Photodegradation of Oxidized Cotton Cellulose

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SYNOPSIS

Different functional groups were systematically introduced into cotton cellulose and their effect on the stability of cotton toward photochemical degradation was examined. First, the cotton was progressively oxidized with sodium metaperiodate up to an oxygen consumption of 2.45 atom per 100 anhydroglucose units (agu) to form 2,3-dialdehyde cellulose. These products were reduced with potassium borohydride to obtain 2,3-dialcohol cellulose or were oxidized with sodium chlorite to obtain 2,3-dicarboxyl cellulose. The chemical modifications of the cellulose structure caused a drop in tensile strength of 34% for the dialdehyde of 2.45 oxygen consumption per 100 agu compared to 27% and 37% in the case of the dialcohol and the dicarboxyl celluloses, respectively. Upon irradiation with UV light, the breaking strengths of the dialcohol and the dicarboxyl celluloses were generally higher up to an oxygen consumption of 0.63 per 100 agu when compared to the dialdehyde and then fell more drastically. The tensile data of the exposed oxycelluloses correlated well with the reciprocal of their intrinsic viscosities ($R^2 = 0.89$). The primary alcohol groups appeared to accelerate the progress of the photochemical degradation. The photochemical effects of the carboxyl groups could not be differentiated from the autohydrolysis to which dicarboxyl cellulose is susceptible. No indication of a change in morphology was detected for any of the treatment types. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Photodegradation of cellulosic fibers has been discussed from both fundamental and practical points of view.[1,2] It is well known that purified cellulose is incapable of absorbing light in the visible region, and it remains uncertain whether absorption takes place in the UV region, and if so, which groups are responsible for the absorption.[1-3] However, irradiation at 2537 Å, the emission wavelength of a mercury light source, was found sufficiently energetic to cause photolytic degradation by formation of free radicals through direct absorption, generating carbonyl and carboxyl groups, and finally leading to chain cleavage.[1,4,5] Rånby[2] found a broad absorption peak at 2650 Å with a shoulder for pure cellulose film. It was suggested that the regularly reoccurring acetal groups at C1 of the nonreducing glucose units form a chromophoric center that produces a band ab-

sorption. Another possible explanation for the observed absorption involves external or internal impurities especially if they contain carbonyl or carboxyl groups.[1] Photodegradation as a surface effect, where the chromophoric centers were primarily formed on the surface, has also been discussed.[6]

Once radiation of appropriate energy is absorbed by the cellulose molecule, electronically excited species are formed that lead to the dissociation of chemical bonds either directly or by energy transfer, followed by irreversible structural changes. According to Desai and Shields,[7] chain scission at the glycosidic bonds is the primary photolytic reaction followed by the formation of some volatile products. Apparently, the presence of oxygen is not a decisive factor in determining the rate of degradation,[1,4] whereas the amount of moisture present in the cellulosic fiber appears to have both promoting and obstructing effects on the progress of deterioration, depending on the applied source of light.[8] Water molecules obviously influence the formation of free radicals as well as their recombination and, thereby, make some impact on the chemical nature of the degradation products. On the other hand, this would

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mean that free radicals are produced preferentially in the amorphous regions of the fiber since water is unable to penetrate the crystalline areas.[1,2]

The objective of the present work was to investigate whether aldehyde, carboxyl, or primary alcohol groups in the cellulose molecules would affect photodegradation. The functional groups were introduced by oxidation using sodium metaperiodate. Although most oxidants are nonspecific in their method of attack, sodium metaperiodate selectively attacks the hydroxyl groups at C2 and C3 with simultaneous cleavage of the C2—C3 bond[9] and aldehyde groups are formed at these positions. The reaction mechanism has been studied in detail, and it is known that as a permutoid reaction the oxidation is not limited to the accessible regions. However, since the reaction is heterogeneous, the distribution of aldehyde groups along the polysaccharide chains cannot be expected to occur uniformly.[10] Further specific functional groups were then introduced by reduction or oxidation of the dialdehyde cellulose. The dialcohol was obtained on reduction with potassium borohydride, and the dicarbon acid, by oxidation with sodium chlorite.[9,11]

Thus, in a series of experiments, the dialdehyde, dialcohol, and dicarboxyl celluloses were exposed to a controlled irradiance and humidity system for various periods of time. The tensile strength, intrinsic viscosity, and surface characteristics of the exposed samples were determined to study the course of the degradation and establish the influence of the different functional groups introduced.

EXPERIMENTAL

A 2-ply (40/2) yarn made of 100% carded cotton was used. The yarn was scoured in 4% sodium hydroxide solution at 100°C for 1.5 h, washed thoroughly, and air-dried before further reactions.

Preparation of Dialdehyde Cellulose

The yarn was used in the loose form and the procedure described by Nevell[11] was followed, applying a 0.01N sodium metaperiodate solution. The oxidized samples were kept in the refrigerator in the dark for further investigation.

Preparation of the 2,3-Dialcohol Cellulose

The reduction of the aldehyde groups in the periodate-oxidized samples by potassium borohydride was carried out in the manner described by Head.[12]

Preparation of the 2,3-Dicarboxyl Cellulose

The oxidation was carried out at 20°C using 50 mL of 0.2M sodium chlorite in 1 M acetic acid for each gram of material.[11] The treatment time was 72 h.

Exposure to Controlled Irradiance and Humidity

For the photodegradation, a Weather-ometer (Atlas Electric Devices Co., USA) was used with a 6500/3500 W xenon burner lamp as light source with borosilicate inner and outer filters. The emission spectrum of the lamp covered the range from about 2800 to 7000 Å, shorter wavelengths being cut off by the borosilicate filters.[13] The products were exposed for up to 672 h, applying a 2 h cycle of 102 min light and 18 min dark. The temperature was set to 49°C maximum for the light part of the cycle and to 20°C for the dark portion. The temperature of the conditioning water was kept at 30°C throughout.

Characterization of the Products

Tensile Tests

The breaking load of the yarns was determined on an Instron Tensile Tester at 65% RH and 21°C using 76.2 mm as the gauge length and 20 mm/min as the rate of extension.

Intrinsic Viscosity

The determination of the intrinsic viscosity of the samples was carried out according to DIN 54 270, Part 3, using Cannon-Fenske viscometers and FeTNa as solvent.[14] The samples were prepared for dissolution by grinding in a Wiley mill to pass through a 20-mesh screen. Values are the average of four determinations. Periodate-oxidized samples were reduced with potassium borohydride before viscosity determinations because of their alkaline susceptibility.[9]

Scanning Electron Microscopy (SEM)

SEM micrographs were obtained using an ISI-DS-130 scanning electron microscope in the manner described before.[15]

RESULTS AND DISCUSSION

Effects of Photodegradation on the Tensile Strength of Periodate-Oxidized Cotton Yarn

Previously, it was found[16] that the tensile strength of cotton yarn decreased significantly during the

Table I   Influence of Photodegradation on the Tensile Strength of Periodate-Oxidized Cotton Yarn

Oxygen Consumption (Atoms/100 agu)	Breaking Load (N) after Irradiation			
	0 h	168 h	336 h	672 h
Control	4.23	4.13	4.02	3.45
0.29	4.01	3.69	3.31	2.60
0.43	3.65	3.45	3.07	2.43
0.55	3.80	3.40	2.98	2.31
0.63	3.58	3.27	2.84	2.28
0.84	3.50	3.18	2.72	2.44
1.35	3.62	3.09	2.65	2.26
1.58	3.19	2.87	2.42	1.88
2.45	2.80	2.27	2.02	1.57

early stage of the periodate oxidation, up to about 15 atoms oxygen per 100 anhydroglucose units (agu) and then rose slightly as the reaction proceeded further. The present project was concerned with the initial stages of the oxidation reaction extending up to an oxygen consumption of 2.5 atom per 100 agu. During this phase, side reactions are not likely to be significant.

The tensile strength decreased by about 15% up to an oxygen consumption of 1.35 atom per 100 agu,

then dropped more drastically and achieved a 34% loss by an oxygen consumption of 2.45 atom per 100 agu (Table I and Fig. 1). This course is attributed to the oxidant attacking the accessible fiber regions first, then slowly penetrating the crystalline areas and gradually breaking down the cellulose structure.[9,16]

Upon irradiation, the breaking strength of the periodate-oxidized yarns decreased faster than did the nonoxidized sample (Table I and Fig. 2). During the first 168 h, an average drop of 7–10% was observed for a given oxidation level, while a nonoxidized sample lost only 2.3% in strength. The following 168 h caused a further decrease of approximately 10–15% compared to 2.4% for the control, and as a result of the subsequent 336 h of exposure, an additional 20% loss in strength, on the average, was obtained while the nonoxidized product dropped by only 14%.

Surprisingly, the observed decrease takes a nearly linear course. A more accelerating effect on photodegradation could have been expected due to the introduced aldehyde groups. However, the aldehyde groups in the C2 and C3 positions are known to combine with water (hemialdals) or with alcohols (hemiacetals).[17] Inter- and intramolecular crosslinking with the hydroxyl group at C6 can take place, leading to the formation of 2,6- or 3,6-hemiacetals in the absence of other suitable reagents.[16] There-
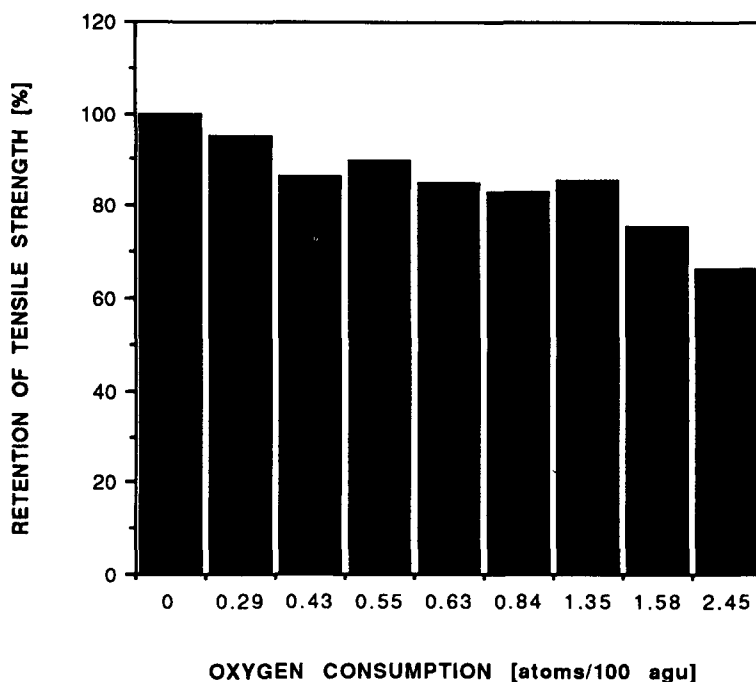

Figure 1   Retention of breaking strength of periodate-oxidized cotton yarn for increasing levels of oxygen consumption.
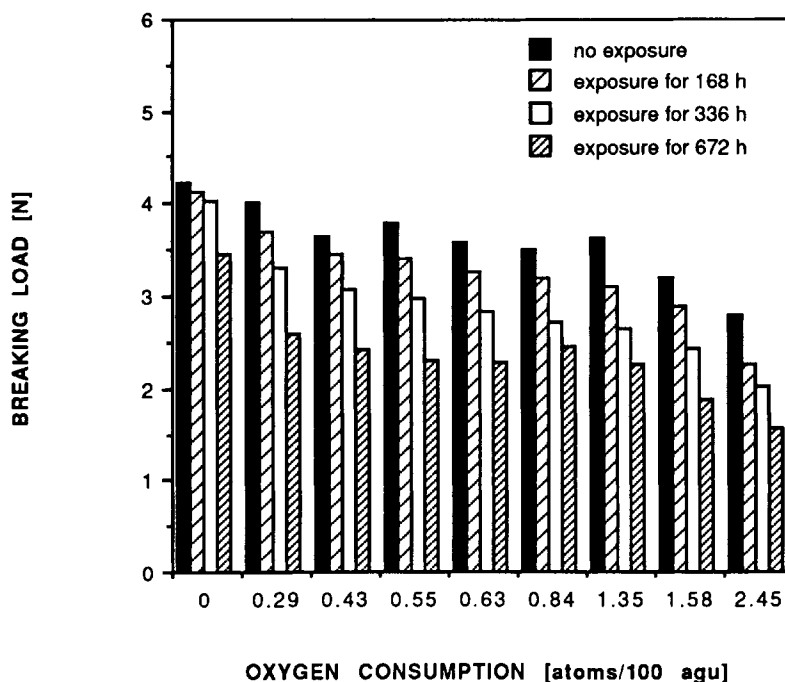
Figure 2 Comparison of the tensile strength of periodate-oxidized cotton after exposure to UV for various periods of time.

fore, only small amounts of free aldehyde groups can be expected to be available for photoreactions.

Changes in Tensile Strength of 2,3-Dialcohol Cellulose upon Photochemical Treatment

With the reaction conditions applied for the reduction with potassium borohydride, all available aldehyde and hemialdal groups as well as the hemiacetal cross-links were converted to alcohol groups. As a result of the destruction of the cross-links, higher breaking strengths were obtained compared to the dialdehyde celluloses due to increased chain mobility and extensibility (Fig. 3; cf. Tables I and II). Up to an oxygen consumption of about 1 atom per 100 agu, the original strength of the starting yarn was almost restored by the reduction, then it gradually dropped to 73% strength retention in contrast to 66% in the case of the counterpart dialdehyde cellulose. The observed slow decrease in strength can be attributed to the effect of chain scission, which occurred primarily during the periodate oxidation.

When the samples were irradiated, it was observed that after 168 h exposure time the tensile strengths of the reduced samples were either higher or equal to the nonreduced counterparts over the entire oxidation range (cf. Tables I and II). After

336 h irradiation, a turning-point around an oxygen consumption of 1 atom per 100 agu appeared where the strength of the oxidized sample remained higher than that of its reduced counterpart. The turning point shifted to 0.63 atom oxygen per 100 agu by the end of the fourth week (Fig. 4). Thus, it seems very probable that, with a certain amount of alcohol groups in the cellulose structure, indeed, chromophoric centers were created that accelerated photochemical deterioration to some extent. The shift of the turning point to lower oxidation levels might be an indication of decomposition reactions due to additional light-absorbing centers induced by these primary alcohol groups.

Changes in Tensile Strength of 2,3-Dicarboxyl Cellulose after Exposure to Light

When dialdehyde cellulose is treated with sodium chlorite, the aldehyde groups are oxidized to carboxyl groups and the products should have higher chain flexibility similar to the dialcohol. In fact, the tensile strength of the dicarboxyl cellulose was 2–4% lower than the breaking strength of the counterpart dialcohol celluloses (cf. Tables II and III), but still it was close to that of the nonoxidized control up to an oxygen consumption of 0.65 atom per 100 agu.
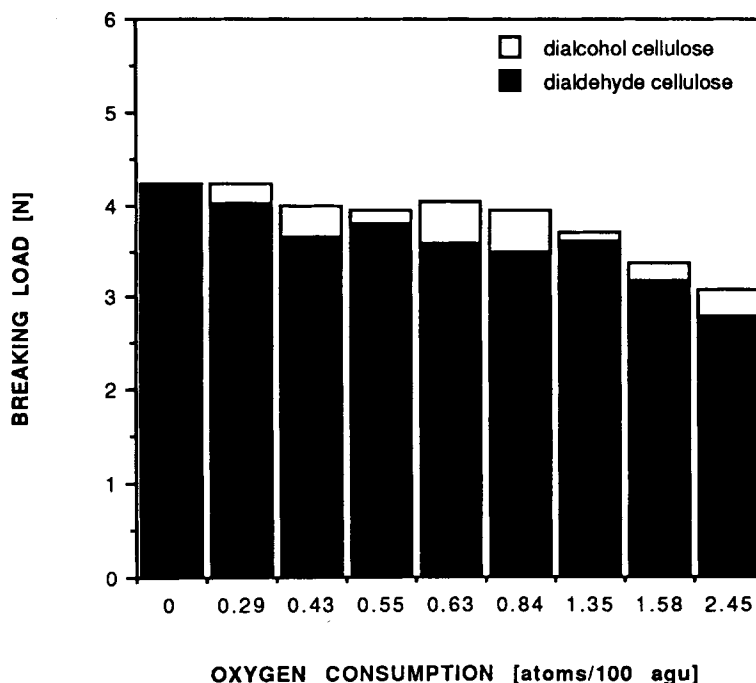
Figure 3 Restoration of breaking strength by reduction of the periodate-oxidized cotton with potassium borohydride.

With increasing oxidation level, the dicarboxyl celluloses lost strength more rapidly and achieved the lowest strength retention (63%) of all three investigated cellulose modifications.

The acidic reaction conditions during the chlorite oxidation made it necessary to treat a nonoxidized sample as a control using the same experimental setup. An initial loss in strength of approximately 3% was obtained and it was mostly maintained during the subsequent light exposure.

Table II Influence of Photodegradation on the Tensile Strength of Borohydride-Reduced Periodate-Oxidized Cotton Yarn

Oxygen Consumption (Atoms/100 agu)	Breaking Load (N) after Irradiation			
	0 h	168 h	336 h	672 h
Control	4.23	4.11	3.91	3.27
0.29	4.23	3.73	3.62	2.81
0.43	4.00	3.67	3.15	2.66
0.55	3.95	3.76	3.09	2.48
0.63	4.03	3.38	3.16	2.30
0.84	3.94	3.23	2.78	2.33
1.35	3.71	3.09	2.51	1.98
1.58	3.37	2.97	2.42	1.67
2.45	3.08	2.27	1.91	1.24

Subjected to light and humidity, the degradative breakdown of the dicarboxyl celluloses proceeded at a rather fast rate (Fig. 5). If compared to the dialdehyde counterparts, a turning point in tensile strength appeared at an oxygen consumption of approximately 0.63 atom per 100 agu, independent of the exposure duration (Fig. 6). For higher degrees of oxidation, the strength loss was higher for the dicarboxyl celluloses than for the dialdehyde samples, and below that point, it was slightly less. Since this was true for the entire irradiation period, only the data for the longest exposure time of 672 h are presented in Figure 6.

By oxidizing the dialdehyde cellulose with chlorite and subsequently subjecting it to light, the highest decreases in tensile strength were obtained compared to the other treatments. Part of this relatively steep drop in strength may be due to autohydrolysis by the carboxyl groups present in the cellulose structure.

Changes in Intrinsic Viscosity after Photochemical Degradation

Intrinsic viscosities were determined for samples with oxygen consumptions of 0.84 and 2.45 atom per 100 agu before and after 672 h of exposure to light (Table IV). The highest viscosities were ob-
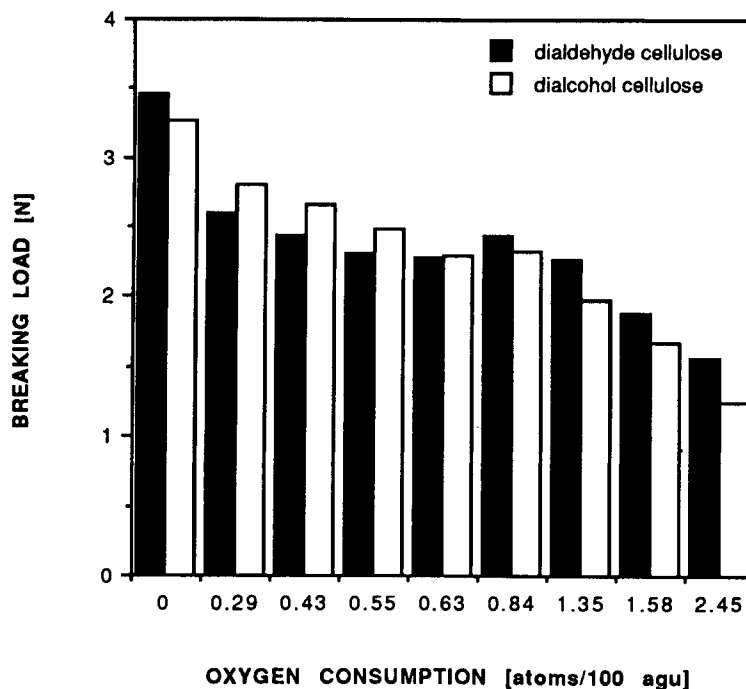
Figure 4 Comparison of the tensile strength of periodate-oxidized and borohydride-reduced, periodate-oxidized cotton after exposure to UV light for 672 h.

tained on periodate-oxidized materials that were subsequently reduced to 2,3-dialcohol. The reduced nonexposed samples also have to be regarded as reference for nonexposed 2,3-dialdehydes since the viscosity of dialdehyde celluloses cannot be deter-

Table III Influence of Photodegradation on Tensile Strength of Chlorite-Treated, Periodate-Oxidized Cotton Yarn

Oxygen Consumption (Atoms/100 agu)	Breaking Load (N) after Irradiation			
	0 h	168 h	336 h	672 h
Control, untreated	4.23	3.92	3.91	3.32
Control, oxidized[a]	4.09	3.98	3.78	3.36
0.29	3.93	3.86	3.29	2.86
0.45	3.91	3.59	3.17	2.45
0.55	3.88	3.72	3.22	2.35
0.65	3.91	3.48	2.76	2.28
0.79	3.72	3.09	2.34	1.91
1.35	3.44	2.69	2.24	1.80
1.58	3.40	2.52	2.02	1.57
2.45	2.66	1.85	1.59	1.03

[a] Control (0.0 atoms/100 agu) oxidized at the same conditions as the periodate oxycelluloses.

mined directly due to their alkali sensitivity.[9,18] Compared to the untreated control, a decrease in viscosity of about 31% was observed for slightly oxidized dialcohol. It can be attributed to the chain scission caused primarily during periodate oxidation. This was also documented by the small decrease in breaking strength that occurred at low degrees of oxidation (Table II).

Subjected to light for 672 h, the intrinsic viscosity of the untreated control fell from 1577 to 521 mL/g, which gives a greater percentage drop in viscosity than in the case of the exposed dialdehyde with an oxygen consumption of 0.84 atom per 100 agu. In this case, the intrinsic viscosity fell from 1081 to 479 mL/g. In contrast, as noted earlier, the periodate-oxidized sample lost more strength than did the nonoxidized sample upon irradiation. Normally, a decrease in strength is accompanied by a decrease in intrinsic viscosity, but it appears that the strength/intrinsic viscosity correlations are different for the nonoxidized and oxidized samples where the strength is lowered by light exposure.

The intrinsic viscosity of the exposed dialcohol dropped to 345 mL/g for the low oxidation level and to 221 mL/g for the higher degree of oxidation, which, in both cases, was distinctly a higher decrease than for the dialdehyde counterparts. Since the ob-
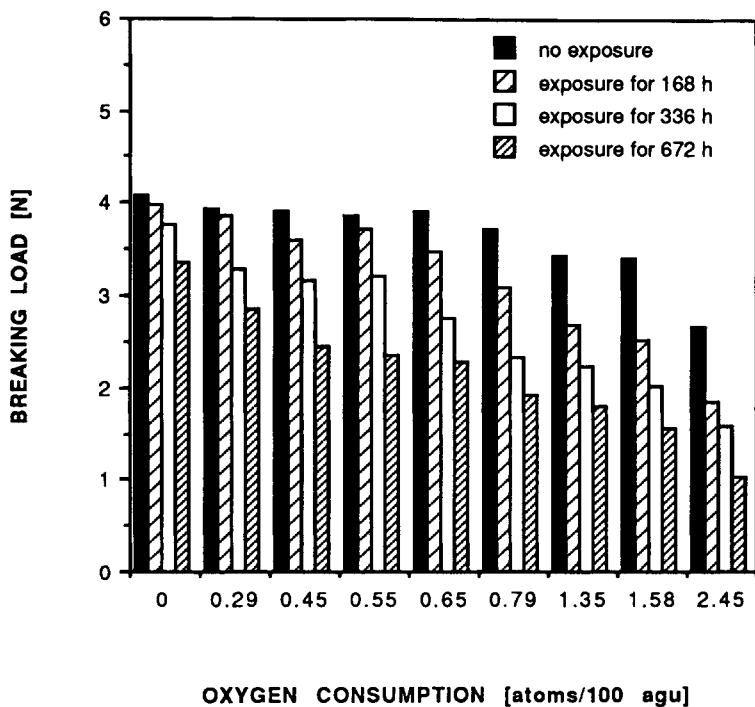
Figure 5   Comparison of the tensile strength of chlorite-oxidized, periodate-oxidized cotton after exposure to UV for various periods of time.
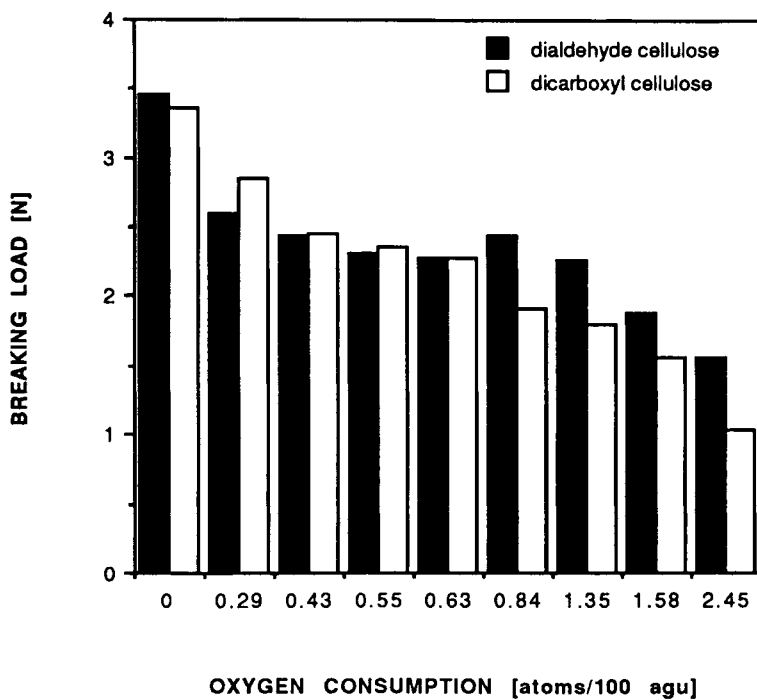

Figure 6   Comparison of the tensile strength of periodate-oxidized and chlorite-oxidized, periodate-oxidized cotton after exposure to UV light for 672 h.

Table IV **Intrinsic Viscosities of Selected Samples before and after Exposure to Light for 672 h**

Sample	Oxygen Consumption (Atoms/100 agu)	Intrinsic Viscosity (mL/g)
Control		
No exposure	0.00	1577
Exposed	0.00	521
2,3-Dialdehyde cellulose		
Exposed	0.84	479
Exposed	2.45	323
2,3-Dialcohol cellulose		
No exposure	0.84	1081
Exposed	0.84	345
No exposure	2.45	644
Exposed	2.45	221
2,3-Dicarboxyl cellulose		
Exposed	0.79	282
Exposed	2.45	178

served decrease proved to be independent of the degree of oxidation if based on the unexposed sample of comparable oxidation level, it follows that the alcohol groups must have a photosensitizing effect and thus actually accelerate the photodegradation. The results for the intrinsic viscosities are in good
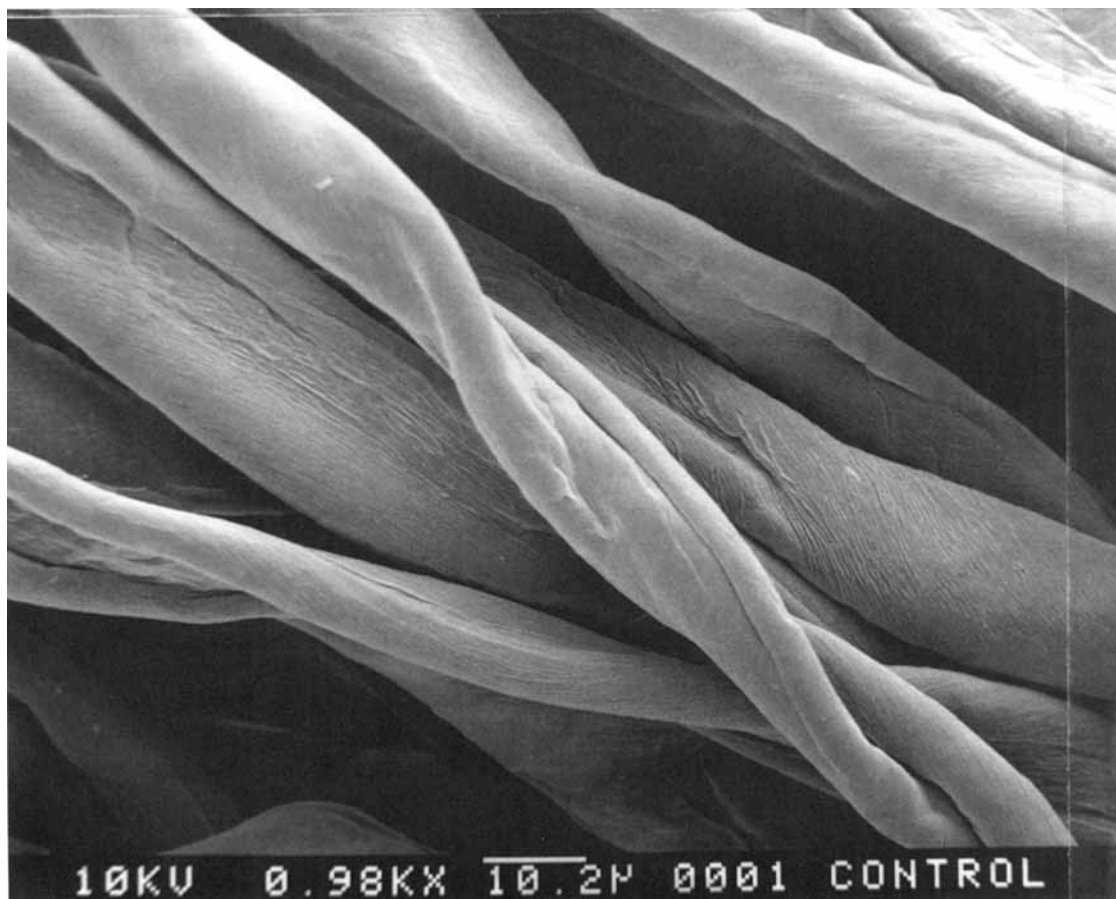
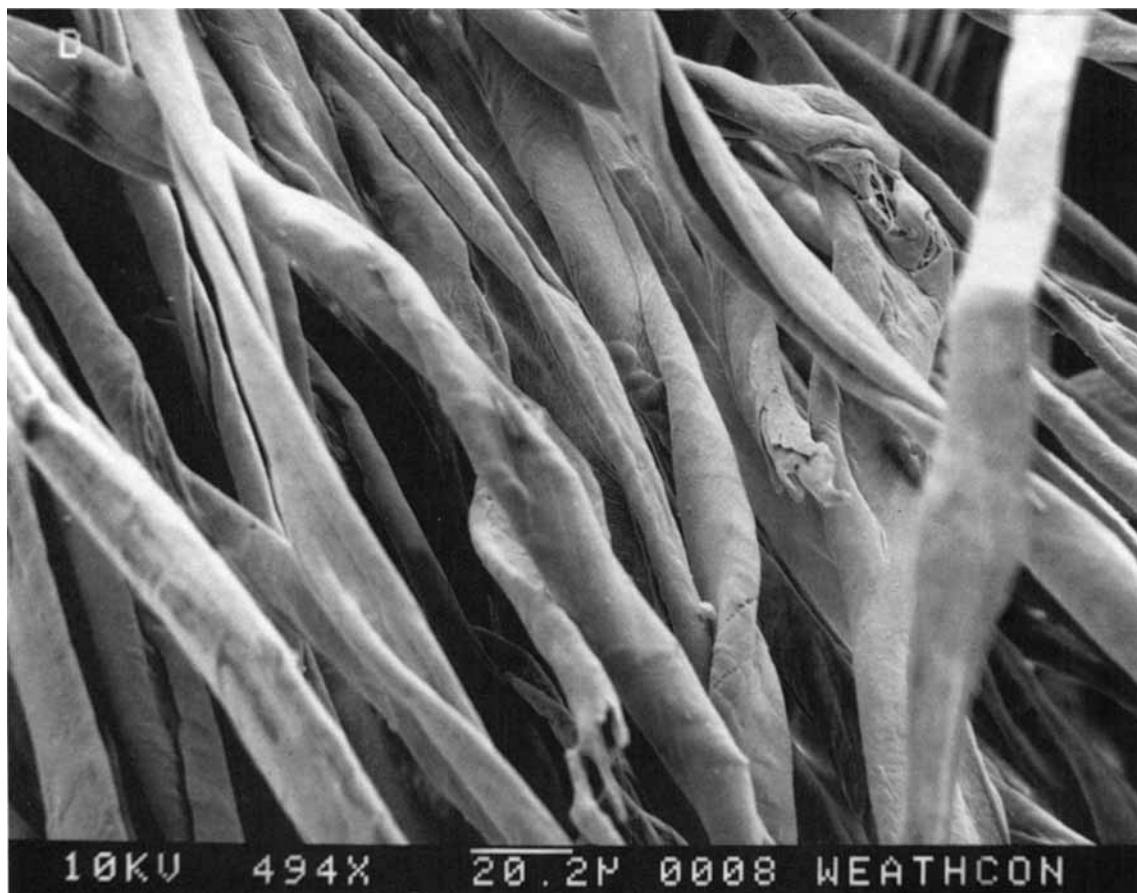**Figure 7** SEM micrograph of untreated cotton.

Figure 8 SEM micrograph of untreated cotton after 672 h exposure.

agreement with the higher strengths obtained for these periodate-oxidized samples in comparison to the borohydride-reduced counterparts (cf. Tables I and II).

In agreement with the moderate tensile strength of the dicarboxyl celluloses, the intrinsic viscosities of these samples turned out to be distinctly lower than those of the dialdehyde and dialcohol samples. It is very likely that the structural breakdown of this material is proceeded by chemical rather than photoinduced reactions, and random chain fracture together with oxidative processes are very likely to be the cause.

When the breaking loads of the dialdehyde, dialcohol, and dicarboxylic celluloses were expressed as a function of the inverse intrinsic viscosities or fluidities, a correlation with $R^2 = 0.89$ was obtained. Thus, irrespective of the treatment type, all data points followed a linear course.

Infrared spectra of the modified exposed samples did not exhibit any differences to the nonexposed. This was true for all discussed treatments. There-

fore, it can be assumed that no major detectable changes in crystallinity occurred.

Surface Characteristics

None of the treatments caused any determinable color changes of the yarns and, macroscopically, they could not be distinguished. Electron microscopy was used to examine the morphology of the 672 h light-exposed samples. In contrast to the smooth surface of the nonexposed sample (Fig. 7), fractured fiber ends and cracks in the fibrillar direction were observed on the light-exposed nonoxidized samples, indicating increased brittleness of the exposed material (Fig. 8).

More and deeper fibrillar cracks were found on the surface of the chemically modified fibers after exposure to UV light. Figure 9 presents the magnification of a typical crack on a borohydride-reduced periodate-oxidized sample. However, there are no extraordinary signs of surface alteration noticeable and the surface can still be considered as relatively smooth.
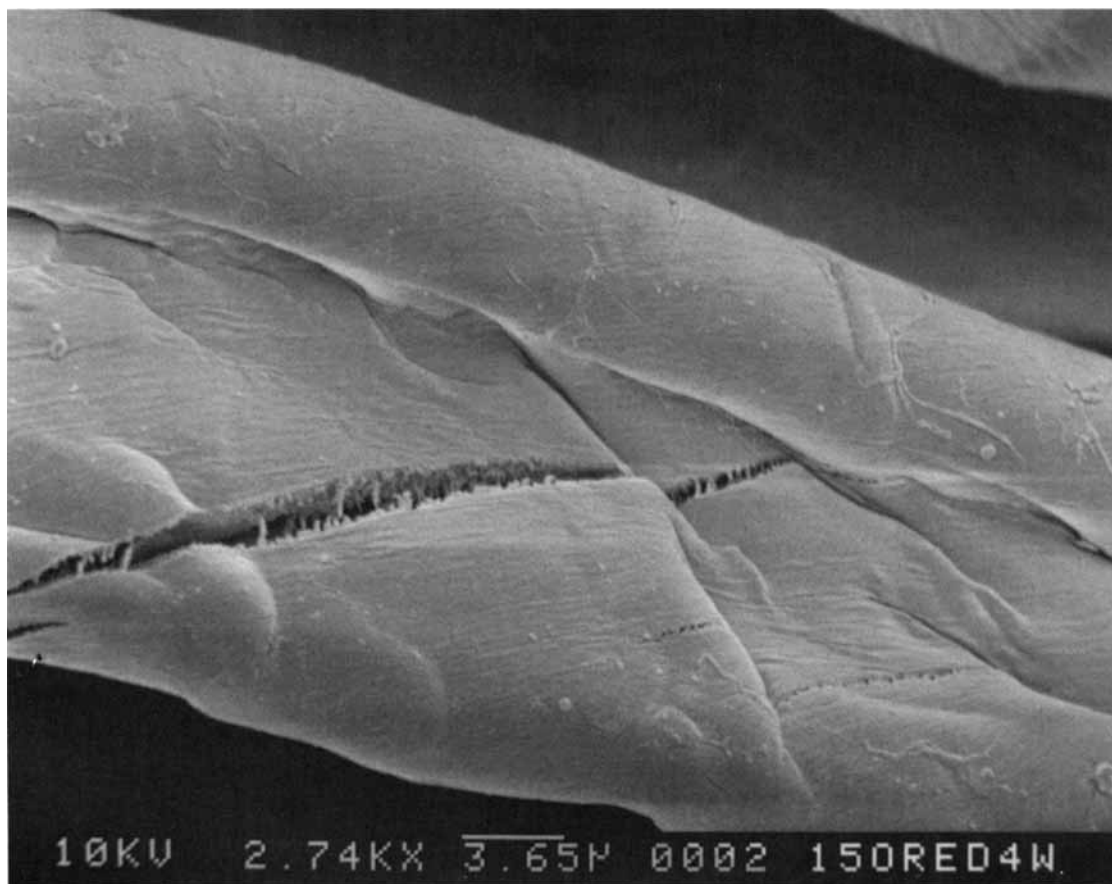
Figure 9 SEM micrograph of borohydride-reduced, periodate-oxidized cotton (oxygen consumption = 2.45 atom per 100 agu) after 672 h exposure.

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