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INFLUENCE OF TEMPERATURE AND HUMIDITY ON PHOTOFADING OF CRYSTAL VIOLET ON POLYMER SUBSTRATES

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ABSTRACT: The effects of humidity and oxygen on the photofading of Crystal Violet (CV) in nylon 6 film were studied in detail. Both moisture and oxygen were necessary for the formation of Michler's Ketone. The effects of temperature and humidity on the photofading of CV in nylon 6 and polyester films were discussed in terms of kinetics. The fading rate was accelerated with rises in temperature and humidity for both films, and the rate was lower in polyester film than in nylon. The quantum yield in film decreased with the progress of decay, whereas it was almost unchanged in solution. The relationship between relative quantum yield (ϕ) in film and absorbance (A) at $\lambda_{\max}$ was expressed by the equation, $\phi = \beta (A - a_0)^m$. The parameter m indicates the ease of decrease of the rate with the progress of decay. The influences of temperature and humidity on the value of m were compared. The value of m depends on the initial absorbance in some cases. At elevated temperatures m has smaller value in almost all the cases.

1. INTRODUCTION

Photofading of dye can be affected by many factors such as photochemical characters of the reaction, aggregation of dye and various physical conditions of the surroundings. Recently the effects of humidity and temperature on the photofading of dye have attracted some interests from practical side. However, few investigation has been done from the fundamental standpoint so far.

In our previous paper the effects of temperature, humidity and oxygen on the formation of the photoproducts of Crystal Violet (CV) in nylon 6 film were discussed¹⁾. Under wet conditions the fading of CV proceeded at elevated temperatures, even in the dark, yielding carbinol as the main product. The irradiation of visible light ($\lambda > 500$ nm), corresponding to the first absorption band of CV, accelerated the fading of CV in the film, especially at elevated temperatures in the presence of humid air.

Analysis using both the least square method and the principal component analysis method revealed

that the photoproducts were leuco compound (CVH), leuco base (CVOH) and Michler's Ketone (MK), accompanied with the formation of other products such as their demethylated compounds.

The present investigation was designed to elucidate the effects of temperature, humidity and oxygen on the photofading of CV in both nylon and polyester films in terms of the photoproducts and kinetics.

2. EXPERIMENTAL

2.1 Materials

Crystal Violet Chloride (C. I. Basic Violet 3), GR grade of Kanto Chemical Co., Ltd., was used as previously reported¹⁾.

Nylon 6 film was same as previously used¹⁾. Poly (ethylene terephthalate) (PET) film drawn biaxially of 9 μ thickness was supplied from Teijin Co., Ltd. PET film was used after being treated in water at 130 °C under pressure for 1 h.

Irradiation was carried out in air or sufficiently deoxidized nitrogen. The effect of oxygen in dry or wet air was also examined. The deoxidization of dry

or wet atmosphere was accomplished by using a deoxidizing agent supplied from Mitsubishi Gas Chemical Co., Ltd.

2.2 Dyeing

Nylon 6 film was dyed at 80 °C for 1 h at various dye concentrations in 500:1 liquor ratio, and PET film was dyed at 130 °C for 1 h under pressure at various dye concentrations in 200:1 liquor ratio. All dyed films were washed successively with water and ethanol in order to remove excess dye on film surface and air-dried at room temperature.

2.3 Irradiation

The dyed film was exposed to visible light ($\lambda > 500$ nm) in a Pyrex cell under the conditions of controlled temperature and humidity as previously described¹⁾. The dry atmosphere was attained by introducing dry air into the degassed cell. The sufficient elimination of oxygen was attained by attaching the deoxidizing agent in a bag in the upper part of the degassed cell. The constant moisture content (0.935 mol/m^3) was obtained by sealing after exposing the cell including the dyed film to saturated CaSO_4 aqueous solution¹⁾.

The irradiation was carried out using a super high-pressure mercury lamp 500 W (USHIO USH 500 D). The course of fading was traced spectrometrically by a SHIMADZU UV210-A spectrophotometer.

3. RESULTS AND DISCUSSION

3.1 Effects of humidity and oxygen on the photoreaction of CV in a nylon 6 film

After exposure to the light, the faded film was boiled with ethanol, and the extract in ethanol was measured spectrophotometrically. The absorption spectra between 280 nm and 400 nm of photofading products were analyzed using both the least square method¹⁾ and the principal component analysis method^{1,2)}. The relative amounts of photofading products are summarized in Table 1.

In the presence of both moisture and oxygen, CVOH and MK were notably formed but CVH was not formed, whereas in the presence of dry oxygen CVH was formed, but CVOH and MK were not formed. These results show that both moisture and oxygen play important roles in the formation of CVOH and MK. Kuramoto and Kitao³⁾ proposed that MK was

formed by direct oxidation by singlet oxygen. On the other hand, our results suggest another mechanism of the formation of MK, because moisture is also necessary for its formation. Tentatively MK is assumed to be produced by photo electron transfer to give CV radical followed by addition of oxygen:

However, more detailed investigation must be done to elucidate the mechanism of the formation of MK.

3.2 Kinetics of photofading of CV in polymer substrates

The concentrations (C_{calc}) of the unchanged dye was calculated using relative amount of dye shown in Table 1. Fig. 1 shows that this concentration (C_{calc}) is proportional to the concentration (C_{obs}) calculated directly using the absorbance of the dyed nylon film

Table 1 The Effects of Humidity and Oxygen on Photofading products of CV in a Nylon 6 Film

Reaction conditions	Component (%)				
	CV	CVH	CVOH	MK	Total
35°C, dry air	61	13	0	1	75
35°C, dry air absence of oxygen	47	21	0	3	71
35°C, 98% air	25	0	16	12	53
35°C, 98% RH absence of oxygen	17	34	0	1	52

Fig. 1 Relationship between C_{obs} and C_{calc} . C_{calc} , concentration of unchanged dye calculated using relative amount of CV obtained by the least square method¹⁾ and C_{obs} , concentration of unchanged dye obtained directly from the absorbance of dyed film at λ_{max} .

at $\lambda_{\max}$ (correlation coefficient, 0.995). Consequently, the concentration of the unchanged dye determined by the absorbance of dyed film at $\lambda_{\max}$ was used throughout this work. The photofading curves of CV show that the fading rate is accelerated with rises in temperature and humidity in both nylon and PET films as illustrated in Fig. 2. The decay was slower in a PET film than in nylon.

3.2.1 Relative quantum yield

The fading rate of absorbance can be written by eq. 1, where the first term in the right-hand side corresponds to the rate of photofading and the second term to the rate of thermal reaction, since the absorbance of the film linearly decreased with time under the dark.

$$-dA/dt = \phi V + k \quad (1)$$

where A is the absorbance at $\lambda_{\max}$, ϕ is quantum yield of the photofading, V is the rate of excitation of dye molecule and k is the zero order rate constant of

thermal reaction.

The reaction conditions are abbreviated by temperature (35, 65 or 89°C), relative humidity (0 or 98% RH) and substrate (nylon (N) or PET (P)), such as 35N(98) for nylon film in 98% RH at 35°C.

The rate constant (k) of the thermal reaction was obtained by analysis of the thermal decay using linear regression. The results are compared in Table 2. The table shows that thermal reaction is rather slower than photoreaction, but can not be neglected under hot and/or wet conditions, and that the fitness of the zero order kinetics for thermal reaction is excellent.

The thermal reaction in a PET film is much slower than in a nylon film as shown in Table 2. Although the thermal reaction was observed also in dry nylon film at higher temperature (65N(0) and 89N(0)), these thermal reactions are tentatively assumed to be reaction between water and the dye.

Fig. 2 Photofading curves of CV in nylon 6 and PET films under dry nitrogen at 35°C (○), 65°C (□), and 89°C (△) or under 98% RH in air at 35°C (●), 65°C (■), and 89°C (▲).

Table 2 The Effects of Temperature and Humidity on Rate Constant of Dark Reaction

Reaction conditions	89N(98)	89N(0)	65N(98)	65N(0)	89P(98)
$k \times 10^3 \text{ sec}^{-1}$	6.083	2.845	2.618	1.043	0.561
Correlation coefficient	-0.9995	-0.9946	-0.9938	-0.9995	-0.9825
Number of data	13	13	13	15	9

Quantum yield is calculated by eq. 2 derived from eq. 1.

$$\phi = -(dA/dt + k)/V \quad (2)$$

The rate of excitation of the dye is expressed by eq. 3 using some assumptions^{4)*1}.

$$V = V_0(1 - (1 - 10^{-A})/2.303A) \quad (3)$$

where V_0 denotes a constant including strength of incident light per unit time and the band width of absorption spectrum, and A is the value at the maximum absorption. Combining eq. 2 with eq. 3, relative quantum yield can be given by eq. 4.

$$\phi V_0 = -(dA/dt + k)/(1 - (1 - 10^{-A})/2.303A) \quad (4)$$

Differential (dA/dt) was calculated from the decay curve of absorbance (A), which was approximated by a polynomials of the fourth order of time. The approximation fitted the decay curve excellently. The relative quantum yield (ϕV_0) is simply written by ϕ hereinafter, since V_0 is constant under all reaction conditions.

In Fig. 3 the experimental fading curves are compared with the theoretical fading curves both in polymer and solution. The theoretical fading curves were calculated by assuming that ϕ was constant with the progress of decay.^{*2} It is evident that the value of ϕ interestingly decreases with the progress of decay in a film, while it was almost unchanged in solution.

Figs. 4 and 5 show the plots of the relative quantum yield (ϕ) in a film against absorbance (A). The profiles of curves are concave upward or downward, thus ϕ is assumed to be approximated by eq. 5.

$$\phi = \beta(A - a_0)^m \quad (5)$$

Value of a_0 can be taken to be zero for almost all the cases except the case of the initial absorbance (A_0) = 1.073 for 35N(98). Parameter m indicates the degree of change of ϕ with the progress of decay; when the value of m is large, the rate of decay is liable to slow down with the progress of reaction and vice versa. The parameter β changes with the initial absorbance

*1 The rate of excitation of dye can be expressed by eq. 3, assuming that the strength of incident light linearly changes with wave length and the spectrum of the dye can be approximated by an isosceles triangle.

*2 The value of ϕ used in the calculation of the decay was determined by following equation

$$\phi = (dA/dt)_0 / (1 - (1 - e^{-2.303A_0})/2.303A_0)$$

where A_0 denotes the initial absorbance.

Fig. 3 Comparison of experimental and theoretical fading curves of CV in a nylon 6 film and $CV^+(CO_2H)(CO_2)^-$ in degassed acetonitrile solution⁵⁾.; calculation by assuming $\phi = \text{const}$.

(A_0) under some reaction conditions. These values are summarized in Table 3.

3.2.2 Values of the parameters in a nylon film under dry conditions

i) 35N(0): Plots of ϕ against A display the change of curvature as shown in Fig. 4 (a). Decrease of the reactivity is rather small at the early period, since the value of m is smaller than unity. However, m increases to larger values with the progress of decay. The value of m at the early period increases with increase in the initial absorbance, while opposite tendency is observed at the later period. Although m and β change with the initial absorbance, plots of ϕ/ϕ_0 against A/A_0 are nearly independent of A_0 as illustrated in Fig. 6.

ii) 65N(0): Both values of m and β increase with increase in the initial absorbance. Since the value of m is smaller than that of 35N(0), an elevated temperature results in suppression of decrease of the rate with the progress of reaction.

iii) 89N(0): The mean value of m (0.75 ± 0.05), except the result at $A_0 = 0.772$, indicates that the reactivity is similar to that of 35N(0). The value of β (0.1 ± 0.02) is almost independent of A_0 .

3.2.3 Values of the parameters in a PET film under dry conditions

The value of m in a PET film is larger than that in a nylon film. Thus ϕ in PET more sensitively de-

Fig. 4 Relationship between relative quantum yield and absorbance under dry conditions. a: 35N(0) for A_0 , 1.179 (○), and 1.536 (●). b: 65N(0) for A_0 , 1.004 (○); 1.236 (●); 1.308 (△); and 1.371 (▲). c: 89N(0) for A_0 , 0.772 (○); 1.470 (●); 1.531 (△); and 1.626 (▲). d: 35P(0) for A_0 , 0.453 (○); 0.477 (●); 1.191 (△); and 1.542 (▲). e: 65P(0) for A_0 , 1.308 (○); and 1.704 (●). f: 89P(0) for A_0 , 0.398 (○); and 0.998 (●).

Fig. 5 Relationship between relative quantum yield and absorbance under wet conditions. a: 35N(98) for A_0 , 1.046 (○); 1.073 (●); 1.200 (△) and 1.898 (▲). b: 65N(98) for A_0 , 1.002 (○) and 1.672 (●). c: 89N(98) for A_0 , 0.833 (○); 1.132 (●) and 1.140 (△). d: 35P(98) for A_0 , 0.427 (○); 0.540 (●); 1.142 (△) and 2.077 (▲). e: 65P(98) for A_0 , 1.45 (○) and 1.80 (●). f: 89P(98) for A_0 , 0.539 (○); 1.075 (●) and 1.843 (△).

Table 3 Values of Parameters m and β

Conditions	A_0	m	$\ln \beta$	r
35N(0)	1.179	0.667	-4.613	0.987
		(2.980)	(-4.298)	(0.993) *)
	1.536	1.429	-3.721	0.999
		(2.102)	(-3.910)	(0.992) *)
65N(0)	1.004	0	-2.453	— ***)
	1.236	0.460	-2.415	0.965
	1.308	0.879	-2.140	0.965
	1.371	0.849	-2.131	0.996
89N(0)	0.772	1.515	-2.191	0.980
	1.470	0.769	-2.690	0.999
	1.531	0.671	-2.641	0.985
	1.626	0.730	-2.332	0.924
35P(0)	0.453	4.986	1.077	0.937
	0.477	3.611	-0.965	0.985
	1.191	3.173	-3.558	0.960
	1.542	4.845	-5.072	0.895
65P(0)	1.308	2.817	-3.423	0.843
	1.704	1.601	-3.305	0.997
89P(0)	0.398	1.991	-0.437	0.988
	0.998	1.550	-2.106	0.931
35N(98)	1.046	0.761	-2.443	0.998
	1.073	0.527	-2.319	0.999 ***)
	1.200	0.758	-2.587	0.997
	1.898	0.937	-2.626	0.993
65N(98)	1.002	1.461	-1.863	0.952
	1.672	1.054	-1.651	0.953
89N(98)	0.833	0.469	-2.123	0.960
	1.132			
	1.140			
35P(98)	0.427	2.020	-1.432	0.979
	0.540			
	1.142			
	2.077			
65P(98)	1.45	1.76	-3.04	— ***)
	1.80	1.79	-3.27	0.972
89P(98)	0.539	0.413	-1.934	— ***)
	1.075	1.213	-2.170	— ***)
	1.843	1.235	-2.167	— ***)

*) The values at later period are shown in parentheses.

**) Correlation result by using $a=0.13$ in eq. 5.

***) The results are less reliable, since plots of $\ln \phi$ vs. $\ln A$ show some scatter.

Fig. 6 Plots of ϕ/ϕ_0 versus A/A_0 in a nylon film under dry conditions at 35°C. A_0 : ○, 1.179 and ●, 1.536.

Fig. 7 Plots of $\ln \beta$ versus $\ln A_0$ in a PET film under dry conditions at 35°C.

creases with the progress of decay than that in a nylon film.

i) 35P(0): The value of m (4.15 ± 1.43) is almost independent of A_0 , but the value of β decreases with increase in A_0 as shown in Fig. 7 (eq. 6).

$$\ln \beta = -(4.18 \pm 1.7) \ln A_0 - (3.094 \pm 1.00) \quad (6)$$

$$(r = -0.96, n = 4)$$

Plots of ϕ against A depend on A_0 as shown in Fig. 4 (d), but plots of ϕ/ϕ_0 against A/A_0 are almost independent of A_0 as shown in Fig. 8 (eq. 7).

$$\ln(\phi/\phi_0) = (3.61 \pm 0.78) \ln(A/A_0)$$

$$+ (0.33 \pm 0.15) \quad (7)$$

Fig. 8 Plots of ϕ/ϕ_0 versus A/A_0 in a PET film under dry conditions at 35°C. A_0 : ○, 0.453; ●, 0.477; △, 1.191 and ▲, 1.542.

Fig. 9 Plots of ϕ/ϕ_0 versus A/A_0 in a PET film under dry conditions at 89°C. A_0 : ○, 0.398 and ●, 0.998.

Fig. 10 Calculated decay curves by assuming the different value of m .

These results suggest that the value of ϕ can be approximated by eq. 8.

$$\phi = \alpha (A/A_0)^n \quad (8)$$

where n and α nearly equal to 4 and 0.45, respectively.

ii) 65P(0) and 89P(0): The value of m decreases with increase in temperature. Plots of ϕ against A of 89P(0) depends on A_0 , while plots of ϕ/ϕ_0 against A/A_0 are independent of A_0 as illustrated in Fig. 4 (f) and Fig. 9 (eq. 9), respectively.

$$\phi/\phi_0 = 0.95 (A/A_0)^{1.4} \quad (9)$$

3.2.4 Values of the parameters in a nylon film under wet conditions (98% RH)

The values of m and β in a nylon film are almost independent of A_0 under 35N(98) and 89N(98) conditions. The value of m decreases with increase in temperature. However, the rate at 65°C is larger and more sensitively suppressed than those at 35°C and 89°C.

3.2.5 Values of the parameters in a PET film under wet conditions

The value of m decreases with increase in temperature, similarly to that in a wet nylon film. Under the

Table 4 Dependency of the Parameter m on the Irradiation Conditions

Conditions	Dependency on A_0	Dependency on temperature
35N(0)	positive ^{*)}	negative ^{**))}
65N(0)	positive	
89N(0)	± ^{*)}	
35P(0)	±	negative
65P(0)	negative ^{*)}	
89P(0)	±	
35N(98)	slightly positive	positive ^{**))}
65N(98)	±	negative
89N(98)	±	
35P(98)	positive	negative
65P(98)	±	
89P(98)	positive	

* "Positive" and "negative" mean increase and decrease of m with increase in initial absorbance, respectively. Notation "±" denotes that m is almost independent of initial absorbance within the range of error.

** "Positive" and "negative" mean increase and decrease of m with increase in temperature.

conditions of 35P(98) the value of m increases slightly with increase in A_0 . The value of β depends on A_0 (eq. 10).

$$\ln \beta = -1.922 \ln A_0 - 2.807 \quad (r = -0.986, n = 4) \quad (10)$$

It is difficult to determine the definite values of m for the cases of 65P(98) and 89P(98) because of their large experimental errors. The values of m were estimated as 0.413 ± 0.766 for $A_0(89P(98)) = 0.539$, 1.213 ± 0.653 for $A_0(89P(98)) = 1.075$ and 1.235 ± 0.551 for $A_0(89P(98)) = 1.843$. However, it can be said that the value of m decreases with increase in temperature.

3.2.6 Dependency of the parameter m on the irradiation conditions

As shown in Fig. 3, the rate of decay in polymer films slowed down with the progress of decay, contrary to the rate in solution. The parameter m in eq. 5 indicates the ease of decrease of the rate. Fig. 10 illustrates decay curves calculated by assuming the initial rate to be unity. Curvature of the decay curve depends on the value of m . The larger the value of m is the more the rate of decay slows down with lap of irradiation time.

In Table 4 dependency of m on the irradiation conditions is roughly compared. The value of m depends on A_0 in some cases. At the elevated temperature m

has smaller value in almost all the cases.

If the dye possesses the sole reactivity (ϕ), m is vanished and the rate can not decrease with the progress of decay. Hence the results suggest that a distribution of reactivity may exist among the dye molecule in a film and it may be affected by temperature and humidity. Kinetic consideration on the parameter (m) will be presented in a subsequent paper by assuming a distribution of reactivity in a film.

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高分子基質上クリスタルバイオレットの光退色に対する温度、湿度の影響

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ナイロンフィルム中のクリスタルバイオレット(CV)の光退色におよぼす湿度、酸素の影響を詳細に検討した。その結果、ミヒラーズケトン(MK)の生成には水分と酸素が共に必要であることが明らかとなった。さらにナイロンおよびポリエステルフィルム(PET)中のCVの光退色におよぼす温度と湿度の影響を速度論的に解析した。両フィルム中において染料の退色速度は温度、湿度の上昇とともに加速された。PETではナイロン中に比べ退色が遅い傾向となった。溶液中ではCVの量子収率

にほとんど経時変化はないが、フィルム中の量子収率は時間とともに減少し、減速効果が認められた。フィルム中における相対量子収率(ϕ)と $\lambda_{\max}$ における吸光度(A)の関係を次式で示した。

$$\phi = \beta(A - a_0)^m$$

式中のパラメーター m は時間による減速のし易さを示すものである。 m 値におよぼす温度、湿度の影響を比較検討した。