Can recycled kraft fibres benefit from chemical addition before they are first dried?

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The goal of this work is to overcome the loss of bonding strength experienced by kraft fibres when they are dried and reslurried. Paper strength was compared in the presence or absence of chemical pre-treatments of the refined, never-dried pulp. Polyelectrolytes of relatively high molecular mass had the greatest beneficial effect on the compression strength of recycled unbleached kraft paper. Results were consistent with the persistent nature of charged complexes formed by polyelectrolytes at fibre surfaces, and the contribution of such complexes to inter-fibre bonding, even after drying and recycling. Differing effects of certain chemicals on compression versus tensile tests suggest that chemicals can affect not only the extent, but also the physical properties of inter-fibre bond sites.

Keywords  
Recycling, dry strength, compression strength, linerboard, unbleached kraft

In 1963 Higgins and McKenzie had a radical idea: treat kraft pulp fibres before they are ever dried in order to improve the strength properties when the once-dried fibres are made into paper (1). The idea was radical because of the times. Relatively little paper
was being recycled, and people were more concerned about strength losses during production of dry-lap pulp. Subsequent work has shown that strength loss is more important in the case of refined pulp for papermaking, compared to the production of dry-lap pulp, which is unrefined (2). To put things in perspective, the utilization rate of waste fibres (OCC) in recycled containerboard in 1963 was reported as 21.1% in the U.S. (3). In 2001 OCC comprises about 67% of the fibre for U.S. containerboard production (4), and the recovery rate of old corrugated containers is approximately 70% when exports are considered (5-6).

All of the treatments discussed in this article will be of the same nature as those described by Higgins and McKenzie (1) – chemical additions to never-dried pulp used to make first-generation handsheets, and then nothing added when making the recycled (2nd generation) handsheets. The cited work identified several types of chemical treatments that yielded measurable improvements in the bonding strength of recycled handsheets, compared to untreated kraft handsheets that had been repulped and formed again. In subsequent years there have been many studies that have added greatly to our understanding of how the drying of kraft fibres can cause essentially irreversible losses in bonding ability (7-22). A few innovative studies have shown that chemical derivatization of fibre surfaces sometimes can prevent strength losses from occurring (20-22). However, relatively little published work describes pre-treatment with non-reactive chemicals that can be added to fibres under typical papermaking process conditions (22-24).

Higgins and McKenzie obtained encouraging results with simple sugars, but very high concentrations were required (1). Those tests have been replicated by others,
including the present authors (22,24). Sugars at very high concentrations appear to inhibit some changes in the fibre surfaces and pores caused by drying (1,7,22), even though they have little affinity for the fibre surface (25). These results show the mechanism of strength loss; however papermakers have not rushed to add sugars to their process.

The present study focuses on chemical pre-treatments that are more likely to adsorb from solution onto fibre surfaces. Unbleached kraft pulp of relatively high freeness was selected for this work because of its importance for the most highly recycled grade of paper, old corrugated containers (OCC) (26).

Given the relative scarcity of data related to the effects of additives on the bonding potential of fibres after they are recycled (22-24), the experimental approach chosen for this initial phase of the project may be described as a “screening” study (see Experimental). Factors used for selecting a range of contrasting candidate materials for the screening tests included the following: (a) presence and degree of carboxylic acid content or other anionic groups, (b) presence and degree of cationic groups, (c) presence of hydrophobic groups, and (d) molecular mass and structure. Self-imposed constraints on the strength-enhancing strategies considered in the work reported here included the following:

- Additives should be water-soluble and non-toxic.
- Additives reported here are added only to the refined, never-dried pulp, not later.
- Other than chemical preparation and feeding, no additional unit operations, e.g. washing stages, should be required.
The main focus is the strength of the “recycled” paper, following a cycle of virgin handsheet forming, oven drying, reslurrying, and secondary sheet formation without further refining or chemical addition.

A condition is to be considered “successful” if the treatment not only improved the strength of the recycled paper, but also gives either a positive effect or no significant effect on the strength of virgin sheets.

**THEORY**

There are at least two ways in which a non-reactive chemical added to never-dried fibres could affect the strength of recycled paper. As illustrated in Fig. 1, one can expect different results if the additive is absorbed into the fibre cell walls (Case A) versus those that tend to stay at the outer surfaces (Case B). Past work has shown that pores in the cell walls of kraft fibres are readily penetrated by water-soluble monomers, as well as by oligomers up to about 10,000 Daltons (25). In principle, much larger macromolecules may absorb into the 5-20 nm slit-like pores of a typical never-dried kraft pulp fibre by a process of reticulation, i.e. snake-like movement (27). In practice, there is insufficient time during papermaking operations for the system to approach an equilibrium state (28). It is safe to assume that macromolecules in excess of 100,000 Daltons do not substantially penetrate into the fibre (25) during typical time periods of contact between the additives and paper fibre slurries. There are excellent reviews describing factors governing adsorption of macromolecules onto surfaces (28-30).
**Case A: How a molecule in a fibre wall may affect recycling**

Let’s first consider the possible mechanistic role of a chemical additive that has penetrated *into* a never-dried fibre. There are at least four ways in which past work suggests a likely bond-enhancing role for chemicals absorbed into the walls of never-dried fibres:

1. As in the pioneering work of Higgins and McKenzie, simple, non-interacting molecules such as a sugar might **inhibit closure of pores** when the fibre is dried \((1)\). Presumably the hard-to-reverse closure of submicroscopic pores results in less conformable fibre surfaces \((31)\), yielding a reduction in relative bonded area \((32)\). The effects of sugar on the strength of recycled kraft fibres have been confirmed in subsequent work by us and by others \((22,24)\). To the extent that this mechanism is active, one would expect a corresponding effect on results of water retention value (WRV) tests of the once-dried fibres \((33-36)\).

2. It is also reasonable to expect that substances filling the pores spaces of fibres can act as either **plasticizers** or **stiffeners** of the cell wall material \((37-38)\). In cases
where this mechanism is important, one ought to be able to observe characteristic effects on strength properties of the recycled paper. For example, compression strength is expected to be critically dependent on individual fibre stiffness (39-40). Fibre stiffness is expected to increase as a consequence of pore closure and other processes during drying (41). By contrast, tensile strength does not require stiff fibres, and a more compliant fibre surface can be expected to result in greater relative bonded area of the recycled paper (32).

3. Results reported by Ellis and Sendlachek (13) suggest that hydrophobic groups might affect strength of recycled fibres. A moderate degree of acetylation of fibre surfaces increases the bonding ability of fibres and the increased bonding ability remains in effect when the fibres are reslurried and formed into recycled sheets. One explanation is that the acetyl groups inhibited formation of hard-to-reverse intra-fibre hydrogen bonding (10,22). Evidence is not clear whether or not the inability of pores to reopen when the fibres are rewetted is due to local crystallization of newly joined cellulose surfaces (42), or other factors (15,17,43-44). In any case, this mechanism suggests that various substances containing hydrophobic groups ought to be included in the screening study.

4. Finally, Lindström and Carlsson (10) showed that it is possible to avoid strength loss during the drying of kraft fibres when two conditions are met. First, the fibre surfaces must have a sufficient density of carboxylic acid groups, an effect that can be achieved in the laboratory by carboxymethylation. Second, the fibres must be dried in a pH range favouring dissociation of those acid sites, i.e. when there are negatively charged surfaces. One ought to expect the same effect if non-reacted carboxylated
species can be persuaded to remain in the pores of kraft fibres. Some “persuasion” strategies considered in the present work included the use of cationic materials or groups (29-30), or hydrophobic groups (1,45-46). Other screening tests were carried out with materials of different molecular mass to achieve a balance between high-affinity adsorption (30) and ability to penetrate into small pores (25).

Past work suggests that monomeric dye molecules can benefit paper strength, especially if they are present during refining (47). While it should be noted that present experiments followed a different procedure, it is worth noting that dye molecules combine the features mentioned in items 3 and 4 above. The hydrophobic character of the chromophoric groups within a dye is expected to help in its adsorption (48). Variation of the number of anionic groups, per molecule of dye or fluorescent whitening agent offers a possible way to achieve the best balance between adsorption tendency and a possible impact on strength loss during drying.

**Case B: How additives on a fibre surface may affect recycling**

Literature related to dry-strength additives leaves little doubt that water-loving polyelectrolytes adsorbed at fibre surfaces can act as bonding agents (49-53). Effects of starch and guar derivatives, and acrylamide copolymers are usually attributed to increased relative bonded area (32,54). In certain cases the data are consistent with increased shear strength of inter-fibre bonds, per unit of area that appears to be bonded, based on light scattering analysis (55).
Less is known about the degree to which the same additives also can contribute to strength when the same fibres are recycled. The ability of an additive to contribute to bonding the second time around when fibres are recycled ought to depend on (a) whether the additive remains adsorbed, and (b) whether the additive is degraded, matted down onto the fibre surfaces, permanently dehydrated, or lost into the cell wall in the course of drying, use, and redispersal of the waste fibres. The approach taken in the present work was to compare a range of contrasting materials. Variations in molecular mass, charge type and density, and the inclusion of materials with hydrophobic groups in the pool of candidate treatments can be expected to affect both adsorption (28-29), and possible mechanisms by which the cell wall loses its bonding ability (7,15,17-21).

Carboxylated polymers at a fibre surface might be expected to benefit the bonding ability of the fibres when they are recycled, but only if they are adsorbed there. Anionic polyelectrolytes typically do not adsorb well on anionic surfaces of kraft fibres. Possible exceptions include guar gum products; these are reported as having special affinity for cellulose (56). Another exception is hemicellulose; hemicellulose that originates with the wood appears able to stay on kraft fibre surfaces and contribute to bonding in recycled sheets (57-58). A common feature of typical guar and hemicellulose products is that they are relatively low in anionic charge. An approach used in this work was sequential addition with a cationic polymer. Figures 2 and 3 illustrate ways to envision what may happen at a molecular level. In these figures black curves correspond to cationic polyelectrolytes and grey curves correspond to anionic polyelectrolytes.

Figure 2 corresponds to a proposed “mordant and glue” model. Here the cationic polymer is added first, taking advantage of its expected high-affinity adsorption to the
fibre surfaces (29-30). The cationic polymer then can serve as a point of attachment for an anionic dry-strength agent such as carboxymethylcellulose (CMC). Addition sequences roughly corresponding to the “mordant and glue” model have been reported in work focusing on the strength of the first generation of paper (59), but no corresponding results have been reported for residual effects of such treatments after fibres are recycled.

**“Mordant and Glue” Model**

**“Polymer Complex” Model**

![Fig. 2. Proposed mechanism for dual treatment of fibre surfaces](image1)

![Fig. 3. Alternative mechanism involving complexation of polyelectrolytes](image2)

Figure 3 shows a limiting model that helps to justify experiments with the opposite order of addition. This “polyelectrolyte complexation” model requires that the two additives have sufficient mobility and time to form a complex (60). This model might reasonably be applied in the case where the first additive is an anionic polymer having a low affinity for the fibre surfaces. Subsequent addition of a cationic polyelectrolyte is then expected to result in precipitation of insoluble complex onto the fibre surfaces. If this type of model is valid, then it is reasonable to expect results to be dependent on contact times, agitation, and orders of addition. Others have considered polyelectrolyte complexes in relation to paper strength (61-64), but no publication has considered possible effects of such treatment persisting after those fibres are recycled.
EXPERIMENTAL

Materials

Never-dried, unbleached pine kraft pulp was obtained from the Mansfield, Louisiana mill of International Paper Company. The sample was collected from high-density storage after the blowline and de-shive refiners. Fresh pulp was screened and centrifuged to 30% consistency. The fibres were fluffed and then refrigerated during storage. These procedures made it possible to carry out experiments from highly consistent master batches of fibre.

Starch products from Penford Products Co. included PenCat® 550, a cationic quaternary ammonium derivative having 0.27% nitrogen by mass. “Anionic starch” consisted of Astro® Gum 3010, having approximately 1% carboxymethylation. “Oxidized starch” was Douglas® 3018, with approximately 0.3% carboxylation. “Hydroxyethyl starch” was Penford® Gum 280.

The “anionic acrylamide copolymer” was Hercobond® 2000, a copolymer based on 92 mole % acrylamide groups and 8 mole % acrylic acid, yielding a charge density of 1.1 microequivalents per gram.

Guar products provided by Hercules, Inc., included the following: “Neutral guar” was Supercol® U, a product having a mass-average molecular mass of about 2 million Daltons. “Depolymerized neutral guar” (code 30M1F), and it had a molecular mass of 200,000 to 300,000 Daltons. “Cationic guar” (SP813D) had a degree of substitution of 0.13 (800 microequivalents per gram) and a molecular mass of 1.1 million Daltons. The “depolymerized cationic guar” (SPX247) had a similar composition as SP813D, but a
lower molecular mass of 500,000 Daltons. The “anionic guar” (GPX241) had a molecular mass between 1 and 2 million Daltons and a degree of substitution of 0.08 to 0.1, corresponding to 0.49 to 0.62 meq/g.

Carboxymethylcellulose (CMC) products provided by Hercules, Inc., were designated by the following codes: 7L, 7M, 7H, 9M8, and 12M8. In these codes the initial number corresponds to ten times the degree of substitution. Because each pyranose unit of cellulose has three available hydroxyl groups, the maximum theoretical degree of substitution is 3, and the samples span the most common range for CMC products. The letters L, M, and H correspond to low, medium, and high molecular mass. Typical molecular mass values corresponding to these categories are 90,000, 250,000, and 700,000 Daltons. An additional CMC product (LT446A) having lower DS of 0.35 and a molecular mass of 200,000 Daltons was obtained from Akzo Nobel. The hemicellulose was a developmental product, code 9673:83 from National Starch, and described as “corn fibre gum.” The stated purity level was 98%.

“High-mass chitosan” was a Vanson product, Natural Biopolymer SC442, a material with 83.5% deacetylation. “Low-mass chitosan” was an 85% deacetylated product, Lot 00-AESQ-0741 from the same source. The chitosan products were solubilized before use by mixing for two hours in 5% acetic acid.

The fluorescent whitening agents were Blankophor® AWP, PL, and UW from Bayer. These were, respectively, di-, tetra-, and hexa-sulfated stilbene compounds. The direct dye was Pontamine® Kraft Orange OCC, from Bayer. Sodium laurylsulfate was of reagent grade.
Low-mass poly-DADMAC was Alcofix® 169, provided by Ciba Specialty Chemicals. The molecular mass is approximately 300,000 Daltons. High-mass poly-DADMAC was Alcofix® 109, having a molecular mass of approximately 1,000,000 Daltons. All chemicals were used on a dry-mass basis.

**Procedures**

Sub-batches of centrifuged pulp were taken from cold storage and refined with a laboratory Hollander-type beater (Valley Machinery, Inc.), following TAPPI method T-200. The pulp was dispersed in the beater for 30 minutes (zero load) then refined for 20 minutes. The pulp was screened, centrifuged to approximately 30% consistency, fluffed, and then refrigerated again until use.

Before making handsheets the refined pulp was dispersed in a disintegrator for 5 minutes. As shown in Fig. 4, chemicals were added to slurry samples of refined pulp. Addition levels were based on the added amount of chemical solid compared to the mass fibre (dry basis). The pulp samples were mixed with chemicals for 12 hours with stirring.

Fig. 4. Treatment procedure
The procedure of TAPPI Standard Method T-205 was used, with the following modifications. Instead of the standard slurry pulp consistency 0.3%, a 0.6% consistency was used. As a result the basis weight of handsheets was 120 g/m², not 60 g/m². At the higher basis weight the samples are not expected to fail in a "buckling" mode during STFI compression strength tests (39). Instead, they are expected to fail by the desired shear/internal bond failure. Handsheets with drying rings were placed in an oven at 105 °C for eight minutes, resulting in approximately 5% moisture content to simulate the effect of drying on a paper machine. Handsheets were stored in a TAPPI standard condition room for 12 hours before testing. Recycled handsheets were formed the same way as primary handsheets, except without further chemical addition.

Water retention values (WRV) were used to quantify fibre swelling capacity (33-36). The procedure followed TAPPI Useful Method 256 with some modifications. Prior to measurement, the pulp was dispersed in a disintegrator for 5 minutes (15,000 revolutions), thoroughly washed in a large excess of de-ionised water, and allowed to stand in water overnight. Following further washing the pulp was collected on a vacuum filter and dewatered to 25% solids. Moist samples of pulp (equivalent to 0.16g dry weight) were placed in sintered centrifuge tubes (pore size 0.22µm, volume 3ml, provided by MSI). Samples were centrifuged at 900g for 30 minutes according to TAPPI UM 256. After centrifuging, the moisture content of the samples was determined by weighing immediately and also after drying at 105 °C for 2 hours and cooling in a desiccator jar for 30 minutes.
RESULTS AND DISCUSSION

Table 1 summarizes results of tests with ten different batches of pulp without added chemicals. The “±” values indicate 95% confidence intervals for the mean. As shown, processes related to the preparation of secondary handsheets, including the fibres’ history of forming, drying, and reslurrying, had significant effects on water retention and physical properties. The first row in Table 1 shows a significant decrease in water retention value due to recycling. As noted by others (13), these results are consistent with a loss of pore volume when kraft fibres are dried. The observed losses in compression strength, tensile strength, and apparent density are consistent with previous work (1-2,8-14). The loss of compression strength is particularly important, due to the likely failure modes of corrugated containers (39-40).

Effects of starch products

Pre-treatment of never-dried pulp with various water-soluble chemicals yielded changes in strength of both virgin and recycled sheets. Figure 5 shows 95% confidence limits for the means for typical experiments with starch products. The first pair of bars corresponds to experiments in which there was no chemical treatment. The remaining sets of bars correspond to cases in which 2% of a chemical, based on the dry mass of fibre, was added only to the refined, never-dried pulp slurry. In each case the shaded (hatched) histogram bars correspond to the STFI compression strength of sheets made from the never-dried fibre with no additional chemical use or further refining. The unfilled bars correspond to sheets made from the same fibres, after being oven-dried under the relatively mild conditions of 105 °C for 8 minutes.
A student-t test of the data in Fig. 5 indicated a significant increase in compression strength of virgin paperboard sheets at an 80% level of confidence following the addition of 2% cationic corn starch relative to the untreated virgin paper. The other starch treatments did not significantly affect STFI compression of the virgin sheets, relative to the untreated control. To place these results in context, the 2% treatment level is about twice what would be considered a typical high level for wet-end addition of starch. However, a lower retention of chemical is usual in handsheet tests compared to paper machines, since paper machines continually reuse whitewater for stock dilution.

Results of tests with recycled sheets in Fig. 5 indicated significant increases in compression strength due to all of the starch treatments, relative to the untreated, recycled control. All of these differences were significant at a higher confidence level of 90%. The recycled sheets with cationic starch treatment were stronger than the corresponding recycled control sheets by a factor of 1.47.
Figure 6 shows corresponding results for tensile strength. Tensile strength is not a primary indicator of likely failure modes of corrugated boxes (39-40), but the results give an indication of inter-fibre bonding (32). The apparent increase in tensile strength of virgin pulp due to cationic starch pre-treatment was not statistically significant. But, once again, some of the starch treatments yielded increases in the strength of recycled sheets, relative to the recycled control. The largest effects were with the cationic starch, followed by uncharged, native starch, and little or no effect in the cases of anionic starches. Possibly cationic polymers are better retained on the pulp or help to retain fines in the handsheets.

![Fig. 7. Effects of starch on WRV](image1)
![Fig. 8. Effects of CMC products](image2)

As shown in Fig. 7, pre-treatment with starch products generally increased the water retention values (WRVs) of recycled fibres, relative to the recycled control. In each case the fibres were re-tested after the initial sheets were dried and then reslurried. The relative increases were significant at the 99% level of confidence, except for the case

of treatment with cationic starch. The fact that the WRV numbers for the recycled, cationic-starch-treated fibres were lower than those of the other starches suggests that WRV may not be the controlling factor governing strength in this case. If one were to assume that WRV is a main indicator of strength potential, then based on the literature (33-36) one would have expected a different trend among the histogram bars in Fig. 7.

**Effects of carboxymethylcellulose (CMC)**

Figure 8 compares effects of ten carboxymethylcellulose (CMC) products of different molecular mass and charge density. The labels give information about the mass and charge density, as described in the Experimental section. As shown, there were no significant effects observed when testing virgin handsheets. Results of testing recycled sheets indicated a trend towards increased strength of some treatments, compared to the untreated, recycled control.

Though the results for CMC samples by themselves were unpromising, the data will be useful as a point of reference when we later consider effects of combinations of chemicals that include CMC products. This is consistent with industry practice; CMC products are typically added in sequence with cationic polymers to achieve improvements in dry strength or to enhance the effectiveness of cationic wet-strength resins.

**Tabulation of results at the 2% level of treatments**

The majority of the screening experiments were carried out at the 2% level of chemical treatment (dry basis) on never dried pulp mass (dry basis). Data in Table 2 are expressed as changes relative to untreated, control samples. For example, in the second
row of data the entry “1.10” means that the cationic-starch-treated virgin handsheet had a compression strength that was 1.10 times as large as the untreated control. The second column of data shows how STFI test values of recycled sheets compared to the controls for the virgin sheets. The third column shows how the recycled treated sheets compared to the corresponding recycled control sheets; rows in the table are sorted by this column of data, with the strongest recycled sheets (relative to the recycled control) at the top of the list. Breaking length data are organized similarly. The final column in Table 2 shows how the water retention values of recycled sheets compared to the recycled control. The first row of data, corresponding to “controls,” is based on pooled data from ten sets of replicated experiments, whereas the remaining rows of data are each related to control data for a given batch of fresh pulp. For this reason, the values in the first row should not be used to calculate exact relationships among the data in the remaining rows.

As can be seen from Table 2, a wide range of chemical additives yielded relative changes in virgin STFI compression strength in the range 0.84 to 1.14. A comparison of the figures in the first and second columns of data shows that the recycled sheets were weaker than the virgin sheets from the same recipe. In other words, the chemicals listed did not fully prevent strength loss, compared to virgin sheets made from the same chemical-treated pulp. On the other hand, certain chemical treatments did have important relative effects, shown in the third column of data, when comparing the results with recycled sheets made from untreated pulp.

Cursory inspection of the tensile strength data, in comparison to the compression strength data, reveals that the two types of test results did not necessarily respond in the same way to various chemical treatments. To make this contrast more apparent, the STFI
compression results corresponding to Table 2 were plotted as a function of tensile strength results. Figure 9 compares the two types of results in the case of recycled sheets, compared with their respective recycled controls.

![Graph 1](image1.png)

**Fig. 9.** Compression strength vs. tensile strength of recycled handsheets

![Graph 2](image2.png)

**Fig. 10.** Compression strength of recycled sheets vs. WRV of the recycled fibres

To understand why certain chemicals affected compression strength to a different degree than they affected breaking length, an initial step was to look for trends based on classes of chemical treatments. Treatments favouring recycled STFI strength over recycled tensile strength included the following: chitosan (low-mass type), anionic starch, oxidized starch, and perhaps cationic starch. Treatments favouring recycled tensile strength over compression strength included direct dye, fluorescent whitening agents (which are chemically related to dyes), an anionic acrylamide copolymer, cationic guar, and hydroxyethyl starch. It is interesting that each of these lists includes some cationic, anionic, and nearly uncharged materials. One difference was that the treatments favouring recycled breaking length over compression strength usually contained

hydrophobic chemical groups. By contrast, the treatments most favouring recycled compression strength were hydrophilic polysaccharide products.

As shown in Fig. 10 there was no consistent relationship between recycled compression strength and the water retention values of the corresponding recycled pulp, from which the sheets were made. Treatments yielding the highest WRVs of recycled fibres included oxidized starch, chitosan, various other starch products, and a certain carboxymethylcellulose of low charge density (LT446A). Treatments yielding the lowest WRVs of recycled fibres included anionic acrylamide copolymer, certain guar products, most of the CMC products, and an anionic surfactant. An initial hypothesis to explain these results is that the higher values were achieved in cases where there was sufficient driving force to retain a higher amount of water-holding polymeric material at fibre surfaces. This requirement is most easily met in the case of cationic materials including cationic starch and chitosan, and the other materials having similar effects were generally on the low end of charge density. Based on theoretical work by McKenzie (65), one can expect better adhesion between fibrous surfaces if polymeric chains on those surfaces are capable of mixing within a three-dimensional inter-phase region. It makes sense that cationic starch should give favourable bonding results, since the positively charged groups provide a driving force for mixing with anionic polymers on an adjacent fibre surface. These observations are of a preliminary nature, indicating factors that deserve attention in future work.

There was no correlation between the compression strength of treated virgin handsheets and the recycled sheets made from the same material, after rewetting the initial sheets, dispersal of the fibres, and forming into recycled sheets. One might expect
additives to have a similar effect in both virgin and recycled paper. A likely explanation was most clearly stated by Pycraft (8). His hypothesis states that conditions most favourable to the formation of strong virgin paper from kraft pulps are also most conducive to the loss of bonding potential through such mechanisms as pore closure or hardening of the fibre surface due to crystallization of polysaccharide chains. Also, one cannot rule out effects of detailed chemical differences, the ability of certain chemicals to affect the formation of the virgin handsheets, and random experimental error. The operations of papermaking, conversion, use, and recycling can be expected to degrade polymers and result in unequal yield losses of different paper components. Because cationic starch was a leader for increasing compression strength of both virgin sheets and recycled sheets made from the pre-treated fibres, that chemical deserves more study, regardless of the mechanisms involved.

**Results of Tests at Lower Treatment Levels**

Low treatment levels make economic sense. An additional motivation here was to be able to test certain chemicals that had undesired effects at 2% addition. For example, attempts to run tests at the 2% level of natural, high-mass guar gum yielded sheets too sticky to be removed from the forming screen of the handsheet mould.

Results of tests with lower chemical dosages are shown in Table 3. With one exception, the relative changes in STFI compression strength were generally similar to those observed with 2% treatment. Effects of chemicals on the compression strength of virgin sheets ranged from positive to near zero. Several of the treatments with guar and chitosan products improved the compression strength of recycled sheets, relative to the
recycled controls. However, treatment with 1.3% poly-diallyldimethylammonium chloride (poly-DADMAC) yielded contrasting results; the relative effect on recycled strength was strongly negative, despite the fact that poly-DADMAC had a positive effect on the strength of the virgin sheets.

A mechanism that may account for the adverse effect of poly-DADMAC on the compression and tensile strength of the recycled sheets involves the ability of such highly charged polyelectrolytes to neutralize the net charge of fibre surfaces. As shown by Lindström and Carlsson (10), kraft fibres that have significant net negative charge at their surface are generally less susceptible to strength loss, compared to those that have a near-neutral charge. Apparently the charged groups either inhibit pore closure or promote rehydration when the paper is rewetted. This explanation is also consistent with the lower value of water retention value in the case of recycled fibres that had been pre-treated with poly-DADMAC.

**Effects of Sequential Treatments with Oppositely Charged Additives**

Table 4 summarizes results of tests involving sequential addition of a cationic additive and an anionic additive. In most tests the cationic material was added first. The combination treatment yielding the largest net gains in both virgin and recycled strength involved chitosan (cationic) and CMC (anionic). The relative effect of the various dual-chemical treatments on compression strength of virgin paper was generally consistent with a linear summation of effects of each additive. For example if one notes that 1.3% low-mass poly-DADMAC (Table 3) yielded a relative change of 1.04, and 2% carboxymethylcellulose (CMC) yielded a relative change of 1.03 (Table 2), it makes
sense to expect a net relative effect of about 1.07 on the compression strength of virgin sheets following sequential treatment by both chemicals. As shown in Table 4, the net effect was 1.10, 1.06, or 1.09, depending on the order of addition and the particular sample of CMC and the amount of poly-DADMAC (not always 1.3%).

Contrasting results were found when comparing the compression strengths after recycling. Except in the case of chitosan, the results of individual treatments would not have suggested the strengths of recycled sheets in the range 1.13 to 1.40 relative to the recycled, untreated controls. For example, 1.3% poly-DADMAC by itself yielded a change of 0.77 relative to the untreated, recycled control, and 2% CMC yielded a relative change that averaged 1.06. Simple addition of the two effects yields an overall relative change of 0.83. Though more sophisticated mathematical treatments could be considered, the results of such calculations do not explain the actual observed values of 1.14 through 1.25 for the compression strengths of recycled sheets, relative to recycled sheets from untreated fibre.

As described in the Theory section, a mechanism that may better account for the effects of dual treatments is based on polyelectrolyte complexation. In principle, pre-treatment by poly-DADMAC is expected to provide adsorption sites for the water-loving, anionic CMC chains. Alternatively, post-addition of poly-DADMAC, after the CMC, is expected to precipitate a complex of the two polymers onto the fibre surfaces. The latter mode of addition yielded higher recycled strength in the one case where that was tried in Table 4. Further work is planned relative to the charge densities and ratios of oppositely charged additives and the relationship between the results and the colloidal charge properties of the furnish.
Results in Table 4 for recycled compression strength were very well correlated with the trend in water retention values. Here again, simple addition of the effects of the individual agents does not predict the observed WRV data. Poly-DADMAC at the 1.3% level yielded 0.97 times the WRV value of untreated, recycled pulp (Table 3), and the main series of CMC samples at the 2% level yielded 0.98 times the recycled control value (Table 2). By contrast, the observed values for combinations of the two polymers (not always at the same dosages) were 0.99 to 1.07, with the higher values at the lower dosage of the cationic polymer. These results suggest that bound water in the adsorbed polyelectrolyte complexes themselves may account for the observed effects on WRV values. This possibility is proposed here as a hypothesis, and a focus of planned follow-up work.

CONCLUSIONS

1. The answer to the question in the title of this article is “yes.” Several water-soluble materials or sequences of two additives increased the strength of recycled handsheets, compared to recycled control handsheets that had not been treated before their first drying.

2. Results were consistent with persistence of adhesiveness of surface-bound polyelectrolytes. These materials at the fibre surface contributed to bonding even after the initial paper had been reslurried and formed into second-generation handsheets. However, the positive effects of polymeric pre-treatments on the strength
of recycled handsheets did not appear to be related to the water-holding ability of fibre cell walls.

3. Tensile versus compression test results were affected differently by certain chemicals. Treatments favouring compression strength included many water-loving polymers, such as polysaccharide products. Treatments favouring tensile strength included chemicals having hydrophobic substituent groups.

4. Based on the screening tests reported in this article, the following candidate treatments appeared most promising for maximizing the strength of recycled paper, or reducing the need for additional strength additives when paper is recycled: cationic starch, various other starch products, depolymerized guar products, chitosan, and sequential addition of a cationic material and an anionic polymer such as carboxymethylcellulose (CMC).

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REFERENCES


Table 1
95% confidence limits for the means of water retention values of pulp and strength properties of resulting handsheets from untreated virgin vs. once-dried fibre

<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
<th>Virgin</th>
<th>Recycled</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water Retention Value</td>
<td>%</td>
<td>212 ± 6</td>
<td>167 ± 3</td>
</tr>
<tr>
<td>STFI Compression</td>
<td>Nm/g</td>
<td>25.4 ± 1.2</td>
<td>19.8 ± 1.2</td>
</tr>
<tr>
<td>Breaking Length</td>
<td>km</td>
<td>5.6 ± 0.6</td>
<td>3.8 ± 0.4</td>
</tr>
<tr>
<td>Apparent Density</td>
<td>g/cm³</td>
<td>0.71</td>
<td>0.66</td>
</tr>
</tbody>
</table>

Table 2
Relative changes in strength and water retention due to drying, as affected by chemical treatment of the never-dried fibre (2% treatment level)

<table>
<thead>
<tr>
<th>Chemical Additive</th>
<th>Change Relative To The Control</th>
<th>STFI Compression</th>
<th>Breaking Length</th>
<th>WRV</th>
</tr>
</thead>
<tbody>
<tr>
<td>UNTREATED</td>
<td></td>
<td>1.00 0.78 1.00</td>
<td>1.00 0.69 1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Cationic starch (PC550)</td>
<td></td>
<td>1.10 1.01 1.47</td>
<td>1.07 0.95 1.36</td>
<td>1.04</td>
</tr>
<tr>
<td>Hydroxyethyl starch (PG280)</td>
<td></td>
<td>0.90 0.87 1.26</td>
<td>0.98 0.84 1.20</td>
<td>1.06</td>
</tr>
<tr>
<td>Anionic starch (CMAG3020)</td>
<td></td>
<td>0.96 0.82 1.19</td>
<td>1.03 0.70 1.00</td>
<td>1.06</td>
</tr>
<tr>
<td>Cationic depol. guar (GPX247)</td>
<td></td>
<td>0.98 0.97 1.17</td>
<td>1.13 0.96 1.27</td>
<td>0.98</td>
</tr>
<tr>
<td>Oxidized starch (D3060)</td>
<td></td>
<td>0.94 0.80 1.16</td>
<td>0.99 0.75 1.07</td>
<td>1.11</td>
</tr>
<tr>
<td>Depolymerized guar (30M1F)</td>
<td></td>
<td>1.14 0.90 1.14</td>
<td>1.11 0.76 1.17</td>
<td>1.01</td>
</tr>
<tr>
<td>Low-mass chitosan (AESQ741)</td>
<td></td>
<td>1.01 0.76 1.11</td>
<td>1.07 0.61 0.87</td>
<td>1.07</td>
</tr>
<tr>
<td>FWA-tetrasulfonated (BlankPL)</td>
<td></td>
<td>1.00 0.82 1.10</td>
<td>1.06 0.80 1.24</td>
<td>1.04</td>
</tr>
<tr>
<td>FWA-hexasulfonated (BlankUW)</td>
<td></td>
<td>0.97 0.82 1.10</td>
<td>1.07 0.81 1.24</td>
<td>1.02</td>
</tr>
<tr>
<td>FWA-disulfonated (BlankAWP)</td>
<td></td>
<td>1.01 0.81 1.09</td>
<td>1.03 0.78 1.20</td>
<td>1.03</td>
</tr>
<tr>
<td>Carboxymethylcellulose (LT446A)</td>
<td></td>
<td>1.02 0.91 1.09</td>
<td>1.10 0.85 1.13</td>
<td>1.06</td>
</tr>
<tr>
<td>Sodium laurylsulfate</td>
<td></td>
<td>0.95 0.89 1.07</td>
<td>1.01 0.84 1.12</td>
<td>1.00</td>
</tr>
<tr>
<td>Hemicellulose (corn fibre gum)</td>
<td></td>
<td>1.03 0.82 1.06</td>
<td>1.03 0.74 1.08</td>
<td>1.00</td>
</tr>
<tr>
<td>Carboxymethylcellulose (average)</td>
<td></td>
<td>1.03 0.82 1.06</td>
<td>1.02 0.69 1.01</td>
<td>0.98</td>
</tr>
<tr>
<td>Anionic guar (GPX241)</td>
<td></td>
<td>1.10 0.88 1.06</td>
<td>1.15 0.85 1.12</td>
<td>1.03</td>
</tr>
<tr>
<td>Cationic guar (SP813D)</td>
<td></td>
<td>1.03 0.80 0.96</td>
<td>0.98 0.82 1.09</td>
<td>1.03</td>
</tr>
<tr>
<td>Direct Orange (Pont KrOrOCC)</td>
<td></td>
<td>0.84 0.70 0.94</td>
<td>0.98 0.77 1.19</td>
<td>1.01</td>
</tr>
<tr>
<td>Acrylamide copolymer (H2000)</td>
<td></td>
<td>1.03 0.74 0.92</td>
<td>1.09 0.75 1.05</td>
<td>0.97</td>
</tr>
</tbody>
</table>

Table 3
Relative changes in strength and water retention due to drying, as affected by chemical treatment of the never-dried fibre (Lower treatment levels)

<table>
<thead>
<tr>
<th>Additive</th>
<th>Change Relative to the Control</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>STFI Compression</td>
</tr>
<tr>
<td>UNTREATED</td>
<td>1.00 0.78 1.00</td>
</tr>
<tr>
<td>Anionic guar (GPX241)</td>
<td>1.13 1.01 1.21</td>
</tr>
<tr>
<td>High-mass chitosan (SC442)</td>
<td>1.01 0.80 1.16</td>
</tr>
<tr>
<td>Cat. depol. guar (GPX247)</td>
<td>0.97 0.93 1.12</td>
</tr>
<tr>
<td>Underivatized guar (SprclU)</td>
<td>1.03 0.87 1.07</td>
</tr>
<tr>
<td>Cationic guar (SP813D)</td>
<td>1.08 0.78 0.94</td>
</tr>
<tr>
<td>Low-mass poly-DADMAC</td>
<td>1.04 0.57 0.77</td>
</tr>
</tbody>
</table>

Table 4
Effects of sequential treatments with oppositely charged polyelectrolytes: relative changes in strength and water retention due to drying

<table>
<thead>
<tr>
<th>Additives</th>
<th>Change Relative To The Control</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>STFI Compression</td>
</tr>
<tr>
<td>UNTREATED</td>
<td>1.00 0.78 1.00</td>
</tr>
<tr>
<td>Chitosan, HM (0.5%) CMC 7M (2%)</td>
<td>1.04 0.96 1.40</td>
</tr>
<tr>
<td>CMC 7M (2%) DADMAC, HM (0.5%)</td>
<td>1.10 0.93 1.25</td>
</tr>
<tr>
<td>Chitosan LM (2%) CMC 7M (2%)</td>
<td>1.05 0.79 1.16</td>
</tr>
<tr>
<td>DADMAC, LM (0.5%) CMC LT446 (2%)</td>
<td>1.06 0.96 1.15</td>
</tr>
<tr>
<td>DADMAC, LM (1.3%) CMC 7M (2%)</td>
<td>1.09 0.84 1.14</td>
</tr>
<tr>
<td>DADMAC, LM (1.3%) FWA-hexa (2%)</td>
<td>0.98 0.84 1.13</td>
</tr>
</tbody>
</table>