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The Effect of Drying Stress and Polyelectrolyte Complexes on the Strength Properties of Paper

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The mechanical properties of dried paper have been shown to correlate strongly with the final drying stress developed during restrained drying. The adsorption of polymers onto fibres influences the development of the strength properties of paper. Drying stress affects bonding negatively and the in-plane strength properties positively. Certain polyelectrolyte complexes seem to have the ability to change these relationships, i.e. they affect the behaviour of the paper network during drying. For example, in some cases cationic polyacrylamide seems to counter the negative effect of drying stress on bond strength.

Les propriétés mécaniques du papier séché sont en forte corrélation avec la contrainte de séchage finale développée pendant un séchage limité. L'adsorption des polymères sur les fibres a une incidence sur le développement des propriétés de résistance du papier. La contrainte de séchage a un effet négatif sur la cohésion et un effet positif sur les propriétés de résistance dans le plan. Certains complexes de polyelectrolytes semblent posséder la capacité de modifier ces relations, c'est-à-dire qu'ils modifient le comportement de la feuille de papier pendant le séchage. Par exemple, en certains cas, le polyacrylamide cationique (C-PAM) semble contrer l'effet négatif de la contrainte de séchage sur la cohésion des fibres.

INTRODUCTION

An interfibre bond can be defined as the zone where two fibres are so close to each other that hydrogen bonding, van der Waals' interaction or molecular entanglement can occur [1]. Formation of interfibre bonds begins as the web's solids content increases during papermaking. At first, bonding occurs through surface tension forces pulling fibres together when water is removed (Campbell effect) [2]. This will change gradually to hydrogen bonding. The bonding layer is formed when external fibrils and fines come close during dewatering and couching, and become pressed and packed between fibres. As the web dries, external fibrils and fines material form the bonding layer [3]. Formation of bonds is promoted by external fibrillation and fines, which link two fibre surfaces more closely together. Internal fibrillation contributes to the swelling and flexibility of fibres and therefore improves interfibre bonding; the adjacent fibres are able to conform onto each other during pressing and drying. Fibre-water interactions also influence bond formation [1].

The structure of bonds is influenced by various processes in papermaking such as beating, pressing and drying. Other important factors affecting the bond structure include fibre morphology and the pulping procedure. Also fines, both from mechanical and chemical pulp, play a significant role in bonding. Flexible fibres can form wrap-around type of bonds, and fibrils and fines form bridges between fibres [1]. Nanko and Ohsawa [3] studied the structure of fibre bonds and they have presented a good schematic illustration of the bond structure. According to their findings, an amorphous bonding layer is formed between the S1 layer of two beaten fibres by external fibrils, and probably by polymer chains as well. The more beaten the fibres are, the thicker the bonding layer and the better the contact between two fibres will be, partly because of the increased amount of fines. They also detected structures like skirts (an elongated part of the S1 layer extending from bond edges) and covering layers consisting of external fibrils and fines covering smooth edges. The skirt and covering layer structures have an important role in strengthening the bond. The mechanical properties of bonds are related closely to the drying stresses that act across every interfibre bond [1].

Fibre segment activation or activation, as a term, is used to describe the phenomenon of modification of originally kinked, curly or otherwise deformed fibre segments into active, load-bearing components of the network (Fig. 1).

Fig. 1. A schematic illustration of activation.
Activation takes place in drying, when lateral shrinkage of fibres is transformed into axial shrinkage of the neighboring fibres in bonded areas. If this shrinkage is restrained, the free fibre segments dry under stress and therefore are removed of their slackness [4,5]. Once the segments are activated, the axial elastic modulus of fibres increases, which leads to a further increase in drying stress. Thereafter, both the segments and bonded areas are capable of bearing load. Activation requires both bonding and shrinkage of fibres. The amount of drying stress needed to activate free segments depends on the morphology of the fibres [6]. Activation can be improved by maximizing the bonded area and average fibre length. Beating of chemical pulp increases the swelling ability (and therefore the shrinkage potential) of fibres and also fibre flexibility. Beating also increases the number of bonds and the number of free segments and decreases the length of the free segments [4,7].

The drying stress that acts on the fibre network has a significant effect on the final strength properties of paper. The changes in mechanical properties caused by drying under load can be related to two main mechanisms: firstly, the increase in crystal lattice orientation and secondly, the more even distribution of stress among fibres [6,8]. The mechanical properties of dried paper have been shown to correlate strongly with the final drying stress developed during restrained drying [9]. This relationship does not depend on the type of pulp, beating or wet pressing. In reality, shrinkage also usually occurs during drying and this will have an effect on the paper properties.

Additives that have been shown to affect interfibre bonding positively are high molecular weight (MW) hydrophilic colloids, either natural or synthetic, such as starch, proteins, vegetable gums and water-soluble resins (particularly polymers of acrylamide) [10]. They act by adsorbing onto fibre surfaces, where fibre-to-binder-to-fibre bonds can evolve and contribute to bond and sheet strength. Retulainen and Nieminen [11] studied the effect of several dry-strength additives on tensile strength. The highest strength increases were obtained by using cationic starch and carboxymethyl cellulose (CMC). Also, two-component systems of oppositely charged polyelectrolytes used commonly as retention aids have been reported to increase both tensile strength and bond strength in paper [11,12]. Polymer complexes are assumed to affect bonding and the structure of a fibre network by changing the swelling, viscoelastic and frictional properties of fibre surfaces and by influencing the consolidation of the paper web and the behaviour of the fibre network during drying [12]. However, not much is known about the mechanisms by which these polymer complexes affect paper strength together with drying stress. Therefore, the aim of this study was to examine the combined effect of drying stress and the adsorption of various polymer complexes on the strength properties of laboratory sheets made from mixtures of bleached kraft pulp and bleached thermomechanical pulp (TMP).

### Table I

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Molecular weight, x 10³ g/mol</th>
<th>Charge density, mol%</th>
<th>Charge density, meq/g</th>
<th>Dosages % on dry pulp</th>
</tr>
</thead>
<tbody>
<tr>
<td>High MW C-PAM</td>
<td>5.8</td>
<td>10</td>
<td>1.1</td>
<td>0, 0.5, 1</td>
</tr>
<tr>
<td>CL C-PAM</td>
<td>1.1</td>
<td>10</td>
<td>1.4</td>
<td>0.1, 2.5, 3.5</td>
</tr>
<tr>
<td>CMC</td>
<td>1.0</td>
<td>50</td>
<td>2.7</td>
<td>1.25</td>
</tr>
<tr>
<td>A-PAM</td>
<td>1.7</td>
<td>10</td>
<td>1.7</td>
<td>0.5, 1</td>
</tr>
</tbody>
</table>

### MATERIALS AND METHODS

The sheets used in this study were made from a 50/50 mixture of elemental chlorine-free bleached softwood market kraft pulp (made of Scots pine, *Pinus sylvestris*) and commercial, bleached TMP (made of Norway spruce, *Picea abies*). The TMP was collected at the mill after the post-bleaching wash press. Before polymer adsorption and sheet forming, the kraft pulp was disintegrated in a Valley beater for 30 min, washed into sodium form and then beaten in the Valley beater for 8 min to Schopper-Riegler (SR)° 15. The TMP (Canadian Standard Freedom (CSF) 25) was hot disintegrated and converted into sodium form. The polymer adsorptions onto fibre surfaces were made on the pulp mixture either by using cationic polymers (a high MW and a crosslinked (CL) cationic polyacrylamide (C-PAM)) or by using two-component complexes of high MW C-PAM (1%) and CMC or CL C-PAM (3.5%) and anionic polyacrylamide (A-PAM). Some properties of the chemicals are presented in Table I. The cationic component was added to the pulp first, followed by the anionic component after 30 min. The consistency in the adsorption experiments was 5 g/L, ionic strength 0.5 mmol/L NaHCO₃ and reaction time under magnetic stirring 30 min. After the adsorption, 60 g/m² handsheets were prepared in a semiautomatic sheet former producing 240 mm x 290 mm test sheets using recirculated white water. NaHCO₃ solution (0.5 mmol/L) was used during sheet forming. The sheets were washed at 400 kPa for 5 min.

Drying of the sheets was carried out with the paper drying rheometer (PDR) device enabling biaxial straining, with 6 x 500 W halogen lamps for drying (Fig. 2). The PDR device is a construction with 6-7 separate clamps for each side of the paper sample. Each clamp is connected to a high-precision sensor that measures position and force throughout the experiment. The drying procedure is controlled with a computer and the measurements from the sensors are recorded on-line with special computer software. The PDR device utilizes both hydraulic and pneumatic drives for moving beams onto which the clamp–sensor constructions are attached. By controlling the beam movement, the paper sample can be subjected to various controlled strains during drying, for example. In this test series, the idea was to achieve different levels of drying stress by straining the sheets just before drying. First, the sheets were attached to the drying device and a preliminary straining was done to obtain a zero stress level. The sheets were strained at the solids content of ~30%, immediately after wet pressing. Then, drying commenced immediately after this. Five strain levels, -1, -0.5, 0, +0.5 and +1%, on both in-plane directions of the test sheet, were used.

The dried sheets were conditioned (23°C, 50% RH) and tested for tensile properties, bond strength (Scott bond strength and elastic breaking strain) and in-plane tear strength, which was measured with an MTS 400 tensile tester (MTS Systems Corp., Eden Prairie, MN, USA) according to the procedure described in [13]. Also, damage analysis was carried out. It produces two parameters, damage width and pull-out width: damage width measures the extent of damage or fibre debonding from the actual crack line, and pull-out width describes the extending of fibre ends from the crack line [14].

Certain assumptions were made when assessing the results of this study. Tensile stiffness or elastic modulus is an indicator of the level of activation in the sheets [15]. Scott bond strength represents the z-directional bond strength, whereas elastic breaking strain, calculated as tensile index divided by tensile stiffness index, gives an indication of bonding in the in-plane direction. A calculated variable (in-
plane tear index divided by damage width) is assumed to combine these two aspects of bonding, at least to a certain extent. Damage width indicates how far a fracture will progress in a paper network, and its extent depends on bond strength and fibre strength in the fibre network.

RESULTS AND DISCUSSION

The adsorption of both high MW C-PAM and CL C-PAM, as different polymer complexes, increases somewhat the overall tensile strength of the sheets. The effect of high MW C-PAM seems to be more of a trend than a clear increase in tensile strength (Fig. 3) although, with certain adsorptions, there are statistically significant differences between the tensile strength values of untreated and adsorbed sheets, depending on the strain level in which the sheets were dried. Combined C-PAM and CMC complexes seem to have the ability to increase tensile strength, and this seems to take place especially in the sheets that have been subjected to higher drying stress. The effect of CL C-PAM (plus A-PAM) is more pronounced and even small additions of single polyelectrolytes show a statistically significant increase in tensile strength (Fig. 4). Combining CL C-PAM with A-PAM to form polyelectrolyte complexes does not seem to increase tensile strength that much and, with the combined 3.5% CL C-PAM and 1% A-PAM treatment, tensile strength is decreased as drying stress increases to its maximum (10% strain).

As for the effect of drying stress on tensile strength, it can be said that the tensile properties of paper are improved generally by increasing drying stress. Especially elastic modulus is affected favourably [16,17]. However, tensile strength increases only slightly with increasing drying stress. It is thought to reflect both activation and bonding. Since drying stress affects bonding negatively and at the same time leads to increased activation, the overall effect of drying stress on tensile strength should be minimal. In the two figures (Figs. 3,4), however, it can be seen that there is a slight increasing trend in the tensile strength of the test sheets with increasing drying stress. It might be that the polyelectrolyte complexes affect interfibre bonds favourably and hence counter the negative effect of drying stress on bonding.

The straightening of initially slack fibre segments leads to an increase in the elastic modulus of the paper web, as has been reported earlier by Huhn [9]. Tensile stiffness values five times the original can be reached with increasing strain [18]. A significant increase in activation is visible in most of the test points, as the drying stress increases (Figs. 5,6). Polyelectrolyte addition does not affect the tensile stiffness of the sheets significantly, except for the two CL C-PAM test points, where drying stress has been the highest (Fig. 6). There, one can see some sort of increase in tensile stiffness with all the C-PAM (plus A-PAM) treatments, although there are no actual statistically significant differences between the treatments – the smallest C-PAM addition increases tensile stiffness as much as the highest complex treatment. On the other hand, this increase in tensile stiffness also can be interpreted as a lack of activation in the untreated sheets: tensile stiffness clearly increases, in some of the cases almost linearly, with increasing drying stress in all other test points (both in Fig. 5 and in Fig. 6), whereas the untreated test points in Fig. 6 do not exhibit such an increase, and tensile stiffness seems even to decrease with increasing drying stress. It is not clear whether this is an actual effect caused by the polyelectrolyte treatment or drying stress: the standard deviation of the tensile stiffness measurements was quite high, and the increase might be explained simply by variation (in sheet structure and adsorption patterns).

Both the MW and the CL C-PAM treatments increase the bond strength of the sheets both in the z direction (Fig. 7) and in the in-plane direction (Fig. 8). Especially the complex forms of high MW C-PAM and CMC seem to

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Fig. 3. The effect of drying stress on the tensile strength of sheets adsorbed with high MW C-PAM and combined C-PAM and CMC complexes.

Fig. 4. The effect of drying stress on the tensile strength of sheets adsorbed with CL C-PAM and combined C-PAM and A-PAM complexes.

Fig. 5. The effect of drying stress on the tensile stiffness of sheets adsorbed with high MW C-PAM and combined C-PAM and CMC complexes.

Fig. 6. The effect of drying stress on the tensile stiffness of sheets adsorbed with CL C-PAM and combined C-PAM and A-PAM complexes.
be effective in improving bonding (Fig. 7). Dry-
ing stress affects the bond strength negatively, although the decrease is statistically significant only between certain test points, usually be-
tween the highest and lowest strains. Increased stress disturbs bonding, reduces the bonded area and even breaks up bonds in the sheet (wit-
tnessed as decreasing sheet density). Similar re-
sults have been published by Wahlström et al. [17]. However, the decrement in Scott bond strength seems to be lower with certain polymer treatments. For example, when 1% high MW C-PAM is added, Scott bond values stay approximately unchanged regardless of the in-
creasing drying stress between strains from -0.5 to 0.5%.

Similarly, the polyelectrolyte treatments have a positive effect on the in-plane direc-
tional bond strength (Fig. 8), especially with a high dosage and in the complex forms. There are no significant differences between the three. Drying stress causes an approximately linear decrease in bonding also in the in-plane direction but, with the polyelectrolyte treatments, the effect is visibly smaller, and deteriora-
rection seems to take place only with higher drying stresses. For example, within the 1% C-
PAM treatment test points, there are no statisti-
cally significant differences between the various strain (drying stress) levels.

All in all, the polyelectrolyte complexes seem to affect the behaviour of the bonded ar-
eas within the paper network, resulting in a structure able to resist the negative influence of straining. This effect could arise from changes in bond structure and changes in water removal from the bonded area during drying.

The rather drastic effect of polyelectro-
lyte complexes on the drying behaviour of the test sheets is seen in Fig. 9. The relationship be-
tween bonding and activation in the untreated kraft–TMP sheets is linear, with activation in-
creasing significantly and bonding deteriorat-
ing somewhat with increasing drying stress. This is what can be expected in most sheets dried and strained similarly, with the extent of increase in activation and deterioration in bonding varying depending on the sheet furnish. In the C-PAM-adSORbed sheets, a similar trend cannot be detected. The improvement in activa-
tion due to the increasing straining of the sheets prior to drying is visible clearly in all of the treatments but, as for bonding, the effect of drying stress is ambiguous. For example, in sheets treated with 1% high MW C-PAM, bonding is improved at first while drying stress increases. Even the higher drying stresses do not cause significant decreases from the ini-
tial bond strength level at -1% strain be-
fore drying. The more polyelectrolyte is added, the less the drying stress affects the bonding, with the exception of the 3.5% C-PAM addition: in those test points, bonding remains level until the highest strain is reached, at which point bonding de-
creases significantly.

The results suggest that, with the right dry-strength chemi-
cal or combination of polyelectrolyte com-
xplexes, it might be possible to counter the negative effect of drying stress on the bond strength of paper and simultaneously to affect the in-plane strength properties (activation) positively. The exact mechanisms of the way these polyelectrolytes affect bonding, bond structure and bond strength are not yet under-
stood fully. However, possible explanations in-
clude the possibility that the polyelectrolytes may form some sort of flexible gel-like layers between fibres at the bonded areas, thus con-
tributing directly to bond strength and the beha-
vior of bonds in drying. Also, an interaction be-
tween the polyelectrolytes and the fines, es-
specially those of the TMP, might in part explain the findings. A considerable part of the polyelectrolytes may actually be adsorbed onto fines instead of onto fibre surfaces. The fines then become retained more readily in the test sheets. The positive effect of fines on paper strength and especially bond strength has been reported widely [6,19,20].

CONCLUSIONS

Both the high MW C-PAM and the CL C-PAM increased the tensile strength of test sheets somewhat. Especially the complex forms of both C-PAMs were effective. Drying stress did not have a significant effect on tensile strength, as this property is affected by both bonding (decreasing with increasing drying stress) and activation (increasing with increasing drying stress). The adsorption of polyelectrolyte complexes onto fibre surfaces did not affect tensile stiffness, i.e. activation, significantly, whereas increasing drying stress did. The adsorption of polyelectrolyte complexes also increased the z-directional and in-plane directional bond strength significantly. The effect of drying stress on bond strength was slightly negative. With some of the C-PAM plus anionic polyelectrolyte complexes, it was pos-
sible to counter the negative effect of drying stress on bonding without impairing tensile strength or activation. In general, activation in-
creases with increasing drying stress whereas
bonding deteriorates, depending on the pulp type. Certain polymers seem to have the ability to change the relationship between bonding and activation, and may affect the behaviour of paper during drying.

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REFERENCES


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