

Expanding the property space of cellulosic materials with multifunctional polymers

Niko Arne



Expanding the property space of cellulosic materials with multifunctional polymers

Niko Aarne

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This work represents a fundamental effort to improve the knowledge how multifunctional polyelectrolytes affect the physical properties of fibers and the paper made from these fibers. Throughout this work, the anionic charge of the fibers were modified with a well-known method: irreversible adsorption of carboxymethyl cellulose (CMC) onto the fibers. This modification amplified the sometimes weak effect that the naturally occurring anionic charge in fibers has on the physical properties of paper.

First, increasing the anionic charge of the fibers increased the strength properties of the paper and also water retention. In contrast, drying and then rewetting the fibers decreased the strength and water retention of the fibers. However, treating the anionically modified fibers with cationic polyelectrolyte could break this correlation and the water retention could be lowered without adverse effect on the strength properties.

Second, a model for cellulosic fibers was developed. The model divides fibre structure to two distinct regions: (i) surface fibrils (ii) cell wall. This model helps to understand how the polyelectrolytes function when dewatering or strength increasing is needed.

Third, multifunctional polymers (ionenes and diblock copolymers) could be used to widen the property space of fibers: (i) to increase the wet strength of the paper or (ii) hydrophobize paper. Ionenes do not have amine reactivity due to their quaternary amine structure like commonly used wet strength agents. Therefore, the results can be used to design more effective wet strength agents. In addition, treatment with diblock copolymer micelles allows hydrophobization of fibers with adjustable layer of hydrophobic material. This could prove valuable as the layer of hydrophobic material can be tuned effortlessly by selecting the starting block copolymer for the desired effect.

Keywords cellulose, fibers, paper, polymer, adsorption, block copolymer, ionene**ISBN (printed)** 978-952-60-5282-3**ISBN (pdf)** 978-952-60-5283-0**ISSN-L** 1799-4934**ISSN (printed)** 1799-4934**ISSN (pdf)** 1799-4942**Location of publisher** Helsinki**Location of printing** Helsinki**Year** 2013**Pages** 156**urn** <http://urn.fi/URN:ISBN:978-952-60-5283-0>

Tekijä

Niko Aarne

Väitöskirjan nimi

Selluloosapohjaisen materiaalin ominaisuuksien laajentaminen multifunktionaalisten polymeerien avulla

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Tämä työ pyrkii esittämään perustavanlaatuista tietoa miten multifunktionaaliset polyelektrolyytit vaikuttavat kuitujen ja näistä valmistetun paperin fysikaalisiin ominaisuuksiin. Tämän työn punaisena lankana on anionisesti muokattu (negatiivisesti varattu) kuitu. Tämä on saatu aikaan adsorboimalla irreversibelisti karboksimeetylliselluloosaa (CMC) kuituihin. Tämä vahvisti joskus heikkojakin vaikutuksia, joita kationisilla polyelektrolyyteillä on käsittelemättömiin kuituihin.

Ensimmäiseksi, lisäämällä kuitujen anionista varausta sekä paperin lujuusominaisuudet että kuitujen vedenpidätyskyky kasvoi. Sen sijaan, kuivattujen ja uudelleenkostutettujen kuitujen käyttö laski paperin lujuutta sekä kuitujen vedenpidätyskykyä. Kuitenkin käsittelemällä anionisesti muokattuja kuituja kationisella (positiivisesti varatulla) polyelektrolyytillä tämä varsin yleinen korrelaatio voitiin katkaista: Vedenpidätyskykyä voitiin alentaa ilman haitallista vaikutusta paperin lujuusominaisuuksiin.

Toiseksi, selluloosakuiduille kehitettiin malli, joka jakaa kuiturakenteen kahteen erilliseen osaan: (i) pinta-fibrilleihin ja (ii) soluseinään. Tämä malli auttaa ymmärtämään, miten polyelektrolyytit vaikuttavat, kun vedenpoistoa tai paperin lujuutta halutaan muokata. Kolmanneksi, monitoimiset polymeerit (ioneenit ja lohkopolymeerit) voidaan käyttää laajentamaan kuitujen ominaisuuksia: (i) Paperin märkälujutta voidaan lisätä tai (ii) paperia voidaan hydrofobisoida. Kvaternäärisistä amiineista muodostuvat ioneenit eivät sisällä reaktiivisia amiineja, kuten tavanomaiset märkälujapolymeerit, joten niitä voidaan käyttää märkälujapolymeerien tutkimuksen ja suunnittelun apuna. Lisäksi lohkopolymeereistä koostuvat misellit mahdollistavat kuitujen hydrofoboinnin säädettävällä polymeerikerroksen paksuudella. Tämä voi olla hyödyllistä, kun kerroksella hydrofobista materiaalia voidaan virittää vaivattomasti valitsemalla tietyn tyyppinen lohkopolymeeri joka miselloidaan ja adsorboidaan kuituun.

Avainsanat polymeeri, adsorptio, lohkopolymeeri, ioneeni, kuitu, paperi**ISBN (painettu)** 978-952-60-5282-3**ISBN (pdf)** 978-952-60-5283-0**ISSN-L** 1799-4934**ISSN (painettu)** 1799-4934**ISSN (pdf)** 1799-4942**Julkaisupaikka** Helsinki**Painopaikka** Helsinki**Vuosi** 2013**Sivumäärä** 156**urn** <http://urn.fi/URN:ISBN:978-952-60-5283-0>

Preface

I came to work at Teknillinen Korkeakoulu (now Aalto University) when my Master's Thesis supervisor from Kemira, Veli-Matti Vuorenvalo, had recommended me that there would be an opportunity for work with prof. Janne Laine. My thesis work had revolved around something called color reversion of paper (the common phenomenon that yellows paper with time). That project as well as the new task had little to do with my basic education, chemistry. But one of the long and memorable talks with my brother Lauri and his rather curious collection of rare wood specimens somehow convinced me that something as ordinary as "wood" and "paper" would be interesting. Then, after the first meeting with Janne, I felt that he is an astonishing professor and I am thankful that he gave me the opportunity to work with him.

My deepest thanks go to my thesis supervisor, Eero Kontturi. We formed with him and Janne, some kind of triumvirate that was able to produce this thesis. Eero's otherworldly ability to transform mundane to extraordinary helped us to publish the results in highly rated academic forums. Janne's vision about the aim of this work and his skill of obtaining the rarest resource available for scientists, funding, was the glue that held this thesis together.

This work had a connection to Finnish paper and chemical industry that mainly financed this thesis under the project ChAD, Chemically Aided Drying. In no particular order I thank Botnia (now Metsä-Fibre), Kemira, UPM, Andritz and TEKES, the Finnish Funding Agency for Technology and Innovation. I am also grateful for all the individuals from these companies who I had privilege to meet.

I thank my co-authors, Dr. Tuomas Hänninen, Ville Rantanen, Dr. Jani Seitsonen, prof. Janne Ruokolainen, Dr. Arja-Helena Vesterinen, and prof. Jukka Seppälä for their valuable contributions.

My coworkers are enormously thanked. I think I met and gained something from all the members of our department. I would like to thank them all: Tuomas (both), Anu, Arcot, Joe, Ilari, Sole, Leena-Sisko, Karoliina, Alexey, Risu, Katri, Markus, Anna, Albert, Marcelo, Akio, Naveen, Iina, Timbe, Carlo, Antti, Paula, prof. Thad Maloney, the laboratory superpersons (Leena, Anu, Marja, Aila, Rita and Risu), Marina, Alina, Michael, Vahid, Kaarlo, Annariikka, Könde, Lidia, Lasse, Evangelos, Minna, Laura, Tiina, Elli and to many others who I worked with. I also want to thank Timo, Ari, Riitta and Sirje for the help in the practical matters. Special thanks goes to my office mates (in chronological order Jani Xuejie, Hannes, my good old friend Petri and Raili), to the members of the "Spanish" lunch team (Leonardo, Alina, Juan, Marc, Mikhail), our music listening group (Marc, Mikko, Pertti and Albert), and to Mikhail and Lidia for all the memorable moments. Also special thanks go to Christian and konehallin pojat for helping me to build all the equipment necessary for this thesis (for example, "Gertrüd"). There were some people that

made all the difference in the atmosphere and therefore I would like to give my very special thanks to Timbe, Risu, Hannes, Tiina, Elli, Raili, Katri, Christian, Lidia, Naveen and Mikhail.

Big thanks to my friends – You know who you are!

I would like to thank all the members of my family: Affe, Ranja, Mamppa, Olli, Outi, Lauri, Aapo and Martti. Your support made this work possible.

To Nela, with all my love, thanks.

List of publications

This thesis is based on the results presented in four publications, which are referred as Roman numerals in the text. Some additional data related to the work is also discussed.

Paper I Niko Aarne, Eero Kontturi, and Janne Laine. 2012. "Influence of Adsorbed Polyelectrolytes on Pore Size Distribution of a Water-swollen Biomaterial." *Soft Matter* 8 (17): 4740.

Paper II Niko Aarne, Eero Kontturi, and Janne Laine. 2012. "Carboxymethyl Cellulose on a Fiber Substrate: The Interactions with Cationic Polyelectrolytes." *Cellulose* 19 (6): 2217–2231

Paper III Niko Aarne, Janne Laine, Tuomas Hänninen, Ville Rantanen, Jani Seitsonen, Janne Ruokolainen and Eero Kontturi. 2013. "Controlled hydrophobic functionalization of natural fibers by self-assembly of amphiphilic diblock copolymer micelles." *ChemSusChem* 7 (6): 1203–1208.

Paper IV Niko Aarne, Arja-Helena Vesterinen, Eero Kontturi, Jukka Seppälä and Janne Laine. 2013. "A Systematic Study of Non-crosslinking Wet Strength Agents." *Ind. Eng. Chem. Res.*, DOI: 10.1021/ie401417e

Author's contribution to the appended joint publications:

- I-IV Niko Aarne was responsible for the experimental design, performed the experimental work, analyzed the results, and wrote the manuscripts (see below).
- I Routine DSC measurements made by Leena Nolvi
- II Anu Anttila made the routine CMC adsorptions, paper sheets and paper testing
- III Tuomas Hänninen did the Raman-imaging, Jani Seitsonen and prof. Janne Ruokolainen performed the TEM measurements and Ritva Kivelä made the AFM images. Ville Rantanen did the computer analysis of the TEM images.
- IV Arja-Helena Vesterinen synthesized the ionenes and performed the Size Exclusion Chromatography experiments.

List of abbreviations

AFM	atomic force microscopy
AKD	alkyl ketene dimer
ASA	alkenyl succinic anhydride
Block-n	In this thesis, Block-n (n=1,2,...,5) refers to the diblock copolymers. The numeral refers to the total molecular weight of the polymer. 1 was the polymer with lowest and 5 had the largest molecular weight.
C-n	A special notation for carbohydrates that signify which of the carbons in the five or six membered rings is referred to.
C18	linear hydrocarbon with 18 carbons and 38 hydrogens. The general form is $C_n = C_nH_{(2n+2)}$
CMC	carboxymethyl cellulose
COBB ₃₀ -test	Cobb test measures the water uptake into a paper in a given time period (30 s in this thesis). Units are grams of water per square meter.
DDA	dynamic drainage analyzer
DLS	dynamic light scattering
DMF	dimethylformamide
DS	degree of substitution
DSC	differential scanning calorimeter
ECF	elementary chlorine free bleaching
GlcA	4-O-methyl-D-glucuronic acid
HexA	4-deoxy- β -L-threo-hex-4-enopyranosyluronic acid
H_m	latent heat of melting
HPLC	high performance liquid chromatograph
IR	infrared
MALS	multi-angle light scattering
MF	melamine-formaldehyde resin
M_w	molecular weight
neutralization	In this thesis, neutralization refers to the process where the negative charge of a polyelectrolyte have been neutralized by adding equal amount of cationic charge polyelectrolyte.
NFW	non-freezing water
NMR	nuclear magnetic resonance
NTP	normal temperature and pressure (20 °C and 1 atm pressure)
PAE	polyamide-co-poly(amine-epichlorohydrin), also known as polyamide epichlorohydrin
PAM	poly(acrylamide)
PDADMAC	poly(diallyl dimethyl ammonium chloride)
PEO	poly(ethyleneoxide)
PES-Na	sodium poly(ethene sulfonate)
PPO	poly(propyleneoxide)
PVAm	poly(vinylamine)
RI	refractive index
SEC	size exclusion chromatography
(cryo-)TEM	(cryo-)transmission electron microscopy
TEMPO	2,2,6,6-tetramethylpiperidine-1-oxy radical
T_g	glass transition temperature
UF	urea-formaldehyde resin
WRV	water retention value
YAG	Yttrium aluminum garnet, a synthetic crystalline material used in, <i>e.g.</i> , lasers.

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1. Introduction and outline of the study

This work consists of several attempts to improve the properties of cellulosic fibers in paper applications. Therefore, the work finds itself in the context of a multitude of previous research. However, one of the factors that distinguish this work from many others is the use of well-characterized fibers and polymers. In addition, substantial differences were found when polyelectrolytes were adsorbed on never-dried fibers (commercially known as virgin pulp) or adsorbed on never-dried fibers and then dried (commercially, market pulp). This kind of approach is rarely reported. An outline of the experimental paths taken in this work is shown in Fig. 1.

The recent progress in the analysis of the pore structure in the wet state by differential scanning calorimeter (DSC) enabled the study on how drying and cationic polyelectrolytes affect the porous structure of fibers (**Paper I**). The detailed analysis of these results improved the current knowledge of cationic polyelectrolyte adsorption.

All attempts to improve the fiber properties in this work were based on the cationic polyelectrolytes ability to adsorb onto the anionic fibers. Sometimes the anionic charge was not sufficient to introduce desired effect. Therefore, a well-known method to increase surface charge was used: irreversible adsorption of carboxymethyl cellulose (CMC) onto the fibers. Both low molecular weight (M_w) and high M_w CMCs were used (Fig. 1). The well-characterized CMCs gave opportunity to further improve the model of cellulosic fiber adsorption. This in turn allowed the use of well-characterized cationic polyelectrolytes to tune the properties of the CMC pretreated fibers (**Paper II**). The paper made from these fibers could be improved in several ways (Fig. 1): (i) The dry strength could be improved by CMC treatment, (ii) The dewatering of the fibers could be improved while retaining the high strength when high and low M_w cationic polyelectrolytes were adsorbed after low M_w CMC pretreatment, (iii) The wet strength could be improved when low M_w polybrene was adsorbed on high M_w CMC pretreated fibers or (iv) the strength after drying and rewetting could be retained with high M_w PDADMAC adsorption after low M_w CMC pretreatment. The wet strength attained by adsorption of polybrene after high M_w CMC pretreatment was a novelty that had not been reported before. Therefore, several similarly structured polymers called ionenes were synthesized to further study this wet strength effect (**Paper IV**).

Finally, the hydrophobization of the cellulosic fibers was attempted. In **Paper III**, a novel way to hydrophobize paper was introduced. Selecting water insoluble diblock copolymers that could be micellated allowed formation of stable suspensions. This enabled a facile method to increase the hydrophobic content of the polymers. The water-insoluble polymers could be rather easily transformed to micellar aggregates that were monodisperse. This avoided the complex adsorption kinetics, which troubles many water-soluble amphiphilic polymers. According to previous literature, it is easy to produce “crew-cut” micelles that have short hydrophilic block and a long hydrophobic block. In addition, they have a high hydrophobic/hydrophilic ratio. The hydrophobic group was varied while the hydrophilic group was kept constant. The “crew-cut” micelles were stable in water and due to the cationic charge, could be effortlessly adsorbed to the fibers. The micelles hydrophobized paper when the molecular weight of the constituent diblock copolymers was sufficiently high (Fig. 1). Furthermore, medium sized micelles hydrophobized paper after heat treatment.

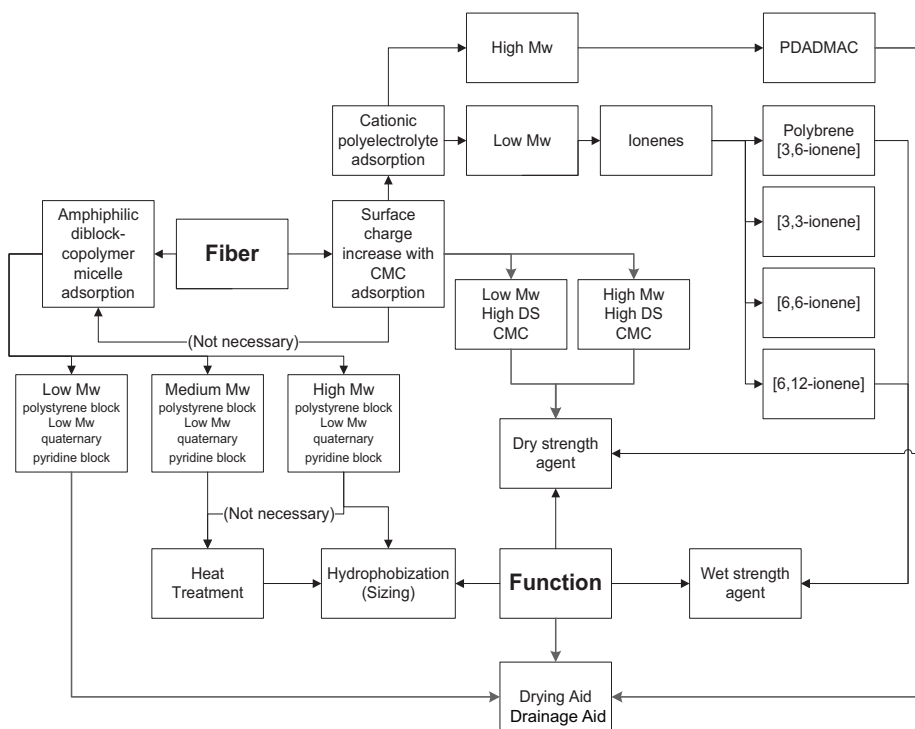


Fig. 1 Outline of the thesis' results. We started with bleached birch kraft pulp fibers without fines. Via polymeric modification we could manufacture multifunctional paper, i.e., increase its dry strength, wet strength, increase the dry matter content after dewatering (drying or drainage aid) and even hydrophobize it. The outline depicts the various routes to obtain desired functional properties. All the tested cationic polyelectrolytes helped dewatering (drainage aid). This is shown in the outline with two examples: (i) PDADMAC+CMC pretreated fibers to demonstrate that it is rare to increase dry strength with cationic polyelectrolytes and (ii) low M_w polystyrene block micelle treated fibers to show that amphiphilic micelles can also be used as drainage aids.

2. Background

2.1 Pulp fiber characteristics

The staggering amount of variety that comes with natural substances such as native-based fibers makes it difficult to choose one source of cellulosic fibers that represents or even tries to mimic the whole. Therefore, substantial simplifications are inevitable. In this work, the source of cellulosic fibers comes from a tree species, namely birch. Birch is particularly suitable for this work since it is commonly applied in the pulp and paper industry and its physical and chemical properties have been extensively covered. The cellulosic fibers were used as bleached products from the kraft process of pulping. This manufacturing method has mostly removed the colored glue-like substance, lignin, and some of the non-cellulosic polysaccharides, known as hemicelluloses as well as the small molecules called extractives. Bleached birch kraft pulp is a porous, soft biomaterial consisting mainly of cellulose and xylan. A detailed representation of a bleached birch kraft fiber is shown in Fig. 2. The sugar monomeric units consist mostly of glucose and xylose with a small amount of mannose, indicating that the polysaccharides in the pulp fibers are cellulose (constructed from anhydroglucose monomeric units) and xylan (constructed principally from anhydroxylose units Fig. 2b). The charge of the fiber is mainly due to xylan, because cellulose backbone ideally lacks charged functional groups. In xylan, the specific nature of the compound responsible for the negative charge is altered when different bleaching methods are employed in the manufacturing processes of chemical pulp. Nevertheless, the main source of negative charge is due to the 4-O-methyl-D-glucuronic acid (GlcA) side units in xylan, most of which have been transformed to 4-deoxy- β -L-threo-hex-4-enopyranosyluronic acid (HexA) during alkaline pulping. According to literature, these acid groups represent approximately 10 mol-% of the total amount of xylan (Fig. 2),¹ which corresponds to the total charge of the fibers in this work as determined from a polyelectrolyte adsorption isotherm.

polyelectrolyte adsorption.¹⁵ Since the adsorbed polyelectrolytes affect the charge of fibers, it is logical to expect that the osmotic pressure towards the pores is consequently influenced. Adsorbed polyelectrolytes also possess a physical volume, which can alter the size of the smallest pores. Paper I was a fundamental effort to explore the actual influence of adsorbed polyelectrolytes on the pore size distribution of chemical pulp fibers.

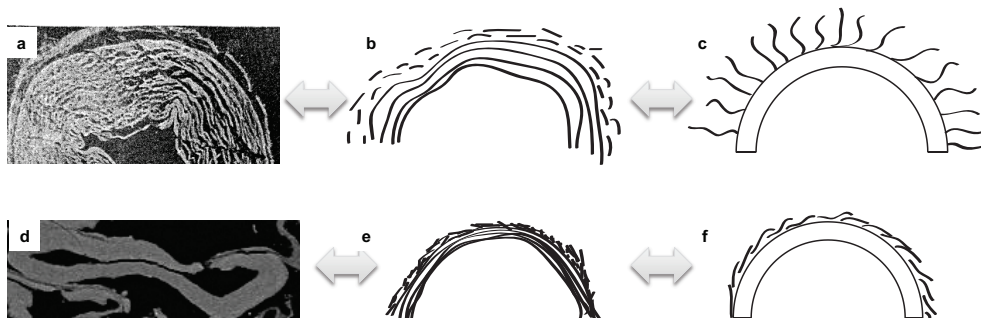


Fig. 3 Schematic representations of a cellulose fiber in wet and dry states. (a) Extremely swollen bleached sulphite spruce fiber (Adapted from Stone and Scallan¹⁶). (b) Schematic representation of a wet fiber. The broken lines form the fibrillar surface while the constant lines describe the lamellar structure of fiber. (c) Idealized representation of fiber divided in surface microfibrils (lines) and thick cell wall (arc). (d) Dried cellulose fiber in a paper cross-section lacking any lamellar features. (Adapted from Eriksen and Gregersen¹⁷) (e) Schematic representation of the dense structure of a dried fiber. (f) Idealized representation of fiber which demonstrates collapsed fibers and smaller cell wall (arc).

2.1.2. Hornification

The term hornification is used to describe structural changes in chemical pulp fibers occurring in fiber drying or recycling. In literature, Jayme is arguably the first person to rigorously study the concept of hornification and therefore to introduce it to the pulp and paper science.¹⁸ He quantified hornification as the loss of water retention (WRV) after drying. The method relied on the centrifugation of a sample at given parameters and it has lately become a standard method (SCAN-C 62:00).

It is remarkable that such a simple method allows the determination of hornification. Unsurprisingly, there has been critique what the term hornification includes.¹⁹ Since Jayme introduced the term in 1944, hornification now covers many effects: It is thought to aggregate the microfibrils irreversibly²⁰, decrease the porosity²¹, increase the crystallinity²² and hinder the refining (beating) of the fibers⁶ among other things. Ageing fibers also demonstrate the hornification effect as well as heat treated fibers.²³ Recently, comprehensive reviews about hornification have emerged and the original WRV reducing effect has effectively changed to deep understanding of the fiber interactions at nano-scale upon drying.^{24,25}

The relevance of hornification to this thesis is limited to the effect of drying. The cationic polyelectrolytes do not appreciably affect hornification, except, perhaps, through the neutralization of the anionic charge of the fibers as the negative charge is known to limit the effect of hornification.^{20,26} The example of added xylan, a polyelectrolyte that inhibits hornification, summarizes these statements: The xylan addition should be more than 4%, preferably 16%, to halve the hornification effect at low ionic strength conditions.²⁷ In this

work, the adsorption percentage of any combination of polyelectrolytes was lower than 4% in all the experiments. Therefore, the reduction of hornification by polyelectrolytes was not considered as an aim for this work. Rather, the negative aspects of hornification (strength loss of paper made out of the hornified fibers) were minimized. For example, polyelectrolytes could reduce WRV while certain physical properties of paper made out of the hornified fibers remained constant, such as tensile strength. In addition, the polyelectrolytes can only reduce the hornification if the negative charge is located inside cell wall. For example, the CMCs in this work were used to modify mainly the surface charge and such CMCs do not affect hornification.²⁸ This is in contrast to bulk treatments that affect the cell wall.

2.2 Polyelectrolyte adsorption

The determination of the amount of polyelectrolyte adsorbed onto fibers has been scrutinized before^{13,14,29-33} and critically compared to other methods.^{13,34,35} The common way to determine the polyelectrolyte adsorption amount is with the adsorption isotherm. In an adsorption isotherm, the equilibrium concentration of the solution is plotted against the adsorbed amount. The equilibrium concentration is determined from the filtrated solute by back-titration of the added polyelectrolyte with a known polyelectrolyte of opposite charge. The adsorbed amount is usually determined by subtracting the equilibrium concentration from the initial polyelectrolyte concentration. Subsequently, the adsorbed amount can be calculated with the help of the charge density of the added polyelectrolyte and the mass of fiber used in the titration.

2.2.1. Theoretical considerations

Polymers adsorb at interfaces much more strongly than the disconnected free monomers (or solute particles). Crudely stated, the (neutral) polymer adsorption onto a surface is due to the thermodynamical “adsorption” energy and entropy reasons. The “adsorption” energy is due to the van der Waals interaction of the surface and polymer. These interactions are also available to smaller particles (and solute particles), so van der Waals interactions alone do not explain the preferred polymer adsorption. In order to understand why polymers adsorb, an abstract thermodynamic quantity called translational entropy is needed. Translational entropy can be thought to be a measure of the particles freedom to move. Free monomers can move (translate) through a solution freely and thus have a relatively high amount of translational entropy. In contrast, the segments in a polymer have much lower translational freedom, since the segments are chained (attached) to each other. When polymer attaches to a surface, it loses only a little of its already low translational freedom, while a confined small (solute) particle lose much more. Therefore, in thermodynamical equilibrium, the (neutral) polymers are more likely

to be found closer to the surface than the solute particles i.e. polymers are adsorbed on to a surface.³⁶

In this thesis, a negatively charged surface (a fiber) and positively charged polyelectrolytes were mostly used. The resulting adsorption for these is surprisingly simple. First, if the ionic strength is very high (high salt concentration) the salt ions mask the charge and the adsorption follows the neutral polymer adsorption stated above. In this thesis a high salt concentration was used to allow CMC to adsorb on to the fibers. Second, if the ionic strength is very low the adsorption follows the physics of electrostatics (negative and positive attract) and the adsorption continues until the surface has been neutralized (charge compensation).¹³ The polyelectrolyte displaces any counter-ions associated with the charged surface due to the higher translational entropy of the small ions compared to the polyelectrolyte. Finally, a reader who is interested on the detailed theory of polymer adsorption on interfaces, is directed to, *e.g.*, the book of Fleer *et al.*³⁷

2.2.2. Adsorption isotherms

The adsorption isotherm for a charged polyelectrolyte (in low ionic strength) has two main features. First, the polyelectrolyte completely disappears from the solution and is adsorbed onto fibers because all the polyelectrolyte is adsorbed at low addition levels due to charge compensation. This kind of sorption is called polyelectrolyte adsorption and in this thesis the adsorption is mostly this kind of sorption. Secondly, a plateau region is reached at higher equilibrium concentrations, because the additional polyelectrolyte remains in solution once the available surface is saturated (Fig. 4).^{13,34,38}

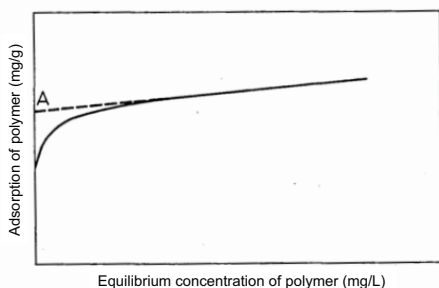


Fig. 4 Schematic adsorption isotherm. The fiber charge can be calculated from the polymer adsorption by extrapolating the curve to zero equilibrium concentration (A).³⁹

In practice, however, the adsorption isotherms often deviate from this prediction, particularly in the case of porous fibers. The rounding of the isotherm is due to at least three effects: (i) The polydispersity of the adsorbing polyelectrolyte causes curved isotherms because high M_w material is preferentially adsorbed at the accessible fiber surfaces, displacing low molecular mass material.⁴⁰ However, for fibers the low M_w polyelectrolytes can displace high M_w material.¹³ (ii) A low molecular mass polyelectrolyte has higher accessibility to charges inside the pores of the fiber cell wall than a high

molecular mass polyelectrolyte.²⁹ (iii) A decrease in stoichiometry for the adsorbed polyelectrolyte molecules, most probably due to an increased interaction between the polyelectrolyte molecules on the surfaces, seen as an expansion of the adsorbed polyelectrolyte layer out from the surface.³⁵ (iv) Some of the low M_w fraction in a polydisperse polyelectrolyte can be adsorbed inside the fiber, especially if the average M_w is high and the composition polydisperse (Fig. 5). This has been also shown for low and high M_w PDADMAC by Wågberg and Hägglund.¹⁴

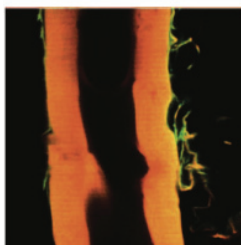


Fig. 5 Fluorescent confocal laser scanning microscope image of a fiber. The fiber has been pre-adsorbed with high M_w high charge density PDADMAC (4.8×10^5 g/mol) that has been modified to fluoresce green. The image shows clearly how a low M_w polyelectrolyte (cationic dextran, 10^4 g/mol) that fluoresces red adsorbs inside the cell wall through the pre-adsorbed layer of high M_w PDADMAC.⁴¹

2.2.3. Importance in papermaking

A wide variety of polymers are commercially used in practical papermaking for diverse applications such as retention of fines, strength improvement and surface sizing (starch) to name a few. Pulp fibers are anionic, and therefore, commercially the most viable polymers have been cationic to improve the adsorption of polymers in the wet end of the paper machine. The most important polymeric properties for papermaking additives have been molecular weight, reactivity and charge density.^{13,32,42,43} The adsorption of charged polymers onto cellulose fibers and its kinetics have been exhaustively studied experimentally and theoretically.^{12–14,32,44,45} Pure polyelectrolyte adsorption, i.e., the electrostatic combining of the cationic polymer and the anionic fiber, have been found to govern the adsorption of most cationic polyelectrolytes.^{13,45} The kinetic studies have brought up the importance of adsorption time, but for practical purposes the polyelectrolyte adsorption is extremely fast (<1 s).⁴⁵ Depending on the molecular weight of a polyelectrolyte, its accessibility into the fiber wall is different. Small molecules can fully penetrate the fiber wall whereas large molecules are constrained to the outer surface of the fibers.^{29,46} Therefore, polyelectrolyte adsorption has been widely used as a method to assess the charge and porosity of cellulose fibers.^{32,35}

However, polyelectrolyte adsorption is not the only way to adsorb polymers on fibers. Also neutral or even anionic polymers can be adsorbed. For example, water soluble cellulose derivatives, vegetable gums, and hemicelluloses, can be adsorbed onto fibers in the absence of electrostatic interactions.^{47,48} The adsorption mechanism is probably due to some specific carbohydrate-carbohydrate interactions between the polymer and cellulose.⁴⁹ The same interactions are found in hemicelluloses, such as xylan, which are

intimately associated to cellulose microfibrils in the fiber wall structures already during the biosynthesis of wood.⁵⁰

The extensive use of cationic polymers in commercial applications has increased the need to maximize adsorption, either to increase strength or other desirable property of paper.⁵¹ Arguably, the simplest approach to increase the adsorption of cationic polyelectrolytes is to increase the anionic charge of the substrate, even though similar effects can be found by altering the cationic polyelectrolyte by decreasing the degree of substitution (DS) of the polymer or by varying the ionic strength of the system. Popular, yet academic, methods to increase the anionic charge of the fiber have been to either oxidize cellulose (with 2,2,6,6-tetramethylpiperidine-1-oxy radical (TEMPO)^{52,53} or other oxidant⁵⁴) or to adsorb negatively charged carbohydrate on the surface of the fiber.⁴⁸ Table 1 lists the effect of some of these treatments on the surface charge of the fiber. The table demonstrates how the surface charge can be increased with these methods. The most common negatively charged commercial carbohydrate derivative has proven to be CMC.^{48,55} It is particularly suitable over oxidation because it is surface selective⁵⁶ and thus most suitable for mainly surface adsorbing cationic polyelectrolytes.²⁹

As mentioned previously, it is customary to study polymer adsorption onto cellulose fibers by measuring adsorption isotherms and kinetics as well as the effects of ionic strength and pH conditions on them. In this work, however, the effect of pH and ionic strength was not studied. These were taken into account by using high enough pH to maintain the carboxyl groups in their ionized form (pKa of carboxyl groups in carbohydrates is approximately 4.5) and low enough ionic strength (less than 10^{-2} M) to conserve the charge stoichiometry.³⁵ All studies have indicated the importance of the polymer shape on the fiber surface, but the direct measurement of shape on the surface of the fiber has remained elusive. Cellulose model surface studies have shown good promise to indirectly evaluate polymer shape.⁵⁷⁻⁶⁰ However, the model surface studies were out-of-scope of this work.

Table 1. Surface charge properties of bleached kraft pulps treated with various methods to 80 ± 10 $\mu\text{eq}\&\text{mol}$ total charge. (Carboxymethylation and TEMPO-oxidation are versatile reactions and can be used to increase charge almost indefinitely. The reactions end when two new polymers from cellulose form: CMC and poly(glucuronic acid), respectively.)

Pulp sample	Total charge ($\mu\text{eq/g}$)	Surface charge ($\mu\text{eq/g}$)
Reference ⁶¹	37	2
Carboxymethylated pulp ⁶¹	89	4
CMC treated pulp ⁶¹	74	21
TEMPO oxidized pulp ⁵²	89	50

2.3 Paper strength additives

The simplest way to increase paper strength has traditionally been refining. Refining is an energy-intensive mechanical process that improves fiber bonding by delamination of the fiber wall (surface and internal fibrillation) and results in stronger paper.⁶² The mechanism of refining in improving fiber bonding and paper strength has been related to fiber swelling, plasticization, fines generation, external fibrillation and other mechanically

attainable changes.⁶³⁻⁶⁵ These mechanical changes yield simple and cost efficient changes to the physical properties of fiber. However, physico-chemical modifications in the form of paper strength additives possess added value to refined fibers, usually in cases where mechanical alteration of fiber does not alone yield the specific desired effect. For example, when the tensile strength of paper needs to be improved without adverse effects to density or when the wet strength of paper should be higher.

Paper strength additives are commonly divided into dry and wet strength additives. Dry strength additives can be regarded as non-reactive adhesives that improve fiber-fiber bonding, while wet strength additives are chemically reactive polymers that form covalent crosslinks to improve the fiber-fiber bonds and to provide additional strength when the water completely negates the adhesive power of the dry strength additives. Some strength enhancing polymers are classified below.^{42,51} The overview serves to rationalize the selection of polymers in this work. For example, the novel wet strength polymers (ionenes, Paper IV) are interesting due to their different structure compared to the commercially available wet strength agents.

2.3.1. Dry strength mechanisms and agents

Recent reviews comprehensively describe how fibers bond and how that affects the paper strength with or without dry strength additives.^{51,66} Also, how the polymer properties affect the paper strength has been elucidated.⁴² The landmark studies on fiber bonding,⁶⁷ cellulose fiber structure,⁶³ and paper strength⁶⁸ have been vital for providing the basis for the materials science of paper. Yet, after countless studies on the effects of strength additives on paper properties, the underlying mechanisms are still somewhat unclear.

Recently, the molecular approach to fiber bonding has evolved.^{69,70} Hubbe emphasized the difference between the conventional and the molecular level views on fiber bonding.⁶⁶ In the molecular view, the role of nano-scale interactions between fibers and strength additives has been stressed as a crucial contribution on the development of fiber bonding and paper strength.^{71,72}

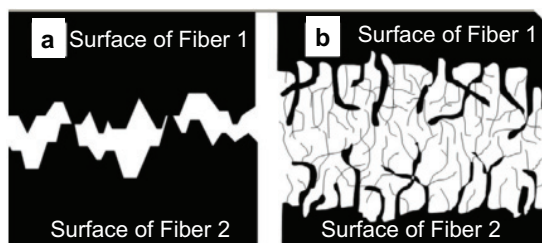


Fig. 6 Schematic views of fiber-fiber bonding. (a) Conventional view of two fiber surfaces. (b) Molecular level view of two fiber surfaces. Adapted from Hubbe.⁶⁶

In this work, this molecular view is taken as a basis to hypothetically explain how the interactions of model polyelectrolytes with the surface fibrils of fiber give rise to the obtained strength properties. Hubbe made an interesting schematics on the molecular

level view of the fiber (Fig. 7).⁷³ The model was originally used to explain why the streaming potential of fibers + cationic polymer (PDADMAC) complex changes with time from positive to negative.⁷⁴ His model (Fig. 7) and the model in this thesis (Fig. 3) share the view that the fiber cell wall should be divided to surface fibrils and porous cell wall to explain the obtained results. In addition, the adsorbed polymer (PDADMAC) is depicted as adsorbing only to the surface fibrils.

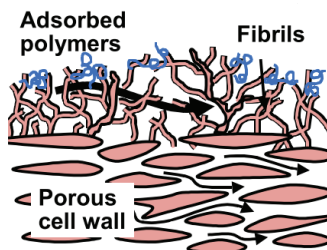


Fig. 7 Schematic view of the fiber. It includes the division of the fiber to surface fibrils and to porous cell wall. The figure includes surface adsorbed polymers (in blue) and water flow (arrows) that were used by Hubbe to explain the charge reversal of the streaming potential. Adapted from Hubbe.⁷³

Starch and dextran. Starch and dextran are both complex polysaccharides similar to cellulose (polymer of $\beta(1\rightarrow4)$ -D-glucose, see Fig. 8). Characteristic bonds in starch are the $\alpha(1\rightarrow4)$ -D-glucose bonds that form the polymer backbone with occasional branches at C-6, while dextran is a $\alpha(1\rightarrow6)$ -D-glucose with occasional branches at C-3. Both starch and dextran usually have a very high molecular weight (more than 10^6 g/mol). Starch is an important paper dry strength additive, while dextran is widely used as a model carbohydrate polymer.^{75,76} They function mainly by increasing the strength of the fiber-fiber bond.⁷⁷ The origin of the improved bond strength lies probably in the entangling of the polymers at the fiber-fiber interface, i.e., the “spaghetti effect”.⁷⁸ They are adsorbed on cellulosic fibers through carbohydrate-carbohydrate interactions only slightly. Therefore, cationized products are commonly used to allow polyelectrolyte adsorption and thus better retention.^{79,80} Starch is economical and offers good improvements to paper strength but is rather poor model to study adsorption, due to the extreme polydispersity. Dextran could be a good model polymer to study the starch adsorption due to the lower branching and polydispersity.⁷⁶ However, starch and dextran were not essential for this thesis since the focus was on the highly charged polyelectrolytes.

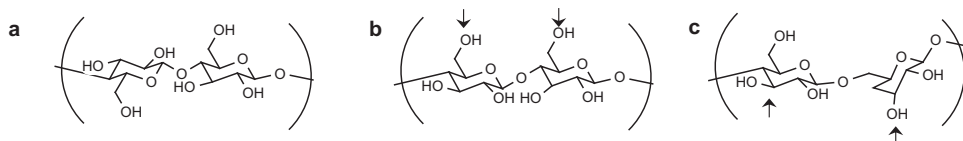


Fig. 8 Simplified representation of polysaccharides. (a) cellulose and the $\beta(1\rightarrow4)$ -D-glucose bond (b) starch and the $\alpha(1\rightarrow4)$ -D-glucose bond (c) dextran and the $\alpha(1\rightarrow6)$ -D-glucose bond. Arrows indicate possible branching points.

Synthetic cationic polyelectrolytes. It is remarkable that most of the strength increasing synthetic cationic polyelectrolytes for paper come from a relatively small subset of water

soluble polymers: poly(acrylamides) (PAM, Fig. 9), polyethylene imines (PEI) and poly(vinylamines) (PVAm).⁴² The molecular weight should be high, arguably to increase the chances to form fiber-fiber connections. Small amounts of cationic groups allow electrostatic adsorption that increases the retention and efficiency of the polyelectrolytes.⁵¹ On the other hand, highly charged polymers such as PDADMAC have no strengthening effect.⁴² The structure does not offer any solution for why it does not offer strength. However, using highly charged cationic polymers in polyelectrolyte multilayers or polyelectrolyte complexes have proven to be efficient way to increase strength.^{81–86} Model studies made with glass fibers have shown that the strength improvement lies in the relative amounts of cationic and anionic groups on the surface with the optimal value near charge neutralization.⁸⁷

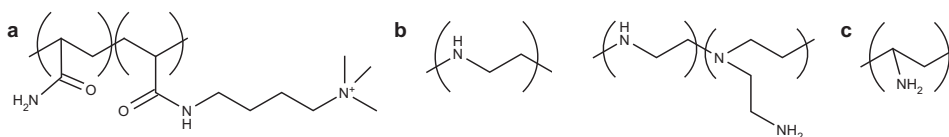


Fig. 9 Synthetic cationic polyelectrolytes. (a) cationic PAM (b) linear and branched PEI (c) PVAm.

PDADMAC. The diallyldimethyl ammonium chloride monomers that form PDADMAC are rather unique in their polymerization behavior: instead of forming a cross-linked structure they polymerize into a linear polymer. It was first synthesized by Butler in 1957.⁸⁸ The quaternary ammonium groups of this polymer guarantee a permanent charge. It was soon realized that the monomeric units of this polymer are cyclic but two possible structures were possible (Fig. 10). Later it was found out that the pyrrolidine (5-membered ring) structure form dominates (>98%).⁸⁹ The water solubility, permanent charge and high charge density make it effective in fixing disturbing anionic substances, e.g., from water circulations. In addition, the linear structure and wide availability has made PDADMAC indispensable in polyelectrolyte multilayer studies. Therefore, it can be regarded as a good model polymer.

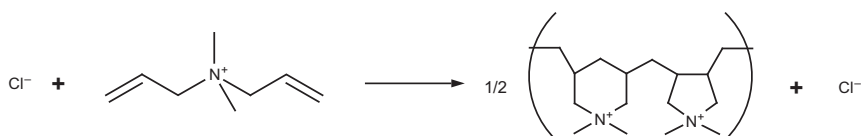


Fig. 10 PDADMAC polymerization reaction. PDADMAC with pyridine and pyrrolidine ring structures. The 5-membered ring (pyrrolidine) structure dominates (>98%).

Polybrene and other ionenes. Polybrene is only a single polymeric species in a large group of polymers called ionenes. They are unique among cationic polyelectrolytes, because the charge is part of the linear backbone of the polymer. Several ionenes were synthesized for this thesis, due to the discovered wet strengthening effect of polybrene (Paper IV). Therefore, we summarize here shortly the history and synthesis of the ionenes.

Commercially available polybrene was first introduced as an antiheparin agent in the 1950s.^{90,91} The use of polybrene in medical research continued further^{92–94} and the use

broadened closer to forest products science when in the 1968 complexation of polybrene with polysaccharides were reported for the first time.⁹⁵ Later, a Swedish group led by Lindström found it as an effective way to determine the charge of cellulosic fibers.^{96,97} Polybrene is an invaluable model polymer for adsorption studies, due to the low molecular weight, high charge density and low polydispersity.

Aliphatic ionenes were first synthesized by Lehman et al. in 1933,⁹⁸ but the name ionene was coined by Rembaum who made several key investigations on their synthesis.^{99–101} Ionenes are polymers of ditertiary amines and dibromides, which polymerize through the Menschutkin reaction.¹⁰² The naming convention is as follows: The length of the linear chain (the number of CH₂ groups) of the ditertiary amine is X CH₂ units and linear chain of the dibromide has Y CH₂ units. The numbers are written inside the brackets, separated by comma to form the chemical formula for the monomer and thus the name of the polymer (i.e. [X,Y]-ionene). Polybrene is [3,6]-ionene. Thus, it is a polymer of *N,N,N',N'*-tetramethyl-1,3-diaminopropane and 1,6-dibromohexane monomers (Fig. 11).

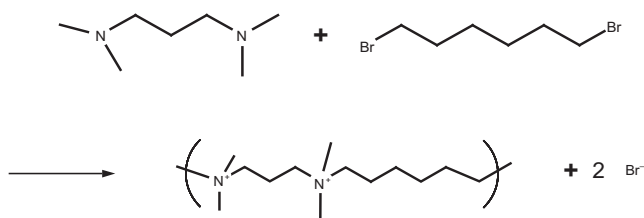


Fig. 11 Polymerization of [3,6]-ionene (polybrene).

CMC is the most common ionic cellulose derivative prepared by etherification (carboxymethylation) of cellulose.⁵⁵ It was first synthesized in 1918.⁵⁵ CMC is produced in a variety of molecular weights and degrees of substitution that influence its solubility and viscosity. The usual range is from DS 0.5 to 1.5 and the molecular weight depends on the reaction conditions and the initial molecular weight of the starting material (cellulosic fibers). The rather high DS of common CMC grades is probably due to the insolubility of CMC at low DS (cellulose is insoluble in water). The distribution of the carboxymethyl groups in cellulose is interesting. First, the reaction to form CMC is governed by the preference of the monochloroacetic acid to react with the hydroxyl groups in C-2 and C-6 positions (Fig. 12).⁵⁵ The low interaction of C-3 hydroxyl groups in etherification reactions is not entirely clear. However, it has similar tendency as nitration and other esterification reactions of cellulose that also have low reactivity in the C-3 hydroxyl groups.^{103,104} Second, the glucose unit in cellulose has three hydroxyl groups that react to form mono-, di- and tri-substituted glucose units.⁵⁵ (The tri-substituted glucose unit being a rarity due to the low reactivity of the C-3) Therefore, it is possible for CMC with DS 1 to have 30% of unsubstituted glucose units, instead of the expected one carboxymethyl group per glucose unit because of the large amount of disubstituted glucose units. It is most likely due to these unsubstituted glucose units why CMC can be adsorbed irreversibly onto cellulose fibers even though the electrostatic repulsion between fibers and CMC is difficult to

overcome.^{47,48,105} Therefore, adsorption of CMC requires suppression of the electrostatic charge.⁴⁸ Fibers modified by CMC have shown excellent dry strength properties and the mechanism lies probably in the extreme swelling capability of the CMC thus improving the chances of the swollen fiber surfaces to form fiber-fiber bonds.^{106–108} CMC is also known to improve paper formation by dispersing the fiber suspension through electrostatic repulsion,¹⁰⁹ and reduced friction between CMC modified cellulose surfaces.^{110,111} The ability of (high M_w) CMC to specifically adsorb to the exterior of the fibers,⁵⁶ makes it an ideal polymer to increase the anionic charge on the surface. Thus, CMC enables the study of the fiber-fiber interactions with minimal changes in the cell wall composition of the fiber.

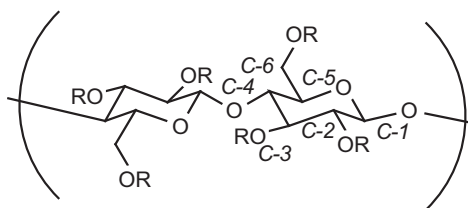


Fig. 12 CMC structure. The carbons indicated by numerals from C-1 to C-6. ($R=CH_2COOH$ or H)

2.3.2. Wet strength mechanisms and agents

In the process of conducting the experiments for Paper II, we found out that the combination of CMC and polybrene gives wet strength after drying and rewetting. This kind of wet strength is rare, since almost all the reported wet strength agents are cross-linking. In addition, there are no mechanisms available to explain how the CMC+polybrene (or CMC+[6,12]-ionene) system functions and yields wet strength for paper (Paper IV). Therefore, it is useful to give a short description of the existing mechanisms and the wet strength agents to summarize which mechanisms are available to the CMC+polybrene system.

The two mechanisms. The mechanisms of action of wet strength additives have been discussed in many publications.^{51,112–116} There are two generally accepted mechanisms that are thought to bring wet strength to fibers. The first one is called the *protection mechanism* and it is based on the fact that if the fiber-fiber bond is covered with hydrophobic material the resulting covering material resists water intrusion and keeps the fibers bonded by protecting the existing fiber-fiber bonds.⁵¹ The other mechanism is known as the *reinforcement mechanism*. As the name suggests, it functions by strengthening the existing fiber-fiber bonds through new – usually covalent – bonds between the fibers themselves. The resulting covalent fiber-fiber bonds resist the dispersing effect of water and wet-strength is attained.⁵¹

The four attributes of wet strength agents. Apart from the two accepted mechanisms how the wet strength agents work, some design parameters have also been suggested.

Espy summarized four attributes that are necessary for a wet strength agent: (i) water-solubility, (ii) cationicity, (iii) polymeric nature and (iv) reactivity.¹¹⁷

Three classes of wet strength adhesion. In addition to the mechanism and design parameters of the wet strength agent, Pelton has suggested three classes of adhesion that describe the function of a wet strength agent:^{42,43,118–124} (i) heat curing, (ii) damp dried and rewetted and (iii) instantaneous wet adhesion. The heat curing polymers are added before the fiber web has formed and they are activated in an already formed sheet by heat treatment in the drying section or other suitable high temperature location in the paper machine. The drying sections of modern paper machines can easily cure paper while it is drying. Therefore, heat curing wet strength agents such as polyamide-co-poly(amine-epichlorohydrin) (PAE) and urea-formaldehyde (UF) resins are common in commercial applications (Fig. 13). In contrast, damp dried systems do not need heat activation. Treating an already formed fiber-web with a wet strength agent and subsequently drying the paper to activate the wet web yields “damp dried” wet strength. PVAm and PEI are examples of damp dried wet strength agents (Fig. 9).^{125,126} Finally, the instantaneous wet adhesion is reserved only for those wet strength agents that form permanent fiber-fiber bonds when fibers are in low concentration in solution, i.e., before the formation of the fiber web. Instantaneous wet adhesion has remained elusive and scientifically advanced concepts such as PVAm boronate¹²⁷ or bioconjugation¹²⁸ are needed to gain wet strength.

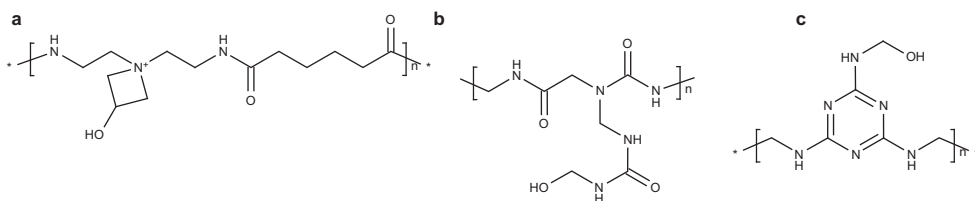


Fig. 13 Commercial wet strength agents. Examples from three commercial polymers. (a) PAE polyamide-co-poly(amine-epichlorohydrin) polymer, (b) UF urea-formaldehyde and (c) MF melamine-formaldehyde resins.

Formaldehyde resins. Formaldehyde can be used alone as a wet strength resin. However, the high temperature and acidity needed has prohibited its commercial use. Through some initial tests during the World War II, urea was found to be a good polymerizing agent for formaldehyde.¹²⁹ In addition to the acidic and heat curing UF resin, melamine-formaldehyde (MF) is another popular acidic and heat curing resin (Fig. 13c).

PAE. The change of papermaking in the 1970s to neutral and alkaline pH rendered the acidic formaldehyde resins impractical. To replace UF and MF resins a new class of polymeric wet strength agents was developed. The amine groups in PAE are reacted with epichlorohydrin to form reactive azetidinium chloride.⁵¹ PAE reacts with carboxylic groups to form covalent bonds that are essential for wet strength development. For this reason, carboxylic group rich CMC is used together with PAE. The similarity of nylon to PAE probably explains how PAE was invented.¹³⁰

PVAm, poly(ethyleneimine) (PEI) and chitosan. The most common linear amine functional polymers known to improve both the wet and dry strength of paper are PVAm,

PEI and chitosan.^{116,122,123,131} The linear amine functionality gives reactivity with the hydroxyl groups of cellulose that improves initial wet strength to some extent. Chitosan (deacetylated chitin, mostly polymerized $\beta(1\rightarrow4)$ -D-glucosamine) has gained interest in many applications, since the polymer is cationic and has carbohydrate backbone.¹³² Both these characteristics improve adsorption on cellulosic fibers.

Wet strength of cellulose. In addition to these wet strength agents, it is important to note that cellulose is capable of resisting water even though usually paper disintegrates readily in water. Cellophane is a well-known example that demonstrates the wet strength of cellulose. Furthermore, an already formed paper can be converted to water resistant paper by dissolving the surface layers of a fiber by strong sulfuric acid and subsequently washing the acid away.¹³³ Drying the paper forms dense crystallized layers between fibers that are impenetrable by water.¹³⁴ This kind of paper is called vegetable parchment and it has been used to package oily products and it is also known by its common name, butter wrap.

2.4 Hydrophobization of paper

The hydrophobization of paper is a widely explored topic and the commercial papermaking has found effective chemicals that hydrophobize paper.¹³⁵⁻¹³⁹ The chemicals usually have a long hydrocarbon chain (C18 or more) and a reactive group that attaches the chemical to fibers. However, in this work, a polymeric approach for hydrophobization was taken (Paper III): An unreactive polymer that has cationic groups for adsorption (polyelectrolyte adsorption) and hydrophobic groups to hydrophobize paper. The obvious challenge was how these polymers can be dispersed in water. A specific class of polymers called amphiphilic diblock copolymers can be micellated and subsequently dispersed in water. These dispersions could be used much like traditional hydrophobization agents: Added to fibers in solution and cured at high temperature to obtain hydrophobized fibers. The following short overviews give information of the traditional hydrophobization agents and amphiphilic block copolymers to let the reader appreciate better the results of this work.

2.4.1. Hydrophobization (sizing)

Hydrophobization (sizing) of paper is an important part of modern papermaking. The traditional sizing chemicals have been rosin sizing (acidic pH), when paper was made in acidic conditions. The shift to neutral and alkaline papermaking brought alkyl ketene dimer (AKD) and alkenyl succinic anhydrides (ASA) as the main chemicals to hydrophobize paper (Fig. 14).

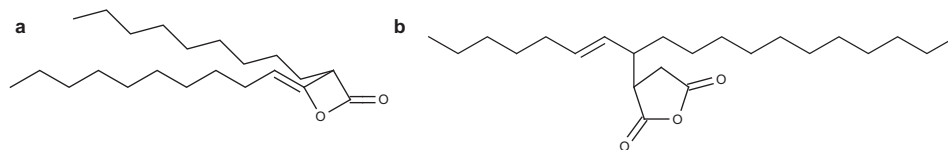


Fig. 14 Sizing agents. Examples from the two commercial types: (a) Alkene ketene dimer (AKD) and (b) alkenyl succinic anhydride (ASA).

2.4.2. Mechanism of neutral sizing

The widely accepted mechanism in both AKD and ASA sizing involves esterification of the reactive chemicals towards cellulosic hydroxyl groups.^{135–137,140} The primary challenges for these molecules is the adsorption (retention) on the fibers and that the adsorbed molecules react. However, one of the most interesting practical aspects of sizing is the spreading of the size on the surface of the fibers. After a while this spread layer that can be molecularly thin, loses its reactivity. This passivated surface is hydrophobic due to the long hydrocarbon chains found in AKD and ASA. In addition, the hydrophilic cellulose OH-groups are shielded from water and thus hydrophobization (sizing) is achieved. ASA and AKD are almost always added as an aqueous emulsion and dispersion, respectively, that has been stabilized with cationic starch.^{135,136,140} The diameter of the dispersed molecules is in the order of 1 μm and the maximum surface coverage is achieved roughly at 10 mg AKD per gram of fiber.¹⁴¹ This amount is in direct contrast to the extremely low amounts necessary for hydrophobized paper where even ~ 0.1 mg/g of AKD is needed to hydrophobize paper.¹³⁸ However, this demonstrates how spreading of AKD evenly on the surface reduces the amount needed for hydrophobization. ASA has arguably similar behavior, but unlike AKD, the reacted ASA has acidic groups that are hydrophilic (above pH 4.5). Therefore, some of the carboxylic groups in hydrolyzed ASA can be complexed with Ca^{2+} or Al^{3+} that possibly improve the hydrophobization.¹⁴²

2.4.3. Amphiphilic diblock copolymers

The amphiphilic diblock copolymers are a wide group of polymers that are generally considered as the macromolecular counterparts of surfactants. Usually, they are water soluble, such as poly(ethyleneoxide)-*block*-poly(propyleneoxide) (PEO-*b*-PPO)¹⁴³, but also water insoluble amphiphilic block copolymers exist.¹⁴⁴

Amphiphilic molecules possess both hydrophilic (literally, water loving) and hydrophobic (literally, water fearing) moieties. The amphiphilic nature of these polymers bestows unique properties in selective solvents, at surfaces and in the bulk, due to separated morphologies. Their characteristic self-organization often results in the formation of aggregates, micelles, and other structures.¹⁴⁵ In aqueous solution, the block copolymer micelles consist of a compact core of the insoluble chains, surrounded by a corona composed of the soluble chains. Based on the length of the soluble block two types

of micelles can be distinguished: “crew-cut” and star-like. Crew-cut micelles have short coronal “hair” and star like micelles have long “threads” extending to the solution (Fig. 15).

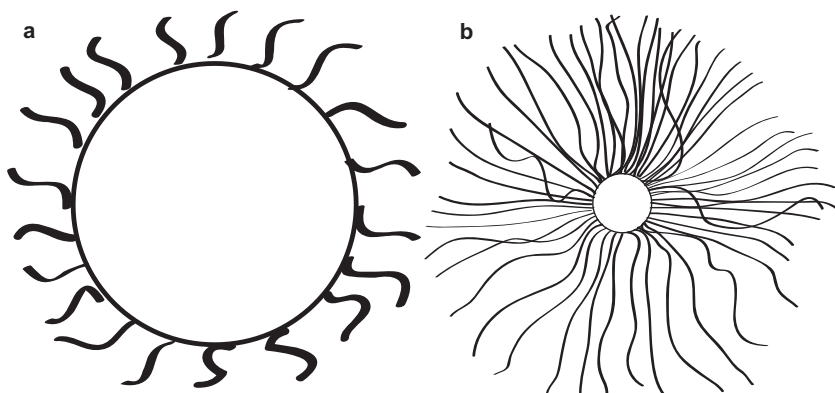


Fig. 15 Schematic representation of diblock copolymer micelles. (a) “Crew-cut” micelle (b) star-like micelle.

The formation of block copolymer micelles is due to two opposite forces: An attractive force between the core-forming (hydrophobic) chains and a repulsive force between corona chains (either ionic or due to solvation). The interplay of these forces prevents the continual growth of the micelles into macroscopic aggregates.^{144,145} Macromolecules are thermodynamically driven to self-assemble in order to minimize the contact between immiscible components.¹⁴⁶

Amphiphilic diblock-micelles in this work. The insoluble block in the polymer allows micellization with a procedure introduced by the Eisenberg’s group.¹⁴⁷ The basis of this approach is that the block copolymer is dissolved in a solvent that solubilizes both blocks. Subsequent (slow) addition of water leads to aggregation of the hydrophobic block to form micelles. By carefully controlling the micellization, this procedure yields a selection of morphologies such as spherical, rod, vesicle and other complex structures.¹⁴⁸ The spherical micelles have the advantage of uniformity (polydispersity index = $M_w/M_n < 1.1$)^{147,149} and the micelles are isotropic i.e. the adsorption of the micelles on a substrate does not depend on the orientation of the micelles, which facilitates the interpretation of the results.

Typical micelles have a rather low aggregation numbers which suggests weaker dependence on the diameter of the micelle to insoluble block than those predicted from scaling theories (diameter \sim (number of monomeric units)^{2/3})^{144,150} This is attributed to the low interfacial tension between the core and the solvent (such as dimethylformamide, DMF) during micellization.¹⁴⁵ The weak dependence is not surprising. The results of Zhang et al. confirm that the block copolymer chain-exchange is completely halted already when H₂O/DMF ratio in the solution is as low as 1/9 and will remain so in completely aqueous solutions (Fig. 16).¹⁵¹ The figure demonstrates the extreme stability and selectivity that is characteristic of amphiphilic block copolymer micelles: The water efficiently freezes the micelle configuration already at low water concentrations. Therefore, the usual dynamics of micelles do not exist, since the polymers are confined into their micelle form and they are no free polymers in solution. Finally, instead of micelles, aggregates or frozen

micelles can be a better definition, since the term “micelle” suggests that the system is in dynamic equilibrium and that continuous chain-exchange with the solvent is prevalent. However, the term micelle has been widely adopted, since the structure of the frozen micelles is similar to proper micelles.¹⁴⁴ In addition, the frozen structure is an advantage, since monodisperse micelles can be obtained relatively easily and the unimers are not hindering the adsorption on surfaces.

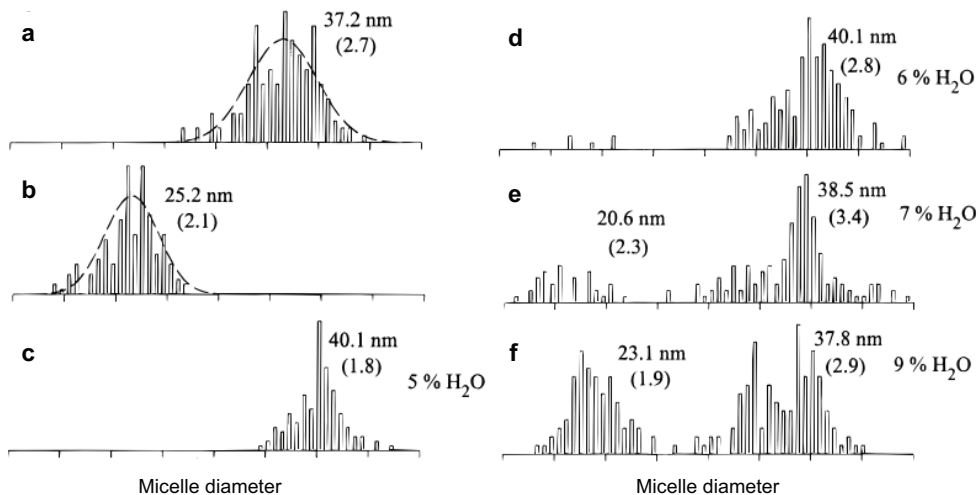


Fig. 16 Aggregation of diblock copolymer micelles. Size distribution of the spherical micelles made from (a) high M_w diblock copolymer and (b) low M_w diblock copolymer. Mixing the above two different copolymer micelle solutions at different water contents: (c) 5 wt % (d) 6 wt % (e) 7 wt % (f) 9 wt % give different distributions. The numbers are the average core diameters with the standard deviations in parentheses for each size distribution. Already at 9% H_2O two distinct micellar aggregates are formed showing the immiscibility and extreme stability of the micelles.¹⁵¹

3. Experimental

This chapter gives a short description of the material and methods used in this thesis. Detailed experimental descriptions are presented in Papers I-IV and their supporting information.

3.1 Materials

3.1.1. Cellulosic fibers

The cellulosic fibers were the basis for this research. The pulp fibers were obtained from fully bleached (elementary chlorine free bleaching, ECF) chemical pulp produced in Botnia, Äänekoski, Finland. Only long fibers section was used, i.e., the fines were removed from the pulp through 200 mesh with 6.0 g/L consistency, mixing and 5.0 L/min flow rate for tap water (conductivity 200 $\mu\text{S}/\text{cm}$) for 1h 30 min to give a clear filtrate (adapted from SCAN-M 6:69 standard). Furthermore, the carboxylic acid groups were ion-exchanged to Na^+ to remove interfering metal cations such as Ca^{2+} and Al^{3+} .³⁹ The standard method ensures that all carboxylic acid groups have the same counter ion (Na^+). First, the counter ions of the carboxylic groups in the fibers were replaced to protons by first washing them with deionized water, then stirring the mixture for 60 min in 10 mM HCl solution and finally washing the fibers with deionized water twice to obtain conductivity $<5 \mu\text{S}/\text{cm}$. The protons were then replaced by sodium ions by using 0.005 M NaHCO_3 and adjusting the pH to >8 by 1 M NaOH. This solution was mixed for 40 minutes, filtrated and washed with deionized water until conductivity was again $<5 \mu\text{S}/\text{cm}$. (Fig. 17a) The fibers were kept refrigerated (4-6 °C) after fines removal and Na-washing at conc. $\sim 20\%$, this conditioning is a rather standard method to preserve the pulp between experiments. We have listed the most important characteristics of the used birch pulp in Table 2 with some literacy values. The long fiber fraction does not have appreciable amount of lignin ($<1\%$) nor extractives, since the bleaching stages have removed effectively all lignin content and the removed fines contained most of the extractives.¹⁵² The fibers were unrefined and thus had high freeness (~ 20 in Schopper Riegler number). Typical length of birch fibers are ~ 1 mm and coarseness ~ 100 g/m.

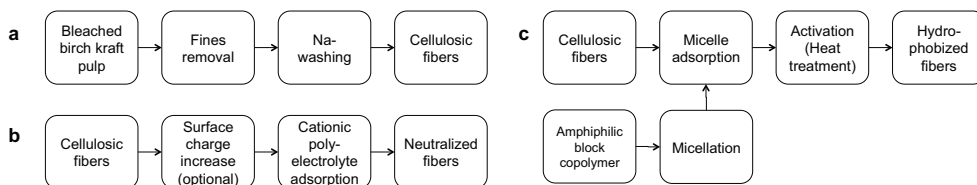


Fig. 17 The experimental pathways for this work. (a) Ordinary bleached birch kraft pulp is treated to prepare cellululosic fibers with controlled size (long fibers) and charge (carboxylic groups in Na-form) (b) The cellululosic fibers are pretreated with different CMCs to increase surface charge. Subsequently different cationic polyelectrolytes are used to obtain neutralized fibers with different characteristics such as wet strength (Papers I,II and IV) (c) The cellululosic fibers are treated with amphiphilic block copolymer micelles that with heat treatment hydrophobize fibers. (Paper III)

Table 2. Typical composition of bleached birch kraft pulp fibers in this work as well as comparison to some literary values.

	In this work	Asikainen et al. ¹⁵²
D-(+)-Glucose (%)	70.8	71.7
D-(+)-Xylose (%)	28.6	26.1
D-(+)-Mannose (%)	0.6	-
L-Rhamnose (%)	<0.1	-
D-(+)-Galactose (%)	<0.1	-
Total charge ($\mu\text{eq/g}$)	100	153.7
Surface charge ($\mu\text{eq/g}$)	9	-
Fines content (%)	~5	4.6

3.1.2. Polymers

Polyelectrolytes. The employed polyelectrolytes were two CMCs (90 000 g/mol DS 0.7 and 700 000 g/mol DS 0.9, as reported by the producer Sigma-Aldrich), hexadimethrine bromide, (polybrene, [3,6]-ionene, $\geq 94\%$, Sigma), polydimethyldiallylammonium chloride (PDADMAC, Sigma) and several synthesized ionenes. The molecular structures of these polyelectrolytes are presented in Fig. 18 and their measured properties are tabulated in Table 3. To determine the charge in polyelectrolyte titrations, sodium poly(ethane sulfonate) (PES-Na, M_w 19 100 g/mol Oy G.W. Berg & CO Ab/BTG Müttek GmbH) was used. The PDADMAC was either used as received or ultrafiltrated before use with Minisette membrane cassette system (300K Omega 0.75 ft², cut off at >300 000 g/mol, Filtron Technology Corporation, Northborough, USA) at 2.0 bar and 1.0 g/L. The CMC was used to increase the surface charge and the cationic polyelectrolytes were used to neutralize the fibers (Fig. 17b).

Ionenes. Several ionenes were synthesized in Paper IV using acetone as a solvent. In a typical synthesis, 10 g of diamine was dissolved in 150 ml acetone at ambient conditions. Subsequently, the reaction flask was placed in oil bath and dibromide was added under continuous stirring. The reaction proceeded 24 hours in which time the synthesized polymer precipitated. This precipitate was further purified and analyzed. Polymer formation was confirmed by ¹H NMR as a peak at 3.3 ppm originating from CH₃ groups in the quaternary ammonium ions. ¹H NMR was measured with 400 MHz NMR (Bruker

Ultrashield 400 Plus) using deuterium oxide as a solvent. The ionenes [3,3], [6,6] and [6,12]-ionenes polymerized effortlessly (Paper IV).

Table 3. The characteristics of the polyelectrolytes used. Molecular weight (M_w), polydispersity index (M_w/M_n) and charge density (CD). (Paper IV).

Polymer	M_w (kDa)	M_w/M_n	CD (meq/g)
Low M_w CMC	66	2.7	3.8
High M_w CMC	690	1.9	4.1
PDADMAC	800	12.6	6.2
[3,3]-ionene	17	2.7	6.0
polybrene i.e. [3,6]-ionene	6.3	1.8	5.3
[6,6]-ionene	25	1.8	4.8
[6,12]-ionene	63	1.2	4.0

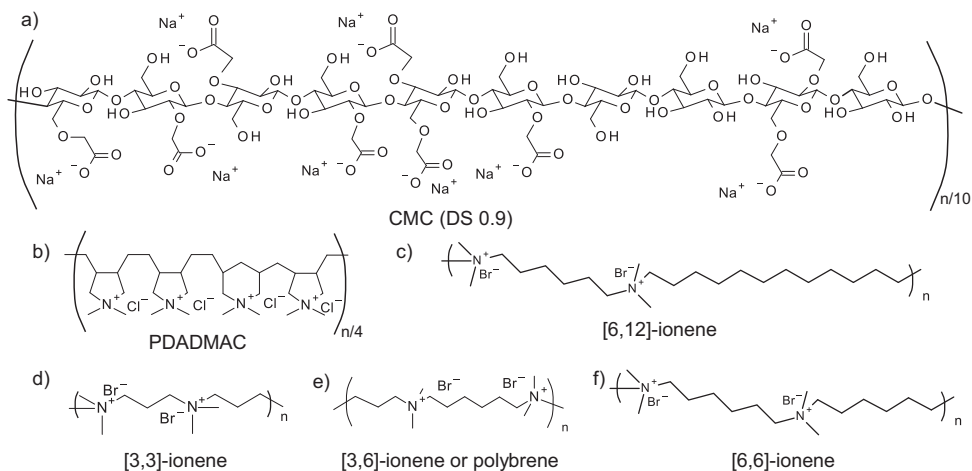


Fig. 18 The polymers used in this work. Polymers used and synthesized for this study. (a) Schematic representation of CMC with DS 0.9. (b) Schematic representation of the high M_w PDADMAC. (c-f) Various ionenes synthesized for this study. (c) [6,12]-ionene (d) [3,3]-ionene (e) [3,6]-ionene or polybrene (f) [6,6]-ionene.

Block copolymers. Several polystyrene-*block*-poly(*N*-methyl-4-vinyl pyridinium iodide) block copolymers were obtained from PolymerSource Inc. (Montreal, Canada, see Fig. 19). We used the polymers as received, due to the extensive characterization given upon purchasing the material: The company provided the polydispersity and molecular weight data based on size exclusion chromatography (available from PolymerSource Inc.) and the company confirmed the complete quaternization by the disappearance of the pyridine band at 1412 cm^{-1} in FT-IR spectrum

Micellation of the block copolymers. Micellation was done according to the procedure described in detail by Gao *et al.* In short, approximately 0.5 g block copolymers were mixed in 10 g DMF (analytical grade, Sigma Aldrich) until dissolved (~ 24 h). The solutions were filtered through Whatman 541 filter paper (GE Healthcare, USA) to remove any undissolved particles. Subsequently, water (MilliQ, conductivity $0.5\ \mu\text{S}/\text{cm}^{-1}$) was slowly added from a peristaltic pump adjusted to $0.25\text{ mL}/\text{min}$, until the solution reached volume of approx. 100 mL. The micellar solutions were dialyzed against distilled water for

3 days in continuous flow dialysis equipment. Spectra/Por dialysis tubes of 6000 M_w cut-off (Spectrum Europe B.V., Breda, The Netherlands) were used for dialysis. Finally, the solution concentration was determined by drying three ~ 1 g samples in oven (105°C). The micelles were adsorbed to cellulosic fibers and used to hydrophobize paper (Fig. 17c).

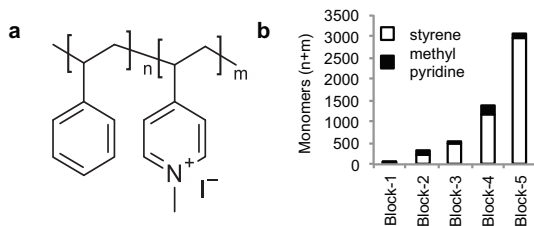


Fig. 19 The properties of the block copolymers and the micelles made from these polymers. (a) Chemical structure of the block copolymer: n , polystyrene and m , polystyrene-*block*-poly(*N*-methyl-4-vinylpyridinium iodide). (b) The 5 chosen block copolymers showing the total monomer content ($n+m$) divided between the styrene (white column) and methyl pyridine (black column). (Paper III).

3.2 Methods

3.2.1. Adsorption isotherms

The charge of the CMC treated fibers was determined from the filtrate by MÜTEK particle charge detector (PCD-03, Mütek Analytic, Herrsching, Germany). A series of additions of polybrene or PDADMAC were added to the fiber suspension (0.25 g of fiber in 50 cm^3 of 0.1 mM NaCl solution). Treatment time was 30 min, time that has been reported to be sufficient for the chosen polyelectrolytes to adsorb into full extent.³⁹ The solutions were filtrated and the cationic polyelectrolyte in the filtrate was titrated with PES-Na solution to the endpoint where the streaming potential changed sign. The amount of titrant was equated to the equilibrium concentration of cationic polyelectrolyte in the solution. The amount of cationic polyelectrolyte in the solution was compared to the added amount and adsorbed cationic polyelectrolyte was calculated from the difference. An adsorption isotherm was plotted according to the adsorbed amount in fiber *vs.* equilibrium concentration in the filtrate (Fig. 20). The amount of surface and total charge were determined from the plot by extrapolation to the zero concentration, by using PDADMAC and polybrene, respectively. (Paper II)

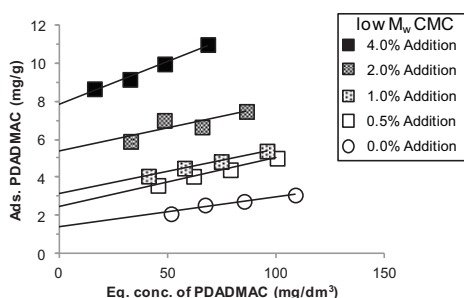


Fig. 20 Typical adsorption isotherms for CMC treated fibers. 4 different additions of PDADMAC (low M_w) were adsorbed on CMC pretreated fibers. The excess PDADMAC were measured with polyelectrolyte

titration and the adsorbed amount determined from the titration. The neutralization point (and surface charge in this case) was determined from the intercept of zero equilibrium concentration of PDADMAC. (Paper II)

3.2.2. Thermoporosimetry

Thermoporosimetry is a method where water held in the capillaries of porous materials melts at a depressed temperature. It is based on the triple-point shift of melting of frozen water inside the cavities, which is summarized by Gibbs-Thomson equation.¹⁵³

$$d = \frac{4VT_0\sigma_{ls}}{H_m\Delta T} = \frac{k}{\Delta T} \quad (\text{Eq.1})$$

where V is the molar volume, σ_{ls} is the interfacial tension between solid (ice) and liquid (water), T_0 is the melting point at NTP and H_m is the latent heat of melting and the constant $k = 43.12 \text{ nm K}$ for cylindrical pores with diameter d . This method was used because it has been adjusted with Hg porosimetry¹⁵³ and extensively calibrated with a series of controlled pore glasses (CPG) and high purity silica gel samples. Isothermal step melting method was chosen because of its suitability for pulp fibres.¹⁵⁴ Mettler-Toledo Differential Scanning Calorimeter DSC 821 with intracooler and autosampler was used. Gas was N_2 . Elaborate calibration was made to achieve $\pm 0.02 \text{ }^\circ\text{C}$ accuracy in the region -50 to $0 \text{ }^\circ\text{C}$.¹⁵⁴ Measurement points were $-33 \text{ }^\circ\text{C}$, $-20 \text{ }^\circ\text{C}$, $-17 \text{ }^\circ\text{C}$, $-14 \text{ }^\circ\text{C}$, $-11 \text{ }^\circ\text{C}$, $-9 \text{ }^\circ\text{C}$, $-7 \text{ }^\circ\text{C}$, $-5 \text{ }^\circ\text{C}$, $-3.5 \text{ }^\circ\text{C}$, $-2.5 \text{ }^\circ\text{C}$, $-1.6 \text{ }^\circ\text{C}$, $-0.8 \text{ }^\circ\text{C}$, $-0.4 \text{ }^\circ\text{C}$, $-0.2 \text{ }^\circ\text{C}$. Each temperature was retained for 7-10 minutes to ensure that all the water had melted before ramping to the next temperature. Ramping speed was $1.0 \text{ }^\circ\text{C}/\text{min}$. The moisture content of the samples varied between $1 - 2 \text{ g/g}$ with most of the samples in the optimal region of $1.2 - 1.5 \text{ g/g}$. Pore volume for a given pore diameter was evaluated from the power-time area in each of the isothermal steps and non-freezing water (NFW) was evaluated by melting and refreezing the sample and subtracting the total freezing water from the moisture content of the sample according to the method described by Maloney and Paulapuro.¹⁵³ The minute differences in the DSC scans shown in Fig. 21 exemplify the difficulties in obtaining the data and multiple samples were measured to obtain the results in Paper I. The polyelectrolytes and their associated thermodynamical properties such as osmotic pressure and pronounced non-ideality at low ionic strengths due to the dissociated counter-ions (Donnan effect) could interfere with this purely thermodynamical measurement. However, (i) the method has been used in many studies involving cellulosic fibers, becoming nearly a standard method.¹⁵³⁻¹⁵⁷ (ii) The cellulosic fibers could be considered to be polyelectrolytes themselves due to the negative charge of the dissociated carboxylic groups.¹⁵⁸ (iii) The results in this thesis and elsewhere showed quantitative differences between never-dried and dried fibers,^{154,159} thus demonstrating that the dissociated counter-ions of the polyelectrolytes do not interfere substantially with the results i.e. the Donnan effect is minimal. (iv) The cationic polyelectrolyte treated fibers showed substantial difference (Paper I), while anionic polyelectrolyte treated fibers (CMC-treated fibers) failed to show drastic differences (see, later in the text.) Finally, (v) the

cryoscopic effect to the melting point is very minor in the applied ionic strength (Paper I, supporting information).

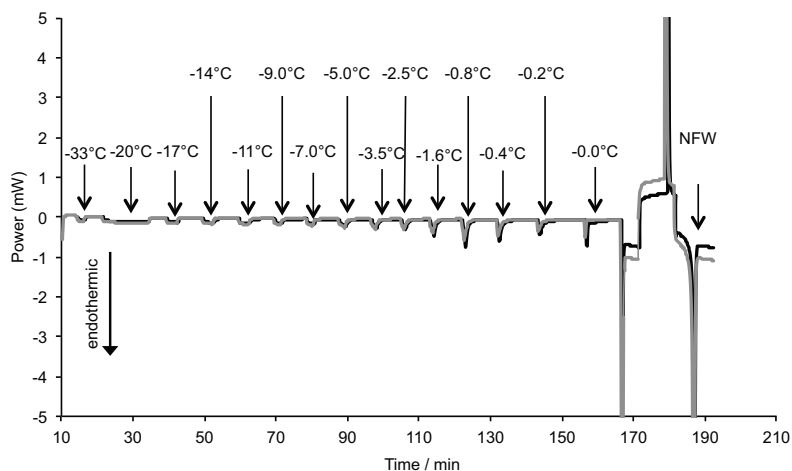


Fig. 21 Example of actual thermoporosimetry data. The measured temperatures are shown in addition to the times that temperature was held until ramped to the next temperature. The black and grey samples demonstrate a single scan of reference fibers and fibers that have been neutralized by polybrene, respectively.

3.2.3. Sheet preparation and testing

Bleached birch kraft pulp fibers without fines section were the standard fiber for all the work in this thesis (see Fig. 22). The fibers were altered by adsorption of CMC and/or cationic polyelectrolyte. Subsequently, these fibers were formed into paper sheets or, alternatively, into thick sheets (dynamic drainage analyzer, DDA filtration) and dried. The latter type of paper mimics thick market pulp sheets and after drying the DDA sheets were rewetted and formed into paper sheets with the same grammage as the paper made from never-dried fibers. Therefore, we obtained never-dried and once dried fibers and could measure the paper properties made out of these fibers.

Pulp drying. DDA was used to obtain sheets with grammage 600 ± 30 g/m². These 10 cm diameter round sheets were clamped with a screw press between heavy rings of aluminum with 10 cm diameter, with sufficient pressure applied to the rim 0.3 cm thick. Sheets were dried with geometrical restriction at 80 °C for 60 min to gain dry-matter content of $95 \pm 1\%$. The pressed area was cut and the remaining sheet was rewetted overnight and disintegrated. (Papers I-II,IV).

Paper drying. Laboratory sheets were prepared according to SCAN-C 26-67, with following modifications: 60 g/m² sheets were done, deionized water was used and the drying was done in press with 1.0 ± 0.1 kg/cm² pressure (~ 0.1 MPa) and temperature 130 ± 1 °C in both press plates for 3 min (dry matter content was 90-91%, Fig. 23). Papers (I-IV)

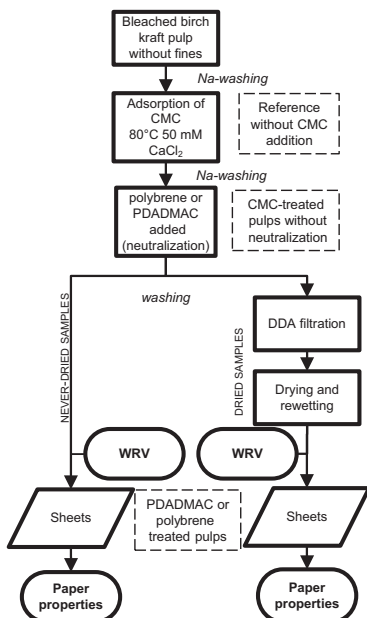


Fig. 22 Detailed workflow for the experiments. Na-washing removed unwanted cations and converted all the carboxylic acids in their carboxylate form. In some cases, the surface charge of the fibers was increased with CMC adsorption. Adding a known amount of cationic polyelectrolyte neutralized the anionic charge. The interplay of the increased charge and the multifunctional cationic polyelectrolytes form the framework of this thesis. After these treatments, both dried and never-dried samples were prepared for WRV and paper testing. (Paper II)

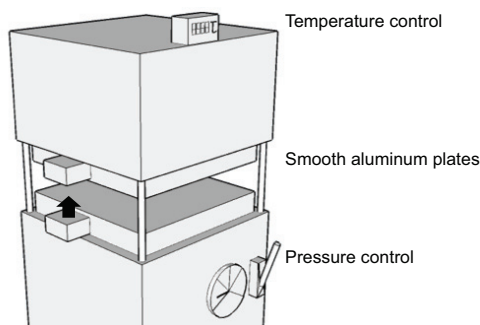


Fig. 23 Restricted drying device. The smooth aluminum plates prevent shrinking of the paper sheet upon drying. The pressure and temperature can be changed to control the drying process.

Wet and dry sample testing. Paper testing was done according to the following standards: Grammage ISO 536, thickness ISO 534, tensile testing (strength, stiffness, stretch and tensile energy adsorption) SCAN-P 38:80, tear strength ISO 1974, zero-span ISO 15361:2000, internal bond (Scott bond) strength T569 pm-00, air permeability SCAN-P 21:67, water adsorption (COBB₃₀) SCAN-P 12:64, opacity, light scattering and absorption coefficients ISO 9416. The wet strength was measured according to the SCAN-20:95 with several modifications: To compare directly the wet/dry strength ratios, the same equipment as tensile test SCAN-P 38:80 was used (Alwetron TH1 Tensile Tester, Lorentzen & Wettre, Sweden). Soaking time was kept minimal (30 s) in order to preserve

the integrity of the reference samples (which with longer soaking times disintegrated in water).

3.2.4. Other methods

Light scattering. To gain deeper information about the amphiphilic block copolymer micelles in Paper III, the hydrodynamic diameters of the micelles (D_h) were determined by Dynamic Light Scattering (DLS) using a Zetasizer Nano90 Instrument (Malvern Instruments, Worcestershire, UK) equipped with a 4 mW He-Ne laser (633 nm wavelength). The scattering angle used for the measurements was 90° and the Stokes-Einstein equation was used to convert the diffusion coefficient into hydrodynamic diameter. The Z-average size calculations were automatically done according to standards: ISO 13321 and ISO 22412. The micellar solutions were filtered through 1.0 μm filters (Acrodisk® CR, PTFE membrane, Pall Life Sciences, Ann Arbor, MI, USA) before analysis.

AFM imaging. AFM was used to visualize the adsorption of amphiphilic block copolymer micelles and the effect of heat treatment on model surfaces in Paper III. AFM images were taken with a Nanoscope IIIa Multimode scanning probe microscope (Digital Instruments Inc., Santa Barbara, CA, USA) equipped with J-scanner. The images were scanned in tapping mode with NSC15/AIBS tips (Ultrascharp μmasch , Tallinn, Estonia) with measured resonance frequency of 280 ± 10 kHz. Typical force constants were 46 ± 25 N/m and the radius of curvature of the tips was < 10 nm, as reported by the manufacturer. (Paper III)

Raman imaging. The location of the adsorption of the amphiphilic block copolymer micelles was determined qualitatively with Raman imaging from the cross sections of the micelle treated fibers. Pulp sheet samples were embedded in epoxy resin (Agar Low Viscosity Resin, Agar scientific, Essex, England) under vacuum and cured overnight before sectioning. Epoxy blocks were sectioned using a razor blade to obtain smooth surface for Raman imaging. Samples were analyzed with an alpha300 R Confocal Raman microscope (Witec GmbH, Germany, www.witec.de) at ambient conditions. The Raman spectra were obtained by using a frequency doubled Nd:YAG laser (532.35 nm, 10 M_w) and a Nikon 100 \times (NA=0.95) air objective. The Raman system was equipped with a DU970N-BV EMCCD camera behind a 600 lines/mm grating. The excitation laser was polarized horizontally. For each Raman image, an integration time and excitation laser power was varied depending on how prone the samples were to burn. The size of one pixel in the image was 0.33 μm . The baselines of the spectra were corrected with WiTec Project 1.94 (WiTec GmbH, Germany, www.witec.de) by employing a fifth order correction. For the Raman-image, the chosen wavenumbers were 999-1006 cm^{-1} for the block copolymer (characteristic for styrene aromatic C-C stretching), 1090-1100 cm^{-1} for the fiber cell wall (characteristic for cellulose C-O stretch) and 1719-1760 cm^{-1} for the epoxy resin. (Paper III)

TEM imaging. To deepen the characterization of the amphiphilic block copolymer micelles cryo-Transmission Electron Microscopy (cryo-TEM) was carried out using field emission cryo-electron microscope (JEOL JEM-3200FSC, JEOL Ltd., Tokyo, Japan).

Cryo-TEM was operating at 300 kV voltage. Images were taken in bright field mode and using zero loss energy filtering (omega type) with the slit width of 20 eV. Micrographs were recorded using Gatan Ultrascan 4000 CCD camera (Gatan Inc., Pleasanton, CA, USA). Specimen temperature was maintained at -255 °C during the imaging. Vitrified specimens were prepared using automated FEI Vitrobot device (FEI Company, Hillsboro, OR, USA) using Quantifoil 3.5/1 holey carbon copper grids (Quantifoil Micro Tools GmbH, Jena, Germany) with the hole size of 3.5 µm. Just prior to use grids were plasma cleaned by Gatan Solarus 9500 plasma cleaner (Gatan Inc., Pleasanton, CA, USA) and then transferred into an environmental chamber of FEI Vitrobot having room temperature and 100 % humidity. Thereafter, 3 µl of sample solution was applied on the grid and the sample was blotted once for 1 seconds and then vitrified in 1/1 mixture of liquid ethane and propane at temperature of -180 °C. The grid with vitrified sample solution were maintained at liquid nitrogen temperature and then cryo-transferred in to the microscope. *TEM image analysis.* The core sizes of the amphiphilic block copolymer micelles were analyzed with computer analysis to avoid laborious manual work that is prone to human errors. For the detection, spherical feature scale detection was implemented. The detection was semi-automatic, or visually guided, to improve detection accuracy. For each group of expected sizes, a guided algorithm was used to find objects at an expected size range. In addition, the algorithm was more accurate with spherical features that had two radii (i.e. ovals). From the two radii, the shorter one corresponded to the actual radius of the micelle and was identified as micelle radius. (Paper III)

Size Exclusion Chromatography (SEC). The size exclusion chromatography is challenging for charged polymers, because the diffusion is hindered with the electrostatic interactions between the tested polyelectrolyte and the columns. However, increasing the ionic strength of the solvent and using extensively tested systems and calibrations have allowed molecular distribution analysis for the polyelectrolytes.¹⁶⁰ (Papers I,II,IV)

PDADMAC and polybrene were analyzed with the following SEC system: Agilent 1100 (Agilent, USA) with refractive index detector, conventional calibration standard (PEO with M_w 1.9×10^3 to 1.3×10^6 g/mol) and column TSK GMPW_{XL} (Tosoh, Japan). The ionic strength was high due to the acetic acid buffer (0.3125 M CH₃COOH and 0.3125 M CH₃COONa, at 35°C). (Papers I, II)

The different CMCs were determined with the following SEC setup: ERC 3315a degasser (ERC Inc., Kawaguchi, Japan), Knauer Smartline Pump 1000 (Knauer, Berlin, Germany) Kontron Instruments HPLC 360 Autosampler (Kontron AG, Eching, Germany) and Wyatt Dawn Heleos (Wyatt Technology Europe GmbH, Germany) multi-angle light scattering (MALS) detector and the measurement parameters were the following: Ionic strength was high due to the NaNO₃ 0.1 M solution with small amount of NaN₃ (0.05%). Columns were PL aquaGel-OH 60, 50 and 40 (Agilent, USA). Calibration was done with pullulan standards (Polymer Standard Services, Mainz, Germany). CMC solutions were made by shaking the samples for 10 days in mobile phase solution and filtering through a 1.2 µm filter (Millipore, USA). (Paper II)

The ionenes ([3,3]-ionene, [6,6]-ionene and [6,12]-ionene) were measured with Waters 510 HPLC Pump and Waters 717plus Autosampler through the following column system: Ultrahydrogel 6*40mm Guard Column and Ultrahydrogel Linear Column 7.8*300mm (Waters), detection was done by combining signals from a refractive index (RI) detector (Waters 2414) and a light-scattering (LS) detector (Wyatt Dawn 8+). Ionic strength was high due to 0.5 M acetate buffer that was diluted with methanol until 10 vol-% methanol content was reached. (Paper IV)

4. Results and discussion

The most important findings of this thesis work are summarized in this chapter. The complete results are presented in the attached Papers I-IV.

4.1 Schematic model for porous structure of fibers based on thermoporosimetry and polyelectrolyte adsorption

The polyelectrolyte adsorption on cellulosic fibers is largely known. In Paper I, the influence of adsorbed polyelectrolytes on the pore size distribution of water-swollen fibers was investigated. The results in that article could be used to generate a model for porosity that is based on the representation of fiber that divides the surface fibrils and cell wall in two distinct regimes (Fig. 7). To generate this model, the results from drying and polyelectrolyte adsorption experiments were combined. The porosity was determined with thermoporosimetry, a method that involved meticulous DSC measurements. In short, three detectable types of water were present in the fiber cell wall: (i) water tightly bound on the surface of the microfibrils (i.e., non-freezing water, NFW), (ii) water residing in micropores (2-220 nm diameter), and (iii) water residing in macropores (>220 nm diameter). NFW and the water in micropores are detectable with thermoporosimetry whereas a WRV measurement quantifies all water, i.e., all of the three types.

4.1.1. Untreated bleached birch kraft pulp fibers

Thermoporosimetry for bleached birch kraft pulp fibers gave a distribution with pores of all sizes between 2-220 nm diameter with a peak in the 54 nm pore diameter (Fig. 24a) and it correlates well with previously obtained data for other cellulosic pulp fibres.¹⁵³ The initial high value of 2.2 nm pores in Fig. 24a is due to the fact that <2.2 nm column contains all the pores measurable in thermoporosimetry below 2.2 nm pore diameter (which equals the temperature range of -33°C – 20°C, Fig. 21) resulting in an initial column with high values.

The distribution has been fitted to a simple model (Fig. 24b). The model shows the cell wall pores explicitly and depicts the surface pores as residing between microfibrils. The model resembles Fig. 3 and Fig. 7, as it is divided to the surface and cell wall. How the

pores are divided between the surface and cell wall cannot be deduced yet. A partial answer can be obtained with a simple physical alteration, drying.

The micropore effect of drying for the untreated fibers is shown in Fig. 25a. Here, the actual pore volume distribution of untreated, never-dried fibers has been expressed in white columns whereas the negative values, denoted by the black columns, correspond to the decrease in pore volume after drying and rewetting the fibers. There was a slight decrease in the <2.2 nm diameter pores and a substantial decrease starting from ~ 17 nm diameter pores. This measurement directly indicated that the pores with diameters 2.5 – 17 nm are scarcely affected by drying and the hornification effect was most pronounced for the large pores (110–220 nm, Fig. 25a). Since all the pores were essentially closed in the dried fibers, the changes upon drying and rewetting gave a clue where the pores in the model (Fig. 24b) might be located. First, the WRV decreased from 1.68 to 1.29 while the micropore volume changed from 0.80 to 0.67 (Fig. 25a and Paper I). The substantial decrease (~ 0.4) in WRV while the micropore volume changes are slight (~ 0.1) is an important result. It is assumed in this thesis that the largest pore closure is assigned to the surface microfibrils in the schematics (Fig. 25c). In addition to drying, polyelectrolyte adsorption experiments could further elaborate the model.

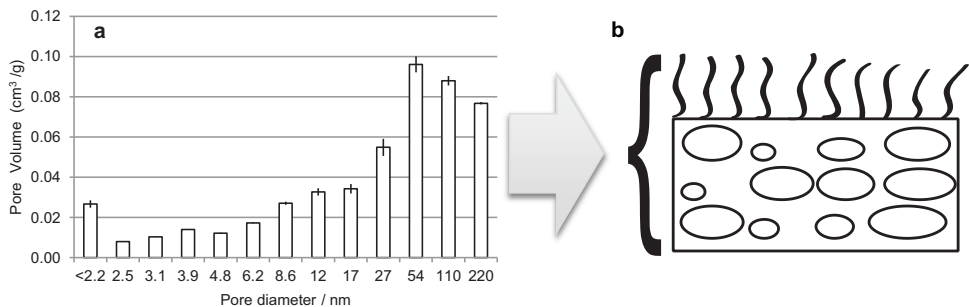


Fig. 24 Thermoporosimetry of untreated (reference) fibers. (a) The pore volume of the never-dried control reference (white columns). (b) Schematic representation of the porosity obtained from thermoporosimetry (Paper I).

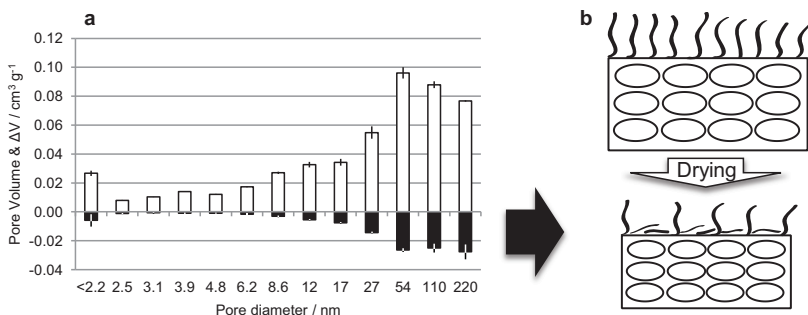


Fig. 25 Effect of drying. (a) The pore volume of the never-dried control reference (white columns) and the changes in the pore volume after drying and rewetting (black columns). (b) Schematic representation of the cell wall before drying as well as after drying and rewetting. The surface microfibrils are mostly affected by drying, while the cell wall also loses some of the porosity (Paper I).

4.1.2. Modification of fibers by cationic polyelectrolyte adsorption and its effect on the porosity of the fibers

The bleached (birch) kraft pulp fibers are inherently anionic (due to the occasional carboxylic acid groups in the hemicellulose xylan, Fig. 2). Therefore, a simple way to modify the fibers is by adsorbing cationic polyelectrolytes. The nature of the cationic polyelectrolytes is essential for modifying the properties of the cellulosic fibers in a desired way.

4.1.3. The effect of molecular weight on the adsorption location of the cationic polyelectrolyte

Usually, the highly charged, high M_w cationic polyelectrolytes adsorb only on the surface of the fiber.²⁹ The cell wall of the fibers can be accessed either by increasing the electrolyte concentration of the solute or lowering the molecular weight of the polyelectrolyte. The former suppresses the electrostatic interactions and allows a normal diffusion process to occur inside the fiber,³⁵ while the latter makes the pores accessible simply by reducing the polyelectrolyte size to the same scale as the pores in the cell wall.⁴¹ Decreasing the charge density of the cationic polyelectrolyte also allows adsorption inside the fiber, but we concentrated in this work on the highly charged cationic polyelectrolytes.⁴⁶ In Paper I, we studied the adsorption behavior of the high and low molecular weight highly charged polyelectrolytes from the point of view of their effect on fiber pores. Three different cationic model polyelectrolytes were used in Paper I: Polybrene as well as fractionated and unfractionated PDADMAC. The molecular weight distributions of the three model polyelectrolytes were analyzed first (Fig. 26a). In the figure the distribution is divided into two parts that separate the well-known division to surface and cell wall adsorbing parts. The dividing line has been in many occasions determined to be approx. 10^4 g/mol for highly charged linear cationic polyelectrolytes.^{35,38} The adsorption isotherms showed a rather flat adsorption isotherm for the fractionated PDADMAC, indicating only surface adsorption (Fig. 26b). Polybrene adsorbed an order of magnitude more indicating that the whole cell wall was accessed (Fig. 26c). The unfractionated PDADMAC adsorbed slightly more than the fractionated one. Based on the SEC data (Fig. 26a) we could hypothesize that the low M_w fraction of the unfractionated PDADMAC adsorbed inside the cell wall. The adsorption of low M_w highly charged cationic polyelectrolyte through a layer of high M_w polyelectrolyte has been shown before (Fig. 5).⁴¹ The hypothetical locations for the adsorption are shown in the insets in Fig. 26.

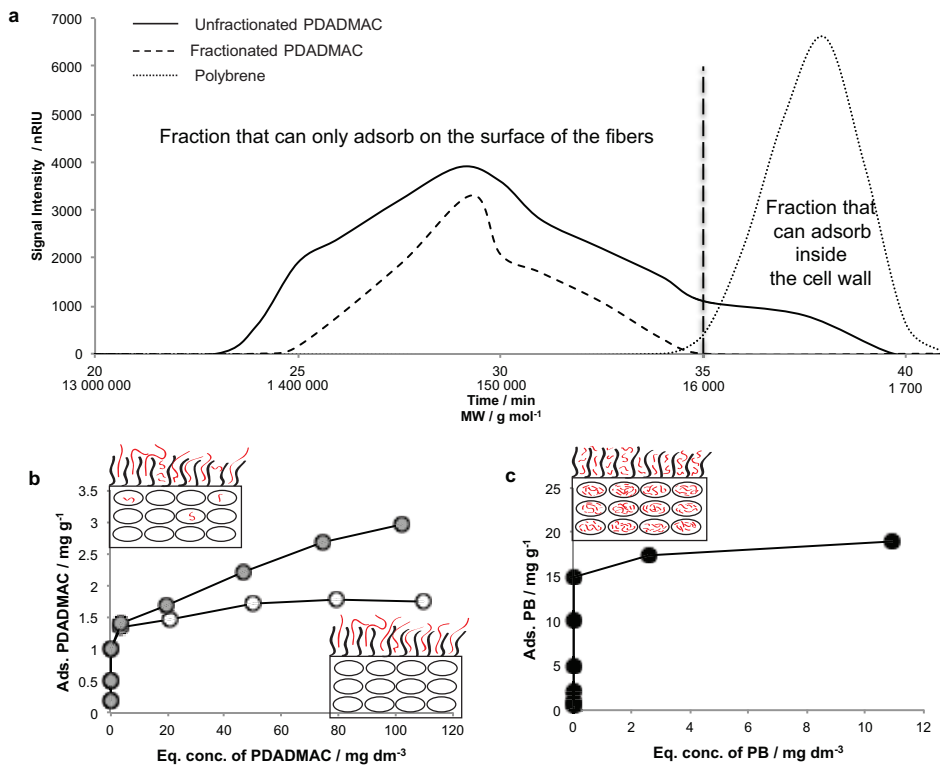


Fig. 26 SEC data and adsorption isotherms for model cationic polyelectrolytes. (a) Molecular weight distribution for model cationic polyelectrolytes. (b) Unfractionated PDADMAC (filled grey circles) adsorbs mainly to the surface, but some additional adsorption can be explained if the low molecular weight fraction is allowed to reach inside the cell wall. Fractionated PDADMAC shows more constant adsorption. (filled white circles) indicating that only surface is reached. (c) Polybrene adsorbs also inside cell wall and therefore has an order of magnitude larger adsorption (filled black circles, Paper I).

4.1.4. The effect of polybrene adsorption on porous structure of fibers

Fig. 27 presents the effect of a low M_w polyelectrolyte polybrene on the pore volume as well as the model from Fig. 24 to indicate where the pores are located. The cationic polyelectrolytes deswell the anionic cellulosic fibers upon their adsorption. The deswelling behavior is quantitatively demonstrated in Fig. 27b, where WRV and pore volume (as measured by thermoporosimetry) values are plotted as a function of the adsorbed polybrene. The total fiber volume could be obtained from WRV measurements (Fig. 27c).^{161,162} The pore volume correlated with the decrease in WRV when incremental amounts of polybrene were adsorbed onto the fibers. WRV and pore volume began to settle at 1.55 and 0.69 g/g, respectively. There exists a limit of how much deswelling can be imposed on a fiber and this was studied in more detail in Paper II. After this nominal value, the dissociated acidic groups of the fiber are effectively neutralized and further addition of the cationic polyelectrolyte does not affect the swelling behavior of the fibers.¹⁶³ The important result was that the polybrene influenced only the micropore

volume and the macropores were left intact, because micropore (thermoporosimetry) and total volume (WRV) values (Fig. 27) decreased by the same amount.

Fig. 28a shows the pore volume differences at a given pore diameter of hardwood kraft pulp fibers after adsorption of varying amount of polybrene. To gain insight into the alterations occurring in the pore size distribution, the control reference values were set to zero (the values in Fig. 24a are set to zero) and the pore volume difference to the control as a function of pore volume were plotted at a given pore diameter. In Fig. 28a, a portion of the largest pores (≥ 17 nm) collapsed as a result of polybrene adsorption. The pore volume between 17–220 nm pore diameter (Fig. 3) shows that the pore volume at a given diameter is gradually reduced when the polybrene amount is increased, indicating that the cationic polyelectrolyte collapsed the structure. Due to spatial considerations, the surface pores must close first and therefore, the surface fibrils are depicted as collapsing in the schematics in Fig. 28b, i.e., when water is evaporated from the fibrils it first disappears from the surface of fiber and therefore affects the surface first. Only the micropores were affected in Fig. 27b. Therefore, when the polybrene adsorption was increased to the maximum of 1.7% (17 mg/g) some of the large pores must have existed inside the cell wall and not in the surface as is the case for dried and rewetted fibers (Fig. 25). This is schematically shown in Fig. 28c.

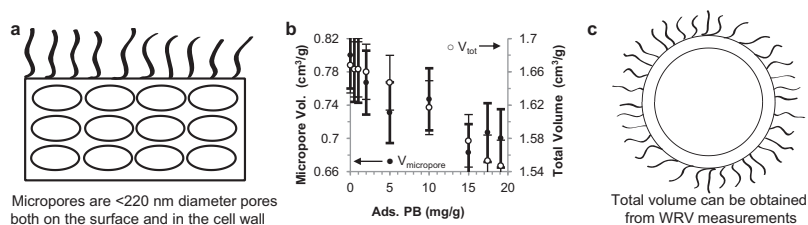


Fig. 27 Effect of polybrene on the micropore and total volume. (a) Micropores are <220 nm and can be found both on the surface as well as in the cell wall. (b) Polybrene adsorption can be detected both in micropores (thermoporosimetry) and in total volume (WRV). (c) WRV measurements give an estimate for the total cell wall porosity (Paper I).

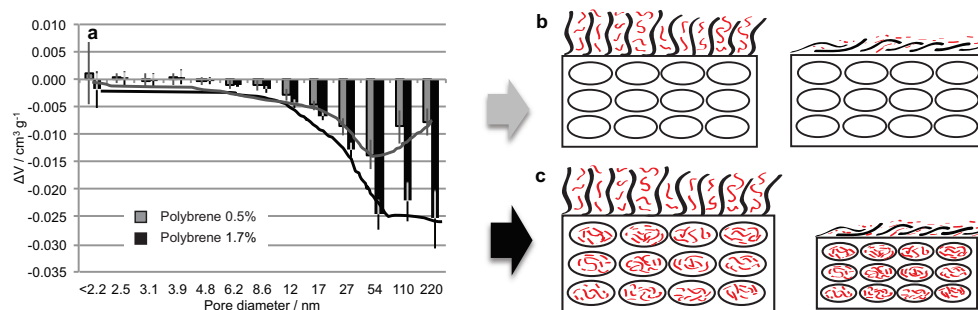


Fig. 28 Never dried samples. Pore volume difference at a given pore diameter (control reference set to zero). (a) Polybrene has increasing effect on the pore closure starting from ~ 12 nm. The different behavior of low addition (0.5%) and high addition (1.7%) is due to the different adsorption location. (b-c) Schematic representation of the pore closure for (b) low addition and (c) high addition of polybrene (Paper I).

4.1.5. The effect of high and low M_w high charge density cationic polyelectrolyte adsorption on the surface pores

The schematic diagram developed in the preceding chapters can be used to explain the effect of fractionated (purely high M_w) PDADMAC and unfractionated PDADMAC (a mixture of high and low M_w polymers, Fig. 26a). Due to steric reasons, both PDADMACs adsorb preferentially onto the surface. In Fig. 29, the reference values have been set to zero and only the difference to those values are reported. First, the unfractionated PDADMAC seems to have the similar pore closure than polybrene that has been adsorbed roughly by the same amount (grey and black columns in Fig. 29). In here, pore closure is defined as the amount of lost volume as measured by thermoporosimetry. The unfractionated PDADMAC had a completely different influence to the pores between 110-220 nm. This was seen as an indication of overcompensation of the positive charge in the surface. It is assumed that the overcompensation is due to the coiling of the polymer or other concentration of positive charge that is related to the length of the polymer. This speculative effect of overcompensation then would not be that substantial for polybrene since its short chains can have only limited coiling. This can be seen clearly, for example, in a more rapid thickness increase of multilayer films with high M_w PDADMAC in contrast to a lower M_w polyelectrolyte.¹⁶⁴ This overcompensation was also seen in the dried fibers that were pretreated with fractionated PDADMAC (Paper I:Fig. 6b).

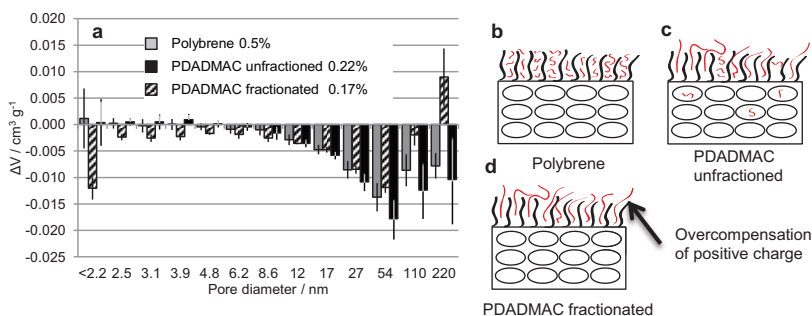


Fig. 29 Never-dried samples with similar amounts of positive charge adsorbed onto the fibers. (a) The columns represent the difference of the pores compared to the control reference. (b-d) Schematic location of the adsorption for (b) polybrene (c) unfractionated PDADMAC and (d) fractionated PDADMAC (Paper I).

4.1.6. Effect of CMC and amphiphilic block copolymer micelles on the pore size distribution

During this thesis also the effect of CMC and amphiphilic block copolymer micelles on the pore size distribution was tested. However, the thermoporosimetry results could not be used to rigorously study their effect on the pore size distribution. The results are summarized here in qualitative terms, as they are in accordance to the model of a cell wall that divides the fiber into cell wall and surface regimes.

Several experiments with low and high M_w CMCs were conducted. Within the error no substantial change in the micropores (i.e. <220 nm) could be detected. This was

surprising as the macropores (measured with WRV) changed drastically. This was likely due to the confinement of CMC to the outer layer of the fibers (Paper II). That way, the relatively free swelling of the surface adsorbed CMC did not create pores measurable by the thermoporosimetry. In the case that CMC would have completely adsorbed to the cell wall, two possible outcomes would probably have occurred: Either an expansion of the cell wall due to the electrostatic repulsion or a simple filling of the pores that would have reduced the porosity of the fibers – or a combination of the two. Therefore, we could not detect substantial micropore changes with the CMC adsorption.

The experiments with the amphiphilic block copolymer micelles (Paper III) included also thermoporosimetry measurements. However, the measurements gave scattered and contradicting results and the validity of these measurements was questioned. The scattering was due to the adsorption of hydrophobic micelles to the fiber. The hydrophobic material probably interfered with the measurement that was based on an equation (Eq. 1) that had been calibrated for hydrophilic material. In addition, the drastic change of interfacial tension by the hydrophobic micelles probably interferes the wetting of the fibers even though interfacial tension *of the surface* is not part of Eq. 1. In short, it is easier to measure the pores of a cellulosic fiber network than, for example, a porous Teflon block in an aqueous environment.

4.2 Influence of CMC and cationic polyelectrolytes on fiber and paper properties

In Paper II, high and low M_w CMCs were adsorbed on bleached birch kraft pulp fibers to increase the charge and swelling of the fibers in a controlled fashion. The M_w was an important factor for CMCs function as a swelling agent as well as a dry strength additive. The (de)swelling was further tuned by two highly cationic polyelectrolytes PDADMAC and polybrene, because of their known ability to neutralize the anionic charge either exclusively on the surface or in the whole fiber, respectively (Chapter 4.3, Paper I).

4.2.1. Adsorption of CMC

CMC adsorption on cellulosic fibers is not usually stoichiometric.⁴⁸ However, during adsorption there exists a balance between the solution concentration of CMC and the adsorbed amount of CMC in the pulp. The average adsorption percentage was ~30% for the pulp treated with the low M_w CMC and ~20% for the high M_w CMC (Fig. 30). The higher adsorption amount of low M_w CMC is usually an indication of sorption also occurring in the cell wall, since surface adsorption limit exists⁴⁸ and charge cannot be increased indefinitely on the surface due to electrostatic repulsion. However, the main part of the adsorption is on the surface (Table 1, Paper II) The adsorption plateau was not reached with our CMCs (see Paper II). The low adsorption amounts could be explained by a model based on the earlier results (Fig. 31). The shape of the CMC is linear in solution in the low ionic strength, but forms coils and even aggregates in high ionic strength.¹⁶⁵ The

high ionic strength screens the charges of the CMC. This allows the CMC aggregates to adsorb on cellulose fibers through carbohydrate-carbohydrate interactions (Fig. 31).⁴⁸ The ionic strength decreases drastically, when the pulp is washed to Na-form. Then, the charges in the CMC molecules are no longer screened and electrostatic repulsion desorbs a portion of the CMC⁴⁸ and the adsorbed CMC molecules take elongated shapes (Fig. 31).

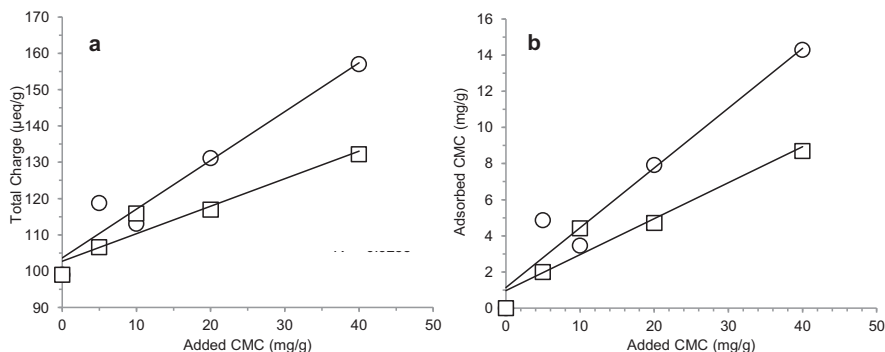


Fig. 30 Adsorption of low and high M_w CMC to cellulosic fibers. (a) Added CMC plotted against total charge. (b) Added CMC plotted against calculated values for adsorbed CMC based on the DS of the CMCs. (square for low M_w CMC and circle for high M_w CMC, Paper II)

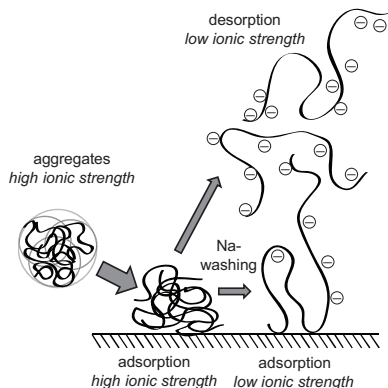


Fig. 31 A schematic representation of the adsorption of high and low M_w CMCs. The adsorption process in high electrolyte concentration renders the CMC molecules effectively without charge and the CMC adsorbs via carbohydrate-carbohydrate interactions. The low ionic strength after conversion to Na-form descreens the molecules, a shape change ensues and a portion of CMC is desorbed (Paper II).

4.2.2. CMC as a cross-linked gel on cellulose fibrils

In Paper II, the adsorbed CMC can be seen to be similar to cross-linked CMC. That is, the adsorbed CMC possess similar swelling characteristics on the surface of fibers as a gel matrix of cross-linked CMC. In addition, it was found out that both the low M_w CMC and high M_w CMC adsorb almost exclusively on to the surface. Therefore, the results from the CMC experiments reflect the changes in the outer surfaces of the fibers. The untreated fibers had 1.6 g/g water retention (Paper II) and the WRV above 1.6 g/g can be attributed to the added charge brought by the CMC. As mentioned previously, CMC absorbs

extensive amounts of water. This value has been reported to be 100-200 g/g WRV for the slightly cross-linked CMCs (Fig. 32a).¹⁶⁶ Extensive cross-linking of CMC decreases the WRV to 20-40 g/g (Fig. 32b).¹⁶⁶ These magnitudes are in accordance with the adsorbed high M_w CMC, as the increase in WRV was 0.8 g/g per 7.4 mg/g of CMC (*i.e.* WRV_{HighM_wCMC} is 108 g/g) and with adsorbed low M_w CMC that had a relatively low value of 30 g/g (WRV_{LowM_wCMC} , 0.4 g/g increase with 14 mg/g adsorption). These values can be understood if we assume that the low and high M_w CMCs have different shapes on the surface: The low M_w CMC assumes mainly flat shape while high M_w CMC can expand freely due to its longer chain length and the elongated loops and tails. The analogue to cross-linked CMCs is that low M_w CMC has shorter interaction free section or “cross-linking distance” compared to the high M_w CMC and therefore lower water adsorption (Fig. 32c,d).

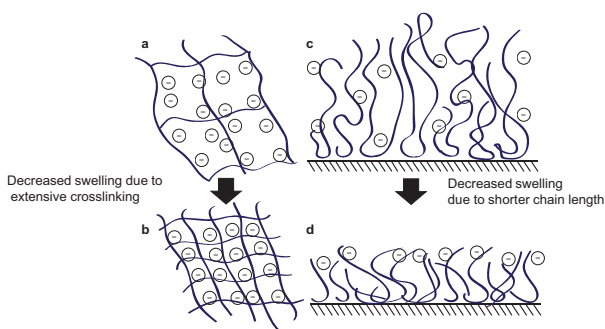


Fig. 32 The resemblance of cross-linked CMC and adsorbed CMC. (a) Slightly cross-linked cellulose can retain over 100 g/g water while (b) extensively cross-linked CMC adsorbs much less (~30 g/g, CMC was cross-linked by radiation).¹⁶⁶ (c) The adsorbed high M_w CMC resembles slightly cross-linked CMC because of the long free chain ends. (d) The adsorbed low M_w CMC is corresponds to highly cross-linked CMC due to low chain length.

4.2.3. The effect of cationic polyelectrolytes on CMC-treated surface fibrils based on the WRV measurements

Further analysis is possible if we separate the effect of surface charge and total charge contribution to the WRV. This can be done by neutralizing the surface charge and the total charge of both high and low M_w CMC modified fibers with PDADMAC and polybrene, respectively.⁶¹ The WRV has been plotted against the (non-neutralized) total charge in Fig. 33. All data points in the series, where the fibers have been neutralized with PDADMAC, show that WRV reached the value of the untreated reference (Fig. 33). This was the case for both of the CMCs used, indicating that mainly surfaces of fibers were modified with CMCs. This effect has been reported before for refined fibers¹⁶³ and for high M_w CMC⁶¹. In addition, the PDADMAC treated fibers had a constant WRV regardless of the adsorbed amount of the CMC. The constant WRV is found also for polybrene treated fibers, albeit at a lower level. This extra WRV decrease can be attributed to the cell wall pore closure (Paper I). It is quite remarkable that also dried fibers exhibit this behavior. After drying, a

drastic decrease in WRV for the reference (1.6 g/g \rightarrow 1.2 g/g) can be seen and the effects of cationic polyelectrolytes are similar to those of never-dried fibers. Furthermore, the fibers retain similar decrease in both low and high M_w CMC cases (Fig. 33c,d). These findings can be understood if we assume that surface changes are distinct from cell wall changes. The results also fit to the hypothetical models that divide the fiber to surface fibrils and cell wall (i.e. Fig. 3, Fig. 7, Fig. 25, Fig. 27).

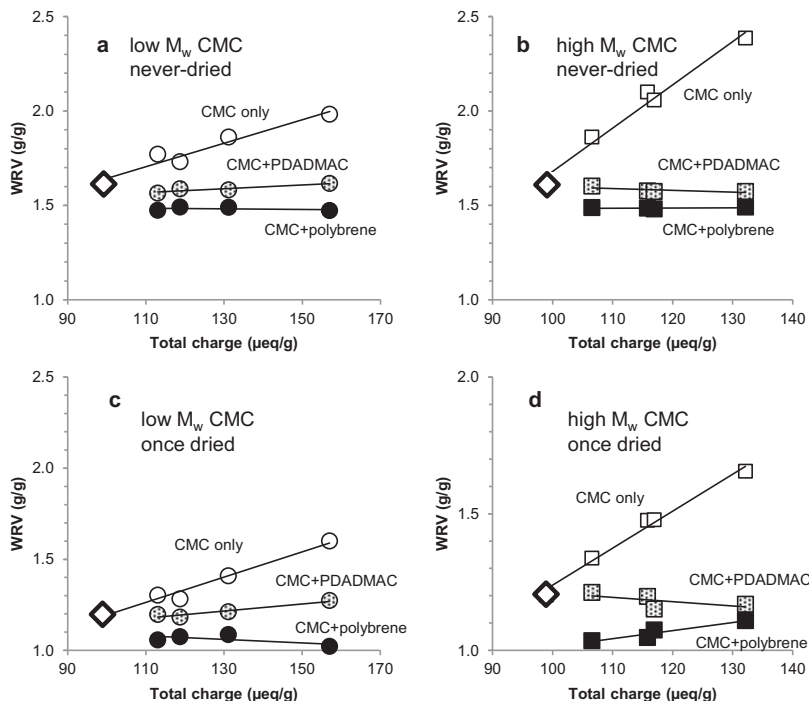


Fig. 33 The effect of CMC and cationic polyelectrolyte additions on WRV. Never-dried fibers: (a) Low M_w CMC treated fibers and (b) high M_w CMC treated fibers. In both cases, the total charge increase corresponds to higher adsorption of CMC. Total charge is the negative charge of the fibers before cationic polyelectrolyte adsorption (*diamond*, the untreated reference) Dried and rewetted fibers: (c) Low M_w CMC treated fibers (d) high M_w CMC treated fibers. The surface charge neutralization of the fibers with PDADMAC in all cases reduces the WRV to the untreated level. The neutralization of the total charge dewater the fibers only slightly more than surface neutralization (~ 0.1 g/g). (Paper II, c and d are unpublished data).

4.2.4. High and low M_w CMC influence the paper properties differently

The strength of the paper made from never-dried fibers was strongly influenced by the adsorption of CMC (Fig. 34). This effect has been reported in many studies before.^{106–108} The result also confirms that CMC is a dry strength agent. The effect of drying is also shown for the CMC treated fibers in Fig. 34. The hornification effect is seen in Fig. 34, i.e. in decreased swelling and decreased tensile strength. However, the most prominent effect is how the slopes change after drying in the tensile strength – WRV graph: The never-dried high M_w CMC treated fibers had a gentler tensile strength-WRV slope compared to the low M_w CMC. A hypothetical model for the shape, based on these results can be made. The surface layer depended, according to previous reasoning, on the M_w of the CMC (Fig. 32). The difference in the slopes (never-dried vs. dried, Fig. 34) is an indication of only the

external surface varying after drying. The effect is different for low M_w CMC treated fibers compared to the high M_w CMC treated fibers. For example, in the low M_w CMC case, the slope variation between the never-dried and dried samples was hard to distinguish (Fig. 34a), while a marked difference could be found in the high M_w CMC case (Fig. 34b). We attribute this to the stabilization of the surface microfibrils with the low M_w CMC (see insets in Fig. 34a). The high M_w CMC can then effectively entangle adjacent microfibrils. This entangled structure then suffers a fiber-wide collapse upon drying (see insets in Fig. 34b) We argued in Paper II, that this is the reason for the paper strength decrease.

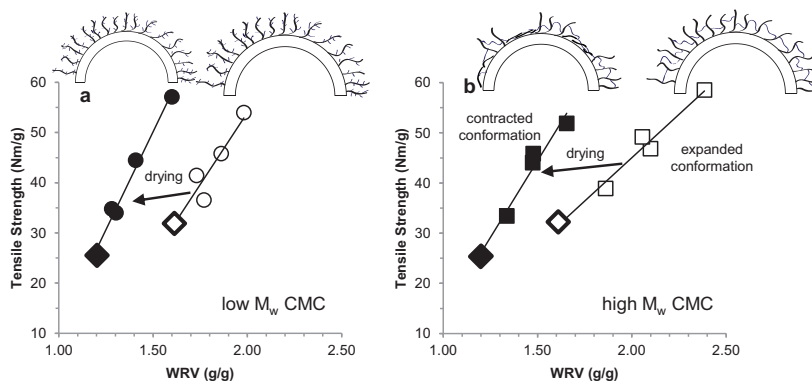


Fig. 34 The effect of drying on the WRV of the fibers and on the tensile strength index of the paper sheets. (a) The slope is similar for the never-dried and dried samples indicating that the low M_w CMC stabilizes the surface microfibrils. (b) The different slopes of never-dried and dried samples indicates that before drying the fibers were in expanded shape and after drying the surface microfibrils suffered an extensive collapse (Paper II).

4.2.5. Cationic polyelectrolytes affect the surface fibrils treated with high and low M_w CMC

The adsorption of PDADMAC on the CMC treated fibers affects only the surface charges and the surface is neutralized.²⁹ Prior to the adsorption the surface charge was measured with polyelectrolyte titration. Therefore, the amount needed to neutralize the surface charge was known. The results of this surface neutralization to the paper strength are shown in Fig. 35. In a combination of low M_w CMC and PDADMAC, the strength increases with roughly constant WRV, while the corresponding effect was minor for the high M_w CMC and PDADMAC system. This result is rather surprising; as it is well known that increasing the molecular weight of the polyelectrolyte usually increases strength (CMC-only treated samples in Fig. 34). This could be explained by the shape (conformation) differences of the CMC itself (Fig. 32). The shape then determines the shape of the second layer (PDADMAC) and two kinds of layers are formed: The low M_w CMC and PDADMAC possibly formed a tighter layer, while the high M_w CMC-PDADMAC complex formed a more loosely bound layer, due to the molecular sizes involved (Fig. 36).^{167,168}

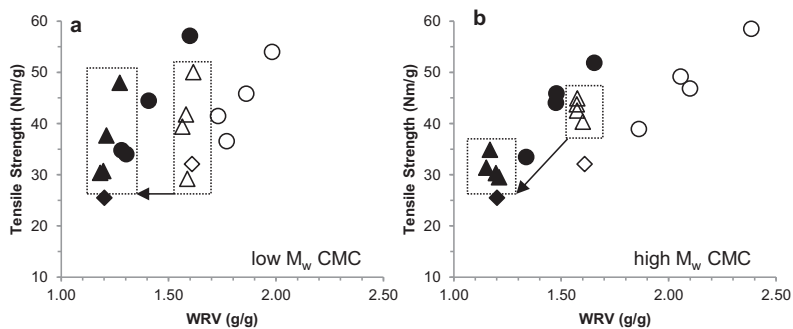


Fig. 35 Effect of polymer adsorptions on WRV of the fibers and tensile strength of the paper. (a) Low M_w CMC samples which were surface neutralized with PDADMAC. (b) Surface adsorbing high M_w CMC surface neutralized with PDADMAC and CMC-only treated samples. Boxes indicate the effect after drying with CMC+PDADMAC treated samples. The graphs show the increase in tensile strength without adverse effect on the water retention usually encountered with dry strength agents. (*circle*, CMC pretreated sample; *filled circle*, dried CMC pretreated sample; *triangle*, CMC pretreated sample where the surface charge has been neutralized with PDADMAC and *filled triangle*, CMC pretreated sample+PDADMAC that has been dried, Paper II).

The differences in paper strength can be then attributed to the model shown in Fig. 37. The cationic polyelectrolyte addition destabilizes the surface fibrils pretreated with high M_w CMC, resulting in a multilayer that has low strength (Fig. 37a). In contrast, the low M_w CMC pretreated surface fibrils are stabilized towards cationic polyelectrolyte addition and form a strong paper (Fig. 37b).¹⁶⁹ This idea is supported by literature where the use of high molecular weight in the anionic counterpart of polyelectrolyte bilayers is known to cause increase in tensile strength of paper when compared to the use of low M_w anionic polyelectrolytes.¹⁷⁰ The situation is more complicated when multiple layers are used, but even then the macromolecular arrangement is important attaining the high strength.^{83 171-}

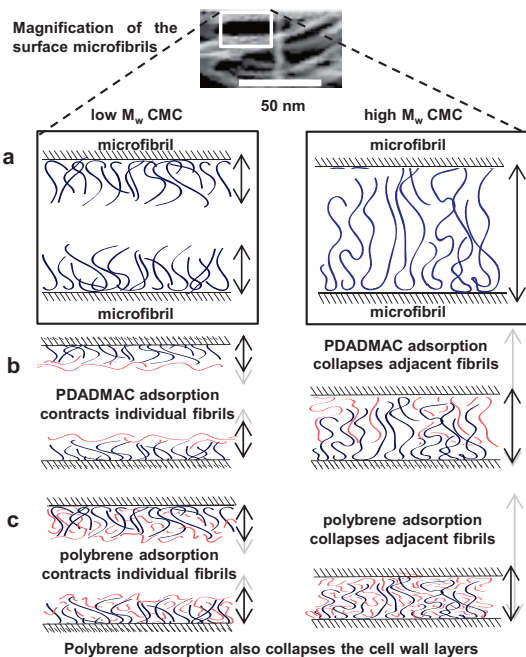


Fig. 36 A close-up of two adjacent microfibril surfaces with adsorbed CMC and after cationic polyelectrolyte treatments. (a) The electrostatic repulsion in the low M_w CMC molecules stabilizes the microfibrils. The high M_w CMC loses this stabilization because the high M_w CMC is able to connect to adjacent microfibrils. (b) The stabilization in the low M_w CMC case is still valid after cationic polyelectrolyte (PDADMAC) adsorption, since the high M_w PDADMAC can form layers on top of the stabilized anionic fibrils. Only a small collapse in the structure is expected. This is in contrast to the high M_w CMC case where the addition of PDADMAC pulls adjacent microfibrils together effectively collapsing the fibrils. (c) The adsorption of low M_w polybrene has a similar effect as PDADMAC, with low M_w CMC being stabilized and high M_w CMC destabilized. However, the small size of the polybrene allows the penetration inside the cell wall and the stabilization is reduced compared to the high M_w PDADMAC (Paper II).

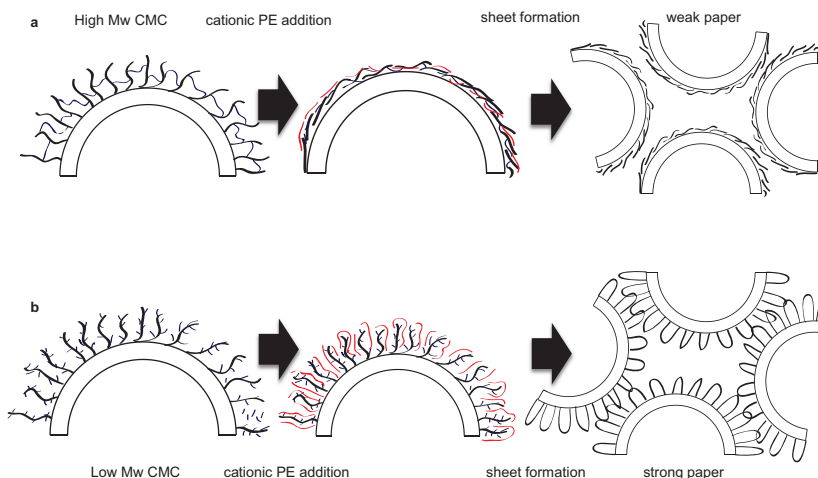


Fig. 37 Schematic representation of the different paper strengths due to high and low M_w CMC after cationic polyelectrolyte (PE) addition. (a) Initially the high M_w CMC treated fibers have highly expanded microfibrils and swollen fibers that easily form strong paper. After cationic polyelectrolyte addition the expanded microfibrils collapse resulting in rather weak fiber web. (b) Low M_w CMC treated fibers have stabilized microfibrils. After cationic polyelectrolyte addition the fibers remain stabilized and the swollen structure easily attains strong fiber-fiber bonds and thus high tensile strength.

4.3 Novel wet strength agent – high M_w CMC and ionenes

The content of this section concerns mainly the results from Paper IV. The CMC pretreated fibers are the same as in Chapter 4.4 and, hence, in Paper II.

4.3.1. Initial results that lead to the new wet strength agent

In the previous discussion most of the results regarding polybrene adsorption on paper strength were omitted. The reason was that in Paper III, drying handsheets containing the total charge neutralized fibers (*i.e.*, neutralized by polybrene) had a peculiar effect on the paper sheets. For example, the normal laboratory disintegrator could not separate the fibers from each other by using the standard method of dispersing. Subsequently, these undispersed fibers produced flocky paper sheets. The flockiness resulted in bad formation and finally to low paper strength, as shown in Fig. 38. In addition, the rewetted fibers demonstrated interesting wet strength behavior. Usually, the redispersing difficulties arise when the fibers are treated with wet strength agents, as the recycling of these fibers has proven to be a challenge.²⁴

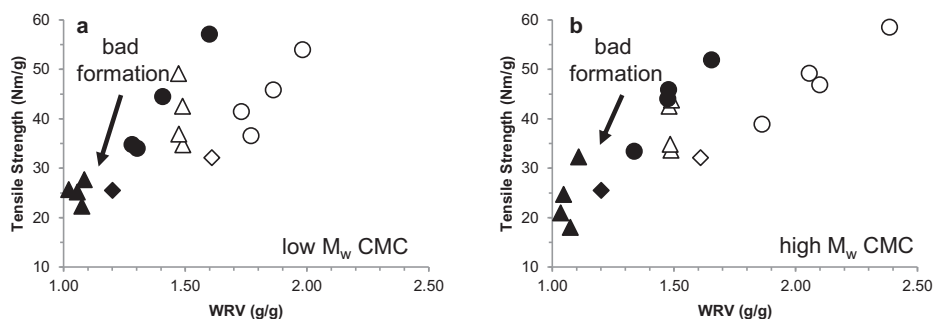


Fig. 38 The low and high M_w CMC pretreated fibers adsorbed with polybrene. (a) The low M_w CMC pretreated fibers (*circle*) and the total charge neutralized fibers (neutralized with polybrene, *triangle*) show initially high strength and low WRV. After drying (*filled circles and triangles*), the rewetting of the fibers was difficult and the resulting paper sheets were flocky. (b) Similar results were found with high M_w CMC. (Paper II and some unpublished data).

4.3.2. Systematic study of the wet strength – CMC and polybrene

The measured wet strength data for polybrene is shown in Fig. 39. The pulp had been pretreated with CMC before the adsorption of polybrene. The polybrene was added in such amounts to neutralize the total charge of the fiber. The actual amount of adsorbed polybrene can be calculated from the charge densities and generally the amount varies between 2-3% (*i.e.*, the reference has been neutralized with ~ 20 mg/g polybrene and the pulp with the highest adsorbed amount of CMC has been neutralized with ~ 30 mg/g polybrene). The effect was much smaller for low M_w CMC treated with polybrene but still measurable. The cationic polyelectrolyte is necessary for the wet strength since CMC alone does not show any wet tensile strength (Fig. 39a). The type of cationic

polyelectrolyte was of utmost importance. For example, the use of PDADMAC as the cationic polyelectrolyte did not give any wet strength (Fig. 39b). Curiously, the effect was the most pronounced when high M_w CMC is neutralized with polybrene. This is in contrast to the dry strength measurements (Fig. 35 and Fig. 38) where usually the low M_w CMC had higher strength. Possibly, the difference lies in how the CMCs alter the microfibrillar structure. Fig. 36a showed the fibrillar point of view of the difference between the low and high M_w CMCs. Consider that the two microfibrils in the figure can also depict *two different fibers*, in addition to fibrils. Then the added cationic polyelectrolyte can pull two adjacent fibers closer together when the charge neutralization collapses the swollen CMC structure. Only high M_w CMC would generate enough fiber-fiber bonds to yield appreciable wet strength effect, because the length of the high M_w polymer is an order of magnitude longer compared to the low M_w CMC. How these fiber-fiber bonds resist water intrusion to maintain the fiber-fiber bonds and why only polybrene induces such bonds is not apparent from the model. The wet strength was notable only with fibers that had been pretreated with CMC. Similar results have been obtained with TEMPO-oxidized fibers and C-PAM, but they argue for the N-acylcarbinolamine cross-linking.⁵²

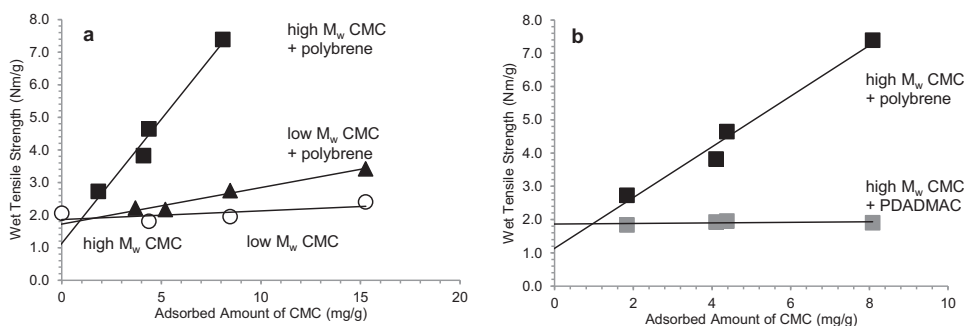


Fig. 39 The effect of polybrene and CMC on wet strength. (a) Polybrene and high M_w CMC together give high wet strength (filled black squares). Low M_w CMC and polybrene give partial wet strength (filled black triangles), while CMC alone (whether high or low M_w) does not give any wet strength (empty circles). (b) Another quaternary amine polyelectrolyte (PDADMAC, filled grey squares) does not yield wet strength (Note the different scale in the x-axes, Paper IV).

The discrepancy between polybrene and PDADMAC wet strength effects is profound, since it is well-known that usually cationic polyelectrolytes do not give wet-strength.¹¹⁷ In Fig. 40, the increase in surface neutralization corresponds to the appearance of wet strength. This clearly demonstrates the surface effect of the attained wet-strength. In addition, Fig. 40 shows that the structure of polybrene has important effect on the attained wet strength, since with similar additions of PDADMAC and polybrene, only polybrene exhibited wet strength.

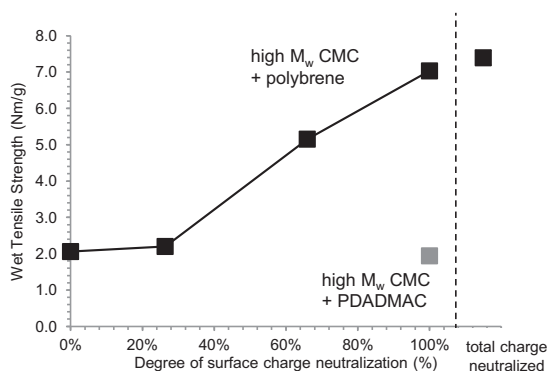


Fig. 40 The effect of surface charge on wet strength. The surface charge is gradually neutralized with polybrene. The 100% surface neutralized pulp is an average of 5 measurements. The last point corresponds to the total charged neutralized where polybrene has been added over twice the amount than in the 100% surface charge addition. Again, PDADMAC does not yield wet strength (Paper IV).

4.3.3. The wet strength of ionenes on CMC pre-absorbed pulp

Polybrene had unique wet strengthening behavior that was not possible to attain with other cationic polyelectrolytes with quaternary amines (e.g., PDADMAC). The hypothesis was that polymer structure explains the attained wet strength, i.e., the charge of the polybrene is part of the polymer backbone unlike in PDADMAC and other quaternary amine containing polymers. Therefore, a series of ionenes was synthesized to obtain further information of the wet strengthening effect. All of them adsorb to the same extent as polybrene, i.e., they could neutralize the total charge of the fibers. They also had comparable molecular weight and charge density (Table 3). Fig. 41 summarizes the results of the prepared ionenes. The main feature was that the ionenes that had similar structure to polybrene (asymmetric charge distribution, e.g. [6,12]-ionene) demonstrated a wet strength effect compared to the reference. In contrast, no significant wet strength effect could be noticed, when the spacing of the charges was identical (e.g. [3,3] and [6,6]-ionenes). Hypothetically, the asymmetric charge distribution is responsible for the wet strength, although the tested polymers consisted only 1:1 symmetry and 1:2-ratio asymmetry.

Theoretically, the long hydrocarbon chains could induce some hydrophobization of the entire fibers, thus giving wet strength simply by adsorbing less water. How this increased hydrophobicity induces wet strength is not known. However, Fig. 41 demonstrates that the wet strength is not due to hydrophobizing effect (i.e. lowering of the water content of the samples), since the wet strength is already attained at ~40% dry matter content. The results were not entirely surprising, since for example [6,6]-ionene is arguably more hydrophobic than [3,6]-ionene.

The wet strength effect could be tentatively explained by the different shapes the ionenes can adopt. For example, the [3,3]-ionene probably forms rather linear structure due to the electrostatic repulsion of the cationic groups. This stiffness is eased when an alternating structure such as [3,6]-ionene is considered. It seems plausible that the alternating long

and short hydrocarbon chains can alleviate the tension caused by the cationic groups by rotation that is prohibited for [3,3]-ionene. However, why this tension relieving shape helps to obtain wet strength together with CMC is not clear. In Paper IV, it was argued that the structure of a CMC + asymmetric ionene would be similar to the cellulosic structures found in cellophane and butter wrap. Both of which are water resistant paper grades formed without any additives and which are purely formed from cellulosic substances. Cellophane is formed from individual polymer chains (compare to CMC) and butter wrap from fibers that have a gelatinous outer layer. Also, both cellophane and butter wrap have to be dried and rewetted to attain wet strength (compare to CMC adsorbed onto cellulosic fibers). Hypothetically, it is the action of the gelatinous CMC layer on the fibers and the subsequent neutralization by conformable ionenes (e.g. polybrene) that attain the wet strength.

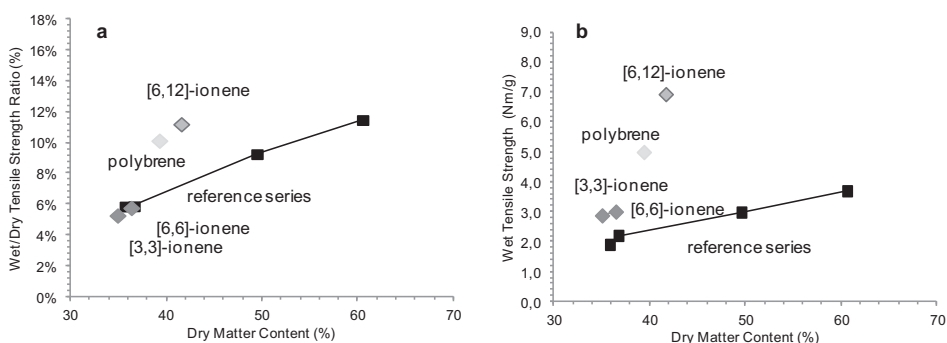


Fig. 41 The wet strength effect of ionenes. Ionenes are shown in diamonds (high M_w CMC pre-adsorbed pulp). A wet strength curve for reference is shown in black to demonstrate that the wet strength of the ionenes is not due to increased dry matter content of the samples (a) The wet/dry tensile strength ratio demonstrates the effective wet strengthening. (b) Wet tensile strength shows the actual measured strengths. (The ionenes had comparable molecular weights, between 6 and 60 kDa, Paper IV).

4.4 Novel hydrophobization treatment – amphiphilic diblock copolymer micelles

The results of this section are mainly from Paper III. Amphiphilic diblock copolymer micelles are polymeric aggregates that have certain similarity with the traditional sizing agents such as ASA and AKD. However, instead of a cationic polymer stabilized colloids, the micelle is self-assembled with hydrophobic core and cationic outer surface. Amphiphilic diblock copolymer micelles were chosen as novel hydrophobizing chemical due to their unreactivity and stability in aqueous solutions i.e. they do not hydrolyze in water like ASA and AKD.

4.4.1. Micelles on a model substrate

The micelles were made from block copolymers as described in the experimental part. The low amount of cationic groups and high amount of hydrophobic groups were chosen to maximize the hydrophobic groups. In the preparation process, water is added to a solvent

that solutes both blocks in the polymer. This changes the polarity in the solution and forces the hydrophilic block of the polymer on the surface and the hydrophobic block inside the core. The resulting micelles are therefore extremely stable.

The amphiphilic copolymer micelles were used to obtain controlled hydrophobicity on bleached birch kraft pulp fibers. The core size of the polymers were dependent on the DP of styrene block, while the hydrodynamic diameter depended on the cationic pyridine block (Fig. 42) The procedure of applying micelles for hydrophobization occurs in a simple two-step procedure: (i) the diblock copolymer micelles adsorbed on a fiber surface from aqueous solution and (ii) the fibers are heated above the glass transition temperature (T_g) of the micelle core, which causes the micelles to open, exposing the hydrophobic core to the exterior of the fiber. To demonstrate the molecular control over the phenomenon, we first tested the procedure on mica. Mica is an anionic model substrate with extreme flatness (atomic scale smoothness, *i.e.*, ~ 1 nm).

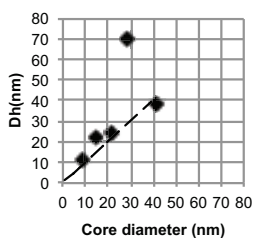


Fig. 42 The hydrodynamic and core diameters of the amphiphilic block copolymer micelles. The measured hydrodynamic diameter (D_h) and core diameter had one-to-one relation (dashed line) for all but one block copolymer micelle (Paper III).

The hydrophobization of a surface by amphiphilic block copolymer micelles can be achieved by micellar opening which exposes the hydrophobic core to the exterior.¹⁷⁴ The model surfaces were heated in oven (130 °C, 3 min) to open the micelles, which was followed with AFM measurements (Fig. 43). The model surfaces were not hydrophobic, as the static contact angle increased only from $\sim 30^\circ$ to $60\text{-}70^\circ$. Similar increases for model surfaces has been previously published.¹⁷⁴ The decrease in hydrophilicity was attributed to the melting of the micelle core after heating. This flattens the surface features as suggested by the decrease in height of the micelles in the AFM images (Fig. 43).

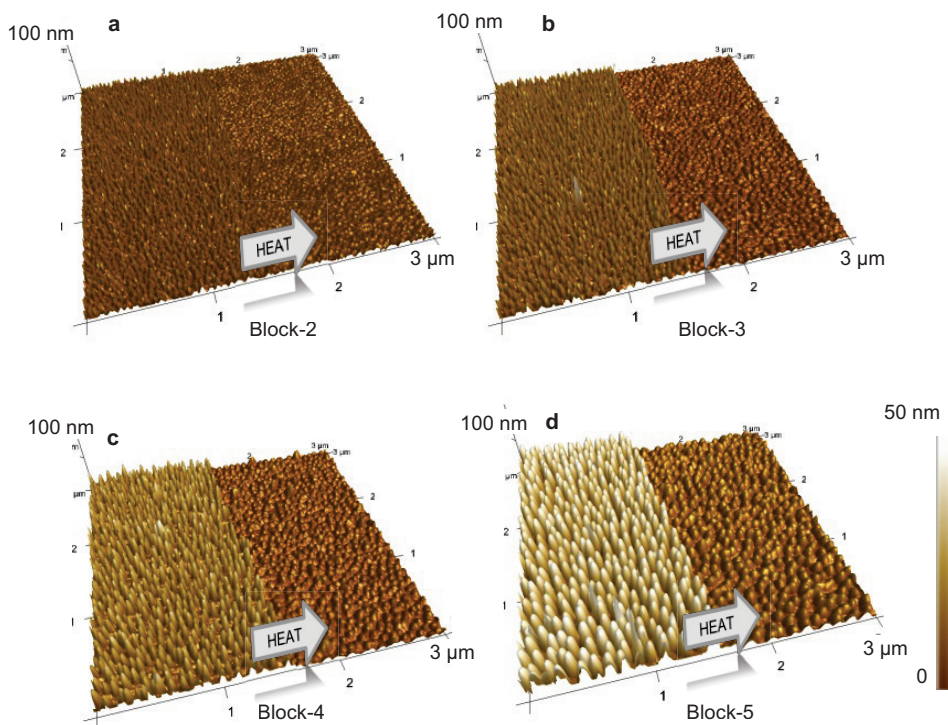


Fig. 4.3 AFM images of amphiphilic block copolymer micelles on mica surface before and after heat treatment (a) Block-2 (b) Block-3 (c) Block-4 (d) Block-5. The decreasing height of the micelles after heat treatment demonstrates the melting and spreading of the micelle core. Scale bar on right. The AFM images are $3\ \mu\text{m} \times 3\ \mu\text{m} \times 0.1\ \mu\text{m}$ (Paper III and some unpublished figures).

4.4.2. Micelles on cellulosic fibers

The cellulosic fibers could be hydrophobized more effectively than model surfaces. The cellulosic fiber shrinks when the fibers dries. The hypothesis is that the hydrophobization improves when the surface adsorbed micelles reorganize (move closer to each other) on the surface of the fiber upon drying.

First, the cationic amphiphilic block copolymers adsorbed on the surface of the fibers in similar fashion than on smooth model surfaces, as revealed by Raman-imaging (Fig. 44a). The image suggests that only the surface of the fibers was coated and the micelles did not reach the porous fiber wall. In addition, upon adsorption of the micelles on cellulosic fibers, the adsorbed amount increased linearly with the (core) size of the polymer (Fig. 44b). From the data, an estimate for surface area of the fiber could be obtained from the coefficient. For 1 g of fiber, the adsorption coefficient is $0.49\ \text{mg}/\text{nm} \approx 0.49\ \text{m}^2$, taking density as unity and assuming uniform layer of micelles on the surface. That is, the surface area is roughly $0.5\ \text{m}^2/\text{g}$, which compares favorably to the surface area of dried fibers, reported to be $\sim 1\ \text{m}^2/\text{g}$ in magnitude. In addition, this kind of surface coating is economical since the micelles are not consumed by adsorption to the interior of the fiber cell wall, which occurs with many low molecular weight polymers such as polybrene.^{29,46}

In this way, the micelles function like the hydrophobic sizes (AKD and ASA) that do not penetrate into the fibers either. However, ASA and AKD are added as hydrophobic colloids whose hydrodynamic diameter is in the range of 1 μm .¹⁴¹

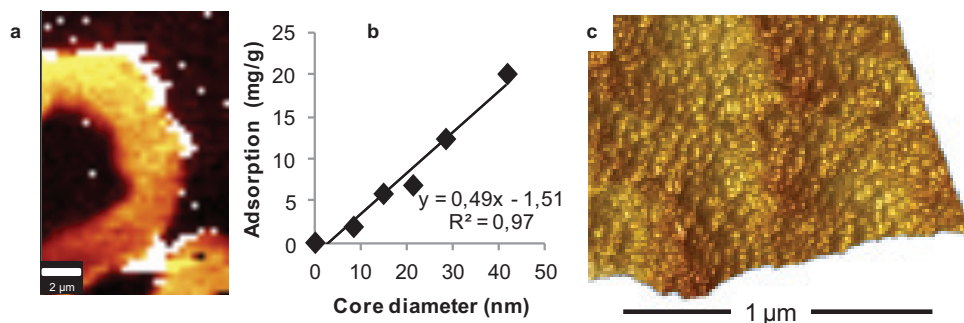


Fig. 44 Adsorption of micelles on cellulosic fibers. (a) Raman imaging cross-section of a single fiber demonstrating the abundance of the micelles on the surface (cellulose in yellow, Block-5 micelles in white color). (b) The adsorption increases linearly with the size of the core diameter. An estimate for surface area of the fiber can be obtained from the coefficient (see text). (c) Close-up of a pseudo-3D AFM image of Block-5 micelles on a single fiber. (Paper III).

Based on Fig. 44b, it can be hypothesized that a monolayer of micelles was adsorbed on the fibers (in the swollen wet state of the fiber), due to the linearity of the graph. It needs solely the assumption that the surface area is constant. However, the monolayer hypothesis forms a good basis for discussion, because with this assumption the diameter of the micelle corresponds to the coating thickness. The hydrophobicity of the fibers is shown in Fig. 45a where the hydrophobicity can be obtained after heat treatment for all coatings that are thicker than ~ 15 nm (see Fig. 19c, Fig. 43 or Fig. 44b for the micelle sizes). The thickest coatings (30 and 50 nm) are hydrophobic without heat treatment but the thicker coating also needs more micelles to fully cover the fibers (maximum adsorptions in Fig. 45b). It is long known that fibers do not need full coating to achieve hydrophobicity.¹³⁸ This is also shown for amphiphilic block copolymer micelles in Fig. 45b where approximately one third of the maximum adsorption (full coating) is needed to lower the water absorption to hydrophobic region (~ 20 g/m² in COBB₃₀ test).

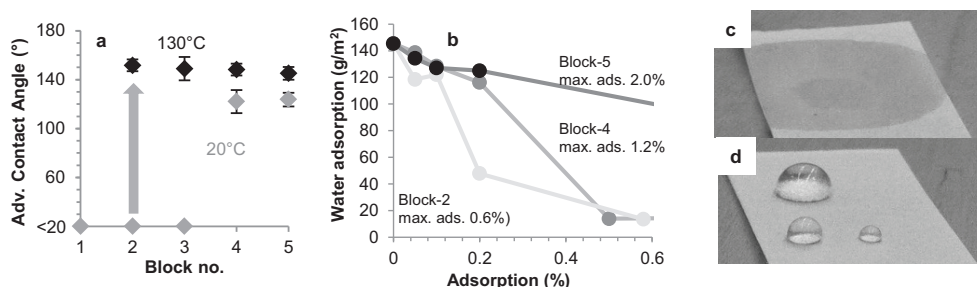


Fig. 45 Hydrophobizing effect of the micelles. (a) Advancing contact angle of the heat treated samples (130 °C) and room temperature dried samples (20 °C) (b) Water adsorbed onto heat treated samples in 30 sec time (COBB₃₀ test). (c) Water adsorbed on a reference paper sheet (~ 140 g/m²). (d) Water adsorbed on a hydrophobized paper sheet (~ 20 g/m², Paper III and some unpublished data).

4.4.3. Comparison between the novel wet strength agents and hydrophobic micelles

Finally, a short analysis of CMC+ionene treated fibers to the fibers treated with block copolymer micelles in terms of paper properties demonstrates important differences between wet strength paper and hydrophobized (sized) paper. A comparison of wet strength properties of ionene treated and block copolymer micelle treated fibers are shown in Fig. 46. The ionenes, hence, demonstrated wet strength. That is, they had a relatively high wet tensile strength compared to the reference. In contrast, the block copolymer micelles hydrophobized the fibers. That is, the fibers were relatively dry compared to the reference. The results show that the smallest micelles (Block 1 in Fig. 46) do not have any particular effect on fibers, since neither hydrophobization nor wet strength were attained. However, the wet strength is high for hydrophobized micelle treated fibers because of the dryness of the fiber (60% Fig. 46). In contrast, the wet strength agent (CMC + polybrene) does not render the fibers hydrophobic and water is free to adsorb inside the fibers. Dry matter content is therefore low (Fig. 46). In the figure it is shown how the hydrophobized micelle treated fibers and the wet strength ionene (polybrene and [6,12]-ionene) treated fibers both exhibit higher wet/dry tensile ratio than the reference. For wet strength ionenes, already 40% dry content has substantial percentage of the dry strength (~15%) while the hydrophobizing block copolymer micelles treated samples reach this threshold at substantially higher dry matter content.

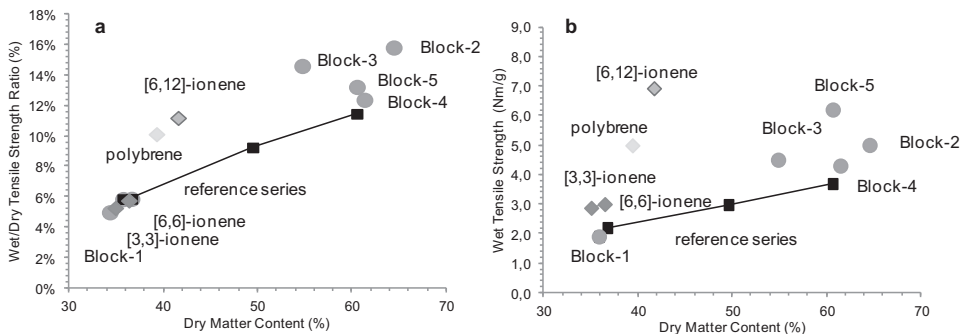


Fig. 46 Summary of the Wet Tensile Strength for different treatments. High M_w CMC pretreatment with neutralization by polybrene or [6,12]-ionene yields the highest wet-strength with lowest dry matter content. The hydrophobizing (sizing) treatments (heat treatment and adsorption of Block-2,3,4,5) have only slightly higher wet tensile strength than reference demonstrating that wet strength agents and sizing agents function in different ways. Finally, some of the treatments do not have any wet strength or sizing effect, namely reference, Block-1; [3,3]-ionene and [6,6]-ionene. (a) The wet/dry tensile strength ratio demonstrates the effective wet strengthening. (b) Wet tensile strength shows the actual measured strengths. All wet strength measurements were done for dried and rewetted fibers. To obtain the reference series, separate measurements of dried and rewetted fibers were done at timed intervals as the samples gained dry matter content through evaporation.

5. Concluding remarks

This work was a fundamental effort to improve the knowledge on how polyelectrolytes affect the physical properties of fibers and the paper made from these fibers. Increasing the anionic charge of the fibers increased the strength properties of the paper and also water retention. In contrast, drying and then rewetting the fibers decreased the strength and water retention of the fibers. The results indicated correlation of water retention and strength. That is, it was difficult to obtain fibers that had low water retention (good dewatering) and good strength properties. However, treating the anionically modified fibers with cationic polyelectrolyte could break this correlation and the water retention could be lowered without adverse effect on the strength properties. Hence, the cationic polyelectrolytes were efficient at dewatering the cellulosic fibers and could prove valuable to the paper and market pulp producing mills that are limited by their drying section capacity.

5.1 Model for cellulosic fibers

A model for cellulosic fibers was developed. The model divides fiber structure to two distinct regions: (i) surface fibrils (ii) cell wall. This distinction is somewhat ideal, since there is no real boundary between surface fibrils and cell wall. This model helps to understand how the polyelectrolytes function when dewatering or strength increase is needed. For example, the dewatering effect of cationic polyelectrolytes was attributed to the cell wall porosity changes in Paper I. Similarly, the fibers treated with CMC had either a stabilizing or destabilizing effect for the surface fibrils. The high M_w CMC treated fibers and the paper made from these fibers had consequently lower strength properties after cationic polyelectrolyte adsorption or drying and rewetting than that of low M_w CMC. The low M_w CMC could stabilize the surface fibrils, resulting in high tensile strength paper after adding a cationic polyelectrolyte.

5.2 Multifunctional polymers

The multifunctional polymers (ionenes and diblock copolymers) could be used to widen the property space of fibers: (i) to increase the wet strength of the paper or (ii) hydrophobize paper. The destabilization with high M_w CMC was important to the wet

strength, since some non-crosslinking polyelectrolytes (polybrene, and [6,12]-ionene) could increase the wet strength in unprecedented way. Since the ionenes do not have amine reactivity due to their quaternary amine structure the results could help to design more effective wet strength agents.

Amphiphilic diblock copolymer micelles could be adsorbed exclusively on the fiber surface by using tunable spherical micelles. The micelles could also be melted by heat treatment. Heating formed a hydrophobic layer on the surface of cellulosic fiber that hydrophobized the fibers. In addition, this kind of treatment allows hydrophobization of fibers with adjustable layer of hydrophobic material. This could prove valuable as the layer of hydrophobic material can be tuned effortlessly by selecting the starting block copolymer for the desired effect.

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