Mechanism of Crosslinking of Papers with Polyfunctional Carboxylic Acids

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SYNOPSIS

Brief thermal curing of papers treated with an aqueous solution of polyfunctional carboxylic acids and NaH_2PO_4 imparts substantial wet strength to the papers. The effectiveness of such carboxylic acids increases with their functionality in the order 1,2,3,4-butanetetracarboxylic acid (BTCA) > tricarballylic acid (TCA) $\gg$ succinic acid. The two main stages of the curing reaction of papers, i.e., pendant attachment of the polyfunctional carboxylic acids via esterification with cellulosic hydroxyl groups, and its further reaction with another cellulose hydroxyl group producing crosslinks of the cellulose fibers were analyzed separately using a combination of acid–base and conductometric titrations. The extent of reaction of the polyfunctional carboxylic acids with paper was followed by pH titration, which shows the total decrease in acid functions as the curing progresses and is directly related to the total consumption of carboxylic acids groups by ester attachment and ester crosslinking steps. The conductometric titration, on the other hand, measures the increase in carboxylic acids bound to cellulose units of the paper as a direct result of previous esterification steps. Our studies reveal that the reaction of BTCA with papers is essentially quantitative after 15 min of curing. The amount of once-reacted BTCA increases in the initial phases of the curing reaction and then decreases as more and more carboxylic acid units are converted into crosslinking sites, while the amount of crosslinked BTCA increases throughout the curing reaction. The reaction profile of papers with TCA differs from that of BTCA in that the curing reaction is initially dominated by the formation of ester appendages; crosslinking becomes the main reaction only after extended curing times. We attribute this difference to the ability of BTCA to form an highly reactive difunctional crosslinking reagent at the outset of the curing reaction, while TCA is initially monofunctional in its reaction with cellulosic hydroxyl groups (formation of a monoanhydride). The relationship between the wet tensile strength of the treated papers and their degree of crosslinking is also discussed.

INTRODUCTION

In previous publications,[1,2] we reported that treatment of papers with an aqueous solution of a series of polyfunctional carboxylic acids in the presence of NaH_2PO_4 imparts wet strength of up to 55% after brief thermal curing. It was found that the effectiveness of such carboxylic acids increased with their functionality in the order *meso*-1,2,3,4-butanetetracarboxylic acid (BTCA) > tricarballylic acid (TCA) > succinic acid. These structurally similar carboxylic acids were chosen based upon their ability to form highly reactive cyclic anhydrides under the thermal reaction conditions of the curing process. The greatly increased reactivity of the *in situ* generated anhydride moiety over the parent polyfunctional carboxylic acids in the reaction with the cellulosic hydroxyl groups permits high conversion of the carboxylic acid moieties into ester linkages at moderate reaction temperatures and short curing times. We view the excellent wet-strengthening properties of polyfunctional carboxylic acids such as BTCA and TCA as a reflection of their ability to form multiple anhydrides during the curing reaction either directly

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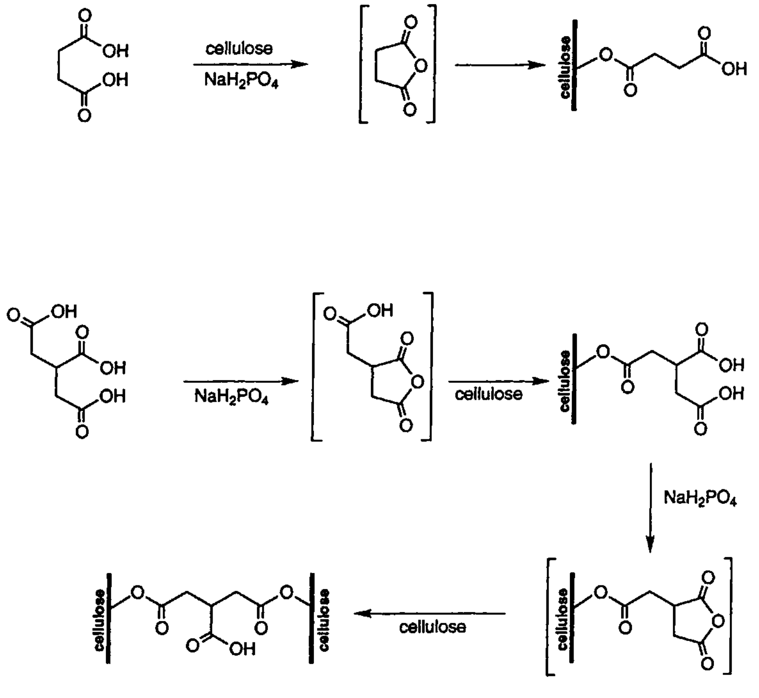
in the form of a dianhydride for BTCA or in a successive, stepwise mode for BTCA and TCA as illustrated in Schemes 1 and 2. This work parallels the treatment of cotton fabrics with polycarboxylic acids developed at the Southern Regional Research Center of the U.S. Department of Agriculture in New Orleans.[4,5] We note that our work on paper fibers employs substantially milder curing conditions. Support for the intermediacy of anhydrides under the curing conditions of the cotton fabrics may be found in Fourier transform infrared spectroscopy studies of reactions using poly(maleic acid)—but not BTCA—where anhydride units, derived from the excess carboxyl moieties in the polymer, were observed in the finished products.[6]

As shown in Schemes 1 and 2, attachment of the carboxylic acid moiety to the paper via esterification reaction of the first cyclic anhydride—generated during the curing process—exposes a new carboxylic acid unit in BTCA as well as in TCA, which has the proper chemical connectivity to form a new intramolecular anhydride moiety with the adjacent carboxylic acid unit. For BTCA, the latter is structurally identical to the product obtained via the reaction of cellulose with an initially formed dianhydride (Scheme 2). Further reaction with cellulose can then lead to crosslinking of the fibers which provides the chemical basis for the observed increase in wet-strength of treated papers. In the case of succinic acid, however, this consecutive sequence is structurally not possible and the reaction leads to a substituted cellulose unit with a single carboxylic acid attached to it. The latter could further react with cellulosic hydroxyl groups but at a much slower rate than that of the anhydride units exposed in the reactions of tricarballylic acid and BTCA. As a result, succinic acid is a very poor wet-strength agent for paper. The sequential attachment of the polyfunctional carboxylic acid to the cellulose—as outlined above—first as a pendant ester attachment and then as a crosslinking bridge between cellulose fibers—is the subject of the present article. Its implication for the development of wet-strength is also discussed.

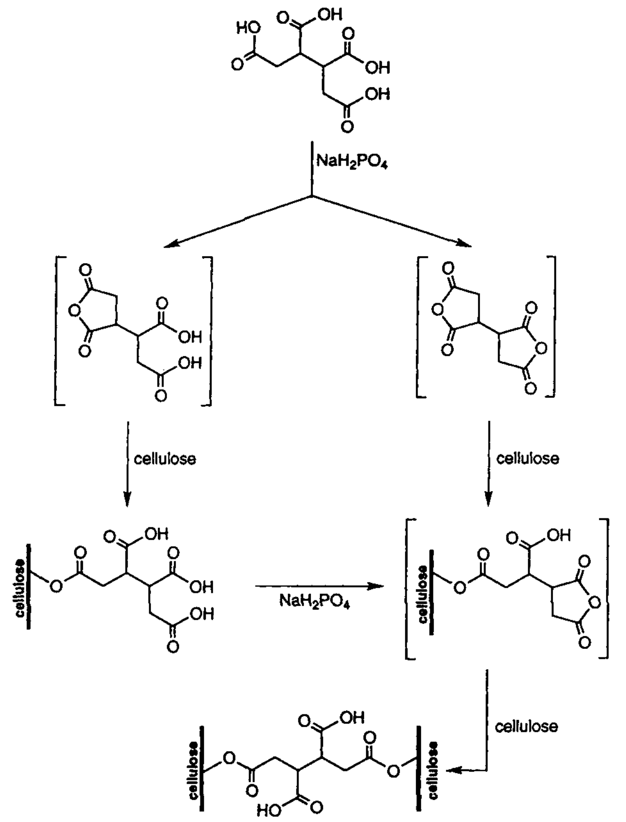
EXPERIMENTAL

Materials

Dried commercial bleached softwood pulp (Riverdale) was used to make handsheets. The pulp was



Scheme 1. Comparison of the reaction modes of cellulose with succinic acid and tricarballylic acid at 150°C in the presence of NaH_2PO_4. (The reactions of cellulose with carballylic anhydride and the subsequently formed cellulose-bound anhydride are shown for illustrative purposes only to occur exclusively with the sterically least encumbered carbonyl group of the anhydrides.)



Scheme 2. Comparison of the direct and step-wise reaction of 1,2,3,4-butanetetracarboxylic acid (BTCA) with cellulose at 150°C in the presence of NaH_2PO_4. (The structure of the monoanhydride as shown in the stepwise reaction of BTCA with cellulose is only for illustrative purposes. It is used here only to facilitate the comparison with the anhydrides of succinic acid and tricarballylic acid shown in Scheme 1. For the structure of the dianhydride of BTCA, see Ref. 3. The reactions of cellulose with the monoanhydride or dianhydride and the subsequently formed cellulose-bound anhydride are shown for illustrative purposes only to occur exclusively with the sterically least encumbered carbonyl group of the anhydrides.)

beaten in a Valley Beater for 30 min (450 CSF). Handsheets were made according to *Tappi* standard T205. Paper was also made on a small pilot machine from dried pulp (40% softwood and 60% hardwood). *meso*-1,2,3,4-Butanetetracarboxylic acid (BTCA), tricarballylic acid (TCA), succinic acid (SA), and NaH_2PO_4 were obtained commercially from the Aldrich Chemical Co.

Paper Treatment

Polycarboxylic acids and NaH_2PO_4 were applied by dipping papers in aqueous solutions containing the acids and NaH_2PO_4 for 30 min. The excess water was wiped out by pressing between blotting papers with a handsheet couch roll. After impregnation, the handsheets were air-dried in a conditioned room (50% RH, 23°C). The machine-made paper was dried on a drum dryer at about 80°C. All samples were then cured in an oven at 150°C for various periods of time.

Testing

The tensile strength was tested in an Inston. For the wet tensile strength, the samples were soaked in deionized water for 1 h before testing. The total acid in the paper was determined by pH titration. Samples (about 3 g) were disintegrated and titrated with 0.1*N* NaOH. Phenolphthalein was used as an indicator. Conductometric titration was used to determine the strong and weak acids in the paper. Samples (about 3 g) were disintegrated and acidified by soaking in 0.1*N* HCl twice (45 min each time). After washing out the HCl, the samples were titrated with 0.1*N* NaOH in 0.001*M* NaCl solution.[7]

DISCUSSION AND METHODOLOGY

The two main stages of the reaction of polyfunctional carboxylic acids with paper, i.e., pendant attachment of the polyfunctional carboxylic acid via esterification with a cellulosic hydroxyl group and its further reaction—via esterification—with another cellulosic hydroxyl group producing the bridging crosslinks of the cellulose fibers can be analyzed separately using a combination of acid–base titration, conductometric titration[7] and kinetic analyses. The extent of reaction of the polyfunctional carboxylic acids with paper—carried out in the presence of NaH_2PO_4—during the curing reaction can be conveniently analyzed by pH titration, which reveals the decreasing number of carboxylic acid functional groups upon incorporation of the starting acids into cellulose units of paper. The actual number of carboxylic acid functional groups incorporated into cellulose units on the other hand, may be calculated conveniently using conductometric titration data. Figure 1 shows a typical conductometric titration curve for untreated paper handsheets made from Riverdale softwood. The initial straight slope shows the neutralization of strong acids present in the paper as a result of prior treatment (e.g., pulping, bleaching). Because these strong acids are present in paper in a very small amount, a little strong acid (0.1*N* HCl) was added in order to obtain the initial slope. After the first equivalence point is reached,

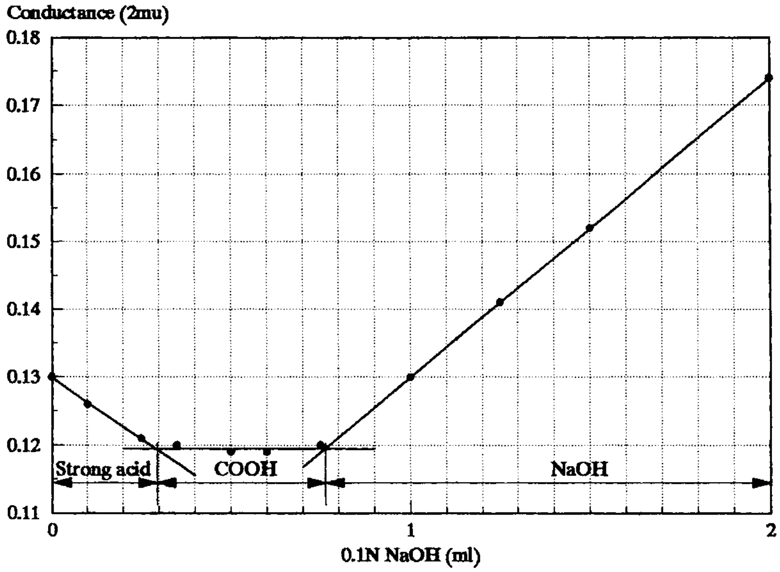


Figure 1 Conductometric titration curve of untreated handsheets made from Riverdale softwood.

further addition of NaOH results in the neutralization of weak acids (i.e., carboxylic acid moieties) present in cellulose. A flat line appears due to the low levels of H_3O^+ in solution from the weak acids. After all acid groups are neutralized, the conductance increases proportionally with excess NaOH. The two equivalence points can be obtained by extrapolating and intersecting the three linear portions of the curve as shown in Figure 1. The weak acid (i.e., carboxylic acid) content of the paper was then determined using the following equation:

$$\text{Carboxylic acid content (mmol/kg paper)} = k \text{ mL NaOH} \times 1000 \times \text{N/g paper}$$

where k = mL of NaOH between inflection points and N = normality of NaOH.

When paper handsheets were dipped into a 1% aqueous solution of BTCA—in the absence of NaH_2PO_4—drum-dried, and then heated at 150°C for 15 min, the conductometric titration showed the same profile as for the untreated handsheets. The strong acid region of the curve did not change in magnitude, whereas the weak acid area of the curve showed a significant increase. This is, of course, attributable to the incorporation of carboxylic acid functionalities in the cellulose units of the paper via partial esterification of one or more carboxyl moieties of BTCA. On the other hand, when paper handsheets were treated with a 1% aqueous solution of NaH_2PO_4 alone—under the same experimental conditions—then the conductometric titration showed an increase in both the strong acid and the weak acid portions of the curve, when compared to the titration results of untreated handsheets. We attribute the increase in the strong acid as well as in the weak acid area of the curve to a chemical reaction of the paper with NaH_2PO_4 during the thermal treatment. This results in the introduction of phosphate groups in some cellulose units of the paper in the form of phosphate monoesters (present originally as their sodium salts and converted into the acid form by the treatment of the paper with HCl prior to the conductometric titration). Such monoesters of phosphoric acid are more acidic than is phosphoric acid itself.[8] Thus, the first ionization of these phosphate esters would contribute to the strong acid area, while the second dissociation would increase the weak acid area. Further evidence in support of this conclusion may be found in the fact that increasing the concentration of NaH_2PO_4 or increasing the reaction time resulted in increasingly more pronounced strong acid areas in the conductometric titration curves. Additionally, the incorporation of phosphorus in the paper was confirmed by solid-state ^{31}P-NMR spectroscopy.[9] This increase in the strong acid area can thus be used as a measure for the introduction of phosphate groups in cellulose.

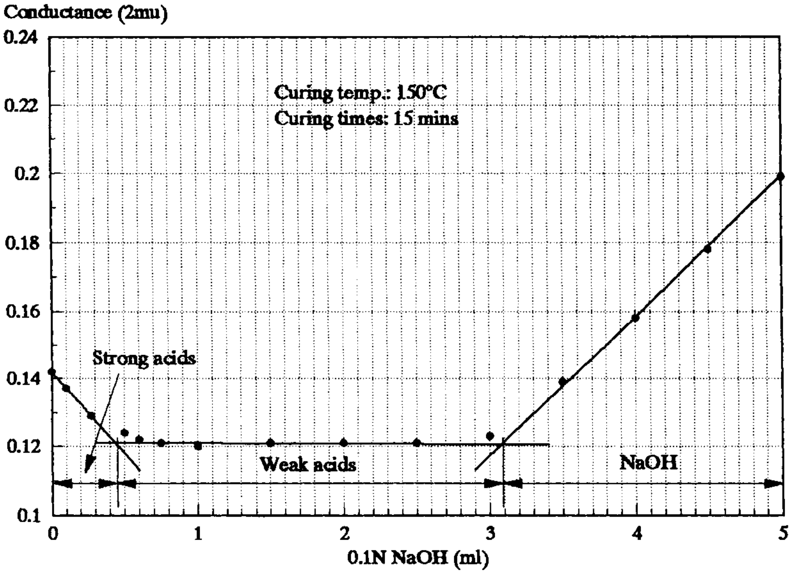


Figure 2 Conductometric titration curve of handsheets (Riverdale) treated with 1% BTCA + 1% NaH_2PO_4, dried, and heated at 150°C for 15 min.

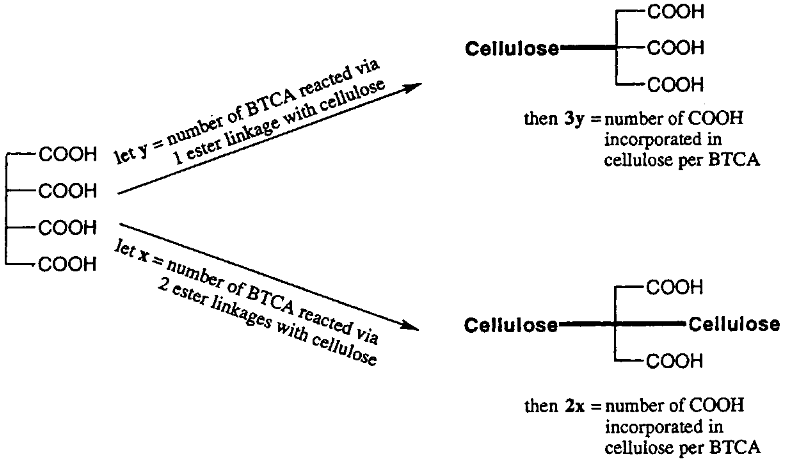
Reaction of Paper with 1,2,3,4-Butanetetracarboxylic Acid (BTCA)

When paper handsheets were treated with a 1% aqueous solution of BTCA and a 1% aqueous solution of NaH_2PO_4, drum-dried, and heated at 150°C for 15 min, then conductometric analysis of the treated paper (Fig. 2) revealed a very pronounced increase in the weak acid area of the curve when compared to the results of the reaction of paper with BTCA in the absence of NaH_2PO_4. Once again, this increase is attributed to the incorporation of carboxylic acid units in the paper by the partial esterification of one or more carboxyl groups of BTCA with cellulose. The comparative conductometric data for the treatments of handsheets are shown in Table I. These data clearly reveal the importance of the presence of NaH_2PO_4 on the rate of reaction between the polyfunctional carboxylic acid and the paper. We attribute this to the catalytic effect of NaH_2PO_4 on the rate of anhydride formation from the polyfunctional carboxylic acid.

As discussed earlier, the reaction of BTCA and cellulosic hydroxyl groups proceeds in sequential fashion, first leading to the incorporation of pendant BTCA residues via anhydride-initiated esterification reaction and then further transformation of these newly formed branches into crosslinking bridges between cellulose fibers, again via anhydride-mediated esterification. Information about the relative importance of these two consecutive reactions during the curing process of paper with BTCA—in the presence of NaH_2PO_4—may be obtained by combining acid–base titration and conductometric titration data. The former provides data about the total decrease of acidic functionalities as the curing

Table I Strong Acid and Weak Acid Contents of Handsheets (Riverdale) Treated at 150°C for 15 Min Determined by Conductometric Titration

	Strong Acids (mmol/kg paper)	Weak Acids (mmol/kg paper)
Untreated Paper	13	20
+1% BTCA	14	48
+1% NaH_2PO_4	18	27
+1% BTCA +1% NaH_2PO_4	19	117



A = 2x + y : Total BTCA reacted with cellulose. Determined by pH titration.

B = 2x + 3y : Total number of COOH incorporated in cellulose. Determined by conductometric titration.

Scheme 3. Schematic representation of the analysis for the dual reaction mode of BTCA with cellulose: **y** = formation of pendant ester;

progresses and is directly related to the total consumption of carboxylic acid groups by the ester attachment and ester crosslinking steps, while the latter measures the increase in weak acids (i.e., carboxylic acids) bound to the cellulose units of the paper as a direct result of previous esterification steps. For this analysis, we assume that further esterification of those carboxylic acid units already involved in the crosslinks with cellulose will be considerably slower than those occurring during the initial phases of the curing reaction. This assumption seems reasonable in view of our short curing times and moderate curing temperatures and the expected accessibility difficulties associated with functional groups located within the crosslinking sites between two cellulose units. Our procedure is schematically outlined in Scheme 3.

The total BTCA *reacted* with cellulose [**A**] is then given by the contribution of the pendant ester formation [**y**] and of the two-step crosslinking reaction [**2x**]. This value is experimentally readily determined by the change in total acidity before and after curing as measured by pH titration. This change is due to the reaction of BTCA with cellulose as well as to the reaction of the paper with NaH_2PO_4 (see above). The needed correction for the contribution of the latter is readily determined by conductometric titration of paper treated with NaH_2PO_4 under typical curing conditions in the absence of BTCA. The total number of carboxylic acids *incorporated* into cellulose [**B**] is given by the contribution of pendant ester formation, which incorporates three carboxylic acid groups [**3y**], and by the two-step crosslinking reaction which produces two COOH groups [**2x**] (see Scheme 3). This value is easily obtained from the weak acid portion of the conductometric titration curve, after appropriate corrections for the carboxylic acid units present in the starting paper and the contribution to the weak acid part of the curve as a result of the reaction of the paper with NaH_2PO_4 (see above).

The two expressions [**A**] and [**B**] shown in Scheme 3 and their easy determination by pH titration and conductometric titration allow for the facile determination of **x** and **y**, i.e., the extent of crosslinking and the formation of ester appendages, respectively, in the reaction of BTCA with paper. In a typical experiment, acid–base titration before curing gave a total acid value of 330 mmol/kg paper; this amount was reduced to 223 mmol/kg after standard curing. This value needs to be corrected for the amount of weak acids introduced in the paper (5 mmol/kg paper) by its reaction with NaH_2PO_4. The weak acid content of the paper, i.e., the carboxylic acid content—determined by conductometric titration—increased from 20 mmol/kg before reaction with BTCA to 143 mmol/kg after curing at 150°C for 15 min, a value that also requires correction for the weak acids introduced into the paper (7 mmol/kg paper) by reaction of the paper with NaH_2PO_4. From these data and the equations in Scheme 3, the following values are obtained: $\mathbf{x}$ = 47.5 mmol/kg paper and $\mathbf{y}$ = 7 mmol/kg of paper, where $\mathbf{x}$ is related to the crosslinking reaction and $\mathbf{y}$ represents a simple pendant ester attachment. The total amount of BTCA that has reacted with the paper is thus 54.5 mmol/kg of paper or 12.7 g/kg of paper. The total amount of BTCA available for the reaction with paper, i.e., the retention of BTCA, was determined gravimetrically by weighing the handsheets before and after soaking in the 1% aqueous BTCA solution. The BTCA retention was also determined by titration before and after the soaking of the sample. The value obtained in the above experiment was 12.4 g/kg of paper. It is evident from this example that the reaction of BTCA with cellulose under our curing conditions is essentially quantitative.

It can also be easily calculated from such titration data and from the relationship between the number of carboxylic acids in the starting BTCA and the cured paper—shown in Scheme 3—that, on average, less than two carboxylic acid moieties from BTCA react with cellulosic hydroxyl groups under limited curing times. Thus, some reactions stop at the introduction of simple ester appendages into cellulose, while others continue to form crosslinks between cellulose fibers. This dual reaction mode during the curing reaction of cellulose with BTCA is further illustrated in Figures 3 and 4, which show the curing profile for reactions carried out at 150°C on handsheets and machine-made paper, respectively. It is seen that the extent of reaction of BTCA increases with the curing time and reaches a quantitative conversion after 15 min. The concentration of once-reacted BTCA (simple esterification with cellulose) increases in the initial phase of the reaction and then decreases as more and more carboxylic acid units are converted into crosslinking sites. The amount of crosslinked BTCA increases throughout the curing reaction. This reaction profile is consistent with the proposed chemical conversions during the curing reaction (see Scheme 2). At the curing temperature and under the influence of NaH_2PO_4, BTCA may be converted into a monoanhydride or a dianhydride. Reaction of the anhydride moieties with cellulosic hydroxyl groups lead to the attachment of the BTCA units to the cellulose via esterification reaction. In the case of an intermediate dianhydride, this leads then immediately to crosslinking of the cellulose units. The reaction of a monoanhydride with cellulose hydroxyl groups releases a new carboxylic acid unit which has the proper chemical connectivity to be converted into a new cyclic anhydride moiety under the curing conditions. Its further reaction with cellulose also leads to crosslinking. From Figures 3 and 4, it can be seen that the amount of crosslinked BTCA is the same or higher than that of once-reacted BTCA (monoesterification) at the beginning of the curing reaction. This probably is a reflection of the competition be-

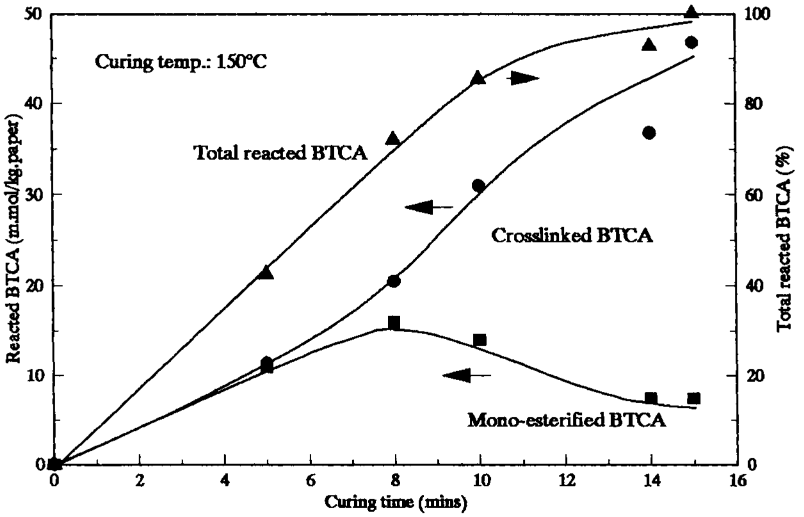


Figure 3 Reaction profile of the curing of paper handsheets with 1% BTCA in the presence of 1% NaH_2PO_4 at 150°C.

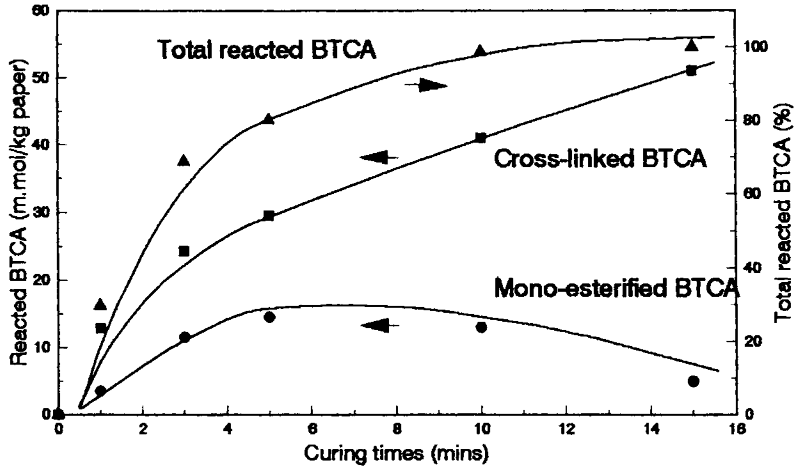


Figure 4 Reaction profile of the curing of machine-made paper with 1% BTCA in the presence of 1% NaH_2PO_4 at 150°C.

tween monoanhydride and dianhydride formation at the beginning of the curing reaction.

Reaction of Paper with BTCA Under Extended Curing Times

As shown in Scheme 2, the crosslinking of cellulose with BTCA results in the incorporation of two carboxylic acid moieties in the immediate vicinity of the crosslinking site. These are properly positioned for additional anhydride formation and, hence, could react further with a cellulosic hydroxyl group in a third esterification reaction. This reaction should be considerably more difficult than are the monoesterification and crosslinking reactions discussed earlier and is expected to occur only after extended curing times. Our analysis for such reactions of BTCA with cellulose through three esterification steps is analogous to that shown earlier in Scheme 3 for the two-stage reaction, under the assumption that at this stage of the curing no monoesterified BTCA in the form of ester appendages is left. The total amount of reacted BTCA [A] and the total number of carboxylic acids introduced into cellulose [B] are then given by the following equations:

$$\mathbf{A} = 2\mathbf{x} + 3\mathbf{z}$$

$$\mathbf{B} = 2\mathbf{x} + \mathbf{z}$$

where $\mathbf{x}$ = number of BTCA reacted via two ester linkages with cellulose and $\mathbf{z}$ = number of BTCA reacted via three ester linkages. The results of our experiments under extended curing times are shown in Table II. It is seen that the amount of BTCA reacted by three groups is relatively small and did not show an increase from 30 to 45 min of curing time.

In an alternative set of experiments, papers cured with BTCA under our standard curing conditions for relatively short periods of time were recured. Thus, papers treated with an aqueous solution of 1% BTCA and 1% NaH_2PO_4 were first cured at 150°C for 9 and 14 min, respectively. The sheets were then washed with water to remove any unreacted BTCA and then retreated with 1% NaH_2PO_4, drum-dried, and reheated at 150°C for

Table II Reaction of BTCA (1%) with Cellulose Under Extended Curing Time at 150°C in the Presence of NaH_2PO_4 (1%)

Curing Time (min)	BTCA Reacted by Two COOH Groups (mmol/kg Paper)	BTCA Reacted by Three COOH Groups (mmol/kg Paper)
30	41	3.5
45	42	4

Table III Reaction of BTCA with Papers: Recuring (see Text)

	Initial Curing (min at 150°C)	Carboxyl Content (mmol/kg Paper)	Wet Tensile Index (m N/g)
Sample 1	9	78	11.2
Sample 2	14	96	23.9
	Recuring (min at 150°C)		
Sample 1	15	68	22.2
Sample 2	15	84	26.2

15 min. The results are collected in Table III. During the initial curing reaction, the carboxylic acid content of the paper increases between 9 and 14 min of curing time. This is the result of the continuing incorporation of BTCA into cellulose. After washing and recuring of the papers, their carboxylic acid content continues to decrease, which is indicative of further crosslinking of the carboxylic acid units already incorporated into the cellulose units.

Reaction of Paper with Tricarballylic Acid (TCA)

The reactions of papers with tricarballylic acid (TCA) follow a reaction profile similar to that of the reaction of paper with BTCA. This can be seen from Figure 5, which shows our kinetic analysis for machine-made paper (40% softwood–60% hardwood) treated with a 2% aqueous solution of TCA and a 2% solution of NaH_2PO_4, drum-dried, and then cured at 150°C. The values shown were derived from the equations shown in Scheme 3 for BTCA, but modified for the lower number of carboxylic acid units present in TCA. Under our curing conditions, the reaction of TCA with papers is essentially quantitative after a 15 min curing time. The two-step nature of the reaction of BTCA with cellulosic hydroxyl groups, i.e., ester appendage and crosslinking, is also observed in the reactions with TCA. However, a comparison between the reaction of the tetrafunctional BTCA and the trifunctional TCA (see Figs. 4 and 5, respectively) reveals that for TCA the curing reaction is initially dominated by the formation of ester appendages (monoesterification), and crosslinking becomes the main reaction only after extended curing times. On the other hand, in the reaction of papers with BTCA (see Fig. 4), crosslinking is found to be the main pathway for the reaction of BTCA throughout the curing process,

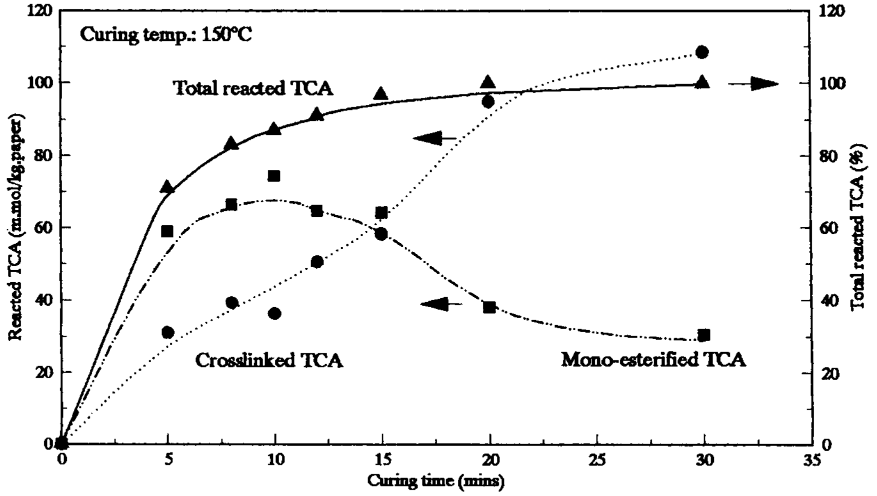


Figure 5 Reaction profile of the curing of machine-made paper with 2% TCA in the presence of 2% NaH_2PO_4 at 150°C.

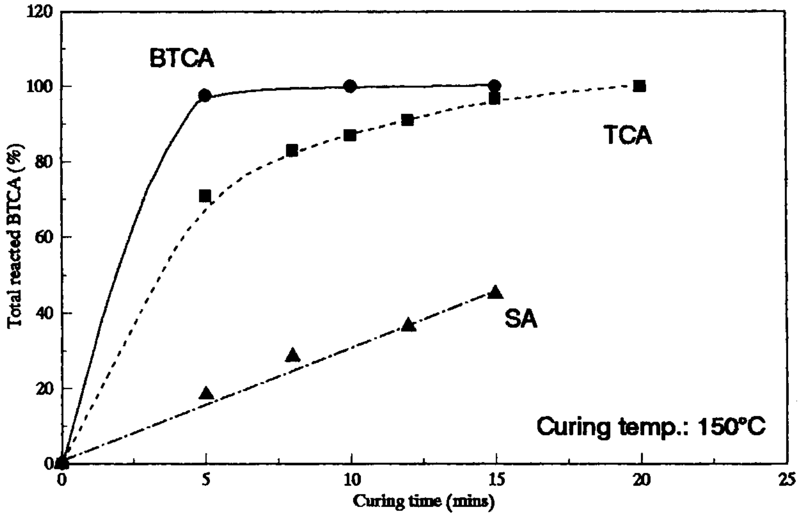


Figure 6 Reactions of polycarboxylic acids (2%) with machine-made paper in the presence of NaH_2PO_4 (2%) at 150°C.

even at its very beginning. We believe that these different curing behaviors are a reflection of the ability of BTCA to form a dianhydride directly from the tetracarboxylic acid, thus providing a highly reactive difunctional reagent for crosslinking of cellulosic hydroxyl groups even at the outset of the curing reaction. For TCA, on the other hand, its trifunctionality permits only the formation of a monoanhydride, which is monofunctional in its reaction with cellulosic hydroxyl groups. After its incorporation into cellulose, a second carboxylic acid unit becomes available for activation to form the needed anhydride moiety to finish the crosslinking process. Apparently, this two-stage process is less efficient than is the direct route available for BTCA. This is also evident from Figure 6 which shows a comparison of the reactions of BTCA, TCA, and SA with machine-made paper under identical curing conditions. This better crosslinking ability of BTCA is also reflected in the better wet-strength properties for papers cured with BTCA over those treated with TCA (see below).

Reaction of Paper with Succinic Acid (SA)

As anticipated, the reaction profile for the structurally similar, but difunctional succinic acid is different from that shown above for BTCA and TCA. Our

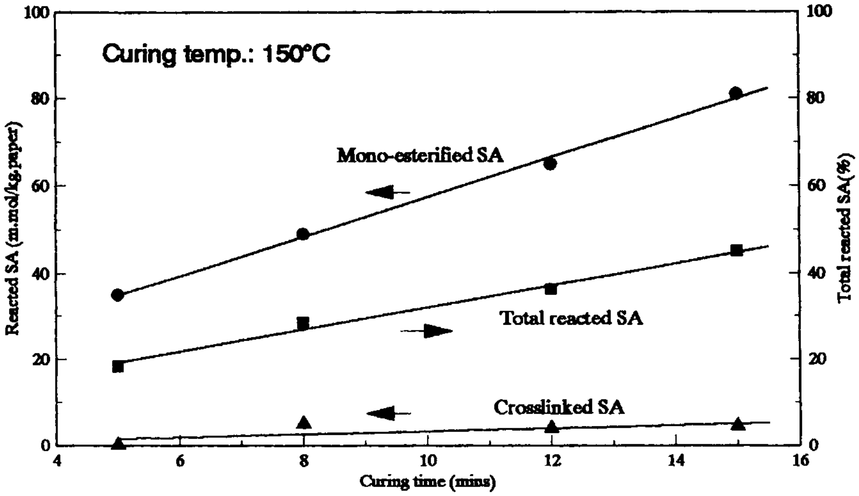


Figure 7 Reaction of succinic acid (2%) with machine-made paper in the presence of NaH_2PO_4 (2%) at 150°C.

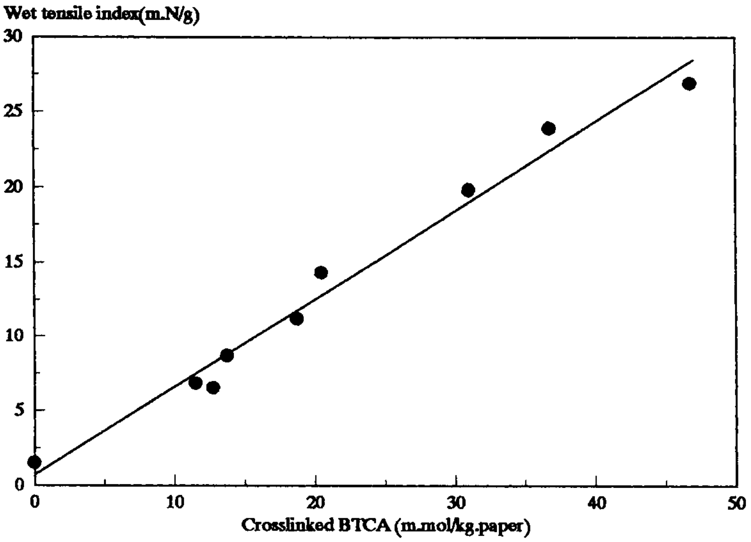


Figure 8 Relationship between wet strength and the number of crosslinking sites introduced by the curing reaction of handsheets with BTCA. (Crosslinked BTCA obtained from titrations and Scheme 3 [see text]).

kinetic analysis for the reaction of succinic acid (2% aqueous solution) with machine-made paper (40% softwood–60% hardwood) in the presence of 2% aqueous solution of NaH_2PO_4 under our standard curing conditions is shown in Figure 7. The analysis is based on the equations shown in Scheme 3 for BTCA and modified for the reduced number of carboxylic acid moieties present in succinic acid. It is seen that the reaction is dominated by the formation of ester appendages which increase linearly with the curing time. We note that under our curing conditions a small amount of crosslinking of the fibers takes place. However, the extent of this reaction does not increase significantly with the curing time.

Relationship Between Wet Tensile Strength and Degree of Crosslinking

In the dry state, paper strength is due mainly to the presence of hydrogen bonds between the hydroxyl groups of cellulose. When the paper is wet, these hydrogen bonds are destroyed, resulting in the loss of strength of the paper. As demonstrated in this article, the reaction of polyfunctional carboxylic acids, such as BTCA and TCA, with cellulose can lead to substitution and crosslinking. It can reasonably be assumed that only crosslinked cellulose can support the paper structure when wet. Since ester linkages are stable in water, the crosslinks introduced during esterification reactions of the cellulosic hydroxyl groups of the paper and the polyfunctional carboxylic acids will prevent the swelling of the fibers and hold them together in the wet condition. This correlation is supported by Figure 8, which shows a good linear relationship between wet strength and the number of crosslinking sites, obtained from titrations based on Scheme 3 (see above) in the indicated range. The introduction of COOH moieties into paper as a result of the esterification reactions may affect water penetration, moisture equilibrium, and other paper surface properties, which also may influence paper strength, but the main wet strength is the result of crosslinks with BTCA and cellulose. This may be seen from Table III, which shows an increase of wet strength upon recuring of the samples as a result of an increasing number of crosslinking sites. A similar relationship between wet strength and the number of crosslinking sites, as established by our analytical procedure, is also found in the initial phases of the curing reaction with TCA. This is shown for machine-made paper in Figure 9, which reveals that the wet strength initially increases with the amount of crosslinked TCA, but then levels off with increasing degree of crosslinking. We attribute this phenomenon to the extended curing times which are necessary to obtain the higher degrees of crosslinking in curing reactions with TCA. Under these conditions, paper fibers deteriorate and gradually lose strength. Paper becomes brittle and both the wet and dry strength are decreased. Papers treated with SA show very little wet strength. Although the number of carboxylic acids introduced in papers as a result of the reaction with succinic acid is high, these moieties occur nearly ex-

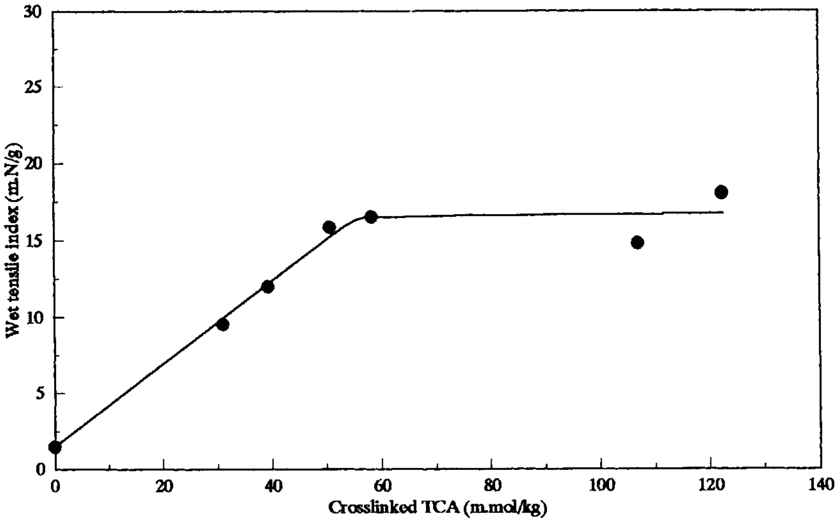


Figure 9 Relationship between wet strength and the number of crosslinking sites introduced by the curing reaction of machine-made paper with TCA.

clusively as pendant functional groups. These are constitutionally not capable (see Scheme 1) to enter into further reactions with cellulosic hydroxyl groups to effect the crosslinking of the cellulose fibers under our curing conditions. This demonstrates that the mere presence of carboxylic acid moieties into paper does not impart wet strength. The observed wet strength of papers upon curing with BTCA and TCA is thus the result of crosslinking reactions of the initially incorporated pendant carboxyl groups.

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