Variations in Crosslink Organization in Formaldehyde-Modified Cotton Celluloses

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Synopsis

Rates of decrease in crystallinity, as measured by x-ray crystallinity index, have been followed throughout periodate oxidations of cotton cellulose and formaldehyde-treated cotton celluloses. Depending upon the conditions under which the agent was introduced, a low level of formaldehyde crosslinks exerted small or large retardation on the rate of decrease of crystallinity index. The extents of decrystallization per unit of oxidation of cotton and crosslinked cotton celluloses are substantially smaller in the initial phase of oxidation than in the later stage, indicative of preferential oxidative attack in the early stage on chain segments of predominantly noncrystalline regions. Relative to unmodified cotton, crosslinked cotton celluloses are characterized by more extensive decrystallization per unit of oxidation in the early phase of oxidative attack (to approx. 40%). From these data, supplemented by electron micrographs and solubilities in cupriethylenediamine hydroxide, uniformity of distribution of crosslinks is shown to increase in this series of formaldehyde-modified cotton celluloses (at the same level of agent) in the order: form D cotton (nonaqueous treatment) < form W cotton (aqueous treatment) < form V cotton (vapor treatment). Effectiveness of crosslinking (i.e., composite of number of linkages, ratio of intermolecular to intramolecular bonds, low degree of polymerization in crosslink) is indicated to increase from form W to form D to form V cotton.

INTRODUCTION

Crosslinks developed by various methods in semicrystalline fibrous polymers may differ in distribution within noncrystalline regions, in ratios of intermolecular bonds to intramolecular rings or substituents, in linkages involving mono-, di-, or polymeric units of the agent and in site of attachment on the structural units of the polymer chain. The profound changes which occur within a fiber on introduction of a crosslinking agent have been reviewed by Valentine,[1] Tovey,[2] and Smith[3] and have been related to theoretical considerations by Gardon and Steele.[4] In spite of considerable progress in relating physical properties of crosslinked fiber structures to the conditions of reaction by Reeves and coworkers,[5,6] Steele,[7] Guthrie,[8] and others,[9–11] little is known about the variations in the basic structural features of the crosslinked compositions. Considerable delineation re-

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mains for an understanding of the distributions and the structures of cross-links which are associated with the various processes of crosslinking and with physical performance characteristics.

Chemical reactivity of modified fibrous polymers reflects presence and nature of crosslinks[12,13] and offers a potential means of assessing parameters related to combinations of the above features.   Among the chemical reactions of polymeric molecules, the periodate oxidation of cellulose is unique in being highly selective for specific structural units, i.e., vicinal hydroxyls, and responsive to different types of molecular order.[14,15]   Davidson[16] showed that the original crystalline order in cellulose is destroyed as oxidation with periodic acid proceeds, and recently we have related the decrease in crystallinity index to degree of periodate oxidation of cotton cellulose.[17] Karrholm[18] found the extent of periodate oxidation of modified rayons to be controlled by the level of chemical crosslinks, and Cousins et al.[12] showed that substantial differences in rates of oxidation characterize formaldehyde-crosslinked cotton celluloses prepared by different techniques to contain the same level of agent.   The latter results are indicative of different organizations of crosslinks in the cotton cellulose structure.

Rates of disappearance of crystallinity during periodate oxidation of chemically modified cotton celluloses appear to offer fruitful means for studying differences in the organizations of the molecular structures of crosslinked celluloses.   It is the purpose of this paper to report studies on a series of three cotton celluloses crosslinked to the same level of formaldehyde (0.4%) by different techniques of reaction and to develop another incremental degree of understanding of the ramifications of crosslinking in semicrystalline polymeric structures.

EXPERIMENTAL

Cotton cellulose utilized was desized, scoured, bleached 80 × 80 print cloth which was treated with reagents to introduce 0.4% formaldehyde in an aqueous system[19] (designated form W cotton), in an acetic acid system[20] (designated form D cotton), and in the vapor phase[21] (designated form V cotton).   The preparation, oxidation, and analyses of the modified cotton celluloses are described by Cousins et al.[12]

X-ray diffractograms were obtained with a General Electric Model XRD-5 diffractometer equipped with copper target, nickel filter, and medium resolution Soller slits.   Operation of the x-ray unit included calibration of beam intensity with a polished brass plate.   The operation of the x-ray unit, the preparation of the sample, and the calculation of crystallinity index [CI = $100(I_{002} - I_{am})/I_{002}$; method very similar to that of Segal[22]] are described in an earlier publication.[17]

To minimize the several sources of variabilty in x-ray diffractograms which are discussed by Segal et al.[22] and Nelson and Schultz,[23] the x-ray measurements were made at fixed tube current and were checked at tube current adjusted to the original calibrated beam intensity.   The correction

of all diffractograms to a common base line and the calculation of crystallinity indices by a suitable and consistent method are major factors in minimizing variations.

Values of crystallinity indices on highly oxidized samples are subject to more than the normal uncertainty, since peak heights are low while instrumental fluctuations remain relatively constant and, thus, variations are magnified. Nevertheless, careful measurements yielded consistent crystallinity indices from the various samples of cotton even to 80–100% oxidation. However, data are insufficient to establish whether differences in crystallinity indices are significant among the various samples at a given degree of oxidation above approximately 60% consumption of oxidant.

In view of high congestion of points at the lower levels of oxidation in Figures 1 and 2, several points are omitted for clarity.
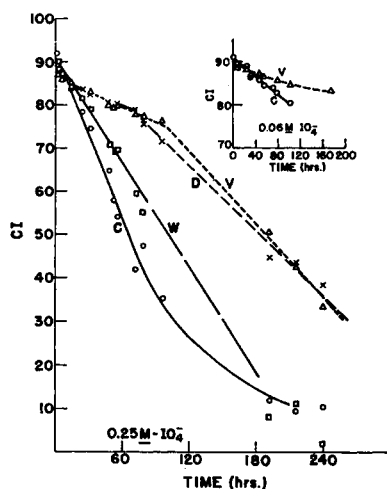

Fig. 1. Decrease in crystallinity index during oxidation with $0.25M$ periodate: (O) cotton; (□) form W; (×) form D; (△) form V. Insert presents data for oxidation with $0.06M$ periodate.

Electron micrographs were made after the ultra-thin (600–800 A.) cross sections of fibers were freed of embedding poly methacrylate and immersed for 30 minutes in $0.5M$ cupriethylenediamine hydroxide (cuene) by the method of Rollins et al.[24,25] The layer expansion technique of these authors[25,26] was also employed in electron micrographic examination of cross sections as an indication of freedom of microphysical structural units in the fibers. Water-beaten fragments of fibers were prepared and examined with the electron microscope by the method of Rollins and Tripp[25] for comparison of fragmentation patterns.

Solubilities of chemically modified cotton celluloses were determined quantitatively in cuene by the method of Bullock et al.[27]
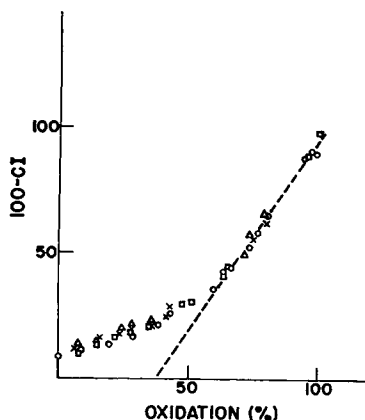
Fig. 2. Noncrystalline index (100 − CI) vs. oxidant consumption (0.25M periodate): (O) cotton; (□) form W; (×) form D; (△) form V.

RESULTS

Progressive decrease in crystallinity index (CI) of cotton cellulose during periodate oxidation has been observed to proceed at a pseudo zero-order rate from an initial CI of 91.7 throughout at least 60% of the decrease in CI (curve C of Figure 1).[17] Similar constancy in rate applied to the oxidative decrease in CI for form W cotton with 0.25M periodate (curve W, Figure 1). The velocity coefficient for form W cotton is substantially lower (0.40 CI/ hr.) than that for unmodified cotton (0.62).   Under the same conditions of oxidation the decreases in CI of forms D and V cotton celluloses are generally similar to each other but deviate substantially from the linear progressions of unmodified cotton and form W cotton.   The ratio of reaction periods required for 50% reduction in CI for cotton/form W/form D/form V is 1.0/1.4/2.8/2.8.

Generally similar differences in rates of oxidative decrystallization between unmodified cotton and form V cotton are observed with more dilute periodate reagent, i.e., 0.06M.   These differences, which are shown in the insert section of Figure 1, are summarized in terms of velocity coefficients for the 10–80-hr. interval of reaction as follows: 0.11 and 0.03 CI/hr. respectively, for cotton and form V cotton with 0.06M periodate and 0.62 and 0.09 CI/hr., respectively, with 0.25M periodate.

With the possible exception of form V cotton, the rates of decrease in CI in the initial oxidative decrystallization (to approximately 10 hr. or CI of 85) are indistinguishable; for this reason data points for form W and D cottons have been omitted for this interval in Figure 1.   There is an indication in Figure 1 (and the insert figure) that form V cotton undergoes greater decrease in CI than unmodified cotton during this initial interval.   Thus, it appears that the anhydroglucose units (AGU) of highly ordered regions of form V cotton are more readily available for oxidation during this stage of the reaction than are those of uncrosslinked cotton.

Crystallinity indices of form D and V cottons decrease at similar retarded rates (velocity coefficients are 0.11) between CI values of 85 and 75 and over periods of approximately 70 hr. for form D cotton and 90 hr. for form V cotton.   These periods of retardation could not be anticipated from rates of consumption of periodate, since these curves[12] are apparently zero-order and linear in this interval.   Subsequent to these periods of retardation for forms D and V cottons, the CI values decrease at rates which approach that of form W cotton; i.e., velocity coefficients for cotton and forms W, D, and V cottons at this stage are 0.62, 0.40, 0.25, and 0.28 CI/hr., respectively.

The progressive penetration into crystalline regions as a function of degree of oxidation for all of the cotton compositions is shown in Figure 2 in terms of increase in noncrystalline index (i.e., 100 − CI) versus extent of consumption of oxidant.   Gross trends are similar for all samples.   The curves are concave with slopes less than one in the first half of the reaction and greater than one in the latter half.   These data indicate that AGU's originally in highly ordered regions constitute a small fraction of the total chain segments undergoing oxidation in these samples of cotton, and especially in unmodified cotton cellulose,[17] during the early phase of reaction.

Significant differences among the cotton compositions are evident in the slopes, i.e., $d(100 - CI)/d(Ox)$, of the curves plotted from 100 − CI versus degree of oxidation during the early stages of oxidation (to approximately 40% consumption of oxidant) as shown in Figure 3.   The formaldehyde-treated cottons exhibit greater increase in 100 − CI in the early stage of oxidation than does uncrosslinked cotton.   The relationship between 100 − CI and degree of oxidation for form W is closest to that shown by uncross-linked cotton; form V cotton deviates to the greatest extent.

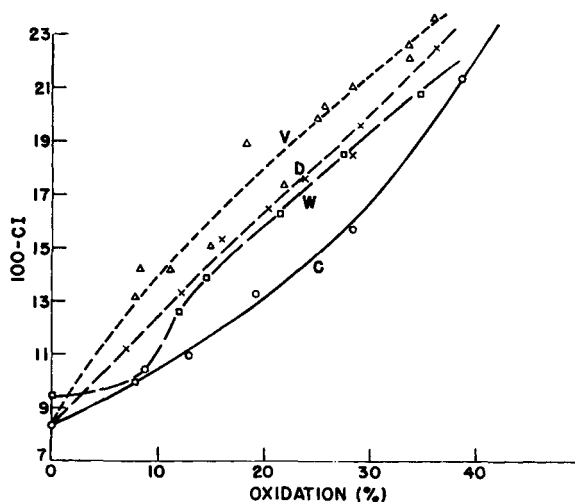Fig. 3. Detailed variations in noncrystalline index (100 − CI) vs. oxidant consumption (0.25M periodate): (O) cotton; (□) form W; (×) form D; (△) form V.   CI values at zero oxidation coincide for cotton, form D cotton, and form V cotton.
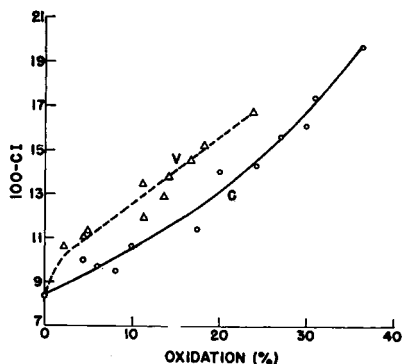
Fig. 4. Detailed variations in noncrystalline index (100 — CI) vs. oxidant consumption (0.06M periodate): (O) cotton; (△) form V.

In oxidations with 0.25M periodate (Fig. 3) and with 0.06M periodate (Fig. 4), form V cotton exhibits higher $d(100 - CI)/d(Ox)$ than uncross-linked cotton up to a level of approximately 20% oxidation; beyond this level the curves for form V cotton and uncrosslinked cotton gradually converge, all points being indistinguishable from a single curve beyond approximately 45% oxidation. The differences among the curves for the cross-linked cottons are most notable in the range of 15–25% oxidant consumption. The increment of change in CI which has occurred to the 15% range of oxidant consumption is 7.8 CI units for form V cotton relative to 3.5 units for unmodified cotton. Forms W and D cottons are intermediate: 4.6 and 6.2, respectively.

The above differences among (unoxidized) crosslinked cottons are further clarified by visual information from electron micrographic examinations of fiber cross sections subjected to various treatments. While thin sections of unmodified cotton fibers disappear from the grid by dissolution on treatment with cuene and those of form V cotton appear to be most inert, results obtained on sections of forms W and D cottons are intermediate. The electron micrographs of form W cotton (Fig. 5) on treatment with cuene suggest an almost transparent, highly expanded structure. Cross sections of form D cotton exhibit many variations, ranging from residues similar to those which characterize form V cotton to those which approach form W cotton. Many form D cross sections show evidence of considerable disruption, suggesting dissolution of parts of the fiber structure.

Differences in internal microstructure among the crosslinked cotton cellu-loses are also readily apparent in electron micrographs of fiber cross sections subjected to layer expansion. Between the patterns exhibited by un-modified cotton and by form V cotton lie the patterns of forms W and D cottons. The normal expansion pattern of cross sections of cotton fibers into concentric rings is very apparent at both levels of magnification (3700× and 32,000× in original prints) in Figure 6 for the uncrosslinked samples; the solid, opaque, unexpanded structure of form V cotton stands
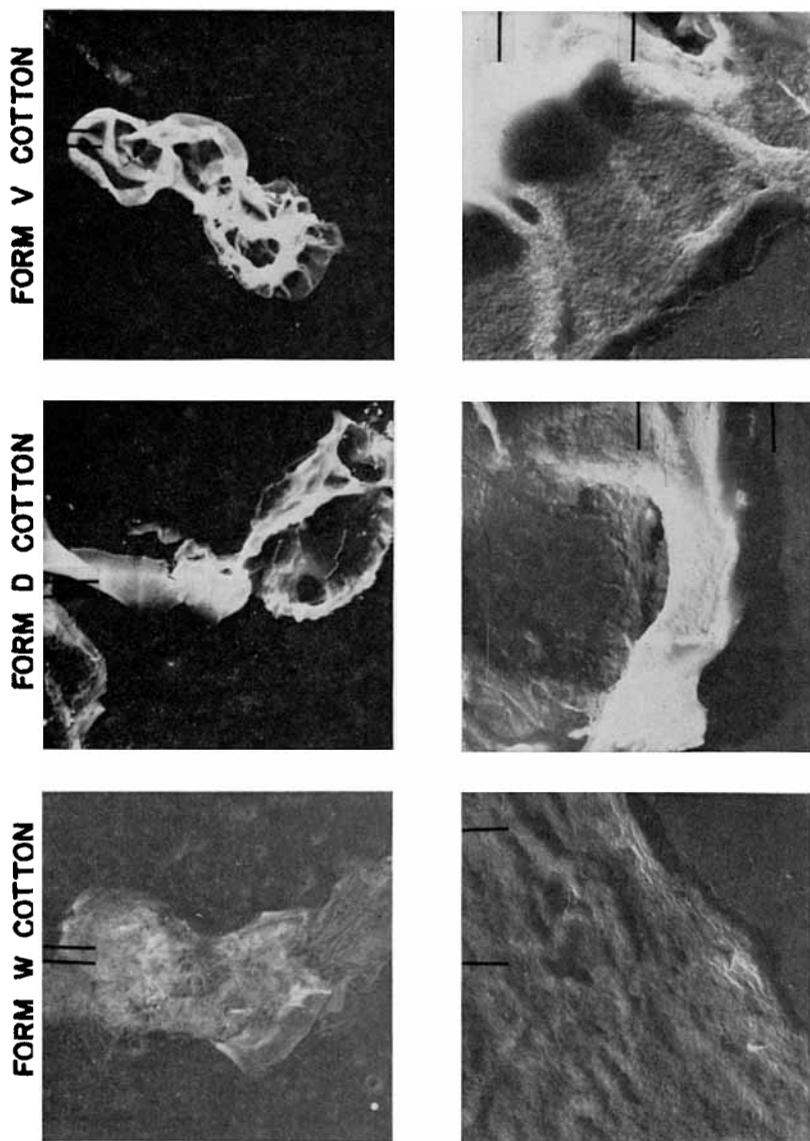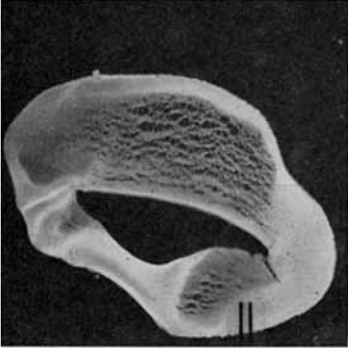
Fig. 5. Electron micrographs at two levels of magnification of fiber cross section following exposure to 0.5M cuene. Distance between markers represents 1 μ.
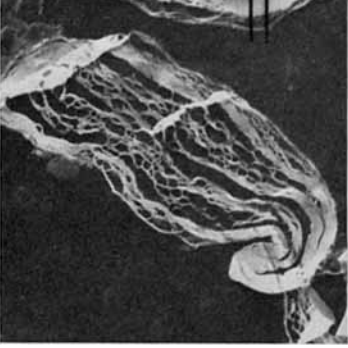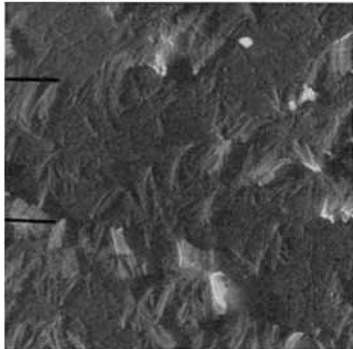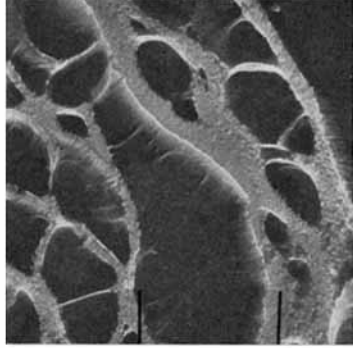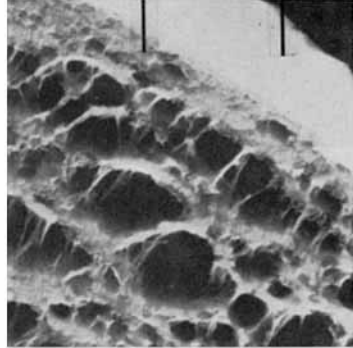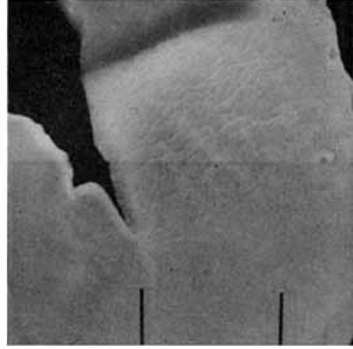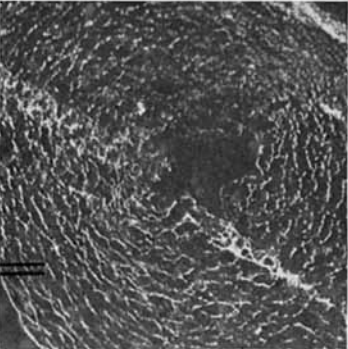
Fig. 6. Electron micrographs at two levels of magnification of fiber cross sections subjected to layer expansion. Distance between markers represents 1 μ.

out in contrast.   Form W cotton varies in expansion pattern, but a common pattern is the type already shown by Frick et al.[26] and pictured here in Figure 6: i.e., a lacy structure containing fewer separations and considerably more substance between separations than unmodified cotton.   Form D cotton is characterized by wide variability in expansion patterns, exhibiting the compactness which is characteristic of the form V fiber in some sections together with a degree of expansion which approaches that of uncrosslinked cotton fiber in other fiber cross sections.   A common pattern for the form D fiber is the type illustrated in Figure 6, where a solid, opaque, unexpanded periphery surrounds an interior which is expanded in part.

Fragmentation patterns of the cotton compositions tell a story which is not uniquely lucid but which is consistent with the differences already noted.   Unmodified cotton exhibits a peeling into thin layers with some separation of fibrils and microfibrils (Fig. 7).   Form V cotton, at the other extreme, fractures and breaks into solid chunks characteristic of a thor-
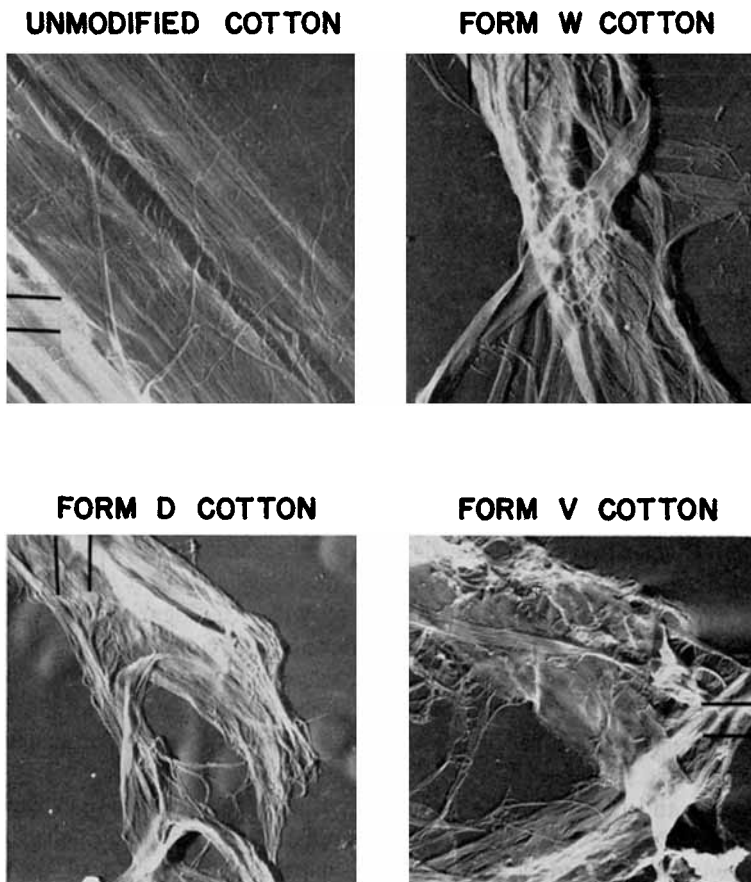
UNMODIFIED   COTTON   FORM W COTTON

FORM D COTTON   FORM V COTTON

Fig. 7. Electron micrographs of fragmentation patterns of cotton fibers.   Distance between markers represents 1 μ.

oughly crosslinked cotton cellulose.   Form W cotton undergoes peeling into layers, shows a relatively low degree of fracturing, and exhibits less separation of fibrils and microfibrils than uncrosslinked cotton.   Form D cotton is variable in this test, as we noted also in earlier cases.   Fractures of solid chunks, as for Form V cotton, are apparent for form D cotton but to a lesser extent.   Individual microfibrils are more difficult to identify in forms D and V cotton samples and appear to be bound into bundles which constitute structural units.

TABLE I
Quantitative Solubilities of Cotton Samples
in Cupriethylenediamine Hydroxide[a]

Composition	W_s, %	W_i, %	W_g, %
Cotton	99; 101	0	0
Form W	0; 0.9	100; 99.1	101.9; 100.5
Form D	12.6; 14.1	87.3; 85.9	84.2; 84.6
Form V	0	100	102.4; 101.8

[a] W_s is percentage of recovered soluble cellulose; W_i is percentage of insoluble material by difference; W_g is percentage of gel component determined gravimetrically.

Quantitative solubilities of the (unoxidized) formaldehyde-modified cotton celluloses in cuene were measured by dissolutions and recovery of soluble cellulose (W_s) with calculation of insoluble fraction (W_i) by difference and by isolation of gel component (W_g).[27]   The values which are summarized in Table I establish that forms W and V cottons at the 0.4% level of formaldehyde are completely insoluble, whereas form D cotton at the same level of formaldehyde is soluble to the extent of approximately 15%.

DISCUSSION

Diffusion-Controlling Factors

In a preceding study[17] we have found that periodate oxidative decrystallization of cotton cellulose proceeds at a pseudo zero-order rate over approximately 60% of the reaction.   We have observed also that a straight line results over the same range of the reaction when the logarithm of the percentage oxidation is plotted against the logarithm of time, a condition which fulfills the Sakurada equation,[28] $x = kt^m$, where x is a measure of the extent of the reaction, t is time of reaction, k is the velocity constant, and m is the average time constant.   This behavior is indicative of a diffusion-controlled process.

Peterson and Livingston[29] have measured a fivefold reduction in permeability to dilute potassium chloride for cellophane membrane on being crosslinked with dialdehyde starch.   It is postulated that rate of diffusion through a crosslinked network will be dependent upon degree of crosslinking and nature of crosslinks.   In a semicrystalline, fibrous structure it is neces-

sary to consider, also, distribution of crosslinks. "Effective crosslinking" will be the consequence, therefore, of the summation of effects of the following factors: (1) number of linkages formed to AGU; (2) ratio of intermolecular to intramolecular linkages; (3) number of units of reagent in each intra- or intermolecular linkage; (4) distribution of crosslinks. In crosslinked compositions incorporating the same level of agent, variations in factors 1 and 3 may be interrelated by formation of a smaller number of long crosslinks (polyoxymethylene) under one set of conditions or a larger number of short crosslinks (oxymethylene) in another case. Guthrie[8] has deduced the variation in crosslink length from performance properties, and Jones[30] has found evidence for oxymethylene and polyoxymethylene linkages from hydrolysis rates. Differences in ratios of inter- to intramolecular linkages have been proposed by Steele,[7] and differences in distribution of crosslinks in the fiber microstructure have been inferred by Frick et al.[11,26]

The penetration of periodate reagent to regions of high order in the cellulose structures under study may be functions of diffusion rates among several types of molecular structures: (a) unmodified cotton AGU, (b) "dialdehyde units" produced by oxidative bond scission between carbons C_2 and C_3 of the AGU, (c) AGU reacted with formaldehyde residues through the hydroxyl groups on C_2 or C_3, (d) AGU crosslinked with formaldehyde through the hydroxyl group on the C_6 and (e) "dialdehyde units" crosslinked with formaldehyde through the hydroxyl group on C_6. Since periodate oxidation at vicinal hydroxyl groups proceeds at velocities manyfold faster than rates of diffusion into cellulose, it is reasonable to expect that AGU having available vicinal hydroxyl groups [types (a) and (d) above] are oxidized rapidly as the reagent permeates progressively into the fibrous structure. The rate of diffusion will be reduced when crosslinked molecular segments [types (c), (d), and (e) above)] are encountered. The rate of oxidation will also be reduced by the lower availability of vicinal hydroxyl groups when the crosslink involves a stable formal linkage through the 2- or 3-hydroxyls of the AGU [type (c) above] which preclude oxidation of that unit. It is noteworthy that Wagner and Pacsu,[31] Datye,[32] and Jones[30] conclude that the (predominant) reaction of formaldehyde is at the 2- (and 3-) hydroxyls; it appears, therefore that the diffusion of periodate reagent will be predominantly through molecular structures of types (b) and (c).

The effect of removal of an AGU in the noncrystalline region from potential reaction with periodate reagent by the development of a linkage with formaldehyde at the hydroxyl groups in the 2- or 3-positions will be to increase the relative extent of oxidation and decrystallization which will occur in regions of high order at any given level of oxidation.

Both the reduction in the rate of oxidative decrystallization and the increase in relative attack on regions of high order will be accentuated by tendency for crosslinks to exclude neighboring AGU from undergoing oxidation. This appears to be a possibility, at least at high levels of crosslinking agent, from results of Karrholm[18] who found the oxidation of cross-

linked rayon to level off below the complete reaction of theoretically available vicinal hydroxyl groups.

The removal of AGU from reactivity with periodate by development of oxymethylene crosslinks through the 2- or 3-hydroxyl groups in the compositions under study may reduce reaction by a maximum of 4.4% in the total composition, and by 21.7% in an accessible region amounting to 20% of tne total. Datye[32] has estimated an accessibility of approximately 20% for cotton cellulose on the basis of the HCl-catalyzed reaction with formalde‐ hyde in aqueous calcium chloride; it is apparent, then, that development of oxymethylene crosslinks in an accessible region of this magnitude will remove a substantial portion of vicinal hydroxyl groups from reaction and will also provide a restrictive barrier to diffusion, as a consequence.

Thus, rates of oxidative decrystallization of crosslinked cotton celluloses are expected to provide a composite measure of factors *1–4* noted above under effective crosslinking. The relative extent of oxidative attack in regions of high order at a given level of oxidation, being independent of time, will provide a measure of factors *1–3*.

Crosslinked Cotton Celluloses

The crosslinked compositions studied were formaldehyde-modified cotton celluloses prepared via HCl catalysis[12] under conditions conducive to different degrees of swelling during crosslinking: in typical aqueous (form W), in nonaqueous (form D), and in vapor (form V) treatments. The level of reagent (0.4% in each case) represents a molar ratio of combined formalde‐ hyde to AGU of $1/_{46}$; the maximum potential of crosslinks is, therefore, one per 46 AGU. By all standards this is a low level of chemical modification; nevertheless, significant differences in physical properties exist among the three modified cottons (Table II), and high wrinkle recoveries are realized, the maximum being obtained with form V cotton.

TABLE II
Formaldehyde-Modified Cotton Celluloses

Composition	Reagent system	Crease recoveries (W + F), degrees[a]		Breaking strength (W), lb.	Tearing strength (W), g.
		Wet	Dry		
Cotton	—	160	180	42	990
Form W	80.2% H_2O, 7.6% CH_2O, 12.2% HCl	250	200	31	580
Form D	17.7% H_2O, 71.3% HOAc, 5.5% CH_2O, 5.5% HCl	240	250	30	480
Form V	CH_2O–HCl vapor, ambient moisture	250	300	27	550

[a] W is warp; F is fill.

Variations in Crosslink Distributions

The constant rate of decrease in crystallinity index (CI) for form W cotton over the entire oxidation, together with conformity to the Sakurada equation over 80% of the reaction, indicates a "simple" diffusion-controlled penetration to chain segments in the highly ordered regions. Additional complexity is evident in the oxidative decrystallizations of forms D and V cottons as indicated by curves in Figure 1 and by the necessity for a second set of constants (k and m) for the Sakurada equation in order to describe the reaction beyond 42 and 36% oxidation for forms D and V cottons, respectively. Based on the deviation from straight-line relationships in Figure 1, we note three distinct phases for reactions for forms D and V cottons. We tentatively interpret the first phase to include oxidative attack on readily available surface areas; to a CI of approximately 85, we recognize no differences in rates among the various cottons with the possible exception that form V cotton exhibits a small but consistent trend (Fig. 1 and insert) toward a more rapid decrease in CI. We suspect that this is a reflection of molecular degradation which, although occurring on surface or in accessible regions, has bearing on the access to crystalline regions.

The existence of an extensive period of slow oxidative decrystallization for forms D and V cottons is evidence of more effective development of crosslinks in these cottons than realized in the case of form W cotton: i.e., the crosslink structures in forms D and V cottons are more restrictive to diffusion and/or oxidation, indicative of a higher number of crosslinks and/or higher proportion of intermolecular linkages and/or shorter length of crosslinks and/or a specific distribution of crosslinks. On this gross basis, the rating for effectiveness of crosslinking in these compositions is form W $\ll$ form D $\leq$ form V.

It is interesting that following the period of slow decrease in CI, forms D and V cottons undergo transitions to more rapid decreases in CI at significantly different times (72 and 96 hr., respectively) but at similar levels of oxidant consumption (36–42%). Since no evidence for hydrolysis of crosslinks has been observed, the increase in rate of oxidative decrystallization appears to result from development of less tortuous paths of diffusion through regions which approach oxidized cotton [type (a) structural segments] in freedom of mobility. An increase in diffusion constant, m, in $x = kt^m$ (Table III) beyond 36–42% oxidation for forms D and V cotton coincides with transition of these crosslinked cottons to more rapid rates of decrease in CI. Thus, these transitions are interpreted as stages at which maximum relaxation of crosslinked segments is realized.

On the basis of electron micrographic observations, it is apparent the form W cotton offers a high degree of internal surface which provides ready access to the microstructure of the fiber. This is consistent with the absence in form W cotton of any major barrier to the oxidative decrystallization (Fig. 1).

In spite of the considerable nonuniformity in form D cotton which is

TABLE III
Values of Constants for Sakurada Diffusion Equation[a]

Composition	m	k	Range of reaction
Cotton	0.60	5.8	To ca. 76% oxidation (time = 0–72 hr.)
	0.22	29.8	From 76% to 99.3% oxidation (time = 72–240 hr.)
Form W cotton	0.58	5.1	To ca. 73% oxidation (time = 0–96 hr.)
	0.37	13.5	From ca. 73% to 100% oxidation (time = 96–240 hr.)
Form D cotton	0.49	4.5	To ca. 43% oxidation (time = 0–96 hr.)
	0.71	1.6	From ca. 43% to 80% oxidation (time = 96–240 hr.)
Form V cotton	0.44	4.9	To ca. 36% oxidation (time = 0–96 hr.)
	0.88	0.7	From ca. 36% to 79% oxidation (time = 96–240 hr.)

[a] $x = kt^m$, where x is percentage consumption of oxidant, t is time in hours, and m and k are characteristic constants; m is the slope in the log/log plot.

observed electron micrographically, and the evidence for incomplete distribution of crosslinks throughout the molecular species from solubility data, form D cotton approaches form V cotton in (slow) rate of oxidative decrystallization. All these data are indicative of effective crosslinking for form D cotton in peripheral regions which limit access of the oxidizing agent to the less effectively crosslinked regions until considerable oxidation has occurred.

We conclude that "effectiveness of crosslinking" measured via relative rates of oxidative decrystallization of the crosslinked cotton celluloses is in the order form V ≅ form D > form W and that this relative rating includes pronounced contribution from distribution of crosslinks and availability of surfaces. It is interesting that the crosslinks of form D cotton which are concentrated in peripheral regions are essentially as effective in retarding oxidative decrystallization of cotton as are the uniformly distributed crosslinks of form V cotton.

Nature of Crosslinks

From the extent of oxidative decrystallization (i.e., the increase in 100-CI) at a specific level of oxidation of crosslinked cottons relative to the corresponding change for unmodified cotton cellulose, we obtain a measure of comparative ease of oxidative attack on chain segments in crystalline versus noncrystalline regions. Since this is a reflection of the extent to which the AGU in noncrystalline regions have become unavailable, it is a measure of the composite of the number of linkages formed, the proportion of intermolecular bonds, and the length (shortness) of linkages.

Differences in slopes, $d(100 - CI)/d(Ox)$, for crosslinked cottons versus unmodified cotton are significant in the range of 0–40% oxidant consumption. Whereas the incremental CI values which separate the curves (Fig. 3 and 4) reach maxima in the range of 15–25% oxidation, the most pronounced differences in slopes of curves exist at the outset of the reaction (form W cotton appears to be an exception). For the initial reaction (i.e., at zero and 10% oxidation) values of $d(100\text{-}CI)/d(Ox)$ for the crosslinked cottons are multiples of that of unmodified cotton; i.e., 3.8 and 1.8 for form V; 2.2 and 1.7 for form D; and 0.3 and 2.6 for form W cotton. The maximum value for $d(100 - CI)/d(Ox)$ in the early stage of oxidation is the 0.74 value which characterizes form V cotton at the outset of oxidation; this is approximately 49% of the value (1.52) associated with attack solely on crystalline regions.[17]

The relative increase of oxidative attack on crystalline regions by virtue of crosslinking in noncrystalline regions is most readily indicated by consideration of areas between the curves for the formaldehyde-modified and unmodified cotton celluloses in the range of 0–45% oxidant consumption; the estimated ranges of convergence for forms W, D, and V curves with the curve for cotton are 41, 45, and 46% oxidant consumptions. These differential areas are in the ratio of 1.0/1.5/2.3 for form W/form D/form V cottons.

It is evident that form V cotton is substantially more effectively crosslinked than either forms D or W cotton. On the tentative assumption that the various hydroxyl groups of the AGU of each of these modified cottons are involved in crosslinks in the same ratio, we propose that form V cotton is characterized by shorter crosslinks, possibly monooxymethylene units, in greater number than either of the other two formaldehyde-modified cottons.

CONCLUSIONS

Crosslinks in cotton cellulose control access to both amorphous and crystalline regions, evidence being lowered rates of oxidation and lowered rates of decrystallization.

Differences in rates of oxidative decrystallization of this series of crosslinked cotton celluloses appear to reflect availabilities of surfaces, both internal and external, together with selective concentrations of crosslinks (as in peripheral regions) as the dominating factors rather than structural characteristics of the crosslinks.

Gross effectiveness of crosslinking, including number of linkages, proportion of intermolecular bonds, and monomeric nature of crosslinks, is indicated to increase in the order form W < form D < form V on the basis of relative extents of oxidative attack on crystalline regions of crosslinked cottons in the early phase of the oxidation reaction.

The dominating characteristics of form W cotton observed here are high interior fiber surface, a broad and uniform distribution of crosslinks throughout the molecular and microphysical structures, but limited interlamellar bonds.

Form D cotton at this level of formaldehyde content exhibits high concentration of crosslinks in peripheral regions, limited interlamellar bonds in interior sections of the fiber, and low uniformity in distribution of crosslinks throughout the molecular species.

Form V cotton exhibits uniform distribution of crosslinks on all bases: molecular, intermicrofibrillar, and interlamellar scales. This composition is indicated to have more and/or shorter crosslinks than form W or D cotton containing the same concentration of agent.

It is notable that the crosslinks which generate only wet crease recovery have relatively small effect in retarding oxidative decrystallization of cotton cellulose whereas those which generate high dry crease recovery (together with high wet crease recovery) are very effective in retarding decrystallization. Highest crease recoveries in this series are associated with the more uniform distribution of shorter crosslinks.

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Résumé

On a mesuré la diminution de la cristallinité de la cellulose de coton et de la cellulose de coton traitée par le formaldéhyde pendant l'oxydation au périodate. Le degré de cristallinité est déterminé par l'indice de cristallinité, obtenu au moyen des rayons-X. Suivant les conditions dans laquelle le réactif est introduit, des petites quantités de ponts dus au formaldéhyde retardent plus ou moins la vitesse de diminution de l'indice de cristallinité. L'importance de la diminution de cristallinité par unité d'oxydation du coton et coton ponté est plus petite au début de l'oxydation qu'à la fin. Ceci prouve qu'au début l'attaque par oxydation est préférentiellement dirigée sur les segments des régions non-cristallines des chaînes. Comparé avec le coton inchangé, le coton ponté est caractérisé par une plus grande diminution de cristallinité au début de l'attaque oxydante (approx. 40%). De ces résultats, confirmés par des micrographies d'électrons et des solubilités dans l'hydroxyde de cupriéthylène-diamine, on observe que l'uniformité de la distribution des ponts augmente dans la série des celluloses de coton, modifiés par la formaldéhyde dans l'ordre suivant: forme D coton (non traité par l'eau) < forme W coton (traité par l'eau) < forme V coton (traitement à la vapeur). L'efficacité du pontage augmente à partir de la forme W à la forme D à la forme V du coton.

Zusammenfassung

Die Geschwindigkeit der Kristallinitätsabnahme, gemessen am Röntgenkristallinitätsindex, wjrde während der Periodatoxydation von Baumwollzellulose und von formaldehydbehandelter Zellulose verfolgt. Je nach den Bedingungen, unter welchen das Reagens eingeführt wurde, bewirkte eine geringe Formaldehydvernetzung eine kleine oder grosse Verzögerung der Geschwindigkeit der Abnahme des Kristallinitätsindex. Das Ausmass der Dekristallisation pro Oxydationseinheit von Baumwolle und vernetzter Baumwollzellulose ist in der Anfangsphase der Oxydation wesentlich kleiner als im späteren Stadium, was für einen bevorzugten oxydativen Angriff vorwiegend auf Kettensegmente in nichtkristallinen Bereichen im frühen Stadium spricht. Im Verhältnis zu nichtmodifizierter Baumwolle ist die vernetzte Baumwollzellulose durch eine starke Dekristallisation pro Oxydationseinheit in der frühen Phase des oxydativen Angriffs (zu etwa 40%) charakterisiert. Anhand dieser Daten, welche durch elektronenmikroskopische Aufnahmen und durch Löslichkeitsdaten in Kupferäthylendiaminhydroxyd ergänzt werden, wird gezeigt, dass die Einheitlichkeit der Vernetzungsstellenverteilung bei dieser Reihe formaldehydmodifizierter Baumwollzellulosen (bei der gleichen Reagensmenge) in folgender Reihenfolge zunimmt: Baumwolle Form D (nichtwässrige Behandlung) < Baumwolle Form W (wässirge Behandlung) < Baumwolle Form V (Dampfbehandlung). Die Vernetzungswirksamkeit (d.h. zusammengesetzt aus Bindungszahl, Verhältnis von inter- zu intramolekularen Bindungen, niedrigem Polymerisationsgrad in der Vernetzung) steigt von Baumwolle der Form W zu Form D und zu Form V an.