

PHOTODEGRADATION OF LINEN BY SUNLIGHT

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ABSTRACT

In order to elucidate the mechanism of degradation of cellulosic fibers, linens have been exposed to sunlight on an underglass-exposure-rack for 3 years and 5 months and changes of their properties have been investigated as a function of incident sunlight energies. Carbonyl groups, especially aldehyde groups, increased remarkably in the samples after early exposure times, while carboxyl groups were not observed to increase. Degree of polymerization (D. P.) decreased with an increase in light energy and became less than 1/6 of the value of the unexposed control at the incident UV light energy of ca. 900 MJ/m². These facts suggest that degradative reactions including oxidation took place at glycosidic bonds as well as hydroxyl groups of cellulose to cause scission of the molecular chains. Their crystallite size of longitudinal dimension decreased markedly at first and then only slowly, while the size of their lateral dimension and crystallinity index remained almost unchanged. These results indicate that the degradation did not proceed from the surface to the inner of the fibers, but proceeded longitudinally. The tensile strength monotonously decreased until ca. 4% of the value of the unexposed control.

INTRODUCTION

Cellulosic materials such as papers, vegetable fibers and woods are inevitably degraded by various factors. It is very important for their good preservation to know how and why their degradation proceeds. In this work, in order to elucidate the mechanism of the degradation of cellulose, linens were exposed to sunlight on an underglass-exposure-rack equipped with an integrating actinometer for these 3 years and 5 months, and changes in their oxidation-stages, degrees of polymerization (D.P.), cellulose crystallinities and mechanical properties were investigated as a function of incident sunlight energies, especially in the UV region.

EXPERIMENTAL

MATERIALS

Plain-weave linen woven with yarns of 25/1 S was used; its thickness was 0.5 mm. The sample linen had been exposed to sunlight with an IS-1 model underglass-exposure-rack equipped with a PH-11M-2AT model integrating actinometer (Suga Test Instruments Co., Ltd.) since March 1988 and collected at various exposure times.

PROCEDURES

Oxidation-stage: Oxidation stages of the samples were evaluated by comparison of amounts of aldehyde, ketone and carboxyl groups formed in the samples with those in the unexposed control. Total carbonyl groups were determined by a semicarbazide method¹⁾ except that the reaction time of the samples and the reagents was prolonged to 192 h. Ketone groups of the samples were determined by the same method after reoxidation with sodium chlorite²⁾. The amount of aldehyde groups was calculated by subtracting the amount of ketone groups from that of total carbonyl groups. The amount of carboxyl groups was determined by a dynamic ion exchange method³⁾. **Degree of polymerization:** Degrees of polymerization of the samples were determined as the derivatives of cellulose triphenylcarbanilates by high performance size exclusion chromatography (HPSEC). Cellulose triphenylcarbanilates were obtained by the treatment of the sample linens with phenyl isocyanate in dry pyridine according to Evans et al.⁴⁾. HPSEC was carried out on a system made up of a Shimadzu LC-6A liquid chromatograph, a Shimadzu CTO-6A column oven, a Shimadzu SPD-6A

UV spectrophotometric detector and a Shimadzu C-R3A chromatopac connected with an FDD-1A floppy disk drive. The column sets used were a series of 1.5×30 cm Shodex columns KF-806, -805 and -804, and a KF-800 guard column (Showa Denko K. K.). Other analytical conditions were the same as that reported by Evans et al.⁴⁾.

TSK standard polystyrene kit (Toyo Soda Manufacturing Co., Ltd.) was used as the molecular weight standards. Cellulose crystallinity: The yarns extracted from the sample linens were used for the X-ray diffraction study. X-ray diffraction traces were obtained on a Rigaku Geiger flex RAD-IIIB X-ray diffractometer using nickel-filtered copper radiation over the angular range 5 to 60. The crystallinity index (CrI) proposed by Segal et al.⁵⁾ was used as a measure of the degree of lateral order. Crystallite size of the cellulose in the linens was determined by measuring the width at half-maximum intensity of the 002 and 020 reflections and using the Scherrer equation⁶⁾. Tensile strength and elongation-at-break: All of the tensile tests were carried out at 20 °C and 65% R. H., using a UTM-4-100 model tensile testing machine (Toyo Baldwin Co., Ltd.). The gauge length was fixed at 100 mm and the stress was applied at a fixed rate of 300 mm/min. Specimens 200 mm long by 25 mm wide were used for the test, which was carried out only in the warp direction. The test was repeated for 4 times in each sample.

RESULTS AND DISCUSSION

Since March 1988, linens had been exposed to sunlight on an underglass-exposure-rack equipped with an integrating actinometer, which measured the amount of incident sunlight energies, separating them into three parts, ultraviolet (300-400 nm), visible (400-700 nm) and infrared (700-1,200 nm). The total amount of the incident sunlight energies during 1988 was 4,448 Mj/m^2 , of which 6.26, 50.30 and 43.54% were the light energies in the UV, visible and IR regions, respectively. The values in the other two years were almost equal. The total amount of the incident light energies for these 3 years and 5 months was 14,352 Mj/m^2 , in which 902, 7,298 and 6,152

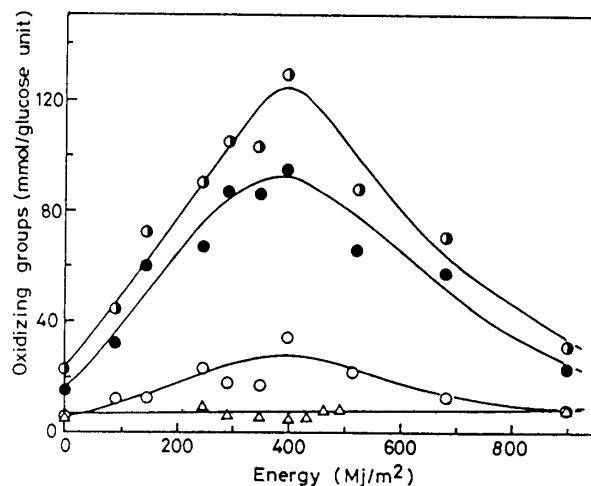


FIGURE 1. RELATIONSHIP BETWEEN OXIDIZING GROUPS FORMED IN LINEN AND INCIDENT UV LIGHT ENERGIES

● : $>\text{C}=\text{O} + -\text{CH}=\text{O}$, ● : $-\text{CH}=\text{O}$,
○ : $>\text{C}=\text{O}$, △ : $-\text{COOH}$

Mj/m^2 were the incident light energies in UV, visible and IR regions, respectively. However, ca. 30% of the UV light and 10% of the others were estimated to be absorbed by the glass of the exposure-rack⁷⁾.

OXIDATION-STAGE

The relationships between the light energies in the UV region and amounts of aldehyde, ketone and carboxyl groups formed in linens are shown in Fig.1. Carbonyl groups ($>\text{C}=\text{O} + -\text{CH}=\text{O}$) were increased with increasing light energies until the total incident UV light energies of ca. 400 Mj/m^2 is reached, and then decreased. On the other hand, carboxyl groups were hardly formed. At the incident UV light energies of 379 Mj/m^2 , 129 mole equivalents of carbonyl group (95 mole equivalents of aldehyde) per 1000 glucose units were formed, which was 5 times that of the unexposed control. When all oxidations are supposed to occur only at glycosidic bonds, formation of carbonyl groups should cause scission of the molecular chains at ca. 65 sites. This corresponds to the lowering of D. P. into ca. 1.6% of that of the unexposed linen. However, the actual D. P. value obtained was 42.3% of the initial value. Therefore, the results indicate that oxidation of cellulose took place at hydroxyl groups and/or ether linkages of glucose residues as well as glycosidic bonds. Decrease of

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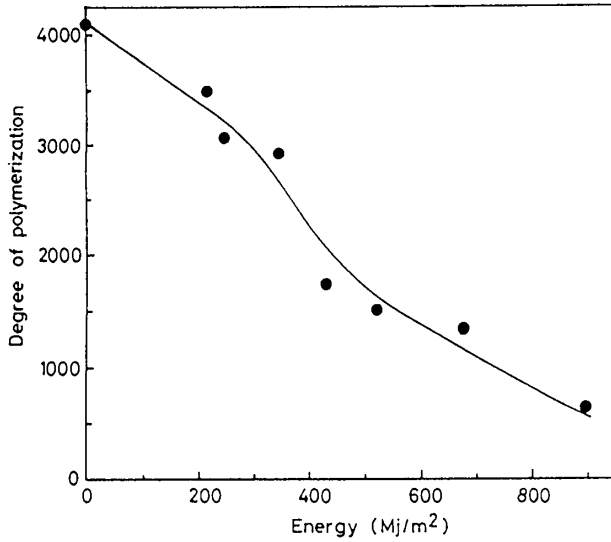


FIGURE 2. RELATIONSHIP BETWEEN D. P. OF LINEN AND INCIDENT UV ENERGIES

carbonyl groups observed in the secondary stage may suggest that they are converted into volatile compounds as reported by Desai and Shields⁸).

DEGREE OF POLYMERIZATION (D. P.)

Fig. 2 shows the D. P. of samples evaluated as their triphenylcarbanilates. The values reduced with an increase in light energies since the early time of the exposure. The value of the sample exposed for the whole period was less than 1/6 of that of the unexposed control. These results distinctly indicate that the degradative reactions including oxidation caused breakage of the molecular chains of cellulose.

CELLULOSE CRYSTALLINITY

Fig. 3 shows the changes of crystallite sizes in lateral (D_{020}) and longitudinal dimensions (D_{002}) and crystallinity indices (CrI) during the exposure to sunlight. The values of D_{020} and CrI were scarcely changed, but the value of D_{002} became lower as the light energies increased, especially in the early stages of the exposure. These results suggest that the degradative reaction probably began to occur in the crystalline region as well as in the amorphous region even in the early stages, and proceeded not from the surface to the inner of the fiber, but longitudinally.

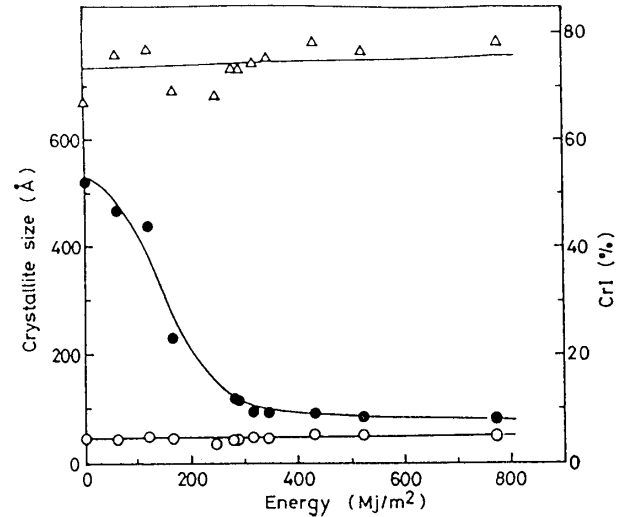


FIGURE 3. RELATIONSHIP BETWEEN CELLULOSE CRYSTALLINITIES OF LINEN AND INCIDENT UV LIGHT ENERGIES
● : D_{002} , ○ : D_{020} , △ : CrI

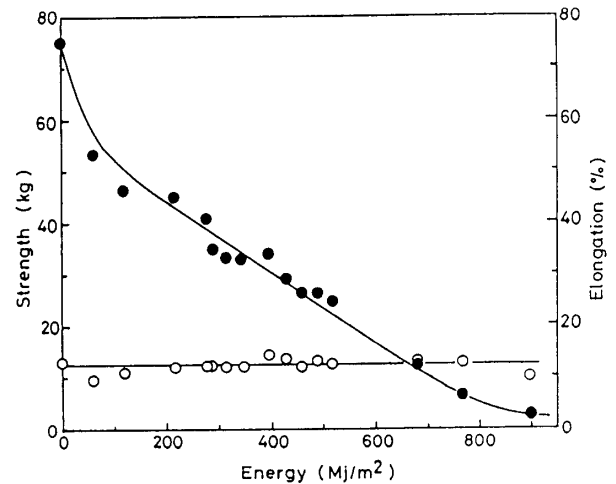


FIGURE 4. RELATIONSHIP BETWEEN MECHANICAL PROPERTIES OF LINEN AND INCIDENT UV LIGHT ENERGIES
● : Tensile strength, ○ : Elongation at break

MECHANICAL PROPERTIES

Tensile strength and elongation-at-break of the samples are shown in Fig.4. The strength began to reduce at the initial stage and became only about 1/25 of that of unexposed linen finally. In spite of

such significant reduction in the strength, distinct alteration was not observed in their elongation properties.

CONCLUSION

The effect of sunlight irradiation on linens was investigated for more than 3 years by the alterations in oxidation-stages, D. P., cellulose crystallinities and mechanical properties. Formation of aldehyde groups, reduction in D. P. and lowering of tensile strength had already begun at the early stages of the exposure to sunlight. Invariance of D_{020} and decrease of D_{002} suggest that the reaction did not proceed from the surface to the inner of the fibers, but did longitudinally. Reduction in D. P. also suggests that the degradative reactions including oxidation took place at glycosidic bonds and hydroxyl groups and/or ether linkages of glucose residues in cellulose, and reaction at the former caused scission of the molecular chains.

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太陽光による麻布の劣化

小原奈津子・中山栄子・豊田春和

セルロースの劣化機構を解明することを最終目的として、アンダーグラス屋外暴露試験台を用いて3年5ヶ月間、麻布を太陽光に暴露し、暴露期間の異なる麻布試料について酸化度（カルボキシル基、ケトン基およびアルデヒド基量）、セルロースの重合度、結晶化度、微結晶粒の幅と長さおよび機械的性質を測定した。この結果、暴露初期では、カルボニル基、特に、アルデヒド基は著しく増加したが、その後減少することが明らかになった。一方、重合度および強度は、受光量の増加と共にほぼ単調に低下した。また、セルロースの微結晶粒の幅には明らかな変化は認められなかったが、長さは受光量の増加と共に減少していたことから、劣化反応は、繊維表面から内部へというよりむしろ、繊維軸に沿って進行していることが予想された。