The Influence of Molecular Adhesion on Paper Strength

Malin Eriksson

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Department of Fibre and Polymer Technology
School of Chemical Science and Engineering
KTH, Royal Institute of Technology
Stockholm, Sweden.
Abstract

This thesis deals with the influence of molecular adhesion on paper strength. By combining the use of high-resolution techniques and silica/cellulose surfaces, with various fibre–fibre and sheet testing techniques, new information regarding the molecular mechanisms responsible for paper strength has been obtained.

Large parts of this research were devoted to the polyelectrolyte multilayer (PEM) technique, i.e. a charged surface is consecutively treated with oppositely charged polyelectrolytes. Application of PEMs incorporating polyallylamine hydrochloride (PAH) and polyacrylic acid (PAA) onto dried, fully bleached softwood fibres, prior to sheet preparation, increased tensile strength. No linear relationship was detected between the amounts of PAH and PAA adsorbed onto the fibres and the developed tensile strength, which suggests that the adsorbed amount is not the only important factor determining the tensile strength. Closer examination of PEM formation on silica indicated that both exponential PEM film growth and the occurrence of a PEM film in which the polyelectrolytes are highly mobile, favour the strength-enhancing properties of sheets containing PEM-treated fibres. This indicates that a water-rich, soft PEM film allows the polyelectrolytes to diffuse into each other, creating a stronger fibre–fibre joint during consolidation, pressing, and drying of the paper. In addition, when PAH capped the PEM film, the paper strength was higher than when PAA capped the film; this could be related to the structure of the adsorbed layer. Further analysis of the sheets revealed that the increase in tensile strength can also be linked to an increase in the degree of contact within a fibre–fibre joint, the number of efficient joints, and the formation of covalent bonds. The relative bonded area (RBA) in the sheets, as determined using light-scattering measurements, indicated no significant change until a certain tensile strength was obtained. The RBA, as determined using nitrogen adsorption via BET analysis, did show significant changes over the whole investigated tensile strength range. From this it can be concluded that light scattering cannot give any direct information regarding molecular interactions within a sheet. Furthermore, it was shown that PEMs involving cationic and anionic starch display an almost linear relationship with out-of-plane strength properties regarding the amount of starch in the sheets, whereas the tensile strength was more dependent on the physical properties of the starch, as was the case with PAH and PAA.

Cationic dextran (DEX) and hydrophobically modified cationic dextran (HDEX) were used to test the importance of having compatible surface layers in order to obtain strong adhesive joints. DEX and HDEX phase separated in solution, however, this incompatibility of HDEX:DEX mixtures was not reflected in wet or dry joint strength. For both wet and dry measurements, adhesion between DEX and HDEX coated surfaces was intermediate to the adhesion of DEX:DEX and HDEX:HDEX surfaces.

In addition, various types of cellulose surfaces, different regarding their crystallinity, were investigated. Depending on the preparation techniques and solution conditions used, i.e. pH and salt concentration, steric, electrostatic, and van der Waals interactions were obtained between the surfaces in aqueous solutions. The adhesion forces between polydimethylsiloxane and cellulose surfaces, measured under ambient conditions, were influenced by the degree of crystallinity. This suggests that amorphous cellulose offers more possibilities for surface groups to arrange themselves to participate in molecular interactions in the joint. Higher relative humidity could increase this adhesion force further, water probably acting as a plasticizer during joint formation.
1 Introduction

1.1 Setting the scene

Paper is made from wood fibres suspended in water. Knowledge of how these fibres interact with each other and with various additives during the paper-making process is important in producing a high-quality, strong paper. The final paper contains fibres, fines, fillers, and dry strength agents that are joined together during consolidation, as water is removed in the pressing and drying process. The properties of the paper are dependent on the adhesion between those constituents. In addition, the physical properties of the added polyelectrolytes (i.e., dry strength enhancers) will greatly influence the resulting paper strength, and research has provided the paper industry with polymer systems for that purpose. The mechanisms involving these additives are, however, poorly understood. To provide the paper-making industry with new and even more efficient strength-enhancing systems, there is a need to understand the mechanisms underlying various strength-enhancing additives. Thus, information is needed regarding fibre–fibre joint formation, a complex process in which several components act co-operatively. This process starts in the fibre suspension, where interactions, such as electrostatic, hydrodynamic and steric interactions, between fibres are important. It continues as the water is removed, when the orientation and interdigitation of the surface molecules affect the molecular adhesion. The process ends by producing a dry fibre network in which the final strength of the paper product is assumed to be determined to a large extent by the number and area of efficient fibre–fibre joints formed and the resulting adhesion within the fibre–fibre joints.

Since wood fibres are rough at a micrometer scale it is difficult to obtain molecular information regarding the fibre–fibre joint. Therefore, in performing a study like the present one it is important to have simple and well-characterised systems to work with. Polyelectrolyte adsorption and the formation of polyelectrolyte multilayer (PEM) films on smooth model surfaces, such as silica and mica, and the interaction between such layers were studied. In order to provide for more relevant studies, it is of great interest to find suitable model cellulose surfaces that can be used for different types of adsorption and interaction
studies. In this work, different cellulose surfaces were prepared and characterised in terms of their surface properties. Furthermore, the dry and wet interaction between such surfaces was also studied.

The results obtained were used in discussing the formation of fibre–fibre joints, fibre–fibre joint strength, and paper strength, especially tensile strength. The choice of tensile strength is based on the availability of established standardized laboratory sheet making and tensile testing. This also makes it possible to relate the results to the extensive literature on paper tensile strength development.

1.2 Objective
The primary aim of this work is to establish knowledge of the molecular mechanisms responsible for adhesion between wood fibres and additives in paper, as well as to develop new and efficient ways to improve the joint strength between fibres. Another aim is to further develop suitable model cellulose surfaces to be used in various interaction studies; such studies would help greatly in contributing to the understanding of paper strength.

1.3 Outline of the thesis
The thesis is divided into seven main chapters. The chapter entitled, *Fibre–fibre interactions and molecular adhesion*, includes short descriptions of surface force interactions in aqueous solutions, relevant for the formation of the fibre–fibre joint. However, the chapter mainly focuses on adhesion theories with respect to fibre–fibre joint strength and paper strength. The polyelectrolyte multilayer (PEM) technique is introduced as a strength-enhancing method. The chapter also presents model studies using high-resolution techniques, to help in understanding fibre–fibre joint formation, fibre–fibre joint strength, and paper strength. The next two chapters are self-explanatory, being entitled *Materials* and *Methods*, respectively. The main results presented in papers I–V are discussed in the chapter *Surface modifications and effects on paper strength*. Papers VI and VII are discussed in the chapter *Interaction studies using model cellulose surfaces*. Finally, the work is summarised and the most important findings are presented in the *Conclusions*.
2 Fibre–fibre interactions and molecular adhesion

2.1 Fibre–fibre joint formation
Wood fibres are negatively charged, due to the carboxylic groups on the hemicelluloses. Hence, electrostatic repulsion and the van der Waals forces are present in a suspension of fibres. When water is removed, the balance between these colloidal and capillary forces (Campbell forces) – due to the water meniscus formed between fibres during pressing and drying – determines how closely the fibres approach each other at a given solid content level [1]. Attractive van der Waals forces exist between all molecules/solids and are a consequence of the movement of the electrons of the atoms, which creates temporary dipoles. A repulsive electrostatic double-layer force exists between charged surfaces in an aqueous medium. The extension of the double layer is determined by the properties of the solvent, where, for example, the salt concentration and valence of the counter ions play a dominant role. In addition, the double-layer forces are dependent on the charge density of the surface and the properties of the aqueous medium, commonly pH, salt concentration, and type of salt. These surface forces will affect the final molecular adhesion between the fibres in a paper sheet and thus the final paper strength [1, 2]. Reduced electrostatic interaction between carboxymethylated rayon fibres has been shown to reduce the joint strength while increasing the overall sheet strength [2]. These results were explained as being a consequence of two different mechanisms: (1) addition of salt screens the fibre charges, which increases the number of created fibre–fibre joints; and (2) at the same time, the higher salt concentration reduces the fibre surface swelling thereby creating weaker fibre–fibre joints.

2.2 Paper strength with a focus on molecular adhesion
From paper physics theories it is concluded that fibre strength, fibre length, and the strength of the joints between individual fibres are the most important factors determining the tensile strength properties of paper [3, 4]. Furthermore, it is known that the strength properties of weak sheets of low density are limited by the fibre–fibre joint strength, while those of strong sheets of high density are more limited by fibre strength [4]. In addition, it is possible to pull out intact fibres from both strong and weak papers, indicating that the weak link in any paper is in fact
the fibre–fibre joint [5]. Studies aiming at improving paper strength should therefore focus on molecular adhesion between fibres and its influence on paper strength.

The fundamental science of adhesion is rather complex and not yet fully understood. In earlier research different theories of adhesion were developed. Three major mechanisms should be mentioned: 1) mechanical interlocking due to surface roughness, 2) molecular inter-diffusion of surface molecules, and 3) chemical interactions/attractions of surface molecules. Depending on the particular systems studied, these adhesion mechanisms may of course operate simultaneously, which will be discussed further below. The confusion regarding adhesion mechanisms mostly stems from the experimental methods for studying joint strength, since these methods themselves bring with them loading factors and additional geometrical factors that are not considered in the theories. A thorough review of the molecular mechanisms underlying adhesion is presented in a recent book by Kendall, which covers important issues regarding both theories and experimental applications [6]. Perhaps the most critical issues are the surface roughness and unavoidable contamination of studied surfaces. In view of this, it is understandable that the adhesion between the rough fibres is not easy to determine exactly, and that addition of different types of strength-enhancing polyelectrolytes introduces further complexity. Attempts have been made to determine the force needed to separate single fibres from fibre–fibre crosses [7, 8]. However, to obtain more exact information about molecular adhesion, more elaborate testing techniques are needed, including smooth model cellulose surfaces and high-resolution techniques.

The rough and highly fibrillated surfaces of wood fibres may be subject to mechanical interlocking. This theory suggests that surface irregularities could lock into each other mechanically (mechanical keying or interlocking), which would contribute to the intrinsic adhesion between the fibres. However, the fact that good adhesion can occur between perfectly smooth surfaces suggests that other interactions must also be of great importance. Since mechanical interlocking can occur without molecular adhesion, it should not be regarded as a type of molecular adhesion but rather as a macroscopic behaviour [6]. Nevertheless, since
some studies indicate that such mechanical interlocking does exist, for example in textiles [9], it is not unlikely that it also comes into play between fibres in a paper sheet.

So, if the rough fibres are considered, how can, for example, hydrogen bonding and van der Waals forces hold them together in a network? If hydrogen bonds are to develop between fibres they must come into very close contact with each other for these specific interactions to occur, since hydrogen bonds are formed at separations of only a few Angstroms. Currently it is accepted, that the fibre surface resembles a polyelectrolyte gel [10, 11] with an elastic modulus in the range of 2–15 MPa [12, 13]. The molecules on the fibre surface could thus diffuse into each other during pressing and drying and orient themselves in such a way that hydrogen bonding is possible. This presents the diffusion theory as suggested by Voiutskii [14], which can be summarised as follows. If polymer chains on surfaces can diffuse into each other they must be soluble in each other or have certain mobility. This inter-diffusion mechanism is also thought to be important in obtaining strong papers [11, 15]. If fibres do come into such close contact, it is natural to suggest that the van der Waals forces should be considered a possible bonding force in the fibre–fibre joint, since these can facilitate bonding between all parts of the fibre surfaces. There are astonishingly few investigations of paper strength in which these forces are mentioned [10, 16-19]. Hydrogen bonding is more frequently discussed in the literature, and it is believed that the hydroxyl groups on the cellulose strongly attract hydroxyl groups on adjacent cellulose surfaces as water is removed [16]. There are theoretical models describing the role that hydrogen bonds play in holding the entire fibre network together in a paper [20]. Experimental results also exist, which indicate that removal of hydroxyl groups by acetylation decreases paper strength, through a reduction in hydrogen bonding [21]. However, these modifications also change the swelling of the fibres, which also could have influenced the obtained results.
2.3 Dry strength additives and their contribution to paper strength

Although it is possible to produce strong papers, using only pulp fibres, such as sack paper and liner board, certain paper grades demand addition of dry strength agents, to the fibre suspension prior to sheet preparation. These dry strength agents, commonly water-soluble cationic polyelectrolytes, will function as an adhesive, i.e., a material that can join surfaces and help them resist separation. A good example is when a paper contains fillers; it is then necessary to add strength enhancers to provide for good adhesion between the filler particles and the fibres [22]. There are several different commercially available dry strength agents, such as starches, acrylamide-based polymers, gums, and hemicelluloses. No intention to cover the literature regarding these substances is made here; instead, the reader is referred to a recent review on the topic [17]. The present work will consider mechanisms by which a selection of additives might function as strength enhancers in forming strong fibre–fibre joints.

Cationic starch (CS) is probably the most common strength enhancer used in paper today, due to its cost efficiency. It has been suggested that CS can increase the number of fibre–fibre joints [23] and/or the specific bond strength [24-27]. Few studies have actually attempted to determine what constitutes this specific bond strength, but it is assumed that the OH groups on the starch contribute to the paper strength through hydrogen bonding, also suggested by Gaspar [24]. It is also quite likely that a highly swollen starch macromolecule on the fibre surface will allow for a greater molecular contact area. Furthermore, a high-molecular-weight starch is more efficient than a low-molecular-weight starch is [28]. It has also been shown in the case of cationic dextran (a polyelectrolyte, i.e., carbohydrate, similar to CS) that the molecular weight did not affect the tensile index when the surfaces were fully saturated [29]. However, molecular weight was shown to be important when smaller additions were made, in which case the higher molecular weight was found to result in a higher tensile index [29]. Furthermore, low-charge-density CS is more efficient than high-charge-density CS is in terms of enhancing strength [30], and the same trend is observed in the case of cationic dextran [31]. This could either be due to the adsorbed amounts (as the adsorbed amount increases with lower charge density) or possibly be an effect of layer conformation, as a low-charge-density polyelectrolyte will adsorb in a more
extended conformation, with loops and tails, whereas a high-charge-density polyelectrolyte will adsorb in a flat structure [32].

Recent research in which carboxymethyl-cellulose (CMC) has been deposited on fibre surfaces has shown to be efficient at increasing the tensile properties of sheets [33-35]. It is suggested that these strength effects are due to an increase in the relative bond strength, since the light scattering coefficient does not change (the applicability of this method will be discussed later) [34]. Furthermore, it can be seen that the ionic groups introduced with the CMC did not contribute to this strength increase due to fibre swelling [34]. Traditionally, ionic groups on the fibre surface affect the degree of swelling and thereby enhance the paper strength.

A review [18] concerning paper strength-enhancing polyelectrolytes emphasised the importance of the polyelectrolyte structure. This review discussed many hypotheses regarding the action of various strength-enhancing polyelectrolytes, identifying, one important factor i.e., the hydrophobicity/hydrophilicity of the polyelectrolytes, suggesting that a hydrophilic polyelectrolyte is likely to give the best strength-enhancing properties. Pelton et al. [15] also showed the importance of compatibility between the molecules on the fibre surfaces in creating strong paper. These authors suggested that compatible surface molecules could diffuse into each other and create stronger joints during the paper pressing and drying. These results also support McKenzie’s theory concerning the inter-diffusion of molecules across the boundaries of adjacent fibres [11].

It is generally accepted that added polyelectrolytes improve the adhesion between the fibres by increasing the molecular contact area and/or the number of efficient fibre–fibre joints [23, 25, 26, 36]. A recent investigation has also shown that increasing the charge of the fibres increases the molecular contact area between them, creating a stronger fibre–fibre joint and hence a stronger paper [37]. The molecularly bonded area is often referred to as the optically bonded area, since light scattering methods are frequently used to determine the degree of “bonding” [38-40]. From light scattering, the RBA concept was derived by Nordman [41], as defined by Equation 2.1:
\[ RBA = \frac{s - s_0}{s_0} \] (2.1)

\( RBA \) is the relative bonded area in a paper sheet, \( s \) is the light scattering coefficient of the sheet of interest, and \( s_0 \) is the light scattering coefficient of a totally unbonded paper sheet.

It must be stressed, however, that optical measurement methods are only sensitive to a separation of approximately 200 nm (half the wavelength of visible light), and can hence not be used to obtain information regarding the true molecularly bonded area. The molecular contact area can be more accurately determined by use of nitrogen adsorption, applying the Brunauer-Emmett-Teller (BET) theory, as nitrogen molecules are approximately 4 Angstroms in diameter [38, 39]. Small-angle X-ray scattering would also be more appropriate, since the wavelength of the X-rays is much smaller than that of light. The specific surface area determined using X-ray scattering produces a specific surface area result five times larger than that of BET analysis [42]. This difference was ascribed to the evaluation of the Porod invariant in analysing the X-ray scattering data. It has recently also been shown that staining a dry fibre–fibre cross with a small dye molecule (i.e., rosaniline) dissolved in acetone allows for the indirect determination of the area in molecular contact between the fibres [43].

2.4 **Polyelectrolyte multilayer (PEM) technique**

A new technique for fibre modification is the PEM technique [44]. In this technique, a charged surface is consecutively treated with oppositely charged polyelectrolytes [45]. This surface engineering technique is very attractive, because it can be used for many water-soluble polyelectrolytes and the actual PEM formation is very simple. Over the past ten years, intense research has focused on this surface engineering technique, which has found a number of useful applications, such as in sensor technology and paper making [44, 46].

When forming multilayers, each adsorption follows the fundamental principles of polyelectrolyte adsorption onto a flat substrate [32]. The key to form multilayers is, however, the ability of the adsorbed polyelectrolytes to induce charge reversal
in the oppositely charged substrate and polyelectrolyte layers. Furthermore, it is important to have a rinsing step between each treatment to remove any non-adsorbed polyelectrolyte and to ensure film stability [47]. Designing a multilayer film with the desired properties involves controlling a number of parameters (as with single polyelectrolyte adsorption), such as the nature of the polyelectrolytes, salt concentration, and pH (if weak polyelectrolytes are used). An extensive summary of recent developments in this area has been published [48].

The PEM technique was first used to modify wood fibres in 1998, with promising results in terms of the strength properties of paper [49]. Perhaps the most interesting result so far has been that the tensile index turns out to be highly dependent on which polyelectrolyte is used in the outer layer [44]. These results indicate that multilayers could be important in controlling adhesion between different types of surfaces. When this thesis research started there were few published studies of PEM technology used on wood fibres; this situation has changed, and several research groups are now working on the topic. The main findings to date are that it is possible to increase the tensile index by increasing the number of adsorbed layers [44, 50-52]. It has also been demonstrated that it is possible to achieve the same strength using PEM technology as can be achieved using conventional beating [44]. Mixing PEM treated fibres carrying cationic polyelectrolytes in the outermost layer with fibres having anionic polyelectrolytes in the outermost layer, has also been shown to improve the tensile strength of the resulting paper, claimed to be due to electrostatic interactions [53]. Another study has shown that a hydrophobic outer surface layer tends to form a stronger sheet than a hydrophilic outer surface layer does [54]. It should also be mentioned that forming PEMs on fibres using a wide range of polyelectrolytes and nanoparticles, can give wood fibres totally new properties under very mild conditions. For instance, the PEM technique has been used for preparing electrically conductive papers [55].
2.5 Model studies for understanding the fibre–fibre joint strength

To obtain new information regarding fibre–fibre joint formation there is a need for model experiments in which smooth surfaces are used. It is natural, as a starting point, to use silica or mica as a model surface for cellulose. Both silica and mica are well-known substrates, commonly used in polyelectrolyte adsorption and interaction studies [56-59]. These surfaces have also been used in model studies aiming to build understanding of polyelectrolyte adsorption onto fibres as well as of interactions between polymer-covered surfaces, all of which should cast new light on paper strength mechanisms [19, 60, 61]. Using techniques such as reflectometry, surface force apparatus (SFA), and contact mechanics, valuable information has been obtained regarding paper-making systems. Typical strength-enhancing polyelectrolytes have been studied using reflectometry, revealing the potential of using silica as a model substrate, for example, when evaluating the influence of polyelectrolytes, charge density, and electrolyte concentrations [60]. This technique has also been used in studies forming multilayers of dissolved and colloidal substances (DCSs). DCSs are often present in paper-making systems and are known to negatively affect the formation of fibre–fibre contacts. The phenomenon has also been thoroughly studied using continuum contact mechanics [61]. A recent work by Rojas et al. [19] demonstrated, with aid of SFA, that strong adhesion was obtained with mica surfaces covered with a high-charge-density polyelectrolyte, due to electrostatic surface–polyelectrolyte–surface bridges. In fact, high-charge-density polyelectrolytes are also known to be efficient for pulps with high surface-charge densities as well as for pulps containing fines and fillers, as also discussed by Rojas et al. [19]. It was further shown that low-charge-density polyelectrolytes gave rise to adhesion, which was suggested to be due to entanglement of the polyelectrolyte chains. This could be of great importance for strength-enhancing agents for bleached kraft pulps, which have a low surface charge density [31]. It is also known that low-charge-density polyelectrolytes are more efficient at improving paper strength, as mentioned earlier.

To perform more precise model studies, surfaces other than mica and silica should be used. A smooth model surface made of cellulose would enable studies that are better able to reveal the fibre–fibre interactions occurring in the paper-making
process. However, some issues regarding the use of cellulose surfaces need to be discussed. First, the instruments available today for studying polyelectrolyte adsorption and molecular interaction may not always be suited for examining cellulose surfaces. Therefore, the preparation of cellulose surfaces has to be specifically designed to suit the instruments, and this is in progress in several research groups. There are currently many different ways to prepare thin cellulose films in which the raw material, dissolving procedures for the raw material and the actual film preparation procedures do differ, which leads to a second issue. These preparation procedures lead to different properties in terms of mechanical properties, surface structure/roughness, degree of crystallinity, and swellability. The Langmuir−Blodgett (LB) technique, using tetra-methyl-silane-cellulose (TMSC), has been shown to produce robust films, but the surface preparation is tedious [62]. Surfaces prepared according to Gunnars et al., where a pulp is dissolved in N-methylmorpholine-N-oxide/dimethylsulphoxide and spin coated (SC) onto a silica surface pre-treated with a cationic polyelectrolyte have been thoroughly characterised [63-65]. These cellulose surfaces are, for example, known to display the same type of swelling behaviour as do the wood fibres used in preparing the surfaces [66]. Nuclear magnetic resonance (NMR) investigation of fibres prepared using the same solvent as used in the SC procedure indicated that the surfaces consisted of para-crystalline cellulose II [63]. Eriksson et al. prepared cellulose surfaces by means of spin coating, by dissolving microcrystalline cellulose in Lithium chloride/dimethylidiacetamide [67]. Furthermore, Edgar and Grey developed a method by which it is possible to prepare cellulose I surfaces, either by placing a droplet of a colloidal suspension of cellulose I nanocrystals onto a mica surface and allowing it to dry under ambient conditions or by using SC [68]. These three last mentioned cellulose surfaces were used with slight modifications in the present work and will be further discussed later. Cellulose spheres have also been used as a model system and are essential in studies using the colloidal probe technique with atomic force microscopy (AFM) [69, 70].

In addition, these different cellulose surfaces/spheres have been used in studying the interactions between two cellulose surfaces, and naturally the results obtained differ depending on the techniques used to prepare the cellulose surfaces. Two
recent AFM investigations, in which SC cellulose II surfaces were used together with a colloidal cellulose probe, found that van der Waals interactions could be detected between the surfaces at low pH and that interaction between the surfaces was dominated by electrostatic interactions at higher pH [71, 72]. However, with the LB cellulose films it was difficult to investigate the true Derjaguin-Landau-Verwey-Overbeek (DLVO) behaviour of the surfaces in water, due to steric interactions between the surfaces, probably due to the highly swollen structure of the LB films [73]. Recently, continuum contact mechanics have been used with the Johnsson–Kendall–Roberts (JKR) theory [74] to investigate the adhesion forces obtained when using model cellulose surfaces [61, 75]. These measurements can also contribute significantly to a better understanding of the adhesion mechanisms between cellulose surfaces. So far, there has been no attempt to systematically compare different types of cellulose surfaces in terms of their ability to give valuable information regarding cellulose–cellulose interactions.

Since wood fibres consist of cellulose, hemicelluloses, and lignin, it is not only important to find suitable cellulose surfaces; appropriate lignin and hemicellulose surfaces must be found as well. Norgren et al. have developed a lignin model surface that has been well characterised [76]. There is also ongoing research to prepare a hemicellulose model surface, with use of galactoglucomannan. This will allow for the investigation of interactions between all three wood polymers.
3 Materials

This chapter presents the polyelectrolytes and model surfaces used, together with the preparation and characterisation details for those materials. For more thorough descriptions, the reader is referred to papers I–VII.

3.1 Polyelectrolytes

Polyallylamine hydrochloride (PAH) and polyacrylic acid (PAA) were chosen to form PEMs on silica and wood fibres. PAH with a molecular weight of 15 kDa and PAA with a molecular weight of 5 kDa were used. These polyelectrolytes are known to form an amide linkage upon heating [77]. The molecular monomer structures of these polyelectrolytes and of the amide formation are presented in Figure 3.1. Both polyelectrolytes are weak and their charge densities are hence dependent on pH. In this research, three pH strategies were used during PEM formation on both fibres and silica surfaces: 1) both polyelectrolytes were adsorbed at pH 7.5, 2) both polyelectrolytes were adsorbed at pH 5.0, and 3) PAH was adsorbed at pH 7.5 while PAA was adsorbed at pH 3.5.

![Figure 3.1](image)

Figure 3.1 Chemical monomer structures of polyacrylic acid (PAA) and polyallylamine hydrochloride (PAH) together with the amide linkage formed between the polyelectrolytes upon heating.

To obtain the refractive index increments (dn/dc), the refractive index was measured for both PAA and PAH at all pH values used, as a function of polyelectrolyte concentration. An Abbe refractometer (Carl Zeiss, Oberkochen, Germany) was used. The dn/dc values are presented in Table 3.1.
Table 3.1 The $dn/dc$ values for PAH and PAA at different pH levels and NaCl concentrations.

<table>
<thead>
<tr>
<th>pH</th>
<th>0.2 M NaCl PAH (mL/g)</th>
<th>PAA (mL/g)</th>
<th>0.1 M NaCl PAH (mL/g)</th>
<th>PAA (mL/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5</td>
<td>0.124</td>
<td>0.132</td>
<td>0.210</td>
<td>0.150</td>
</tr>
<tr>
<td>5.0</td>
<td>0.150</td>
<td>0.175</td>
<td>0.209</td>
<td>0.147</td>
</tr>
<tr>
<td>7.5</td>
<td>0.162</td>
<td>0.175</td>
<td>0.156</td>
<td>0.174</td>
</tr>
</tbody>
</table>

Anionic and cationic starches were also used for PEM formation on silica and on wood fibres. Potato starch is a carbohydrate with a small net anionic charge, due to a small number of phosphorus groups. Potato starch consists of approximately 20% linear amylose and 80% branched amylopectin [78]. Cationically modified starch with a quaternised ammonium group is used in paper-making as a strength-enhancing additive, to obtain optimal retention of fillers and fines and to improve printing quality. In this research, four different types of starches were used, obtained from Lyckeby Industrial AB (Kristianstad Sweden): cationic amylose-rich potato starch, cationic amylopectin-rich potato starch, cationic potato starch, and an anionic potato starch. Chemical structures of the cationic starch (CS) and the anionic starch (AS) are presented in Figures 3.2 and 3.3, respectively. The CS and the AS had a degree of substitution (DS) of approximately 0.06.

Figure 3.2 Chemical structure of quaternised potato starch (CS).
Figure 3.3 Chemical structure of sulphonated potato starch (AS).

Dextran is often used as a model polymer for starch, due to its similar chemical structure. In this research, the dextran was made cationic with a quaternary ammonium ion using a method described elsewhere [79] and was also modified by means of esterification, using roughly the same method as described by Bamford et al. [80], resulting in cationic hydrophobically modified dextran (HDEX) and cationic dextran (DEX) samples. The modified groups are illustrated in Figure 3.4.

Figure 3.4 Chemical structure of HDEX showing the cationic and the hydrophobic modification. On average there is about one hydrophobic butyric ester on every other carbohydrate ring whereas there are about 30 rings per quaternary ammonium group.
The degree of substitution (DS) of the modified dextrans was determined using $^1$H-NMR. A Bruker AV 200 NMR spectrometer was used to record the spectra. D$_2$O was used as the solvent and 100 mg of dextran was dissolved in 3.5 mL D$_2$O. The degree of quaternary ammonium ion substitution was reported relative to the peak assigned to the anomeric proton, and the degree of fatty acid substitution was reported relative to the same peak [81]. The cationic dextran (DEX) had a DS of 0.034 and the hydrophobically modified cationic dextran (HDEX) had a hydrophobic DS of 0.61 and a cationic DS of 0.036.

The refractive index increment (dn/dc) values were determined, using a differential refractometer, and found to be 0.137 mL/g for HDEX and 0.139 for DEX in 0.05 M NaCl, similar to the value for unmodified dextran, 0.151 mL/g in 0.1 M NaCl [82].

Static light scattering was used to determine the molecular weight (MW) and radius of gyration ($R_g$) of the modified dextrans, using a photon-counting device supplied by Hamamatsu. The light source was a 3-mW He–Ne laser with a wavelength of 632.8 nm. These measurements indicated that the HDEX and DEX had molecular weights of 617,000 and 475,000 g/mol, respectively, and $R_g$ values of 470 and 350 Å in 0.05 M NaCl.

3.2 Model surfaces
The silicon wafers (150 mm, p-type) were purchased from MEMC Electronics Materials, Novara, Italy. They were treated in different ways, depending on the end use. For adsorption studies, the wafers were washed consecutively with ethanol and milli-Q water, blown dry with nitrogen, and oxidised in an oven at 1000°C for 3 hours. The silica surfaces were then hydroxylated to obtain a fully wetted surface, by placing them in a 10% (w/w) aqueous solution of NaOH for 30 seconds. They were then rinsed with an excess of milli-Q water and blown dry with nitrogen. The surface roughness, as determined using tapping-mode AFM (Picoforce SPM, Veeco Inc., Fremont, CA), did not change significantly during this step. Finally, the oxidised wafers were treated in a plasma cleaner (Model PDC 002, Harrick Scientific Corporation, NY, USA) for 30 seconds. The thickness of the oxide layer on each strip was also directly measured using a
Rudolph ellipsometer (model 437, Rudolph Research, Flanders NJ, USA) and was found to be in the range from 90 to 92 nm.

Silica-coated quartz crystals, Q-Sense (Göteborg, Sweden), used for the quartz crystal microbalance with dissipation (QCM-D) measurements, were treated with a mixture of sulphuric acid (3 parts) and hydrogen peroxide (1 part) for 1 minute and then rinsed with excess milli-Q water and finally blown dry with nitrogen gas.

The mica (kindly provided by Mark Rutland, KTH, Stockholm, Sweden) was carefully cleaved several times on both sides before being mounted in the AFM liquid cell.

Polydimethylsiloxane (PDMS) hemispherical caps and sheets were prepared using a two-component system, as described earlier [83]. Droplets of the reaction mixture were placed on a clean glass slide treated with fluorodecyltrichlorosilane, and PDMS sheets were prepared by pouring the mixture into a Petri dish made of glass. The PDMS was then cured for 1 hour at 105°C. The cured caps/sheets were extracted in heptane for 12 hours to remove unreacted monomer. Finally, they were oxidised in a plasma cleaner in air for different times ranging from 0 to 5 minutes at power levels of the plasma cleaner ranging from 7 to 30 W.

Contact-angle measurements were performed against water and methyleneiodide, using a CAM 200 contact-angle meter (KSV, Helsinki, Finland) on PDMS sheets, both before and after plasma treatment for 1 minute. The results are presented in Table 3.2. Using the contact angles obtained between methyleneiodide ($\gamma_i^d \approx \gamma_i = 50.8$ mJ/m$^2$) and PDMS/oxidised PDMS (OxPDMS), the dispersive part of the surface energy ($\gamma_s^d$) was calculated according to Equation 3.1, which is valid when the interactions between the liquid and the surface are dominated by dispersive interactions [84].

$$2\sqrt{\gamma_s^d \gamma_i^d} = \gamma_i (1 + \cos \Theta)$$  \hspace{1cm} (3.1)
These values, presented in Table 3.2, agree well with those from previous studies, ranging from 21 to 22.5 mJ/m$^2$ for a PDMS surface, as determined using contact-angle measurements [85].

Table 3.2 Static contact angles (with an error of ±2) and the calculated dispersive part for the surface energies for PDMS and OxPDMS sheets.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Water ($^\circ$)</th>
<th>Methyleneiodide ($^\circ$)</th>
<th>$\gamma_s^d$ (mJ/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS</td>
<td>110</td>
<td>72</td>
<td>22</td>
</tr>
<tr>
<td>OxPDMS</td>
<td>0</td>
<td>44</td>
<td>38</td>
</tr>
</tbody>
</table>

The preparation of dextran films on PDMS caps was performed according to a procedure described earlier in the literature [86]. Before any surface treatment, the prepared PDMS caps were oxidised in a plasma cleaner (model PDC 002, Harrick Scientific Corporation, NY, USA; power level, 7 W) for 15 minutes, to provide a surface with good adherence for the used dextrans [86]. The silicon wafers were treated in the same manner. Silica and OxPDMS surfaces were placed in a beaker containing a solution of cationically charged dextran (with or without hydrophobic modification) at pH 8, with a polymer concentration of 1 g/L, for 45 minutes. Thereafter the excess polyelectrolyte was rinsed away with milli-Q water and the surfaces were dried with a nitrogen stream. All surfaces were subsequently stored in a dust-free environment set to the relative humidity (RH) at which the measurements were performed in, i.e., 50% RH.

To test whether the dextran-coated surfaces displayed any differences in wetting behaviour depending on the type of dextran used (i.e., DEX or HDEX), the contact angles of the two different surfaces against water were measured using a CAM 200 contact-angle meter (KSV, Helsinki, Finland). The DEX surface was found to be hydrophilic with a contact angle of 7±1$^\circ$, whereas the HDEX surface was shown to be less hydrophilic with a contact angle of 48±1$^\circ$. 
3.3 Wood fibres
For fibre modifications and sheet preparation, dried, totally-chlorine-free (TCF) softwood kraft fibres from SCA Forest Products (Östrand Mill, Sundsvall, Sweden) were used. The fibres were soaked in deionised water overnight and then defibrated in a disintegrator for 30,000 revolutions according to the ISO 5263-1:1997 method. Before use, the counter ions in the pulp were exchanged with sodium ions according to a previously described procedure [87].

A dissolving-grade pulp from Domsjö Fabriker (Domsjö, Sweden) was used as the raw material for preparing amorphous cellulose thin films and cellulose II (para-crystalline) thin films. The pulp was extracted in acetone before use. A similar northern softwood dissolving-grade pulp, Temalfa 93 (Tembec Inc., Temiscaming, QC, Canada), was used to make the cellulose I nanocrystal suspension, which was used to prepare cellulose I thin films.

3.4 Model cellulose surfaces
Three model cellulose thin films, each different with regard to crystallinity, were prepared. Amorphous cellulose spheres, prepared from a lithium chloride (LiCl)/dimethyldiacetamide- (DMAc) solution, were kindly provided by MonoGel AB (Helsingborg, Sweden). The amorphous surface was prepared from a cellulose solution, in which the pulp was dissolved in a LiCl/DMAc solution, without the derivatising agent, according to a previously described method [88]. The cellulose II surface was prepared from a cellulose solution in which the pulp was dissolved in N-methylmorpholine-N-oxide (NMMO) and dimethylsulfoxide (DMSO) [64]. Finally, the cellulose I surface was prepared from a colloidal suspension of cellulose nanocrystals (kindly provided by Derek Grey, McGill University, Montreal, Canada).

In brief, the cellulose solutions/colloidal cellulose suspensions were spin coated, using a KW-4A spin coater (Chemat Technology Inc., Northridge, CA), onto silica surfaces, pre-treated with polyvinylamine or glyoxylated polyacrylamide, according to previously developed methods [64, 67, 68]. The amorphous cellulose and the cellulose II surfaces were precipitated in milli-Q water to remove the
solvents, and the cellulose I surfaces were heat treated at 90°C for 4 hours to remove most of the sulphate groups on the cellulose surface.

Tapping-mode atomic force microscopy using a Picoforce SPM (Veeco Instruments Inc., Fremont, CA) was used to determine the morphology and surface roughness of the cellulose surfaces/spheres used. The different types of cellulose surfaces were all shown to have similar structures with round aggregates. However, the cellulose II surface had larger aggregates than the other two did, as depicted in Figure 3.5a–c. This difference in aggregate size is likely linked to the dissolution process. The dissolution of cellulose in NMMO is known to form a fringe micellar-type arrangement before regeneration to the cellulose II structure in water [89]. The surface roughness, together with the film thickness of the prepared cellulose surfaces as determined using a Beaglehole Scanning Imaging Ellipsometer (Beaglehole, New Zealand), are presented in Table 3.3. The cellulose spheres were found to be a bit rougher than the cellulose surfaces, having an RMS value of 6 nm over a 1 µm² image, as determined by means of reverse imaging using AFM [90].

Table 3.3 Root mean square (RMS) values and the thickness of the different cellulose surfaces, measured for areas of 1 µm² and 100 µm².

<table>
<thead>
<tr>
<th>Sample</th>
<th>RMS value (nm) 1 µm²</th>
<th>RMS value (nm) 100 µm²</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cellulose I</td>
<td>2.3</td>
<td>3.1</td>
<td>120</td>
</tr>
<tr>
<td>cellulose II</td>
<td>3.9</td>
<td>5.7</td>
<td>30</td>
</tr>
<tr>
<td>amorphous</td>
<td>1.9</td>
<td>2.5</td>
<td>44</td>
</tr>
</tbody>
</table>
Figure 3.5a–c AFM tapping-mode height images of cellulose thin films on silica: a) cellulose I, b) cellulose II, and c) amorphous cellulose.
Static contact-angle measurements were performed against water and methyleneiodide, using a CAM 200 contact-angle meter (KSV, Helsinki, Finland). The results are presented in Table 3.4. Using the values of the contact angles between methyleneiodide ($\gamma_d = \gamma_s = 50.8 \text{ mJ/m}^2$) and the three cellulose surfaces, the dispersive part of the surface energy ($\gamma_s^d$) was calculated according to Equation 3.1. These values are also presented in Table 3.4. From this table it can be seen that the $\gamma_s^d$ of the cellulose surface exceeds the polar contribution, since the surface energy of cellulose is known to be approximately $54.5 \text{ mJ/m}^2$ [84], as determined by contact-angle measurements. The $\gamma_s^d$ of cellulose has been determined by contact-angle measurements to be $40 \text{ mJ/m}^2$ and $44.0 \text{ mJ/m}^2$ [83, 84]; this is similar to the values in the present investigation.

### Table 3.4

<table>
<thead>
<tr>
<th>Sample</th>
<th>Water (°)</th>
<th>Methyleneiodide (°)</th>
<th>$\gamma_s^d$ (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cellulose I</td>
<td>19.5</td>
<td>34</td>
<td>42</td>
</tr>
<tr>
<td>cellulose II</td>
<td>17</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>amorphous</td>
<td>18</td>
<td>37</td>
<td>41</td>
</tr>
</tbody>
</table>
4 Methods

In this chapter, all the instruments and methods used during the course of the research are presented, except for those presented in the previous chapter. For more detailed information regarding the experiments, the reader is referred to papers I–VII.

4.1 Stagnation point adsorption reflectometry (SPAR)
Polyelectrolyte adsorption onto silica surfaces was studied using stagnation point adsorption reflectometry (SPAR). The method and its underlying theory are well covered by Dijt et al. [91] and will not be discussed in detail here. Using this method, the adsorption kinetics of polyelectrolytes or surfactants onto a flat, optically well-defined surface can be studied under controlled-flow conditions. Figure 4.1 presents a schematic representation of the set-up.

![Figure 4.1 Schematic representation of the SPAR experimental set-up. The linearly polarised laser beam enters the cell, passes through the injected solution, and hits the reflecting surface. The reflected beam is then divided into parallel and perpendicular components, which are both detected by photodiodes and recorded separately (illustration courtesy of Lars-Erik Enarsson).](image)

Typically, an oxidised silicon surface is mounted in the liquid cell. A polarised laser beam enters the cell through a 45° glass prism, is reflected by the silica surface, and leaves the cell through a second 45° glass prism. A reflectivity ratio \((S)\) is defined from the reflectivity of the laser light in both directions of
polarisation. Upon adsorption onto the surface, the refractive index of the surface layer changes, altering the reflection of the incident laser beam to a certain extent. Thus, both the change in the parallel and perpendicular components of this reflected laser beam (\(\Delta S\)) and their ratio (\(\Delta S/S\)) can be determined. The theory, which is based on a four-layer (silicon, silicon oxide, polyelectrolyte, and solvent) optical model, can be used to calculate the adsorbed amount (\(\Gamma\)) which is proportional to \(\Delta S\), according to Equation 4.1.

\[
\Gamma = \frac{1}{A_s} \times \frac{\Delta S}{S}
\]  

(4.1)

\(A_s\) is a sensitivity factor proportional to the refractive index increment, \(dn/dc\), of the studied species. \(A_s\) is also highly sensitive to the thickness of the oxide layer on the silicon wafer.

When the SPAR equipment was used to study PEM formation, the data were presented as a relative change (\(\Delta S/S\)) in the reflected signal and not as a surface excess. This was because the polyelectrolytes are likely to diffuse into each other to a certain extent, constructing a film with an unknown \(dn/dc\) value.

4.2 Quartz crystal microbalance with dissipation measurements (QCM-D)

Polyelectrolyte adsorption was also studied using QCM-D equipment supplied by Q-Sense (Göteborg, Sweden). Figure 4.2 presents a schematic representation of the set-up of the crystal and the electric circuit of the equipment. This device examines the adsorption of polyelectrolytes onto a resonating, silica-coated piezoelectric quartz crystal. Adsorption onto the crystal is sensed as a decrease in the resonance frequency. If the adsorbed species is flat, uniform, and rigidly attached, the change in resonance frequency is directly proportional to the added mass and can be calculated using the Sauerbrey relationship, as shown in Equation 4.2 [92].

\[
\Delta m = -\frac{C_{qcm}}{n} \Delta f
\]  

(4.2)
$C_{qcm}$ is the mass sensitivity constant (17.7 ng/cm$^2$), $n$ is the overtone number, and $\Delta f$ is the change in resonance frequency of the AT-cut quartz crystal. Deviations from the Sauerbrey relationship occasionally occur upon polyelectrolyte adsorption. These deviations are due to both the conformation of adsorbed polyelectrolytes, which can be adsorbed as tails and loops, and to the coupled water, which also influences the decrease in resonance frequency and contributes to the detected mass uptake.

![Diagram of QCM-D set-up](image)

Figure 4.2 A schematic representation of the QCM-D set-up. The quartz crystal oscillates at a constant resonance frequency. When a substrate is attached to the surface the frequency decreases, indicating mass uptake. When the power source is disconnected it is also possible to study how the amplitude of the oscillation decreases. A change in dissipation is usually also observed upon adsorption. High dissipation indicates a mobile (water-rich) layer, while low dissipation indicates a rigidly attached substance (illustration courtesy of Lars-Erik Enarsson).

The change in energy dissipation during adsorption can also be examined, yielding information about the visco-elastic properties of the adsorbed film. To determine these properties, the electric current to the oscillating crystal is stopped so that the decay of the amplitude of the crystal can be measured. This decay is proportional to the visco-elastic properties of the layer, which are partly dependent on the amount of water trapped in the adsorbed layers. For a rigidly attached species, no change in dissipation will be observed during adsorption. For an adsorbed visco-elastic (water-rich) layer, the energy dissipated through the layer will increase during adsorption. The dissipation factor ($D$) is defined in Equation 4.3, and the change in dissipation can, according to the simplest view, be regarded as a change in the stiffness of the adsorbed layer.
\[ D = \frac{E_{\text{dissipated}}}{2\pi E_{\text{stored}}} \]  

(4.3)

\( E_{\text{stored}} \) is the energy stored in the oscillating system and \( E_{\text{dissipated}} \) is the energy dissipated during one oscillation period [93].

### 4.3 Atomic force microscopy (AFM)–colloidal probe technique

AFM–colloidal probe technique was used to examine the forces between different types of surfaces on approach and on separation, in wet conditions. The measurements were preformed using a Picoforce scanning probe microscope (Veeco Ltd., Santa Barbara, CA). A detailed description of the force measurements is presented elsewhere [94]. The colloidal probe technique, first introduced by Ducker et al. [95], was used in the present investigation. A schematic representation of the experimental set-up is presented in Figure 4.3.

![Schematic representation of the AFM set-up](image)

Figure 4.3. A schematic representation of the AFM set-up. As the sample and probe are brought into contact and then again separated, the deflection of the beam is measured via laser reflection from the cantilever. The reflected laser light is collected by the detector, and the change in position is monitored as a function of the voltage applied to the piezoelectric tube. Before the surfaces make contact the tip of the probe may bend upwards (due to long-range repulsive force) or downwards (due to long-range attractive force). After contact the cantilever starts to retract and the extra force (pull-off force) needed to separate the surfaces can be related to the adhesion between them.

A triangular voltage wave is applied to a piezo-electric tube, which causes the two surfaces to be brought towards and away from each other while the cantilever deflection signal from the photodiode is monitored as a function of the voltage.
applied to the piezo-electric tube. These force curves were subsequently converted into curves of force versus apparent separation. To accomplish this conversion, zero force and zero separation are defined. Zero force is defined as the force existing when the surfaces are far from each other, which is when the deflection is constant. Zero separation occurs when the movement of the cantilever is linear with respect to sample displacement at high force.

To measure forces between asymmetrically covered surfaces, a glass cell was built with a dividing wall (see Figure 4.4). The flat surface and the colloidal probe were hence separated during polyelectrolyte adsorption. After adsorption, the polyelectrolyte solution on both sides was removed by flushing the cell with excess electrolyte solution. The entire glass cell was then filled with the electrolyte solution, and the cantilever with the attached colloidal probe was moved over the dividing wall in the glass cell to the section of the cell where the substrate was stored, without exposing the probe to air. This set-up allows the adsorption of two different polyelectrolytes onto the colloidal probe and onto the flat surface, respectively, without exposing either the probe or the flat surface to air, which would undoubtedly dry the surfaces and change the conformation of the adsorbed layer.

Figure 4.4 Schematic representation of the liquid cell used in the AFM force measurements. After adsorption of two different polyelectrolytes in the separate sections (A) (for example, DEX on the right and HDEX on the left in the divided liquid cell) each side of the cell was rinsed with excess NaCl solution to remove any unadsorbed polyelectrolytes. The entire cell was filled with NaCl solution of uniform concentration and pH, so that it overtopped the dividing wall (B) and the probe could be moved to the left section without being exposed to the air. The probe was then in the same section as the mica surface and the measurement could start (C).
4.4 Micro adhesion measurement apparatus (MAMA)

In a typical experiment using MAMA, an elastic lens (PDMS cap) is stepwise pressed towards a lower, flat smooth surface, comprising material such as silica or cellulose [75, 85]. When a predetermined maximum load is reached, unloading begins and is performed in the same way as the loading, until the surfaces are pulled apart. Since the PDMS lens is transparent, the increase/decrease in contact area can be directly imaged through a microscope connected to a computer via a CCD camera (see Figure 4.5). The adhesive properties between two elastic bodies can be evaluated using JKR theory [74]. According to Equation 4.4, the JKR theory provides a relationship between the cube of the contact radius \((a^3)\) and the load \((F)\).

\[
a^3 = \frac{R}{K} \left[ F + 3\pi WR + \sqrt{6\pi WRF + (3\pi WR)^2} \right]
\]  

(4.4)

\(W\) is the adhesion energy, \(K\) is the elastic constant of the system and \(R\) is a function of the radii of the undeformed bodies as presented in Equation 4.5 and 4.6, respectively.

\[
K = \frac{4}{3} \left[ \frac{(1-\nu_1^2)}{E_1} + \frac{(1-\nu_2^2)}{E_2} \right]^{-1}
\]  

(4.5)

\[
R = \frac{R_1 R_2}{(R_1 + R_2)}
\]  

(4.6)

\(\nu_1\) and \(\nu_2\) are Poisson’s ratios, \(E_1\) and \(E_2\) are Young’s moduli and, \(R_1\) and \(R_2\) are the radii of curvature, of the two elastic bodies used. In the present work the adhesion measurements were performed between an elastic cap and a flat surface. Equation 4.6 reduces to Equation 4.7 and the elastic constant for the system is expressed in Equation 4.8.

\[
R_2 \to \infty \Rightarrow \frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_2} = \frac{1}{R_1} + \frac{1}{\infty} = \frac{1}{R_1} \Rightarrow R = R_1
\]  

(4.7)
\[
\frac{1}{K} = \frac{1}{K_{\text{lens}}} + \frac{1}{K_{\text{flat}}}
\]  

(4.8)

R₁ and R₂ are calculated by measuring (using a light microscope) the dimensions of the PDMS caps, i.e., the width and height. In the present work, the values were found to be approximately 1 mm.

The adhesion energy at minimum load, \( W_{\text{min}} \), is determined from the pull-off force, \( F_s \), according to Equation 4.9.

\[
F_s = \frac{3}{2} \pi R W_{\text{min}}
\]  

(4.9)

Figure 4.5 Schematic representation of the micro adhesion measurement apparatus (MAMA) constructed to measure interaction between, for example, cellulose surfaces and additives typically used in paper-making. An enlargement of the PDMS cap in contact with the lower surface is also shown. Adapted with permission from Rundlöf [96].
4.5 Hand sheet preparation and sheet evaluations

The pulp was consecutively treated with cationic and anionic polyelectrolytes according to a method described earlier [44]. In brief, the cationic polyelectrolyte was added to the fibre suspension and allowed to adsorb onto the fibres. The excess polyelectrolyte was filtered off and the fibre pad was rinsed with water/electrolyte solution. The fibre pad was then again suspended in water/electrolyte solution and the anionic polyelectrolyte was added and allowed to adsorb. The excess polyelectrolyte was again filtered off and the fibre pad was rinsed with water/electrolyte solution. This procedure was repeated until the desired number of polyelectrolyte layers was achieved.

Polyelectrolyte titration was used to determine the amounts of PAH and PAA consecutively adsorbed at pH 7.5 and 3.5, respectively, from solutions of 0.01 M NaCl, according to methods described elsewhere [97, 98]. In short, PAH was allowed to adsorb onto the fibres and the excess was titrated using potassium polyvinyl sulphate in the presence of an indicator, orto-toulidine blue (OTB). By repeating this procedure, with different amounts of PAH added to the fibre suspension, it was possible to determine an adsorption isotherm. The adsorbed amount of PAA was determined by adding it to fibres with a preadsorbed layer of PAH. Excess PAA was titrated using polyberen in the presence of OTB. The colorimetric endpoint was determined using the optical two-beam method developed by Horn et al. [99]. These procedures were performed for each of up to five adsorbed layers.

Hand sheets with a grammage of 100 g/m² were made according to the standard method, ISO 5269-2:1998, using Rapid Köthen sheet preparation equipment (Paper Testing Instruments – PTI, Pettenbach, Austria). The sheets were dried at 93°C and 90 kPa for 10 minutes. Some sheets containing PAH and PAA were also further heat treated at 160°C for 30 minutes. The grammage (mass per unit area), thickness, and density of the sheets were evaluated according to the Scandinavian standards for pulp and paper manufacturing (SCAN) SCAN-C 28:76 method.
Dry tensile testing, i.e., determining the stress–strain curves of paper strips, was conducted according to the method SCAN-P 67:93. The strength of paper can be expressed in several ways, tensile index being one common measure; the tensile index is the force at break per unit width and unit grammage (Nm/g).

Scott bond testing was performed according to the Tappi 833 pm-94 method, which determines sheet strength in the z-direction. In this method a test specimen (a piece of hand sheet) is laminated, and the rupture energy is expressed in energy units for a unit of surface produced (J/m²).

The light scattering coefficients ($s$) were determined for hand sheets, by applying Kubelka–Munk theory, according to the ISO 2471:1998 standard method. The sheets were exposed to diffuse light, in front of both a black background and a thick pad of sheets of the same material, and the reflectance of the light was measured.

To determine the molecularly non-bonded areas of hand sheets, an ASAP 2010 Accelerated Surface Area and Porosimetry Analyser (Micromeritics; Norcross, GA) was used. With this device, nitrogen gas is allowed to adsorb onto a paper sample. From the adsorbed amount of nitrogen and the size of the nitrogen molecule it is possible to determine the specific surface area of the paper using BET methodology [39, 100]. In the present study, sheets were cut into pieces, typically weighing approximately 3 gram, and treated in an external vacuum at 100°C for 5 hours to remove any adsorbed water. Samples were then placed in the ASAP 2010 sample container to determine nitrogen adsorption at different nitrogen pressures. From the initial part of the adsorption isotherm, i.e., at low relative vapour pressures, the monolayer coverage of nitrogen on the paper was determined, and from this amount the specific surface area of the paper was determined.

The nitrogen content of the dried sheets was analysed to determine the adsorbed amount of PAH using an ANTEK 7000 nitrogen analyser (Antek Instruments, Houston, TX, USA). A piece of a sheet, typically weighing 15–30 mg, was combusted in an oxygen-poor atmosphere. During combustion, all chemically
bonded nitrogen is transformed into \(-\text{NO}\), which forms \(\text{NO}^2\) upon reaction with ozone. As the excited molecule decays, light is emitted and sensed by a photomultiplier tube. Reference curves for known amounts of PAH were used to determine the adsorbed amount of PAH in the sheets.

The adsorbed amount of starch in dried hand sheets was detected using enzymatic treatment, according to a procedure outlined earlier [101]. Approximately 1 gram of a hand sheet was dispersed in 50 mL of water and 5 mL of potassium hydroxide, and then heat treated for 5 minutes at 95°C. The pH was then adjusted to 5.0 with acetic acid, followed by the addition of 2.5 mL of calcium chloride (50%) and 100 µL of α-Amylas. The suspension was heat treated for 1 hour at 95°C; 100 µL of amyloglukosidas (AMG) was then added, followed by heat treatment for 1 hour at 60°C. Using these enzymes, the starch is completely degraded to glucose units. The remaining fibres were filtered off and the filtrate was diluted to 200 mL and a sample is injected into a high-pressure liquid chromatograph.

Fourier transform infrared–attenuated total reflectance (FTIR–ATR) spectroscopy was used to analyse sheets containing PAH and PAA. The spectrometry equipment used was a Spectrum 2000 system (PerkinElmer, Kent, UK)

### 4.6 Fibre–fibre measurements

Fibre crosses were prepared according to the method initially outlined by Stratton and Colson [8], except that the fibres were not dyed [7]. The chemical conditions were the same as during paper formation. Fibre-cross preparation was made more efficient by preparing a very dilute fibre suspension, a small volume of which was placed on a Teflon-faced silicon disc, 8 mm in diameter. The fibres were allowed to sink to form a thin web of only a few fibres. A second Teflon disc was then placed face down on top of the fibres. The fibre web was then put under a nominal compressive load of 0.12 MPa and allowed to dry at 160°C for 2 hours. Perpendicular fibre crosses were chosen and carefully collected from the dry fibre web; these fibre crosses were stored at 50% RH and 23°C until testing.
A tensile testing stage was designed at Mid Sweden University for determining the mechanical properties of the fibre crosses. The fibre–fibre cross was mounted across the stage jaws. One of the stage jaws was held stationary, while the other was displaced during testing at 2 µm/s. A load cell with a working range of 0.150 gram was used. The sample was fixed to the table of the load bench with Loctite 401 glue. For each measuring point, 25–50 fibre crosses were tested.

The contact zones of the fibres were investigated using a light microscope, operating in the diffraction interference contrast mode. Hand sheets were soaked in an acetone solution containing 1 g/L hexamethyl-P-rosaniline chloride (C\textsubscript{25}H\textsubscript{30}ClN\textsubscript{3}, 407.99 g/mol). The van der Waals dimensions of the hexamethyl-p-rosaniline chloride crystal are 1.47 × 0.47 nm when dissolved in ethanol [102]. The sheets were then allowed to dry before being delaminated to expose the contact zones. The idea underlying this evaluation method is that acetone will not disrupt the molecular contacts between the fibres, so the dye can only reach the areas between the fibres that are not in molecular contact. By removing the excess acetone and evaporating the solvent, the dye will be left only in the non-joined areas of the fibre–fibre joint, which will increase contrast in images of the contact zones. The method for calculating the degree of contact (DOC) of the zones was outlined in an earlier publication by Torgnysdotter et al. [43]. DOC is calculated as the ratio between the areas in molecular contact, visualised via the rosaniline staining technique, and the macroscopic contact zone between the fibres. Approximately 25 contact zones, i.e., 25 fibre–fibre crosses, were analysed at each measuring point in order to determine the relative value of the degree of contact between the fibres.
In this research, polyelectrolyte adsorption and particularly the polyelectrolyte multilayer (PEM) technique have proven to be useful tools for modifying the properties of fibre surfaces and different model surfaces (e.g., silica surfaces). From comparisons with paper strength data and model experiments (papers I-IV), it was possible to obtain more detailed information regarding the action by which PEM films affect the strength properties. Furthermore, an attempt was made in paper V to understand the importance of polymer compatibility for the formation of strong joints.

5.1 PEM formation on silica (papers I and IV)

Stagnation point adsorption reflectometry (SPAR) was used to study the formation of PEMs from the chosen polyelectrolytes (PAH and PAA) under the influence of different pH regimes (as mentioned earlier). The possibility of using cationic and anionic starches to form PEMs was also examined. In making these measurements, silica surfaces were consecutively treated with cationic and anionic polyelectrolytes, with a rinsing step between each treatment. Figure 5.1 depicts the consecutive adsorption of PAH and PAA onto silica surfaces, using different pH strategies, in an electrolyte concentration of 0.01 M NaCl.

Figure 5.1 The change in reflectometer signal upon consecutive adsorption of PAH and PAA, using different pH strategies during adsorption, i.e., pH 7.5/3.5 (black), pH 7.5/7.5 (red), and pH 5.0/5.0 (grey). Rinsing was performed with a NaCl solution (of the same pH as the previous adsorbing solution) between each polyelectrolyte adsorption. The background electrolyte concentration was 0.01 M NaCl.
Multilayers do form using all three pH strategies, as a change in the signal was detected every time the polyelectrolytes were introduced. The figure also shows that there are large differences in PEM formation, depending on the pH used during adsorption. PEM growth when both polyelectrolytes were adsorbed at pH 7.5 was linear, while at pH 5.0 the growth could be characterised as exponential. When PAH was adsorbed at pH 7.5 and PAA at pH 3.5, PEM growth was even more markedly exponential. Shiratori and Rubner found similar trends when they used ellipsometry to investigate layer thickness as a function of pH [103]. These authors suggested that these transitions in film thickness are largely dependent on differences in the charge densities of PAA and PAH, which changes with pH.

Figure 5.2 shows PEM formation with amylose-rich cationic potato starch and with anionic potato starch, at pH 7.0, in a salt concentration of 0.01 M NaCl.

Even though the adsorption kinetics did not indicate as clear a formation as was demonstrated in Figure 5.1, it is obvious from Figure 5.2 that PEM formation does occur between CS and AS, as a change in the signal can be detected with each starch treatment. This indicates that such large and bulky polyelectrolytes of relatively low charge density (DS=0.065) also have the ability to form multilayers. The adsorption results presented in Figures 5.1 and 5.2, as detected using SPAR equipment, confirm that the chosen polyelectrolytes can be
successfully studied using reflectometry, as can also be done with other systems [47, 104].

5.2 PEM formation on wood fibres (papers I and IV)

Since silica presents a non-porous surface, in contrast to the heterogeneous, nanoporous fibre surface, it is also crucial to evaluate the adsorbed amounts of the studied polyelectrolytes as applied to the fibres prior to sheet making. The sheets prepared from fibres treated with PAH and PAA were analysed for their PAH content and the sheets prepared from starch-treated fibres for their starch content. The results are presented in Figure 5.3, showing that the adsorbed amount of PAH increases as the preadsorbed layer of PAA decreases its charge density (lower pH resulting in a lower charge density). This was expected both from previous studies of the same system [103] and from the SPAR results presented above. This figure also shows that it is easier to adsorb larger amounts of starch than of PAH onto the fibres, using the PEM strategy. Since most of the starch is adsorbed onto external parts of the fibre wall, due to the molecular size, this difference can only be explained by the much lower charge densities of the starches compared to those of PAH and PAA.

![Figure 5.3](image)

Figure 5.3 The total amount of PAH adsorbed onto the fibres as a function of every odd number of layers, (after treatments 1, 3, 5, and 7) using different pH strategies during PEM formation with PAH and PAA (▲ = pH 7.5/7.5, ● = pH 5.0/5.0, and ■ = pH 7.5/3.5). The figure also shows the total amount of starch adsorbed onto the fibres, as a function of the number of layers (which is the same as the number of starch treatments). The fibres were consecutively treated with CS and AS to produce three layers, i.e., CS/AS/CS (Δ = cationic amylpectin-rich starch, □ = cationic potato starch, and ○ = cationic amylose-rich starch).
Since no method for detecting the adsorbed amount of PAA in the dried sheets was available, PEM formation on fibres was studied using polyelectrolyte titration. Adsorption isotherms were derived for up to five layers using the 7.5/3.5 pH strategy. The results are presented in Figure 5.4, and indicate that PAA adsorbs in larger amounts in layers 2 and 4 than PAH did in layers 1 and 3. The adsorbed amounts of PAH correlate well to the adsorbed amount as detected in the sheet analysis. However, slightly higher adsorbed amounts of PAH were actually detected by means of polyelectrolyte titration; this finding could depend on several factors, but likely there was not a complete 1:1 stoichiometry between the polyelectrolytes used for the titration and the PAH/PAA. Nevertheless, it is clear that PAA adsorbed in at least equal, or even greater, amounts in comparison to PAH.

Figure 5.4 (Unpublished data) Adsorption isotherms for PAH and PAA onto fibres, using the 7.5/3.5 pH strategy. ○ = PAH and △ = PAA. The adsorptions were performed in a background electrolyte solution of 0.01 M NaCl. The adsorbed amounts presented in the figure are from the last adsorbed layer as indicated.
5.3 PEM formation on silica and wood fibres – a comparison (papers I and IV)

It is of interest to compare the amount adsorbed onto silica surfaces with the amount adsorbed onto the fibres. One obvious difference between these two surfaces is their geometry, which raises the possibility of polyelectrolytes penetrating into the interior of the porous fibres. This could produce different relationships between the amounts adsorbed in the different layers, when comparing silica surfaces and fibres. In Figure 5.5 the adsorption data from the SPAR is plotted against the amount adsorbed onto the fibres. As can be seen, it is not simple to qualitatively transform the data from the SPAR experiments to the actual adsorbed amount as determined from the dried sheets – at least not for the starch multilayers. Considering the large differences between the starches in terms of the amount adsorbed onto silica and fibres, it is likely that the differences are due to both the geometries of the surfaces and the physical properties/compositions of the starches used. It is thus possible that starches possess a different ability to recharge a flat silica surface than a nano-porous fibre surface. However, the PAH/PAA systems indicate that the same general trends can be found in adsorption onto silica surfaces as in adsorption onto fibres.

![Figure 5.5](image-url) (Unpublished data) The change in reflectometer signal upon adsorption of PAH and CS/AS as a function of amounts of PAH and CS/AS in the dried sheets. PAH/PAA was adsorbed using different pH strategies, i.e., pH 7.5/7.5 (■), pH 7.5/3.5 (▲), and pH 5.0/5.0 (●). In the experiments with CS and AS, a cationic amylose-rich starch (□), a cationic potato starch (△), and a cationic amylopectin-rich starch (○) were used.
5.4 Effects of PEM-treated wood fibres on paper strength (papers I, III, and IV)

The multilayer technique has been shown to improve paper strength in terms of both in-plane and out-of-plane properties. Figure 5.6a-b shows how the tensile index (a) and fibre–fibre joint strength (b) increase with layer number, using two different adsorption strategies for PAH and PAA at different pH levels. The results indicate that a lower charge density, as obtained at pH 3.5 for PAA and at pH 7.5 for PAH, made it possible to achieve both a stronger fibre-fibre joint and a stronger sheet. A difference in strength that depends on the polyelectrolyte used in the outermost layer is also detected. Finally, additional heat treatment can improve the tensile strength even further.

![Figure 5.6a–b Tensile index of sheets (a) and fibre–fibre joint strength (b) as a function of number of layers of PAH and PAA using different pH strategies, pH 7.5/7.5 (▲/△) and pH 7.5/3.5 (■/□). Filled symbols indicate heat treatment. The adsorptions were carried out in an electrolyte concentration of 0.01 M NaCl.](image)

The tensile index values for three different starch series, in which the chemical composition of the cationic starch was altered, are presented in Figure 5.7. An amyllose-rich starch acts as a better strength enhancer than does a potato starch, which has a much higher relative amount of amyllopectin. There may be several explanations to these differences, but probably the mechanical properties of the layers as such and their ability to anchor to the porous fibres are the most important factors. Amylose may penetrate into the fibre wall, thus strengthening the mechanical properties of the fibre wall during tensile testing. It is also known that films cast from pure amyllose are elastic, while films cast from amyllopectin
are very brittle (Olle Wikström, Lyckeby Industrial AB, private communication). This is also reflected in the strain at break of the sheets, where a sheet containing an amylose-rich starch has a strain of approximately 3% and a sheet containing an amylopectin-rich starch has a strain of approximately 2%.

![Figure 5.7 Tensile index of sheets as a function of starch treatments (CS/AS/CS) performed at pH 7 in a background electrolyte concentration of 0.01 M NaCl. A cationic potato starch (Δ), a cationic amylopectin-rich starch (●), and a cationic amylose-rich starch (■) were used.](image1)

The improvement in paper strength properties with the number of treatments could depend on the adsorbed amount of polyelectrolytes used. However, as indicated in Figure 5.8, the correlation between adsorbed amount and increase in tensile index is not straightforward.

![Figure 5.8 Tensile index of sheets as a function of cumulative adsorbed amount of PAH (pH 7.5)/PAA (pH 3.5), as determined using polyelectrolyte titration (▼) and CS/AS (in the sheets). In the experiments with CS and AS, a cationic potato starch (Δ), a cationic amylose-rich starch (□), and a cationic amylopectin-rich starch (○) were used. All adsorptions were carried out in a background electrolyte concentration of 0.01 M NaCl, at pH 7](image2)
Adsorption of anionic starch or PAA resulted in little or no improvement in the tensile strength of the sheets, with reference to previous adsorbed layer, despite the relatively high adsorbed amounts. All series show that the adsorbed amount in the sheets/on the fibres is not directly correlated to the tensile index. This leads to the conclusion that the nature and/or structure of the polyelectrolytes must be important for the efficiency of the formed layers.

However, the nature and/or structure of the polyelectrolytes used does not seem to be as important for the out-of-plane properties when starches are used (measured using Scott bond testing), as indicated in Figure 5.9. In this figure, the adsorbed amount is shown to be more important, and an increase in Scott bond can be seen for the three-layer treatments for all starches used, despite the differences in chemical composition.

Figure 5.9 Scott bond properties of sheets containing different types of starches, presented as a function of amount of starch adsorbed in the sheets. The fibres were treated with CS and AS consecutively to produce three layers, i.e., CS/AS/CS. A cationic potato starch (■), a cationic amylose-rich starch (●), and a cationic amylopectin-rich starch (▲) were used. All adsorptions were carried out at pH 7 in a background electrolyte concentration of 0.01 M NaCl. The lines included in the figure merely serve to guide the eye.

It is important to investigate how sheet density may be affected by these polyelectrolyte treatments; an increase in the sheet density will have negative effects on other sheet properties, such as bending stiffness. A summary of the different experimental series presented in papers I, III, and IV is presented in Figure 5.10, showing tensile index as a function of sheet density. A series in
which the sheet density was changed by wet pressing untreated sheets is also included. This figure indicates that most of the strength enhancement is due to the polyelectrolyte treatments, since there is great increase in tensile index upon PEM treatment without any significant increase in sheet density. It should be noted that a cationic amylopectin-rich starch influences sheet density more than the other starches do; this again indicates that a cationic amylose-rich starch is better for strength improvement than the other starches are.

Figure 5.10 Tensile index as a function of sheet density for untreated, wet-pressed sheets (+) compared to all the sheets made of PEM-treated fibres, as described in papers I, III, and IV. Unfilled symbols represent PAH/PAA, ○ = pH strategy 7.5/3.5, ∆ = pH strategy 5.0/5.0, and □ = pH strategy 7.5/3.5. Filled symbols represent CS/AS, ● = a cationic amylose-rich starch, ▲ = a cationic potato starch, and ▲ = a cationic amylopectin-rich starch.

5.5 A study of the internal and external structure of PEM films (paper II)

PEM films prepared using PAH and PAA (pH 7.5/3.5 strategy) had a more positive effect on the paper strength properties than did PEM films constructed using the pH 7.5/7.5 strategy (Figures 5.6a). In addition, PAH in the outermost layer had a more positive effect on paper strength than did PAA (Figure 5.8). To achieve a more fundamental understanding of these two intriguing results, it was decided to study PEM structure in more detail. PEM formation using PAH and PAA and the internal and external structures of these layers were therefore studied with the aid of QCM-D and AFM–colloidal probe technique.
From QCM-D measurements, the visco-elastic properties of the formed PEMs were examined from the changes in energy dissipation as the multilayers formed on the silica surfaces. Additional information was obtained about the mass uptake as a decrease in frequency, and the reader is referred to paper II for these results. Figures 5.11 and 5.12 display the change in energy dissipation during PEM formation with PAH and PAA, using two different pH strategies, i.e., pH 7.5/7.5 (Figure 5.11) and pH 7.5/3.5 (Figure 5.12) for PAH and PAA, respectively. When PEM formation was carried out at pH 7.5 for both polyelectrolytes, there was an increase in energy dissipation when PAH was adsorbed and a rapid decrease when PAA was adsorbed. PEM formation with PAH at pH 7.5 and PAA at pH 3.5 displayed similar trends. However, there was also an overall larger increase in dissipation, which indicates a more open and less rigid structure for the films formed at pH 7.5/3.5. These results also indicate that PAA in the external layer creates a more rigid structure than does PAH; this holds true for both pH strategies.

![Graph](image-url)

**Figure 5.11** The change in energy dissipation (ΔD) upon consecutive adsorption of PAH and PAA at pH 7.5. A pH-adjusted background electrolyte solution of NaCl with a concentration of 0.01 M was used during the rinsing step. The data are from the third overtone (15 MHz).
Figure 5.12 The change in energy dissipation ($\Delta D$) upon consecutive adsorption of PAH and PAA at pH 7.5 and 3.5, respectively. A pH-adjusted background electrolyte solution of NaCl with a concentration of 0.01 M was used during the rinsing step. The rinsing solution always had the same pH as the next adsorbing polyelectrolyte solution. The data are from the third overtone (15 MHz).

Further information regarding the external layers could be obtained from the AFM force measurements. Figure 5.13a-b presents the interaction between silica surfaces bearing PEMs, constructed at pH 7.5/3.5 (a) and 7.5/7.5 (b) with PAH as the outer layer, on approach. In all cases, throughout the build-up, PAH displayed a steric repulsive interaction that increased with the number of bilayers. Interestingly, the steric repulsion after the third bilayer is more significant with PAH in the outermost layer using the pH 7.5/7.5 strategy than for the pH 7.5/3.5 strategy. This is perhaps surprising considering the dissipation data as measured using QCM-D (Figures 5.11 and 5.12). However, more detailed inspection of the figures reveals that the pH 7.5/7.5 strategy produces a higher change in energy dissipation when PAH is adsorbed (after the third bilayer) than does the 7.5/3.5 strategy. This possibly indicates that PAH is adsorbed in a slightly more extended conformation in the pH 7.5/7.5 strategy. As the colloidal probe measurement technique is only sensitive to the outermost layer, this could explain why PAH in the outer layer using the pH 7.5/7.5 strategy did display a more significant steric repulsion.
The interaction between adsorbed multilayers when PAA formed the outermost layer, adsorbed under both pH strategies (i.e., pH 7.5/7.5 and pH 7.5/3.5 for PAH and PAA, respectively), was also studied. To clarify the behaviour of PAA when these two pH strategies are used, two typical force curves of the multilayer assembly with PAA as the outermost layer, adsorbed at pH 7.5 and pH 3.5 were compared. Figure 5.14 presents this comparison of the force curves with PAA as the outermost layer, in a log–lin diagram, for the fifth bilayer. The PAA-capped multilayers at pH 7.5 displayed electrostatic repulsion, whereas the PAA-capped multilayers at pH 3.5 displayed a typical steric repulsive interaction (recognised as S shaped). This result is perhaps not surprising considering the QCM data (Figures 5.11 and 5.12), which indicates that PAA adsorbed using the 7.5/7.5 pH strategy always displays almost zero energy dissipation, indicating a flat adsorbed layer, whereas PAA adsorbed using the 7.5/3.5 pH strategy always displays increased energy dissipation, indicating a more extended conformation. Earlier studies examining the adsorbed layer conformation of differently charged polyelectrolytes onto charged surfaces found similar trends [58].
Figure 5.14 (Unpublished data) Comparison of a typical normalised force–distance profile existing between multilayer-covered silica surfaces with PAA as the outermost layer, as a function of the pH of the adsorbing solution. A background electrolyte concentration of 0.01 M NaCl was used. Data are shown for the fifth bilayer. ▲ = PAA in the outer layer adsorbed under the pH 7.5/3.5 strategy and △ = PAA in the outer layer adsorbed under the pH 7.5/7.5 strategy. A scan size of 1000 nm and a scan rate of 0.5 Hz were used for all measurements.

Another interesting feature detected in the AFM force measurements was the adhesion interaction measured on separation of the PEM-treated surfaces. These results are summarised in Figure 5.15, which presents the pull-off force as a function of number of layers for PEM formation at pH 7.5/7.5 (for PAH and PAA, respectively). As shown in this figure, the adhesive interaction increases as the number of bilayers increases. Furthermore, the adhesive interactions were much higher when PAH was used as the outermost layer. It is suggested that this is due to the obtained contact area when these surfaces are pressed together. PAH in the outermost layer results in a softer layer than when PAA is outermost (as already discussed). As these surfaces are pressed towards each other, the softer layer will achieve a higher degree of contact, and this in turn leads to a higher adhesion force. This has also been demonstrated for the pH 7.5/3.5 adsorption strategy as well as in the case of PEMs using polydimethylammoniumchloride (polyDADMAC) and polystyrene sulphonate (PSS) [54].
Figure 5.15 A summary of the pull-off force data obtained from the adhesion measurements made using the AFM–colloidal probe technique. Both PAH (▲) and PAA (●) were adsorbed at pH 7.5 at a background electrolyte concentration of 0.01 M NaCl. A scan size of 1000 nm and a scan rate of 0.5 Hz were used for all measurements.

After comparing all these results to the paper strength data, it can be suggested that when the PEMs are constructed of highly charged PAH and PAA, a compact and rigid film is obtained, which contributes to a moderate increase in tensile strength. Furthermore, it was also shown that by making the adsorbed structure of PAA less rigid, by simply changing the pH of the adsorbing solution (i.e., lowering the charge density of PAA), it was possible to create a film with a less rigid structure and a greater mobility of polyelectrolytes within the film. This leads to significant strength enhancement in these films by improving adhesion between the fibres, as indicated by the better strength properties of the sheets obtained using the pH 7.5/3.5 adsorption strategy (for PAH and PAA, respectively). The strength improvements obtained with these systems are possibly due to: 1) molecular mixing, where a soft, water-rich layer is more likely to permit inter-diffusion to occur between adjacent fibre surfaces, and 2) an increase in contact area between the fibres, where the contact area possibly increases with the softness of the adsorbed layers. Other researchers have suggested that the inter-diffusion/interpenetration mechanism is important in creating strong fibre–fibre joints [11, 15]. The possibilities of an increase in contact area will be further addressed below.
5.6 Influence of PEM on the bonded areas within the sheets (paper III)

The effect of polyelectrolyte treatment on the bonded areas was investigated using three different techniques: BET analysis, light scattering coefficient determination, and a new method, developed by Torgnysdotter et al. [43], by which the degree of contact (DOC) within a fibre–fibre joint can be determined. For the 7.5/7.5 pH strategy using PAH and PAA, no large changes (except in the first adsorbed layer) in the DOC between the fibres were detected with increasing layer number, as shown in Figure 5.16. However, when the 7.5/3.5 pH strategy was used there was a significant increase in the first two layers, whereafter there was no further increase in DOC.

![Figure 5.16 Degree of contact (DOC) within a fibre–fibre joint as a function of number of layers of PAH and PAA, formed under different pH conditions. ■ = pH 7.5 (PAH)/pH 3.5 (PAA) adsorption strategy and ▲ = pH 7.5 (PAH)/pH 7.5 (PAA) adsorption strategy.](image)

Figure 5.16 reveals that the extent of apparently non-joined areas decreased with increasing sheet density and increasing number of layers. The results obtained also indicate large differences between the different methods. BET analysis reveals a much larger specific surface area, as well as a larger relative change with density and number of polyelectrolyte treatments, than the light scattering determinations did. The area, as determined using BET analysis is much larger than the area detected with visible light. However, both methods reveal linear relationships between sheet density and number of layers, as indirectly indicated in Figure 5.17. This is in accordance with the findings of earlier investigations comparing light scattering, nitrogen adsorption, and X-ray scattering [38, 39, 42].
Figure 5.17 Light scattering coefficients and BET areas of sheets as a function of number of layers of PAH and PAA, formed under different pH conditions. Squares refer to use of the pH 7.5 (PAH)/pH 3.5 (PAA) adsorption strategy, ■ = the BET area, and □ = the light scattering coefficient. Δ = pH 7.5 (PAH)/pH 7.5 (PAA) adsorption strategy, and represent the light scattering coefficient. All analysed hand sheets were heat treated. The lines serve only to guide the eye.

The relative bonded area (RBA) could be calculated from both light scattering data and nitrogen adsorption data according to Equation 2.1. From Figure 5.18a-b the BET area was extrapolated to 0.9 m²/g at zero tensile index (a), and similarly, the light scattering coefficient was extrapolated to 37 m²/kg at zero tensile index (b). These values correspond well to the values presented by Haselton [39]. In his work, zero tensile index corresponds to 0.82 m²/g (BET), or 35-40 m²/kg (as estimated from the light scattering data), for a bleached sulphite pulp. The RBA values are presented in Figure 5.19, together with the results obtained from the DOC measurements (Figure 5.16). Figure 5.19 shows that the RBA, as determined from the BET area, responds directly and increases almost linearly with tensile index. In contrast, the RBA as calculated from the light scattering stays almost constant from the beginning, only responding after a tensile index of 40 Nm/g. It has been suggested that strength-enhancing additives, such as starch, do not contribute to an increase in RBA, despite an increase in the tensile index.

Hence, the conclusion was made that starch contributed by increasing the specific fibre–fibre joint strength [25].
Figure 5.18a-b (Unpublished data) BET area (a) and light scattering coefficient (b) as a function of tensile index for sheets prepared with multilayered fibres, using PAH and PAA and the pH 7.5/3.5 adsorption strategy.

Figure 5.19 (Unpublished data) RBA values calculated from light scattering and BET analysis together with DOC values for the pH 7.5/3.5 series. ■ = RBA values calculated from BET analysis and □ = RBA calculated from light scattering data. Δ = DOC within a fibre–fibre joint. The lines serve only to guide the eye.
From the present investigation it is shown that light scattering cannot reveal information on a molecular level. If this is true for PAH and PAA, it must also be considered to be true for starch – but this must be tested. Even though BET area and light scattering indicate linear relationships, as demonstrated in the present work and by others [38-40], light scattering can not provide information regarding molecular adhesion. Additionally, from Figure 5.19 it can be seen that the DOC within a fibre–fibre joint increases immediately and at a tensile index of approximately 30 Nm/g, it levels out. This, and the fact that the RBA as determined using BET analysis continues to increase even after a tensile index of 30 Nm/g, suggests that there is initially an increase in contact area in the fibre–fibre joint, contributing to the increased tensile index. The effect of contact area then diminishes, and the increase in tensile index comes to be dominated by an increase in number of efficient fibre–fibre joints.

5.7 Development of covalent bonds in the sheets (paper III)
From Figure 5.6a it was clear that heat treating the sheets further increased the tensile strength. The hypothesis was that this increase was due to the formation of amide linkages, which are known to be formed between PAH and PAA [77]. The FTIR–ATR measurements presented in Figure 5.20 indicate that amide linkages were formed between PAH and PAA, both after drying the sheet at 93°C and after further heat treatment at 160°C, since the characteristic peak for amide linkages appears at 1550 cm\(^{-1}\). These chemical changes were more easily detected in the pH 7.5 (PAH)/3.5 (PAA) series than in the pH 7.5 (PAH)/7.5 (PAA) series. The ratio of the amount of cellulose to the amounts of PAH and PAA was probably too low to enable reliable detection of the amide formation in this latter pH series. Based on the results of the FTIR–ATR measurements (Figure 5.20), it is suggested that amide formation contributed to the further increase in tensile index for both series, as indicated in Figure 5.6a.
Figure 5.20 FTIR–ATR spectra of sheets. The analysed sheets were made from wood fibres treated consecutively with PAH and PAA to obtain a PEM film of eight polyelectrolyte layers a) reference (no polyelectrolyte treatment), b) pH 7.5 (PAH)/pH 7.5 (PAA), c) pH 7.5 (PAH)/pH 7.5 (PAA) heat treated, d) pH 7.5 (PAH)/pH 3.5 (PAA), and e) pH 7.5 (PAH)/pH 3.5 (PAA) heat treated.

5.8 Studies of wet and dry adhesion between compatible and incompatible dextran-covered surfaces, aiming to understand paper strength (paper V)

This part of the thesis was inspired by research by Pelton et al. demonstrating the importance of chemical surface compatibility for obtaining strong paper [15]. The main finding of that work was that a smaller increase in paper strength was obtained in sheets made from fibres modified with differing ratios of cationic dextran (DEX) and hydrophobically modified cationic dextran (HDEX), as compared to symmetrical combinations of the adsorbing polyelectrolytes, i.e., DEX:DEX and HDEX:HDEX. It was postulated that the decrease in paper strength was due to the inability of the polymer layers to inter-diffuse during the consolidation and drying of the paper [15]. Since paper is a complex material, it was decided to test this hypothesis at the molecular level. The main objective of the present study was hence to investigate whether the adhesion between dissimilar dextran-covered surfaces of different degrees of hydrophilicity would be weaker compared to the adhesion of dextran-covered surfaces of the same degree of hydrophilicity.

Despite the short hydrocarbon chain of the modified dextran (HDEX), it has earlier been shown that intramolecular association does occur between the
hydrophobic moieties in solution [81]. Based on QCM-D and SPAR measurements in the present investigation, it is believed that intra-association between the hydrocarbon chains also occur in the adsorbed structure of HDEX. QCM-D measurements are presented in Figure 5.21a, showing the change in frequency (third overtone) and dissipation upon adsorption of DEX and HDEX onto silica. The change in frequency was essentially the same regardless of the type of dextran used. Interestingly, significant differences in the dissipation values were obtained and the adsorption of HDEX resulted in the lower dissipation value. From the QCM-D data, the adsorbed amount of the dextrans, including the coupled water, could be calculated using Equation 4.2, showing values of about 11 mg/m$^2$ for both DEX and HDEX. From SPAR measurements, the adsorbed amounts of dextran were calculated using Equation 4.1, and are presented as a function of time in Figure 5.21b. There was no significant difference between DEX and HDEX regarding the calculated adsorbed amount, approximately 1.25 mg/m$^2$ in both cases. From these two values it can be concluded that the adsorbed structures of DEX and HDEX contain approximately 90% water, meaning that both polyelectrolytes adsorb in an extended structure with loops and tails, which is reasonable due to the low charge density (approximately 3.5%) of the dextran.

In addition, these adsorption results are in good agreement with the results presented by Plunkett et al. [105], showing through the use of QCM-D that a polyelectrolyte with a charge density of 1% contained a large amount of coupled water (80%) in its adsorbed structure. However, since the adsorbed layers in the present investigation contain the same amount of coupled water, this cannot account for the detected differences in dissipation. This suggests that an intra-association between the hydrocarbon chains on the HDEX does occur, and this can be explained by the lower dissipation for HDEX, indicating a stiffer adsorbed layer than that formed by DEX, as indicated in Figure 5.21a. Schematic representations of the adsorbed structures of DEX and HDEX are presented in Figure 5.22.

In solution, DEX and HDEX formed an aqueous biphase as shown in Figure 5.23; this was as expected and has been reported earlier [81]. It was thus anticipated that incompatibility of the polymer solutions would be reflected in the interactions of adsorbed layers.
Figure 5.21a–b Adsorption of DEX (triangles) and HDEX (squares) with the use of QCM-D (a) and SPAR (b) from a solution of 50 mg/L dextran in 0.01 M NaCl at pH 8. Both the initial baseline and the final rinsing step were performed using a NaCl solution of 0.01 M at pH 8. (a) The two lower curves with open symbols represent the change in frequency upon adsorption onto the oscillating silica-coated quartz crystal. The two upper curves with closed symbols represent the change in dissipation due to adsorption of DEX and HDEX. (b) The adsorbed amount of dextran was calculated from the data collected from the SPAR measurements using Equation 1 and is presented as a function of time.

Figure 5.22 Schematic representations of possible structures of adsorbed layers of DEX (left) and HDEX (right) on solid surfaces. The hydrophobic hydrocarbon chains on the HDEX may associate during adsorption, forming a stiffer adsorbed layer than DEX does while still containing the same amount of coupled water.

Figure 5.23 Biaqueous phase separation of DEX and HDEX in a 10% (w/w) concentration in 0.01 M NaCl. These conditions were chosen, since the QCM-D and reflectometry data indicated that the amount of water in an adsorbed dextran layer was approximately 90%, in the cases of both DEX and HDEX. The upper phase, A, is rich in HDEX and the lower phase, B, is rich in DEX.
From the wet adhesion determined using the AFM–colloidal probe technique, as obtained between the three different combinations (i.e., DEX:DEX, HDEX:HDEX, and DEX:HDEX), there was no clear indication that the phase separation indeed occurred, while the asymmetric case displayed an intermediate adhesion force, as shown in Figure 5.24. The wet adhesion correlates well with the solvency behaviour of the polyelectrolytes. HDEX:HDEX displays the strongest adhesion force on separation, possibly due to a rearrangement of the hydrophobic moieties on the HDEX. The hydrocarbon chains on opposite surfaces possibly associate; this would result in a higher adhesion force as the surfaces are separated and the hydrophobic chains are pulled into a poorer solvent that is less favourable entropically than continued contact. The DEX:DEX interaction has a much lower adhesion in water; this likely originates in the hydrophilic nature of the polyelectrolyte. High water solubility will lead to a much lower adhesion force upon separation. The intermediate adhesion force detected for the DEX:HDEX system is suggested to be due to a preferred mixing of HDEX with DEX instead of being surrounded by the solvent molecules.

![Figure 5.24 Interaction forces between dextran-covered surfaces (a silica sphere, with a diameter of 10 µm, and a freshly cleaved mica surface) on separation as determined using the AFM–colloidal probe technique. The dextrans were adsorbed from a solution of 50 mg/L in an electrolyte concentration of 0.01 M NaCl at pH 8. The force measurements were made in the same background electrolyte concentration and pH. Red = DEX:DEX, Black = DEX:HDEX and Grey = HDEX:HDEX.](image-url)
The dry adhesion measurements, presented in Figure 5.25, did indicate the existence of adhesion hysteresis in all three investigated systems, as outlined above. It is clear that the introduction of hydrophobic units on the dextran leads to a less pronounced adhesion hysteresis and a lower work of adhesion at minimum load (\(W_{\text{min}}\)), as calculated from the pull-off forces using Equation 4.9. DEX:DEX displayed a \(W_{\text{min}}\) of 590±69 mJ/m\(^2\), while DEX:HDEX and HDEX:HDEX displayed values of 148±33 mJ/m\(^2\) and 55±3 mJ/m\(^2\), respectively. Similar to the wet adhesion measurements, there is no evidence of incompatibility playing a role since the adhesion force between the asymmetric surfaces was intermediate. These effects on adhesion hysteresis and the presence of OH groups have been studied previously, showing a decrease in adhesion hysteresis with removal of OH groups from the surface [106, 107]. It seems reasonable to suggest that the presence of butyrate groups on HDEX interfere with hydrogen bonding, resulting in weaker adhesion. This is further supported by the contact angle measurements, clearly showing that the DEX surface is more hydrophilic than the HDEX surface. The higher contact angle for the HDEX surface can be attributed to the removal of the polar OH groups and the introduction of the hydrophobic moieties.

![Figure 5.25 Results from MAMA measurements of adhesion between dextran-covered silica surfaces and OxPDMS surfaces. The adhesion was measured between combinations of DEX:DEX- (Δ / ▲), DEX:HDEX- (● / ○), and HDEX:HDEX- (□ / ■) covered surfaces. Open symbols refer to the loading data and closed symbols refer to the unloading data. The measurements were made in air at 50% RH and a temperature of 23°C](image-url)
The present results indicate no direct link with the paper strength data presented by Pelton et al. [15]. However, the results once again highlight the complex mechanism responsible for fibre–fibre joint formation and strength development in paper. Perhaps the surfaces possess an inherent potential to form strong joints between adjacent surface layers. However, to efficiently exploit this potential the surfaces must be in close contact with each other, otherwise no strong adhesion will occur. This could also explain why the asymmetric case, DEX:HDEX, results in a weaker paper despite the fact that the ability to develop specific interactions, such as hydrogen bonding between the surfaces, is greater than that of HDEX:HDEX, as indicated by the MAMA experiments.

5.9 Why are certain polyelectrolytes good as strength enhancers while others are not?

On the basis of the present results and the hypothesis proposed by Pelton [18], basically suggesting that hydrophilic polyelectrolytes are more efficient strength-enhancing additives than hydrophobic polyelectrolytes, it might be suggested that a hydrophilic polyelectrolyte can retain more coupled water even in its adsorbed state. This would create mobile and soft surface layers offering good potential for mixing as the two fibre surfaces approach each other, thus establishing strong fibre–fibre joints with large contact areas. In contrast, when a more hydrophobic polyelectrolyte is adsorbed onto a fibre surface, it would retain less coupled water, resulting in poorer mixing as water is removed during joint formation. Possibly, a smaller contact area and a weaker joint is then formed. This hypothesis must be further critically examined, and it would be interesting to test a set of different polyelectrolytes of different degrees of hydrophilicity, but with the same molecular weight and charge density. Adsorption measurements should be performed using QCM-D and SPAR, to determine the coupled water in the adsorbed structures. The strength properties of hand sheets, prepared from wood fibres treated with the same polyelectrolytes should be tested in order to determine whether there is a relationship between the paper strength and the polyelectrolytes ability to hold water. Below is an attempt to test this hypothesis.

The relationship between tensile index (y-axis) and dissipation factor (x-axis) for different polyelectrolyte systems are tested in Figure 5.26. Some cautions should
be taken in drawing conclusions from this figure, as the polyelectrolytes used differ in terms of both charge density and molecular weight. Ideally, the coupled water of the adsorbed polyelectrolyte structures should be determined, as mentioned above. However, only QCM-D data are available. These measurements give a good indication of the visco-elastic properties of the surfaces, which are closely related to the amount of coupled water. The figure should be regarded as an inspiration for possible continuation of this work. There seems to be a correlation between the dissipation factor and the obtained tensile index, indicating that starch is an effective strength enhancer, while polyDADMAC contributes little to the tensile index. Furthermore, it is evident that PAH falls into the same category as polyDADMAC, and use of the multilayer technique with PAH and PAA (8 layers, pH 7.5/3.5) can significantly improve the tensile index by creating a quite soft and water-rich PEM film. Finally, if covalent bonding is developed, the strength can be further increased, as is seen with the use of PAH and PAA.

Figure 5.26 Tensile index as a function of change in dissipation (ΔD) as determined using QCM-D. The dissipation value indicates the amount of coupled water in the adsorbed layer structure, and the higher the value the greater the water content. Data come from the present work; data regarding the tensile index for polyDADMAC come from Lingström [52] and regarding the dissipation value of polyDADMAC from Ondaral et al. [108]
6 Interaction studies using model cellulose surfaces

Considering the options for the preparation of model cellulose surfaces, it was decided in this research to compare three different cellulose surfaces with different degrees of crystallinity (papers VI and VII). The aim of this was to build a platform for future cellulose–cellulose/cellulose–lignin/cellulose–hemicellulose interaction studies, in which different research groups could use the same type of cellulose surface. This would allow the comparison of results and hence an integrated way to understand fibre–fibre interactions in paper products. Three different cellulose surfaces were prepared (as described earlier), one crystalline surface (cellulose I), one para-crystalline surface (cellulose II), and one amorphous surface, which were all smooth in the nanometre range. Interaction studies were performed under both wet and dry conditions.

6.1 Studies of wet interaction between cellulose surfaces (paper VI)

Using the AFM–colloidal probe technique, the three different cellulose surfaces were compared based on the force profiles of their interactions with a hornified amorphous cellulose sphere. The amorphous flat cellulose surface displayed a steric interaction profile under all investigated solution conditions, with pH ranging from 3.5 to 8.5 and salt concentrations ranging from 0.1 to 10 mM NaCl. Figure 6.1 presents the interaction profile for 1 mM NaCl and pH 3.5

![Figure 6.1 Normalised force–distance curve for the interaction of an amorphous cellulose sphere and an amorphous cellulose flat surface at pH 3.5 and an ionic strength of 1 mM NaCl. No attempt was made to fit the data to the DLVO theory.](image-url)
This steric interaction between cellulose surfaces has also been detected by others [70, 109], and it has been suggested to be due to tangling tails of cellulose protruding into the solution. This explanation is unlikely since cellulose is not soluble in water. Instead, this steric or sometimes electrosteric interaction is suggested to be due to the swelling behaviour of the surfaces. Amorphous cellulose surfaces prepared from LiCl/DMAC are known to swell to double their volume in water [67].

The force profiles of the cellulose II surface displays both van der Waals and electrostatic interactions depending on the solution conditions, as shown in Figure 6.2a–b. When the electrostatic contributions were removed, i.e., at low pH or high salt concentrations, attractive van der Waals forces were detected. If either the pH was raised or the salt concentration was lowered, the interaction with the cellulose II surface indicated an electrostatic repulsion.

![Figure 6.2a Normalised force–distance curves for a cellulose sphere and cellulose II surface: a) at pH 5.5 as a function of ionic strength. Grey symbols correspond to 0.1 mM (Debye length = 25 nm) and black symbols correspond to 1 mM. b) in a background electrolyte concentration of 0.1 mM as a function of pH. pH 3.5 correspond to black symbols, pH 5.5 correspond to red symbols, and pH 8.5 correspond to grey symbols.](image)

The cellulose I surface exhibited an electrostatic repulsion under all investigated solution conditions, as summarised in Figure 6.3a–b. Despite making the measurements at pH 3.5 (Figure 6.3a), electrostatic repulsive interaction was still dominant, which was suggested to be due to the presence of the sulphate ester
groups introduced by acid hydrolysis [68]. The low $pK_a$ value of approximately 1.9 suggests that these charges on the cellulose I surface were almost completely dissociated under these solution conditions.

![Diagram](image)

Figure 6.3a–b Normalised force–distance curves between a cellulose sphere and cellulose I flat surface: a) at a background ionic strength of 0.1 mM as a function of pH, pH 3.5 (black), pH 5.5 (red) and pH 8.5 (grey). The data can be fit to DLVO theory with a measured Debye length of 32 nm. b) at pH 8.5 as a function of ionic strength, for 0.1 mM (grey), 1 mM (red), and 10 mM (black) NaCl. The fitted Debye lengths were 32, 10.5 and 3.5 nm, respectively.

Figure 6.4 presents a comparison of the measured interaction potentials of the three different cellulose surfaces used in this study at pH 3.5 and 1 mM aqueous NaCl solution, which highlights the differences between these surfaces. The cellulose I interactions are characteristic of an electrostatic repulsion, the cellulose II sample displays a combination of electrostatic and dispersion force interactions, whilst steric interactions predominate in the case of the amorphous sample. Thus, the preparation procedure of the cellulose thin film clearly has a great influence on the measurable surface forces, even though similar raw materials were used for each sample. Based on the present investigations, it is suggested that the cellulose II surface offers the greatest potential for further study of force interactions.
Figure 6.4 Comparison of the interaction force–distance curves between a cellulose sphere and the cellulose I, II and amorphous cellulose surfaces at pH 3.5 and in 0.1 mM aqueous NaCl solution. The interaction with the cellulose I sample (red) is characterised by an electrostatic repulsion, while van der Waals forces and steric interactions predominate with the cellulose II sample (black) and amorphous cellulose sample (grey), respectively.

6.3 Studies of adhesion between polydimethylsiloxane (PDMS) and cellulose surfaces (paper VII)

Using the micro adhesion measurement apparatus (MAMA), the adhesion forces between PDMS and the three different cellulose surfaces were measured at two different RH levels, 30 and 50%. These data are presented in Figure 6.5a–b.

Figure 6.5a–b Adhesion between PDMS and cellulose I (Δ / ▲), cellulose II (○ / ●), and amorphous cellulose (□ / ■) at (a) 50% RH and (b) 30% RH. Unfilled symbols represent the loading data while filled symbols represent unloading data.
Direct comparison of the figures is always difficult, and to allow for quantitative comparison of the different surfaces and RH levels, the work of adhesion was calculated. If the load data are first considered, it was possible to use Equation 4.4 to obtain $W_A$ and $K$ for the three studied systems, and those values are presented in Table 6.1. Furthermore, using the dispersive parts of the surface energies of PDMS and the cellulose surface (as shown in Tables 3.2 and 3.4, respectively), it was possible to calculate the work of adhesion due to the dispersive interaction ($W_{12}^d$) between the investigated systems, using Equation 6.1 [84].

$$W_{12}^d = 2\sqrt{\gamma_1^d \gamma_2^d}$$  \hspace{1cm} (6.1)

A summary of these calculations and the experimental values obtained with contact mechanics are presented in Table 6.1.

Table 6.1 The work of adhesion, $W_A$, (loading data) and $K$ values, as determined using JKR measurements together with the calculated dispersive contribution to the work of adhesion.

<table>
<thead>
<tr>
<th>System</th>
<th>30% RH $W_A$ (mJ/m$^2$)</th>
<th>30% RH $K$ (MPa)</th>
<th>50% RH $W_A$ (mJ/m$^2$)</th>
<th>50% RH $K$ (MPa)</th>
<th>50% RH $W_{12}^d$ (mJ/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS/cellulose I</td>
<td>49±6</td>
<td>3.2±0.2</td>
<td>45±4</td>
<td>3.2±0.2</td>
<td>61</td>
</tr>
<tr>
<td>PDMS/cellulose II</td>
<td>47±3</td>
<td>2.9±0.2</td>
<td>47±3</td>
<td>3.1±0.2</td>
<td>59</td>
</tr>
<tr>
<td>PDMS/amorphous</td>
<td>40±4</td>
<td>2.7±0.1</td>
<td>46±4</td>
<td>2.9±0.2</td>
<td>60</td>
</tr>
</tbody>
</table>

From Table 6.1 it can be seen that there are no large differences in the $W_A$ between the different cellulose surfaces at 50% RH. However, at 30% RH, the $W_A$ seems to correlate with the degree of crystallinity, showing a lower $W_A$ for an amorphous surface. Considering the calculated values of $W_{12}^d$ (which indeed is somewhat larger than the experimentally determined work of adhesion), it can be concluded that the $W_A$ consists mainly of dispersive interactions.
On examining Figure 6.5a–b again, it is clear that the adhesion hysteresis is significant and that it depends on both the degree of crystallinity and the RH. For further quantification of these differences, $W_{\text{min}}$ was calculated according to Equation 4.9. The data from these calculations are summarised in Table 6.2, showing even more clearly the differences between the different surfaces.

Table 6.2 Calculated $W_{\text{min}}$ between PDMS and cellulose surfaces, with different degrees of crystallinity. The measurements were carried out at a RH of 30 or 50%, as indicated in the table.

<table>
<thead>
<tr>
<th>Sample</th>
<th>RH 30% $W_{\text{min}}$ (mJ/m$^2$)</th>
<th>RH 50% $W_{\text{min}}$ (mJ/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS/cellulose I</td>
<td>213±32</td>
<td>289±29</td>
</tr>
<tr>
<td>PDMS/cellulose II</td>
<td>347±14</td>
<td>389±32</td>
</tr>
<tr>
<td>PDMS/amorphous</td>
<td>337±31</td>
<td>472±32</td>
</tr>
</tbody>
</table>

The detected differences in the adhesion hysteresis (Fig 6.5a–b) and $W_{\text{min}}$ (Table 6.2) correlate with the degree of crystallinity of the studied cellulose surfaces, a highly crystalline cellulose surface displaying the lowest adhesion force and the amorphous cellulose surface displaying the highest adhesion force. This is possibly due to the cellulose surfaces adjusting themselves and orienting their OH groups towards the PDMS surface. Amorphous regions on the cellulose offer greater potential for mobility of the surface groups, thereby allowing for more specific interactions than crystalline regions do. The largest adhesion hysteresis, as well as the highest $W_{\text{min}}$ values, for all three investigated surfaces, were obtained at 50% RH. This finding could probably be linked to the ability of the surfaces to adsorb/absorb water. The highest $W_{\text{min}}$ value was obtained for the amorphous surface, followed by the cellulose II surface and the cellulose I surface, respectively. This correlates well with the assumed water uptake, assuming that the amorphous parts of the cellulose have the largest water uptake. From earlier research it is known that the amorphous surface can swell to double its thickness when exposed to water [67]. At 50% RH one can also detect a difference in the obtained $W_{\text{min}}$ between the amorphous and the para-crystalline surfaces, which was impossible from the measurements made at 30% RH as shown in Table 6.2. This could possibly be explained by the ability of the water to
plasticize the amorphous parts of the cellulose, which in turn would allow stronger joints to form. Furthermore, the mobility of the surface OH groups is perhaps more favoured at a higher RH.

Since the measurements were performed in a humid environment, it is important to consider the possibility of capillary condensation. An investigation using AMF–colloidal probe technique demonstrated that a distinct increase in adhesion between two cellulose surfaces was detected at 60% RH [110]. Given this background, it is suggested that the achieved adhesion indicated by these measurements is not due to capillary condensation.

Earlier studies demonstrated that the adhesion between either LB cellulose or cellulose II surfaces and PDMS were of similar magnitude as presented in the present investigation [75, 83]. The measurements with the LB film were made under conditions ranging from 33 to 47% RH, making direct comparison with the results of the present investigation difficult [75]. However, the values are similar to those presented here, and $W_A$ ranged from 47.4 to 51.6 mJ/m$^2$ and $W_{\text{min}}$ was 201 mJ/m$^2$. The cellulose II measurements were made at a RH of 50% in the earlier study, and can thus be directly compared with those from the present study: the earlier study found that $W_A = 43$ mJ/m$^2$ and $W_{\text{min}} = 400$ mJ/m$^2$ [83], while the present study found similar values of $W_A = 47\pm3$ mJ/m$^2$ and $W_{\text{min}} = 389\pm32$ mJ/m$^2$.

From this comparison it is obvious that differences in cellulose crystallinity are not as critical as when the cellulose interactions are measured in aqueous conditions. However, it is clear that a highly crystalline cellulose surface did result in a lower adhesion hysteresis and lower $W_{\text{min}}$ (as determined from the pull-off force) than did the amorphous cellulose surface. These differences can be attributed to the ability of the cellulose surface to adsorb water and rearrange its surface groups to participate in joint formation, which is suggested to be more favourable in the case of an amorphous cellulose surface.
7 Conclusions

The polyelectrolyte multilayer (PEM) technique, using polyallylamine hydrochloride (PAH) and polyacrylic acid (PAA), as well as cationic and anionic potato starches, was applied to wood fibres. The following conclusions can be made regarding strength properties (papers I–IV):

1. For the out-of-plane sheet strength properties, the adsorbed amount of starch is the dominant factor.

2. The adsorbed amount of strength-enhancing additive is not the only factor contributing to the in-plane paper strength properties. The structure of the formed film is also important.

3. PEM formation on silica indicated that both exponential PEM film growth and the occurrence of a PEM film in which the polyelectrolytes are highly mobile, favour the strength-enhancing properties of sheets. This indicates that a water-rich, soft PEM film allows the polyelectrolytes to diffuse into each other which has a positive effect on the obtained adhesion between the fibres, contributing to stronger sheets.

4. The physical properties of the polyelectrolytes used and the type of polyelectrolyte, which forms the outermost layer, will greatly influence the paper strength. Again, the adsorbed structure is shown to be important.

5. The measured tensile index of sheets containing PAH and PAA can be related to an increase in both degree of contact within a fibre-fibre joint and the number of efficient fibre–fibre joints, without significantly affecting sheet density.

6. Using PAH and PAA, it is also possible to form amide linkages that contribute further to paper strength.

7. Nitrogen adsorptions using BET analysis can detect changes in the molecularly bonded area of the sheets that are not detected by light-scattering measurements.

Using cationic dextran (DEX) and hydrophobically modified cationic dextran (HDEX), the following conclusions can be made (paper V):

1. Phase separation can not be detected from adhesion measurements between surfaces covered with DEX and HDEX.
(2) Wet adhesion measurements indicate stronger adhesion due to the presence of hydrophobic moieties on the modified dextran, which is suggested to be due to the association of the hydrophobic parts of the preadsorbed HDEX.

(3) Dry adhesion measurements demonstrate the ability of the surfaces to develop specific interactions between them, where hydrogen bonds are considered to contribute to the adhesion. Hence, this bonding is weaker when either or both surfaces consist of HDEX.

From studies of interaction between different cellulose surfaces, the following conclusions can be made (papers VI and VII):

(1) The type of cellulose surface used is more important in interaction studies in aqueous solutions than in adhesion measurements made under ambient conditions.

(2) In aqueous salt solutions an amorphous surface displays large steric repulsion regardless of pH and salt concentration, probably due to the swelling of the amorphous surface.

(3) In aqueous salt solutions a cellulose I surface displays electrostatic repulsions at all investigated pH levels and salt concentrations, suggesting being due to the presence of weakly ionisable groups.

(4) In aqueous salt solutions a cellulose II surface displays pure van der Waals interactions at low pH or higher salt concentrations, and predominantly electrostatic interactions at high pH or lower salt concentrations.

(5) Under ambient conditions the work of adhesion, as determined from the loading data between polydimethylsiloxane (PDMS) and cellulose surfaces with different degrees of crystallinity, does not differ to any large extent.

(6) Under ambient conditions the extension of the adhesion hysteresis between PDMS and cellulose decreases with crystallinity. It is suggested that a surface with amorphous parts offers greater potential for surface groups to orient themselves in such a way that specific bonding occurs between the cellulose and PDMS surfaces.
(7) Humidity affects the adhesion force, and a larger adhesion hysteresis was obtained between PDMS and cellulose under higher RH conditions. This could be because the water acted as a plasticizing agent, contributing to formation of a stronger joint

Finally, it should also be emphasised that high-resolution techniques together with ordinary paper testing methods can be used to investigate interactions at different length scales – from molecular to network interactions. A combination of these techniques provides new important and interesting insight into the complex molecular mechanisms responsible for the fibre–fibre interactions in paper.
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