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Dependence of Sheet Properties on the Location of Adsorbed Polymer

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SUMMARY

By choosing the point of addition of the strength aid, the papermaker can control its location in the sheet. This study explored the effect of various points of addition on dry (50% RH) and moist (92% RH) tensile and compressive strength and on wet tensile strength. A combination of polyamide polyamine epichlorohydrin (PAE) and carboxymethylcellulose (CMC) was used with a southern pine unbleached kraft pulp.

Strength aids added separately to the classified pulp components (long fiber and fines) produced the highest strengths when adsorbed on the long fiber only. Attempts to achieve this effect (without classifying the pulp) by adding the strength aid before beating were unsuccessful.

The much larger percentage enhancement of strength for classified compared with whole pulps was shown to be due to a shift in the mechanism of failure. Untreated sheets have a strength that is governed by the bond strength between the fibers. With the addition of a strength aid, the bond strength is increased and the individual fiber properties (fiber axial and wall strengths) become the limiting factor.

Wet-end addition of strength aids was shown to be much more effective than external additions. It is important to have the polymer within the crossover region between two fibers (i.e., the bonded area) and not just around the periphery of the bond. The combination of PAE and CMC produced greater
strength than PAE alone. Both tensile and compressive strengths could be improved by the combination, but the relative effect of the two polymers on the two strengths was different.
INTRODUCTION

The recent trend in papermaking is toward weaker sheets. This is a result of several factors: (1) lower basis weights, and increasing percentages of (2) hardwood, (3) secondary (recycled) fiber, and (4) mineral fillers. Despite these changes papermakers would like to maintain or even enhance the strength of the paper. To accomplish this, they have turned increasingly to the use of chemical strength aids. Although effective, these usually polymeric materials are rather expensive. It is essential to use them efficiently.

Strength aids may be added at a variety of points in the wet end or at the size press. The particular point of addition gives the papermaker some control over the ultimate location of the strength aid within the sheet. The work presented below was undertaken to clarify whether this "location" had a strong influence on the resulting sheet properties.

In the following discussion the "location" of the strength aid will be used in either of two senses. First, it will be concerned with whether the polymer is adsorbed on the long fiber fraction or the fines fraction of the pulp. In the second case it will refer to whether the polymer(s) is within the fiber/fiber bonded area or whether it is only external to this area. Both of these "locations" can be influenced by the point of addition.
EXPERIMENTAL

Materials

Southern pine unbleached kraft pulps were used. Because this work extended over a period of several years, a number of similar but distinct pulps were employed. All were in the 47-49% yield range. The pulps were beaten in a Valley beater to a level of about 350 mL CSF unless stated otherwise. In some cases the beaten pulps were classified by two passes at very dilute consistency (0.01%) over the IPC Web Former. The separated fines were saved for later read- dition to the long fiber fraction.

A wet-strength aid, polyamide polyamine epichlorohydrin (PAE), which has also been shown to improve dry strength (1), was used in conjunction with carboxymethylcellulose (CMC). Espy (1) has shown that the latter provides a synergistic effect with PAE on the strength properties. The CMC was a low viscosity material with a 0.7 degree of substitution. Our exploratory studies showed that an addition ratio of 0.4:1.0 (CMC:PAE) was optimum in agreement with previous work (1). Unless otherwise indicated the addition rate was 1% PAE and 0.4% CMC based on o.d. pulp.

Tap water was used throughout and was adjusted to a pH of 4.5 unless otherwise indicated.

Procedures

Handsheets

The required amount of PAE solution, (1% w/v) was added to a vigorously stirred batch of pulp at 0.5% consistency. Moderate stirring was
then continued for five minutes. The CMC solution (1% w/v) was then added under similar conditions. A series of handsheets was then formed from this treated batch of pulp. An aliquot of the pulp sufficient to form a 62 g/m² sheet was diluted to 0.04% consistency in a Noble & Wood sheet mold. After formation, the sheet was couched from the 100 mesh monel wire onto blotters. The sheet/blotter sandwiches were pressed at 50 psi for five minutes and then dried on a steam drum at 105°C for seven minutes.

Tub Sizing

For some experiments sheets were formed as above but without one or both of the additives. These (dried) sheets were then immersed in a tray containing a solution of the additive at a concentration necessary to give the desired pickup. After immersion for 30 sec, the sheet was passed through a squeeze roll and dried on the steam drum at 105°C for seven minutes. Pickup (dosage) was based on the wet weight of the squeezed sheet and the air dry weight of the sheet before immersion. This assumes pickup is by imbibition of the polymer solution only and neglects polymer adsorption effects. These should be small at the short time and stagnant (no mixing) conditions of the immersion. Sheets dipped in water-only trays served as controls to ascertain the effects of rewetting the sheets and of additional drying (curing) time on the physical properties.

Beating

For some experiments the strength aids were added before refining in the following manner. A batch of pulp at 1.8% consistency was circulated in the Valley beater with no load on the bedplate. The pulp was treated with 1% PAE (based on o.d. pulp) and circulation was continued for two minutes. Treatment
with 0.4% CMC followed with further circulation for three minutes. (The shorter
times used here, compared with the handsheet studies, reflect the higher pulp
consistency and thus collision frequency.) After the polymers were added and
adsorbed, weight was added to the bedplate and beating for the desired time
was carried out. The beaten pulp was diluted to 0.5% consistency and handsheets
were formed as described above.

Testing

The dried handsheets were preconditioned at 20% RH, 73°F for 24 hours
and then conditioned at 50% RH, 73°F for 24 hours before testing. Dry and wet
tensile tests were performed according to the TAPPI Standard Methods T494 and
T456, respectively. Samples to be tested "moist" were conditioned at 92% RH,
73°F for 24 hours and then tested at those conditions.

Polymer Adsorption

The amount of PAE adsorbed on the pulp under the standard conditions
(0.5% pulp consistency, 5 minute contact time, moderate agitation) was deter-
mined by difference by measuring the amount of unadsorbed PAE. Samples of a
beaten pulp (350 mL CSF) were treated with various dosages of PAE (0.9–4.5% based
on o.d. pulp) according to the standard conditions listed above. At the end of
the contact time, the pulp slurry was quickly filtered on a Nuclepore 2.0 µm
membrane under vacuum. The filtrate was analyzed for PAE using a colloid titra-
tion method (2) with spectrophotometric detection.
RESULTS AND DISCUSSION

Polymer Adsorption

Because arguments in the following sections depend upon an assumed location of the strength aids, it is important to determine what fraction of the polymers are adsorbed under the standard conditions. The unadsorbed fraction may, of course, adsorb on the pulp's surface at a later time or form a complex in solution with an oppositely charged polymer. This latter event would defeat the effectiveness of both polymers.

When determining the adsorption of a polymer on a pulp containing fines, it is essential to separate the pulp from the supernatant solution by using a very small pore filter. Otherwise polymer adsorbed on colloidal-sized fines will be present in the supernatant and may be measured as unadsorbed polymer. The choice of a 2.0 μm pore size filter was a compromise between the conflicting goals of eliminating fines in the filtrate and of achieving a reasonable flow rate through the filter.

The adsorption at pH 4.5 of PAE on a beaten whole pulp was measured as described in the Procedures section. The results in Fig. 1 show that, at the dosage used in most of the experiments to be discussed (1% based on o.d. pulp or equivalently here 50 mg/L), approximately 96% of the PAE is adsorbed. A negligible amount remains unadsorbed, and hence the location of the PAE in the system can be assigned unambiguously.

(Figure 1 here)

The zeta potential of the fines of the PAE adsorption samples (and of other samples at lower dosages) was determined by microelectrophoresis. The isoelectric point is at a dosage of about 0.15%. The zeta potential at a PAE
dosage of 1% is +14 mV. At higher dosages it appears to reach a plateau of +18 mV. It is interesting that almost 100% adsorption is still possible at 1% dosage when the surface is strongly cationically charged.

It should be mentioned that the curve in Fig. 1 is not an equilibrium adsorption isotherm. Adsorption was measured after a contact time of five minutes. At low dosages equilibrium may have been reached, but certainly at the higher dosages with the concomitant highly charged pulp surfaces, more adsorption will occur with time.

Having proved the virtually complete adsorption of the PAE under our experimental conditions, we turn our attention to the subsequent adsorption of the CMC. Here Neal (3) has shown, over a similar range of dosages of PAE and CMC, that the CMC is completely adsorbed. Thus, we can be confident in the following studies that the PAE and CMC added to the pulp are essentially 100% adsorbed.

**Location on Fibers and Fines**

It is well-known that the presence of fines in a pulp enhances the strength properties. The exact mechanism is not clear. Likewise, how strength aids interact with fibers and fines to improve strength is not known. To distinguish the effects of strength aid adsorption on fibers and fines, we used a classified pulp and its associated fines. The whole pulp before classification had 12% fines determined by a Bauer-McNett classification through a 200 mesh screen. The several pulps and components were each treated with 1.5% PAE (based on o.d. pulp) and the four samples are denoted as follows:
a) Classified - Only the long fiber is treated and used to prepare handsheets.

b) Whole - The unclassified pulp is treated and used. This is equivalent to the typical addition method in the mill.

c) Separately - The classified pulp and the separated fines are each treated with PAE. The treated components are then blended in an 88/12 fiber to fines ratio, and handsheets are formed.

d) Fiber only - The classified pulp is treated and is then mixed in an 88/12 ratio with untreated fines.

The results are listed in Table I.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Breaking Length, km</th>
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<tbody>
<tr>
<td></td>
<td>Dry</td>
</tr>
<tr>
<td>Classified</td>
<td>5.4</td>
</tr>
<tr>
<td>Whole</td>
<td>6.3</td>
</tr>
<tr>
<td>Separately</td>
<td>6.8</td>
</tr>
<tr>
<td>Fiber only</td>
<td>7.1</td>
</tr>
</tbody>
</table>

The effect of including the fines in the furnish can be seen by comparing the results for the "classified" and "whole samples". Fines increase all three strength properties. It is well-known that fines adsorb a disproportionate share of additives because of their large surface area (4-6). This is reflected in the results here on the "whole" and "separately" samples. Carrying out the PAE adsorption so that the fiber and fines receive equivalent dosages
based on their weight ("separately") rather than on their surface area ("whole") leads to increased strength. It is perhaps surprising that treatment of just the long fiber ("fiber only") produces greater strength than the treatment of both fines and fiber ("separately"). It is possible that not treating the fines reduces their tendency to attach to the long fiber prior to formation. This in turn would decrease the interference of the attached fines with fiber/fiber bonding. This hypothesis assumes that the fines contribute their positive effect (cf. "classified" vs. "fiber only" samples) by attachment to the fibers along the periphery of the fiber/fiber bond. Such a location of the fines would occur naturally due to surface tension forces during drying and would help to bolster the bond strength at the periphery where stress concentrations are highest. Further work is required to verify this hypothesis.

The above results suggest that treatment of just the long fiber with a strength aid is one method to maximize strength. Since classifying refined stock in the mill is probably not economically feasible, an alternate scheme was sought. One possible method would be to treat the pulp before refining. The strength aid could then only adsorb on long fiber. So long as most of the fibers' outer walls (containing the adsorbed polymer) remained intact during subsequent refining, the method should be successful. Obviously, the more outer wall removed during refining to form fines, the lower the fraction of the polymer that will be associated with the long fiber.

To test the proposed method, we added the strength aids to the beater before refining as described in the Procedures section. The treated pulp was then beaten for one of several intervals, and handsheets were then prepared as usual. For comparison untreated pulp was beaten for the same periods of time.
after which strength aid addition and sheet formation proceeded as usual. Treated and untreated pulps had similar freenesses after a given interval of refining.

The results for moist tensile and compressive strengths are presented in Fig. 2 and Fig. 3, respectively. Evidently, either method of strength aid addition enhances the properties, but addition after refining is the more effective. The data point at 50 minutes for "after refining" in Fig. 3 is believed to be in error, because all other physical properties (including dry STFI compressive strength) showed an increase from 25 to 50 minutes. Both dry (50% RH) and wet tensile strengths showed similar behavior to that in Fig. 2 and Fig. 3. In the case of "before refining" addition, apparently sufficient wall material is removed via fines production during the beating process that the advantage of adsorbing the polymers just on the long fibers is lost.

(Figure 2 and 3 here)

The results in Fig. 2 are replotted as the tensile factor (i.e., the ratio of the tensile strength with additives to that without the additives) in Fig. 4. Here the decreased effectiveness of the strength aids with refining is clear. The strength enhancement is cut almost in half at 50 minutes beating time (450 mL CSF) compared with the unbeaten pulp.

(Figure 4 here)

To clarify this behavior, we added the strength aids (1% PAE, 0.4% CMC) to a whole pulp beaten to 350 mL CSF and to the same pulp after the fines had been removed. The results for the (dry) tensile strength are presented in Table II.
Table II. Influence of Fines on Strength Aid Effectiveness

<table>
<thead>
<tr>
<th></th>
<th>Breaking Length, km</th>
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<tbody>
<tr>
<td></td>
<td>No strength aid</td>
<td>With strength aid</td>
<td>Enhancement, %</td>
</tr>
<tr>
<td>Whole Pulp</td>
<td>6.1</td>
<td>8.3</td>
<td>36</td>
</tr>
<tr>
<td>Classified Pulp</td>
<td>3.9</td>
<td>7.8</td>
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</tbody>
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The greater effectiveness with the classified pulp is striking. Two hypotheses can be suggested.

1. Because of the much greater surface area of the whole pulp, the strength aid dosage used may lead to the polymers being spread too thinly to achieve the maximum potential enhancement. For the classified pulp the used dosage may be much nearer the optimum.

2. Sheet strength is a function of both fiber/fiber bond strength and individual fiber tensile strength (7). Upon incorporation of the strength aids into the sheet, we may have so strengthened the bonds that the fiber strength is now the "weak link".

To test the first hypothesis we treated a whole pulp with a range of dosages of PAE and CMC keeping the CMC/PAE ratio at 0.4 as shown to be optimum (1). The results are plotted in Fig. 5 where the dosage is the sum of the PAE and CMC percentages. A similar pattern is exhibited by the tensile strength for each moisture level. There is a rapid initial rise in strength enhancement followed by a plateau. The dosage used in the work described above (Fig. 2-4 and Table II) was equivalent to 1.4% on the abscissa of Fig. 5. This is near the beginning of the plateau or maximum strength possible with this pulp and strength aid. Apparently this dosage is adequate to provide sufficient polymer
adsorption to both fines and fiber to produce strong bonding. Further increments of strength aid add nothing more to the strength.

(Figure 5 here)

Such behavior suggests that the second hypothesis may be viable. Fiber strength is now the weak link; it is generally believed that polymeric strength aids such as those used here do not improve fiber strength. Evidence for this hypothesis was sought by examining the fibers in the region of failure of tensile test specimens. Typical results are shown in Fig. 6 and Fig. 7 at 9x and 50x magnification, respectively. Evidence for bond failure is a predominance of fiber pull-out with little fiber rupture. Predominantly fiber failure should result in little fiber pull-out. The progression from left to right in Fig. 6 and Fig. 7 corresponds to dosages of 0, 0.7, and 2.8%. In Fig. 5 the latter two are seen to lie in the steeply rising and plateau portions, respectively. From 0 to 2.8% there is a steady progression of decreasing fiber pull-out and increasing fiber rupture. We conclude that the strength aid has shifted the mode of failure. This result agrees with the findings of previous workers (8, 9). They compared pulps which were untreated or treated with 10% locust bean gum. Using dyed fibers, they were able to quantify the fraction of fibers broken as a function of treatment. By increasing the bond strength either by refining or by chemical additive, they observed more fiber breakage.

(Figure 6 and 7 here)

This finding also helps to explain the behavior seen in Fig. 4. At zero beating time the strength aids contribute a large enhancement to the stiff, poorly-bonded fibers. With increasing beating the fibers are rendered more flexible and conformable, and fines are produced. Both of these factors lead to improved bond strength, and the potential for further sheet strength enhancement with additives is concomitantly reduced.
Strength aids can also affect the locus of bond failure. For single fiber/fiber bonds, we have shown (10) that for untreated fibers the failure occurs between the two fibers with little or no disruption of the walls (top of Fig. 8). When the fibers are treated with PAE and CMC as above, the failure now occurs within the wall of one or both fibers (bottom of Fig. 8). The location of the failure has been changed and the bond strength has been increased (10).

(Figure 8 here)

**Location in the Vicinity of the Bond**

It is generally believed that polymeric additives improve strength by one or more of the following factors:

a) by increasing the total number of (hydrogen) bonds per unit fiber to fiber crossover area because of the ability to bridge across the gap between the rough surfaces of the fibers,

b) by increasing the bonded area because of the ability to bridge the larger gap between the fibers around the periphery of the fiber/fiber bond,

c) by increasing the toughness of the bond because of the long chain nature of the polymer and its ability to permit deformation in the bonded area without bond failure, and

d) as a result of b) and c) above the polymer-treated fibers can better withstand the stress concentrations that naturally arise around the periphery of the bond.

In addition, for some materials including those used here (1), covalent bonds formed between the additive and the fiber surface replace or supplement the much
weaker hydrogen bonds between the untreated fibers. Such materials are also wet strength aids. For this use they are believed (11) to function by either: 1) forming a covalent, water-insensitive bond between the fibers ("reinforcement") or, 2) forming a crosslinked network around the fibers ("protection"), thereby preventing water penetration to the traditional hydrogen bonds between the fibers and also minimizing fiber swelling.

These hypothesized mechanisms for wet and dry strength additives suggest that the detailed location of the polymer in and/or around the fiber/fiber bonds will influence the sheet strength. To determine whether the location is indeed important, we used a series of internal and/or external methods of treating the fibers. These would correspond, respectively, to wet-end addition and tub sizing-type processes in the mill. Sheets were formed from untreated (U), treated with 1% PAE (TP), or treated with 1% PAE followed by 0.4% CMC (TPC) classified unbleached softwood kraft pulp. The fines had been removed from the beaten pulp (before treatment) to heighten the differences among the several internal and external treatments and to eliminate the strength-enhancing effect of the fines. Because the polymer additives also act as fines retention aids, comparison of the effect of the several strength aid treatments could be obscured by concomitant variations in fines retention if unclassified pulp were used.

Some of the dried sheets (U, TP, TPC) were subsequently immersed in trays containing water, PAE solution, or CMC solution as described in the Procedures section. The various sequences of treatment were chosen to apply the strength aids to particular surfaces. An example of a sheet whose fibers had been treated by wet-end addition of PAE (coded TP) followed by subsequent sheet
immersion in CMC solution is shown schematically in Fig. 9. It is assumed here that fiber/fiber bonding is not disturbed by immersion in CMC solution and that the latter cannot enter the bonded regions. This is a reasonable assumption when PAE (or PAE/CMC) is the bonding agent because of the covalent bonds formed with the fibers (1). It is less clear whether this also holds for untreated (U) sheets. However, the relatively short immersion time (30 sec) and the substantial wet web strength of the sheets reflected in their ease of handling through the steps of removal from the immersion bath and passage through the squeeze rolls imply that extensive fiber/fiber bonding was maintained in this case, also.

(Figure 9 here)

The results from these experiments are displayed in Fig. 10-13. For dry tensile strength (Fig. 10), moist compressive strength (Fig. 11) and wet tensile strength (Fig. 12) several trends are evident. a) Introducing a strength aid, either PAE or CMC, at the wet end, produces greater strength than if the polymer is added externally. This implies that supplementing the bonding in the crossover area between the fibers is an important mechanism for these agents. For wet tensile strength this suggests that the "reinforcement" mechanism predominates over that of "protection". b) Increases in strength of PAE-containing sheets produced by subsequent immersion in water and redrying reflect additional crosslinking of the PAE with itself and/or additional reaction of PAE's azetidinium groups with carboxylate groups on the fibers (or CMC, if present). c) When the untreated sheet (U) is immersed once or twice in water, the dry and moist compressive and tensile strengths (and also the values not reported here for tensile energy absorption, extensional stiffness, and strain at failure) suffer severe losses. This suggests loss of bonding during the immersion and incomplete recovery of the bonding during the subsequent squeezing
and drying processes. The absence of a corresponding significant loss in density and the high level of solids (40%) out of the squeeze roll (cf. 37% solids after pressing for 5 min at 50 psi), however, do not support this explanation. It is difficult to rationalize the losses in strength due to water immersion because the drying conditions (time, temperature, and amount of restraint) were the same for all sheets.

(Figure 10-13 here)

The combination PAE/CMC has rather different effects on the compressive and tensile strengths as shown in Fig. 13. Adding PAE externally to an untreated sheet or internally (wet-end addition) produces a large increase in tensile strength. Subsequent external treatment with CMC provides only a small additional increment. A somewhat larger effect is seen when the CMC is added internally (cf. TP and TPC) showing the importance of the latter within the bonded (crossover) area. For compressive strength the opposite is found. Adding PAE only, whether internally or externally produces little or no improvement. However, when CMC is incorporated either internally (cf. TP and TPC) or externally, substantial increases result. Apparently, tensile strength and compressive strength are dependent in different ways on the bonding produced by the strength aid(s). This suggests that a more detailed study of the interactions between the polymers and the cellulose surfaces and between the polymers themselves could produce the understanding needed to design still more effective strength aids.
CONCLUSIONS

The optimum location of the strength aid is on the long fiber, not the fines. Strength aids can improve the bond strength to the point where fiber failure in the axial direction or within the cell wall becomes the limiting factor (weak link). Because wet-end addition is much more effective than external addition, the function of the strength aids is to increase the bond strength within the bonded area.
ACKNOWLEDGMENTS

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LITERATURE


Fig. 1. Adsorption isotherm for PAE on a whole beaten softwood unbleached kraft pulp. Contact time is five minutes.
Fig. 2. Evolution of moist (92% RH) tensile strength with beating as influenced by mode of strength aid addition.
Fig. 3. Evolution of moist (92% RH) STFI compressive strength with beating as influenced by mode of strength aid addition.
Fig. 4. Variation with beating of the ability of the strength aid (PAE/CMC) to enhance the moist tensile strength.
Fig. 5. Influence of strength aid dosage (% PAE + % CMC) on the tensile strength of sheets made from a whole beaten softwood unbleached kraft pulp. CMC:PAE is 0.4.
Fig. 6. Photomicrographs of the failure region of tensile test specimens at the indicated strength aid dosages. Magnification 9X.
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Fig. 8. SEM photomicrographs of the formerly bonded region of a fiber/fiber pair after bond breakage. Top: no strength aid. Bottom: treated with 1% PAE/0.4% CMC.
Fig. 9. Schematic of a portion of a fiber/fiber bond showing location of PAE and CMC when the PAE has been added at the wet end and the CMC has been added after sheet formation.
Fig. 10. Effect of a sequence of internal and external treatments on the dry (50% RH) tensile strength. U = untreated, TP = PAE added internally, TPC = PAE followed by CMC added internally. Codes above the arrows refer to immersion of dried sheets into baths of aqueous solutions of the indicated components.
Fig. 11. Effect of a sequence of internal and external treatments on the moist (92% RH) STFI compressive strength. Codes same as Fig. 10.
Fig. 12. Effect of a sequence of internal and external treatments on the wet tensile strength. Codes same as Fig. 10.
Fig. 13. Comparison of the relative effects of PAE and CMC on the compressive and tensile strength. Codes same as Fig. 10.