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Adhesion of Colloidal Polyelectrolyte Complexes to Wet Cellulose

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The adhesion of wet regenerated cellulose to colloidal complexes formed between carboxymethyl cellulose (CMC) and polyvinylamine (PVAm) was evaluated by measuring the force to delaminate pairs of regenerated cellulose membranes bound together with polyelectrolyte complex. The most important parameter was the surface composition of the colloidal complex particles. High delamination forces corresponded to using complexes coated with excess PVAm whereas low adhesion was observed for both CMC coated complexes and complexes in which the PVAm was replaced with polymer bearing quaternary amine groups. Adhesion with complexes was highest at pH 4 and rather insensitive to pH from 6 to 9. Finally, mild TEMPO/NaBr/NaClO oxidation of the cellulose gave much stronger adhesion when PVAm was in excess but not with the CMC rich complexes.

Introduction

Paper and paperboard are remarkably strong when dry,[1] however, to function in a wet or humid environment, it is necessary to reinforce fiber−fiber joints with synthetic wet strength polymers such as polyamide−epichlorohydrin (PAE).[2] Recently, the papermaking technology literature has seen a resurgence of interest in using polyelectrolyte complexes formed between oppositely charged water-soluble polymers. Papermaking with complexes can give high levels of polymer incorporation which will improve dry strength.[3] Perhaps the most elegant example of the use of polyelectrolyte complexes is Wågberg et al.'s layer-by-layer deposition of oppositely charged polymers on fiber surfaces to give strong paper.[4] However, most studies involve either preforming polyelectrolyte complexes[5,6] and adding them to a fiber suspension or generating complexes in situ in the papermaking suspension.[3,7]

We are interested in establishing the links between polyelectrolyte complex composition and the ability of the complex to adhere to wet cellulose, thus imparting wet strength to paper. The standard approach to evaluating wet paper strength enhancing polymers is to make laboratory paper sheets with the polymers and then measure strength. However, with this approach, it is often difficult to expose the underlying mechanisms because the complexes are often poorly characterized, the quantity of polymer adsorbed on the fibers cannot be controlled and must be measured, and polymer adsorption often induces fiber flocculation which in turn influences paper sheet structure. In an effort to isolate the adhesion phenomena from papermaking and testing issues, we have developed an alternative method for comparing wet adhesives. In our approach, two regenerated cellulose films are laminated using the polymer mixtures as an adhesive. The wet peel delamination force then gives a direct measure of adhesion.[8−11] Furthermore, the quantity of adhesive can be carefully controlled, and the locus of joint failure is well defined.

Herein, we report the results of a systematic study of the wet adhesion to cellulose of well-defined dispersions of complexes on the basis of mixtures of carboxymethyl cellulose (CMC) and polyvinylamine (PVAm). This paper follows from our previous characterization of the phase behaviors of aqueous dispersions of CMC:PVAm complexes as functions of composition and pH.[12] CMC was chosen for this research because it is commonly used in papermaking. By contrast, PVAm is relatively new as a commercial polymer, and it was chosen because it shows strong adhesion to wet cellulose. A few results involving poly(diallyldimethyl ammonium chloride) (PDADMAC) are also presented for comparison because this cationic polymer is commonly used in the paper industry.

Experimental Section

Materials. Three sodium carboxymethyl cellulose (CMC) powders were obtained from Aldrich with molecular weight and degree of substitution (MW/DS) of 90 kDa/0.7, 250 kDa/0.7, and 250 kDa/1.2. The polymers were purified by dialysis. Two poly(vinylamine-*co*-vinylformamide) copolymers samples, with ∼10% of the formamide groups hydrolyzed to amines, were provided by BASF, one based on poly(*N*-vinylformamide) with MW 340 kDa and the other with MW 150 kDa. The copolymers were further hydrolyzed to give polyvinylamine (PVAm) using 5% NaOH at 75 °C for 48 h under nitrogen purge.[13] The hydrolyzed polyvinylamine samples were exhaustively dialyzed and freeze-dried. Complete hydrolysis of the copolymer was evidenced by ^{1}H NMR confirming the disappearance of the proton in formamide at 7.8 ppm. The equivalent weights of stock solutions of purified polyvinylamine were measured by conductometric titration. The PVAm 150 kDa solution had an equivalent weight of 72 g per mol of total nitrogen whereas the value for PVAm 340 kDa was 92 g per mol of total nitrogen. Poly(diallyldimethyl ammonium chloride) (PDADMAC) MW 400−500 kDa in 20% solution was from Aldrich and was dialyzed before use.

Regenerated cellulose membrane (Spectra/Por 2, 12 000 MWCO) was purchased from Spectrum Laboratories, Rancho Dominguez, CA. Membranes were washed with Milli-Q water for 24 h to remove preservatives. Some membranes underwent oxidation with 2,2,6,6-tetramethyl-1-piperidinyoxy radical (TEMPO), sodium bromide, and sodium hypochlorite following Kitaoka et al.'s method.[14] The concentrations were TEMPO 0.034 g/L, NaBr 0.34 g/L, and NaClO 2.8 wt % on the basis of dry cellulose. Oxidation was carried out at 23 °C under magnetic stirring. The pH was maintained at 10.5 with sodium hydroxide, and the oxidation was stopped after 20 min by adding ethanol

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to the suspension. The oxidized cellulose membranes were then removed and were rinsed repeatedly with Milli-Q water. Finally, the treated membranes were stored in 4 °C water with a small quantity of ethanol.

Preparation and Characterization of Complexes. PVAm and CMC were separately dissolved in sodium chloride solution and were stirred for 24 h. After adjusting the pH, polymer solutions were filtered using 0.45 μm filters. CMC solution was then added dropwise into the PVAm solution under magnetic stirring. Finally, the complex colloids were stirred for an additional 30 min.

Particle size and surface charge were characterized by dynamic light scattering (DLS) and electrophoretic light scattering (ELS). DLS measurements were carried out at 25 °C, at a scattering angle of 90°, with a Brookhaven (Holtsville, NY) 256 channel BI-9000 AT digital correlator and a Lexel 300 mW He−Ne 514 nm laser. The correlation function of the scattered light intensity was analyzed by the program CONTIN to obtain the particle size (diameter). Each reported particle size was the average of 10 measurements. All measurements were carried out after complexes had been prepared for 24 h.

Electrophoretic mobility measurements were carried out at 25 °C using a Brookhaven ZetaPlus analyzer operating in phase analysis light scattering (PALS) mode. The reported mobility was the average of 10 runs.

Laminate Preparation and Delamination Force Measurement. Two wet cellulose membranes were pressed onto a smooth stainless steel plate, and excess water was removed with tissue. A strip of 1 cm wide Teflon tape was placed along the top edge of the 3 × 6 cm^2 membrane to facilitate separation after lamination. A 15 μL polymer or colloidal complex was placed on one end of this membrane. Then, a 2 × 6 cm^2 wet cellulose membrane was progressively placed over the bottom membrane to give laminates. The laminated wet membranes were pressed on a Hot Plate (Carver, Wabash, IN) at 18.5 MPa and at room temperature for 10 min and were equilibrated at 23 °C and 50% humidity for 24 h.

After equilibration, the laminated membranes were soaked for 30 min in sodium chloride solution with ionic strength and pH the same as those of the applied polymer solution. Following removal of excess water on the membrane surface using a tissue, the wet laminated membranes were mounted onto the aluminum peeling wheel with a layer of adhesive tape (3M Polyethylene Medical Double Coated Tape) applied to the wheel before mounting. The wheel was fixed to the bottom jaw of an Instron 4411 universal testing system (Instron Corp., Norwood, MA), located in a humidity-controlled room and fitted with a 50 N load cell. The top membrane was then separated from the bottom membrane at the edge and was clamped to the upper jaw of the Instron. The top membrane was peeled off at 90° and at a crosshead rate of 20 mm/min. The result of the peel test was recorded as peel force (width-normalized) versus displacement. The adhesion force was expressed as an average of steady-state peel forces. Each reported force is the average of four measurements.

Results

The ability of polymers and polyelectrolyte complexes to promote adhesion between wet cellulose layers was evaluated by measuring the peel force required to separate two wet regenerated cellulose films laminated with a layer of adhesive.[9,10] This approach was originally described by McLaren,[15] and variations have been used by others.[8] Figure 1 shows three typical raw data sets where the peel delamination forces were divided by the sample width to give a normalized value. The results in each peel trace were averaged to give the adhesion force, and all experiments were repeated four times.

The behaviors of three wet adhesives are illustrated in Figure 1. The strongest laminate (the top curve) was obtained using a wet adhesive formed by mixing carboxymethyl cellulose (CMC) and polyvinylamine (PVAm). Herein, the amount of adhesive in the laminate is called the coverage and is expressed as mg of dry polymer per square meter of cellulose/cellulose interface. The results for PVAm laminate in Figure 1 showed intermediate strength, whereas CMC alone gave very weak laminates. Interestingly, the CMC delamination force was identical to a value reported by Ben-Zion and Nussinovitch for wet cellulose acetate films laminated with CMC.[8] Finally, in the absence of polymeric adhesive, the wet cellulose/cellulose laminates spontaneously delaminated.

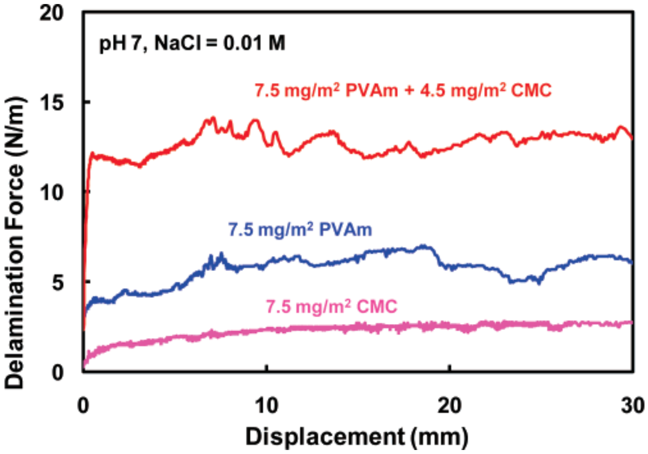

Figure 1. Wet cellulose delamination peel force versus displacement for PVAm (150 kDa), CMC (90 kDa, DS 0.7), and CMC:PVAm complex. The polymer coverage in the cellulose/cellulose joint is expressed as mg of dry polymer per square meter of joint.

A series of polyelectrolyte complex mixtures was prepared by adding increasing volumes of CMC stock solution into PVAm. The resulting mixtures were used to prepare a series of laminates. A second series of polyelectrolyte complex adhesives was prepared by using poly(diallyldimethyl ammonium chloride) (PDADMAC) instead of PVAm. Figure 2A shows the laminate strengths as functions of the overall composition of the adhesive mixtures expressed as the mass ratio of dry CMC to dry PVAm. The coverages of PVAm and PDADMAC were constant (7.5 mg/m^2), whereas the overall adhesive coverage increased with CMC addition.

In all cases, the PDADMAC adhesives gave weak laminates the inability of the relatively hydrophobic quaternary ammonium polymer to give wet adhesion as has been reported by Espy.[2]

The maximum adhesion occurred with a CMC:PVAm mass ratio of 0.6:1, whereas adhesive mixtures with high CMC contents gave very weak adhesives even though the coverage was high. This is consistent with the observation that CMC alone is a very poor wet adhesive for cellulose (see Figure 1).

The diameter and electrophoretic mobilities of the colloidal phase are shown as a function of overall composition in Figure 2B. In our previous paper, we reported the composition of the colloidal polyelectrolyte complex and the equilibrium solution properties as functions of polymer mixing ratios.[12] The colloidal complex particle size is rather insensitive to composition, whereas the sign and the magnitude of the charge on the colloidal complexes is very sensitive to the CMC:PVAm ratio.[12] A key result, also reported by others,[16] is that complex formation is not stoichiometric. At low CMC dosages, the colloidal complexes are positively charged reflecting excess protonated amine groups. By contrast, at high CMC dosages, the complexes are negatively charged and there is excess CMC in solution. The open circle in the mobility plot denotes the point of zero net charge calculated from the ionization behavior of CMC and PVAm. The charge content modeling was described previously.[12]

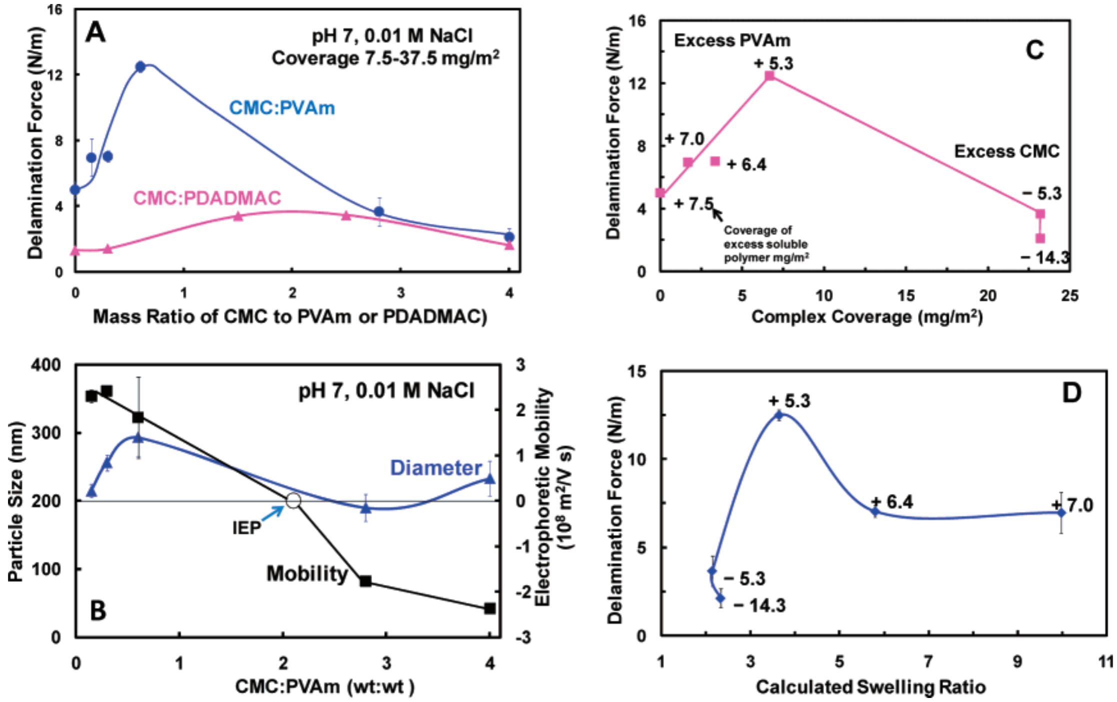

Figure 2. Two series of complexes prepared from 0.5 g/L PVAm 150 kDa or PDADMAC and a range of CMC 90 kDa, DS 0.7 concentrations. The isoelectric point (IEP) was calculated from the ionization behavior.[12] The labels in C and D give coverage of excess soluble polymer where + is for PVAm and − denotes CMC. Swelling ratios (wet mass/dry mass) were calculated from a model.[17] All solutions were at pH 7 in 0.01 M NaCl.

The adhesion results in Figure 2A are complicated by the fact that the adhesives are a mixture of colloidal polyelectrolyte complex and excess PVAm or CMC. Figure 2C shows the same PVAm adhesion data in Figure 2A plotted as a function of the coverage of colloidal CMC:PVAm complex in the adhesive joint. The numbers beside the data points give the corresponding coverage of free polymer, and the sign gives the type of polymer, that is, the negative values correspond to excess CMC whereas the positive values denote excess PVAm. Together, Figure 2B and 2C shows that the most important compositional property related to high adhesion is the presence of excess amine groups as evidenced by the correlation between high adhesion and positive electrophoretic mobility. By contrast, the CMC rich mixtures were negatively charged, indicating excess carboxyl groups which gave poor adhesion.

Figure 2C also shows that adhesion increased with coverage as long as the amine groups were in excess. In earlier work, we have shown that wet adhesion with PVAm alone increases with coverage up to about 10 mg/m^2, above which adhesion is constant.[10]

Polyelectrolyte complexes are hydrogels whose degree of swelling is determined by the balance of elastic forces opposing swelling versus a combination of solvation and Donnan forces promoting swelling. Since the mechanical properties of most elastic materials are degraded by swelling, we estimated the degree of swelling of the polyelectrolyte complexes in the laminates using a swelling model we validated with macroscopic CMC:PVAm complex films.[17] Figure 2D shows the adhesion data from Figure 2A plotted as functions of the calculated complex swelling ratios (i.e., swollen volumes divided by dry volume). There is no data point in Figure 2D corresponding to PVAm with no CMC, because PVAm is soluble and there is no equilibrium swelling. Complex swelling does not appear to correlate with adhesion. The lowest estimates of swelling corresponded to the higher CMC contents which gave weak adhesion.

The results in Figure 2 are somewhat difficult to digest because both adhesive composition and coverage varied. Figure 3 shows adhesion from a series of experiments where the adhesive composition was varied at constant total coverage in the laminate. The lower part of Figure 3 shows the relative amounts of colloidal complex and excess polymer in the adhesive mixtures. As before, the amine-rich mixtures gave the highest adhesion. When compared at constant coverage, the complexes did not give significantly higher wet adhesion than PVAm alone.

Both CMC[18] and PVAm[19] are pH sensitive polymers. At low pH, CMC bears little negative charge, whereas PVAm is highly positively charged. High pH shows the opposite effects. In previous work, we showed that wet adhesion to cellulose with PVAm alone was maximum and approximately constant from pH 3 to 9, while it decreased outside this range.[10] Figure 4 shows the pH dependence of a 3:1 CMC:PVAm complex. The adhesion was greatest at pH 4, lowest at pH 5, and approximate constant from pH 6 up to pH 9. The lower figure shows the corresponding complex electrophoretic mobility and particle size as functions of pH. The higher adhesion values correspond to the smaller particle size complexes. Perhaps smaller complexes give a more uniform adhesive layer.

CMC is characterized by the average molecular weight and the degree of carboxymethyl substitution (i.e., the average number of carboxyls per sugar ring). Figure 5A shows the influence of CMC molecular weight and DS on adhesion versus overall adhesive composition. In this series of experiments, the PVAm coverage was constant (7.5 mg/m^2) and the CMC content in the adhesive increased going from left to right. The greatest adhesion trend was for the highest MW and DS CMC sample, with the maximum peel delamination force almost 3 times greater than the value for PVAm alone. By contrast, addition of the high MW but low DS CMC did not improve adhesion. Compared to PVAm alone, all three CMC samples lowered adhesion when added at concentrations sufficiently high to give

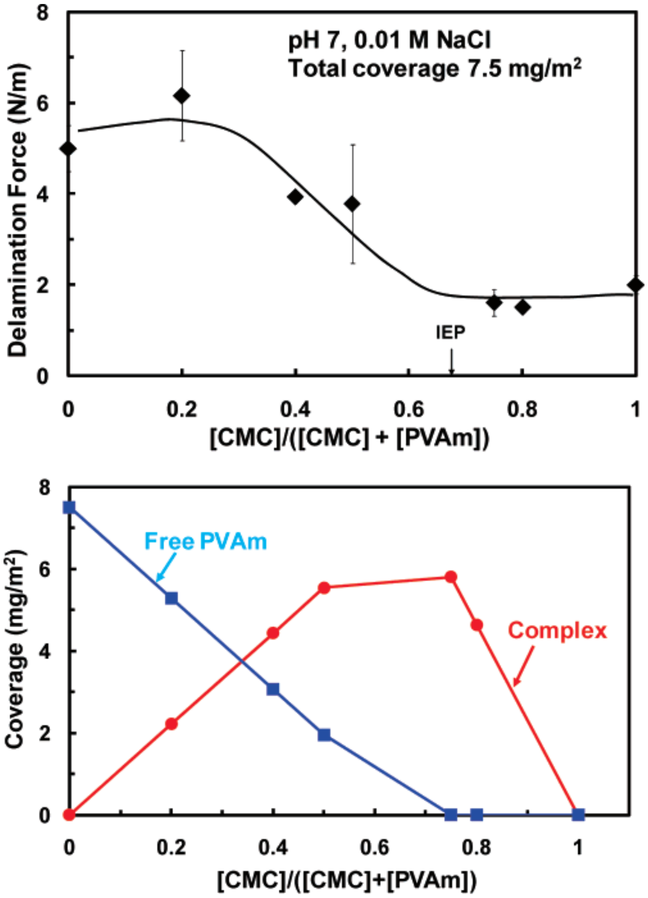

Figure 3. Influence of polyelectrolyte complex composition at constant total coverage. PVAm 150 kDa, CMC 90 kDa, DS 0.7.

negatively charged colloidal complexes. The calculated isoelectric points are shown as open circles.

Figure 5B shows the influence of CMC structure on the electrophoretic mobility versus overall composition. As expected, the high DS CMC reversed the complex mobility at a lower CMC dosage. The two CMC samples with the same DS displayed approximately the same electrokinetic behaviors.

Figure 5C shows the influence of CMC DS on the calculated swelling ratio of the complexes predicted by our swelling model. In the excess PVAm regime, where adhesion values were greatest, the lower DS CMC was predicted to give greater swelling, reflecting the lower concentration of potential ionic cross-links in the hydrogels. Perhaps excessive swelling of the low DS CMC gels explains the poor adhesion characteristics (see Figure 5A).

The results in Figure 5 again emphasize that the highest adhesion corresponds to the positively charged complex which has an excess of amine groups. In addition, the maximum adhesion increased with CMC molecular weight and DS. In previous studies of the mechanical properties of dry, homogeneous CMC:PVAm complex films, we found the opposite trend; the tensile strength of dry complex films deceased with increasing CMC molecular and DS.[20] We do not have a good explanation for the role of CMC molecular weight and degree of carboxylation.

Previously, we have shown that PVAm alone gives substantially higher adhesion when the cellulose films are slightly oxidized by TEMPO/NaBr/NaClO.[10] Both our work and that of Saito and Isogai[21,22] indicate that amine groups react with hemiacetals on oxidized cellulose to form imine and aminal linkages. Figure 6 shows the influence of oxidation on adhesion with CMC:PVAm complexes. Like PVAm alone, cellulose oxidation increased the maximum adhesion by more than a factor of 3. Also with oxidation, the maximum adhesion corresponded to a lower CMC content. The inability of oxidation to improve adhesion with the CMC rich compositions (right-hand side of Figure 6) suggests that the positive benefits of oxidation are associated with the presence of excess amines in the adhesive layer.

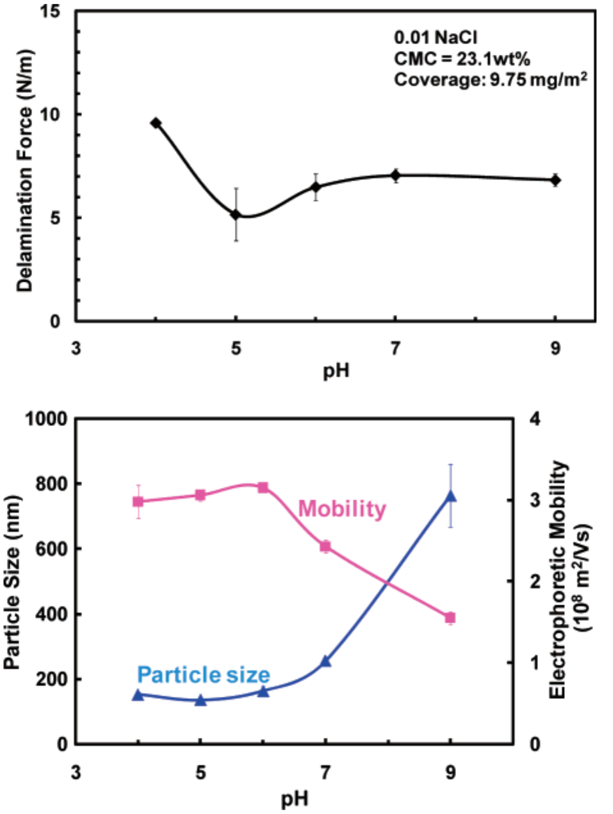

Figure 4. The influence of pH on adhesion and on the properties of the colloidal polyelectrolyte complex particles prepared with 0.5 g/L PVAm (150 kDa) and 0.15 g/L CMC (90 kDa, DS 0.7).

Discussion

The perennial question in adhesion research involves identification of the locus of failure: cohesive failure of either the substrate or adhesive versus adhesive failure of the adhesive/substrate interface. For situations involving very thin adhesive layers, Sharpe makes a strong case for considering an interphase where the distinction between adhesion and cohesion blurs.[23] Nevertheless, on the basis of our previous work, some comments about the cohesive strength of CMC:PVAm complexes can be made. Using homogeneous cast films prepared from CMC:PVAm mixtures, we have shown that the minimum swelling and maximum cohesive strength of complex films correspond to conditions where there exists a charge balance between the carboxylate groups and the ammonium ions.[17] Charge balance corresponds to the maximum density of electrostatic cross-links in the complex gel, giving minimum swelling and maximum strength. By contrast, this work shows that the maximum adhesion to cellulose film corresponds to the maximum concentration of amine groups. For example, Figure 2A shows maximum adhesion when the CMC:PVAm ratio is 0.6:1, and Figure 3 suggests that there is little advantage in adding any CMC. The implications are that failure occurs at the polymer cellulose interface and not within the polymer complex film.

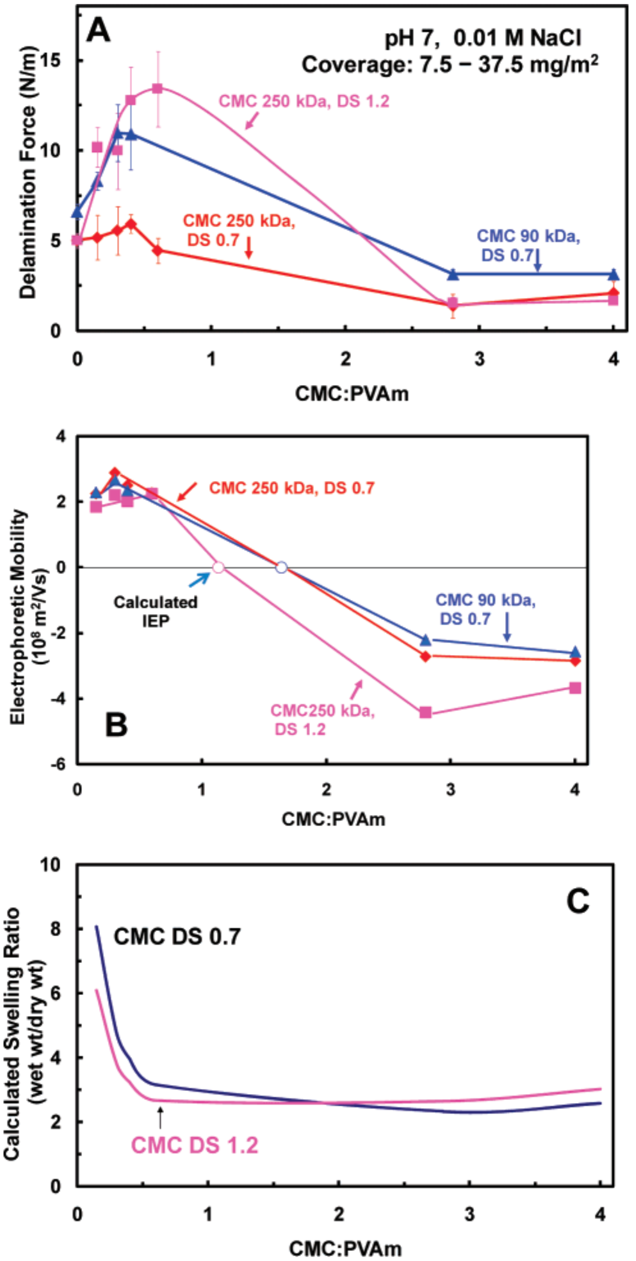

Figure 5. Influence of CMC molecular weight and DS wet adhesion. PVAm 340 kDa, CMC 90 kDa, DS 0.7, 250 kDa, DS 0.7, 250 kDa, DS 1.2.

Further evidence for this conclusion is shown in Figure 6, which shows that delamination work increased substantially when the cellulose film was oxidized.

A casual glance at Figures 1, 2, or 5 leaves the impression that CMC improves wet adhesion, perhaps displaying some synergism. However, in each of these cases, the polymer coverage (mass/area) in the cellulose−polymer−cellulose joints was varying because CMC was added to a constant loading of PVAm. Only Figure 5 illustrates the contribution of CMC at a constant total coverage of CMC + PVAm in the joint. Pure CMC gave very weak adhesion, and the more CMC was replaced with PVAm, the stronger was the wet adhesion. With oxidized cellulose, the results are even more dramatic (see Figure 6): the more CMC added, the weaker the joint.

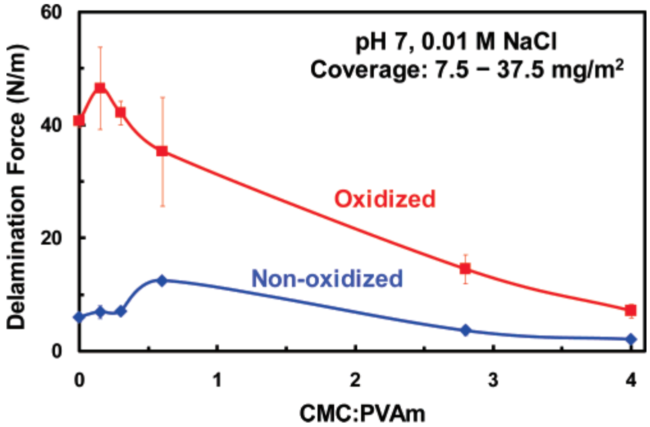

Figure 6. Influence of cellulose film oxidation on the adhesion to complexes at pH 7, 0.01 M NaCl. PVAm 150 kDa, 0.5 g/L, CMC 90 kDa, DS 0.7.

If CMC does not improve wet adhesion with PVAm, why use it? Colloidal complexes offer advantages to conventional papermaking technology. Strength-enhancing polymers are usually added to the cellulose fiber suspension before paper is made. Thus, the maximum polymer content in the paper corresponds to a saturated adsorbed monolayer. For linear-soluble polymer, this limit is about 1 mg/m^2, whereas for deposited colloidal complexes it could be much higher. High polymer contents are an advantage because the work required to disrupt many adhesive joints increases with adhesive thickness.[24] Furthermore, with rough fiber surfaces, we have shown that bulky adsorbed microgels give much stronger adhesion than do thin layers of adsorbed linear polymer.[25]

This work does highlight a practical difficulty in using polyelectrolyte complexes to strengthen paper. The strongest wet adhesion corresponds to the situation with excess amine groups on the complex. However, this case also corresponds to the coexistence of significant quantities of excess free PVAm, see Figure 3. In other words, optimizing polymer mixing ratios for maximum colloidal complex yield will not give maximum adhesion.

In conventional papermaking technology, strength-enhancing polymers are adsorbed onto fiber surfaces in dilute aqueous solution before paper sheets are formed by filtration. Many papermaking polymeric additives have quaternary ammonium charge groups to promote electrostatic driven adsorption onto anionic cellulose fibers in water. Although electrostatic interactions promote polymer adsorption from dilute aqueous solution, polymer adsorption does not ensure strong wet adhesion when two polymer coated cellulose surfaces are brought together. A good example is poly(diallyldimethyl ammonium chloride) (PDADMAC) which strongly adsorbs onto cellulose[26] but gives weak wet adhesion (Figure 2 and Espy's work[2]). Presumably, this reflects the inability of the quaternary ammonium groups to participate in acid/base interactions, hydrogen bonding, and covalent bond formation with the cellulose surface. By contrast, primary amines in polyvinylamine are basic, are hydrogen bond acceptors, and can form covalent bond with hemiacetals on the end of cellulose chains.[10,21,22]

Finally, it is interesting to note that these results involve wet adhesion. Our previous work suggests that the opposite trends occur with dry or nearly dry adhesion. We have shown that the tensile strength of dry homogeneous films based upon CMC:PVAm mixtures increases with CMC content.[20] In the dry state, PVAm acts as a plasticizer weakening the CMC films. Therefore, optimizing complex composition may depend upon the type of strength improvements desired.

Conclusions

The wet delamination force for pairs of regenerated cellulose films was used as a measure of the wet adhesion between CMC:

PVAm polyelectrolyte complexes and cellulose. The major conclusions from this work are the following.

1. For a given adhesive coverage on relatively flat cellulose surfaces, CMC:PVAm complex is no more effective than PVAm alone as a wet adhesive for cellulose.

2. CMC:PVAm complexes bearing excess amine groups gave far higher adhesion than did complexes with excess carboxyl groups.

3. Adhesion of amine-rich complex was greatest at pH 4 and is insensitive to pH over the range 6−9.

4. Excess linear polymer virtually always coexists with complex, particularly for those compositions giving the greatest wet adhesion.

5. On the basis of indirect observations, it appears that failure occurs at the cellulose complex interface and not within the complex itself.

6. Primary amines promote adhesion to wet cellulose, whereas quaternary amines and carboxyl groups do not.

7. TEMPO/NaBr/NaClO oxidation of cellulose increases wet adhesion to complexes with excess amines but not with excess carboxyls.

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References and Notes

(1) Pelton, R. *Appita J.* **2004**, *57*, 181−190.
(2) Espy, H. H. *Tappi J.* **1995**, *78*, 90−99.
(3) Heermann, M. L.; Welter, S. R.; Hubbe, M. A. *Tappi J.* **2006**, *5*, 9−14.
(4) Wagberg, L.; Forsberg, S.; Johansson, A.; Juntti, P. *J. Pulp Pap. Sci.* **2002**, *28*, 222−228.
(5) Gardlund, L.; Wagberg, L.; Gernandt, R. *Colloids Surf., A* **2003**, *218*, 137−149.
(6) Hubbe, M. A. *J. Pulp Pap. Sci.* **2005**, *31*, 159−166.
(7) Lofton, M. C.; Moore, S. M.; Hubbe, M. A.; Lee, S. *Tappi J.* **2005**, *4*, 3−8.
(8) Ben-Zion, O.; Nussinovitch, A. *Food Hydrocolloids* **1997**, *11*, 429−442.
(9) Kurosu, K.; Pelton, R. *J. Pulp Pap. Sci.* **2004**, *30*, 228−232.
(10) DiFlavio, J. L.; Bertoia, R.; Pelton, R.; Leduc, M. In *13th Fundamental Research Symposium*; FRC: Cambridge, U.K., 2005; pp 1293−1316.
(11) Li, X.; Pelton, R. *Ind. Eng. Chem. Res.* **2005**, *44*, 7398−7404.
(12) Feng, X.; Pelton, R.; Leduc, M.; Champ, S. *Langmuir* **2007**, *23*, 2970−2976.
(13) Chen, X. N.; Wang, Y.; Pelton, R. *Langmuir* **2005**, *21*, 11673−11677.
(14) Kitaoka, T.; Isogai, A.; Onabe, F. *Nord. Pulp Pap. Res. J.* **1999**, *14*, 279−284.
(15) McLaren, A. D. *J. Polym. Sci.* **1948**, *3*, 652−663.
(16) Chen, J. H.; Heitmann, J. A.; Hubbe, M. A. *Colloids Surf., A* **2003**, *223*, 215−230.
(17) Feng, X.; Pelton, R. *Macromolecules* **2007**, *40*, 1624−1630.
(18) Aggeryd, I.; Olin, A. *Talanta* **1985**, *32*, 645−649.
(19) Katchalsky, A.; Mazur, J.; Spitnik, P. *J. Polym. Sci.* **1957**, *23*, 513−30.
(20) Feng, X.; Pelton, R.; Leduc, M. *Ind. Eng. Chem. Res.* **2006**, *45*, 6665−6671.
(21) Saito, T.; Isogai, A. *Tappi J.* **2005**, *4*, 3−8.
(22) Saito, T.; Isogai, A. *Ind. Eng. Chem. Res.* **2007**, *46*, 773−780.
(23) Sharpe, L. H. *J. Adhes.* **1998**, *67*, 277−289.
(24) Kendall, K. *Molecular Adhesion and its Applications-The Sticky Universe*; Plenum: London, 2001.
(25) Miao, C.; Chen, X.; Pelton, R.; Leduc, M. *Appita.* **2006**, to appear.
(26) Horvath, A. E.; Lindstrom, T.; Laine, J. *Langmuir* **2006**, *22*, 824−830.

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