DYEING OF PET TEXTILE FIBERS AND FILMS IN SUPERCRITICAL CARBON DIOXIDE

Ki-Hyeok Chang, Hyo-Kwang Bae[†] and Jae-Jin Shim

Dept. of Chem. Eng., Yeungnam University, 214-1 Tae-dong, Kyongsan City, Kyongbuk 712-749, Korea

Abstract – Polyethylene terephthalate (PET) textile fibers were dyed with a disperse dye in the presence of supercritical carbon dioxide at three temperatures of 333.2, 363.2 and 393.2 K and at pressures between 15 and 25 MPa. The PET film was also dyed at 393.2 K. It was found that the dye uptake in the fiber increased 2-5 times when a small amount of acetone was added as a cosolvent. The equilibrium dye uptake increased with increasing pressure at all temperatures. At 393.2 K the pressure effect appeared to be much larger. It was explained with the shift of the glass transition temperature of the polymers at high pressures. These results may be useful in designing and developing the pollution-free supercritical dyeing technique, a potential alternative to the conventional dyeing of polyesters that produces a lot of wastewater.

INTRODUCTION

Conventional dyeing of textiles requires huge amount of water and discharges the same amount of wastewater. Therefore, dyeing industry suffers from increasing costs of process water and of wastewater treatment. Large amount of dispersing agents and surfactants must be added into the dyeing liquor to dye the unmodified PET fibers since, with the help of the agents and surfactants, dyes can overcome the hydrophobicity of the fibers and evenly penetrate into the fibers. Dispersing agents and surfactants are normally hard to be destroyed by conventional biological treatment. Thus wastewater treatment has become a major problem in dyeing industry. The best solution to this problem would be the pollution-free supercritical dyeing technique that dyes textiles in supercritical fluids, especially in the supercritical carbon dioxide.

Supercritical dyeing technique completely eliminates water pretreatment and wastewater treatment before and after the dyeing process. Since fabrics that are dyed in the supercritical fluid will be completely dry after reducing the pressure of the fluid to the atmospheric, the drying step may be eliminated and therefore the energy corresponding to this step could be saved [Saus et al., 1993]. Dyeing in the supercritical carbon dioxide needs no auxiliary agents such as surfactants and dispersing agents since the medium is not water. Saus et al. [1993] reported that they obtained high degrees of dyeing level and dye exhaustion in the supercritical dyeing process. Any remaining dyestuff is also easily recovered after reducing the pressure of the system. Furthermore, supercritical dyeing requires only a very short dyeing time. There is no need of aftertreatment processes such as reductive washing and finishing that are necessary in the convention dyeing process.

Since the supercritical fluids have a lot of fancy properties, they have mainly been used in processing of the natural prod-

ucts up to 1970's [McHugh and Krukonis, 1994]. In the 1980's the scope of supercritical fluid technology has been widened to include material processing of complex molecules such as polymers, surfactants, and biomolecules [Johnston, 1989]. Polymer processing with supercritical fluids which has been received significant attention since mid-1980's include fractionation of polymers, formation of porous polymers, and polymer impregnation and purification [McHugh and Krukonis, 1994]. Supercritical fluids swell polymers so that they may be impregnated rapidly with additives such as pharmaceuticals, flavors, etc., for controlled release applications [Sand, 1986; Berens et al., 1988], or with additives such as pigments, stabilizers, plasticizers, etc., to modify the properties of polymers [Shim and Johnston, 1989]. Since textile fibers are special form of polymers, dyeing fibers may be considered to be an equivalent to the polymer impregnation.

For commercialization of the supercritical dyeing process, a lot of basic dye-solubility data and dye sorption data are required, but are very rare. Bae and Her [1996] reported some dye-solubility data for two disperse dyes in supercritical carbon dioxide. The supercritical dyeing has rarely been studied except for Saus et al. [1993] and Gerbert et al. [1994]. In this study the PET fibers and films are to be dyed by the novel supercritical dyeing technique. The pressure and temperature effects on dye sorption are to be investigated experimentally. The cosolvent effects on dye solubility and dyeing level are also to be studied.

EXPERIMENTAL

1. Materials

The disperse dye (C. I. Disperse Blue 79) was kindly supplied without dispersing agents by Lucky Metal Co., Ltd. Lumps of the dye were ground to 0.177-0.250 mm (60-80 mesh) to improve its solvency in the supercritical fluids. It has a very good dyeing characteristics and a fairly good abrasion

---

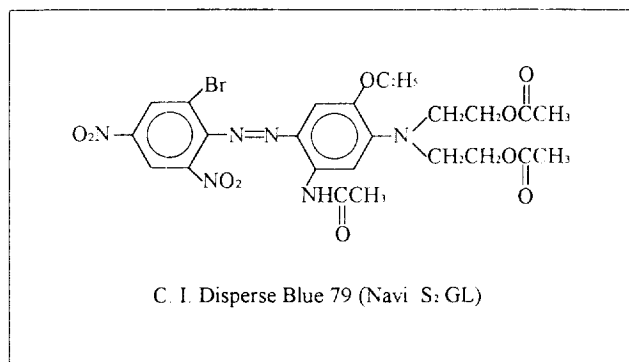[†]To whom all correspondences should be addressed.

C. I. Disperse Blue 79 (Navi S₂ GL)

Fig. 1. Molecular structural formula of the C. I. Disperse Blue 79 dye.

A : Gas cylinder   B : Liquid pump   C : Cooling unit
D : Pressure regulator   E : Dyeing vessel   F : Expansion valve
G : Cold trap   H : Rotameter   I : Wet gas meter
TC : Temperature controller TI : Temperature indicator

Fig. 2. Schematic diagram of the experimental supercritical dyeing apparatus.

resistance. It is an important dye used in matching the dark-blue or black colors. Its structure is shown in Fig. 1. Carbon dioxide used as the dyeing medium had a purity of above 99.8 %. Chlorobenzene was purchased from Yanssen Chemical and acetone, from Katayama Chemical. They were of extra-pure grade and were used as-received. The PET textile [84 picks/in, DTY 150/48(SD), 1000 T/m] was supplied by Samyang Co., Ltd. The PET film, about 9 mil (23 mm) thick, was supplied by Kolon Co., Ltd.

2. Experimental Equipment

The supercritical extraction equipment (Nikkiso, Model 08U-06-50-FS-S : modified the Autoclave Engineers' Autoclave) was modified again for dyeing the PET fibers in the presence of supercritical fluids as shown in Fig. 2. The dyeing vessel (300 mm long by 17 mm diameter) was packed with glass wool, glass beads of 2-mm diameter, glass wool, and about 2.5 gram of dyestuff, in series. The glass beads were employed to make the uniform flow-distribution of the supercritical fluid, and the glass wool, to prevent the dyestuff from being entrained in the fluid. One more series of the same layers of packings were placed at the top of the dyestuff layer. The upper-dyestuff layer was covered with glass wool again. The overall height of the bed was about 150 mm and the total amount of dyestuff was about 5 gram. The PET textile was cut into 50 mm × 35 mm pieces. Two pieces (about 0.25 g) were laid one after another upon a 200 mesh stainless steel cloth, and the combination was rolled into a spiral. One roll was then placed at the top of the packing in the dyeing vessel. In case of the PET film it was cut into a piece of 77 mm by 37 mm and was placed in the vessel with a support (ring structure).

The CO₂ cylinder was held upside-down to charge the liquid carbon dioxide to the high pressure micrometering pump (LDC/Milton Roy, miniPump NSI-33R). The line from the cylinder to the pump was cooled below -12°C with the cooling unit (Tokyo Rikakikai, Cool Ace CA-100) to liquefy any remaining CO₂ vapor. Pressure in this line was measured to ±6 psig by a pressure gauge (3D Instrument). The pressure in the dyeing vessel was regulated within ±1 psig by a back pressure regulator. The temperature of the vessel was controlled to ±0.5°C by a temperature controller. A metering valve was used to keep the pressure and flow rate of the fluid to the desired values. The valve was heated to 70°C to prevent it from being clogged with the dry ice formed by the Jule-Thompson expansion of the fluid. The unused dye in the fluid was collected at the cold
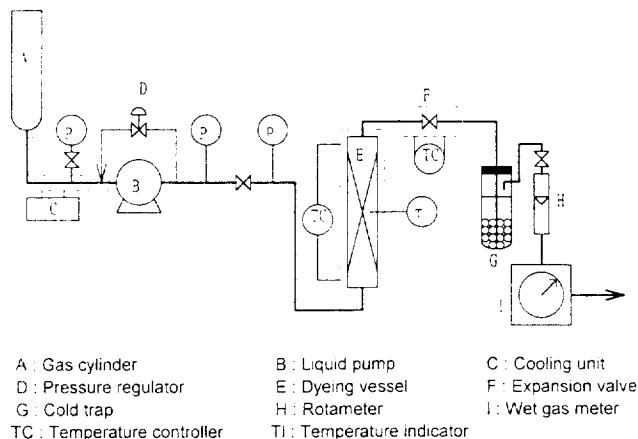
trap that were filled with acetone and glass beads. Acetone is a good solvent for the dye and the beads can improve the mass transfer of dye in carbon dioxide by breaking the gas bubbles into many smaller ones. Therefore the dye molecules remaining in the fluid can easily be dissolved in acetone kept at room temperature. Two flowmeters, a rotameter (Kojima, RK-600A) and a wet gas meter (Sinagawa, W-NK-1A), were placed at the downstream of the cold trap to measure the flow rate of the supercritical fluid.

3. Experimental Procedure

The dyeing vessel was packed with glass wool, glass beads, and powders of the dye as described in the previous section, and a piece of textile sample with a known weight (measured to ±10⁻⁴ g) was placed in the vessel. After the vessel was connected to the pump and the expansion valve, air in the vessel and in the line was purged by low pressure carbon dioxide. Then the vessel was heated to the desired temperature. When the temperature was reached to a set point and controlled at steady state, the vessel was pressurized by supplying liquid carbon dioxide using the metering pump. The flow rate of the fluid was set to a desired value by adjusting the opening of the expansion valve. When the desired pressure in the vessel was attained, the dyeing experiment was begun.

After a certain amount of time was elapsed, the supply of the solvent mixture was stopped and the vessel was depressurized. The dyed textile or film sample was taken out from the vessel. The textile was washed with soapy water to remove the dye particles precipitated on the surface of the textile fibers. The textile was then dried in the oven to remove the water. On the other hand, the dye precipitated on the surface of the film was wiped out with a piece of gauze damped with acetone. The film was then cut off the edges to minimize end effect and the weight was measured. The textile or film was put in the boiling chlorobenzene for 30 minutes to extract the dye impregnated in them. Complete extraction of dyestuff from the fibers can be easily confirmed by just observing the color of the textile or the film, since the naked PET textile is white and the film is clear and transparent. After taking out the textile or the film, the solution cooled down to room temperature. UV absorbency of the solution was then measured by scanning it in the range of wavelength 400-800 nm with a UV-Visible Spec-
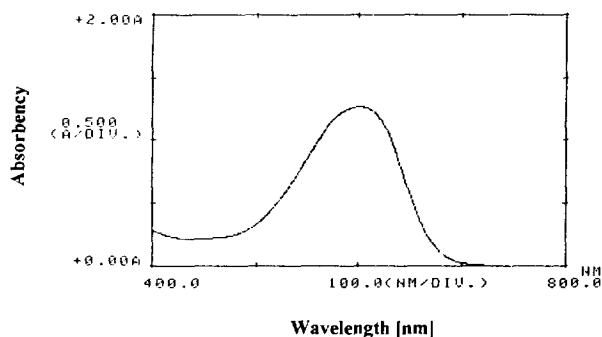
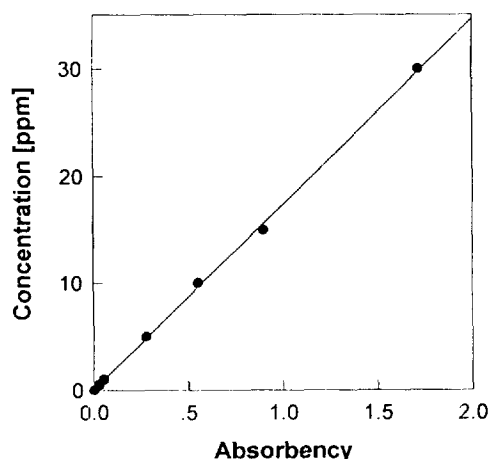Fig. 3. Absorption curve of the C. I. Disperse Blue 79 dye obtained by a UV-Visible Spectrophotometer.

Fig. 4. Concentration of the C. I. Disperse Blue 79 dye in chlorobenzene versus its light absorbency.
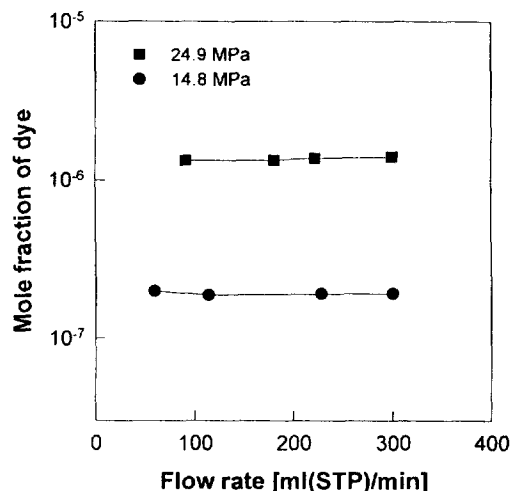

Fig. 5. The range of the flow rate of the supercritical carbon dioxide that does not change in solubility of the C. I. Disperse Red 60 dye in the fluid phase at 393.2 K [Her, 1994].

trophotometer (Shimadzu, UV-160A). The resulting UV-Visible absorption curve is shown in Fig. 3 for C. I. Disperse Blue 79 dye in chlorobenzene. The dye has a single broad peak with a maximum near the wavelength of 605 nm. To calibrate the concentration several dye solutions with different concentration were prepared and their UV-absorbency at the maximum wavelength was measured. Since the absorbency has a linear relationship with the concentration (Fig. 4), the dye concentration can readily be obtained from the UV-absorbency of the solution.

RESULTS AND DISCUSSION

1. Solubility of Dye in the Supercritical Fluids

The solubility of the C. I. Disperse Blue 79 dye was measured at temperatures between 333.2 and 393.2 K and at pressures between 15 and 25 MPa [Bae and Her, 1995]. They showed that the solubility of dye in the supercritical carbon dioxide was very small and in the order of 10^{-7}-10^{-9} in mole fraction. Her [1994] measured the solubility of the C. I. Disperse Red 60 dye at various flow rate between 60 and 300 ml(STP)/min, of carbon dioxide at a fixed pressure and temperature. He got a constant solubility of the dye for the entire range of flow rate tested in his study (Fig. 5). Since we have used the same equipment and method as he used except for the dyestuff, we may assume that the supercritical fluid was in a similar degree of saturation. On the basis of this assumption

we have used flow rates of the fluid below 150 ml(STP)/min, sufficiently lower than 300 ml/min, the largest flow rate proved to have the same solubility.

Solubility of the dye is so small in pure supercritical carbon dioxide that it is necessary to increase it for commercialization of this supercritical dyeing process. Dobbs et al. [1986, 1987] reported that the solubilities of certain solids were increased markedly in supercritical carbon dioxide by adding small amount of various cosolvents. For example, the addition of only 3.5 mol% methanol increased the solubility of 2-aminobenzoic acid 620%. In this study, acetone was chosen as a cosolvent since it had the strongest dye-dissolving power among the solvents tested. Since there may be a chance that the PET textiles are damaged when it comes in contact with acetone solution of higher concentration, the concentration of acetone in the supercritical carbon dioxide was restricted to a little bit lower value, 2 mol%, for the entire dyeing experiments. Actually there was no evidence that the textiles were damaged by the supercritical fluid-acetone mixture at this concentration.

To prepare the acetone-CO_2 mixture we measured the pressure of the pure CO_2 in the cylinder and calculated the density by the equation of state proposed by Huang et al. [1985]. Since the internal volume of the cylinder is known, the amount of pure CO_2 in the cylinder was easily obtained by multiplying the density and the volume. Then, a known amount of acetone (2 mol%) was pumped into the CO_2 cylinder by a high pressure metering pump and the cylinder was shaken for about 30 minutes to blend them.

2. Effects of Pressure and Temperature on the Dye Uptake in the PET Textile Fibers

To determine when to stop the dyeing experiment, it is necessary to know how long it takes for the textile fibers to be fully-saturated with the dye. To measure this equilibration time, the uptake of dye (C. I. Disperse Blue 79) in the PET fibers in the presence of supercritical carbon dioxide was measured at various dyeing times. The results are plotted in Fig. 6 for three different dyeing conditions. This figure shows that, after 80

minutes, the amount of dye uptake became constant for all cases. Therefore we placed and kept the fibers in the dyeing vessel for 80 minutes, which is enough time for the dye molecules to penetrate into the fibers and to equilibrate with the fluid phase.

Uptake of the C. I. Disperse Blue 79 dye in the PET textile fibers in the presence of supercritical carbon dioxide and acetone (2 mol%) mixture was measured at three temperatures 333.2, 363.2, and 393.2 K for pressures between 15 and 30 MPa as described in the experimental section. The results are
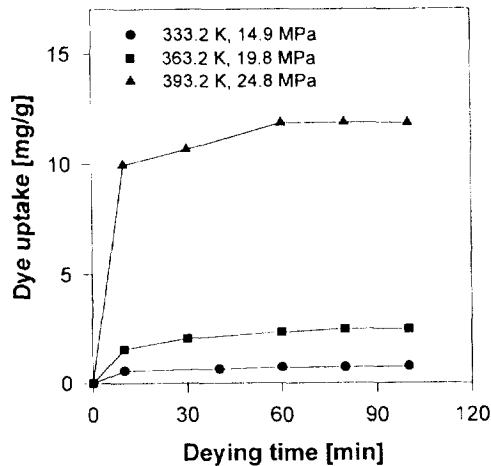

Fig. 6. Uptake of the C. I. Disperse Blue 79 dye in the PET textile fibers with dyeing time.

Table 1. Uptake of the C. I. Disperse Blue 79 dye in the PET textile fibers in the presence of supercritical carbon dioxide containing 2 mol% acetone as a cosolvent [mg/g textile]

Pressure [MPa]	Temperature [K]		
	332.2	363.2	393.2
15.20	1.06	3.94	12.35
19.88	0.79	5.76	17.47
24.71	1.30	6.28	22.92
30.22	2.09	6.57	24.93

shown in Table 1 and compared in Fig. 7 with the sorption data in the presence of pure supercritical carbon dioxide [Bae and Her, 1996]. At the lowest temperature (333.2 K) the difference between them was small, but it became pronounced with increasing temperature. At the highest temperature (393.2 K) the dye uptake in the presence of mixed cosolvent was 2 to 5 times that in the presence of pure carbon dioxide. At this temperature and 30 MPa the uptake of dye reaches to about 25 mg/g fiber. By adding the cosolvent we could lower the pressure by 10 MPa at 393.2 K or the temperature by 30°C at 17 MPa to get the same amount of dye uptake.

In Fig. 8, various colors are shown for the same textiles dyed with the same dye, C. I. Disperse Blue 79. This photograph indicates that the dyeing level is changing with pressure and temperature in supercritical dyeing. The color of the textile becomes darker as the pressure increases at the same temperature. This may be due to the unique property of supercritical fluids, i.e., the large adjustability of their solubilities of solutes for a small change in pressure or temperature near
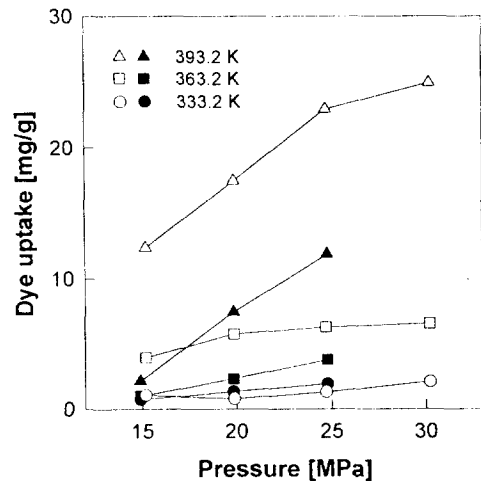

Fig. 7. The difference in the amount of dye (C. I. Disperse Blue 79) uptake with the pure fluid and with the cosolvent-laden fluid (Open symbols represent CO_2 with 2 mol% acetone; solid symbols, pure CO_2).

Results of Dyeing of PET in Supercritical Carbon Dioxide
(C.I.Disperse BLUE 79)

Carbon Dioxide only

Pressure [atm] \ Temp.[°C]	60	90	120
147.1			
195.4			
244.8			

Carbon Dioxide + Acetone 2%mol

Pressure [atm] \ Temp.[°C]	60	90	120
150.0			
196.2			
243.9			
298.3			

Fig. 8. The colors of the PET textiles dyed with the C. I. Disperse Blue 79 dye in supercritical carbon dioxide with or without cosolvent.

Table 2. Dye uptake in the PET film vs. dyeing time for the C.
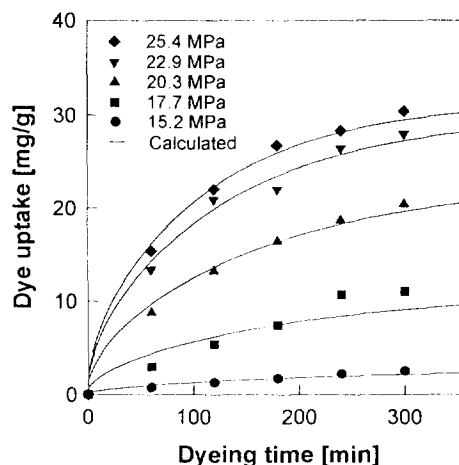I. Disperse Blue 79 dye at 393.2 K

Press. [MPa]	Dye uptake [mg/g]				
	1hr	2hr	3hr	4hr	5hr
15.19	0.74	1.27	1.71	2.21	2.52
17.74	2.95	5.39	7.40	10.69	11.04
20.29	8.76	13.20	16.39	18.68	20.41
22.91	13.34	20.91	21.97	26.48	28.00
25.39	15.32	22.00	26.75	28.34	30.43

their critical conditions. Bae and Her [1996] showed the solubilities of the two dyes (C. I. Disperse Red 60 and C. I. Disperse Blue 79) increased dramatically, about 2 orders of magnitude, when the pressure increased from 15 to 25 MPa. Since the sorption of dye is greatly influenced by the dye solubility in the fluid phase and since the solubility is varies with the fluid pressure, it is easy to understand that the sorption is very closely related to the pressure. In the conventional dyeing there is no pressure effect on dyeing level since the solubility of dye in water does not change with pressure but with temperature.

It is also seen that, at the same pressure, the color of the textile is clearly darker at higher temperature than at lower temperature. Since the PET textile is a polymer with its glass transition temperature of about 353 K [van Krevelen, 1990], the amount of dye-sorption in the glassy PET textile is small at 333.2 K. But we have to note that the glass transition temperature may be dropped when the polymer is placed in a high pressure supercritical fluid [Saus et al., 1993; Wissinger and Paulaitis, 1987]. Saus et al. estimated that the glass transition temperature of PET was lowered by 20-30°C due to swelling of the textile in the supercritical fluid. Wissinger and Paulaitis [1987] reported that, for polystyrene, the glass transition temperature was lowered by about 10% when the concentration of carbon dioxide in the glassy polymer is 5%. The PET is also a glassy polymer but does not sorb carbon dioxide a lot since a part of it may crystallize in the presence of carbon dioxide. Therefore the effect of carbon dioxide sorption on the polymer morphology may not be as large as Saus et al. estimated. It will be verified in our future study.

At 363.2 K the dye molecules can be easily impregnated into the textile since it is transformed into rubbery state. The equilibrium sorption of the dye is also higher at this temperature than at 333.2 K. At 393.2 K the color of the textile is dark blue and becomes darker as the pressure increases. This may be explained by the fact that the crystalline melting point as well as the glass transition temperature is lowered as the fluid phase pressure increases [Wissinger and Paulaitis, 1987]. Polymers are swollen and softened in supercritical fluids so that their glass transition and melting temperatures are lowered significantly. Therefore the polymers are impregnated rapidly and significantly with additives.

Fig. 8 shows that the textiles dyed in the presence of co-solvent are much darker at 363.2 and 393.2 K. As mentioned above, the concentration of dye in the supercritical carbon dioxide and properly chosen-cosolvent mixture is higher than that in the pure fluid. Therefore the dye uptake of the textile must be larger in the fluid mixture than in the pure fluid. At 333.2

Fig. 9. Uptake of the C. I. Disperse Blue 79 dye in the PET film at 393.2 K.

K the textile is in its glassy or near glassy state, and the sorption is not much affected by the presence of the cosolvent.

3. Dye Uptake of the PET Films

The amount of dye sorption in the PET film was measured at 393.2 K in the presence of pure carbon dioxide. The results are shown in Table 2 and Fig. 9. The curves in the figure were obtained by regressing the experimental data with the equation for the unsteady state mass transfer in the slab (see Chang [1995] for details). The amount of dye uptake increased with increasing pressure and dyeing time. As the pressure (density) of the fluid increases, the solubility of dye in the fluid phase increases and thus the dye uptake also increases. Polymers are easily swollen at temperatures above their glass transition temperatures, but the degree of swelling varies with pressure and temperature. At the experimental temperature of 393.2 K, about 40°C higher than its glass transition temperature, the PET film might be much swollen by the supercritical fluid and become a very flexible rubbery state. The polymer chains in the film are so loosened that the free volume in the film increases a lot. The sorption of dye in the film, therefore, increases with pressure.

In conventional dyeing, dyes are not dissolved very well in the dyeing medium, water, even though dispersing agents are employed. This is why the dyeing uniformity has been a problem in dyeing industry [Etters, 1994, 1995]. In the supercritical dyeing, however, the PET film did not show any blot on the surface. This good dyeing uniformity comes from the excellent transport properties of supercritical fluid dyeing media. Supercritical fluids have such large diffusion coefficients that the solute molecules can diffuse easily in the polymers as well as in the fluids. The dye concentration in the fluid is constant at any time, while the concentration is almost constant everywhere at the same depth of polymer. Therefore, polymers are uniformly dyed in the supercritical fluid.

The dye uptake in the PET film is plotted versus density of carbon dioxide in Fig. 10. The density of pure carbon dioxide was calculated by the equation of state proposed by Huang et al. [1985]. The dye uptake appeared to increase almost linearly with fluid density. This behavior is quite different from the result of Shim and Johnston [1989]. They reported that the
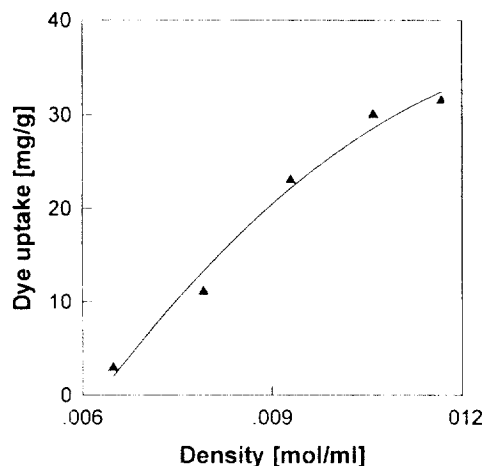
Fig. 10. Uptake of the C. I. Disperse Blue 79 dye in the PET film in the presence of supercritical carbon dioxide expressed as a function of fluid density.

sorption of toluene at 308.2 K increased with increasing pressure up to 4 MPa and then decreased rapidly up to 10 MPa, and that a maximum in sorption occurred near 4 MPa, where the partial molar volume of toluene in the fluid phase is the same as that in the polymer phase. Part of the reason for this difference is that the experimental conditions of the two studies are quite different each other. In their experiment, the concentration of toluene in supercritical carbon dioxide remained constant regardless of pressure, while, in this study, the concentration of dye varied with total pressure. Since they used much lower temperatures than this study, there is no dramatic change in density or fugacity coefficient. The principal reason is, however, that the dye is almost nonvolatile and has a extremely small vapor pressure compared to toluene. Therefore, the dye has a much smaller solubility in the fluid phase than toluene and it may follow Henry's law up to a very large pressure (density), while toluene follows the law up to about 4 MPa (less than 0.10 g/ml).

The increasing tendency of dye uptake in Fig. 10 may be further explained by the following phase equilibrium relationship between the solutes in the polymer phase and in the fluid phase [Shim and Johnston, 1989]:

$$\Phi_2 = \frac{y_2 \phi_2 P}{\Gamma_2 P_2^{sat} \phi_2^{sat} \exp\left(\dfrac{\bar{v}_2^P(P - P_2^{sat})}{RT}\right)} \tag{1}$$

where Φ_2 is the volume fraction of dye in the polymer phase, y_2 is the mole fraction of dye in the fluid phase, ϕ_2 is the fugacity of dye in the fluid phase, P is the system pressure, Γ_2 is the activity coefficient of dye, P_2^{sat} is the saturation pressure of dye, ϕ_2^{sat} is the fugacity of dye at the saturation pressure, and $\bar{v}_2^P$ is the partial molar volume of dye in the polymer phase. The solubility of solute, y_2, increases but the fugacity and the activity coefficients, ϕ_2 and Γ_2, of solute decrease with increasing pressure. The resulting Φ_2 value and thus the amount of sorption (dye uptake) would increase with pressure. The data of dye sorption in the film may be useful in analyzing the dyeing kinetics and mechanism. The dye sorption in the film will be

discussed in our article that is now in preparation [Chang et al.].

CONCLUSIONS

The amount of dye uptake in the PET textile fibers increased 2 to 5 times when a small amount of cosolvent (2 mole percent acetone) was added in the supercritical carbon dioxide. This may be due to the increase in solubility of dye in the fluid phase by the cosolvent. This adjustable-solubility effect was pronounced especially when the dyeing temperature was 393.2 K, which is above the glass transition temperature of the polymer (textile). When the system was pressurized at the same temperature, the textile fiber took in more dye molecules as the fiber was more swollen and was lowered its glass transition temperature. At 333.2 K below its glass transition temperature the pressure effect seems to be negligible. The darkness of the dyed textile was found to have a very close relationship with solubility of dye. Therefore it is possible to match colors of the dyed-textiles just by a small change in pressure and/or temperature in the supercritical dyeing.

It was found that the supercritical dyeing yields a very good dyeing uniformity. This enables us to solve the dyeing nonuniformity problem that the conventional dyeing carries. The time necessary to get complete dyeing of the PET textile fibers was less than 80 minutes. The flow rate of carbon dioxide below 150 ml (STP)/min was enough to make sure that the dye concentration in the fluid phase was kept constant during the experiment. The increasing behavior of the dye uptake with pressure at a fixed temperature was explained well using the phase equilibrium relationship.

NOMENCLATURE

P : the system pressure
P_2^{sat} : the saturation pressure of dye
$\bar{v}_2^P$: the partial molar volume of dye in the polymer phase
y_2 : the mole fraction of dye in the fluid phase
Φ_2 : the volume fraction of dye in the polymer phase
ϕ_2 : the fugacity of dye in the fluid phase
ϕ_2^{sat} : the fugacity of dye at the saturation pressure
Γ_2 : the activity coefficient of dye

REFERENCES

Bae, H. K. and Her, B. K., "Solubility of Disperse Dyes in Supercritical Carbon Dioxide", *HWAHAK KONGHAK*, 34(3), (1996).

Berens, A. R., Huvard, G. S. and Korsmeyer, R., "Application of Compressed Carbon Dioxide in the Incorporation of Additive into Polymers", Paper No. 48b, AIChE Meeting, Washington, DC, (Nov., 1988).

Chang, K.-H., "Development of Dry Dyeing Techniques with Supercritical CO₂", M. S. Thesis, Yeungnam University, Kyongbuk, Korea, 1995.

Chang, K.-H., Shim, J.-J. and Bae, H.-K., "Diffusion of a Dye in PET Film Swollen with Supercritical Carbon Dioxide", in preparation.

Dobbs, J. M., Wong, J. M., Lahiere, R. J. and Johnston, K. P., "Modification of Supercritical Fluid Phase Behavior Using Polar Cosolvent", *Ind. Eng. Chem. Res.*, **26**(1), 56 (1987).

Dobbs, J. M., Wong, J. M. and Johnston, K. P., "Nonpolar Co-solvents for Solubility Enhancement in Supercritical Fluid Carbon Dioxide", *J. Chem. Eng. Data*, **31**(3), 303 (1986).

Etters, J. N., "Kinetics of Dye Sorption: Effect of Dyebath Flow on Dyeing Uniformity", *Am. Dyestuff Reporter*, 38 (January, 1995).

Etters, J. N., "Sorption of Disperse Dye by Polyester Fibers: Boundary Layer Transitional Kinetics", *Textile Res. J.*, **64**(7), 406 (1994).

Gerbert, B., Saus, W., Knittel, D. and Buschmann, H.-J., "Dyeing Natural Fibers with Disperse Dyes in Supercritical Carbon Dioxide", *Textile Res. J.*, **64**(7), 371 (1994).

Her, B. K., "A Fundamental Study on the New Dyeing Technique with Supercritical Fluid", M. S. Thesis, Yeungnam University, Kyongbuk, Korea, 1994.

Huang, F.-H., Li, M.-H., Lee, L. L. and Starling, K. E., "An Accurate Equation of State for Carbon Dioxide", *J. Chem.*

Eng. Japan, **18**(6), 490 (1985).

Johnston, K. P., "New Directions in Supercritical Fluid Science and Technology", in Supercritical Fluid Science and Technology, Johnston, K. P. and Penninger, J. M. L., eds., ACS Symposium Series 406, American Chemical Society, Washington, DC, 1 (1989).

McHugh, M. A. and Krukonis, V. J., "Supercritical Fluid Extraction, Principles and Practice", 2nd ed., Butterworth-Heinemann, Boston, 1994.

Sand, M. L., "Method for Impregnating a Thermoplastic Polymer", U. S. Patent 4,598,006 (Jul. 1, 1986).

Saus, W., Knittel, D. and Schollmeyer, E., "Dyeing of Textiles in Supercritical Carbon Dioxide", *Textile Res. J.*, **63**(3), 135 (1993).

Shim, J.-J. and Johnston, K. P., "Adjustable Solute Distribution between Polymers and Supercritical Fluids", *AIChE J.*, **35**(7), 1097 (1989).

Van Krevelen, D. W., "Properties of Polymers", 3rd ed., Elsevier Science, Amsterdam, The Netherlands, p. 144, 1990.

Wissinger, R. G. and Paulaitis, M. E., "Swelling and Sorption in Polymer-CO_2 Mixtures at Elevated Pressures", *J. Polym. Sci.: Part B: Polym. Phys.*, **25**, 2497 (1987).