INFLUENCE OF CARBOHYDRATE PHYSICAL STATE ON PULPING AND BLEACHING CHEMISTRY

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ABSTRACT

The viscosities of pulp, cotton linters, crystalline cellulose, and amorphous cellulose samples have been measured as a function of time during simulated soda and soda/AQ pulping, oxygen delignification, and hydrogen peroxide bleaching. Typical drops in viscosities for amorphous cellulose samples were 90%; while crystalline cellulose showed, under identical conditions, drops of 40% during simulated pulping and 0–10% during simulated oxygen delignification and hydrogen peroxide bleaching. Anthraquinone did not cause significant chain cleavage in amorphous cellulose. The addition of metals to oxygen/alkali reactions of amorphous cellulose gave trends similar to that observed in pulp reactions. The occurrence of very large molecular weight changes suggests that amorphous cellulose will be an ideal substrate for studying carbohydrate chain cleavage reactions under a variety of simulated pulping and bleaching conditions.

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INTRODUCTION

The goal of chemical pulping and bleaching of wood is to remove lignin without excessive degradation of the carbohydrate components. Unfortunately, current processes exhibit large carbohydrate losses, together with a reduction of the carbohydrate chain length. The latter leads to decrease pulp strength. Studies by Haas et al. in 1967[1] and by Gentile et al. in 1987[2] demonstrated that the cellulose physical state is more important than chemical termination mechanisms in preventing yield losses during alkaline treatments. The term carbohydrate "physical state" refers to whether the carbohydrate is (a) soluble in the medium and free to rotate, ring flip, etc., (b) insoluble but able to flex (i.e., amorphous cellulose), or (c) insoluble and fixed in space (i.e., crystalline cellulose).

We have been interested in the chemistry of cellulose chain cleavage, having examined the influence of restricted ring flipping,[3] insoluble cellulose models,[4] and the chemistry of amorphous and crystalline cellulose in typical pulping and bleaching reactions.[5,6] This report details the latter work and serves as an introduction for the ozone chemistry of amorphous and crystalline cellulose.[7]

RESULTS AND DISCUSSION

The samples examined were cotton linters and crystalline and amorphous cellulose that were prepared from cotton linters.[8,9] Linters are primarily crystalline cellulose, along with a small amount of the amorphous cellulose. The samples were reduced with sodium borohydride to minimize (peeling-type) yield losses when the samples are exposed to alkali.

Initially, both gel phase chromatography (GPC) and viscosity changes were used to estimate to the extent of carbohydrate chain cleavage reactions. The GPC method involved carbanilation of the carbohydrate hydroxyl groups with phenyl isocyanate, followed by determination of molecular weight distributions.[10] Viscosity measurements, which are much less time-consuming, provide *average* molecular weights, rather than *distributions*. In our case, the two methods correlated well (Figure 1); consequently, the faster method was most often used.

Non-Oxidative Degradations

Each cellulose sample exhibited a viscosity loss upon heating in 1 M NaOH at 150–152°C (Figures 2 and 3). After 2 h, the percent changes in
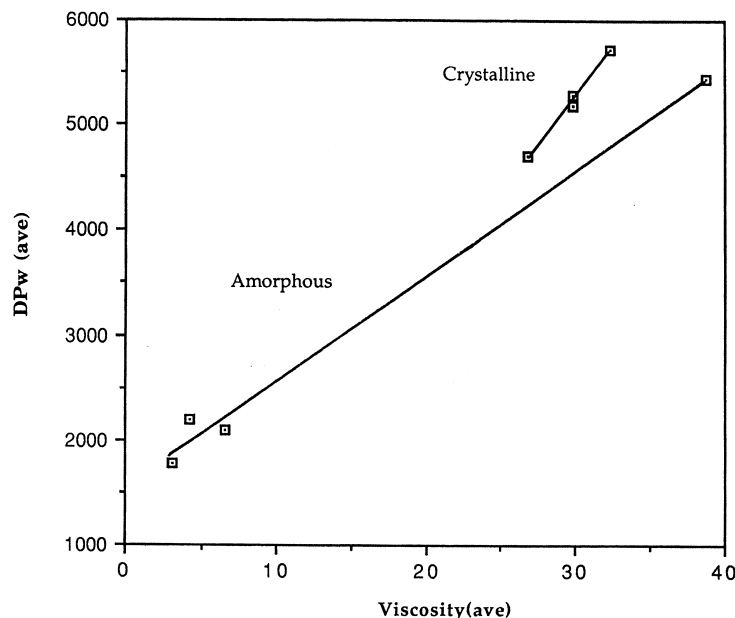
Figure 1. Correlation of DP_W and viscosities (cps) for cellulose samples that were treated with oxygen/alkali/cobalt.
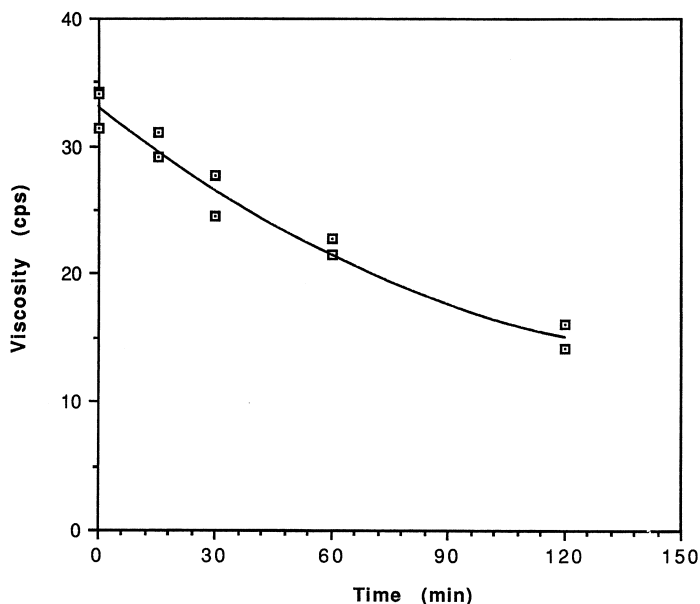
viscosities were: crystalline cellulose −50%, cotton linters −70%, and amorphous cellulose −90%. Most of the viscosity loss in the amorphous case occurred in the first 15 min; the slow drop after 15 min probably reflects the occurrence of crystallization. Gentile et al. report that amorphous cellulose converts to crystalline cellulose at 60–80°C in alkali.[2]

Anthraquinone (AQ) in alkali has been reported to cause oxidation of alcohol groups[11] and more rapid degradation of amylose[12] than comparable experiments done in the absence of AQ. In both cases, the AQ was interacting with a soluble substrate. Does such chemistry also occur with an insoluble carbohydrate? To answer this question, we briefly examined the interaction of AQ with amorphous cellulose. High levels of AQ were employed since the system is not set up to regenerate AQ, as is the case with the pulping of wood.[13] The temperature and time of the treatments were also lowered in order to decrease the amount of degradation and provide greater differences; a direct comparison to cotton linters was also performed. The data are presented in Table 1.

In 3 of the 4 samples, the cooks done in the presence of large levels of AQ had slightly bigger viscosity drops. Based on the limited data

collected, we conclude that AQ causes few chain cleavage reactions for insoluble carbohydrate substrates. This was the expected result for two reactants that are completely insoluble in alkali at high temperatures.[14] Our results do not rule out that AQ *species* cause chain cleavage reactions,

Figure 2. Viscosity changes as a function of time for heating crystalline cellulose at 150°C in 1 M NaOH.

Table 1. Cellulose Viscosities (cps) after Heating in 1 M NaOH with/without AQ[a]

Linters, 148–150°C, 60 Min			Amorphous, 135–137°C, 10 min		
Starting viscosity	No AQ viscosity	AQ viscosity	Starting viscosity	No AQ viscosity	AQ viscosity
64.0	27.5 (27.1–28.0)[b]	29.3 (28.2–30.5)[b]	34.8	16.2 (14.0–18.0)[b]	14.6 (13.9–15.5)[b]
67.2	35.8 (32.5–38.4)[c]	32.4 (31.3–33.4)[c]	51.9	24.9 (21.7–26.8)[c]	22.1 (18.0–24.1)[c]

[a]Anthraquinone moles equivalent to the moles of glucose units in the cellulose.
[b]Range for triplicate sample cooks to give the average listed above.
[c]Range for six cooks to give the average listed above.
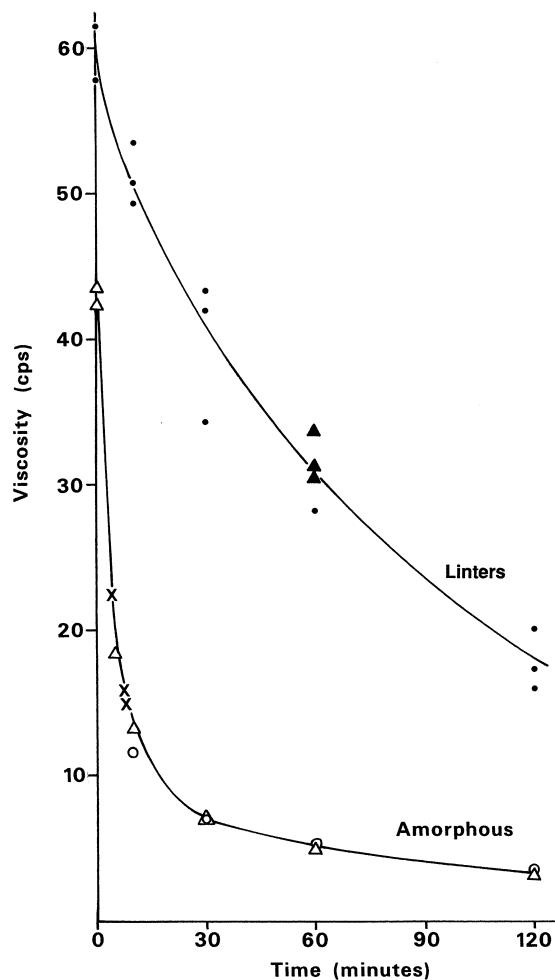
Figure 3. Viscosity changes as a function of time for heating cotton linters and amorphous cellulose at the 152°C in 1 M NaOH. The different symbols for each curve represent determinations done on different days.

since anthrahydroquinone radical anion, a soluble intermediate oxidation state of AQ present during pulping,[13] may be a carbohydrate oxidizer.

A mild alkaline degradation of amorphous cellulose, which was per-formed in the presence of 0, 25, 50, and 100 mg of NaCl, gave nearly the same viscosity values as a function of time. Thus, increasing the ionic

strength (dead load) of the system appeared to have little effect on the extent of carbohydrate chain cleavage.
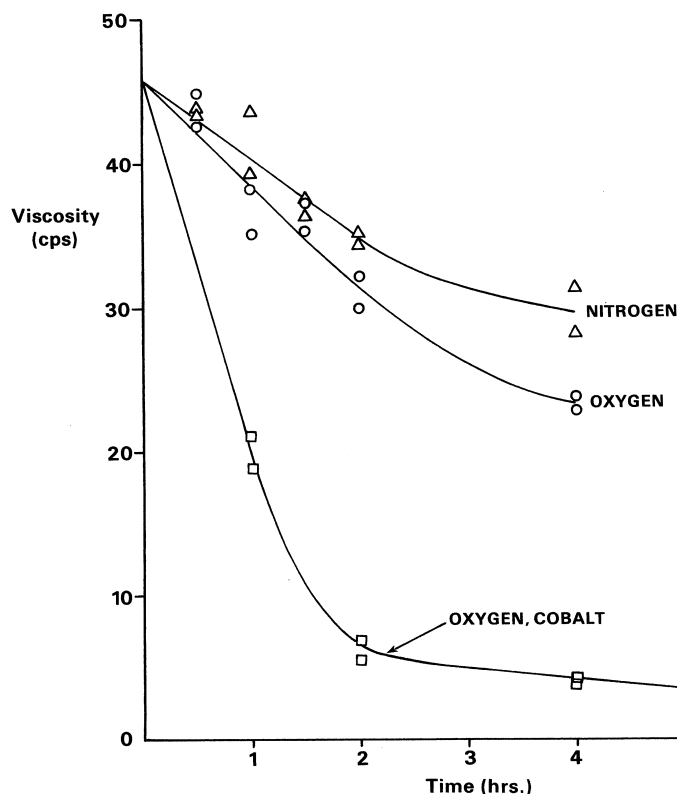
Degradation by Oxygen/Alkali

The viscosities observed when heating amorphous cellulose at 100°C for different time periods in 0.1 M NaOH under selected conditions are given in Table 2 and Figure 4. The presence of oxygen led to a more rapid viscosity loss, especially in the case of cobalt. The other metal tested, magnesium, had a stabilizing effect (Table 2). The amorphous cellulose viscosity loss was not, however, completely retarded in both the oxygen and nitrogen control cases in the presence of magnesium. Surprisingly, the combination of magnesium and cobalt caused a greater loss in viscosity than when cobalt was used alone (Table 2).

The two metals chosen for study, cobalt and magnesium, are known to cause chain cleavage reactions in the presence of oxygen in models[15] and stabilized pulps,[16–17] respectively. The results observed here are parallel to these known properties, but are unusual in a few aspects. The data indicate that the magnesium protecting effects are not lasting and apparently are not

Table 2. Viscosities Changes Associated with Heating a 46-cps Amorphous Cellulose at 100°C in 1 M NaOH with/without Oxygen and Certain Metals

| Gas	Metal	Viscosities (cps) – Average (Duplicates)			
		1 Hour	2 Hour	4 Hour	6 Hour
N_2	–	41.5 (39.2, 43.7)	34.9 (34.6, 35.2)	29.9 (31.5, 28.2)	–
O_2	–	36.7 (38.2, 35.1)	31.1 (29.9, 32.2)	23.3 (23.7, 22.8)	–
N_2	1% Mg	39.5 (38.3, 40.6)	35.1 (35.2, 35.1)	31.7 (32.2, 31.1)	28.0 (29.3, 26.7)
O_2	1% Mg	36.9 (36.3, 37.5)	38.5 (41.5, 35.5)	32.8 (32.9, 32.7)	26.2 (25.3, 27.0)
N_2	0.308 µmole Co	35.6 (35.6, 35.7)	31.1 (29.4, 32.7)	21.7 (21.5, 22.0)	20.5 (21.5, 19.5)
O_2	0.308 µmole Co	20.0 (18.9, 21.1)	6.2 (6.8, 5.5)	3.9 (4.2, 3.6)	3.2 (3.5, 2.9)
O_2	1% Mg and 0.308 µmole Co	8.0 (7.5, 8.4)	4.0 (4.1, 3.9)	3.1 (2.9, 3.2)	–

Figure 4.   Viscosity variations as a function of time following duplicate treatments of amorphous cellulose at $100°C$ in 0.1 M NaOH with the indicated chemicals; cobalt sulfate was 0.308 mole/100 g sample.

helpful in the presence of cobalt; the Mg-Co interaction was unexpected.[18] Also, cobalt promoted degradation in the nitrogen control case, possibly indicating that simply bubbling nitrogen, instead of oxygen, through the solution did not give a completely oxygen-free condition.

The response of the amorphous cellulose-oxygen-alkali system to different levels of cobalt is shown in Figure 5. The cobalt appears to have little effect below a level of 0.162 mole of $CoSO_4$/100 g of amorphous cellulose. Above this level, there was a rapid drop in viscosity with increasing amounts of cobalt.

A comparison of the reactivities of cotton linters, kraft pulp, and amorphous and crystalline cellulose samples towards oxygen at $100°C$ in
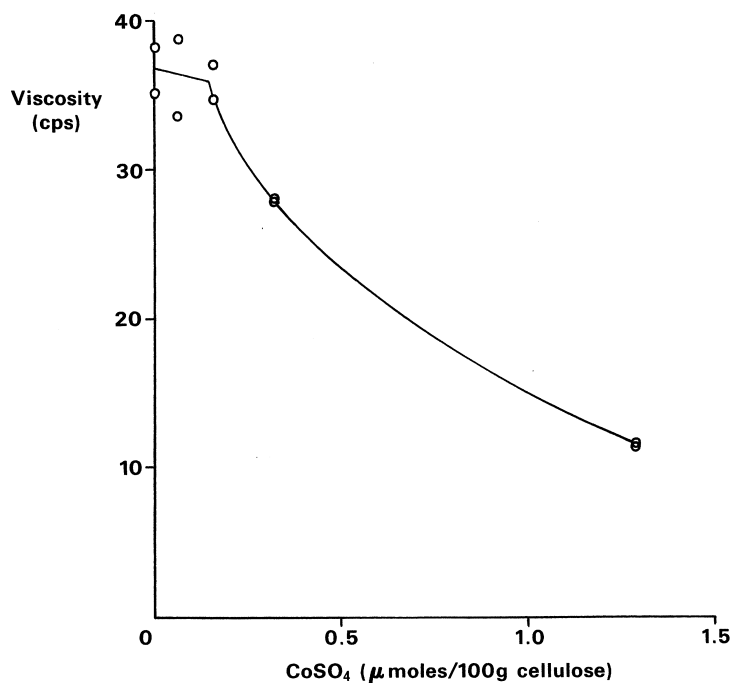
Figure 5. Variations in amorphous cellulose viscosities with different levels of cobalt for samples heated at 100°C for 1 h in 0.1 M NaOH; duplicates were done at each cobalt level.

alkaline solutions that contained cobalt is shown in Figures 6 and 7. After 4 h, the viscosity of the linters is roughly one-half that of the starting viscosity, while in the amorphous case it is one-tenth. The initial rapid drop in viscosity for the linters was likely due to the amorphous cellulose present in the sample. The viscosity losses for a cellulose sample towards oxygen-alkali-cobalt were slight.

As seen in the figures, there is a dramatic difference in reactivity between the crystalline and amorphous cellulose. The viscosity profiles for the amorphous cellulose and pulp samples in Figures 6 and 7 are not identical; the reasons for this are not clear. Two different amorphous cellulose samples were used to generate the data in the figures; possibly one of the samples still contains a small amount of crystalline material. Also, small differences in impurities between runs can have an impact on bleaching reactions that are very sensitive to metals.
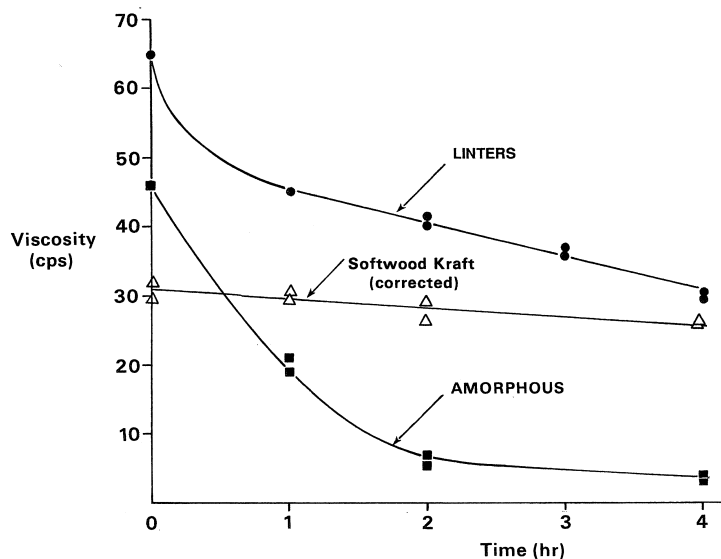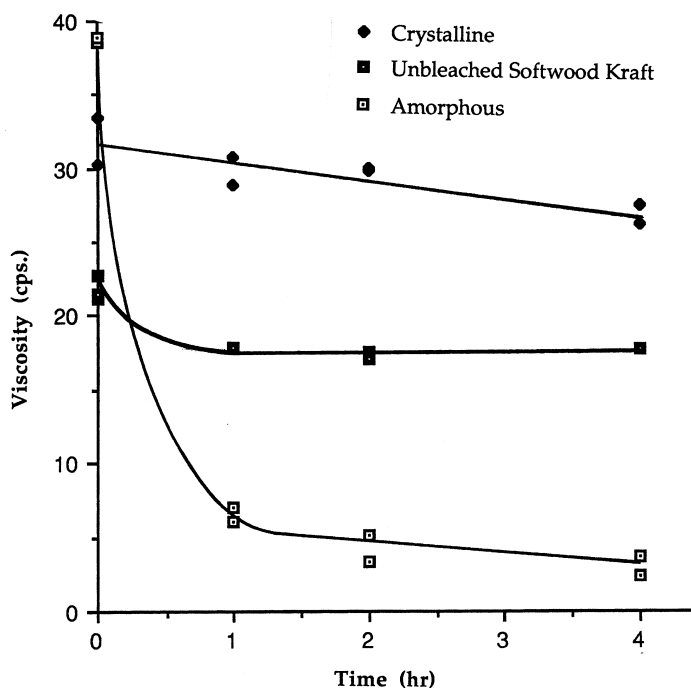
Figure 6. Viscosity variations as a function of time for treatment of different cellulose samples with oxygen, 0.1 M NaOH, 0.323 μmoles Co/100 mg sample at 100°C; duplicates were done in most cases.

The viscosity losses for a bleached kraft pulp under the oxygen-alkali-cobalt conditions were small. The data in Figure 6 show a straight-line response for the kraft pulp, with a slope similar to crystalline cellulose; the absolute values of the viscosity determinations were not, however, available in this case due to a wrong, but consistent sample dilution. The data in Figure 7 show that the kraft pulp lost some viscosity initially and then became stable. Oxygen-alkali-cobalt treatment of a new unbleached kraft pulp produced no loss in viscosity over 4 h. Obviously, kraft pulps are relatively stable to the conditions and must be fairly free of amorphous material, which is rapidly degraded.

Degradation by Hydrogen Peroxide

The results of several alkaline hydrogen peroxide reactions are given in Table 3. As expected, the viscosity drop of amorphous cellulose increased with increasing peroxide application. Also, the addition of magnesium and silicate stabilized the amorphous cellulose towards extensive degradation. Copper also seemed to have a small stabilizing effect; however, this effect is

Figure 7. Viscosity variations as a function of time for treatment of different cellu-
lose samples with oxygen, 0.1 M NaOH, 0.323 µmoles Co/100 mg sample at 100°C;
duplicates were done in most cases.

Table 3. Viscosities Values After Treating a 46-cps, 12% Consistency Amorphous
Cellulose Sample with Different Levels of Hydrogen Peroxide and Metal Salts at
60°C for 1 h, and an Initial pH of 11[a]

Peroxide (%)	Alkali (%)	Additive	Viscosity (cps) duplicates
–	0.033	–	44.5, 43.2
0.2	0.10	–	12.3, 10.7
0.4	0.15	–	7.1, 7.8
1.0	0.39	–	4.4, 4.5
0.4	0.14	0.37 M CuSO$_4$	13.8, 10.1
0.4	0.13	0.2% MgSO$_4$ and 4.5% Na$_2$SiO$_3$	39.8, 35.1

[a]All reaction samples were basic at the conclusion of the heating period.

probably related to copper-induced decomposition of the hydrogen peroxide, which would lower the level of the peroxide available for reaction.[19]

A time study of the reaction of crystalline, amorphous, and cotton linters cellulose with 0.2% hydrogen peroxide at 50°C produced the data shown in Figure 8. The initial rapid 10% drop in viscosity in the crystalline case was not seen in a subsequent study with a new crystalline sample; here the viscosity showed no loss with time over a 0–40 min period. There is some uncertainty as to which set of data more accurately reflects the true response of crystalline cellulose towards peroxide; the data in Figure 8 imply that our first sample of crystalline cellulose may have had some amorphous cellulose
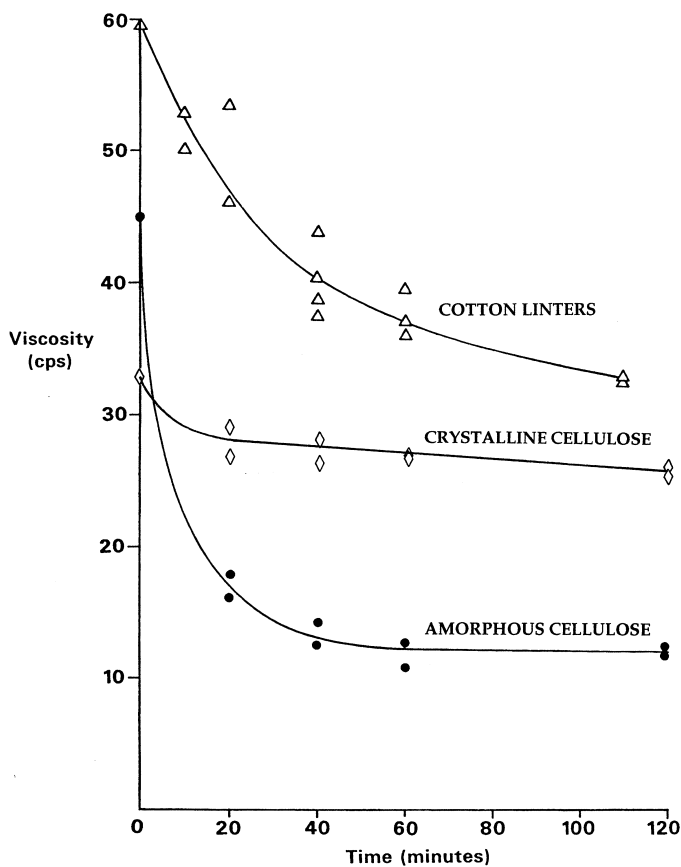
Figure 8. Viscosity variations as a function of time for the treatment of 12% consistency cellulose samples with 0.2% H_2O_2/0.10% alkali at 50°C.

present.Our data clearly show that, in the absence of stabilizers, hydrogen peroxide causes severe chain cleavage of amorphous cellulose and little, if any, cleavage of crystalline cellulose.

CONCLUSIONS

Our studies establish that there are large reactivity differences between crystalline and amorphous cellulose during simulated pulping and bleaching. Reactions that cause harmful carbohydrate chain cleavage are greatly amplified in the case of amorphous cellulose; crystalline cellulose is basically unreactive. Because reactivity is closed tied to the physical state, the chemistry displayed by wood and pulp might simply reflect reactions occurring with only the amorphous components in the pulp.

EXPERIMENTAL

Cellulose Samples

Hercules, Inc. provided cotton linters to us; initially we used grade ER4500 and later grade 351. Amorphous cellulose was prepared by dissolving 2.5-g of dried hydropulped cotton linters in $DMSO/Et_2NH/SO_2$ and precipitating into methanol/water.[9] Mild acid hydrolysis of cotton linters for an extended period removes any amorphous material, providing crystalline cellulose.[8] Reactions were first performed to define the proper conditions. Ten-gram samples were soaked in 2.5 L of 0.25 N HCl for 2, 4, 8, and 24 h at room temperature. The samples were washed with $(4 \times 500\,mL)$ distilled water, or until acid-free, next washed with $(2 \times 125\,mL)$ 5% NH_4OH and $(5 \times 500\,mL)$ distilled water, and then freeze-dried. The sample viscosity leveled out after 8 h. In general, a 24-h treatment time was employed. There was a drop in viscosity with each operation: linters at 60 cps viscosity $\rightarrow$ 33 cps crystalline cellulose and 45 cps amorphous cellulose.

A sodium borohydride reduction step consisted of mixing a 10-g sample of cellulose with 1.5 L of 0.25 N $NaBH_4$ on a shaker for 2–3 days. The sample was washed with 2 L of 0.1 N NaOH and $(6 \times 1\,L)$ distilled water to a neutral pH and then freeze-dried.

The amorphous and crystalline and cellulose samples were analyzed by x-ray diffraction. Amorphous cellulose has a very broadband diffractogram, while crystalline cellulose has one large sharp signal separated from two closely spaced, semi sharp smaller signals.[20] The pulp used in our studies was a 38%-consistency unbleached loblolly pine pulp of kappa number 32.

Alkali Reactions at 150°C

Reaction mixtures were prepared under a nitrogen atmosphere in a glove bag with NaOH solutions using 30% ultra-pure NaOH in deionized, deoxygenated water in an attempt to minimize metals and oxygen in the solution. The cellulose samples and anthraquinone, where used, were weighed into small metal tube reactors inside a glove bag. The reactors, which were warmed and evacuated in a desiccator prior to use, were sealed before removal from the glove bag. The reactors were rotated in a constant-temperature oil bath over a specified period, generally at a temperature of 135–150°C. The temperature occasionally varied by 2°C for what were intended to be identical cooks. The tubes were cooled and opened and the contents filtered and washed extensively with deionized water. Viscosities were determined on 40 mg of dry samples in 80 mL of solutions (0.5%) using the TAPPI standard T230 method.

Oxygen–Alkali Reactions

Numerous trials were conducted to determine the best way to conduct oxygen-alkali reactions on a small scale; the following procedure worked well for us. For this and other procedures described below we used sodium hydroxide solutions that were prepared with 30% ultra-pure NaOH in deionized water in an attempt to minimize metals in the solution. Approximately 2 L of 0.1 N NaOH solution was placed in a 4-L beaker and the level of the water marked on the beaker. As the water level dropped during the experiment, boiling water was added to keep the alkali level constant. For experiments with metal salts, we added specific concentrations of metals at this point. Oxygen was delivered through a gas dispersion tube that was fitted, by means of a rubber stopper, into the middle of a desiccator plate (a flat ceramic plate with numerous holes). The plate, which was placed near the bottom of the beaker, helped spread the gaseous bubbles throughout the solution. Cellulose samples (100 mg) were weighed into crucibles that had sinter-glass on one end and were open on the other end. The open end was covered with a 160×160-mesh polypropylene cloth that was stable at high temperature. The opening was secured by a strip of polypropylene.

The NaOH solution was brought to a boil and either oxygen or nitrogen was delivered through the dispersion tube, causing generous bubbling throughout the beaker. The crucibles containing the cellulose samples were pushed under the water level to begin the reaction. Crucibles were removed at specific time intervals, drained of their alkali solution, submerged briefly in distilled water to dilute the residual alkali, and the polypropylene cloth

removed. The reacted cellulose was washed several times with distilled water, transferred to weighed vials, and freeze-dried. Dry weights were recorded and viscosities determined on 40-mg samples at 0.5% TAPPI standard T230. Select samples were also analyzed by GPC by a method described by Schroeder and Haigh.[10]

Peroxide Bleaching Reactions

Hydrogen peroxide solutions were prepared from a 31% stock solution and titrated to determine an accurate peroxide level. A combination of 0.05 and 0.001 N NaOH solutions were used to give a pH of 11.0 and a consistency of 12%. An alkaline peroxide solution (0.833 mL) was mashed into a 100-mg cellulose sample inside a vial. The vial was sealed with a screw cap and Teflon septa, placed in a lead-foil holder, and submerged in a 50°C oil bath. After a specific time period, the vial was removed and cooled. The sample was washed several times with distilled water, quantitatively transferred to a weighed vial, and freeze-dried. The dry weight was recorded and viscosities determined on 40-mg samples at 0.5% TAPPI standard T230.

ACKNOWLEDGMENTS

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