〔報 文〕

Journal of the Korean Society
of Clothing and Textiles
Vol. 16, No. 2 (1992) p. 181～187

Photodegradation of Cellulosics

—Part 1: Effects of Temperature and Humidity on Tear Strength Reduction—

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면섬유의 Photodegradation에 대한 연구

—온도, 습도가 인열강도 감소에 미치는 영향—

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(1992. 1. 27 접수)

국문초록

일반적으로 면섬유는 햇빛에 의해서 변색되거나 약해지며 또 그 외에도 여러가지 물리적, 화학적인 변화를 일으키게 된다. 구체적인 화학반응의 메카니즘은 사용되는 광선의 스펙트럼, 대기조건(실내인 경우는 실내 환경조건), 산소의 유무 그리고 염료 등 첨가물의 종류와 같은 여러 요소에 의해 크게 영향을 받게 된다. 환경조건 중에서 산소의 존재는 매우 중요하지만 open system에서 산소의 농도가 일정하다고 가정할 때 면섬유가 접하고 있는 환경조건 중에서 온도와 습도는 photodegradation의 속도를 결정짓는 중요한 요인으로 작용하게 된다. 박물관, 기념관, 도서관 등의 소장품이 자연광선이나 인공조명으로부터 손상되는 것을 막기 위해서는 먼저 이들의 photodegradation 현상에 대한 연구를 필요로 한다.

본 연구에서는 면시험포를 자연광선과 가장 흡사한 스펙트럼을 가진 xenon arc lamp를 사용한 내후도 시험기내에서 온도와 습도를 조절하여 이에 따른 반응속도의 차이를 인열강도의 감소와 중합도 저하로 측정하였다. 1차 반응식은 실험결과를 설명하는데 유용하였으며 온·습도의 증가는 반응속도를 증가시키는 것으로 나타나 기존의 상반된 연구결과의 차이를 입증하였다. 또 온도와 습도는 상호관련이 있는 것으로 나타났으며 고온인 경우 습도의 영향을 더 크게 받는 것으로 분석되었다. 반응의 활성에너지는 30～75% RH에서는 12 kcal/mole 정도이며 수분의 함량이 낮을수록 활성화에너지는 커지는 것으로 나타나 수분은 섬유소 분자구조내에서 가소제(plasticizer)의 역할을 하는 것으로 판명되었다.

I. Introduction

The absorption of light by cellulosic material leads to yellowing, reduction in its degree of polymerization, embrittlement, weakening and increase in acidity. Although the destruction of cellulosic materials can be initiated by light, the specific chemical reactions are dependent upon many factors such as the energy of the light absorbed, the purity of the material and the presence or absence of oxygen, etc.

When the wavelength is less than 340 nm, the breaking of chemical bonds of cellulose can occur[1]. However, this process called 'Direct Photolysis' is not of major concern in the museum environment, where materials are usually protected by glass or UV filters. In near UV light at wavelengths between 340 and 400 nm, light of this energy cannot cause chemical bonds to break, but can raise impurities in the cellulose to an excited state. These excited species can then induce the cellulose molecules to react with oxygen or other reactive species in the environment. This process is called 'Photooxidation' and may, under some circumstances, be the dominant mode of the aging of textile objects.

The environmental conditions to which cellulosic material is exposed can strongly influence its rate of photodegradation reaction. The effect of temperature on photooxidation has not been well studied, although it has been recognized that the influence of this parameter is very complex[2]. First, the reaction rate should change as a function of temperature; with an overall activation energy following the well-known Arrhenius relationship[3]. However, the activation energy for photooxidation of cellulose has not been reported. In addition, the moisture content of cellulosic materials changes when the temperature is altered[4]. Consequently, an increase in temperature, which raises the chemical reactions, decreases the moisture content, which may also change the reaction rates.

The effect of moisture on photooxidation has been studied, but the results are, as yet, inconclusive. Hackney and Hedley[5] observed no significant difference between yarns exposed, at room temperature, to sunlight at 35~40% RH and those exposed at 60~65% RH. However, Daruwalla, et al.[6] found that increasing moisture content led to progressive inhibition of chemical damage up to a critical stage and when moisture content was increased beyond this critical stage, chemical damage was increased. Hon [7] supported this finding by the measurement of free radicals; showing that the moisture content greatly influenced the formation of free radicals in cellulose irradiated with UV light and confirmed that the moisture content in the range of 5~7% led to a significant decrease of radical formation and alternatively, when moisture content was lower or higher than this range, the formation of free radical was increased.

In an open system the concentration of oxygen is constant, so that temperature and moisture content are the major environmental factors to be studied.

In order to develop appropriate strategies and techniques for the conservation of cellulosic materials exposed to natural or artificial light, it is necessary to understand the mechanisms of degradation and the effects, if any, of temperature and relative humidity. In this report, the first in a series, the author reviewed some literature on the photochemical deterioration of cellulosic materials, and discussed the effects of changes in temperature and relative humidity on tear strength and degree of polymerization of cotton fabric.

II. Experimental Procedures

1. Material and Equipments

The fabric used in this study was cotton print cloth (width 44", style 400) obtained from Testfabrics, Inc., Middlesex, NJ. The cloths were washed twice and dried as per AATCC Test Method No. 124, rinsed in deionized water and air-dried before use. The device used for irradiation was a Weather-Ometer (Model 25 WR 123, Atlas Electronic Devices Co.) with a xenon arc lamp which provides the emission spectrum closest to natural sunlight. The lamp was fitted with a soda-lime outer filter and a borosilicate inner filter to simulate sunlight behind glass. Standard Xenon Reference Fabric for calibrating the Weather-Ometer was supplied by the AATCC.

2. Experimental Methods

Exposure to light was carried out at air temperatures of 32, 40, 50 and 56℃ and the relative humidities of 30, 50 and 75% RH. Four warpwise and four weftwise specimens were cut from each exposed sample. All the measurements were done in an atmosphere of 65% RH and 21℃ after specimens were conditioned overnight. Tensile strength of a cloth is not sensitive to aging time until tear strength has dropped to about 60% of the initial value[8]. Thus, tear strength was adopted as a mechanical property and measured by the Elmendorf Falling Pendulum Apparatus with a 1600 gram weight according to ASTM D 1424. The experimental procedures and calculation of degree of polymerization followed Roy[9]. The viscosity average degree of polymerization, $\overline{DP}v$ was measured with Cannon-Ubbelohde Four-Bulb Shear Dilution Type Viscometers.

III. Results and Discussion

1. Reaction Kinetics

A statistical analysis[10], independent of reaction mechanism, reveals that for a small degree of conservation the degree of polymerization ($\overline{DP}v$) should follow the equation (1),

$$1/\overline{DP}-1/\overline{DP}_0=k*t \qquad (1)$$

where $\overline{DP}$ and $\overline{DP}_0$ are the degree of polymerization after and before irradiation, respectively, k is the first-order reaction rate constant and t is the reaction time.

In property kinetics the degradation processes are assumed to affect macroscopical properties of the cellulosic material, such as tensile and tear strength. In such a manner, the chemical kinetics can be modeled by the kinetics of the property being measured[11,12]. The measurements of loss of tear strength and decrease of DP of cotton sample irradiated with xenon arc lamp are shown in Fig. 1. Insofar as these two properties are so well correlated ($R^2=0.94$), it was possible to extend the investigations of the photochemically induced changes in cotton cloth to the measurements of tear strength. Therefore, one should find that

$$1/\overline{DP}-1/\overline{DP}_0 \propto 1/SR-1/SR_0,$$
$$1/SR-1/SR_0=k'*t \qquad (2)$$

where SR and SR_0 are the percent tear strength retention after and before irratiation, respectively, k'is the first-order reaction rate constant and t is the reaction time.

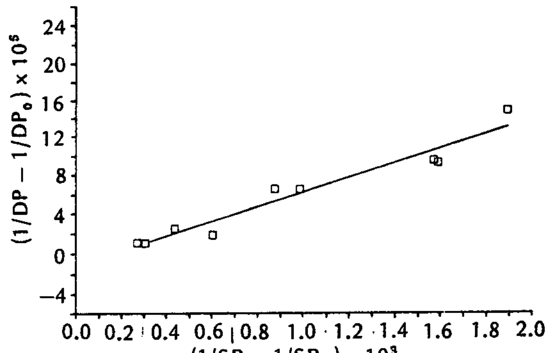

Fig. 1. Correlation between Depolymerization and Loss of Tear Strength for Cotton Fabric Irradiated with Xenon Arc Lamp.

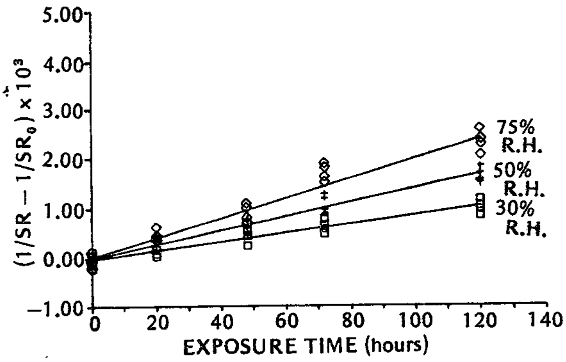

Fig. 2. Loss of Tear Strength vs Exposure Time for Cotton Fabric Irradiated with Xenon Arc Lamp at 40℃.

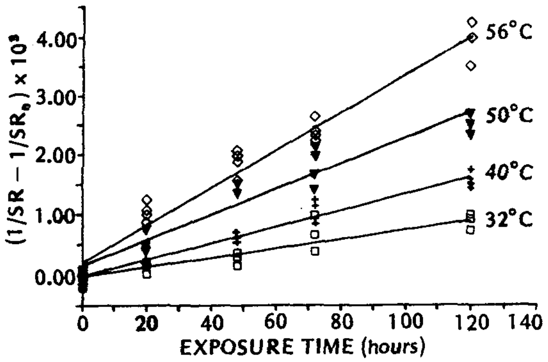

Fig. 3. Loss of Tear Strength vs Exposure Time for Cotton Fabric Irradiated with Xenon Arc Lamp at 50% RH.

2. Decreases of Tear Strength at Different Conditions

Some typical results, the percent loss of tear strength vs exposure time, are drawn in Figs. 2 and 3. Fig. 2 shows a plot of the loss of tear strength for cotton fabric exposed to xenon arc lamp at 40℃ and relative humidities of 30, 50 and 75%. In Fig. 3, the effect of temperature at constant humidity are shown. The lines are plots of the regression equations.

Table 1. Reaction rate constants at different temperatures and RH ($\times 10^{-3}$)

	Relative Humidity (%)		
	30	50	75
Temperature (℃)			
32	*	7.85±0.84 (.83)	11.68±1.27 (.82)
40	8.68±0.67 (.90)	13.71±0.73 (.95)	19.43±0.86 (.97)
50	16.30±1.13 (.92)	21.42±1.52 (.92)	32.04±1.24 (.97)
56	23.93±1.18 (.96)	31.53±1.37 (.97)	*

The values in parentheses are R^2 s of regression lines.
*denotes outside of range of Weather-Ometer.

Table 1 is a summary of the results of this portion of the study, in which the reaction rate constants, calculated using the equation (2), for the degradation of cotton cloths at different temperatures and humidities are listed. The numbers in parentheses are the regression coefficients for the linear regression lines. The values of R^2 are larger than 0.90 except for the data at 32℃, where the strength losses are relatively small. Fig. 4 depicts the data in Table 1. Here, the reaction rate constants are shown as a function of

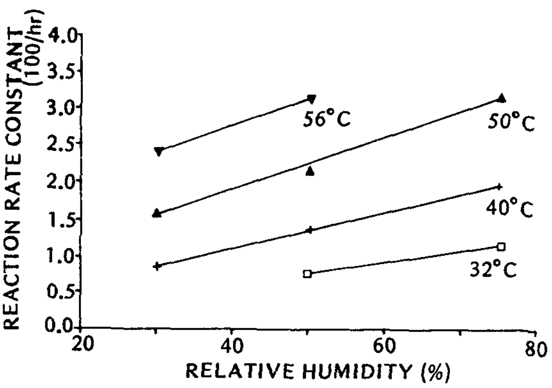

Fig. 4. First-order Reaction Rate Constants vs Relative Humidity for Cotton Fabric Irradiated with Xenon Arc Lamp at Different Temperatures.

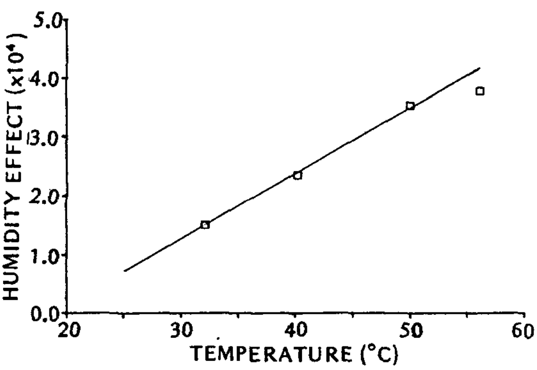

Fig. 5. Humidity Response as a Function of Temperature for Cotton Fabric Irradiated with Xenon Arc Lamp.

relative humidity for each temperature. It is clear that 1) the rate increases with increasing temperature for each relative humidity and 2) the rate at each temperature increases with rising relative humidity. It is also of interest to note that the slopes of the lines increase with increasing temperature. That is, at the lower temperatures moisture is less important than at the higher temperatures.

A more detailed analysis is shown in Fig. 5, where the slopes of the lines in Fig. 4 are plotted as a function of temperature. The line is the regression line ($R^2=0.99$), calculated from the lower three points. It is observed that the effect of relative humidity decreases linearly as the temperature decreases. Thus, it would be expected that at ambient temperatures, about 20℃, changes in humidity would have no discernible effect unless the exposure time is long enough. Since the influence of moisture is less at lower temperatures than at high, these results may also explain why Hackney and Hedley[5] did not find relative humidity to be an important factor in their investigation. It is not clear if the datum point 56℃ indicates a roll-off in the effect of moisture. Further work is needed to clarify the humidity effects at higher temperatures.

For light in the far UV region, most photons would have sufficient energy to rupture bonds, so that direct bond scission would be the major cause of strength loss. Cotton has its maximum density at moisture contents of 4~6%[4], where some water molecules are in a fundamental chemical combination with cellulose. Therefore, the chemically bound water, by absorbing photon energy, may restrict the formation of free radicals, leading to less degradation.

However, in the near UV region, the light energy is not sufficient to cause direct molecular change in cellulose, but is able to excite the surrounding atmospheric oxygen molecules, which then attack the cotton. When water is present in the system, the activated oxygen may react with it to form hydrogen peroxide. The combination of activated oxygen and peroxide then brings about a more rapid oxidation of the cellulose. The presence of water vapor would allow the acidic species produced as a degradation process[13] to be ionized more easily, and at a given temperature help the cellulose to be more readily degraded. Therefore, a high moisture content would cause more degradation than a low moisture content.

3. Activation Energies

The Arrhenius equation[3] is a convenient method for assessing the temperature dependence of the rate constant for a chemical reaction and changes in physical properties resulting from the chemical reaction. For the system changing temperature from T_H to T_C, the equation will be written as follows:

$$\mathrm{Ln}\ k_H/k_C = -Ea/R * (1/T_H - 1/T_C) \qquad (3)$$

k_H=reaction rate constant at high temperature

k_C=reaction rate constant at low temperature

T_H=high temperature (°K)

T_C=low temperature (°K)

Ea=activation energy

R=gas constant (1.98 cal $°K^{-1}\ g^{-1}\ mole^{-1}$)

Fig. 6 is the plot of Ln k (k, the first-order reaction

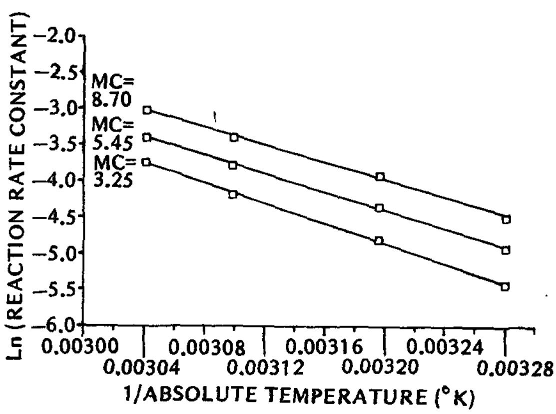

Fig. 6. Arrhenius Plots for the Loss of Tear Strength for Cotton Fabric Irradiated with Xenon Arc Lamp.

rate constant) vs 1/T (T, absolute temperature). The activation energy can be obtained from the experimental values of k and T by applying the least square method, using the equation (3). The relative humidity of cotton cloth changes as temperature does. Thus, it is desirable to adopt moisture content instead of relative humidity. The conversion between the two factors was based on Wiegerink[14]. The relative humidities 30~75% approximately correspond to moisture content 3.25~8.70.

The activation energies calculated from the regression lines are summarized in Table 2. The activation energies for the different moisture contents are about 11~13 kcal/mole. Even though the activation energies differ statistically, they show very little difference in the moisture content 3.25~8.70. It is of interest to investigate how it changes at much lower moisture content. In Fig. 7 the activation energies are presented as a function of moisture content. It is obvious that the lower the moisture content, the higher the activation energy. The lower activation energy also means that the degradation reaction rates are less sensitive to the changes of temperature. This result provides strong evidence that the role of moisture is to open up the fiber structure and provide a pathway whereby chemical species may more readily interact.

Table 2. Activation Energies at Different Moisture Contents

Moisture Content	Activation Energy (cal/mole)	R^2
3.25	13,463±323	.99
5.45	12,380±332	.99
8.70	11,682±379	.99

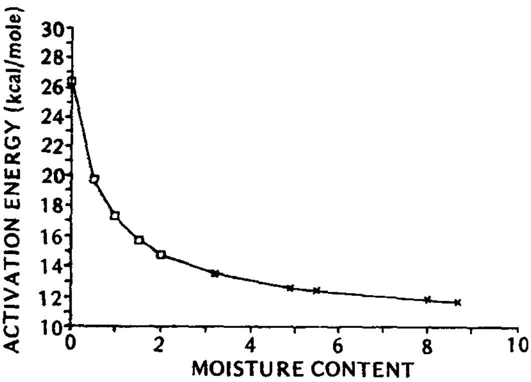

Fig. 7. Activation Energy vs Moisture Content.

IV. Conclusions

The effect of changes in temperature and relative humidity on tear strength retention was determined for cotton cloth exposed to the xenon arc lamp of an Atlas Weather-Ometer. Atmospheric conditions ranged from 32 to 56℃ and 30 to 75% RH.

It is shown that, over the range studied, the rate of light-induced degradation of cotton cloth increases monotonously with both temperature and humidity. The effects of temperature and moisture are found to be interrelated within the ranges studied, i.e., moisture is more important at the higher temperatures than at the lower temperatures. Also the effect of changes in relative humidity approaches zero at room temperature.

The activation energy is about 11~13 kcal/mole in moisture content 3.25~8.70. As moisture content is lower, the activation energy increases. Thus, the role of moisture in the photodegradation process is to open up the fiber structure and provide a pathway to interact with the chemical species more easily.

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