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Wet reinforcement of paper with high-molecular-weight multifunctional carboxylic acid

YUFENG XU, CHARLES Q. YANG, AND CHIA-MING CHEN

ABSTRACT

Multifunctional carboxylic acids show promise as environmentally benign wet-strength chemicals. These acids improve the wet performance of paper and board through ester crosslinking of the cellulosic components of papermaking fibers. The major drawback is embrittlement of the acid-treated sheets. This study evaluates the effect of molecular weight on the wet-strength performance of multifunctional carboxylic acids. A high-molecular-weight polymeric carboxylic acid (EMA, polyethylene maleic acid), and a low-molecular-weight acid (BTCA, 1,2,3,4-butanetetracarboxylic acid) were used as crosslinking agents on sheets of unbleached kraft, bleached paper, and corrugating medium. Similar results were obtained for all three types of paper. The wet strength obtained with EMA was significantly higher than that achieved with BTCA at equivalent acid consumption. More importantly, the folding endurance—a measure of embrittlement—increased remarkably up to a very high treatment level for EMA-treated sheets. However, the high-molecular-weight EMA was less effective than the low-molecular-weight BTCA in achieving high dimensional stability and wet stiffness. These results can be explained by differences in the proportion of inter- and intrafiber bonds formed with acids of widely diverging molecular weights.

Application:

Examines the feasibility of using environmentally benign multifunctional carboxylic acids to increase the wet strength of paper and board.

In a previous study *(1)*, we discussed the application of two polymeric carboxylic acids—a homopolymer of maleic acid (PMA) and a terpolymer of maleic acid, acrylic acid, and vinyl alcohol (TPMA)—to improve the wet performance of kraft paper. Although these two acids are both effective and economically feasible, papers treated with PMA and TPMA suffer from embrittlement, as exemplified by a severe loss in folding endurance. Addition of plasticizers did not prevent embrittlement.

It is reasonable to infer that acid degradation of fiber cellulose at elevated temperature is the predominant reason for the reduction in folding endurance. The curing process for acid-impregnated paper is similar to that in accelerated paper aging, and the role of pH on paper aging is well known. However, in a study by Horie and Biermann *(2)*, the folding endurance for BTCA-treated (1,2,3,4-butanetetracarboxylic acid) paper dropped from an original value of 840 to approximately 640 when no catalyst was used in the acid solution. When the molar ratio of catalyst/COOH was increased from zero to 1/2.3, the folding endurance decreased from 640 to near zero. The catalyst promotes crosslinking, which increases with increasing catalyst addition. Moreover, the catalyst, which is weakly basic in nature, does not lower the pH of the acid solution any further. Therefore, the reduction in folding endurance with increasing catalyst addition suggests that crosslinking itself might be another important reason for the reduction in folding endurance.

However, this embrittlement effect does not occur with the conventional wet-strength resins, even those for which a "cocrosslinking" strengthening mechanism has been strongly suggested, such as glyoxalated polyacrylamide (PAM) and dialdehyde starch (DAS). Indeed, in both cases, resin addition improved the folding endurance. Despite the interference of unreacted amide groups on the PAM resins and hydroxyl groups on the DAS resins, it is safe to conclude that crosslinking in both cases does not have a severe detrimental effect on the folding endurance of paper. Among other possible explanations for these differences in folding endurance—such as the method of application and the amount of resin used—it is noteworthy that conventional wet-strength resins are high-molecular-weight polymers.

Cellulose fiber is a porous material. Low-molecular-weight reagents can penetrate the pores of the fiber cell wall and crosslink the accessible area within the fiber (intrafiber crosslinking). However, as the reagent's molecular weight increases, it tends to adhere to the periphery of the fiber, and crosslinking becomes increasingly concentrated between fibers (interfiber crosslinking). Given these facts, it is possible that only the intrafiber crosslinks contribute to the embrittlement of the paper.

The pore-size distribution within the fibers depends on the chemical and mechanical treatments to which the fibers have been subjected as well as other processing factors such as drying, recycling, and the power of the applied swelling agent. Data reported by different researchers vary, depending on the materials and

experimental methods used *(3–7)*. For chemical wood pulp, the pore-size distributions are generally within the range of less than 8 Å to 400 Å, with a peak between 20 Å and 100 Å.

The diffusion or penetration of large reactants into the fiber matrix is limited by the size and shape of the pore opening. If the opening is circular, the molecule can penetrate only if the pore is at least four times larger than the molecule. If the opening resembles parallel slits, the polymer can penetrate a pore that is twice as large or larger. The openings or pores of cellulose fiber can reasonably be expected to assume an elliptical shape, and a penetration factor of three has been proposed *(3)*.

If the reagent takes a hydrodynamic coil shape in aqueous solution, its diameter can be calculated by the Einstein–Stokes formula *(4, 6)*. However, for the multifunctional carboxylic acids we used in the previous research—PMA, TPMA, and BTCA—an accurate calculation of the molecular diameter is impossible because of the lack of data about the molecular modeling and diffusion coefficient. Nevertheless, an accurate calculation is not necessary for our purpose. If we assume these carboxylic acids follow the same pattern in this respect as the sugars and dextrans used by Stone and Scallan in their pore-size distribution study *(6)*, the estimated molecular diameter of the three acids would be less than 20 Å. Considering the similarity in structures of polycarboxylic acids and dextrans, such an estimation seems reasonable. There is no doubt that these acids could readily penetrate into a large portion of the pores in the fiber wall and form intrafiber crosslinks. It was also found that dextran molecules with a molecular weight of 40,000 or larger could not penetrate into the fiber pores of kraft pulp *(6)*.

The loss of strength when paper is wetted is presumably due to the failure of fiber–fiber bonds in resisting the disrupting action of water. Thus interfiber crosslinking will be sufficient to render paper wet strength. By using a multifunctional carboxylic acid that is large enough to be excluded from penetrating the fiber pores, the crosslinking can be limited to the interfiber area. This might result in improved wet strength without embrittling the paper.

In this research, a high-molecular-weight polyethylene maleic acid (EMA) was used to improve the wet performance of various papers, and the results were compared with that from the treatment with BTCA.

EXPERIMENTAL

Materials

The unbleached kraft paper (74 g/m^2) used in this study was a commercial product made by Georgia-Pacific. Bleached paper (58 g/m^2) containing 70% hardwood and 30% softwood was made on the laboratory paper machine at Western Michigan University. Corrugating medium (122 g/m^2) was provided by International Paper.

BTCA and sodium hypophosphite (NaH_2PO_2) were supplied by Aldrich. The EMA solution was prepared by hydrolyzing polyethylene maleic anhydride in powder form (average molecular weight of 100,000, Zeeland Chemicals) in distilled water with heating.

Procedures of paper treatment

Sample sheets measuring 25 × 25 cm^2 were brought to equilibrium in a conditioned room at 25°C and 50% RH (relative humidity). The conditioned sheets were then soaked for 30 s in BTCA or EMA solutions of prescribed concentration. Sodium hypophosphite (NaH_2PO_2) was used as catalyst. All the solutions maintained a constant 1:2 weight per weight (w/w) catalyst-to-carboxyl ratio. The sheets of unbleached kraft paper and corrugating medium were pressed between squeezing rolls at 40 psi after soaking, and the bleached paper sheets were pressed between blotting paper to remove the excess acid solution. The pressed sheets were dried on a photographic dryer at 80°C to prevent curling. Individual sheets were then cured in a forced-draft oven at 170 ± 1°C for 2 min. The cured sheets were rinsed in running water for 15 min to remove unreacted acid and catalyst and, finally, dried. After standard conditioning (TAPPI T 402 om-93), the physical properties of these samples were measured. Control references were established by soaking the paper sheets in distilled water instead of an acid/catalyst solution and then subjecting them to the same treatment procedures as the treated sheets.

Paper performance evaluation

Tensile strength and folding endurance of the samples were evaluated according to TAPPI T 404 om-87 and T 511 om-88, respectively. The wet tensile strength and wet stiffness were tested after soaking 15-mm-wide paper strips in water for 12 hours. Stiffness was expressed as Young's modulus of elasticity *(8)*. These mechanical properties were measured in the machine direction. Dimensional stability was calculated according to the formula specified by Caulfield *(9)*:

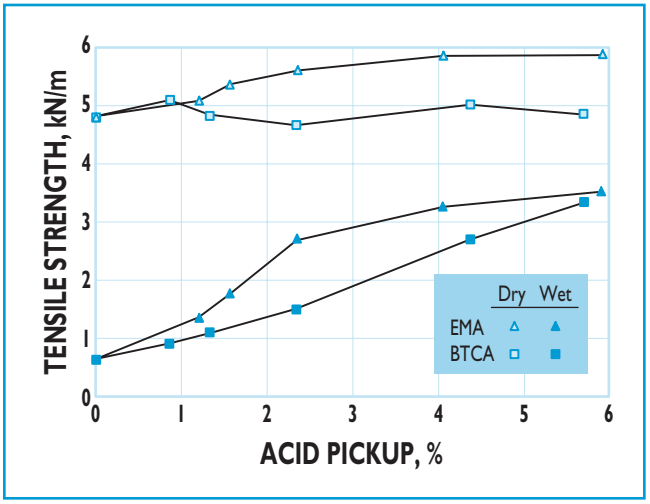
$$DS = 100 \times \frac{L_u - L_t}{L_u}$$

where

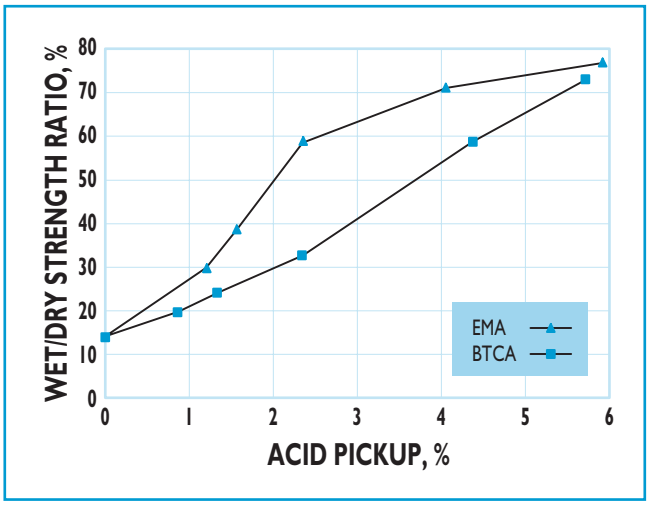
L_u = change in linear dimension (between water soak and 50% RH) for untreated sheets

L_t = change in linear dimension (between water soak and 50% RH) for treated sheets

The samples were cycled once before testing between water soaked and 50% RH to release internal strains. For each physical property, ten specimens randomly selected from five different treated sheets were tested. A normalized *Z* score of



1. Wet and dry tensile strength of kraft paper as a function of acid pickup for two wet-strength acids



2. W/D ratio for kraft paper as a function of acid pickup for two wet-strength acids

±3 was used as a standard to detect outliers. The acid pickup levels were determined by titration using a standard 0.1*N* NaOH solution. (Sheets were first ground into powder in a Wiley mill to improve sample uniformity.) The end point of the titration, pH 9.2, was determined with a pH meter. The acid pickup level (% w/w) was calculated by the formula:

$$\text{Acid pickup} = \frac{V_{NaOH}\, C_{NaOH}\, q}{W} \times 100$$

where

V_{NaOH} = volume of NaOH, mL
C_{NaOH} = concentration of NaOH, mmole/mL
q = equivalent coefficient
W = vacuum dry weight of the sheet, mg

and where the equivalent coefficient q is 73.0 and 58.5 for EMA and BTCA, respectively.

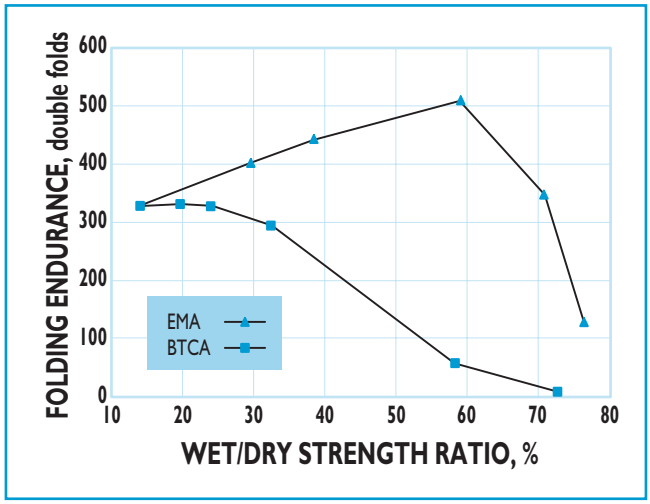
RESULTS AND DISCUSSION

The wet and dry tensile strengths of kraft paper treated with EMA and BTCA at different acid concentrations are presented in **Fig. 1**. At the same acid pickup level, the wet strength of EMA-treated paper was significantly higher than that of BTCA-treated paper, indicating that the high-molecular-weight carboxylic acid is more effective in improving the wet strength of paper. In contrast to the BTCA-treated paper, where the dry tensile strength remained relatively constant, the EMA-treated paper showed an increase in dry tensile strength. The relative constancy of the dry tensile strength of BTCA-treated paper can be interpreted as a balance between the strengthening effect of fiber-to-fiber bonding by ester crosslinking and the detrimental effect of acid degradation of the fibers. If this is the case, then the crosslinking effect must overshadow the fiber degradation in EMA-treated paper. The increase in dry strength suggests that EMA treatment would be useful for upgrading recycled furnishes, reducing the softwood pulp or chemical pulp requirement in the manufacture of some paper grades, or even saving fiber materials by merely lowering the basis weight of paper.

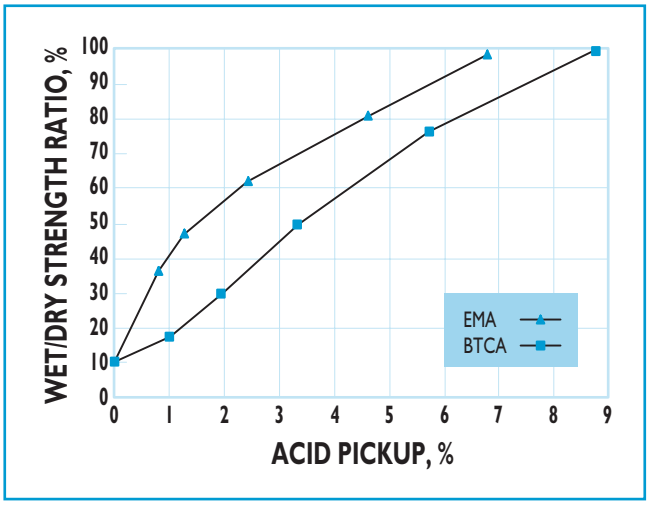
Paper wet strength is traditionally expressed as the percentage of wet tensile strength over dry tensile strength of the treated paper. However, results expressed in those terms can be quite misleading because resin addition also changes the dry strength. One resin might give higher absolute values of both dry and wet tensile strengths and still show about the same wet/dry percentage as another resin, thus masking improvements in wet strength. More consistent results are obtained by expressing paper wet strength as the percentage of wet strength of treated paper over the dry strength of *untreated* paper (W/D ratio). This is the method used to express wet strength throughout this paper.

Figure 2 shows the change in wet/dry percentage rather than the actual wet-strength values of kraft paper subjected to different treatments with EMA or BTCA. The response pattern is not altered, but the quantitative relationship is in better focus. At an acid pickup of 2%, a wet strength of 50% of the original dry strength was sustained with EMA-treated paper, while that from BTCA treatment was only 30%. To achieve a wet strength of 50%, about 3.8% of BTCA is required. Thus the efficiency of BTCA relative to EMA at this test level is only 53%. Note that the result reported here is for a short curing time of 2 min at 170°C, so the acids are not reaching their full capacity. The amount of acid required to provide a given wet strength could be further reduced by extending the curing time or curing at a higher temperature.

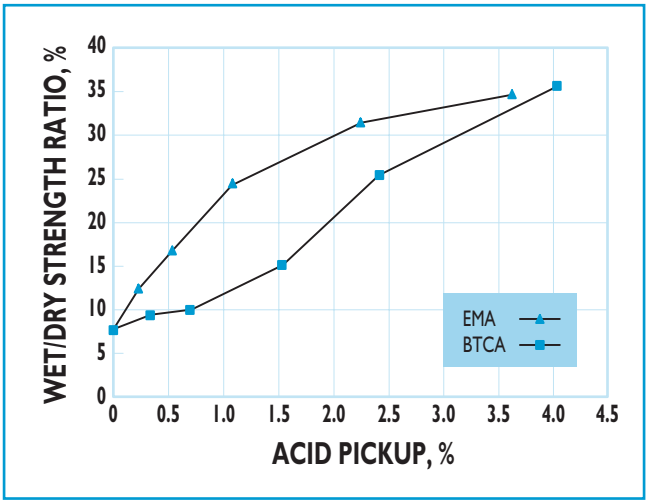
Figure 3 shows the folding endurance of acid-treated kraft paper. As expected, below wet strength of about 59%—which is high enough



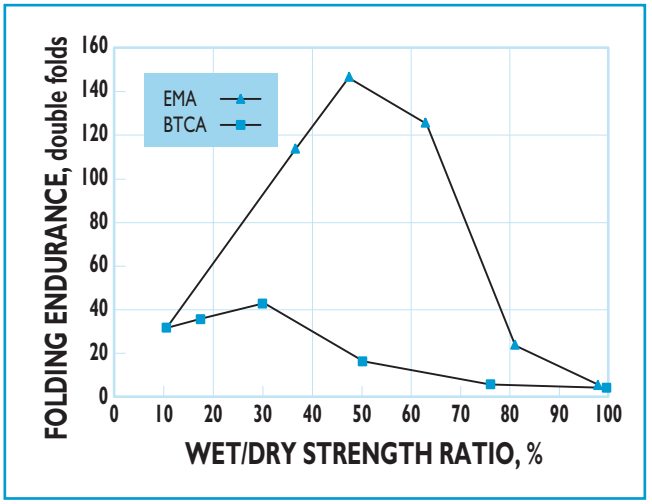
3. Folding endurance of kraft paper as a function of W/D ratio for two wet-strength acids



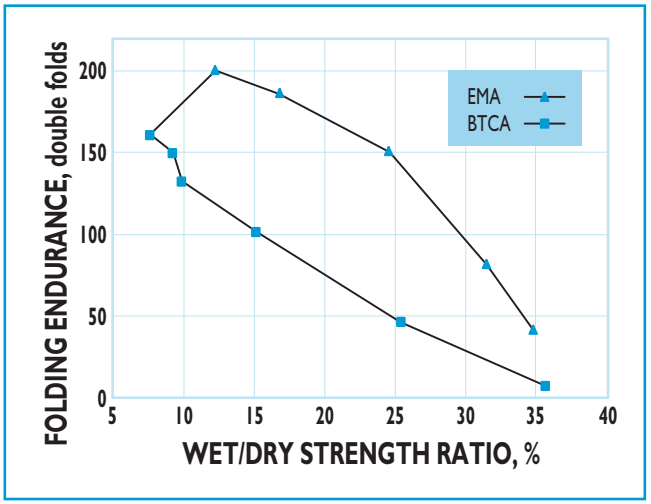
4. W/D ratio for bleached paper as a function of acid pickup for two wet-strength acids



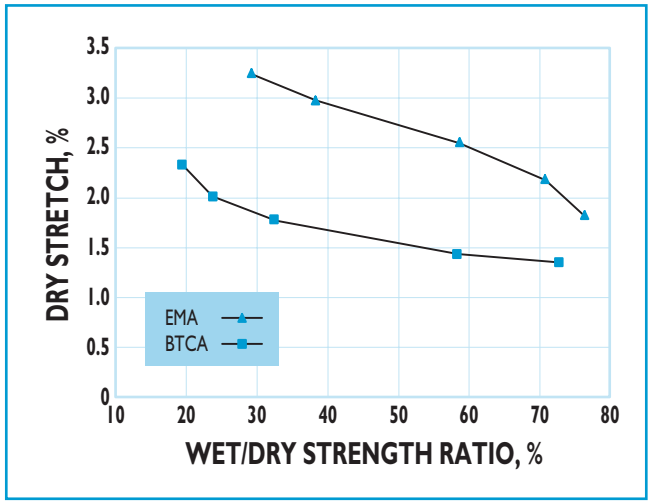
5. W/D ratio for corrugating medium as a function of acid pickup for two wet-strength acids



6. Folding endurance of bleached paper as a function of W/D ratio for two wet-strength acids



7. Folding endurance of corrugating medium as a function of W/D ratio for two wet-strength acids



8. Dry stretch of kraft paper as a function of W/D ratio for two wet-strength acids

to meet most of the wet-strength requirement—EMA treatment increased the folding endurance significantly. At the wet strength of 59%, the folding endurance of EMA-treated paper was 509, a 55% increase from the original value of 328 for the untreated paper. At the same wet strength, folding endurance of BTCA-treated paper dropped to 55, about sixfold lower than the original value. When the wet strength exceeded 59%, folding endurance fell off even for EMA-treated paper. This drop is either the result of severe acid degradation at high acid pickup levels, or excessive crosslinking, or perhaps both. If the goal is to achieve a wet strength as high as possible without negatively affecting the folding endurance, then a wet/dry value of more than 70% can be obtained, which is exceptionally high compared with wet strengths obtained using conventional wet-strength resins.

To test this phenomenon further, we treated two other substrates—bleached paper and corrugating medium—with BTCA and EMA. The original properties of bleached paper and corrugating medium are, of course, significantly different from unbleached kraft paper.

The wet strengths of acid-treated bleached paper and corrugating medium are illustrated in **Figs. 4 and 5**, respectively. In both cases, higher wet strength was obtained with the EMA-treated samples at equivalent levels of acid pickup, which is in agreement with the results for kraft paper. However, the absolute wet-strength increment of acid-treated corrugating medium was lower compared with the tremendous increment in kraft paper and bleached paper. Corrugating medium is made from chemimechanical pulp, where the hydroxyl groups in the fiber are less accessible because of the relatively larger amount of lignin. Thus the extent of crosslinking was not large enough to give the corrugating medium a high level of wet strength.

The folding endurances of EMA- and BTCA-crosslinked bleached paper and corrugating medium are given in **Figs. 6 and 7**, respectively. Surprisingly, the EMA-treated bleached paper showed an increment in folding endurance that was more than four times the original value over a wet-strength range of 40–65%. A modest increment in folding endurance at low acid pickup levels was obtained for the BTCA-treated bleached paper. We attribute this large upgrade in the folding endurance of EMA-crosslinked bleached paper to the weakness of the bonds in the untreated sheet. The folding endurance of the EMA-treated corrugating medium was also significantly higher than that treated with BTCA, mirroring the trends observed for the kraft paper and the bleached paper.

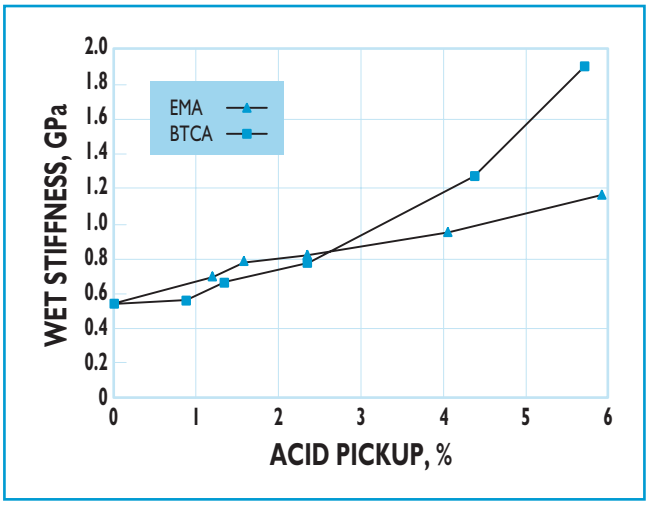
There are two possible explanations for the difference in folding endurance of EMA- and BTCA-treated papers:

First, EMA-induced crosslinks are concentrated in the interfiber area, with little intrafiber crosslinking. While these interfiber crosslinks increase the bonding force between fibers, they would not increase the stiffness of the fibers themselves. The fibers remain flexible enough to relax in response to the stress applied during the test. Because folding endurance depends both on fiber bonding and flexibility, the net result is an increase in fold. In contrast, a significant amount of intrafiber crosslinks are formed within the BTCA-treated paper. These intrafiber crosslinks, together with interfiber crosslinks, greatly restrict the flow property of paper and cause embrittlement. The results of stretch testing in **Fig. 8** show that the EMA-crosslinked sheets were significantly more flexible than the BTCA-treated sheets.

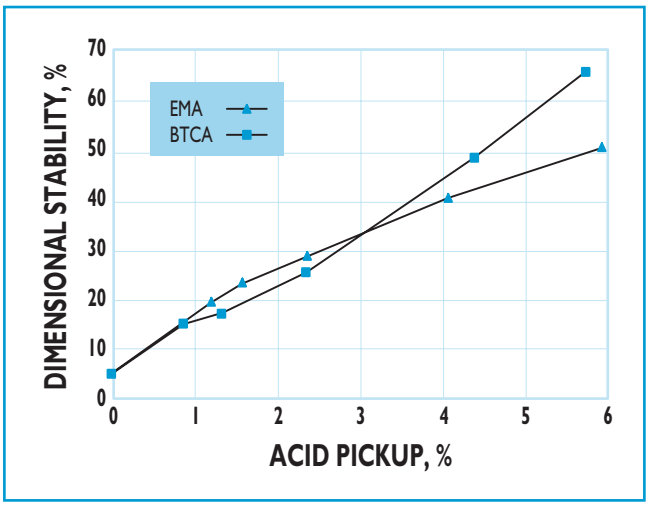
Second, EMA-induced linkages between two fibers may be longer than those induced by BTCA. Because there are only four adjacent carboxylic acid functional groups in the BTCA molecule, the linkage length is limited. EMA is a long-chain copolymer, and there may be a series of unreacted ethylene maleic acid units between the connecting points. Thus the bridge formed between reacted hydroxyl groups will be markedly longer than it is for BTCA. Quantitative analysis of the reacted and unreacted carboxyl groups, which we will discuss in greater detail in a future paper, showed that this is theoretically the case. The crosslinked network formed in EMA-treated paper will thus be looser and will not cause embrittlement.

Considering the results from other wet-strength-resin applications and the dry stretch reduction of BTCA- and EMA-treated kraft paper (Fig. 8), the first explanation appears to be most correct. Note that the two explanations are not mutually exclusive of each other. It is possible that a combination of both explanations provides a more thorough account of the differences between EMA- and BTCA-treated paper.

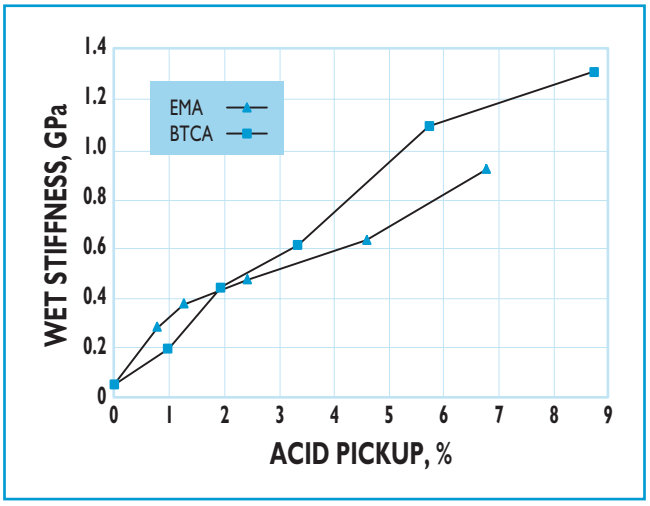
An interesting phenomenon—one that has a direct bearing on this work—is that the method of applying the wet strength agent appears to affect performance. When synthetic wet-strength resins were first used on an industrial scale, urea–formaldehyde was applied to paper as a tub size or surface application treatment, which is similar to the method we used in this study. One negative aspect of this treatment was that the paper tended to become embrittled, as evidenced by the reduction in folding endurance *(10–12)*. Attempts to minimize this drop in folding endurance with various cures, accelerators, and even plasticizers were complete failures.



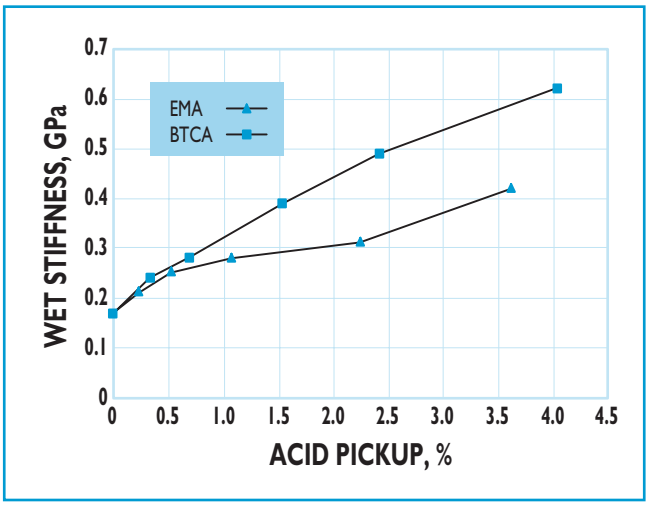
9. Wet stiffness of kraft paper as a function of acid pickup for two wet-strength acids



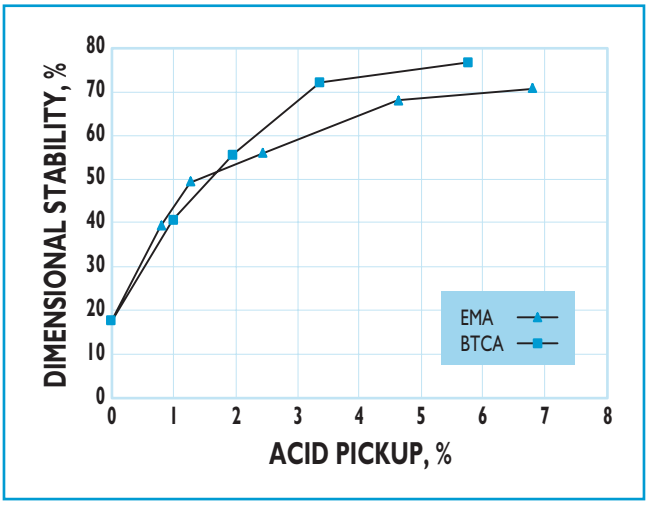
10. Dimensional stability of kraft paper as a function of acid pickup for two wet-strength acids



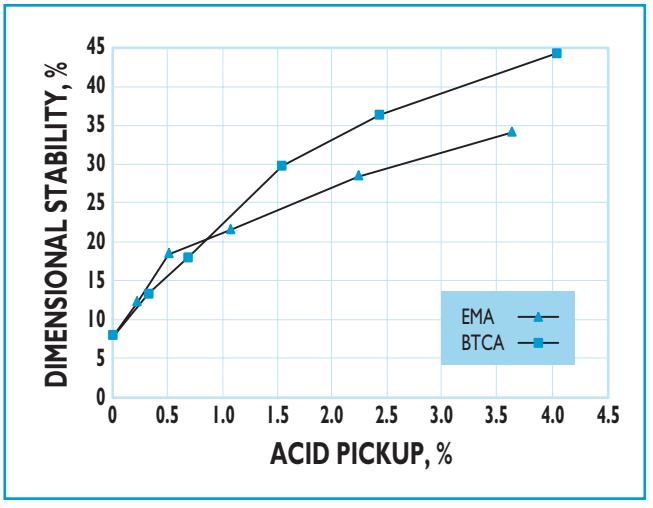
11. Wet stiffness of bleached paper as a function of acid pickup for two wet-strength acids



12. Wet stiffness of corrugating medium as a function of acid pickup for two wet-strength acids



13. Dimensional stability of bleached paper as a function of acid pickup for two wet-strength acids



14. Dimensional stability of corrugating medium as a function of acid pickup for two wet-strength acids

When the method of resin application evolved from tub size to stock addition, there came a rather astonishing discovery: the folding endurance of the resin-treated paper was higher than that of comparable untreated papers. No further explanation has been found in the literature than the difference in "method of application" *(12)*.

The facts behind this difference in application method lead us to believe that this interesting phenomenon also reflects differences in intra- and interfiber crosslinking. First, the urea–formaldehyde used for tub size had a low degree of polymerization, while that used for stock addition was characterized by a high degree of polymerization *(11)*. Second, the molecular weight of urea–formaldehyde condensate used for stock addition is not uniform. High-molecular-weight fractions tend to be more substantive to fibers and are more easily trapped in the fiber mat than low-molecular-weight materials, which can wash away with the white water. Third, urea–formaldehyde resin for stock addition is charged. The resins tend to be adsorbed on the fiber surface because of electrostatic forces. If the resins manage to enter the large pores in the fiber wall after prolonged contact time, they adhere to the inner surface of the pores and form a monolayer, leaving the central portion of the pores unoccupied. The resins used for tub size are uncharged, and the resin concentration employed is much higher than that used for stock addition. Resin molecules, especially small ones, have more opportunities to penetrate into the fiber cell wall and fill the pores. Given these tendencies, it is clear that tub size application of urea–formaldehyde produces a much higher level of intrafiber crosslinking, resulting in embrittlement of paper. While the chemistry of crosslinking with urea–formaldehyde is different from that of carboxylic acids, the mechanism runs parallel.

Figure 9 shows the wet stiffness values of kraft paper treated with EMA and BTCA. The increase in wet stiffness for EMA-treated kraft paper proceeded more slowly than for the BTCA-treated paper, although the EMA-treated paper was slightly higher at low levels of acid pickup. To achieve higher levels of wet stiffness, crosslinks are required both within the cell wall and between fibers. Once a sufficient level of bonding forces between fibers has been developed, intrafiber crosslinking becomes more important. The results from this study are in agreement with Van den Akker's conjecture that stiffness is more of a matter of individual fiber rigidity *(13)*.

The dimensional stability of EMA- and BTCA-treated kraft paper is illustrated in **Fig. 10**. EMA has a small advantage over BTCA in achieving a moderate level of dimensional stability but has difficulty reaching a high level. This trend also reflects the relative importance of interfiber and intrafiber crosslinking.

Corresponding data of wet stiffness and dimensional stability from bleached paper and corrugating medium are given in **Figs. 11–14**, respectively. Although there are some minor differences compared with the results from kraft paper, the general trends are the same. In this respect, small carboxylic acids are more effective than large ones in achieving good wet stiffness and dimensional stability.

CONCLUSIONS

High-molecular-weight polyfunctional carboxylic acids are more effective wet-strength agents than low-molecular-weight acids. Moreover, the fiber–fiber crosslinks induced by high-molecular-weight acids increase the sheet's folding endurance, while folding endurance drops for sheets treated with low-molecular-weight carboxylic acids. On the other hand, high-molecular-weight carboxylic acids are less effective in obtaining high wet stiffness and dimensional stability. We tentatively attribute differences in the behaviors of papers treated with high- and low-molecular-weight carboxylic acids to differences in the extent of interfiber and intrafiber crosslinking. **TJ**

Xu is a post-doctoral associate at the Institute of Paper Science and Technology, 500 10th Street, Atlanta, GA 30318. Yang is a professor in the Department of Textile, Merchandising and Interior at the University of Georgia, Athens, GA 30602. Chen is a senior research scientist in the School of Forest Resources at the University of Georgia, Athens, GA 30602.

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LITERATURE CITED

1. Xu, Y. F., Chen, C. M., and Yang, C. Q., *TAPPI J.* 81(11): 159(1998).
2. Horie, D. and Biermann, C. J., *Tappi J.* 77(8): 135(1994).
3. Nelson, R. and Oliver, D.W., *J. Polymer Sci. Part C* 36: 305(1971).
4. Carpita, N., Sabularse, D., Montezinos, D., *et al.*, *Science* 205: 1144(1979).
5. Stone, J. E., Treiber, E., and Abrahamson, B., *Tappi* 52(1): 108(1969).
6. Stone, J. E. and Scallan, A. M., *Pulp Paper Mag. Can.* 69(6): 69(1968).
7. Berthold, J., "Water adsorption and uptake in the fiber cell wall as affected by polar groups and structure," Doctoral dissertation, Royal Institute of Technology, Sweden, 1996.
8. Casey, J. P., *Pulp and Paper Chemistry and Chemical Technology*, John Wiley & Sons, New York/Chichester, U.K., 1979, p. 1809.
9. Caulfield, D. F., *Tappi J.* 77(3): 205(1994).
10. Wiltshire, W.A., *World's Paper Trade Review* (supplement), Aug. 14, 1947, p. 45.
11. Britt, K. W., *Paper Mill News* 70(39): 106(1947).
12. Maxwell, C. S., "Dry strength from wet strength agent," in *Dry Strength Additives*, TAPPI PRESS, Atlanta, 1980.
13. Van den Akker, J. A., *Tappi* 33(8): 398(1950).