BONDING OF OXIDIZED CELLULOSE FIBERS AND INTERACTION WITH WET STRENGTH AGENTS

Raymond A. Young

Assistant Professor of Wood Chemistry, Department of Forestry
University of Wisconsin, Madison, WI 53706

ABSTRACT

A sulphite pulp was oxidized with dichromate in oxalic acid to introduce primarily aldehyde groups into the fibers. Compared to unmodified pulps, this method results in greater wet strength, which can be further enhanced by heat treatment. Addition of a high molecular weight carbonyl containing additives, such as dialdehyde starch, was found to have a synergistic effect on the wet strength. Although acetal and hemiacetal bonds may contribute to this wet strength, an additional crosslinking reaction has been postulated to more satisfactorily explain the experimental observations. An aldol condensation type reaction between adjacent carbonyl groups has thus been suggested as a primary reaction in the development of wet strength in pulp systems containing aldehyde groups. Confirmation of this theory, however, awaits model compound studies.

Keywords: Cellulose fibers, bonding, oxidization, wet strength.

INTRODUCTION

Techniques that result in oxidation of polymer surfaces have been utilized by numerous previous investigators to alter bonding behavior of polymer systems. Corona discharge in oxygen or air, for example, is known to introduce carbonyl groups at the surface of both hydrophilic cellulose (Goring and Suranyi 1967), and hydrophobic polypropylene (Sradal and Goring 1975) and polyethylene (Kim and Goring 1971) polymers; and these newly introduced functional groups have been implicated, at least in part, in the enhanced bondability of the respective materials.

Recent investigations by Johns et al. (1977, 1978) on the nonconventional bonding of wood have demonstrated that wood surfaces can be effectively bonded by "activating" the wood surfaces through oxidative techniques. A variety of oxidizing agents have been utilized and include nitric acid, peroxyacetic acid, hydrogen peroxide, hypochlorite, and perchlorates. Mechanisms of bond formation with oxidized wood, however, are quite complex and remain obscure.

Another important effect is the wet strengthening of paper and rayon sheets through prior oxidation of the fiber surfaces. Thus, Meller (1958) demonstrated that oxidation of a bleached sulphate pulp by periodic acid and by potassium dichromate (in oxalic acid solution) had a beneficial effect on wet strength of paper sheets made from the oxidized pulps. Both Luner et al. (1967a, b, c) and Meller showed that further oxidation with chlorous acid or reduction with sodium borohydride caused the wet strength to revert to the original low level. As a result of these observations, both investigators suggested that carbonyl groups are im-

portant to wet strength development of oxidized pulps. In terms of mechanisms, both hemiacetal and acetal linkages have been suggested to explain the wet strength increase (Mack and Reeves 1961).

It seems pertinent to establish the type of bonding responsible for wet strength as a result of oxidation if significant progress is to be achieved in the area of cellulose modification or additives for wet strength in paper. An attempt is therefore made in this investigation to gain further insight into the nature of bonding in oxidized systems by interacting oxidized pulp fibers with compounds containing different types of functional groups. A series of wet strength agents were used for this purpose because they are designed to be compatible with pulp systems, and their behavior with, and effect on, unmodified pulp systems are well established. Enhanced or synergistic effects on wet strength should be realized if specific reactions occur with the oxidized pulp. The three wet strength agents utilized were urea-formaldehyde resin, dialdehyde starch (DAS), and glyoxal. Specific mechanisms of wet strength development through each of the additives will be discussed.

EXPERIMENTAL

Wet strength agents

The urea-formaldehyde resin (Uformite 700) used in this study was a cationic type available as a 30% solids solution from the Rohm and Haas Company. The glyoxal was obtained as a 30% solids solution and was diluted to a 4% solids solution for tub sizing of the preformed sheets.

The anionic dialdehyde starch was prepared using the following procedure suggested by Hofreiter (1965): 20 g of a native pearl cornstarch (O.D. basis) was slurried by adding it to 233 ml of a solution containing 32 g of sodium periodate. The addition was made over a course of time sufficient to prevent excess temperature rises that would partially swell the granules and make recovery and washing difficult. The reaction was carried out in the range of 20–30 C for 7 h. The product was isolated by filtration and washed in distilled water until free of iodate. The product was given a final wash in acetone and after equilibration had a moisture content of about 10%. The identification of the formation of the dialdehyde starch was made by the appearance of a carbonyl band of 1730 cm^{-1} in the infrared spectrum of DAS as a KBr pellet.

Pulp preparation

An unbleached sulfite pulp was refined to 360 ml Canadian Standard Freeness in a Hollander-type laboratory beater. The refined pulp was then separated into two portions—one portion to have no further treatment and the second portion for oxidation.

A dichromate oxidation was performed on two separate batches of 40 g of pulp (O.D. basis) at 3% consistency (Luner et al. 1967a). The pulp was suspended in oxalic acid (final concentration 0.2 N) and then potassium dichromate solution was added (final concentration 0.1 N) with occasional stirring. The reaction was run for 45 min at room temperature. After the reaction, the pulp was washed rapidly with water on a glass filter until the original pulp color returned. The pulp was then treated with oxalic acid (0.2 N) for 20 h to remove traces of dichromate

and was given a final wash with distilled water. This oxidation method primarily introduces aldehyde groups at the C#6 position of the cellulose molecule with lesser amounts of carboxyl and other carbonyl groups also being introduced. Detailed analyses of the proportions of aldehyde and carboxyl groups produced by this technique have been published elsewhere by Luner et al. (1967a).

Handsheet preparation

The following procedure was carried out for both the oxidized and unoxidized pulps. The refined pulp was dispersed in a Waring blender and then diluted to a consistency of 0.15%. When urea-formaldehyde and dialdehyde starch wet strength agents were used, the pH of the slurry was adjusted to 4.5 ± 0.2 with dilute hydrochloric acid.

The urea-formaldehyde was added at the 3% level oven-dry pulp basis after the pH was adjusted to the proper working level (4.5). The DAS was first dispersed in water at 3% concentration in the presence of 15% sodium bisulfite (DAS weight basis) by cooking at 92 C for 45 min. Two separate pulp solutions were made up, one containing 10% alum (O.D. pulp basis) and the other without alum. The pH was then adjusted to 4.5, and the DAS was added at the 5% level (O.D. pulp basis) at a concentration of about 0.6%. After addition of the wet strength agents, the slurries were allowed to agitate for 5 min. Handsheets were then prepared according to Tappi standard, except that the pH of the slurry was again adjusted to 4.5 in the sheet mold. The sheets were then dried overnight under controlled temperature and humidity. All samples were given a 10-min cure in a forced air circulation oven at 105 C and allowed to recondition. The sheets that were not treated with wet strength agents were made similarly but with no pH adjustments.

One set each of the oxidized and unoxidized sheets, which were not treated with wet strength agents, were set aside for glyoxal treatment. These sheets were dipped in a 4% aqueous solution of glyoxal, rolled free of excess solution, and allowed to dry overnight under the controlled conditions. The treated sheets were then cured in a 105 C oven for 10 min and reconditioned. Although glyoxal and dialdehyde starch do not require curing, the heat treatment was performed to standardize the procedure.

Testing

The testing of the handsheets was done according to the procedures given in the Tappi Standard methods. For wet strength, the test strips and sheets were immersed for 15 min in distilled water at room temperature. With the sheets studied, this was found to be sufficient time for complete wetting. In the wet tensile test, the strips (twenty per condition) were removed from the water, blotted to remove excess water, and tested within one minute. The percent wet strength was obtained from the following equation:

$$\% \text{ Wet Strength} = \frac{\text{wet strength}}{\text{dry strength}} \times 100$$

DISCUSSION OF RESULTS

The mechanical properties of the unmodified and oxidized pulps, both with and without additives, are shown in Table 1. The changes were assessed on the basis of percent wet tensile strength factor.

TABLE 1. *Mechanical properties of unmodified and oxidized pulp.*

Treatment	Unmodified Pulp				Oxidized Pulp			
	Dry	Breaking Length (meters)	Wet	% Wet Strength	Dry	Breaking Length (meters)	Wet	% Wet Strength
Untreated	5,394 ± 265		207 ± 10	3.8	5,140 ± 257		390 ± 20	7.6
10-min cure								
at 105 C	5,404 ± 270		207 ± 10	3.8	5,250 ± 263		630 ± 32	12.0
U-F-treated	6,540 ± 327		2,427 ± 121	37.1	5,860 ± 293		2,193 ± 110	37.4
DAS-treated								
no alum	5,213 ± 262		260 ± 13	5.0	5,507 ± 275		1,313 ± 66	23.9
with alum	6,507 ± 325		947 ± 47	14.6	5,893 ± 295		1,553 ± 78	26.4
Glyoxal-								
treated	4,720 ± 236		1,747 ± 87	37.0	5,334 ± 267		1,900 ± 95	35.6

The dichromate oxidation method utilized in this investigation is known to produce large amounts of C#6 aldehyde groups (Meller 1958; Luner et al. 1967a, b). As depicted in Table 1 the oxidation decreases the dry strength of the sheets. This effect has been noted by previous investigators (Meller 1958; Luner et al. 1967a, b, c) and Luner et al. (1967a, b, c), also detected a corresponding decrease in sheet density with the introduction of the aldehyde groups. Oxidation by chlorite to form carboxyl groups or reduction with sodium borohydride to the original alcohol groups was found to result in a return of the density and most of the original dry strength properties (Meller 1958; Luner et al. 1967a, b, c). These results indicate that the introduction of oxidized groups, and especially aldehydic groups, decreases interfiber hydrogen bonding by reducing the ability of the fibers to come into close contact.

As depicted in Table 1, the 10-min heat treatment had essentially no effect on the wet strength of the unmodified pulp, while this same heat treatment gives a definite wet strength increase with the oxidized pulp, approximately 4% greater as assessed by tensile factor. Although it is possible that the cure treatment densified the oxidized pulp sheet, possible enhancement of specific chemical reactions with higher temperature is an equally plausible explanation for the effect of heat on the wet strength of the modified pulp. With curing, the paper dries and surface tension pulls the fibers closer together such that new fiber-to-fiber bonds may be formed. It appears that with the oxidized pulp the heat treatment has created bonds of greater strength or greater water resistance.

Urea-formaldehyde (U-F) treatment

Addition of urea-formaldehyde to the unmodified pulp gives a marked increase in the wet strength as expected (Table 1), with the average wet tensile strength at 37.1%. The cationic urea-formaldehyde has the advantage of giving high wet strength without the use of retention aids such as alum. Essentially the same wet strength is obtained with the oxidized pulp treated with U-F resin as shown in Table 1. The closeness of the wet strength values indicates that the oxidation procedure does not interfere with mechanisms of wet strength development with U-F resins. Apparently carbonyl groups do not enter into the curing reaction of the U-F resin.

Dialdehyde starch (DAS) treatment

The unmodified pulp was treated with DAS, both with and without the use of alum as a retention aid (Table 1). The wet tensile was only 5% without the alum, as compared to 14.6% with prior addition of alum. Obviously, the anionic DAS requires the retention aid to achieve reasonable paper wet strength. The same trend was noted for the wet burst strength. The wet strength achieved with DAS was considerably less than that obtained with the U-F resin; for tensile strength this was 37.1% versus 14.6%. Although retention values were not determined, it is possible that at least part of the difference between these two wet strength treatments is related to the poorer retention of the DAS. This conclusion is supported by the work of Mirza et al. (1964), who employed a cationic DAS and obtained wet strength equal to or greater than that obtained with U-F resin.

The mechanism by which DAS promotes wet strength appears to be quite different than with the U-F resin. As shown in Table 1, the wet strength obtained after treatment of the oxidized pulp with DAS was much greater than that obtained from the DAS-treated unmodified pulp. Also, the effect of alum was much less significant in the treatment of the oxidized pulp. Thus, without the use of alum as a retention aid, the wet tensile strength was 23.9%; while with the aid of alum, the wet tensile was only slightly greater, 26.4%. It was further noted that there was a synergistic effect on wet strength with the DAS-treated oxidized pulp. Thus, the wet strength obtained is greater than the additive effect of oxidation plus DAS (with or without alum) treatment.

The presence of carbonyl groups in the pulp obviously makes DAS more substantive to the pulp. It is possible that DAS incurs wet strength through the formation of fiber-to-fiber bonds, which are of greater strength or of greater water resistance. The enhanced wet strength also appears to be closely aligned with the presence of aldehyde groups as previously noted. Proposed mechanisms must therefore account for the interaction of carbonyl groups with each other or with other specific functional groups in the pulp to account for the good water resistance of the resulting sheets.

Glyoxal treatment

Because glyoxal lacks specific substantivity to cellulose, it must be applied to the web after sheet formation. This makes direct comparison with the other two types of wet strength agents somewhat more difficult. However, general interpretations are probably valid.

The glyoxal was applied as a tub size at a high level of addition, 14%. At this level, good wet strength was achieved for the unmodified pulp with the wet tensile at 37%. Eldred and Spicer (1963) proposed that both hemiacetal and acetal linkages were responsible for the wet strength of glyoxal-treated paper as shown in Figs. 1 and 2.

The oxidized pulp treated with glyoxal exhibited about the same wet tensile strength (35.6%). A significantly higher wet strength was expected with the glyoxal-treated oxidized pulp since the interaction of carbonyl groups appears to play a major role in the development of wet strength through treatment with DAS. Two explanations that would account for the absence of a synergistic effect on wet strength of the glyoxal-oxidized pulp system are: (1) the tub application of glyoxal acts only at the surface of the sheet and the glyoxal therefore does not
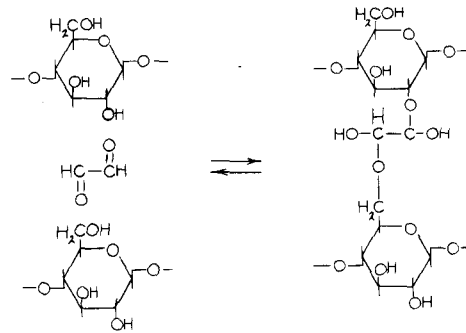
Fig. 1. Formation of hemiacetal linkage between glyoxal and cellulose.
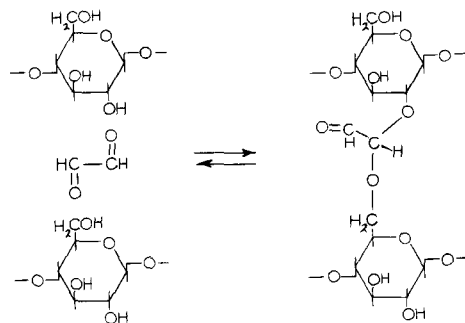

Fig. 2. Formation of acetal linkage between glyoxal and cellulose.

enter into extensive inter fiber-to-fiber bonding, and/or (2) the small glyoxal molecule is not large enough to "bridge" fibers as would be possible with the high molecular weight DAS.

Mechanism of wet strength development

There seems little doubt that the presence of carbonyl groups in cellulose pulp fibers enhances the wet strength of the final sheet, even with a loss in dry sheet density. One interpretation for the enhanced strength is that bonds of greater strength and water resistance result from oxidation of cellulosic fibers. The synergistic effect of dialdehyde starch addition suggests that the effect can be compounded by incorporation of structures that also contain carbonyl groups. There are a number of additional factors that must also be considered in interpretations of the effect of additives, such as ionic effects and improved retention due to physical adsorption. These alternate explanations have not been totally ruled out in this work, and they may contribute to some extent to the wet strength improvement. However, the cumulative evidence provided in this and previous investigations suggests that a more permanent, high enthalpy change type interaction would better account for the wet strength improvement through oxidation.

Postulation of hemiacetal or acetal linkages seems valid, and such bonds probably do affect the wet strength to some extent. However, the presence of such
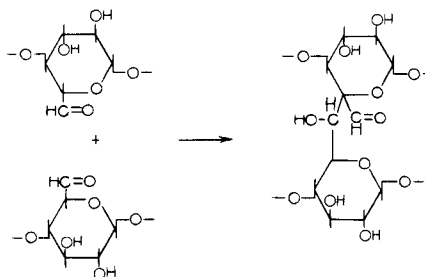
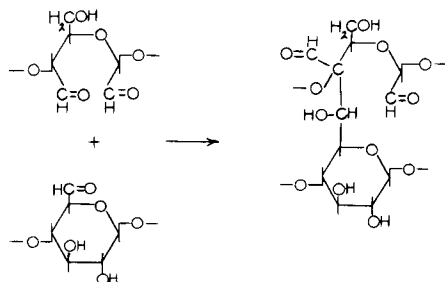Fig. 3.   Aldol condensation-type reaction with oxidized cellulose.

Fig. 4.   Crossed aldol condensation-type reaction between dialdehyde starch and oxidized cellulose.

bonds does not sufficiently explain the observation by Luner et al. (1967a) that the wet strength of oxidized pulps is decreased in alkaline solution but is unaffected by acidity. Such behavior is contrary to the anticipated behavior of covalent bonds of the hemiacetal type. The presence of high enthalpy change hydrogen bonds also does not explain the increase in the wet strength (Young et al. 1970) since hydrogen bonds are readily broken by water.

A more stable bond that involves the carbonyl group may be operative in the development of wet strength in oxidized pulps and synergistic wet strength development of oxidized pulps with high molecular weight carbonyl containing additives. A reasonable postulation to explain these observations is a reaction of two carbonyl groups in an aldol condensation. An aldol condensation-type reaction would occur with oxidized pulps, while a crossed aldol condensation reaction would be expected with oxidized pulps containing additives with carbonyl groups such as DAS. Aldol condensation reactions are catalyzed in both dilute acid and base—conditions that are met in most papermaking operations.

These reactions are depicted in Fig. 3, for the reaction of aldehyde groups in oxidized pulps and in Fig. 4, for the interaction of oxidized pulp with dialdehyde starch. The reaction in both cases is through the aldehyde group at carbon 6 of the glucose moiety, but involves carbons 2 or 3 in the interaction of DAS. The formation of these covalent bonds is one of the means of explaining the high wet strength at decreased sheet density. Confirmation of this hypothesis awaits further model compound studies under similar conditions.

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