Fundamental Studies on Solvent Dyeing with Tetrachloroethylene.   I. Diffusion of Disperse Dyes in Poly(ethylene Terephthalate)

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Synopsis

The diffusion of C.I. Disperse Violet 1 and Violet 8 in poly(ethylene terephthalate) (PET) was investigated by the method of cylindrical film roll.   The effect of tetrachloroethylene (TCE) on the properties of PET was also studied.   The treatment of PET with TCE brought about a strong effect on the thermal properties without degradation of PET.   The diffusion of disperse dyes in PET from the TCE dyebath was faster than that from the aqueous dyebath.   The activation energies of diffusion in the temperature range of 60° to 95°C from the TCE dyebath were smaller than those from the aqueous dyebath.   Some break points were observed in the Arrhenius plots of diffusion coefficients in PET from the TCE dyebath.   They were lower than those observed at dry and water-swollen states.

INTRODUCTION

Extensive studies on solvent dyeing have been carried out, and a number of reports on this subject have appeared in the recent literatures.[1–15]   Halogenated hydrocarbons, especially tetrachloroethylene (TCE), have been concluded to be the most suitable solvent for textile processing in organic media from a number of viewpoints.[10–14]

Fundamental studies on solvent dyeing are needed to elucidate the dyeing mechanism and to establish the dyeing technology in organic solvents.   White and Suda have investigated the equilibrium adsorption of dipserse dyes from organic solvents and have found partition-type adsorption isotherms in almost all cases.[1–3]   On the other hand, Kojima,[4,5] Datye et al.,[6] and Senner et al.[7,8] have investigated the kinetics of disperse dyeing from various organic solvents. Milićević and Gebert have reported the theory and practice of disperse dyeing from the TCE dyebath.[10–13]   These results show that the solvent dyeing mechanism of disperse dye on hydrophobic fibers is independent of the kind of solvent used.[15]   The partition and diffusion coefficients of disperse dyes for each system may be determined by the interaction strength among dye, solvent, fiber, and additives.

On the other hand, the solvent effect on the crystallization and mechanical behavior of poly(ethylene terephthalate) (PET) have been extensively stud-

ied.[16-27] Some solvents as well as water depress the glass transition temperature T_g of PET.[28-30] Recently, Ribnick et al. have found that some solvents had the capability of lowering the T_g of PET well below room temperature.[24,25] Morita et al.[30] have found two transitions in the Arrhenius plots of diffusion coefficients of disperse dyes and their model compounds in PET from the water dyebath. And Ito et al.[31] have observed multiple transitions in the penetrant diffusion in PET without water by the sublimation method.

In the present paper, the diffusion of disperse dyes in PET from the TCE dyebath is investigated by the cylindrical film-roll method, and the transitions of the PET–TCE system are discussed. Some comparisons are made between the systems of water and TCE in the diffusion of disperse dyes in PET. The stability of PET in TCE at high temperatures and the solvent effect on the thermal properties of PET are also studied.

EXPERIMENTAL

Films

Biaxially oriented PET film (Mylar C-25, du Pont) and nonoriented PET film were used. They were cut 2.5 cm wide and 55 cm long. The thickness of these films was measured by a thickness gauge (Peacock Upright Dial Gage, Ozaki Seisakusho) to be 6.78 and 35 μm, respectively.

Penetrants

1,4-Diaminoanthraquinone (C.I. Disperse Violet 1) and 1,4-diamino-5-nitro-anthraquinone (C.I. Disperse Violet 8), supplied by Nippon Kayaku Co., Ltd., were recrystallized by organic solvents and dried in a vacuum drier for more than a week. Absence of impurities was checked by thin-layer chromatography.

Stability of PET in TCE

The PET film was wound so tightly on a stainless steel rod (ϕ = 1 cm) in TCE that no bubbles were between the consecutive film layers and the film end was fixed by a glass rod and cotton thread. The film roll was treated with TCE in a stainless steel dyeing bottle for a definite time and then was immediately cooled by running water. The treated film was dissolved into a mixed solvent of m-cresol and phenol (1:1 by wt), and the viscosity was measured with a Cannon-Fenske viscosimeter at 20°C.[32] TCE of technical grade (Toa Gosei Kagaku Kogyo Co., Ltd.) and the other organic solvents of reagent grade were used throughout without purification.

Thermal Analysis of PET Treated with TCE

The nonoriented PET films treated with TCE were thermally analyzed by a Rigaku Thermoflex series thermal analyzer (heating rate: 10°C/min; temp. range: room temp. $\sim$ 260°C; sensitivity of DSC: 2 mcal/sec). The measurements were carried out in nitrogen atmosphere. About 10 mg PET was used in a thermal analysis test. A blank pan was used as the reference substance. The biaxially oriented PET films were also examined in comparison with the nonoriented ones.

TABLE I
Dyeing Conditions with TCE

Dyebath	C.I. disperse Violet 1		Violet 8, 0.3 g/100 ml TCE
	Temp., °C	0.2 g/100 ml TCE	
Diffusion time	40	744 hr	—
(examples)	50	600 hr	—
	60	72 hr	—
	70	25 hr	—
	80	10–15 hr	72 hr
	90	60 min	150 min
	100	—	60 min
	120	30 min	50 min
	140		30 min

Diffusion

In order to establish the surface concentration constant during the diffusion experiment, the dyeing was carried out from an infinite dyebath. Diffusion times were so decided by some preliminary experiments that the film roll was regarded as a semiinfinite substrate and that the absorbance of 5 to 8 respective layers could be measured. Examples of dyeing condition are shown in Table I. The biaxially oriented PET film after heat set at 160°C for 1 hr in water was wound so carefully on a glass tube or a stainless steel rod in the same solvent as dyeing that no bubbles of air entered between the layers. Glass dyeing bottles were used below 95°C in the water system and below 120°C in the TCE system. Above these temperatures, a high-temperature dyeing apparatus was used.[33] The dyeing bottle was inserted in a thermostat set at a given temperature to dissolve dye for more than 6 hr in water or 2 hr in TCE. Then, a film roll was immersed in the bottle. As to the high-pressure dyeing bottle, a test tube, in which a given weight of dye and a little dyeing solvent were added, and a film roll were fitted in the bottle. The bottle was kept at a given dyeing temperature for a prescribed time to dissolve dye in the test tube, and then was turned upside down several times in order to mix completely the solution in the test tube with the dyeing solvent. The time was regarded as the initial time of diffusion. After dyeing, it was immediately cooled by running water. The optical densities of the dyed film removed were measured to obtain the dye concentration of respective layers by a Shimadzu spectrophotometer D-40S. The concentration of dye on the film was calculated by the use of calibration curves.

Calculation of Diffusion Coefficient (Sekido-Matsui Method[34])

The film roll may reasonably be taken as a semiinfinite substrate in the direction of radius within a limited diffusion time. The diffusion equation along the radial direction of the film roll can be described by Fick's law,

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \tag{1}$$

where D (cm²/min) is the diffusion coefficient, C (g dye/kg substrate) is the concentration of dye in PET, t (min) is the diffusion time, and x (cm) is the distance

from the surface along the radial direction of the film roll. As the dyebath is infinite, the initial and boundary conditions are given by

$$C = 0, x > 0, t = 0$$
$$C = C_0, x = 0, t > 0 \tag{2}$$

where C_0 (g/kg) is the surface concentration. On applying the Laplace transform, the solution of eq. (1) satisfying conditions (2) is given by

$$C = C_0 ercf \frac{x}{2\sqrt{DT}} \tag{3}$$

where

$$erfc \; z = \frac{2}{\sqrt{\pi}} \int_2^{\infty} e^{-\xi^2} d\xi. \tag{4}$$

The adsorption of penetrant M_i (g) in the ith layer of the film roll of layer thickness ϵ (cm) is given by

$$M_i = \int_{(i-1)\epsilon}^{i\epsilon} C dx$$
$$= 2C_0\sqrt{Dt} \left\{ ierfc \; \frac{(i-1)\epsilon}{2\sqrt{Dt}} - ierfc \; \frac{i\epsilon}{2\sqrt{Dt}} \right\} \tag{5}$$

where

$$ierfc \; z = \int_z^{\infty} erfc\xi d\xi. \tag{6}$$

If the average concentration in the ith layer is C_i, $M_i = \epsilon C_i$. Putting

$$\frac{\epsilon}{2\sqrt{Dt}} = \zeta \tag{7}$$

the ratio of adsorption (i.e., that of average concentration) of neighboring layers is

$$\frac{M_{i+1}}{M_i} = \frac{C_{i+1}}{C_i} = \frac{ierfc \; i\zeta - ierfc(i+1)\zeta}{ierfc(i-1)\zeta - ierfc \; i\zeta} \tag{8}$$

and that of surface adsorption M_0 and ith layer is

$$\frac{M_i}{M_0} = \frac{2\sqrt{Dt}}{\epsilon} \left\{ ierfc \; \frac{(i-1)\epsilon}{2\sqrt{Dt}} - ierfc \; \frac{i\epsilon}{2\sqrt{Dt}} \right\} \tag{9}$$

where $M_0 = \epsilon C_0$. It is understandable from eqs. (8) and (9) that for different values of $i = 1, 2, \ldots, n$, the relation between M_{i+1}/M_i or M_i/M_0 and ζ can be calculated. If this relation is tabulated or drawn (cf. Figs. 4 and 5 in ref. 34), the value of ζ corresponding to the experimental value M_{i+1}/M_i is obtained directly from the relation for different layers $i = 1$ to 6 or 7, and the average value of ζ is used for the calculation of the diffusion coefficient.

On rewriting eq. (7), the diffusion coefficient is calculated from
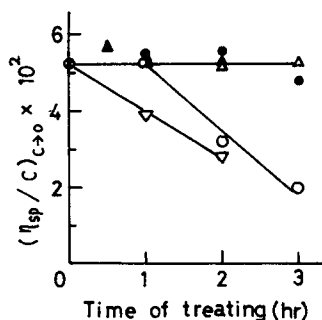
$$D = \frac{\epsilon^2}{4t\zeta^2}. \tag{10}$$

Fig. 1. Change of viscosity by treating with TCE or water (*m*-cresol:phenol = 1:1 (wt), 20°C). TCE: (●) 160°C; (▲) 180°C; H₂O (measured at 25°C)[30]: (△) 140°C, (◐) 160°C; (▽) 180°C.

In the concentration range where Beer's law holds, the value of M_{i+1}/M_i can be directly obtained from the optical density of the respective layers without being converted into concentration.

The value of M_i/M_0 corresponding to ζ obtained above for different layers is similarly obtained from the relation of eq. (9), and the average value of C_0 can be calculated with ease from them. The surface concentration was assumed to be equal to the equilibrium adsorption.

RESULTS AND DISCUSSION

Solvent Effect on PET

Viscosities of PET treated with TCE at high temperatures are shown in Figure 1. The viscosities of PET treated at 160° and 180°C were not decreased below that of no treatment. However, TCE was pyrolyzed by treating for longer than 30 min at 180°C, and was colored brown, with an offensive odor, by treating for 2 hr. The PET film was also colored, but no degradation occured by the TCE treatment even at 180°C for 2 hr, while the treatment of PET by water at 160°C for longer than 1 hr gave rise to a viscosity drop.[30] The degradation of PET by TCE treatment is much smaller than that by water. The most severe pretreatment condition by a solvent which does not degrade the PET films is the treatment with water for 1 hr at 160°C. Then, all the films, except some, were treated by the most severe condition.

Thermal Analysis

The thermogram (DSC) of nonoriented PET film shows three peaks, at 82°, 130°, and 252°C, corresponding to T_g, crystallization, and melting, respectively. Treatment of PET with TCE even at room temperature reduces the crystallization peak (Fig. 2, curve 3), and that at 40°C for 2 hr only shows a T_g peak at 76°C (a decrease in T_g), a trace of peak which may correspond to crystallization at about 83°C, and a distinct melting peak at 252°C in the DSC diagram, respectively. Treatment of PET for 33 hr at 40°C only shows the melting peak in the DSC diagram. Treatment with TCE even at 40°C promotes the crystallization of PET and reduces T_g owing to plasticization. Peaks of T_g and crystallization can no longer be detected, except for melting in the thermogram of PET of the
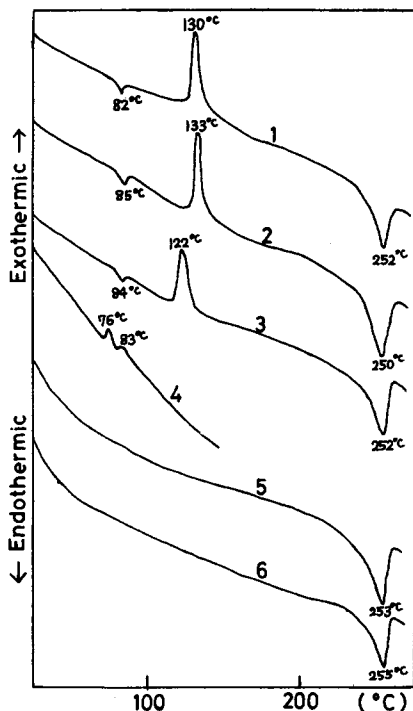
Fig. 2. DSC curves for PET treated by TCE: curve 1, no treatment; curve 2, 2 hr at room temp.; curve 3, 33 hr at room temp.; curve 4, 2 hr at 40°C; curve 5, 33 hr at 40°C; curve 6, 29.5 hr at 90°C.

more severe treatment than that at 40°C. These phenomen have been found by Scott and Hughes.[21,35] The peaks of T_g and crystallization are raised at first and then reduced gradually by the more severe treatment. This phenomenon of T_g has also been observed by Thompson and Woods.[36] No peaks except melting have been detected in the thermograms of all the biaxially oriented films.

Diffusion

The diffusion coefficients of C.I. Disperse Violet 1 and 8 in PET from the TCE dyebath over various temperatures are shown in Figure 3 as Arrhenius plots. Some experiments were carried out with the use of different PET films treated with water at 95°C for 24 hr. There were no differences in the diffusion coefficients of Violet 1 in PET films treated with water under different conditions (95°C, 24 hr, and 160°C, 1 hr) within experimental errors. This was confirmed by some experiments in the temperature range of 90° to 60°C.

The diffusion of Violet 1 was always faster than that of Violet 8 over the temperature range tested, in the same way as the PET—water system.[30] The diffusion coefficient of Violet 1 from the TCE dyebath at 60°C was nearly similar to that from the water dyebath at 100°C, and that of Violet 8 from TCE at 90°C to that from water at 120°C. The differences in diffusion coefficients between both systems, however, become smaller with increase in temperature. Activation energies of diffusion are shown in Table II. The activation energy in the TCE system is considerably smaller than that in the water system. Dyeing in the

TABLE II
Activation Energies of Diffusion in PET

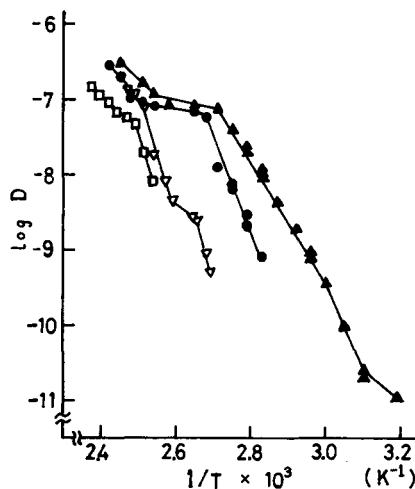| Dye	Dyebath	Temp. range, °C	Activation energy, kcal/mole
Violet 1	TCE	50–60	67.4
		60–95	33.0
	water[30]	below 103	85.3
Violet 8	TCE	below 100	56.2

Fig. 3. Arrhenius plot of diffusion coefficients in PET from the TCE or water[30] dyebath. Violet 1: (▲) from TCE; (▽) from water[30]; Violet 8: (●) from TCE; (□) from water.[30]

TCE system at high temperature, for example, 120°C, is not always recommended.

Transition Phenomena

In the TCE system, there are some transition points and regions (Fig. 3) which are the same phenomena as in water system reported earlier.[30] A transition point (about 60°C) and a transition region (95°–110°C)are observed in the diffusion of Violet 1, and a transition region (100°–130°C) in the diffusion of Violet 8. The transition of Violet 1 at 50°C may be a transition region below this temperature. In water system, on the other hand, two transitions at about 130°C and about 110°C have been observed and assigned to the crystallization transition and T_g, respectively.[30] In comparison with the water system and thermal analysis, the transition between 95° and 130°C in the TCE system may be assigned to crystallization transition, although the lower limit was reduced to 95°C.

On the other hand, Milićević reported the depression of T_g by TCE treatment from 70° to 47°C from the thermal analysis of PET.[12] Ribnick et al. have recently found the T_g of PET in TCE to be 22°C from isothermal and dynamic shrinkage.[24,25] From this point of view, the transition region below 50°C may be

assigned to T_g. However, there was also a transition at 60°C which could be considered to be T_g. A similar phenomenon was also observed in the diffusion of a dye in PET from the trichloroethylene dyebath, although the transition region was depressed to below 40°C.[37] From these results, it may be concluded that the transition region below 50°C was the T_g of PET in TCE and that the transition at 60°C was the inherent transition of PET remaining in the PET–TCE system.

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