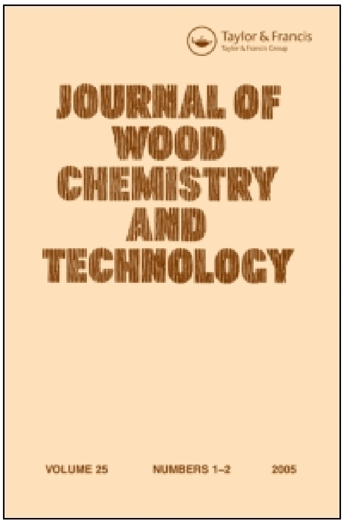

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NOTE

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INTRODUCTION

Alkaline depolymerization of cellulose occurs by successive endwise elimination of monomer units (peeling reaction)[2–4] and random cleavage of internal glycosidic linkages.[4,5] The cellulose molecule becomes stable to peeling by formation of an acidic end group (chemical stopping reaction).[4,6,7] Both the peeling reaction and random cleavage of glycosidic linkages are moderated by the degree of structural ordering of the cellulose chains.[8–10]

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In sodium hydroxide, cellulose undergoes peeling at a much faster rate than the competing stabilization reaction.[11] However, divalent metal hydroxides are known to greatly enhance the stopping reaction relative to the peeling reaction.[12,13] Strontium hydroxide was found to be particularly effective in this respect and thought to be capable of converting almost all of the reducing end groups to acidic end groups.[12] Consequently, treatment of cellulose with 1.0 M strontium hydroxide (100°C, 10 h) was employed in one study to as a means of indirect measurement of reducing end groups.[9] The observed increase in acidic end groups was assumed to approximate the initial reducing end group content of the cellulose.

While testing a new method for determination of reducing end groups,[10] we used the same strontium hydroxide treatment for comparative purposes. In this article we report the results of that study.

RESULTS AND DISCUSSION

Two cellulose substrates were used, a fibrous cotton hydrocellulose[10] and its amorphous analog, prepared through regeneration of the hydrocellulose from its solution in dimethylsulfoxide-paraformaldehyde.[14,15] Both substrates were treated with 1.0 M aqueous strontium hydroxide for 10 h at 100°C. Yield, reducing end groups, acidic end groups, DP_N, and hydroxyl accessibility data for the substrates before and after the reactions are presented in the Table 1.

Peeling lengths of 16 and 19 were estimated for the fibrous and regenerated substrates, respectively, from the ratio of the yield loss to the mole fraction of acidic end groups formed (Table 1). Since both peeling lengths are considerably less than those observed in similar sodium hydroxide degradations (>100),[10] the strontium hydroxide did enhance acidic end group formation (stopping) relative to the peeling reaction.

T1

However, the strontium hydroxide also caused significant increases in the total end group contents of both of the cellulose substrates (Table 1). The number of end groups in the fibrous hydrocellulose increased by 47%, while the number in the amorphous, regenerated hydrocellulose increased by 85%. The difference in the end group changes between the two substrates roughly reflects the difference in the hydroxyl accessibilities of the two samples. The increase in the total number of end groups in the cellulose substrate indicates that, although the strontium hydroxide did enhance stabilization (stopping reaction) toward the peeling reaction, it also caused significant random chain clea-

Table 1. Data from cellulose degradation in strontium hydroxide.[a]

	Fibrous hydrocellulose		Amorphous hydrocellulose	
	Initial	Degraded	Initial	Degraded
Yield loss	—	0.029	—	0.121
Reducing end groups	0.00126	0.00057	0.00345	0.00083
Acidic end groups	0.00110	0.00290	0.00099	0.00739
Total end groups	0.00236	0.00347	0.00444	0.00822
DP_N[b]	420	280	230	110
Hydroxyl accessibility (%)	50	49	98	91

[a] End groups are reported as a mole fraction of the cellulose monomer units in the initial substrate.
[b] DP_N was calculated as the inverse of the total end groups times the yield.

vage to occur in the cellulose substrates. The relative rates of the random chain cleavage in the two substrates were approximately the same as the relative hydroxyl accessibility of the substrates.

CONCLUSIONS

The utilization of a strontium hydroxide treatment of cellulose to estimate reducing end groups could involve several potential sources of serious error. First, all reducing ends are not converted to acidic end groups, as was assumed,[9] by the treatment (Table 1). Second, random chain cleavage induced by the alkaline reagent can lead to additional end groups, some which are converted to acids, and thereby yield a high value for the initial reducing end group content. Third, inaccessible reducing end groups would not be evaluated by this approach without first converting the substrate to a highly accessible (amorphous) form.

EXPERIMENTAL

Cellulose Substrates

Raw cotton fiber was purified by extraction with chloroform; 95% ethanol; and boiling, oxygen-free sodium hydroxide.[11] Fibrous hydrocellulose was made by treating the purified cotton fiber with 1.0 M HCl at 40°C for 20 h. The fibrous hydrocellulose was washed with distilled water (until neutral) and then freeze-dried. Amorphous hydrocellulose was prepared by regenerating the hydrocellulose from a dimethylsulfoxide-paraformaldehyde solution of the fibrous hydrocellulose[14] in 0.2 M sodium alkoxide in methanol:2-propanol (1:1, Vol.).[15] The regenerated cellulose was successively washed with 0.2 M sodium alkoxide in methanol:2-propanol (1:1, vol), methanol, 0.1 M HCl, and distilled water (3 ×), and then freeze-dried. Both substrates were stored under anhydrous conditions.

Strontium Hydroxide Reactions

Hydrated strontium hydroxide was prepared by crystallization of chemically-pure grade strontium hydroxide (Amend Drug Co.) from distilled water.

The cellulose substrate (0.400 g o.d.), hydrated strontium hydroxide (10.1 g), and oxygen-free, distilled water (34.8 mL) were loaded into tubular 316 stainless steel reaction vessels while under a nitrogen atmosphere. The vessels were sealed and rotated end-over-end (ca. 3 rpm) in a 100°C oil bath for 10 h. The reactors were cooled to 20°C in an ice bath and the cooled reaction mixtures were neutralized with 1 M HCl. The degraded hydrocelluloses were washed with 0.1 M HCl (300 mL) and distilled water (until neutral), and then freeze-dried.

Analytical Methods

Cellulose acidic end groups were determined by methylene blue absorption.[16,17] Reducing end groups were measured on regenerated samples[15] using an adaptation of a sodium borohydride-^{3}H reduction method developed by Richards and Whelan.[16,18] Cellulose hydroxyl group accessibility was obtained by the deuterium exchange technique (D_2O) of Rouselle and Nelson,[19] with the exchange time extended to 12 h.

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