Crosslinking Cotton Cellulose with Ethyleneurea Derivatives Having Varying Hydrogen-Bonding Capabilities. II. Accessibility Determinations

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Synopsis

In a continuation of previously reported work of the effect on cotton cellulose of ethyleneurea crosslinking agents modified with ring substituents of varying hydrogen-bonding capabilities, accessibilities of the cellulosic hydroxylic protons to exchange with deuterium oxide vapor were determined by means of infrared spectroscopy. In analyzing these values with respect to previously reported data on physical properties of the treated fabrics, it was found that accessibility to deuterium oxide did not correlate with moisture regain of the resin-treated samples as has been reported for physically modified celluloses. It appears that the different resins did have some effect on the structure of water adsorbed by the fiber and also that the solvent affected the manner in which the resins attached themselves to the cellulose and eliminated water from the structure. Values of accessibility were not found to correlate well with crease recovery, although a weak trend was indicated. Accessibility was found to decrease as the infrared band for ring stretching decreased.

INTRODUCTION

In previous work,[1] cotton fabric was treated with a series of ethyleneurea derivatives modified at the ethylene portion of the ring with groups of varying hydrogen-bonding capabilities. The ethyleneurea derivatives were applied to the fabric using two different hydrogen-bond breaking solvent systems, water and dimethyl formamide (DMF). The combination of the effects of crosslinking and hydrogen bonding of the cellulose with the "resin" was then studied with reference to the physical properties of the fabric and the hydrogen-bonded structure of the molecules. The stimulus for this work was attempts in the last several years[2,3] to modify and expand previously accepted crosslinking theories of resiliency with a more detailed concern for the hydrogen-bonded and water structures, as well as for their interactions, in the cellulose system. A number of questions regarding the roles and relative importance of crosslinking, hydrogen bonding, and water in the cellulose system have arisen.

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Previous work[1] showed that when the ethyleneurea derivatives were applied to the cellulose from DMF, a greater percentage of methylene crosslinks was formed in the fibers than when the crosslinking agents were applied from water solutions. In addition, different resins produced different types of bonds, e.g., inter- or intramolecular. Hydrogen bonding of the cellulose with substituents on the crosslinking reagent did not appear to be significant in producing changes in the physical properties of the fabric. The reactivity of the compounds and the type of crosslink formed with the cellulose seemed to be the major reasons for observed differences in physical properties and fine structure.

In this work, the accessibilities of the cellulosic hydroxylic protons of the various chemically modified celluloses to exchange with deuterium oxide vapor were determined. These accessibilities were then studied to determine if any relationship existed between them and the crease recovery properties of the samples or the specific changes observed in the hydrogen-bonded structure of the cellulose. The relationship of the accessibilities and the moisture regains of the samples was also investigated in view of a known relationship of this type which exists for physically modified celluloses.[4]

EXPERIMENTAL

Preparation of Samples

The fabric used was a scoured and bleached 80 $\times$ 80 cotton print cloth. All reagents, unless otherwise specified, were analytical grade. The crosslinking agents, which were all synthesized and purified in the laboratory according to methods described previously,[1] were the following:

1,3-bis(hydroxymethyl)-2-imidazolidinone, or dimethylol ethyleneurea (DMEU)

1,3-bis(hydroxymethyl)-4,5-dihydroxy-2-imidazolidinone, or dimethylol dihydroxy ethyleneurea (DMDHEU)

4,5-dihydroxy-2-imidazolidinone, or dihydroxy ethylene urea (DHEU)

1,3-bis(hydroxymethyl)-4,5-dimethoxy-2-imidazolidinone, or dimethylol dimethoxy ethyleneurea (DMDMxEU)

1,3-bis(hydroxymethyl)-4,5-bis(β-hydroxyethoxy)-2-imidazolidinone, or dimethylol dihydroxyethoxy ethyleneureaa (DMDHeEU)

1,3-bis(hydroxymethyl)-4,5-dibenzoxy-2-imidazolidinone, or dimethylol dibenzoxy ethyleneurea (DMDBEU)

The treating solutions were $0.55M$ in crosslinking reagent and $0.03M$ in catalyst, $Zn(NO_3)_2 \cdot 6H_2O$. Fabric samples were padded to a final wet pickup of 80–90%, dried at 60°C and cured for 3 min at 160°C. They were then given an afterwash in a home-type laundry unit using a nonionic detergent, rinsed, and tumble-dried.

Degree of substitution, per cent add-on and crease recovery properties of the fabrics are given in Table I. These data were determined by methods previously reported.[7]

TABLE I
Degree of Substitution and Crease Recovery Properties
of the Resin-Treated Celluloses

	Add-on, %	N, %	HCHO, %	CL/agu	CL length	Crease-recovery Angle ($W + F$)	
						Dry	Wet
Untreated	—	—	—	—	—	185.5	163.2
Solvent							
water	—	—	—	—	—	190.3	156.1
DMF	—	—	—	—	—	173.3	164.0
Catalyst							
water	—	—	—	—	—	196.2	190.3
DMF	—	—	—	—	—	172.3	187.7
DMEU							
water	5.1	1.58	2.43	0.042	2.35	287.8	281.3
DMF	2.6	1.59	2.27	0.033	3.05	273.2	296.6
DMDHEU							
water	5.1	1.39	2.43	0.054	1.55	302.1	284.8
DMF	3.7	1.43	2.03	0.019	3.10	286.4	294.5
DHEU							
water	1.1	1.21	0.00	0.074[a]	1.00[a]	275.3	259.4
DMF	2.5	1.24	0.00	0.076[a]	1.00[a]	267.9	247.4
DMDMxEU							
water	6.0	1.44	2.25	0.042	2.18	283.4	271.0
DMF	4.2	1.48	2.36	0.045	2.10	277.9	268.7
DMDBEU							
water	23.5	2.48	2.74	0.005	29[b]	217.6	244.2
DMF	6.0	1.19	1.52	0.015	5.00	249.6	244.1
DMDHeEU							
water	5.9	1.33	0.86	0.086[a]	1.00[a]	253.3	247.1
DMF	7.3	1.46	1.00	0.094[a]	1.00[a]	238.5	247.5

[a] CL (crosslink) length = 1.00 assumed; therefore, CL/agu was derived from % N only.

[b] This crosslink could only be approximated because the point lies on the part of the curve where the slope approaches zero.

Deuteration Technique

Vapor phase deuterations of the samples were carried out according to the general method of Mann and Marrinan[5] as modified by Åsnes and Wickman[6] for the use of KBr pellets. Deuterium oxide (25 g) was transferred to a 250-ml Erlenmeyer under a dry nitrogen atmosphere in a drybox, hooked into the system, purged with dry nitrogen for a few minutes, and subsequently isolated from the system.

The samples, which were ground in a Wiley Mill to pass a 20-mesh screen, weighed to give a dry weight of 1.8 mg, and stored in 1-dram vials over P_2O_5 for six days, were loaded into a 400-ml beaker under dry nitrogen and hooked into the system. The nitrogen, isolated from the D_2O, was passed over the samples for approximately 3 min, after which the D_2O was introduced into the system and the deuteration was continued for 4 hr. At the

end of this time, the D_2O was again isolated and the dry nitrogen was passed over the samples for 2 hr.

The samples were then isolated and disconnected from the system and placed in the nitrogen-filled drybox. Spectral-grade KBr (250–300 mg), which was ground with a mortar and pestle, weighed into individual vials, dried in an oven at approximately 200°C, and stored in an oven at 110°C, was added to each of the sample vials. The contents were then mixed and pellets were pressed in an evacuated die under 16,000–17,000 lb pressure for approximately 2 min. Samples were not exposed to the air until after they were pressed, and they were then quickly placed in their holder and transferred to the dry nitrogen-purged Perkin-Elmer Model 421 infrared spectrophotometer. Samples were run with a blank KBr pellet in the reference beam using a scan time of 10 min. An identical technique was used to obtain spectra of the undeuterated controls.

The relative concentrations of OH and OD were obtained from the infrared spectra as follows:[5]

$$\frac{\log (I_0/I)_{OD}}{\log (I_0/I)_{OH}} = \frac{k_{OD} C_{OD}}{k_{OH} C_{OH}}$$

where $k_{OD}/k_{OH} = 1.11$, which is the ratio of the extinction coefficients, and $C_{OD} + C_{OH} = 1$. I_0 and I were measured from the infrared spectra using a baseline technique.

DISCUSSION OF RESULTS

Several workers[4,7] have demonstrated a correlation between the moisture sorption of various physically modified celluloses and their accessibilities to exchange with deuterium oxide vapor as a measure of the degree of order of these samples. In fact, it is claimed[8] that exactly the same quantities are measured in moisture sorption studies as are measured in exchange studies with D_2O.

The moisture sorption and accessibility data obtained in this study for the chemically modified celluloses and the respective controls are given in Table II. Accessibilities of these samples, corrected to account for OH groups removed in crosslinking or added by the resin, are also reported in this table and were obtained by the method given in Appendix A.

A plot of the sorption ratio versus per cent accessibility for the chemically modified celluloses is shown in Figure 1. The line drawn is that reported in the literature for physically modified celluloses—cotton, fortisan, mercerized viscose rayon, and viscose rayon.[8] The large scattering of points around this line should be noted; accessibility values are believed to be accurate to ±1%. A correlation analysis of these data yielded $r = -0.28$. Thus, no significant correlation was found between the moisture sorption of these chemically modified celluloses and their accessibilities to exchange with deuterium oxide vapor. A correlation of the type reported in the

TABLE II
Sorption and Accessibilities

	Moisture regain, %	Sorption ratio	$\dfrac{k_{OH}C_{OD}}{k_{OD}C_{OH}}$	Accessibility,[a] %	
				Uncorrected	Corrected
Untreated	5.9	1.00	0.590	37.1	—
Solvent					
water	6.1	1.03	0.530	34.6	—
DMF	6.1	1.03	0.556	35.7	—
Catalyst					
water	6.0	1.02	0.510	33.8	—
DMF	5.8	0.98	0.570	36.3	—
DMEU					
water	5.1	0.86	0.364	26.7	28.8
DMF	6.6	1.12	0.391	25.5	29.5
DMDHEU					
water	3.8	0.64	0.444	30.7	29.4
DMF	6.6	1.12	0.363	26.6	23.8
DHEU					
water	5.6	0.95	0.501	33.4	36.7
DMF	5.7	0.97	0.410	29.1	32.7
DMDMxEU					
water	4.7	0.80	0.528	34.6	36.4
DMF	5.2	0.88	0.391	28.1	30.3
DMDBEU					
water	5.8	0.98	0.361	26.5	26.8
DMF	5.0	0.85	0.352	26.0	26.8
DMDHeEU					
water	5.8	0.98	0.359	26.4	30.3
DMF	6.6	1.12	0.456	31.3	35.6

[a] See Appendix A for the procedure for calculating the corrected per cent accessibility values.

literature for the physically modified celluloses would require a positive r value near unity.

Enderby[9] has proposed a theory for the absorption of water by polymers containing hydrophilic groups, e.g., cellulose, in which it is assumed that the initial tendency of such a process is the addition of water molecules which are able to form hydrogen bonds with the cellulose which saturate the bonding potential of the water molecule. This is termed a primary site and requires a free hydroxyl in the system. Secondary sites are those where the entering water molecule is able to form hydrogen bonds with additional water molecules to form a "polymeric aggregate" of water molecules within the cellulose network.

It is possible that the addition via the crosslinking agent of carbonyl groups which are capable of entering into hydrogen bonding may affect the amount of moisture held in the system. However, per cent nitrogen values (Table I) were almost identical (with the exception of DMDBEU) within each solvent pair for each resin, indicating that the number of carbonyls added should also be identical. The addition of carbonyl groups, therefore,

Fig. 1. Comparison of found versus theoretical relationship between moisture sorption and accessibility in various celluloses: (□) literature; (●) H_2O experimental; (○) DMF experimental; (■) untreated cotton control.

Fig. 2. Relation between dry crease recovery and per cent accessibility: (●) H_2O; (○) DMF.
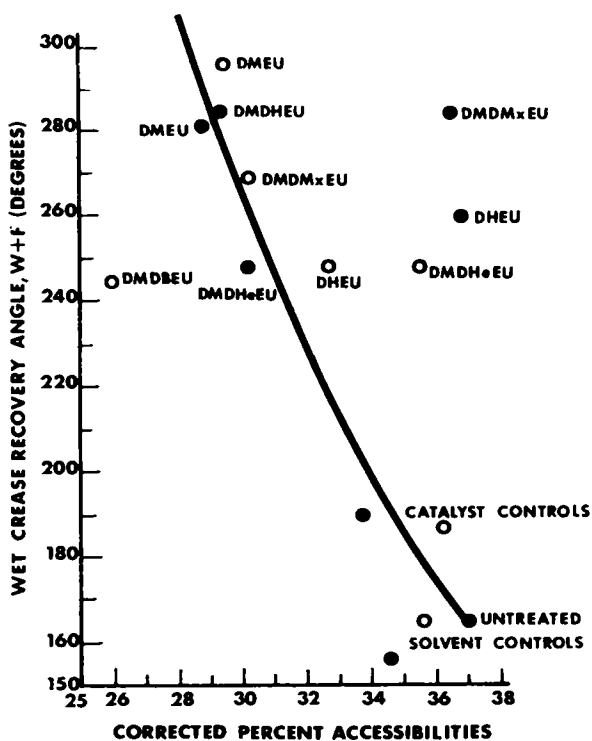
Fig. 3. Relation between wet crease recovery and per cent accessibility: (●) H₂O; (O) DMF.

would not explain the large differences in moisture regain observed within each solvent pair.

It is possible, however, that the nature of the "tails" on the resins used in this study along with the manner in which the resins became "added" to the cellulose may have altered the structure of water sorbed by the cellulose. It is interesting to note in Figure 1 that, with respect to a line of the same slope drawn through the lower of the two points in each resin pair, the DMF-treated sample, in all cases except two, lies above the water-treated sample. The exceptions to the above observations were DMDHeEU, where the two solvents were on the same line, and DMDBEU, a pair which would be expected to give erratic results with respect to each other owing to poor solubility of the resin in water. It is interesting to speculate on the meaning of these results in view of Benerito's theory[3] of a hydrogen bond-breaking solvent creating voids in the hydrogen-bonded structure of cellulose for the reactant molecules, which in turn prevent the entrance of water molecules into their original absorption sites. In the case in point, it appears that the DMF has not been as effective as the water in creating voids, and, thus, more water may return into the cellulose structure at secondary adsorption sites.

Fig. 4. Relation between infrared out-of-phase ring stretching (11.1 μ) and accessibility
ratio: ($\bullet$) H_2O; (O) DMF.

Values found for per cent accessibility did not correlate with the cal-
culated degree of substitution or with the adsorbed water peak (6.1 μ) in the
infrared.   A weak trend may be indicated (Figs. 2 and 3) in the combination
of the crease recovery data with per cent accessibilities corrected for OH
groups removed in crosslinking (Table II).   It is tempting to try to cor-
relate an increase in crease recovery angle with a decrease in accessibility.
However, the points scattered from the curve drawn are not consistent as a
group with respect to resin, solvent, or any properties found thus far for the
fabric samples.   Speculation on the relationship mentioned, therefore, can
only be made with a great deal of caution.

The only infrared band discussed in the previous study[1] with which any
type of correlation with accessibility may be made is the 11.1 μ peak due to
the out-of-phase ring stretching (Fig. 4).   Caution must again be observed
in such an analysis since the standard deviation for this peak value is quite
sizable (δ = 0.02) with respect to the total change (range = 0.08).   In
presenting these data, no cause-and-effect relationship is necessarily
indicated; it is presented merely as a point of interest.   It would seem

likely, however, that an increase in stiffness of the cellulose chain would lead to a decrease in OH accessibility, since the decreased motion of the chain would enable a more tightly "packed" system.

APPENDIX A

Values for per cent accessibility of crosslinked celluloses obtained by the deuterium exchange techniques would be low for per cent accessible OH groups since a certain percentage of OH groups which should appear in the accessible regions of the cellulose have reacted with the crosslinking agents and thus do not appear at all as OH groups. To obtain a value for per cent accessibility of the cellulose itself, for certain uses, these groups may be accounted for. Assuming that two cellulose OH groups are reacted per crosslink,

$$\text{no. of OH groups reacted/agu} = 2(\text{crosslinks/agu})$$

$$\text{no. of OH groups/agu available} = 3$$

$$\% \text{ "accessible" OH groups made nonaccessible} = 2\left(\frac{\text{crosslinks/agu}}{3}\right) \times 100 = X$$

For reacted cellulose, $\%C_{OD} + \%C_{OH} + X = 100\%$; the final accessibility, therefore, is $\%C_{OD} + X$.

However, where the crosslinking resin contains OH groups which do not react, the concentration of accessible OH groups measured would be increased, assuming the length of the ethyleneurea residue to be greater than one, and assuming these OH groups remain accessible after crosslinking occurs. (If the length of the crosslink were one ethyleneurea residue, the number of accessible OH groups added would equal the number of accessible OH groups removed, and no correction would be necessary, i.e., $\%C_{OD} + \%C_{OH} = 100\%$).

Then:

$$\text{no. of OH groups added/agu} = 2(\text{no. of EU residues/CL})(\text{CL/agu})$$

$$\%\text{OH groups added} = \frac{\text{no. of OH groups added/agu}}{\text{no. of OH groups/agu}} \times 100$$

$$\text{net } \%\text{OH added} = \%\text{OH groups added in EU residues} - \%\text{OH reacted}$$

$$= \frac{2(\text{residues/CL})(\text{CL/agu}) \times 100}{3} - \frac{2(\text{CL/agu}) \times 100}{3}$$

$$= \frac{2(\text{CL/agu}) \times 100}{3}(\text{no. of EU residues/CL} - 1)$$

$$= X(\text{no. of EU residues/CL} - 1) = Y$$

Thus, $\%C_{OD} + \%C_{OH} - Y = 100\%$, and the final per cent accessibility for celluloses crosslinked with resins containing OH groups is $\%C_{OD} - Y$.

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