

Combination of Bifunctional Aldehydes and Poly(Vinyl Alcohol) as the Crosslinking Systems to Improve Paper Wet Strength

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Received 10 August 2003; accepted 23 November 2003

DOI 10.1002/app.20593

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Two bifunctional aldehydes (i.e., glyoxal and glutaraldehyde) are used as the crosslinking agents to improve paper wet strength in the presence of fully hydrolyzed poly(vinyl alcohol) (PVA) as a co-reactant. These bifunctional aldehydes alone improve paper wet strength but diminish its folding endurance. The use of PVA as a co-reactant not only improves paper wet strength but also increases its dry strength and folding endurance. Glutaraldehyde is able to impart much higher levels of wet strength to the treated paper than glyoxal when a catalyst is present. The wet strength of the treated paper increases as the amount of PVA added is increased, and it also increases as the molecular weight (M_w) of the PVA increases. The data

suggest that the reaction between glutaraldehyde and PVA promotes the formation of interfiber crosslinking, thus improving the wet strength without diminishing the flexibility of the treated paper. The use of a catalyst is critical to achieve high levels of durable wet strength of the treated paper. We studied the effects of different Lewis acids as the catalysts for crosslinking of pulp cellulose by glutaraldehyde and found that $Zn(NO_3)_2$ is the most effective one. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1673–1680, 2004

Key words: brittle cellulose; crosslinking; folding endurance; functionalization of polymers; glyoxal; glutaraldehyde; paper; pulp; wet strength

INTRODUCTION

Since the 1980s, the academic and industrial communities have made continuous efforts to develop new paper wet strength agents without emission of formaldehyde or absorbable organic chlorides (AOX).^{1–4} In our previous research, we found that polycarboxylic acids of small molecular sizes, such as 1,2,3,4-butanetetracarboxylic acids and poly(maleic acid) (PMA) with M_w of 800, improve wet strength but also diminish folding endurance of the treated paper.^{5–6} We also found that the use of copolymers of maleic acid with high M_w as the crosslinking agents improves both wet strength and folding endurance.^{7,8} We believe that the crosslinking systems with high M_w promote the formation of interfiber bonding, thus improving the flexibility of treated paper.

The use of multifunctional carboxylic acids as wet strength agents requires curing temperature as high as 170°C, which is significantly higher than the temperatures used in conventional paper production. To reduce the curing temperature, we used two bifunctional aldehydes (i.e., glutaraldehyde and glyoxal) as

the crosslinking agents for paper.⁹ We found that glutaraldehyde is very effective in improving wet strength of paper at relatively lower curing temperatures (110–120°C).¹⁰ Similar to the polycarboxylic acids of small molecular sizes, glutaraldehyde also causes paper embrittlement and diminishes its folding endurance.⁹

Previously, we found that combining a polymeric co-reactant, such as poly(vinyl alcohol) (PVA), together with a crosslinking agent of small molecular size significantly improves both wet strength and folding endurance of the treated paper.^{10,11} In this research, we investigated and compared the performance of glutaraldehyde and glyoxal as the wet strength agents for paper when PVA was used as a co-reactant. We compared the wet strength of the paper treated with glutaraldehyde in combination with PVA of different M_w 's. We also studied the effects of catalysts on the performance of the paper crosslinked by the glutaraldehyde/PVA system.

EXPERIMENTAL

Materials

The paper used was an unbleached Kraft paper with grammage of 65 g/m² and was supplied by Southwest Paper (Wichita, KS). Glutaraldehyde was a 50% aque-

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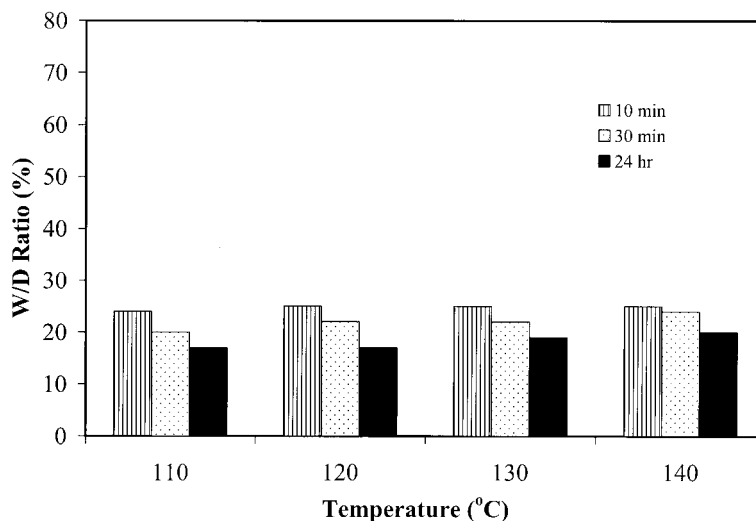


Figure 1 Wet strength (soaked in water for 10 min, 30 min, and 24 h) of the paper treated with 2.00% (0.20 mol/L) glutaraldehyde and 1.17% PVA without a catalyst, pH 4.3, and cured at different temperatures for 1.5 min.

ous solution (supplied by Union Carbide, South Charleston, WV). Fully hydrolyzed poly(vinyl alcohol) (PVA) had a viscosity of 62–72 cps (PVA). The PVA with a lower M_w had a viscosity of 28–32 cps (PVA-LMW). Both PVA samples were supplied by Airproducts (Allentown, PA). The catalysts [$Zn(NO_3)_2$, $AlCl_3$, $MgCl_2$, and NH_4Cl], citric acid, sodium hydroxide, and glyoxal were all reagent grade chemicals supplied by Aldrich (Milwaukee, WI).

Paper treatment

The Kraft paper sheets with a size of $25 \times 25 \text{ cm}^2$ were immersed in a solution for 30 s, then pressed between the squeezing rolls of a laboratory padder to remove the excess liquid and to reach a wet pick-up around 95%. The impregnated sheets were dried on a hot plate dryer at 85°C for 3 min to prevent curling. Each sheet was cured in a forced draft oven at a specified temperature for 1.5 min. The cured sheets were rinsed in water for 15 min to remove unreacted chemicals and then dried. The control sample was treated with water, dried, and cured at 130°C . All the treating solutions contained either 1.16% glyoxal (0.20 mol/L) or 2.00% glutaraldehyde (0.20 mol/L) in combination of different amounts of PVA. Citric acid and NaOH were used to prepare the glutaraldehyde/PVA solutions with different pH values.

Paper mechanical properties evaluation

Dry tensile strength, wet tensile strength, and folding endurance of the treated paper sheets were evaluated according to TAPPI standard test methods T 494 om-96, T456 om-87, and T 511 om-96, respectively. For wet tensile strength measurements, the specimens were

immersed in distilled water for different times (10 min, 30 min, or 24 h) before testing. Ten measurements were performed and averaged for each tensile strength data point. The wet strength (W/D ratio) was expressed as a ratio of the wet strength of treated paper to the dry strength of the control sample. The change in dry strength was expressed as a percentage increase over that of the control sample.

RESULTS AND DISCUSSION

The paper was treated with 2.00% (0.20 mol/L) glutaraldehyde and 1.17% PVA at pH 4.3 without a catalyst and then cured for 1.5 min at temperatures ranging from 110 to 140°C . The wet strength (W/D ratio) of the control paper after soaking for 24 h is only 10%. After curing, the wet strength of the treated and cured sheets reach 17–20% after soaking for 24 h (Fig. 1). Apparently, the glutaraldehyde/PVA only provides marginal improvement in the wet strength of the paper without a catalyst.

Presented in Figure 2 is the wet strength of the paper treated with 1.16% glyoxal and 1.17% PVA without a catalyst and cured in the same temperature range. The treated sheets were also soaked in water for 10 min, 30 min, and 24 h. One observes that the treatment with glyoxal/PVA without a catalyst results in only temporary wet strength. The wet strength reaches above 40–47% when the paper is soaked in water for 10 min, but it decreases to 30–33 and 12–13% when the soaking time increases to 30 min and 24 h, respectively (Fig. 2). It is apparent that different curing temperatures do not have a significant effect on the wet strength of the treated paper, similar to the treatment with glyoxal without a catalyst observed in our previous research.⁹ It is known that aldehydes react

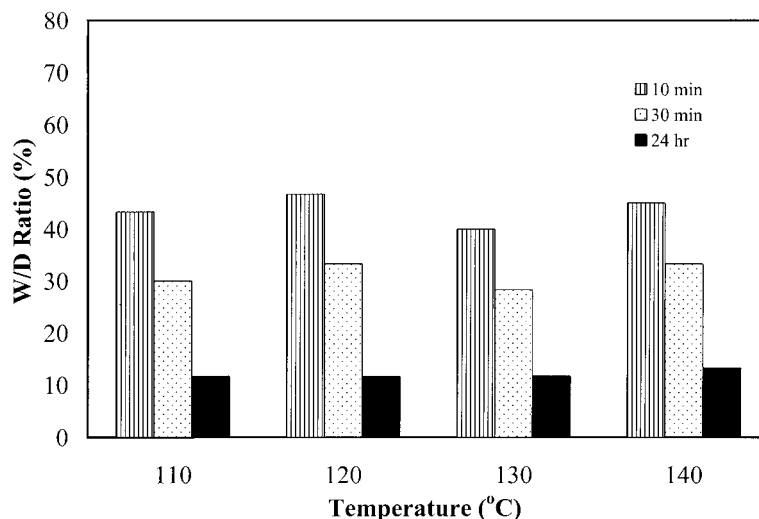


Figure 2 Wet (soaked in water for 10 min, 30 min, and 24 h) of the paper treated with 1.16% (0.20 mol/L) glyoxal and 1.17% PVA without a catalyst, pH 4.3, and cured at different temperatures for 1.5 min.

with hydroxyl groups to form semiacetal,¹² which is easily hydrolyzed in water. The aldehyde groups of glyoxal are more electronic deficient and thus more reactive than those of glutaraldehyde. Therefore, glyoxal is able to react with hydroxyl of PVA and cellulose to form more semiacetal crosslinks on cellulose fibers, thus providing a higher level of temporary wet strength than glutaraldehyde, as shown in Figure 2. The performance of the combination of glutaraldehyde or glyoxal with PVA without a catalyst presented above is similar to that of glutaraldehyde or glyoxal without PVA reported previously.⁹

The paper was treated by 2.00% glutaraldehyde and 1.17% PVA in the presence of 0.76% $\text{Zn}(\text{NO}_3)_2$ as a catalyst and cured at different temperatures. The wet

strength of the paper thus treated is shown as a function of the curing temperature in Figure 3. The paper thus treated shows wet strength 25–30% even without exposure to elevated temperatures, indicating that glutaraldehyde starts to react with cellulose and PVA at room temperature when a catalyst is present. The wet strength increases from 35–40 to 70–72% as the curing temperature increases from 110 to 150°C (Fig. 3). The decrease in wet strength of the treated paper after 24 h soaking is insignificant, especially when the curing temperature reaches 130° and above, thus indicating that the wet strength is durable to hydrolysis (Fig. 3). Evidently, the catalyst plays a critical role in the crosslinking of wood pulp cellulose through acetalization of glutaraldehyde.

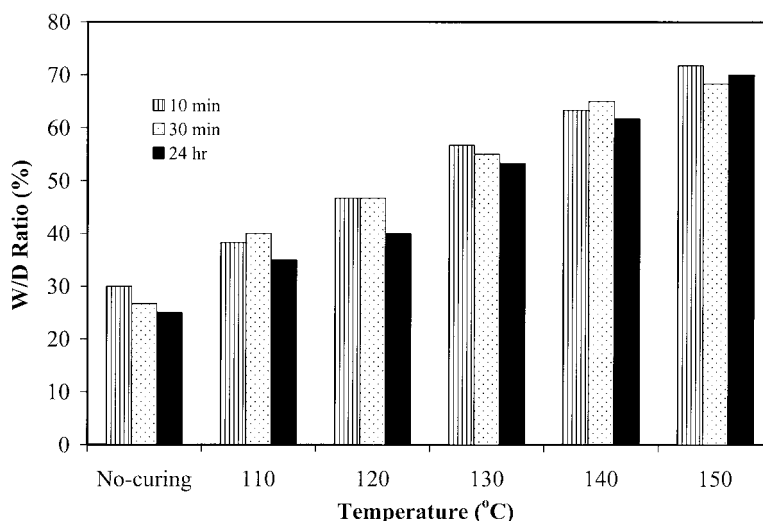


Figure 3 Wet strength (soaked in water for 10 min, 30 min, and 24 h) of the paper treated with 2.00% (0.20 mol/L) glutaraldehyde, 1.17% PVA, and 0.76% $\text{Zn}(\text{NO}_3)_2$, pH 4.3, cured at different temperatures for 1.5 min.

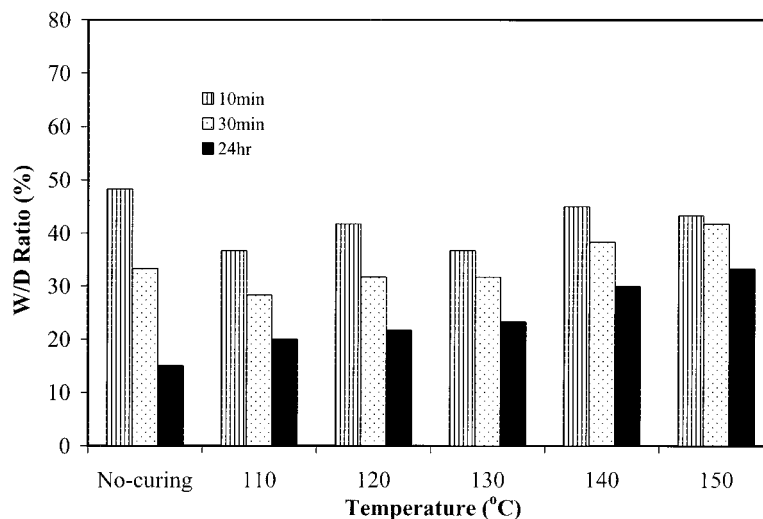


Figure 4 Wet strength (soaked in water for 10 min, 30 min, and 24 h) of the paper treated with 1.16% (0.20 mol/L) glyoxal, 1.17% PVA, and 0.76% $\text{Zn}(\text{NO}_3)_2$, pH 4.3, and cured at different temperatures for 1.5 min.

Presented in Figure 4 is the wet strength of the paper treated with 1.16% glyoxal and 1.17% PVA in the presence of 0.76% $\text{Zn}(\text{NO}_3)_2$ as a catalyst and cured at different temperatures. The initial wet strength (after soaking in water for 10 min) of the paper thus treated (Fig. 4) is similar to that treated with glyoxal/PVA without a catalyst (Fig. 2). When a catalyst is present, however, the wet strength of the treated paper after 24 h soaking is significantly higher than that treated without a catalyst. The W/D ratio after 24-h soaking increases from 20% at 110°C to 35% at 150°C. Thus, the data indicate that the wet strength becomes more resistant to hydrolysis when a catalyst is used in the glyoxal/PVA system, and the durability increases as the curing temperature increases. In the presence of a catalyst, adding PVA as a co-reactant to the crosslinking system remarkably increases the wet strength of the treated paper compared to that treated with glyoxal and glutaraldehyde alone in our previous study.⁹

There are two fundamental differences between the paper treated with glyoxal/PVA and that treated with glutaraldehyde/PVA when $\text{Zn}(\text{NO}_3)_2$ is used as a catalyst. The glutaraldehyde/PVA system imparted much higher levels of durable wet strength to the paper than glyoxal/PVA at all curing temperatures. For the paper treated with glutaraldehyde/PVA and cured at 150°C, its W/D ratio is 70% after 24-h soaking, whereas it is only 33% for the paper treated with glyoxal/PVA. Second, the wet strength of the paper treated with glutaraldehyde/PVA is more durable to hydrolysis than that treated with glyoxal/PVA. The W/D ratio of the paper treated with the glutaraldehyde/PVA and cured at 150°C remains practically unchanged during the 24-h soaking (Fig. 3), whereas that for the paper treated with glyoxal/PVA and

cured at the same temperature decreases from 43 to 33% after a 24-h soaking (Fig. 4). Therefore, the data clearly show that glutaraldehyde/PVA is a more effective crosslinking system to improve paper wet strength than glyoxal/PVA.

The improved durability of paper wet strength can be attributed to the formation of acetal crosslinks instead of hemiacetal crosslinks. Aldehyde reacts with hydroxyl groups to form hemiacetal, and the reaction proceeds further to form acetal under the catalysis of a Lewis acid.¹² Consequently, hemiacetal is easily hydrolyzed by water, whereas acetal is stable under neutral and alkaline conditions. Hemiacetal crosslinks of cellulose only lead to temporary wet strength, whereas acetal crosslinks bring about durable wet strength. High-curing temperature increases acetalization rate, thus increasing the amount of acetal crosslinks formed.¹² As a result, wet strength increases as curing temperature increases. The different effectiveness of glyoxal and glutaraldehyde is possibly due to their different molecular structures and consequently different reactivity for acetalization. For glyoxal, the two aldehyde groups are too close to each other, making them difficult to react with four hydroxyl groups of cellulose or PVA simultaneously to form acetal-based crosslinks.

Lewis acids, such as magnesium chloride, have been used as the catalysts for the crosslinking of cotton cellulose by formaldehyde-based crosslinking agents.^{13–14} We compared the effectiveness of different catalysts for the crosslinking of wood pulp cellulose by glutaraldehyde/PVA. The paper was treated with 2.00% glutaraldehyde and 1.17% PVA in the presence of three different Lewis acids [i.e., $\text{Zn}(\text{NO}_3)_2$, AlCl_3 , and MgCl_2] with the same mole concentration and at different pHs, then cured at 130°C for 1.5 min. The wet strength (after 24 h soaking)

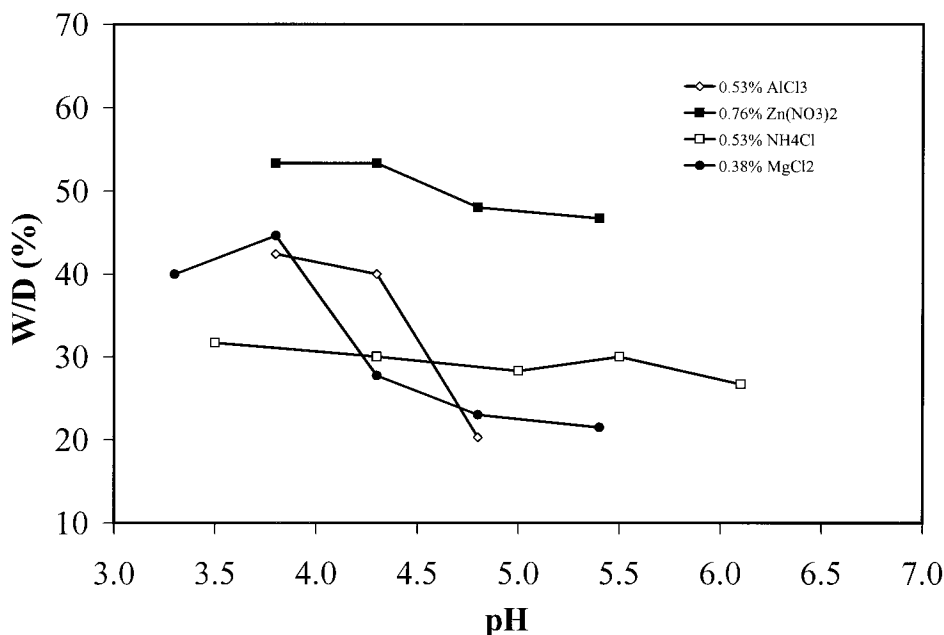


Figure 5 Wet strength (soaked in water for 24 h) of the paper treated with 2.00% glutaraldehyde, 1.17% PVA, and different catalysts at the same mole concentration, and cured at 130°C for 1.5 min as a function of pH.

of the treated paper is shown in Figure 5. We find that the wet strength of the paper treated with AlCl₃ and MgCl₂ as catalysts decreases notably when pH is higher than 4.0. Zn(NO₃)₂ remains highly effective at pH as high as 5.4 with the W/D ratio at 47%. This result indicates that Zn(NO₃)₂ is the most effective catalyst for the acetalization of glutaraldehyde by cellulose and PVA. For the purpose of comparison, NH₄Cl is also included

in the study. We find that NH₄Cl provided a relatively constant W/D ratio around 30% in the pH range from 3.5 to 6.1 (Fig. 5).

The wet strength and percent increase in dry strength of the paper treated with 2.00% glutaraldehyde, 0.76% Zn(NO₃)₂, and different amounts of PVA are presented in Figures 6 and 7, respectively. The W/D ratio (after 24 h soaking) increases from 51%

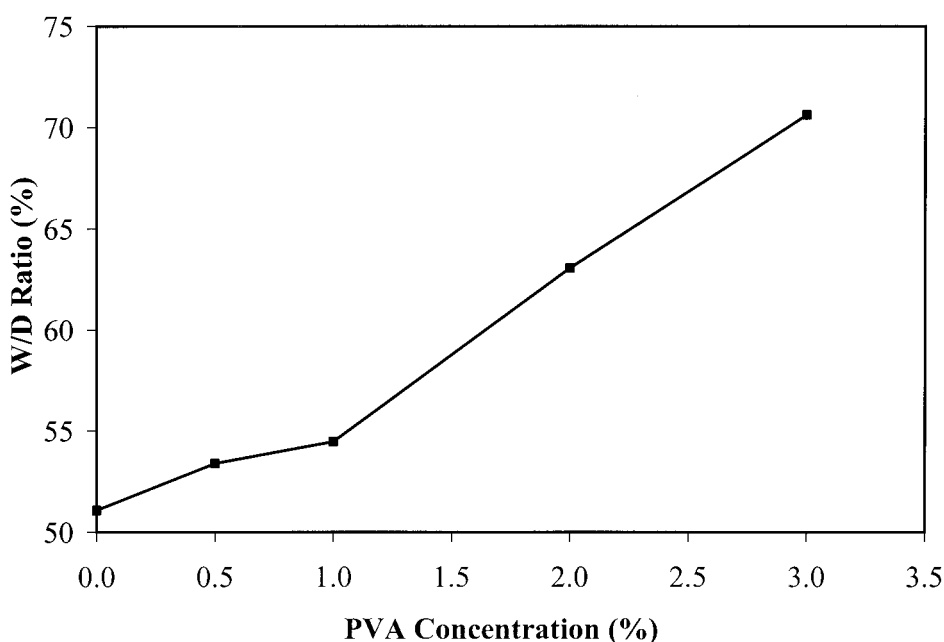


Figure 6 Wet strength (soaked in water for 24 h) of the paper treated with 2.00% glutaraldehyde, 0.76% Zn(NO₃)₂, and PVA, pH 5.3, and cured at 140°C for 1.5 min as a function of the PVA concentration.

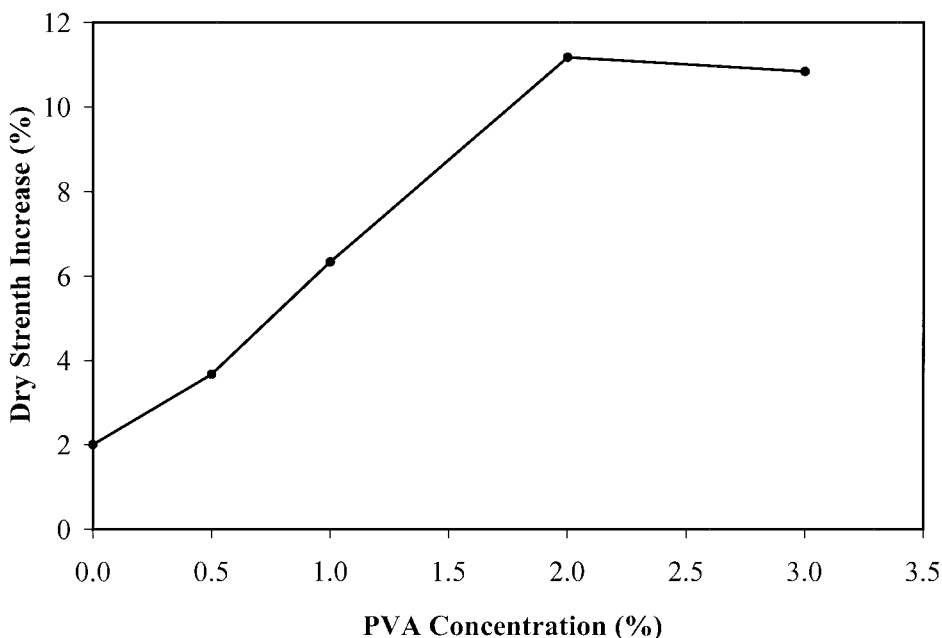


Figure 7 Dry strength increase of the paper treated with 2.00% glutaraldehyde, 0.76% $\text{Zn}(\text{NO}_3)_2$, and PVA, pH 5.3, and cured at 140°C for 1.5 min as a function of the PVA concentration.

without PVA to 71% with 3.0% PVA added (Fig. 6). The dry strength also increases by 11% when 2.0% PVA is presented (Fig. 7). The amount of PVA added has such a profound impact on the wet strength of the treated paper as shown in Figure 6, indicating that PVA plays an important role in the crosslinking of cellulose by glutaraldehyde.

The importance of PVA is also shown by the effect of its M_w on the wet strength of the treated paper. The paper was treated with 2.00% glutaraldehyde and 0.76% $\text{Zn}(\text{NO}_3)_2$ in combination with 1.0% PVA of different M_w 's. The PVA with a higher M_w , abbreviated as PVA here, has a viscosity of 62–72 cps, whereas the one with a lower M_w , abbreviated as

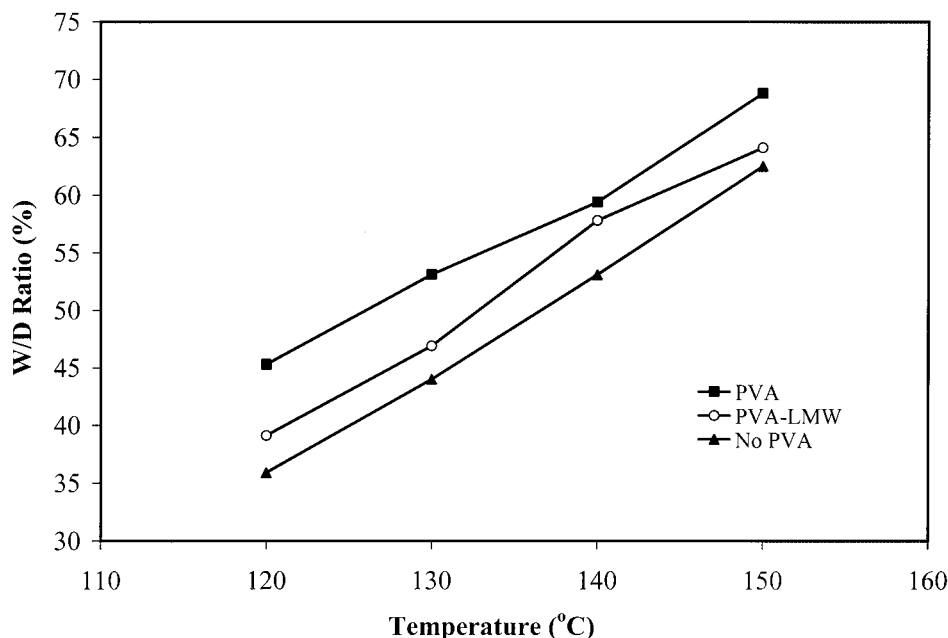
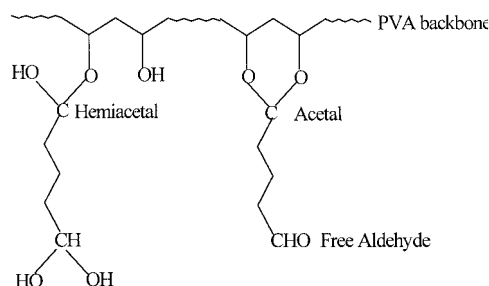


Figure 8 Wet strength (soaked in water for 24 h) of the paper treated with 2.00% glutaraldehyde, 0.76% $\text{Zn}(\text{NO}_3)_2$ without PVA, and with 1.0% PVA of different molecular weights, pH 4.3 and cured for 1.5 min, as a function of the curing temperature.



Scheme 1 Structure of pentane dialated PVA.

PVA-LMW, has a viscosity of 28–32 cps. The wet strength (after 24 h soaking) is presented as a function of the curing temperature in Figure 8. In the entire curing temperature range, the use of the higher M_w PVA as the co-reactant results in a significantly higher W/D ratio than the use of the lower PVA (PVA-LMW) (Fig. 8). When the curing temperature is 130°C, the W/D ratio increases from 44% without PVA to 47% when 1.0% PVA-LMW is added. When 1.0% PVA is used, the W/D ratio increases further to 53%. The combination of glutaraldehyde and the higher M_w PVA probably forms more interfiber bonding, thus becoming more effective in improving the wet strength of the crosslinked paper than the combination of glutaraldehyde and the lower M_w PVA.

The important role of PVA for improving the wet strength of the paper treated with glutaraldehyde is probably due to its participation in the cellulose

crosslinking by glutaraldehyde. PVA reacts with glutaraldehyde and chains up the small glutaraldehyde to form a bulky pentane-dialated PVA, as shown in Scheme 1, which carries highly reactive aldehyde and hemiacetal groups to react with cellulose to form crosslinking networks. Because of its bulky size, the PVA molecules cannot penetrate into fiber interior but stay on fiber surface and fiber crossing areas. Therefore, the reaction of PVA with glutaraldehyde promotes the formation of interfiber crosslinking. Consequently, the glutaraldehyde/PVA system becomes more efficient in improving the wet strength of the treated paper.

For crosslinking agents of small molecular sizes, the improvement in paper wet strength is always achieved in the expense of paper folding endurance.^{1–3,5,6} When a high molecular weight polymeric crosslinking agent is used, we found that both wet strength and folding endurance of the treated paper is increased in our previous research.^{7,8} The paper is treated with glyoxal, glyoxal/PVA, glutaraldehyde, and glutaraldehyde/PVA and cured at 110, 120, 130, and 140°C for 1.5 min. All the solutions used to treat the paper contain 0.76% $Zn(NO_3)_2$ as a catalyst. In all treated paper samples, the wet strength of treated paper increases and the folding endurance decreases as curing temperature is raised. The folding endurance of the paper thus treated is plotted against the W/D ratio (after 24 h soaking in water) in Figure 9. For the paper treated with 2.00% glutaraldehyde, the presence of 1.17% PVA as a co-

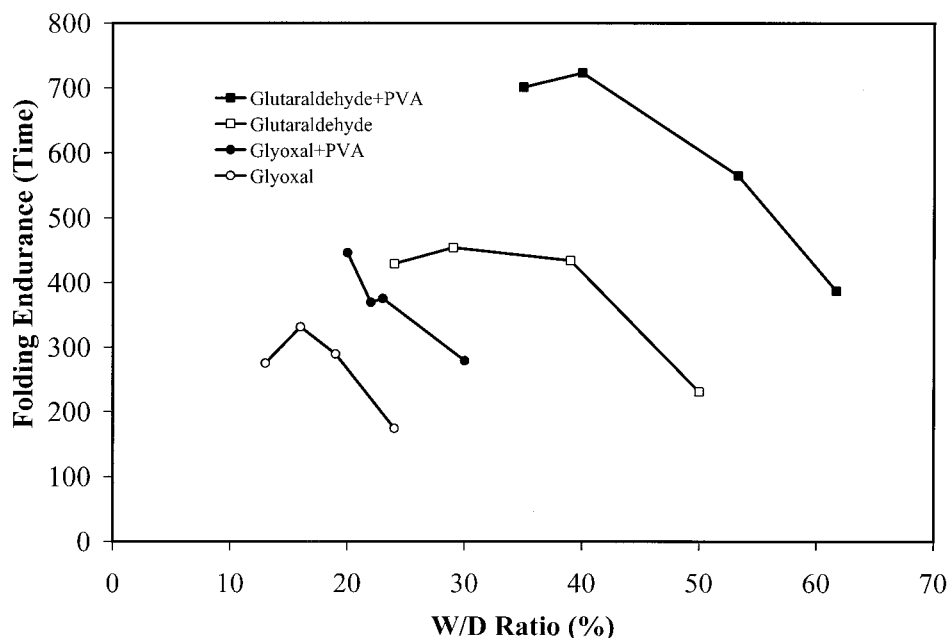


Figure 9 Folding endurance as a function of W/D ratio (soaked in water for 24 h) for the paper treated with 1.16% glyoxal, 1.16% glyoxal/1.17% PVA, 2.00% glutaraldehyde, and 2.00% glutaraldehyde/1.17% PVA, pH 4.3, and cured at 110, 120, 130, and 140°C for 1.5 min. All the treating solutions contain 0.76% $Zn(NO_3)_2$ as the catalyst.

reactant not only increases W/D by 24–46% in the curing temperature range, but also improves the folding endurance by 131–272 double folds at the same W/D ratios. Combining PVA with glyoxal also significantly improves both W/D and folding endurance of the treated paper (Fig. 9). This is another indication that the glutaraldehyde/PVA crosslinking system promotes the formation of interfiber crosslinking on the treated paper.

CONCLUSION

The glutaraldehyde/PVA crosslinking system demonstrates high effectiveness for increasing paper wet strength and folding endurance when a catalyst is present. Among the four catalysts investigated, $\text{Zn}(\text{NO}_3)_2$ is the most effective one. Glutaraldehyde/PVA is significantly more efficient in improving paper wet strength than glyoxal/PVA. The wet strength of the treated paper not only increases with the added amount of PVA, but also increases with the M_w of added PVA. This is probably due to the reaction of PVA with glutaraldehyde, which pro-

motes the formation of interfiber crosslinking on the paper.

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