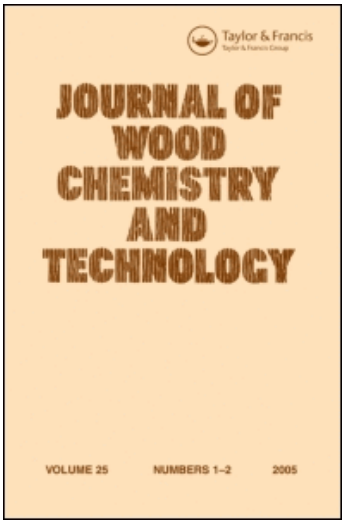

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Leland R. Schroeder[a]; Victor M. Gentile[a]; Rajai H. Atalla[a]
[a] The Institute of Paper Chemistry, Appleton, Wisconsin

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NONDEGRADATIVE PREPARATION OF AMORPHOUS CELLULOSE

Leland R. Schroeder[1], Victor M. Gentile, and Rajai H. Atalla
The Institute of Paper Chemistry
Appleton, Wisconsin 54912

ABSTRACT

Amorphous (noncrystalline) cellulose was prepared by dissolving cotton hydrocellulose in the dimethylsulfoxide-paraformaldehyde solvent system and regenerating the cellulose by slow addition of the resultant methylol cellulose solution to stirred 0.2M sodium alkoxide in methanol:2-propanol (1:1 vol.). The regenerated celluloses, essentially devoid of residual methylol substituents (ca. 0.002 m.s.), had x-ray diffractograms, Raman spectra, and solid-state ^{13}C-n.m.r. spectra characteristic of amorphous cellulose. In addition, 98-100% of the cellulose hydroxyl groups were accessible to proton exchange with deuterium oxide. For small scale (< 2 g) preparations, the d.p. and end group composition of the cellulose were essentially unaltered by the regeneration process.

INTRODUCTION

Amorphous (noncrystalline) cellulose is useful as a reference material in studies of the morphology of cellulosic samples.[2-4] Since cellulose reactivity is dictated to a considerable extent by the morphology of the cellulosic sample,[4-7] amorphous cellulose is also useful in studies of cellulose reactivity and derivatization. In addition, a convenient method of preparing amorphous cellulose, particularly if it is nondegrading, would facilitate techniques for cellulose functional group and degree of polymerization analysis.

Amorphous cellulose has been prepared by two primary methods, precipitation from solution and mechanical or chemical treatment

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of the solid substrate.[8] Ball-milling[9-10] is frequently used to prepare standard "amorphous cellulose",[3] but decrystallization of cellulose fibers with such drastic mechanical action causes significant degradation of the polymer. Amorphous cellulose has also been prepared by precipitation from cadmium ethylenediamine (cadoxen),[11-12] cuprammonium hydroxide (cuam),[13] and phosphoric acid,[14] but these solvents degrade the cellulose and, with the alkaline solvents, alter its functional groups. Nonaqueous saponification of cellulose acetate[13,15,16] and regeneration of nonaqueous cellulose xanthate solutions[13] also yield highly accessible celluloses. However, the conditions required for formation of these derivatives typically result in significant cellulose degradation.

In this paper we report a method for preparing amorphous cellulose by dissolving the cellulose in the dimethylsulfoxide-paraformaldehyde solvent system[17-19] and regenerating it from the resultant methylol cellulose without recrystallization or appreciable degradation.

RESULTS AND DISCUSSION

Preparation - Chemical Characterization

The mechanism by which cellulose dissolves in the dimethylsulfoxide (DMSO)-paraformaldehyde (PF) solvent system involves formation of a hemiacetal, methylol cellulose,[17-19] as shown in Figure 1. Although addition of formaldehyde to OH-6 is probably preferred, OH-2 and OH-3 may also be substituted, with the distribution and the molar degree of substitution (m.s.) dependent on the dissolution conditions.[18-20] Formation of the methylol cellulose and its dissolution can be effected without degradation of the cellulose.[19,21]

Cellulose can be regenerated from methylol cellulose by heating[18-19] or a variety of reagents, particularly bases, which cause breakdown of the methylol (hemiacetal) substituents. Our initial criteria for regeneration were no recrystallization, no

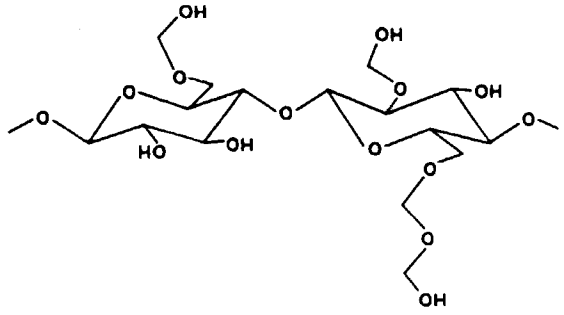

Figure 1. Methylol cellulose.

loss in the degree of polymerization (d.p.), and no change in the functional groups of the cellulose. A variety of regeneration media were tried. The reclaimed celluloses were evaluated for residual methylol substitution, d.p., end groups, crystallinity, accessibility, yield, and appearance. We avoided aqueous regeneration media at elevated temperature, since these have the potential to induce crystallization and cause d.p. loss.[19,22]

While not necessarily the optimum regeneration medium, 0.2M sodium alkoxide in methanol:2-propanol (1:1 vol.) gave excellent results. Regeneration in this medium gave essentially quantitative yields of amorphous cellulose. The molar degree of methylol substitution (m.s.) of the regenerated cellulose was ca. 0.002, or approximately one molecule of residual formaldehyde per cellulose molecule. Thus, regeneration of the cellulose was essentially complete. In addition, ash contents of both the fibrous and regenerated celluloses were ca. 0.02%, indicating that the regeneration process did not introduce additional inorganic contaminants into the regenerated cellulose.

An important variable in the regeneration process was the concentration (viscosity) of the methylol cellulose solution being added dropwise to the regeneration medium. If the polymer solution was too concentrated (>0.2%, wt. cellulose/vol. DMSO), the

droplets would not disperse adequately in the regeneration bath, resulting in incomplete removal of the methylol substituents.

Other critical factors were the washing sequence and the drying technique. Solvent exchange with methanol, anhydrous diethyl ether, and pentane resulted in a discolored, hornified product after vacuum drying. However, when the regenerated cellulose was washed with methanol, dilute hydrochloric acid, and water, and then freeze-dried, a fluffy, white product was obtained.

Potential degradation during regeneration was assessed through analyses of the cellulose d.p. and end groups. The molecular weight distribution was obtained from gel permeation chromatographic (g.p.c.) analysis of the tricarbanilate derivative.[23] Acidic end groups were determined by methylene blue uptake[24] and reducing end groups by reduction with sodium borohydride-^{3}H. The reducing end group analysis is a modification of the basic method reported for determining reducing end groups in soluble polysaccharides.[25]

G.p.c. analyses of the fibrous and amorphous celluloses are shown in Figure 2. The number-average degrees of polymerization ($\overline{d.p._n}$) are reported in Table 1. The data clearly indicate that the regeneration process caused, at most, only a slight reduction in the cellulose d.p. The d.p. decrease corresponds to cleavage of ca. 0.012% of the glycosidic linkages, or one cleavage in ca. 5% of the cellulose molecules. However, the d.p. drop may be an artifact of the g.p.c. derivatization process. Carbanilation of cellulose can cause degradation if the reaction conditions are too harsh.[23] While the carbanilation procedure used in this study is reportedly nondegrading for fibrous substrates,[23] the highly accessible physical structure of the amorphous cellulose would be more susceptible to degradation reactions.

As indicated in Table 1, the fibrous and regenerated celluloses contained essentially the same numbers of acidic and reducing end groups. The number of reducing end groups in the fibrous cellulose and its regenerated counterpart would not necessarily have to be equal because of the potential for inaccessible groups in the

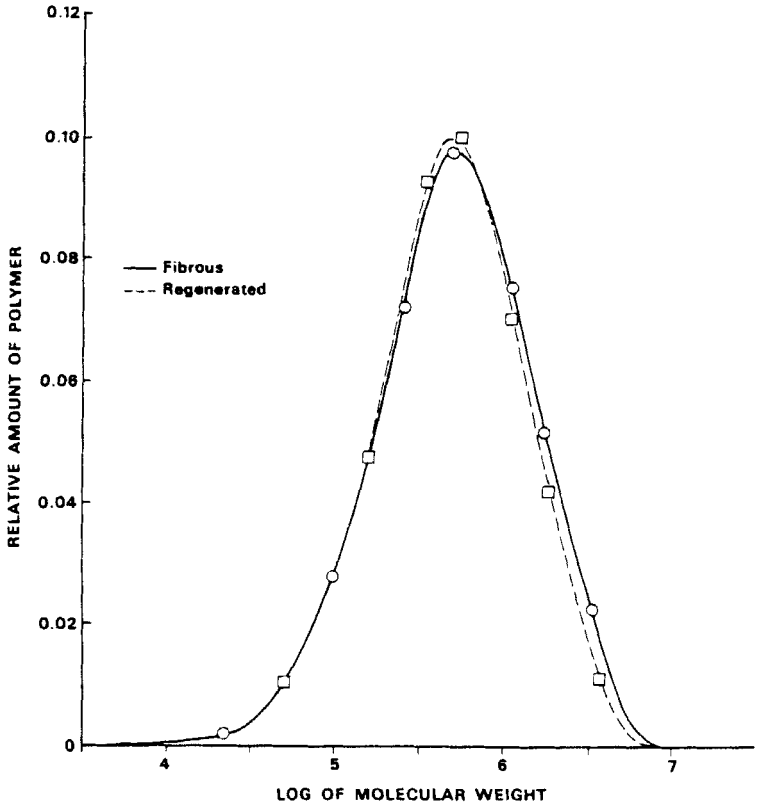

Figure 2. G.p.c. molecular weight distributions of the fibrous and regenerated hydrocelluloses.

TABLE 1

End Group and Degree of Polymerization Data

Hydrocellulose	End Groups[a]		$\overline{d.p.n}$	
	Reducing	Acidic	End groups	g.p.c.
Fibrous	1.40×10^{-3}	0.94×10^{-3}	427	407
Regenerated	1.41×10^{-3}	0.95×10^{-3}	424	390

[a]Mole fraction of cellulose monomer units.

fibrous material.[26] However, the $\overline{d.p.}_n$ values calculated from the total end group contents, in addition to being essentially the same for both celluloses, are in good agreement with the g.p.c. data. Thus, the analytical methods lend credence to one another and are consistent with the regeneration process of this scale (<2 g) being nondegrading. However, preparation of larger quantities (ca. 20 g) of amorphous hydrocellulose for other studies did result in some cellulose degradation in the scaled-up regeneration process.[26]

Physical Characterization

Regenerated celluloses prepared by this technique exhibited hydroxyl accessibilities of 98-100% as measured by proton exchange with liquid deuterium oxide. The key factor in achieving total accessibility appears to be regeneration under anhydrous conditions in a medium of low polarity. Neither the room temperature aqueous washes nor the freeze-drying caused any significant loss in accessibility.

Crystalline characteristics of the regenerated cellulose were assessed by x-ray diffraction. X-ray diffractograms of the starting fibrous cellulose, regenerated cellulose, and ball-milled Whatman CF-1 cellulose (amorphous standard)[27] are shown in Figure 3. The diffractogram of the fibrous cellulose contains well-defined reflectances of the 002, $10\bar{1}$, and 101 planes of the cellulose I crystalline lattice, indicating a relatively high degree of cellulose I crystallinity.[2,4] In contrast, the regenerated cellulose exhibits a diffuse scattering pattern similar to that obtained for the ball-milled cellulose, and characteristic of amorphous or noncrystalline cellulose.[28]

Molecular conformations associated with the different cellulose crystalline lattices produce distinct signals in Raman[27] and solid-state ^{13}C-n.m.r.[29-33] spectroscopy. In addition, in both spectral methods signals characteristic of particular cellulose polymorphs become more intense as the ratio of crystalline to amorphous components increases.

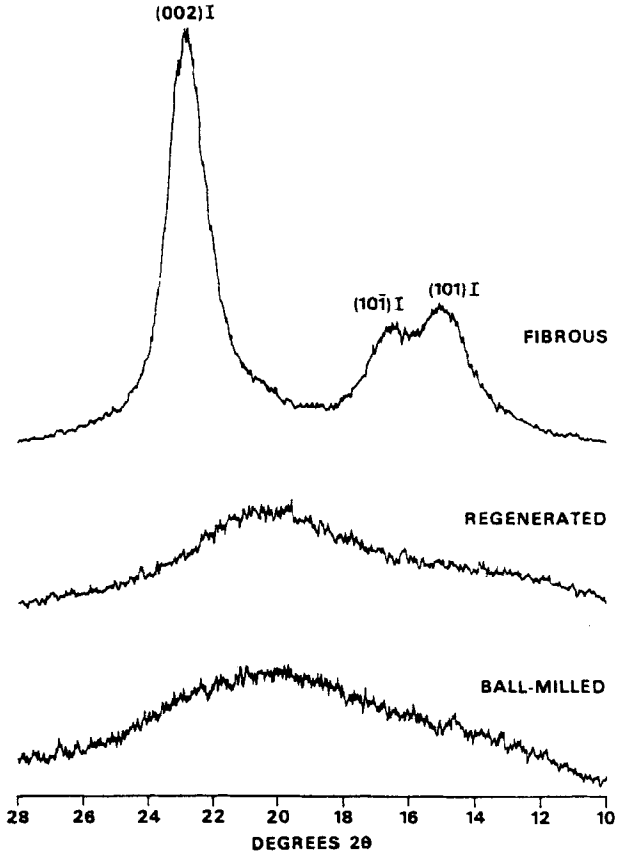

Figure 3. X-ray diffractograms of the fibrous and regenerated hydrocelluloses, and ball-milled Whatman CF-1 cellulose.

The low frequency regions of Raman spectra of the fibrous, regenerated, and ball-milled celluloses are shown in Figure 4. The spectrum of the fibrous cellulose has relatively intense cellulose I bands, e.g., 378 cm^{-1}. In contrast, the Raman spectra of the regenerated and ball-milled samples exhibit broad diffuse bands indicative of irregular sequences of conformations along the cellulose chains.[27]

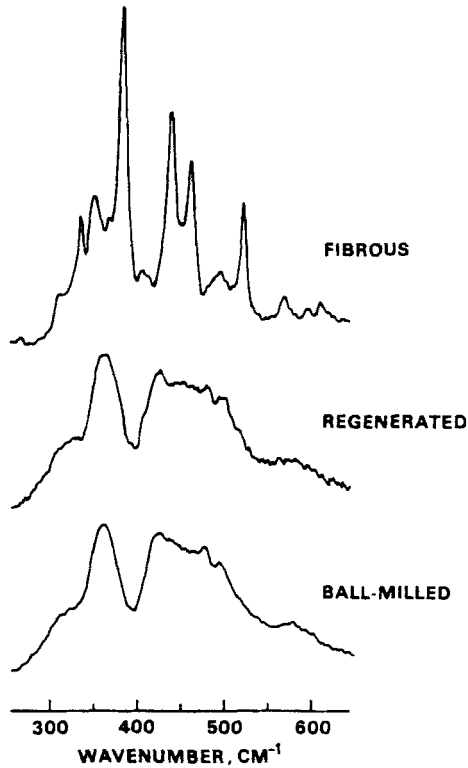

Figure 4. Raman spectra of the fibrous and regenerated hydrocelluloses, and ball-milled Whatman CF-1 cellulose.

Solid-state ^{13}C-n.m.r. spectra of the fibrous, regenerated, and ball-milled celluloses obtained by the cross polarization-magic angle spinning technique[29,30] are shown in Figure 5. The fibrous cellulose spectrum exhibits several sharp resonances indicative of the cellulose I polymorph.[30,31] The accepted assignments of resonances to carbon atoms in the anhydroglucose monomeric units are as indicated in the spectrum. The broader resonances appearing slightly upfield of the sharp C-4 and C-6 resonances are thought to be C-4 and C-6 resonances of monomeric units associated

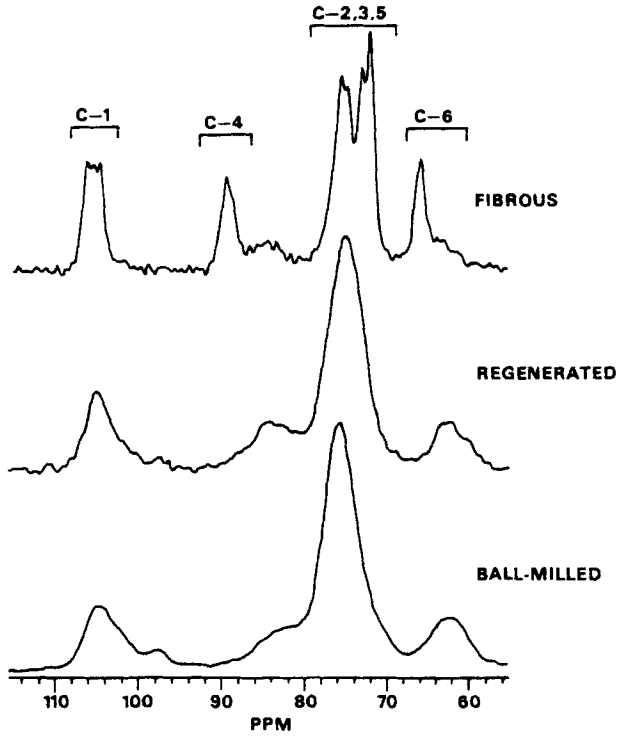

Figure 5. Solid-state ^{13}C-n.m.r. spectra of the fibrous and regenerated hydrocelluloses, and ball-milled Whatman CF-1 cellulose.

with regions of disorder and crystallite surfaces.[32] The analogous C-1, C-2, C-3, and C-5 resonances are overlapped by the corresponding sharper resonances and therefore not evident in the spectrum. The spectra of the regenerated and ball-milled celluloses are similar, but in contrast to the spectrum of the fibrous cellulose, exhibit only diffuse and unresolved resonances indicative of no significant structural order.

EXPERIMENTAL

Preparation of Amorphous Cellulose

A stirred mixture of purified fibrous cotton hydrocellulose[34] (1.0 g) and DMSO (100 mL) was heated to 125°C. Paraformaldehyde (5.0 g; Fluka, A. G.) was added to the mixture and stirring was continued until a clear solution was obtained.[17-19] The methylol cellulose solution was diluted with DMSO (400 mL), allowed to cool to room temperature, filtered through a glass microfiber pad (1.2 μm pore size), and added dropwise to a stirred regeneration bath of 0.2M sodium alkoxide in methanol:2-propanol (1:1, vol.; 2 L). For convenience in handling, the cellulose precipitate was divided into four equal portions. Each portion was successively washed with 0.2M sodium alkoxide in methanol:2-propanol (1:1, vol.; 150 mL), methanol (3 x 150 mL), 0.1M HCl (150 mL), and distilled water (3 x 150 mL); and then freeze-dried. The yields of amorphous cellulose were 95-100%.

General Analytical Methods

Cellulose tricarbanilate derivatives were prepared under non-degrading conditions for gel permeation chromatography.[23] The analyses were performed on Styragel columns calibrated by a dispersion-compensated universal technique.[23,35]

Carboxylic acid groups were measured by methylene blue adsorption.[24,34] Cellulose hydroxyl accessibility was determined by hydrogen-deuterium exchange with deuterium oxide over 24 h.[34,36]

X-ray diffractograms were recorded on a Norelco instrument using nickel-filtered, CuK_α radiation. Raman spectra were acquired on a Jobin Yvon spectrophotometer utilizing a 100-mw argon laser. Solid-state ^{13}C-n.m.r. spectra were obtained on General Electric S-100 instruments.

Bound Formaldehyde Analysis

Regenerated cellulose (ca. 0.1 g) was mixed with distilled water (12.5 mL) and 85% phosphoric acid (2.5 mL). The mixture was refluxed for 1 h and then distilled. Two 10-mL volumetric flasks,

connected in series and cooled in ice, were used as receivers. Each volumetric flask initially contained ca. 1 mL of distilled water. Approximately 8 mL of distillate were collected. The distillate in each volumetric flask was diluted to volume. Aliquots of the diluted distillates (0.5 mL) were combined with 0.5% (w/v) chromotropic acid solution (0.4 mL) and 81% sulfuric acid (3.2 mL). The resulting solutions were heated at 60°C for 20 min, and their absorbances at 570 nm were determined. A solution of distilled water (1.8 mL) and 81% sulfuric acid (6.4 mL) was used as the blank for the spectrophotometric measurements. A linear calibration curve for the procedure was obtained with standard formaldehyde (distilled) solutions (0 to 10 mg L^{-1}). The combined formaldehyde content of the two receivers was used to calculate the residual methylol substitution of the cellulose sample.

Reducing End Group Analysis

Blanks for cellulose analyses were prepared by reacting cellulose (0.050 g) with 0.25M $NaBH_4$ (50 mL) for 24 h. Excess borohydride was decomposed by adding 3M acetic acid (10 mL). The reduced cellulose was washed with 0.1M HCl (50 mL) and distilled water (100 mL), and freeze-dried.

D-Glucose (calibration standard), D-glucitol (blank for D-glucose), cellulose samples, and cellulose blanks (50 mg each) were reacted individually for 24 h with 0.25M $NaBH_4$ (50 mL) containing sodium borohydride-^{3}H (New England Nuclear Corp., 350 mCi $mmol^{-1}$, 0.007 mg mL^{-1}).

The reactions of D-glucose and D-glucitol were terminated by adding Amberlite IR-120 (H+) resin (20 mL). The solutions were filtered and concentrated to dryness in vacuo. The residues were concentrated to dryness from methanol (20 mL) three times. The resultant D-glucitol from each sample was crystallized from absolute ethanol, rinsed with anhydrous diethyl ether, dried in vacuo, weighed into a glass scintillation vial, and dissolved in distilled water (1.0 mL). Scintisol liquid scintillation cocktail was added,

and the D-glucitol was analyzed for its tritium content with a Beckman LS-100 instrument.

Reductions of the cellulose samples and blanks were terminated by adding 3M acetic acid (10 mL). The reduced cellulose samples were washed with 0.1M HCl (50 mL) and distilled water (100 mL), freeze-dried, and hydrolyzed with trifluoroacetic acid.[35,37] The resulting hydrolyzates were concentrated to dryness in vacuo. The residues were reduced with 0.25M $NaBH_4$ (50 mL) for 24 h, and the D-glucitol was isolated for analysis of its tritium content as described for the reduction of D-glucose.

The reducing end group contents of the cellulose samples were calculated from the specific activities of the various D-glucitol samples according to Equation 1.

$$X_{re} = (A_c - A_{cb})/(A_g - A_{gb}) \quad (1)$$

where X_{re} = reducing end group content, mole fraction of total monomer units,

A_c = specific activity of the D-glucitol from the cellulose sample (counts min^{-1} mg^{-1}),

A_{cb} = specific activity of the D-glucitol from the cellulose blank (counts min^{-1} mg^{-1}),

A_g = specific activity of the D-glucitol from D-glucose (counts min^{-1} mg^{-1}), and

A_{gb} = specific activity of the D-glucitol (counts min^{-1} mg^{-1}) subjected to the reduction procedure.

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