Cellulose의 광분해에 관한 연구(Ⅱ)

— 광조사된 면섬유의 화학적 성질을 중심으로 —

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Photodegradation of Cellulosics(Part Ⅱ)

— Chemical Properties of Irradiated Cotton —

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(1993. 7. 19 접수)

Abstract

본 연구에서는 면시험포와 cellophane film을 이용하여 xenon arc lamp 를 사용한 인공기후조 안에서 광선의 파장에 따른 강도의 변화와 변색을 조사하였다. Pyrex와 quartz filter를 사용하여 광선의 파장이 섬유의 성질을 변화시키는 중요한 요인임을 밝히고 first-order kinetic model 을 사용하여 반응속도를 측정하였다. 또 면섬유의 황변현상을 화학적으로 분석하여 파장이 긴 자외선과 가시광선의 영역에서는 황변과 동시에 표백효과가 있음을 알게 되었고 그 속도를 측정하였다. 세가지의 중요한 말단기분석을 통해 carbonyl기의 양이 제일 많고 carboxyl기와 peroxide기도 존재함을 분석하였고 또 이들의 양은 온도와 습도에 따라 변화하는 것으로 나타났다. Cellulose chain의 중합도를 측정하고 이를 cellulose bond scission과 연결시켜서 중합도와 섬유의 강도저 하와의 관계를 연구하였다.

I. Introduction

The energy of light, E, is defined in Joule by

$$E = h * v = h * C / \lambda$$

in which　　h = Planck's constant $(6.626 \times 10^{-34}$ J · sec)
C = speed of light$(2.998 \times 10^8 m/sec)$
v = frequency
λ = wavelength(m)

The shorter the wavelength, λ, the higher the energy level. In order to relate light energy to chemical bond strength, we have to consider a mole of quanta(Nhv ; N = Avogadro's number, 6.022×10^{23} mol^{-1}) called an Einstein [1,2,3]. The energy is given in kilocalories and can be evaluated from the following expression :

$$E(kcal/mole) = \frac{2.858 \times 10^4}{\lambda(nm)}$$

This equation gives the energy level for the light source of given wavelength.

The chemical bonds in cellulose are C-H, O-H, C-O

and C-C bonds and the bond dissociation energies are about 80-100 kcal/mole [4,5], which correspond to wavelength shorter than 340 nm. Light of wavelength greater than 340 nm cannot induce degradation of cellulose directly in vacuo[6]. Therefore, for near ultraviolet irradiation in the presence of oxygen, the mode of degradation is photooxidation.

In spite of the many studies intended to explain the photooxidation of cellulose, the detailed mechanism is still very uncertain. Many investigators have drawn some analogy with acid hydrolysis[2]. Daruwalla et al.[7] proposed the scheme for photooxidation of alcohol groups to carbonyl and carboxyl groups. In their scheme, the primary step is the abstraction of a hydrogen atom from the carbon atom. Following the abstraction of the hydrogen atom, a free radical site is formed on the cellulose backbone and, at this site, further reactions can take place[8].

The fundamental procedure of all the investigations concerned with the photodegradation of polymer is to expose a sample to light, either natural or artificial, and then examine the changes of some selected properties of the sample[9, 10]. For outdoor weathering tests using natural sunlight, a standard[11] has been established by ASTM for exposure sites and conditions. But the instability of weather makes it difficult to perform outdoor weathering tests precisely. The interruption of solar radiation during the night cycle is a major disruption. Moreover, outdoor testing is invariably slow, and long exposure periods are required for the evaluation[12].

These complex problems have led to the development of standardized methods and many powerful light sources for artificial weathering devices. Therefore, well-controlled intensifying indoor test, so-called 'Accelerated Weathering Test', is useful for clarifying the mechanisms involved in cellulose photodegradation. Several different types of artificial light sources can be used depending on the test conditions, fiber types and the equipment employed. The most widely used sources of irradiation are the carbon arc, mercury arc, xenon arc and fluorescent lamp [9, 10]. Xenon arc lamp approximates the spectrum of sunlight better than any other commercially available light sources. For this reason, it is widely used in commercial equipments for indoor testing. The result of experiments using this instrument have been found to correlate well with that of outdoor tests[13].

In photooxidation, cellulose materials are deteriorated over the period of exposure. Degradation can be easily assessed by loss of breaking strength and change in color. The degree of polymerization will be related to bond breakage and the formation of functional groups will help to understand the reaction mechanisms. In an earlier report[15], the relationship between breaking strength and degree of polymerization was discussed and also the effect of environmental factors such as temperature and relative humidity on degradation reaction was reported. In the present paper, the effect of wavelength of light sources on strength retention and color change will be examined. The yellowing of cotton will be carefully investigated. The chemical changes of irradiated cotton will be also analyzed by measuring functional groups.

II. Experimentals

The fabric used in this study was cotton print cloth (Testfabric style #400). The film was unplasticized cellophane provided by E. I. duPont de Nemours & Co. The details of sample preparation were reproted in the earlier paper of the author[15].

The device used for irradiation was a Weather-Ometer with a xenon arc lamp. Several filters and filter combinations are commercially available[16]. To examine the effect of light energy, the xenon arc lamp was fitted with quartz/quartz as well as Pyrex(borosilicate)/soda lime filters.

The color change of irradiated samples was measured with a Hunterlab Colorimeter Model D25M-2 and the Yellowness Index (YI) of each specimen was calculated by the following equation[17] ;

$$Yellowiness\ Index = (1.28X - 1.06Z)/Y$$

where $X = (L^2 * 0.01 + a * L/175)/1.02$

$$Y = L^2 * 0.01$$

$$Z = (L^2 * 0.01 - b * L/70)/0.847$$

For spectroscopic analysis, a Beckman Model 25 UV-Visible Spectrometer was used to determine the ultraviolet spectra.

The method developed by Marraccini and Kleinert[18] was adopted to measure the content of peroxide groups in the light irradiated samples. ASTM D 1926-63[19] provides a standard test method for determining the carboxyl group content of cellulose based on the procedures developed by Davidson.[20] The method used to measure total carbonyl group content was that of Lewin[21].

III. Result and Discussions

1. Effect of Filter System

The quartz/quartz filter system has a cutoff point at about 235 nm and permits shorter wavelength than Pyrex/soda lime filter system. But Pyrex filters more closely match the spectrum of natural sunlight than the quartz filters. The percent strength losses for cotton exposed to xenon arc lamp at 50℃, 75% R.H. using the two filter systems are measured and the data are fitted to the first-order reaction model[15].

$(1/SR - 1/SR_o) = k * t$

where SR is the percent strength retention after irradiation, SR_o the initial percent strength, k the reaction rate constant and t the exposure time. The results are illustrated in Fig. 1 and the reaction rate constants are listed in Table 1. It can be seen that the reaction proceeds about 2.6 times faster when quartz filters are used. The filter types are critical to energy output of xenon arc lamp and are directly related to bond scissions of cellulose chains.

To investigate the color change of different filter types, Yellowness Indexes were measured. With a quartz filter system the cotton samples show more yellowing than with Pyrex one. The ratio of reaction rate constants

Table. 1. Photolysis rate constants for different filter systems*($\times 10^{-3}$)

Pyrex filter	Quartz filter
32.04 ± 1.24	82.13 ± 4.44
(0.97)	(0.95)

Parenthesis are the R^2s of the regression lines in Fig. 1.
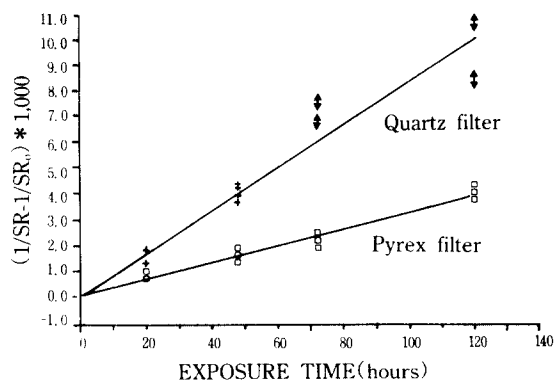*Samples were exposed at 50℃, 75% R.H.

Fig. 1. Loss of tear strength vs. exposure time for cotton irradiated with xenon arc lamp at 50℃, 75% R.H.

of color change is about 2.3, indicating that the ratio is close to that of loss of tear strength of the same samples with different filter types.

2. Yellowing

Yellowing is the loss of brightness and change in color through the discoloration that occurs during use and storage[6, 22]. Fig. 2 shows the time variation of the yellowness Index(YI) for cotton fabric exposed at 50% and 75% R.H. at constant temperature of 50℃. A larger value of YI indicates more yellowing. In general, the YI increases as exposure continues. Yellowing is more severe in 75% R.H. than in 50% R.H. It is apparent that high humidity accelerates yellowing.

The ultraviolet absorption spectra shown in Fig. 3 illustrate the bleaching effect of near UV light. Curve A is the spectrum of the cellophane film thermally aged at 140℃ for 70 hours in a Thelco forced-draft oven.
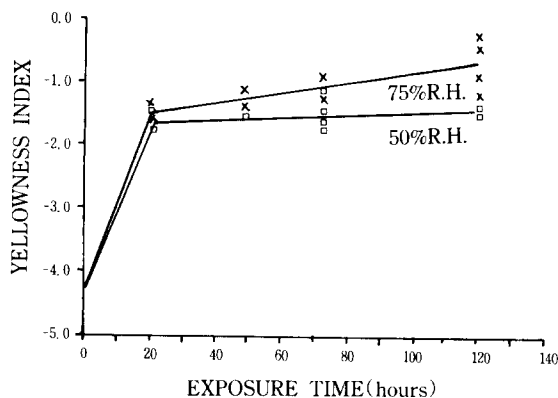
Fig. 2. Yellowness index vs. exposure time for cotton ir-
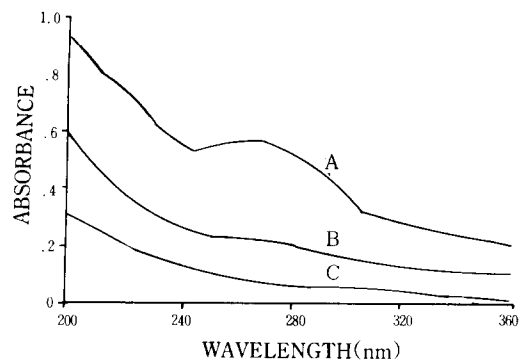radiated with xenon arc lamp at 50°C

Fig. 3. UV spectra of cellophane films
(A) : oven-aged for 70 hrs at 140°C,
(B) : (A) + exposed under xenon arc lamp for 140
hrs,
(C) : unexposed original

After baking the cellophane film turns to yellow and
a peak is formed around 265 nm in UV specturm. It
has been shown[23,24] that this peak is associated with
carbonyl species, which are known to be the primary
cause of yellowing[25]. After the aged cellophane film was
exposed with xenon arc lamp for 140 hours at 40°C,
50% R.H. in the Weather-Ometer(Curve B), the peak
has been greatly reduced. This result can only happen
when the color centers are formed during thermal aging
and afterwards broken down by irradiation in air and
moisture.

It should be noted in Fig. 2 that the YI increases
rapidly in the first 20 hours, but after that it changes
very little in both humidites. Especially at the lower
humidity, YI has increased very slowly after 20 hours.
It seems that the color centers are created during the
initial exposure period, and then the color centers are
still formed but at the same time some of them are
removed. Near UV and visible light in the presence
of oxygen break some bonds in yellowed material so
as to make it lose strength but gain whiteness.

If it is assumed that

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$
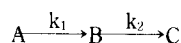
where A is cellulose before reaction, B is the yello-
wing substance, C is the bleached substance, and k_1,
k_2 are the reaction rate constants, then

$$-dA/dt = k_1 * A,$$
$$dB/dt = k_1A - k_2B$$

The solutions to these equations are[26] :

$$A = A_0e^{-k_1t},$$
$$B = [A_0k_1/(k_2 - k_1)] * (e^{-k_1t} - e^{-k_2t})$$

where A_0 is the initial concentration of reactant A. If
one defines $K = k_2/k_1$, then it will permit an estimation
of the relative efficiencies of yellowing and bleaching.
The value of k_1, the initial rate of formation of carbonyl
species which has been known as yellowing color cen-
ters[23,24,25], was measured to be 0.0096/hr experimentally.
This value was then used to calulate K, and it was found
to be between 0.05 and 0.1 for exposure at 50°C and
75% R.H.

When oxidation reactions leading to yellowing occur,
the C2 and/or C3 in cellulose molecule are attacked
by excited oxygen. Free radical sites are formed and
further reactions can take place that lead to the forma-
tion of hydrogen peroxide. The colored ketonic species
may react with hydrogen peroxide to form colorless
hydroperoxide. Then the hydroperoxides may also react
with aldehydes and ketones to form peroxides, which
are also colorless.

3. Chemical Analysis of Irradiated Cotton

Even though photooxidation may involve a free radical mechanism, previous studies[8] have failed to detect radicals in cotton samples exposed to wavelengths longer than 300 nm at room temperature. It is hard to monitor the free radicals because they are short-lived and unstable at ambient temperature. Thus, the functional group concentrations of carbonyl, carboxyl and peroxide groups that are possibly formed in the irradiated cotton were measured.

Fig. 4 shows the changes in content of carbonyl, carboxyl and peroxide groups in cotton cloth irradiated in a Weather-Ometer at 50°C, 75% R.H. with a xenon arc lamp with a Pyrex/soda lime filter system as a function of exposure time. The concentrations of three functional groups increase as exposure continues. Carbonyl group content is much larger than carboxyl and peroxide groups. Carboxyl group and peroxide group contents increase very slowly after 48 and 72 hours, respectively.
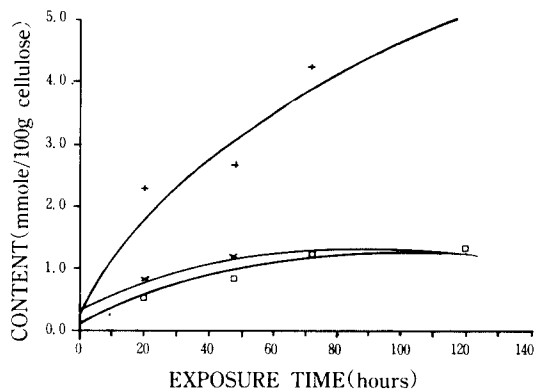

Fig. 4. Functional group content vs. exposure time for cotton irradiated with xenon arc lamp at 50°C, 75% R.H. + carbonyl group, x carboxyl group, □ peroxide group

The effect of environmental conditions of exposure are shown in Table 2, where carbonyl, carboxyl and peroxide group contents after exposure for 48 hours

are listed. In all three functional groups, the concentration has increased as temperature and humidity go up. Carbonyl group seems to be the major cause of yellowing and a major contributor to chain scission in both thermal and light-induced degradation[25, 27]. If the carboxylic acid species are formed by the transition of carbonyl groups, the concentration of carboxyl group should be lower than carbonyl group. As previously noted, the rate of removal of carbonyl speices is estimated as 1/10 to 1/20 of the rate of formation.

The degradation processes will finally lead to chain scission and decrease in degree of polymerization. Saku-

Table. 2. Functional group concentration (millimole/100g cellulose)

Carbonyl group content

	Temperature(°C)			
	32	40	50	56
R.H. (%)				
30	*	0.39	0.70	1.17
50	1.09	1.25	1.64	2.27
75	1.48	2.01	2.66	*

Carboxyl group content

	Temperature(°C)			
	32	40	50	56
R.H. (%)				
30	*	1.09	1.16	1.21
50	0.75	1.17	1.17	1.30
75	1.11	1.20	1.22	*

Peroxide group content

	Temperature(°C)			
	32	40	50	56
R.H. (%)				
30	*	0.42	0.60	0.63
50	0.37	0.45	0.69	0.78
75	0.45	0.52	0.83	*

Samples were exposed for 48 hours under xenon arc lamp with borosilicate/soda lime filter system.

* dentoes outside of range of the Weather-Ometer.

rada and Okamura[28] has derived an equation which relates the change in DP to the number of scissions per chain for random scission :

$$DP_f/DP_i = 2*(s-1+e^{-s})/s^2$$

where s is the number of sicssions per chain and DP_f and DP_i are the final and initial degrees of polymerization, respectively. The above equation can be solved by the Newton-Raphson iteration technique and plotted in Fig. 5 to reveal the relationship between reduction of degree of polymerizaiton, $DP_f DP_i$, and bond scissions per chain, s. In this study s is less than 3.1($DP_i=6025$ and minimum $DP_f=2732$), so that the usual simplifying assumptions for the kinetics model can be applied[15].
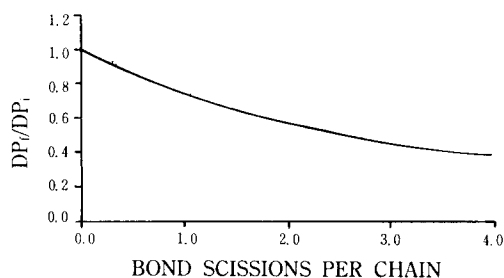

Fig. 5. Relation between depolymerization and bond scissions per chain.

The degree of polymerization of cotton fabric photooxidized under different test conditions are listed in Table 3. The values in parentheses are the average numbers of bond sicssion per chain. For the higher humidities and temperatures, the degree of polymerization decreases more than for the lower values. Therefore, both high humidity and high temperature contribute to depolymerzation.

IV. Summary and Conclusions

Natural sunlight was simulated by a xenon arc lamp in a Weather-Ometer with Pyrex filters. Cotton print cloth and cellophane film were used as cellulose materials. The analysis included the measurement of tear

Table. 3. Degree of Polymerization

	Temperature(℃)			
	32	40	50	56
R.H. (%)				
30	*	5235	4320	3855
		(0.44)	(1.09)	(1.52)
50	5637	5407	3806	3162
	(0.20)	(0.33)	(1.57)	(2.34)
75	5626	4287	2732	*
	(0.21)	(1.12)	(3.02)	

DP of unexposed original is 6025.

Samples were exposed for 48 hours under xenon arc lamp with borosilicate/soda lime filter system.

The parentheses are number of bond scissions per chain.

*dentoes outside of range of the Weather-Ometer.

strength reduction, color change(yellowing), UV spectrum, formation of functional groups and depolymerization.

The use of quartz/quartz filters in place of Pyrex/soda lime filters increased the reaction rates by the factor of 2.6 in loss of tear strength and that of 2.3 in yellowing. The power output of xenon arc lamp was directly influenced by the filter system employed.

With exposure the samples became more and more yellow. Color change rose quickly in the first 20 hours and much more slowly thereafter. These results indicate that discoloration and bleaching occur simultaneously. A hypothesis of bleaching was corroborated by measuring the UV spectra of previously darkened baked cellophane film. It was found that the rate of bleaching was about 0.05-0.1 of the rate of darkening.

The formation of carbonyl group was dominant to other functional groups. Concentrations of both carboxyl and peroxide groups were found to rapidly reach low steady state values that increased slightly with increasing temperature and relative humidity. Since the degradation of cellulose samples was in the initial stage and the conversion of glycosidic bonds and hydroxyl groups were very small, it was found that changes in the physical and chemical properties could be fitted to

a first-order reaction model.

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