounts while the primary oxidant is NaBr. The reaction takes place in acidic, aqueous condi-

tions. The OH groups are converted via aldehyde to carboxylate groups. The carboxylate groups introduce negative charge onto the cellulose fibrils, loosening the interfibril adhesion and increase the electrostatic repulsion between fibrils⁵. Oxidation occurs selectively on the microfibril surface which helps to retain the original fibrous morphology. TEMPO oxidized NFC fibers have a quite constant diameter of 3-4 nm independent of the wood species, indicating that they are individual microfibrils. The length may vary but it can be over 2 μm ^{1, 26} depending on the oxidation and disintegration methods used³⁷. NFC fibers form an almost transparent dispersion in water with a very high viscosity and yield stress²⁶.

2.2 Flocculation of MFC suspensions

MFC fibers form an inherently entangled network in water suspension. The network is not uniform but there are local mass concentrations called flocs. The floc structure is to some extent similar to pulp suspensions³⁸; although MFC fibers have significantly smaller dimensions and a higher aspect ratio than pulp fibers. The flocculation of pulp fibers has been studied extensively since the early 20th century due to its relevance for paper making. MFC flocculation is a less-studied topic and therefore, the research of pulp flocculation is also reviewed here to give a broader perspective to the flocculation of cellulosic fibers.

The fibers in the network are interconnected, and the strength of the network is dependent on the number of contact points between the fibers and cohesive forces in these contacts³⁹. Within the flocs, there are higher amount of contact points which makes them stronger than the network on average. Under flow these interconnected flocs rupture from the network and flow as individual flocs. Figure 3 shows schematically the fiber network at rest and under flow.



Figure 3. Schematic representation of the flocs in the fiber network at rest (on the left) and as individual entities under flow (on the right).

According to Soszynski and Kerekes⁴⁰, three important aspects can be observed in the flocculation of a suspension. The state of flocculation describes the degree of uniformity in the fiber network at a given moment. The flocculation process relates to the dynamics of flocculation between two states of flocculation separated by certain time. The nature of flocculation is related to the flocculation mechanisms and forces at fiber contact points.

MFC fibers are inherently entangled after the preparation of the material but new contacts can be formed between the fibers under flow. Fibers can collide due to relative motion between the fibers in translation and rotation. Flowing fibers tend to rotate about their center and thus collide with other flowing fibers assuming that the concentration is sufficiently high. Collisions between the fibers are dependent on the volumetric concentration of the fibers⁴¹.

Existing contacts between fibers can also be broken when the suspension is under flow. Two mechanisms have been proposed for pulp flocs: erosion of the fibers from the floc surface and splitting of a floc into two⁴². If flocs are weak, hydrodynamic forces can break flocs and the released fibers can form new flocs. Flocs which break and reform are called transient flocs. The size of transient flocs is dependent on the shear rate. Flocs that persist through the flow as identifiable entities and do not disperse upon dilution of the suspension are called coherent flocs⁴⁰.

The flocculated structure of pulp suspensions has been studied by imaging^{43, 44, 45, 46, 47}, but flocculation of MFC is less studied³⁸. Beghelli⁴⁸ and Wågberg and Nordqvist⁴³ used very similar measuring systems consisting of a flow loop through pipe and video camera to detect the flocculation of pulp suspensions. Instead, Björkman⁴⁹ utilized a large Couette instrument resembling commercial rotational rheometers equipped with a camera. Chen et al.⁴⁶ also utilized a rotational device using plate and plate geometry and a high speed CCD camera.

In pulp suspensions, the prevailing floc structure and size are dependent on shear rate and flow type. The floc structure in turn affects the rheological properties of the suspension^{50, 51}. Furthermore, flocculation can be affected by adding polyelectrolytes⁴³ or salts^{48, 52} to fiber suspensions or by adjusting pH⁴⁸. Rheological properties such as viscosity at different shear rates and flocculation are essential information for both the processing of MFC and its applications. The state of flocculation affects the rheology of MFC suspension. Forces affecting the flocculation of cellulosic fibers are presented in the following section 2.2.1 and the effect of polymers on the flocculation after that in section 2.2.2.

2.2.1 Forces between the cellulosic fibers

Colloidal forces

Colloidal forces acting between cellulosic fibers can be described by DLVO theory which is named after the first researchers presenting it, Derjaguin and Landau⁵³, and Verwey and Overbeek⁵⁴. The theory describes two types of forces: van der Waals and electrostatic double layer forces. Van der Waals interactions arise from the transient, induced, or permanent electronic dipoles in the molecules on the surface. These interactions are attractive between similar surfaces. Electrostatic double layers are formed by charged surfaces and the ions which gather near the charged surface in water suspensions. Electrostatic double layers cause repulsion between negatively charged cellulosic surfaces.

Figure 4a shows the electronic double layer repulsion and van der Waals attraction and their additive effect as a function of the distance between the surfaces. At larger separations, double layer repulsion dominates the interactions, thus stabilizing the suspension. At closer distance, van der Waals forces are important, causing aggregation, if the energy barrier is first overcome. Depending on the mutual magnitude of these forces, there may be a secondary minimum inducing aggregation, as presented in Figure 4b.

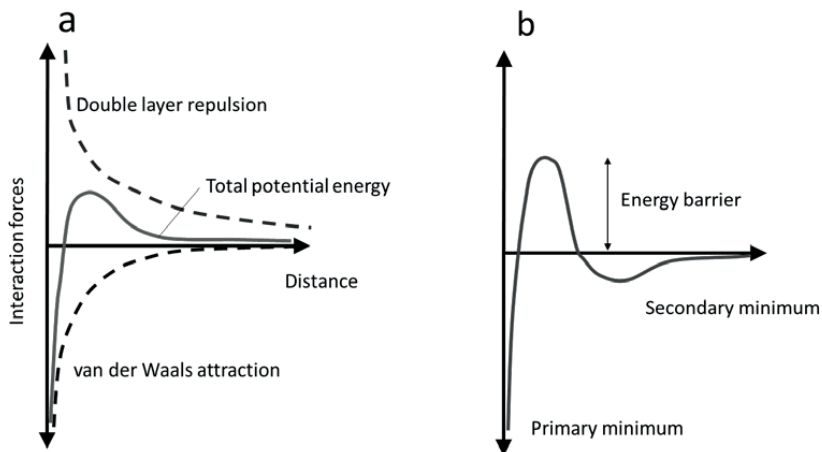


Figure 4. Schematic representation of the interaction forces between two surfaces predicted by DLVO theory (according to ref³⁴). a) Stable suspension and b) suspension with a secondary minimum.

Unmodified surfaces of cellulosic fibers have a net negative charge in aqueous suspensions which are due to the carboxylic groups on hemicellulose³⁴. It causes repulsion between the fibers as they collide with each other and prevent van der Waals interactions which would lead to permanent aggregation. The surface charge of unmodified MFC is low, but especially when excess ions are removed by washing, the electrostatic double layer is expected to be sufficient to reduce flocculation and permanent aggregation of the fibers. The negative charges attract oppositely charged counter-ions and there is an excess of positive ions near the cellulosic surface compared to the bulk of the suspending medium⁵⁵. The length of this layer is called the Debye length (κ^{-1}), and it is determined as follows:

$$\kappa^{-1} = \left(\frac{\varepsilon \varepsilon_0 k_B T}{\sum_i (z_i e)^2 n_i} \right)^{\frac{1}{2}} \quad (1)$$

where z_i is the valence of the ion “i”, n_i is its concentration in consistent units, e is the elementary charge, ε_0 is the permittivity of vacuum, ε is the dielectric constant of the suspending medium, k_B is Boltzmann’s constant, and T is the absolute temperature. When the electrostatic double layers of two surfaces start to overlap, it gives rise to osmotic pressure and creates repulsion between

the surfaces. The Debye length is dependent on the ionic strength but not on the surface charge of the fibers. Earlier, it has been found that increased ionic strength causes severe aggregation in MFC suspensions^{38, 52}, showing that surface charges cause repulsion between the fibers and screening them with salt ions leads to aggregation.

DLVO theory is a simplification of the real pulp fiber or MFC fiber surface, receiving some criticism, since it assumes, for instance, a flat surface and uniformly spread charges⁵⁶. Despite the limitations, it is useful for describing cellulosic surface interactions^{57, 58}.

Mechanical surface linkage

For pulp suspensions, mechanical flocculation is more important than colloidal forces causing flocculation⁵⁹. MFC fibers have smaller dimensions and therefore colloidal forces can be more important for them than for pulp fibers. However, since the length of the fibers is normally several microns, it is likely that flocculation also occurs due to mechanical entanglements.

When the mechanism of flocculation is purely mechanical, at least three contacts per fiber are needed to form a network³⁹. The number of contacts is dependent on the amount of fibers per volume. To describe this relationship in pulp suspensions, Kerekes et al.³⁹ introduced a crowding number, N , which specifies the amount of fibers in the volume swept by a length of a fiber.

$$N = \frac{2}{3} C_V \left(\frac{L}{d} \right)^2 \quad (2)$$

where C_V is volumetric concentration, L fiber length, and d fiber diameter. Fiber suspensions can be divided into different regimes based on crowding factor. When $N < 1$, the suspension is dilute and there is a chance for a collision. N between 1 and 60 is called semi-concentrated and in that region, fibers are forced to collide. $N > 60$ is the concentrated region, where there are continuous contacts between the fibers. The idea of a crowding factor has been further developed in later publications. Martinez et al.⁶⁰ introduced a gel crowding factor at $N=16$, at which fibers start to interact significantly but do not become immobilized like they do at $N=60$. Celzard et al.⁶¹ suggested that $N=16$ should be used as a threshold for connectivity of the fibers and $N=60$ for flocculation. Crowding factor has been widely used to predict flocculation of pulp suspension but not for MFC suspensions, and therefore, it is not clear if the same relationship holds for MFC suspensions.

Mechanical cohesion can be divided into three categories⁴⁰: linking or hooking of fibers ($N > 1$), interlocking by the elastic bending of the fibers ($N \geq 60$) and spinning of the fibers into threads. Illustrations of hooking of fibers and elastic bending are shown in Figure 5. Elastic interlocking of fibers occurs in the decelerating flow⁶². In the flowing suspensions, the suspensions bend, and when the flow stops, the bent fibers straighten. Since there are other fibers around them, the fibers are locked between them due to frictional forces. Schmidt et al.⁶³ have shown by simulation that flocculation can occur purely by mechanical means (interfiber friction) without any attractive forces between the fibers.

In that case, flocculation is dependent on the coefficient of friction, fiber stiffness, equilibrium shape, and concentration. Interfiber friction inhibits contacting fibers from sliding, assists in clutching and deforming fibers, and resists their dispersion.

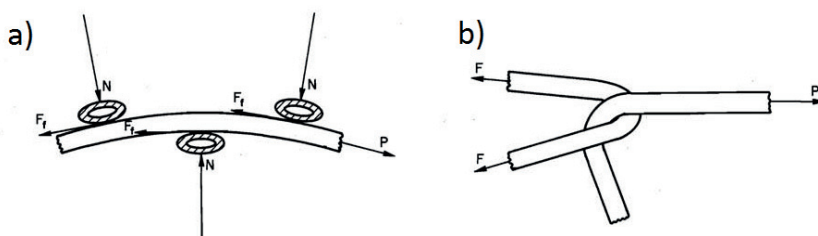


Figure 5. Illustration of elastic bending, showing the normal and frictional forces, (a) and hooking (b) of the fibers in the suspension. Modified from ref⁴¹.

Mechanical flocculation is dependent on the fiber properties, such as fiber length and electrostatic charge of the fiber surface, and on suspension properties including concentration, hydrodynamic forces, ionic strength, and pH^{39, 63}. Decreased stiffness reduces flocculation due to decreased elastic energy storage of the strained fibers. Therefore, flocs break up more easily in unbound shear flow as fiber stiffness is decreased⁶³. In addition, fiber equilibrium shape and dimensions affect the bending behavior of single fibers and the first normal stress differences in flexible fiber suspensions. Highly irregular fiber shapes induce more fiber interactions and faster aggregation⁶³. The threshold concentration for flocculation decreases when the fiber length increases. Moreover, for a given fiber length, the threshold concentration increases when the diameter of the fiber increases. Soszynski and Kerekes⁴⁰ found that above a certain fiber diameter, no flocs formed in nylon fiber suspension.

Viscosity of the suspending medium also affects the elastic interlocking of the fibers. Increased viscosity reduces flocculation. Soszynski and Kerekes⁴⁰ observed that above a certain viscosity (0.14 Pas) nylon fibers did not form flocs at all. At low viscosity of the suspending liquid, the fibers do not tend to follow the flow of the liquid, but crowd where the flow decelerates. At higher viscosities of liquid, the fibers follow the flow of the suspending liquid more closely. Fibers also align themselves within the flow at higher viscosities.

Mechanical flocculation is favored by two characteristics of MFC. First, MFC fibers have a high aspect ratio²⁸, which enables them to bend elastically. As elastically bent fibers come to rest, they may become restrained by adjacent fibers inducing normal forces at fiber contact points and together with frictional forces inhibit movement between fibers^{39, 41}. Secondly, the morphology of fibers is irregular since there are also only partially fibrillated fibers⁶, which favors mechanical hooking.

2.2.2 Dispersing mechanisms of polymers

Polymers are used widely in paper making to flocculate and deflocculate pulp fibers. Presumably, same polymers can be used for MFC suspensions although the mechanisms and influence may be slightly different than for MFC fibers. Polymers used as dispersants and flocculants can be anionic, cationic or neutral. The molecular weight and charge density of the ionic polymers are the most characteristic properties of the polymer additives⁶⁴. Polymer-induced forces are dependent on solvent-polymer interactions, surface coverage, polymer concentration, and whether the polymer adsorbs (irreversibly or reversibly)³⁴. Often, adsorption of the polymer is needed and the interactions causing that may be electrostatic interactions, hydrogen bonding, hydrophobic interactions, or ion binding⁶⁴. In addition, the conformation of the adsorbed polymers is important for flocculation. Polymers adsorbing with loops and tails extend into the solution, whereas flat polymers act at smaller distances. Within time, the conformation may also change towards a flatter conformation³⁴.

Adsorption of polymers

Polymers can adsorb on charged or neutral surfaces. If the surface and polymer are charged, the charges can be of same sign or opposite sign. Depending on the above mentioned factors, there are different forces governing adsorption. Neutral homopolymers adsorb on the surface if there is polymer-surface affinity⁶⁵. The interactions causing that may be, for instance, hydrogen bonding or hydrophobic interactions. The amount adsorbed is dependent on the polymer molecular weight; the higher the molecular weight, the higher the adsorbed amount. For copolymers, the structure is also important. Random copolymers often behave similarly to homopolymers but block copolymers may have substantially higher adsorbed amounts, if one block is acting as an adsorbing anchor on the surface and the other block points out of the surface as loops and tails.

The most common system in industry is the adsorption of charged polyelectrolytes on an oppositely charged surface. For instance, cationic polyelectrolytes are used widely as strength additives in paper making⁶⁵. When the polyelectrolyte and the surface are oppositely charged, the main driving force for the adsorption is electrostatic interactions. In addition, the entropy of the system increases, since small counter ions are released from the surface and replaced by more constrained polymer chain. On the other hand, the adsorbed segments carrying the same charge repel each other which can hinder adsorption. Increasing salt concentration reduces the repulsion between the polyelectrolyte segments but also the attraction between the polyelectrolyte and the surface. If the adsorption is based only on the electrostatic interactions, the adsorbed amount is lower in the presence of salt. If the polyelectrolyte has high affinity towards the surface, salt can increase the adsorbed amount of the polyelectrolyte⁶⁶.

The adsorbed layer is expected to be flat in the case of oppositely charged polyelectrolyte and surface, since only next to the surface the segment-segment repulsion can be overcome by segment-surface attraction⁶⁵. Salt con-

centration has a great effect on the conformation of polyelectrolytes: at low concentrations a polyelectrolyte adopts an extended conformation, which makes the adsorption layer thin. At increased salt concentrations, polyelectrolytes adopt a coiled conformation, leading to a thicker adsorption layer with loops and tails. The adsorbed amount may decrease or increase depending on the non-electrostatic polymer-surface affinity⁶⁵. Similarly, high charge density results in a flat conformation on the surface and also a higher amount of adsorbed polymer. On the other hand, low charge density polyelectrolytes adsorb with loops and tails, especially if the surface is highly charged.

The adsorption of oppositely charged polyelectrolytes onto the charged surface affects the interactions between the surfaces (cellulosic fibers). Adsorption of a minute amount of the polyelectrolyte leads to neutralization of the surface and removal of the electrostatic double layer force. However, increasing the polyelectrolyte concentration normally leads to small recharging of the surface and reappearance of the electrostatic double layer⁶⁵.

If the surface is neutral, there must be sufficiently high non-electrostatic polymer-surface affinity for any adsorption to occur. The system's entropy decreases upon adsorption and the charged segments in the polyelectrolyte chain repel each other, which reduce the adsorption. Increasing the salt concentration enhances the adsorption in this case⁶⁶.

Adsorption of the polyelectrolyte onto a similarly charged surface is even more unfavorable, since the polyelectrolyte and surface repel one another. In that case, the affinity of the polyelectrolyte towards the surface must be very high for any adsorption to occur, since the polymer-surface repulsion and the entropy penalty of adsorption must be overcome. The adsorption occurs most easily at high salt concentrations⁶⁶. Salts with divalent cations, like calcium or magnesium, can bind negatively charged polymers onto negatively charged surface⁶⁴.

An example of similarly charged polymer-surface adsorption is the adsorption of many polysaccharides onto cellulosic surfaces³⁵. This is attributed to the similarities between polysaccharides and the cellulose backbone structure. In particular, carboxymethylcellulose (CMC) has a high affinity towards the cellulose surface⁶⁷. Using high temperature, long adsorption time, and sufficiently high salt concentration, CMC adsorbs nearly quantitatively onto the cellulose surface. Uncharged segments of the CMC chain resemble a cellulose chain structure and that is believed to be the driving force of the adsorption. However, at low salt concentrations the adsorption of CMC onto NFC surface is reversible³⁰.

Forces between cellulosic surfaces in the presence of adsorbing polymers

Polymers can be used to stabilize or flocculate cellulosic fiber suspensions. The effect which the polymer has on the stability, depends on whether the polymer adsorbs onto the surface, the amount of adsorbed polymer and conformation of the polymer on the surface (which can be time dependent⁶⁴). The strength of fiber flocs in the presence of polymers in the system is a combined effect of cellulose-cellulose and cellulose-polymer-cellulose interactions.

If the fiber surface is partially covered by a polymer, it can lead to flocculation by two mechanisms: i) patch-like adsorption of the polymer or ii) bridging. Patch-like adsorption of the polymer causes aggregation especially if the polymer is positively charged and has low molecular weight leading to a flat conformation on the fiber surface^{34, 42}. Charged patches formed by the adsorbed polymer attract uncovered cellulose surfaces, leading to aggregation. Charged patches are likely to form on the low surface-charge cellulose surface if the polyelectrolyte is highly cationic and has a low molecular weight⁶⁴. Polyelectrolytes at low concentrations can also cause charge neutralization, thus aggregating the suspension. Typically, flocs formed by patch-like adsorption or charge neutralization break easily under shear. Adding high molecular weight polymer, which adsorbs with loops and tails, may cause polymer bridging where the same polymer molecule is adsorbed onto two fibers and pulls them together^{34, 64}. A maximum rate of bridging flocculation is expected when approximately half of the fiber surfaces are covered by the polymer. The most effective bridging agents are high molecular weight, linear polymers.

Cationic starch and poly(diallyldimethylammonium chloride) (PDADMAC) are examples of polymers that can form charged patches on the cellulose surface, thus aggregating the fibers. Cationic starch is commonly used for flocculation of pulp, and it has also been shown to aggregate MFC⁶⁸. Highly cationic, small molecular weight PDADMAC was observed to adsorb with a flat conformation¹⁵, favoring the formation of charged patches on the fiber surface.

Cationic polyacrylamides (CPAM) typically adsorb with loops and tails and flocculate pulp by bridging^{43, 69, 70}. Myllytie et al.⁶⁸ observed using optical microscopy that CPAM can also flocculate MFC fibers. The same polymer can in some cases have a dispersing and flocculating effect on pulp. Wågberg and Lindström⁷⁰ showed that about 50% surface coverage by CPAM led to flocculation but when the CPAM surface coverage was close to 100%, redispersion of pulp fibers occurred.

Flocs produced by bridging are normally very strong and stable even in turbulent conditions⁶⁴. Mosse et al.⁷¹ discovered that flocs formed from pulp suspension with CPAM were clearly stronger than flocs from neat pulp suspension. They also compared CPAM and small molecular weight, cationic polyethyleneimine (PEI) as flocculants and observed that although PEI increased the floc strength compared to neat pulp, the increase was much smaller than with CPAM. This is explained by the different flocculation mechanisms: CPAM mainly forms bridges between the fibers whereas PEI aggregates by patch-like adsorption.

A high amount of polymer adsorbed onto the fibers can sterically stabilize the system⁶⁴. This is attributed to the loops and tails protruding into the solution from the surface. If approaching fibers are covered with thick polymer layers, the polymer chains are forced to adopt a denser configuration, resulting in a loss of entropy. In the case of a polyelectrolyte, electrostatic interactions also repel one another, and therefore, it is called electrosteric stabilization. On the other hand, if oppositely charged polyelectrolyte is adsorbed onto the cellulose surface, it often adsorbs in higher amounts than is sufficient to screen

the surface charge, causing charge reversal and stabilization. In this mechanism, charge density is normally the most important factor to determine the stabilization. Low molecular weight of the polymer favors stabilization by charge reversal, since bridging is not likely to occur.

Coating the fiber surface with polymer may act as a lubricant layer between the sliding fibers. Some polymers, such as gums and mucilages⁷² and CMC⁶⁷, are known to adsorb on cellulosic fibers, thus reducing the fiber-fiber friction, and in turn, mechanical flocculation⁴⁸. It has been experimentally shown that polyelectrolytes can lower the sliding friction forces between the cellulose surfaces^{73, 74}.

Forces between cellulosic surfaces in the presence of non-adsorbing polymers

Polymers can act as dispersants also when they are not adsorbed onto the cellulosic surfaces. High molecular weight anionic polymers can be used as dispersants for pulp and MFC, even if they do not adsorb onto cellulosic surfaces at low electrolyte concentration. They can deflocculate the suspension by changing the shear⁷⁵ or elongational⁷⁶ viscosity of the suspending medium. Even though no increase is observed in shear viscosity at low molecular concentrations, the elongational viscosity may increase substantially. An increased shear or elongation viscosity of the suspending medium reduces the turbulence intensity and the velocity of the approaching fibers, thus diminishing flocculation^{44, 75, 76, 77}. When flocs are formed, they experience higher viscous forces dispersing them⁷⁵. High molecular weight anionic polyacrylamides (APAMs) are an example of polymers that do not adsorb onto cellulose surfaces. They were observed to be effective in improving sheet formation⁷⁶, which indicated that the original suspension was less flocculated when the molecular weight of APAM was higher.

Polymers can also reduce flocculation by causing repulsion between approaching fibers. If the diffusion of the polymer chains between the approaching fibers is slow, osmotic pressure may resist the contact of fibers and flocculation⁶⁶. Wasser⁷⁸ speculated already in the 1970's that high molecular weight, anionic polyelectrolytes were effective dispersants, since they adopt an extended conformation in water, thus preventing close contacts due to their large physical size. Later, it has been proposed that CMC can prevent flocculation of pulp although it is not adsorbed on the fibers. This was attributed to the CMC molecules between the fibers that form a non-adsorbed layer near the fiber surfaces, thus reducing fiber-to-fiber friction due to the large physical size of the CMC molecules⁷⁹, or that anionic CMC molecules create repulsive forces between the fibers and thus prevent flocculation⁸⁰.

Non-adsorbing polymers can also cause flocculation in some cases. The surfaces confine the movement of the polymer chain and reduce the available conformations and thus the chain entropy, leading to depletion flocculation⁶⁵. However, depletion flocculation has not been reported for pulp or MFC fibers.

2.3 Rheology of fiber suspensions

Solid particles (for instance fibers) in liquid change the rheological behavior of the liquid. Firstly, the particles cause a hydrodynamic disturbance to the flow field, increasing the viscosity. Secondly, interactions between the particles can increase the viscosity of the suspension enormously. Additionally, the behavior of the suspension deviates from Newtonian behavior. The suspension can be shear thinning or shear thickening. Furthermore, there might be time effects when the interaction forces between the particles are adjusted, causing thixotropy⁸¹.

Measuring techniques are also different for suspensions compared to pure liquids, since wall depletion is very likely to occur in these kind of systems when using conventional rotational rheometer⁸². A depletion layer forms when fibers and flocs drift from the geometry walls due to flow and the actual shear is mostly or totally restricted to this fiber-poor layer of suspending medium. This can be a serious problem especially when making flow measurements. On the other hand, oscillation measurements occur in the linear viscoelastic region and the problems with wall depletion are expected to be diminished with small stresses and strains^{50, 82, 83}.

Several researchers have employed roughened surfaces to avoid wall depletion^{84, 85, 86, 87}. However, to efficiently prevent wall depletion in a flowing suspension, the scale of the roughness should be the same or larger than the particle size (floc size) in the suspension⁸³. Therefore, a rough surface is normally not sufficient to prevent slipping in MFC suspensions. Another method to avoid wall depletion is the vane method^{88, 89}. In this method, a vane rotor with four blades is rotated in an infinite cup⁹⁰ or baffled cup^{48, 91}. The suspension is trapped between the blades and it is assumed to form a cylindrical surface with a diameter close to that of the vane. The vane can be placed in a cup with baffles, which hinder the slippage, or in a sufficiently large cup where the shear stress decreases below the yield stress before the shear reaches the surface of the cup (infinite cup). This measuring system has been used for yield stress measurements of pulp^{90, 91, 92} and MFC⁹³, and also to measure flow properties of pulp⁹⁴. However, proper flow curve measurements for MFC suspensions have not been reported in the literature.

The fiber network strength of a suspension can be determined using two types of measurements, oscillation measurements and yield stress measurements. In addition to the network strength, the flow properties, that is, shear stress and viscosity as a function of shear rate, are often of interest. In the oscillation measurement, a sinusoidal stress or strain is applied to the suspension and stored and lost energy is measured (storage and loss modulus, G' and G''). If the storage modulus is higher than the loss modulus, the suspension behaves like a gel. In the opposite case, the behavior is liquid-like. The level of the storage modulus is related to the gel strength of the suspension.

In yield stress measurements, increasing force is applied on the suspension starting from rest. At first, the network is assumed to deform elastically but at some point the network breaks and the suspension starts to flow. This is ob-

served as a sudden increase in the shear rate or decrease in shear stress. A flocculated suspension has weaker areas between the flocs, and the suspension is assumed to first yield between the flocs. In theory, the suspension has another yield stress related to the contacts in the floc, however in practice it can be challenging to separate these two. The difference between the intra- and inter-floc yield stress is depicted in Figure 6. The concept of yield stress is useful in practical applications like mixing, pumping, or dispersing the suspension. However, it must be noted that the yield stress values are often dependent on the method used to measure them. The network strength is also dependent on the sample preparation and shear history⁸⁵.



Figure 6. Schematic presentation of four-bladed vane rotor in a flocculated suspension. As the suspension yields, flocs inside the dashed line start to flow and the others stay stationary. Red flocs must either rupture or move and deform, while breaking contacts with neighboring flocs. Adapted from Mosse et al.⁷¹.

2.3.1 Pulp fibers

Similarly to flocculation, the rheology of pulp suspensions has been extensively studied over the years. Since it is expected that there are common properties in pulp and MFC suspensions, the literature regarding the rheology of pulp suspensions is briefly considered before continuing to MFC suspension rheology.

Pulp fibers form an interconnected network in water suspension, which gives it a solid-like behavior. In order to flow, the network must be broken and the stress needed to facilitate that is called yield stress. The network breaks to flocs and their size is dependent on the shear conditions. Once flowing, the fibers align within the flow. This together with the decreasing floc size results in shear-thinning behavior. Ongoing exposure to shear may gradually break down the structures in the pulp which leads to time-dependent flow properties, referred to as thixotropy⁹². The yield stress and viscosity of pulp suspensions is highly dependent on the fiber concentration^{84, 85, 91}. In many studies, a power law relationship has been found for storage modulus as function of concentra-

tion. The value of power is dependent on the concentration range, pulp type, and degree of beating among others.

As was discussed in the previous section, polymers can be used to modify the flocculation of cellulosic fiber suspensions. The state of flocculation also directly affects the rheology of the suspensions⁹⁵. In general, polymers which induce aggregation of a particle suspension also increase the viscosity and yield stress. On the other hand, polymers dispersing the suspension and causing repulsion between the particles typically lower the viscosity and yield stress^{1, 96}. Pulp concentration determines how significant of an effect polymers have on the rheology of pulp suspension. Swerin et al.⁸⁵ observed that CPAM did not have any influence on the rheological properties of a pulp suspension at concentrations of 3-8%. The fiber network strength was probably so high at these concentrations that the additives did not have a significant contribution to the measured values. Instead, at lower pulp concentrations (0.69%), CPAMs had a large effect on the shear moduli⁵¹. The large molecular weight CPAMs increased the number of active fibers in the network and increased the strength in the points of contact between the fibers.

Mosse et al.⁷¹ studied 2% pulp suspension and found that the yield stress was dependent on the CPAM concentration. The yield stress reached a maximum before the fiber surfaces were completely covered with the polymer. This indicates that the increased yields stress was due to increased attraction between the fibers by polymer bridging. When the polymer amount was further increased, the yield stress started to decrease, since the charge reversal started to cause repulsion between the fibers. Despite this repulsion and lower yield stress, the flocs still remained strong and did not start to disperse. This was explained by the history of the pulp suspensions and kinetics of polymer-pulp interactions. Since the polymer was added to an already-flocculated suspension, the polymer chains adsorbed mostly onto the floc outer surface causing repulsion between the flocs, making them actually stronger although the overall strength of the suspension was reduced.

Horvath and Lindström⁸⁷ studied the yield stress of CMC grafted pulp and observed that CMC decreased the dynamic yield stress. They attributed the decrease to increased surface charge and electrostatic repulsion. Beghello and Lindström⁴⁸ also studied carboxymethylated pulp and discovered that the floc size and yield stress decreased with increasing amount of carboxymethylation. They explained it with decreased fiber-fiber friction. Giri et al.⁸⁶ also found that adsorbing CMC onto pulp fibers reduced the yield stress, which was attributed to reduced surface friction. Interestingly, Liimatainen et al.⁷⁹ found that CMC can decrease the yield stress, regardless if it was adsorbed on the pulp fibers or not. They claimed that even though CMC did not adsorb on the fibers, it forms a non-adsorbed layer that prevented fiber contacts due to the large physical size of the CMC molecules.

According to Swerin⁵¹, the flocculation by polymers gives non-equilibrium structures. Therefore, the floc structure is dependent on sample preparation and prevailing shear conditions. Since the flocculated state strongly influences

the rheological results, sample preparation has a significant effect on the obtained data.

2.3.2 Rheology of microfibrillated cellulose suspensions

Compared to pulp fibers, MFC and NFC fibers have smaller dimensions and higher aspect ratios. In addition, they have a large specific surface area. This brings some new aspects to the rheological behavior of NFC and MFC suspension, for instance, colloidal forces may be more important for nanocellulosic fiber suspensions than for pulp suspensions. On the other hand, there are also similarities, such as the identical chemical structure of the fibers and flocculation tendency.

MFC suspensions are strongly shear-thinning and their viscosity is dependent on concentration^{6, 97, 98}. Flow properties of suspensions have been studied with regard to concentration^{6, 97, 99, 100}, temperature^{22, 98}, ion concentration^{22, 38, 97}, and pH^{6, 97}. MFC suspensions show a power law relationship between the concentration and storage modulus of the gel, similar to pulp. Exponent values between 2.25 and 3.0^{6, 97, 100} have been reported. The viscosity and moduli dependence on pH of the suspension is not straightforward but dependent on the suspension concentration. Agoda-Tandjawa et al.⁹⁷ did not observe any difference between different pHs from 4.5 to 9 for 1% MFC suspension. On the contrary, Pääkkö et al.⁶ reported that the viscosity was dependent on the pH between pH 2 and 10 when the MFC concentration was 0.25%. The viscosity of 0.25% MFC suspension decreased with increasing pH which was explained by higher electrostatic repulsion between the fibers⁶. It seems that at lower concentrations, changes in the surface charge caused by the pH are sufficient to change the interactions between the fibers. Instead at higher concentration, the network strength of the fiber network is so high that the contribution of pH does not show in the results.

According to Lowys et al.²², the storage and loss moduli of MFC suspensions are not dependent on temperature between 25 and 60 °C. On the other hand, Iotti et al.⁹⁸ found that the viscosity of the MFC suspension decreased with increasing temperature from 25 to 60 °C, and similarly Ono et al.⁵² observed decreasing viscosity between a temperature range of 30-80 °C. The reduction in the viscosity was explained by the decrease in the water viscosity with temperature and deswelling of the fibers at higher temperatures. The reason for these different results is not clear but Lowys et al.²² used a lower concentration (0.4%) than Iotti et al.⁹⁸ and Ono et al.⁵² (1 % and 2 %, respectively).

Salt ions can screen the negative charges on MFC fibers. This leads to stronger interactions between fibers and further aggregation. Agoda-Tandjawa et al.⁹⁷ observed that 0.05 and 0.1 M NaCl or CaCl₂ increased the loss and storage modulus of 0.5% MFC suspension. Lowys et al.²² obtained similar results when using 0.05-0.3 M NaCl, with the optimum (highest G' value) at 0.2 M NaCl. Saarikoski et al.³⁸ found that adding salt (10⁻² – 1 M NaCl) to MFC suspension causes flocculation and that was reflected as lower shear stresses in

the flow measurements. The drop in shear stress was mainly attributed to increased wall depletion rather than changed interactions between the fibers.

MFC has been reported to show hysteresis and time dependent flow behavior^{97, 98, 101}. The hysteresis in the flow curves has been generally attributed to time-dependent changes in the suspension structure, but there has not been a detailed study about the actual reason for this observed behavior.

Compared to MFC, TEMPO-oxidized NFC suspensions are similar in many ways: they show gel-like behavior in oscillation measurements, shear-thinning and viscosity dependence on the concentration^{32, 101}. On the other hand, a lower threshold concentration for gel-like behavior has been reported for NFC than MFC suspensions (0.03%³² for NFC compared to ~0.1%⁶ for MFC).

Few studies have been published about MFC/polymer suspensions and their rheology. Gómez Martínez et al.¹⁰² added MFC to κ -carrageenan suspension and measured dynamic moduli as a function of temperature. They found that MFC increased the strength and stability of the κ -carrageenan gel. Lowys et al.²² studied three different charged polymers as additives in MFC suspensions: anionic CMC, anionic polyacrylate (PAA), and cationic polyacrylamide derivative. In their study, all polymers decreased the storage and loss modulus of the suspension, even the cationic one. This was somewhat surprising but it was not further explained in the study.

Vesterinen et al.¹⁰³ mixed 0.5% MFC with 0.5% of different polymers: cationic starch (CS), CPAM, CMC, and poly(ethyleneoxide) (PEO). Addition of negatively charged CMC or PEO removed the apparent yield stress of the suspension whereas cationic CS and CPAM maintained yielding behavior of the suspension. In the oscillation tests, CMC and PEO increased tan delta of the suspension over 1, indicating that the suspensions were liquid-like. This was attributed to the dispersing effect of the polymers.

Measuring MFC suspension rheology is not straightforward as was described above. The first challenge is to find a measuring method which avoids the problems of wall depletion. In addition, flocculation can cause error for the interpretation of results. Moreover, the sample history has a huge effect on the measured values. This thesis studies the flocculation and rheology of MFC and tries to determine the mechanisms of how polymers can affect these two properties. For that purpose, new methods for measuring the rheology reliably and simultaneously with flocculation are developed.

3. Experimental

3.1 Materials

3.1.1 Microfibrillated celluloses

Microfibrillated cellulose (MFC, obtained from UPM-Kymmene Corporation) was prepared from never-dried bleached kraft birch pulp by mechanical disintegration. Slightly different procedures were used in different papers: MFC was ground three (papers II, IV, and V) or five (paper I) times with a grinder (Supermasscolloider, Masuko Sangyo, Japan), or passed once through a Voith refiner (Voith AG, Heidenheim, Germany) and then seven times through Fluidizer M7115 (Microfluidics Corp., Newton, MA, USA) (paper III). The pulp was changed to its sodium form and washed with deionized water to an electrical conductivity of less than 10 $\mu\text{S}/\text{cm}$, according to a procedure introduced by Swerin et al.¹⁰⁴, except in paper III where the pulp was not washed prior grinding. MFC suspension was in its sodium form and washed, as it was received and was used without further purification. The initial concentration was approximately 2% (w/w).

The properties of the raw material have been reported in the literature³⁵: carbohydrate composition was 72.8% glucose, 25.6% xylose, and 1.4% mannose and the charge of the pulp $\sim 65 \mu\text{eqg}^{-1}$. Similar never-dried kraft birch pulp has been used as raw material for every MFC grade used in this study. Therefore, the hemicellulose content and surface charge is assumed to be approximately the same for every MFC. As was discussed in chapter 2, the size of MFC is difficult to determine exactly, since the size distribution is so large. Vartiainen et al.²⁸ examined similar MFC as was used in Paper I and found that the smallest fibers had diameters even below 10 nm, but some of the fibers were even visible by optical microscopy. Size and morphology most probably vary slightly in MFCs used in this study but based on the rheological characterization the difference is negligible.

Similar never-dried bleached birch kraft pulp was used as a raw material for nanofibrillated cellulose (NFC). First, the pulp was oxidized by TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl radical) similarly to a previously described procedure²⁶. Oxidized pulp was diluted with tap water in a Diaf dissolver to provide a cellulose suspension. Two different procedures were employed to prepare fibers with different lengths. Long NFC fibers were prepared using rotor-rotor dispergator, 4 passes in 2.5 % consistency, while short NFC fibers were fibrillated using a homogenizer using 1500 bar, 3 passes, 1.5 % consistency. Diameters and lengths of the fibers were estimated from cryo-

TEM and AFM images. Diameters were mainly 2-6 nm for both materials. Shorter NFC fibers were mainly between 0.5-1 μm and longer NFC fibers were 1-10 μm in length. The carboxylate content of the pulp titration was determined by conductometric after the oxidation of the pulp. It was 0.95 mmol (COOH)/(g pulp) for longer fibers and 1.02 mmol (COOH)/(g pulp) for shorter fibers. The preparation of TEMPO oxidized NFC and dimensional analysis were performed by the manufacturer (UPM Kymmene).

3.1.2 Polymers

Three cationic and five anionic polymers were studied as modifiers for MFC suspensions. They are listed in Table 1. The cationic polymers were

- commercial cationic polyacrylamide (CPAM, Fennopol K3400R, Kemira)
- cationized poly([2-(methacryloyloxy)ethyl] trimethyl ammonium iodide) (PDMQ)
- cationized statistical copolymer of 2-(methacryloyloxy)ethyl trimethyl ammonium iodide (META1) and stearyl methacrylate (SMA) (PSMA13Q).

The synthesis of prepolymers for PDMQ and PSMA13Q was performed in bulk phase with radical polymerization and cationic groups were obtained by post-modification. A detailed description of the synthesis and polymer characterization, including rheological characterization of the polymers, is reported elsewhere¹⁰⁵. The synthesis of PDMQ and PSMA13Q was performed by Arja-Helena Vesterinen.

Table 1. The properties of polymers used in the experiments. The molecular weights are given by the producer and the charge densities are determined by conductometric titration unless otherwise stated.

Polymer	Molecular weight (M_w) (10^6 gmol^{-1})	Charge density (CD) (meqg^{-1})	Paper
PDMQ	0.063 ^a	6.32 ^b	III
PSMA13Q	0.051 ^a	4.8 ^b	III
CPAM	6-7	1	Unpublished
CMC	0.7	-4.2 ^b	IV
xanthan gum	- ^c	-1.6	IV
LMW-LCD	7	-1.1	V
LMW-HCD	7	-3.5	V
HMW-HCD	15-17	-3.2	V

^afrom ref¹⁰⁶, determined by gel permeation chromatography

^bcalculated from the molecular structure

^cmesh size 381 μm

The anionic polymers were

- carboxymethylcellulose (CMC) from Sigma-Aldrich (M_w 700 000 g/mol, degree of substitution (DS) 0.9, sodium salt)
- xanthan gum from CP Kelco (Kelzan XG, mesh size 381 μm)
- three different anionic polyacrylamides (APAM, Kemira). They are listed in Table 1.

The charge of xanthan gum was determined to be approximately 1.6 meqg⁻¹ by conductometric titration with cationic polydiallyldimethylammonium chloride. The APAMs were classified according to molecular weight (low molecular weight (LMW) and high high molecular weight (HMW)) and charge density (high charge density (HCD) and low charge density (LCD)). The molecular weights for the anionic polymers were provided by the producer. Charge densities were determined via polyelectrolyte titration or calculated from the chemical structure. All polymers were used without purification.

3.1.3 Suspension preparation

Dilution of the MFC suspension to different concentrations was made with deionized Milli-Q water (electrical conductivity $<0.2 \mu\text{S cm}^{-1}$ at 25°C) in order to avoid excess electrolytes. The dilution was performed with a propeller mixer (diameter 58 mm, RZR 2051 control, Heidolph Instruments, Germany) using a speed of 1400 rpm for 10 min in a beaker with a diameter of 66 mm. The conductivity of the 0.5% MFC suspension was 22 $\mu\text{S/cm}$ and pH 6.18.

The cationic PSMAQ13 and PDMQ were dissolved in distilled water to desired concentrations. PSMA13Q required heating to 60°C. The MFC suspension was diluted from 1.6 wt% to 1 wt%, then the polymer solution was poured to the MFC suspension and mixed with a magnetic stirrer for 45 min. The final concentration of MFC was 0.5 wt% and polymer concentrations were 0.25, 0.5, 1, 2, or 4 wt%.

CPAM, CMC and xanthan gum were dissolved in Milli-Q water at room temperature and mixed with a magnetic stirrer for at least 2 h. The MFC suspensions were diluted with Milli-Q water and mixed with the propeller mixer at 1400 rpm for 10 min. After that, the polymer solution was poured into the MFC suspension, and the resulting suspension was again mixed with the propeller mixer at 1400 rpm for 10 min. APAMs were dissolved in distilled water, then combined with diluted MFC suspension and ultrasonicated (Branson digital sonifier 450, USA) for 2 minutes at 25% amplitude.

The pH of the MFC suspensions was between 5 and 7, slightly depending on the MFC concentration and the polymer added.

TEMPO-oxidized NFC suspensions were diluted to desired concentrations (0.25-1%) with MilliQ water and mixed with a domestic blender 4 times at 10 s intervals. After every 10 s mixing, the suspension was stirred with a spoon to ensure the mixing of the whole suspension volume.

3.2 Methods

3.2.1 Rheological characterization

The rheological measurements were performed using a dynamic rotational rheometer (ARG2, TA Instruments), with a standard (ISO 3219/DIN 53 019) metal concentric cylinders geometry (bob and cup radii 14 and 15 mm). For measurements with imaging, a transparent polymethylmethacrylate (PMMA) outer cup was used together with the same inner cylinder. The measurements were performed at 25 °C.

Viscosity of the polymer solutions

Polymer solutions viscosities were measured from 0.02 to 1000 s⁻¹ (PDMQ and PSMA13Q), from 500 to 0.01 s⁻¹ (CPAM and APAM (LMW-HCD)), or 0.01-1000 (CMC and xanthan gum). Point time was 1 min (PDMQ, PSMA13Q, and APAM) or 15 s (CPAM, CMC, and xanthan gum).

Preshear

Before starting the actual measurements, a 20 min preshear interval at 500 s⁻¹ (neat MFC suspensions and suspensions with APAM) or 250 s⁻¹ (suspensions containing CMC, xanthan gum, or CPAM) was applied on the sample. The intensive pre-shear period was implemented to break down the flocculated MFC network structure and ensure similar shearing history for all samples. Then the sample was left to rest for at least 10 min with the application of a small oscillation at 6.25 rads⁻¹ and 0.5% strain, which is within the linear viscoelastic region. Stopping the flow of the suspension after the pre-shear period relaxes the MFC network strained in shear, pushing it into better contact with the cylinder walls, thus decreasing the likelihood of depletion in the following oscillation measurements.

Oscillation measurements

Oscillation measurements were performed after the preshear and rest periods. Frequency sweep was measured from 0.02 to 200 rads⁻¹ at 0.5% strain and amplitude sweep from the strain 0.01 to 1000% at a frequency of 6.283 rads⁻¹. The measurements with PDMQ and PSMA13Q were performed slightly differently: Before measuring, the samples were allowed to rest 15 min in the geometry. In the strain sweep, the strain was from 0.1 to 1000% at an angular frequency of 1.0 rads⁻¹. After this, the samples were allowed to rest for 30 min. Next, a frequency sweep was performed at 0.2% strain, in the linear viscoelastic region, varying angular frequency from 300 to 0.05 rads⁻¹.

Flow curve measurements

The flow curve was measured strain-controlled from 0.01 to 1000 s⁻¹ with a point time of 15 s (MFC and NFC). For the suspensions with PDMQ or PSMA13Q, flow was measured by raising the shear rate from 0.002 to 1000 s⁻¹ with point time of 1 min. For the CMC and xanthan gum containing suspensions, the flow curve was measured strain controlled from apparent shear rates

of 500 (MFC) or 300 (suspensions with polymers) to 0.1 s^{-1} with a point time of 15 s.

Constant shear

Selected suspensions were photographed after constant shearing to study their floc structure. Suspensions were sheared at four constant shear rates (500, 30, 5, and 0.5 s^{-1}) for 10 min using the transparent cylinder. After each shear rate period, a 10 min oscillatory time sweep was measured at 0.5% strain and 1 Hz frequency. The photographs were taken immediately after shearing the suspension.

The vane method

TEMPO-oxidized NFC suspensions were measured with an improved measuring system. The geometry consisted of a standard vane rotor (height 42 mm, radius 14 mm) and a cup (radius 33 mm) with eight 5-mm-baffles at the wall. The assumed gap was between the tips of the vane and baffles, that is, 16.5 mm. The measurement was started with a 10 min preshear at 100 rads^{-1} followed by a 10 min rest period. The suspensions were measured between 31.62 and 0.01 rads^{-1} , six points per decade. At the lowest velocity, the point time was 10800 s and the other point times were defined to keep the total displacement constant, while keeping the point time at least 600 s. The maximum velocity, where the flow of the suspension was still laminar, was carefully ensured for each sample by introducing a trace of blue ink into the suspension. The vane rotor was rotated at stepwise increasing velocity, while visually observing the ink displacement. At some shear rate, Taylor vortices appeared in the suspension, and only shear rates below that were used for the analysis.

3.2.2 Photographing and floc size analysis

In addition to standard metal outer geometry, a tailor-made transparent polymethyl methacrylate (PMMA) outer geometry was used in the rheological experiments in order to photograph changes in suspension structure during the measurements. The cup was placed into a transparent water container to prevent reflections. The temperature in the water container was not controlled, but it was assumed to be close to room temperature. The photographs were taken with Nikon D90 camera (Nikon Corporation, Japan) with a macro objective controlled by NKRemote software (Breeze Systems Limited, UK).

Floc size analysis was done using the method presented by Karema et al.¹⁰⁷. Uneven illumination in each image was corrected using the average image of all acquired images and all the remaining intensity variations in the corrected images are due to changes in suspension properties. The dominant factor causing these variations is the suspension's local concentration. Floc size analysis was performed as described earlier by Saarikoski et al.³⁸ and was carried out by Juha Salmela (Technical Research Centre of Finland, VTT).

3.2.3 Optical coherence tomography

The OCT device used in this study was a Spectral Domain OCT (Telesto SD-OCT, Thorlabs Inc) with a central wavelength of 1325 nm. In the SD-OCT, a light beam of low coherence is emitted from a super luminescent led light source and split into the sample arm and the reference arm of the Michelson interferometer. The backscattered interference pattern carries information about the sample scattering index from different depths. Slice images are constructed from a series of adjacent lateral scans. In Doppler OCT mode, the velocity data is acquired using Kasai autocorrelation function of adjacent scans¹⁰⁸.

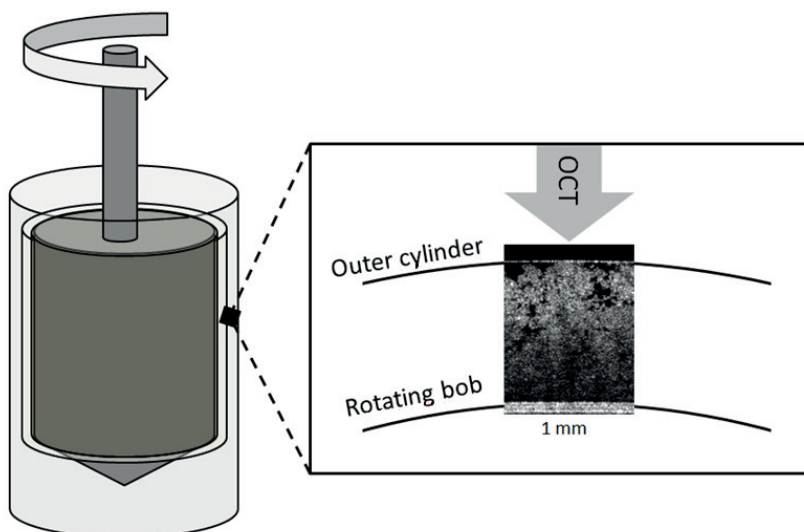


Figure 7. Schematic presentation of the set-up with rheometer and OCT.

The OCT was utilized in visualizing the MFC suspension structure during the stepped flow measurements. OCT recording and analysis were carried out by Sanna Haavisto (Technical Research Centre of Finland, VTT). The device was set to acquire 2D slice images consisting of 500 radial scans across a lateral width of 1 mm. The set-up is presented in Figure 7. The resolution and frame rate of the slice images are determined by the light beam properties (central wavelength, coherence length, and dimensions) and the radial scan rate. With the current device, the radial resolution in water was approximately 5 μm and the lateral resolution was 15 μm . Three discrete values, 5.5, 28 and 91 kHz, were available for the radial scan rate. The value was selected based on the shear rate, aiming to minimize the structure motion between two sequential slice images to the detriment of image quality. At the highest radial scan rate, a mean frame rate of 12 ms was achieved.

A sequence of 2D images was recorded at each shear rate during the stepped flow measurements. In addition to structural characterization, the images were utilized to determine the radial mean velocity profile by tracking the horizontal displacement of the MFC flocs between sequential structure images. The tracking was realized with an optical flow algorithm developed for fiber flocculation studies¹⁰⁹. The presented experimental setup allowed structure

motion to be tracked across shear rates from 0.1 to approximately 50 s⁻¹ in the vicinity of the outer cylinder wall. The velocity profiles could be built up over a shear rate range of 0.1 to approximately 15 s⁻¹, however the profile span was limited by the image quality.

4. Results and discussion

The rheology and flocculation of MFC suspensions as such and with polymer additives were studied using rheometer and imaging methods. The aim was to study the effect of various charged polymers and surface modification on the MFC suspension properties. The selected polymers were novel polymers and commercial polymers. These commercial polymers have been used, for instance, in paper making. This section starts with a short discussion on MFC rheology and flocculation without any additives. Then, the effect of cationic and anionic polymer additives will be explored, and last, the effect of surface charge and fiber length will be briefly considered.

4.1 Flocculation and rheology of MFC suspensions

Figure 8 shows the flow curves and frequency sweeps for microfibrillated cellulose suspensions at different concentrations. The well-known properties of MFC suspensions, shear thinning and gel-like behavior, are evident in these rheograms. If we first consider the flow curve, we see that it can be divided in three regions: first shear thinning region, transition region and second shear thinning region. The apparent shear thinning behavior suggests that the structure is changing when the suspensions is sheared with increasing shear rate. The suspension structures related to these regions are discussed more in detail later in this chapter. The measured viscosity of the MFC suspensions is highly dependant on the concentration of the suspensions.

Looking now at the frequency sweep in Figure 8, it shows that the suspensions at concentrations 0.1-2% have higher storage (G') than loss (G'') moduli, indicating gel-like structure. This stems from the strong network structure of the fibers. The storage modulus represents the ability of the suspension to restore energy, and therefore, it is regarded as the gel strength of the suspensions. The storage modulus is highly dependent on the MFC concentration. This is because more fibers per volume make the suspension stronger. At the lowest concentration 0.1%, the loss modulus starts to increase at lower frequency which suggests that this concentration is close to the threshold concentration for gel-like behaviour.

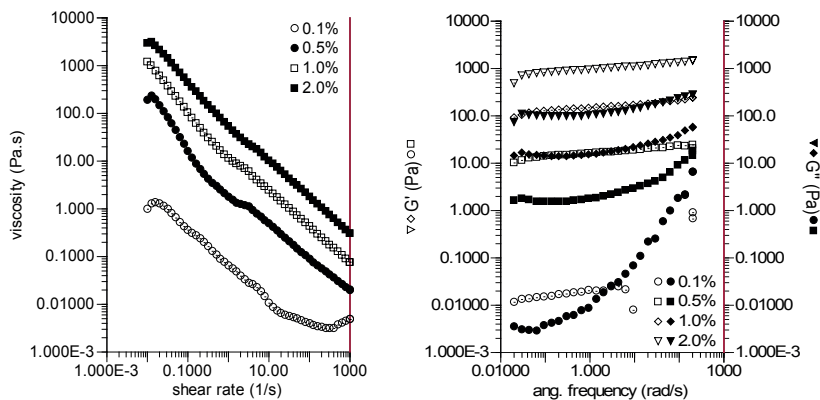


Figure 8. Flow curve and frequency sweeps for MFC suspensions at different concentrations (paper I).

MFC fibers form a three dimensional network where the junction points are partially disintegrated fibers or mechanical entanglements. The small negative surface charge ($65 \mu\text{eqg}^{-1}$ according to Eronen et al.¹¹⁰) that the fibers have causes slight repulsion between the fibers, thus inhibiting aggregation to some extent. Within the network, there are more concentrated areas which can be regarded as flocs. Under flow, the linkages between the flocs break and large flocs, visible to the naked eye, are formed. Figure 9 shows the floc structure of 1% MFC suspension with increasing shear rate. The structure in the first picture (a) represents the structure at the apparent shear rate of 0.1 s^{-1} . However, the shear is mostly located in the depletion layer near the outer cylinder wall at this low shear rate, as will be shown later. Therefore, the structure is basically what was created in the previous high shear interval. The image shows an even network of very small flocs evenly distributed. In this region, the suspension shows decreasing viscosity (see Figure 8). In the Figure 9b, the shear rate is sufficient to start to deform the fiber network and it breaks into large, irregular flocs. This is seen as a transition region in the flow curve. In the last image of Figure 9c, the whole suspension is under shear and small, separate flocs are rolling in the flow. This is the second shear thinning region shown in the flow curve in Figure 8.

Figure 10 shows the floc diameter in x (along the flow) and y (across the flow) directions calculated from the flow curve images. First, the floc size is small and not changing, since the shear is not actually deforming the bulk of the suspension, as was discussed above. Then an increase in floc size is observed, followed by decreasing floc size with increasing shear rate. The increase in floc size is related to the transition region in the flow curve and rupture of the fiber network. After that, the floc size starts to decrease, since the suspension is under flow. Shear thinning behavior of the MFC suspension observed in Figure 8 is due to decreasing floc size and orientation of the fibers in the suspension in the second shear thinning region.

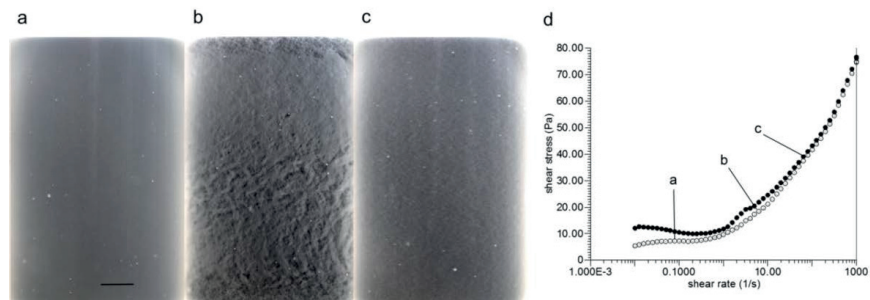


Figure 9. Flow curve and floc structure for 1% MFC suspension. The suspension is photographed through the outer cylinder of the concentric cylinders geometry, and the gap between the cylinders is 1 mm. The images are from three different regions from the flow curve: a) shear rate 0.1 s^{-1} constant stress, b) shear rate 5 s^{-1} transition region, and c) shear rate 63.1 s^{-1} increasing shear stress. The inner cylinder rotates to the left. Rheograph d) shows flow curves with the metal cup (filled circles) and the transparent cup (empty circles) and the positions of the images. The length of the scale bar is 5 mm (paper I).

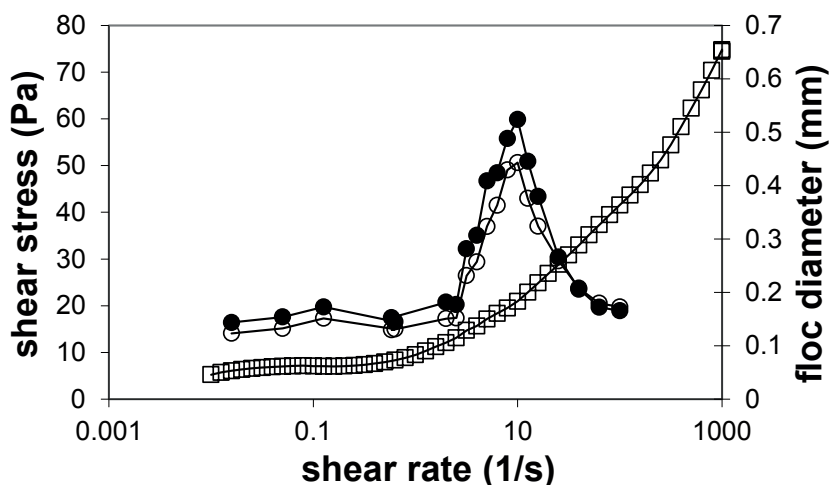


Figure 10. Floc sizes in x direction (empty circles) and y direction (filled circles) for 1% MFC suspension together with shear stress (empty squares) (paper I).

Understanding of the MFC suspension structure and flow during the changing shear rate was complemented with OCT analysis. It is a method which uses visible light to depict the suspension structure and velocity in the suspension. The set-up utilized in this study enables imaging of the sample through the gap between the cylinders. In addition, the velocity of the structures can be calculated from the consecutive frames to obtain the velocity profile in the gap. For the interpretation of the rheological data, the velocity profile is normally assumed to be linearly decreasing to zero towards the outer cylinder wall. Figure 11 shows the structure of the MFC suspensions imaged through the 1-mm-gap, and the velocity profile is drawn on it. The maximum of the x-axis is equal to the velocity of the bob surface. The images together with the velocity profiles by OCT and rheometer in Figure 11 clearly show that the velocity profile is not ideal. The suspension is not under shear at low shear rates but there is a deple-

tion layer at the outer cylinder surface. Therefore, the shear stress and viscosity calculated from the results assuming linear velocity profile do not represent the real properties of the suspension.

Figure 11 shows 0.5 and 1% MFC suspensions at apparent shear rates 0.6–12.3 s^{-1} . Flocculated structure is evident at this scale as well. The first row presents MFC suspension at a concentration of 0.5%. The velocity profile reveals that the suspension slips at both geometry surfaces. In addition, the velocity profile is quite irregular due to the inhomogeneous structure of the suspension, where flocs rotate as bigger entities.

The rheological properties observed below yielding of the fiber network are mostly related to formation and properties of the depletion layer. In Figure 8, the observed shear thinning can arise from properties of the depletion layer (it may contain nanoscale fibers and dissolved components), changing thickness of the depletion layer, or the friction which is caused by the fibers sticking out of the bulk of the suspension at the depletion layer interface. Based on these measurements, the phenomena cannot be distinguished. The method used in these experiments was restricted to apparent shear rates under approximately 20 s^{-1} , which is the transition region in the flow curve. Following this, the method was developed further, and velocity profiles and structures from higher shear rates were obtained¹¹¹. The results in those experiments show that after the yield stress, the suspensions slips but the bulk is under shear. That is, flow properties measured at higher shear rates represent more accurately the actual suspension properties. OCT results also confirm that the floc size decreases with increasing shear rate at higher shear rates where photographing is no longer possible¹¹¹.

The second row in Figure 11 shows the 1% MFC suspension observed by OCT. The suspension is more crowded than the 0.5% suspension, and there are less black areas presenting water in the images. At the lowest shear rate 0.6 s^{-1} , the suspension is attached to the inner cylinder and rotating with it as a plug. At two higher shear rates, the velocity profile starts to resemble that of 0.5% MFC suspension: rolling flocs within the suspension cause irregularity to the curve and wall depletion occurs at both geometry walls. It seems that the flocs become denser, since there is more water between them.

It is evident from the results that measuring the flow curves for MFC suspensions with smooth concentric cylinders geometry suffers from wall depletion. However, the particular geometry was utilized since it enables the use of imaging methods, photographing and OCT, and detect the floc structure at different shearing conditions. As was discussed above, the high shear rate results represent the suspension properties to some extent. Moreover, the oscillation measurements are expected to describe the suspension properties when the strains and stress are kept sufficiently small^{51, 83, 112}. Therefore, the rheological characterization of MFC suspensions is based on oscillation measurements and the flow measurements are only used to study the flocculation behaviour in this thesis. To measure flow curves without wall depletion, a different type of geometry must be employed. One option is the vane method. Later in this thesis, an example of using that for TEMPO-oxidized NFC is given.

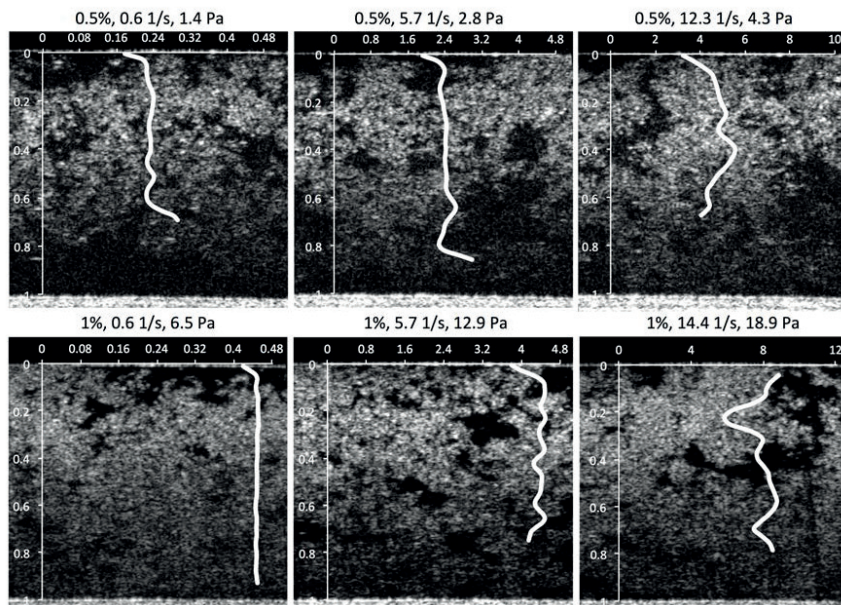


Figure 11. Structure image with calculated shear rate distribution from inner geometry boundary to outer geometry boundary, at different apparent shear rates in a stepped flow measurement. The abscissa shows the velocity in mm/s with the maximum value equaling the bob surface velocity. The ordinate shows the position inside the gap in mm (paper II).

By applying different shear rates on the MFC suspensions, it is possible to create a certain floc structure in the suspension. Figure 12 shows the floc structure of 1% MFC suspension after 10 min shearing at different shear rates. The higher the shear rate, the smaller the flocs. A high shear rate (500 s^{-1}) creates an even structure with small flocs. Decreasing the apparent shear rate induces a coarser structure. The same trend was observed for the concentrations 0.1–2% (results not shown). However, in the dilute suspensions, the fibers spun into rolling “logs” at the lowest shear rate shown in Figure 13. Between the rollers, there is visibly fiber-free water. This illustrates how flow induces collisions between the fibers and thus flocculation. Simultaneously, the shearing is too low to disperse the flocs, creating the rollers. Later in this thesis, the low apparent shear rate 0.5 s^{-1} will be used to compare the ability of different polymers to flocculate or deflocculate MFC suspensions.

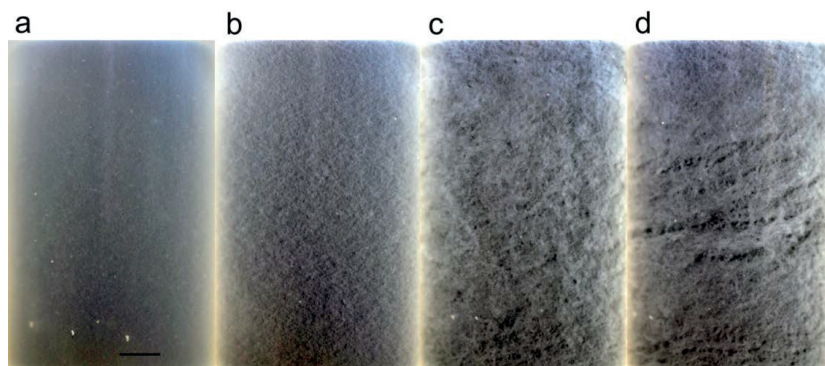


Figure 12. 1% MFC suspension immediately after peak holds at a) 500 s^{-1} , b) 30 s^{-1} , c) 5 s^{-1} , and d) 0.5 s^{-1} . The inner cylinder rotates to the left. The length of the scale bar is 5 mm (paper I).



Figure 13. 0.1% MFC suspension immediately after shearing the suspension at apparent shear rate 0.5 s^{-1} for 10 min (paper I). The length of the scale bar is 5 mm.

4.1.1 Comparison of different MFC batches

Figure 14 compares the storage and loss moduli of 0.5% MFC suspensions made from the different batches and slightly different mixing procedures used in this thesis. MFC is made from natural raw material which means that its properties may vary from batch to batch. Its properties change also during storage and its shelf life is limited. In addition, manufacturing methods were developed during this thesis. Therefore, the morphology of the fibers used in the papers I-V may differ, thus affecting the rheological performance. Figure 14 shows that the MFC used in paper III had the lowest moduli. This is probably because the mixing of the suspension after dilution was made only with a magnetic stirrer. Later, a propeller mixer was used, which can disperse the fibers better. The MFC used in papers II, IV, and V had the highest moduli although it is passed only three times through the grinder and the MFC used in paper III is passed five times. This shows that the grinding procedure was developed over the time enabling better disintegration of the fibers with fewer passes through the grinder. MFC for the measurements in paper V were mixed

with ultrasound after dilution. That had only a minor effect on the gel strength of the suspension compared to the propeller mixer.

Since there are differences in the rheological performance between the materials, the rheological comparisons in this thesis are only made within the samples from the same MFC batch prepared with the same procedure. On the other hand, based on previous experience, trends observed with one batch are expected to hold for unmodified MFC in general. The exact dimensions and especially size distribution for each batch are difficult to evaluate, since the sizes vary by several decades. Rheology is sensitive to different dimensions and size distributions and it gives an overall description of the suspensions.

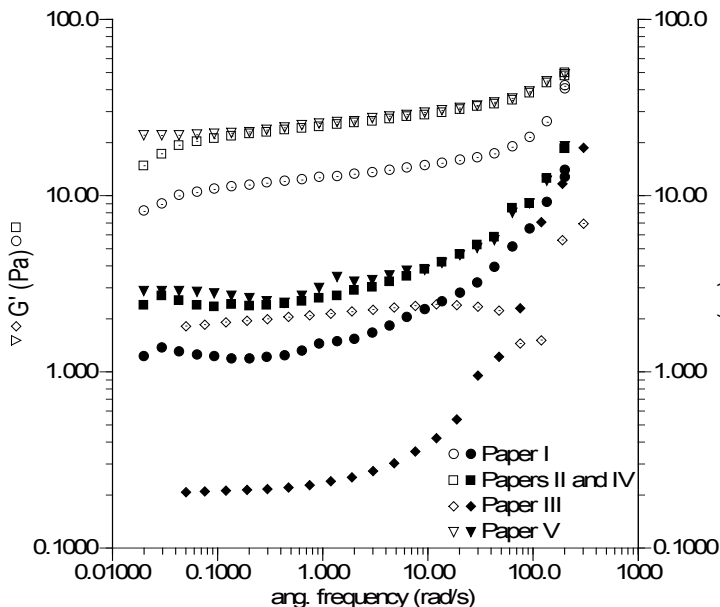


Figure 14. Comparison the storage and loss moduli of the MFC suspensions from papers I-V at a concentration of 0.5%.

4.2 Polymers as flocculants and deflocculants

In this chapter, the effect of cationic and anionic polymers on the gel strength and flocculation of MFC suspensions is discussed. Based on the studies with pulp suspensions, at least the following properties are important for a polymer's ability to flocculate or deflocculate cellulosic fibers: molecular weight, charge density, possible adsorption of the polymer on the cellulose surface⁴², and viscosity of the polymer solution⁷⁶. Polymers with different molecular weights and charge densities were chosen for this study and they are listed in Table 1 in chapter 3.1.2. The cationic polymers were expected to adsorb onto the MFC fibers based on the earlier results in the literature^{106, 113}. The anionic polymers were not expected to adsorb in large amounts, since excess ions were removed from the suspensions which hinders the adsorption of the polyelec-

trolyte to the similarly charged surface. QCM-D results (paper IV and V) confirmed that CMC, xanthan gum and APAMs did not substantially adsorb on the NFC model surface. Figure 15 shows the viscosities for polymers at the highest concentration at which they were used in this study (i.e. 0.11% or 4%). The small molecular weight cationic PDMQ and PSMA13Q were used at higher concentrations than the higher molecular weight polymers; therefore, their viscosity is shown at higher concentration. Still, their viscosity is clearly lower than the viscosity of the other polymers. CPAM, xanthan gum, and APAM have a very high viscosity at low shear rates but they are shear thinning which lead to rather low viscosity at higher shear rates. Instead, CMC has clearly lower viscosity at low shear rates but it is not as shear-thinning as CPAM, xanthan gum, and APAM. Thus at high shear rates, its viscosity is the highest of these polymers.

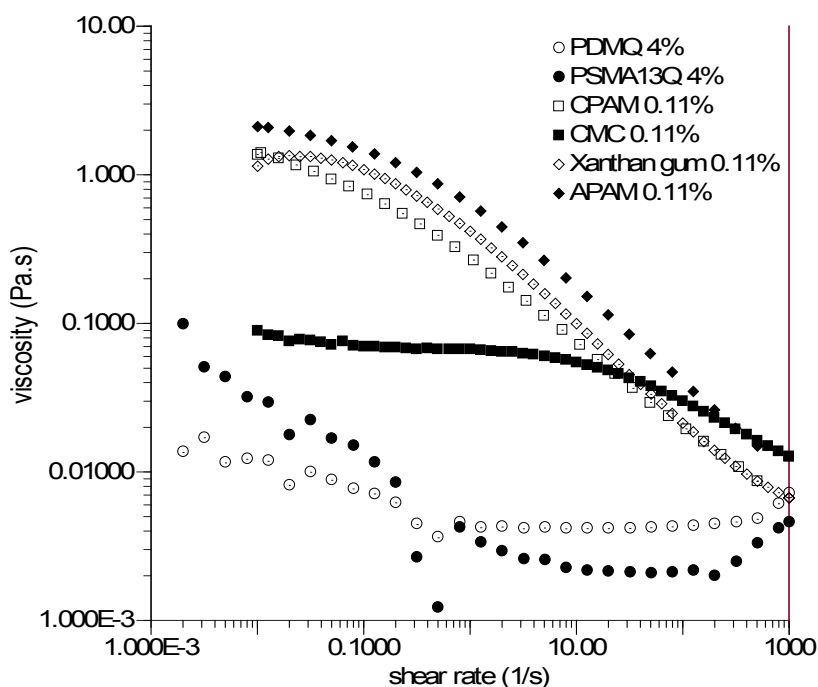


Figure 15. Viscosities of the polymer solutions. APAM is HMW-HCD. Note that PDMQ and PSMA13Q are at higher concentrations than the others.

4.2.1 Cationic polymers

Cationic polymers adsorb readily onto the slightly negative MFC surface. They are widely used as flocculants for pulp suspensions. The adsorption and conformation of the polymer on the surface affects the flocculation mechanism.

Small molecular weight polymethacrylates

Cationic PDMQ and amphiphilic, cationic PSMA13Q are low molecular weight, high charge density polymers which are expected to adsorb onto MFC fibers¹⁰⁶. Cationic PDMQ adsorbs in flat conformation, whereas amphiphilic PSMA13Q is assumed to adsorb in more coiled conformation resulting in a thicker adsorption layer.

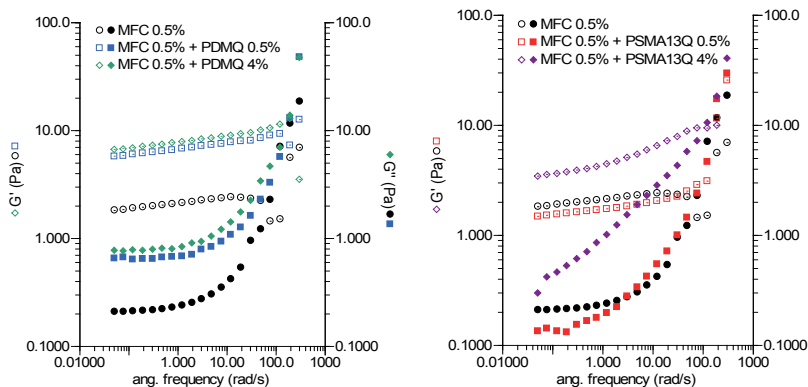


Figure 16. Frequency sweeps for pure MFC suspension at 0.5% concentration and with polymer addition (paper III).

Figure 16 shows the frequency sweeps for MFC suspensions at a concentration of 0.5%, with 0.5 or 4 % PDMQ or PSMA13Q. Cationic homopolymer PDMQ increased the gel strength at both concentrations. Instead, PSMA13Q slightly decreased the gel strength at a concentration of 0.5% and increased the gel strength at 4% concentration. Based on the molecular weight and charge density of PDMQ, patch-like adsorption is likely to occur. Patch-like adsorption of a cationic polymer onto the slightly negative cellulose surface increases the attraction between the polymer-covered and neat areas on the MFC fibers. Recharging of the surface is also possible, introducing a higher, cationic surface charge to the fibers. An increased surface charge is known to lead to higher gel strength¹¹⁴.

Amphiphilic PSMA13Q contains hydrophobic stearyl methacrylate (SMA) units in addition to cationic dimethylaminoethylmethacrylate (DMAEMA) units. This clearly reduced its ability to increase the gel strength, and caused even a slight decrease in gel strength at 0.5% concentration. PSMA13Q is assumed to adsorb as a thicker layer, which also means that the surface coverage is lower at the same mass concentration compared to PDMQ. In addition, the charge density of PSMA13Q was lower than that of PDMQ. PDMQ was more effective to increase the gel strength, which suggests that charge reversal was the mechanism behind the observed change.

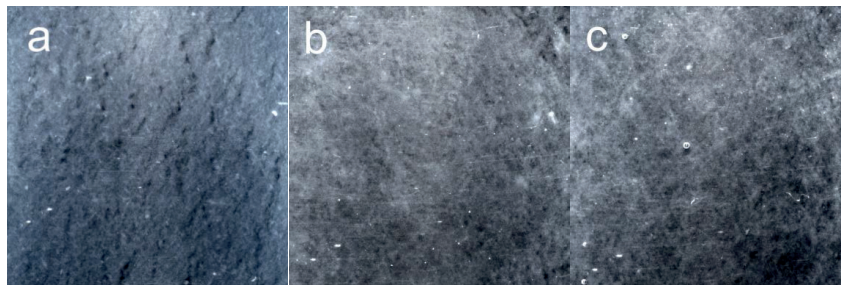


Figure 17. 0.5% MFC (a) and 0.5% MFC suspensions with 0.5 PDMQ (b) and PSMA13Q (c) after 10 min shearing at an apparent shear rate of 0.5 s^{-1} . The photographed area is $20 \times 20 \text{ mm}$ (unpublished data).

Figure 17 shows the flocc structure of MFC/polymer suspensions at polymer and MFC concentration of 0.5% after 10 min shearing at 0.5 s^{-1} . Compared to neat MFC suspension, the structure of PDMQ and PSMA13Q containing suspensions is very similar, even slightly better dispersed. Based on these images, PDMQ and PSMA13Q do not disperse or aggregate the MFC suspensions strongly, although they changed the gel strength.

Large molecular weight cationic polyacrylamide

High molecular weight cationic polyacrylamides are known to adsorb on cellulosic surfaces¹¹³ and cause bridging flocculation in pulp suspensions^{43, 70, 95, 115}. Compared to PDMQ and PSMA13Q used in the previous section, the CPAM has a higher molecular weight ($6\,000\,000 \text{ g mol}^{-1}$) and lower charge density. Therefore, it forms thicker and looser polymer layer on the MFC fibers with loops and tails protruding into the suspending medium.

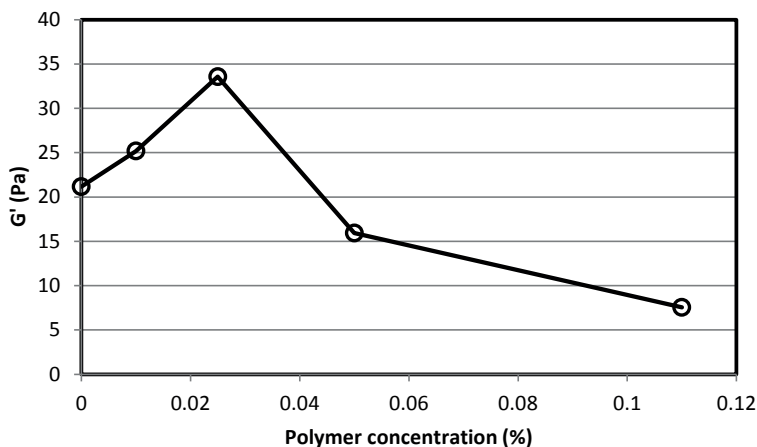


Figure 18. Storage modulus for 0.5% MFC suspension with different amounts of CPAM. Measured at 1 Hz frequency and 0.05% strain (unpublished data).

Figure 18 shows the storage moduli for MFC suspension at 0.5% with 0.01–0.11% CPAM. Storage moduli are taken from the amplitude sweep measurements at 1 Hz frequency and 0.05% strain. This is within the linear viscoelastic region meaning that the deformation of the structure is reversible. The gel strength of 0.5% MFC suspensions first increases with 0.01 and 0.025% of CPAM. The initial increase in gel strength is attributed to stronger contacts between the fibers. Since CPAM has a rather high molecular weight and low charge density, it is assumed to form bridges between the MFC fibers, thus strengthening the gel. With higher amounts of CPAM (0.05 and 0.11%), the gel strength decreases compared to the neat MFC suspension. This may first seem unexpected, since more polymer should form more bridges between the fibers. However, it is possible that higher amounts of CPAM induce the formation of stable, stronger flocs and weaker areas exist around the flocs, which weaken the total strength of the suspension. The increased viscosity of the suspending medium may also reduce contacts between the flocs or fibers.

Opposite to these results, Lowys et al.²² reported that cationic polyacrylamide derivative lowered the moduli of MFC suspension. The authors provided no interpretation, although one possible explanation is that the concentrations used were so high that the effect of the cationic polymer was decreasing already (compare to the results presented in Figure 18). However, when they studied the dispersion effect of different polymers after drying the suspension, cationic polyacrylamide derivative did not work at all, which was attributed to the patch-like adsorption of the polymer.

Mosse et al.⁷¹ reported a similar trend as in these presented experiments in the yield stress of pulp suspension with CPAM addition. First CPAM increased the yield stress, but larger amounts started to decrease it. They explained the increase with polymer bridging, charged patching, and reduction of electrostatic repulsion. Instead, the decline in yield stress was caused by the recharging of fibers and thick polymer layers between the fibers causing repulsion. This was explained to occur in particular between the flocs, since the flocs were still strong, and the yielding was assumed to occur in the less-dense region between the neighboring flocs. In addition, similar first increasing and then declining storage modulus has been reported for pulp suspensions by Swerin⁵¹. This was also attributed to the bridging of CPAM.

Figure 19 shows the suspension structure of MFC/CPAM suspensions after 10 min shearing at an apparent shear rate of 0.5 s⁻¹. The structure is very different compared to neat MFC suspension (see Figure 17a). The two lowest concentrations of CPAM, 0.01 and 0.025%, caused the formation of rollers in the suspensions. At lower concentrations, all fibers appear to be in these rollers, whereas at 0.025% concentration, there is a layer of suspension at the outer cylinder wall and the rollers are moving below it. At these two concentrations, the gel strength was higher than for neat MFC suspensions, which, together with the stronger flocculation tendency, indicates stronger interactions between the fibers. Under slow flow, the increased interactions lead to roller formation, since fibers collide and get stuck in the rollers but the low shearing is insufficient to break the contacts between the fibers.

The suspension with 0.05% CPAM is qualitatively similar or slightly better dispersed than neat MFC suspension. Probably, the increased viscosity of the suspending medium reduces the shear-induced flocculation and diminishes the effect of increased interactions between the MFC fibers due to polymer bridges. Furthermore, the presence of the polymer chains between the fibers may cause steric hindrance to collisions at high polymer concentrations. With the highest amount of CPAM, 0.11%, there are coherent flocs in the suspension which remain there regardless of the shear rate. This indicates that CPAM is able to make strong flocs via bridging. Strong flocs surrounded by lower concentration and weaker areas explain why the gel strength starts to decrease with higher CPAM concentrations. On the other hand, there are not fiber-free areas like those observed in the neat MFC suspension after low shearing, which is attributed to increased viscosity of the suspending medium.

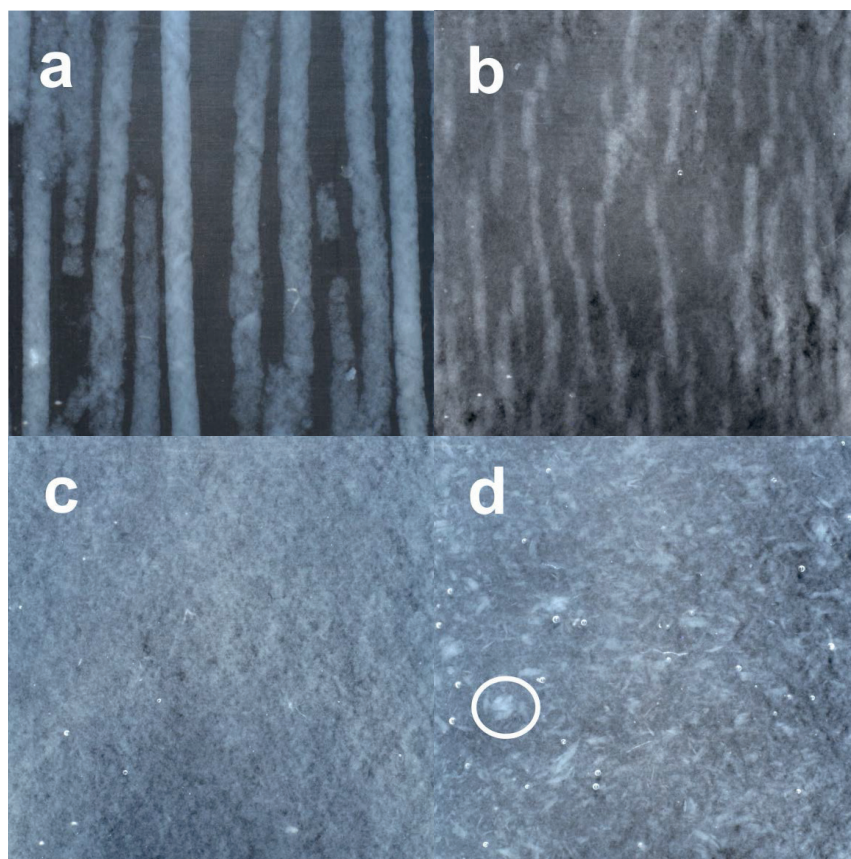


Figure 19. Suspension structure of 0.5% MFC suspension with 0.01% (a), 0.025% (b), 0.05% (c), and 0.11% (d) CPAM after shearing the suspension at an apparent shear rate of 0.5 s^{-1} for 10 min. In image d, a coherent floc is highlighted. The photographed area is 20 x 20 mm (unpublished data).

Comparison of different cationic polymers

The effect of cationic CPAM on the rheological properties and floc structure of MFC was completely different from that of PDMQ and PSMA13Q. The small molecular weight, high charge density polymers PDMQ increased the gel strength. PSMA13Q, which is otherwise similar except it contains hydrophobic segments, caused decreased gel strength of MFC suspensions at 0.5% PSMA13Q concentration. At 4% PSMA13Q concentration, the gel strength was increased compared to neat MFC suspension, although not as much as with 4% PDMQ. These polymers did not have any significant effect on the floc structure. The high molecular weight, low charge density CPAM instead first increased and then started to decrease the gel strength of the MFC suspension, and caused flocculation of the suspension. Under low shearing, a small amount of CPAM induced roller formation into the suspension due to stronger interactions between the fibers. At higher concentration such rollers were not observed, probably due to the high viscosity of the suspending medium which reduced collisions between the fibers. Instead, the highest amount of CPAM, 0.11% created stable flocs which remained in the suspension regardless of the shearing. From this, it can be concluded that polymers forming bridges between the fibers are more effective flocculants than polymers forming charged patches on the fiber surface.

The amount of polymer needed to impart the maximum effect on the rheology and flocculation of the MFC suspension varied considerably for these polymers. The small molecular weight PDMQ and PSMA13Q had the greatest effect on the Herschel-Bulkley yield stress at the highest measured concentration (4%, paper III), whereas high molecular weight CPAM increased the gel strength the most at a concentration of 0.025%.

4.2.2 Anionic polymers

In general, anionic charge of polymers inhibits their adsorption onto cellulosic surfaces, since the surface is also weakly anionic. In this study, the conditions were such that most of the polymer was dissolved in water and did not adsorb onto the fibers.

Polysaccharides

CMC and xanthan gum were studied as dispersants for MFC suspensions. They are polysaccharides and have a similar polymer backbone as cellulose. Xanthan gum has trisaccharide side chains attached to the main chain. Some of the side chains carry acetic and pyruvic acid groups which make the polymer anionic¹⁶. CMC consists of cellulose chain where some of the OH groups are replaced with carboxymethyl groups, making the polymer negatively charged. In this study, CMC with on an average 0.9 carboxymethyl groups per one glucopyranose unit was used. QCM-D measurements showed that only a negligible amount of the polymers adsorbed onto the NFC model surface in the conditions used in this study (paper IV).

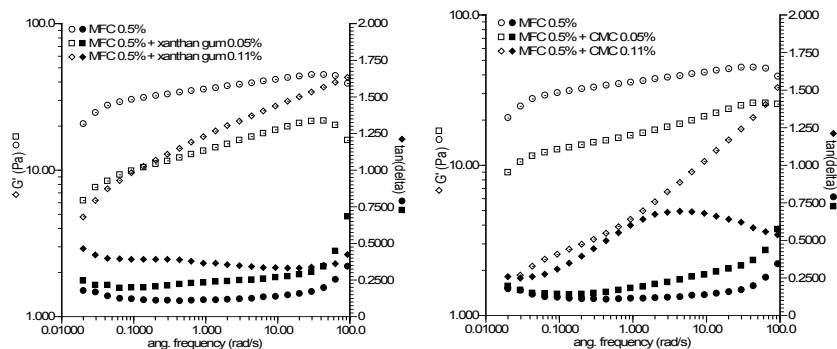


Figure 20. Frequency sweeps for 0.5% MFC suspensions as such and with polysaccharide additives.

Figure 20 shows the frequency sweeps for MFC suspensions with CMC or xanthan gum compared to MFC suspension without any additive. Both polysaccharides decreased the storage modulus and increased tan delta. Lower amount of polymer, 0.05%, decreased the storage moduli slightly and the shape of the curves remained approximately the same as for neat MFC suspension. The higher amount of polymer, 0.11%, changed the behavior of the storage modulus, increasing it with frequency. CMC lowered the storage modulus more than xanthan gum at both concentrations, and at 0.11% concentration the difference to neat MFC suspension was tenfold at low frequencies.

The decrease in gel strength is attributed to a reduced number of contacts between the fibers and lower cohesive forces at these contacts. The storage modulus provides information about the strength of the fiber network at rest which is dependent on the strength of the average fiber-fiber contact and the number of contact points between the fibers¹¹⁷. Earlier studies have shown that CMC lowers the yield stress^{48, 87} and moduli⁸⁶ of pulp suspensions and it has been connected to better dispersion of the pulp fibers. Lower moduli suggest that both polymers dispersed the MFC suspension and weakened the interactions between the fibers. The more liquid-like behavior (higher tan delta) observed with 0.11% polymer concentration also suggests that there were fewer or weaker contacts between the fibers. At 0.11% polymer concentration, CMC lowered the storage modulus more than xanthan gum, suggesting that CMC dispersed the MFC fibers better than xanthan gum. CMC had a higher charge density which could explain its greater effect on the gel strength. Furthermore, xanthan gum solution had a higher gel storage modulus than CMC solution, which may be the reason for higher strength in MFC/xanthan gum suspensions compared to MFC/CMC suspensions. Dispersion mechanisms of the anionic polymers are further discussed at the end of this section.

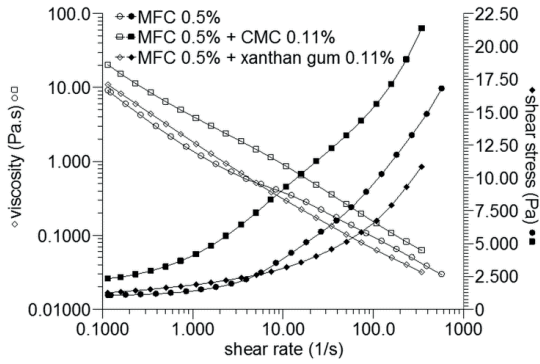


Figure 21. Flow curves for MFC suspensions with CMC and xanthan gum measured with transparent cup (paper IV).

Figure 21 shows the flow curve for the MFC/CMC and MFC/xanthan gum suspensions measured with the transparent cup. The suspensions were simultaneously photographed (Figure 22) and recorded with OCT (Figure 23) through the transparent rheometer geometry. Compared to neat MFC suspension, xanthan gum increased and CMC decreased the apparent viscosity at high shear rates. At low shear rates, both polymers increased the apparent viscosity. The structure of the suspension is more homogeneous with both polymer additives than without them in Figure 22. Especially at low shear rates, the neat MFC suspension is flocculated, whereas the MFC/CMC and MFC/xanthan gum suspension show even structure. This illustrates that the polysaccharides prevented shear induced flocculation in the suspensions.

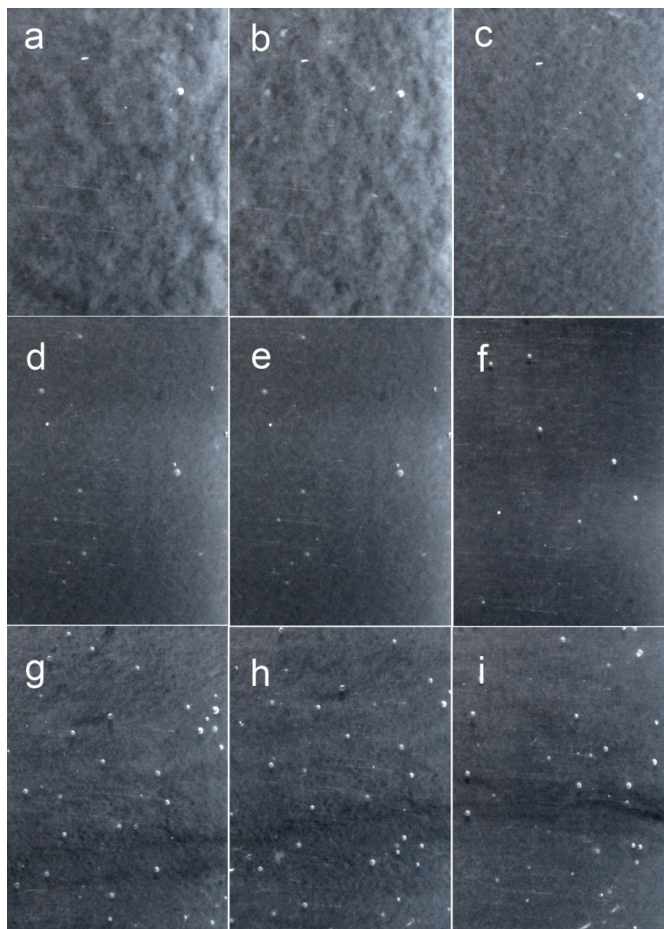


Figure 22. Photographs from the suspensions at three apparent shear rates: 0.5% MFC suspension at apparent shear rate a) 0.6 s^{-1} , b) 6 s^{-1} , c) 64 s^{-1} from the flow curve measurements. 0.5% MFC suspension with 0.11% CMC at apparent shear rate d) 0.6 s^{-1} , e) 6 s^{-1} , f) 64 s^{-1} . 0.5% MFC suspension with 0.11% xanthan gum at apparent shear rate g) 0.6 s^{-1} , h) 6 s^{-1} , i) 64 s^{-1} . The width of the photographed area is 10 mm.

OCT images show the structure of the suspensions in smaller scale (Figure 23) over the gap at intermediate and low shear rates. The pure MFC suspension showed flocs and water between them. The addition of CMC or xanthan gum resulted in better dispersion in the suspension through the gap, although the structure appeared slightly more flocculated towards lower shear rates. At this scale, there are also some flocs visible in the suspensions with CMC or xanthan gum at two lower shear rates presented in Figure 23. At intermediate shear rates, the black areas representing water disappear from the suspensions with CMC or xanthan gum but neat MFC suspension is still flocculated (note that the images are from slightly different apparent shear rates for each suspension). A more homogeneous structure of polymer-containing suspensions is also reflected in velocity profiles, which are smoother for MFC/CMC and MFC/xanthan gum suspensions. The velocity profiles also show that pure MFC

suspension (first row) slips at both geometry boundaries and flows as a plug flow. For xanthan gum (third row in Figure 23), the situation is similar, although it slips more at the inner cylinder compared to pure MFC. Instead, the suspension with CMC (the second row in Figure 23) shows some deformation within the bulk at shear rate 5.7 s^{-1} , which further suggests that the forces between the flocs were weaker in the MFC/CMC suspension. Unfortunately, it was not possible to calculate the velocity profile for the higher shear rate due to the recording frequency in the MFC/CMC suspension being too low. Due to the observed wall depletion, the viscosities presented in Figure 21 must be considered as apparent ones as was observed for the neat MFC suspensions.

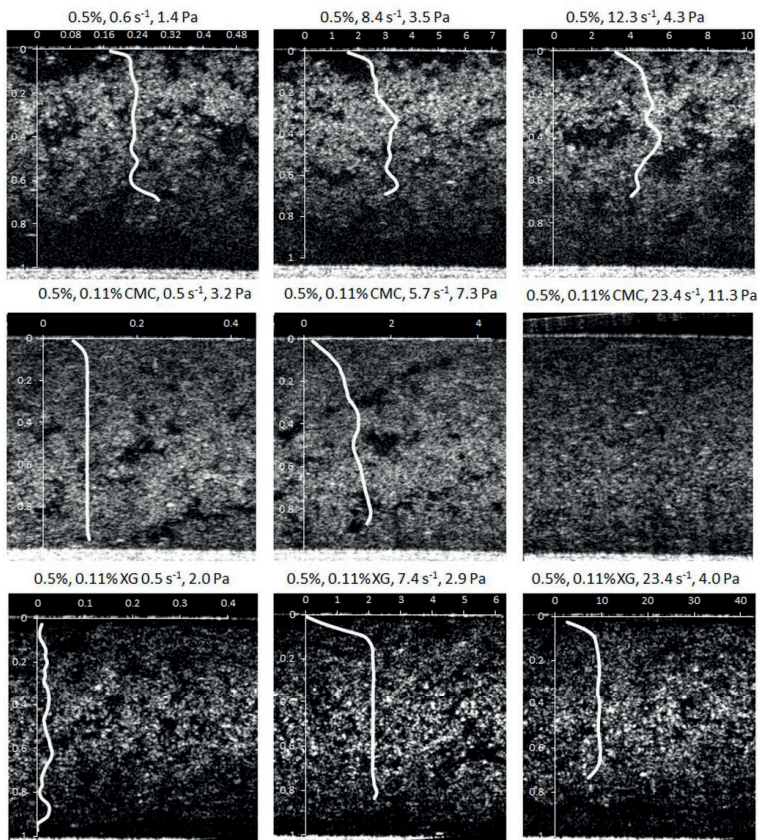


Figure 23. OCT images of the MFC suspensions as such and with CMC or xanthan gum (XG). The velocity profiles over the gap are calculated from the consecutive frames and shown on the top of the structure images. First row: 0.5% MFC suspension, second row: 0.5% MFC with 0.11% CMC, and third row: 0.5% MFC with 0.11% xanthan gum. The abscissa shows the velocity in mm/s with the maximum value equaling the bob surface velocity. The ordinate shows the position inside the gap in mm (paper IV).

Anionic polyacrylamides

Anionic polyacrylamides (APAMs) are linear polymers that do not adsorb substantially onto cellulose surfaces (paper V). In this study, three different APAMs were tested: low molecular weight and low charge density APAM (LMW-LCD), low molecular weight, high charge density APAM (LMW-HCD), and high molecular weight, high charge density APAM (HMW-HCD). The molecular weights and charge densities are given in Table 1 in chapter 3.1.2.

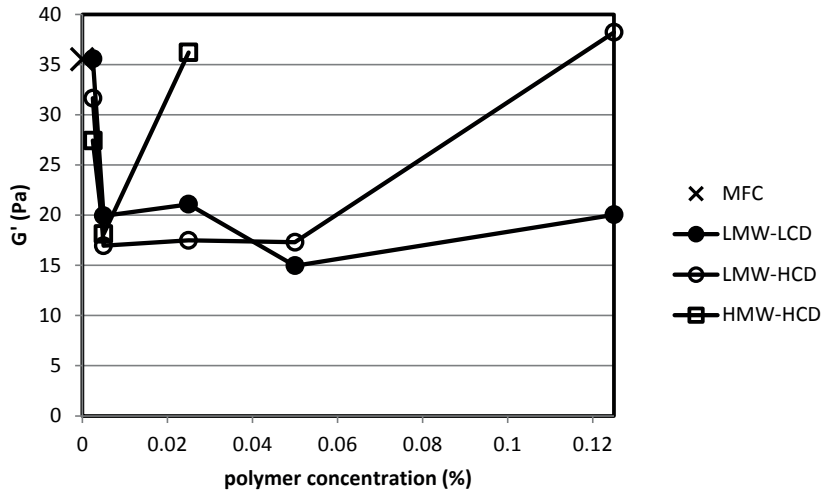


Figure 24. Storage modulus for 0.5% MFC suspensions with three different APAMs. Measured at 0.05% strain and 1 Hz frequency (paper V).

Figure 24 shows the storage moduli for 0.5% MFC suspensions with different amounts of each APAM. First, the low molecular weight APAMs were considered. LMW-HCD and LMW-LCD initially decreased the gel strength of the MFC suspension. Then there was a quite constant gel strength at polymer concentrations of 0.005 to 0.05% for the low molecular weight, high charge APAM (LMW-HCD) and slightly declining gel strength for low molecular weight, low charge APAM (LMW-LCD). The initial decrease was caused by the dispersive effect of the polymers, which decreases the contacts between the fibers and thus weakens the gel. This is an opposite effect compared to the results obtained with CPAM addition which increased the interactions between the MFC fibers (see Figure 18). With high charge density APAM, the minimum of the gel strength was achieved at lower concentration than with the low charge density APAM. This indicates that the amount of negative charge in the system is part of the dispersing mechanism. The viscosity of LMW-HCD is higher than for LMW-LCD, which may also cause lower gel strength.

With the highest amount of the polymer, 0.125%, the gel strength started to increase again, especially with the high charge, low molecular weight APAM. The highly charged polymer chains are extended and rigid, displaying gel-like behavior at higher concentrations. This increases the stiffness of the whole suspension. The higher charge density of LMW-HCD, compared to LMW-LCD,

results in a higher storage modulus of the suspending medium, which is also reflected in the higher gel strength of the whole suspension.

Now turning to high molecular weight APAM, it is clear that the greatest reduction in gel strength occurred at the two lowest concentrations (0.0025 % and 0.005%). This indicates that a high molecular weight anionic polymer is most effective to weaken the gel strength of the MFC suspension at low polymer concentrations. Compared to low molecular weight APAMs, the viscosity of HMW-HCD APAM is higher which may be one of the reasons for its superior dispersing ability. For the high molecular weight APAM, the gel strength started to increase already at 0.025% concentration. This can be explained by the very high molecular weight and hence a high viscosity of the polymer solution which starts to dominate the MFC/APAM gel strength. For higher HMW-HCD concentrations, no reliable results could be obtained due to the high viscosity of the polymer solution.

The gel strength is dependent on the strength of the average fiber-fiber contact point and the number of contact points in a certain volume. According to the adsorption tests (paper V), APAMs did not substantially adsorb onto the MFC surface. The polymer chains may get trapped between approaching fibers and introduce steric hindrance between the slightly negative MFC fibers. In addition, they increase the viscosity of the suspending medium, which decreases the turbulence in the flow and results in weaker flocs⁷⁵.

The lower gel strength of the MFC/APAM suspensions was also reflected in the floc structure observed after 10 min constant shearing at 5 s^{-1} . Figure 25 shows the MFC suspension as such and with 0.005% low molecular weight, high charge density APAM (optimized concentration based on the gel strength in Figure 24). The suspension with APAM contains smaller flocs than neat MFC suspension. However, the dispersion effect of APAM disappeared after lower apparent shear rate 0.5 s^{-1} , as will be shown next.

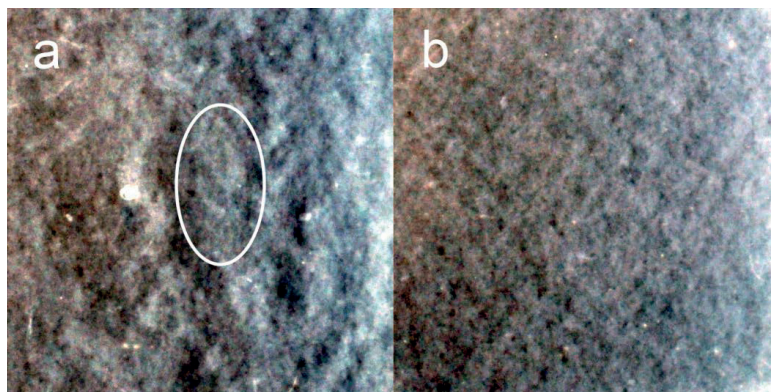


Figure 25. Images of the MFC suspension structure after shearing at 5 s^{-1} for 10 min in the rheometer. a) MFC 0.5 w-% (a floc highlighted), b) MFC 0.5 w-% with 0.005 % APAM (LMW-HCD). The area of the photographs is 10 mm x 10 mm (paper V).

Comparison of different anionic polymers

Figure 26 shows images after 10 min constant shear for the 0.5% MFC suspensions with 0.11% CMC, 0.11% xanthan gum, or 0.005% LMW-HCD APAM. CMC and xanthan gum clearly dispersed shear induced flocs in long, slow shearing at 0.5 s^{-1} , whereas APAM was not as effective. Figure 26c shows that even few rollers appeared at the inner cylinder in the suspension containing APAM. However, a better dispersion was achieved at 5 s^{-1} with APAM compared to neat MFC suspension (see Figure 25). The better dispersed structure of the suspensions containing anionic polymers was also observed in frequency sweeps where the suspensions with polymer had lower moduli than the pure MFC suspension. Negatively charged APAM also lowered the storage modulus of the MFC suspensions at low concentrations but the effect was lost at higher concentrations.

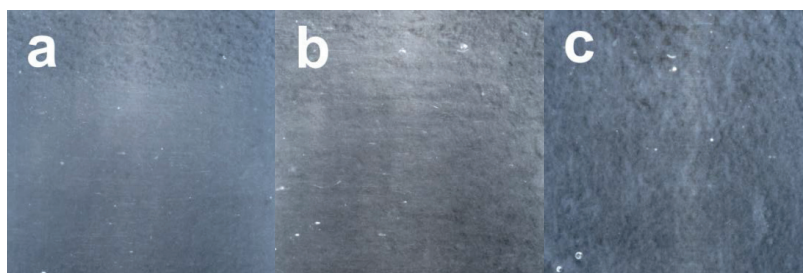


Figure 26. 0.5% MFC suspension with 0.11% CMC (a), 0.11% xanthan gum (b), and 0.005% APAM after 10 min shearing at 0.5 s^{-1} . The photographed area is 20 x 20 mm.

CMC has been studied widely as a dispersant for pulp fibers^{72, 74, 79, 80, 86, 118} and MFC fibers^{103, 119}. CMC's ability to disperse pulp has mainly been attributed to lowering the friction between the fibers and thus preventing mechanical flocculation^{72, 74, 86, 118}. This mechanism requires adsorption of the polymer onto the fibers. However, in this study, a negligible amount of the polymers adsorbed onto the fibers. Therefore other mechanisms must be considered. Lee and Lindström⁷⁶ observed that APAM dispersed pulp and attributed that to

increased elongational viscosity of the suspending medium. Increased elongational or shear viscosity of the suspending medium has been shown to decrease mechanical flocculation in other studies as well^{75, 77, 120}, since it reduces the relative motion of the fibers. The rheology of the suspending medium can also affect how much the fibers bend in the flow and thus how strained they are when they come to rest. Therefore, higher viscosity should lead to higher capability to disperse fibers⁷⁵. The optimized APAM dosage was clearly lower than for CMC or xanthan gum and thus the increase in shear viscosity was probably lower. Xanthan gum had higher zero shear viscosity than CMC; however, CMC seemed to be more effective than xanthan gum or APAM based on the images after 10 min shearing at the apparent shear rate of 0.5 s^{-1} and the moduli levels in the frequency sweeps. Unfortunately, direct comparisons of gel strengths between CMC and APAMs cannot be made, since the mixing procedures were different. However, the decrease in MFC/CMC suspension was relatively larger than in MFC/APAM suspensions.

These observations suggest that there are factors other than just viscosity affecting the dispersing ability of the polymer. The presence of negative polymer chains between the fibers may have prevented collisions between the MFC fibers^{79, 80}. CMC had the highest charge density of these polymers. On the other hand, the charge density of xanthan gum was the same or lower than APAMs but it dispersed MFC better after slow shearing. Therefore, it does not seem that charge density alone is responsible for the dispersion ability, although it is definitely important.

Xanthan gum was more structured and had intermolecular interactions based on the solution rheology, which has been related to diminished ability to disperse pulp fibers^{72, 121}. On the other hand, the molecular structure of APAM is completely different from the polysaccharides. Compared to xanthan gum and APAMs, CMC is linear and unsubstituted parts of the chain are similar to the cellulose backbone. It might be that CMC molecules are in closer proximity of the MFC fibers in the suspension, and they are more likely to be trapped between the approaching fibers upon flow, preventing collisions and flocculation.

As was observed for the cationic polymers, the amounts needed to achieve the maximum effect, that is, dispersion with different polymers were very different. It seems that the molecular weight of the polymer is important when optimizing the concentration of the dispersants. Measuring the gel strength is an easy way to optimize the polymer concentration.

4.3 The effect of surface charge

Modifying the surface properties of the MFC fibers changes the rheological and flocculation behavior of the suspension. However, if the modification is performed before grinding, the dimensions and morphology of the fibers are also affected. Figure 27 shows the frequency sweep results for two different NFCs made from TEMPO oxidized pulp and reference MFC. Compared to

MFC, both NFC grades have a smaller diameter and the surface charge is clearly higher. In addition, the mixing of the NFC suspensions was performed with a domestic blender, whereas MFC suspension was mixed with a propeller mixer. The NFC grades have the same surface charge and diameters but their lengths differ. Short NFC fibers are approximately 0.5-1 μm long and long NFC fibers approximately 1-10 μm long. As was discussed earlier, the length of MFC fibers is difficult to determine, but it has been estimated to be several microns. The storage and loss moduli for MFC and long NFC suspensions are approximately the same. This is somewhat surprising since, the higher surface charge³² and smaller diameter⁴⁰ of the fibers is assumed to increase the moduli of NFC suspension. It is possible that surface modification affects the morphology of the fibers and especially the physical links between the fibers. Moreover, the smaller diameter may make the fibers more flexible, which is related to reduced flocculation.

The short NFC suspension displayed lower storage and loss moduli than long NFC suspension. Moreover, the storage modulus was lower than the loss modulus in the short NFC suspension, indicating that it was not a gel at 0.5% concentration, and the suspension lacked a network of fibers that would provide solid-like behavior. This shows that the length of the fiber is essential for gel behavior and gel strength. The threshold concentration for gel-like behavior is higher if the fibers are shorter.

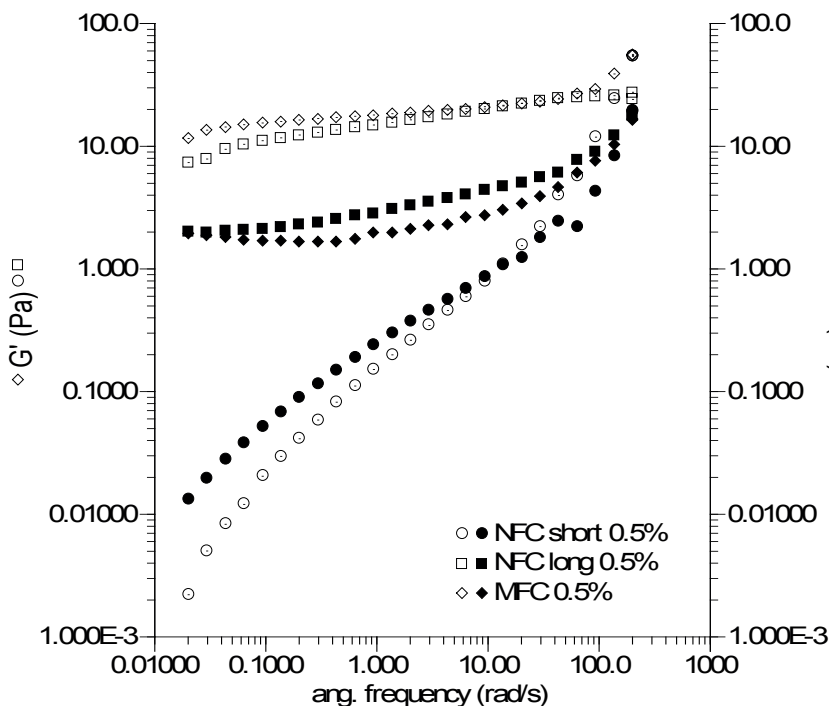


Figure 27. MFC and two different TEMPO-oxidized NFC at concentration 0.5% (unpublished data). Note that NFC suspension have been mixed with a domestic blender and MFC suspension with a propeller mixer after dilution.

The smaller dimensions of the NFC fibers make the suspension transparent. Therefore, similar analysis of the flocculation, as was applied on the other materials, was not possible for NFC suspensions. However, acquiring information about the structure along one line with OCT enabled a structure image of the suspension to be obtained. Figure 28 shows the structure image of 0.5% long TEMPO-oxidized NFC fibers recorded that way. OCT is based on visible light which means that individual fibers cannot be seen with it. However, the image contains white areas, which are presumably fiber aggregates, indicating that TEMPO-oxidized NFC fibers also form flocs.

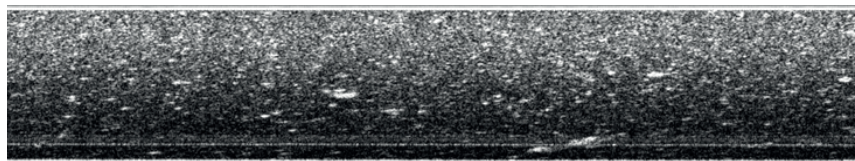


Figure 28. Long TEMPO oxidized NFC fibers measured with OCT at apparent shear rate 5 s^{-1} . The gap between the cylinders is 1 mm. (unpublished data measured and analyzed by Sanna Haavisto).

Figure 29 shows the shear stress as a function of shear rate for long TEMPO oxidized NFC fibers measured with the large gap vane method, where the suspension is measured in a large cup with vane rotor to avoid wall depletion. The cup must be sufficiently large so that the shear rate decreases to zero before it reaches the cup wall, thus preventing slipping at the outer wall. In this case, the gap was 16.5 mm, and the maximum vane velocity was visually evaluated by introducing a minute amount of ink to the suspensions and observing at which velocity secondary flows appeared to the cup. The results show that the shear stress is highly dependent on the concentration in NFC suspensions. Moreover, the samples showed hysteresis, that is, the shear stress was lower during the downward sweep compared to the same shear rate during the upward sweep. When the shear rate changes stepwise, the suspension starts to adopt a new steady state. This requires some time, and since hysteresis was observed in the flow curve, it means that the suspension did not have enough time to reach a full steady state although very long point times were used. The hysteresis is more pronounced for the two lower concentrations, 0.25% and 0.5%, whereas at the two higher concentrations, 0.5% and 0.75%, the downward and upward curves are close to each other. It was assumed that the steady state viscosity and stress are the average of the downward and upward curves. The black lines show the Herschel-Bulkley fits based on the average values, which can be assumed to be the steady state behaviour of the suspensions.

Since imaging methods did not give information about the possible flocculation behaviour of TEMPO-oxidized NFC, the data of the 0.5% NFC suspension was fitted to a model which assumes aggregation of the fibers and adaption of the aggregate size to shearing conditions (paper VI). The model represented the data fairly well, indicating that the fibers probably form aggregates similarly to coarser MFC. The simulations revealed that the structural adaption to

new shear rate occurred in two time scales. The two time scales may come from two mechanisms by which a floc can grow and diminish: floc splitting and erosion. A floc splitting in two or aggregation of two flocs together is a faster process. Erosion of the fibers from the floc surface or attachment of new fibers to the floc, is a slow process. This indicates that surface charge does not prevent flocculation totally. However, the aggregate size is significantly smaller than in MFC suspensions.

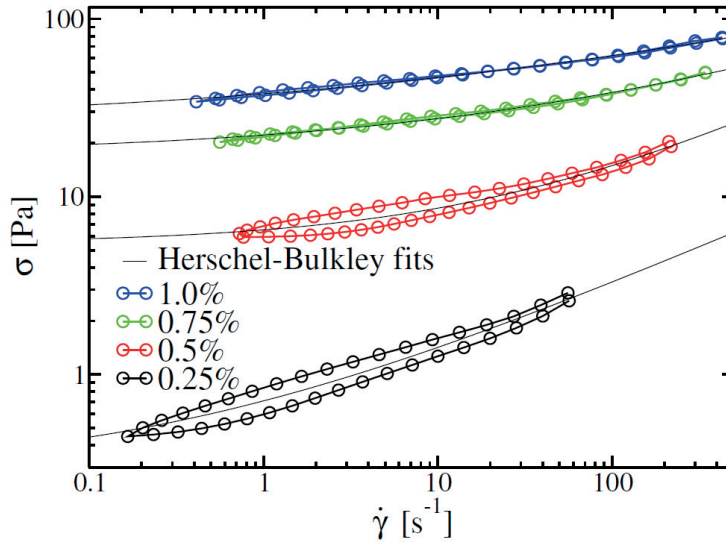


Figure 29. Shear stress as a function of shear rate measured with large gap vane system for long TEMPO oxidized NFC fibers at different concentrations. Shear rate is gap corrected. Black lines show the Herschel-Bulkley fits as an average of the downward and upward sweeps (paper VI).

5. Concluding remarks

The aim of this research was to develop methods for modifying the rheology and flocculation of MFC fibers suspensions using polyelectrolytes or surface modification. The polyelectrolytes were cationic and anionic and they had different charge densities and molecular weights. First, the rheology and flocculation of neat MFC suspensions were studied. The floc structure of the suspensions was dependent on the shear conditions, and wall depletion occurred during the flow measurements. The ability to create large flocs within the suspension was utilized when comparing the effect of different polymers with the flocculation tendency of MFC. For evaluation of the rheological properties of the suspensions, oscillation measurements with small deformations were used, since they suffer less from wall depletion.

Cationic polymers are attracted by the negatively charged MFC fibers. They enhance the interactions between MFC fibers by patch-like adsorption or polymer bridging. The adsorption of cationic polymethacrylates led to a stronger MFC gel, but no clear changes were observed in the floc structure upon their addition to the MFC suspension. Instead, the bridging by CPAM caused strong flocculation in the MFC suspensions and even coherent flocs at sufficiently high polymer concentrations. The overall gel strength first increased and then decreased with increasing CPAM concentration.

Anionic CMC, xanthan gum, and different APAMs were studied as dispersants. They all dispersed the MFC suspensions, leading to a lower gel strength, although APAMs started to increase the gel strength at higher polymer concentrations. The dispersing mechanism is probably a combination of the increased viscosity of the suspending medium and the steric hindrance of the polymer chains between the fibers. At low, long shearing, CMC and xanthan gum were more effective than APAM in preventing shear-induced flocculation. This may be due to the better ability of xanthan gum and in particular CMC to be in close proximity of MFC fibers, which efficiently prevents collisions between the fibers. Comparing APAMs with different molecular weight and charge density showed that higher molecular weight and charge density decreased the amount of polymer needed to achieve the maximum dispersing effect.

Modifying the surface of the fibers by TEMPO oxidation produces fibers with smaller dimensions and increased the surface charge. Due to smaller fiber dimensions, NFC is a transparent gel and its flocculation cannot be followed with the same methods which were used for MFC suspensions. Some indication of the aggregation of the fibers was gained with OCT. In addition, modeling based on the rheological behaviour supported the theory that the NFC

suspension is flocculated and the aggregate size is dependent on the shear rate. Contrary to expectations, the gel strength of the charged NFC was close to that of native MFC. This might be related to the morphological and dimensional changes that follow from the surface modification.

This method, a combination of imaging and rheology, was successfully used to study the effect of different polymers on the interactions between MFC fibers and more generally cellulosic surfaces. Rheology alone could lead to an incorrect interpretation, but combined with the observations of the structure, better conclusions can be drawn. On the other hand, looking at the floc structure alone may be misleading, since it is based on qualitative judgments, which is always subjective. Together with rheology, subtle differences may be detected. Hence, the combination of these two methods is preferable. It can be used to optimize flocculant and deflocculant dosage in processing or in certain application of MFC. Moreover, using this method for MFC suspensions gives information about inter-fibrillar cellulose interactions and between cellulosic fibers and polymers in general. A comprehensive characterization of this new nanomaterial helps to develop new, value-added products from wood raw materials.

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