

# Applications of Bifunctional Aldehydes to Improve Paper Wet Strength

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**ABSTRACT:** Glyoxal and glutaraldehyde behave very differently for improving wet strength of paper. It is found that glyoxal is very efficient for improving temporary wet strength of paper without the presence of a catalyst and exposure to elevated temperatures. When a metal salt, such as  $\text{Zn}(\text{NO}_3)_2$ , is used as a catalyst and the curing temperature is increased, the durable wet strength of glyoxal-treated paper increases at the expense of its flexibility, as shown by reduced stretch and folding endurance. Glutaraldehyde is not able to provide any improvement in wet strength to paper, even under high curing temperatures, provided no catalyst is used. With the aid of a metal salt catalyst, glutaraldehyde imparts excellent durable wet strength to paper without significantly sacrificing folding endurance, and the wet strength of glutaraldehyde-treated paper increases steadily as curing temperature increases. The different behavior of glyoxal and glutaraldehyde may be attributed to their different reactivity toward cellulose. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2539–2547, 2002

**Key words:** wet strength; dry strength; wet-to-dry strength ratio; glyoxal; glutaraldehyde; folding endurance

## INTRODUCTION

Environmental consideration has been the driving force for the papermaking industry to develop new wet-strength resins without the emission of carcinogenic formaldehyde and adsorbable organic halides (AOX).<sup>1</sup> Polycarboxylic acids have been investigated for enhancing the wet performance of paper.<sup>2–11</sup> Among the carboxylic acids of relatively small molecular sizes, 1,2,3,4-butanetetracarboxylic acids (BTCA) and poly(maleic acid) (PMA) were the most effective crosslinking agents.<sup>5,7</sup> However, the treatment with BTCA and PMA causes paper embrittlement, thus severely reducing its folding endurance.

We have discovered two approaches to improve the flexibility of paper crosslinked by polycar-

boxylic acids.<sup>9–11</sup> We treated paper with high molecular weight maleic acid copolymers, including poly(ethene-*co*-maleic acid) and poly(methyl vinyl ether-*co*-maleic acid),<sup>9,10</sup> and found that the high molecular weight maleic acid copolymers not only exhibit higher efficiency for improving wet strength but also significantly improve the dry strength and folding endurance of the treated paper. To improve the cost effectiveness of the treatment, we used poly(maleic acid) in combination with poly(vinyl alcohol) to treat kraft paper and found that the use of poly(vinyl alcohol) as a coadditive notably improves the dry strength, folding endurance, and wet strength of treated paper.<sup>11</sup> However, the use of polycarboxylic acids requires a curing temperature as high as 170°C for effective crosslinking, which is beyond the operating temperature range of current papermaking machines.

In the past, bifunctional aldehydes were studied as crosslinking agents of cellulose to impart wrinkle resistance to cotton fabric.<sup>12–14</sup> The mul-

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**Table I Dry Properties of Kraft Paper Treated by 1.16% (0.20 mol/L) Glyoxal and 2.0% (0.20 mol/L) Glutaraldehyde Without a Catalyst, Cured at Different Temperatures**

Dialdehyde	Temperature (°C)	Change in Dry Strength (%)	Change in Stretch (%)	Folding Endurance (times)
Glyoxal	No curing	6.5	-20.1	386
	110	6.5	-17.4	387
	120	4.8	-15.6	476
	130	0	-19.4	439
	140	1.6	-14.1	334
Glutaraldehyde	No curing	-3.2	-3.5	495
	110	-4.8	-5.4	469
	120	1.6	-5.2	418
	130	0	-3.9	439
	140	-1.6	-10.6	452

For control sample, W/D = 9.8%, dry strength = 4.11 kN/m, stretch = 7.6%, and folding endurance = 489 times.

tifunctional aldehydes include glyoxal, glutaraldehyde, succinaldehyde, and their acetal derivatives. The reaction between dialdehydes and cellulose is catalyzed by metal or ammonium salts.<sup>15,16</sup> The most frequently used catalysts include aluminum, magnesium, and zinc salts of inorganic acids.<sup>16</sup> Glyoxal was also used to provide temporary wet strength for paper.<sup>17-19</sup> These multifunctional aldehydes enjoy the advantage of low curing temperatures (~ 120°C), which are consistent with the current papermaking condition.

The object of this study is to evaluate the feasibility of using glyoxal and glutaraldehyde as wet strength agents for paper.

## EXPERIMENTAL

### Materials

An unbleached kraft paper with a grammage of 65 g/m<sup>2</sup> was used in this research. Glutaraldehyde was a 50% aqueous solution. Glyoxal was a 40% aqueous solution. Zn(NO<sub>3</sub>)<sub>2</sub> was a reagent-grade chemical. The aldehyde-to-Zn(NO<sub>3</sub>)<sub>2</sub> ratios (w/w) in all solutions were 1.16 : 0.758 for glyoxal and 2.0 : 0.758 for glutaraldehyde. The pH of all solutions was adjusted to 4.3 with NaOH and citric acid.

### Paper Treatment

The kraft paper sheets (25 × 25 cm<sup>2</sup>) were immersed in a solution for 30 s, then pressed between squeezing rolls to remove the excess liquid, to reach about 90% wet pickup. 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 force-draft oven at specified temperatures for 1.5 min. The control sample was the paper subjected to the same treating procedure, except for using deionized water instead of a solution. Five specimens were treated under each condition.

### Paper Performance Testing

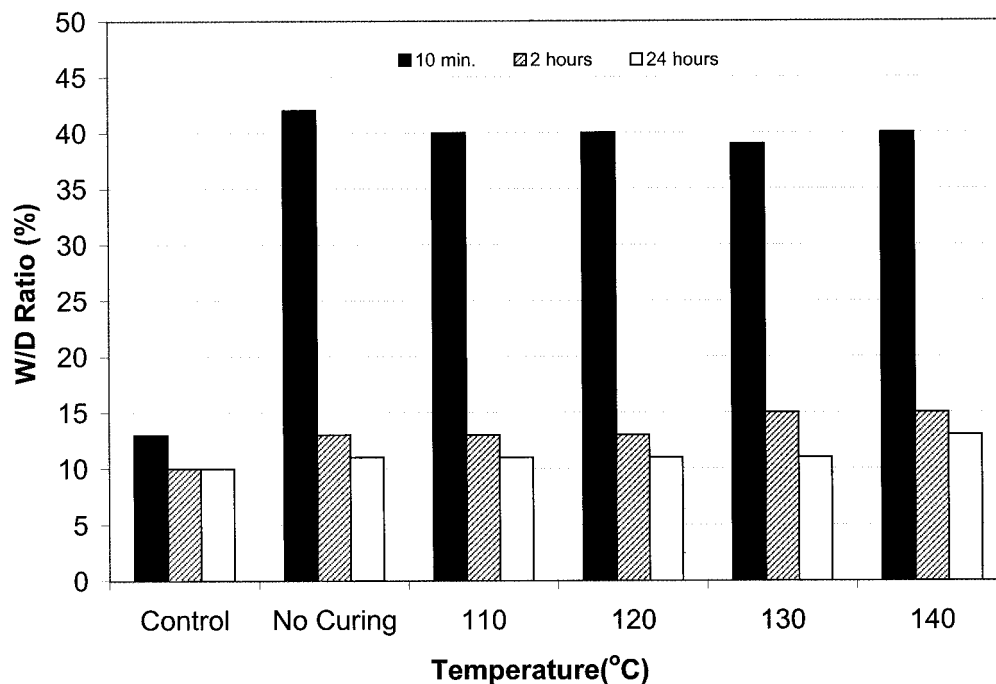
Dry tensile strength, wet tensile strength, and folding endurance of the treated paper sheets were evaluated according to Technical Association of the Pulp and Paper Industry (TAPPI) standard test methods T 494 om-96, T 456 om-87, and T 511 om-96, respectively. For wet tensile strength, the specimens were immersed in deionized water for 10 min, 2 h, or 24 h before testing. Ten measurements were performed for each testing procedure.

The wet strength (wet-to-dry [W/D] strength ratio) was defined as the ratio of the wet strength of treated paper to the dry strength of the control sample. The dry strength and stretch were expressed as percentage changes over those of the control sample. The folding endurance was expressed as the number of double folds before the specimen would break. The properties of the control sample are shown in the footnote to Table I.

## RESULTS AND DISCUSSION

### Properties of the Paper Treated With Dialdehydes Without a Catalyst

The kraft paper sheets were treated with 1.16% (0.20 mol/L) of glyoxal without using a catalyst,



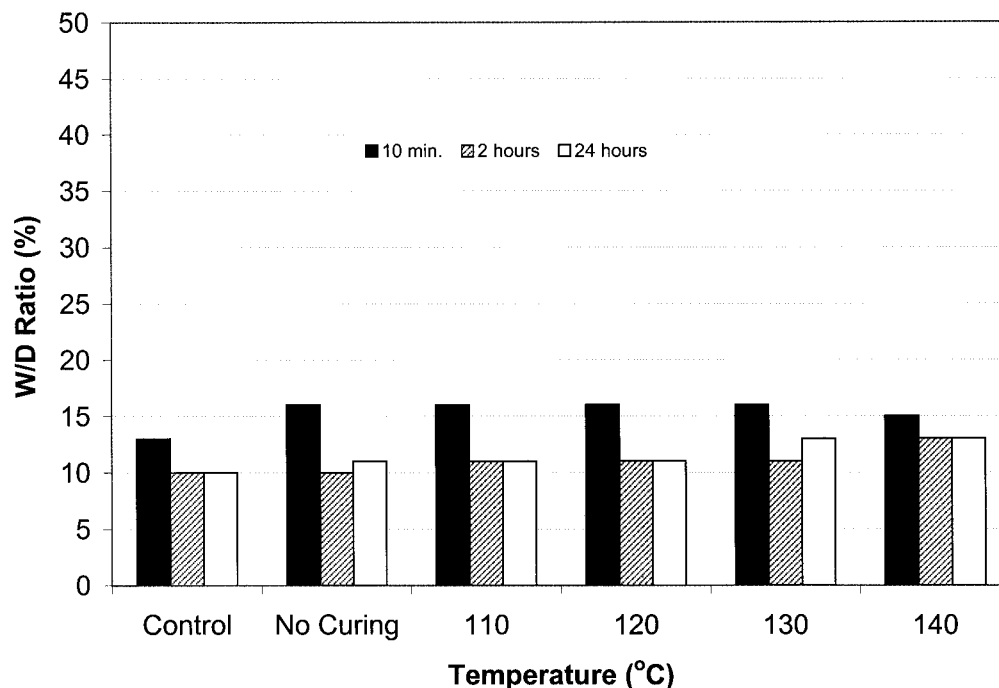
**Figure 1** Wet strength of the paper treated with 1.16% (0.20 mol/L) glyoxal without a catalyst after being soaked in water for 10 min, 2 h, and 24 h.

and cured at different temperatures for 1.5 min. The cured paper was then soaked in water for different lengths of time before its wet strength was tested. The W/D strength ratios of the treated kraft paper are presented in Figure 1. One observes that different curing temperatures did not result in significantly different wet strength of treated paper. All samples cured at temperatures ranging from 110 to 140°C exhibited wet strength similar to those without curing. All treated paper samples showed high levels of wet strength with W/D ratios around 40% after being soaked in water for 10 min, but the wet strength deteriorated quickly as the soaking time was increased. The W/D ratio decreased to 10–15% after 2 h of soaking in water (Fig. 1). The wet strength of the treated paper cured under different temperatures was close to that of the control sample after soaking for 2 h. It indicates that the glyoxal-treatment without a catalyst imparts only temporary wet strength to the paper.

The wet strength of glyoxal-treated paper is a result of the crosslinking of cellulose by glyoxal. Glyoxal is able to react with hydroxyl groups of cellulose to form hemiacetal bonds between cellulose molecules.<sup>20</sup> The improved wet strength of the glyoxal-treated paper without curing suggests that the hemiacetals form so easily as the water is removed from the treated paper during

the drying process that further curing is not needed. The hemiacetal bonds produced by glyoxal between cellulose molecules, however, are sensitive to water and can be replaced by hemiacetal bonds with water when the paper is saturated by water for a short period of time. Consequently, the wet strength imparted by glyoxal is only temporary.

Figure 2 shows the wet strength of paper treated by 2.0% (0.20 mol/L) glutaraldehyde without the use of a catalyst. The initial wet strength of paper treated by glutaraldehyde was around 15% compared with 40% for the glyoxal-treated paper. Similar to the case of glyoxal treatment, different curing temperatures have little impact on the wet strength of treated paper. The wet strengths of the paper cured under different temperatures after soaking for different lengths of time were similar to those of the control sample. Apparently, glutaraldehyde did not provide significant improvement in the wet strength of paper. The results indicate that glutaraldehyde possesses low reactivity toward cellulose, even at high temperatures, if no catalyst is present. The difference in reactivity between glyoxal and glutaraldehyde may be attributed to the fact that the carbonyl groups in glyoxal are more electron deficient than those in glutaraldehyde. The



**Figure 2** Wet strength of the paper treated with 2.0% (0.20 mol/L) glutaraldehyde without a catalyst after being soaked in water for 10 min, 2 h, and 24 h.

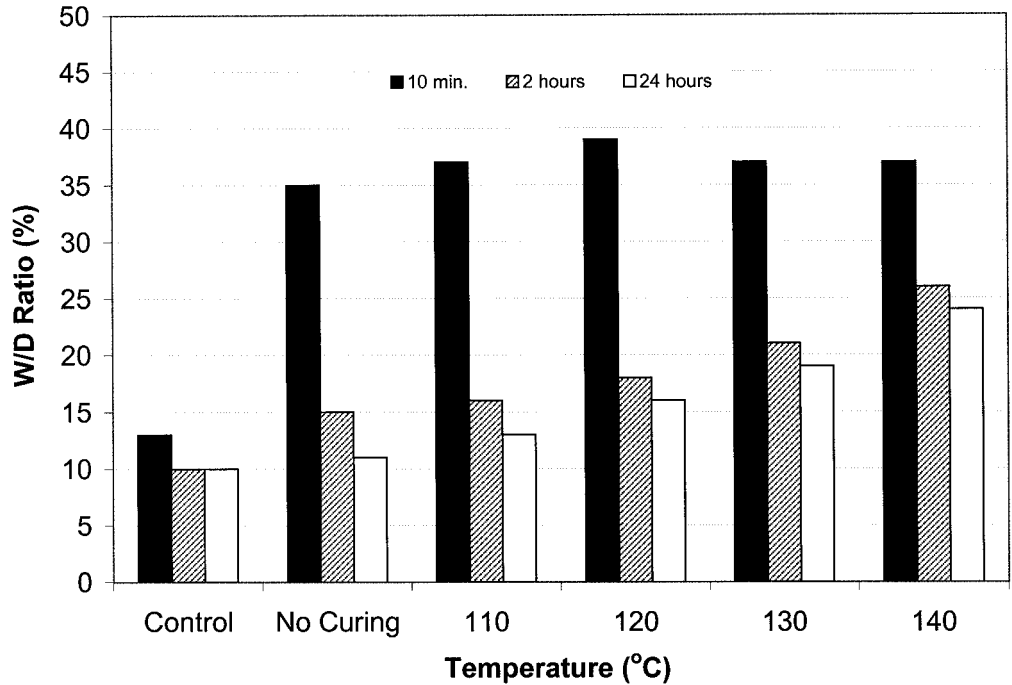
hemiacetals are easily formed and relatively stable for those aldehydes whose carbonyl group is strongly electron deficient.<sup>20</sup>

The dry properties of the paper treated by glyoxal and glutaraldehyde are shown in Table I. The data show no significant change in dry strength after the chemical treatment with both glyoxal and glutaraldehyde. However, the dialdehyde treatment does reduce the dry stretch, particularly in the case of glyoxal. The treatment by glyoxal causes much more reduction in stretch than that by glutaraldehyde. The high loss of stretch of the sample treated by glutaraldehyde and cured at 140°C may result from the unexpected experimental error or sample handling. The reduction of stretch is possibly a result of crosslinking between the cellulose molecules. The short linkage between cellulose molecules produced by glyoxal limits the mobility of cellulose molecules and thus reduces the stretch of the paper network. The reduced stretch is also consistent with the decreased folding endurance. The short and rigid crosslinkage reduces the flexibility of paper and diminishes the folding endurance. Consequently, paper treated with glyoxal showed more significant loss of stretch and folding endurance than that treated with glutaraldehyde.

#### Properties of the Paper Treated with Dialdehydes with $\text{Zn}(\text{NO}_3)_2$ as a Catalyst

The wet strength of paper treated with 1.16% (0.20 mol/L) of glyoxal and 0.758%  $\text{Zn}(\text{NO}_3)_2$  and cured at different temperatures is shown in Figure 3. The data indicate that the initial wet strength (after being soaked in water for 10 min) of the treated paper is independent of curing temperatures. The wet strengths were slightly lower than those of paper treated with glyoxal of the same concentrations without a catalyst, as shown in Figure 1. The wet strength after being soaked for 2 and 24 h, however, increased gradually as curing temperature was increased. The W/D ratio after a 24-h soaking increased from 13% at 110°C to 24% at 140°C. It means that the wet strength becomes more durable at higher curing temperatures. It is well known that aldehyde reacts with the hydroxyl group to form acetal under catalysis of Lewis acids.<sup>20</sup> Acetal is stable under neutral and alkaline conditions. The data show that high curing temperature increases reaction rate and shifts the reaction equilibrium to the direction of acetal formation.

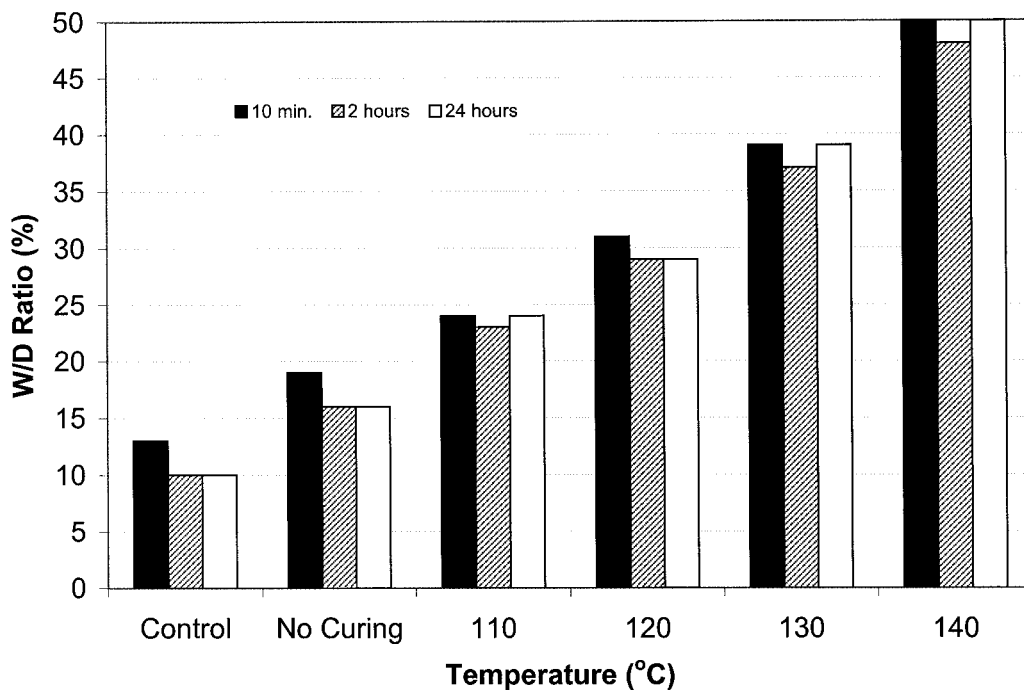
The wet strength of kraft paper treated by 2.0% (0.20 mol/L) glutaraldehyde and 0.758%  $\text{Zn}(\text{NO}_3)_2$  and cured at different temperatures is illustrated in Figure 4. There are two major dif-



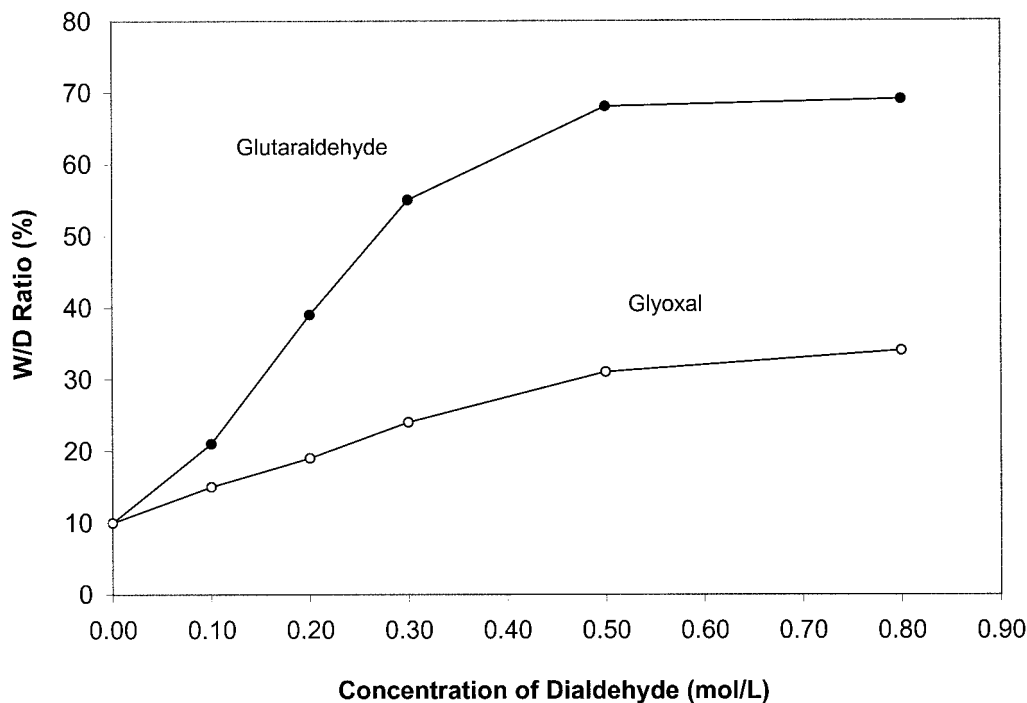
**Figure 3** Wet strength of the paper treated with 1.16% (0.20 mol/L) glyoxal and 0.758%  $Zn(NO_3)_2$  after being soaked in water for 10 min, 2 h, and 24 h.

ferences between glyoxal and glutaraldehyde. The first is that the wet strength of glutaraldehyde-treated paper is more durable than that of

glyoxal-treated paper at all curing conditions. For the glutaraldehyde-treated paper, its W/D ratios remained almost unchanged during the 24-h



**Figure 4** Wet strength of the paper treated with 2.0% (0.20 mol/L) glutaraldehyde and 0.758%  $Zn(NO_3)_2$  after being soaked in water for 10 min, 2 h, and 24 h.



**Figure 5** Wet strength (after being soaked in water for 24 h) of the paper treated with glyoxal and glutaraldehyde of different concentrations and  $\text{Zn}(\text{NO}_3)_2$ , and cured at  $130^\circ\text{C}$  for 1.5 min.

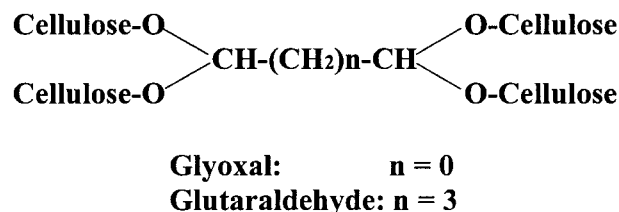
soaking in water. The second difference is that the wet strength increased steadily as the curing temperature was raised from  $110$  to  $140^\circ\text{C}$ . The W/D ratio after the 24-h soaking increased from 15% at  $110^\circ\text{C}$  to 50% at  $140^\circ\text{C}$  (Fig. 4), which is much greater in magnitude than that of glyoxal-treated paper, as shown in Figure 3.

The wet strength of the paper treated with a bifunctional aldehyde increased steadily as the concentration of the dialdehydes was increased (Fig. 5). At the same concentrations, glutaraldehyde is much more efficient than glyoxal for improving the wet strength of paper. When the concentration exceeded  $0.20$  mol/L, the glutaraldehyde-treated paper showed a W/D ratio more than twice that of glyoxal-treated paper. One also observes a leveling-off effect as the concentration reaches  $0.50$  mol/L (Fig. 5).

The significantly improved wet strength is possibly a result of the formation of acetal crosslinkages between cellulose molecules by glutaraldehyde. The acetal formation is strongly affected by steric and conformational factors.<sup>20</sup> As demonstrated in **Scheme 1**, one glutaraldehyde molecule may react with four cellulose hydroxyl groups by acetalization. For glyoxal, however, the two aldehyde groups are too close to each other to

allow them to reach cellulosic hydroxyl groups to form crosslinkages.

The dry properties of paper treated by 1.16% ( $0.20$  mol/L) glyoxal and 2.0% ( $0.2$  mol/L) glutaraldehyde are listed in Table II. The dry strength remained statistically unchanged. The stretch was significantly reduced, particularly for the glyoxal-treated paper. This phenomenon is similar to that of paper treated with polycarboxylic acids of small molecular sizes.<sup>3,4,7,8,10</sup> The reduction of stretch is shown as a function of wet strength (after a 24-h soaking) in Figure 6. At the same wet-strength levels, the paper treated with glyoxal showed more reduction in stretch than that treated with glutaraldehyde. The relatively higher loss of stretch may also be attributed to the shorter crosslinkage formed by glyoxal than that



**Scheme 1** Acetalization of cellulose by dialdehyde.



**Table II** Dry Properties of Kraft Paper Treated by 1.16% (0.20 mol/L) Glyoxal and 2.0% (0.20 mol/L) Glutaraldehyde with 0.758%  $\text{Zn}(\text{NO}_3)_2$  as Catalyst, Cured at Different Temperatures

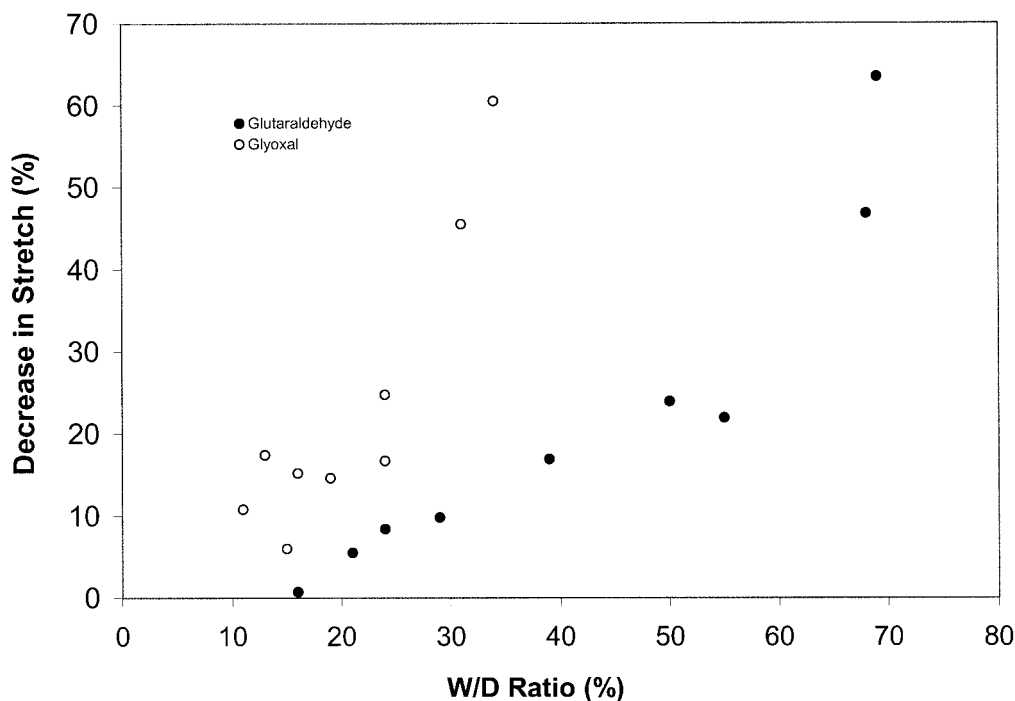
Dialdehyde	Temperature (°C)	Change in Dry Strength (%)	Change in Stretch (%)	Folding Endurance (times)
Glyoxal	No curing	1.6	-10.8	398
	110	3.2	-17.4	275
	120	1.6	-15.2	331
	130	1.6	-14.6	289
	140	-4.8	-16.7	174
Glutaraldehyde	No curing	1.6	0.7	474
	110	-1.6	-8.4	429
	120	4.8	-9.8	454
	130	4.8	-16.9	434
	140	-4.8	-23.9	231

formed by glutaraldehyde. Shorter crosslinkage is more effective in restraining the mobility of cellulose molecules, thus increasing the heterogeneity of the fiber network and brittleness of paper sheet.

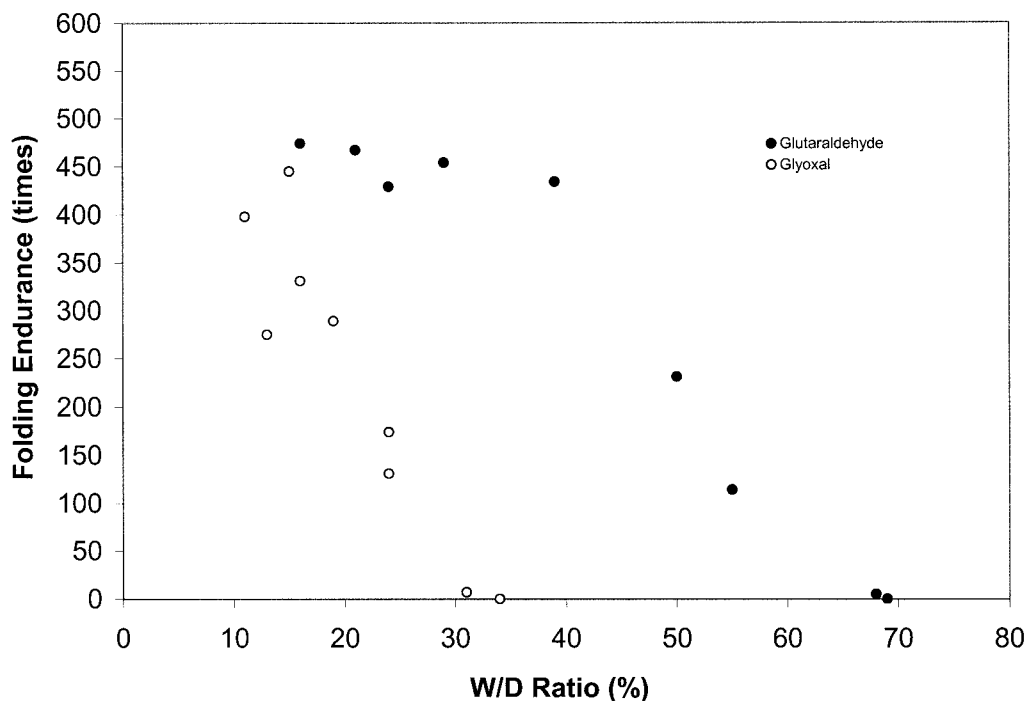
One disadvantage for wet strength agents of small molecular sizes is their adverse impact on the folding endurance of treated paper. The folding endurance of paper treated with glyoxal and glutaraldehyde is presented as a function of W/D in Figure 7. The glyoxal-treated paper reduced its

folding endurance to zero at a W/D ratio of approximately 34%, whereas the glutaraldehyde-treated paper still maintained its original folding endurance at a W/D ratio of approximately 40%. When the W/D ratio exceeded 40%, the folding endurance decreased gradually to zero at a W/D ratio of 68%.

Folding endurance is the ability of paper to resist breaking when folded under load. It is related to the flexibility of paper.<sup>21</sup> Lack of adequate foldability can be the result of lack of fiber length,



**Figure 6** Decrease in stretch as a function of W/D ratio (after being soaked in water for 24 h) of the paper treated with glyoxal and glutaraldehyde and  $\text{Zn}(\text{NO}_3)_2$ .



**Figure 7** Folding endurance as a function of W/D ratio (after being soaked in water for 24 h) of the paper treated with glyoxal and glutaraldehyde and  $\text{Zn}(\text{NO}_3)_2$ .

inadequate fiber bonding, or brittleness of paper. Crosslinking of cellulose increases the brittleness of paper sheet. The reasons that glyoxal-treated paper exhibits lower folding endurance than that of glutaraldehyde-treated paper are similar to those for the difference in loss of stretch, as discussed earlier.

## CONCLUSIONS

Glyoxal and glutaraldehyde show significantly different reactivity toward cellulose and thus their ability to improve wet strength of paper. Glyoxal is able to react with cellulose without the use of a catalyst and elevated temperatures to provide temporary wet strength to paper. The use of  $\text{Zn}(\text{NO}_3)_2$  as a catalyst improves the durability of the crosslinkage formed by glyoxal to some extent, but it also causes severe embrittlement and loss of folding endurance of the treated paper.

Without a catalyst, glutaraldehyde is not able to impart any wet strength to paper, even under elevated curing temperatures. In the presence of a catalyst such as  $\text{Zn}(\text{NO}_3)_2$ , glutaraldehyde is very efficient in crosslinking cellulose, thus improving paper wet strength. Glutaraldehyde is also able to retain stretch and folding endurance

of the treated paper as wet strength is developed. Compared to the paper treated with glyoxal, the paper treated with glutaraldehyde exhibits both a higher level of wet strength and a higher retention of its flexibility.

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