



CHALMERS
UNIVERSITY OF TECHNOLOGY

Fundamental aspects of the non-covalent modification of cellulose via polymer adsorption

Downloaded from: <https://research.chalmers.se>, 2026-04-04 01:07 UTC

Citation for the original published paper (version of record):

Arumughan, V., Nypelö, T., Hasani, M. et al (2021). Fundamental aspects of the non-covalent modification of cellulose via polymer adsorption. *Advances in Colloid and Interface Science*, 298. <http://dx.doi.org/10.1016/j.cis.2021.102529>

N.B. When citing this work, cite the original published paper.



Historical Perspective

Fundamental aspects of the non-covalent modification of cellulose via polymer adsorption

Vishnu Arumughan^{a,b,*}, Tiina Nypelö^{a,c}, Merima Hasani^{a,b,c}, Anette Larsson^{a,b,c,d,*}

^a Department of Chemistry and Chemical Engineering, Chalmers University of Technology, Gothenburg, Sweden

^b AvanCell, Chalmers University of Technology, Gothenburg, Sweden

^c Wallenberg Wood Science Center, Chalmers University of Technology, Gothenburg, Sweden

^d FibRe Vinnova Competence Center, Chalmers University of Technology, Gothenburg, Sweden



ARTICLE INFO

Keywords:

Polymer adsorption
Cellulose
Polyelectrolyte adsorption
Specific ionic effects
Layer-by-layer assembly

ABSTRACT

The increasing need for new material applications based on cellulose demands increased functional diversity and thus new functionalisation/modification approaches. The non-covalent modification of cellulose fibres via the adsorption of functional polymers has emerged as a promising route for tailoring the properties of material. This review focuses on fundamental aspects of polymer adsorption on cellulose surfaces, where the adsorption of polyelectrolytes and non-polyelectrolytes are treated separately. Adsorption studies on model surfaces as well as cellulose macro-fibres are reviewed. A correlation of the adsorption findings with the Scheutjens-Fleer polymer adsorption theory is provided, allowing the fundamentals behind the polymer adsorption phenomenon and its context in utilization of cellulose fibres to be understood.

1. Introduction

The adsorption of functional polymers on cellulose has been traditionally employed in the papermaking process to improve both the processability and physical properties of paper-based materials; it has gained attention due to the need of developing non-synthetic functionalisation strategies for fibres. Development in the layer-by-layer assembly on cellulose fibres for creating advanced materials has fueled research in this area further [1–4]. The nature of a polymer is of paramount importance to its adsorption on surfaces. The polymers used in adsorption studies are classified as polyelectrolytes and non-polyelectrolytes; the adsorption of polyelectrolytes on surfaces differs fundamentally from that of non-ionic polymers [5]. Different synthetic and non-synthetic polyelectrolytes have been utilized to functionalise cellulose materials and, by careful selection of the polyelectrolyte and other functional entities (such as carbon nanotubes, conducting polymers and quantum dots), it is possible to create interactive and reactive surfaces for various advanced applications [6–11]. The fundamental aspects of polyelectrolyte adsorption on cellulose have been reviewed and discussed in depth by Wågberg [12]. However, there have been developments in this area in recent years with respect to both fundamental understanding and applications. The major focus of this review is the fundamental aspect of polymer adsorption on cellulose materials

between the years 2000–2021.

2. Modification of cellulose via polymer adsorption

Cellulose possesses physical robustness provided by the supramolecular structure and chemical stability stemming from the abundance of hydroxyl groups that provide the chain with conformational stabilization. However, the need for new material applications based on cellulose requires increased functional diversity and new functionalisation/modification approaches have therefore been developed, using both chemical and physical procedures [13].

Chemical modification of cellulose usually involves the conversion of hydroxyl groups in the cellulose chains into ethers, esters, acids, etc. The intrinsic reactivity of hydroxyl groups is less important in chemical reactions of cellulose, since the accessibility of reagents is primarily regulated by the supramolecular structure, which is important especially in reactions that are performed in cellulose suspensions. Cellulose reactions can also be performed in cellulose solutions in which the supramolecular structure has vanished completely [14–17]. The majority of chemical reactions performed industrially are, however, heterogeneous, or are to begin with at least, and the supramolecular structure is affected as the reaction proceeds. Heterogeneous reactions usually lead to non-uniform substitutions, with a preference for accessible low-

* Corresponding authors at: Department of Chemistry and Chemical Engineering, Chalmers University of Technology, Gothenburg, Sweden.

E-mail addresses: vishnukarumughan@gmail.com (V. Arumughan), anette.larsson@chalmers.se (A. Larsson).

<https://doi.org/10.1016/j.cis.2021.102529>

Received in revised form 24 September 2021;

Available online 29 September 2021

0001-8686/© 2021 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

ordered regions. A swelling media can be used to increase accessibility and ensure the uniform distribution of substituents to some extent. Reactions performed in non-swelling media usually restrict the modification to the surface and low-ordered regions.

The location of the functional groups in cellulose fibres is decisive in facilitating the fibre-fibre bonding to enable the formation of a strong fibre network [1,18–20]. It has been shown that papers made with toposelectively carboxylated cellulose fibres in non-swelling media such as isopropanol-methanol mixture exhibited good tensile properties [19,20]. In practical terms, however, the use of non-swelling media for topochemical reactions is limited due to environmental concerns.

Surface modifications of the fibres can be achieved by polymer adsorption without compromising the physical integrity of their structure. This non-covalent modification strategy is topochemically selective compared to the covalent modification of cellulose, provided that the adsorbing polymer molecules are too large to diffuse into the fibre walls [18].

Modification of cellulose with hemicellulose is often of interest [21]. The dissolution of hemicelluloses is inevitable during the chemical pulping and consequently, re-depositing the dissolved hemicelluloses back onto the cellulose fibres is one way of enriching the pulping process with hemicellulose. The key phenomenon acting in this re-deposition process is the adsorption of dissolved hemicellulose chains on the fibre surface. The retention of hemicellulose can not only increase the pulp yield significantly but also improve the beatability of the pulp by shortening the beating time. More importantly, the retained hemicellulose also enhances properties such as pulp strength, softness and reduction of dust [22].

Interest in the adsorption of polymers onto cellulose has increased during the past years as new areas of application, such as health-care materials and diagnostic platforms, have shown an increased demand for functionalised bio-based surfaces with controlled properties [23,24]. Understanding the polymer adsorption process and the properties of the adsorbed layer is therefore necessary for developing the next generation of cellulose-based materials and fundamental studies of polymer adsorption are still necessary.

2.1. Cellulose model surfaces for adsorption studies

According to Cohen Stuart et al., an ideal surface for fundamental adsorption studies should fulfil the following requirements [25]:

- 1) The chemical composition of the surface should be completely known
- 2) The surface charges of the substrate should be thoroughly characterized
- 3) The morphological structure of the surface should be well-characterized, including surface roughness and porosity
- 4) The surface should have a defined curvature
- 5) The crystallinity of the exposed surface should be known
- 6) No exchange of materials across the solid/liquid interface should occur

The surface of cellulose fibres, with their chemical and structural heterogeneities, do not in fact fulfil these criteria and are thus not ideal for fundamental studies of polymer adsorption [25,26]. Cellulose materials originating from pulping processes often contain residual amounts of other wood components, or negative charges that originate from the pulping process. Cellulose fibres almost always contain a certain amount of negative charges even when they are often considered uncharged and, if not, further functionalized [27]. Moreover, the distribution of these charges in cellulose fibres is also heterogeneous.

Polyelectrolyte titrations are used to characterize the surface charges, whereas the total charges of the fibres includes charges both distributed on the surface as well as within the fibres walls and can be characterized using conductometric titrations [28,29]. While surface roughness, porosity and surface curvature in the aforementioned criteria can be defined, the semicrystalline nature of cellulose is more problematic because it is easy to detect but notoriously difficult to quantify [30]. Even though cellulose surfaces are far from perfect, there has nevertheless been a need for understanding the physicochemical interactions that occur between polymers with these cellulosic surfaces. This, in turn, requires the utilization of accurate surface sensitive techniques such as Quartz Crystal Microbalance with Dissipation (QCM-D), Surface Plasmon Resonance spectroscopy (SPR) and ellipsometry. Surface sensitive analytics, with detection limits in nanograms per square centimetre, demand substrates that are closer to the requirements stated by Cohen Stuart et al. [25] than those of the typical cellulose products such as paper.

Cellulose model surfaces have been developed in order to circumvent the shortcomings of using cellulose as a substrate in fundamental studies. So far, Langmuir-Blodgett (LB) deposition and spin coating are the major techniques used for preparing cellulose model film [31]. Both methods suffer from the limitation that the depositing materials need to be in liquid form. Considering the insolubility of cellulose in most common solvents, generating cellulose model surfaces with these techniques has been challenging. Solvents such as trifluoroacetic acid (TFA), *N*-methylmorpholine *N*-oxide (NMO) and mixtures of urea-sodium hydroxide (NaOH) have been used to dissolve cellulose and deposit it on substrates like silica and mica [32–34]. These regenerated films do not, however, represent the native form of cellulose in terms of crystallinity or crystalline structure (cellulose I), but rather that of cellulose II. An alternative method for obtaining cellulose model film surfaces is to spin-coat cellulose derivatives, followed by regeneration to cellulose by cleaving away the substituents on the surfaces [35,36]: the selectivity, efficiency and ease of performing the regeneration reaction are all important in this case. The most commonly used method for the preparation of regenerated model films is via trimethylsilyl cellulose (TMSC) films. The regenerated cellulose model films also show diffraction features and hence display some crystalline order, but not equivalent to that of cellulose I [37]. Fig. 1a shows AFM micrograph of regenerated cellulose films where no fibrillar features are visible. Another alternative is to spin-coat colloidal suspensions of nanocellulose, either cellulose nanocrystals (CNC) or cellulose nanofibers (CNF), on a silica substrate to form ultra-thin cellulose model films: these films are more equivalent to native cellulose [38]. Spin coated CNF and CNC films also show 3D morphological features (see Fig. 1 b and c). Adhesion between cellulose nanofibrils and the silica substrate is improved by using an anchoring layer of polyethyleneimine (PEI) or aminopropyltriethylsilane (APTES) [24,39,40]. It has been shown that anchoring a positively-charged layer can impart non-negligible effects to surface forces [41]. Recently, the recommendation was made that “all cellulose” thin films should be used in adsorption studies in order to avoid interference from positively-charged anchoring layers [42–44].

The well-defined morphology and ultrathin nature of cellulose model films has transformed fundamental adsorption studies, making them easier to undertake and less ambiguous. A comprehensive description of the preparation, characterization and challenges of cellulose model films has been provided by Kontturi and Österberg, and is recommended for further reading [31]. The cellulose surfaces need to be selected appropriately, depending on the subject being researched in the adsorption study; the choice of film is relevant to the phenomenon being modelled. The selection process needs to take into consideration that regenerated surfaces often provide consistent and reproducible results compared to

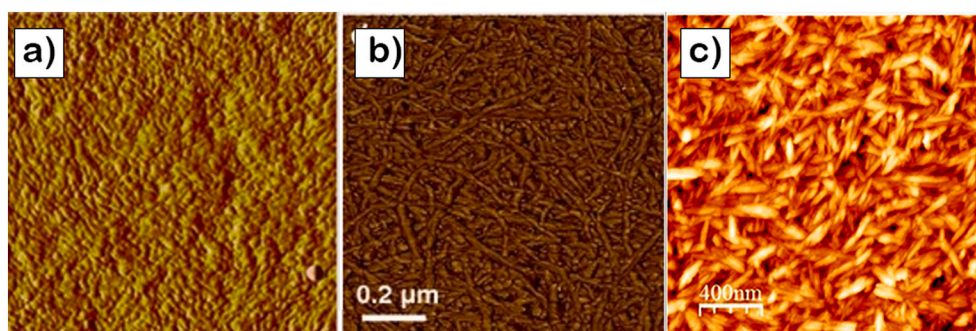


Fig. 1. AFM micrograph of different cellulose model films prepared by spin coating. a) regenerated cellulose films from TMSO reprinted from Niegelhell et al. [48] with permission from Elsevier, b) CNF model films with an anchoring layer of polyethyleneimine reprinted from Nypelö et al. [40] with permission from Springer and c) CNC model films reprinted from Villares et al. [49] with permission from Royal society of Chemistry.

nanocellulose model surfaces, whereas the latter have the advantage of being both physically and chemically more equivalent to cellulose-rich fibres. Cellulose nanofiber films are therefore recommended when the intention is to extrapolate the adsorption results from model studies to macro-fibres.

It is also important to mention that, alongside usage as an experimental model system for fundamental studies, ultra-thin cellulose films have extended their horizons to various material applications, including bio-sensing and thermoelectric applications [23,45]. A recent review by Kontturi and Spirk discusses cellulose thin films from a material perspective [46].

Here, the adsorption of polymers on cellulose surfaces using both conventional and model system approaches are reviewed. The discussion section is divided into two parts: the adsorption of polyelectrolyte and the adsorption of non-ionic polymers.

2.2. Polyelectrolyte adsorption on cellulose

The general polymer adsorption theory introduced by Scheutjens and Fleer [5] describes polyelectrolyte adsorption process in terms of four parameters: χ , χ_s , q_m , σ_0 , where χ and χ_s are the Flory-Huggins parameters accounting for the polymer-solvent interactions and the polymer segment-surface interaction, respectively. Both χ and χ_s have a positive linear dependence on the amount adsorbed. The terms q_m and σ_0 represent the surface charge and polymer segmental charge, respectively, and account for the coulombic interactions in polyelectrolyte adsorption [5,47]. The Scheutjens and Fleer theory can effectively predict the adsorption behaviour of different polymers, polymer adsorption isotherms, segmental density distributions and “tail-and-train” distributions. Wågberg [12] linked published results on the adsorption of different cationic polyelectrolytes on cellulose fibres to predictions made by the Scheutjens and Fleer theory. Here, we review the adsorption of different polymers on cellulose surfaces in relation to the terms of Scheutjens and Fleers’ adsorption parameters and considers thermodynamical aspects of adsorption.

2.2.1. Adsorption of negatively charged polyelectrolytes on cellulose

Cellulose substrates typically contain some negative charges that originate from the native lignocellulose matrix (hemicellulose, extractives, etc.) and the preparation process (introduction of oxidized groups). Hence, the interactions of negatively charged polyelectrolytes with the cellulose surface should be governed firstly by the electrostatic repulsion, providing these electrostatic forces are not overcome by other chemical interactions. The addition of salts is a way of modulating the interaction that occurs between the polyelectrolyte and the cellulose surface. Fig. 2 shows a predicted adsorption isotherm with increasing salt concentration for the particular case of adsorption of negatively charged polyelectrolytes on a likely-charged substrate. It is important to note that, in this model, only the addition of monovalent salts is

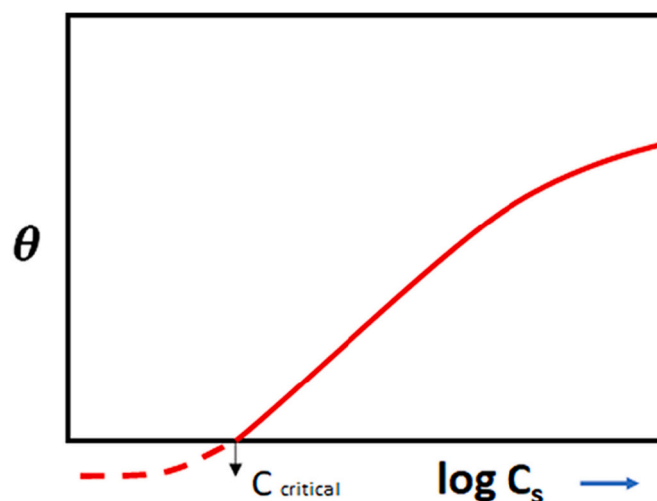


Fig. 2. A predicted adsorption isotherm of a negatively charged polymer on a likely-charged surface. θ : amount adsorbed and C_s : concentration of monovalent salt Adapted from Fleer et al. [5] with permission from Springer.

considered, where the ionic strength is equal to the salt concentration C_s [5].

The figure shows that, at lower salt concentrations, electrostatic repulsion dominates, and no adsorption takes place via electrostatic attraction: this is typically known as depletion and is illustrated by the dotted line. At a critical salt concentration, $C_{critical}$, the charges on the polymer and the surface are masked by the cations in the salt solution, and the depletion is switched to adsorption. At higher salt concentrations, the contribution made by repulsive electrostatic forces to the adsorption energy vanishes and the adsorption is considered to be dominated by non-electrostatic forces [5]. According to van de Steeg, these cases are termed “screening enhanced adsorptions” [50].

The most studied example of the adsorption of negatively charged polymer on cellulose is the adsorption of carboxymethyl cellulose (CMC). Carboxymethyl cellulose is a water-soluble cellulose derivative prepared by the carboxymethylation of cellulose [51–54]. CMC has been used as a viscosity modifier in food products, pharmaceuticals and cosmetics.

The study of the adsorption of CMC on the surface of cellulose is motivated by the fact that it is a resource-efficient way of increasing the number of carboxylic groups on the fibre surface [1,18,55–57]. The presence of charges on the fibres has a significant effect on various unit operations in pulp and papermaking, as well as on the final properties of the paper produced [19]. The adsorption of high molecular weight CMC has been shown to introduce charges on the fibres toposelectively, and substantial improvements in tensile properties have been observed

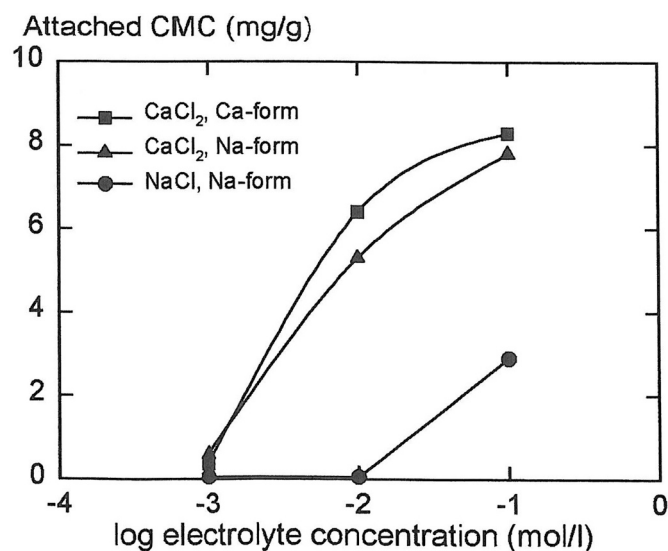


Fig. 3. Adsorption of CMC on cellulose fibres (ion-exchanged with Ca^{2+} and Na^+) as a function of electrolyte concentration. Reprinted from Laine et al. [18] with permission from De Gruyter.

[1,18,55]. An extensive adsorption study of CMC on cellulose fibre was carried out in a seminal work by Laine et al. in which it was shown that an increase in the concentration of electrolyte in the system facilitated the attachment of CMC onto the fibre surface [18], as can be seen in Fig. 3.

The shape of this binding isotherm is somewhat similar to that predicted by Fleer et al. (Fig. 2) and no adsorption can be observed at the low salt concentration (i.e., no added electrolyte). This corresponds to the depletion phenomenon predicted by Fleer et al. [5]. Fig. 3 also shows that the valency of the cations in the electrolyte has a substantial influence on the adsorption process. The presence of CaCl_2 enhances the adsorption of CMC on fibres compared to NaCl [18].

Other factors, such as pH, temperature and degree of substitution (DS) of the CMC, have also been shown to influence the adsorption process [18,58]. At low pH (close to pH 2), for example, adsorption was found to be enhanced [18]. Similar observations have been reported by Kargl et al. [58], too, where enhanced adsorption was attributed to the complete protonation of carboxylic groups in the CMC and the reduced solubility of the polyelectrolyte. The change in pH of the solution not only affects the CMC chains but also the cellulose surface: a lower pH will reduce the segmental charge of the CMC chains (σ_0) and the surface charge of the cellulose fibre (q_m).

Table 1 presents the findings to elucidate the influence of the degree of substitution (DS) of the CMC on its adsorption on bleached kraft pulp: the amount of CMC adsorbed on the fibre surface decreases as the degree of substitution increases. The DS has a profound effect whereby both the

solubility (χ) and the segmental charge (σ_0) of CMC polymer chains increase with increasing DS, which are unfavourable for the adsorption process.

Laine et al. also made the observation that the adsorption of CMC was temperature dependent: elevated temperature facilitated the adsorption process and resulted in higher amounts being attached [18]. The structural similarity of the cellulose backbone of CMC and cellulose gave rise to a co-crystallization mechanism being suggested in the literature for the irreversible attachment of CMCs on cellulose surfaces [18]. Interactions governing this co-crystallization process, however, remain unidentified. The enhanced adsorption seen at elevated temperature suggests that adsorption is an endothermic process, which devalorizes the possibility that hydrogen bonding is involved as a driving factor in adsorption processes [59].

Kargl et al. have studied the adsorption of CMC on cellulose model surfaces of varying chemical compositions, including regenerated cellulose from TMSC, deacetylated cellulose acetate and cellulose acetate, under different pH conditions [58]. They observed an adsorption trend that was pH dependent for both deacetylated and regenerated TMSC cellulose films, which was assumed to be due to the involvement of specific interactions between CMCs and the cellulose surface. This is in line with the prediction made by Scheutjens and Fleers that the adsorption of polyelectrolytes on likely-charged surface is governed by non-electrostatic forces [5] as depicted in Fig. 4.

In another study of model systems, CMC adsorption on regenerated cellulose surfaces was monitored using QCM-D and SPR [60]. The combination of these two techniques provided quantification of the adsorption based on both gravimetric and optical responses. It was observed that, when compared to NaCl , CaCl_2 enhanced the adsorption of CMC at the same ionic strength. This suggests that the presence of divalent ions contributes towards adsorption, in addition to electrostatic screening. The enhanced adsorption of CMC in presence of divalent ions such as Ca^{2+} could be also due to changes in solubility and/or conformational changes of the polymer in the presence of divalent salts [61,62]. Recent investigation has shown that the structures of CMC solutions in monovalent and divalent ions differ significantly, which could have a profound effect on adsorption behaviour [63,64]. These structural changes in polymer solutions have been overlooked in previous adsorption studies. Recently Arumughan et al. [65] studied the structural changes induced by Ca^{2+} ions in CMC solutions and its effects in adsorption of CMC on cellulose surface. It was observed that presence of Ca^{2+} ions facilitated the multichain association of CMC chains and increased the hydrodynamic size with increase in ionic strength of CaCl_2 . A correlation has been observed between the both the hydrodynamic size and electrophoretic mobility of CMC and adsorbed mass per unit area on the cellulose surface. The adsorbed mass increased monotonically with the hydrodynamic diameter. However, no such relation has been observed when comparing the zeta potentials of the CNF (the adsorbing surface) in different ionic strength and the adsorbed mass of CMC per unit area from corresponding CaCl_2 which suggest that the adsorption of CMC in presence of CaCl_2 is more governed by the changes

Table 1

Effects of the degree of substitution on the attachment of CMC to elemental chlorine free (ECF)-bleached softwood kraft pulp. Adapted from Laine et al. [18] with permission from De Gruyter.

CMC-product	D-S	M_w	Attached amount mg/g	Total charge increase $\mu\text{mol/g}$
CMC 2690	0.39	1.0×10^6	11.8	24
Finnfix WRH	0.52	1.0×10^6	8.7	23
Cekol DVG	0.64	1.7×10^6	8.2	27
Cekol FF2	0.71	2.8×10^6	8.1	29
Cekol MVG	0.80	1.0×10^6	7.9	28

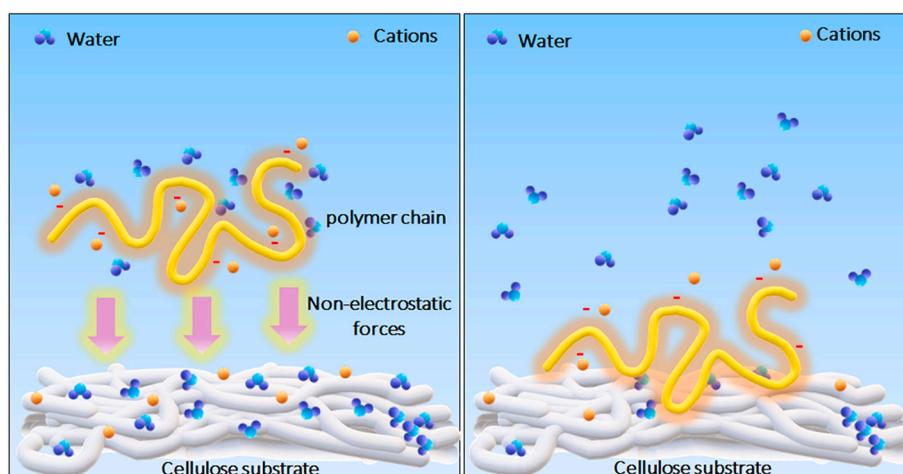


Fig. 4. Diagram illustrating the involvement of non-electrostatic forces in polyelectrolyte adsorption on a likely-charged surface.

CMC solutions rather than the bridging interaction between the CMC and the surface. As many of the interfacial processes, CMC adsorption on cellulose has also found to be depend on ion identity. A recent study by Arumughan *et al.* [66] reported specific ion effects in adsorption of CMC on cellulose. Presence of Ca^{2+} ions was more favourable for the adsorption of CMC on cellulose surface than Mg^{2+} ions. The distinction in the adsorption behaviour in the presence of Mg^{2+} and Ca^{2+} is suggested to be due to the differences in the polarizability of the ion.

Recently, an alternative mechanism has been in focus for the adsorption of polyelectrolytes on likely-charged surfaces in particular in the theoretical community [67]. According to this newly-proposed mechanism, the multivalent ions induce charge inversion on either the surface or the polymer chains, which promotes the adsorption of negatively-charged polyelectrolytes on likely-charged surfaces [67–69]. Charge inversion, or over-charging, is an observation that the sign of a surface charge can reverse in the presence of interacting species such as surfactants, polyelectrolytes, proteins and multivalent ions [70]. An excellent example of charge inversion is the reversal of the surface charge of cellulose caused by the adsorption of positively-charged polyelectrolytes [71].

The concept of charge inversion and its effect on the adsorption of polyelectrolytes on like-charged surfaces can be seen as concurring with the bridging between CMC and negative cellulose surfaces that is mediated by Ca^{2+} ions, as suggested by Liu *et al.* [60] (See Fig. 5). However, the charge inversion due to multivalent ions has not yet been reported for cellulose materials, which may be due to the experimental challenges involved.

Apart from the obvious influence cations have on the association of negatively-charged cellulose particles, anions are also found to influence the self-assembly of negatively-charged cellulose fibres in the state-of-the-art flow-focusing process used to make ultra-strong biofibres [72]. A Hoffmeister effect has been observed in the interaction of these particles and, in turn, in the physical properties of the fibres made under different salt environments [72]. Even though this is a completely different process, such effects may also be applicable to the adsorption of polymers on cellulose surfaces. It would be of interest to investigate this in a systematic manner: understanding the anionic influences in adsorption may become useful in tuning both the behaviour of adsorption and properties of adsorbed layers.

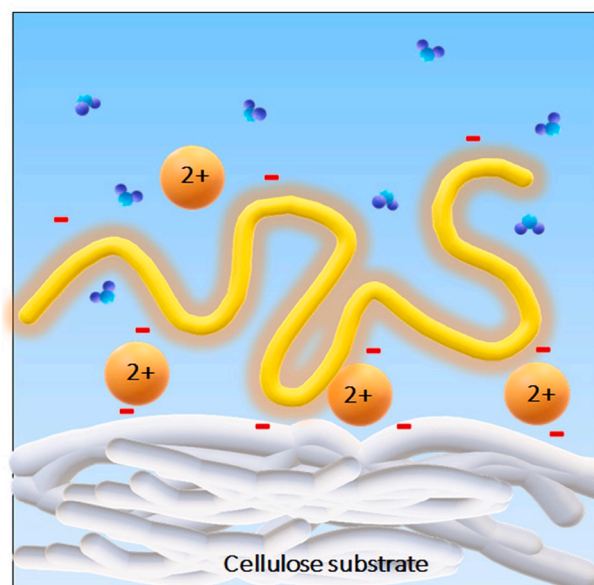


Fig. 5. Diagram illustrating bridging between an anionic polyelectrolyte and cellulose fibres, mediated by multivalent ions.

The properties of the adsorbed layer, such as stability, conformation and thickness, can be decisive for the properties of the final materials that are produced from the modified fibres.

The stability of adsorbed layers is important to consider when it comes to practical applications. Depending upon the conditions of environment that the modified surface is exposed to, the layer properties may change drastically and sometimes cause desorption. The adsorbed layer stability can be accessed using QCM-D by exposing the adsorbed layer to various conditions. For instance, Kargl *et al.* has studied the stability of adsorbed CMC layers by exposing it to water as well as sodium bicarbonate solutions, see Fig. 6.

The CMC layers adsorbed from solutions with pH 4 and pH 7 were not stable when exposed to water which resulted in sharp increase in frequency. On the other hand, the layer adsorbed from solution with pH

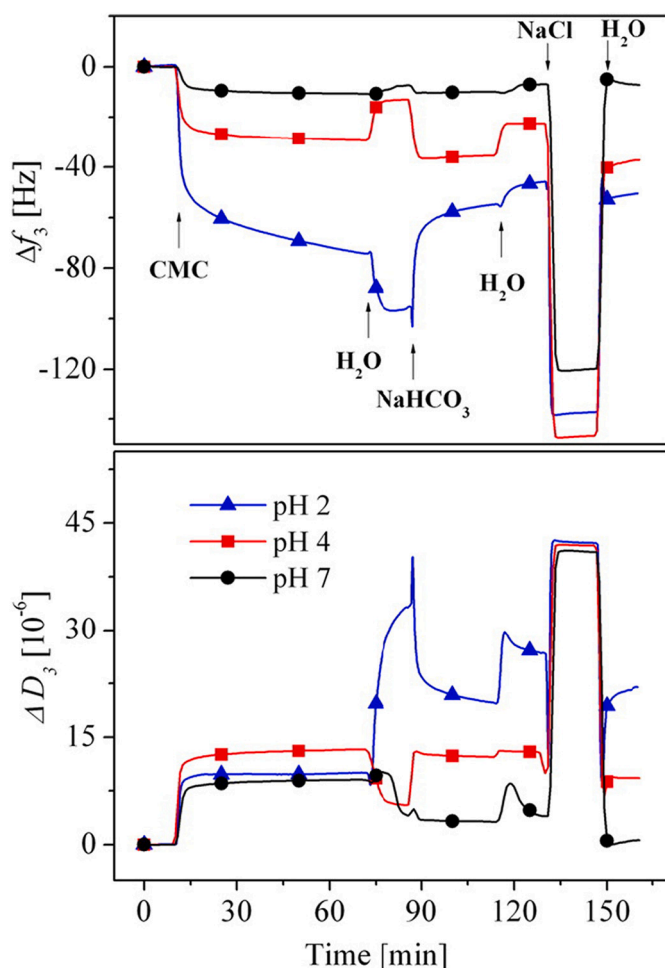


Fig. 6. Adsorption of CMC on a cellulose film at pH 2, 4, and 7. The frequency and dissipation changes of the third overtone of the oscillation are shown. Reprinted from Kargl et al. [58] with permission from American Chemical society.

2 were stable when exposed to water, but their conformation changed, which was evident from the large decrease in frequency and increase in dissipation. Liu et al. has shown that the CMC layer adsorbed from CaCl_2 solutions are more stable than the one adsorbed from NaCl solutions of same ionic strength [60].

The adsorbed layer conformation is another property that needs to be studied in detail to utilize the modified surfaces with their full potential. Gustafsson et al., studied wet adhesion between CMC modified cellulose surfaces laminated with polyvinyl amine adhesive [73], see Fig. 7. Bulky carboxymethylated cellulose membranes were used in a control experiment, as these have a surface chemistry equivalent to that of CMC

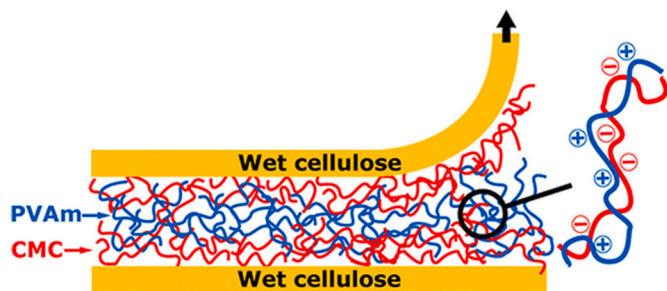


Fig. 7. Diagram illustrating interdigitation and the formation of complexes between layers of CMC adsorbed on cellulose and polyvinyl amine reprinted from Gustafsson et al. [73] with permission from American Chemical society.

modified cellulose fibres. They observed that a 10 nm thick CMC layer was necessary to achieve a superior interfacial wet adhesive property. It was proposed that the interdigitation of polyvinyl amine into CMC layers contributed more to the wet adhesive property than to the formation of poly-complexes between the CMC adsorbed and the polyvinyl amine.

The properties of the adsorbed layer play a pivotal role in the interdigitation process. It has been shown that the presence of different types of counter-ions can influence the formation of polyelectrolyte multilayers. In-depth knowledge of ion-specific effects in polymer adsorption would enable adsorption to be tailored in terms of the amount adsorbed and properties of the adsorbed layer, such as conformation and layer viscosity. It would facilitate the usage of polymer adsorption in applications in paper-based diagnostics, water purification, etc. It is important to note here that the aforementioned interdigitation process can also be affected by the conformation of the layer; wet adhesion via interdigitation can be controlled by changing the conformations of the adsorbed layers.

The adsorption behaviour of CMCs can also be modulated by chemical functionalisation. It has recently been shown that hydrophobically modified CMC adsorbs on cellulose surfaces more than unmodified CMC does [74], see Fig. 8. The hydrophobic groups in the CMC chains can contribute to changes in the solubility and conformation of the polymer chains in the solutions which can, in turn, alter the adsorption behaviour. Interestingly, a non-monotonic behaviour was also observed in adsorption when the degree of substitution (DS) of hydrophobic groups was increased, where the CMC derivative with a hydrophobic substituent of DS 0.41 adsorbed less than that with a DS of 0.2. Extensive functionalization of CMCs could affect the interaction energy of the polymer segment and the surface (χ_s) which, in turn, can reduce the adsorption tendency. In fact, it is almost impossible to vary these parameters independently and thereby determine their separate effects in experimental situations [75]. Grigory et al. [76] proposed that there should be a hydrophilic-hydrophobic balance in polymers to make adsorption possible, which is actually the balance between χ and χ_s . This rationale was used by Grigory et al. to make a water-soluble photo-responsive derivative of CMC that could adsorb on the fibre surfaces and exhibit photo-responsive cross-linking [76]. The same authors also developed fluorescent fibres by utilizing the adsorption of a fluorescent CMC derivative [77].

The adsorption of a poly(3,4-ethylenedioxythiophene):poly(styrenesulphonate) (PEDOT:PSS) system on cellulose can be

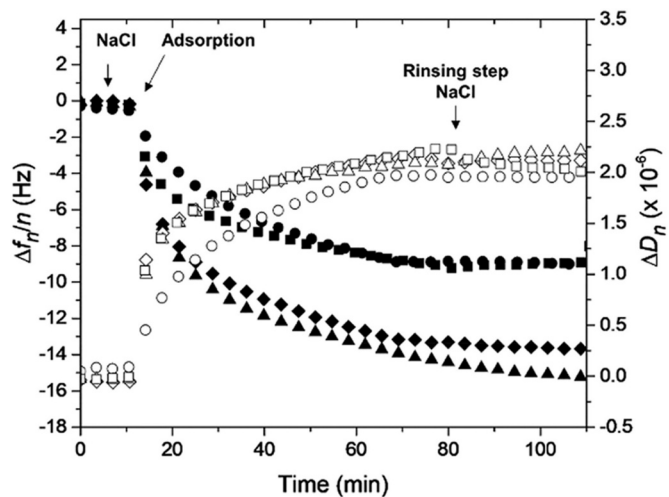


Fig. 8. QCM-D adsorption curve for the adsorption of CMC isocyclohexyl products on cellulose, where DS = 0.07 (● and ○), 0.2 (▲ and △) and 0.41 (◆ and ◇). Reprinted from Pettignano et al. [74] with permission from American Chemical society.

considered as an example of adsorption of a negatively-charged polymer on cellulose fibres as well [79]. PEDOT is a water-insoluble conducting polymer and is usually doped with an anionic polyelectrolyte to form spherical PEDOT:PSS particles: Jain et al. have recently studied the particle morphology and solution behaviour of such particles using a coarse-grained model and dynamic light scattering [78].

It was found that PEDOT occupies the inner region, with a span of up to around 8 nm. PSS forms a shell with a thickness of about 4 nm around the PEDOT (See Fig. 9). Interactions between PEDOT:PSS and cellulose surfaces have already been used to create cellulose-based, flexible and light-weight electronic materials [10,80–83].

Seen from a theoretical perspective, the adsorption of PEDOT:PSS on cellulose differs from the adsorption of CMC on cellulose due to its poly-complex nature and particle morphology. Jain et al. have recently carried out an extensive study to distinguish the factors controlling the interaction of PEDOT:PSS with cellulose surfaces [84]. They observed that the adsorption of anionic PEDOT:PSS particles on cellulose surfaces could be tuned by altering solution parameters such as pH, ionic strength, temperature and presence of different counter-ions. It was suggested, due to the endothermic nature of the PEDOT:PSS adsorption process, that adsorption is driven by the gain in entropy resulting from the release of water molecules from the surface. However, this investigation did not consider changes in the colloidal behaviour of PEDOT:PSS at elevated temperatures. The endothermic behaviour of polyelectrolyte adsorption could arise due to changes in solvent-polymer interaction at elevated temperatures. High temperatures can induce insolubility in

polyelectrolytes, which could result in higher adsorption [85,86]. The endothermic behaviour of CMC adsorption observed by Laine et al. could also be caused by changes in polymer-solvent interaction at high temperatures [18].

Despite several efforts being made to understand the adsorption of negatively charged polymers on cellulose, a conclusive statement on the adsorption mechanism cannot be formulated. Although the involvement of both entropic and enthalpic factors in adsorption is apparent, quantitative determinations of these factors require systematic thermodynamic evaluations.

Recently, it has been suggested that QCM-D can be used to evaluate the thermodynamics of binding interactions of carbohydrate-binding proteins to cellulose surfaces [87–89]. The authors have fitted the adsorption data to the Langmuir model to extract the equilibrium constant of the process and used it for further calculation of entropy and enthalpy of the process. Even though the data fits well with the Langmuir adsorption model, the applicability to the specific system of interest should be considered. Langmuir model assumes that only a monomolecular layer of non-interacting solute is formed on the adsorbent surface, with all adsorption sites being of equal adsorption energy. All these criteria seems to be violated in the adsorption of protein or other polymers on cellulose surfaces; therefore, equilibrium constants calculated from the Langmuir plot should be considered with caution and should not be used for quantitative assessment of thermodynamic parameters, as mentioned by Latour [90]. Alternatively, use of direct methods such as isothermal titration calorimetry is recommended for thermodynamic evaluations [91].

2.2.2. Adsorption of positively charged polyelectrolytes on cellulose surfaces

The adsorption of positively charged polymers on cellulose is important in paper making, since they are used as additives to improve the performance of paper and as retention aid. Several studies have been devoted to probing the adsorption behaviour of cationic polyelectrolytes with respect to cellulose fibres. A review by Wågberg has linked different cases predicted in Scheutjens and Fleers' theory with published data of the adsorption of mostly positively-charged polyelectrolyte on cellulose fibres that was available at the time [12]. The adsorption of positively charged polyelectrolytes has also been studied, using surface-sensitive techniques such as QCM-D and reflectometry [92]. The interaction of cationic polyelectrolytes with negatively-charged fibre surfaces is driven by entropy gain due to the counterion release (See Fig. 10), consequently the adsorption process is therefore highly sensitive to the concentration of the electrolyte [93].

Counter-ions are released into the solutions from both the polymer chains and the surface during the process of adsorption of

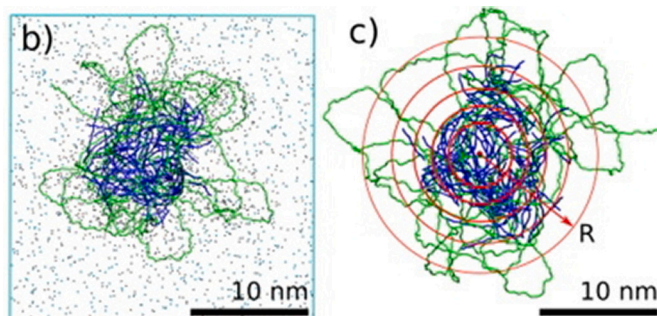


Fig. 9. (b) Simulation image of a PEDOT:PSS complex in dispersion, where water molecules are not displayed for clarity and Na^+ and Cl^- ions are shown as dots. (c) Schematic illustration of a particle dividing into shells of radius R , where the red dot is the centre of its mass. Reprinted from Jain et al. [78] with permission from Elsevier. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

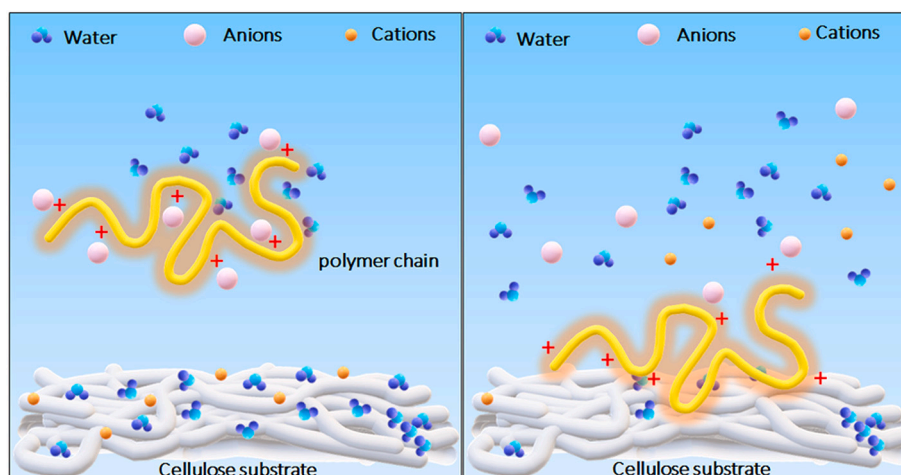


Fig. 10. Diagram illustrating the adsorption of cationic polymers on a cellulose surface, driven by the release of counter-ions.

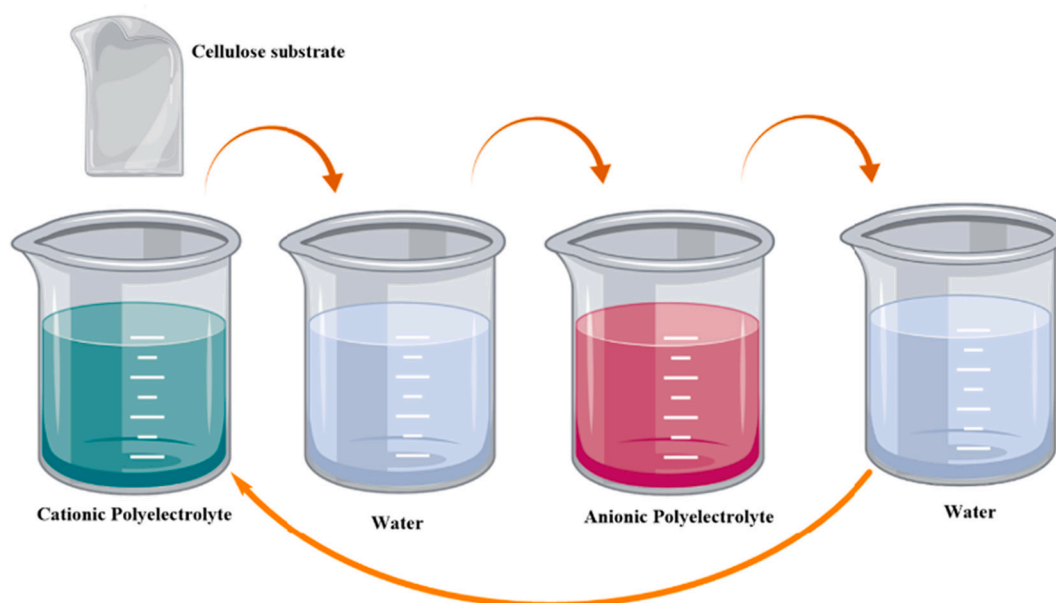


Fig. 11. Schematic representation of the Layer-by-layer technique.

polyelectrolytes on cellulose, which leads to an increase in the translational entropy of the system. This results in a gain in the free energy that is sufficient to make adsorption favourable [12,93,92]. The addition of salt reduces the gain in entropy because the amount of counter-ions released during the adsorption process decreases, and thus adsorption is reduced. Even though the adsorption of positively charged polyelectrolytes on cellulose is considered to be well understood, there are certain aspects where more detailed investigations are still necessary. In the theoretical treatment of polyelectrolyte adsorption [5], it has been mentioned that the adsorption of specific counter-ions on surfaces can alter the adsorption behaviour due to the competition between the counter-ions interacting with either the surface or the polymer segments, which could result in reduced polymer adsorption. To the best of the authors' knowledge, a systematic study of the specific adsorption of counter-ions on cellulose surfaces, and its effect on polymer adsorption, has not been carried out thus far.

2.2.3. Layer-by-layer assembly of cellulose surfaces

Layer-by-layer (LbL) assembly is an established technique for coating substrates with polymers, colloids, biomolecules and even biological cells. It offers superior control and versatility when compared to other thin-film deposition techniques and has been widely used in both research and industrial applications [94–96]. In the LbL technique, charge reversal is achieved by coating a charged surface with an oppositely charged polymer or particle dispersion (See Fig. 11). Subsequent deposition of alternating positively and negatively-charged layers on the surface then builds up a multi-layered system [97]. The thickness of the adsorbed layer depends on the treatment conditions, e.g. concentration, ionic strength, pH and temperature [98]. The adsorption of both positive and negatively-charged polymers on cellulose has opened up possibilities for tailoring the properties of the material for advanced applications such as energy storage, water filtration and bacterial resistant films [2,8,99,100]. It has been shown that the LbL technique can be used to prepare stable cellulose films on a SiO₂ substrate; a positively-charged polyelectrolyte layer is anchored on the substrate, on top of which a CNF layer is adsorbed [40]. Although a detailed discussion of the LbL technique and its applications is omitted here, since it falls outside the scope of this review, the authors can recommend review by Wågberg et al. for further reading [11].

2.3. Non-ionic polymer adsorption on cellulose

Many non-ionic polymers, including hemicelluloses and other polysaccharides adsorb on cellulose surfaces; such interactions are already being utilized in traditional papermaking processes as well as in advanced applications for functional materials [101–103].

Several investigations have sought to understand the interactions governing this adsorption process. The challenge, however, is to isolate the driving force of adsorption for a diverse set of polymer structures (branching) and hydrophilicities.

The absence of coulombic interactions means that the adsorption of non-ionic polymers differs fundamentally from that of polyelectrolytes. Only χ and χ_s are considered in the theoretical treatment of adsorption of non-ionic polymers on surfaces. The adsorption of non-ionic polymers is not as sensitive to ionic strength as polyelectrolytes, but the presence of specifically-interacting counter ions may nevertheless alter the adsorption process because these can compete with polymer segments for adsorption sites on the adsorbing surface [5].

Köhnke et al. investigated how the degree of substitution and the substitution pattern of arabinoxylans influenced adsorption on cellulose surfaces [101]. Arabinoxylans with low ratios of arabinose to xylose were found to adsorb more onto cellulose surfaces, which is likely due to the decreased solubility of arabinoxylans with decreasing arabinose to xylose ratio. The substitution pattern along the polymer chains can influence both χ and χ_s , depending on the conformation that is assumed by the polymers in the solution.

Xyloglucan (XG) is one of the most studied hemicelluloses where adsorption on cellulose is concerned. In a recent article, Kishani et al. suggested that there is a cluster formation and phase separation of XG molecules at a cellulose/water interface induced by an increase in its concentration close to the surface, which contributes to the driving force for adsorption [104] (See Fig. 12). Linder et al. [105] studied the adsorption of xylans on cellulose surfaces, observing that globular xylan particles were formed on the cellulose surface even after short treatment times. This suggested that the surface structures are formed by the adsorption of preformed xylan aggregates from solution rather than being built up at the cellulose surface over time by the multilayer adsorption of xylan. This concurs with observations made by Kishani et al. [104]. Adsorption on cellulose assisted by globular form of modified xylans have been reported by Nypelö et al. [106].

The abundance of hydroxyl groups on both the XG and cellulose

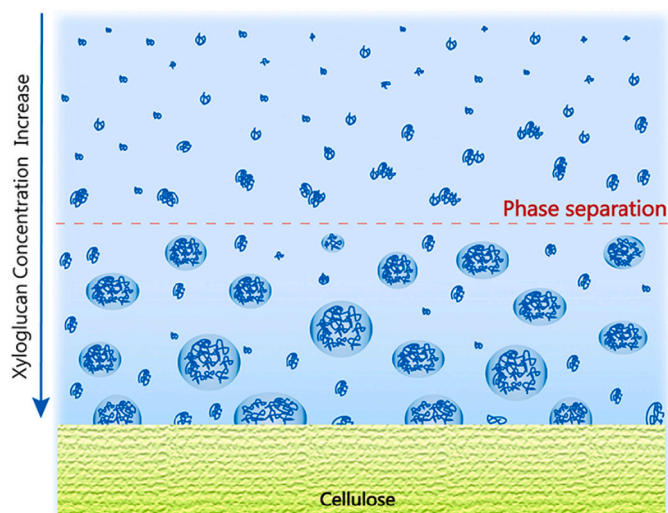


Fig. 12. Schematic diagram of xyloglucan adsorption on cellulose. Reprinted from Kishani et al. [104] with permission from American Chemical society.

surface has led to claims being made that the driving force is enthalpic in origin. Hanus et.al [107] further supported this with molecular dynamic simulations that demonstrated the interaction of xyloglucan with cellulose surface is predominantly by polar components such as hydrogen bonding, it is important to note that in the simulation the presence of water was not considered. Isothermal titration calorimetry (ITC) is a sensitive technique which enables thermodynamic profiling of binding events [108]. Lima et al. [109] performed ITC studies of interaction of xyloglucan with cellulose and showed that the adsorption is an exothermic process with a small heat change. Sundman et al. also supported involvement of hydrogen bonding in the adsorption of non-ionic cellulose derivatives on cellulose surfaces [109–111]. Hu et.al observed that the non-ionic polymers such as Hydroxypropyl guar (HPG), Hydroxyethylcellulose (HEC), and Locust beam gum (LBG) adsorbs to cellulose nanocrystal surfaces, whereas dextran did not show any adsorption to cellulose surface [112]. Significant changes in adsorption behaviours of chemically similar polysaccharides suggest that there are subtle differences in their interactions with cellulose and adsorption is not probably driven by the common ability to form hydrogen bonds [93]. Nevertheless, the hydrogen bonds between non-ionic polymers such as HEC and XG can be easily replaced by hydrogen bonds with water, therefore short-range specific interactions such as hydrogen

might not be the sole driver of the adsorptions. Recent articles supports this picture; Benselft et al. observed endothermic nature of adsorption of xyloglucan on cellulose surface [59]. Elevated temperature would reduce the efficiency of formation of hydrogen bonding interactions making them unlikely driving force for adsorption. It has been suggested that in the case of highly hydrated cellulose surfaces, adsorption is driven by the entropy gain due to the release of structured water from the surface during the adsorption process, (see Fig. 13) [57,90]. Kishani et al. have recently supported this further, with results they obtained from molecular dynamic simulations [113].

However, the endothermic behaviour might not directly link to the water release from the cellulose surface. It could be also due to the solubility changes in the polymer solutions.

According to Kishani et al. [104] the XG chains form associated structures at higher temperature which result in larger average size and wider size distribution (See Fig. 14). This result indicates that the solubility of XG decreases with increase in temperature. The decreased solubility can also favour the adsorption of XG on the surface and which

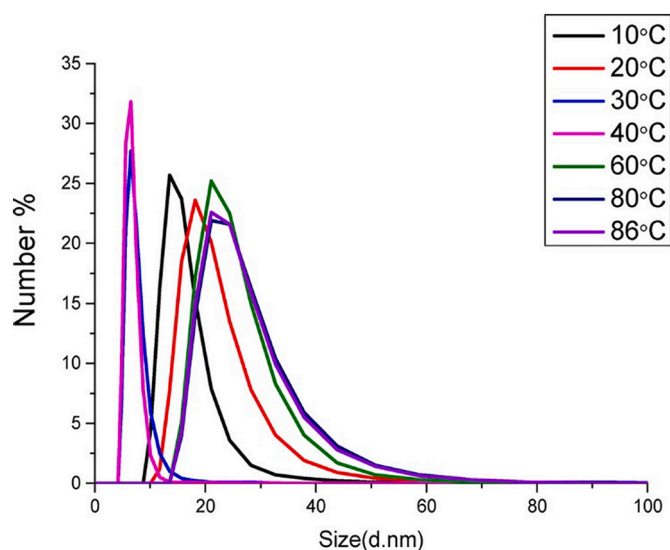


Fig. 14. Number distribution of the high molecular weight sample of xyloglucan at 1 g/L prepared at different temperatures, as evaluated from DLS measurements. Reprinted from Kishani et al. [104] with permission from American Chemical society.

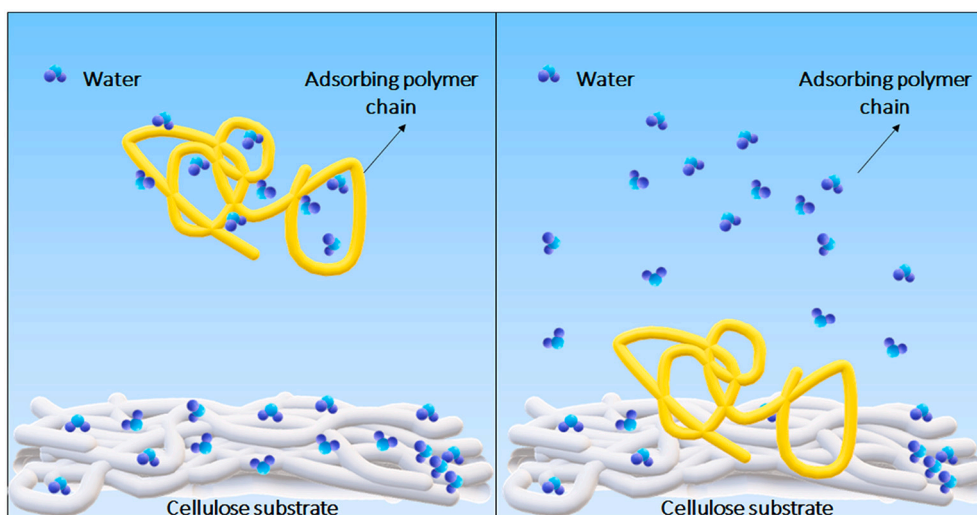


Fig. 13. Diagram illustrating the entropy-driven adsorption of non-ionic polymers on a cellulose surface.

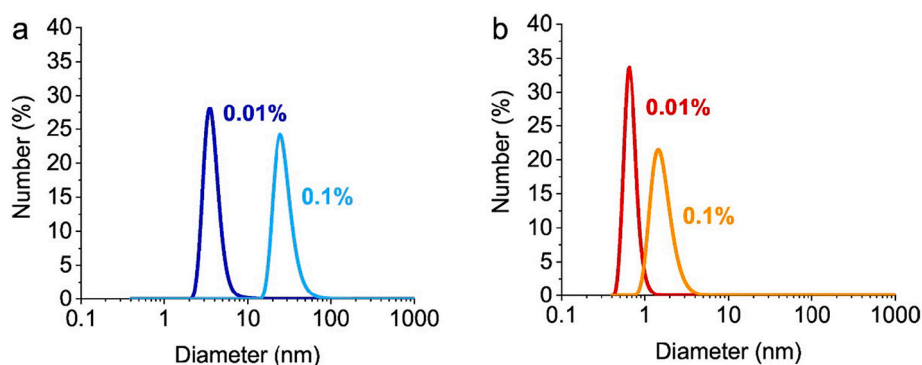


Fig. 15. Size distribution by number of HX (a) and LX (b) dispersed in PBS buffer at concentrations of 0.1 and 0.01 wt% determined at 22 °C. Reprinted from Palasingh et al. [114] with permission from Elsevier.

could explain the endothermic behaviour.

Linder et al. [105] observed temperature induced aggregation of xylans and it was found that there was a considerable reduction of 4-*O*-methyl glucuronic acid groups in xylan after the heat treatment in autoclave. The reduction in the 4-*O*-methyl glucuronic acid groups resulted significant reduction in the solubility which in turn increased the interactions of xylans with cellulose surface [105].

Recently Palasingh et al. has observed that the molecular mass of the oxidized xylan is crucial in determining the solubility and in turn the adsorption behaviour on CNF and TEMPO oxidized CNF surfaces [114].

Fig. 15 shows the hydrodynamic size distribution of different grades of oxidized xylans in two different concentrations. It was observed that the hydrodynamic diameter of the high molecular weight oxidized xylans increased by 6.8 fold when the concentration changed from 0.01 wt % to 0.1 wt% whereas the low molecular weight xylans exhibited an increase of 2.5 fold.

These solubility changes of different grades of oxidized xylans were reflected in their adsorption on different cellulose surfaces. Fig. 16 shows the adsorbed mass of high molecular weight xylan (HX) and low molecular weight xylan (LX) probed using QCM-D and SPR. The oxidized xylan with high molecular weight were adsorbed more on both the CNF surface whereas the oxidized xylan with low molecular weight adsorbed less compared to the larger ones.

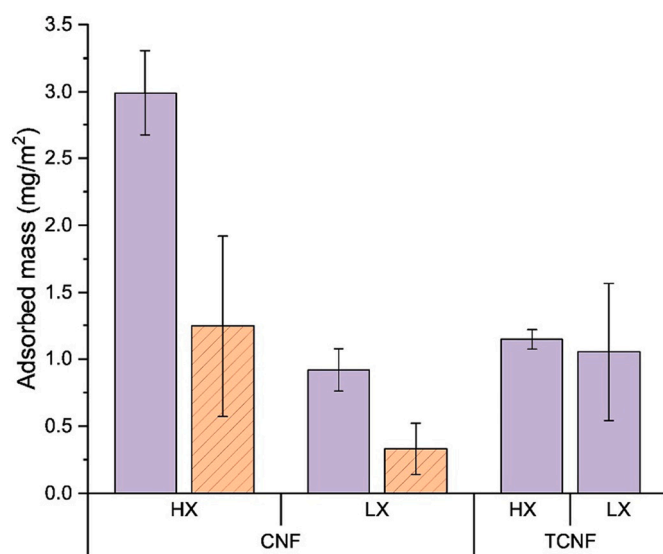


Fig. 16. Adsorbed mass of HX and LX on CNF and TCNF films using QCM-D (■) and SPR (▨). Reprinted from Palasingh et al. [114] with permission from Elsevier.

3. Conclusions and future outlook

The need for non-synthetic strategies for cellulose modification is undisputed. Non-covalent modification by means of polymer adsorption has been found to be a successful method for introducing new functionalities to cellulose materials. It has traditionally been used in the papermaking industry to achieve mechanical paper properties. Developments in layer-by-layer technology has meant that, after the 2000s, the direction of research in this area has shifted to applications of advanced engineering materials. Even though a plethora of investigations have sought out the fundamentals behind the polymer adsorption process, gaps in knowledge remain that need to be filled: the adsorption of negatively-charged polyelectrolytes on cellulose surfaces in particular requires in-depth study to identify the driving force behind the adsorption process. Although the involvement of both entropic and enthalpic factors in adsorption are obvious, the dominating factors should be identified by systematic thermodynamic evaluations.

It is well known that multivalent ions can promote the adsorption of anionic polyelectrolytes on cellulose, and it has been suggested that they act as a bridge between the cellulose surface and the polyelectrolytes. Structural changes in the solution induced by multivalent ions, along with the solubility of polyelectrolytes, have been overlooked while describing the adsorption process. In addition, the adsorption of anionic and cationic polyelectrolytes is prone to specific ionic effects but such effects on the polymer adsorption process on cellulose surfaces have not yet been studied.

In addition to addressing these knowledge gaps as a prerequisite for further development of adsorption-based functionalisation routes, the future work in this area will likely be focused on identifying strategies to efficiently tune the properties of the target surfaces and find large scale processing solutions for resource efficient adsorption steps.

In the context of tuning the surface properties, the adsorbing conditions would have a profound influence on the properties of an adsorbed layer; properties such as conformation and hydration would have a significant impact on the interaction of a modified surface with other entities, e.g., proteins, enzymes and other active molecules. Achieving a layer in which the properties are controlled opens the possibility of customising a cellulose surface, thereby making it suitable for various applications such as antifouling surfaces, paper-based diagnostics, water filtration and antimicrobial surfaces.

Turning to processing solutions, integration of polymer adsorption step with current pulping stages has shown to be feasible [115]. This paves a resource efficient way of making fibres with tailored properties in accordance with demands in the market. Similarly, polymer adsorption could be also possible to integrate with production of regenerated cellulose fibres such as viscose fibres [116] and lyocell fibres [117,118].

Declaration of Competing Interest

The authors declare no competing interest.

Acknowledgements

This project is part of the AvanCell network. It is financed partially by Tresearch, BIOINNOVATION VINNOVA, and Södra Foundation for Research, Development and Education, which are gratefully acknowledged. Wallenberg Wood Science Center is acknowledged for funding and support.

References

- Laine J, Lindström T, Glad Nordmark G, Risinger G. Studies on Topochemical modification of cellulosic Fibres. Part 2. *Nord Pulp Pap Res J* 2002;17:50–6.
- Ottenhall A, Henschen J, Illergård J, Ek M. Cellulose-based water purification using paper filters modified with polyelectrolyte multilayers to remove bacteria from water through electrostatic interactions. *Environ Sci Water Res Technol* 2018;2070–9. <https://doi.org/10.1039/c8ew00514a>.
- Wågberg L, Forsberg S, Johansson A, Juntti P. Engineering of fibre surface properties by application of the polyelectrolyte multilayer concept. Part I: modification of paper strength. *J Pulp Pap Sci* 2002;28(7):222–8.
- Eriksson M, Notley SM, Wågberg L. The influence on paper strength properties when building multilayers of weak polyelectrolytes onto wood fibres. *J Colloid Interface Sci* 2005;292(1):38–45. <https://doi.org/10.1016/j.jcis.2005.05.058>.
- Fleer GJ, Cohen Stuart MA, Scheutjens JM, Cosgrove T, Vincent B. *Polymers at interfaces*. Springer Science & Business Media; 1993.
- Larsson E, Sanchez CC, Porsch C, Karabulut E, Wågberg L, Carlmark A. Thermo-responsive nanofibrillated cellulose by polyelectrolyte adsorption. *Eur Polym J* 2013;49:2689–96. <https://doi.org/10.1016/j.eurpolymj.2013.05.023>.
- Utsel S, Malmström EE, Carlmark A, Wågberg L. Thermo-responsive nanocomposites from multilayers of nanofibrillated cellulose and specially designed N-isopropylacrylamide based polymers. *Soft Matter* 2010;6:342–52. <https://doi.org/10.1039/b910481j>.
- Hamedí M, Karabulut E, Marais A, Herland A, Nyström G. Nanocellulose aerogels functionalized by rapid layer-by-layer assembly for high charge storage and beyond. *Angew Chem Int Ed* 2013;125(46):12260–4. <https://doi.org/10.1002/ange.201305137>.
- Junka K, Guo J, Filpponen I, Laine J, Rojas OJ. Modification of cellulose nanofibrils with luminescent carbon dots. *Biomacromolecules* 2014;15(3):876–81. <https://doi.org/10.1021/bm4017176>.
- Belaineh D, Andreasen JW, Palisatis J, Malti A, Håkansson K, Wågberg L, et al. Controlling the organization of PEDOT:PSS on cellulose structures. *ACS Appl Polym Mater* 2019;1(9):2342–51. <https://doi.org/10.1021/acsapm.9b00444>.
- Wågberg L, Erlandsson J. The use of layer-by-layer self-assembly and Nanocellulose to prepare advanced functional materials. *Adv Mater* 2020;33(28):2001274. <https://doi.org/10.1002/adma.202001474>.
- Wågberg L. Polyelectrolyte adsorption onto cellulose fibres - a review. *Nord Pulp Pap Res J* 2000;15(5):586–97. <https://doi.org/10.1515/9783110213447>.
- Tang J, Sisler J, Grishkewich N, Tam KC. Functionalization of cellulose nanocrystals for advanced applications. *J Colloid Interface Sci* 2017;494:397–409. <https://doi.org/10.1016/j.jcis.2017.01.077>.
- Tsuji W, Nakao T, Ohigashi K, Maegawa K, Kobayashi N, Shukri S, et al. Chemical modification of cotton fiber by alkali-swelling and substitution reactions—acetylation, cyanoethylation, benzylation, and oleoylation. *J Appl Polym Sci* 1986;32(5):5175–92. <https://doi.org/10.1002/app.1986.070320533>.
- Swenonson B, Larsson A, Hasani M. Probing interactions in combined hydroxide base solvents for improving dissolution of cellulose. *Polymers (Basel)* 2020;12(6):1310. <https://doi.org/10.3390/POLYM12061310>.
- Swenonson B, Larsson A, Hasani M. Dissolution of cellulose using a combination of hydroxide bases in aqueous solution. *Cellulose* 2020;27(1):101–12. <https://doi.org/10.1007/s10570-019-02780-8>.
- Gunnarsson M, Bernin D, Östlund Å, Hasani M. The CO₂ capturing ability of cellulose dissolved in NaOH(aq) at low temperature. *Green Chem* 2018;20(14):3279–86. <https://doi.org/10.1039/c8gc01092g>.
- Laine J, Lindström T, Nordmark GG, Risinger G. Studies on topochemical modification of cellulosic fibres. Part 1. Chemical conditions for the attachment of carboxymethyl cellulose onto fibres. *Nord Pulp Pap Res J* 2000;15(5):520–6. <https://doi.org/10.3183/NPPRJ-2000-15-05-p520-526>.
- Barzyk D, Page DH, Ragauskas A. Acidic group topochemistry and fibre-to-fibre specific bond Strength. *J Pulp Pap Sci* 1997;23(2):J59–61.
- Barzyk D, Page DH, Ragauskas A. Carboxylic acids and fibre bonding. In: Baker CF, editor. *The Fundamentals of Papermaking Materials*. Cambridge: Trans. of the Xth Fund. Res. Symp.; 1997. p. 893–907.
- Miletzky Albrecht, Fischer Wolfgang J, Czibula Caterina, Teichert Christian, Bauer Wolfgang, Schennach Robert, et al. How xylan effects the breaking load of individual fiber–fiber joints and the single fiber tensile strength. *Cellulose* 2015;22:849–59. <https://doi.org/10.1007/s10570-014-0532-8>. <https://link.springer.com/article/10.1007/s10570-014-0532-8>.
- Ban W, Van Heiningen A. Adsorption of hemicellulose extracts from hardwood onto cellulosic fibers. I. Effects of adsorption and optimization factors. *Cellulose Chemistry and Technology*. 1st45; 2011. p. 57.
- Orelma H, Filpponen I, Johansson LS, Laine J, Rojas OJ. Modification of cellulose films by adsorption of cmc and chitosan for controlled attachment of biomolecules. *Biomacromolecules* 2011;12(12):4311–8. <https://doi.org/10.1021/bm201236a>.
- Orelma H, Teerinen T, Johansson LS, Holappa S, Laine J. CMC-modified cellulose biointerface for antibody conjugation. *Biomacromolecules* 2012;13(4):1051–8. <https://doi.org/10.1021/bm201771m>.
- Cohen Stuart MA, Cosgrove Terence, Vincent Brian. Experimental aspects of polymer adsorption at solid/solution interfaces. *Adv Colloid Interface Sci* 1986;24:143–239. [https://doi.org/10.1016/0001-8686\(85\)80030-0](https://doi.org/10.1016/0001-8686(85)80030-0). <https://www.sciencedirect.com/science/article/pii/0001868685800300>.
- Wågberg L, Odberg L. Polymer adsorption on cellulosic fibers. *Nord Pulp Pap Res J* 2007;4:135–40. <https://doi.org/10.3183/npprj-1989-04-02-p135-140>.
- Sjostrom E. The origin of charge on cellulosic fibers. *Nord Pulp Pap Res J* 2007;4(2):90–3. <https://doi.org/10.3183/npprj-1989-04-02-p090-093>.
- Winter L, Wågberg L, Odberg L, Lindström T. Polyelectrolytes adsorbed on the surface of cellulosic materials. *J Colloid Interface Sci* 1986;111:537–43. [https://doi.org/10.1016/0021-9797\(86\)90057-3](https://doi.org/10.1016/0021-9797(86)90057-3).
- Horvath AE. The effects of cellulosic fiber charges on polyelectrolyte adsorption and fiber-fiber interactions. PhD diss KTH 2006.
- French AD. Increment in evolution of cellulose crystallinity analysis. *Cellulose* 2020;27:5445–8. <https://doi.org/10.1007/s10570-020-03172-z>.
- Kontturi E, Tammelin T, Österberg M. Cellulose - model films and the fundamental approach. *Chem Soc Rev* 2006;35(12):1287–304. <https://doi.org/10.1039/b601872f>.
- Zhang L, Ruan D, Zhou J. Structure and properties of regenerated cellulose films prepared from cotton linters in NaOH/urea aqueous solution. *Ind Eng Chem Res* 2001;40(25):5923–8. <https://doi.org/10.1021/ie0010417>.
- Gunnars S, Wågberg L, Cohen Stuart MA. Model films of cellulose: I. Method development and initial results. *Cellulose* 2002;9(3):239–49. <https://doi.org/10.1023/A:1021196914398>.
- Neuman RD, Berg JM, Claesson PM. Direct measurement of surface forces in papermaking and paper coating systems. *Nord Pulp Pap Res J* 2007;8(1):96–104. <https://doi.org/10.3183/npprj-1993-08-01-p096-104>.
- Schaub M, Wenz G, Wegner G, Stein A, Klemm D. Ultrathin films of cellulose on silicon wafers. *Adv Mater* 1993;5(12):919–22. <https://doi.org/10.1002/adma.19930051209>.
- Weißl M, Hobisch MA, Johansson LS, Hettrich K, Kontturi E, Volkert B. Cellulose carbamate derived cellulose thin films: preparation, characterization and blending with cellulose xanthate. *Cellulose* 2019;26(12):7399–410. <https://doi.org/10.1007/s10570-019-02600-z>.
- Jones AOF, Resel R, Schrode B, Machado-Charry E, Röthel C, Kunert B, et al. Structural order in cellulose thin films prepared from a Trimethylsilyl precursor. *Biomacromolecules* 2020;21:653–9. <https://doi.org/10.1021/acs.biomac.9b01377>.
- Edgar CD, Gray DG. Smooth model cellulose I surfaces from nanocrystal suspensions. *Cellulose* 2003;10(4):299–306. <https://doi.org/10.1023/A:1027333928715>.
- Ahola S, Salmi J, Johansson LS, Laine J, Österberg M. Model films from native cellulose nanofibrils. Preparation, swelling, and surface interactions. *Biomacromolecules* 2008;9(4):1273–82. <https://doi.org/10.1021/bm701317k>.
- Nypelö T, Pynnönen H, Österberg M, Paltakari J, Laine J. Interactions between inorganic nanoparticles and cellulose nanofibrils. *Cellulose* 2012;19(3):779–92. <https://doi.org/10.1007/s10570-012-9656-x>.
- Cranston ED, Gray DG, Rutland MW. Direct surface force measurements of polyelectrolyte multilayer films containing nanocrystalline cellulose. *Langmuir* 2010;26(22):17190–7. <https://doi.org/10.1021/ja1030729>.
- Foster EJ, Moon RJ, Agarwal UP, Bortner MJ, Bras J, Camarero-Espinosa S, et al. Current characterization methods for cellulose nanomaterials. *Chem Soc Rev* 2018;47(8):2609–79. <https://doi.org/10.1039/c8cs00895j>.
- Reid MS, Villalobos M, Cranston ED. Cellulose nanocrystal interactions probed by thin film swelling to predict dispersibility. *Nanoscale* 2016;8(24):12247–57. <https://doi.org/10.1039/c6nr01737a>.
- Niinivaara E, Faustini M, Tammelin T, Kontturi E. Water vapor uptake of ultrathin films of biologically derived nanocrystals: quantitative assessment with quartz crystal microbalance and spectroscopic ellipsometry. *Langmuir* 2015;31(44):121710–6. <https://doi.org/10.1021/acs.langmuir.5b01763>.
- Orelma H, Filpponen I, Johansson LS, Österberg M, Rojas OJ, Laine J. Surface functionalized nanofibrillar cellulose (NFC) film as a platform for immunoassays and diagnostics. *Biointerphases* 2012;7(1):61. <https://doi.org/10.1007/s13758-012-0061-7>.
- Kontturi E, Spirk S. Ultrathin films of cellulose: a materials perspective. *Front Chem* 2019;7:488. <https://doi.org/10.3389/fchem.2019.00488>.
- Fleer GJ, Scheutjens JM. Adsorption of interacting oligomers and polymers at an interface. *Adv Colloid Interface Sci* 1982;16(1):341–59. [https://doi.org/10.1016/0001-8686\(82\)85024-0](https://doi.org/10.1016/0001-8686(82)85024-0).
- Niegelhell K, Chemelli A, Hobisch J, Griesser T, Reiter H, Hirn U. Interaction of industrially relevant cationic starches with cellulose. *Carbohydr Polym* 2018;179:290–6. <https://doi.org/10.1016/j.carbpol.2017.10.003>.
- Villares A, Moreau C, Dammak A, Capron I, Cathala B. Kinetic aspects of the adsorption of xyloglucan onto cellulose nanocrystals. *Soft Matter* 2015;11(32):6472–81. <https://doi.org/10.1039/c5sm01413a>.

- [50] van de Steeg HGM, Stuart MAC, de Keizer A, Bijsterbosch BH. Polyelectrolyte adsorption: a subtle balance of forces. *Langmuir* 1992;8(10):2538–46. <https://doi.org/10.1021/la00046a030>.
- [51] Fechter C, Heinze T. Influence of wood pulp quality on the structure of carboxymethyl cellulose. *J Appl Polym Sci* 2019;136(34):47862. <https://doi.org/10.1002/app.47862>.
- [52] Heinze T, Liebert T, Klüfers P, Meister F. Carboxymethylation of cellulose in unconventional media. *Cellulose* 1999;6(2):153–65. <https://doi.org/10.1023/A:1009271427760>.
- [53] Swintosky JV, Kennon L. A note on the preparation of powdered carboxymethyl-cellulose and linseed acids. *J Am Pharm Assoc Am Pharm Assoc (Baltim)* 1953;42: 505. <https://doi.org/10.1002/jps.3030420815>.
- [54] Karabinos JV, Hindert M. Carboxymethylcellulose. *Advances in Carbohydrate chemistry*. 9; 1954. p. 285–302.
- [55] Fras Zemljic L, Stenius P, Laine J, Stana-Kleinschek K. Topochemical modification of cotton fibres with carboxymethyl cellulose. *Cellulose* 2008;15(2):315–21. <https://doi.org/10.1007/s10570-007-9175-3>.
- [56] Rodríguez K, Rennecker S, Gatenholm P. Biomimetic calcium phosphate crystal mineralization on electrospun cellulose-based scaffolds. *ACS Appl Mater Interfaces* 2011;3(3):681–9. <https://doi.org/10.1021/am100972r>.
- [57] Laurila E, Thunberg J, Argent SP, Champness NR, Zacharias S, Westman G, et al. Enhanced synthesis of metal-organic frameworks on the surface of electrospun cellulose nanofibers. *Adv Eng Mater* 2015;17(9):1282–6. <https://doi.org/10.1002/adem.201400565>.
- [58] Kargl R, Mohan T, Bračć M, Kulterer M, Doliška A, Stana-Kleinschek K, et al. Adsorption of carboxymethyl cellulose on polymer surfaces: evidence of a specific interaction with cellulose. *Langmuir* 2012;28(31):11440–7. <https://doi.org/10.1021/la302110a>.
- [59] Benselfelt T, Cranston ED, Ondaral S, Johansson E, Brumer H, Rutland MW, et al. Adsorption of xyloglucan onto cellulose surfaces of different morphologies: an entropy-driven process. *Biomacromolecules* 2016;17(9):2801–11. <https://doi.org/10.1021/acs.biomac.6b00561>.
- [60] Liu Z, Choi H, Gatenholm P, Esker AR. Quartz crystal microbalance with dissipation monitoring and surface Plasmon resonance studies of Carboxymethyl cellulose adsorption onto regenerated cellulose surfaces. *Langmuir* 2011;27(14): 8718–28. <https://doi.org/10.1021/la200628a>.
- [61] Moreno-Villoslada I, Rivas BL. Competition of divalent metal ions with monovalent metal ions on the adsorption on water-soluble polymers. *J Phys Chem B* 2002;106:9708–11. <https://doi.org/10.1021/jp013345s>.
- [62] Chen Y, Pu KY, Fan QL, Qi XY, Huang YQ, Lu XM, et al. Water-soluble anionic conjugated polymers for metal ion sensing: effect of interchain aggregation. *J Polym Sci Part A Polym Chem* 2009;47:5057–67. <https://doi.org/10.1002/pola.23558>.
- [63] Lopez CG, Richtering W. Influence of divalent counterions on the solution rheology and supramolecular aggregation of carboxymethyl cellulose. *Cellulose* 2019;26(3):1517–34. <https://doi.org/10.1007/s10570-018-2158-8>.
- [64] Sharratt WN, O'Connell R, Rogers SE, Lopez CG, Cabral JT. Conformation and phase behavior of sodium Carboxymethyl cellulose in the presence of mono- and divalent salts. *Macromolecules* 2020;53:1451–63. <https://doi.org/10.1021/acs.macromol.9b02228>.
- [65] Arumugan Vishnu, Nypelö Tiina, Hasani Merima, Larsson Anette, et al. Calcium ion-induced structural changes in carboxymethylcellulose solutions and their effects on adsorption on cellulose surfaces. *Biomacromolecules*. Submitted for publication.
- [66] Arumugan Vishnu, Nypelö Tiina, Hasani Merima, Brelid Harald, Albertsson Sverker, Wågberg Lars, et al. Specific ion effects in the adsorption of carboxymethyl cellulose on cellulose: the influence of industrially relevant divalent cations. *Colloids Surf A Physicochem Eng Asp* 2021;626:127006. <https://doi.org/10.1016/j.colsurfa.2021.127006>. <https://www.sciencedirect.com/science/article/pii/S092777572100875X>.
- [67] Tiraferri A, Maroni P, Borkovec M. Adsorption of polyelectrolytes to like-charged substrates induced by multivalent counterions as exemplified by poly(styrene sulfonate) and silica. *Phys Chem Chem Phys* 2015;17(16):10348–52. <https://doi.org/10.1039/c5cp00910c>.
- [68] Turesson M, Labbez C, Nonat A. Calcium mediated polyelectrolyte adsorption on like-charged surfaces. *Langmuir* 2011;27(22):13572–81. <https://doi.org/10.1021/la2030846>.
- [69] Pastré D, Hamon L, Landousy F, Sorel I, David MO, Zozime A, et al. Anionic polyelectrolyte adsorption on mica mediated by multivalent cations: a solution to DNA imaging by atomic force microscopy under high ionic strengths. *Langmuir* 2006;22(15):6651–60. <https://doi.org/10.1021/la053387y>.
- [70] de Vos WM, Lindhoud S. Overcharging and charge inversion: finding the correct explanation(s). *Adv Colloid Interface Sci* 2019;274:102040. <https://doi.org/10.1016/j.cis.2019.102040>.
- [71] Brockman AC, Hubbe MA. Charge reversal system with cationized cellulose nanocrystals to promote dewatering of a cellulosic fiber suspension. *Cellulose* 2017;24:4821–30. <https://doi.org/10.1007/s10570-017-1477-5>.
- [72] Mittal N, Benselfelt T, Ansari F, Gordeyeva K, Roth SV, Wågberg L, et al. Ion-specific assembly of strong, tough, and stiff biofibers. *Angew Chem Int Ed* 2019; 131(51):18735–42. <https://doi.org/10.1002/anie.201910603>.
- [73] Gustafsson E, Pelton R, Wågberg L. Rapid development of wet adhesion between Carboxymethylcellulose modified cellulose surfaces laminated with Polyvinylamine adhesive. *ACS Appl Mater Interfaces* 2016;8(36):24161–7. <https://doi.org/10.1021/acsami.6b05673>.
- [74] Pettignano A, Daunay A, Moreau C, Cathala B, Charlot A, Fleury E. Sustainable modification of Carboxymethyl cellulose by Passerini three-component reaction and subsequent adsorption onto cellulosic substrates. *ACS Sustain Chem Eng* 2019;7(17):14685–96. <https://doi.org/10.1021/acssuschemeng.9b02634>.
- [75] Cohen Stuart MA, Scheutjens JM. The role of the solvent in polymer adsorption: displacement and solvency effects. In: *ACS Symp. Ser. 240. American Chemical Society*; 1984. p. 53–65. Chapter 4.
- [76] Grigoray O, Wondraczek H, Heikkilä E, Fardim P, Heinze T. Photoresponsive cellulose fibers by surface modification with multifunctional cellulose derivatives. *Carbohydr Polym* 2014;111:280–7. <https://doi.org/10.1016/j.carbpol.2014.04.089>.
- [77] Grigoray O, Wondraczek H, Pfeifer A, Fardim P, Heinze T. Fluorescent multifunctional polysaccharides for sustainable supramolecular functionalization of fibers in water. *ACS Sustain Chem Eng* 2017;5(2):1794–803. <https://doi.org/10.1021/acssuschemeng.6b02539>.
- [78] Jain K, Mehandzhyski AY, Zozoulenko I, Wågberg L. PEDOT:PSS nano-particles in aqueous media: a comparative experimental and molecular dynamics study of particle size, morphology and z-potential. *J Colloid Interface Sci* 2021;584:57–66. <https://doi.org/10.1016/j.jcis.2020.09.070>.
- [79] Montibon E, Järnström L, Lestelius M. Characterization of poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonate) (PEDOT:PSS) adsorption on cellulosic materials. *Cellulose* 2009;16(5):807–15. <https://doi.org/10.1007/s10570-009-9303-3>.
- [80] Wistrand I, Lingström R, Wågberg L. Preparation of electrically conducting cellulose fibres utilizing polyelectrolyte multilayers of poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonate) and poly(allyl amine). *Eur Polym J* 2007;43(10):4075–91. <https://doi.org/10.1016/j.eurpolymj.2007.03.053>.
- [81] Tkalya E, Ghislandi M, Thielemans W, Van Der Schoot P, De With G, Koning C. Cellulose nanowhiskers templating in conductive polymer nanocomposites reduces electrical percolation threshold 5-fold. *ACS Macro Lett* 2013;2(2): 157–63. <https://doi.org/10.1021/mz300597j>.
- [82] Alam KM, Kar P, Thakur UK, Kisslinger R, Mahdi N, Mohammadpour A, et al. Remarkable self-organization and unusual conductivity behavior in cellulose nanocrystal-PEDOT: PSS nanocomposites. *J Mater Sci Mater Electron* 2019;30: 1390–9. <https://doi.org/10.1007/s10854-018-0409-y>.
- [83] Wang X, Grimoldi A, Håkansson K, Fall A, Granberg H, Mengistie D, et al. Anisotropic conductivity of cellulose-PEDOT:PSS composite materials studied with a generic 3D four-point probe tool. *Org Electron* 2019;66:258–64. <https://doi.org/10.1016/j.orgel.2018.12.023>.
- [84] Jain K, Reid MS, Larsson PA, Wågberg L. On the interaction between PEDOT:PSS and cellulose: adsorption mechanisms and controlling factors. *Carbohydr Polym* 2021;260:117818. <https://doi.org/10.1016/j.carbpol.2021.117818>.
- [85] Holmberg K, Jönsson B, Kronberg B, Lindman B. *Surfactants and Polymers in Aqueous Solution*. 2nd. John Wiley & Sons; 2004.
- [86] Salomäki M, Vinokurov IA, Kankare J. Effect of temperature on the buildup of polyelectrolyte multilayers. *Langmuir* 2005;21:11232–40. <https://doi.org/10.1021/la051600k>.
- [87] Zhang Y, Yang F, Hu F, Song J, Wu S, Jin Y. Binding preference of family 1 carbohydrate binding module on nanocrystalline cellulose and nanofibrillar cellulose films assessed by quartz crystal microbalance. *Cellulose* 2018;25: 3327–37. <https://doi.org/10.1007/s10570-018-1803-6>.
- [88] Zhang Y, Wang X, Wang P, Song J, Jin Y, Rojas OJ. Interactions between type a carbohydrate binding modules and cellulose studied with a quartz crystal microbalance with dissipation monitoring. *Cellulose* 2020;27(7):3661–75. <https://doi.org/10.1007/s10570-020-03070-4>.
- [89] Liu T, Zhang Y, Lu X, Wang P, Zhang X, Tian J, et al. Binding affinity of family 4 carbohydrate binding module on cellulose films of nanocrystals and nanofibrils. *Carbohydr Polym* 2021;251:116725. <https://doi.org/10.1016/j.carbpol.2020.116725>.
- [90] Latour RA. The Langmuir isotherm: a commonly applied but misleading approach for the analysis of protein adsorption behavior. *J Biomed Mater Res - Part A* 2015; 103:949–58. <https://doi.org/10.1002/jbm.a.35235>.
- [91] Lombardo S, Gençer A, Schütz C, Van Rie J, Eyley S, Thielemans W. Thermodynamic study of ion-driven aggregation of cellulose nanocrystals. *Biomacromolecules* 2019;20(8):3181–90. <https://doi.org/10.1021/acs.biomac.9b00755>.
- [92] Enarsson LE, Wågberg L. Polyelectrolyte adsorption on thin cellulose films studied with reflectometry and quartz crystal microgravimetry with dissipation. *Biomacromolecules* 2009;10(1):134–41. <https://doi.org/10.1021/bm8010193>.
- [93] Reid MS, Villalobos M, Cranston ED. The role of hydrogen bonding in non-ionic polymer adsorption to cellulose nanocrystals and silica colloids. *Curr Opin Colloid Interface Sci* 2017;29:76–82. <https://doi.org/10.1016/j.cocis.2017.03.005>.
- [94] Decher G, Hong JD, Schmitt J. Buildup of ultrathin multilayer films by a self-assembled process: III. Consecutively alternating adsorption of anionic and cationic polyelectrolytes on charged surfaces. *Thin Solid Films* 1992;210–1. [https://doi.org/10.1016/0040-6090\(92\)90417-A](https://doi.org/10.1016/0040-6090(92)90417-A).
- [95] Decher G. Fuzzy nanoassemblies: toward layered polymeric multicomposites. *Science* 1997;277(5330):1232–7. <https://doi.org/10.1126/science.277.5330.1232>.
- [96] Richardson JJ, Björnmalm M, Caruso F. Technology-driven layer-by-layer assembly of nanofilms. *Science* 2015;348(6233). <https://doi.org/10.1126/science.aaa2491>.
- [97] Dubas ST, Schlenoff JB. Factors controlling the growth of polyelectrolyte multilayers. *Macromolecules* 1999;32(24):8153–60. <https://doi.org/10.1021/ma981927a>.

- [98] Hammond PT. Engineering materials layer-by-layer: challenges and opportunities in multilayer assembly. *AIChE J* 2011;57(11):2928–40. <https://doi.org/10.1002/aic.12769>.
- [99] Ottenhall A, Illergård J, Ek M. Water purification using functionalized cellulosic fibers with nonleaching Bacteria adsorbing properties. *Environ Sci Technol* 2017; 51(13):7616–23. <https://doi.org/10.1021/acs.est.7b01153>.
- [100] Chen C, Petterson T, Illergård J, Ek M, Wågberg L. Influence of cellulose charge on Bacteria adhesion and viability to PVAm/CNF/PVAm-modified cellulose model surfaces. *Biomacromolecules* 2019;20(5):2075–83. <https://doi.org/10.1021/acs.biomac.9b00297>.
- [101] Köhnke T, Pujolras C, Roubroeks JP, Gatenholm P. The effect of barley husk arabinoxylan adsorption on the properties of cellulose fibres. *Cellulose* 2008;15 (4):537–46. <https://doi.org/10.1007/s10570-008-9209-5>.
- [102] Hatton FL, Engström J, Forsling J, Malmström E, Carlmark A. Biomimetic adsorption of zwitterionic-xyloglucan block copolymers to CNF: towards tailored super-absorbing cellulose materials. *RSC Adv* 2017;7(24):14947–58. <https://doi.org/10.1039/c6ra28236a>.
- [103] Cerclier Carole, Guyomard-Lack Aurélie, Moreau Céline, Cousin Fabrice, Beury Nadège, Bonnin Estelle, et al. Coloured semi-refractive thin films for biomass-hydrolyzing enzyme detection. *Adv Mater* 2011;23:3791–5. <https://doi.org/10.1002/adma.201101971>. <https://onlinelibrary.wiley.com/doi/10.1002/adma.201101971>.
- [104] Kishani S, Vilaplana F, Ruda M, Hansson P, Wågberg L. Influence of solubility on the adsorption of different xyloglucan fractions at cellulose-water interfaces. *Biomacromolecules* 2020;21(2):772–82. <https://doi.org/10.1021/acs.biomac.9b01465>.
- [105] Linder A, Bergman R, Bodin A, Gatenholm P. Mechanism of assembly of xylan onto cellulose surfaces. *Langmuir* 2003;19(12):5072–7. <https://doi.org/10.1021/la0341355>.
- [106] Nypelö Tiina, Laine Christiane, Colson Jérôme, Henniges Ute, Tammelin Tekla. Submicron hierarchy of cellulose nanofibril films with etherified hemicelluloses. *Carbohydr Polym* 2017;177:126–34. <https://doi.org/10.1016/j.carbpol.2017.08.086>. <https://www.sciencedirect.com/science/article/pii/S0144861717309621?via%3Dihub#!>.
- [107] Hanus J, Mazeau K. The xyloglucan-cellulose assembly at the atomic scale. *Biopolymers* 2006;82:59–73. <https://doi.org/10.1002/bip.20460>.
- [108] Archer WR, Schulz MD. Isothermal titration calorimetry: practical approaches and current applications in soft matter. *Soft Matter* 2020;16:8760–74. <https://doi.org/10.1039/d0sm01345e>.
- [109] Lima DU, Loh W, Buckeridge MS. Xyloglucan-cellulose interaction depends on the sidechains and molecular weight of xyloglucan. *Plant Physiol Biochem* 2004;42 (5):389–94. <https://doi.org/10.1016/j.plaphy.2004.03.003>.
- [110] Eronen P, Junka K, Laine J, Österberg M. Interaction between water-soluble polysaccharides and native nanofibrillar cellulose thin films. *BioResources* 2011;6 (4):4200–17. <https://doi.org/10.15376/biores.6.4.4200-4217>.
- [111] Sundman O. Adsorption of four non-ionic cellulose derivatives on cellulose model surfaces. *Cellulose* 2014;21(1):115–24. <https://doi.org/10.1007/s10570-013-0105-2>.
- [112] Hu Z, Cranston ED, Ng R, Pelton R. Tuning cellulose nanocrystal gelation with polysaccharides and surfactants. *Langmuir* 2014;30:2684–92. <https://doi.org/10.1021/la404977t>.
- [113] Kishani S, Bensselfelt T, Wågberg L, Wohler J. Entropy drives the adsorption of xyloglucan to cellulose surfaces – a molecular dynamics study. *J Colloid Interface Sci* 2021;588:485–93. <https://doi.org/10.1016/j.jcis.2020.12.113>.
- [114] Palasingh C, Ström A, Amer H, Nypelö T. Oxidized xylan additive for nanocellulose films – a swelling modifier. *Int J Biol Macromol* 2021;180:753–9. <https://doi.org/10.1016/j.ijbiomac.2021.03.062>.
- [115] Ekeväg P, Lindström T, Gellerstedt G, Lindström ME. Addition of carboxymethylcellulose to the Kraft cook. *Nord Pulp Pap Res J* 2004;19(2):200–7. <https://doi.org/10.3183/npprj-2004-19-02-p200-207>.
- [116] Anufrijeva O. Chemical modification of viscose fibres by adsorption of carboxymethyl cellulose and click chemistry. Master's Thesis Aalto 2014. <https://aaltodoc.aalto.fi/handle/123456789/13973>.
- [117] Jiang X, Bai Y, Chen X, Liu W. A review on raw materials, commercial production and properties of lyocell fiber. *J Bioresour Bioprod* 2020;5:16–25. <https://doi.org/10.1016/j.jobab.2020.03.002>.
- [118] Payerl C, Bračić M, Zankel A, Fischer WJ, Kaschowitz M, Fröhlich E, et al. Nonspecific protein adsorption on cationically modified Lyocell fibers monitored by zeta potential measurements. *Carbohydr Polym* 2017;164:49–56. <https://doi.org/10.1016/j.carbpol.2017.01.088>.