Studies of the Solvent Dyeing of Poly(ethylene terephthalate) with Disperse Dyes from Trichloroethylene and Isooctane

Zenzo Morita, Shinji Hiraoka,* Toshiyasu Yamamori, and Hiromi Motomura
Department of Textiles and Polymer Science, Faculty of Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184

(Received February 8, 1975)

The diffusion of 1,4-dihydroxyanthraquinone and C. I. Disperse Orange 3 in poly(ethylene terephthalate) (PET) from the trichloroethylene (TRI) and isooctance (ISO) dyebath was investigated by the method of the cylindrical film-roll. The stability of PET in TRI and ISO at high temperatures was also examined. The degradation of PET by solvents was in the following order: water>TRI>tetrachloroethylene (TCE) and ISO. The diffusion coefficients of Orange 3 from various solvents at 90 °C were in the order: TRI>TCE>water>ISO. The activation energy of diffusion from ISO was much larger than that from TRI, the latter being nearly identical to that from TCE. The Arrhenius plots of the diffusion coefficients in PET indicated some transitions. The glass transition temperature of PET in TRI was lower than that in TCE. The diffusion coefficient and the surface concentration of Orange 3 from ISO were increased by the addition of water, while those from TRI were not changed within the range of experimental error.

Solvent dyeing with disperse dyes from ISO has been studied by Schuler,[1] that from *n*-octane, by Kojima,[2] and that from TRI, by Parkins and Hall recently.[3,4] A bimodal relation between the effects of the solvents on PET and the solubility parameter, δ, has also been observed.[5,6] According to Ribnick *et al.*, the bimodal relation suggests that the specific groups of PET molecules interact differently with two types of solvents. One maximum, near $\delta=10$, is due to the interaction between the solvent and the hydrophobic group of PET, while the other one, near $\delta=12$, is due to that between the solvent and the hydrophilic ester group of PET. The difference between the solubility parameters of TCE and TRI is small, while that between the dyeing characteristics of these solvents is large.

There are also large differences in the diffusion coefficients of the disperse dyes from the solvents used in the present study, though all the solvents have a hydrophobic character. The diffusion coefficients from TRI and TCE are larger than that from water, though that from ISO is smaller.

The addition of water to the ISO and TCE dyebath has given rise to an increase in the diffusion coefficients and the equilibrium adsorption of the disperse dyes.[1,7] The addition of water to the TRI dyebath, however, has not yet been reported.

In the present paper, we wish to examine the diffusion of disperse dyes in PET from the TRI and ISO dyebath and the effect of water added to the solvent dyebath by means of the cylindrical film-roll method. The results and the transition phenomena of the PET-TRI system will be discussed and compared with those of the PET–water and PET–TCE systems reported earlier.[8,9]

Experimental

Materials. Biaxially oriented PET films (Mylar C-25. du Pont), TRI (commercial grade—Toa Gosei Kagaku Kogyo Co., Ltd.), and ISO (reagent grade) were used. 1,4-Dihydroxyanthraquinone (reagent grade) and C. I. Disperse Orange 3 recrystallized from ethanol were used as penetrants.

Stability of PET in TRI and ISO. The film was wound on a stainless steel rod ($\phi=1$ cm) in TRI or ISO so that there were no bubbles between the consecutive film layers, and the film end was fixed. The film-roll was then treated by TRI or ISO in the same dyeing bottle as before under definite conditions.[9] After drying, the viscosities of the PET films treated were measured by means of a Cannon-Fenske viscosimeter at 20 °C in the same manner as before.[9]

Diffusion. The biaxially oriented PET film treated by water at 160 °C for 1 hr was wound on glass tubing ($\phi=1$ cm) in the experiment with a glass diffusion bottle or on a stainless steel rod in the ISO system above 135 °C with a high-pressure diffusion bottle, in the same solvents as in the dyeing. The diffusion experiments were carried out in the same manner as before under the conditions shown in Tables 1—3.[9] The experiments above or near the boiling point of the dyeing solvent were done under pressure using a high-pressure diffusion bottle.

Before beginning the diffusion experiment, the diffusion bottle was inserted into a thermostat set at a given temperature to dissolve the water, if necessary, and then the dye for a long time (*cf.* Table 3). After that, a film-roll was immersed in the bottle. In the case of a high-pressure diffusion bottle, a test tube in which a given weight of the dye and a little of the dyeing solvent had been added and a film-roll were placed in the bottle in which the dyeing solvent was put. The bottle was kept at a given temperature for a prescribed time to dissolve the dye in the test tube and was then quickly turned upside down several times in order to mix completely the solution in the test tube with the dyeing solvent. The time when the solution began mixing was regarded as the initial time of diffusion. After diffusion and drying, the optical densities of the dyed film were measured by means of a Shimadzu MPS-50L recording spectrophotometer at the wavelength of maximum absorption. The concentration of dyes on the film was confirmed to obey Beer's law under the present experimental conditions.

The diffusion coefficients and surface concentrations were calculated by the Sekido-Matsui method from the concentration profile obtained experimentally.[10]

Results and Discussion

The Effect of Solvent on PET. The solution viscosities of PET treated by TRI and ISO are shown in Fig. 1. The treatment of PET with ISO at 180 °C for

---

* Present address: Fuji Spinning Co., Ltd., 2-3 Nihonbashi-Ningyo-cho, Chuo-ku, Tokyo 103, Japan.

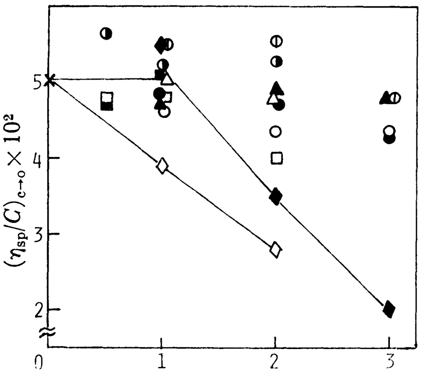

Fig. 1. Change of viscosity by treating with some solvents at high temperature (m-cresol: phenol = 1: 1 (wt), 20 °C).

Solvent	140 °C	160 °C	180 °C
ISO	○	△	□
TRI	●	▲	■
TCE[9]	—	⦶	◑
H_2O[8]	—	◆	◇
no treatment	×		

2 hr and with TRI at 180 °C for 1 hr brought about almost no change in the viscosity. However, during the treatment of PET with TRI at 180 °C for 2 hr, the TRI turned brownish and smelled offensively, and the film-roll could not be opened. No coloration of TRI was observed below 160 °C. On the other hand, the treatment of PET with water at 160 °C for more than 1 hr brings about a profound decrease in the viscosity.[8] That with TCE at 180 °C for less that 2 hr produces no change in the viscosity, but there is the decomposition of TCE above 180 °C, and the film-roll of PET treaed with TCE even at 200 °C for 1 hr could be opened.[9] Therefore, the degradation (in molecular weight) of PET by the solvents is in the following order: water>TRI>TCE and ISO. The order of TCE and ISO could not be determined by viscometry.

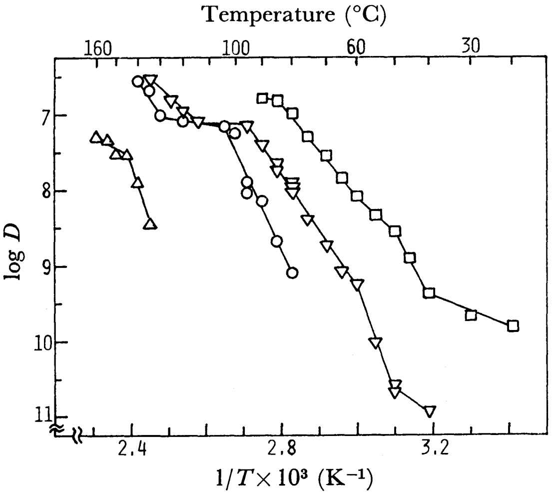

Fig. 2. Arrhenius plot of the diffusion coefficient (cm²/min) of dye in PET from the solvent dyebath.
△: quinizarine from ISO, ○: C. I. Disperse Violet 8 from TCE,[9] ▽: Violet 1 from TCE,[9] □: Orange 3 from TRI.

Table 1. The diffusion and adsorption of C. I. disperse orange 3 from the solvent dyebath

Solvent	Temp. (°C)	Dyebath (g dye/100 ml solvent)	Diffusion time (min)	D (cm²/min)	C_0 (g dye/kg PET)
TRI	20	0.2	15710	1.51×10^{-10}	4.62
TRI	30	0.4	8487	2.19×10^{-10}	8.05
TRI	40	0.1	5800	4.22×10^{-10}	4.28
TRI	45	0.4	1440	1.26×10^{-9}	7.30
TRI	50	0.3	1080	2.92×10^{-9}	5.62
TRI	55	0.4	600	4.52×10^{-9}	6.00
TRI	60	0.3	480	8.09×10^{-9}	5.09
TRI	65	0.3	300	1.41×10^{-8}	4.67
TRI	70	0.4	90	2.78×10^{-8}	5.12
TRI	70	0.2	120	3.34×10^{-8}	2.18
TRI	75	0.4	100	5.11×10^{-8}	4.72
TRI	80	0.4	60	1.04×10^{-7}	4.85
TRI	85	0.4	30	1.60×10^{-7}	4.00
TRI	90	0.4	20	1.59×10^{-7}	3.34
TCE	90	0.2	120	6.52×10^{-8}	3.63
H_2O	90	0.3[a]	11355	3.83×10^{-10}	12.6
ISO	90	0.2	12870	3.07×10^{-11}	6.47

a) saturated solution

Table 2. The diffusion and adsorption of 1,4-dihydroxyanthraquinone from the ISO dyebath

Temperature (°C)	Diffusion time (min)	D (cm²/min)	C_0 (g dye/kg PET)
135	420	3.54×10^{-9}	39.3
140	300	1.26×10^{-8}	31.6
145	240	2.97×10^{-8}	27.5
150	180	3.05×10^{-8}	26.3
155	90	4.70×10^{-8}	22.2
160	77	4.88×10^{-8}	21.2

Diffusion from the TRI and ISO Dyebath. The diffusion coefficients, D, and the surface concentrations, C_0, of Orange 3 and 1,4-dihydroxyantraquinone from the TRI and ISO dyebath are shown in Tables 1 and 2 and in Fig. 2 as the Arrhenius plots. It is well known that the diffusion of penetrants in a polymer correlates with the intrinsic mobility of polymer molecules.[11] However, in the case of the diffusion in a polymer which is in a swelling equilibrium with a solvent, such as in dyeing, it also correlates with the swelling or plasticization of the polymer by the solvent.[8,9,12] The diffusion coefficients of Orange 3 from various solvents at 90 °C were in the order: TRI>TCE>water>ISO (Table 1). This order, therefore, is considered to be due to the plasticization effect of the solvents on PET or to the solvent-polymer interaction.

Orange 3 is one of the few kinds of dyes which can be dyed from various solvents. In the case using the ISO dyebath, the diffusion of even a small penetrant may be difficult below 100 °C. The activation energies for the diffusion of Orange 3 from the TRI dyebath and that of quinizarine from the ISO one were 30 (60—85 °C) and 80 kcal/mol (135—145 °C) respectively. That from ISO was very much larger than that from TRI, the latter being nearly identical with that from TCE.[9]

The surface concentrations from the TRI and ISO dyebaths, shown in Tables 1 and 2, decreased with an increase in the temperature.

Transition Phenomena. A transition region was found above 145 °C in the Arrhenius plots of the diffusion coefficient from ISO (Fig. 2). In those from TRI, it was considered that there were three transitions—above 85 °C, between 50 and 60 °C (a shoulder), and below 40 °C. According to Ribnick, the glass-transition temperature, T_g, of PET has been reduced to a lower temperature by TRI than by TCE.[6] In a previous paper, a transition point at 60 °C and two transition regions between 95 and 110 °C and below 50 °C have been observed in the diffusion of C.I. Disperse Violet 1 from the TCE dyebath (*cf.* Fig. 2).[9] In comparison with the case from the TCE dyebath, it can be concluded that the transition region below 40 °C is the T_g of PET swollen by TRI, though the upper limit of T_g is reduced to 40 °C. A transition region between 50 and 60 °C, appearing as a shoulder in Fig. 2, may correspond to the transition at 60 °C from the TCE dyebath, though the lower limit is reduced to 50 °C.

The transition correlated with the maximum crystallization rate of PET[13] was observed as a trasition region above 145 °C in the diffusion in PET from the ISO dyebath and as a transition region above 85 °C in that from the TRI one. It has been observed as a transition region between 125 and 145 °C in water[8] and as one between 95 and 130 °C in TCE.[9] The lower limit of this transition in ISO was higher than that in water and TCE, while that in TRI was lower. Therefore, ISO has no capability to affect the properties of PET, the transitions in PET–ISO system being considered to be nearly identical with those of PET in the dry state. On the other hand, TRI has a more profound effect on PET than do water and TCE.

TABLE 3. DYEING OF C. I. DISPERSE ORANGE 3 FROM THE TRI AND ISO DYEBATH (0.2 g dye/100 ml solvent) IN ADDITION WITH WATER

Dyebath		Diffusion time (min)	D (cm^2/min)	C_0 (g dye/ kg PET)
Solvent (Temp.)	Water added (ml)			
TRI (70°C)	0	120—150	3.34×10^{-8}	2.18
	0.1	120—150	3.33×10^{-8}	2.38
	0.3	120—150	3.58×10^{-8}	2.30
	0.5	120—150	3.45×10^{-8}	2.20
	1.0	120—150	3.47×10^{-8}	2.36
ISO (90°C)	0	12870	3.07×10^{-11}	6.47
	0.1	12860	3.50×10^{-11}	10.5
	0.3	12860	3.75×10^{-11}	9.20
	0.5	12865	3.84×10^{-11}	9.41

Standing times in the TRI system for dissolving water and dye added were about 1 and 1—2 days, respectively. Those in the ISO system were 28 and 20 hrs, respectively. Glass-stoppered diffusion bottles were used to keep the dyebath from evaporation.

Mean values were shown in the diffusion coefficient and surface concentration of the TRI system.

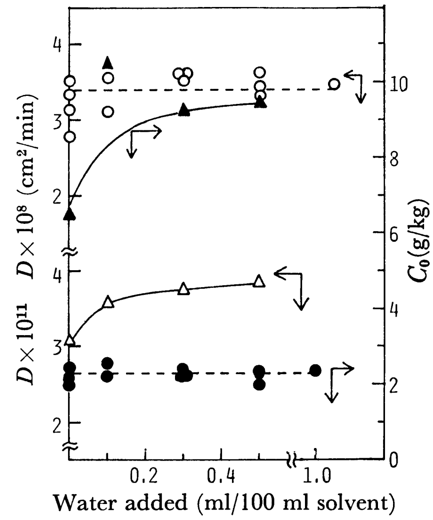

Fig. 3. The diffusion coefficients D and surface concentration C_0 of C. I. Disperse Orange 3 when water was added to the solvent dyebath (0.2 g dye/100 ml solvent).

Dyebath	D	C_0
ISO (at 90 °C)	△	▲
TRI (at 70 °C)	○	●

The Effect of Water Added to the Solvent Dyebath. The effect of the addition of water to the ISO dyebath on the diffusion and adsorption of Orange 3 at 90 °C is shown in Fig. 3 and Table 3. The solubility of water in ISO can be estimated from the data reported by Englin *et al.* to be about 0.3 wt% at 90 °C.[14] The diffusion coefficients and surface concentrations of Orange 3 from ISO increased with an increase in the addition of water to the dyebath. On the other hand, it has been observed that the water added to the TCE dyebath has the capability of accelerating the diffusion of disperse dyes.[7] In the solvent dyeing of nylon 6, the diffusion of C. I. Disperse Violet 1 from the TCE dyebath has been slower than that from the aqueous one.[15] The water added to the TCE dyebath, however, has accelerated the diffusion in nylon. These facts show that the water added to the TCE and ISO dyebath promotes the diffusion of disperse dyes in PET and nylon.

In order to elucidate these phenomena, the effect of the addition of water on diffusion and adsorption from the TRI dyebath has been examined. The solubility of water in TRI at 90 °C can be estimated from McGovern's data to be 0.15 g water/100 g TRI.[16] The results in Fig. 3, however, show that the diffusion coefficients and the surface concentrations of Orange 3 did not change within the range of experimental error when water was added to the TRI dyebath. It may be considered that, as TRI with an active hydrogen atom is adsorbed on both the hydrophilic and hydrophobic groups of PET and the water added to the TRI dyebath on the former, the adsorption of water brings about a decrease in that of TRI as a result of their competition. In the TRI system, therefore, there may be no addition effect of water. The effect of the addition of water to the TCE dyebath on the diffusion and adsorption of some disperse dyes in PET is more complicated than that investigated in the present study; it is currently under investigation.

The authors should like to thank Prof. Kiichiro Sakaoku for his helpful discussions. Acknowledgements are also due to Nippon Kayaku Co., Ltd. for its staff's assistance in the preparation of this paper.

References

1) M. Schuler, *Text. Res. J.*, **27**, 352 (1957).

2) H. Kojima, *Kogyo Kagaku Zasshi*, **70**, 183 (1969).

3) W. S. Parkins and D. M. Hall, *Tex. Res. J.*, **43**, 115, (1973).

4) W. S. Parkins and D. M. Hall, "Textile Solvent Technology—Update '73," American Association of Textile Chemists and Colorists, p. 49 (1973).

5) W. R. Moore and R. P. Sheldon, *Polym.*, **2**, 315 (1961).

6) A. S. Ribnick and H.-D. Weigmann, *Text. Res. J.*, **43**, 316 (1973).

7) K. Gebert, *Melliand Textilber.*, **52**, 710 (1971); *J. Soc. Dyers Colour.*, **87**, 509 (1971)

8) Z. Morita, K. Koyama, and T. Iijima, *Nippon Kagaku Kaishi*, **1972**, 1522.

9) Z. Morita, R. Kobayashi, K. Uchimura, and H. Motomura, *J. Appl. Polym. Sci.*, **19**, 1095 (1975).

10) M. Sekido and K. Matsui, *Sen-i Gakkaishi*, **20**, 778 (1964).

11) J. Crank and G. S. Park, "Diffusion in Polymers," Academic Press, London (1968).

12) R. E. Pattle and P. J. A. Smith, *Trans. Faraday Soc.*, **62**, 1776 (1966).

13) N. D. Scott, *Polym.*, **1**, 114 (1960).

14) B. A. Englin, A. F. Plate, V. M. Tugolukov, and M. A. Pryanishnikova, *Khim. i Technol. Topliv. i Masel*, **10**, 42 (1965); *Chem. Abstr.*, **63**, 14608 (1965).

15) Z. Morita, K. Uchimura, and H. Motomura, This Bulletin, **48**, 1081 (1975).

16) E. W. McGovern, *Ind. Eng. Chem.*, **35**, 1230 (1943).