Preferred citation: P. Luner, Y.J. Zhou, P. Caluwe and B. Tekin. Wet reinforcing of paper and board by novel crosslinking chemicals. In **Products of Papermaking**, *Trans. of the Xth Fund. Res. Symp. Oxford, 1993*, (C.F. Baker, ed.), pp 1045–1072, FRC, Manchester, 2018.
DOI: 10.15376/frc.1993.2.1045.

WET REINFORCING OF PAPER AND BOARD BY NOVEL CROSSLINKING CHEMICALS

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ABSTRACT

Among the most extensively used chemicals in the paper industry are wet strength resins. They enhance the performance of paper products ranging from tissue to board. Environmental concerns are questioning the use of several of these additives and a strong effort is being made to replace these chemicals with benign ones. This paper reports one such study.

Highly water soluble polyfunctional carboxylic acids — succinic acid, citric acid, tricarballylic acid, and 1,2,3,4-butanetetracarboxylic acid (BTCA) — when applied in a 1% solution to paper, dried, and heated (120 - 150 °C) with a catalyst develop wet strength as high as 55%. The effectiveness of these acids is in the order tetrafunctional > trifunctional > difunctional. This sequence is a reflection of their ability to form multiple anhydrides. Additional experiments indicate that the wet strength is the result of crosslinking of the hydroxyl groups in cellulose. The wet reinforced papers are easily dispersed under alkaline conditions. The crosslinking of the papers results in an increased dimensional stability.

Most wet strength chemicals are added at the wet-end where they are substantively adsorbed on the pulp and cured during the drying process. In contrast, the chemicals used in this study are water soluble and therefore are applied to the paper by a saturation technique. Additional research will focus on the optimization of their delivery.

INTRODUCTION

It has long been recognized that paper products are significantly improved and their use extended by increasing their resistance to high humidities and water. This is accomplished by a wide variety of chemical additives either at the wet-end, size press or coating operation.

Currently, several of these chemicals such as urea-formaldehyde, melamine-formaldehyde and other wet strength chemicals containing epichlorohydrin have come under scrutiny as generating suspected carcinogens (1,2). In view of these environmental concerns, the U.S. Bureau of Printing and Engraving has launched a research effort to find alternative wet strength agents especially for currency papers which are environmentally safe and are compatible with current manufacturing practices and product performance.

Rather than searching for methods to reduce the "potential" carcinogens of commercial chemicals to acceptable levels, we are proposing novel bonding agents for currency papers which will be non-toxic and environmentally acceptable. While this is our immediate goal, the broader objective is to develop a wet strength chemical which will be applicable to a wider range of paper products.

LITERATURE REVIEW

A brief overview of the wet-strength chemicals used to reinforce paper and their mechanism will serve as background for this study. More comprehensive reviews can be found in TAPPI monograph series Nr. 29 (3,4) and reviews by Stannett and coworkers (4,5) and by Ward (6). A more recent review on the newer alkaline type wet strength additives is given by Espy (7) and in a TAPPI *Wet and Dry Strength Course* (8).

"A paper which retains more than 15% of its dry strength when completely wetted with water may properly be called a wet strength paper"(9). This very broad definition of wet strength leaves open how "wet strength" is measured. The measurement of wet strength depends greatly on the end-use of the paper. Thus, consumer products such as paper towels, facial tissues and napkins require a moderate temporary improvement in wet tensile, while packaging papers used in corrugated medium require a high wet stiffness *i.e.* wet modulus. Specialties, such as photographic paper, disposables and currency papers may require a balance between wet tensile, wet modulus and absorbency.

Paper strength, *i.e.* elastic modulus, tensile breaking length, originates from the hydrogen bond dominated system. The loss in tensile strength and modulus when exposed to water vapor or water is a result of the decrease in hydrogen bonding. When chemicals are added to protect, and/or reinforce these bonds the paper becomes more water resistant and the wet tensile and wet stiffness is increased.

Wet Strength by Heat Treatment

When paper is heated to temperatures above 100 °C for relative short periods, considerable wet tensile and wet stiffness is developed (10,11). This effect is enhanced by the addition of salts to the papers or preoxidation of the pulp fibers. Dimensional stability is also increased. However, depending on the severity of the conditions, such treatments can lead to paper brittleness as exemplified by the folding endurance test. On the basis of these results, it was concluded that the wet strength originates from the formation of acetal and hemiacetal linkages. The term auto-crosslinking has been given to this treatment (10).

Wet Strength by Formaldehyde Treatment

The reaction of formaldehyde with paper, wood and fibers have been studied at the Forest Products Laboratories by Stamm (12,13) and Caulfield (14). Their work has greatly clarified how crosslinking with formaldehyde alters the wet and dry mechanical properties of paper and board. Caulfield has also shown (15) how the microporous structure of fibers is changed by formaldehyde crosslinking and its consequences on the wet mechanical properties *i.e.* tensile and stiffness. The formaldehyde reaction serves to show that internal crosslinking leads to high wet stiffness. Caulfield showed that formaldehyde crosslinking leads to a systematic decrease in the fiber saturation point, an increase in the wet modulus and increase in the dimensional stability of the paper along with extensive changes in the surface area and hence pore structure. They concluded that the dominant factors influencing the tensile modulus of paper is the amount of water within the cell walls and that the extent of the water-cellulose interface crosslinks limits the access of water into the structure, thus protecting the preexisting hydrogen bonds. On the basis of these results, it would appear that this mechanism is also operative in the auto-crosslinking of paper during heating and oxidation, but to a lesser degree. In our view the formaldehyde treatment represents one "clean" mechanism to achieve high wet strength and stiffness. Commercial application of this process has been abandoned due to the potential carcinogenic activity of formaldehyde.

Wet Strength by Bulking

Another method to achieve wet strength is to deposit or introduce into fibers chemicals of molecular size small enough to penetrate the cell wall. This may be done by direct esterification of cellulose (16,17) Thus, the introduction of acetyl groups (~15-20%) (18) into wood or paper results in the improvement in dimensional stability and wet strength. The grafting of paper and fibers with such monomers as ethyl acrylate, acrylonitrile, or a hydrophobic polymer can greatly reduce the moisture regain or fiber saturation points. Thus the dimensional stability and wet mechanical properties are enhanced. A good example of this is illustrated by the work of Caulfield (19) who impregnated paper with a fiber penetrating phenolic resin and after curing subsequently swollen in sodium hydroxide solutions. The fiber saturation points and moisture regains were determined. The linear and volumetric swelling showed that the linear dimensional stability is directly correlated with cell wall stability. The ratio of Ew/E50 wet-to dryness modulus was directly related to the fiber saturation point (F.S.P.) for all resin contents. Caulfield concluded that the wet stiffness depends upon the resin content only in so far as the resin content is effective in reducing cell wall swelling measured by the fiber saturation point of the paper.

Wet Strength by Polymer Reinforcement

By far the largest group of chemicals used for the wet reinforcement of paper are heat setting polymers. The urea-formaldehyde and melamine-formaldehyde systems have been extensively investigated by Stannett and coworkers (4,5). On the basis of the reaction of model compounds and kinetics of wet strength development and wet strength loss with various pulps and glass fibers, they concluded that the primary reaction in wet strength is the polycondensation of the resin itself and not the reaction with the fiber. Thus, the wet strength resin protects or "waterproofs" the existing fiber-to-fiber bonds by forming a crosslinked network of resin molecules over or in bonding areas. However, other evidence which include the effect of hemicelluloses, starch or pulp composition on wet strength development suggests that some covalent linkage and polymer complexation (20) may also occur with these heat-setting urea-formaldehyde and melamine-formaldehyde resins. Indeed, the decrease in moisture regain found by addition of wet strength in some of these systems suggests that not only covalent linkages but even "bulking" may be involved in the wet strength development of these resins.

Attention in recent years has shifted from acid-curing to alkaline-curing wet strength resins. These are the polyamide-epichlorohydrin or polyamine-epichlorohydrin resins. These resins are compatible with alkaline papermaking and unlike the acid-curing resins do not alter the absorbency of paper. Reviews on the use of these resins are given by Espy (7) and in the TAPPI publication (8). The primary mechanism for wet strength development involves the homo-crosslinking between the azetidinium functional groups and remaining secondary amine groups in the backbone structure. The polymer forms an insoluble network around existing fiber-fiber bonds. These polymers develop considerable wet strength of the permanent type. Bates (21) showed that PAE resins did not react appreciably with hydroxyl groups of β-methylglycosides. Additional work by Espy and Rave (22) confirmed these results with model compounds. They showed additionally that model amines containing epoxy groups react covalently with cellulose as determined by solubility tests in Cuen after curing.

Wet Strength : Temporary Type

As noted previously, oxidized fibers when heated develop considerable wet strength when made into paper (23). Indeed, when pulp fibers are oxidized specifically (24) to form dialdehyde or aldehyde groups, wet strength is obtained without heating. This wet strength is rapidly lost when paper is wetted. Cationic dialdehyde starches have been commercially developed to impart wet strength of a labile nature. It is believed that both hemiacetal and acetal linkages may be formed in these systems as water is removed (25). The cationic starches also give dry-strength improvement. When paper is saturated with water, these bonds are rapidly destroyed with a rapid loss in wet strength.

Polyacrylamide-glyoxal resins have largely replaced dialdehyde starches. These resins are prepared by crosslinking a low molecular weight polyacrylamide with glyoxal under controlled conditions (8). These resins perform in much the same way as cationic starches *i.e.* they increase the dry as well as wet strength, which is rapidly lost when saturated with water. Very little work has been done with these systems to elucidate the basic reaction mechanism of their action.

The foregoing overview of paper wet strengthening has shown that wet strength is achieved by three main mechanism : bulking, crosslinking of cellulose, and polymer reinforcement of the existing hydrogen bonded paper. Covalent linkage between resin and cellulose cannot be ruled out. Several mechanisms may be operating simultaneously within a given system, and insufficient test criteria exist to clearly establish the dominant mechanism. Clearly this is an area for additional research and is another objective of this study.

CURRENT METHODOLOGIES

The crosslinking of cellulosic materials is generally carried out by forming ether type linkages or via acetal/hemiacetal formation. Considerable research has been devoted to other crosslinking methodologies as a replacement strategy for the use of formaldehyde especially in durable press finishing agents for cotton textiles. Work at the Southern Regional Research Center of the U.S. Department of Agriculture in New Orleans has shown that certain structurally well defined polyfunctional carboxylic acids are highly effective durable press finishing agents (26 - 28). These finishes are durable even after a very large number of laundry cycles under alkaline conditions. These studies show clearly that the ester linkages obtained through these polyfunctional carboxylic acids are hydrolytically stable, contrary to the widespread belief that ester linkages in general provide inferior hydrolytic stability. In view of the similarity of this type of crosslinking reaction to formaldehyde it seemed logical that reaction of these polyfunctional carboxylic acids with paper would lead to wet strengthening of paper.

This paper discusses the development of new wet strength agents and methodologies based on the reaction of paper with polyfunctional carboxylic acids with at least three carboxyl units that are structurally capable of thermal anhydride formation according to Blanc's rule (29). This study encompasses three main areas:

1. Reaction of papers with low molecular weight polyfunctional carboxylic acids that obey Blanc's rule of thermal anhydride formation. These studies deal principally with 1,2,3,4-butanetetracarboxylic acid (BTCA).

2. Evaluating the wet and dry mechanical properties of papers treated with polyfunctional carboxylic acids.

3. Mechanism of wet strength development in relation to the chemical modification of the papers.

EXPERIMENTAL SECTION

Materials

A bleached pulp (90% softwood, 10% hardwood) was used throughout this study. The pulp was beaten in a Valley Beater for 30 minutes (CSF around 450 ml). TMP, a hardwood and cotton fiber were only used to study the effect of pulp types on wet strength development. The linerboard was a commercial sample and had a basis weight of 210 g/m^2. 1,2,3,4-

Butanetetracarboxylic acid (BTCA), other acids and catalysts were obtained from Aldrich Chemical Co. and SIGMA.

Paper Treatment

The acids and catalyst were added at a weight ratio of 1:1. The handsheets were made according to TAPPI standard T205. In method 1 the handsheets were prepared using a solution of 1% BTCA and 1% catalyst. In method 2 the handsheets were first formed and air-dried. The handsheets were then dipped in a solution containing 1% BTCA and NaH_2PO_4 for 15 minutes (30 minutes for linerboard). The excess water was removed by pressing between blotting paper. The handsheets impregnated with BTCA and catalyst were air-dried in a conditioned room (50% RH, 23 °C) and then cured in a forcing air circulating oven at various temperatures and times.

Testing

Tensile strength testing was carried out in an Instron. For the wet tensile strength, the samples were soaked in deionized water for one hour before testing. The water retention test was used in this work to estimate the swelling of the fibers. Handsheets were disintegrated in a blender for 4 minutes. The pulp was then diluted to 0.25%. The pad (about 0.7 g in weight) was formed in a specially designed cylinder with an inner diameter of about 26 mm with a wire at one end. The pad was centrifuged in a IEC CENTRA-8 at a speed of 5,000 RPM for 30 minutes, and then weighed and dried at 105°C. The infrared spectra were obtained on a Nicolet 5DDX spectrometer fitted with a diffuse reflectance accessory. The spectra were obtained at a resolution of 4 cm^{-1} and using 64 scans. KBr was used as reference material. The handsheets used for the infrared spectra were treated with 5% BTCA and NaH_2PO_4 and were cured in an oven for 15 min. at 150 °C. The handsheets were washed with dilute NaOH and deionized water to remove unreacted BTCA and neutralize the carboxylic acid moieties. Dimensional stability of the linerboard (C.D.) was measured by soaking 1.5 x 10 cm paper strips in water overnight and measuring the dimensional increase. The dimensional stability was expressed as:

$$\% \text{ Dimensional Stability} = (\Delta L_b - \Delta L_t / \Delta L_b) \times 100$$

where ΔL_b : Change in length of untreated sample by soaking in water

ΔL_t : Change in length of treated sample by soaking in water

RESULTS AND DISCUSSION

Wet Strength Development of Paper with BTCA

Guided by the curing temperatures and catalysts developed by U.S.D.A. for durable press fabrics (26 - 28) a series of experiments were performed using paper and BTCA. Fig. 1 shows the wet strength development at several temperatures. Wet strength values in the range of 50% are developed at high temperatures. While curing was only made in an oven, other methods of curing are being studied. Fig. 2 compares two methods of adding BTCA to the paper. Method 1 consisted in using a 1% solution of BTCA and catalyst in the sheet mold while in method 2 the preformed dry sheet was saturated in a 1% solution of BTCA and catalyst. Fig. 2 shows that similar wet strength values were developed by the two methods. An analysis of the two papers showed that both methods contained ~1% BTCA. Saturating the papers in a 2% BTCA solution gave somewhat higher rates of wet strength development and wet strengths in the range of 65%. Similar wet strength values were developed in pulps ranging from TMP to cotton. It is important to note that the effective concentration of BTCA in our experiments with pulp (1%) is much lower than those employed in the durable press treatment of fabrics (6 - 10%) (26 - 28).

Effect of Catalysts

For BTCA to be effective in preparing durable press fabrics a catalyst must be used. Fig. 3 shows the wet strength development with BTCA at different weight ratios of NaH_2PO_4/BTCA (based on a 1% solution of BTCA). The wet strength reached a limiting value at a ratio of 1. Fig. 4 shows that the two most effective catalysts are NaH_2PO_2 and NaH_2PO_4. A similar conclusion was reached in the durable press experiment (30). Based on these experiments most of our work involved saturating dry handsheets or papers in a 1% solution of BTCA containing a weight ratio

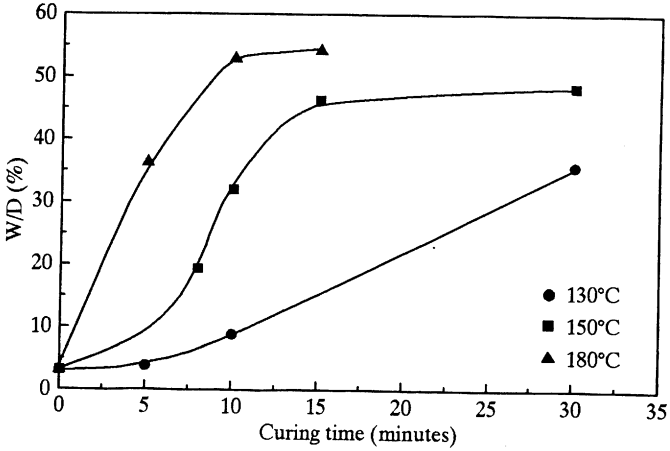


Fig. 1 Effect of curing temperature and time on wet strength development.

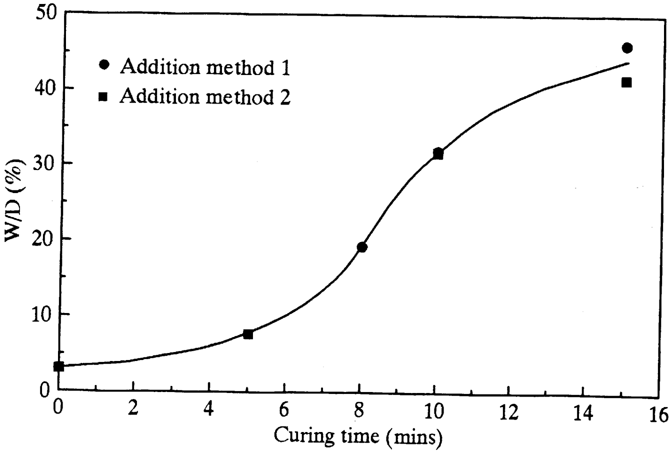


Fig. 2 comparison of two addition methods on wet strength development.

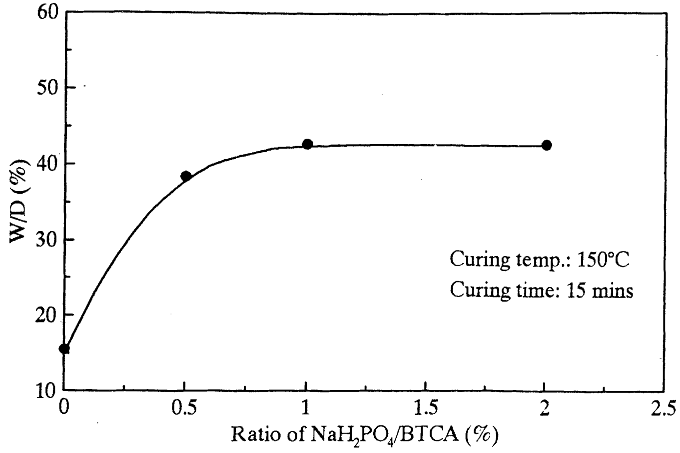


Fig. 3 Effect of ratio of catalyst/BTCA on wet strength.

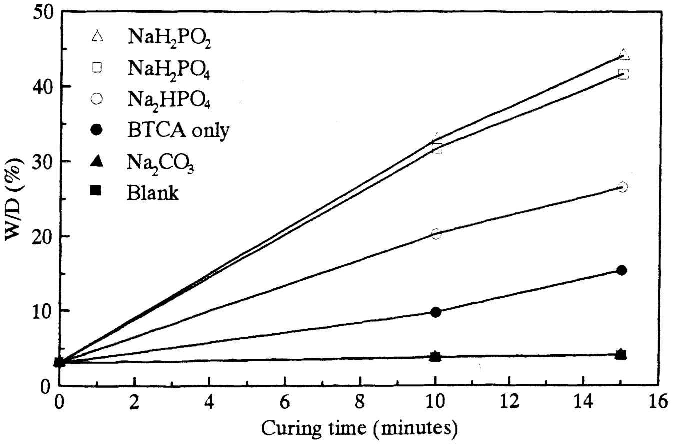


Fig. 4 Effect of catalysts on wet strength development at 1% BTCA. BTCA/Catalyst = 1

of catalyst : BTCA of 1. These results show that to develop high wet strength values with BTCA higher temperatures are necessary than normally required for developing wet strength with resins (3). Wet strength in the range of 20% require no catalysts. The exact chemical role of the catalysts in developing wet strength needs further clarification.

Relationship between Wet and Dry Mechanical Properties of Papers Cured with BTCA

A few selected results from the dry and wet mechanical properties of handsheets and linerboard are shown in Table 1a,b and Table 2. The dry tensile index for the handsheet decreased somewhat on BTCA treatment while for the linerboard treated paper the tensile index increased (6%). The dry modulus and ring crush values are relatively constant after treatment but the zero span values for the handsheets suffer a 30% loss. We conclude that the fibers have been damaged by the acid environment during the curing step. In contrast to the dry strength properties, the BTCA treatment considerably enhances all wet strength properties except the wet zero-span values. Table 2 shows that BTCA treatment is very effective in enhancing the wet/dry mechanical properties. The values obtained with 1% BTCA are greater than those obtained with a PAE resin or a PAE and CMC resin system. The BTCA treatment has not been fully optimized with regard to all the process variables.

Table 1a

WET AND DRY MECHANICAL PROPERTIES OF HANDSHEETS

	Untreated		Treated*	
	Dry	Wet	Dry	Wet
Tensile index, Nm/g	55.0	2.5	53.69	21.40
Modulus x 10^9, N/m^2	4.39	0.97	4.41	2.08
Zero s. break, length, km.	39.35	32.88	30.26	27.05
T/Z	0.143	0.008	0.181	0.081
Ring crush, kN/m	0.27	0.04	0.27	0.09

*: Cured at 150°C for 15 min.

Table 1b

WET AND DRY MECHANICAL PROPERTIES OF LINERBOARD

	Untreated		Treated**	
	Dry	Wet	Dry	Wet
Tensile index, Nm/g	75.92	12.16	82.47	40.40
Modulus x 10^9, N/m^2	4.17	0.76	4.17	2.17
Ring crush, kN/m	4.42	0.50	4.50	1.04

**: Cured at 150°C for 30 min.

Table 2

WET:DRY PROPERTIES

Handsheets

	Untreated	Treated
Tensile index, W/D	4.54	39.86
Elastic modulus, W/D	22.10	47.16
Ring crush, W/D	14.81	32.58
Dimensional stability	---	72.88

Linerboard

	Untreated	Treated
Tensile index, W/D	16.02	49.00
Elastic modulus, W/D	18.23	52.03
Ring crush, W/D	11.31	23.11
Dimensional stability	---	47.28

Recycling of BTCA-treated Papers

In today's world of environmental awareness it is essential that papers be repulpable and recyclable. Fig. 5 shows that high alkalinity at 23 °C is quite effective in decreasing the wet strength. Under these conditions the papers break up completely. The loss in wet strength and break up of the paper is greatly accelerated at higher temperature. This behavior is in line with the hydrolysis of ester linkages. Fig. 6 shows that when papers are cured with BTCA and mechanically disintegrated and reformed there is a significant increase in bulk. These bulk values are maintained in proportion to their weight composition when mixed with untreated pulp as shown in Fig. 7. The increased bulk values achieved by BTCA treatment may offer a means of enhancing some types of paper products.

Establishing the Chemical Basis for Wet Strength

Based on the wet strength development with BTCA and previous work (26 - 28) the sequence of individual steps that occur during the curing reaction may be visualized as shown in Scheme 1. The reaction may start with the thermal generation of a monoanhydride unit (shown in Scheme 1 as a 2,3-anhydride) in the curing step; its reaction with an hydroxyl group of cellulose leads to an ester linkage with concomitant regeneration of a carboxylic acid unit. This newly formed acid moiety is suitably located to permit a facile second thermal cyclic anhydride formation reaction with the terminal carboxylic acid unit of the BTCA residue. Reaction of this anhydride with another cellulosic hydroxyl group completes the crosslinking reaction (Scheme 1). Alternatively, the reaction may proceed by initial thermal formation of a dianhydride, followed by a double acylation reaction of the cellulosic OH groups. It is important to note that BTCA induced crosslinking of cellulose units is accompanied by the introduction of two free carboxylic acid units at the crosslinking site. It is conceivable that these two moieties may further react with formation of a six-membered ring anhydride which would permit an additional esterification reaction with another cellulosic hydroxyl group.

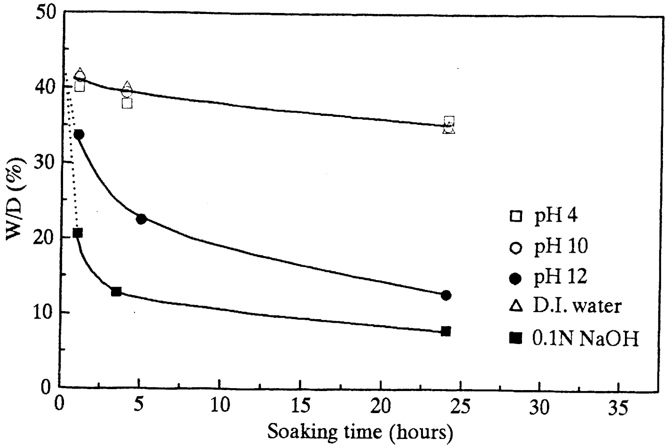


Fig. 5 Effect of soaking time on wet strength of paper at 23°C.

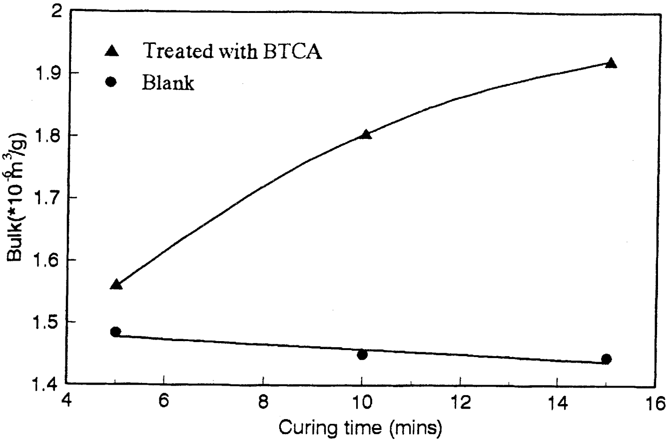


Fig. 6 Bulk of paper treated with 1% BTCA.

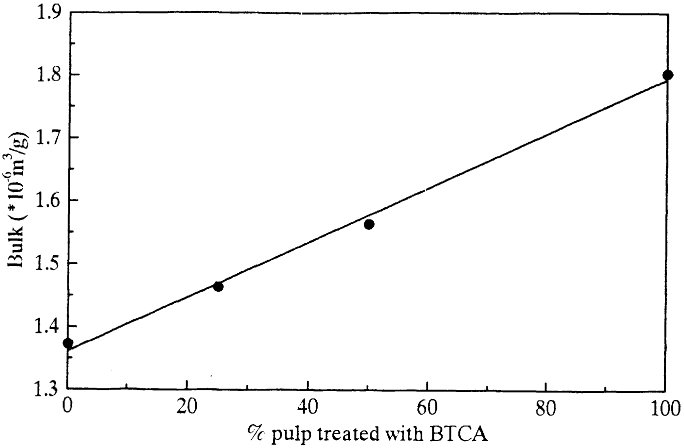


Fig. 7 Effect of BTCA-treated pulp on paper bulk.

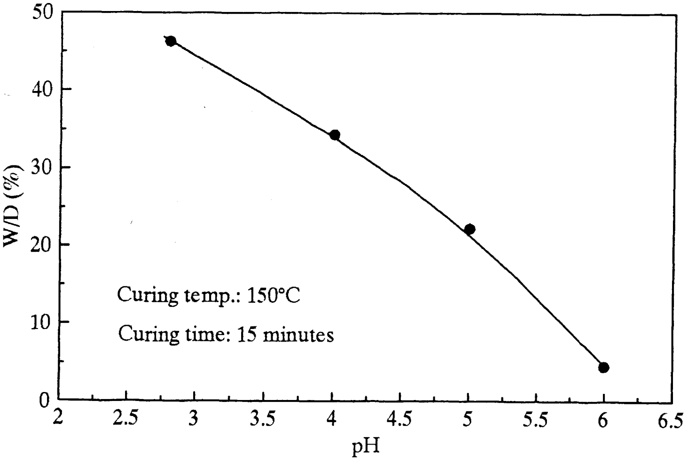
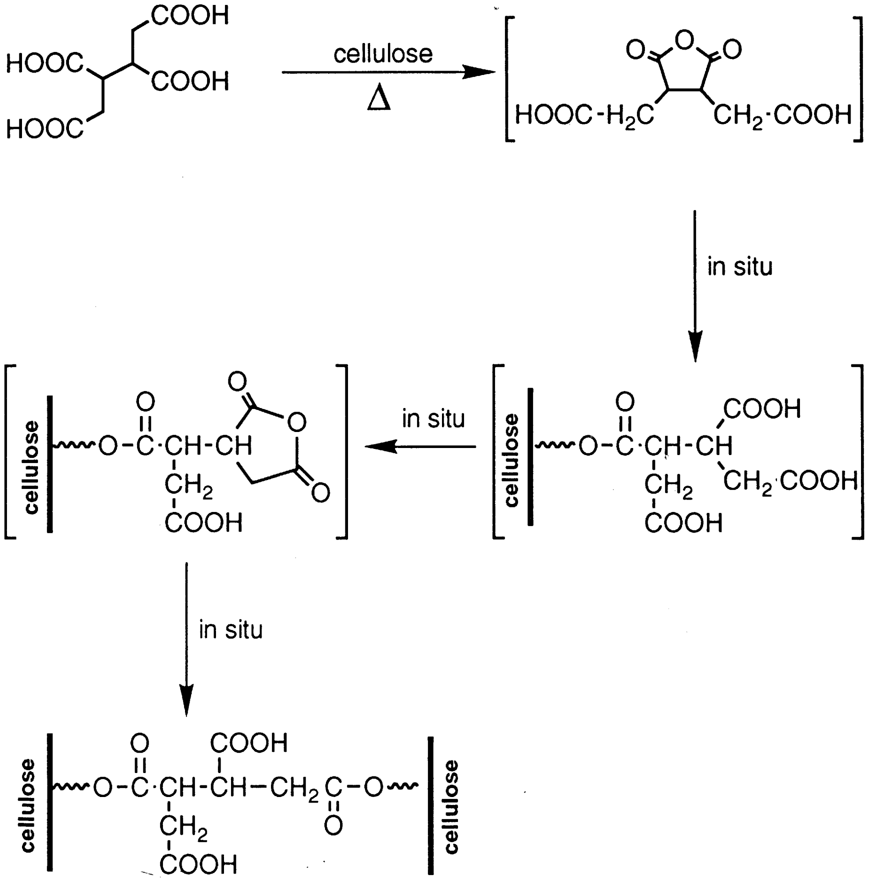


Fig. 8 Effect of pH on wet strength of BTCA treated paper.

Scheme 1

Mechanism of Thermal Crosslinking of Cellulose with BTCA



Effect of pH on Wet Strength Development

According to this reaction mechanism for the development of wet strength, neutralization of one or more carboxylic acid groups in BTCA would reduce the functionality of the system by conversion of carboxyl groups — needed for anhydride formation — into inert carboxylate moieties. This decrease in functionality will lead to lower crosslinking and hence to lower wet strength. This pH dependency of wet strength development is confirmed in Fig. 8. A reduction of the wet strength from 46% to 35% was observed when BTCA-treated papers were cured at pH 4 — a pH range corresponding to the neutralization of one carboxyl group of BTCA. It is noteworthy that at pH 5 a 22% wet strength is still observed.

Functionality of Carboxylic Acids

These results suggest that carboxylic acids of lower functionality than BTCA may also be capable of developing wet strength. Fig. 9 shows that tricarballylic acid and citric acid are quite effective in developing wet strength. These acids also performed well as durable press materials (31). Fig. 10 shows that citric acid can be a very effective wet strength agent at higher concentrations than those employed for BTCA. Cotton and TMP pulps also developed wet strength with citric acid. The lower effectiveness of citric acid and tricarballylic acid is due to their reduced anhydride functionality when compared to BTCA. The mechanism for the crosslinking of cellulose with tricarballylic acid is analogous to that discussed earlier for BTCA and is shown in Scheme 2. We note that this crosslinking reaction delivers only a single free carboxylic acid unit to the crosslinking site, in contrast to BTCA where two free carboxylic acid units are incorporated at the reaction site with cellulose (see above). The low wet strength values observed with succinic acid and maleic acid are due to the inability of these systems to form the necessary second anhydride moiety needed for the crosslinking of two cellulose units. To confirm the critical role of thermal anhydride formation in wet strength development of BTCA, adipic acid and valeric acid were tested as wet strength agents at the 1% concentration used in the BTCA experiments. The former is a dicarboxylic acid that does not produce a thermally induced anhydride, the latter is monofunctional and hence incapable of crosslinking reactions. Both acids were ineffective in developing wet strength.

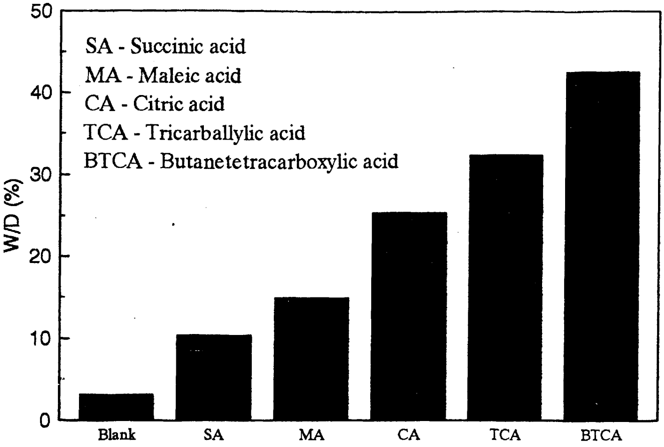


Fig. 9 Wet strength development of paper treated with various acids at 1%.

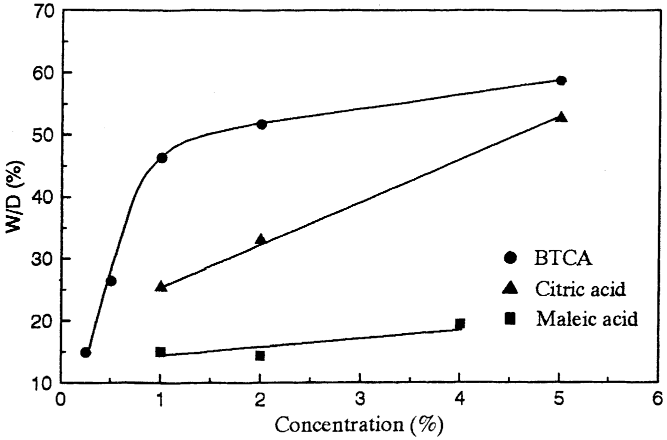
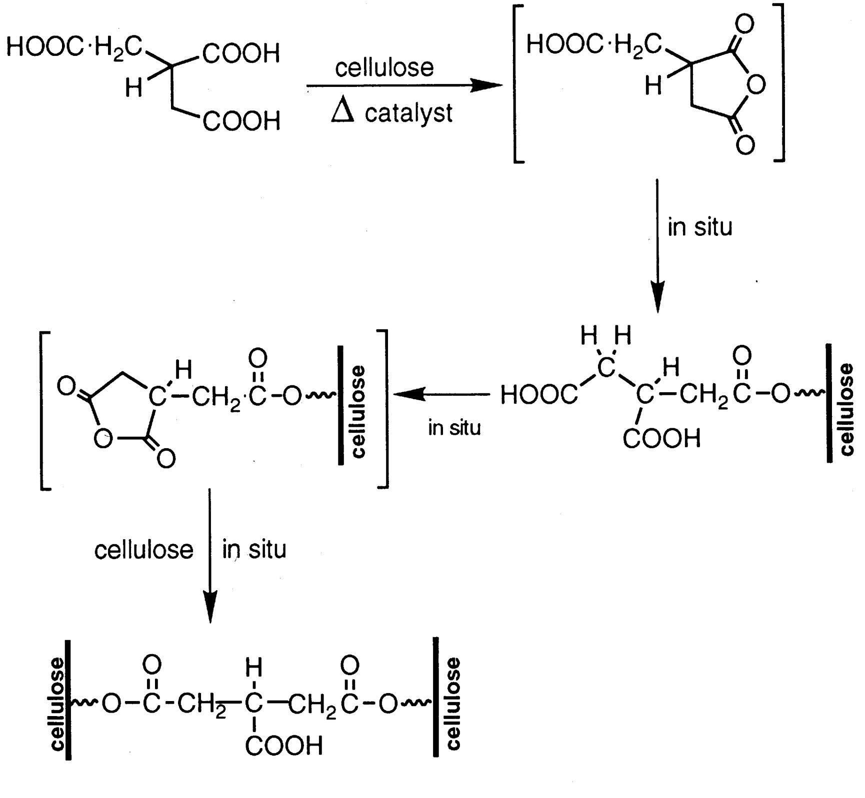


Fig. 10 Effect of concentration on wet strength development for BTCA, citric acid, and maleic acid.

Scheme 2

Crosslinking of Cellulose with Tricarballylic Acid



FTIR Investigation of BTCA Esterification of Cellulose

In order to test the existence of the esterification of cellulose with BTCA, handsheets treated with the tetracarboxylic acid were examined by FTIR spectroscopy. The characteristic carbonyl peaks for the uncured sample impregnated with BTCA are shown in Fig. 11a. The peak at 1726 cm^{-1} is attributed to the carbonyl moieties of BTCA; the peak at 1644 cm^{-1} is due to the carbonyl groups in cellulose. In our proposed reaction mechanism hydroxyl groups of cellulose react with BTCA via a succession of intermediate thermally induced cyclic carboxylic acid anhydrides. Such esterifications are accompanied by the formation of free carboxylic acids which become an integral part of the crosslinks. Direct FTIR analysis of the cured samples was not informative since the peaks of the newly incorporated ester moiety and the carboxylic acid functionality overlapped (Fig. 11b). However this complexity was easily resolved by converting the latter in its carboxylate form by washing the cured sample with dilute NaOH at room temperature (Fig. 11c). A similar approach was used successfully to elucidate the BTCA-crosslinking in durable press fabrics with FTIR photoacoustic spectroscopy (32,33). This treatment resulted in a new peak at 1574 cm^{-1}, attributed to the carboxylate anion; the remaining peak at 1726 cm^{-1} can now be assigned unequivocally to the ester linkage between BTCA and cellulosic hydroxyl groups. Acidification of the sample results in the disappearance of the peak at 1574 cm^{-1} with regeneration of the original spectrum. We note that washings of an uncured sample with dilute NaOH leads to complete disappearance of the peak at 1726 cm^{-1}, indicating the complete removal of BTCA.

Wet Strength, Dimensional Stability, and Wet Stiffness

Stamm (12) and Caulfield (14) showed that when papers and board are reacted with formaldehyde the increase in wet strength is accompanied by an increase in dimensional stability. Caulfield further showed that this treatment greatly improves the wet stiffness as well. He concludes that this is the result of crosslinking of the cellulose surfaces. This lowers the fiber saturation which limits the access of water to the hydrogen bonded system when wetted.

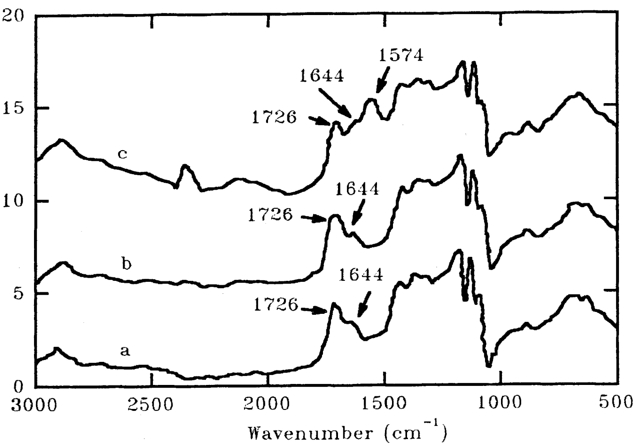


Fig. 11 FTIR spectrum of BTCA-treated papers. a) uncured, b) cured, c) cured and neutralized.

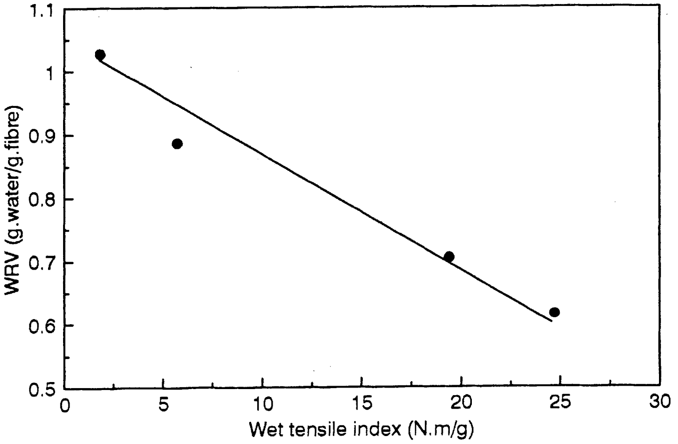


Fig. 12 Relationship between wet strength and WRV.

To verify whether the BTCA-treated papers behave in a similar manner, the wet stiffness, dimensional stability and water retention values were determined on linerboard. Fig. 12 shows that the WRV of BTCA-treated papers decreases as the wet strength increases. This behavior reflects the lowering of the fiber saturation point. Fig. 13 shows that as the wet stiffness increases with BTCA treatment the dimensional stability is greatly enhanced. The improvement in dimensional stability applies as well to various humidities as shown in Table 3. The increments obtained are however somewhat lower than that obtained with formaldehyde (14,19). This behavior is to be anticipated as the BTCA-crosslinks are longer and more polar due to the ester linkages and the presence of carboxylic acid groups. Indeed, moisture regain experiments resulted in only a slightly lower moisture regain for the BTCA treated samples. This is in contrast to formaldehyde crosslinking where large decreases in moisture regain occur on crosslinking (34,35). The exact role of the carboxyl groups on the mechanical properties can be studied by examining the mechanical properties of crosslinking with the tri- and difunctional acids and by chemically blocking the carboxyl groups. Such studies are underway. Nevertheless, while the chemistry of crosslinking with BTCA is greatly different from that of formaldehyde the effect on paper properties run parallel.

Table 3

DIMENSIONAL STABILITY OF LINERBOARD TREATED WITH BTCA AT VARIOUS RELATIVE HUMIDITIES

	Wet to 50% RH		92% to 50% RH		86% to 50% RH	
	Treated	Blank	Treated	Blank	Treated	Blank
% Dimensional increase	1.88	3.21	1.83	2.75	1.01	1.40
Dimensional stability, %	47.28		31.19		24.80	

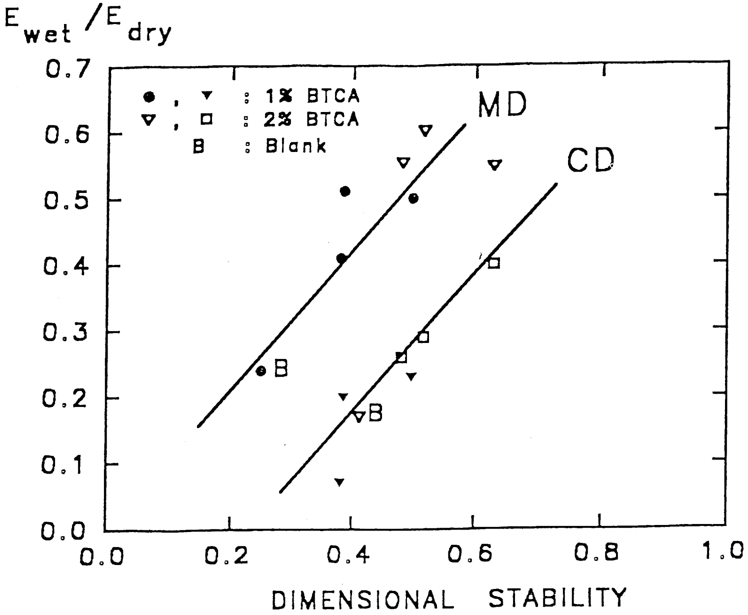


Fig. 13 The relationship between tensile modulus ratio and the linear dimensional stability of BTCA cross-linked linerboard. Blanks represent uncured samples.

Concluding Remarks and Further Prospects

We have shown that when low molecular weight polyfunctional acids such as 1,2,3,4-butanetetracarboxylic acid, citric acid, and tricarballylic acid are absorbed from a 1% solution onto paper and heated in the presence of a catalyst the wet strength of paper is greatly enhanced. This method of applying wet strength chemicals is in sharp contrast to the current industrial practice of applying cationic resins at the wet end. By this method the resins are deposited on or between fibers and on curing, the polymerized resin acts as a barrier to water penetration.

It appears that for commercial application of BTCA or other polyfunctional acids unique methods for their incorporation into paper need to be developed. Machine spraying, size press application, or coating techniques should be explored. It may be speculated that by applying the crosslinking acids in these ways additional product benefits may result. We are currently pursuing some of these avenues.

ACKNOWLEDGMENT

We appreciate and thank the National Science Foundation and the U.S. Bureau of Printing and Engraving (Grant # 9010493) who sponsored this study. Additional support was received through a McIntire-Stennis grant and from the Empire State Paper Research Institute.

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