

# Paper Wet Performance and Ester Crosslinking of Wood Pulp Cellulose by Poly(carboxylic acid)s

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**ABSTRACT:** Poly(carboxylic acid)s have been used as crosslinking agents for wood pulp cellulose to increase the wet strength of paper. In this research, we evaluated the effects of two multifunctional carboxylic acids, i.e., 1,2,3,4-butanetetracarboxylic acid (BTCA) and poly(maleic acid) (PMA), on the wet strength retention, dimensional stability, wet stiffness, and folding endurance of the treated paper. We observed that the wet strength retention, dimensional stability, and wet stiffness of the treated sheets increase, whereas the folding endurance decreases as the poly(carboxylic acid) concentration applied to those sheets increases. We measured the ester carbonyl band absorbance in the spectra of the treated paper. The linear correlation between the ester carbonyl band absorbance and wet strength, dimensional stability, and wet stiffness indicates that the improvement in the wet performance of the treated paper is directly attributed to the ester crosslinking of the wood pulp cellulose by poly(carboxylic acid)s. The data presented in this article also indicate that FTIR spectroscopy can be used for predicting the performance of the paper crosslinked by poly(carboxylic acid)s. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 649–658, 1998

**Key words:** carboxylic acids; cellulose; crosslinking; esterification; infrared spectroscopy; paper; wet strength resins; wood pulp

## INTRODUCTION

Crosslinking agents for cellulosic materials are used to improve the wrinkle resistance of cotton fabrics and the wet strength of paper products in the textile and paper industries, respectively.<sup>1–10</sup> A poly(carboxylic acid) crosslinks cellulose molecules through esterification. The use of poly(carboxylic acid)s as crosslinking agents for cotton cellulose was first documented in the 1960s.<sup>11,12</sup> In 1988, Welch reported that 1,2,3,4-butanetetracarboxylic acid (BTCA) provides effective crosslinking for cotton cellulose, thus imparting high levels of wrinkle resistance to cotton fabrics.<sup>2</sup>

Welch and Andrews also discovered the use of sodium hypophosphite as the catalyst for the esterification and crosslinking of cotton cellulose by poly(carboxylic acid)s, which significantly improved the effectiveness of the acids.<sup>13</sup>

Multifunctional carboxylic acids have also been investigated for improving the wet performance of paper.<sup>7–10</sup> It was reported in the literature that significant improvement in the wet strength retention and dimensional stability was achieved when the paper was treated with BTCA.<sup>7–9</sup> Among the various poly(carboxylic acid)s investigated, BTCA has been the most effective crosslinking agent for both cotton and wood cellulose. However, the exceedingly high cost of BTCA has prevented its application on a commercial scale.

In our previous research, we investigated the use of polymers of maleic acid for enhancing the

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wet performance of cotton fabrics.<sup>14–18</sup> We applied Fourier transform infrared (FTIR) spectroscopy to make a quantitative measurement of the reactant [poly(carboxylic acid)], the reactive intermediate (anhydride), and the product (ester) on cotton fabrics.<sup>14–19</sup> We also used FTIR spectroscopy to study paper crosslinked by poly(carboxylic acid)s.<sup>20</sup>

In this research, we measured the ester carbonyl band absorbance in the spectra of the kraft paper treated with poly(maleic acid) (PMA) and BTCA, and studied the correlation between the esterification and crosslinking of cellulose and the wet performance of the treated paper.

## EXPERIMENTAL

### Materials

The paper used in this research was a commercially available unbleached kraft paper (74 g/m<sup>2</sup>) made by Georgia Pacific. BTCA and sodium hypophosphite (NaH<sub>2</sub>PO<sub>2</sub>) were supplied by Aldrich. PMA with a number-average molecular weight of 800 is an aqueous solution with 50% solid content and is a commercial product made by the FMC Corp.

### Procedures of Paper Treatment

The paper was first cut into 25 × 25 cm sheets. Each sheet was soaked in a PMA or BTCA solution of a prescribed concentration, ranging from 0.5 to 8%, for 30 s. Sodium hypophosphite (NaH<sub>2</sub>PO<sub>2</sub>) was used in the solution as a catalyst. All the solutions maintained a constant 1 : 2 (W/W) catalyst-to-acid ratio. The soaked paper was pressed between the squeezing rolls at 40 psi pressure and dried on a drum dryer at 80°C to prevent curling. The individual sheet was then cured in a forced draft oven at 170°C for 2 min. The temperature variation was less than ±1°C. The cured sheets were rinsed in running water for 15 min to remove the unreacted acid and the catalyst and finally dried. The physical properties of those samples were measured after the sheets were conditioned according to the TAPPI standard.

### Paper Performance Evaluation

The dry tensile strength and folding endurance (MIT tester) of the paper were evaluated according to the TAPPI standard methods T404 om-

87 and T511 om-88, respectively. The wet tensile strength was tested after soaking the paper strips with a width of 1.5 cm in water for 12 h. The wet stiffness was expressed as the Young's modulus of elasticity. The mechanical properties described above were measured at the machine direction. The dimensional stability (DS) was measured at the cross machine direction. A paper strip of 1.5 × 10 cm was conditioned under 50% relative humidity for 24 h; then, the length of the strip was measured. The strip was soaked in water for 24 h; then, the length of the water-soaked strip was measured. The linear dimensional change (*L*) was calculated by subtracting the length of the strip (before soaking) from the length of the strip (after soaking). The DS was calculated according to the formula specified by Caufield<sup>8</sup> shown as the following:

$$DS = [(L_u - L_t)/L_u] \times 100\%$$

where *L<sub>u</sub>* and *L<sub>t</sub>* are linear dimension changes of the paper strip not treated and that treated with an acid solution, respectively.

### Infrared Spectroscopic Measurements

All the infrared spectra in this research are diffuse reflectance spectra collected with a Nicolet 510 FTIR spectrometer and a Specac diffuse reflectance accessory and are presented in the absorbance mode (−log *R/R<sub>0</sub>*). The resolution for all the infrared spectra is 4 cm<sup>−1</sup>, and there were 100 scans for each spectrum. Potassium bromide powder was used as a reference material to produce a background diffuse reflectance spectrum. The ester carbonyl band absorbance was normalized against the 1320 cm<sup>−1</sup> band associated with the C—H bending mode of cellulose.

### Chemical Analysis of the Treated Paper

The carboxyl concentration on the paper was determined by titrating the treated sheets before curing using a standard NaOH solution. The sheets were first ground into a powder in a Wiley mill to improve sample uniformity. The end point of the titration was at pH 9.2 determined by a pH meter. The carboxyl concentration on the paper (%) was calculated by the formula [(volume of NaOH in mL) × (concentration of NaOH in mmol/mL) × (44 mg/mmol) ÷ (dry weight of the sheet in mg)] × 100.

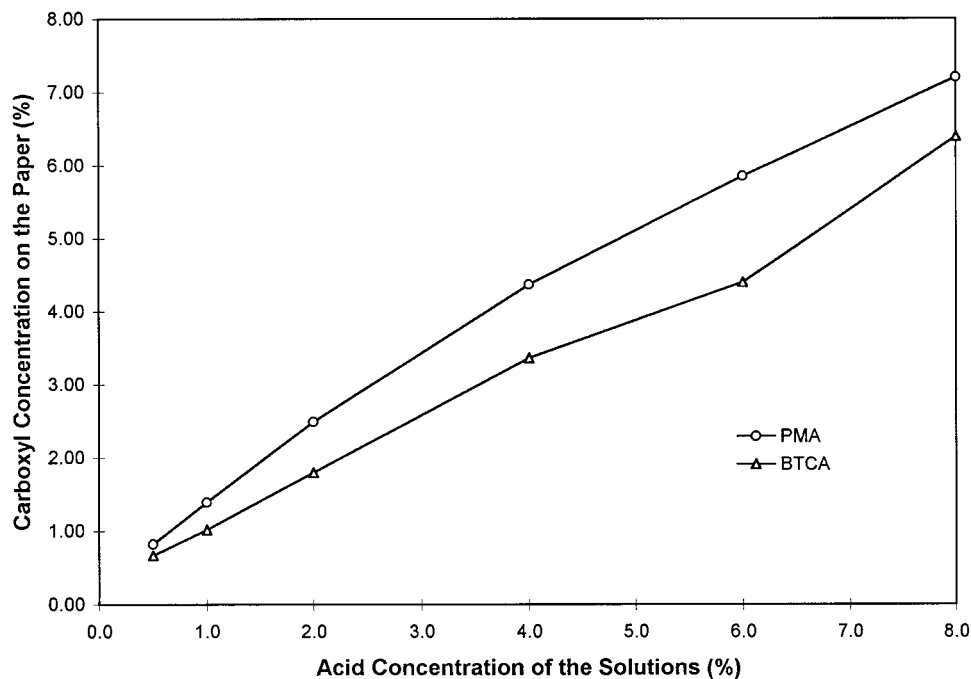
**Table I The Dry and Wet Tensile Strength (kg) of the Kraft Paper Treated with the BTCA and PMA Solutions of Different Concentrations**

Acid Concentration	BTCA		PMA	
	Dry Strength	Wet Strength	Dry Strength	Wet Strength
0.0	7.36	0.98	7.36	0.98
0.5	7.79	1.38	7.26	1.46
1.0	7.38	1.69	7.64	1.97
2.0	7.14	2.28	7.31	3.05
4.0	7.64	4.10	7.84	4.72
6.0	7.37	5.11	7.89	5.82
8.0	7.54	5.63	7.81	6.53

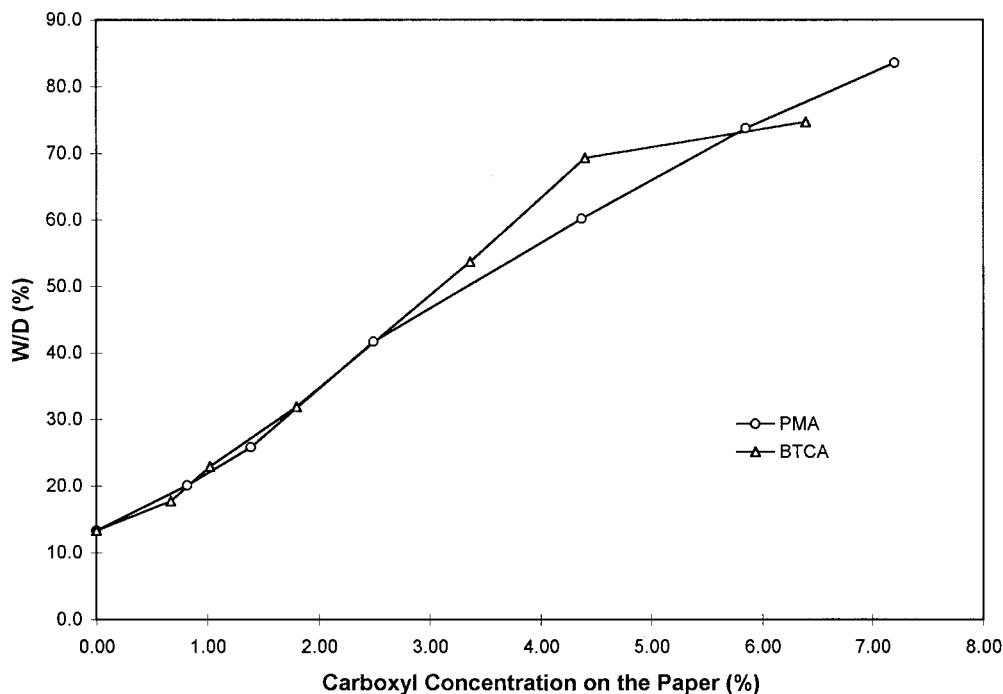
**RESULTS AND DISCUSSION**

The kraft paper sheets were treated with the BTCA and PMA solutions, whose concentration ranged from 0.5 to 8.0%. The treated sheets were cured at 170°C for 2 min. The dry and wet tensile strength of the sheets treated with the BTCA and PMA solutions are presented in Table I. One observes in Table I that the treatment by the multifunctional carboxylic acids has little effect on the dry strength whereas it significantly increases the wet strength of the paper. One also observes that the wet strength increases as the acid concentration increases.

The paper sheets treated with the PMA solutions show higher wet strength than those treated with the BTCA solutions of the same concentration (Table I). We determined the carboxyl concentration on the treated sheets before curing using an acid–base titration. The carboxyl concentration on the sheets treated with the PMA and BTCA solutions are shown in Figure 1. It can be seen that the sheets treated with the PMA solutions had higher carboxyl concentrations than did those treated with the BTCA solutions of the same concentration (Fig. 1). We also found that the carboxyl concentration in the PMA solutions decreased after it was used for the treatment of the



**Figure 1** Carboxyl concentration on the sheets treated with PMA and BTCA as a function of the concentration of the acid solutions.



**Figure 2** *W/D* ratio of the sheets treated with PMA and BTCA and cured at 170°C for 2 min as a function of the carboxyl concentration on the sheets before curing.

paper. Thus, the data indicate a preferential absorption of PMA by the kraft paper.

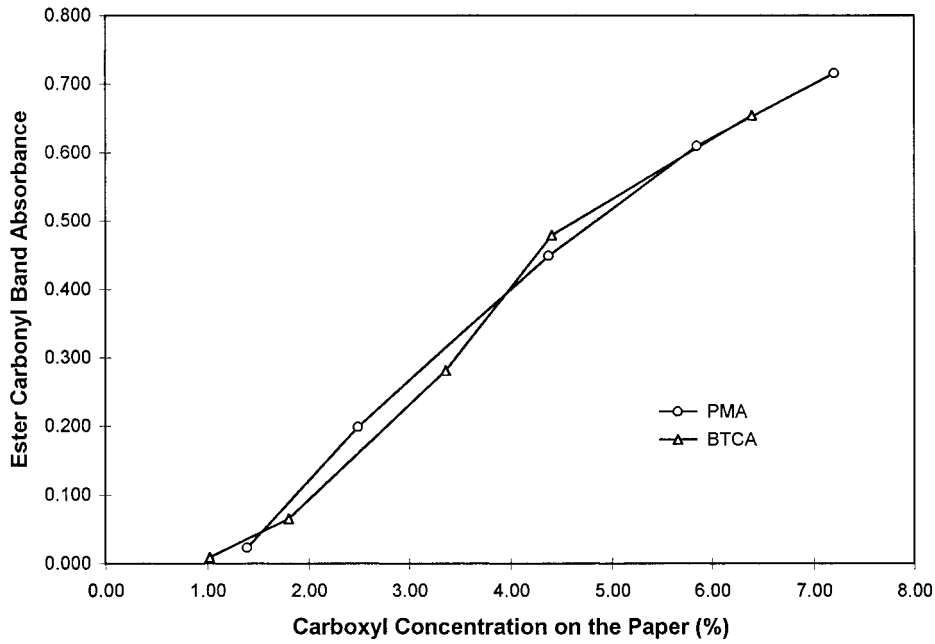
To compare the effectiveness of these two acids for improving the wet performance of the paper, we plotted the wet strength-to-dry strength ratio (*W/D* ratio) of the treated sheets against the carboxyl concentration on those sheets before curing (Fig. 2). The curves of the *W/D* ratio vs. the carboxyl concentration on the paper appear to be similar for the PMA- and BTCA-treated sheets, indicating that the effectiveness of PMA as a paper wet strength agent is comparable to that of BTCA (Fig. 2).

In our previous research, we measured the ester carbonyl band absorbance in the infrared spectra of cotton fabric and paper crosslinked by poly(carboxylic acid)s.<sup>14–20</sup> We found that the carbonyl band at 1730  $\text{cm}^{-1}$  in an infrared spectrum of a paper sheet with a poly(carboxylic acid) is due to an ester when the sheet is rinsed with a dilute NaOH solution to convert the free carboxyl to carboxylate anions.<sup>20</sup> Consequently, the ester carbonyl band absorbance can be used as the basis for evaluating the ester crosslinking of wood pulp cellulose by the poly(carboxylic acid).<sup>20</sup> The ester carbonyl band absorbance of the sheets treated with PMA and BTCA is plotted against the carboxyl concentration on the sheets before curing

(Fig. 3). The data indicate that the amount of ester formed on the PMA-treated and BTCA-treated sheets have nearly the same correlation with the amount of carboxyl applied to those sheets (Fig. 3).

The linear regression curves for the correlation between the *W/D* ratio and the ester carbonyl band absorbance of the sheets treated with PMA and BTCA are presented in Figure 4. One observes a perfect linear regression model between the *W/D* ratio and the ester carbonyl band absorbance of the PMA-treated sheets with an  $r^2$  value of 0.999 (Fig. 4). A similar linear correlation with an  $r^2$  value of 0.962 exists for the sheets treated with the BTCA solutions (Fig. 4). Thus, the data indicate that the improvement in the wet strength of the paper treated with poly(carboxylic acid)s is a direct result of ester crosslinking of the wood pulp cellulose in the paper by those acids. The slopes for the PMA- and BTCA-treated sheets are 81.9 and 81.6, respectively, indicating that the effectiveness of the esterification of cellulose by the two acids for enhancing the wet strength of the treated paper are virtually identical.

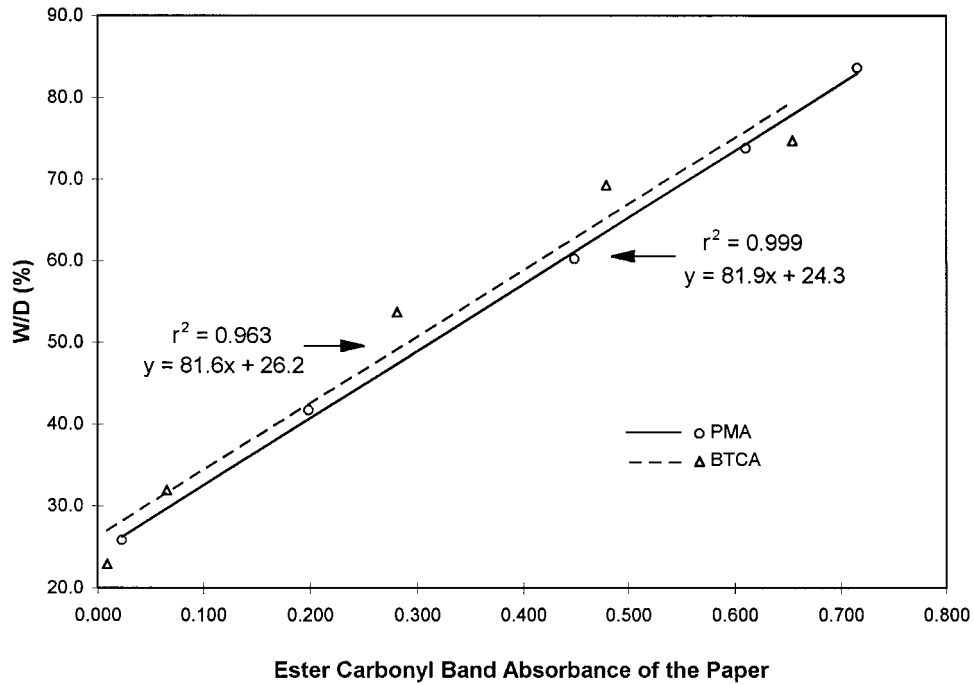
The dimensional stability of the sheets treated with PMA and BTCA is shown in Figure 5. One observes that the dimensional stability increases



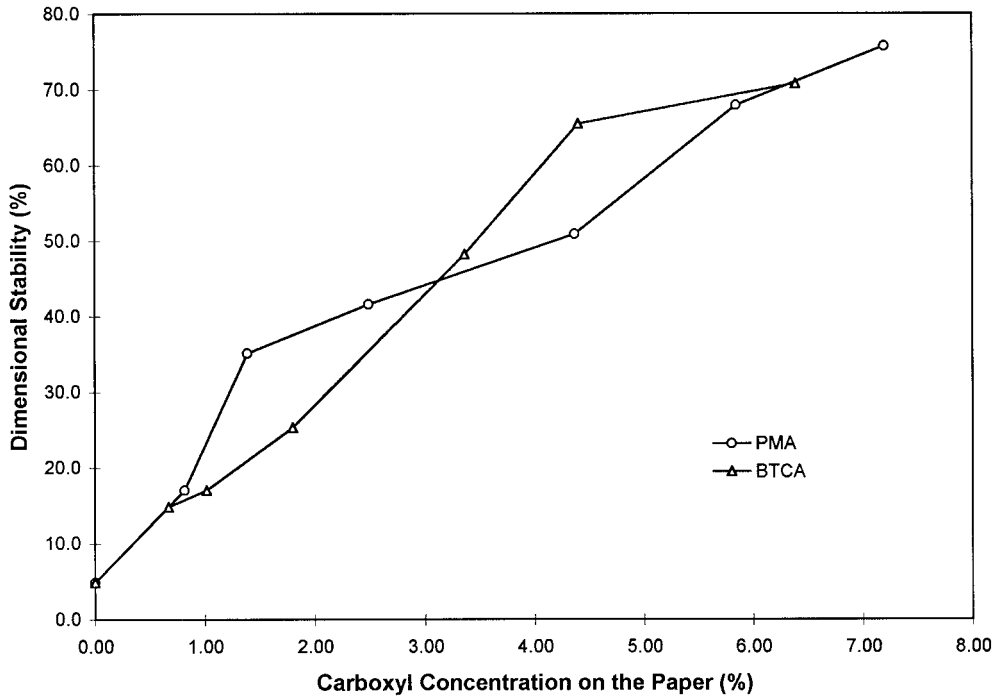
**Figure 3** Ester carbonyl band absorbance of the sheets treated with PMA and BTCA and cured at 170°C for 2 min as a function of the carboxyl concentration on the sheets before curing.

as the carboxyl concentration on the paper increases (Fig. 5). The linear regression models between the dimensional stability and the ester car-

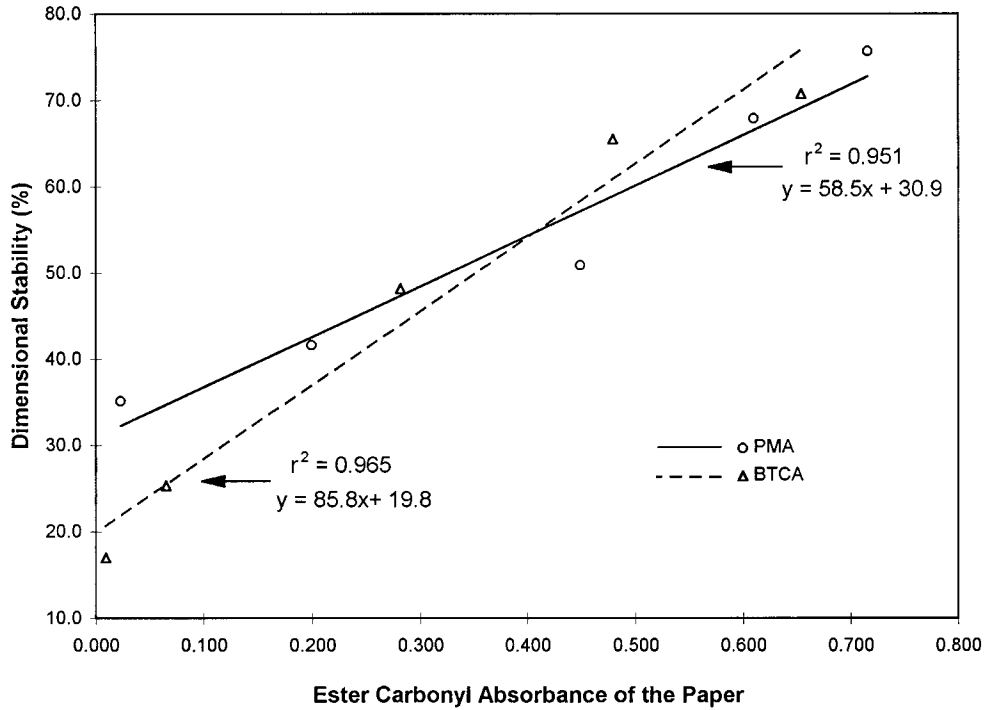
bonyl band absorbance have  $r^2$  values of 0.951 and 0.965 for PMA- and PMA-treated sheets, respectively as demonstrated in Figure 6.



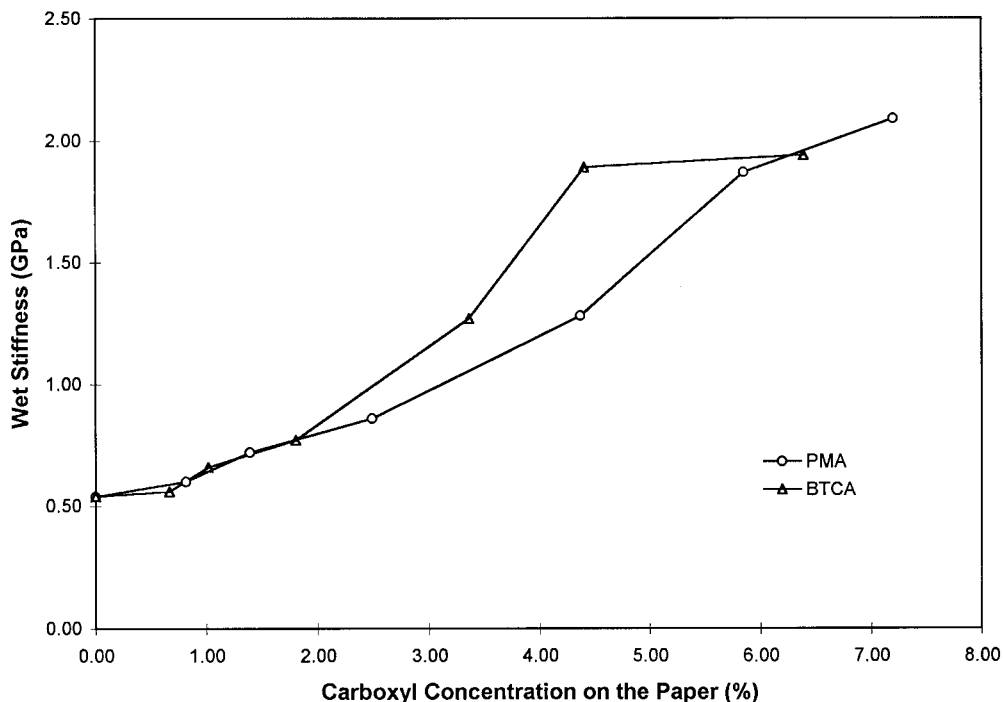
**Figure 4** The linear regression curves of  $W/D$  ratio vs. ester carbonyl band absorbance for the sheets treated with PMA and BTCA.



**Figure 5** Dimensional stability of the sheets treated with PMA and BTCA and cured at 170°C for 2 min as a function of the carboxyl concentration on the sheets before curing.



**Figure 6** The linear regression curves of dimensional stability vs. ester carbonyl band absorbance for the sheets treated with PMA and BTCA.



**Figure 7** Wet stiffness of the sheets treated with PMA and BTCA and cured at 170°C for 2 min as a function of the carboxyl concentration on the sheets before curing.

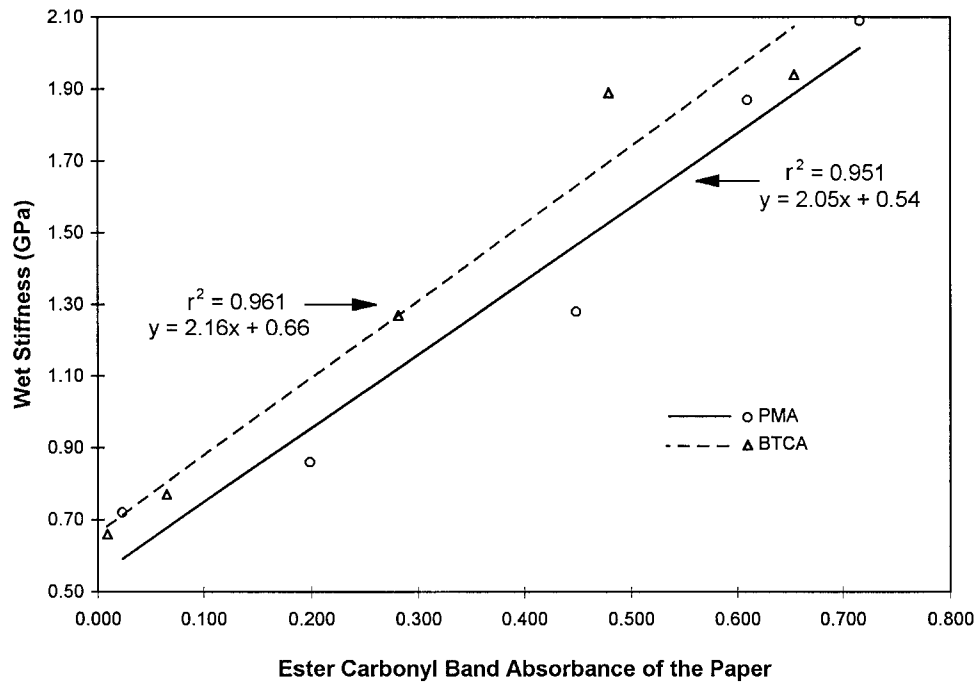
The change in dimensional stability depends on the dispersion of fibers in the paper and the swelling of the fibers. Intrafiber crosslinking of cellulose taking place upon the curing of a treated sheet restricts the swelling of fibers, thus improving the dimensional stability of the sheets. Interfiber crosslinking probably also occurs on the treated sheets, thus further improving the dimensional stability of the paper. One observes that the dimensional stability of the PMA-treated sheets are significantly higher than that of the BTCA-treated sheets when the amount of ester formed on the paper is small, whereas the slope of the linear regression curve of the dimensional stability vs. the ester carbonyl band absorbance is significantly higher for the BTCA-treated sheets than for the PMA-treated sheets (Fig. 6).

We also investigated the change in the wet stiffness of the paper as a result of the treatment with the poly(carboxylic acid)s. The wet stiffness of the treated sheets was plotted against the carboxyl concentration on the paper (Fig. 7). The data show that the wet stiffness of the treated paper increases as the carboxyl concentration on the paper increases (Fig. 7). The improvement in the paper wet stiffness is moderate when the carboxyl concentration is below 2%, and it becomes more significant when the carboxyl concen-

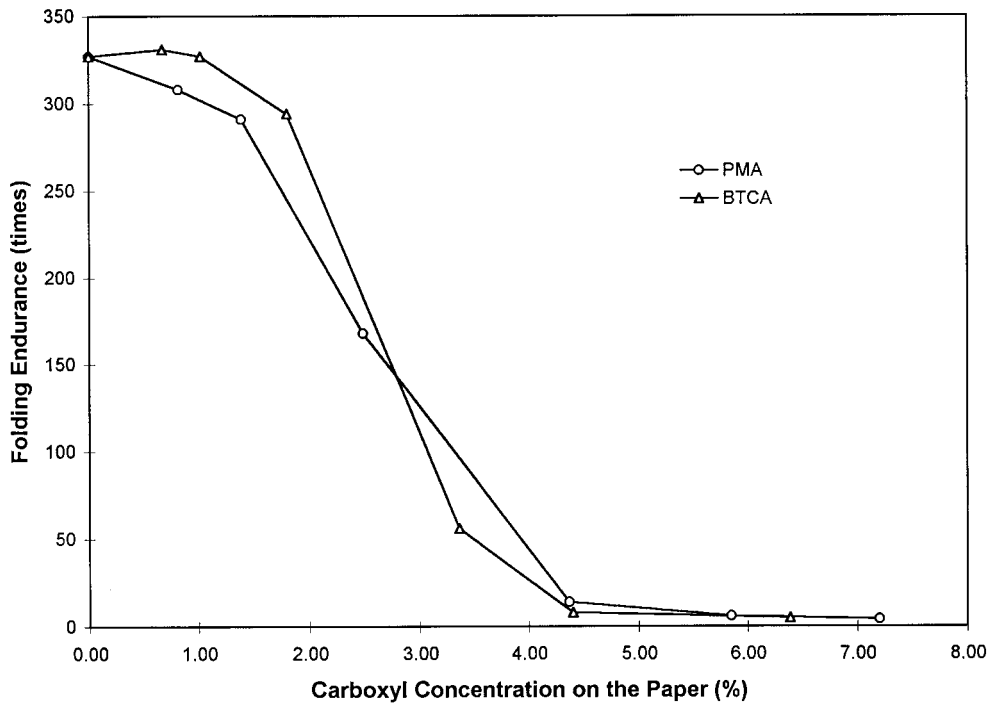
tration is above 2% (Fig. 7). The linear regression models between the wet stiffness and the ester carbonyl band absorbance have  $r^2$  values of 0.951 and 0.961 for the PMA- and BTCA-treated sheets, respectively (Fig. 8). Thus, the data indicated that the increase of the wet stiffness of the treated paper is also attributed to the ester crosslinking of the cellulose by the poly(carboxylic acid)s. The two linear regression curves shown in Figure 8 have almost the same slopes, indicating the effectiveness of the ester crosslinking of cellulose by PMA and BTCA for improving the paper wet stiffness is practically identical.

The folding endurance of the treated sheets at different levels of carboxyl concentration on the paper is presented in Figure 9. Contrary to the changes in the wet strength, dimensional stability, and wet stiffness, the folding endurance decreases sharply as a result of the treatment by the poly(carboxylic acid)s. At low levels of the carboxyl concentration, the treated sheets still retain a certain degree of flexibility. The folding endurance becomes close to zero when the carboxyl concentration on the paper reaches above 4%, indicating extreme paper brittleness.

The folding endurance as a function of the ester carbonyl band absorbance for the treated sheets is shown in Figure 10. The data indicate a drastic

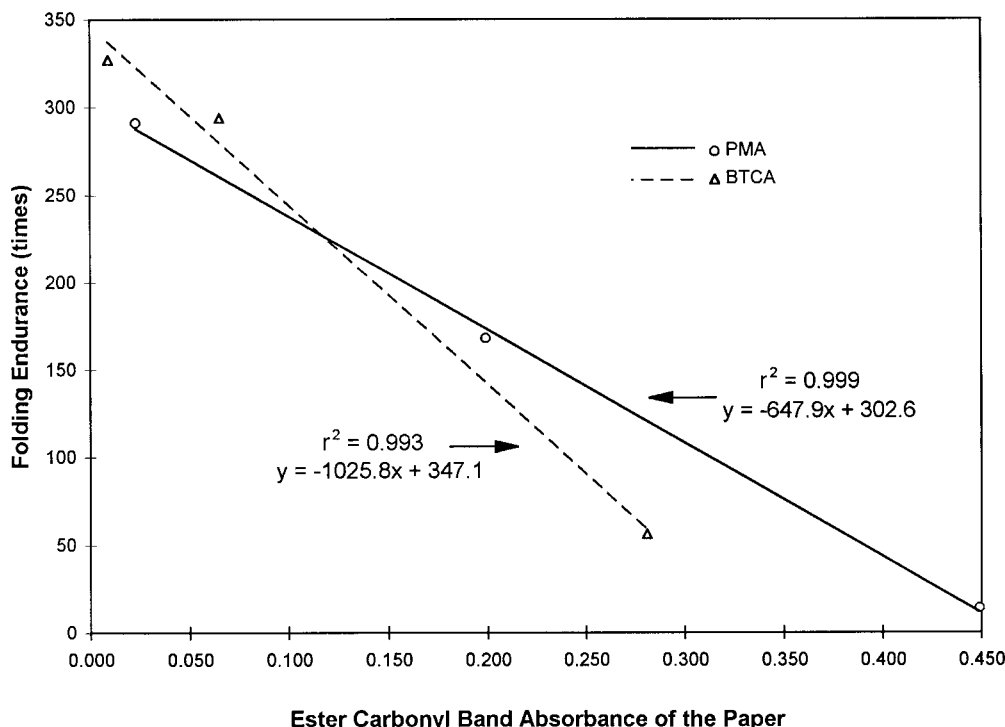


**Figure 8** The linear regression curves of wet stiffness vs. ester carbonyl band absorbance for the sheets treated with PMA and BTCA.



**Figure 9** Folding endurance of the sheets treated with PMA and BTCA and cured at 170°C for 2 min as a function of the carboxyl concentration on the sheets before curing.





**Figure 10** The linear regression curves of folding endurance vs. ester carbonyl band absorbance for the sheets treated with PMA and BTCA.

decrease in the paper's folding endurance as the amount of ester formed on the treated paper increases. The linear regression models between the folding endurance and the ester carbonyl band absorbance for the PMA- and BTCA-treated sheets have  $r^2$  values of 0.999 and 0.993, respectively (Fig. 10). Evidently, the ester crosslinking of the wood cellulose on the paper causes the brittleness of the treated paper, thus diminishing the folding endurance of the treated paper. The treated paper loses all its flexibility when the esterification of cellulose reaches a certain level (Fig. 10).

In summary, the use of the two poly(carboxylic acid)s to treat the kraft paper improves the wet strength, wet stiffness, and dimensional stability. The normal paper wet strength retention imparted by the use of commercial wet strength resins, such as polyaminoamide-epichlorohydrin and urea-formaldehyde resins, is less than 50%.<sup>21</sup> Therefore, the multifunctional carboxylic acids investigated in this research can be considered as effective paper wet strength agents. The effectiveness of the ester crosslinking of paper using PMA and BTCA for improving the paper wet performance is comparable. Paper brittleness and low folding endurance are the major disadvantages

for the poly(carboxylic acid)s as paper wet strength agents. However, a moderate improvement in the paper wet performance can be achieved without significant loss in the folding endurance at low acid add-on levels. PMA has a greater potential than does BTCA to become a commercial paper wet strength agent because of its low cost.

## CONCLUSIONS

Poly(maleic acid) (PMA) and butanetetracarboxylic acid (BTCA) have demonstrated their comparable effectiveness in crosslinking wood pulp cellulose and in improving paper wet strength, wet stiffness, and dimensional stability. The folding endurance of the treated paper was drastically reduced as a result of the esterification and crosslinking of cellulose by the poly(carboxylic acid)s. The linear correlation between the amount of ester formed on the paper and the wet strength, dimensional stability, and wet stiffness of the paper has proved that the improvement in the wet performance of the treated paper is directly attributed to the ester crosslinking of wood pulp cellulose on the paper. The data presented in this

article have also demonstrated that FTIR spectroscopy can be used for predicting the performance of the paper crosslinked by poly(carboxylic acid)s based on the ester carbonyl band absorbance of the treated paper.

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