

THE WET ADHESION OF POLYVINYLAMINE TO CELLULOSE

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Abstract

A systematic investigation of Polyvinylamine (PVAm) as a strength-enhancing polymer for wet paper was undertaken through the development of a new test method that simulates the influence of polymers on fibre-fibre bonding in paper. Pairs of wet regenerated cellulose membranes were laminated using the paper strength-enhancing polymer as the lamination adhesive. The resulting laminates served as a physical model for fibre-fibre bonds in paper and the wet laminate strength was determined by ninety degree peeling experiments. Key experimental parameters and sources of error were identified. Since the wet cellulose delamination procedure was first developed in 2003 , delamination results have appeared in 16 publications and patent applications.

The mechanism of PVAm paper wet strength enhancement was explored by the wet cellulose delamination procedure. Initial results showed that PVAm was a poor wet adhesive for cellulose unless the cellulose was lightly oxidized. The adhesion was found to be a strong function of the concentration of amine and of the cellulose oxidation products. This led to the hypothesis that there are two mechanism in action; the first being the well-accepted electrostatic bonding theories and the second being covalent bond formation between acetal/hemi-acetals/aldehydes and the amine.

A thorough investigation of the surface chemistry and morphology was conducted to confirm the hypothesis of covalent bond formation between aldehydes and amines. Oxidized regenerated cellulose was laminated with PVAm and the peeled surfaces analyzed by X-ray Photoelectron Spectroscopy (XPS). It was shown that the wet delamination force correlated to the acetal/hemi-acetal/aldehyde surface concentration. It was concluded that the delamination force would be increased by a cumulative strengthening of both the cellulose surface and adhesive interface.

Finally, the main legacy of this work is a new, superior method for evaluating adhesives for wet cellulose as was a detailed understanding the factors influencing wet adhesion of PVAm to cellulose.

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Chapter 1 Literature Review

Paper products for writing and packaging are one of the hallmarks of modern society. We use paper to wrap our food, to protect sterile medical supplies, and until very recently, paper was the primary storage media of all knowledge. An important subset of paper products are those products that must function while wet. In some cases, such as common toilet paper, we want paper structures that fall apart when wet in order to facilitate transport to sewage treatment plants. On the other hand, coffee filters, cardboard boxes and many other paper products must maintain their mechanical integrity when wet. Therefore, “wet strength”, as it is known in the industry, is a very important characteristic. This thesis is focused on two major issues: 1) the development of a new laboratory method for evaluating wet strength resins, polymers designed to increase wet strength; and, 2) the first systematic evaluation of the potential for polyvinylamine (PVAm), a new polymer, to increase the wet strength of paper.

1.1 Fibre bonding in paper

Paper is made by the filtration of an aqueous suspension of cellulosic wood fibres (~ 20µm by 1000µm). With drying, capillary forces bring overlapping fibres into intimate contact and once dry, fibre-fibre bonds adhere strongly due to hydrogen bonding [1]. The mechanical properties of paper products depend upon both the strength of the component fibres and on the adhesion between individual fibres in the paper sheet.

An individual paper fibre can vary in physical and chemical composition but has certain common elements. All fibres contain cellulose which is an alternating, chiral polymer of β-D-glucose, which is arranged in both crystalline and amorphous regions. The amorphous regions are readily penetrated with water, while the crystalline regions are not. This gives the fibres the property of swelling in water but not dissolving. Chemically they are hydrophilic with some pockets of hydrophobic lignin and are weakly anionic [2].

On a larger scale wet fibres have been described as a rough, fibrillated surface covered in water soluble carbohydrates with extending chain ends [3]. During the removal of water the fibres are brought into close contact through surface tension forces until the fibre bonds are developed [4]. At this stage the

never dried paper sheet needs to possess enough strength to endure further processing, this property is called the 'wet-web' strength. On further drying the fibres shrink and fibrillated surfaces were observed to align with neighbouring fibres to facilitate bond formation [5]. When fully dried the paper sheet strength can be related to the strengths of the individual fibre and the fibre bonding, as described by Page [6]. The bond formation in paper sheets has been well summarized in many texts [1, 7].

When the newly formed paper is reintroduced to water it will lose almost all of its cohesion. There is little debate as to why wet paper is weak; the fibre-fibre joints swell in water causing them to weaken. More advanced studies have focused on the swelling of individual fibres and the corresponding slipping of interfibre bonding [8]. Molecular-scale theories describing fibre-fibre bonding, including hydrogen bonding [9], van der Waals forces or interdiffusion of surface polymers [10, 11], all predict that water will weaken fibre-fibre interactions.

1.2 Wet strength

In order to combat this deficiency paper wet strength can be increased by either treatment (modification) of fibres with small molecules or by surface treatment with macromolecules, typically called wet strength resins. The delineation between the two treatments can be simply be that an additive that can penetrate the fibre wall (molecules smaller than 1,000Da) can be considered a small molecule treatment, whereas, an additive that cannot penetrate the interior and only resides on the surface of the fibre can be considered a macromolecular treatment. While the molecular weight is a good guide in classification, it is worthwhile to consider the actual dimensions of the molecule in relation to the pore size distribution of the fibres. The average pore size of fibres when wet has been estimated to range between 80nm-100nm, which is larger than most polymers, however the distribution is skewed towards the lower end [12].

Alteration of the chemical nature of fibre surfaces can lead to improvements in the wet strength through different mechanisms. In the literature there is an agreement to the function of wet strength agents in paper, which have been summarized as acting by either a "protection" or "reinforcement" mechanism [13]. Both mechanisms have common characteristics, in that the wet strength agent are; water soluble, possess a cationic charge, and be reactive polymers (or polymerize *in situ*). Another distinction between mechanisms is in the type of bonding, namely with whether the wet strength agent

will react with itself (homo-crosslinking) or the cellulose (co-crosslinking). In the papermaking industry there has been a gradual movement from the polymers which homo-crosslink to those that co-crosslink.

1.3 Fibre Modification with Small Molecules

The improvement of paper wet strength by the addition of small molecules generally act by either producing reactive sites which can form hydrolytically stable covalent bonds or by modifying the chemical nature in a way that enhances further treatment. An example of the latter category is the increase in the electrostatic charge improving polyelectrolyte adsorption. In the former category the bonding can take place both within the fibre and between neighbouring fibres. If such bonds can form spontaneously without drying then they will contribute to the wet-web strength of paper.

1.3.1 Cross-linking

Glyoxal was first proposed as an effective wet strength chemical, which provides temporary wet strength [14]. Glyoxal will not adsorb significantly onto pulp fibres so it needs to be added after sheet formation. The reactions between the aldehyde and the cellulose hydroxyl can form unstable hemiacetals, yet at acidic conditions can proceed to the more stable acetal. Gluteraldehyde was more recently found to impart considerable wet strength gains with the use of a zinc nitrate catalyst [15]. The downside to these modifications is the eventual stiffening of the fibres in the dry state, leading to an loss of dry strength.

Another treatment method similar to dialdehydes are polyfunctional carboxylic acid containing species [16]. The authors used monobasic sodium phosphate along with high temperature curing (150°C) to produce cyclic anhydrides between adjacent carboxyl groups, which in turn reacted with cellulose hydroxyl groups to form ester bonds. Increasing the number of adjacent carboxylic acid groups also gave more potential anhydride formation and potential cross-links between cellulose chains. As with the dialdehydes this treatment resulted in an increase in sheet stiffness and brittleness of the paper sheet [17].

As mentioned, the use of cross-linking molecules is effective in developing wet strength because they act both to increase fibre-fibre bonding and to restrict the swelling of amorphous cellulose. A loss in plasticity of the fibres can result from cross-linking which leads to undesirable dry mechanical

properties. Therefore strategies using small molecule cross-linkers alone have not seen much use in industrial applications, though the potential of pairing them with a polymeric treatment appears promising [18].

1.3.2 Chemical modifiers

Often the development of a novel treatment for paper is limited by the chemical nature of the pulp fibre surfaces. The ability to engineer the fibre surface by physical or chemical adsorption of small molecules has given researchers the ability to develop a wide variety of final properties from a common pulp stock. Treatments that increase the hydrophobicity will reduce the swelling in the surface layers, although as the extent of hydrogen bonding is reduced, the dry strength will likewise be reduced. Similarly, the alteration of the native charge will influence the swelling and affect the behavior of the fibres towards further treatment.

There has been a significant amount of work exploring the modification of paper fibres by carboxymethylation of cellulose. Used alone this modification has been shown to increase swelling and inter-fibre bonding in the dry state [19] but had no improvement in the wet strength [20]. However, when poly(aminoamide)-epichlorohydrin (PAE) was added to the modified fibres the retention of the polymer was increased with a corresponding increase in the wet strength. Other anionic modifications, such as sulfonates, would likewise be expected to improve the retention of cationic polymers to the surface of cellulose [21].

Other charge modifications have been investigated. Inclusion of amino-acid based zwitterions on the fibre surface produced an increase in paper wet strength, dependent on heating [22]. It was observed that the ionic bonds between fibres gave wet strength increases, but reduced the dry strength.

A chemical modification that can reduce the swelling of the paper fibres would reduce the stress on the fibre-fibre bonding area and impart wet strength. Some examples of these modifications are the adsorption of aminosilanes onto fibres and reaction during drying [23] and the acetylation of phenolic lignin in unbleached pulps [24]. If the decrease in swelling is accompanied by a loss of hydrogen bonding sites, then analogous to the cross-linking system, the dry strength will be reduced.

Small molecule modification of the fibres can alone provide improvements in the development of wet strength yet if combined with polymer additives then more control could be had over the final properties. As mentioned the introduction of more anionic groups would facilitate the adsorption of more cationic polymer which can improve wet strength. The simplest way to increase anionic groups is through oxidation of cellulose hydroxyl groups to carboxylic acids.

1.3.3 Oxidation

The oxidation of pulp fibres occurs indirectly in chemical pulps during the bleaching step. The knowledge that oxidized pulp fibres produce papers with higher wet strength had been recognized long ago by Meller [25]. His conclusion that the aldehyde intermediate directly led to wet strength development was confirmed by others [26] [27]. As described, aldehydes are very reactive and will form hemiacetals and acetals during the drying phase with nearby hydroxyls.

More recently a new method was developed to selectively oxidize the primary hydroxyl groups to carboxyl ones using 2,2,6,6-tetramethyl-1-piperidinyloxy radical (TEMPO) and NaBr as catalysts [28]. Application of this reaction by Kitoka *et al.* to pulp fibres showed increases in the wet tensile index of untreated and polyamide-epichlorohydrin (PAE) treated paper [29]. The improvement of the wet strength with PAE was related to the carboxyl content, showing that the PAE was better retained at higher pulp carboxyl concentrations. Interestingly as the oxidation was progressed to higher levels the wet strength decreased which was probably due to the depolymerization of the cellulose and solubilization, rather than the increase in hydrophilicity as concluded. A follow up study by Saito and Isogai (after publication of the work in Chapters 3 and 4) led to the conclusion that aldehyde intermediates played a much more significant role in the wet strengthening of paper by TEMPO mediated oxidation [30]. The conclusion reached is that oxidized cellulose can enhance the efficiency of most cationic water-soluble polymers.

Thus, aldehydes are a key functionality in producing wet strength. Furthermore they can couple with alcohols to form hemiacetals or acetals, with other aldehydes to form aldols, or with amines to give imines or amins. These reactions can occur under papermaking conditions in water and do not require high temperature curing, but most likely require dehydration to give high concentrations. In comparison, the condensation reaction of carboxyls with alcohols to give esters, or amines to give

amides, require high (120°C-180°C) temperatures. There has been interest in developing technologies to effectively produce aldehydes at the surface of paper fibres [31] and discovering new methods of controlled oxidation [32].

1.4 Fibre Modification with Polymers

A wide variety of polymers have been shown to have efficacy as wet strength resins [13, 33, 34] and they share some general features in contrast to the small molecules used for fibre treatment. Size scale is an obvious difference between grafting individual functional groups versus macromolecules on fibre surfaces. A monolayer of water-soluble polymer on a surface will span 5 to 50nm in water whereas most functional groups, formed by oxidation or grafting of small molecules, are sub nanometre in size. Polymers can have many functional groups which, depending upon the polymer chemistry, can crosslink multiple polymer chains together to form a network. Therefore macromolecules are more likely to participate in and enhance inter-fibre bonding, which is crucial for paper strength in the wet state.

1.4.1 General Considerations

Wet strength polymers are usually reactive cationic polyelectrolytes which are added in the wet end where they spontaneously adsorb on fibre surfaces. These should be distinguished from wet strength resins which are oligomeric molecules that form polymeric networks *in situ*. If added alone, polymers will give a maximum fibre coverage corresponding to an adsorbed monolayer, which is approximately 1 mg per square meter of accessible surface [35]. When two polymer-coated fibres come together in the sheet consolidation process, a number of interactions are possible in the fibre-fibre joint. The polymer-fibre interactions may be physical (hydrogen bonding, van der Waals attraction) or chemical (covalent bonds formed through grafting). Similarly, the inter-polymer interactions, dictating the cohesive strength of a distinct polymer layer, can include physical and chemical bonds (covalent crosslinks).

The response of a wet strength polymer to water will depend upon the chemical properties of the polymer. In the extreme case, a hydrophobic polymer film such as polystyrene will not swell because it is insoluble in water. By contrast, a hydrophilic polymer such as polyacrylamide will dissolve in water, unless it is crosslinked, in which case it will only swell.

1.4.2 Formaldehyde based wet strength resins

The first additives for wet strength enhancement were condensation polymers of urea-formaldehyde resins and melamine-formaldehyde colloids [36]. Added to the pulp as oligomers to ensure water solubility, they undergo further polymerization and cross-linking reactions at acidic conditions during sheet formation with corresponding wet strength increase with the cure time. Being one of the first commercially successful additives, there have been many detailed studies in regards to the mechanism [37-39]. From these studies it has been concluded that no appreciable covalent bonding to fibre surfaces occur and that the primary mechanism is the formation of a heavily cross-linked network throughout the fibre surface. The advantage of these additives over the small molecule cross-linking is that the dry strength is not reduced, which is a result of the larger size resins being limited to the near-surface and pores. Taylor also expressed this idea while showing that increasing treatment with these resins resulted in fibre wall breakage, providing indirect evidence that the fibre walls were not involved in cross-linking [40].

1.4.3 Polymeric amine-epichlorohydrin

The current industrial benchmark is wet strength additives based on the alkylation of diamine containing condensation polymers with epichlorohydrin. This class of additives are very effective due to a cationic charge promoting adsorption and a cyclic ether bond which is very reactive. The cyclic ether, being an azetidinium ring or an epoxide depending on the amine, is very reactive and can form crosslinks or bond to fibre surfaces by mechanisms summarized in Espy's review [41]. Espy also makes the case that epichlorohydrin containing polymers will react much more strongly to carboxyl functionalities in the system, either on the PAE polymer, another additive polymer (CMC) or bleached or oxidized fibre surfaces. FTIR analysis of PAE resins added to carboxymethylated pulps has shown the existence of ester linkages [20]; however the relative importance of the bonding is not known and is likely to be secondary to the formation of a cross-linked network.

1.4.4 Aldehyde-Containing Polymers

As mentioned in Section 1.3.3, the oxidation of pulp fibres to give aldehyde products resulted in wet strength gains and similarly the use of oxidized starch has been shown to give the same improvement

[42, 43]. Other approaches to produce aldehyde containing wet strength additives are based upon the reaction of water soluble polymers with glyoxyl [36]. The use of carbohydrates as wet strength polymers has the advantage of being inexpensive and biodegradable while the synthetic polymers can be engineered to fit the final application. However, in terms of wet strength mechanism, both are understood to function similar to that of oxidized pulps, namely that:

1. Aldehyde polymers are always more effective when introduced to pulp at acidic pH inferring that acetals are formed along with hemiacetals;
2. The final wet strength is proportional to the concentration of aldehyde in the paper and less so on the number and size of the polymer chains;
3. High temperature drying will increase the final wet strength.

These ideas were confirmed in a study of aldehyde containing starch [44] and dextran [45]. Both hemiacetals and acetals would contribute to the final wet strength with an acid catalyst needed for the formation of acetals. In the absence of acid, rapid drying of the system will also promote the formation of acetals with the cellulose hydroxyls through dehydration.

One unresolved issue pertained to the ability of the aldehyde containing carbohydrate to provide wet-strength; which was not observed in the dextran study. Theoretically, covalent bonds can form in water, and although they will be readily hydrolyzed the multiplicity of attachments arising from the polymeric nature could provide stable adhesion. The difference between the two conclusions could be explained by the starch having cationic charge and thus being adsorbed on the pulp surface more readily, as opposed to the dextran which was uncharged and might not adsorb at high water concentrations.

In this sense, it is again important to note that adsorption of the wet strength macromolecule is critical to wet strength development. Oxidized carbohydrates being uncharged or weakly anionic has no additional driving force for adsorption to the surface of pulp fibres. This can be overcome by introducing a cationic group; for example by reacting the aldehydes with hydrazine [46] or more simply by introducing a cationic polymer to form a polymer complex [47]. Finally, as the aldehyde group can react with both hydroxyls and other aldehydes on neighbouring carbohydrate chains a suspension or solution of these additives are not stable and need to be stored in the acetal form. There is continuing

interest in applying more efficient methods of producing reactive aldehyde containing starch which would overcome the problems of depolymerization that occurs with harsh oxidizing reagents [48].

1.4.5 Biological Polymers

Apart from the use of starch and cellulose derivatives the investigations of biological macromolecules in paper strengthening has been increasing. The potential for creating wet strength agent that possess the specificity and selectivity of proteins is attracting new approaches to the old problem of paper wet strength. There has been a long interest in isolating and replicating the functionality of the cellulose binding domain (CBD) of cellulase and using it as an ideal adhesive for cellulose [49]. Kitaoka and Tanaka were the first to report the use of cellulose binding domain as a paper strength agent by attaching it to anionic polyacrylamide [50]. They observed an intermediate increase in the wet strength of handsheets made from bleached hardwood kraft pulp compared to PAE; and more importantly demonstrated that the CBD containing polyacrylamide provided wet strength virtually independent of the pulp conductivity. The current opinion of CBD action is that the adsorption is a mixture of hydrophobic, ionic and hydrogen bonding, all optimized in terms of cellulose structure [51].

More recently, the potential of a variety of common polypeptides and proteins as adhesives for wet cellulose has been explored using the method developed in this work. The first of these studies focused on polypeptides of lysine, with inclusions of tyrosine, tryptophan and phenylalanine [52]. Following this the wet adhesion of a wide series of proteins were measured with respect to drying temperature, pH and cellulose oxidation [53, 54]. Some general conclusions can be made from these studies, the first being that most proteins are effective as wet strength agents provided that the protein content in the interface is high and that the system undergoes high temperature drying. The second conclusion is that the amino acids lysine and arginine correlate well with the wet adhesion to cellulose, demonstrating that the primary amine provides the best opportunity for covalent bonding.

A parallel can be made to the amine containing carbohydrate chitosan. Laleg and Pikulik explored the mechanism of paper strength enhancement of mechanical pulps [55] and of bleached hardwood kraft pulps [56]. The authors explored the paper strength and physical properties as a function of water content, chitosan dosage, and pH. Additionally, it was shown that chitosan can introduce some wet-web strength. Below pH 5 both wet-web and wet strength were drastically reduced, this being

attributed the change in solubility of chitosan in water. These results were corroborated in a paper study using different sources of fibres (virgin and recycled) [57].

1.4.6 Polymeric amines

Polymers containing amine groups are well suited for use in paper manufacturing as they possess a cationic charge and, excluding tertiary amines, can form hydrogen bonds. The beneficial effect on wet strength seen with biological polymers containing amine groups is likewise seen with synthetic polymers of high amine content. However the mechanism by which these amine polymers increase wet strength is not well understood.

1.4.6.1 Poly(ethyleneimine)

Poly(ethyleneimine) (PEI), structurally analogous to polyethyleneoxide, when commercially prepared is highly branched and contains primary, secondary and tertiary amines. Early studies by Trout have shown that PEI will adsorb to pulp fibres driven by ion-exchange and that the wet strength was proportional to the amount adsorbed [58]. Continuing on this work, Sarkanen analyzed the effect of PEI on various paper properties and again showed that the wet strength development was proportional to the PEI retention [59]. Furthermore it was found that wet strength proportionality to total retention was not as important as when the adsorption was aided using anionic polyelectrolytes; indicating that PEI contact with the cellulose is important. Finally, Sarkanen also indicated that the irreversible adsorption of PEI was due to bond formation to the cellulose, and speculated that these might be due to the strength of the ionic exchange.

Challenging this viewpoint, Allan proposed that at the isoelectric point, PEI would enter into small pores on the pulp surface and would subsequently be difficult to remove at any pH below this due to electrostatic repulsion increasing the hydrodynamic volume [60]. This seems to address the seemingly irreversibility of the PEI adsorption, discounting the idea that high affinity ionic bonds are the cause, although it ignores the typical irreversibility of polymer adsorption and alone gives no insight into the wet strength behaviour. Discounting the importance of entrapment, Strazdins showed that PEI adsorption to microcrystalline cellulose showed similar adsorption/desorption behaviour and concluded that the whole process is controlled by the electrostatic interaction between the cellulose and PEI [61].

Putting all the adsorption and retention considerations aside, there is still some indication that strong bonding happens between PEI and the pulp cellulose surface. Espy notes that ionic bonding is not important since polymers with quaternary amines do not provide wet strength [62]. Condensation of primary amines and carboxyl groups to form amide links is a possibility, but this reaction requires high temperatures and there has been no confirmation of significant amide formation in paper sheets. Studies into the nature of PEI and chitosan promoted discoloration of paper have proposed and provided evidence of imine formation [63-65].

1.4.6.2 Polyvinylamine

Poly(vinylamine) (PVAm) differs from PEI in that it has a linear hydrocarbon backbone containing only primary amines. Applications of this polymer to papermaking have followed from a recent discovery of a commercial pathway involving the monomer N-vinylformamide. Hydrolysis of poly(N-vinylformamide) (PNVF) produces primary amino groups and formic acid or sodium formate, depending on whether the reaction is acid or base catalyzed. Application of PVAm to improving wet strength was reported by Wang and Tanaka, which showed an increase in both dry and wet tensile strength of paper proportional to the addition of 87:11 PNVF:PVAm co-polymer [66]. While this result was secondary to the main purpose of the work, which was to determine PVAm effectiveness as a sizing agent, there have been few studies that followed up on the wet strengthening property of PVAm. Pelton and Hong investigated the properties of newsprint impregnated with PVAm/PNVF and found that wet strength achieved almost 30% that of the dry strength [67]. Some key results from this work were that the wet strength was reversible, the degree of hydrolysis (reported as % amine groups) did not greatly influence the wet strength between 56% and 100% and that at higher pH values the wet strength increased.

1.4.7 Polyelectrolyte Complexes/Multilayers

Combinations of oppositely charged polyelectrolytes have been found to improve the wet strength of paper, for example the wet strengthening effects of adding PVAm and PAE to paper pre-treated with poly(alkyl succinate) [68]. Investigations into developing multilayers of opposite charged polyelectrolytes at the fibre surface were conducted with the expectation that the cohesive strength of the multilayer will provide improved adhesion. This was observed for multilayers of PAE and carboxymethylcellulose (CMC) through paper testing dry state [69]. This can be considered an extension of an earlier study

using CMC treated fibres with subsequent adsorption of PAE [70]. More recently a CMC and PVAm system was tested using the model system to be described in subsequent chapters [71].

1.4.8 Summary

Wet strength development using polymers requires bonds to persist in the presence of water. Covalent bonds, for example, acetal and imine bonds, will hydrolyze giving temporary wet strength. The integrity of physical bonds in the presence of water is more complicated. Hydrogen bonds between alcohols are weaker than those between an alcohol and water. Thus, water disrupts untreated fibre joints based on hydrogen bonding between carbohydrates. Electrostatic attraction of a charged polymer with an oppositely charged surface is another form of physical bond. These bonds do persist in the presence of water, otherwise cationic polymer would not adsorb onto pulp. On the other hand, as pointed out by Espy [62], poly(dimethyldiallyl ammonium chloride), (PDADMAC), a common papermaking chemical has quaternary ammonium groups which adhere to wet pulp but impart no wet strength improvement. Based on this observation, Espy argues that electrostatic bonds alone are insufficient to give wet strength improvement. It should also be noted that PDADMAC will not crosslink, so the cohesive strength of a PDADMAC film will be very low, giving low wet strength, in spite of strong adhesion to fibre surfaces.

While the end result of polymer addition is easily measured by paper testing, the specific mechanism is not, owing to the complexity of its action. There are many different mechanisms that have been put forth to explain the strength enhancement of different polymers, all supported by some combination of paper or model experimentation.

1.5 Non-paper testing of wet-strength

In order to accurately measure the wet adhesive forces between polyvinylamine and cellulose a more specific measurement should be utilized. Traditionally, testing of a wet strength agent required the laboratory preparation of paper and subsequent determination of the change in the mechanical properties, typically a wet tensile measurement. There are inherent difficulties with this approach which are often difficult to resolve such as; the attribution of strength increase to the fiber bond or the fiber itself, [40] the quantity and location of adsorbed polymer, and the analysis of chemical bond

formation with chemically heterogeneous pulp fibers. To bypass these often difficult problems a distinct simplification of the system is required. Pelton has long ago described the need to accurately represent the pulp fibre surface using a molecular gel [3].

Determination of adhesion to paper and cellulose has been performed in the past for a wide variety of polymeric materials, typically to determine the permanence of inks, and can provide a wide variety of information. For example, McLaren's early work with regenerated cellulose sheets highlighted the importance of polymer polarity to achieve good adhesion[72]. Other investigations into the fundamental adhesion to crystalline films of cellulose can provide valuable information but tend to be more of academic interest [73]. Excluding these idealized cases, most surface adhesion measurements are performed in a relatively dry state. The closest experiment that measures wet adhesion was a study of the adhesive properties of hydrocolloid wet glues on cellulose acetate and a skin-surface model [74].

1.6 Objectives of This Work

The objectives of this research work were the following:

1. Develop a method that would measure the adhesion of cellulose materials in the wet state. The intrinsically complex nature of paper does not readily allow for the rapid and detailed study of adhesion to wet cellulose. Through the development of a model system to represent inter-fibre bonding, mechanistic studies of the role of polyvinylamine could be made. The robustness of the model test method was validated and applied to many different systems.
2. Identify the mechanism of wet strength development of polyvinylamine. Using the aforementioned model system the mechanism by which polyvinylamine produces wet strength was explored. Starting from the existing hypothesis on amine containing polymer wet strength, the model system was put through controlled conditions to reach novel conclusions.
3. Determine the role of oxidation in enhancing the wet strength of amine containing polymers. Based on the observations that oxidized pulp and cellulose generated higher wet strengths using polyvinylamine, a thorough study of the physical and chemical nature of the interactions was made to identify the nature of the adhesive bonding and limitations on strength gains.
4. Prepare chemically modified surfaces of cellulose and relate to wet adhesion.

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Chapter 2: Wet Cellulose Delamination Methodology

2.1 Introduction

The testing of a polymer as a paper wet-strengthening agent is a cumbersome practice. Preparation of paper and subsequent determination of the change in the mechanical properties requires either the use of a paper machine or laboratory handsheet equipment. The former method is costly and the latter laborious and both require a large quantity of material. Also, there are inherent difficulties with any attempts to understand mechanisms with this direct approach, since additives can affect the many processes that occur during papermaking. The two major scientific challenges with conventional paper testing are the identification of the locus of failure [1] and changes in the fibre network structure (i.e. paper “formation”) induced by the strength enhancing polymer addition to the pulp suspension. The polymers can cause fibre flocs to form which gives less uniform and thus weaker paper. Therefore, while fibre/fibre adhesion might be improved, the mechanical properties of paper can be degraded. In summary, it is difficult to obtain fundamental information about the influence of polymers on fibre/fibre adhesion with conventional paper testing approaches. The goal of this work was to develop a test method for comparing the ability of polymers to improve the adhesion between wet fibre surfaces.

As pulp fibres are primarily composed of cellulose, any effect of a strength enhancing polymer will depend on the interactions of that polymer and cellulose. Investigations into the fundamental adhesion to crystalline films of cellulose can provide valuable information but tend to be more of academic interest and are not easily applied to paper [2]. Some workers have used individual pulp fibres in mechanical testing with mixed results [3]. The experimental approach taken here is based on a combination of both McLaren’s early work with adhesion of polymers to regenerated cellulose sheets [4] and a study of the adhesive properties of hydrocolloid wet glues on cellulose acetate [5].

Laminates were made using regenerated cellulose membrane films adhered using a polymer of interest. The resulting laminate was then pressed and dried. For adhesion testing, the dried laminate is immersed in water and separated in a ninety degree peeling geometry while wet, thereby yielding a force which is representative of the adhesive strength of the polymer. Although such peel delamination approaches are widely used in other industries, [6] they have been rarely employed in paper technology. The new wet adhesion method described in this chapter has subsequently been used by a number of

researchers in Pelton's research group and is briefly summarized in the "Impact of This Work" section of the final chapter.

2.2 Experimental

2.2.1 Polymers

Polyethyleneimine (PEI, Polymin SK) and poly-N-vinylformamide (950 kDa) were supplied by BASF AG. Polyvinylamine was prepared by hydrolyzing the poly-N-vinylformamide (12wt%) with NaOH (5wt%) at 70°C for 3 days [7]. Boronic-acid modified polyvinylamine (B-PVAm) was prepared according to the method found in Chen *et al.* [8]. Polyamide-epichlorohydrin (PAE) resin was supplied by Hercules as Kymene 557H in a 12.5wt% solution. Poly(DADMAC) (400-500kDa) and carboxymethylcellulose (CMC) (250kDa, 0.9DS) were purchased from Sigma-Aldrich and cationic polyacrylamide (CPAM) was purchased from Allied Colloids (PERCOL 175). All polymers were made to 0.5g/L concentration in a 1mM NaCl solution and the pH was adjusted to 7 using dilute HCl or NaOH.

2.2.2 Cellulose Preparation and Modification

Regenerated cellulose membranes were purchased as dialysis membranes from Spectrum Laboratories Inc. (Spectra/Por[®] 4 product No:132709 12kDa MWCO). The membranes were cut into rectangular strips along the roll direction with the inside surfaces being used for adhesive contact. The dimensions of all laminates used unless otherwise specified are shown in Figure 1. The cut membranes were cleaned by Soxhlet extraction using water for 24hrs followed by acetone for 24hrs and then air dried at ambient conditions and weighed.

Cellulose films were oxidized with NaClO (11-14%) using 2,2,6,6-tetramethyl-1-piperidinyloxy radical (TEMPO) and NaBr as catalysts [9] following Kitaoka's method for pulp [10]. The concentration of TEMPO and NaBr was fixed at 0.034g/L and 0.34g/L respectively and the concentration of sodium hypochlorite was 3wt% based on dry cellulose. All reactions took place at 23°C under mild stirring (magnetic stirring bar) in a 1L glass beaker treating up to 7g cellulose. The pH was maintained at 10.5 by sodium hydroxide and the oxidation was stopped by adding ethanol to the suspension. The cellulose was removed and rinsed first in ethanol and then repeatedly with deionized water.

2.2.3 Laminate Formation

Adhesive specimens were made by bringing two wet cellulose membranes together with a thin layer of polymer between them and a strip of poly(tetrafluoroethylene) (PTFE) tape (G.F. Thompson Co. Ltd, TWB480P) to act as a release point. Two methods were used to apply a polymer adhesive to the cellulose films, henceforth referred to as **direct application** and **adsorption application**. For the adsorption application method, the top cellulose film was covered in 0.6mL of a solution of 0.5g/L polymer dissolved in 1mM NaCl with the pH adjusted to the desired value. After soaking for 30min the films were rinsed gently for 5min in pH adjusted 1mM NaCl solution. We assume that by rinsing off excess polymer that the resulting cellulose films were coated with a saturated monolayer of adsorbed polymer [11]. The laminates were constructed by first placing the wet bottom membrane on a blotting paper. The PTFE tape was placed across one end of the bottom membrane. In the next step the top membrane was placed on the bottom membrane, followed by blotting paper.

In the direct application method, the bottom cellulose membrane was placed on a stainless steel plate and excess surface water removed by dabbing with a lint free tissue. The PTFE tape strip was placed at the edge of the bottom membrane and a small drop (10 μ L for 15mm wide laminates and 15 μ L for 20mm wide laminates) of polymer solution was applied using a 20 μ L micropipette (Gilson) onto the base membrane near the PTFE tape. The top membrane was progressively placed over the bottom membrane starting at the end with the PTFE tape. If done carefully, the micro-volume polymer solution droplet spread between the top and bottom membrane with negligible loss of polymer solution.

The laminated structure was then pressed between blotting paper under a constant load (9060 kg unless otherwise specified) using a Carver Press (*model 3892*) for 30min and dried under no load for at least 12hrs at 23°C and 50%RH. Prior to testing the laminates were soaked in a dilute salt (1mM NaCl, pH 7) solution for 30min and then blotted free of excess water. The laminates were then fixed to a free moving aluminium wheel running on rubber sealed radial bearings (SKF 608-2RS1) by means of moisture-resistant two-sided tape (3M Polyethylene Medical Double Coated Tape 1522). This set-up is illustrated in Figure 2, along with a close up of the delamination geometry in Figure 3. All testing was done using an Instron 4411 universal testing system (Instron Corporation, Canton, MA) fitted with a 50N load cell (Model 2530-437).

2.2.4 Paper Testing

Handsheets were made and tested according to TAPPI standards T 205 and T 494 respectively using unbeaten softwood bleached kraft pulp. The pulp was oxidized with NaClO (11-14%) using 2,2,6,6-tetramethyl-1-piperidinyloxy radical (TEMPO) and NaBr as catalysts [9] following Kitaoka's method for pulp [10]. PVAm was added to the pulp slurry of 12 g/L consistency at a concentration of 0.5 wt% (polymer/dry pulp) and then the slurry was diluted to a final consistency of 3 g/L. The pH of the papermaking slurry was near neutral in all cases.

2.2.5 Interfacial PVAm Content

Polyvinylamine (PVAm8) was conjugated with 4-hydroxybenzoic acid using 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide (EDC) as a zero-length cross-linker to a final substitution of approximately 15% and is henceforth termed PVAm-Ph [8]. This polymer was then labelled with a radioactive iodine isotope (I^{125}) (ICN Pharmaceuticals Inc, Radiochemical Division, Irvine, CA, USA) using the iodogen technique [12] at a 5% label concentration. The labelled PVAm-Ph was separated from any excess unattached iodine by exhaustive cartridge dialysis against deionized water. The PVAm-Ph was then diluted to the desired concentration using 1mM NaCl solution. For each experiment, a calibration curve of the polymer content against the radioactivity was made. Laminates were prepared using the direct application method and after drying, 0.65cm diameter circle punches were taken along the length and measured for radioactivity.

2.3 Results

2.3.1 Reproducibility

The wet delamination force is meant to represent the strength of adhesion (or resistance to separation) between cellulose sheets bound with polymer. As this method is meant to be a tool to measure the effectiveness of polymers as wet adhesives, it is desirable to summarize the complete delamination event into one value. The raw data from a peeling event is represented by the load or force. Plots of these data for a series of delamination tests all performed at the same conditions are given in Figure 4 labelled I to IV. Taken as the load normalized by the unit width of the laminate, the individual traces show the forces required to initiate failure and propagate the separation until termination of the test.

The trace can thus be separated into two distinct regions; the initial propagation and the steady-state delamination. As the transition between these regions will vary slightly for each specimen, for example due to the slack in mounting, an arbitrary displacement of 10mm was chosen as the transition point with this value being well past the delamination initiation effects. The average of all values of the force past 10mm was then taken as being the delamination force for that specimen. The mean, the standard deviation of the mean and the coefficient of variance for each specimen trace is shown below the individual traces in Figure 4. For all traces the coefficient of variance is less than 10% of the mean.

The mean of individual values of the delamination force at identical displacement values were taken and plotted as an average delamination force trace. The same procedure was done with the standard deviation. Along with the original traces, these average and standard deviation traces are shown in bold in Figure 5. Therefore the overall mean and variance between each trace can be represented in two ways; firstly as the bold curves shown in Figure 5 and secondly as the mean of the trace means and the standard deviation of this mean. For the traces shown in Figure 4, the overall mean is 28.8N/m with a standard deviation of 2.14N/m, while the mean of the average curve is 28.8N/m and the mean of the standard deviation curve is 2.39N. All further results herein which give the average delamination force will use the former method of calculating the mean with the error bars representing the standard error.

During the drying of the laminates a constant load was applied in order to remove air pockets and increase interfacial contact. The load was varied from 1000 kg to 9060 kg (the upper limit of the press) and the delamination force of PVAm bound laminates measured, as seen in Figure 8. The delamination force is constant at 26.5 N/m up to 4500 kg after which the delamination force increases to 35.5N/m at a 9060kg load.

As mentioned the average force required to separate the laminates at a constant rate is divided by the laminate width. Figure 7 gives the non-normalized delamination force of oxidized cellulose and PVAm laminates versus the width of the top laminate. For the range of 10mm to 30mm the relationship between force and width is linear, giving a slope of 35.5N/m, which is equivalent to the normalized peel force for these conditions.

2.3.2 Peeling Rate

The influence of the peeling rate on the average delamination force was measured using oxidized cellulose with two forms of polymer application; the first being PVAm deposited at 7.5mg/m^2 and the second being PVAm adsorbed onto the top laminate, to give an approximate concentration of 1.2mg/m^2 . The results of this experiment are shown in Figure 9. For the high interfacial concentration the average peel force increases from 33 N/m at 5 mm/min to 45 N/m at 500 mm/min. The laminates prepared with a low interfacial polymer concentration shows no discernable pattern over the peeling rate range and is constant at approximately 20 N/m.

2.3.3 Water Content

Laminates made with oxidized cellulose and adsorbed PVAm are approximately 46% water by mass immediately after blotting. The laminates lose approximately 1% water by evaporation for every minute of exposure to air at 23°C and 50% relative humidity. Figure 10 gives the average peel force as a function of the water mass fraction, which was changed by varying the evaporation time between blotting and mounting onto the peeling wheel. There are no error bars as each point represents only one measurement. Given the peel rate, 20 mm/min, and the maximum peeling length, 50mm, then the time needed to conduct one measurement is 2.5 minutes. The mounting time for the laminate was at most 30 seconds so there was an approximate delay of 3 minutes from the blotting to the end of the test. The average peeling force for these conditions with no additional evaporation time is 35.5 N/m. After 10 minutes of additional evaporation time, corresponding to an average water mass fraction of 0.345, the delamination forces reached stable values around 66 N/m. Between 0.43 and 0.40 moisture contents, the peel forces vary from 38 N/m to 56N/m indicating that the water content might not be uniformly distributed.

2.3.4 Comparing Delamination to Conventional Paper Testing

A comparison of the wet delamination force was made to conventional wet paper tensile testing with adsorbed PVAm being used as the wet strength agent for both tests. The pH of the soaking water was adjusted from 2 to 12 in order to produce a change in wet strength. The resultant wet tensile was plotted against the wet peel force for the same pH conditions, separated according to the cellulose/pulp

treatment and is plotted in Figure 11. For the untreated pulp and cellulose there is a non-linear correlation between the two testing methods with the delamination force being more sensitive to the environmental changes. The relationship changes for the oxidized systems, for example an increase in tensile index from 2.7 to 4.7 Nm/g corresponded to a wet peeling force increase from 29 to 42 N/m. Not all of the pH effects were identical between the two tests for the oxidized substrates, specifically at pH 12 where the wet paper maintained its strength at 3.6Nm/g while the wet cellulose laminates were reduced from 46 to 15N/m.

2.3.5 Comparing Wet Strength Polymers

The ninety degree wet delamination test was used to test a series of water-soluble polymers. All polymers were used at identical conditions to give an interfacial concentration of approximately 10mg/m². The results are given in Table 1 for both untreated regenerated cellulose and oxidized regenerated cellulose. For the untreated cellulose both poly(DADMAC) and CMC gave no measurable strength as laminates fell apart spontaneously when wetted. B-PVAm gave the highest peel force for untreated cellulose at 5.02 N/m. Cationic PAM, PVAm and PEI gave similar strengths at same addition levels for untreated cellulose and agrees with previous ranking as wet strength agents [13]. The oxidation of the cellulose resulted in the increase of the peel force of all polymers tested. Kymene gained the most from the oxidation increasing from an initial value of 0.73N/m to 31.60 N/m.

2.4 Discussion

The wet cellulose delamination test demonstrated in this work is an attempt to simulate the forces needed to separate individual paper fibres adhered with polymer in the wet state and therefore a representation of the overall paper wet strength. The use of this model system allows for more control in experimental parameters and serves as an attempt to isolate the interaction of polymer and substrate rather than measuring the total effect of adding polymer to the papermaking process. Comparison of the delamination force to the wet tensile index in Figure 11 shows that there is a non-linear correlation between the two methods that changes when the cellulose or pulp is oxidized.

The differences can be explained by considering the different nature of the two substrate materials. The regenerated cellulose is relatively pure compared to the pulp fibres which contain hemicelluloses, some

trace phenolics (lignin) and low molecular weight wood extractives [14]. The physical differences are also important; where the paper fibres have a fibrillated surface with large pores, the regenerated cellulose is smooth and has no pores exceeding several nanometers. Hence the interaction with polymers will not be identical between these two materials, yet the chemical similarities compensate for this, for example both show the enhancing effect of oxidation. It should be noted that there is no null value for the delamination test; without polymer the cellulose laminates fall apart under handling stress.

The advantage of the wet cellulose delamination method is that the results are readily compared between different conditions without concern of changing material properties. In future chapters the regenerated cellulose membranes were chemically treated to modify the surface chemistry. In order to make reasonable comparisons the variation between specimens needs to be kept to a minimum by controlling some key experimental parameters.

The surface chemistry of the cellulose before lamination will strongly affect the adhesion, and so good control is necessary. Impurities on the regenerated cellulose membranes (glycerine, sulphides and heavy metals) are effectively removed using water and acetone although some hydrophobic contaminants remain in the near surface [15]. Surface contaminants of this type are always present and provided they remain constant it is unlikely they will increase variability.

Therefore care needs to be taken during cellulose preparation so not to contaminate or damage the adhering surfaces; in the latter case any gross abrasions or scratches of the contacting surface will reduce contact area and could provide a site for failure propagation through the cellulose. The cellulose width should be as accurate as possible, since the relationship between width and the delamination force is linear. For example a 1mm variation in width for a target width of 20mm translates to an error of 5% in the delamination force; thus larger widths would reduce this error. Also related to testing geometry is the need to mount the specimen properly, as any mounts not parallel to the wheel direction will result in an apparent change in width and affect the result in a similar manner.

Using the method of direct polymer application results in losses of approximately one third (15 μ L on 20mm wide) or one half (10 μ L on 15mm wide) of the total polymer. Furthermore this polymer loss is not uniform throughout the laminate length but according to Figure 6 decreases opposite the direction of spreading giving a polymer concentration gradient. This can be significant depending on the system;

for oxidized cellulose adhered with polyvinylamine the effect of polymer gradient along the laminate is not significant but for unoxidized cellulose it is very significant. The variation of delamination force along the length of different specimens has been observed (see Figure 4 I. and IV.) and could be attributed to the polymer gradient in laminate. If the polymer concentration gradient affects the delamination force by a linear relationship then the average delamination force will represent the same energy as one of an evenly distributed polymer of the same average value, however this assumption would need to be tested for each polymer. It should be noted that delamination traces that displayed large gradients (slope greater than 1% of the average value) or step gradients were removed from inclusion in the average delamination force. Application of polymer by adsorption removes the gradient but requires the measurement of surface concentration in order to compare pure adhesive effects.

The most important factor in the variability of the delamination force is the water content of the laminate during testing. The influence of water will be strongest for those systems that depend upon the cohesive strength of water soluble polymer and those polymers that react through the formation of condensation type covalent bonds and as such will be reversed by hydrolysis. Furthermore, as the amorphous regions in the cellulose swell, the strength will decrease[16] and present a lower resistance to fracture. For the system with oxidized cellulose and PVAm (Figure 10) it is clear that strict control of the water content prior to and during testing is necessary for consistent data. Even a small decrease in the water mass fraction from 0.46 to 0.41 will result in an astonishing range of 10-60% change in the delamination force. It could be useful to measure the delamination force at different water contents in order to identify differences in the relationship (slope) and interpolate to a constant value.

Low values of delamination force, particularly using untreated cellulose and ineffective wet-strengthening polymers, require attention when attempting to compare results. In Table 1 the lowest value of the delamination force is 2.13N/m which corresponds to an average load of 32mN. In the set-up used the accuracy of the load cell is 0.025% of the rated output of 50N, so each measurement is $\pm 12.5\text{mN}$ or for a 15mm wide specimen, $\pm 0.83\text{N/m}$. Higher values of the delamination force are equal to total loads of 0.5N. The delamination at low forces also affects the geometry of the peeling arm, in that the actual angle of peeling, θ_o , is reduced. For these experiments the delamination force is compared without correction for angle. While it is known that the true angle is less than 90° close to the crack front (Figure 3), it is assumed to be constant, and hence any changes when measuring weak

laminates will lead to error. Therefore when the angle near the front changes appreciably, the delamination force alone no longer provides a good representation of the laminate adhesion and a more complex analysis is needed such as that provided by Kinloch et al. [6]. Similarly care must be made in attempting to compare results using peeling arms of different thickness or different bending stiffness since enough energy needs to be provided to bend the peeling arm which serves to preserve the angle of peeling to a near-constant level.

In all measurements of adhered material strength it is important to identify the locus of failure. Visual evidence of the failure mode is not easily measured due to the thin layer of polymer used and the translucence of the backing. The locus of failure will depend upon the system conditions, and as such no generalizations can be made, though it should be pointed out that there are three possible independent failure loci; adhesive failure between polymer and cellulose and cohesive failure both within the polymer and the cellulose. Consider the case of polyvinylamine bound cellulose laminates. It can be inferred from Figure 9 that there is some viscous process occurring within the failure zone, and since this effect is not seen with the thinnest possible polymer layer (adsorption limited), it can be concluded that it is not due to plastic deformation of the cellulose itself or any other rate effect. Thus the polyvinylamine is deforming which has faintly been observed as fibrillation near the peel front.

Results from previous studies using fluorescently labelled polyvinylamine have shown that there is a dominant cohesive mode of failure with linear polymer and adhesive failure with polymer hydrogels; both at a coverage of $15\text{mg}/\text{m}^2$ [17]. Clearly the linear polymer is able to deform and fails within the fibrillating elements, while the hydrogel, possessing a much higher elastic modulus does not rupture at all and detaches from the cellulose surface. The strength of the individual strings will be a function of the polymer concentration and water content. The future chapters will address the role of oxidation in the enhancement of wet delamination forces.

The behaviour of the polymer strings will determine the mode of failure and hence the ultimate delamination force of thick-layer polymer laminates. The polymer strings are composed of many polymer chains which are limited in motion by attachments to other polymer chains or the interphase region (amorphous cellulose). If the cellulose-polymer bond is strong then the polymer will deform to its cohesive maximum therefore absorbing more energy and increasing the overall delamination force. Alternately if the cellulose-polymer bond is weak then the polymer will detach from the cellulose before

maximum extension is reached and less energy is consumed. There is also the possibility of chain scission of the polymer, yet this is unlikely unless the chains are covalently cross-linked. Additionally the quantity and strength of the binding sites on the cellulose could affect the number, size and formation probability of individual fibrils. Given these possibilities then the interphase strength of the polymer and the cellulose will influence the string properties and regardless of failure mechanism we would still be able to relate the delamination force to the interphase properties. Again it should be noted that the cellulose material itself may fail thereby leading to a measure of the surface strength and ultimately leading to an upper strength limit of the test. This idea that the cellulose strength itself is limiting has also been observed in wet paper testing long ago [1] In the case of adsorbed polymers the system is simplified, since polymer stringing is not expected, the measured delamination force will be simply a property of the polymer-cellulose interaction or the cellulose cohesive strength.

2.5 Conclusions

1. The wet delamination of cellulose membranes is a useful method for distinguishing the effectiveness of polymers to produce wet strength papers.
2. The delamination force is inversely proportional to the water content of the laminate. Therefore strict control of the water content is necessary to obtain good data.
3. The delamination force is insensitive to the choice of experimental conditions such as the width and pressing load up to 6000kg, after that the final wet peeling force increases slightly with the load.
4. Very thin polymer layers are independent of peel rate over the range of 5-500mm/min whereas thicker layers give rate dependence typical of viscous losses.
5. Comparison of wet peeling force to the wet tensile strength of handsheets at the same conditions show a changing power law correlation where the peel force increases at a greater rate than the tensile.

2.6 Tables

Table 1 Average delamination peel force of cellulose laminates made with different water soluble polymers. The interfacial concentration is fixed at approximately 10.5mg/m² for all polymers by adding 15µL of 0.5g/L solution to the interface. All solutions were made in 1mM NaCl and adjusted to pH 7.

Polymer	Details	Average Delamination Force, N/m			
		Untreated Cellulose	Std Error	Oxidized Cellulose	Std Error
poly(DADMAC)	400-500kDa	0.00	-	5.05	0.97
CMC	250kDa, DS 0.9	0.00	-	6.09	1.30
PAE	557H	2.13	0.24	31.60	1.80
PEI	Polymin SK	2.13	0.24	17.79	0.70
c-PAM	Percol 175	2.36	0.40	7.78	0.99
PVAm	950kDa	2.91	0.42	41.51	2.70
B-PVAm	150kDa	5.02	1.28	36.37	4.12

2.7 Figures

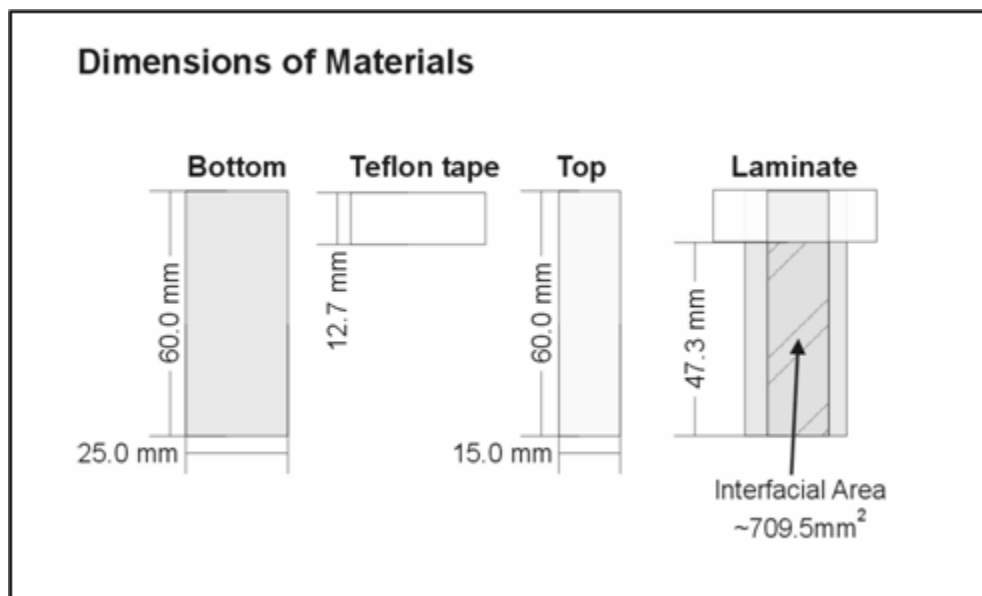


Figure 1. Dimensions of the cellulose materials used to create the laminates. The default width of the top laminate is 15.0mm and this gives an interfacial area of approximately 709.5mm².

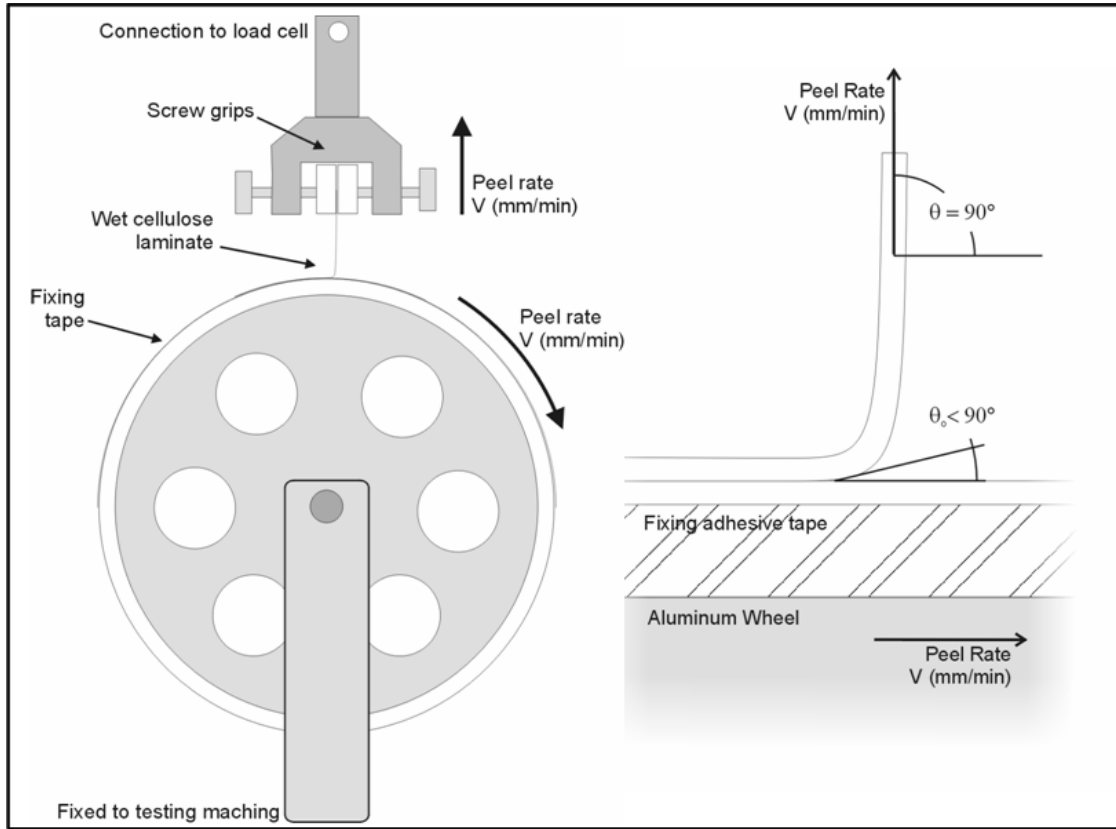


Figure 2. The peeling wheel used in all experiments along with a close up of the delamination area. The default peel rate (V) was 20mm/min and the peel angle (θ) was 90° . The actual angle at the crack front is given by θ_0 and is less than θ . Drawing is not to scale.

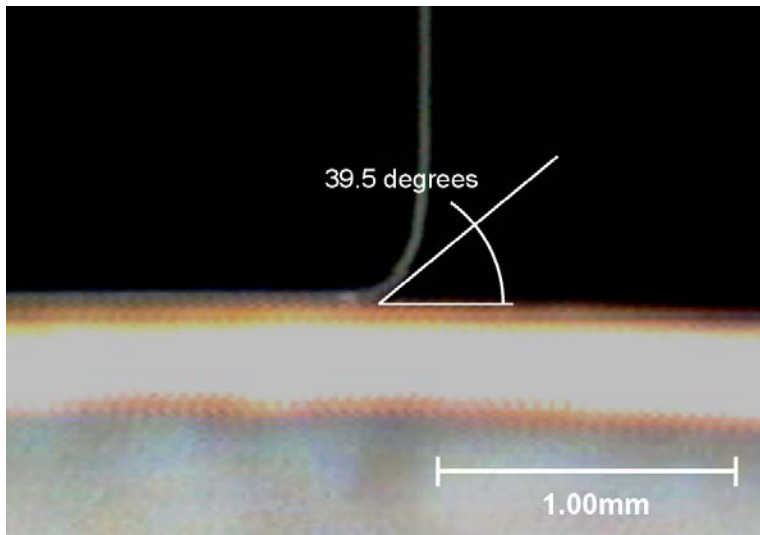


Figure 3. Captured image of delamination event at peel front.

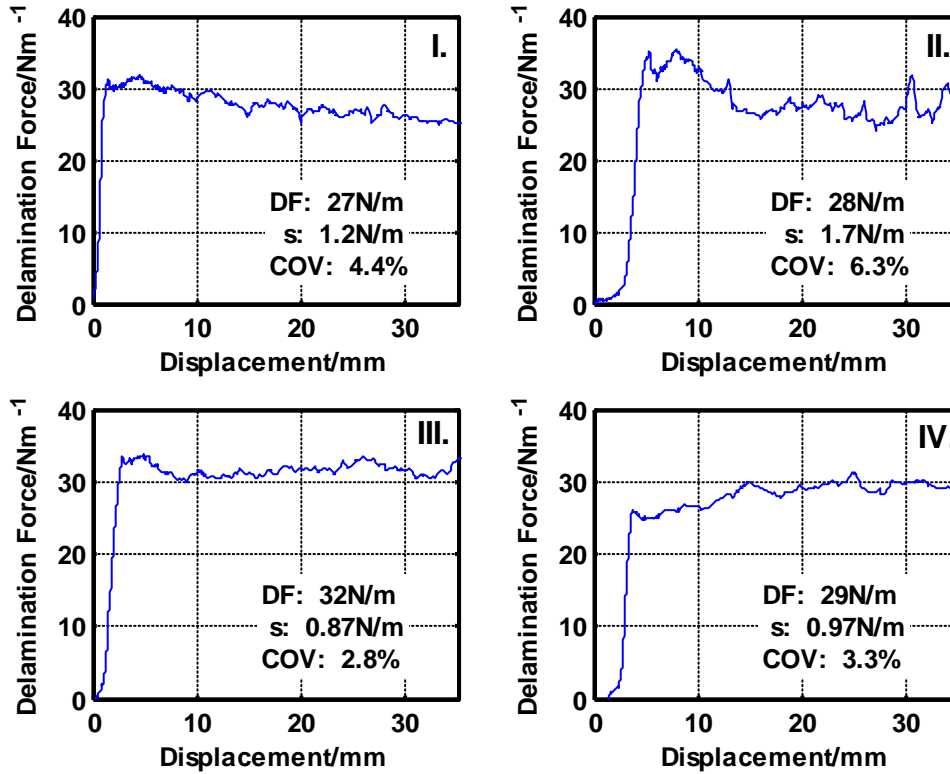


Figure 4. Force versus displacement of the delamination of four identical specimens (corresponding to 15mm width of Figure 7). The inserts give the average (DF), standard deviation (s) and coefficient of variance (COV) for the values of force past 10mm displacement.

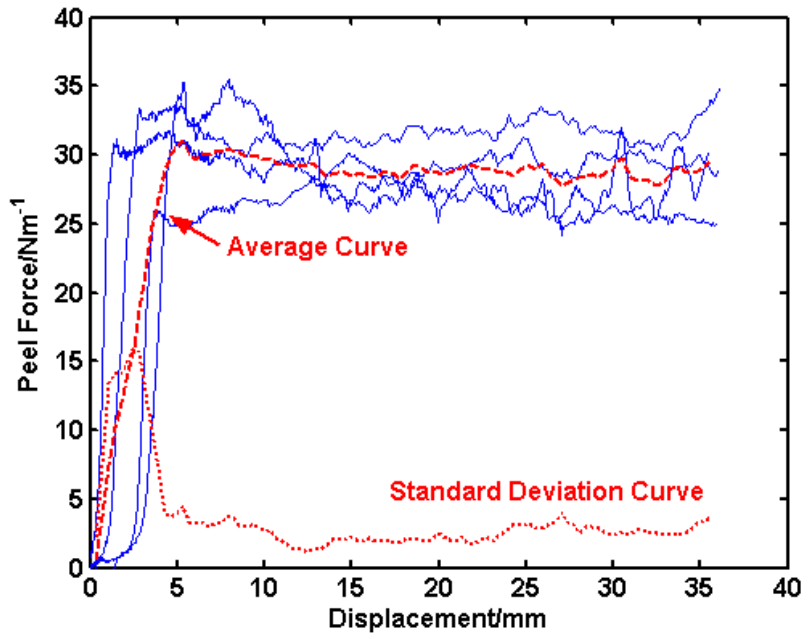


Figure 5. Collection of all specimens shown in Figure 4 on the same axes along with the average (dashed) and standard deviation (dotted) curves.

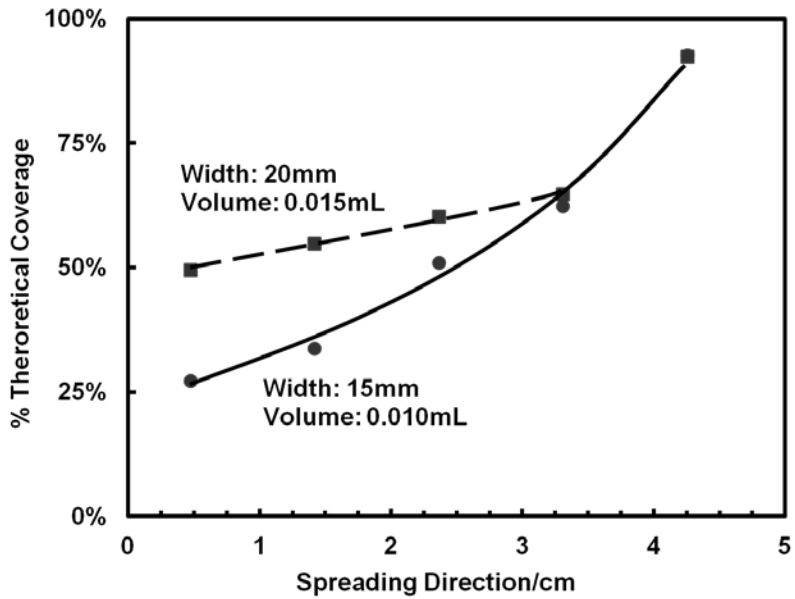


Figure 6. PVAm-Ph interfacial concentration (as % theoretical coverage) along the laminate spreading direction after pressing and drying. The concentrations were measured from 0.65cm diameter punches at intervals of 0.5cm.

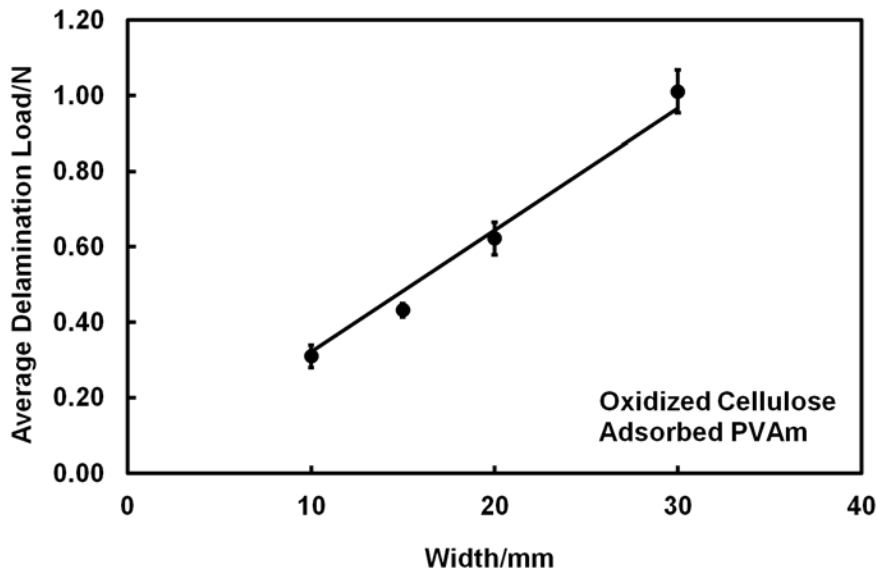


Figure 7. The average delamination load (N) of oxidized cellulose-PVAm laminates for different top layer widths. The slope of the line is equal to 32.2N/m.

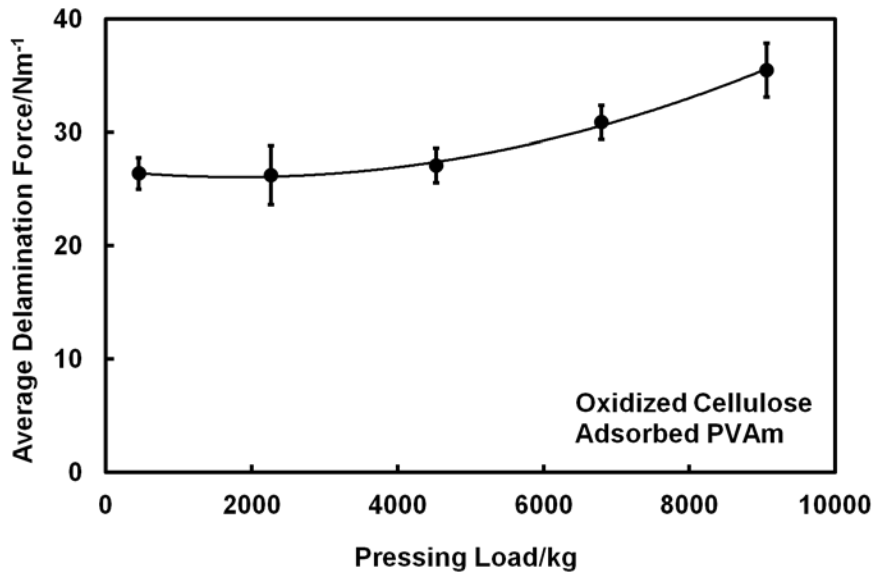


Figure 8. The effect of pressing load on the average delamination force of oxidized cellulose-PVAm laminates.

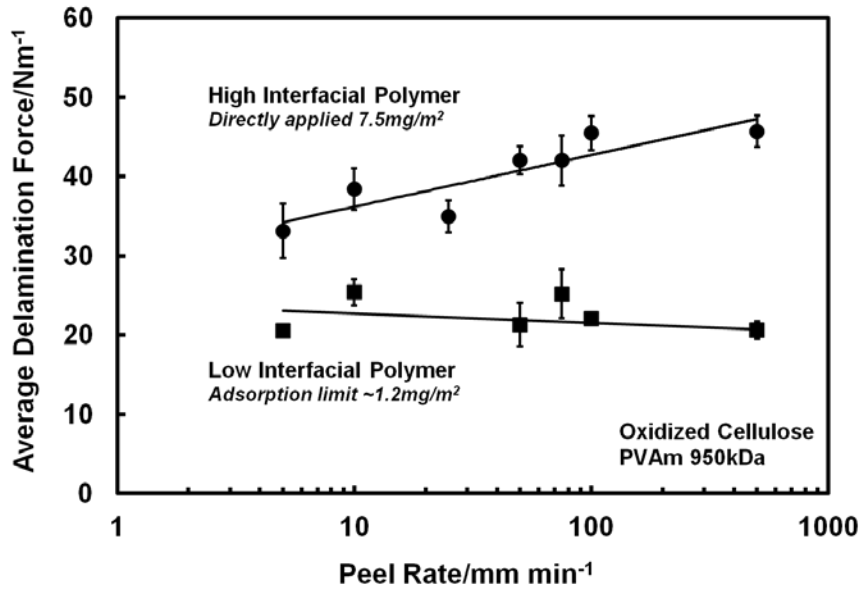


Figure 9. Average delamination force change with peel rate for oxidized cellulose-PVAm laminates with deposited polymer (7.5mg/m²) and adsorbed polymer (~1.2mg/m²).

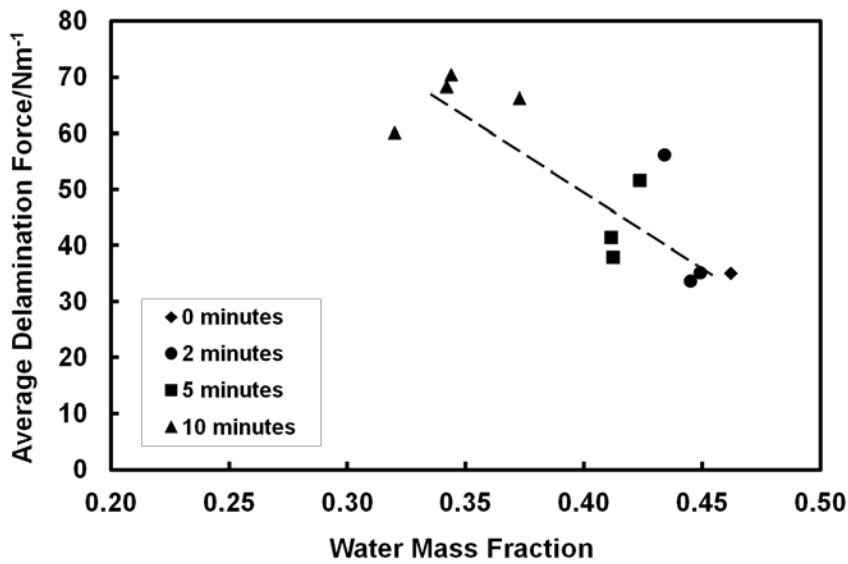


Figure 10. Water content of the laminates prior to testing and the influence on the delamination force. The water content was reduced by evaporation at 23°C and 50%RH for the given amount of time.

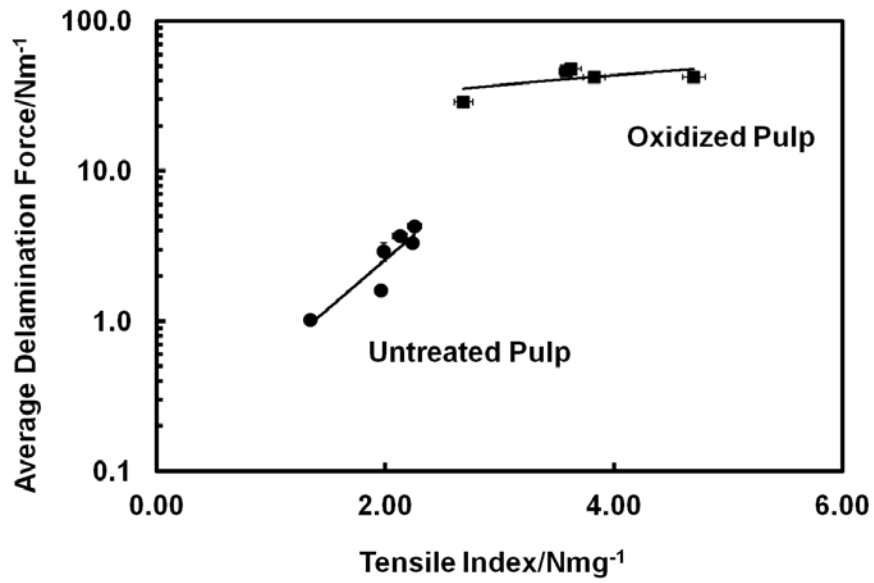


Figure 11. Comparison of wet tensile index and wet delamination force. The points represent the respective properties at identical changes to the pH of the soaking solution.

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Chapter 3 The Mechanism of Polyvinylamine Wet Strengthening

In this chapter the mechanism of Polyvinylamine wet strength enhancement was explored in a phenomenological approach using the wet cellulose delamination method. This work was published as a contribution to the Transactions of the 13th Pulp and Paper Fundamental Research Symposium (FRC), 2005. A lengthy review was included in this paper which is in part a reproduction of the Chapter 1 Literature Review

All experiments were designed by the author with the help of an undergraduate student (Robert Bertoia). All data was processed and plotted the author with assistance in the interpretation of the results provided by Dr. Pelton and Dr. Leduc. Dr. Pelton and Dr. Leduc also provided corrections and comments during the writing of this manuscript.

THE MECHANISM OF POLYVINYLAMINE WET-STRENGTHENING

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ABSTRACT

Regenerated cellulose films were laminated with polyvinylamine, PVAm, and the wet peel delamination forces were used to explore the mechanism by which PVAm increases the wet strength of paper.

Conventional wet strength resins contain highly reactive chemical groups which can crosslink the resin and graft it to fibre surfaces. By contrast, it is not obvious how PVAm provides wet strength.

The delamination experiments revealed that PVAm gives strong adhesion which was approximately independent of drying temperature (23 to 110°C), pH 3 to 9, PVAm molecular weight (34,000 to 1,500,000Da), and PVAm coverage (monolayer to 70mg/m²). By contrast the adhesion increased with the amine content of PVAm and with the degree of oxidation of the cellulose films. It is proposed that the PVAm adhesion is a combination of electrostatic and covalent bonding. The electrostatic bonding is between protonated amines, which are positively charged, and carboxyl groups on the cellulose. Whereas the covalent bonds, aminal and imine linkages, are formed between amines and aldehyde groups on the oxidized films.

3.1 Introduction

Approximately 50 years ago it was reported that polyvinylamine (PVAm), a simple polymer containing primary amine groups (see Scheme 1), increased paper wet-strength [1]. In his excellent review of wet-strength resin technology, Espy stated that the reason why a related polymer, polyethyleneimine, increased paper wet strength was unknown – the same situation is true for PVAm [2]. This paper is our first report of a fundamental investigation aimed at understanding the mechanism by which PVAm increases paper wet strength.

The mechanical properties of wet paper and paperboard are important in many situations. The repulping of paper broke and paper recycling are examples of applications where the tendency of paper to disintegrate in water is an advantage. Conversely, packaging, towels and tissue require paper to maintain some level of mechanical strength when wet. There is little debate as to why wet paper is weak; the fibre-fibre joint swells in water causing it to weaken. Molecular-scale theories describing fibre-fibre bonding, including hydrogen bonding [3], van der Waals forces or interdiffusion of surface polymers [4, 5], all predict that water will weaken fibre-fibre interactions.

From a more pragmatic perspective, wet strength can be increased by either surface treatment (modification) of fibres with small molecules or by surface treatment with macromolecules, called wet strength resins. Some important conclusions from the literature are now summarized to provide a context for our new results. Waterborne molecules smaller than 1,000Da can access most of the interior surfaces in a fibre wall, whereas, high molecular weight polymers are excluded from small pores. Thus, these two classes of surface treatment chemicals are considered separately.

3.1.1 Fibre modification with small molecules

The presence of surface functional groups which will generate hydrolytically stable covalent bonds in the fibre joint will increase wet strength. Furthermore, if such bonds can form in the wet end of the papermachine, they will contribute to wet-web strength. Thus, aldehydes, acetals, and carboxyls will increase wet strength. Aldehydes can couple with alcohols to form acetals or hemiacetals, with other aldehydes [6] (Scheme 2), or with amines to give imines or aminateds (Scheme 4). The amine reactions can occur under ambient conditions in water, potentially contributing to wet web strength [7]. In

comparison, the reaction of carboxyls with alcohols to give esters, or amines to give amides, require high (120°C–180°C) temperatures with water removal.

Three types of fibre modification with small molecules have been described in the literature: 1) oxidation to generate surface carboxyl and aldehyde groups [8-10]; 2) surface grafting with carboxymethyl groups [11, 12], zwitterions [13], sulfonates [14], silanes [15], acetyls [16]; and, 3) polyfunctional (usually polycarboxylate) species which crosslink and thus stiffen the fibre wall [17, 18].

Finally, increasing the carboxyl contents on fibres may not only improve the wet strength directly but also increases the retention of cationic polymers and gives more grafting sites for wet strength resins. For example, poly(aminoamide)-epichlorohydrin (PAE) retention was found to correlate with the carboxyl content of the fibres [11, 19]. These authors found that the effect of oxidation and PAE content on wet strength was synergistic; although with increasing carboxyl content the pulp became more hydrophilic and thus reduced wet strength gains.

3.1.2 Fibre modification with macromolecules

A wide variety of polymers have been shown to have efficacy as wet strength resins [2, 20, 21] and they share some general features in contrast to the small molecules used for fibre treatment. Size scale is an obvious difference between grafting individual functional groups versus macromolecules on fibre surfaces. A monolayer of water soluble polymer on a surface will span 5 to 50nm in water whereas most functional groups, formed by oxidation or grafting of small molecules, are sub nanometre in size. Polymers can have many functional groups which, depending upon the polymer chemistry, can crosslink multiple polymer chains together to form a network. Therefore macromolecules are more likely to participate in inter-fibre bonding, which is crucial for paper strength in the wet state.

Wet strength resins are usually cationic polymers which are added in the wet end where they spontaneously adsorb on fibre and fines surfaces. If added alone, polymers will give a maximum fibre coverage corresponding to an adsorbed monolayer, which is approximately 1 mg per square meter of accessible surface [22]. When two resin-coated fibres come together in the sheet consolidation drying process, a number of interactions are possible in the fibre-fibre joint. The resin-fibre interactions may be physical (hydrogen bonding, van der Waals attraction) or chemical (covalent bonds formed through

grafting). Similarly, the resin-resin interactions, dictating the cohesive strength of a resin film, can include physical and chemical bonds (covalent crosslinks).

The response to water of a wet strength resin containing fibre joint will depend upon the chemical properties of the polymer. In the extreme case, a hydrophobic polymer film such as polystyrene will not swell because it is insoluble in water. By contrast, a film based on a hydrophilic polymer, such as polyacrylamide, will dissolve in water unless it is crosslinked in which case it will swell. Examples of these two situations can be found in wet-strength resin technology. Early wet strength resins were based on hydrophobic condensation polymers of urea-formaldehyde resins and melamine-formaldehyde colloids [23]. These condensation resins crosslink upon curing to give polymer networks that are more or less insoluble. Interestingly, it seems that these chemistries do not form grafts to the fibre surfaces [24-26]. By contrast, glyoxylated polyacrylamide is an example of a resin which is hydrophilic and water soluble yet is insoluble when crosslinked and when grafted to fibres [23]. The most common wet strength resins today are PAE resins. PAE forms crosslinks by mechanisms summarized in Espy's review [2]. Espy also makes the case that PAE will graft to carboxyl groups and not to hydroxyls; this debate is not resolved and is beyond the scope of this paper [11, 27].

To summarize, wet strength requires polymer-polymer and polymer-fibre bonds to persist in the presence of water. Covalent bonds, for example, acetal and imine bonds, will hydrolyze giving temporary wet strength. The integrity of physical bonds in the presence of water is more complicated. Hydrogen bonds between alcohols are weaker than those between an alcohol and water. Thus, water disrupts untreated fibre joints based on hydrogen bonding between carbohydrates. Electrostatic attraction of a charged polymer with an oppositely charged surface is another form of physical bond. We know that these do persist in the presence of water, otherwise cationic polymer would not adsorb onto pulp. On the other hand, as pointed out by Espy [28], poly(dimethyldiallyl ammonium chloride), (PDADMAC), a common papermaking chemical has quaternary ammonium groups which adhere to wet pulp but impart no wet strength improvement. Based on this observation, Espy argues that electrostatic bonds alone are insufficient to give wet strength improvement. It should also be noted that PDADMAC will not crosslink, so the cohesive strength of a PDADMAC film will be very low, giving low wet strength, in spite of strong adhesion to fibre surfaces.

The mechanisms by which PVAm or polyethyleneimine (PEI) increases wet strength are not obvious since neither crosslinking nor grafting seem likely. There have been some studies on PEI and PVAm wet strength and these are now reviewed.

Early studies by Trout have shown that PEI will adsorb onto pulp fibres driven by ion-exchange and that the wet strength was proportional to the amount adsorbed [29]. Sarkanen analyzed the effect of PEI on various paper properties and showed that the wet strength development was proportional to the PEI retention [30]. Interestingly, he found that when anionic polyelectrolytes were used as a retention aid the wet strength proportionality to the PEI retention was less than adding PEI alone.

Polyvinylamine (PVAm) is one of the newest polymers available to papermakers. It is manufactured in a two step procedure (see Scheme 1). The first step is the preparation of poly(N-vinylformamide), (PNVF), which is a nonionic water soluble polymer isomeric to polyacrylamide. In the second step, the amide groups are hydrolyzed to give amine groups. If the hydrolysis is complete, the product is PVAm, whereas partial hydrolysis yields a copolymer, PNVF-co-PVAm. For simplicity, we use the term PVAm to refer to both the homopolymer and the copolymer. The main features of PVAm are the molecular weight and the degree of hydrolysis which correlates with charge density.

Weisgerber's patent appears to have been the first report that PVAm gave wet strength [1]. More recently Pfohl reported a wet/dry strength ratio of 26% for a 1wt% PVAm in sulfite pulp (equal mixture of pine and beech) at pH 7.5 [31]. Wang and Tanaka reported that PVAm at 11% hydrolysis (reported as % amine groups) increased the wet/dry strength ratio of commercial hardwood bleached kraft pulp handsheets from approximately 5% to 30% [32]. Pelton and Hong investigated the properties of newsprint impregnated with PVAm and found that wet strength achieved almost 30% of the dry strength value [33]. Some key results from this work were that the wet strength was constant for up to 1 hr soaking and was not affected by the degree of hydrolysis between 56% and 100%. The wet tensile was higher when the paper was treated at pH 10 compared with pH 3 and pH 7.

3.1.3 Wet strength evaluation

The traditional laboratory approach to wet strength evaluation is to prepare hand sheets with resin-treated fibre suspensions and measure the wet tensile as a function of polymer content. Handsheets should be prepared to give a range of densities so wet tensile results can be compared at equal dry

sheet density. This procedure requires independent measurement of resin retention and it is assumed that sheet formation is not influenced by wet strength resin addition.

In an attempt to learn more about the details of wet strength enhancement we have developed a model adhesion experiment in which two regenerated cellulose films are laminated together using the wet strength resin [34]. The ninety degree peel delamination force gives a measure of adhesion. If the laminate was never dried, the delamination, or peel force, corresponds to the wet-web strength; whereas, laminates which are dried and re-wetted simulate conventional wet strength measurements. Our approach is similar to that described by Ben-Zion and Nussinovitch who used wet cellulose as a model substrate for the characterization of skin adhesives [35]. The advantage of this approach is that the amount of polymer in the laminate can be carefully controlled, the measurements are rapid and reproducible, and the surfaces can be characterized before and after peeling. In this paper we show the influence of a number of parameters on the strength of cellulose-PVAm- cellulose laminates. From these results conclusions are made regarding the various contributions to wet adhesion.

3.2 Experimental

3.2.1 Polymers

Polyvinylamine, PVAm, was supplied by BASF (Aktiengesellschaft, Germany). PVAm of varying molecular weights were prepared by the base hydrolysis of poly(N-vinylformamide) – see Scheme 1. So, in addition to molecular weight, an important variable is the degree of hydrolysis (usually expressed as a mole percent). All polymers were supplied at a 95% degree of hydrolysis as measured by formic acid formation. All polymers were purified by exhaustive dialysis against distilled water. The resulting dilute solutions were dried in a Heto Drywinner vacuum freeze drier and stored in a desiccator at room temperature. The specific charge content of the polymer was determined by conductometric titration with 0.1N NaOH using a Burivar-I2 Automatic Buret (minimum injection volume 1 μ L, ManTech Associates) controlled by PC-Titrate software (version 2.0.0.79). Proton NMR was used to determine the degree of hydrolysis. The properties of the polymers used in this investigation are summarized in Table 1.

PVAm8 (see Table 1) was prepared by further hydrolyzing PVAm3. In this procedure 15g of PVAm3 was added to a round bottom flask and diluted with deionized water to 3wt%. Concentrated NaOH was added to give a final concentration of 5wt% (1.25 N). The reaction vessel was then placed in an oil bath on a magnetic stirrer (IKA RET Basic) with temperature control (IKA ETS D4 fuzzy) and set at 78°C. Air was purged from the system using a low flow of nitrogen gas. The reaction continued for 4 days under constant stirring and positive nitrogen pressure. Finally the solution was purified by dialysis. No further formamide groups could be detected by proton NMR.

3.2.2 Cellulose preparation and modification

Regenerated cellulose dialysis tubing (Spectra/Por® 4 product No:132682 12kDa MWCO, Spectrum Laboratories, Inc.) was cut to the following dimensions: top membrane (2cm by 6cm) and the bottom membrane (3cm by 6cm). Samples were cut with the long axis in the roll direction, and only the interior surface of the tubing was used to study adhesion. Cellulose film strips were soaked in room temperature water for 24hrs to remove any preservatives (glycerine). The cellulose films were then rinsed thoroughly and stored in water with a small amount of methanol (to prevent spoilage) at 4°C. Most of the cellulose films were oxidized with 2,2,6,6-tetramethyl-1-piperidinyloxy radical (TEMPO), NaBr and NaClO (11–14%) [47] all supplied by Sigma-Aldrich following Kitaoka's method [19]. The concentration of TEMPO/NaBr was fixed at 0.034g/L and 0.34g/L respectively and the concentration of sodium hypochlorite was 3wt% based on dry cellulose. All reactions took place at 23°C under mild stirring (magnetic stirring bar) in a 1L glass beaker treating up to 7g cellulose. The pH was maintained at 10.5 by sodium hydroxide and the oxidation was stopped by adding ethanol to the suspension. The cellulose was removed and rinsed first in ethanol and then repeatedly with deionized water. The treated films were stored at 4°C with a small quantity of methanol.

3.2.3 Polymer application

Two methods were used to apply PVAm to the cellulose films – direct application and adsorption application. For the adsorption application method, the top cellulose film was covered in 0.6mL of a solution of 0.5mg/mL PVAm dissolved in 1mM NaCl with the pH adjusted to the desired value. After soaking for 30 min the films were rinsed gently for 5min in pH adjusted 1mM NaCl solution. We assume

that by rinsing off excess polymer that the resulting cellulose films were coated with a saturated monolayer of adsorbed PVAm [22, 36]. The laminates were constructed by first placing the wet bottom membrane on a blotting paper. A 40 × 12.7mm long piece of Teflon tape

Thompson Co. Ltd, TWB480P) was placed across one end of the bottom membrane (see Figure 10, right hand side). The purpose of the Teflon tape, which was removed before peel testing, was to give two cellulose film tails for attachment to Instron clamps and to give a uniform crack in the laminate. In the next step the top membrane was placed on the bottom membrane, followed by blotting paper. The wet laminate was pressed between blotting paper at 89kN and room temperature for 30min. After pressing, the laminates and blotting paper were equilibrated at constant temperature (23°C) and humidity (50%) for at least 12 hours under no load.

In the direct application method, the bottom cellulose membrane was placed on a stainless steel plate and excess surface water removed by dabbing with a lint free tissue. The Teflon tape strip was placed at the edge of the bottom membrane and a 15µL drop of aqueous PVAm was applied using a 20µL micropipette (Gilson) onto the base membrane near the Teflon tape (see Figure 10, left-hand side). The top membrane was progressively placed over the bottom membrane starting at the end with the Teflon tape. If done carefully, the 15µL polymer solution droplet uniformly spread between the top and bottom membrane with negligible loss of polymer solution. The PVAm solutions varied in concentration, salt content (NaCl) and pH. Base conditions were 0.1wt% PVAm, 1mM NaCl, and pH 7. The laminated membranes were then dried and conditioned in the same fashion as described previously.

3.2.4 Wet adhesion testing

Before testing, the laminated membranes were soaked for 30min in 50 mL of deionized water at the ionic strength and pH of the applied polymer solutions, after which excess water was removed by uniform pressing (2.4kg roll wheel) between two pieces of blotting paper. The wet, laminated membranes were then mounted using a 4cm wide fluid resistant two sided tape (3M Polyethylene Medical Double Coated Tape; Model No: 1522) onto a 14cm diameter, 40mm wide aluminium peeling wheel running on SKF-6,8–2RS1 radial bearings – this configuration gives a 90 degree peel angle [37]. The wheel was fixed to the bottom jaw of an Instron 4411 universal testing system (Instron Corporation,

Canton, MA) fitted with a $5\text{N} \pm 0.005\text{N}$ load cell. The top membrane was separated from the base membrane at the edge with the Teflon tape and clamped into the upper jaw of the Instron. The samples were tested at a crosshead rate of $20\text{mm}/\text{min}$. The steady-state force was taken for each membrane with the result divided by the membrane width (20mm) to give a width-normalized force in units of N/m .

3.3 Results

Laminates were prepared by pressing and drying ($50\% \text{RH}$, 23°C) a sandwich of two wet cellulose films with a layer of PVAm acting as an adhesive. A summary of the polymers used is given in Table 1. Two methods were used to apply the PVAm to the cellulose films. For most of the experiments the polymer solution was directly spread on the wet cellulose – we call this the **direct application** method. For some experiments, one or both cellulose films were exposed to a PVAm solution to give saturation adsorption – we call this the **adsorption application** method. Finally, for most experiments, the cellulose films were oxidized by NaClO with a NaBr and TEMPO (2,2,6,6-tetramethyl-1-piperidinyoxy radical) catalyst in order to introduce carboxyl and aldehyde surface groups. For testing, the dried laminates were soaked in aqueous solution and kept wet during the peel force measurements. Figure 1 shows the force versus displacement traces for three laminates which differ in the extent of oxidation. Adhesion increased significantly with cellulose oxidation.

A single peel force was extracted from each curve by averaging the data over the range of steady-state peeling which in most cases occurs between 10mm and 35mm . The three curves in Figure 1 illustrate that the noise within a peeling trace varies with sample properties. Most of the following results are based on 4 replicated experiments and the error bars were calculated as the standard error of the mean steady-state peel force.

The influence of surface oxidation is further illustrated in Figure 2 which shows the variation of peel force with the residence time of the cellulose in oxidizing solution. There appeared to be an induction period up to about 1 minute where peel force increased slowly. The largest increases in peel force occurred with oxidation times between 1 and 4 minutes. Longer oxidation times did not produce further changes in peel force. For most experiments, an oxidation time of 10 minutes was used, which is not in the sensitive regime of oxidation time.

Adhesion is usually sensitive to the quantity of adhesive in a joint. Figure 3 shows peel force as a function of PVAm which is expressed as mg/m^2 based on the macroscopic area of the adhesive joint (usually 20mm by 50mm). Peel force increased with PVAm coverage up to about $10\text{mg}/\text{m}^2$ after which the peel force was approximately constant. Figure 3 also shows an individual point obtained using the adsorption application method. We did not know the corresponding coverage value; however, based on a PVAm adsorption study [38], we estimated that the equivalent of two adsorbed monolayers is about $0.5\text{mg}/\text{m}^2$. Thus, for low surface coverage the adsorption application gives much stronger adhesion than the direct application.

Figure 4 shows the peel force as a function of PVAm molecular weight. The peel force was about $37\text{N}/\text{m}$ and was independent of molecular weight over the range investigated ($34,000$ to $1,500,000\text{Da}$). The regenerated cellulose films, based on dialysis tubing, have fine pores. The molecular weight cut off (MWCO) is shown in the Figure 4 and the PVAm samples were too large to penetrate the membrane. The results have not yet been extended to low molecular weight PVAm, however, we anticipate that adhesion will decrease perhaps as shown in the dashed line since ethylenediamine, gives poor wet strength [39].

A basic assumption in this work is that a cellulose film laminated with PVAm is a model for fibre-fibre adhesion. One obvious difference between paper testing and our experiments is the length scale of the joint. Fibres are roughly $20\mu\text{m}$ wide whereas the laminate strips are 20mm wide. It could be argued that during the soaking step, water transport into the laminate and PVAm diffusion out of the joint will be artificially slow in the laminates. A series of experiments were conducted in which the only variable was the laminate soaking time before peeling and the results are summarized in Figure 5. Our standard soaking time is 30min. The shortest soaking time in this series of experiments was 10min and the longest was 65 days. There was a slight decrease in peel force between the first and second point followed by an increase in peel adhesion with soaking time. Thus there were no slow processes which lower adhesion such as diffusion of polymer out of the joints.

PVAm is prepared from the hydrolysis of PNVF (see Scheme 1). In previous work we measured the wet strength of commercial newsprint impregnated with PVAm of varying degrees of the hydrolysis [33]. PNVF (i.e. approximately 0 degree of hydrolysis) gave no wet strength improvement whereas newsprint wet tensile increased to a maximum value with 56% hydrolysis; higher degrees of hydrolysis gave little

further advantage at polymer retention values greater than 2%. The results from the corresponding cellulose delamination experiments are shown in Figure 6, which includes data obtained using both application methods (direct and adsorption) for treating the cellulose films with PVAm. In agreement with our previous handsheet work, there was little advantage having degrees of hydrolysis greater than 55%. Furthermore, the two application methods gave the same results.

In an effort to gain some insight into the factors controlling adhesion, measurements were made as a function of pH and drying temperature. Figure 7 shows adhesion as a function of drying temperature. The higher temperature data were noisier and the adhesion increased slightly with drying temperature. Gravimetric analysis indicated that the laminates were about 20% water after conditioning at 50% RH, 23°C, which corresponds to the lowest point in Figure 7. Although this seems like rather ineffective drying it is significant, as laminates which were not conditioned gave no measurable wet strength. Thus, the drying stage is critical to the wet-strength mechanism and as such PVAm is unlikely to increase wet web strength.

Figure 8 shows the influence of pH on wet adhesion for both PVAm application methods. It should be noted that there were slight differences in the PVAm used in the two sets of experiments – see the figure captions for details. The peel force was a strong function of pH. The direct application data showed a sharp drop below a pH of 2.75 and a gradual decline from pH 5 to 12. The adsorption application results showed the same trends although the maximum adhesion values were higher. Any explanation of the mechanisms of PVAm wet-strengthening must account for the results in Figure 8. The adhesion was approximately constant from pH 3 to 9, whereas at pH 3 nearly every amine group on PVAm is charged (protonated), while at pH 9 the PVAm is nearly uncharged. Thus, the wet adhesion was independent of the extent of PVAm protonation (i.e. the charge content) over a broad range.

3.4 Discussion

Conventional wet strength resins such as PAE and glyoxylated polyacrylamide function by forming covalent grafts between the resin polymer chains and the cellulose fibre, and by crosslinking themselves giving a covalently bonded polymer network in the fibre joint. At first glance, PVAm does not appear capable of crosslinking or grafting to cellulose. Hence, why does it give wet strength? It is convenient to separately consider covalent bonds and physical bonds.

3.4.1 PVAm Covalent bonding chemistries

The results in Figure 3 show that good adhesion was achieved with a PVAm coverage of 70mg/m². This corresponds to approximately 50 layers of PVAm chains, which in turn, means the cohesive strength of the PVAm layer must be high. This is difficult to understand because a cast PVAm film will dissolve in water suggesting that PVAm does not spontaneously crosslink. There is one potential type of bond between PVAm chains. The formamide groups on partially hydrolyzed PVAm can covalently bond to neighbouring amine groups (see Scheme 3) to give a ringed amidine structure (route A). Alternately, the formamide group can react with a non-neighbouring amine on the same chain or another chain (route B) to give an amidine linkage. The amidine is thermodynamically stable due to the delocalization of the double bond and, therefore, route A is preferred over route B. Reaction route A has been found to occur during the palladium catalyzed hydrolysis of PNVF in water at high temperatures [40][38]. Reaction route B is facilitated at lower temperatures when PVAm reacts with acetaldehyde (a hydrolysis product) or an additional aldehyde cross-linker [41][39]. It seems unlikely that amidine groups formed during the laminate preparation and less likely that cross-linking occurred via route B. Therefore, we conclude that PVAm crosslinking does not occur, with the possible exception of during the high drying temperature experiments (Figure 7).

While there is little possibility for covalent cross-links, PVAm will graft onto cellulose films. The only potentially reactive groups on pure cellulose are the many hydroxyl groups and the hemiacetal/aldehyde group at one end of each cellulose chain. These few terminal aldehyde groups, which are accessible to PVAm, will react with amines in PVAm, therefore, we conclude that PVAm should not form many covalent bonds to untreated cellulose.

PVAm gave low adhesion to untreated cellulose whereas TEMPO oxidized cellulose gave strong adhesion. This treatment converts the C6 cellulose hydroxyl to carboxyl and aldehyde groups which will react with the amine groups on PVAm. Amines will couple to aldehydes to form imines – see Scheme 4. This is a reversible reaction that occurs at room temperature in water through the carbinolamine intermediate and is catalyzed by acid. Typically, an excess of acid will reduce the rate of imine formation due to the protonation of the amine and reduction in the initial nucleophilic attack. Therefore, in general, the rate curve will display a bell shape with an optimal pH range of 4–5 [42, 43]. Imine

formation has been proposed as an important contribution to the ability of chitosan to increase wet strength [7].

Imines can react with amine groups to give aminals [44, 45]. If the imine shown in Scheme 4 reacts with a neighbouring amine group then the result is the six-membered aminor. This product is thermodynamically preferred due to the structure, however both imines and aminals are susceptible to hydrolysis at moderate temperatures.

TEMPO oxidation also gives carboxyl groups on the C6 carbon of cellulose. In an initial investigation we showed that the carboxyl content was 2 meq/100g cellulose after 30 min of oxidation [34]. Amines will condense with carboxylic groups to give amide groups – see Scheme 5. Amide formation generally requires temperatures greater than 150 °C to produce a significant yield of amide and usually occurs under conditions in which free water is removed [46]. Amide formation at moderate temperatures (70–100 °C) does occur [47]. Furthermore, amines couple to formic acid under mild conditions. Nevertheless, it seems unlikely that amide formation is significant in our experiments because the contact times are short and the conditions mild.

In summary, we propose that no crosslinks form between PVAm chains, whereas imine and aminor bond formation do contribute to PVAm-cellulose wet adhesion. However, the occurrence of strong adhesion from pH 3 to 9 (Figure 8), which is beyond the range of imine or aminor formation, suggests that physical bonding is also significant.

3.4.2 PVAm Physical bonding

The chemical properties of PVAm are a strong function of solution pH. At pH 3 virtually every primary amino group is protonated ($-NH_3^+$) giving the polymer a high positive charge whereas at pH 10.5 most of the amine groups are not protonated ($-NH_2$). Between these two extremes the degree of protonation decreases linearly with pH – this is illustrated in Figure 9 [48]. Therefore, at low pH we would expect PVAm to interact with cellulose, or other surfaces, by electrostatic attraction to negatively charged surface sites.

The oxidized cellulose films will have a negative surface charge due to carboxyl groups. We would expect a fraction of the charged carboxyls to give the pH dependence shown in Figure 9. This figure also

shows the pH dependence of PVAm ionization. The overlap area indicates the pH range over which electrostatic interactions should occur.

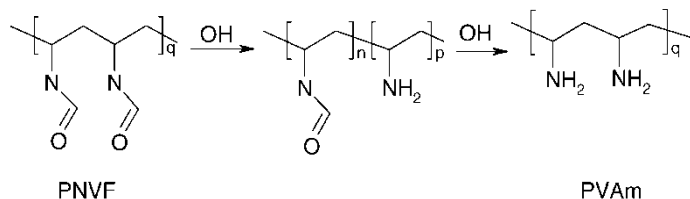
In summary, we propose that PVAm strengthening is due to a combination of covalent bond formation and electrostatic bonding. We hypothesize that covalent bonding is the most important. Based on the current data, it is impossible to decouple the effects of electrostatic and covalent bond formation. Resolving this unanswered question is important since it will point to the best strategies for fibre surface modification to optimize PVAm wet strengthening performance.

3.5 Conclusions

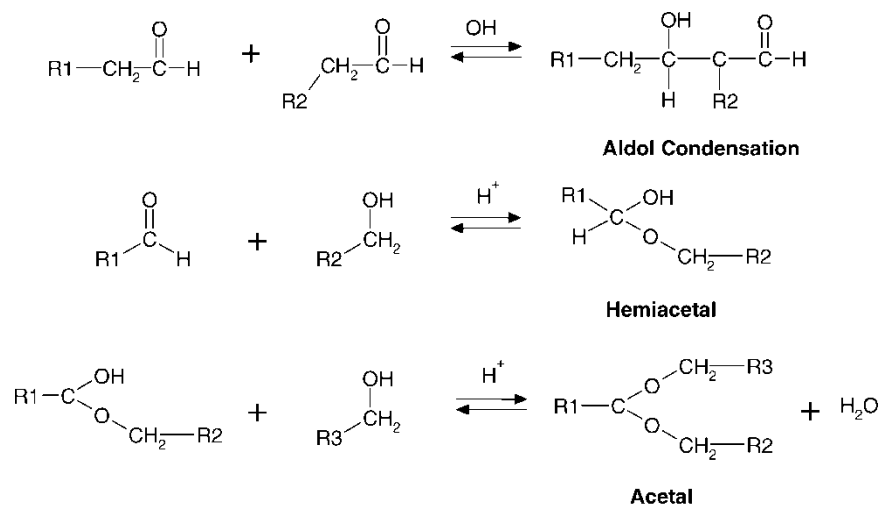
The main conclusions from this work are:

- PVAm gives adhesion between wet cellulose films provided that the laminates were conditioned at 23°C and 50% RH. This is in agreement with published handsheet data. The adhesion results do not predict an improvement in wet web strength.
- Although drying is important, adhesion is weakly dependent on drying temperature over the range 23 to 130°C (Figure 7).
- The primary amine groups on PVAm are the active agents for wet strength since adhesion increases with PVAm amine content.
- The oxidation of cellulose gave a six-fold increase in wet adhesion supporting the hypothesis that imine and aminal bonds between cellulose and PVAm contribute to wet strength.
- Above monolayer coverage, adhesion is virtually independent of PVAm content (Figure 3) and molecular weight (Figure 4) suggesting that wet PVAm has high cohesive strength even in the absence of covalent bonds between neighbouring PVAm chains.
- Because peel strengths are independent of soaking time up to months, the cellulose laminates were tested under conditions of equilibrium swelling. Furthermore, the slow diffusion of PVAm from the joints was not significant.
- Wet adhesion was remarkably independent of pH between 3 and 9 suggesting that in addition to covalent bonding, electrostatic interactions between carboxyls and amines contributed to wet adhesion.

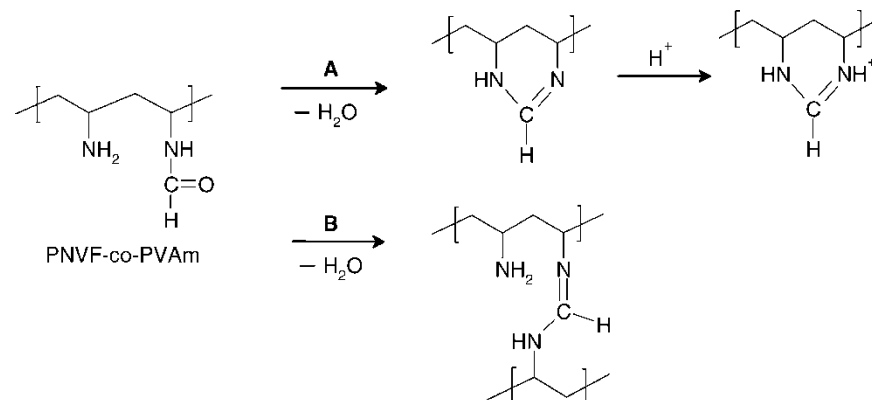
3.6 Schemes



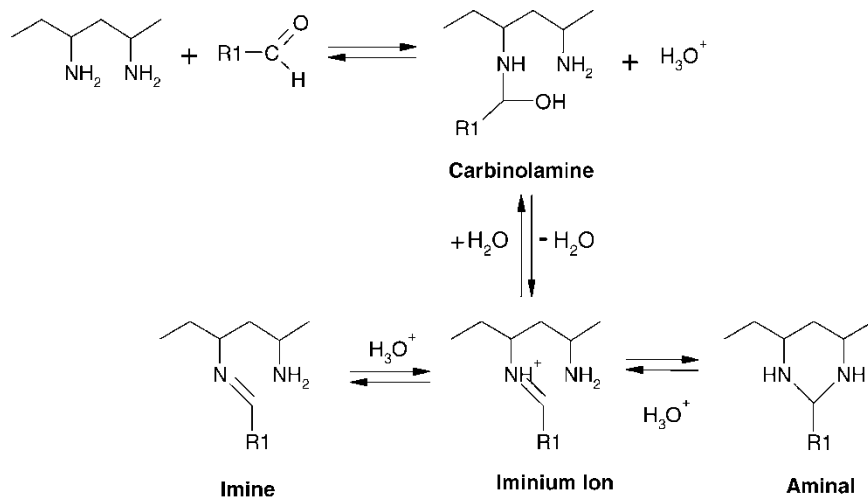
Scheme 1 The preparation of PVAm from the base hydrolysis of poly(N-vinylformamide) (PNVF).



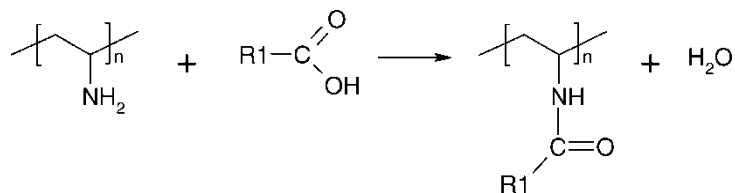
Scheme 2 Relevant reactions of aldehydes.



Scheme 3 The reaction of an amide with an amine to give an amidine. Route A gives a ringed amidine. Only route B gives a crosslink between chains.



Scheme 4 Reaction of an amine with an aldehyde to form an amina through two possible routes.



Scheme 5 Condensation of an amine with a carboxyl to give an amide. This reaction would proceed slowly between cellulose bound carboxyl groups and amino groups on PVAm and thus contribute little in wet strength development.

3.7 Tables

Table 1 List of polymers used in this study and some properties.

Designation	Mw (kDa)	% DH	Charge Content (meq/g)
PVAm1	34	86.3	13.60
PVAm2	70	81.4	13.40
PVAm3	150	96.6	12.40 ± 0.57
PVAm4	300	96.1	–
PVAm5	350	–	14.00
PVAm6	950	90.5	13.20
PVAm7	1500	94.6	13.68
PVAm8	150	>98	13.2 ± 0.76
PVAm9	1500	1.0	–
PVAm10	1500	8.1	–
PVAm11	1500	23.2	–
PVAm12	1500	33.3	–
PVAm13	1500	53.6	–

3.8 Figures

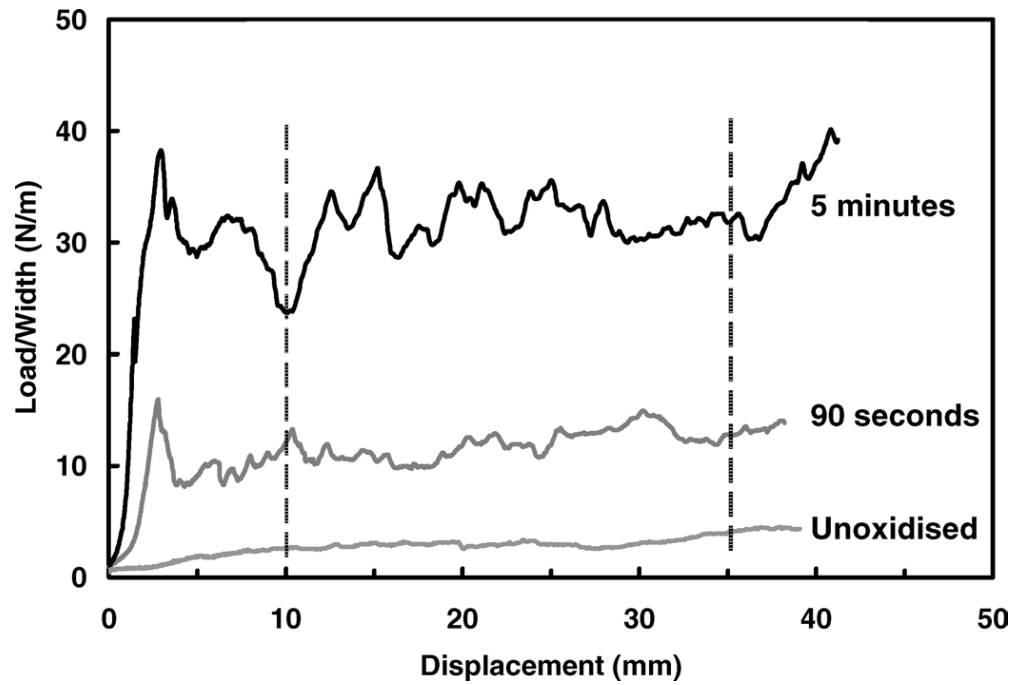


Figure 1 Force versus the displacement data for three wet laminates peeled at 90°. The labels indicate the residence time of the cellulose in the oxidizing solution and in the conditions are given in Figure 2. The dashed lines denote the range over which the data were averaged to give the peel force for the sample.

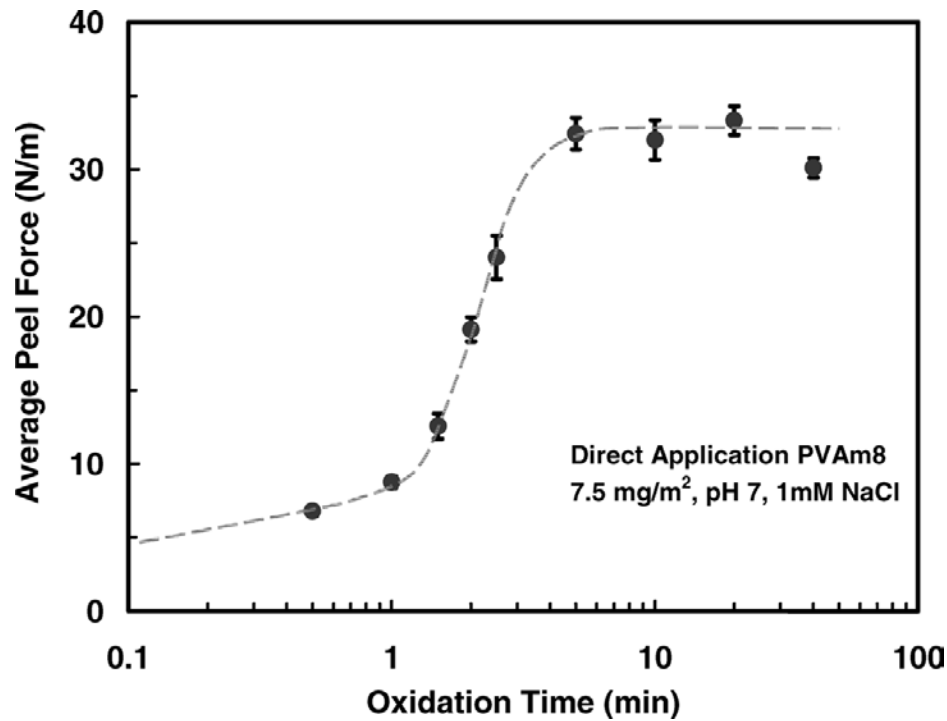


Figure 2 Peel force as a function of the time used to oxidize the cellulose membranes in TEMPO/NaBr/NaClO solution. See insert for details.

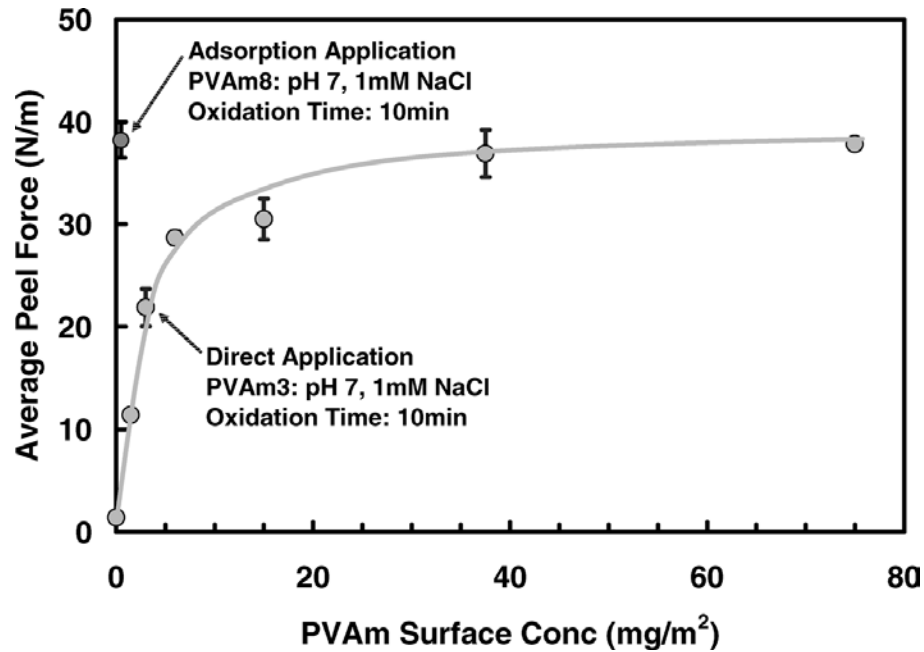


Figure 3 The influence of PVAm coverage on peel force. The cellulose was oxidized with TEMPO/NaBr/NaClO for 10 min.

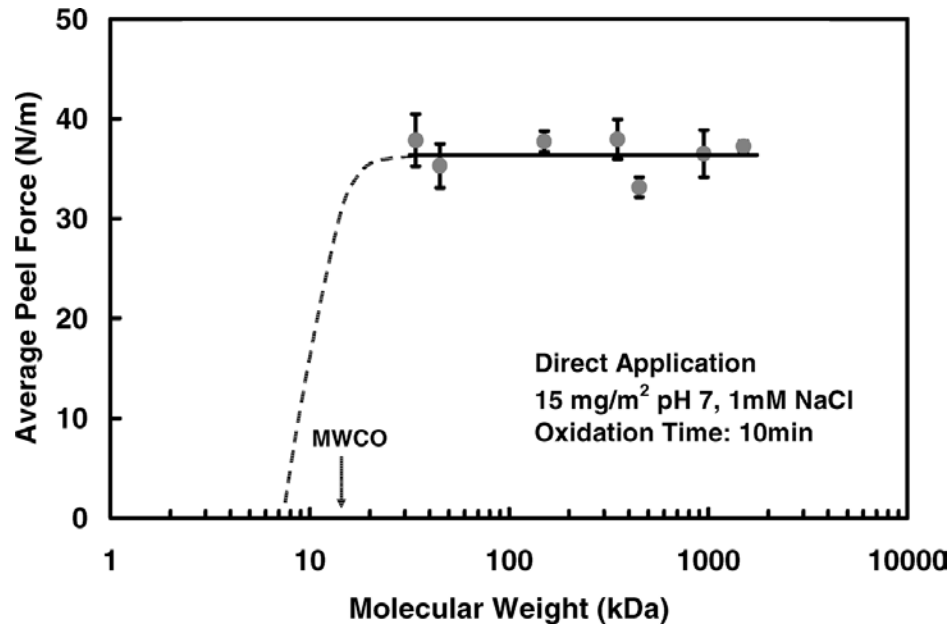


Figure 4 The effect of PVAm molecular weight on the laminate strength of regenerated cellulose membranes.

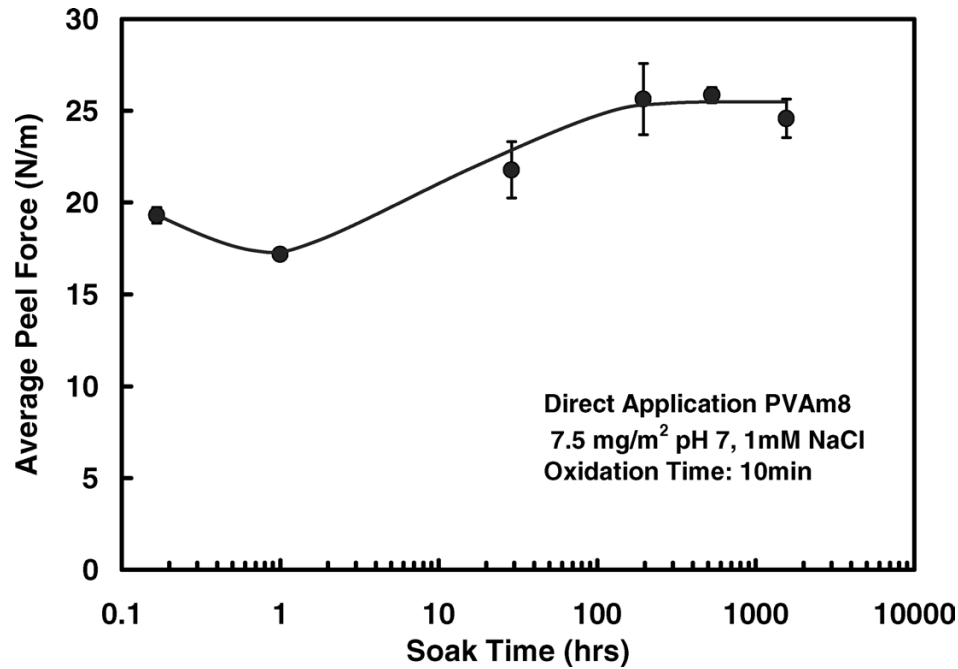


Figure 5 Change in the peel force with soaking time of the laminates in 1mM NaCl prior to peeling.

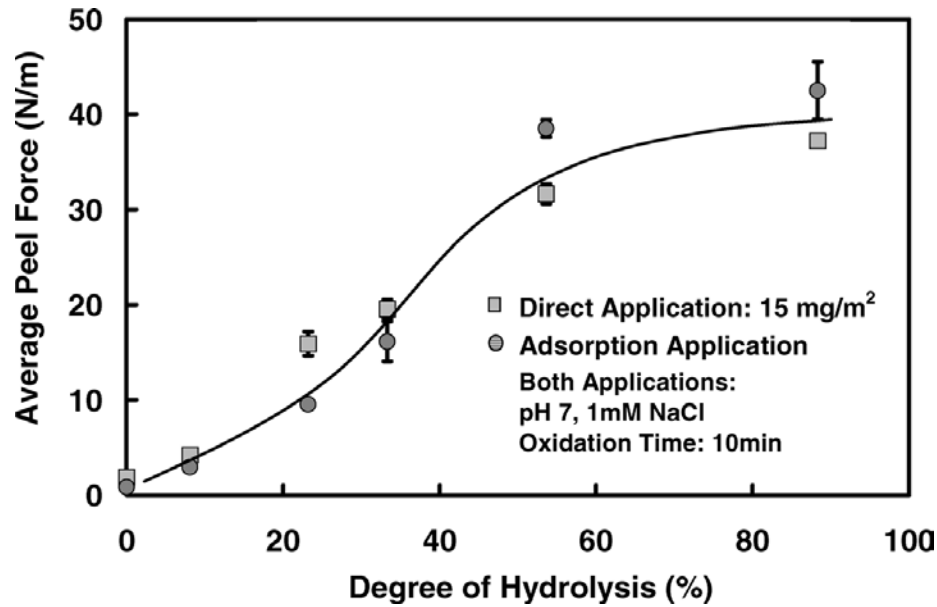


Figure 6 The effect of PVAm hydrolysis degree on the delamination force. The molecular weight of the parent PNVF was 1,500 kDa.

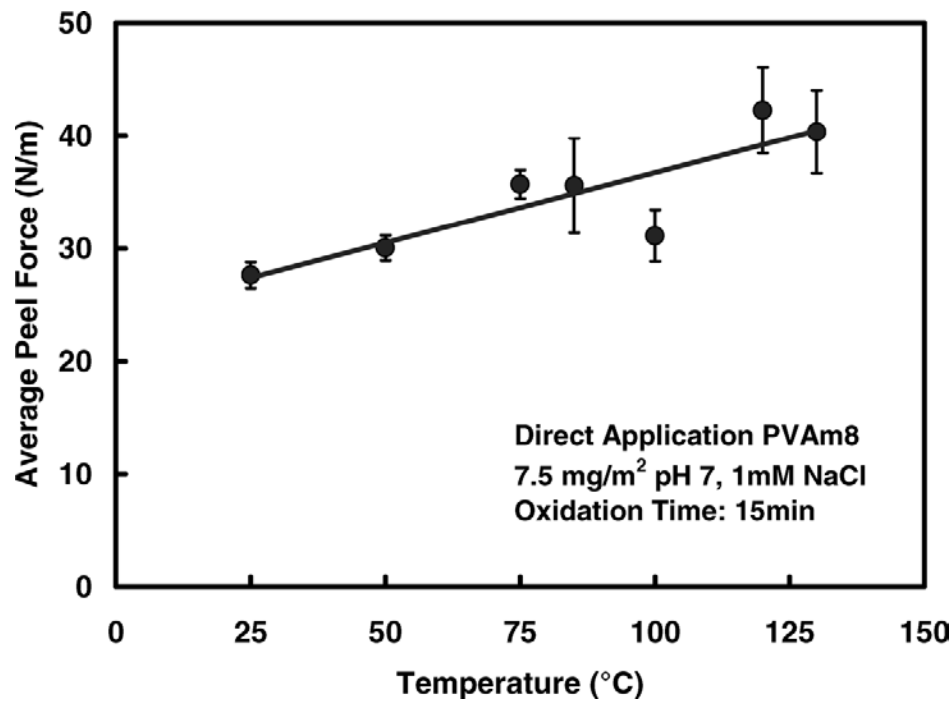


Figure 7 The influence of laminate drying temperature on adhesion. The cellulose was oxidized for 10min and the laminates were heated for 20 min.

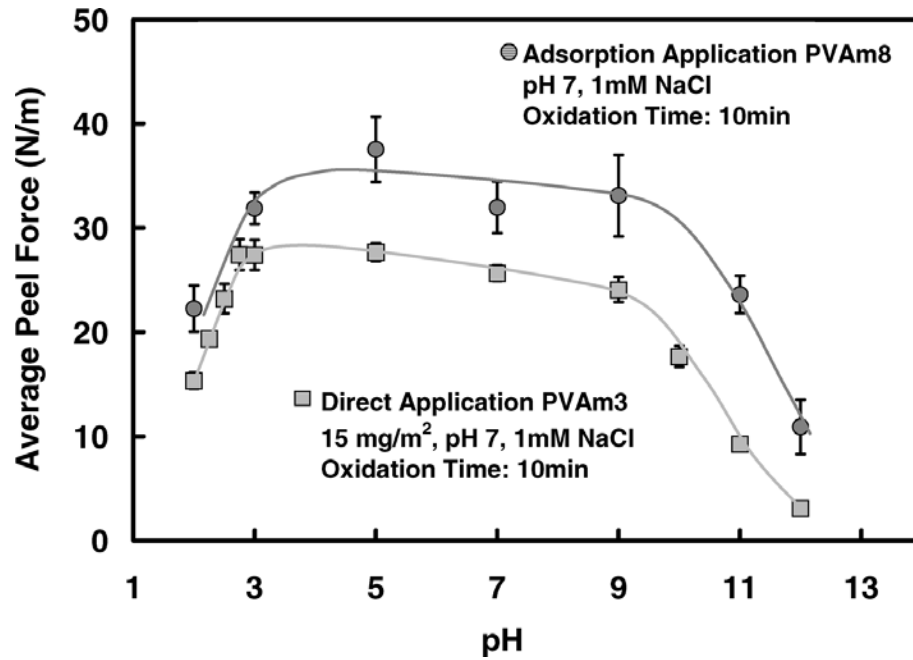


Figure 8 The influence of pH on PVAm adhesion. The same solution pH was used for polymer application and pre-test soaking. The squares represent direct application of PVAm3 at a coverage of 15 mg/m². The circles represent the adsorption application of PVAm8 on only the top film.

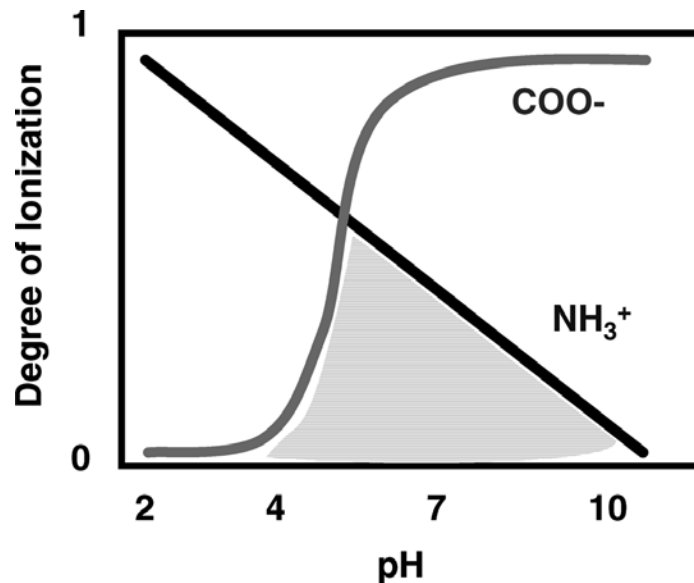


Figure 9 Schematic illustration of pH dependence of the fraction of charged amine groups on PVAm and of charged carboxyl groups on oxidized cellulose.

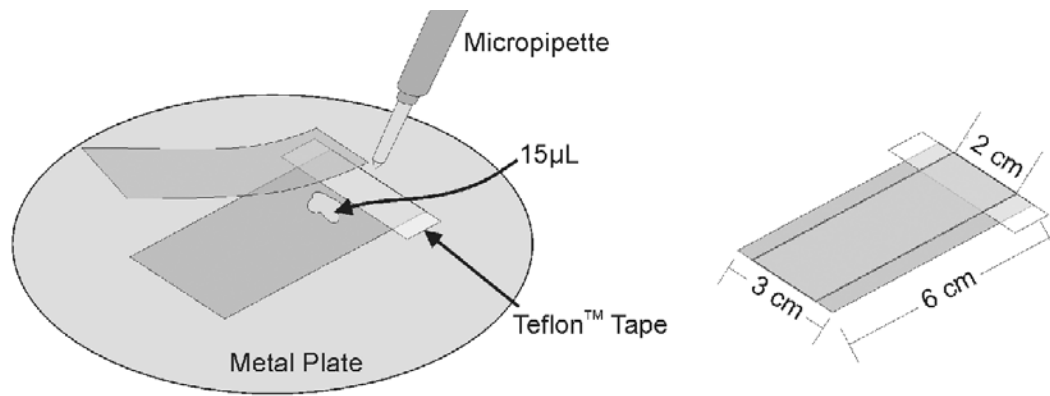


Figure 10 Illustration showing the direct application of PVAm (left) and the final dimensions of the laminates used in this study (right).

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Chapter 4 Chemical Interactions of Polyvinylamine and Oxidized Cellulose

In this chapter the role of oxidation in the enhancement of wet delamination force was investigated using surface analysis of the peeled laminates. The work was published in the journal *Cellulose* in 2007.

All experiments were designed and conducted by the author with the help of an undergraduate student (Robert Bertoia). XPS, SEM and ATR-FTIR analysis was performed at BASF (Ludwigshafen) by technical staff. The data was processed and plotted by the author with assistance in the interpretation of the results provided by Dr. Pelton, Dr. Leduc, Dr. Essig, Dr. Champ and Dr. Frechen. Dr. Pelton provided corrections and comments during the writing of this manuscript.

The role of mild TEMPO-NaBr-NaClO oxidation on the wet adhesion of regenerated cellulose membranes with polyvinylamine

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Abstract

X-ray Photoelectron Spectroscopy (XPS) was used to characterize the functional groups present on regenerated cellulose films after mild oxidation with TEMPO-NaBr-NaClO and the results were correlated with the adhesion forces holding together two wet cellulose films laminated with a thin (i.e. less than 10 mg/m²) layer of polyvinylamine (PVAm). There was no correlation between adhesion and carboxyl content, whereas wet adhesion was proportional to the total content of aldehyde and hemiacetal groups on the cellulose. It is proposed that aldehyde groups react with neighboring cellulose chains to form hemiacetals which serve as crosslinks strengthening the cellulose surface. The hemiacetals can also be attacked by primary amines to give imine and aminal covalent linkages to the PVAm adhesive layer.

Keywords

Oxidation, TEMPO, wet adhesion, XPS, aldehyde, hemiacetal

4.1 Introduction

Paper and paperboard are strong materials when dry because of the intrinsic strength of cellulose fibers and because of strong fiber-fiber adhesion due mostly to hydrogen bonding [1], polymer interdiffusion [2], and polymer compatibility [3]. On the other hand, wet paper can be very weak because fibers swell in water disrupting fiber-fiber joints. For applications where paper must have some wet strength, papermakers employ waterborne, reactive polymers called wet strength resins [4]. In order to explore the detailed mechanisms by which some polymers strengthen wet cellulose-cellulose joints, we have developed model adhesion experiments in which two regenerated cellulose strips are wet-laminated using a very thin layer of the wet strength resin as the adhesive [5, 6]. Wet adhesion is measured as the 90 degree peel delamination force. During the development of this method, we discovered that to get significant adhesion forces with many polymers, it was necessary to lightly oxidize the cellulose strips with TEMPO-NaBr-NaClO, following a recipe published by Kitaoka, Isogai and Onabe [7].

Much of our work has focused on understanding why polyvinylamine (PVAm), a linear carbon chain with pendant primary amines on alternating carbons, gives good wet strength [6, 8]. The goal of the work described herein was to determine which functional groups on regenerated cellulose, mildly oxidized by TEMPO-NaBr-NaClO, increase wet adhesion with PVAm. For this we correlate FTIR and X-ray Photoelectron Spectroscopy (XPS) analysis of cellulose surfaces with the wet adhesion behaviour with PVAm.

4.2 Experimental

Adhesion testing was done at McMaster University, Hamilton, Canada, while all spectroscopic experiments were performed at BASF AG, Ludwigshafen, Germany.

Regenerated cellulose dialysis tubing (Spectra/Por® 4 product No:132682 12kDa MWCO, Spectrum Laboratories, Inc.) was cut to rectangular dimensions (6cm long by 2cm wide) with the long axis in the roll direction of the tubing. In all experiments the inside surface of the tubing was used. Cleaning was performed with a Soxhlet extractor using water for 24hrs and followed by acetone for 24hrs. The cellulose was then air dried at ambient conditions and weighed.

Cellulose films were oxidized for various times at two temperatures, one at 4°C and the other at room temperature (23°C). The colder temperature was chosen so that any effects of cellulose depolymerization could be avoided [9]. Approximately 1g of cellulose films were immersed in 200mL of an aqueous solution containing 0.034g/L of 2,2,6,6-tetramethyl-1-piperidinyloxy radical (TEMPO) and 0.34g/L NaBr. The TEMPO/NaBr concentrations are based on Kitaoka's method for oxidized wood pulps [7]. All chemicals for the 4°C oxidation were supplied by Sigma-Aldrich and for the 23°C oxidation by Acros Chemicals.

The solid cellulose content was set at approximately 3.4g/L. For the 4°C system the temperature was kept constant using a Lauda RM6 refrigerated temperature bath and the suspended cellulose films were stirred continuously with a magnetic stirring bar. No temperature control was employed for the room temperature series. After 30min of conditioning in the TEMPO/NaBr solution, sodium hypochlorite, NaClO (11-14%), was added to the mixture to give a concentration of 3 wt% by mass of dry cellulose. This amount of NaClO corresponds to 3.3% of the stoichiometric requirement to oxidize all the primary alcohols on the cellulose to primary carboxyls. The pH was then adjusted and maintained throughout the reaction at 10.5 using 1N NaOH.

Approximately 20 mL of 95% ethanol was added to stop the reaction. The cellulose was removed and first rinsed with ethanol, and then with deionized water. Any sodium counterions in the film were replaced with protons by soaking the cellulose in dilute (0.1N) HCl for one hour, followed by repeated washed with deionized water. Cellulose intended for adhesion testing was used directly in the wet form within several days of preparation. Cellulose meant for surface analysis was dried in a desiccator with Silica gel prior to analysis. To minimize contamination, the membranes were folded and the inside surfaces were analyzed. The cellulose samples were stored in sealed glass vials for several days prior to testing.

4.2.1 Wet Cellulose Delamination

Laminates consisting of two cellulose films glued together with a very thin layer of polyvinylamine (PVAm) were prepared by: treating one or both wet cellulose strips (6 x 1.5 cm) with PVAm; wet pressing with a pressure of 1.68MPa; and drying at 23 °C and 50% relative humidity. Two polymer treatment methods were used. For the films oxidized at 4 °C, one side of the top laminate was exposed

to PVAm solution (0.5 g/L in 1mM NaCl at pH 7) for 30 minutes and the excess polymer was rinsed (to 1mM NaCl solution at pH 7). Published work suggests that adsorption from this concentration gives a PVAm coverage of approximately 0.2 mg per square meter of cellulose [10]. For the films oxidized at 23 °C, the polymer was directly coated on the wet films to give an average PVAm density of 7.5 mg per square meter of laminated joint. The coating procedure has been described previously [6]. Cellulose laminates prepared without any PVAm came apart spontaneously when re-wetted therefore the adhesion could not be measured.

The dried laminates were soaked (re-wetted) in electrolyte solution (1mM NaCl) for thirty minutes and the adhesion was measured by a 90 degree peeling test at a peel rate of 20mm/min. Details of the peeling apparatus and method were recently described [5]. Since for most experiments, the peel force was stable at peel distances between 10mm and 30mm, the reported adhesion values are the average force over this range divided by the width of the cellulose strip over this range. At least 3 samples were delaminated for each experimental condition.

4.2.2 FTIR

FTIR measurements were made on a Bio-Rad, FTS-Excalibur Spectrometer with a DuraScope Diamond ATR unit having an internal angle of 45°. The scanning depth of this set-up is 2.38µm and the optical resolution is 2cm⁻¹. Cellulose was dried in a vacuum oven at 50°C overnight and tested directly out of the oven. No moisture control was employed during the analysis.

4.2.3 XPS

Many authors have characterized surface function groups on paper and cellulose surfaces with X-ray Photoelectron spectroscopy.; [11-13] For our work, the XPS measurements were made using a Physical Electronics GmbH, Multi-Technique System 5600LS. The X-ray source was a standard Mg_{Kα} (1253.6 eV) with an analyzer area of 13mm² and analyzer angles of 5°, 45° and 90° - the corresponding penetration depths are approximately 1, 7, and 10 nm. The X-ray source was run at 300W with 23.5 eV high resolution analyzer pass energy, and used a multi-channel detector (MCD). Each cellulose sample had a measurement taken in two different locations for comparison purposes. The published binding energies, summarized in Table 2 were used to interpret the results [14].

4.3 Results

Laminates were prepared by pressing PVAm treated wet cellulose films together and allowing them to dry at room temperature. The laminates were re-wetted in neutral 1 mM NaCl and the delamination peel forces were measured. Figure 12 shows the delamination force as a function of oxidation time for two series of cellulose oxidation experiments, one at 4 °C and the other at 23 °C. Each point represents the average of four delamination experiments with the error bars representing the standard error. The average peel force of laminates made from cellulose that was never oxidized is 3.5N/m, which is very low. Both series showed a sharp increase from this initial value to a maximum of 32-35N/m. At 4°C, the average peel force passed through a maximum of 35N/m at 45min to a stable value of approximately 27.5N/m for all times after 60min. For oxidation at 23°C the average peel force reached a maximum of 32N/m for all times longer than 5min. At oxidation times longer than 40min all of the laminates ripped within the top layer of the cellulose films, indicating catastrophic cohesive failure of the cellulose. While these curves do not allow for a direct comparison due to a difference in polymer application they show that the most important feature in the enhancement of wet adhesion is the combination of oxidation temperature and time.

X-ray Photoelectron Spectroscopy (XPS) was used to characterize the cellulose films oxidized at room temperature. Figure 13 illustrates the theoretical changes in the carbon and oxygen oxidation states when the anhydroglucose C6 repeat unit of cellulose is oxidized to give an aldehyde and then a carboxyl. Based on the literature, we assume that only the primary hydroxyl is reacting [15]. The right hand structure in Figure 13 shows a hemiacetal linkage which will form when a neighboring alcohol couples with the primary aldehyde. The labels beside each carbon and oxygen denote the oxidation states, and the number of atoms in each oxidation state are tabulated below the structures.

The theoretical O/C ratio for pure cellulose is 0.83 (5/6) and will not change when the primary alcohol is converted to an aldehyde. If the oxidation proceeds to the formation of a carboxyl group, the O/C ratio will change to 1. High resolution analysis reveals more details. For example, oxidation to give a primary aldehyde will increase the ratio of C3/C2 from 0.20 to 0.50 and subsequent conversion to the primary carboxyl will change the ratio of C4/C2 from 0 to 0.25. The C1 content of cellulose and its oxidation products should be zero; however, this was not the case.

The washed, untreated cellulose films were analyzed by XPS and the O/C ratio was 0.65 at a 45° analyzer angle. This is significantly lower than the theoretical values of 0.83. High resolution scans on the carbon peak show that approximately 10% of the peak area was C1. The lower than expected oxygen content and the presence of C1 in all samples are most probably caused by alkane contamination. The scanning depth of the materials was varied by changing the incidence angle of the sample, and the corresponding O/C ratios are shown seen in Figure 14. For never-oxidized cellulose, the content of C1 was 25% of all atoms at 5°, dropping to approximately 10% at 45° and 90°. Therefore contamination was higher near to the surface, but was also present up to the maximum depth of the XPS instrument (i.e. 10nm at 90°). Subtracting the C1 from the total carbon and using this correction gives an O/(C-C1) ratio of 0.85 at an analyzer angle of 5°. This is close to the theoretical value of 0.83. At larger angles the value of O/(C-C1) decreases to approximately 0.80. We do not know the source of the contamination; however, both the XPS and the adhesion results were reproducible so the C1 was treated as a constant background.

Figure 15 shows the relationships between the wet adhesion strengths of the laminates (Figure 12, 23°C oxidation) and various atomic ratios for data collected at an analyzer angle of 45°. The left hand data shows adhesion versus C4/C2 ratio which is an indicator of carboxyl group formation. The analysis in Figure 13 predicts that for pure cellulose C4/C2 = 0, whereas C4/C2 = 0.25 when all the primary alcohol groups are converted to carboxyls. The maximum experimental C4/C2 was 0.07, only 30% of the 0.25 theoretical maximum. Although adhesion increased monotonically with C4/C2 ratio, the wet adhesion is rather insensitive to carboxyl content. Over the final three data points, adhesion increased by 150% whereas, within experimental uncertainty, the C4/C2 ratio was constant.

The next (2nd leftmost) data set in Figure 15 is the C3/C2 ratio which theoretically is equal to 0.2 for pure cellulose and 0.5 if the primary alcohol is converted to aldehyde (see Figure 13). Complete oxidation to a carboxylate gives C3/C2 = 0.25. Finally reaction of the aldehyde with a neighboring hydroxyl to give a hemiacetal also gives C3/C2 = 0.5. The experimental C3/C2 ratios varied from 0.22 to 0.32 suggesting that, at most, 40% of the primary alcohols were converted to aldehyde and/or hemiacetal groups. Except for one outlier, the laminate strength showed a strong positive correlation with C3/C2.

The oxygen ratio O2/O1 also shows a strong correlation with adhesion (Figure 15). The analysis in Figure 13 shows that O2/O1 = 0.66 for pure cellulose, = 1 for the aldehyde, = 1.5 for the acid and 1.5 for the hemiacetal which forms when the aldehyde couples to a neighboring alcohol. However, the

experimental range of O₂/O₁ ratios was only 0.28 to 0.60 which is much less than the theoretical maximum of 1.5

Finally the overall O/C ratio changed little over the range of adhesion measurements. The analysis in Figure 13 indicates that the O/C ratio should not change when the primary alcohol is converted to the corresponding aldehyde or hemiacetal. To summarize, the XPS results are consistent with the hypothesis that adhesion increases with the aldehyde/hemiacetal content of the cellulose, whereas carboxyl groups appear unimportant for wet adhesion. Unfortunately, we could not obtain unequivocal surface functional group concentrations from the high resolution XPS analysis.

The results of the ATR-FTIR measurements are found in Figure 16. A series of cellulose samples ranging from untreated cellulose to 60min of oxidation time at 23°C was scanned between 900cm⁻¹ to 4000cm⁻¹. Each spectra was normalized by dividing by the intensity at 2900cm⁻¹ which corresponds to CH stretching and should not change during the reaction [16]. For the generation of oxidation products we would expect a change in the 1600-1800cm⁻¹ range which corresponds to carbonyl vibrations. The peak at 1645cm⁻¹ can be attributed to carboxylate ions (COO⁻) but could also be a result of adsorbed bound water. Nevertheless, this region does not change appreciably with oxidation time. In fact all spectra appear to be identical, indicating that there is no significant change in the cellulose within the whole 2.38µm thickness.

Scanning electron microscopy (SEM) was used to characterize the cellulose films before and after oxidation. In this series of experiments the oxidations were conducted at 4 °C to minimize side reactions [9]. This was done so that only oxidation effects on the cellulose surface microstructure would be seen. Figure 17 shows images of the 4°C series of dry cellulose samples at times of 0, 10, 30, and 120 minutes of oxidation. All the images displayed a corrugated microstructure with no obvious change between the non-oxidized and the oxidized cellulose.

Images were also taken of the peeled surfaces – see Figure 18. For all oxidized samples the peeled surfaces show blistering and thin film delamination, which indicate a mixed mode of failure. The unoxidized sample showed no blistering indicating an interfacial mode of failure. The dried PVAm film thickness was 7nm on average, based on the coverage and polymer density. However, there is no contrast between the cellulose and PVAm, thus we cannot distinguish PVAm from cellulose in these

images. Finally, within each sample there is a large variation in the fracture pattern. In some regions the surface appears to remain intact, while in other regions large amounts of material have been separated from the bulk (Figure 18b).

In order to obtain a better picture of the wet cellulose structure, untreated cellulose film and room temperature oxidized cellulose film (120min) were frozen quickly using liquid nitrogen. Both samples had the same wetting/drying history. The ice was then sublimed in a vacuum chamber and the surface was Pt sputtered. Since the membranes were frozen and sublimed, these structures are representative of the swollen surface of the regenerated cellulose membranes. These images are shown in Figure 19 where **a-c** is the unoxidized cellulose and **d-f** is the oxidized cellulose. The frozen samples appear to be heterogeneous, with some regions identical to the dried samples and others possessing distinct features, such as fibrillation and porosity. In contrast to the dried cellulose surfaces, which showed very little change with the oxidation time, the frozen surfaces showed a slight difference between the two conditions. The untreated cellulose appears to contain more topological features than the oxidized cellulose, but could not be quantified.

The main conclusion from the electron microscopy is that the regenerated cellulose films were complex, fibrillated structures showing some indication of cohesive failure, such as blistering and peeling.

4.4 Discussion

In previous publications we have reported that mild TEMPO-NaBr-NaClO oxidation of regenerated cellulose films increased wet adhesion when two wet cellulose films were laminated together with a very thin layer of polyvinylamine [6], polylysine [5], or with a variety of proteins[17]. Our oxidation conditions were based Isogai's work, wherein they reported that wet paper strength is enhanced by mild oxidation of the cellulose pulp fibers [18]. The goal of the work summarized herein was to determine which functional groups produced by the oxidation contribute to enhanced wet adhesion.

The use of TEMPO-NaBr-NaClO to modify primary hydroxyls on cellulose [19-22] and related carbohydrates [15, 23] has been reported since the mid nineties. Most of the early work was aimed at quantitatively converting primary hydroxyls to carboxylic acids, while minimizing side reactions and chain degradation. In the case of regenerated cellulose, complete primary hydroxyl conversion gives a water soluble polyuronic acid [24]. Thus, for paper applications, TEMPO mediated oxidation must be

restricted to low conversions to conserve fiber mechanical properties – this approach was proposed first in the scientific literature by Isogai's group [7].

High conversion TEMPO oxidation gives carboxyl groups in a multi-step process in which the corresponding aldehydes are an intermediate. Kinetic analysis revealed that aldehyde conversion to acid is faster than the initial alcohol to aldehyde step [25] and that the overall activation energy is about 66.2 kJ/mol [26]. The patent application by Cimecioglu and Thomaides [27] describes mild TEMPO-NaBr-NaClO oxidations to maximize aldehyde contents in starch and other soluble carbohydrates. They reported typically 5 to 10 mole% conversion to aldehyde with usually 2 to 5 mole% of the corresponding acid. Note, they measured aldehyde concentration by hydroxylamine hydrochloride titration, which measures the acid generated when the oxime is formed ($\text{RCHO} + \text{NH}_2\text{OH} \cdot \text{HCl} \rightarrow \text{RCHNOH} + \text{HCl}$). We believe that this method measures both primary aldehyde groups and the corresponding hemiacetals (see Figure 13 for structures). Thus, based on the literature, our lightly oxidized cellulose surfaces should contain a mixture of carboxyl groups and aldehydes + hemiacetals. The contribution of each of these functional groups to wet adhesion is now discussed.

The role of fiber carboxymethylation on the wet strength of paper has been reported by a number of authors. Using soluble carboxymethyl cellulose as a model, Espy and Rave [28] showed that PAE forms covalent bonds with carboxyl groups. Wågberg and Bjorklund [29] showed that carboxymethylated fibers could adsorb more cationic PAE resin than untreated fibers. In addition, they showed that for a fixed sheet density and PAE content, wet strength increased with carboxymethylation. They explained this by proposing covalent bond formation between PAE resin and carboxyl groups on the fiber surfaces. The analogous reaction in our work is the condensation of a primary amine with a carboxyl to form an amide. Amide formation generally requires temperatures greater than 150 °C to produce a significant yield of amide, and usually occurs under conditions in which free water is removed [30]. However, amide formation at moderate temperatures (70–100°C) in dilute aqueous solution has been reported [31].

Because our laminates were dried at room temperature in 50% relative humidity, it seems unlikely that amide formation was significant in this work. The XPS results in Figure 15 show that the adhesion increased by 150% with oxidation, whereas the carboxyl content was relatively constant. Therefore we

conclude that TEMPO-NaBr-NaClO induced carboxyl groups are not responsible for enhancing wet adhesion with PVAm.

It has been long known that aldehyde containing polymers and small molecules [32, 33] increase the wet adhesion between cellulose fibers in paper. Aldehydes react with alcohols to give hemiacetals and acetals (see Scheme 1) and with amines to give imines and amins.

There are commercial examples of aldehyde-containing polymers in paper manufacturing applications. Glyoxylated polyacrylamide and dialdehyde starches are known to give temporary wet strength in paper products [4]. However, aldehyde-containing polymers do not have long term stability since aldehyde groups readily oxidize to acids or undergo side reactions such as the base catalyzed aldol condensation reaction. One approach to stabilizing aldehydes is to have them present as acetals which are stable in neutral pH, for example, acetal containing starches [34] and polyacrylamide copolymers [35]. The corresponding aldehydes are regenerated by lowering the pH to 3 [36].

Our FTIR results (Figure 16) showed no evidence of aldehyde groups on the oxidized cellulose surface. The inability to detect aldehydes on carbohydrates has been reported before. For example, Varma et al. [37] could not detect the aldehydes on dialdehyde guar. The explanation is that the aldehydes are converted to hemiacetals by reaction with neighboring alcohol groups on cellulose. Furthermore, the hemiacetals are difficult to detect in a carbohydrate such as cellulose [38]. Nevertheless, the results in Figure 15 show a positive correlation between wet adhesion and C3/C2, a measure of the combined aldehyde and hemiacetal content. These hemiacetal groups serve to crosslink the cellulose film, strengthening the surface near the cellulose/PVAm/cellulose joint. Furthermore, since primary amines are stronger nucleophiles than alcohol groups, we propose that amine groups can displace the alcohol to give imine and amination linkages, making the laminate more resistant to water. We do not know which mechanism is more important – hemiacetal strengthening of the cellulose vs. coupling with PVAm. However, we have observed that TEMPO-NaBr-NaClO oxidation improves wet adhesion with virtually every polymer and protein we have measured. Furthermore, Isogai recently reported that mild TEMPO-NaBr-NaClO oxidation of pulp fibers improves wet strength with unreactive cationic polyacrylamide. Perhaps the widespread utility of mild TEMPO-NaBr-NaClO for increased performance of wet adhesives, irrespective of the polymer structure, results from hemiacetal reinforcement of the weak cellulose substrate.

4.5 Conclusions

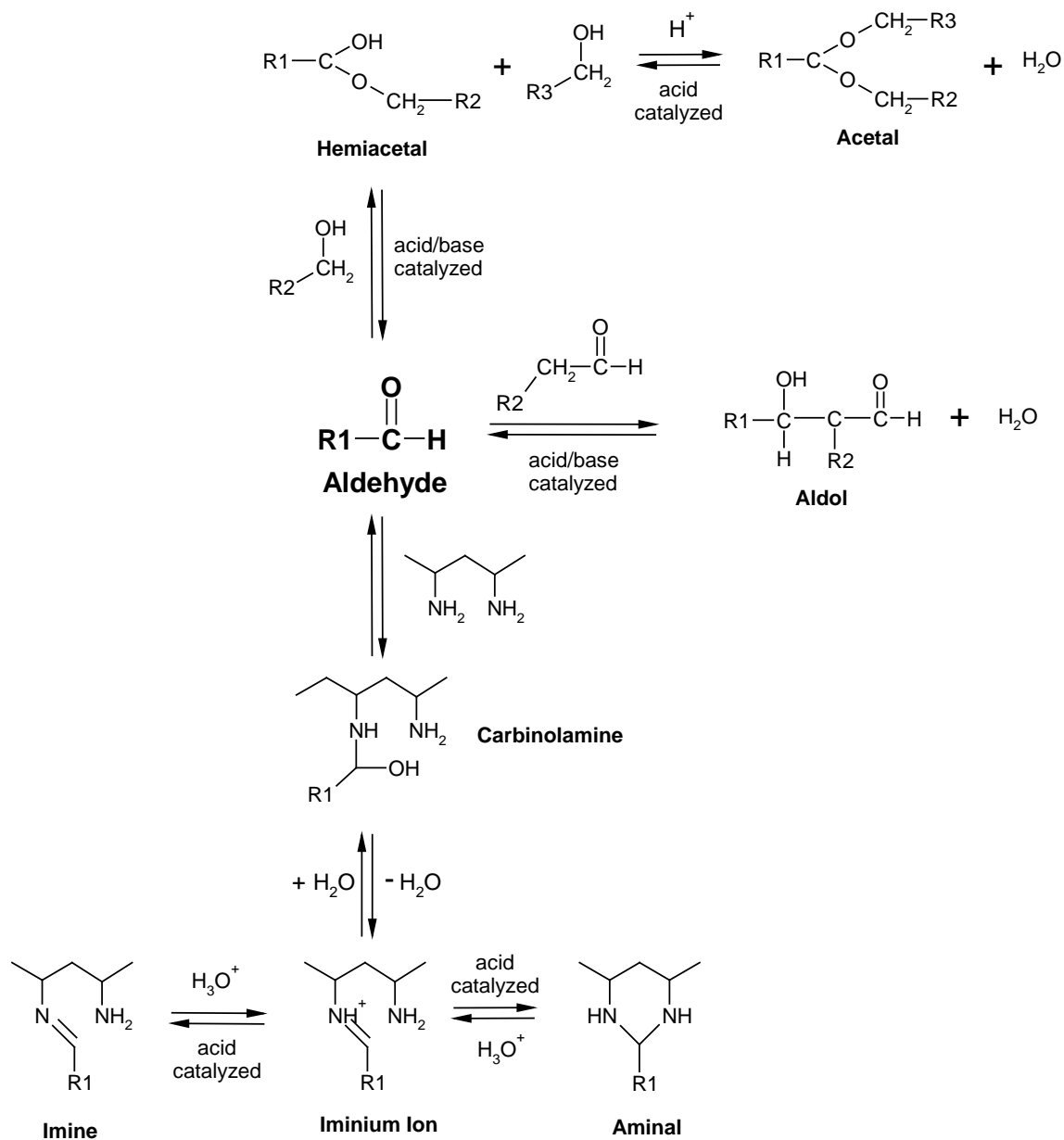
1. Aldehydes produced by the TEMPO catalyzed oxidation of regenerated cellulose film are primarily present as hemiacetal groups formed by the interaction of primary aldehydes with alcohol groups on neighboring cellulose chains.
2. There is a linear correlation between the wet adhesion and the combined concentration of aldehyde and hemiacetal groups.
3. The hemiacetals serve as crosslinks strengthening the cellulose surface and as sites for subsequent covalent coupling to PVAm and other amine-containing polymers. The ability of TEMPO catalyzed oxidation to improve wet adhesion with a wide range of polymers suggests that cellulose crosslinking may be more important than covalent coupling to PVAm.
4. Laminate wet adhesion was virtually independent of the concentration of carboxyl groups which are also produced by TEMPO mediated oxidation.
5. Extended TEMPO catalyzed oxidation weakens the cellulose films giving cohesive failure within the film during peel delamination.

4.6 Tables

Table 2 – Designation of atomic binding states measured by high-resolution XPS [14].

	<i>C1</i>	<i>C2</i>	<i>C3</i>	<i>C4</i>	<i>O1</i>	<i>O2</i>	<i>O3</i>
Oxidation State	<i>C-H,</i> <i>C-C</i>	<i>C-OH,</i> <i>C-O-C</i>	<i>O-C-O,</i> <i>C=O</i>	<i>O=C-O</i>	<i>C-OH</i>	<i>O-C-O</i>	<i>C=O</i>
Binding Energy (eV)	<i>284.8</i>	<i>286.7</i>	<i>288.1</i>	<i>289.5</i>	<i>532.9</i>	<i>533.5</i>	<i>531.2</i>

4.7 Schemes



Scheme 1 Reactions of aldehyde groups with alcohol and amines

4.8 Figures

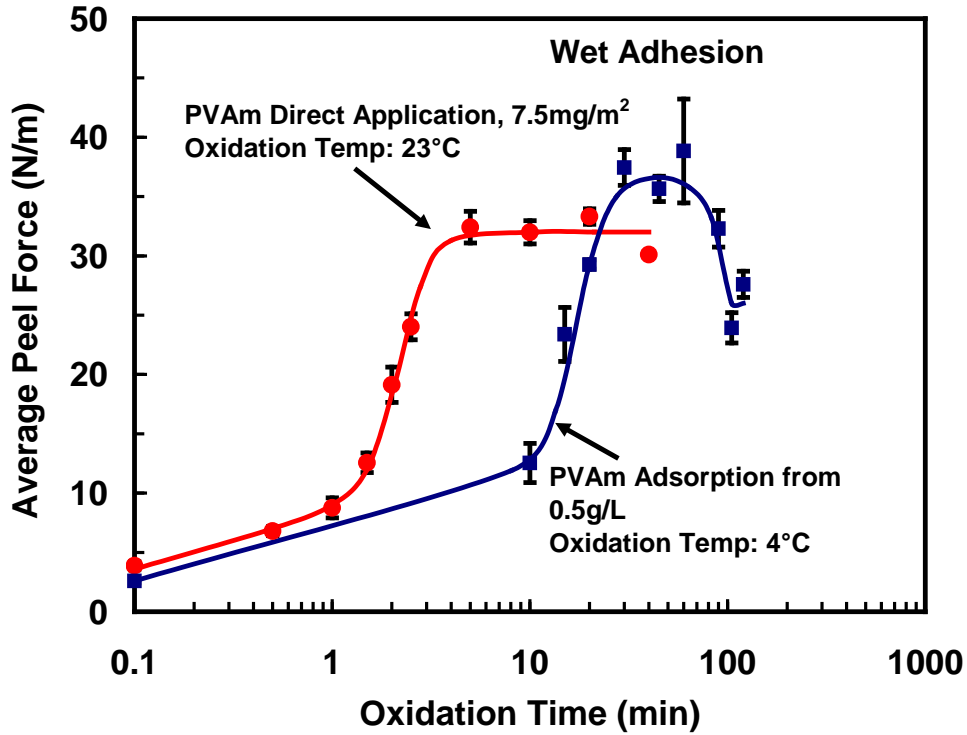


Figure 12 The influence of cellulose oxidation time on the 90 degree delamination force for wet cellulose/PVAm/cellulose laminates. 0.1 mM NaCl at pH 7 was used for both PVAm treatment and for re-wetting of the laminates for adhesion testing.

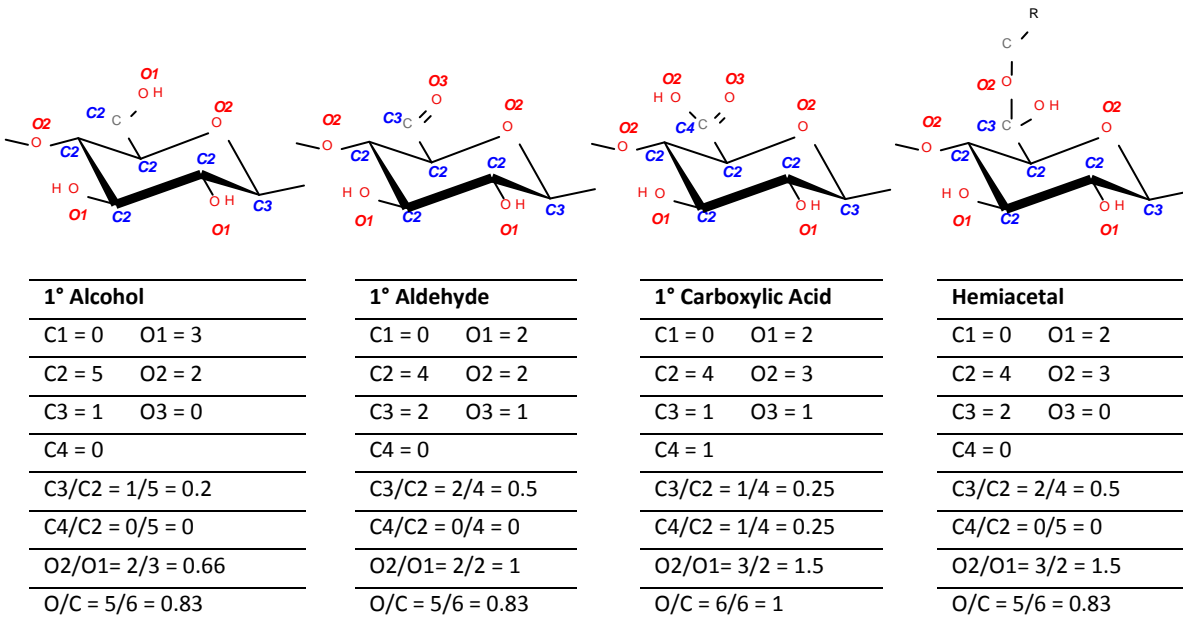


Figure 13 The oxidation states of carbon and oxygen in anhydroglucose and its derivatives. The hemiacetal structure is formed by the attack of a neighbouring alcohol (R-OH). The tabulated atomic ratios were used to interpret the XPS data.

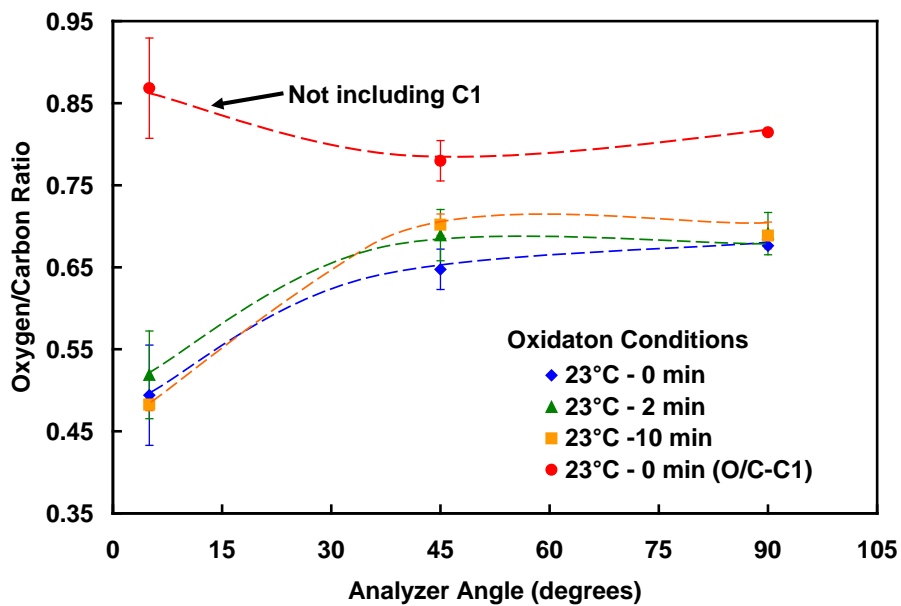


Figure 14 Oxygen/carbon ratio as function of analyzer angle. The cellulose films were oxidized at 23 °C.

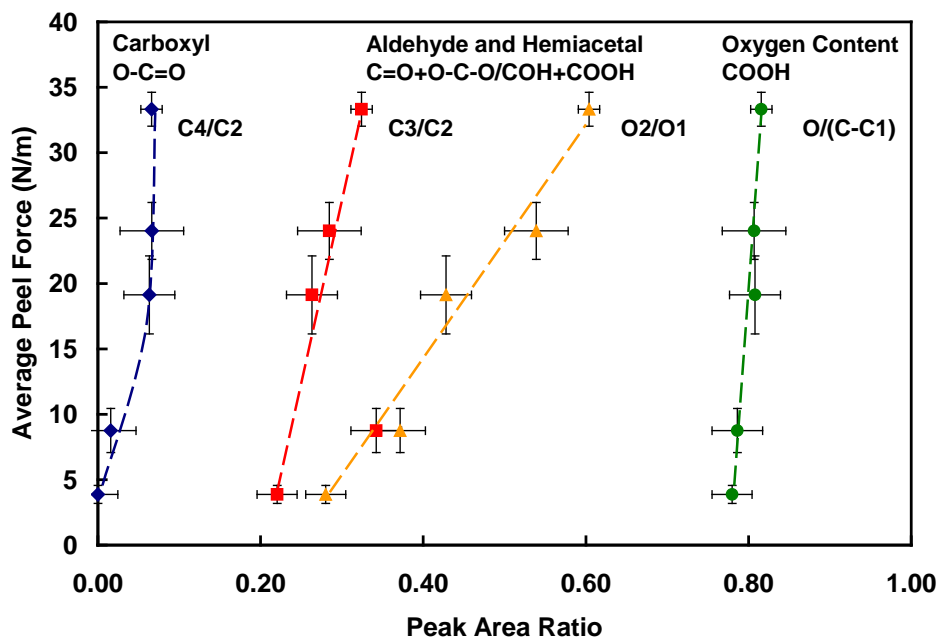


Figure 15 Correlation of average peel force with the various carbon oxidation state ratios as determined by a fit of the high resolution XPS data taken at an analyzer angle of 45°. The cellulose was oxidized at 23 °C.

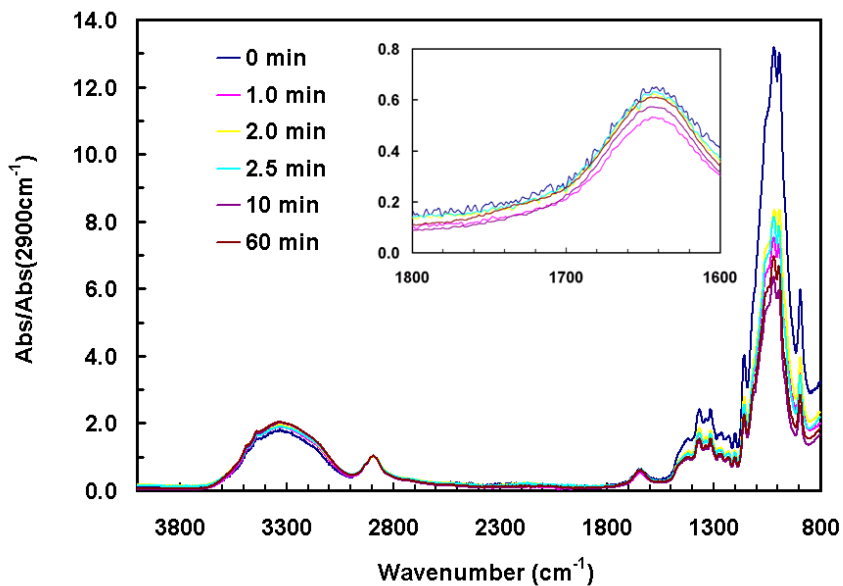


Figure 16 ATR-FTIR spectra of cellulose oxidized at 23°C for various times. The absorbance is normalized by dividing each spectra by the 2900cm⁻¹ peak.

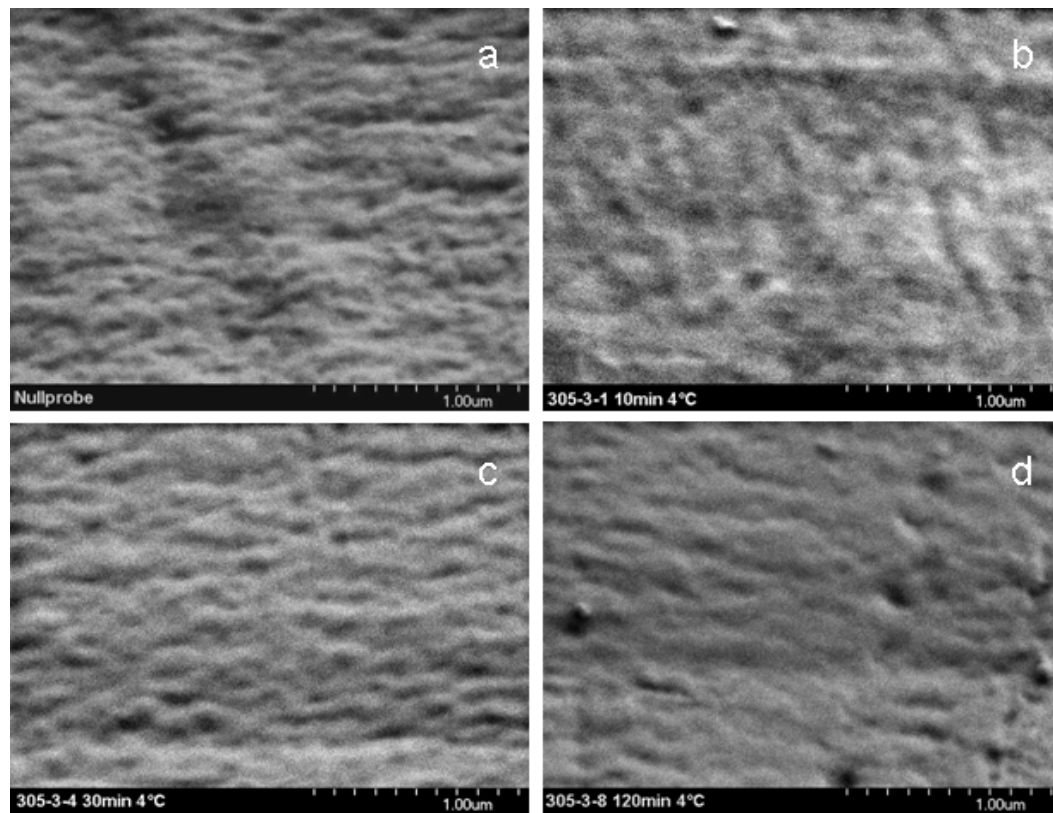


Figure 17 SEM images of dried cellulose films oxidized at 4°C. The images, taken approximately 2 months after the oxidation reactions, are: a) untreated cellulose, b) 10min oxidized, c) 30min oxidized, and d) 120min oxidized. All images are at the same magnification.

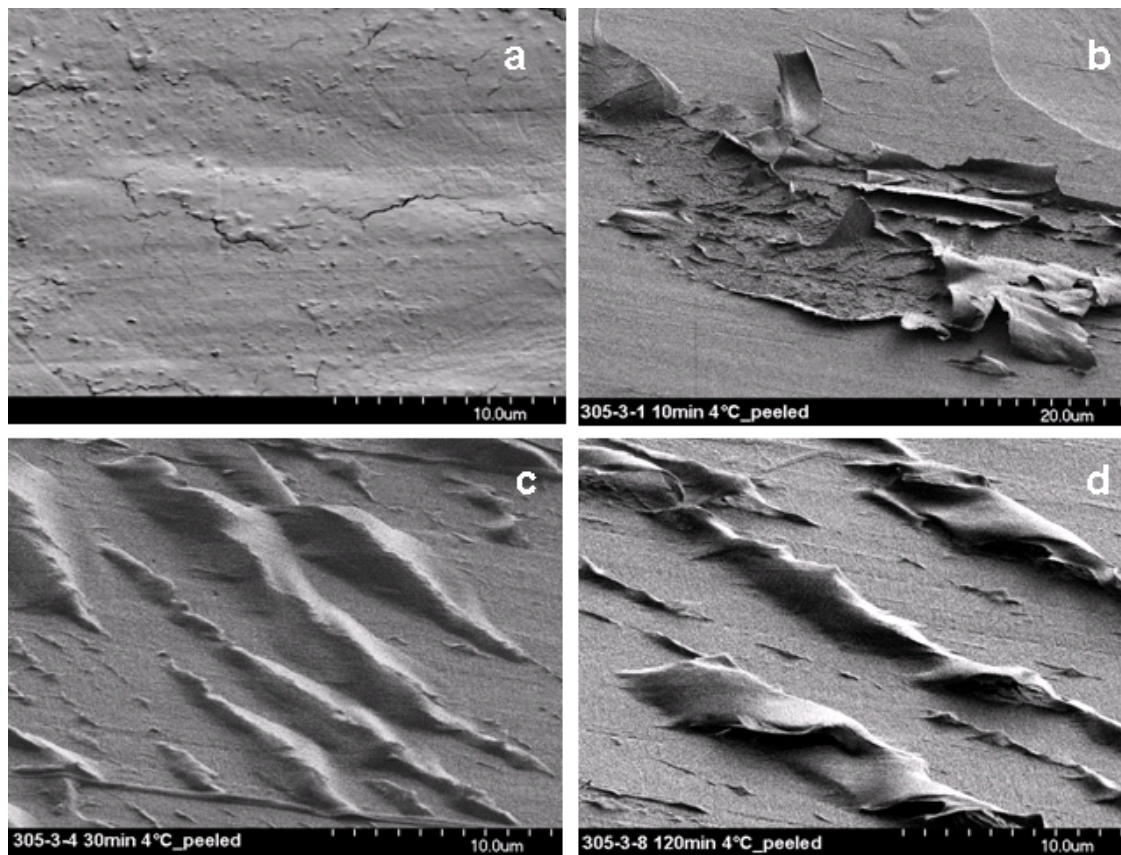


Figure 18 SEM images of cellulose membrane surfaces after delamination. The cellulose membranes were oxidized at 4°C before application of PVAm via adsorption. The oxidation times were a) 0min b) 10min, c) 30min, and d) 120min.

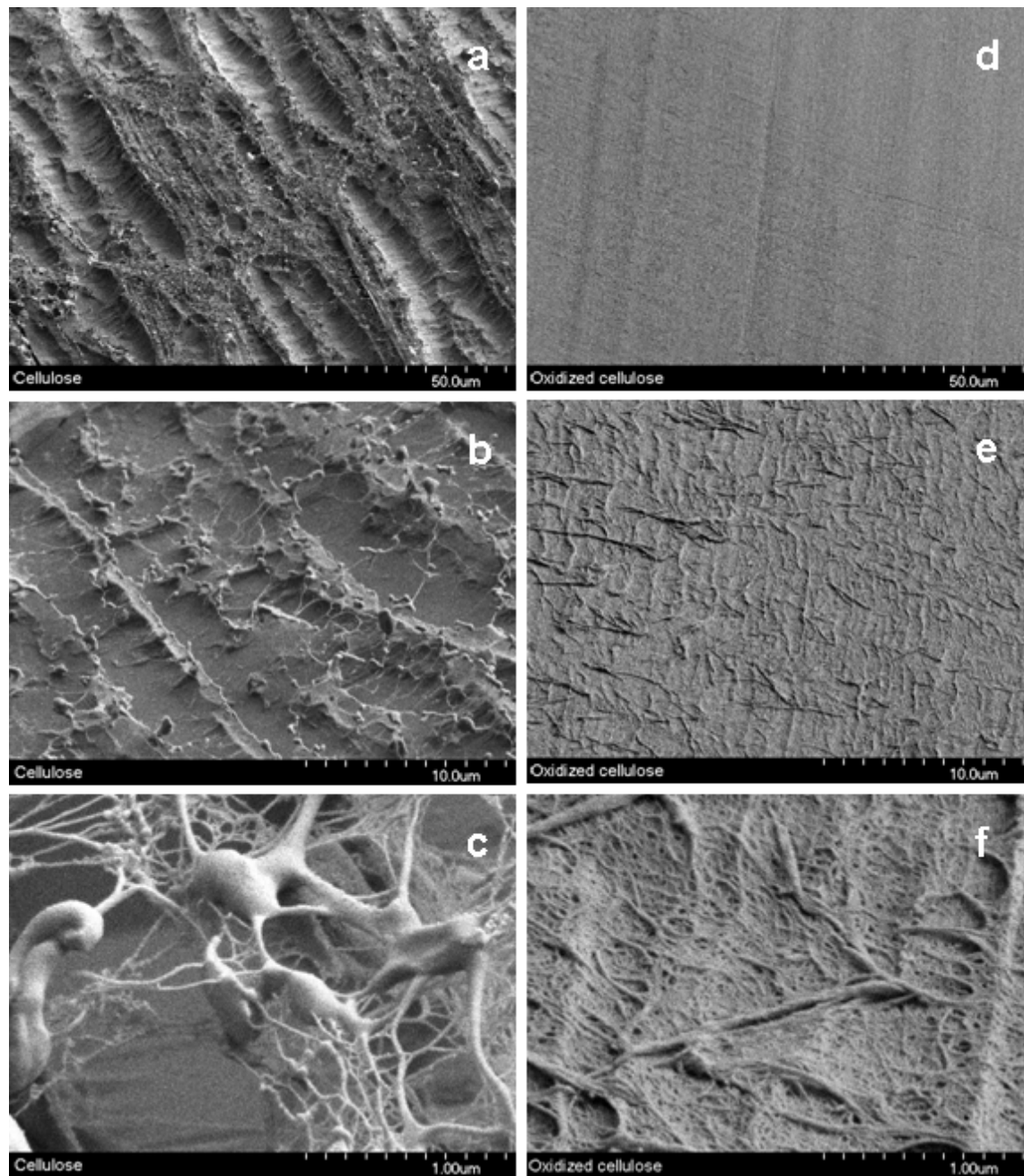


Figure 19 Cryo-SEM images of cellulose frozen from the wet state before (a-b-c) and after (d-e-f) TEMPO-oxidation.

4.9 References

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Chapter 5 Chemical Modification of Cellulose for Enhanced Wet Adhesion

5.1 Introduction

The current polymers that are commonly used in enhancing wet strength of paper rely upon the formation of covalent bonds between reactive amino functional groups. Much of the focus on the improvement of paper wet-strength has been on the design of wet-strength resins and the method of resin application in the papermaking process [1]. The most innovative new approach for application is the layer-by-layer assembly of polymers on fibre surfaces first described by Wågberg [2].

Compared to the significant efforts to wet-strength resin properties to improve wet adhesion between cellulose surfaces, there have been few recent investigations into the possibility of engineering fibre surfaces for enhanced wet strength performance with or without wet-strength polymers. Fibre oxidation to introduce aldehydes is the most common approach [3-10]. However improved wet strength through amino acid derivatization [11] and dielectric barrier discharge [12-14] have recently been described.

The key to chemically altering cellulose is to adjust the surface properties while retaining the desirable bulk properties. For example in improving the hydrophobicity of cellulose fibres by etherification/esterification for use in polymeric composite materials the original structure of the cellulose was preserved [15]. Silane addition to fibres are less likely to alter the bulk physical properties of cellulose but rather form a cross-linked surface coating [16, 17]. Alternately the use of biological molecules is finding fashion for the purpose of modifying cellulose. Triglycerides have been employed to increase the hydrophobicity of cellulose fibres using the etherification/esterification processes [18]. There are biological analogues to the silane surface coverage such as the adsorption onto cellulose of modified xyloglucans [19].

The wet cellulose delamination test, developed in this work provided a unique opportunity to explore the linkages between cellulose surface chemical modification and wet adhesion. The results of an introductory study are now presented.

5.2 Experimental

5.2.1 Materials

Polyvinylamine, PVAm, was supplied by BASF (Aktiengesellschaft, Germany) as hydrolyzed poly(N-vinylformamide). The molecular weight was given as 950kDa with a degree of hydrolysis of 90.5% and an charge density of 13.20meq/g [20]. Regenerated cellulose membranes were purchased as dialysis membranes from Spectrum Laboratories Inc. (Spectra/Por[®] 4 product No:132709 12kDa MWCO). All other chemicals used were supplied by Sigma and are listed in Table 3.

5.2.2 Wet Delamination Testing

Details of the experimental procedure for measuring wet adhesion forces are explained in Chapter 2. PVAm8 (150kDa, >98%DH) was applied using the direct method, at an application of 15 μ L of a 0.5g/L solution.

5.2.3 Anhydride modification

1g of cellulose and 1mL of triethylamine catalyst were added to 200mL of pyridine. To this mixture 8.0mmol of succinic anhydride was then added dropwise and allowed to react under mild stirring and a nitrogen blanket for 18 hours. The cellulose was then removed from the pyridine and rinsed with ethanol to remove excess anhydride followed by soxhlet extraction in acetone [21].

5.2.4 Acid Halide modification

Cellulose was added to pyridine (1g/200mL) which was heated to 80°C and kept under a constant nitrogen atmosphere. To this mixture, 2mL of the pure acid halide, or 25mL of a 0.5wt% 4-toluene sulfonyl chloride in pyridine, was added slowly and then allowed to react for 2 hours. After this the cellulose was rinsed with 80wt% ethanol(aq) and then cleaned by Soxhlet extraction with methanol for 24 hours. The cellulose was then suspended in water prior to adhesion testing.

5.2.5 Silane modification

A solution of 500 μ L of 3-glycidoxypropyltrimethoxysilane in 10mL of aqueous ethanol solution (80% v/v) was prepared and allowed to stand for 2 hours. Approximately 1g of cellulose was suspended in

100mL of an aqueous ethanol solution (80% v/v) and to this 1mL of the silane solution was added. The combined cellulose suspension was then stirred for 2hrs after which the cellulose was removed and dried at room temperature for 24hrs. After this the cellulose was then heated to 120°C under a nitrogen gas atmosphere for 2 hours. The cellulose was then suspended in water prior to use for adhesion testing.

5.2.6 Contact Angle

Decane contact angle in water was measured using a Kruss Drop Shape Analyzer (DSA v1.50), in an inverted glass cell. To ensure that no dynamic wetting processes occurred the contact angle was measured repeatedly until the values were constant for 5 minutes.

5.3 Results

Cleaned, regenerated cellulose films were derivatized with various chemicals and Table 1 summarizes the various cellulose film treatments. The concentration of the grafted groups on the surface was not measured. The wet delamination force of regenerated cellulose and regenerated cellulose modified with aromatic functional groups are shown in Figure 21. The regenerated cellulose gave a delamination force of $3.8 \pm 0.1 \text{ N/m}$. Note that these adhesion forces are low because the cellulose films were not oxidized.

Modification with benzoyl chloride led to a reduction of delamination force to $1.3 \pm 0.5 \text{ N/m}$ however modification using 4-tert butyl benzoyl chloride resulted in an overall increase to $5.6 \pm 1.5 \text{ N/m}$. The use of naphthoyl chloride gave laminates that did not adhere enough to prevent spontaneous separation during handling.

The modification of cellulose using various hydrophobic molecules and the resultant wet delamination force using PVAm is seen in Figure 22. The trimethyl modification increased the wet delamination force from $3.8 \pm 0.1 \text{ N/m}$ to 9.5 ± 0.9 which corresponds to the use of tert-butyl phenyl group mentioned above. Straight chain alkanes produced two different results as the 9 length carbon reduced wet delamination force to $1.3 \pm 0.1 \text{ N/m}$ while a 13 length carbon chain gave an increase to $9.3 \pm 0.8 \text{ N/m}$. It should be noted that the concentration of the two modifications were not identical. The fluorine containing butyl group reduced the adhesion to non-measurable levels.

Figure 23 shows the effect of polar groups on the wet delamination force. The reaction of succinic anhydride at the surface of cellulose gave an increase from the untreated regenerated cellulose to a value of $8.9 \pm 1.3 \text{ N/m}$. Acetic anhydride modified cellulose gave a decrease in the delamination force to $2.4 \pm 1.0 \text{ N/m}$. This is expected since the acetic anhydride results in an ester bound methyl group while succinic anhydride would result in an ester bound pendent carboxyl group which has the possibility to react with PVAm. The modification to carboxymethylcellulose (CMC) produced cellulose with a slippery feel and gave laminates with a reduced delamination force of $2.8 \pm 0.5 \text{ N/m}$. It is likely that the modification resulted in a soluble layer of CMC which failed easily during testing.

The contact angle of water at the decene/water/cellulose interface for the different modified cellulose materials, was taken and the results compared to the delamination force. This is shown in Figure 24. The delamination force was proportional to the water contact angle, with forces decreasing with increasing contact angle. At the maximum contact angle the laminate made with this modification (Tosyl cellulose) would spontaneously fall apart yielding a zero value.

Figure 25 shows the effect of including an epoxy silane onto the surface of the cellulose and the resultant wet delamination with PVAm. When the PVAm was applied at pH 7 the delamination force was $28.0 \pm 3.1 \text{ N/m}$, which is comparable to delamination forces of oxidized cellulose. To promote the reaction of the epoxide with the amine the PVAm was applied at pH 11 the delamination force was $50.2 \pm 3.0 \text{ N/m}$. At basic pH the epoxide ring opening is catalyzed and the deprotonated amines are nucleophilic.

5.4 Discussion

The strong adhesion observed between PVAm and oxidized cellulose is dependent on the formation of covalent bonds as demonstrated in the previous chapter. A covalent bond is 10-20 times greater in strength than a hydrogen bond and thus only a relative few need bonds to be formed to enhance adhesion. With the exception of the reducing end, pure cellulose has very few reactive sites. Introducing highly reactive groups onto the surface of cellulose is therefore a sound strategy for increasing the wet strength with PVAm. Preferably the reactive group should be a source of electrophilic carbon since the primary amine is a good nucleophile.

Epoxydes are highly reactive functional groups that can react with the cellulose and the PVAm according to Schemes 1 and 2. The actual reaction product of the epoxy silane with the cellulose is expected to be complex, but based on the delamination forces observed and their dependence on pH, the epoxide groups are available for bonding to the PVAm and cellulose. It is important to note that the proposed siloxane bond to the cellulose is easily hydrolyzed and that the silane is more likely to bond to other silanol groups [22]. Even with the possibility for hydrolysis the adhesive interphase region may be inaccessible to water and therefore retain its strength.

Electrostatic interactions are expected to provide some contribution to the wet strength development of PVAm to oxidized cellulose, however, the poor performance of the carboxylated cellulose suggests electrostatic effects may be small. Our limited data set and lack of surface characterization means it is difficult to form solid conclusions about the contributions of surface carboxyl groups.

The contact angle results in Figure 5 suggests that hydrophobic patches on cellulose surfaces do not promote wet adhesion with PVAm on cellulose. However, it may be worthwhile to consider the interactions of the hydrophobically modified surfaces with hydrophobically modified PVAm [23].

5.5 Conclusions

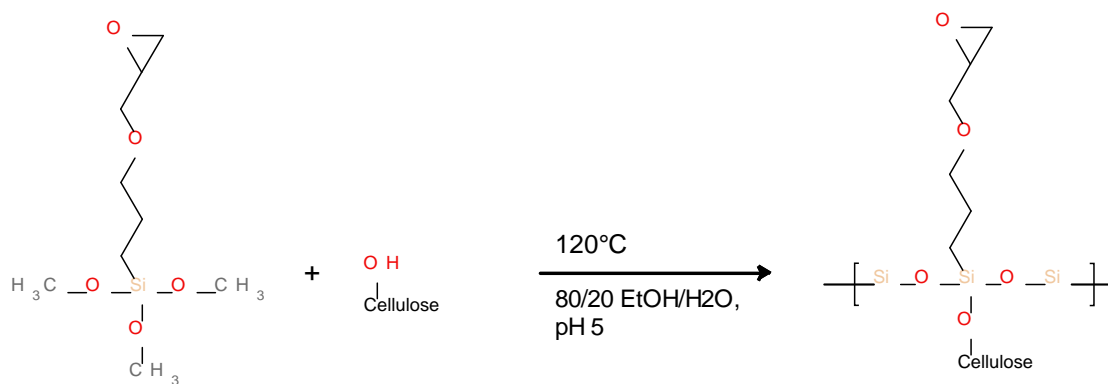
1. The best strategy for improving wet adhesion with PVAm is to introduce functionalities that can form covalent bonds.
2. Adsorption of epoxy silane gives strength comparable to oxidized cellulose at neutral pH and superior adhesion at elevated pH.
3. The introduction of carboxyl groups onto cellulose does not significantly improve wet adhesion over the blank cellulose at the same PVAm coverage.
4. The delamination force decreases with increasing water contact angle against decane on wet cellulose, indicating that wet adhesion is not promoted by hydrophobic domains on the cellulose surface.

5.6 Tables

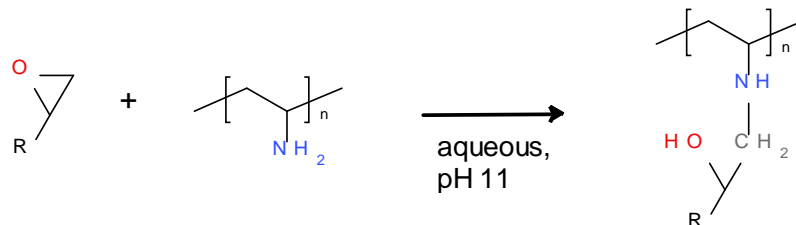
Table 3. Summary of the various cellulose film treatments.

Modifying Agent	ID	Treatment Dosage(moles/g cellulose)
Blank (none)	RC	
Benzoyl chloride	B	17.2
4-tert butyl benzoyl chloride	4tb-B	11.0
1-naphthoyl chloride	N	13.3
Trimethylacetyl chloride	3Me	16.3
Dodecanoyl chloride	C-9	9.1
Myristoyl chloride	C-13	7.4
Perfluorobutyryl chloride	FC-3	13.4
Succinic Anhydride	SA	8.0
Acetic Anhydride	AA	7.8
4-toluenesulfonyl chloride	TC	
Epoxy silane (pH 7)	E	
Epoxy silane (pH 11)	E(11)	

5.7 Schemes



Scheme 2. Reaction of silane coupling agent with cellulose surface hydroxyl groups and other silane molecules. This schematic does not represent the true nature at the cellulose surface as it is equally possible that most of the original silane molecules react with other silanes to form a cross-linked adsorbed layer on the cellulose.



Scheme 3. Reaction of an epoxide with the primary amine on a PVAm molecule at pH 11. This is the expected reaction between the PVAm and the epoxy silane adsorbed onto the cellulose surface.

5.8 Figures

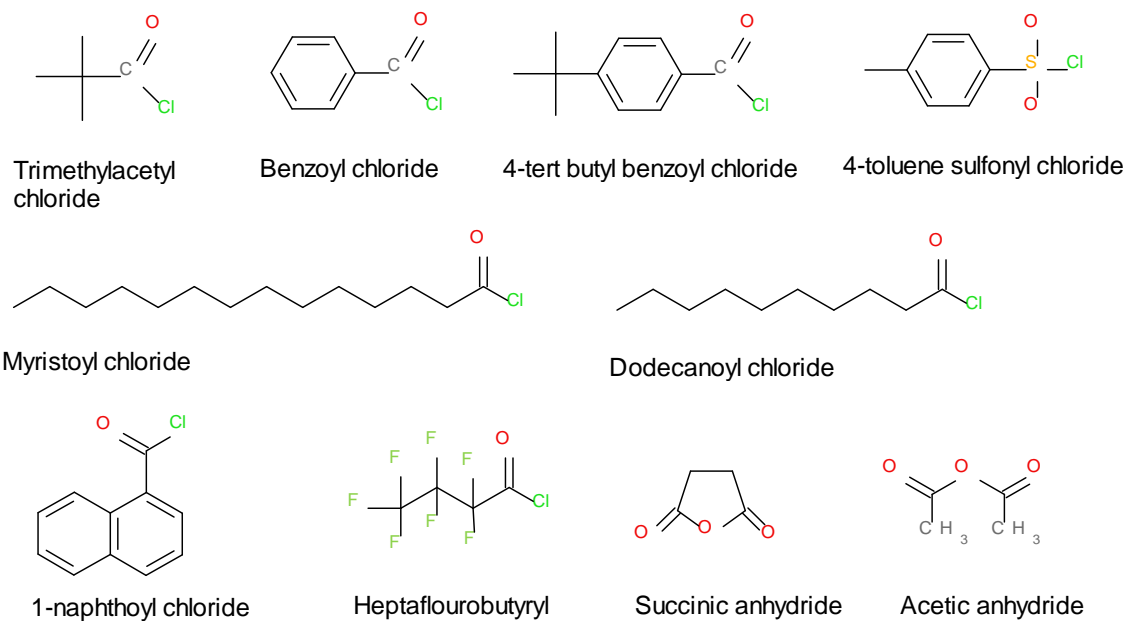


Figure 20. Structures of the chemical used to modify cellulose.

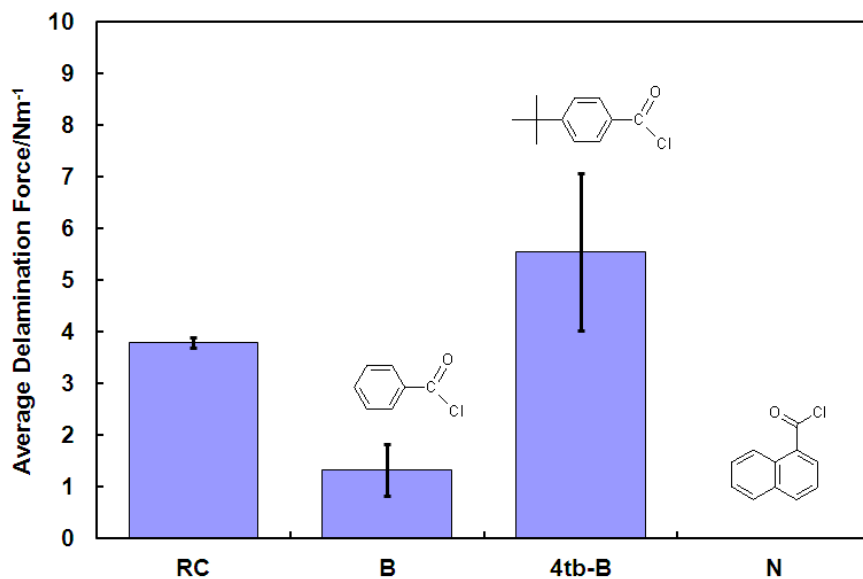


Figure 21. The influence of aromatic modification of cellulose on the wet delamination force for laminates. The modified cellulose surfaces were further treated by direct application a layer of PVAm8. See Table 3 for modification codes.

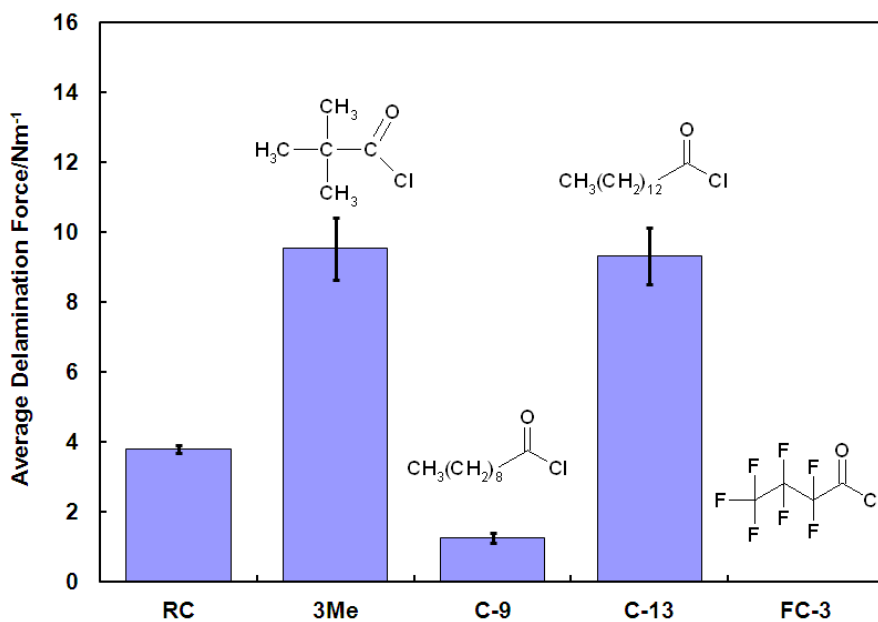


Figure 22 Comparison of average delamination force of regenerated cellulose (RC) with modified cellulose using various acid chloride. The modified cellulose surfaces were further treated by direct application a layer of PVAm8. See Table 3 for modification codes.

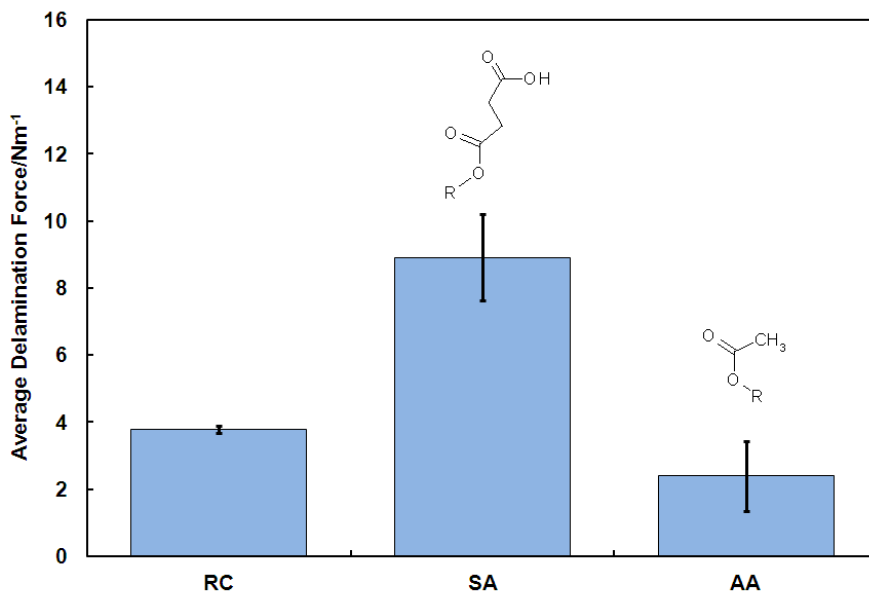


Figure 23. Comparison of average delamination force of regenerated cellulose (RC) with modified cellulose using succinic anhydride (SA) and acetic anhydride (AA). The modified cellulose surfaces were further treated by direct application a layer of PVAm8. See Table 3 for modification codes.

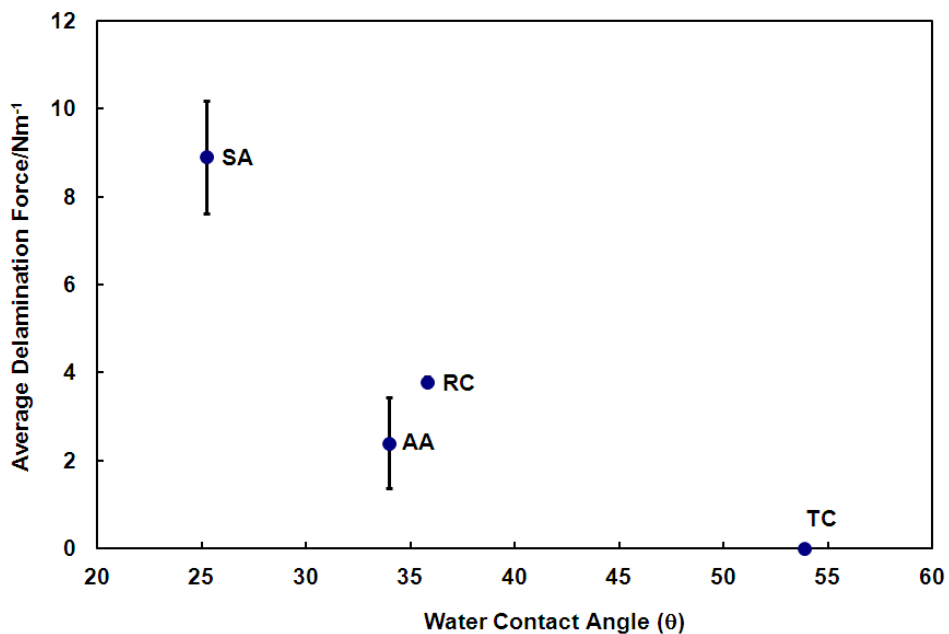


Figure 24. Plot of the wet delamination force of PVAm bound chemically modified cellulose as a function of the water contact angle against decane.

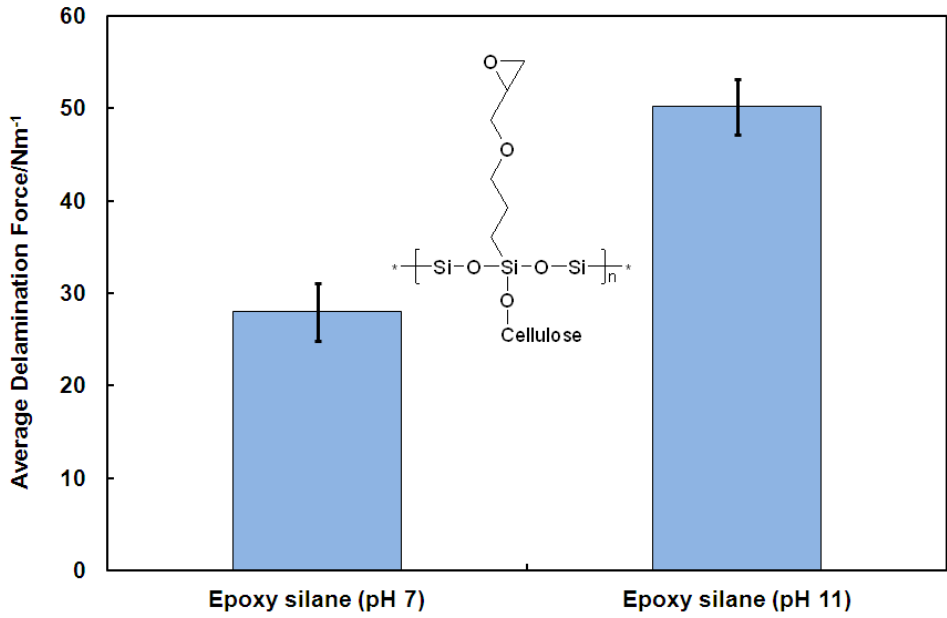


Figure 25. Average delamination force of epoxy silane modified cellulose. The modified cellulose surfaces were further treated by direct application a layer of PVAm8. The pH represents that of the PVAm solution during laminate formation and the soaking water prior to testing.

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Chapter 6 Concluding Remarks

The work summarized in this thesis has been a contribution in two major areas: 1) the development of a new experimental approach to accessing and comparing wet-strength enhancing polymers; and, 2) understanding the factors and the mechanisms by which polyvinylamine can enhance the wet adhesion between wet cellulose surfaces. This work is important because in the last decade PVAm has become widely used in the manufacture of paper. The specific accomplishments include:

1. The conception and validation of the wet cellulose delamination test allowing strict control of experimental conditions including the coverage and distribution of adhesive, the crack growth rate, the average water content in the laminate, and the nanoscale assembly of complex structures such as layer by layer assemblies. In addition, after delamination the composition and topology of the fracture plane can be characterized. Finally, the problems associated with conventional paper testing including formation effects, unknown distribution of wet-strength resin, and high variability are circumvented by the wet cellulose delamination procedure.
2. The mechanism of PVAm wet-strength development was determined as functions of ; PVAm properties, cellulose surface properties and re-wetting properties. Of all these the most important factors were the system pH, the amine content and most importantly the oxidation state of the cellulose. For oxidized systems the pH of the system was found to affect PVAm adsorption but this did not correlate to the delamination forces, which were approximately constant from pH 3 to 10. The delamination force increased with PVAm coverage, even in the absence of oxidation. This demonstrates that the PVAm in the laminates had a high cohesive strength in spite of being water soluble.
3. Confirmed the presence of aldehydes and hemiacetal groups after TEMPO mediated oxidation through XPS and FTIR.
4. Concluding that polyvinylamine promotes wet adhesion between oxidized cellulose film because of the formation of imine and aminal linkages between the primary amine groups of PVAm and the C6 aldehydes on cellulose. This hypothesis explains all of the PVAm results herein and on-going results after my work (see below).

6.1 Impact of this work

The delay between the completion of research work, and the submission of this thesis, has provided the unique opportunity to include an initial indication of the impact of this work. In the Pelton research group 4 Ph.D. thesis, 3 masters thesis and three current researchers (including a visitors from Sweden and China) are using the wet cellulose delamination test. In addition Pelton's researchers have advanced the PVAm technology by evaluating wet cellulose adhesives based on PVAm complexes with CMC [1, 2], PVAm microgels [3-7], boronic acid derivatives of PVAm [8-10], and PVAm bearing pendant TEMPO moieties [11-13].

Outside of the Pelton group, the first two publications from this thesis [14, 15] have been cited 12 times according to ISI [16-28] However, the first paper that was published in FRC conference has only recently been indexed by ISI and we know that although this was cited in 10 of the Pelton papers, only 5 instances appear on ISI. Indeed a paper that came online today (August 1, 2013) references the FRC publication [29].

Finally, although this work was started 11 years ago (September 2002) none of the mechanistic conclusions have been refuted and the postulated role of imine and aminal groups were mentioned in the publication that first appeared today [29].

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Appendix A

Cellulose Tensile Properties

Purpose:

Supplemental information on the mechanical properties of the regenerated cellulose membranes before and after oxidation.

Experimental:

Regenerated cellulose membranes (Spectra/Por[®] 4 product No:132709 12kDa MWCO, 41 $\mu\text{m}\pm 0.2\mu\text{m}$ thickness) were cut into strips of 15mm width and 145mm length and cleaned or modified as described in Chapter 2. The strips were then mounted in an Instron 4411 universal testing system (Instron Corporation, Canton, MA) fitted with a 50N load cell (Model 2530-437). The gauge length was set at 100mm and the extension rate at 25mm/min.

Cellulose films were oxidized with NaClO (11-14%) using 2,2,6,6-tetramethyl-1-piperidinyloxy radical (TEMPO) and NaBr as catalysts [9] following Kitaoka's method for pulp [10]. The concentration of TEMPO and NaBr was fixed at 0.034g/L and 0.34g/L respectively and the concentration of sodium hypochlorite was 3wt% based on dry cellulose. All reactions took place at 23°C under mild stirring (magnetic stirring bar) in a 1L glass beaker treating up to 7g cellulose. The pH was maintained at 10.5 by sodium hydroxide and the oxidation was stopped by adding ethanol to the suspension. The cellulose was removed and rinsed first in ethanol and then repeatedly with deionized water.

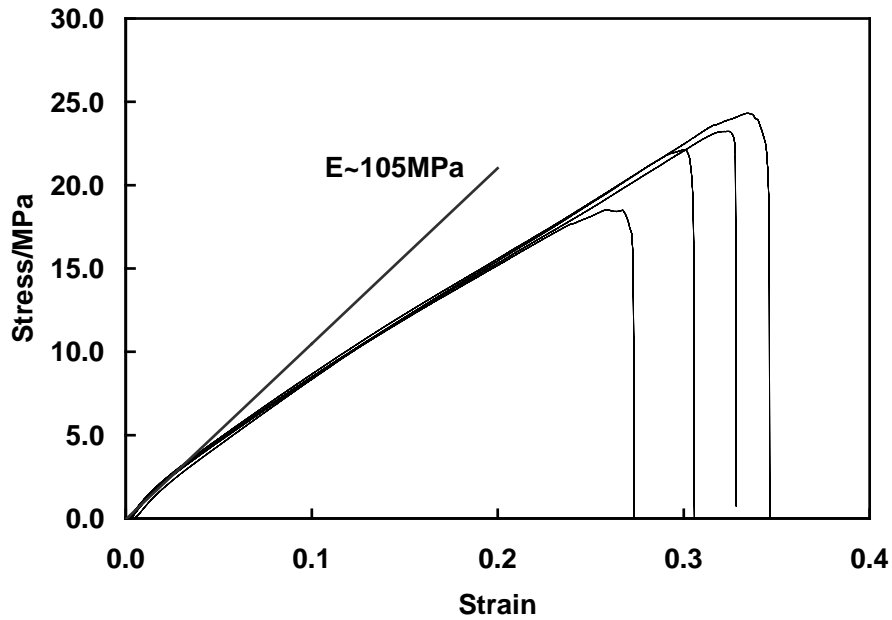


Figure 26. Repeat measurements of tensile stress versus strain for the SpectraPor4 cellulose membranes in the wet state. The response shows that the cellulose retains elasticity until break.

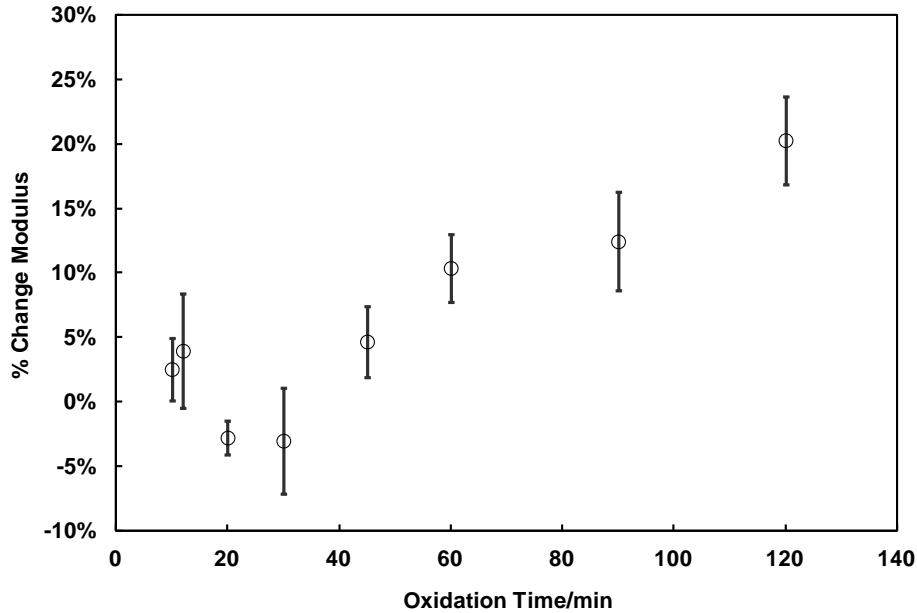


Figure 27. Effect of oxidation time on the percent change in the modulus of regenerate cellulose membranes (SpectraPor4)

Appendix B

Roughness of Regenerated Cellulose Membranes

Purpose

Supplemental information on the surface roughness properties of the regenerated cellulose membranes at different conditions.

Experimental

Roughness of cellulose membranes was measured by the Wyko NT1100 Interferometer (Veeco Metrology Inc.) which uses the interference patterns of light to construct a three dimensional representation of a surface. There are two modes available: VSI (Vertical Scanning Interferometry) and PSI (Phase-Shifting Interferometry); the former being used for height differences >160nm in the sample while the latter is used for small height differences (<160nm). This limit is due to the inability of the PSI mode to resolve adjacent pixels that differ by 160nm, therefore it is possible to acquire a PSI image of surface with a roughness greater than 160nm but unless the surface is wavy significant data will be corrupted.

Average Roughness: R_a

Is the absolute height deviation from the mean line (2D) or surface (3D), given by:

$$2D: \quad R_a = \frac{1}{n} \sum_{i=1}^n |Z_i - \bar{Z}|$$
$$3D: \quad R_a = \frac{1}{MN} \sum_{j=1}^N \sum_{i=1}^M |Z_{ij}|$$

It is similar to the variance of the height distributions though the differences are absolute and not squared. This measure is most commonly used and allows for comparison between similar surfaces. This method does not give any indication of the type of distribution so the same R_a could describe bumpy surface or a wavy one.

Root Mean Square Roughness: R_q

Represents the standard deviation of the surface heights in a profile, given by:

$$2D: R_a = \sqrt{\frac{1}{n} \sum_{i=1}^n (z_i - \bar{z})^2}$$
$$3D: R_a = \frac{1}{MN} \sum_{j=1}^N \sum_{i=1}^M Z^2(x_i, y_j)$$

Power Spectral Density:

Breaks down (Fourier decomposition) the X and Y lines through the data into its component spatial frequencies, *i.e.* it shows how different sine waves would combine to construct the original line. This is averaged over all the X and Y lines. This plot can reveal interesting features about the surface, for example:

- Monotonically decreasing profiles are most common and represent a surface with changing roughness at different scales
- Flat PSD profiles give a surface which has little or no change in roughness at different scales,
- A spike will indicate that a feature occurs periodically at that spatial frequency and indicates some processed effect
- A shoulder will indicate that the surface roughness is uniform over that spatial frequency range and indicates some processed effect
- The difference between the X and Y PSD will give the direction of the non-random effect – however the orientation of the sample will affect the resulting PSD traces.

Interferometer Settings

As the roughness of a dry cellulose membrane is close to the 160nm it is possible to use the PSI mode of profiling but due to large (>160nm) imperfections in the surface (craters, pits, scratches, dust etc.) the VSI mode provides more consistent results at all magnifications. Also it would be impossible to measure roughened surfaces like a peeled surface with the PSI mode.

At low magnification (5.12x) the PSI and VSI mode give similar results of R_a , although the PSI mode loses data in some small regions. The results are the same because both modes capture the wavy structure which dominates the height variation.

At higher magnifications (20.64x and 51.00x) the VSI gives a much higher (double) value of R_a than the PSI. The most obvious reason is that the VSI mode includes a larger lateral dimension (15 μ m) than the PSI mode (160nm) and therefore includes more peaks and pits. The resolution difference will also

contribute, as the PSI mode possesses a better vertical resolution than the VSI mode (0.3nm and 3nm respectively).

Table 4 Ra as measured by both the VSI and PSI modes for regenerated cellulose membranes (washed and dried) at identical locations for each magnification. Each roughness is calculated from surfaces constructed from the average of three scans.

Magnification	VSI R _a (nm)	PSI R _a (nm)
5.12	214.80	217.09
20.64	49.56	24.33
51.00	28.76	14.31

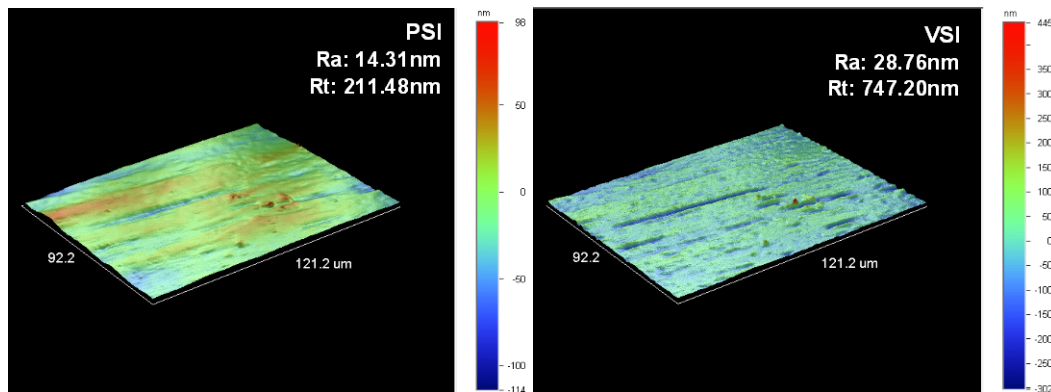


Figure 28 Comparison of the two profiling modes both taken at an identical location at 51x magnification and averaged over three measurements. The VSI gives higher roughness parameters such as Ra due to the fact that larger defects are included in the measurement. This can be seen clearly by the parameter Rt which gives the absolute maximum height difference in the sample.

The regenerated cellulose membranes measured are not self-similar surfaces, meaning that they display different profiles at different length scales. Over large areas the major contributor to the roughness are large scale waviness most likely associated with the manufacturing process. At higher magnifications the roughness is smaller as the large waves and imperfections do not appear as frequently.

The power spectral density (PSD) of each magnification gives some more information about the pattern of the surface. At low magnifications (Figure 29) the PSD shows that the surface is essentially wavy with some regular patterns at large spatial frequencies. At higher magnifications (Figure 30 and Figure 31) the Y-PSD shows that there is a shoulder at 10-200mm⁻¹ which indicates that the roughness is due to this range of frequencies, and primarily in one direction. This fits the observed profile which has a waviness/roughness in one direction of the material, most likely the extrusion direction. According to

these patterns are likely to repeat between 5-100 μm , while below this the surface is smoother. Strict orientation control would be expected to increase the difference between the X-PSD and Y-PSD.

Table 5 Ra as measured by VSI mode for regenerated cellulose membranes (washed and dried) at different locations. The value reported is the average of Ra with its standard error for all measured locations. Each individual spot is scanned three times.

Magnification	Ra (nm)	Rq (nm)
5.12	234.83 \pm 11.03	301.70 \pm 14.06
20.64	53.88 \pm 2.94	76.58 \pm 2.82
51.00	34.38 \pm 2.14	51.31 \pm 3.86

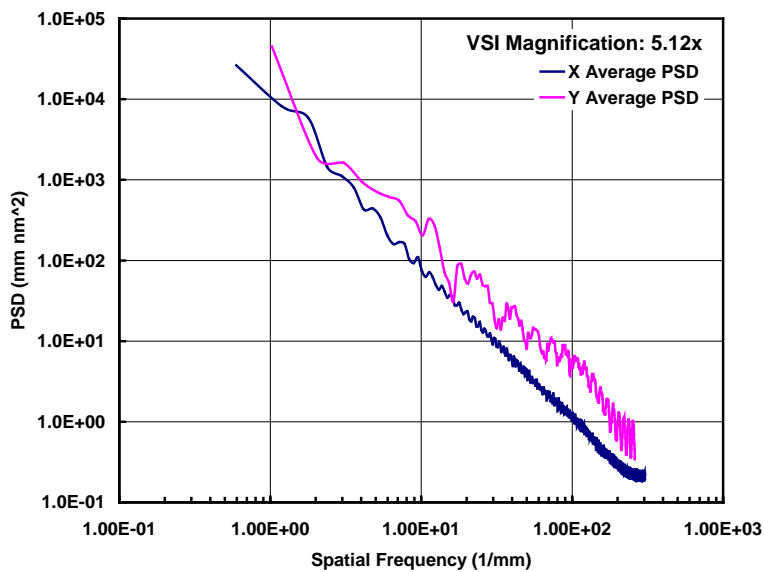


Figure 29 The PSD function for the X and Y direction for regenerated cellulose membranes measured in the VSI mode at 5.12x magnification. The X-PSD shows a random roughness pattern with waviness. The Y-PSD shows that same waviness but with more distinct repetitive features.

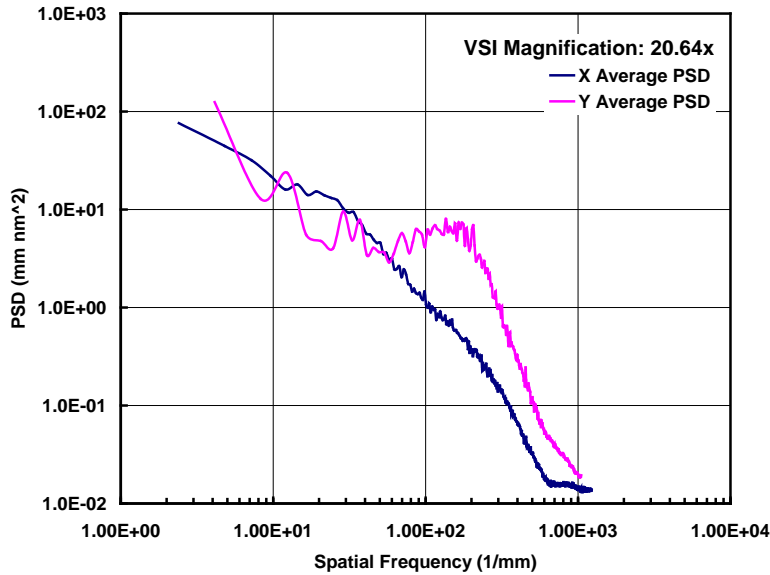


Figure 30 The PSD function for the X and Y direction for regenerated cellulose membranes measured in the VSI mode at 20.64x magnification. The X-PSD shows mostly random features with a slight shoulder at 1-30mm⁻¹ and again at 700-1000mm⁻¹. The Y-PSD gives a strong shoulder between 10-200mm⁻¹ which contains several peaks.

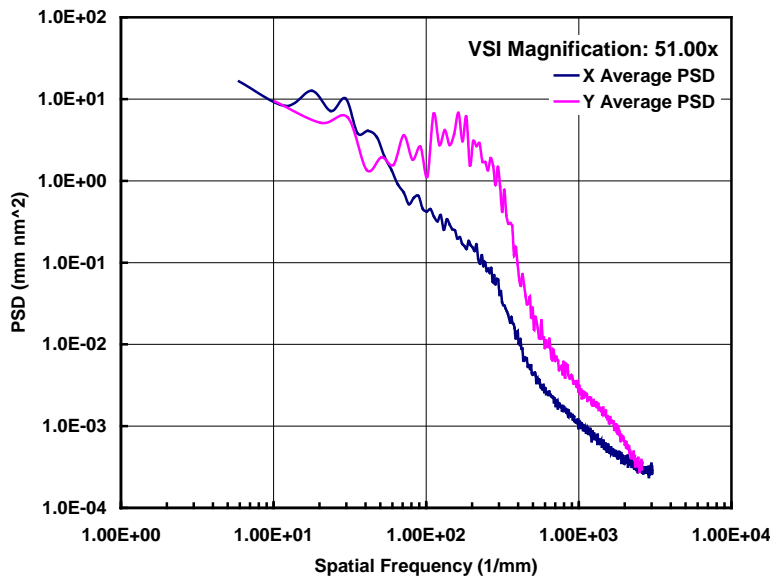


Figure 31 The PSD function for the X and Y direction for regenerated cellulose membranes measured in the VSI mode at 51.00x magnification. The X-PSD has some peaks between 10-100mm⁻¹ and drops off after 200mm⁻¹. The Y-PSD gives a strong shoulder between 10-200mm⁻¹ which contains several peaks.

It is possible to summarize changes in the membrane surfaces using only the R_a averaged over many measurements. Table 6 shows the R_a as measured at 51.00x magnification in VSI mode of SpectraPor4 ($41\mu\text{m}\pm 0.2\mu\text{m}$ thickness) regenerated cellulose membranes. The oxidation of the cellulose does not produce an appreciable change in the R_a parameter, while the use of acidic or basic water does decrease the roughness slightly. Peeled cellulose (PVAm) surfaces show a small increase in the roughness while oxidized cellulose with the same polymer content shows a significant change in roughness.

Table 6 R_a values as measured in the VSI mode, 51x magnification, of regenerated cellulose membrane surfaces at different conditions.

Test Conditions	Average R_a (nm)	Standard deviation	Standard Error (10rep)
Dry cellulose – Outside	81.84	20.47	6.17
Dry cellulose – Inside	57.56	12.29	3.71
Oxidized Air Dried	56.47	6.27	1.98
Cellulose in pH 2 Air Dried	43.20	8.60	2.72
Cellulose in pH 10 Air Dried	43.48	7.06	2.22
Peeled cellulose – Pure	82.38	4.84	1.53
Peeled cellulose – Oxidized	462.18	76.49	25.50
PVAm Adsorption Air Dried	47.63	16.62	5.25

Appendix C

Radioactive Labeling of Polyvinylamine

Purpose

Supplemental information regarding the adsorption of PVAm onto cellulose and its influence on the wet delamination force.

Experimental

Polyvinylamine (PVAm8, 150kDa, >98% DH) was conjugated with 4-hydroxybenzoic acid using 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide (EDC) as a zero-length cross-linker to a final substitution of approximately 15% [2]. The phenyl substituted PVAm was then labelled with a radioactive iodine isotope (I^{125}) (ICN Pharmaceuticals Inc, Radiochemical Division, Irvine, CA, USA) using the iodogen technique [3] at a 5% label concentration. The I^{125} labelled PVAm-Ph was separated from any excess unattached iodine by exhaustive cartridge dialysis against deionized water. The PVAm-Ph was then diluted to the desired concentration using 1mM NaCl solution. For each experiment a calibration curve of the polymer content against the radioactivity was made. The labelled PVAm-Ph solution was then adsorbed onto 0.65cm diameter disks of TEMPO-oxidized or unoxidized regenerated cellulose.

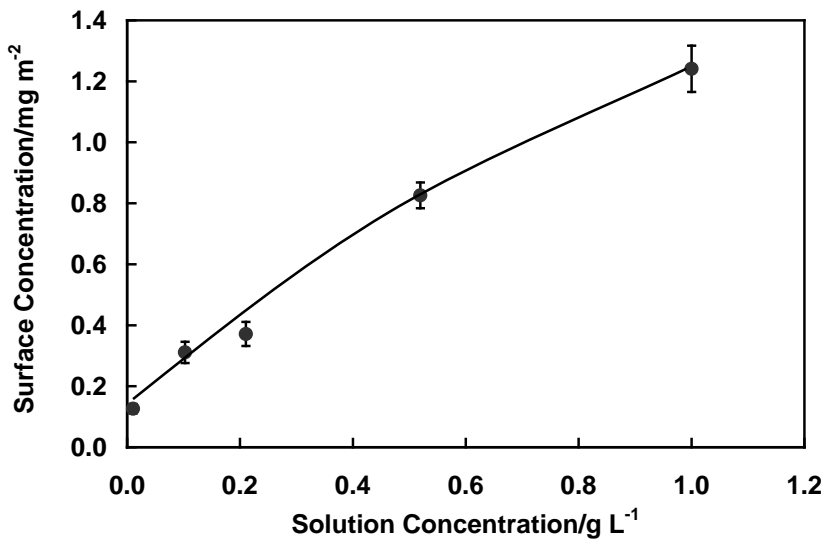


Figure 32. Surface concentration of I¹²⁵ PVAm-Ph adsorbed onto TEMPO-oxidized regenerated cellulose membranes. The adsorption solution was fixed at pH 7 and the adsorption time was 2hrs.

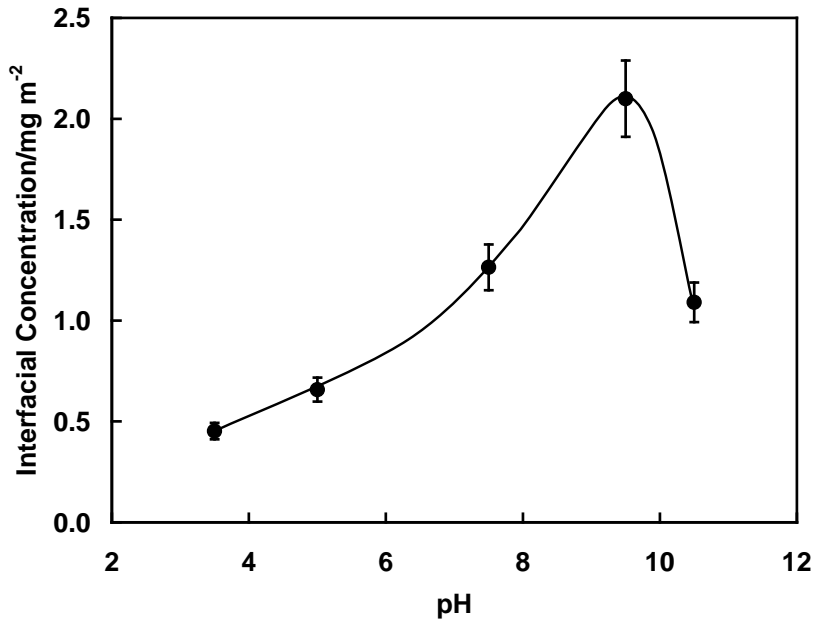


Figure 33. I¹²⁵ PVAm-Ph adsorption onto TEMPO oxidized cellulose membranes from a solution of 0.5gPVAm-Ph/L.

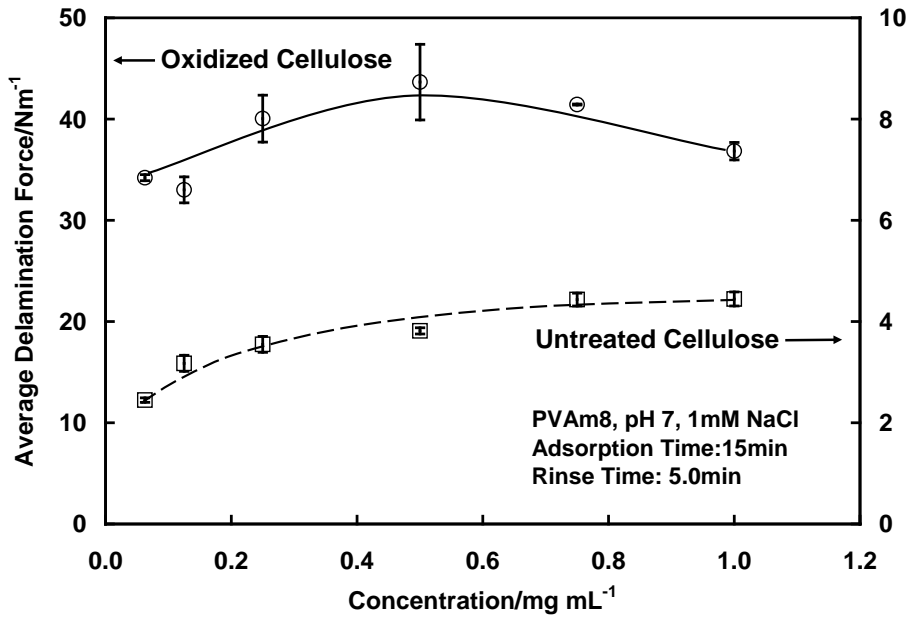


Figure 34. Adsorption effects on the average delamination force for PVAm bound laminates.

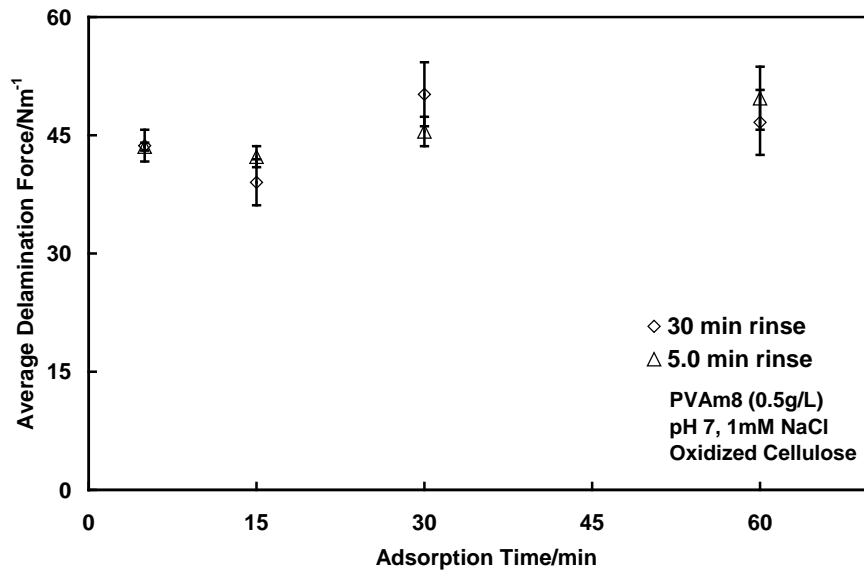


Figure 35. The adsorption time of PVAm (0.5g/L solution) on oxidized cellulose is not a significant factor in the development of wet adhesion. There is also no significant difference between the two rinse times.

Appendix D

Direct Application of PVAm

Purpose

Supplemental information comparing the effect of pH on direct deposited PVAm laminates made with untreated regenerated cellulose membranes.

Experimental

The procedure for the direct application of PVAm to the regenerated cellulose membranes is described in Chapter 2. The volume of the application was the same (15 μ L) while the PVAm concentration was changed to produce laminates with different surface coverages.

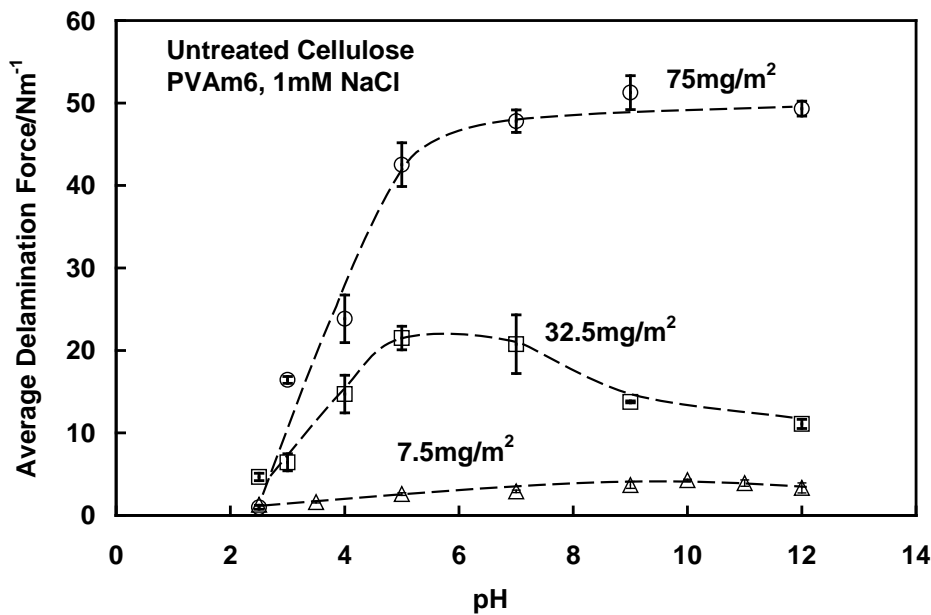


Figure 36 Wet delamination force as a function of pH for regenerated cellulose (unoxidized) laminates with different interfacial concentration. The PVAm was applied using the direct method.

Appendix E

Paper Testing

Purpose

Supplemental information showing results of paper testing using PVAm as a wet strength agent.

Experimental

Handsheets were made according to Chapter 2, Section 2.2.4.

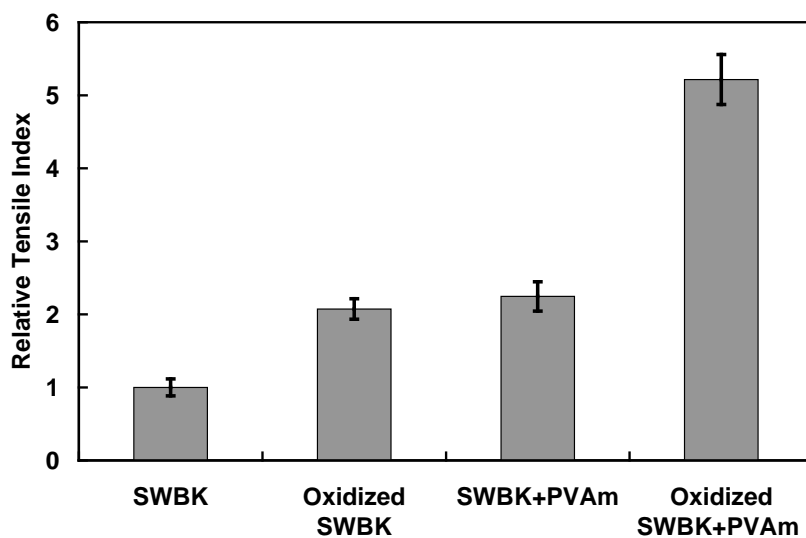


Figure 37. Comparison of the effect of oxidation and PVAm addition on paper wet tensile index. All results are divided by the untreated paper strength. SWBK stands for softwood bleached kraft pulp.

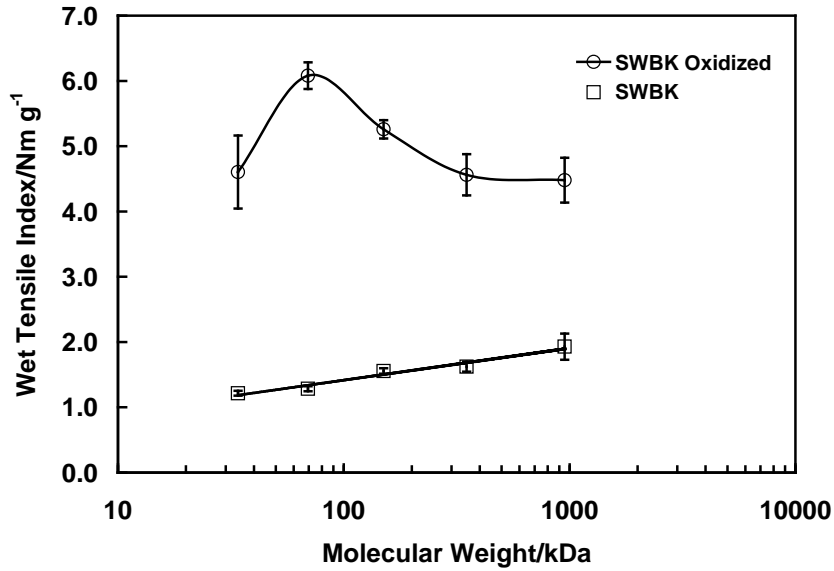


Figure 38. Comparison of wet tensile index of different molecular weight PVAm containing paper made from softwood bleached kraft pulp (SWBK) and oxidized SWBK.

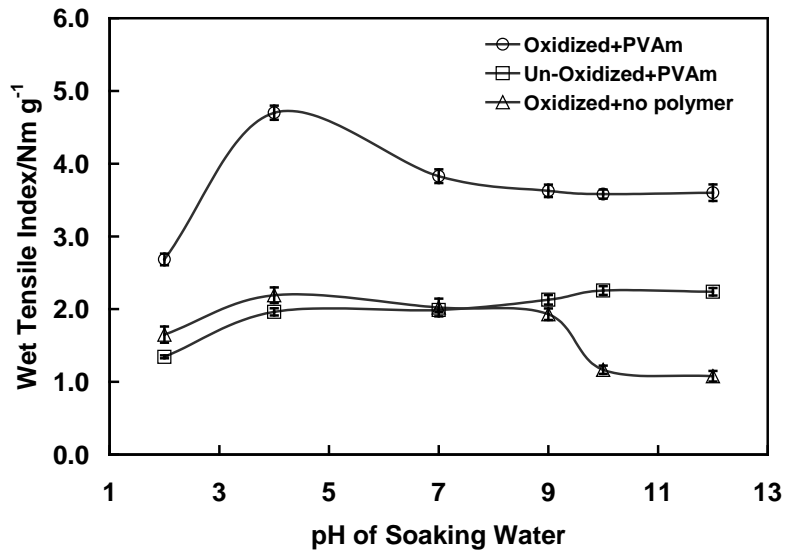


Figure 39 Comparison of wet tensile index of PVAm containing paper made from softwood bleached kraft pulp (SWBK) and oxidized SWBK. The pH of the water used during sheet formation was near neutral.