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**RHEOLOGICAL CHARACTERIZATION OF POLYSACCHARIDE
GELS**

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TIIVISTELMÄ

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Polysakkaridigeelien reologinen karakterisointi

Diplomityö

2015

78 sivua, 36 kuvaa, 10 taulukkoa ja 4 liitettä

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Hakusanat: Reologia, virtauskäyttäytyminen, viskositeetti, viskoelastiset ominaisuudet, selluloosa, geeli

Tässä diplomityössä on tutkittu eri valmistusmenetelmin tuotettujen polysakkaridigeelien reologisia ominaisuuksia ja kehitetty näytteille sopivat mittaussuunnitelmat. Tuloksia on hyödynnetty pohjatietona laajemmassa tutkimuskokonaisuudessa, jonka tavoitteena on kartoittaa mahdollisia käyttökohteita tutkituille näytteille. Potentiaalisten sovellusten selvittämiseksi ja tarvittavien ominaisuuksien ymmärtämiseksi tutkittujen geelien ominaisuuksia on verrattu kaupallisiin hydrokollodeihin, joiden sovelluskohteet ja vaatimukset materiaaleille tunnetaan. Vertailukohteina tutkituille materiaaleille käytettiin anionisia polymeerejä, kuten NaCMC:tä, ksantaania sekä guarkumia.

Työn teoriaosassa on perehdytty tarkemmin reologian peruseräisiin sekä selitetty keskeisimmät käsitteet. Tämän lisäksi työssä on esitelty lyhyesti tutkitut materiaalit sekä yleisiä käyttökohteita reologian muokkaajille. Työn kokeellisessa osassa keskityttiin selvittämään näytteille ominaiset reologiset piirteet ja niihin liittyvät ilmiöt. Erityisesti näytteiden geelimäisyys, geelin vahvuus sekä vesiliuoksien stabiilisuus olivat tarkemman tutkimuksen kohteita.

Näytteiden karakterisoinnissa on käytetty niin rotaatio- kuin oskillaatiotestejä, jotka suoritettiin Anton Paar MCR302 reometrillä. Tutkitut polysakkaridigeelit osoittautuivat luonteeltaan vahvasti leikkausoheneviksi sekä tiksotrooppisiksi materiaaleiksi. Lisäksi näytteillä havaittiin voimakas kyky muodostaa geeli alhaisillakin konsentraatioilla, mistä johtuen viskositeetit tietyillä alueilla olivat jopa korkeampia kuin ksantaanilla. Reologisia ominaisuuksia tarkasteltiin myös konsentraation, lämpötilan sekä polyelektrolyyttien funktiona. Näytteissä havaittiin selkeitä eroja näiden ulkoisten parametrien vaikutuksesta.

ABSTRACT

Lappeenranta University of Technology
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Rheological characterization of polysaccharide gels

Master's thesis

2015

78 pages, 36 figures, 10 tables and 4 appendices

Examiners: Prof. Kaj Backfolk
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Keywords: Rheology, flow behavior, viscosity, viscoelastic properties, cellulose, gel

In this Master's Thesis work the rheological properties of different polysaccharide gels have been studied. The results of this study are used as a starting point for further investigations of potential applications. In order to understand rheological behavior of studied materials, the commercial hydrocolloids such as sodium carboxymethyl cellulose, xanthan gum and guar gum were used as reference and comparison material for rheological studies. As a part the rheological research the development and implementation of proper measurement methods for studied materials were carried out.

In the literature review, short introductions of studied materials and application areas of rheological modifiers are summarized. In addition, basic rheological concepts and key fundamentals are explained. In the experimental part the focus was on the rheological characterization of aqueous suspensions of studied materials. Especially, gel strength and solution stability were investigated.

The rheological measurements included both rotational and oscillatory measurements in different conditions, where several chemical and physical properties were measured with Anton Paar MCR302 dynamic rotational rheometer. Studied polysaccharide gels can be clearly defined to be shear thinning and thixotropic materials. They have strong gel forming properties even at low concentrations, which explains the superior thickening behavior for some of the samples. Along with rheological characterization of selected materials the factors behind different phenomena were investigated. To reveal value and potential use of polysaccharide gels the influence of various factors such as concentration, temperature and ionic strength were determined. The measurements showed a clear difference between studied materials under investigated external parameters.

ACKNOWLEDGEMENT

This Master's Thesis has been carried out on behalf of Stora Enso as part of the joint project at Lappeenranta University of Technology. I would like to express my special thanks to my Professor Kaj Backfolk and my supervisor Heidi Saxell from Stora Enso for giving this opportunity to me and making this MSc thesis project possible. I am grateful for this interesting and challenging subject which has led me to this new scientific field.

I would also like to thank the former Biomaterials staff in LUT and both Stora Enso's research centers in Imatra and Karlstad for their help and cooperation regarding the manufacturing and characterization of samples. I also want to thank staff of Anton Paar for their support.

These years during my studies in Lappeenranta have been instructive, eventful and altogether incredible. It has been an exciting journey to grow, learn and meet new people. I have had a lot of fun thanks to my friends; there are so many great memories to look back because of you guys. I also want to express my gratitude for my loving and caring family whom has believed in me and has been there for me when needed. Especially mom and dad, I am ever grateful to you for the guidance and support you have given me. I am also grateful to my siblings, who have challenged me to do the funniest and craziest things and therefore have taken care that my life wouldn't ever be boring. Finally, my most loving thanks to Oskari for his love, continuous support and encouragement during my studies and throughout this experience. Your help and belief in me has been invaluable and I am so grateful that I have you in my life.

Lappeenranta, 16.09.2015

Iida Ollikainen

LIST OF ABBREVIATIONS AND SYMBOLS

List of symbols

G'	Storage modulus (Pa)
G''	Loss modulus (Pa)
T	Temperature (°C)

Greek Letters

$\dot{\gamma}$	Shear rate (s ⁻¹)
η	Shear viscosity (Pa.s)
η^*	Complex viscosity (Pa.s)
η_r	Relative viscosity (-)
ζ	Zeta-Potential (mV)
ω	Angular frequency (rad/s)

Abbreviations

AFM	Atomic force microscopy
CaCl ₂	Calcium chloride
DP	Degree of polymerization
DS	Degree of substitution
LVE	Linear viscoelastic range
MFC	Microfibrillated cellulose
NaCl	Sodium chloride
NaCMC	Sodium carboxymethyl cellulose

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1 INTRODUCTION

Increased environmental awareness, oil prices fluctuations and/or increase together with decreasing oil reserves has led to the fact that forest industry is looking for new materials and more sustainable solutions to replace petrochemical based products. Particular interest in bio-based nanomaterials produced from cellulosic sources has increased exponentially during the last few decades. Cellulose is the main component in woody plants and thus world's most abundant natural biopolymer source which provides an excellent source of raw material to manufacture various materials and chemicals. The research and development of advanced cellulosic materials like cellulosic nanoparticles has been of great interest because these derivatives offer great bio-based substitutes throughout the industry.

The great interest for nano-scale materials, such as microfibrillated cellulose (MFC), can be explained by their versatile features. MFC is a non-toxic, lightweight material which has an ability to form strong network structure. MFC suspensions show interesting rheological properties and it has a potential to substitute many hydrocolloids. Due to its high aspect ratio, nanoscale dimensions and capacity to form gel-like structure even at very low concentrations, microfibrillated cellulose's usage has been studied in several industrial applications, including food, cosmetics, automotive, construction, packaging and paper and board products. (Ankerfors, 2012; Karppinen, 2014).

In this Master's Thesis, the focus was on rheological characterization of different grades of microfibrillated cellulose. To fully understand the possibilities of MFC, rheological characteristic of different types of reference hydrocolloids were investigated. The rheological study of MFC is an important part of developing MFC and materials comprising it. In order to understand the performance of microfibrillated cellulose in different industrial applications, like processing, storage and transport, the knowledge of rheological behavior is needed. With rheological measurements it is possible to investigate how material responds to the applied force, which gives information about material's flow behavior and viscoelastic properties in certain conditions.

2 OBJECTIVES OF THE STUDY

Microfibrillated cellulose has multifunctional properties, which will provide a wide range of possibilities in addition to the use in paper and board applications. In addition to the use as strength enhancement for example in lightweight material composites, MFC has also potential to be used as a hydrocolloid and rheology modifier. Versatile properties and wide range of end-use applications of MFC are the reasons of growing interest to manufacture it. So, the knowledge about MFC's rheological characteristics and flow behavior are important issues when commercializing and engaging specific commercial products.

In this Master's Thesis the main target was to understand rheological differences between selected MFC grades and to compare them against commercial hydrocolloids. The first step was to develop and implement a reliable method to determine the rheological behavior of MFC suspensions. After validation of proper measurement methods rheological characterization of selected materials were conducted. However the focus of this work was limited to the rheological characterization of MFC suspensions, so the research and development of valid measurement method was not reported in detail.

The rheological studies included characterization of three MFC samples, which were chosen based on the different level of fibrillation and degree of substitution. Different types of rheological measurements and other analysis were conducted in order to gain understanding of the factors affecting the rheological properties. Also few of the market's most used commercial hydrocolloids were chosen to include in the study to provide application orientated information. These certain rheology modifiers were measured to understand their rheological profiles better as well as to understand unique features of MFC.

In the literature part of this work there is given needed background information of studied materials and rheology. The purpose was to shortly explain the rheological key features to understand the results shown in experimental part and familiarize reader with rheological terms. Also the commercial hydrocolloids, their properties and different application possibilities are briefly presented in literature part.

In the experimental part, the used measurement methods are presented in more detail. The study contains few generally used rotational and oscillation rheology measurements which

are selected so that flow behavior along with viscoelastic properties of samples can be investigated. The results presented in this work can be used as a base for further studies of microfibrillated cellulose's rheological behavior and in benchmarking process of future materials.

LITERATURE PART

In the literature part, hydrocolloids, their functionality and applications are introduced. The theoretical part assembles the current knowledge of the selected materials but focuses on the MFC and its rheology. The basic theory of rheology and properties of materials such as deformation and flow behavior is presented to facilitate the analysis in the experimental part.

3 HYDROCOLLOIDS

Hydrocolloid is a colloidal system, which forms a viscous dispersion or gel when dispersed in water. A colloidal system contains at least two components, such as solid particles which have dispersed evenly into dispersing medium. Also colloidal system requires that at least one particle dimension is between 1nm and 1 μ m (IUPAC, 2014). Hydrocolloids are a heterogeneous group of long chain polymers, such as polysaccharides and proteins, which have a large number of hydroxyl (-OH) groups and great affinity towards water. The hydroxyl groups increase the affinity for binding water molecules which in addition to the molecular structure affects their functional properties as rheological modifiers. (Milani & Maleki, 2012; Saha & Bhattacharya, 2010)

Hydrocolloids are a very wide group of high molecular weight polymers which occur naturally or can be obtained from natural sources by chemical derivatisation. The most hydrophilic colloids can be extracted from plants, seeds, seaweed or animal tissue. However some of the hydrocolloids, such as xanthan gum, are produced with microbial synthesis. Hydrocolloids can be roughly divided into five categories by their origin. The commercially important ones and their sources are introduced in the Table I. (Milani & Maleki, 2012)

Table I. Commercially important hydrocolloids (Modified from Phillips & Williams, 2009)

Plant hydrocolloids
Cellulose
Cellulose ethers and derivatives
NaCMC, MC, HEC,
MCC
Starch
Hemicellulose
Mannans & galactomannans, Xyloglucans, Glucomannans, Arabinoxylans
β -D glucans, Arabinogalactan
Pectins
Exudite gums
Gumarabic, Tragacanth gum, Gum karaya, Gum ghatti
Mucilage gums
Psyllium gum, Yellow mustard gum, Flaxseed mucilage
Fructans
Seeds
Guar gum, Locust bean gum, Tara gum
Seaweed
Alginated
Carrageenans
Agar
Microbial
Xanthan gum
Pullulan
Gellan gum
Animal
Chitin & chitosan
Gelatin
Chemically modified

Hydrocolloids are used in many industrial fields such as in pharmaceuticals, food, oil drilling, paints and many other chemicals. Yet, there are numerous application possibilities because their extensive range of functional properties and variety of raw materials. The growing awareness of sustainable products and changes in modern lifestyle has created the market gap for clean-label hydrocolloids, which can help to increase product value. Hydrocolloid usage in the cakes and pastries segment has reached over 300 000 tons and the value of food and drink market is around 4.4 billion dollars per year and it is constantly growing. The demand of hydrocolloids has increased quite steady over recent years at the rate of 2-3% which offers a great opportunity to new materials and applications enter to the market. Market volumes of individual hydrocolloids used in food and beverages are presented in the graph below (Fig.1). (Phillips & Williams, 2009)

Market volume of food hydrocolloids

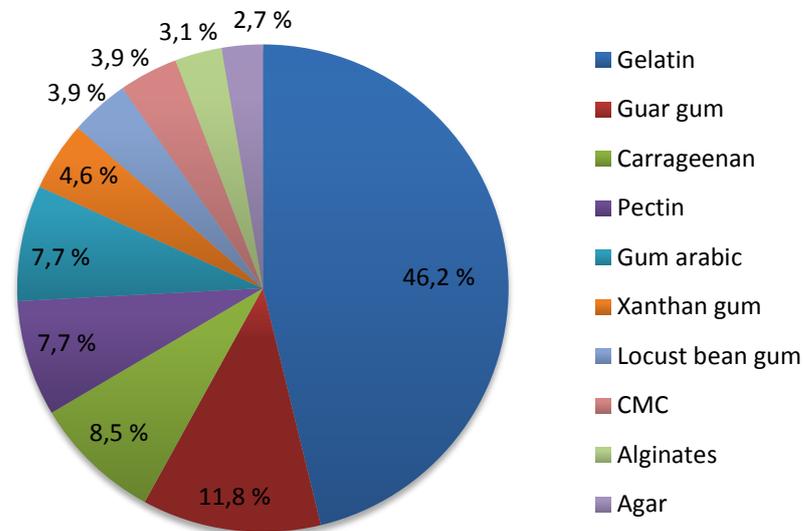


Figure 1. An overview of world's food hydrocolloid market volume (Fixed from Phillips & Williams, 2009)

4 STRUCTURES OF STUDIED HYDROCOLLOIDS

There are various different hydrocolloids on the market. Beside the functional properties, the market selection is dictated by price and security of supply of hydrocolloids. For these reasons starches and gelatin are the most commonly used as thickening and gelling agents whereas NaCMC is widely used throughout industry due to its favorable price and performance ratio. However the interest for other hydrocolloids, like xanthan gum and cellulose derivatives with unique rheological behavior, has increased over the time. (Phillips & Williams, 2009) By chemical modification of cellulose a cheap, water-soluble and environmentally benign materials can be derived. Cellulose itself is not water soluble in its native form, therefore it must be modified in order to obtain hydrophilic character like different cellulose ethers, such as NaCMC, MC, HEC. Whereas, different cellulose ethers are obtained by modifying functional groups, nanoscale materials such as MCC and MFC are manufactured by modifying the size of cellulose fiber components. (Makuuchi & Cheng, 2012) In the next chapter cellulose derivatives and other studied hydrocolloids and their structures are presented shortly.

4.1 Cellulose

Cellulose is a linear polysaccharide polymer which consist of β -D- glucopyranose units linked with (1 \rightarrow 4)-glycosidic bonds. Molecular formula of glucose chains $(C_6H_{10}O_5)_n$ is shown in Figure 2. The sub-index n of formula informs the degree of polymerization of the molecule. The degree of polymerization, DP, describes how many saccharide components are joined in chain. In the native state, cellulose molecule may have a length of 10 000 to 15 000 glucose units which are attached through an acetal oxygen covalently bonding. (Zhou & Wu, 2012)

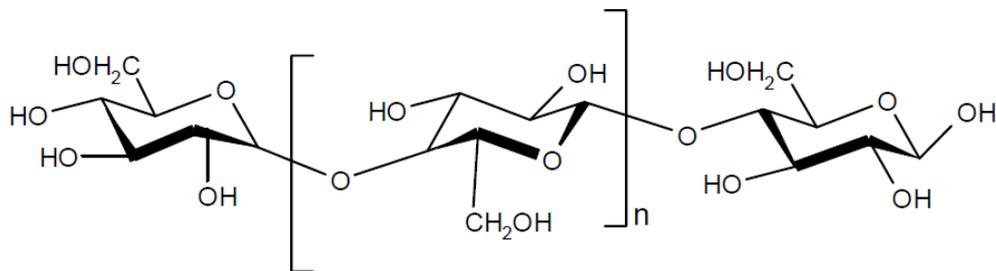


Figure 2. Structure of cellulose molecule (Tuulos-Tikka, 2002)

Cellulose molecules have a strong tendency to form intermolecular hydrogen bonds which are increasing outward from center of microfibril. Cellulose molecules form elementary fibrils so-called microfibrils, which can be arranged crystalline, semi-crystalline or amorphous regions. Cellulose microfibrils are surrounded by an amorphous matrix which makes elementary fibrils flexible so that they don't break so easily when treated. (Fernandes *et al.*, 2011; Sjöström, 1981; Zhou & Wu, 2012)

4.2 Sodium carboxymethyl cellulose

Sodium carboxymethyl cellulose, known as NaCMC, is more specifically sodium carboxymethyl cellulose which is derived from cellulose. The cellulose used in NaCMC manufacturing is carefully selected to meet quality requirements of the end product. Cotton linters are used to prepare high-viscosity NaCMC grades and wood pulp for medium to low viscosity types. Usually, bleached dissolving pulp, high cellulose content, is used to manufacture NaCMC. Commercially sodium carboxymethyl cellulose is produced in a two-stage process, which involves mercerization and etherification stages which are usually carried out in water-alcohol mixtures. The NaCMC manufacturing process steps are presented in Figure 3. (Ambjörnsson *et al.*, 2013; CP Kelco, 2006)

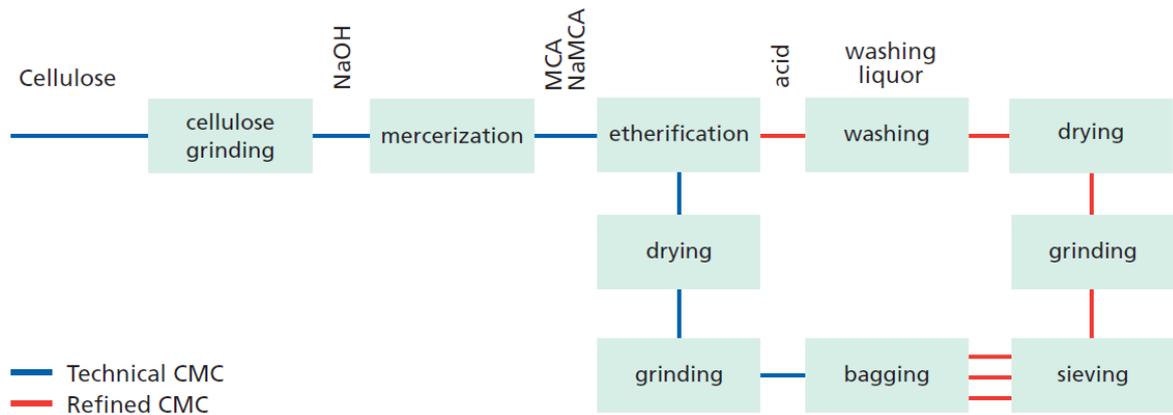


Figure 3. The block diagram of NaCMC manufacturing process (CP Kelco, 2006)

NaCMC is made water-soluble by a chemical reaction where carboxymethyl groups are introduced along cellulose chain. The unit structure of NaCMC is shown in Figure 4. The degree of substitution of this particular NaCMC is 1.0. However the remaining two hydroxyl groups still can be substituted to give a maximum DS of 3.0. (CP Kelco, 2006) Commercial water-soluble carboxymethyl celluloses are typically sold in sodium salt form with DS values from 0.7 to 1.2. The degree of substitution increases tolerance to acidic systems and dissolved ions. (Hercules Inc., 2010; Nussinovitch & Hirashima, 2014). Since NaCMC is biodegradable, nontoxic and reasonably-priced, it can be found in a high number of applications for example in food, health care and also pharmaceutical products for example as a thickener or to stabilize emulsions.

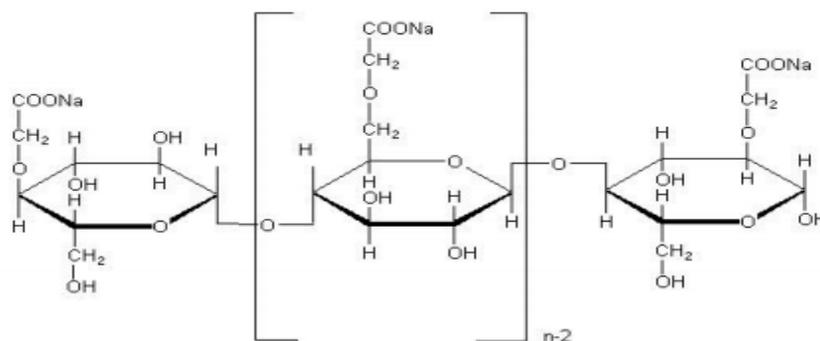


Figure 4. An idealized unit structure of NaCMC (Hoefer, 2008)

NaCMC products vary from low molecular weight to very high molecular weight polymers, which has a great effect on its solubility and rheological properties. The lower molecular weight NaCMC has faster rate of solution, however dissolution is also highly dependent on DS. NaCMC solutions can exhibit almost Newtonian flow behavior, but also

strongly pseudoplastic characteristics, which are result of long chain molecules tending to orient in the direction of flow. As the applied force is increased the viscosity of solution is decreased. Generally, pseudoplasticity decreases with increasing degree of polymer's substitution and lower molecular weight. In solutions uneven distribution of substituted carboxymethyl groups, higher molecular weight and lower substitution grades of NaCMC can lead to thixotropic behavior. (Wüstenberg, 2015)

NaCMC solutions are stable within wide pH range from 4 to 11 (CP Kelco, 2006). However they are relatively sensitive for physiologically relevant variables such as temperature changes and to ionic strength variations (Sannino *et al.*, 2009). Under normal conditions the viscosity of NaCMC solution is reversibly temperature dependent, which means that the original viscosity is regained when temperature is lowered to the starting value. Though prolonged heating period and high temperatures over 100°C can cause permanent loss of viscosity. (Wüstenberg, 2015) The influence of electrolytes depends on the ability of electrolyte to form soluble salt with NaCMC. The changes in viscosity are also dependent on whether the ions are mono-, di-, or trivalent. Monovalent ions (Na^+) have only slight effect, whereas divalent ions such as Ca^{2+} has more prominent effect on structure of NaCMC, which leads to the decreased viscosity. Trivalent ions can make the NaCMC insoluble and also cause gelation via their complexing with carboxylic groups. Also the addition point of electrolyte affects to the properties of NaCMC. In general, the viscosity of NaCMC solution is less affected if electrolyte is added to a water solution after dissolving the NaCMC. If the electrolyte is added prior, viscosity of solution decreases, because the salt restrains disaggregation. (Nussinovitch & Hirashima, 2014)

4.3 Microfibrillated cellulose

Materials prepared from cellulosic raw materials, which have fibers with at least one dimension between 1-100nm can be called nanocellulose. It covers various types of materials with different raw-materials, physical properties and manufacturing processes. Mechanically produced nanocellulose with long and entangled fibers are generally called micro- or nanofibrillated (MFC/NFC) cellulose, whereas chemically prepared shorter, rod-like fibers are called nanocrystalline cellulose (NCC), cellulose whiskers, cellulose micro- or nanocrystals (CNC). (Ankerfors, 2012, Karppinen, 2014) In this Master's Thesis the

focus is on microfibrillated cellulose obtained by mechanical homogenization of pulp fibers.

Microfibrillated cellulose is also known as microfibrillar cellulose or as a cellulose gel. MFC is cellulosic material, which is composed of elementary nanofibril aggregates called microfibrillated cellulose. (Lavoine et al., 2012) MFC has a high surface area and such as cellulose it also contains both amorphous ($> 1\mu\text{m}$) and crystalline parts, shown in Figure 5. Length of MFC is several micrometers and its diameter is in the range of 20-60 nm. There are several unique characteristics of MFC particles such as; nanoscale dimensions, high specific area, lightweight and extensive hydrogen- bonding ability make it a versatile material for new high-value applications. (Lavoine et al., 2012; Iotti et al., 2011)

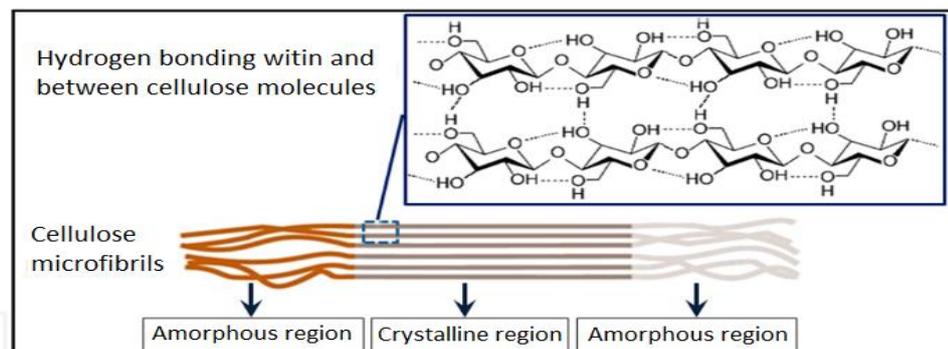


Figure 5. Scheme of interaction between cellulose molecular chains and cellulose microfibrils (Zhou & Wu, 2012)

Microfibrillated cellulose can be practically obtained from any cellulose source like wood, non-wood plants, crops, fruits bacteria, algae or micro-organisms. In general, the isolation of elementary fibrils can be achieved with high- pressure conditions, where nanosized fibrils are liberated from matrix (Wüstenberg, 2015). The fibrillation of cellulosic fibers can be carried out with mechanical disintegration by shearing and impact forces or alternatively by chemical treatment. Generally used mechanical methods are refining, grinding, fluidization, cryocrushing and ultrasonic treatments whereas acid hydrolysis, alkali and enzymatic treatment, partial carboxymethylation and TEMPO-oxidation are the main chemical treatments. The most common mechanical methods to produce MFC are presented in Figure 6. (Ankerfors, 2012; Lavoine *et al.*, 2012; Taipale, 2010)

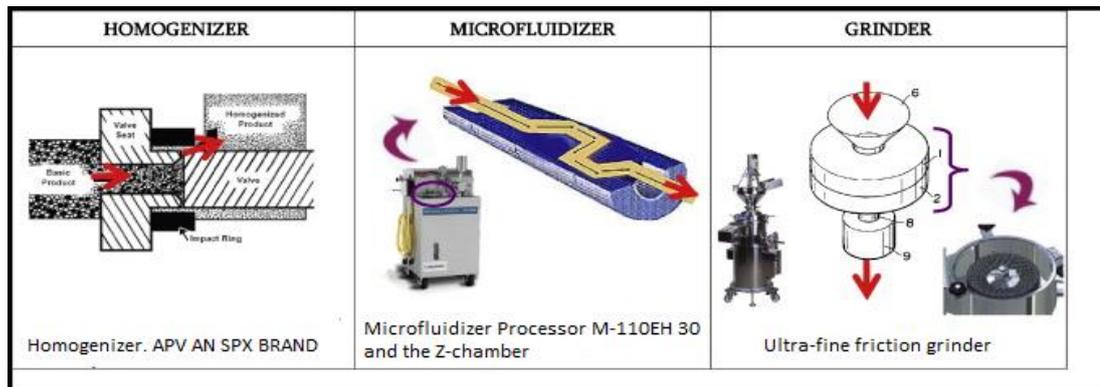


Figure 6. Mechanical equipment used in the fabrication of MFC: the homogenizer, the microfluidizer and the grinder. (Lavoine et al., 2012)

Mechanical fibrillation of untreated lignocellulosics consumes significant amount of energy, for example, 30MWh and over per tonne are not uncommon (Wüstenberg, 2015). The high energy consumption increases the price of MFC, which is undesirable and different pre-treatments are used to address this problem. Generally used pre-treatment methods, such as acid hydrolysis, enzymatic pretreatment, mechanical cutting, and the introduction of charged group, are combined to decrease the energy consumption by promoting the fiber cell wall delamination process. (Thakur, 2015; Wüstenberg, 2015) The studies have proven that energy consumption can be decreased with pretreatment methods and values even below 1 MWh per ton can be reached (Wüstenberg, 2015).

Treating wood-based cellulose fibers at high pressure and rapid collision against a surface, a gel-like MFC can be obtained. Microfibrillated cellulose fibrils, particularly anionic, form a strong hydrogel structure in aqueous systems, which exhibit high viscosity and strong shear-thinning behavior. MFC hydrogels, particularly native grades, are relatively inert to electrolyte concentration and pH changes. (Ankerfors, 2012; Karppinen 2014) Earlier studies have shown that increasing electrolyte concentration decreases the swelling of microfibrils, since the electrostatic repulsion is reduced. Monovalent ions such as sodium can assist the fibers to achieve the maximum swelling, which can be seen as increased viscosity. While divalent ions like calcium reduces the swelling of the fibrils. (Ankerfors, 2012) However the stability of suspension is highly dependent on the concentration. For example, the viscosity is more sensitive for the temperature changes in higher concentrations than lower dry matter contents of MFC. (Karppinen 2014, Lavoine *et al.*, 2012)

4.4 Xanthan gum

Xanthan gum is a natural polysaccharide and one of the microbial hydrocolloids. It is produced by *Xanthomonas campestris* bacterium at cell wall surface by a complex enzymatic process during the normal lifecycle. Commercially produced xanthan is manufactured by an aerobic, submerged fermentation process. The process is carried out in several stages and when the final fermentation step is finished the xanthan gum is recovered by precipitation. (Phillips & Williams, 2009)

Xanthan gum is a branched extracellular heteropolysaccharide which has a linear cellulosic backbone formed by (1->4)-linked β -D-glucose units (same as cellulose). The primary structure of xanthan gum, shown in Fig. 7, consists of two glucose units, two mannose units and one glucuronic acid unit which together form repeated pentasaccharide units. Trisaccharide side chains are attached on every other glucose unit linked at C-3 position. The trisaccharide side chain contains a glucuronic acid residue between two D-mannose units. (Balaghi, 2014;García-Ochoa *et al.*, 2000; Phillips & Williams, 2009)

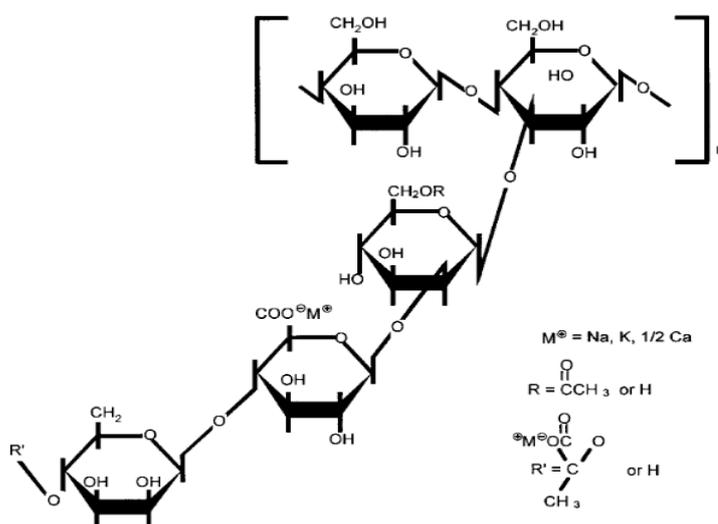


Figure 7. Repeating structural unit of xanthan (Phillips & Williams, 2009)

Xanthan gum is soluble in both hot and cold water. It forms a highly viscous solution and exhibit highly pseudoplastic flow even at low concentrations. The extreme viscosity is amplified at low shear rates. Xanthan solutions show a significantly higher viscosity in comparison with other gums such as guar gum or locust bean. Xanthan gum is also very stable colloidal material and its viscosity is not influenced to any great extent by changes

in pH or temperature nor the presence of electrolytes. (Balaghi, 2014;Phillips & Williams, 2009). These unique functional properties make it very effective stabilizer and thickener in water based systems. Xanthan gum has a great commercial significance and it can be used widely at different industrial applications, however its manufacturing process makes it quite expensive hydrocolloid on the market. (Phillips & Williams, 2009; García-Ochoa *et al.*, 2000)

4.5 Guar gum

Guar gum is one of the best known galactomannans alongside locust bean and tara gums. Galactomannans are macromolecular carbohydrates which can be extracted from different albuminous or endospermic seeds. Guar gum is endosperm of the seed obtained from the leguminous shrub *Cyamopsis tetragonoloba L*, known as the guar plant. (Balaghi, 2014) To extract the guar gum from the seeds, the seed is cracked and hull is removed mechanically. Then the seeds are divided into the endosperm halves which are screened, purified and powdered. The fluctuation in guar gum prices is dependent on crop situation; raw material prices and volume of raw materials, which primarily determines the pricing of material. (Mudgil *et al.*, 2012; Phillips & Williams, 2009)

Guar gum is composed from linearic (1→4)-linked β-D-mannopyranose backbone with α-D-galactopyranose units linked to O-6 positions. Molecular structure of guar gum is presented in Figure 8. The galactose content of guar gum is approximately 33-44-wt% and galactose to mannose ratio is 1:2. The pure mannose is insoluble in the water, but increasing galactose substitution of the guar gum the solubility will increase. Guar has exceptionally high molecular weight, 0.1 to 2.8 million, for naturally occurring and water soluble polymer. The high viscosity is partially explained by the high molecular weight. (Murwan *et al.* 2012; Venugopal & Abhilash, 2010)

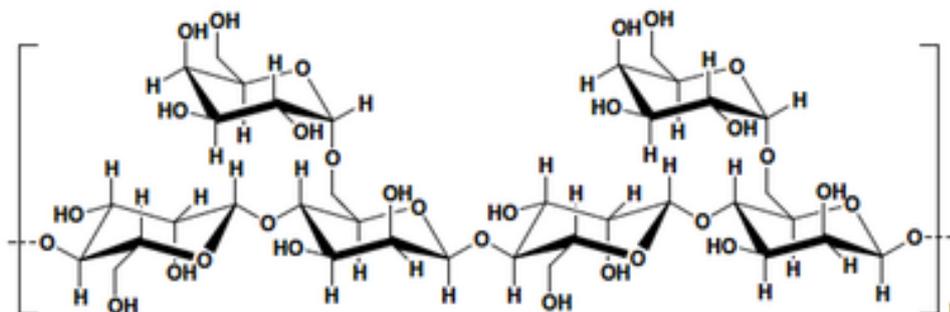


Figure 8. Molecular structure of guar gum (Kawamura, 2008)

Guar gum is non-toxic and non-ionic hydrophilic polymer which is one of the most efficient water binder and viscosity enhancer. It increases the viscosity of the aqueous base even at small concentrations. (Mudgil *et al.*, 2012; Phillips & Williams, 2009) Guar based solutions exhibit non-Newtonian flow behavior. Being non-ionic guar has high pH stability over pH 2-10, but it is still sensitive to high acidic media and temperature changes. However the viscosity is regained after the temperature is lowered. (Wüstenberg, 2015)

5 FUNCTIONALITY AND APPLICATIONS OF HYDROCOLLOIDS

Hydrocolloids are a versatile group of polymers which are used to modify rheological properties of water based solutions and suspensions. For this reason selecting the appropriate hydrocolloid for each application requires understanding about the chemical and structural properties of the hydrophilic materials but also requirements for the product itself. Hydrocolloids are water-soluble and they are characterized by their behavior when dispersed in water. Functional properties of hydrocolloids depend on the different characteristics of material. Macromolecular shape, conformation, intermolecular structure, charge, particle size and particle size distribution are important parameters concerning of the functional properties of hydrophilic colloids. These parameters have a dominant effect for example to the rate of hydration, water binding capacity, rheological behavior and stability. (Phillips & Williams, 2009; Bloor & Wyn-Jones, 1990)

5.1 Functional properties

The functionality and properties are influenced by molecular weight, the polymer monosaccharide backbone, type of side chains, distribution of side chains and intermolecular association. These structural properties define how material responds to the applied stress and chemical modification. Molecular weight is one of the most influencing properties, when it comes to the flow behavior and viscosity. Also the gel formation of hydrocolloids is major property affecting the rheological properties. Gel-like structure is formed by association or cross-linking of the polymer chains, which form three dimensional network structure that absorbs water within. (Milani & Maleki, 2012; Sadar, 2004; Saha & Bhattacharya, 2010)

Polymer suspensions usually exhibit increasing viscosity with growing dosage, but also with increasing molecular weight. This improves the thickening effect, which leads to the development of so-called superstructures, which is obtained with most hydrocolloids. (Wüstenberg, 2015) Flow and deformation properties are strongly depending on the chemical structure of the polymer. Particularly with NaCMC, the degree of substitution and substituent distribution has a considerable influence on the solution properties. The viscosity increases rapidly as a function of concentration, degree of polymerization and fibrillation. (CP Kelco, 2006; Hoefler, 2008) Longer molecular chain will occupy multiple times larger volume and is more likely to collide with an adjacent chain. This produces more friction between molecular chains, but also increases water-polymer contact, which resist the flow and explains the increased viscosity. In addition to long chain structure, fiber length will also increase flow resistance. (Milani & Maleki, 2012; Sadar, 2004)

Linearic structure, side chains and composition of the backbone affect to the rheological stability of hydrocolloids. Branching nature of a polymer, such as xanthan gum, provides more stable suspension against heat, acid, alkali and enzymes. This is because linear cellulosic backbone is shielded by trisaccharide side chains, which produce a rather stiff and rod-like structure. The monosaccharide composition influences ability to interact with the matrix in aqueous systems whereas side chain distribution can determine cold water solubility and synergistic effects. (Hoefler, 2008; Sadar, 2004; Sahin & Ozdemir, 2004)

The interaction between suspension structure and rheological properties is an important issue for development and processing materials. The structural properties of the

hydrophilic suspensions have a significant affect to the stability and rheological behavior of hydrocolloids. Some of the colloidal systems are stable by their nature; however in general the structure and the interactions between molecules can be changed by adding salt, polyelectrolytes or by modifying the pH. Some characteristic of the most major hydrocolloids are presented in Table II. (Sorvari et al., 2013; Karppinen et al., 2012)

Table II. Important commercial hydrocolloids and their characteristics (Fixed from Foster& Wolf, 2011; Saha & Bhattacharya, 2010)

HYDROCOLLOID	PROPERTIES	FUNCTION
Xanthan gum	Highly shear-thinning Extreme viscosity at low shear rate and low concentration High stability over electrolytes, temperature and pH Weak gel formation providing suspending properties Acid stability: Very good Clarity: Fair	Thickener, stabilizer, emulsifier and foaming agent Synergistic effects with gluco- and galactomannans
Carboxymethyl cellulose (NaCMC)	High viscosity, which reduced by adding electrolytes or reducing pH DS determines decrease in viscosity with increased ionic strength Acid stability: Fair Clarity: Excellent	Thickener, stabilizer
Galactomannans (Guar gum)	Very high low-shear viscosity and highly shear-thinning Independent of electrolytes but degrade and lose viscosity at high and low pH and at high temperatures Non-gelling Acid stability: Fair Clarity: Fair	Thickener, stabilizer and emulsifier Viscosity enhancement with xanthan

5.2 Applications

As non-toxic water-soluble materials, hydrocolloids are beneficial in different industrial sectors, including food, pharmaceuticals, cosmetics, textiles, construction, oil recovery and paper- and packaging. There is a wide range of different functions needed within industries. NaCMC is one of the most commonly used water-soluble cellulose derivate, which is widely used as rheological modifier throughout industries. (Sannino *et al.*, 2009) Sodium carboxymethyl cellulose offers an excellent excipient for sophisticated pharmaceuticals and different formulations, because of its high chemical and microbiological purity and stability. NaCMC is also free of odor and taste, which makes it suitable for different kinds of food, cosmetics and personal care applications. (Sannino *et al.*, 2009, Wüstenberg, 2015)

Food industry is one of the major users of hydrocolloids. For example, food hydrocolloids are used for generating mouth-feel, texture, extend to shelf-life, retain moisture and provide freeze-thaw stability. For example in ice creams hydrocolloids, like xanthan and guar gum, are used for various purposes such as provide better mouth-feeling, spoonability, a broader adhesivity and stability range and also improvement of melting resistance. (Balaghi, 2014; Wüstenberg, 2015) In addition to food products xanthan gum is also widely used for oilfield products and personal care products like lotions, body washes and cosmetics where it helps to thicken the solutions and suspend particles. Guar gum is used especially in food industry in desserts, bakery and dairy products. (Phillips & Williams, 2009)

Hydrocolloids are widely used as rheological modifiers. The most common functions for hydrocolloids are thickening and gelling agents in aqueous solutions. However they are used also as stabilizing and emulsifying agents in various applications. Other important uses of hydrocolloids are improving the stability, film-forming, shape retention, foaming aqueous solutions and also water holding. In Table III there is presented typical shear rates for various technical processes and applications. Within specific shear range it is possible to compare how different materials are behaving and are they suitable for a certain end-use purposes. (Mezger, 2011; Mudgil et al., 2012; Phillips & Williams, 2009)

Table III. Typical shear rates for different industrial processes (Mezger, 2011)

PROCESS	SHEAR RATES (s^{-1})
Sedimentation of particles	0.001-0.01
Surface levelling of coatings and printing inks	0.01-0.1
Sagging or dripping of coatings	0.01-1
Dip coating and paper coatings	1-100
Chewing and swallowing	10-100
Spreading	10-1000
Pipe flow, mixing and stirring	10-10 000
Spraying	1000-10 000

6 RHEOLOGY AND FUNDAMENTAL KEY FACTORS

Rheology is field of science which examines flow and deformation of various materials in different phases. In other words rheology defines how materials respond the forces applied to them and describes the interrelation between force, deformation and time. This kind of relevant information about the behavior of substances is obtained with different types of rheological measurements. Rheology is used as semi-quantitative tool in characterization and quality control of materials. It is also an essential tool for development of the materials. The correlation between the structure and rheological properties gives an important instrument of understanding and predicting the behavior of matter. (Goodwin & Hughes, 2008; Huggenberger et al., 2000)

There are many different kinds of properties to describe rheological features of material. One of the most common used parameter is viscosity, but also stress and viscoelastic modulus are used general in the characterization of materials. By determining these parameters, structural and material properties such as stiffness, elasticity, stability, flow behavior and gel-like structure can be defined and overall nature of material described. Rheological measurements can provide information about what kind of effects different parameters, like measurement conditions, additives, chemical, mechanical and thermal treatments have on material's flow behavior, structure and stability. Understanding these rheological properties is needed to optimize process conditions and develop materials with the desired processing and end-use properties. The relationship between structure and rheological features is essential to the development of new materials. (Goodwin & Hughes, 2008; Huggenberger et al., 2000)

6.1 Deformation and flow behavior

Rheological properties are defined as mechanical features which result in deformation or the flow of material under the applied stress. In classical mechanics there are separate physical laws to describe the behavior of solids and liquids. Hooke's law presents ideally deformation of solid whereas Newton's law describes ideally viscous flow. Hookean linear elasticity is valid in the ideally solid state. For example stone, steel and even some foods act according to the law of Hooke's. Whereas ideal fluids like water and oils behave as Newtonian. However there is also a variety of products that exhibit intermediate behavior.

Rheological classification of material's response to applied force is presented in Figure 9. (Gresham, 2008; Kim, 2002; Sahin & Sumnu, 2006)

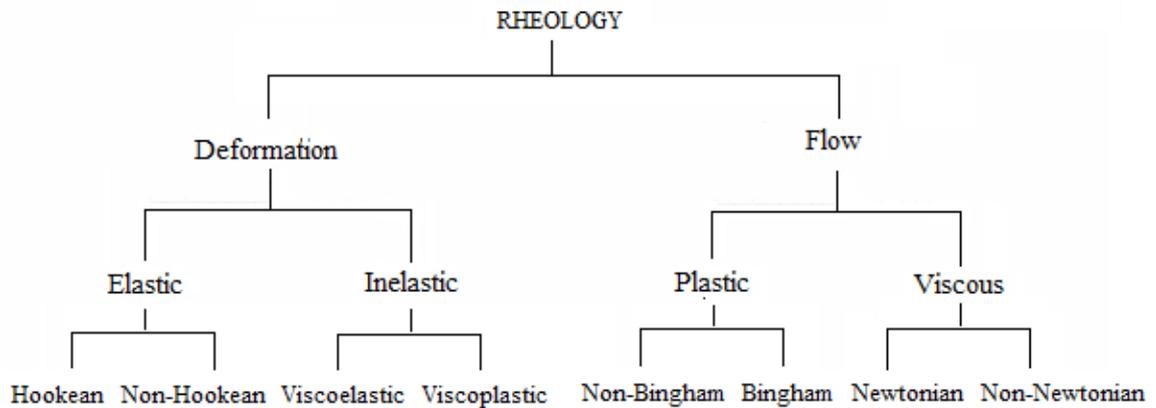


Figure 9. Classification of rheology (Sahin & Sumnu, 2006)

Viscous material does not stretch, but it flows under the applied force. The stress that develops during viscous flow depends on the rate of deformation. Viscous material resists a flow as a result of internal friction and when the force is removed it does not return its original shape. Under the stress these materials can exhibit also viscoelastic behavior which means that their response can be expressed in terms of a viscous and an elastic component. Once the stress is removed the viscoelastic materials has a limited degree of recovery. This kind of viscoelastic behavior is typical for different polymers, such as gels and glues. (Hackley & Ferraris, 2001; Kim, 2002; Sahin & Sumnu, 2006)

Bingham plastic and Non-Bingham (Herschel-Bulkley) fluids present materials which have a yield point. The network of intermolecular bonding forces prevent individual volume components to be displaced when material is at rest so the fluid remains rigid when the magnitude of stress is smaller than the yield stress. The yield stress represents the point where the external forces exceed the internal bonding forces and the material will start flowing. So the yield point or stress represents the force, which is required to initiate flow. It is an important characteristic of materials that exhibits solid like behavior below a finite yield stress.

The yield point is an essential property to many different applications such as toothpastes, cake frostings, margarines, ketchups, lipsticks, sealants and emulsion paints etc. With this kind of applications it is important that material do not flow its own, but become thin upon

the force like spreading, squeezing, pressing or chewing. For example with toothpaste it is important that it does flow out of the tube when squeezed, but not drain when it is applied in toothbrush. A High yield stress also helps the materials' ability to stabilize the solid particles in suspensions. (Huggenberger *et al.*, 2000; Mezger, 2011; Steffe, 1996; Sahin & Sumnu, 2006)

6.2 Definition of rheological parameters

Rheological features of materials define physical properties of liquids and solids. Rheological properties can be illustrated with the simple parallel plate model which is shown in Figure 10. In rheological measurements material is undergoing simple shear between parallel plates. When a force (F) is applied to the plate, the upper plate is moving at a particular velocity (v) and the lower plate is stationary. The distance between these parallel plates is described by h and moving plate area by A. This geometric structure can be used to define fundamental rheological parameters. (Huggenberger *et al.*, 2000; Rheotec, 2010)

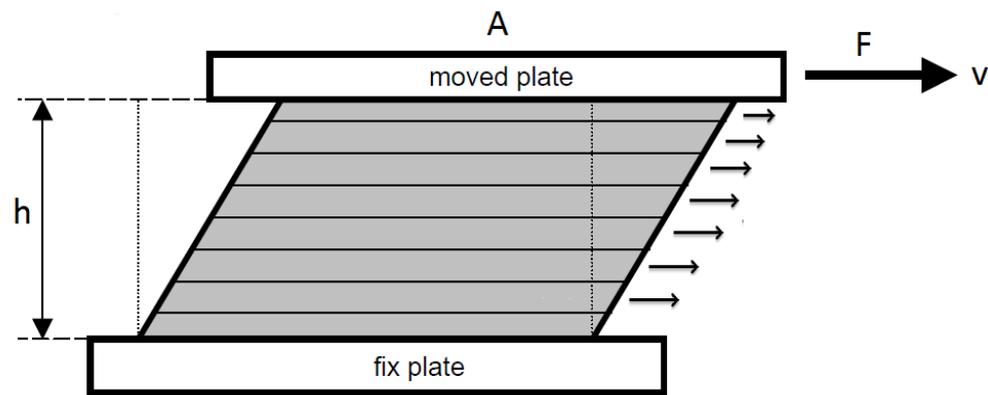


Figure 10. Parallel plate model of rheology (Rheotec, 2010)

6.2.1 Shear stress

The stress describes the force divided by area over which it is applied. Shear stress (τ) is defined as the force per unit area. The shear stress is component of force that is needed to achieve a given deformation. It causes successive parallel layers of a material body to move relative to each other. (Huggenberger *et al.*, 2000; Goodwin & Hughes, 2008)

$$\text{Shear stress } \tau = \frac{\text{Force } F}{\text{Area } A} = \frac{N}{m^2} = \text{Pa} \quad (1)$$

6.2.2 Shear rate

The shear rate describes the ratio of velocity (dv) and distance (dh). The shear rate defines the change of shear strain, relative deformation in shear, per unit time. The shear rate will increase if velocity of the upper plate increases and/or the gap between the two plates narrows. The equation of shear rate is shown in the formula below. (Huggenberger *et al.*, 2000; Barnes *et al.*, 1989)

$$\text{Shear rate } \dot{\gamma} = \frac{dv}{dh} = \frac{\text{Velocity } v}{\text{Distance } h} = \frac{\text{m/s}}{\text{m}} = \text{s}^{-1} \quad (2)$$

6.2.3 Viscosity

Viscosity (η) describes material's resistance to flow which is defined as the ratio of shear stress and shear strain rate. Viscosity is a feature that describes the internal friction of a moving material, because the fluid between parallel plates resists the movement of the upper plate. A fluid with high viscosity resists motion because its molecular structure gives it a lot of internal friction while fluid with low viscosity flows easily because there is very little friction when it is in motion. The equation of dynamic viscosity is illustrated in formula below. The unit used for shear viscosity is Pascal-seconds (SI units) also poise (1cP = 1mPas) have been used to describe the resistance of flow. (Huggenberger *et al.*, 2000, Mezger, 2011)

$$\text{Dynamic Viscosity } \eta = \frac{\text{Shear stress } \tau}{\text{Shear rate } \dot{\gamma}} = \frac{\text{Pa}}{\text{s}^{-1}} = \text{Pas} \quad (3)$$

Viscosity has an important role in many applications, since it has a great effect on fluid properties like transporting, mixing and heat and mass transfer. Due to this, viscosity is one of the key properties used in material, especially polymer, characterization. In Table IV there is presented viscosities of some familiar materials at room temperature and pressure. (Barnes *et al.*, 1989; Huggenberger *et al.*, 2000, Rheotec, 2010)

Table IV. The viscosity values of familiar materials (Mezger, 2011; Holmberg, et al., 2003)

MATERIAL	Viscosity η [mPas]
Gases/Air	0.01 to 0.02
Water	1.00
Light oils	10
Olive oil	100
Motor oils	50 to 1000
Glycerol	1000
Honey	10 000
Silicone	10 to 100kPas
Bitumen	0.5 MPas
Glass	10^{40} Pas

6.3 Viscoelastic behavior

Most materials are neither ideally viscous nor elastic. Viscoelastic materials exhibit both viscous and elastic characteristics simultaneously under the applied stress. Viscoelastic deformation is recoverable when the force applied is removed part of energy stored in the body will be released. As the result, the elastic part is recovered and the viscous part is permanently deformed. (Brummer, 2006; Hackley & Ferraris, 2001)

Viscoelastic behavior is a time-dependent feature which is often associated with polymer solutions and gels. The properties of viscoelastic materials can be characterized with oscillatory rheology which is a beneficial tool to study a wide range of timescales and behaviors. The oscillatory tests, most often an oscillatory shear experiment, are used to define viscoelasticity of material. Material's response to the applied sinusoidal stress or strain can be defined with shear modulus (G), the formula is presented below. (Huggenberger *et al.*, 2000, Rheotec, 2010)

$$\text{Shear modulus } G = \frac{\text{Shear stress } \tau}{\text{Strain } \gamma} = \frac{\text{Pa}}{1} = \text{Pa} \quad (4)$$

Viscoelastic behavior of system can be characterized by the storage modulus (G') which describes elastic response and the ability of the material to store energy. The loss modulus (G'') is respectively a measure of viscous component and provides information on the ability of the material to dissipate energy. With oscillatory measurements the solid-like and fluid-like contributions to the measured stress response is featured. The correlation

between material's structure and the storage and loss modulus is presented in Table V. The loss factor, $\tan\delta$, presents the ratio of the viscous and elastic portion of viscoelastic deformation behavior. The smaller the loss factor is the more gel character the material shows. The gel point is the critical transition point, which classifies material as a liquid before it and as a solid afterwards. (Huggenberger *et al.*, 2000, Grillet *et al.*, 2012)

Table V. Conversion between storage modulus, loss modulus and viscoelastic properties. (Mezger, 2011)

Ideally viscous flow behavior	Behavior of a viscoelastic liquid	The gel point, viscoelastic behavior 50/50 ratio	Behavior of viscoelastic gel or solid	Ideally elastic deformation behavior
$\delta = 90^\circ$	$90^\circ > \delta > 45^\circ$	$\delta = 45^\circ$	$45^\circ > \delta > 0^\circ$	$\delta = 0^\circ$
$\tan\delta \rightarrow \infty$	$\tan\delta > 1$	$\tan\delta = 1$	$\tan\delta < 1$	$\tan\delta \rightarrow 0$
$(G' \rightarrow 0)$	$G'' > G'$	$G' = G''$	$G' > G''$	$(G' \rightarrow 0)$

7 RHEOGRAM AND VISCOSITY FUNCTIONS

The response of material to applied force depends on the type and magnitude of the stresses. For solid materials the elastic properties are the most important, whereas the flow properties are the most important to liquid materials. Graphically displayed flow curve of correlation between shear stress and shear rate defines the flow behavior. There are two general classes of flow behavior which are Newtonian and non-Newtonian. Newtonian fluids have a constant viscosity while non-Newtonian fluids have a shear rate dependent viscosity. (Huggenberger *et al.*, 2000)

These flow behaviors can be classified according to their characteristic shape. In Figure 11 there are illustrated typical flow curves for Newtonian and non-Newtonian fluids. Shear-thinning and shear-thickening behaviors are the most common types of non-Newtonian flow behavior. Flow curve for Newtonian fluids is a straight line and its slope defines the viscosity. For shear-thinning materials, the viscosity decreases with increasing shear rate and the viscosity of shear-thickening increases. (Huggenberger *et al.*, 2000; Steffe, 1996)

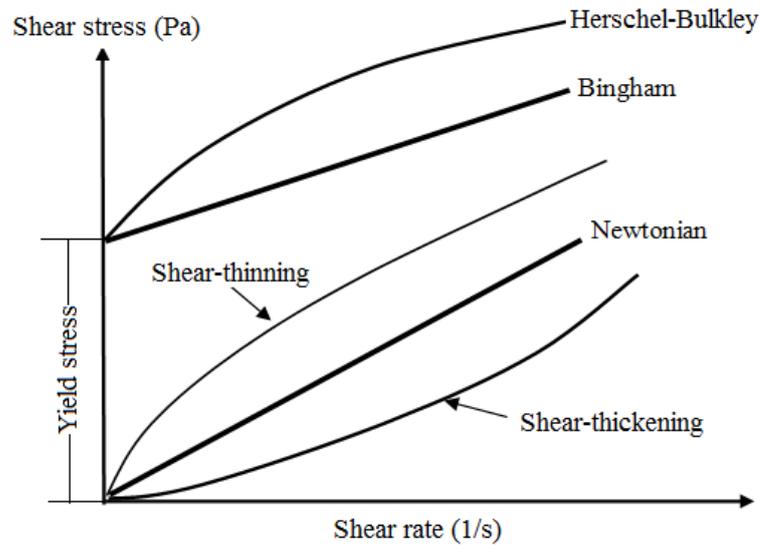


Figure 11. Flow curves of Newtonian and Non-Newtonian fluids (Modified from Steffe, 1996)

Bingham plastics flow like the Newtonian fluids when the shear stress exceeds the yield stress. Typical examples of Bingham plastic fluids are toothpaste, mayonnaise and ketchup. Non-Bingham Plastic fluids also have a yield point but the graph is not linear so the fluid can be either shear-thinning or shear-thickening. For example minced fish and raisin paste are Non-Bingham plastics which obey Herschel-Bulkley model. (Sahin & Sumnu, 2006)

Measurement conditions together with internal forces and chemical structure affect how the substances are behaving under the applied stress. The viscosity depends on the shear applied and most cases viscosity is changing depending on the external force. However measuring the Newtonian fluids viscosity remains constant under different shear rates. When the shear stress is increased, resistance to flow will decrease and vice versa. With applied force, one of the most dominating measurement parameter is temperature. Viscosity measurement requires precise temperature control because substances become less viscous when temperature is rising. Rheological behavior also depends on the previous history of forces applied to the matter, for example, network strength is dependent on the shear history and sample preparation. (Huggenberger *et al.*, 2000; Rheotec, 2010; Saarinen *et al.*, 2009)

7.1 Shear-rate dependent rheology

The Newtonian fluids form the basis for classical flow mechanics. The Newtonian fluids follow the same scientific laws and exhibit characteristics of ideally viscous fluids. Newtonian fluids have a linear relation between shear stress and shear rate which means that flow curve is a straight line starting from zero. In Newtonian flow model the coefficient of viscosity is the constant of proportionality and independent of shear rate. Non-Newtonian material's flow in an unusual way and their flow properties can differ a lot from Newtonian. Non-Newtonian material's flow curve is not linear because the shear stress is not proportional to the applied shear rate and the viscosity of non-Newtonian fluids may increase or decrease with increasing shear rate. (Gresham, 2008; Kim, 2002; Sahin & Sumnu, 2006)

Common liquids, gases and solutions of low molecular weight substances are Newtonian. Substances like water, air and ethanol are good examples from Newtonian fluids whereas paints, foams, blood and toothpaste are non-Newtonian. Usually non-Newtonian materials are aqueous solutions of high molecular weight polymers and suspensions of fine particles. (Hackley & Ferraris, 2001; Kim, 2002) However non-Newtonian materials can also exhibit viscoelastic properties and gel-like networks. Polymers, which have strong tendency to develop interchain hydrogen bonds between the molecular chains, can produce a gel-like network and are defined as viscoelastic materials. (Wüstenberg, 2015)

The Non-Newtonian substances can be categorized by the shear rate dependence of viscosity. Shear –thinning (pseudoplastic) and shear- thickening (dilatant) behaviors are the two most common types of non-Newtonian fluids. The shear-thinning is more common feature than the shear-thickening behavior which generally occurs only at higher shear rates. For example polymers, paints, glues and gels are pseudoplastic materials while starches and dispersions which have a large amount of solid material are dilatant. (Gresham, 2008; Huggenberger *et al.*, 2000; Kim, 2002)

The viscosity of pseudoplastic fluids decreases with increasing shear rate during steady shear flow, whereas dilatant fluid's resistance to shear increases with increasing shear rate. Shear –thinning behavior is often resulting of orientation of particles, droplets or polymer chains in the direction of flow. Also polymer chains or particle aggregates breaking during

flow can cause shear-thinning behavior. The viscosity of shear-thickening fluids increases with shear rate because they contain suspended solids which become close packed under the stress. (Gresham, 2008; Huggenberger *et al.*, 2000; Kim, 2002)

7.2 Time-dependent rheology

There are two types of time-dependent rheological flow behavior. Thixotropy and rheopexy are properties exhibited by non-Newtonian liquids. The viscosity of thixotropic system decreases with time, however it returns to its original viscosity after the shear force is ceased to act. In other words a thixotropic material becomes thinner when the force is applied, but after the shearing forces are removed the internal structure of the fluid can be rebuild. So material will additionally return to its original viscosity after a material-specific period of rest. (Huggenberger *et al.*, 2000; Rheotec, 2010)

The viscosity of rheopectic system increases with time. These kinds of materials exhibit greater viscosity under the shear stress. In a rheopectic system an increase of viscosity is result of shear-induced buildup of internal structure. The original viscosity of rheopectic material is only restored with a delay after the shear stress is removed, by disintegrating this structure. (Huggenberger *et al.*, 2000; Rheotec, 2010)

Thixotropic is quite common for example in paper coating formulations whereas rheopectic behavior is quite rare in actual practice. Thixotropy and rheopexy are generally measured through a shear ramp where the shear rate is increased and then decreased back to the starting value. The viscosity of these time-dependent materials depends on prior shear history. (Huggenberger *et al.*, 2000; Rheotec, 2010)

8 RHEOLOGY OF CELLULOSE FIBER AND MFC SUSPENSIONS

The fiber suspensions are quite different from other solutions of polymers or even solid-liquid systems. Fibers are solid particles which cause a hydrodynamic disturbance to the flow that changes rheological behavior of the liquid. Investigating fluid dynamics and flowing properties of fiber suspensions are extremely important to papermaking processes. Rheological modelling of pulp and other cellulosic fiber solutions is needed because their features are not uniform. (Beghello, 1998; Hämäläinen *et al.*, 2011; Karppinen, 2014) Similar to pulp, also MFC form an interconnected and heterogeneous network in water

suspensions. These fiber suspensions consists various layers which each have different orientations and material properties. (Karppinen, 2014)

8.1 Forces between the cellulosic fibers

The unique interactions between fibers affect to the flocculation and rheology, especially viscosity, of suspension. Cellulose fiber contacts at the suspension are influenced by both supramolecular interactions and mechanical forces. Colloidal forces are supramolecular interactions between cellulosic fibers. These forces can be divided into van der Waals and electrostatic double layer forces. Van der Waals interactions are acting between similar surfaces whereas H-bonding, electrostatic double layers are formed by charged surfaces and the ions. With unmodified fiber surfaces the charge is low and flocculation and permanent aggregation of fibers are reduced. (Beghello, 1998; Karppinen, 2014)

During the flow, suspension will bend and after the shear bent fibers will straighten. The colloidal forces aren't dominant under the conditions of flow. For cellulose fiber suspensions mechanical entanglement is more probable cause for flocculation than colloidal forces. Mechanical interactions can be formed by linking, hooking, interlocking by elastic bending or spinning of the fibers into threads. Elastic bending and hooking of fibers are illustrated in Figure 12. (Karppinen, 2014; Kerekes, 2006)

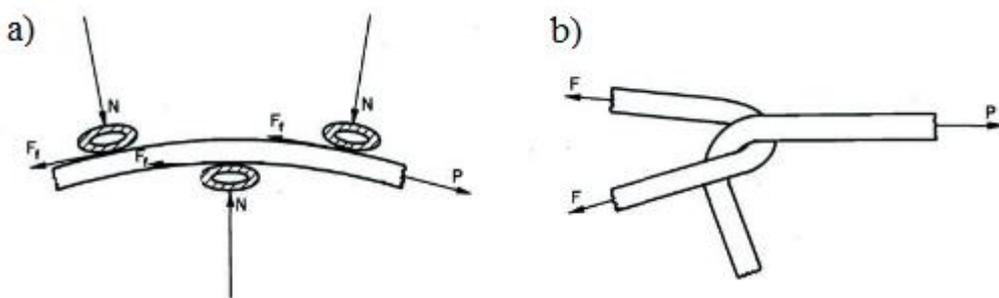


Figure 12. Elastic bending of mechanical forces (a) and hooking mechanism (b) of the fiber suspensions (Karppinen, 2014)

Microfibrillated cellulose fibers have smaller dimension parameters, which increase the effect of colloidal forces compared to pulp suspension. However mechanical entanglement, and thus flocculation, is favored by high aspect ratio and morphology of MFC. High aspect ratio of MFC fibers enables elastic bending and irregular shape of fibrillated fibers favors

mechanical hooking which induces more fiber interactions and faster aggregation. (Beghelli, 1998; Karppinen, 2014; Kerekes, 2006)

8.2 Rheological properties of microfibrillated cellulose

There are some structural and rheological similarities between cellulose fiber suspensions and MFC suspensions. Fibers and elementary nanofibrils have identical chemical structure and strong tendency to flocculate. On the other hand considerably smaller dimensions, higher aspect ratio and large specific surface area bring some new aspects to the rheological behavior of MFC suspensions. (Karppinen, 2014) However, microfibrillated cellulose fibers have smaller dimensions, higher aspect ratio, great affinity towards water and large specific surface area which give interesting rheological characteristics to suspensions. MFC has an interconnected network in water suspensions which must be broken to initiate flow. The strength of the network and entanglements between fibers determines the yield stress needed to achieve the flow. A high yield stress is related to the suspension's ability to stabilize solid particles in dispersion. (Karppinen, 2014; Milani & Maleki, 2012)

MFC has quite complex rheological profile but in general MFC water suspensions exhibit a highly pseudoplastic behavior. Under the shear the fiber network disintegrates and fibrils start to flow in flocs. Once the suspension is properly flowing the fibers will align within flow also with the increasing shear rate the average floc size decreases, which explain the shear-thinning behavior. However at very high shear rates over 100 1/s MFC suspensions can also exhibit shear-thickening behavior when a shear induced structure is formed. With a high enough shear rate the fibrils can get the close enough to organize formation with temporary hydrogen bonds or Van der Waals interactions. (Iotti et al., 2011; Milani & Makeni, 2012; Moberg & Rigdahl, 2012)

MFC suspensions are not only viscous but exhibit also solid-like behavior. These viscoelastic properties are due to the three dimensional network structure. In water suspensions MFC can form gel like structure even at low concentrations, starting from 0.1% (Karppinen, 2014). The stability of MFC suspensions have been studied as a function of concentration, temperature, pH and electrolyte concentration. The viscosity and gel properties of MFC suspensions are strongly dependent on concentration. At low

concentrations the pH modifications results as viscosity decrease, which is due to change in the surface charge and interactions between fibers. Also increase in temperature and electrolyte addition is reducing the viscosity. (Iotti et al., 2011; Karppinen, 2014; Milani & Makeni, 2012) The rheological properties and findings of microfibrillated cellulose reported in earlier studies are gathered in Table VI.

Table VI. Rheological properties of microfibrillated cellulose in different conditions

RAWMATERIAL AND PREPARATION OF MFC	MEASUREMENT CONDITIONS	RHEOLOGICAL PROPERTIES	REFERENCE
MFC from purified sugar-beet pulp cellulose- based residue by strong mechanical treatments	0.25-3wt % 20°C	Shear thinning behavior plateau region between 15-40s ⁻¹ Yield stresses 0.4 -40 pa $G' > G''$, $G' \approx 8 - 4000$ Pa $\tan \delta \approx 0.1$	Agoda-Tandjawa et al., 2010
High concentrated MFC gel manufactured with microfluidizer from unbleached Kenaf kraft pulp	0.52- 2.25% 23°C relative humidity 50%	non-Newtonian, pseudoplastic behavior $G' \approx 76 -5325$ Pa, $G'' \approx 17- 1516$ $\tan \delta$ between 0.22 and 0.28 Critical yield strain 0.52 %	Charani et al., 2013
MFC from birch kraft pulp by ultra-fine friction grinder (Supermasscolloider)	1-4 % 23°C	Gel-like behavior $G' > G''$ $\tan \delta$ between 0.3 and 0.2	Dimic-Misic et al., 2013
MFC from bleached sulphate pulp produced by homogenization	1% 25°C	Shear thinning behavior, $G' > G''$ Yield stress detected at a concentration of 1% At high shear rate, over 15000s ⁻¹ , exhibits dilatant behavior	Iotti et al., 2010
MFC from never-dried bleached kraft birch pulp by mechanical disintegration	0.1-2%	Shear-thinning Transition region observed between two shear thinning regions Gel-like behavior, $G' > G''$ Flocculation detected under the shear	Karppinen, 2014
MFC from never -dried birch pulp by mechanical disintegration (Refiner + Microfluidizer)	0.5wt % 23°C	Strongly shear thinning Gel-like behavior $G' > G''$ Transition region at shear rates 2-20s ⁻¹ Moduli roughly independent of the angular frequency, $G' \approx 2$ pa	Karppinen et al., 2011
MFC from never-dried bleached kraft birch pulp prepared by mechanical disintegration (Supermasscolloider)	0.1- 2% 25°C	Extremely shear thinning Two shear thinning regions Lowest gel concentration $\approx 0.1\%$ 0.1% suspension exhibited dilatant behavior at high shear rates	Karppinen et al., 2012

MFC from never-dried sulphite pulp by TEMPO-oxidation	0.053-0.78% 23°C	Pseudoplastic and thixotropic behavior Superior shear thinning for higher concentrations Critical concentration of 0.23%, Constant viscosity detected from 0.1-100 s ⁻¹ for 0.15% suspension	Lasseuguette et al., 2008
Enzymatic and carboxymethylated MFC from bleached sulphite-softwood-dissolving pulp	2 % 25°C	Up to the critical stress $G' > G''$ Critical shear stress 10- 30Pa Storage modulus $G' \approx 3000\text{Pa}$	Moberg & Rigdahl, 2012
MFC from bleached sulfite softwood cellulose pulp by pre-treatment steps and homogenization	0.125-5.9wt % 25°C	Gel-like behavior, $G' > G''$ 1.5Pa to 10 ⁵ Pa; 3wt % $\approx 10^4$ Pa $\tan \delta$ between 0.24 and 0.17	Pääkkö et al., 2007
MFC from never-dried bleached kraft birch pulp prepared by mechanical disintegration (Supermasscolloider)	0.5wt % 23°C -25°C	Drastically shear thinning, two shear thinning regions can be detected with small plateau between them Viscosity ≈ 150 to 0.03 between shear rates 0.01-1000s ⁻¹	Sorvari et al., 2013

8.3 Flocculation of MFC suspensions

The flocculation in aqueous suspension is typical phenomenon for cellulosic fibers and thus applies also for MFC (Karppinen, 2014). In water suspensions microfibrillated cellulose fibers form entangled and heterogeneous network where local mass concentrations and particle aggregation can occur. Flocs may exist also as isolated entities. In the presence of flocs they exert a profound effect on suspension rheology which causes some challenges to characterizing the rheological behavior. However, flocculation can be a desired or undesired property of the MFC suspensions. For example, flocculation can be beneficial for pumping and drying of the suspension, whereas flocculation is unfavorable feature, when good transparency and mechanical endurance have to be achieved, since fibers must be evenly dispersed. (Karppinen, 2014; Kerekes, 2006; Taipale, 2010)

The strength of the network depends on the forces between cellulosic fibers but also the number of contact points between the fibers and cohesive forces (Karppinen, 2014). Floc-forming is a result of relative motion which brings fibers together. However anionic nature of fibrils decreases the flocculation behavior by keeping the fibers separated from each other. The mechanical entanglement increases the amount of contact points and gives rise to the cohesive forces which make flocs stronger than the network on average. This means

that under the shear flow interconnected flocs will rupture from the network and flow as individual. Floc formation is illustrated in Fig.13. (Karppinen, 2014; Kerekes, 2006)

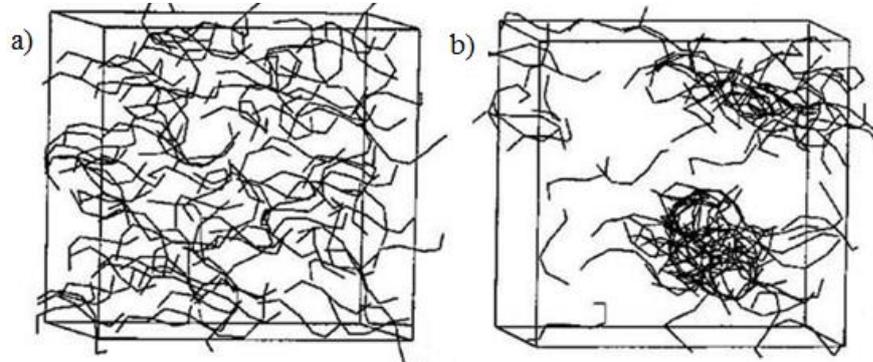


Figure 13. Schematic presentation of flocs in the network (a) and floc forming in simple shear flow (b). (Kerekes, 2006)

The flocculation affects structure and rheological profile of the suspension. The rheological behavior is affected by the floc structure and size which are dependent on shear rate, flow type and surface properties of the suspension. The average size of flocs will decrease as a function of shear rate. The higher applied shear rate is, the smaller floc size will be. Also different additives, like polyelectrolytes or salts, have influence in flocculation and overall viscosity behavior depending of MFC suspensions. When adding salt to the suspension, colloidal particles can form larger aggregates. Furthermore, charge of colloidal particles increases the opportunity to develop flocs. However the contacts between fibers can be broken when the suspension is under flow. The rupture of flocs can be result of erosion of the fibers or hydrodynamics forces which can break them. (Karppinen, 2014; Karppinen et al., 2012; Kerekes 2006)

EXPERIMENTAL PART

The aim of the experimental part was to systemically characterize the rheological behavior of two different types of microfibrillated cellulose (native and anionic) and to provide a reference for further rheological studies. To be able to identify special features of MFC suspensions they were compared against selected rheological modifiers that represent a broad spectrum of rheological behavior and end uses from different fields. The comparisons were made to clarify the possible benefits of microfibrillated cellulose gels in contrast to commercial products. The rheological behavior of studied materials has been investigated with rotational rheometer using rotational and oscillation tests. In order to get comprehensive view of the rheological characteristics of MFC suspensions the effect of various factors such as MFC concentration, temperature, presence of electrolytes and ionic strength were studied.

9 MATERIALS AND METHODS

Studied MFC samples were obtained from Stora Enso Oyj. Three different grades of microfibrillated cellulose suspensions were selected to be studied; one native grade (MFC 1) and two anionic samples MFC 2 and MFC 3. The anionic MFC were selected based on their different charge densities (Table VI). The native MFC was prepared without chemical treatment step by mechanical disintegration, whereas the two anionic grades were manufactured using a chemical pre-treatment steps prior to fibrillation. The final fibrillation and disintegration step for all samples was a similar treatment using a fluidizer (Microfluidics, M-110EH-30) at a fiber concentration of 2wt %.

As a reference for MFC suspensions sodium carboxymethyl cellulose, xanthan gum and guar gum were studied. The selection of high molecular weight polysaccharides was based on the structural similarities with cellulose and they also represent commercial products with different molecular structure, chemistry and rheological behavior utilized in a wide variety of applications. As described in previous section, NaCMC and xanthan gum are anion rheology modifiers, whereas guar gum represents nonionic rheological additive. Both NaCMC and guar gum are polysaccharides with a Newtonian behavior, while xanthan gum is a branched polymer with strongly shear-thinning flow behavior. The studied MFC suspensions and used reference materials are presented in Table VII.

Table VII. The studied materials

SAMPLE	GRADE
MFC 1	Native
MFC 2	Anionic (DS 0.04)
MFC 3	Anionic (DS 0.12)
CMC 1	Oil drilling
CMC 2	Paint industry
CMC 3	Food products
GUAR GUM	Industrial
XANTHAN GUM	Industrial

9.1 Sample preparation and development of the method

To find appropriate preparation method for MFC suspensions, different mixing and stirring techniques from magnetic stirrers to high-performance dispersing instruments, such as Ultra-Turrax, were tested. Also the length of processing time and intensity of different treatments were studied to guarantee homogeneous suspensions even with 1.0wt % anionic MFC suspensions, which were showing strong gel-like structure. The preparation method for studied samples was selected to ensure high quality of rheological measurements by manufacturing uniform suspension efficiently and avoiding the excess of air bubbles. This way the extensive picture of rheological properties of MFC suspensions without artifacts could be achieved. Also different measurement geometries (PP50, CC27) with rheometer were tested and compared to find out optimal measurement method for studied MFC suspensions. The cylindrical geometry was selected, because of diversity and low concentrations of suspensions. The CC27 was decided so that all the samples could be measured with same measurement geometry.

Studied suspensions with different concentrations were prepared by dispersing the appropriate amount of stock solutions (2wt %). The suspensions were diluted to target concentrations with ionized water to minimize impurities, especially to avoid excess electrolytes. The pH values of the diluted suspensions varied from 6 to 8. The mixing of aqueous MFC suspensions (200 ml) was carried out at the speed of 1400 rpm for 10 minutes using propeller mixer (diameter 50 mm, RZR 2051 control, Heidolph Instruments, Germany). After mixing, all the samples were stored overnight in a cold room (7 °C). This way samples were allowed to rest before the rheological measurements and the effect of shear history can be minimized. The prepared solutions were given to equilibrate one hour

at room temperature, before performing the measurements. Because of the effects of shear history sample handling prior to the measurements was carried out as controllably as possible.

9.2 Characterization methods

Besides investigating the rheological properties, different techniques were used to characterize other properties of MFC suspensions. Different physical and chemical tests were carried out in order to find out the key factors affecting flow behavior and other rheological properties. For this purpose the ionic strength, transmittance, fibrillation stage, microscopic structure and also visual differences were studied. The commercial hydrocolloids were only used as rheological references so the structural characterization was not included in this work.

9.2.1 Zeta potential measurements

Zeta potential is a measure of electrokinetic mobility that particle acquires in a specific suspension medium. Zeta potential is used to determine the magnitude potential at the slipping plane (Fig. 14). The magnitude of the zeta potential gives an indication of the stability of the colloidal systems. With large negative or positive zeta potential values, particles will tend to repel each other, which prevent the flocculation. Whereas low zeta potential values, less than -15mV, represent onset of agglomeration. Particles with values greater than +30 mV or more negative than -30mV are considered colloidal stable suspensions, because of sufficient mutual repulsion. However it is also possible to achieve colloidal stable suspension at low zeta potential values, via e.g. steric stabilization or electrostatic stabilization at low ionic strength. (Zhou et al., 2012; Clogston & Patri, 2011)

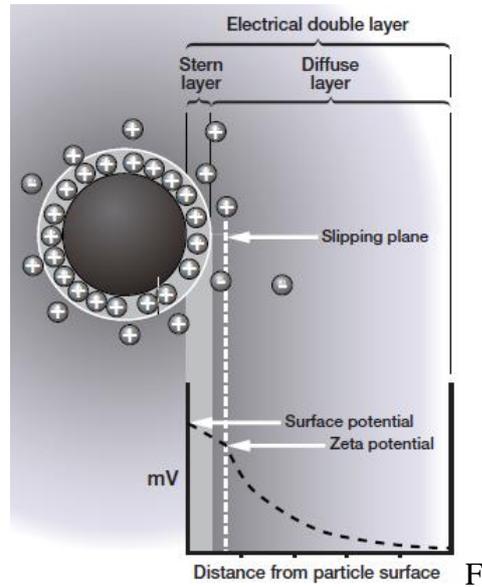


Figure 14. The definition of zeta potential and the electrical double layer surrounding particle (Malvern, 2012)

Malvern Instruments Zetasizer Nano ZS (ZEN 3500) was used to characterize zeta potential of MFC particles suspended in water. The calculation of zeta potential is based on determining the electrophoretic mobility using Laser Doppler Velocimetry (LDV). In the measurement an electric field is applied across an electrolyte where charged particles are attracted towards the electrode of opposite charge. When equilibrium is reached the electrophoretic mobility can be evaluated and zeta potential values are obtained by application of the Henry equation, Eq. 5, where U_E denotes electrophoretic mobility and ϵ is the dielectric constant of dispersion medium (ionized water). The zeta potential is described as z and η is the dynamic viscosity of the suspension medium. (Clogston & Patri, 2011; Hunter, 1986)

$$U_E = \frac{2\epsilon z f(ka)}{3\eta} \quad (5)$$

It should be taken into account that zeta potential is very sensitive to pH level, valency of the ion, ionic strength of the suspension and also particle shape and size. The model for calculation of zeta potential values assumes that particles are spherical objects with certain radius. Therefore, zeta potential values are not considered as exact values for non-spherical particles, such as microfibrillated cellulose, but rather used only as comparison for different MFC grades in this Master's thesis. The measurements were carried out using the

very dilute suspensions (0.1wt %) for enabling laser detection of particle movement. Ion exchanged water was used to dilute suspensions and the temperature during the measurement was 25 °C. The electrical conductivity (EC) and pH of the suspensions were adjusted by titrating suspensions with 0.1M NaOH, so that measurement conditions would be same for all samples. The measurements were carried out at the 1.0 mV/cm and pH 7.5. The reported zeta potential values are an average of eight measurements and standard deviations of parallel measurements were calculated.

9.2.2 **Optical microscopy and digital imaging**

The microscopic structure, degree of fibrillation and appearance of MFC suspensions were studied with light microscope and from micrographs captured with digital camera images. Precise quantification of the microstructure of MFC suspensions is difficult to achieve so two optical approaches were used to determine both internal and external structural characteristics. Photomicrographs of different MFC grades were obtained using Leica Microsystems DMR (DC300) optical light microscope. The microscope images were acquired by viewing the drop of original suspension (2wt %) between two slides of glass. The suspensions were reviewed with 4× and 10× magnifications to get a proper overall picture of fibrillation level and amount of non-fibrilled fibres visible with light microscope.

Two sets of digital images were taken for visual observation of the transparency, homogeneity and gel-like structure. Firstly, pictures from original suspensions were taken to get clear image of how strong gel-like properties MFC grades are exhibiting. Also visual comparison of transparency can be carried out. Secondly, the suspensions' degree of homogeneity and turbidity were visually evaluated from diluted samples. In addition the presence of flocculated structures and air bubbles were investigated. For this purpose original MFC samples were diluted to concentration of 0.2wt %. The photos were taken from above the sample in Petri dishes against black background and Stora Enso's logo.

9.2.3 **Transmittance measurements**

For more accurate studies about the turbidity and transparency of MFC samples, the transmittance measurements were carried out. While transparency describes material's physical property to let light through, the turbidity refers to the degree of cloudiness in water caused by the suspended particles. When a beam of light is directed to material, it

can be scattered, absorbed or transmitted. The higher the transmittance is, the higher is the transparency of suspension. The transmittance measures the intensity of light going through a sample and reaching a detector. The remaining light is the fraction of the light absorbed by the sample. If all the light goes through a sample, the transmittance is 100% and absorbance is zero. However if all the light is absorbed by the sample then percent transmittance is zero and absorption is infinite. However the suspended particles affect to the adsorption and scattering at the molecular, but also atomic level. Absorption and light scattering affect to the change in light intensity, which can be described by the Lambert-Beer law. (Freiser, 1992)

Transmittance values of MFC suspensions were measured using UV/VIS spectrophotometer (Perkin Elmer Lambda 900 UV-visible spectrophotometer). Samples were stirred with a paddle mixer for 10 minutes and shaken for one minute just before the measurement. The measurements were performed within 20 minutes of the preparation of samples. Samples were measured at the concentration of 0.1wt% at wavelengths 200-800nm using 1nm measurement step.

9.2.4 **Rheological measurement methods**

Rheological properties of microfibrillated cellulose water suspensions and hydrocolloids were measured with Anton Paar MCR 302 dynamic rotational rheometer, using the RheoPlus software. All measurements were performed using concentric cylinder geometry, CC27, with bob and cup diameters 26.66 and 28.92 mm. The concentric cylinder geometry was chosen based on preliminary tests. Also the heterogeneous suspension structure and tendency to flocculate during measurements were taken into account. Coaxial cylinder measuring system used in this study is presented in Figure 15.

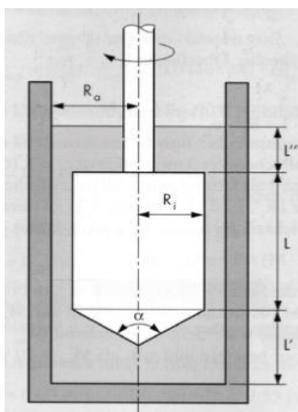


Figure 15. The schematic of cylindrical geometry CC27. (Saarinen et al., 2009)

The sample volume used for each measurement was 19.4 ml and all measurements were performed at 25°C unless otherwise indicated. The temperature was maintained constant at $25 \pm 0.1^\circ\text{C}$ during the measurements. Measuring vessel was heated for higher temperatures by using integrated water bath. To eliminate the effect of loading and immediate time dependence, the samples were allowed to rest in the geometry before measurements. After the spindle was immersed in the sample and thermal equilibrium was reached the waiting time of five minutes started.

All the baseline measurements were carried out at the concentration of 0.5wt %. The used fiber suspension concentration was chosen based on the preliminary tests. Because of the diversity of studied samples the concentration was selected so that all the suspensions could be measured with the cylindrical geometry to guarantee the comparability of results. Moreover, the effects of gap setting and flocculated suspension structure are smaller. Also with dilute suspensions there are no trapped air bubbles to induce unwanted variance into measurements.

9.2.5 Rotational measurements

The flow behavior and viscosity of suspensions were investigated with shear controlled rotational measurements. The measurements were carried out at low shear rates from 0.01 to 1000 s^{-1} . In rotational measurements there was used logarithmic profile with the slope of five points per decade. Measurement point duration decreased logarithmically from 50 to 5 seconds.

9.2.6 Oscillation measurements

Viscoelastic behavior of suspensions was studied with oscillatory measurements. Oscillation measurements use the technique where a sinusoidal strain is applied. In this work amplitude and frequency sweeps were performed for structural characterization of suspensions. Amplitude sweep was used to define linear viscoelastic range of samples and thereby the right strain for frequency sweeps. It is important to continuously excite the sample, but not exceed a strain large enough to destroy the structure. The amplitude sweep was measured from the strain 0.01 to 1000% with angular frequency of 10 rad/s. In order to facilitate the interpretation of the results, the LVE ranges are studied at the range of 0.01- 100%. The Frequency sweeps were performed in the linear viscoelastic region with angular frequency from 100 to 0.01 rad/s, using 1% constant strain. The used strain was selected based on the length of LVE ranges, so that the samples wouldn't be overstrained and the elastic structure destroyed because of too high strain.

9.2.7 Temperature sweep

Temperature dependency of suspensions was measured with shear and temperature controlled rotational test. The measurement was performed from 5 to 60 °C with constant shear rate of 10 s^{-1} . The measurement consisted of 12 measuring points with point duration of five minutes. The samples were taken straight from the cold room (7°C) to avoid temperature variations before the measurement.

9.2.8 Concentration and electrolyte addition measurements

Viscosities of MFC suspensions were studied as a function of concentration and with three electrolyte concentrations. The same measurement parameters were used with basic viscosity measurements in order to find out how the MFC or the polymer concentration and the addition of electrolytes were affecting on flow behavior of studied samples. The effects of MFC or electrolyte concentration on rheological behavior were studied at 0.1, 0.25, 0.5 and 1.0wt %.

The samples for electrolyte measurements were prepared with dilution of 2wt % suspensions and 1M electrolyte solutions were added before mixing the samples. The additions of electrolytes were carried out in hydrated state and before mixing, to ensure salt

spreading evenly in the suspension. The effects of electrolytes on the stability of the suspensions were studied with sodium chloride (NaCl) and calcium chloride (CaCl₂) at the concentrations of 0.5mM, 1mM and 10mM. In this way an insight into colloidal stability of the suspensions at different electrolyte concentration could be achieved.

10 RESULTS AND DISCUSSION

In this chapter the results of studies conducted in the experimental part are presented and discussed. Firstly, in this section data from different analyses have been reviewed and the effects and the importance of these properties on rheological behavior have been considered. Then, the results of rheological characterization are explored and discussed. Finally, the effect of concentration, temperature and electrolytes were studied.

10.1 Optical microscopy and visual comparison

The original microfibrillated cellulose suspensions were analyzed with an optical light microscope in order to visualize the internal structure of MFC samples. The internal structure is identified with fiber features and describes the fiber network of MFC suspensions, which helps to understand the factors behind certain rheological properties. The properties of interest were the size, degree of fibrillation and uniformity of residual fiber fragments in suspensions. The differences between native and anionic grades after the fibrillation were studied. Especially, the amount of the residual damaged fibers can be compared. The microscope images of MFC suspensions at 4× and 10× magnification are presented in Figure 16.

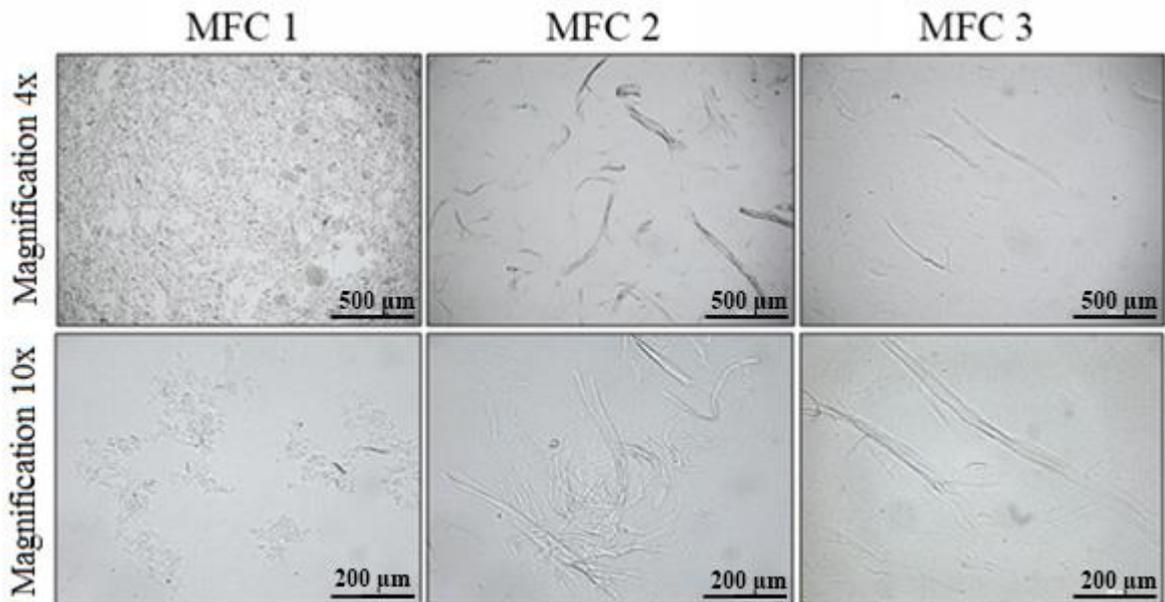


Figure 16. Optical light microscope images of MFC suspensions at a concentration of 2%

From the micrographs a clear difference between native and anionic grades can be seen. There is considerably more non-fibrillated material detected with MFC 1 than seen for the anionic MFC grades. With anionic MFC grades there are only few bigger fiber fragments seen in the micrographs, since the nanoscale material is not detected under the microscope. This confirms that anionic MFC suspensions fibrillate easier and have a higher level of fibrillation under these fibrillation conditions. From the images it can also be observed that native MFC has more homogeneous macrostructure than the anionic grades which have quite big difference between the sizes of fibrils. The homogenous fiber structure indicates that the manufacturing process has been more uniform with MFC 1. However, the anionic grades are showing great results of fibrillation. Higher degree of fibrillation with anionic MFC suspensions can be indicated by an increase in the transparencies of material as a result of invisible nanoscale fibrils. With MFC 2 and MFC 3 also most of the fibers and fiber fragments seen in the micrographs were transparent. Also fiber walls are partially or fully delaminated which indicates that the fibrillation was not superficial, but rather the entire fibers were fibrillated properly. (Dimic-Misic et al., 2013; Sim et al., 2014). Whereas with MFC 1 the fibrillation stage was lower and dark fibrils were actually detected, which indicates that the material is not as transparent and gel-like as anionic MFC samples.

The physical appearances of MFC samples are shown in Figure 17. With digital images of original suspensions the external structure can be studied. Particularly the gel-like properties and transparency of MFC grades are visually evaluated. As can be seen, native suspension differs by its physical characteristics from anionic grades. It can be clearly detected that MFC 1 is a white suspension with weak gel-like characteristics, whereas MFC 2 and 3 are more transparent and strongly gel-like materials. Especially, MFC 3 is a quite transparent and exhibiting strong semi-solid properties.

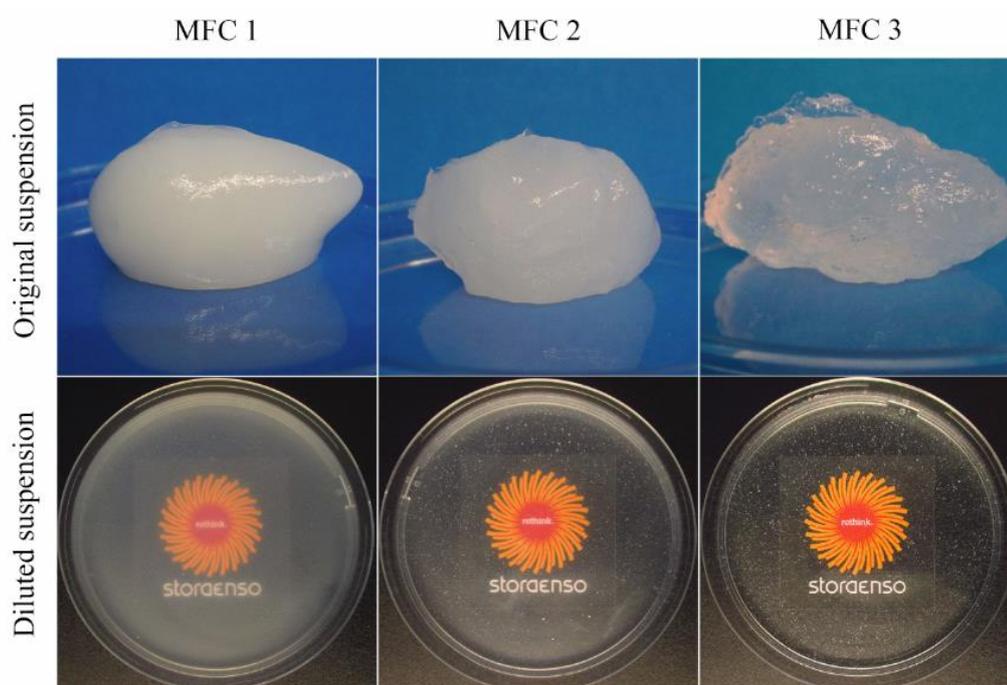


Figure 17. Images of original (2wt %) and diluted (0.2wt %) suspensions of MFC.

From the digital images made on diluted MFC suspensions, the differences between transparency and volume of aggregated structures can be detected. MFC 1 is clearly more turbid than the other two MFC samples. This can be explained by the nature of native MFC suspension, thus this sample is more prone to the form larger fibril aggregates than charged suspensions, whereas large aggregates and residual fiber fragments scatter more light, which results in more turbid suspension. This result can be expected as the anionic fibers have repulsion forces that prevent flocculation. The flocculation shows as fibril agglomerations in diluted suspension while the anionic grades are smooth and clear, only tiny air bubbles are trapped in gel-like suspensions.

10.2 Zeta potential measurements

The electrokinetic mobility of MFC suspensions, presented here as zeta potential measurements were measured in order to evaluate colloidal stability of MFC suspensions. The results of zeta potential measurements are presented in Figure 18. Results show that higher zeta potential values were detected with anionic MFC grades, which means a higher electrokinetic mobility is achieved due to higher anionic charge and obviously less hydrodynamic resistance.

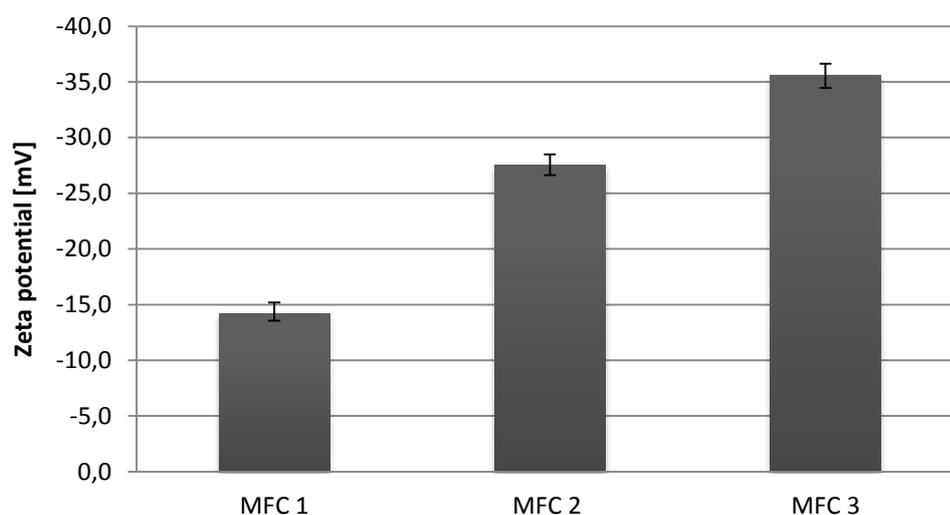


Figure 18. Zeta potential values of MFC aqueous suspensions at the concentration of 0.1wt %

It can be concluded from the results that all of the MFC suspension are negatively charged and the magnitude of zeta potential is increasing as a function of DS. The stronger the anionic charge of microfibrils, the higher the Zeta potential value is. The native MFC has the lowest zeta potential (-14.2 mV) whereas chemically pre-treated MFC grades have higher anionic charges. With lower DS, MFC 2 suspension has a weaker zeta potential (-27.5 mV) than MFC 3 (-35.6 mV) having higher DS. The lower zeta potential value of native MFC grade indicates a weaker electrostatic colloidal stability of suspension. With MFC 3 the suspension's electrokinetic mobility is a high enough to give mutual repulsion, which leads to good colloidal stability.

10.3 Transmittance measurements

Transmittance measurements were carried out to get more accurate picture of transparency of MFC samples. The results of transmittance measurement are presented in Figure 19. The transmittance values are confirmed with the visual evaluation of MFC suspensions. The MFC 1 has lowest transmittance of 52.7%, which was also seen as whitish color and turbidity of suspension. The native MFC is also a coarser grade than anionic MFC suspensions and it is not so well dispersed in water, which partially explains the lower transmittance. However, lower degree of fibrillation and residual fibers detected in the micrographs resulted in increased light scattering reducing the transmitted light (Qing et al., 2013). With anionic grades higher transmittance values are detected as a function of DS. The transmittance for MFC 2 is little bit higher (64.7%) than with native MFC, but not as high as measured for MFC 3 (93.5%). MFC 2 is more gel-like and the suspension is not as white as native grade, but it still exhibits quite high turbidity even though it is well dispersed in water. The MFC 3 has a low absorbance due to high transparency of suspension. When compared anionic suspensions, it can be assumed that the higher transmittance of MFC 3 is a result of high level of fibrillation and more narrow size distribution than with MFC 2 (Qing et al., 2013).

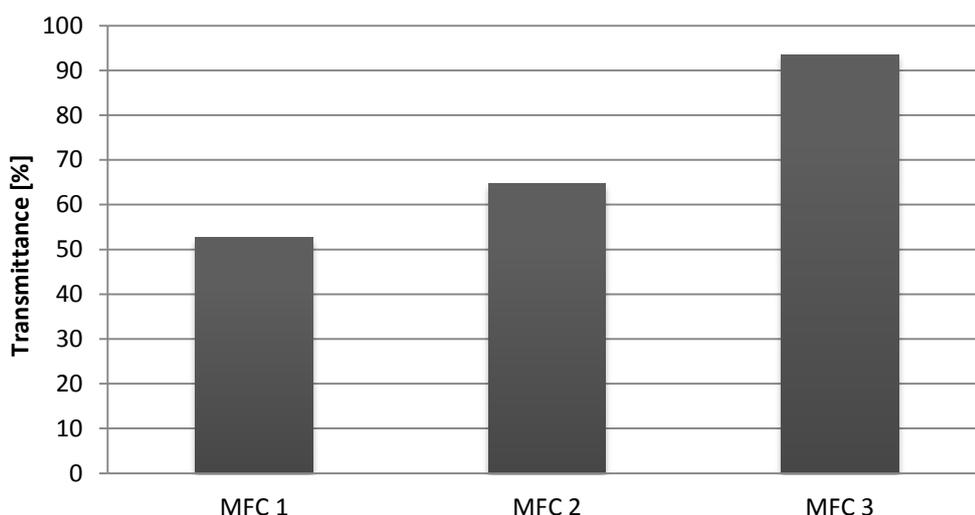


Figure 19. Transmittance results of MFC suspensions at the concentration of 0.1wt % at the wavelength 800nm

10.4 Rheological flow properties

In this chapter the results of rotational tests and the flow behavior of suspensions are presented. The viscosity values and flow curves are measured with the rotational tests as a function of shear rate from 0.01 to 1000%. At low shear rates suspension's flow behavior at the start of the structure's deformation can be studied whereas flow properties at high shear rates are beneficial in manufacturing processes and different applications, such as mixing, coating, spraying and rubbing, where high stresses are applied. The results of flow behavior are reviewed in two groups; MFC suspensions and commercial hydrocolloids.

10.4.1 Viscosity curves

The viscosities of studied aqueous MFC suspensions were measured with low shear rate rotational measurement. In Figures 20 and 21 shows the viscosity curves for 0.5% suspensions. The results reveal that all the studied materials are showing shear-thinning behavior at some level, which correlates with findings in the previous studies (Karppinen, 2014; Tipvarakarnkoon & Senge, 2008). MFC suspensions and xanthan gum are strongly pseudoplastic materials where viscosity is drastically decreasing as a function of increased shear rate. Whereas NaCMC and guar gum are considerable less shear-thinning materials which means that the decrease in viscosity over the applied stress is lower. At very low shear rates NaCMC and guar gum solutions are approaching Newtonian flow behavior and a short Newtonian plateau can be detected between the shear rates 0.01 to 0.1 %.

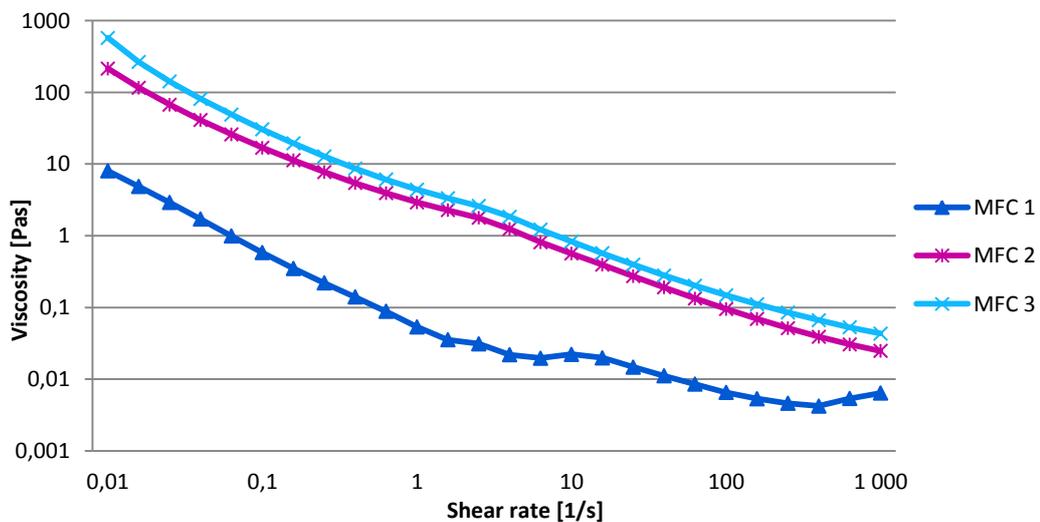


Figure 20. Viscosity curves for MFC suspensions at concentration of 0.5wt %

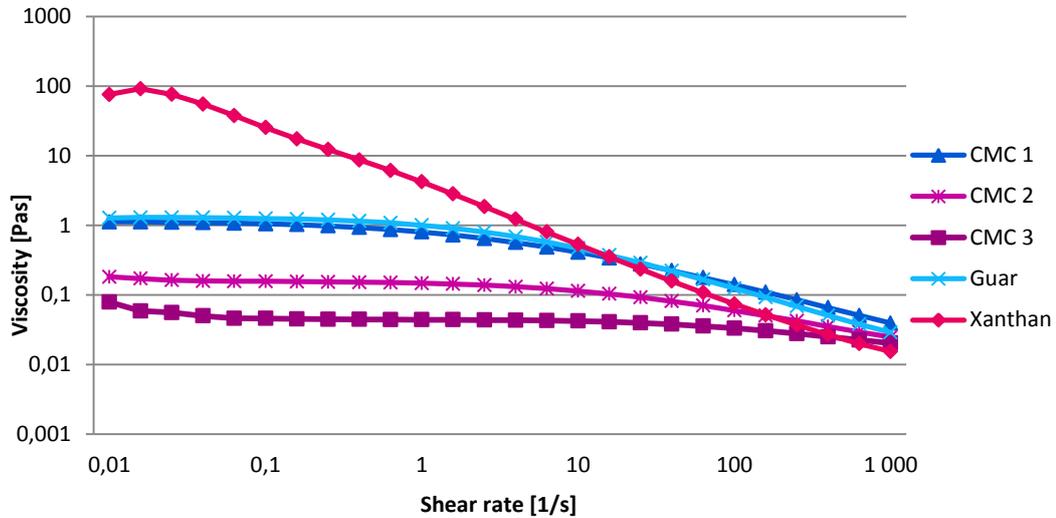


Figure 21. Viscosity curves for commercial hydrocolloids at concentration of 0.5wt %

Anionic MFC suspensions have the highest viscosity values at the start of the test, i.e. at low shear rates, where the internal network structure is not interrupted and still able to resist the shear forces. With increasing shear rate, the three dimensional network of microfibrillated cellulose suspensions will slowly rupture. At first, it is expected that the MFC network will degrade to chain-like floc formations, and then at higher shear rates to individual flocs. The disentangled fibrils are more or less aligned with the flow direction, which reduces the flow resistance. (Sorvari et al., 2013) This is causing the loss of viscosity as a function of increasing shear rate. The bigger the gradient of the viscosity curve is, the faster the network structure of suspension is falling apart.

From Figure 20 it can be detected that the flow behavior of MFC suspensions were nonlinear and viscosity is decreasing quite drastically as a function of shear rate. Thus, the studied MFC suspensions showed strong shear-thinning behavior, as reported in earlier studies (Pääkkö et al., 2007; Iotti et al., 2011). Nonlinear behavior indicates that structural deformation of three dimensional fiber network is uneven in measured shear rate range. Observed structural changes in MFC suspensions were similar with findings reported by Saarikoski et al. (2012). Since, anionic MFC grades are exhibiting stronger shear thinning behavior than native MFC suspension the difference between the viscosities are gradually decreasing as a function of shear rate. However, despite of this the anionic MFC grades are maintaining a higher viscosity throughout the measurement region.

For all MFC samples, three different shear-thinning regions can be identified. Transition region, i.e. a small plateau in the flow curve, could be detected at shear rates from 1 to 20 $\%$. At low shear rates the structure of suspension is adapting to changes, but the floc network is still relatively intact so the viscosity is high. At intermediate shear rates, the increasing shear rate may also increase the collision between the fibrils and flocs which is causing formation of new contacts and thus seen as transition peak in the flow curves. However, with anionic grades the increase in viscosity is not as prominent as native MFC grade. After the transition phase the fibrils are flowing as separate small flocs which do not resist the flow as much as flocculated network structure. For the native MFC grade a second transition region in the viscosity curve was detected at shear rate above 500 $\%$. This high shear rate can disperse and slightly fibrillate or disintegrate flocs so that the fibrils expand and are occupying more volume, which can cause the dilatant behavior momentarily.

As shown in Fig. 21, xanthan gave a very high viscous solution at 0.5wt % and a slight increase in the low-shear range can be detected. This transient viscosity peak is indication of too short measurement point duration, which means the whole suspension is not yet flowing in the time given with slowest shear rates (Mezger, 2011). On the contrary NaCMC grades and guar gum are not so highly viscous solutions, which have plateau value of zero-shear viscosity. Actually oil-grade CMC (1) and guar were exhibiting very similar flow behavior and there is crossover point detected when shear rate exceeds 40 $\%$. Differences between NaCMC solutions are related to the molecular weight and degree of substitution. CMC 1, with the longer molecule chains and higher DS, has higher viscosity. Because it's long chains tend to orient in the direction of flow solution exhibit more pseudoplastic character than CMC 2 or especially CMC 3 which are only slightly shear-thinning materials. In order to compare the flow behavior of studied materials the viscosity values at different shear rates and characteristics of flow profiles are assembled and presented in Table VIII.

Table VIII. Characteristics of flow behavior of studied samples at the concentration of 0.5%

SAMPLE	Viscosity [Pas] shear rate 1 1/s	Viscosity [Pas] shear rate 100 1/s	Flow characteristics
MFC 1	0,52	0,01	Shear-thinning, two plateaus
MFC 2	2,95	0,10	Strongly shear-thinning, one plateau
MFC 3	4,48	0,15	Strongly shear-thinning, one plateau
CMC 1	0,80	0,14	Shear-thinning, zero-shear plateau
CMC 2	0,15	0,06	Slightly shear-thinning, long zero-shear viscosity plateau
CMC 3	0,04	0,03	Slightly shear-thinning, long zero-shear viscosity plateau
GUAR	1,01	0,13	Shear-thinning, short zero-shear viscosity plateau
XANTHAN	4,22	0,07	Very strongly shear-thinning, linear flow profile

10.4.2 Apparent yield stress

The shear stress as a function of shear rate was measured to study the strength of the fiber network (fiber-interlocking) by identifying the possible yield points. Figures 22 and 23 are shows shear stress as function of shear rate at the concentration of 0.5wt%. The flow properties of MFC suspensions differ considerable from commercial solutions. It can be detected that NaCMC and guar gum solutions do not have a clear yield point but rather exhibit liquid like behavior. These suspensions are flowing from the start of the measurement without indication of yield stress. Particularly the flow behavior of CMC 2 and CMC 3 were approaching linear Newtonian flow. Also the native MFC suspension has no significant yield stress, whereas anionic MFC suspensions have quite high yield values. Besides the anionic MFC suspensions also xanthan exhibited a clear apparent yield stress, unlike other studied hydrocolloids.

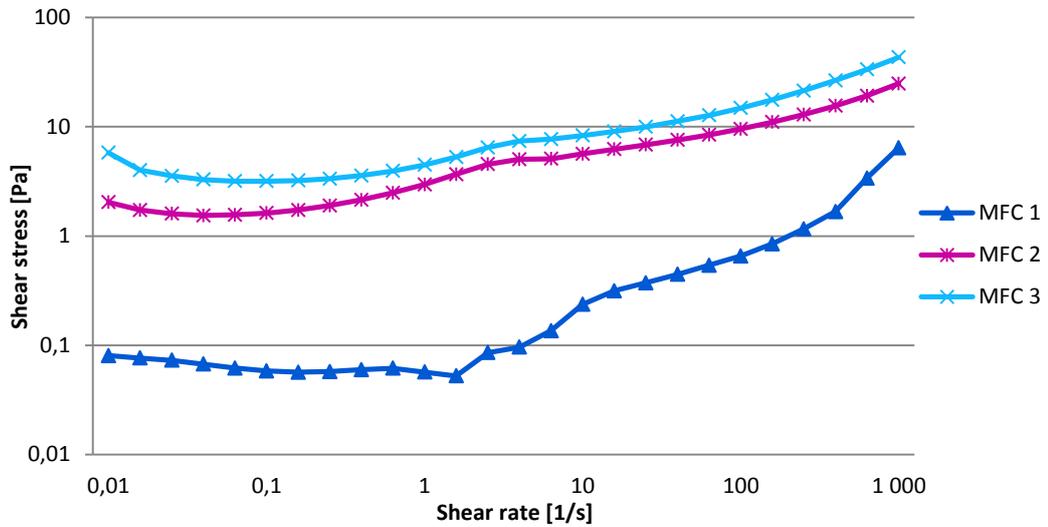


Figure 22. Flow behavior curves of MFC suspensions at concentration of 0.5 wt %

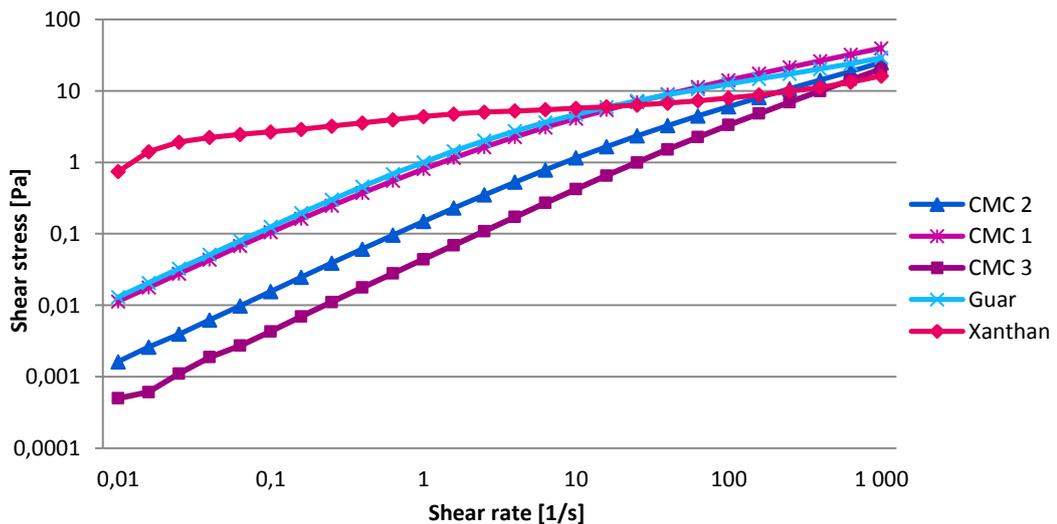


Figure 23. Flow behavior curves of commercial polysaccharide solutions at 0.5wt % concentration

The determined yield stress values are presented in Table IX. A clear difference can be detected between stress values of MFC suspensions and hydrocolloids. Thus the yield stresses are complying with the viscosity results; anionic MFC grades and xanthan gum exhibited the highest yield points. However, even the difference between anionic MFC grades was quite significant, since the yield stress of MFC 3 (5.78 Pa) is over two times higher than with MFC 2 (2.04 Pa). This indicates that MFC 3 is already exhibiting viscoelastic solid properties to some extent at the concentration of 0.5wt %. The high yield stress values are also indicating that anionic MFC suspensions together with xanthan solution have more stable and stronger internal suspension structure than other studied samples. The samples with higher yield points will resist more stress and so the force

needed to interfere with suspension structure is considerably bigger than with samples, which have yield stress value near zero.

Table IX. From the flow curves determined yield stress values for studied materials at the concentration of 0.5wt %

SAMPLE	YIELD STRESS [Pa]
MFC 1	0,08
MFC 2	2,04
MFC 3	5,78
CMC 1	0,01
CMC 2	0
CMC 3	0
GUAR	0,01
XANTHAN	0,77

10.5 Viscoelastic properties

In order to evaluate the gel-like characteristics of studied materials each suspension was measured using dynamic mechanical analysis (DMA). The viscoelasticity determination was conducted with amplitude and frequency sweeps. These DMA tests were carried out in the stress range, where material is continuously stressed, while sample structure is maintained undisturbed. With oscillatory tests the elastic properties such as deformation behavior and stability were examined. The LVE ranges of different materials were measured with amplitude sweep to ensure that the structure of samples is intact. To evaluate gel strength of samples the storage and loss modulus of suspensions were measured with frequency sweeps in the determined LVE range. The viscoelastic properties of CMC 3 weren't studied due to its strong liquid like structure. It would only represent irregularities at chosen measuring range, which was selected to be appropriate for the more viscoelastic studied materials.

10.5.1 Amplitude sweep

The oscillation tests started with the amplitude sweep, which was performed to determine the linear viscoelastic region of materials. The results of amplitude sweeps are presented in Figures 24 and 25. In the linear viscoelastic range both the G' - and G'' -curve are displaying constant plateau values with different levels. With MFC samples and xanthan

gum the elastic behavior is dominating the viscous one ($G' > G''$) which is indication of gel-like consistency in the low-shear range. NaCMC samples and guar are exhibiting fluid characteristics, where viscous behavior dominates the elastic one.

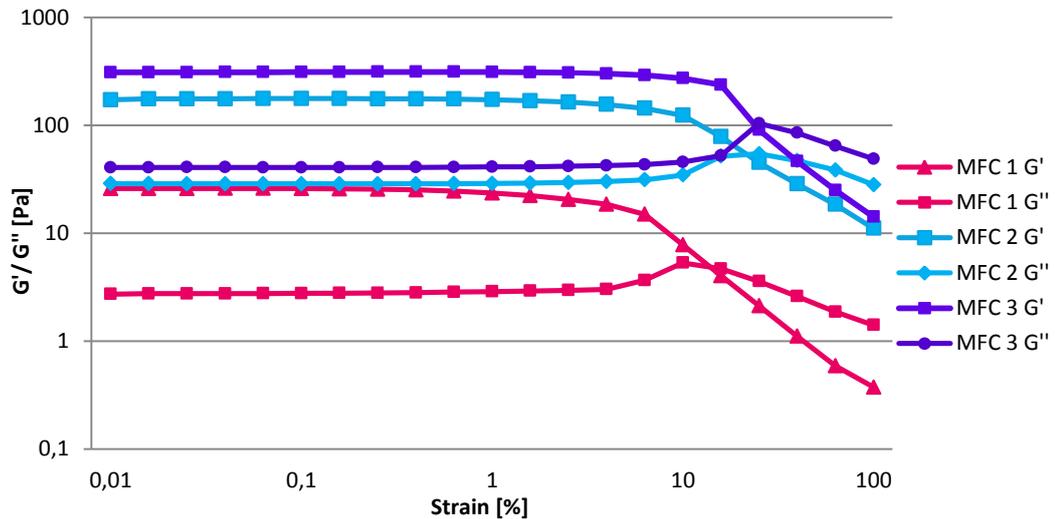


Figure 24. The storage (G') and loss (G'') modulus at 10 rad/s for MFC suspensions as a function of the applied strain at the concentration of 0.5wt %

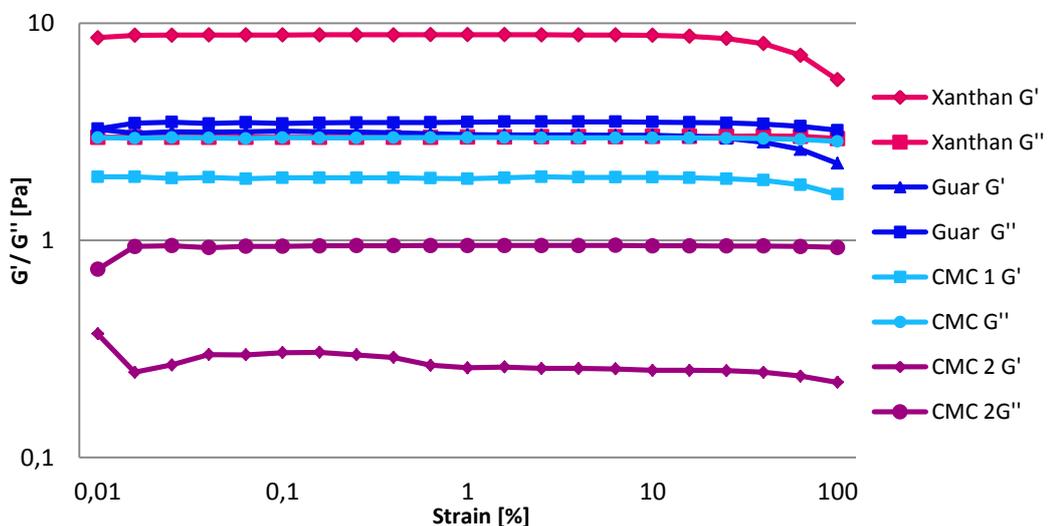


Figure 25. The storage (G') and loss (G'') modulus at 10 rad/s for commercial polymers suspensions as a function of the applied strain at the concentration 0.5wt %

The amplitude sweeps show that anionic MFC grades have longer linear viscolastic (LVE) range than native MFC grade, which indicates that anionic suspensions have more stable internal structure. When the critical strain amplitude is exceeded and the value of storage modulus begin to decrease this is interpreted as a break-down point of network structure.

The breakdown point of structure occurred earlier with native MFC, meaning that less stress is needed to disturb the structure and it will break down more easily. At the crossover point ($G' = G''$) the gel-like character changes to fluid like and MFC samples are flowing as whole.

In the case of NaCMC and guar, where $G'' > G'$, suspensions are flowing in the entire measuring range. Comparison of MFC suspensions shows that anionic MFC grades are also showing stronger gel character than native grade. For the commercial hydrocolloid products, xanthan exhibit very high elastic response to the applied stress. Compared to the commercial hydrocolloids, MFC suspensions are exhibiting stronger viscoelastic properties and more gel-like characteristics at the 0.5% concentration. However xanthan solution has a higher resistance to the applied stress and thereby better suspension stability which is seen as a longer LVE range. In Table X, the loss factor values are presented. Values are calculated based on amplitude sweep results so that the viscoelastic character of suspensions can be described.

Table X. Gel character of studied samples at the concentration of 0.5wt %

SAMPLE	Loss factor [tanδ]	Viscoelastic characteristics
MFC 1	0,27	Viscoelastic solid
MFC 2	0,23	Viscoelastic solid, gel-like
MFC 3	0,21	Viscoelastic solid, gel-like
CMC 1	1,55	Viscoelastic liquid
CMC 2	3,66	Viscoelastic liquid
GUAR	1,14	Viscoelastic liquid
XANTHAN	0,36	Viscoelastic solid, gel-like

With the loss factor values the viscoelastic nature i.e. gel character of studied materials can be compared. The ratio of viscous and elastic portion (G''/G') of the viscoelastic deformation will reveal how strongly material exhibit the gel-like behavior. The samples with loss factor values > 1 are exhibiting viscoelastic liquid behavior whereas suspensions with $\tan\delta < 1$ are showing viscoelastic gel or solid behavior. From the loss factor values, it can be detected that NaCMC samples and guar gum are showing viscoelastic fluid like

characteristics whereas other samples are exhibiting strong viscoelastic gel-like or even semi-solid viscoelastic properties. With guar gum $\tan\delta$ is approaching value one which means that the sample structure is almost at the gel point where viscoelastic behavior is showing 50/50 ratio of the viscous and elastic portions. the gel transition point which means. Because of fluid like nature of NaCMC solutions, they are nicely flowing even when only a little force is applied. However MFC and xanthan gum suspensions have more rigid network structure which needs more stress to get the structure to deform and whole sample to flow.

10.5.2 Frequency sweep

Amplitude sweeps were carried out that the strain used in frequency sweeps could be determined. Based on the results of amplitude sweeps it was decided to use 1% strain for the frequency sweep measurements. The 1% strain is high enough to get valid data even from more structural stable samples like anionic MFC suspensions and xanthan gum. However it is not too high for CMC and guar solutions, which are in this case representing the lower viscosity samples. (Benchabane & Bekkour, 2008) With frequency sweep the stability, viscoelastic nature of the material and time-dependent deformation behavior were investigated. The short-term behavior was observed with rapid motion, where anionic MFC suspensions showed a good stability and gel-like structure while native MFC was expressing dominant viscous behavior at high angular frequencies. However, the long-term behaviors of all three MFC suspensions were indicating stable and gel-like structure over the low motion region. (Mezger, 2011) All MFC suspensions exhibited a higher storage modulus (G') than loss modulus (G''), as shown in Figure 26.

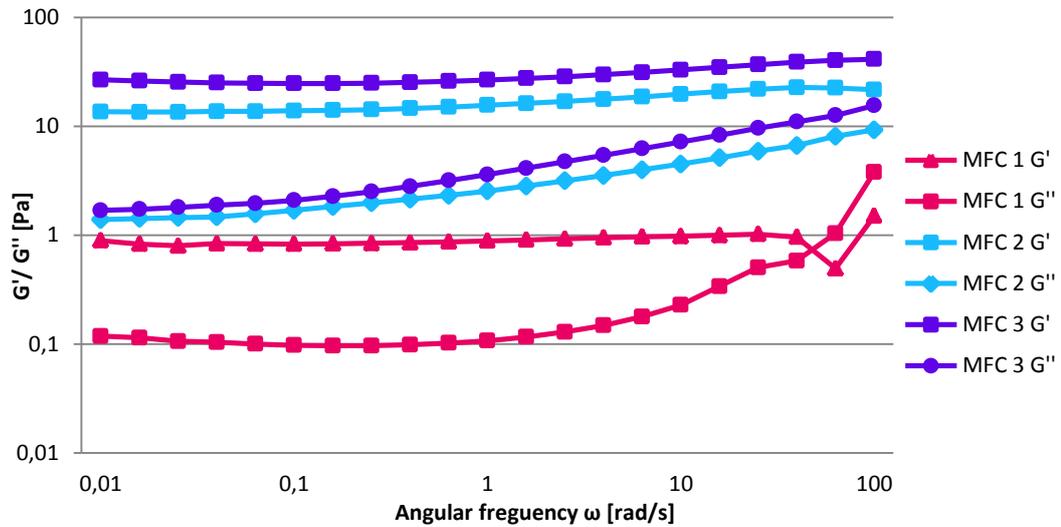


Figure 26. The storage (G') and loss (G'') modulus as a function of the angular frequency for MFC suspensions at the concentration of 0.5wt %.

Since G' and G'' were roughly independent over the entire angular frequency range, which means the systems are gelled and showing little change in viscoelastic characteristics. This indicates that all three MFC suspensions have good physical stability, because the structure is not easily disturbed. However differences in gel strength between native and anionic MFC grades can be detected. Strength of the gel structure is higher with anionic samples which are exhibiting increasing values of G' and G'' towards lower frequencies. Based on the higher values of storage (G') and loss modulus (G''), it can be assumed that anionic MFC suspensions have stronger intra-fibrillar interactions. (Mezger, 2011). Therefore anionic MFC suspensions are displaying better structural strength and rigid structure at gel-like state, whereas native MFC grade has softer viscoelastic structure.

When comparing the structural characteristics of MFC sample and commercial hydrocolloids, the most similar behavior is exhibited by xanthan gum. Xanthan is showing a gel-like structure and it also has quite constant moduli over the wide range of angular frequencies. Therefore, it can be assumed that xanthan is able to form time-independent intermolecular associations and interactions in solutions. Xanthan gum with a high degree of cross-linking is showing strong undisturbed structure at rest, which is indication of good long-term physical stability. Whereas guar gum and both CMC solutions are exhibiting constantly falling values of G' and G'' toward lower angular frequencies, which is typical behavior for unlinked polymers. The frequency sweeps of xanthan gum and other anionic polysaccharides are presented in Figures 27 and 28.

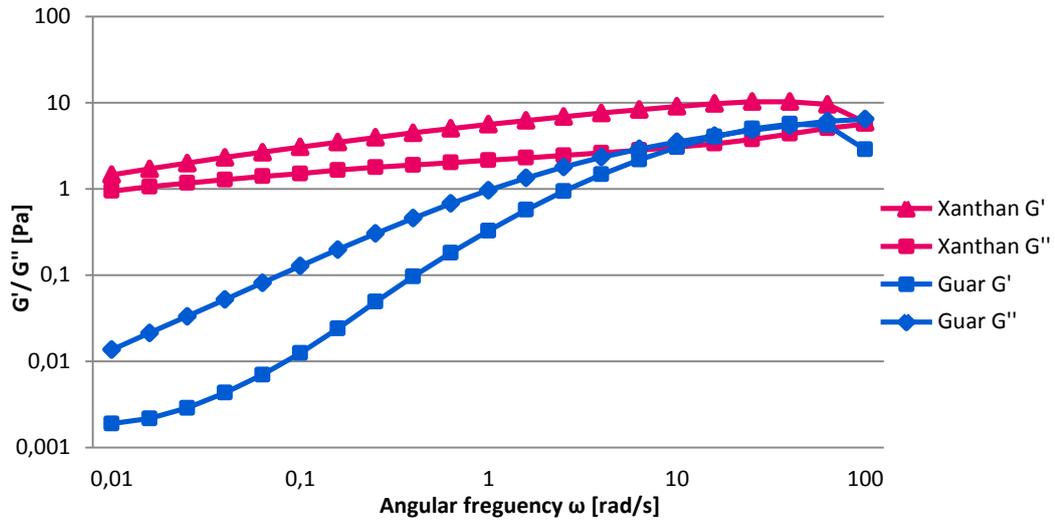


Figure 27. The storage (G') and loss (G'') modulus as a function of the angular frequency for xanthan and guar gum solutions at the concentration of 0.5wt %.

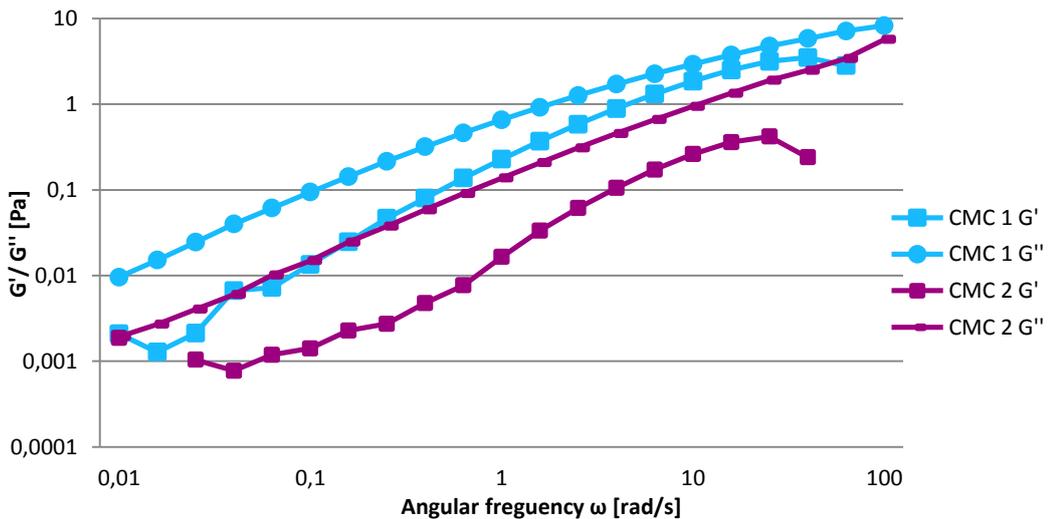


Figure 28. The storage (G') and loss (G'') modulus as a function of the angular frequency for NaCMC solutions at the concentration of 0.5wt %.

The frequency sweeps revealed the structural differences between MFC samples and anionic polymers. Especially, NaCMC grades and guar are quite different from gel-like MFC and xanthan gum. With both NaCMC samples G' and G'' -curves are showing rather deep slope indicating a poor suspension stability as a result of high tendency to phase separation. Also NaCMC grades are exhibiting viscoelastic liquid behavior not gel-like characteristics because the G'' -curve is dominating the storage modulus over the whole frequency range. With liquid like samples, such as CMC 2, at higher angular frequencies some irregularities in the curve can be observed. Frequency sweep is indicating that CMC 2 has little internal network, which can be easily disturbed. CMC 2 is not also exhibiting

elastic structure at higher angular frequencies, which can be caused by overstraining the sample so that the structure is destroyed. These phenomena do not represent real sample characteristics, but are a result of measuring system limitations and limits of sample structure in the measurement range.

The studied guar gum solution showed similar rheological behavior than NaCMC grades. However at the high frequencies guar gum is exhibiting briefly equal G' and G'' - values meaning that sol/gel transition point i.e. structural gel point is momentarily reached at the concentration of 0.5wt %. Otherwise, guar gum is showing purely the liquid like characteristics, which is quite a clear by G'' dominance. In fact, the ratio between G'' and G' is increasing with guar gum and NaCMC solutions, when angular frequency is decreasing. This indicates that viscous like behavior is strengthening and stability of solutions weakened over time.

From the results of the conducted oscillatory tests, the structural stability and gel strength of aqueous suspensions can be ranked as a follow: anionic MFC > xanthan gum > native MFC > guar gum > NaCMC. Based on these results, it can be assumed that MFC samples and xanthan gum are exhibiting semi-solid characteristics whereas guar gum and NaCMC samples exhibit purely high viscous non-Newtonian fluid behavior. Similar findings have been reported by Tipvarakarnkoon & Senge (2008).

10.6 Influence of chemical and physical parameters on rheological behavior

The changes in rheological properties as a function of physical and chemical parameters give an indication of structural stability and material's tolerance under different circumstances. These are important factors to take into account when developing new materials and planning the production and processing conditions. To be able to identify the benefits of MFC as a rheological modifier or structurant few commercial samples were selected as a reference. The viscosity and flow behavior were studied as function of dry matter content, temperature and electrolyte concentrations.

10.6.1 Effect of MFC concentration

The changes in the concentration of MFC affect to the suspension structure and thereby the homogeneity of floc structure and rheological properties of the samples (Karppinen et al., 2012). The influence of MFC concentration on viscosity was studied at three different concentrations (0.25, 0.5 and 1wt- %) and in addition the flow behavior of MFC samples was examined also at 0.1wt % concentration. The ratio between viscosity and concentration was investigated at the shear rate 0.01 s^{-1} , where the fiber network structure is undisturbed and still intact. The viscosity values of MFC suspensions and three commercial hydrocolloids as a function of concentration are presented in Fig. 29.

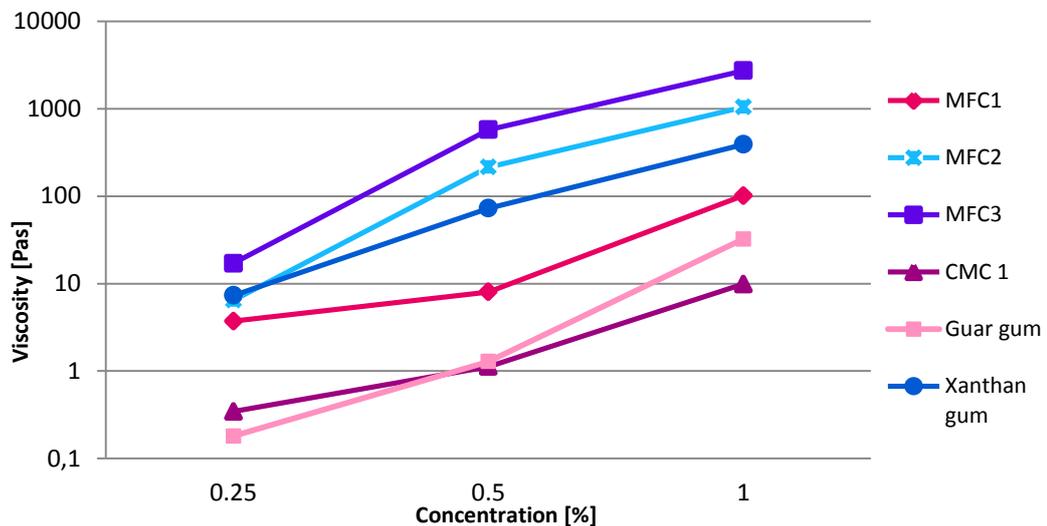
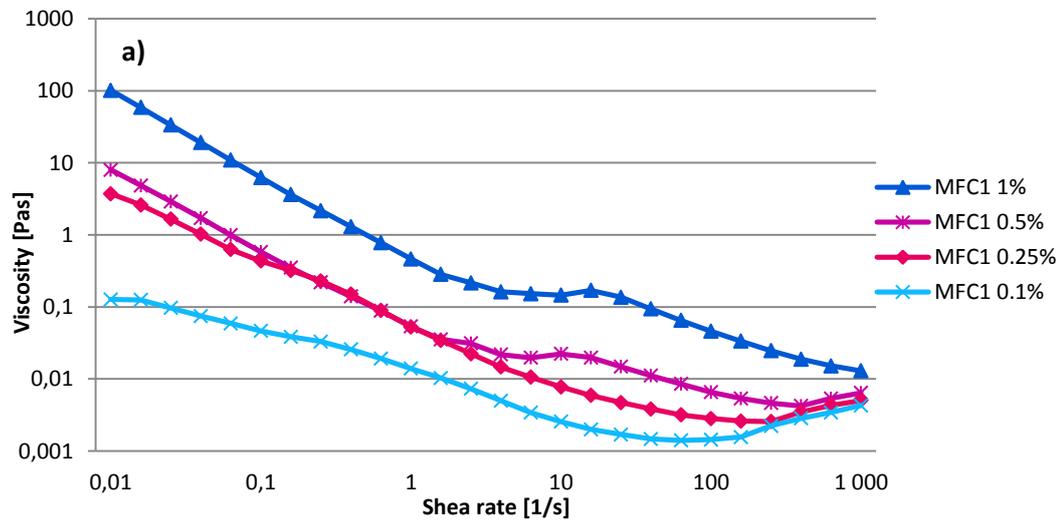


Figure 29. The viscosity as a function of concentration at the shear rate 0.01 s^{-1}

It can be detected from the results, that the measured viscosity is highly dependent on the concentration of the suspensions. The commercial hydrocolloids exhibited a quite linear dependence between viscosity and concentration. Particularly, with xanthan gum the linear correlation between viscosity and concentration can be seen; the viscosity is approximately ten times bigger when dry matter content is doubled. As can be observed from Fig. 29, MFC samples have not so straightforward ratio between viscosity and concentration as a reference material used polymeric hydrocolloids. The difference in viscosity increase can be explained by the structural difference of samples. As reference materials used hydrocolloids are polymers with certain homogeneous structure, whereas MFC suspensions are fibrous materials where size distribution affects to the forming of three dimensional network structure.

It can also be seen, that anionic MFC grades and guar gum have significantly higher increase in viscosity over the whole concentration range, when compared to other samples. When concentration was quadrupled (0.25wt % to 1.0wt %) the viscosity of guar gum increased 180 times as big and with anionic MFC grades the corresponding figure was roughly 160. Whereas with CMC and native MFC the viscosity was 30-fold and with xanthan 50-fold, when compared to starting value at 0.25wt % concentration. With the native MFC grade, the viscosity increase is not that significant at lower concentrations. However, when dry matter content is crossed 0.5wt %, the viscosity level is increasing much more. With anionic grades the effect is the opposite, the strong gel-like characteristics is obvious at low concentrations and after 0.5wt %, the viscosity growth slows down. Eventually, the critical dry matter content is reached, where the viscosity growth is not anymore so remarkable that the concentration should be raised.

With MFC samples, the viscosity as a function of shear rate in different concentrations was studied in more detail. The viscosity curves were measured with all four concentrations to investigate the changes in the flow properties. The viscosities of MFC suspensions at different concentrations are shown in Fig. 30a, b, c, respectively.



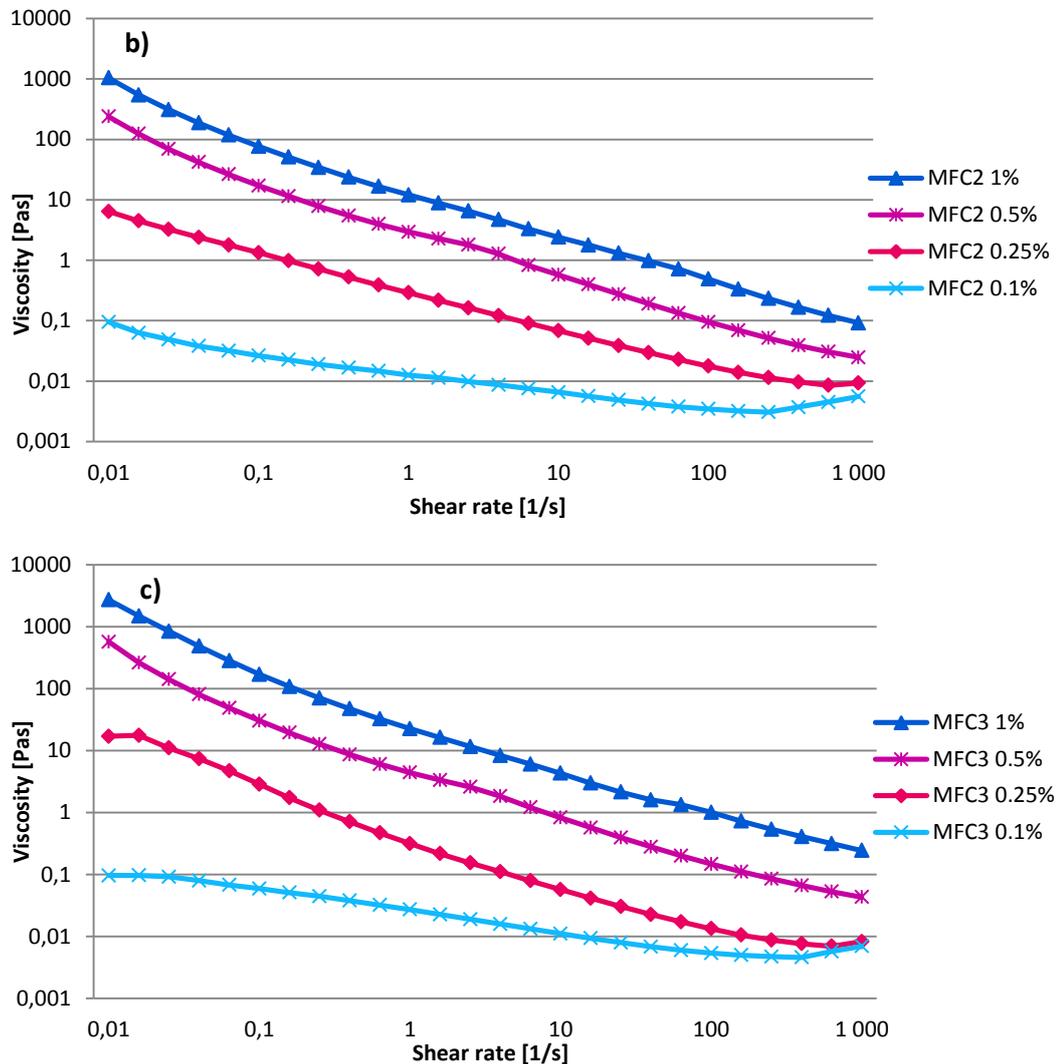


Figure 30. Viscosity versus shear rate dependence for **a)** MFC 1, **b)** MFC 2 and **c)** MFC 3 suspensions at different concentrations

With the lower dry matter contents, more irregular flow behavior especially with native MFC could be detected. At higher concentrations, MFC suspensions exhibited more steady flow, which is expected due to homogeneous structure of samples. At lower concentrations the instability of MFC suspensions is increased, because of weaker and uneven network structure. Therefore, more irregularities can be observed especially with the native MFC grade. The occurring transition regions, i.e. instabilities, can be seen as increase in viscosity between shear rates 10 to 100% and over 200 %. The irregularities observed at flow curves can be explained by changes in floc structure, however at higher shear rates the increased viscosity can also be caused by turbulent vortexes (Karppinen et al., 2012). While native MFC exhibits quite instable flow curves at lower concentrations, anionic

MFC grades, with high anionicity and strong three dimensional network are quite structural stable even at the concentration of 0.1wt %.

10.6.2 Effect of temperature

Temperature sweep was carried out to investigate the viscosity behavior as a function of increasing temperature. The influence of temperature on viscosity behavior was investigated between 5 to 60°C at the shear rate of 10 %. The results of temperature sweep are presented in Figure 31.

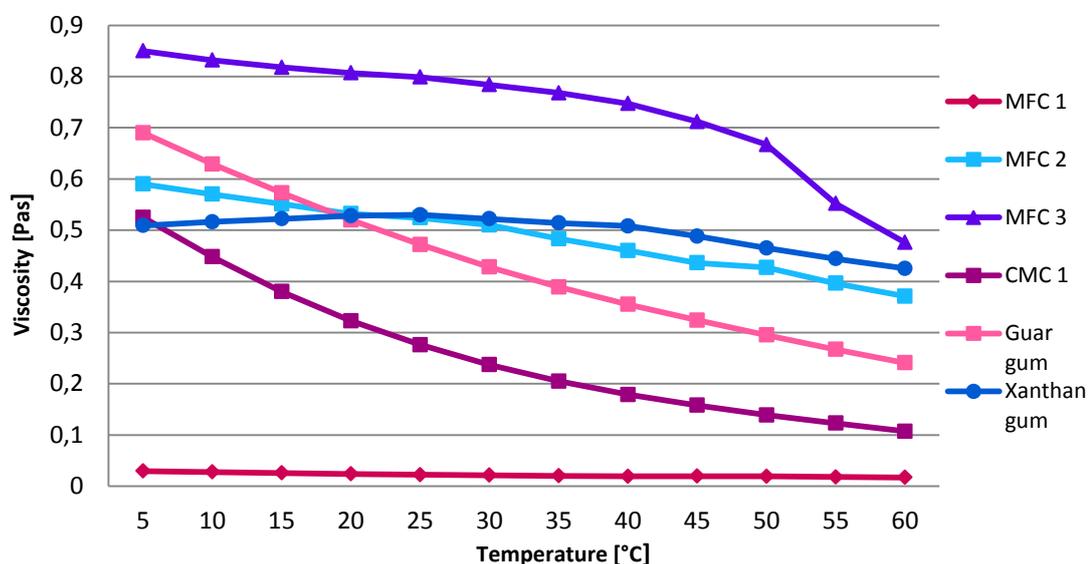


Figure 31. Viscosity as a function of temperature at shear rate 10 s^{-1} at the concentration of 0.5wt %

Figure 31 reveal a clear difference between the temperature stability of studied samples. The MFC suspensions and xanthan gum have quite good temperature stability over the studied temperature region, whereas NaCMC and guar gum were immediately affected, when increasing temperature. With NaCMC and guar gum the viscosity decreased evenly over the temperature range, whereas with MFC 1, there is not detected significant decrease in viscosity. When comparing the anionic MFC samples, it can be observed that MFC 2 maintains its viscosity level better than more gel-like MFC 3. With MFC 3 at some point of the measurement the viscosity starts to drop more drastically which indicates that gel structure begins to break down when a high enough temperature is reached. With MFC 2 the viscosity starts to slowly decrease gradually after the 35°C is exceeded whereas MFC 3 is a little more resistant at low temperatures. However the viscosity drop is more drastic once the structure starts to break when critical temperature point of 45°C is exceeded.

From the studied materials xanthan gum maintain its viscosity level the best over the measured temperature range. Moreover there can be detected a little increase in viscosity between 20 to 35°C where the gel-like structure is its strongest.

The effect of temperature on viscosity levels is also presented in bar chart in Figure 32 to clarify the differences between viscosities at different temperatures. The viscosity values are presented for three different temperatures (10°C, 30°C and 60°C). From the viscosity values can be detected that MFC samples have good thermal stability up to 30°C whereas samples like NaCMC has a weaker resistance and the viscosity is already reduced by half when 30°C is reached. All three MFC suspensions have relative small viscosity changes over the measured temperature range which is an indication of good structural and thermal stability.

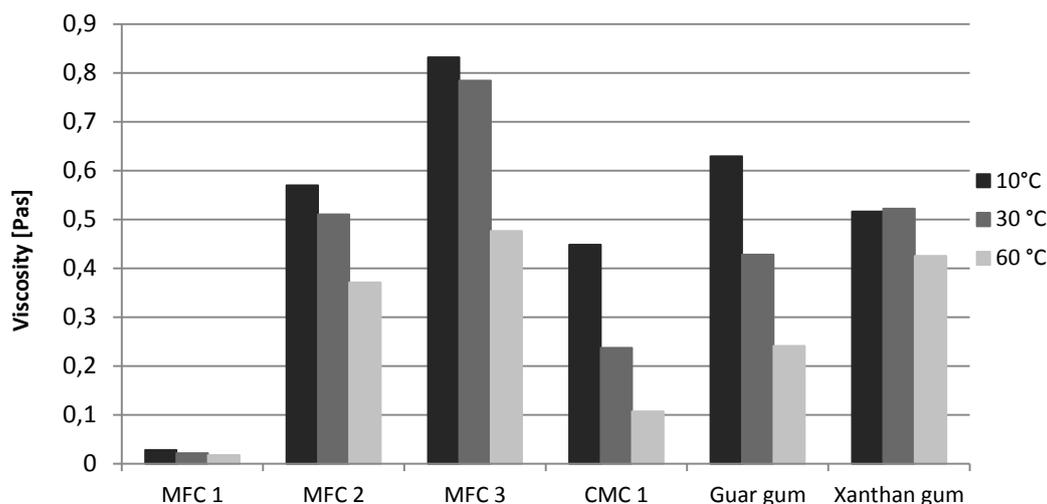


Figure 32. Dependence of the viscosity on the temperature for 0.5 wt % aqueous suspensions at 10°C, 30°C and 60°C with the shear rate 10 s^{-1}

10.6.3 Effect of electrolytes

Various electrolytes, such as Na^+ , Cl^- and Ca^{2+} , are part of various products used in daily life. This sets certain requirements for the materials used in applications where salts or electrolytes are present. The measurements with electrolytes were carried out in order to investigate their influence on the viscosity and tendency to form larger aggregates. To study the effects of salts on the rheological behavior of MFC suspensions, different amount of sodium chloride (NaCl) and calcium chloride (CaCl_2) were added to the aqueous suspensions. The viscosity values as a function of electrolyte concentrations are presented

in Fig. 33 a) and b). The viscosity dependence on electrolyte concentrations were measured at low shear rate of 10 s^{-1} . The effects of salts were illustrated at low motion, because the differences between the viscosity levels are diminishing, when shear rates are high and thus the impact of electrolytes is not detected so clearly.

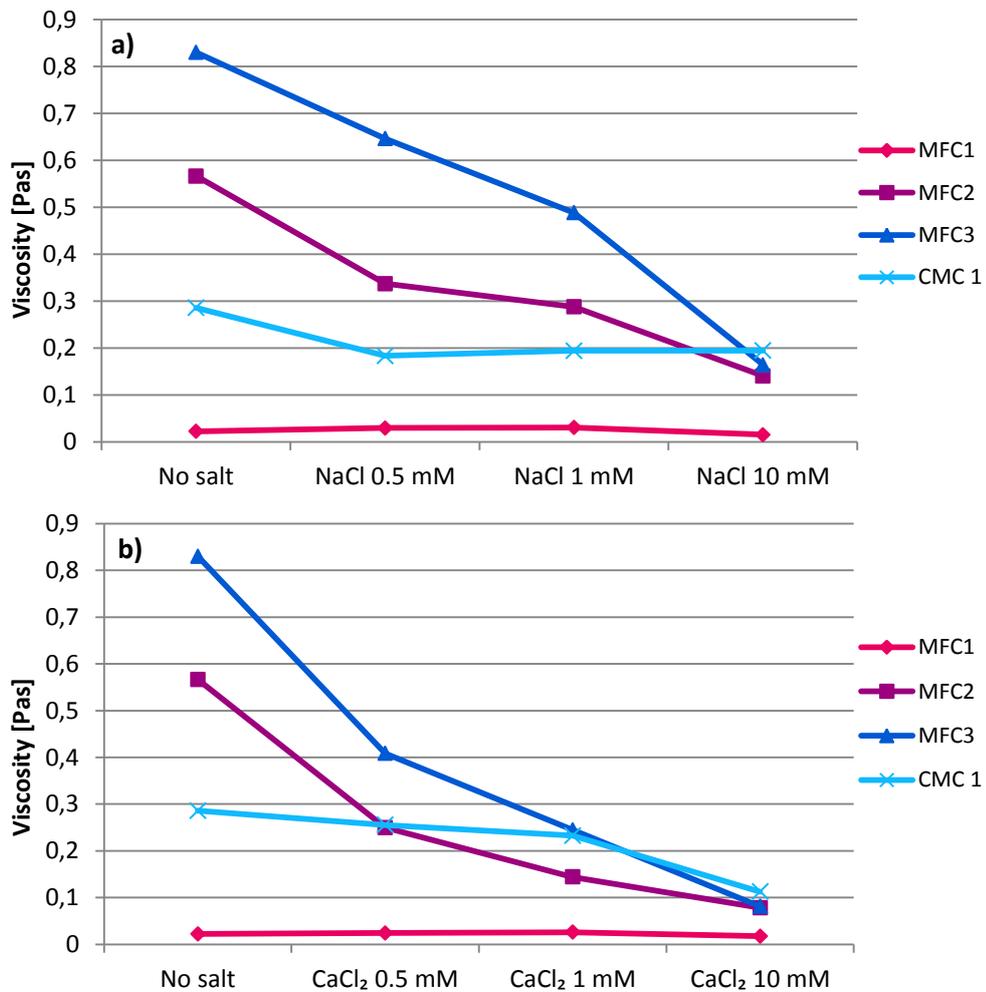


Figure 33. Viscosity dependence on electrolyte concentration of a) NaCl and b) CaCl₂ at 0.5wt % aqueous suspensions at the shear rate 10 s^{-1}

As can be seen in Fig. 33 a) and b), it's clear that native MFC and NaCMC are more resistant to the electrolyte additions than anionic MFC samples. When NaCl is added to these suspensions, the viscosity remains almost constant at measured electrolyte concentration range. On the contrary anionic MFC grades exhibited relatively significant viscosity reduction. With MFC 2 the viscosity decreased to one third and with MFC 3 to quarter of initial values.

When comparing the effects of selected salts it can be clearly observed that divalent CaCl_2 has a stronger effect on the structure of samples, which is seen as more drastic decrease in viscosity. From the results, it can be roughly evaluated that the divalent cation is two times as effective as the monovalent cation, at least with the higher salt concentrations. In particular, the viscosity of anionic MFC grades drops quite significantly even with the lowest, 0.5mM, addition of calcium chloride. The strong influence of divalent CaCl_2 , can be explained by its effect on structure of the suspensions and hydrodynamic properties of fibers. Calcium chloride increases the flocculation tendency, which together with reduced hydrodynamic volume of fibers, decreases the resistance of the flow and thereby viscosity. Also, comparison of anionic MFC suspensions reveals that the addition of electrolytes has slightly greater effect on the viscosity of MFC 3 suspension, which has higher charge and DS than MFC 2. To study the stability and aggregation of MFC suspensions under the influence of electrolytes the flow curves were measured. The flow curves of MFC suspensions in the presence of 10mM NaCl and CaCl_2 are presented in Fig. 34 and 35.

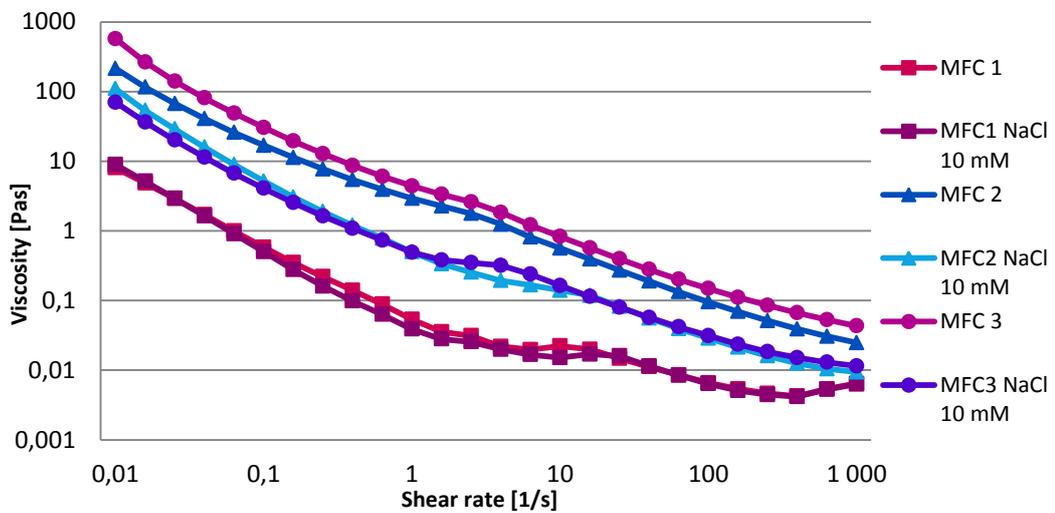


Figure 34. Viscosity versus shear rate dependence for 0.5wt % MFC suspensions at different NaCl concentration

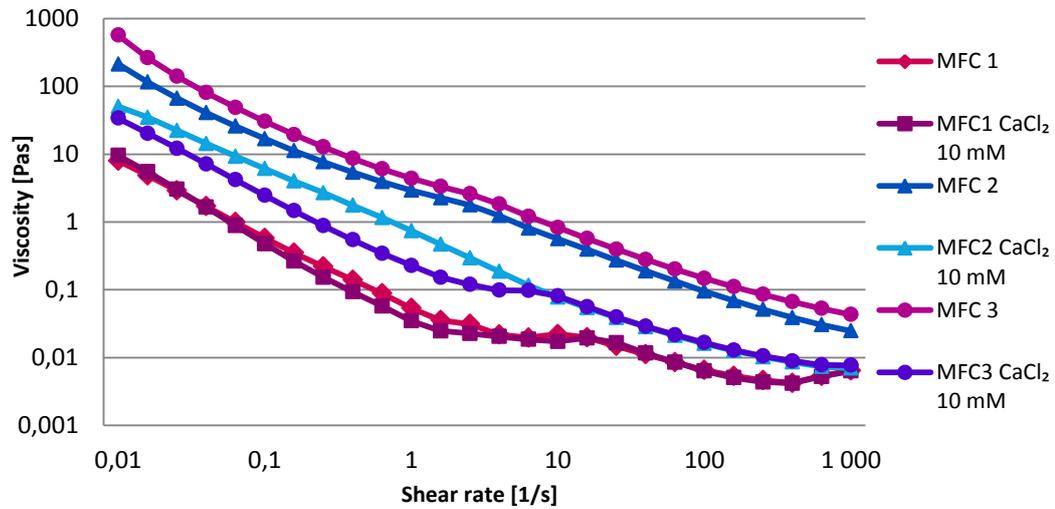


Figure 35. Viscosity versus shear rate dependence for 0.5wt % MFC suspensions at different CaCl_2 concentrations

As can be seen the electrolyte additions caused a significant viscosity decrease and changed the flow profile of anionic grades, which are gel-like materials. The structure of hydrogel is interfered when electrolytes are added to the suspension. The viscosity decreases because the electrolytes are disturbing the hydrogen bonding between MFC particles leading to the formation of weaker gel structure. Also as a result of electrolyte addition, instabilities in flow behavior has been detected especially with MFC 3. Due to the higher charge density of MFC 3 the flocculation tendency increases and it exhibits a slight flocculation between shear rates 10 to 100s^{-1} . Unlike the anionic MFC grades, the native MFC suspension is not affected by electrolyte additions within these volumes because of low charge of the fibrils.

10.6.4 Combined effect of temperature and electrolyte addition

Also the synergistic effects of temperature and electrolyte addition were studied. The measurements with electrolyte suspensions as a function of temperature were carried out at the highest electrolyte addition (10mM) using CaCl_2 . The interaction between salt and temperature in aqueous suspensions can be seen in Figure 36.

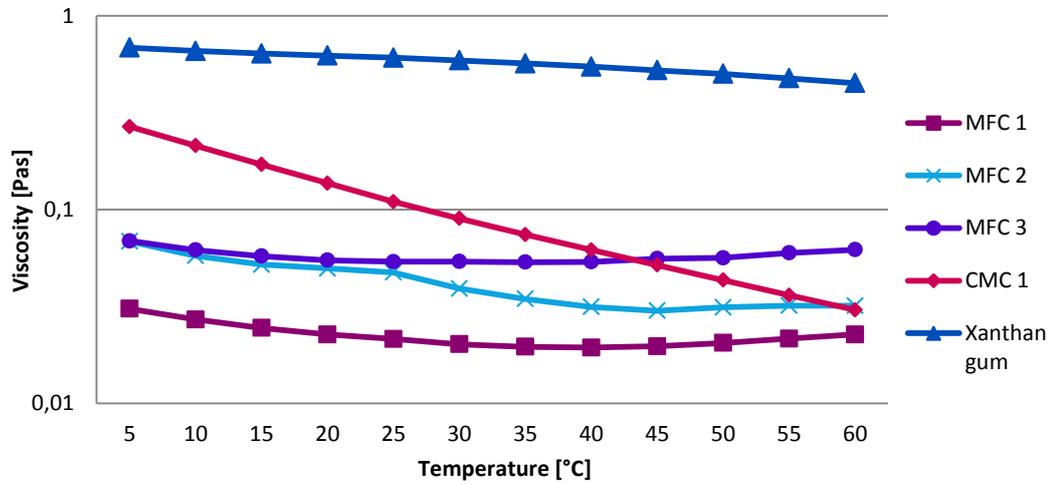


Figure 36. Viscosity dependence on electrolyte addition and temperature at 0.5wt % aqueous suspensions with shear rate 10s^{-1}

From the results it can be observed that all three MFC samples are exhibiting only a slight decrease in viscosity when salt and temperature were both present. In this temperature range there is not detected any significant changes or increased impact with temperature. At higher temperatures over 45°C there can be seen a small increase in viscosity with MFC 1 and MFC 3 due to the slow shear rate, which allows the fibrils to dry up on the hot inner surface of the cup geometry. When compared to the results of temperature measurement presented in Fig. 30, can be detected that samples are exhibiting similar behavior even when electrolytes are added to the suspensions. However the addition of salts is affecting clearly to the viscosity levels of suspensions, which is seen more strongly with MFC grades than polymeric thickeners. Nevertheless, MFC suspensions and xanthan gum are displaying a quite good stability as a function of temperature, while viscosity of CMC solution drastically decreased when temperature is increased. Xanthan gum exhibit a strong resistance for both variables, while NaCMC seems to be more sensitive to temperature than electrolyte addition. Whereas the MFC suspensions are much more sensitive to the electrolyte addition than the temperature changes. With the exception of native MFC, which provides a suspension that is not influenced to any great extent by changes in neither temperature nor the presence of electrolytes.

11 CONCLUSIONS

The aim of this Master's Thesis was to study and characterize rheological properties of selected MFC suspensions and supply valuable information regarding the possible applications for further studies. The first step was to develop and implement a reliable method to determine the rheological behavior of MFC suspensions. In order to carry out benchmarking for MFC suspensions, comparisons between commercial hydrocolloids were made. First, the rheological features of native and anionic MFC suspensions were determined. Rheological measurements showed a clear difference in viscosity levels and strength of the viscoelastic properties between anionic and native MFC. Nevertheless it was also possible to identify certain rheological characteristics common for all MFC samples.

The most apparent characteristics of MFC suspensions are high viscosity, strong shear-thinning behavior and thixotropic properties. All MFC suspensions exhibited strong shear-thinning behavior similar to xanthan gum. However there can be detected some differences in flow properties, because native MFC grade exhibited a clear flocculation under the shear. The native MFC was more sensitive to flocculation than anionic grades, since the low surface charge wasn't strong enough to keep the fibrils separated. The flocculation tendency caused heterogeneous structure and momentarily increased viscosity, which affects to the flow profile, rheological properties and thereby processing of the material. Measurements showed that more irregularities appeared in flow curves at lower concentrations, where the fiber network structure was less strict and fibrils were able to move more freely. The occurred irregularities indicated more instable suspension, which explain the elevated flocculation tendency at lower concentrations.

Microfibrillated cellulose fibrils, particularly with anionic charge, form a strong hydrogel structure in aqueous systems. Anionic MFC grades exhibited strong semi-solid viscoelastic structure, whereas native grade was more viscoelastic liquid material. However all MFC suspensions were purely viscous at the concentration of 0.1wt %. By increasing the concentration of the suspensions up to the 0.25wt %, particularly charged MFC grades, already exhibited viscoelastic structure, whereas at concentration of 0.5wt % all MFC suspensions presented strong gel-like structure. The strong three dimensional network,

higher fibrillation stage and degree of substitution provided stronger and transparent gel-like structure especially for anionic suspensions.

When comparing the anionic and native MFC grades it can be detected that charged MFC grades are more sensitive to environment, but provide suspensions with high yield stress and transparency. On the contrary, coarser, native MFC suspension has a higher tolerance for temperature and electrolyte additions. However, it is more prone to phase separation and not clearly as transparent as anionic MFC grades. Between anionic grades MFC 3 exhibit stronger gel-like structure and better colloidal stability due to high enough to result mutual repulsion. However based on the results it can be observed that there is no clear advance achieved with MFC 3 when compared to the MFC 2. Thus it would be more reasonably and cost-effective to use smaller chemical modifications when manufacturing MFC.

A comparison between reference materials and MFC suspensions provided also useful information of benefits of MFC. The results showed that studied MFC suspensions exhibited a superior viscosity when compared to selected NaCMC and guar gum grades. The anionic MFC grades also exceeded the viscosity levels of xanthan gum, though xanthan gum has considerably better tolerance for various external variables. However with native MFC quite good resistance is reached and suspension's rheological properties are not greatly affected by electrolyte additions or temperature changes.

MFC suspension rheology is highly dependent on the concentration, charge and the fibrillation stage of the material. Raising the consistency increases the viscosity quite considerably and strengthens the viscoelastic properties of suspensions. It was clear that the single most important variable affecting rheological properties of MFC suspensions was the dry matter content of samples. Also shear-history, preparation of sample and measurement conditions has a significant impact on rheological features of MFC aqueous suspensions.

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APPENDICES

Appendix I	Analysis data
Appendix II	Electrolyte concentration calculations
Appendix III	Viscosity data
Appendix IV	Frequency sweep data

Appendix I 1(1) Analysis data

Table XI. Analysis data for MFC suspensions

Sample	DS	pH	Electrical conductivity [mV/cm]	Zeta potential [mV]	Standard deviation (SD)	Transmittance T% (800nm)
MFC 1	-	7,4	1,0	-14,2	0,655	52,66
MFC 2	0.05	7,5	0,9	-27,5	0,872	64,706
MFC 3	0.13	7,4	1,0	-35,6	1,178	93, 526

Appendix II 1(1) Electrolyte concentration calculations

Table XII. Used electrolyte concentrations (mM) calculated for unit g/l

Salt concentration (mM)	mol/l	NaCl (g/l)	CaCl₂ (g/l)
10	0,01	0,6	1,1
1	0,001	0,06	0,1
0,5	0,0005	0,03	0,06

Appendix III 1(1) Viscosity data

Table XIII. The viscosity values for studied materials at the concentration 0.5wt %

Shear rate [1/s]	MFC 1 [Pas]	MFC 2 [Pas]	MFC 3 [Pas]	CMC 1 [Pas]	CMC 2 [Pas]	CMC 3 [Pas]	Guar gum [Pas]	Xanthan gum [Pas]
0,01	8,02	214,67	573,00	1,12	0,18	0,08	1,28	75,73
0,0158	4,86	116,00	265,00	1,12	0,17	0,06	1,30	91,73
0,0251	2,91	67,23	141,33	1,11	0,16	0,06	1,30	76,23
0,0398	1,71	41,03	80,93	1,09	0,16	0,05	1,29	55,13
0,0631	0,99	25,93	48,97	1,08	0,16	0,05	1,28	37,73
0,1	0,58	16,90	30,50	1,05	0,16	0,05	1,26	25,37
0,158	0,35	11,30	19,50	1,02	0,16	0,05	1,24	17,43
0,251	0,22	7,73	12,83	0,98	0,15	0,04	1,20	12,33
0,398	0,14	5,44	8,68	0,93	0,15	0,04	1,15	8,73
0,631	0,09	3,94	6,08	0,87	0,15	0,04	1,09	6,15
1	0,05	2,93	4,42	0,80	0,15	0,04	1,01	4,22
1,58	0,04	2,27	3,34	0,73	0,14	0,04	0,91	2,83
2,51	0,03	1,78	2,60	0,65	0,14	0,04	0,80	1,87
3,98	0,02	1,25	1,84	0,57	0,13	0,04	0,69	1,23
6,31	0,02	0,81	1,22	0,49	0,12	0,04	0,58	0,81
10	0,02	0,57	0,83	0,41	0,11	0,04	0,47	0,53
15,8	0,02	0,39	0,57	0,34	0,10	0,04	0,37	0,35
25,1	0,01	0,27	0,40	0,28	0,09	0,04	0,29	0,24
39,8	0,01	0,19	0,28	0,22	0,08	0,04	0,22	0,16
63,1	0,01	0,13	0,20	0,18	0,07	0,04	0,17	0,11
100	0,01	0,10	0,15	0,14	0,06	0,03	0,13	0,07
158	0,01	0,07	0,11	0,11	0,05	0,03	0,09	0,05
251	0,00	0,05	0,09	0,09	0,04	0,03	0,07	0,04
398	0,00	0,04	0,07	0,07	0,04	0,03	0,05	0,03
631	0,01	0,03	0,05	0,05	0,03	0,02	0,04	0,02
1 000	0,01	0,02	0,04	0,04	0,02	0,02	0,03	0,02

Appendix IV 1(2) Frequency sweep data

Table XIV. Storage (G') and loss (G'') modulus values for 0.5wt % MFC suspensions

Angular frequency ω [rad/s]	MFC1 G' [Pa]	MFC1 G'' [Pa]	MFC2 G' [Pa]	MFC2 G'' [Pa]	MFC3 G' [Pa]	MFC3 G'' [Pa]
0,01	0,891	0,118	13,600	1,390	26,700	1,690
0,0158	0,828	0,114	13,500	1,420	26,100	1,730
0,0251	0,797	0,106	13,500	1,450	25,500	1,800
0,0398	0,836	0,104	13,700	1,470	25,100	1,890
0,0631	0,831	0,100	13,700	1,570	24,800	1,960
0,1	0,829	0,097	13,900	1,690	24,700	2,090
0,158	0,833	0,096	14,000	1,830	24,700	2,270
0,251	0,842	0,096	14,200	1,980	24,900	2,510
0,398	0,854	0,098	14,600	2,140	25,300	2,800
0,631	0,868	0,102	15,000	2,320	25,900	3,170
1	0,885	0,107	15,600	2,540	26,600	3,600
1,58	0,905	0,116	16,200	2,820	27,500	4,110
2,51	0,925	0,129	16,900	3,150	28,500	4,720
3,98	0,947	0,148	17,700	3,530	29,800	5,410
6,31	0,966	0,178	18,600	3,980	31,200	6,230
10	0,978	0,228	19,700	4,500	32,900	7,180
15,8	0,996	0,339	20,800	5,120	34,800	8,290
25,1	1,020	0,504	21,900	5,880	36,800	9,610
39,8	0,960	0,580	22,700	6,650	38,900	11,000
63,1	0,494	1,040	22,500	8,090	40,300	12,600
100	1,500	3,780	21,700	9,250	41,300	15,500

Appendix IV 2(2) Frequency sweep data

Table XV. Storage (G') and loss (G'') modulus values for 0.5wt % hydrocolloid suspensions

Angular frequency ω [rad/s]	Xanthan G' [Pa]	Xanthan G'' [Pa]	Guar G' [Pa]	Guar G'' [Pa]	CMC 1 G' [Pa]	CMC 1 G'' [Pa]	CMC 2 G' [Pa]	CMC 2 G'' [Pa]
0,01	1,460	0,945	0,002	0,014	0,002	0,010	0,002	0,002
0,0158	1,710	1,060	0,002	0,021	0,001	0,015	0,000	0,003
0,0251	1,990	1,170	0,003	0,033	0,002	0,025	0,001	0,004
0,0398	2,320	1,280	0,004	0,052	0,007	0,040	0,001	0,006
0,0631	2,660	1,400	0,007	0,081	0,007	0,061	0,001	0,010
0,1	3,060	1,500	0,012	0,127	0,014	0,094	0,001	0,015
0,158	3,480	1,650	0,024	0,197	0,025	0,143	0,002	0,025
0,251	3,960	1,780	0,049	0,304	0,047	0,215	0,003	0,038
0,398	4,470	1,890	0,096	0,458	0,080	0,319	0,005	0,059
0,631	5,020	2,020	0,181	0,676	0,137	0,463	0,008	0,090
1	5,610	2,150	0,327	0,965	0,228	0,657	0,017	0,137
1,58	6,230	2,290	0,571	1,340	0,370	0,919	0,033	0,207
2,51	6,890	2,440	0,942	1,800	0,582	1,260	0,061	0,309
3,98	7,590	2,620	1,470	2,330	0,889	1,710	0,105	0,455
6,31	8,320	2,810	2,180	2,910	1,310	2,260	0,172	0,659
10	9,060	3,050	3,040	3,510	1,860	2,930	0,261	0,941
15,8	9,760	3,340	4,020	4,130	2,510	3,750	0,361	1,340
25,1	10,300	3,750	4,980	4,810	3,160	4,770	0,419	1,900
39,8	10,300	4,340	5,670	5,420	3,500	5,840	0,240	2,490
63,1	9,550	5,050	5,460	6,100	2,810	7,140	0,000	3,410
100	5,940	5,660	2,870	6,430	0,000	8,250	0,000	5,700