

Ester crosslinking to improve wet performance of paper using multifunctional carboxylic acids, butanetetracarboxylic and citric acid

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ABSTRACT: *Butanetetracarboxylic acid and citric acid are two multifunctional carboxylic acids that have potential for use in formaldehyde-free durable press finishing of fabrics. In this study, these acids were investigated as cellulose crosslinking agents for modifying the wet performance of paperboard. The crosslink reaction involves the formation of two ester linkages per acid molecule to the hydroxyl-rich surface of cellulose to form a covalently linked structure that restricts the swelling action of water. All wet properties of ester crosslinked paperboard were significantly improved, as were dimensional stability and creep performance; two important dry properties—stretch and tensile energy absorption—were seriously decreased. For specialty products where water-soak properties of stiffness, dimensional stability, and reduced creep are important and dry toughness is not important, ester crosslinking may be a solution to material needs. Ester crosslinking eliminates the problems that are encountered with formaldehyde crosslinking. It also affords a pad-dry-cure process that is compatible with paper machine operation and yet has the advantage of a delayed cure option.*

KEYWORDS: *Carboxylic acids, creep, crosslinking, dimensional stability, esters, swelling, wet strength.*

Water and humid environments cause most shortcomings of paper, but the problem of wet-strength has largely been remedied by the use

of wet-strengthening resins, whose mechanisms are now well understood (1, 2). However, three remaining interrelated problems have to be over-

come before the full potential of paper as a material of construction can be achieved. These problems are the poor wet-stiffness and dimensional stability of paper as well as a tendency to creep and deform under load (especially in cyclic humidity environments). These shortcomings not only limit the performance of paper in packaging applications, but also limit the use of paper and other wood-fiber materials in engineered structural applications. One way to remedy these problems is chemical crosslinking (3). However, it is important to find an economical and environmentally sound procedure for crosslinking in a manner compatible with other fiber processing operations.

Cellulose crosslinking markedly improves the wet performance of paper by improving the wet modulus of elasticity (MOE), dimensional stability, and creep properties. The mechanism by which low levels of covalent crosslinks introduced into a cellulosic material can function to improve wet performance is well understood in terms of an explanation compatible with the hydrogen bond theory of paper (4). Chemical crosslinks improve the wet MOE and dimensional stabil-

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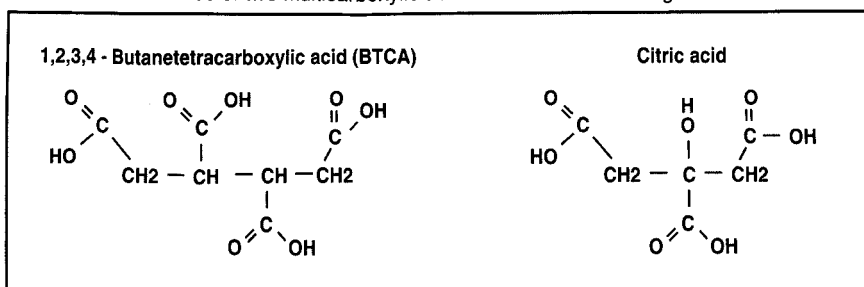
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ity of paper by decreasing the moisture sensitivity of the cellulose network to the swelling action of water. Below the fiber saturation point, the effect of water in decreasing the MOE of crosslinked paper is quantitatively the same as that of uncrosslinked paper. Wet-stiffening arises only from the decrease in the fiber saturation point that the crosslinks create. The role of crosslinks as load-bearing elements is not important in wet-stiffening. Rather, crosslinks function as swelling restraints to the network, so that a larger fraction of the preexisting hydrogen bonds function to retain a larger fraction of the MOE of the paper. In this respect, the mechanism by which crosslinks improve the wet MOE of paper is quite different from the mechanism by which crosslinks improve the dry MOE. Crosslinks in paper limit the swelling of the bonded network and protect the preexisting hydrogen bonds from the disrupting and dissolving action of water. The same crosslinks that are responsible for dimensional stability and MOE retention are also responsible for reduced creep. The arrays of moisture-sensitive hydrogen bonds are stabilized by a few covalent bonds such that the tendency of the hydrogen-bonded arrays in a stressed structure to "flicker" or creep into stress-relaxed configurations is decreased.

One effective way to introduce chemical crosslinks into paper is by reaction with formaldehyde (5). The acid-catalyzed reaction of cellulose with formaldehyde creates short acetal bridges between cellulose surfaces. The state of swelling at the time of crosslinking largely determines the effectiveness of crosslinking in terms of retaining MOE. The SOFORM method of crosslinking with formaldehyde (catalyzed by sulfur dioxide in a dehydrating environment) has been studied extensively (6-8). In spite of considerable initial interest in the process, it became clear that crosslinking with formaldehyde would not be commercially accepted. One main reason for reluctance by industry to accept

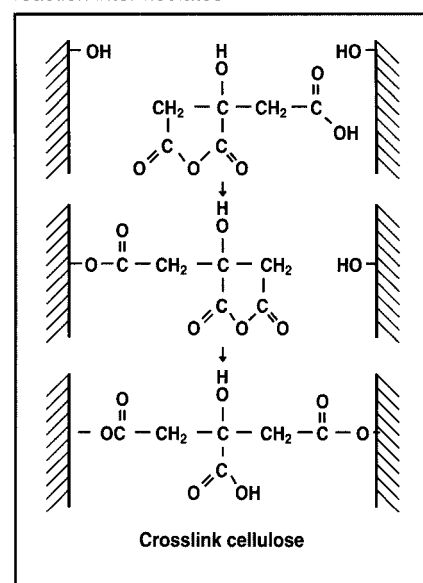
1. Chemical structures of two multicarboxylic acids used for crosslinking



this method has been an unrelenting and growing concern about the dangers of formaldehyde use. Increasingly stringent restrictions on formaldehyde vapor emissions in the workplace have been imposed, and formaldehyde use in many consumer products faces restrictions (9). This is especially true for products that are intended for use with food, for example, chicken boxes and fruit containers. With so many environmental concerns, paper companies have been understandably reluctant to introduce new sources of formaldehyde. It has been generally concluded that the health and environmental problems presented by formaldehyde use are considerable and probably should be avoided. Industries that use formaldehyde, such as wood and textile, have been searching for alternatives.

The textile industry has been actively seeking formaldehyde-free crosslinking methods for cotton fabric finishing to impart qualities of easy care, for example, wrinkle resistance, permanent press, etc., (10). One formaldehyde-free method that has been investigated is ester crosslinking using multicarboxylic acids (11, 12). Two chemicals that have received renewed investigation are 1,2,3,4-butanetetracarboxylic acid (BTCA) and citric acid (**Fig. 1**). The method of fabric treatment that utilizes these crosslinking agents is known as a pad-dry-cure process. This process is inherently suited to a paper treatment compatible with an operation in which the reagents could be applied as aqueous solutions at the size press, dried on the paper machine drums, and cured at a

2. Suggested mechanism for crosslinking reaction involving internal anhydride rings as reaction intermediates



later time by applying an elevated temperature. The desired properties of fabrics to be improved by crosslinking are not necessarily the same as those desired for paper. For example, wet-stiffness, although desirable for structural applications of paper, may not be a desirable characteristic in fabric (11). It is important to assess the range of property improvements achievable with BTCA and citric acid on a typical grade of paper for which wet property improvement would be of value, for example, linerboard.

For cotton fabric treatments, these multicarboxylic acids were shown to be more effective crosslinking agents than were the more common dicarboxylic acids. The reason suggested for their increased effectiveness as

I. Mechanical property values of board crosslinked with multicarboxylic acids

Treatment	Condition	Tensile strength, kN/m	Breaking stress, MPa	Elongation at break, %	Modulus of elasticity, GPa	Extensional stiffness, kN/m	Tensile energy absorption, MPa	Ring crush, kN/m
None	Dry	5.13	17.22	5.32	2.02	602	0.734	2.14
	Wet	0.294	0.971	4.59	0.172	52.0	0.034	---
Cured	Dry	5.99	20.13	4.69	2.58	769	0.772	2.19
	Wet	0.355	1.14	5.75	0.146	42.4	0.051	---
BTCA 4%	Dry	6.39	20.29	2.12	2.85	897	0.317	3.01
	Wet	2.84	8.94	7.25	0.386	122	0.414	0.52
BTCA 6%	Dry	6.23	18.79	1.63	2.55	848	0.209	3.83
	Wet	3.26	9.83	5.51	0.560	186	0.350	1.19
BTCA 10%	Dry	6.27	19.10	1.52	2.12	697	0.188	3.77
	Wet	3.67	10.85	4.13	0.684	232	0.299	1.53
Citric acid 4%	Dry	5.26	16.92	2.36	2.79	866	0.326	2.67
	Wet	1.20	3.79	7.12	0.278	87.5	0.191	0.26
Citric acid 6%	Dry	4.92	15.28	2.31	2.31	741	0.271	2.71
	Wet	1.61	5.09	7.44	0.267	84.9	0.263	0.46
Citric acid 10%	Dry	4.64	13.62	2.26	2.08	710	0.237	2.86
	Wet	1.91	5.70	6.77	0.307	103	0.264	0.78

II. Percentage improvement in wet property

Property	Improvement, %					
	BTCA, 4%	BTCA, 6%	BTCA, 10%	Citric acid, 4%	Citric acid, 6%	Citric acid, 10%
Tensile strength	866	1,008	1,148	308	448	550
Modulus of elasticity	124	226	298	61.6	55.2	78.5
Stretch	57.9	20.6	-10.0	55.1	62.1	47.5
Tensile energy absorption	1,132	942	790	469	683	686

III. Percentage change in dry property

Property	Change, %					
	BTCA, 4%	BTCA, 6%	BTCA, 10%	Citric acid, 4%	Citric acid, 6%	Citric acid, 10%
Tensile strength	24.6	21.4	22.2	2.53	-4.1	-9.6
Modulus of elasticity	41.1	26.4	5.0	38.1	13.9	2.9
Stretch	-59.5	-68.8	-70.9	-55.3	-56.6	-57.5
Tensile energy absorption	-56.9	-71.6	-74.4	-56.6	-63.1	-67.8
Ring crush	40.5	77.4	76	24.7	26.6	33.8

crosslinking agents is the facile, five-membered, intramolecular anhydride ring structure proposed as a reaction intermediate during dehydration and ester bond formation (13). Two ester bonds must be formed in order to create one crosslink. After one ester bond has formed, at least two additional carboxylic groups must remain to facilitate the formation of the additional intramolecular anhydride ring and subsequent ester bond. Dicarboxylic acids are incapable of crosslinking by this proposed mechanism, which requires the formation of two intramolecular anhydride rings either simultaneously or sequentially. **Figure 2** depicts a possible crosslink reaction sequence involving two sequentially formed anhydride ring intermediates. However, BTCA can form two simultaneous anhydride rings. Other reaction mechanisms for citric acid crosslinking might also include the formation of a lactone reaction intermediate during the dehydration step.

Materials and procedures

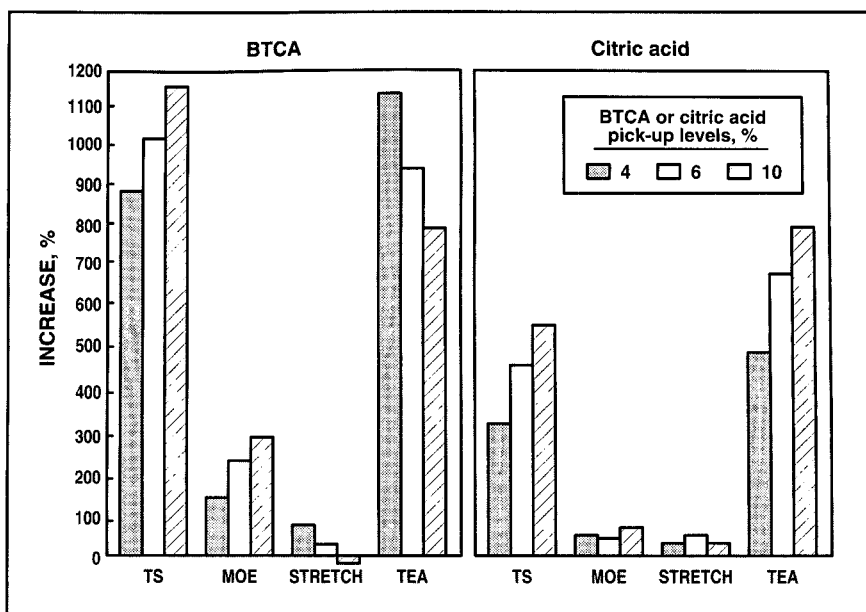
The principal material for this study was MR 7316, a 205-g/m² paperboard made from 100% loblolly pine unbleached kraft furnish on the USDA Forest Service, Forest Products Laboratory* (FPL) pilot-scale fourdrinier paper machine. Paperboard density was 620 kg/m³, and thickness was 0.338 mm. Mechanical properties were measured in the cross-machine direction on specimens cut from treated and untreated paperboard. The properties evaluated, both wet and dry, were tensile strength, MOE, elongation at break, and ring crush. A similar material, MR 6756, a 205-g/m² paperboard made from 100% upper U.S. midwest softwood kraft pulp, was used for the creep stabilization evaluation. This material was selected because it could be compared more effectively with a similar sample that had been crosslink stabilized with formaldehyde using the SOFORM method.

Paperboard treatments were accomplished by a modified pad-dry-cure process (12). Sheets (200 mm x 250

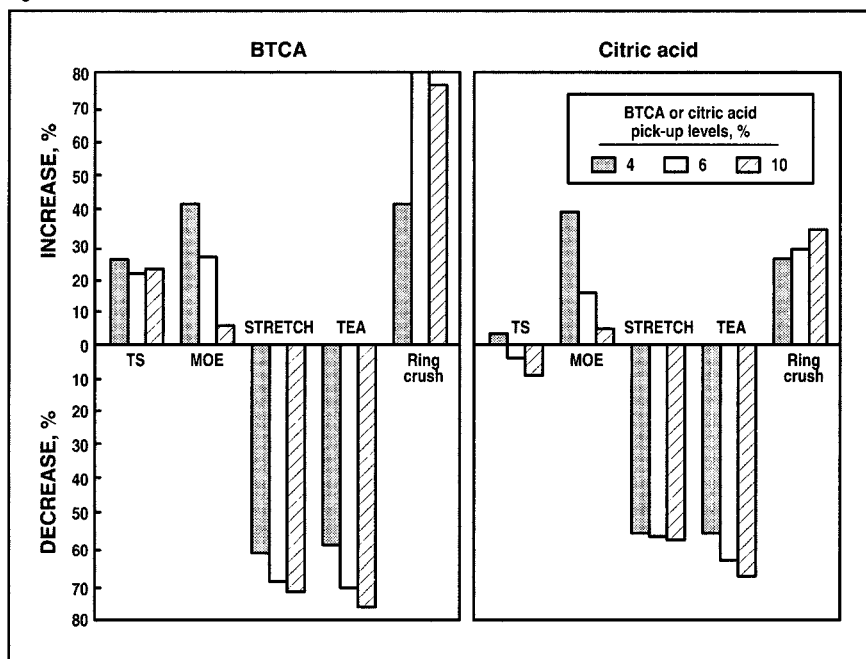
mm) were immersed in solutions of carboxylic acid and catalyst for 30 s and blotted to achieve reproducible pickup of reagents. Solution concentrations were adjusted so that the carboxylic acid (either BTCA or citric acid) pick-ups were 0%, 4%, 6%, and 10%. At each level, the catalyst, sodium hypophosphite, was adjusted to be equal to one-half the concentration of carboxylic acid. These levels were arrived at as reasonable values based on similar crosslinking reactions with cotton fabrics. The sheets were dried on the surface of a photographic dryer to remove enough water to prevent curling. The surface temperature of the paper sheet did not significantly exceed 100°C because the sheets were removed from the photographic dryer before reaching complete dryness. The sheets were then completely dried in an oven at 85°C for 15 min and stored for later curing. The sheets were cured in a forced draft oven. Individual sheets were cured at 180°C for 90 s. After standard TAPPI conditioning (50% RH, 25°C), tests were performed. Ring crush was measured according to TAPPI Test Method T 818. Values of tensile strength, MOE, and elongation to break were determined using a uniaxial tensile testing method originally developed at the FPL (14). Analysis of the stress-strain curves, which involved application of a three-parameter hyperbolic tangent model, has been described elsewhere (15). Tensile energy absorption (TEA) was evaluated as the integrated area under the stress-strain curve. The same tests were also performed wet, after a 24-h soak in tap water at 25°C.

Dimensional stability, or the resistance to swelling, of the sheets has been demonstrated to correlate well with wet-stiffness and was a convenient measurement of the effectiveness of crosslinking (16). Dimensional stability was determined from measurements of cross-machine direction strips cut from untreated and treated sheets. Unrestrained specimens were cycled several times between the water-soaked state and the dry state

3. Wet property improvement of ester-crosslinked paperboard shown as percentage



4. Dry property improvement and decline of ester-crosslinked paperboard shown as percentage



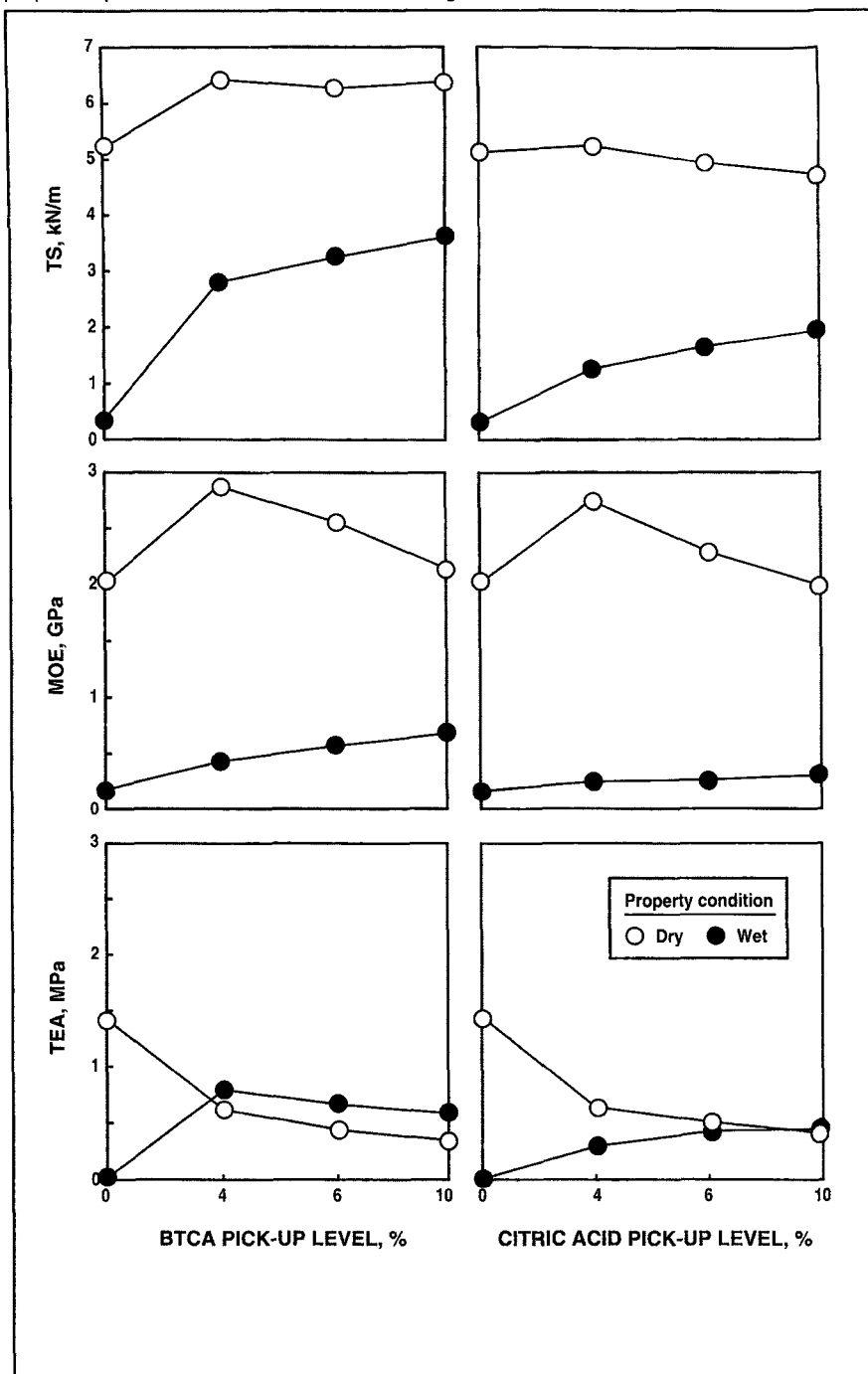
(50% RH) to relieve internal residual strains. When constant dimensions were achieved at both the water-soaked and the dry states and conditions were completely reversible, dimensional stability was evaluated from Eq. 1:

$$D_i = [(L_u - L_t)/L_u] \times 100 \quad (1)$$

where L_u and L_t refer to the linear dimension change between equilibrium water soak and 50% RH of the untreated and treated sheets, respectively.

For MR 7316 untreated and treated paperboards, water sorption isotherms (25°C) were measured on the desorp-

5. Tensile strength, modulus of elasticity, and tensile energy absorption of dry and wet properties plotted as X function of crosslink reagent add-on



tion branch and used to evaluate the water-accessible surface area by means of the "t" plot (17).

The MR 6756 used for the demonstration of the effect on creep stabilization was treated with BTCA at the level of 7.7% add-on by the modified pad-dry-cure method described ear-

lier. Creep performance was evaluated using a method described previously (18). Cross-machine direction tensile specimens were loaded to 25% of their tensile strength (measured at 50% RH), and RH was cycled between 30% and 90%. Creep deformation was measured as a function of time. Creep

in a cyclic humidity environment was compared on similar specimens of MR 6756: untreated, wax-dipped (pick-up 0.56 g/g), and SOFORM-treated (8) with a bound formaldehyde content of 1.5%.

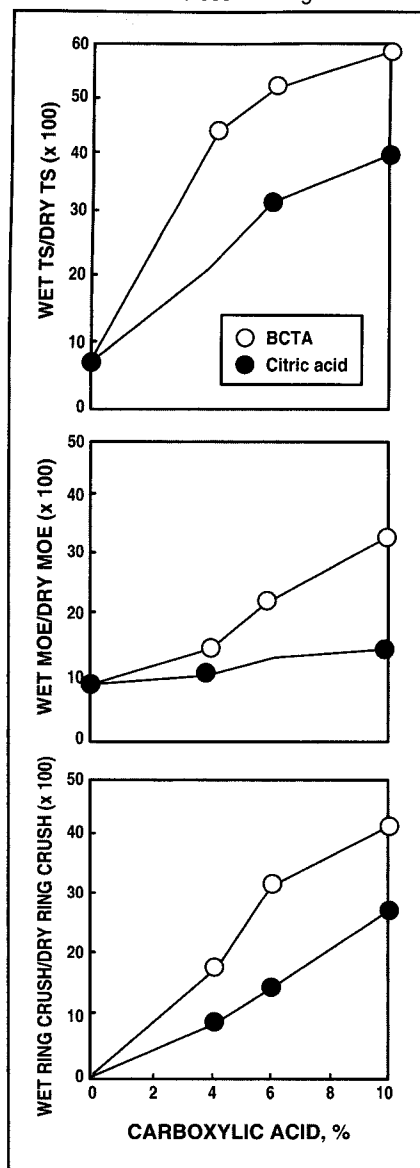
Results

The results of the mechanical property testing are summarized in **Tables I through III** and in **Figs. 3 through 6**. As expected, the wet properties after crosslinking tended to be favorable compared to the wet properties of the untreated paperboard. For crosslinked specimens, wet properties of tensile strength, MOE, and tensile energy absorption were improved several hundred percent (Fig. 3), largely because the properties for untreated wet paperboard are notoriously poor. On the other hand, changes in the dry properties showed a mixture of improvements and declines (Fig. 4). Although tensile strength, MOE, and ring crush showed improved dry values (roughly 20–70% improvement), stretch and tensile energy absorption showed marked decreases of 60–80%. Figure 5 is a composite plot of tensile strength, MOE, and tensile energy absorption as a function of crosslink reagent add-on. From this plot, one can see the trends in the property as the level of crosslinking increased. Similarly, Figure 6 depicts wet tensile strength, wet MOE, and wet ring crush expressed as a percentage of the respective dry property of treated material as a function of extent of crosslinking by both BTCA and citric acid.

Table IV lists dimensional stabilization values that resulted from crosslinking with the multifunctional carboxylic acids BTCA and citric acid. Also included in Table IV are the measured water-accessible surface areas as determined by the "t" plot method from the descending branch of the water vapor sorption isotherm. From the measured surface area, assessing the percentage of surface lost for each

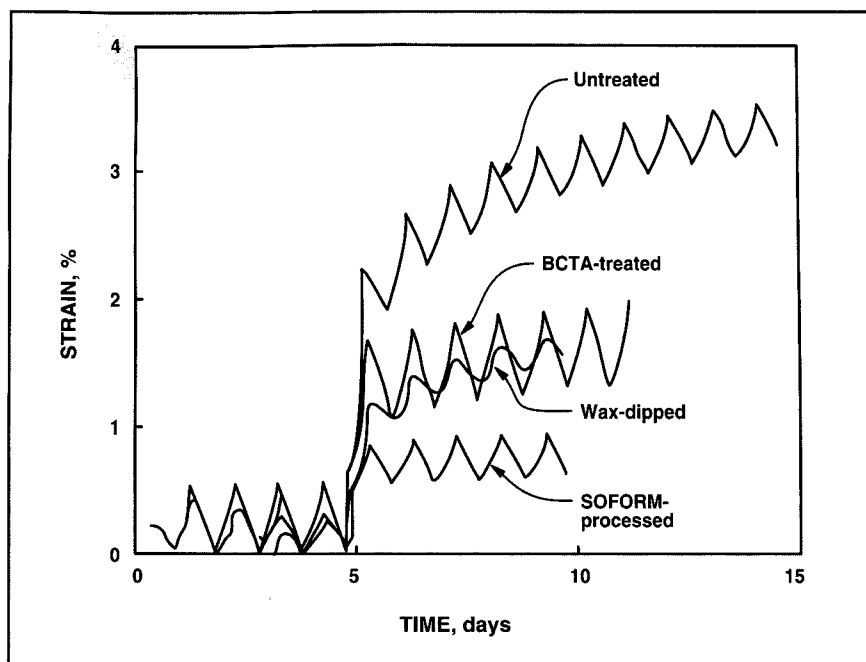
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6. Wet properties as percentage of dry properties of ester-crosslinked paperboard plotted as function of crosslink reagent add-on



crosslinking level was possible. These surface area losses were compared with the dimensional stabilization values or the percentage decrease of swelling for that crosslinking treatment. Although dimensional stabilization values showed substantial stability improvement in the water-soaked state (up to 60%), the losses in water accessible surface area (over the range of 30–90% RH) were considerably smaller. These results are in general agreement with results on the stabilization of paper by formaldehyde

7. Effect of BTCA crosslinking on long-term creep of paperboard loaded in tension and exposed to daily cyclic humidity environment (30–90% RH)



crosslinking except that formaldehyde was more effective in decreasing swelling. The decrease in swelling achieved with 6% BTCA can be achieved with as little as 1.5% formaldehyde.

Figure 7 shows the effect of crosslinking with BTCA on decreasing the long-term creep of paperboard loaded in tension and exposed to a daily cyclic humidity environment (30–90% RH). The creep response of the BTCA-treated paperboard was markedly decreased compared to that of untreated specimens. After 5 days of exposure, creep of the treated specimen was 50% that of the untreated specimen or about that of a specimen treated with 56% wax. Also included in Fig. 7 for comparison is a paperboard crosslinked with formaldehyde. Its creep deformation was even smaller; creep was less than one-third that of the untreated control.

Discussion

Apparently, ester crosslinking provides a means for modifying the wet performance of paper by essentially the same crosslink mechanism pro-

vided by acetal bonds introduced with formaldehyde (19). Crosslinks do not greatly decrease the available surface area accessible to water as determined by the "t" isotherm (Table IV), because the small water molecule can apparently diffuse past the crosslink restriction. However, these bonds do impose a swelling restraint so that volumetric swelling is impeded. The striking effect of crosslinking is the decrease of swelling in the water-soaked state and the subsequent effect on water-soaked mechanical properties. The multifunctional carboxylic acids, BTCA and citric acid, by their action as cellulose crosslinking agents are effective to varying degrees in modifying the wet-performance characteristics of paperboard. At levels of 4–10%, both substantially improve wet performance in terms of tensile strength, MOE, stretch, tensile energy absorption, and ring crush. The improvement in these properties achieved with BTCA is approximately twice that achieved with citric acid. Although some dry properties are also improved (namely, MOE and ring crush), two important dry properties—

IV. Effect of crosslinking on swelling and water-accessible surface area

Treatment	Linear swelling ^a , L, %	Dimensional stability, D _p , %	Surface area ^b , m ² /g	Decrease in surface area, %
None (cured)	2.22	---	259	---
BTCA 4%	1.42	36.1	240	7.3
BTCA 6%	0.87	60.9	214	17.4
BTCA 10%	0.87	60.9	210	18.9
Citric acid 4%	1.67	24.8	265	-2.3
Citric acid 6%	1.55	30.1	243	6.2
Citric acid 10%	1.08	51.1	223	13.9

^a Measured in the cross-machine direction between dry state (50% RH) and water-soaked state.
^b Evaluated from the desorption isotherm between 90% and 30% RH by means of the "t" plot.

stretch and tensile energy absorption—are severely decreased. These losses stem from embrittlement that results when crosslinks prevent relative movement between adjacent cellulose chains. Although wet properties are greatly improved (in some cases, over 1000%), it is rare in actual practice when the importance of wet properties is overriding. Often, dry toughness, especially during fabrication processes, is an essential property. One potential advantage of the multifunctional carboxylic acid crosslinking is the delayed cure feature, where the crosslinking or cure step can be delayed until after fabrication.

For some materials where toughness is not an important feature, reduced creep may be a very desirable characteristic. In large-dimension, fiber-based insulating ceiling panels, for example, dry toughness may not be needed but dimensional stability and decreased creep in cyclic humidity could be highly desirable. Combining multifunctional carboxylic acid crosslinking with an effective fire retardant treatment might eventually

provide a viable process for such a specialty product.

One significant drawback to multifunctional carboxylic acid crosslinking is material costs. Formaldehyde, for example, costs only US\$ 0.449/kg (based on US\$ 0.075/lb for 37% formalin). The carboxylic acids cost considerably more. Citric acid costs between US\$ 1.80/kg and US\$ 1.96/kg, and BTCA is not yet a commodity chemical. But even if a large-scale marketing effort for BTCA were undertaken, it is estimated to cost US\$ 1.65/kg for a 12% solution (equivalent to US\$ 13.75/kg) (20). However, the acids do not present the environmental problems that formaldehyde does. Citric acid, for example, is immediately suitable for use with materials in contact with foodstuffs. If the effectiveness of crosslinking with citric acid could be made equal to that with BTCA (by catalyst improvement, for example), the economic viability of the method would be considerably improved.

In addition to the delayed cure feature and the use of environmentally acceptable chemicals, ester crosslinks provide reversible base hydrolyzable

bonds, unlike the nonreversible acetal bonds afforded by formaldehyde crosslinking. This is important for recycling of crosslinked materials.

Concluding remarks

The multifunctional carboxylic acids, 1,2,3,4-butanetetracarboxylic acid (BTCA) and citric acid, which have been shown to have potential as finishing agents for cotton fabrics, are also potential crosslinking agents for modifying the wet tensile performance of paperboard. In this study, wet tensile strength, wet modulus of elasticity, wet tensile energy absorption, and ring crush were markedly improved. Although some dry properties were improved, there were marked losses in dry stretch and dry tensile energy absorption that would seriously limit the toughness properties of any crosslinked material. The BTCA- and citric-acid-treated paperboard exhibited greatly improved dimensional stability, and in a single test, the creep deformation of BTCA-treated paperboard was greatly improved. The BTCA was more effective as a crosslinking agent compared to citric acid but was much less effective, especially on a weight basis or on a cost basis, compared to formaldehyde. The advantages of a potential ester crosslinking process using multifunctional carboxylic acids are the delayed cure feature and greater environmental acceptability compared to the use of formaldehyde. ■

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The author acknowledges the assistance of Marguerite Sykes with sample treatments, Anne Fuller with test measurements, and Dennis Gunderson and Ty Tobey with creep measurements.

Received for review Jan. 27, 1993.

Accepted March 14, 1993.