Effect of carbohydrate degradation on zero-span tensile strength

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ABSTRACT: Depolymerization of wood carbohydrates in alkaline pulping by primary and secondary peeling is studied. Wood holocellulose fibers are pulped to varying times. The effect of the different modes of degradation on zero-span tensile strength is determined. Primary peeling is found to improve fiber strength at the expense of a higher yield loss. The relationship between pulp viscosity and fiber strength is greatly affected by the occurrence of primary peeling and by the presence of hemicellulose. This study shows that it is necessary to consider the effect of pulping conditions on each type of carbohydrate degradation in order to better understand the relationship between pulping variables and fiber strength.

KEYWORDS:Alkaline pulping, carbohydrates, degradation, depolymerization, hemicelluloses, peeling, pulp properties, zero-span tensile strength.

Pulp strength is determined by the initial properties of fibers in wood and by changes that occur during pulp processing. There are a multiplicity of factors that can affect pulp strength. While the key issues in making strong pulp are known, not all observations related to pulp strength are completely understood. Efforts to relate pulping conditions directly to strength have always resulted in models of limited usefulness which apply to a particular situation only. The fundamental relationships between physical/chemical changes in fibers during processing and pulp strength need to be studied. This paper presents results from a preliminary study of the relationship between pulp strength and carbohydrate degradation. The role of carbohydrate reactions as a connecting link between strength and pulping conditions is explored. In particular, the relationship between zero-span strength and pulp viscosity is analyzed with respect to different types of carbohydrate reactions in pulping.

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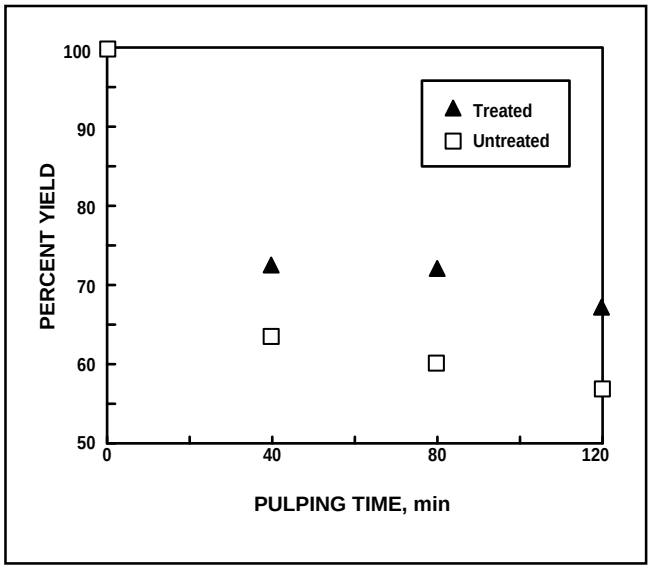
Carbohydrate degradation

Degradation of wood carbohydrates during alkaline pulping is usually accompanied by a reduction in strength and yield. Mechanistic and kinetic aspects of carbohydrate reactions in hot alkali have been studied earlier *(1-4)*. At least three distinct modes of carbohydrate loss are active in the alkaline pulping of wood.

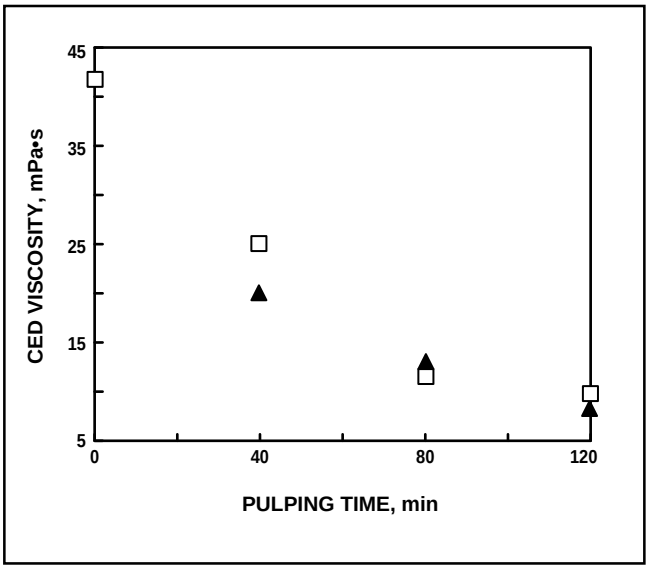
1. Rapid direct dissolution of low DP (degree of polymerization) hemicellulose in alkali
2. End-initiated depolymerization, also referred to as primary peeling
3. Chain-scission initiated depolymerization, also termed as secondary peeling.

Direct dissolution of hemicellulose leads to significant yield loss. The extent of dissolution depends on alkali concentration *(4)*. Primary peeling occurs from reducing end groups in wood carbohydrates that act as initiation sites. Successive glucose moieties are removed from the chain end until a competing termination reaction produces an alkali-stable end group. Yield loss depends on the initial number of reducing end groups. For Western hemlock, up to 18% of wood dissolves by primary peeling and direct dissolution *(5)*. Secondary peeling, on the other

1. Variation of yield with time for borohydride treated and untreated holocellulose



2. Viscosity vs. time for untreated and borohydride treated holocellulose



hand, is initiated by chain scission. The most important effect of this mode of degradation is a rapid decrease in DP of cellulose because of the chain split. Yield loss by secondary peeling is slower than for primary peeling.

Depolymerization mechanisms can range from pure endwise degradation to pure chain scission. Endwise degradation causes weight loss without a change in the number of chains, provided complete dissolution of chains does not occur. On the other hand, chain scission can lead to an increase in the number of chains with little or no weight loss. For wood carbohydrates, the nature of the degradation process lies between these two extremes. The relationship between pulp viscosity, yield loss,and strength is probably dependent on the extent to which each type of degradation occurs.

It is the aim of this study to explore the impact of primary and secondary peeling on the zero-span tensile strength of pulp. Zero-span strength is an index for fiber strength. The effect of each type of degradation on the relationship between fiber strength and viscosity is also investigated.

Experimental

Holocellulose fibers are prepared by peracetic acid delignification of wood shavings *(4)*. Delignified fibers are used in this study to avoid interference from lignin in strength measurements. Peracetic acid holocellulose has 0.2 meq/g of reducing end groups as compared to 0.15 meq/g in wood *(6)*. Part of the holocellulose is treated with sodium borohydride *(4)* to remove the reducing end groups.

Borohydride treated holocellulose and untreated holocellulose (hereafter referred to as BTH and UH, respectively) are pulped at 170°C in 50 g/L NaOH (liquor-to-wood ratio 9:1) for 40, 80, and 120 min. The heatup time is less than 5 min. The following analysis is performed for each sample.

1. Percent yield on holocellulose
2. CED viscosity (TAPPI Method T 230)
3. Wet zero-span tensile strength on a Pulmac tester with 40 g/m^2 strips and 5 replicates.

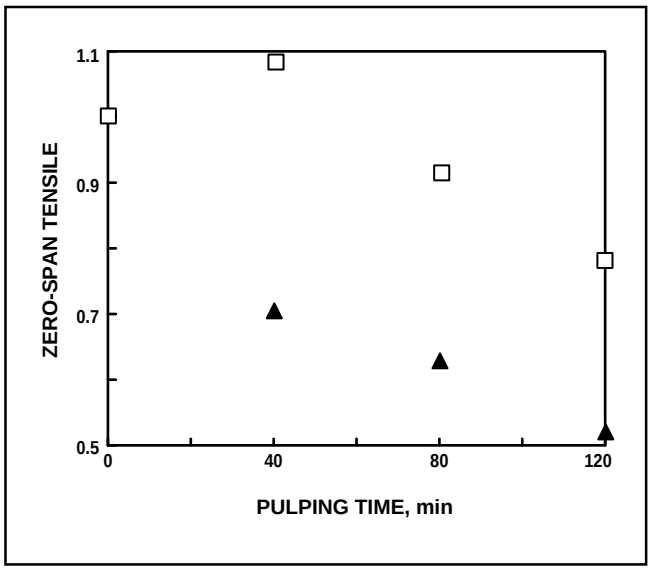
Results and discussion

Borohydride treated holocellulose does not undergo primary peeling during pulping because initiation sites are absent. This part of the holocellulose is used to study the impact of chain- scission initiated depolymerization alone. The untreated sample, on the other hand, undergoes depolymerization by both chain end and chain scission initiation. The observed effect on strength and other properties can, in this case, be attributed to both of these mechanisms. Because UH contains more reducing end groups than native wood, primary peeling is likely to be more pronounced for the experiments in this study than for wood pulping.

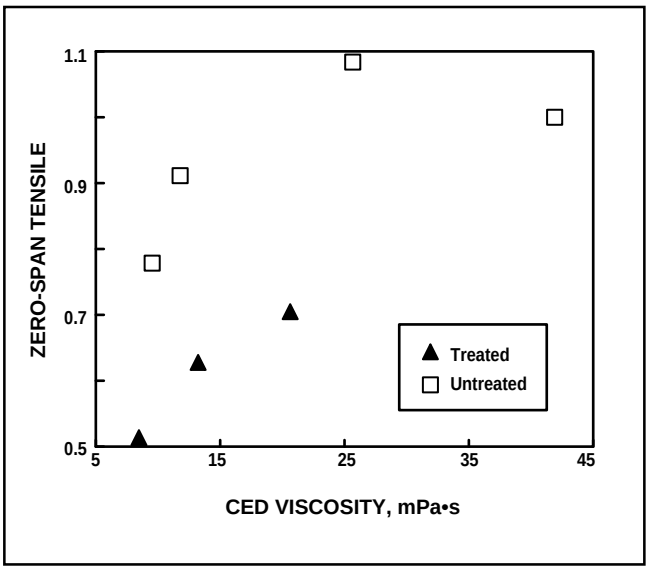
Pulping yield

In the initial phase of pulping, a large decrease in yield is observed mainly because of direct dissolution of low-DP carbohydrates and primary peeling. **Figure 1** shows that the initial yield loss of BTH (28% dissolved in 40 min) is smaller than that for UH (37% dissolved in 40 min). Rapid primary peeling in UH from the reducing end groups can account for the observed difference. As initiation sites for depolymerization are con-

3. Variation of zero-span strength with time for treated and untreated holocellulose



4. Relationship between viscosity and zero-span strength



sumed, primary peeling is retarded. After 40 min of reaction time, primary peeling does not have a significant influence and the rate of yield loss is similar for UH and BTH.

CED viscosity

Figure 2 shows that viscosity decreases continuously with reaction time for all pulped samples. The occurrence of primary peeling does not have a significant effect on pulp viscosity. In studies on hemicellulose degradation *(7)*, it has been shown that primary peeling at relatively low temperature does not cause a significant decrease in viscosity. Also, for primary peeling in cotton hydrocellulose *(3)*, the viscosity is found to be fairly constant with time. The observations in this study are in agreement with some of the earlier findings. Wood carbohydrates can dissolve by primary peeling without having a notable effect on pulp viscosity.

Zero-span tensile strength

Figure 3 shows the difference in zero-span tensile strength for the treated and untreated holocellulose. Consistently higher zero-span tensile strengths are obtained for UH samples (30–40% greater than for BTH samples) at all cookingtimes. A maximum in strength is observed for the UH sample as the strength increases in the initial phase where primary peeling and direct dissolution are active. In the later phase of the reaction, secondary peeling dominates and the strength decreases with time for both BTH and UH. These observations lead us to conclude that primary peeling probably has a beneficial influence on fiber strength. However, the increase in strength is not reflected by the viscosity as shown in Fig. 2. This is one instance in which viscosity and strength do not follow the same trend, and it shows clearly the limitation of viscosity measurement as an indicator of strength.

Primary peeling has been found to increase the number average DP, DP_n, of cotton hydrocellulose at a constant viscosity *(3)*. The increase in DP_n is explained by complete depolymerization of lower DP chains leading to a reduced polydispersity (DP_w/DP_n). Wood holocellulose possibly has a similar behavior. The initial increase in fiber strength for the untreated holocellulose sample shown in Fig. 3 may be attributable in part to an increase in number average DP, DP_n. It is clear from **Fig. 4** that UH has a significantly higher strength at the same viscosity. The effect of reducing end groups which are known to be present in wood holocellulose is therefore not entirely deleterious. In particular, stronger fibers can result at the expense of a higher yield loss.

Extraction with 5% NaOH

Viscosity and zero-span strength were also measured for each holocellulose sample after extraction with 5% NaOH at room temperature. It is found that dissolution in 5% NaOH is small for pulped samples, as might be expected. Consequently, viscosity and strength for the pulped samples is found to be largely unaffected by alkaline extraction. The original BTH before pulping shows 13.5% dissolution in 5% NaOH. Cold alkaline extraction of the original BTH simulates the effect of direct dissolution of low-DP hemicellulose during pulping. Primary and secondary peeling are absent in this case. Dissolution of hemicellulose is accompanied by a 15% drop in zero-span tensile strength and an increase in viscosity from 42 mPa.s to 58 mPa.s. This ob-

servation is from a single experiment and is therefore of limited reliability. However, the observed decrease in strength agrees with earlier work *(6, 8)* that reports a detrimental effect of hemicellulose removal on fiber strength. Selective removal of low DP carbohydrates in the absence of primary or secondary peeling increases the viscosity of holocellulose.

Cold alkaline extraction increases viscosity though the fiber becomes weaker. This is in contrast with the observed behavior for primary peeling where strength increases at a constant viscosity.

Conclusion

A preliminary study to investigate the effect of each type of carbohydrate degradation on pulp strength and viscosity has been conducted. This study points to the need to distinguish between the three modes of carbohydrate degradation, i.e., initial dissolution, primary peeling, and secondary peeling. Each of the three modes of degradation affects pulp properties differently. **Table I** summarizes the effect of each type of degradation on pulp properties. It can be expected that the relationship between different pulp properties (e.g., viscosity and strength) is also affected by the extent of each type of degradation.

Yield loss by primary peeling occurs rapidly in the initial phase of pulping. Somewhat surprisingly, fiber strength is found to increase at the same viscosity because of primary peeling (Fig. 4). A change in pulping conditions or in the pulping process that affects the extent of primary peeling is likely to alter the viscosity-strength relationship. The initial number of reducing end groups present in a particular wood species will partly determine yield loss by primary peeling and strength of the pulp produced. Direct dissolution and dissolution by primary peeling differ in their impact on strength. After the initial phase of pulping, secondary peeling is the dominant effect and it causes both strength and viscosity to decrease.

It is suggested that a stepwise approach be utilized to establish the dependence of pulp quality on process conditions. A more unified and generally applicable method can be developed by first predicting the effect of pulping on each type of degradation and then the effect of degradation on strength.

The viscosity-fiber strength relationship is by no means unique. We found the relationship to be significantly influenced by the occurrence of primary peeling and by the presence of hemicellulose. By studying the dependence of pulp strength on molecular weight distribution of wood carbohydrates, it might be possible to evolve a better way of indirectly estimating pulp strength. TJ

I: Effect of each type of reaction on properties. Increase ⇑, decrease ⇓, and small or no change ⇔.

Reaction	Viscosity	*Strength*
Initial dissolution	⇑	⇓
Primary peeling	⇔	⇑
Secondary peeling	⇓	⇓

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