

DYEING OF POLYESTER, ARAMID AND POLYPROPYLENE FIBERS IN SUPERCRITICAL CO₂

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Polyethylene terephthalate (PET) and polytrimethylene terephthalate (PTT) fibers as well as difficult-to-dye fibers such as aramid and polypropylene were dyed using supercritical carbon dioxide at pressures between 10 ~ 33 MPa and temperatures between 35 ~ 150 degrees Celsius. Special co-solvents were employed to promote the dye sorption. The equilibrium sorption of dye increased with pressure or density as well as temperature. Dye-sorption was analyzed with a sorption model. Colors other than the three primary colors were obtained by using various amounts of dye mixtures with different dye ratios. The optimum amount of co-solvent was also investigated. These sorption data will provide a basis for replacing the current dyeing process with the supercritical fluid dyeing process that does not yield any pollution problem but allows us to save a large amount of energy. Furthermore, the sorption model may reduce the required number of experiments considerably, leading to a low initial investment cost for the new dyeing process.

INTRODUCTION

Application of supercritical fluids to polymer processing has been received significant attention since 1980's [1,2]. Among them the supercritical fluid polymer impregnation has been focused [2,3] and is now on the verge of practical application. Supercritical fluid dyeing (SFD) is one of the typical examples in this field. It has been studied in 1990's throughout the world [4,5]. The conventional wet-dyeing method must fade out before soon because the conventional dyeing of polyester textile requires a lot of dispersing agents and surfactants producing a lot of hard-to-destroy little-biodegradable wastewater. On the other hand, the environmentally friendly supercritical fluid dyeing does not require any water, dispersing agents and surfactants in the dyeing process. It can also offer us to save energy as it does not require any drying stage after dyeing. However, supercritical fluid dyeing has not been adopted in any of the world dyeing industry yet due to the high initial investment cost. Therefore, it may be better to apply the SFD to the hard-to-dye materials such as aramid, PE and PP fibers and films.

Though extensive studies have been performed by several researchers, only limited amount of basic dye-sorption data are available [4-6]. The amount of dye sorption in polymers in the presence of supercritical carbon dioxide is closely related to both the solubility of dye in the fluids and the distribution of dye between the fluid and the polymer phases. The mobility of dye molecules between polymer chains is generally enhanced due to the swelling of polymers in the supercritical fluids [2,3,7]. In this study the sorption amount of disperse dyes in the PET, PTT, Kevlar, PE, and PP textile fibers were measured in a high-pressure sorption cell equipped with a magnetic pump. SFD with dye mixture and SFD in the presence of polar co-solvent were also performed. Experimental data are correlated with semi-empirical equation similar to the dual-mode sorption model. Distribution coefficients are also calculated from the previously reported dye solubility [8-10] and the present dye sorption data. These impregnation data will

provide a basis for replacing the current dyeing process with the supercritical fluid dyeing process that does not yield any pollution problem but allows us to save a large amount of energy.

EXPERIMENTAL

Materials

C. I. Disperse Blue 60 (B60), C. I. Disperse Red 60 (R60), C. I. Disperse Yellow 54 (Y54), and C. I. Disperse Orange 30 (O30) disperse dyes (Figure 1) were obtained from LG Chemical Co., Ltd. Carbon dioxide of 99% in a cylinder equipped with a dip tube was obtained from Daedong Oxygen Co. An extra pure grade of chlorobenzene was purchased from Yanssen Chemical. Ethanol (99.5%) and special grade acetone were obtained from Kanto Chemical and Yakuri Pure Chemical, respectively. N-methylpyrrolidone was from Aldrich. These materials were used without further purification. PET and PTT textiles were obtained from Hyosung Dyeing Co. and Namseung Textile Co., respectively. The former textile sample was pretreated, but the latter came untreated so that it was treated in the laboratory before dyeing. Kevlar knit fabric was obtained from Texland Co., and polypropylene spun-bonded fabric sample, from Toray Saehan Co., Ltd.

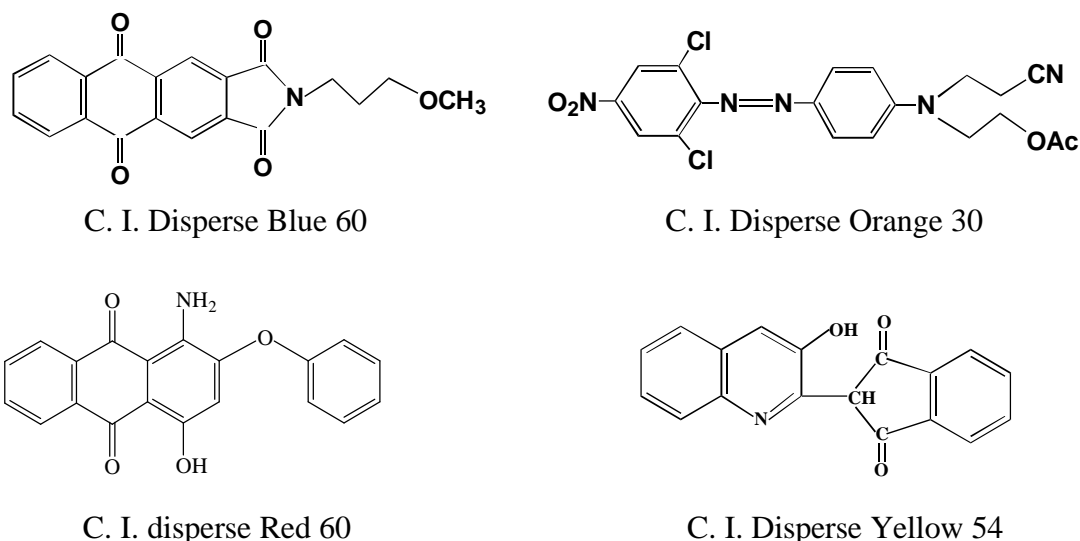


Figure 1 : Molecular structure of Disperse Dyes used in this study.

Experimental Equipment and Procedures

A closed-loop high-pressure sorption apparatus (batch-type) circulated by a magnetic pump was placed in a constant temperature air bath controlled within ± 1 K. A small amount of dye powder, R60, B60, O30 or Y54, was placed in one part (upstream side) of a stainless steel dye reservoir with both sides plugged with glass wool to prevent the dye powder from being entrained. Polymer strips or textile samples, separated by thin wire screen to prevent direct contact of samples, were then packed in the other part (downstream side) of the tube. After evacuation carbon dioxide was introduced into the system and was circulated in the loop with a magnetic pump. The magnetic pump consists of a small cylinder with a piston inside and a roll of concentric coil outside. When the piston jumps up and down continuously, the fluid is

circulated in the loop. One set of Sensotec TJE pressure transducer and Sensotec GM signal conditioner/ indicator reads the pressure to ± 14 kPa. The polymer ample strips were taken out from the cell after 200 minutes (500 minutes for textile samples) and the dye sorbed in the polymer sample was extracted with chlorobenzene at its boiling point. The dye concentration in the resulting chlorobenzene solution was then analyzed by Perkin-Elmer Lambda 40 UV/Visible spectrometer. Other experimental details are described in our previous research [11]. For dyeing in the cosolvent laden supercritical fluid, ethanol, acetone, or N-methylpyrrolidone was introduced in the dyeing vessel.

RESULTS AND DISCUSSIONS

PET and PTT fibers were easily dyed with Y54 and other disperse dyes. The amount of sorption of Y54 dye in the crystalline polyester textile fibers increased with increasing pressure up to 33 MPa at various temperatures (Figures 2). The amount of sorption for PTT was (about 10%) larger than that for PET because PET has a high degree of crystallinity of 30% which is larger than that for PTT. Dye molecules are generally large and their diffusion rate is very small. They may penetrate into a polymer matrix under supercritical fluid conditions. As the smaller supercritical fluid molecules diffuse into the polymer matrix, the polymer is swollen and thus the larger dye molecules can easily get into the polymer. A partially crystalline polymer is consisted of two parts: a crystalline part and a glassy part. The crystalline part does not allow dye molecules below its melting point. However, the glassy part can be swollen by small solvent molecules, creating rooms for the large dye molecules. Therefore, polymers with smaller crystallinity must have lower dye sorption.

At high pressures the increasing rate was slowed down, indicating the polymer was almost saturated with the dye molecules. At pressures lower than 5 MPa, we did not measure sorption because of the experimental difficulty and inaccuracy (due to too little sorption). At temperatures up to 423.2 K, the amount of sorption increased with temperature at the same pressure. The higher the temperature is, the higher the rate of sorption becomes. It was mainly due to the increase in dye solubility in supercritical carbon dioxide with temperature [7]. It may be partially due to the decrease in sorption of carbon dioxide with increasing temperature

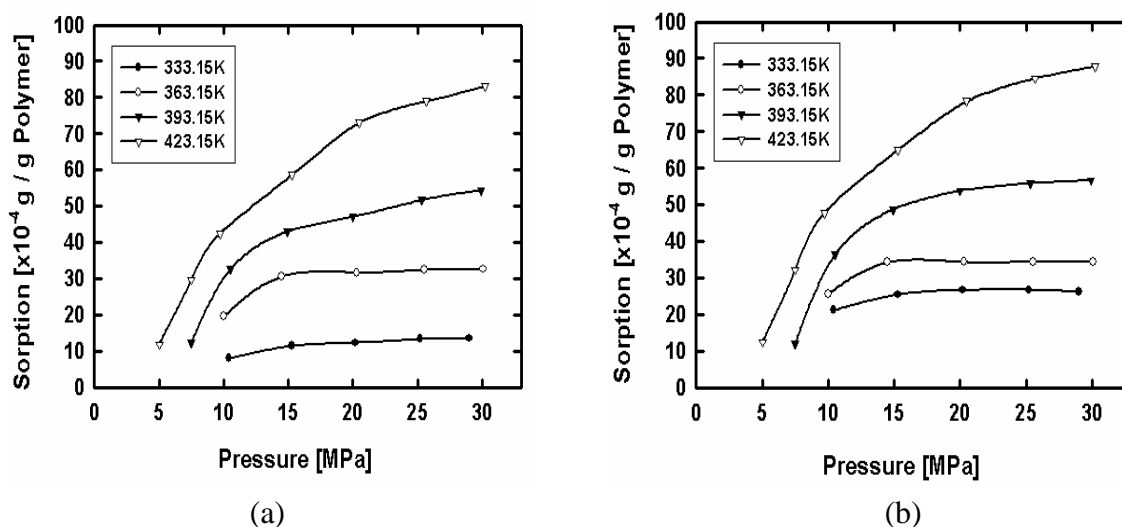


Figure 2 : Experimental sorption of Y54 dye in (a) PET textile and (b) PTT textile in the

presence of supercritical carbon dioxide.

[13]. As the CO₂ sorption increases, the space increases in the polymer that makes the dye molecules penetrate.

An interesting tendency for the dye sorption at low pressures below 150 bar was observed that the amount of sorption was going down rapidly with pressure, leading very small sorption values near zero at around 50 bar. The dual mode sorption scheme may be said that it does not describe the sorption very well. Therefore we tried to use a density representation instead of a pressure representation. Figure 3(a) shows that the sorption of O30 at low density is nearly proportional to the density of the fluid phase. The amount of sorption increases slowly at densities higher than about 0.5 g/cm³, which indicates that the polymer is almost saturated with dye and carbon dioxide at the temperature. The experimental data were analyzed with non-random Langmuir sorption model (curves in Figure 3(a)).

Figure 3(b) shows a linear decreasing behavior of logarithm of the distribution coefficient (K) versus density (r). K is defined as follows:

$$K = \frac{C_i^p}{C_i^f} \cong \frac{S \cdot r^p}{w \cdot r^f} = \frac{S \cdot M_1 \cdot r^p}{y \cdot M_2 \cdot r^f} \quad (1)$$

where C_i^p and C_i^f are the concentrations of i in the polymer phase and fluid phase, respectively, S is the amount of solute sorption, w is the mass fraction of solute in the fluid phase, r^p and r^f are densities of the polymer and the fluid, respectively, y is the mole fraction of solute in the fluid phase, M_1 and M_2 are molecular weights of the fluid and the solute, respectively. The distribution coefficient diminished to one-hundredth when the density increased 0.4 g/cm³. However, all the distribution coefficient isotherms are almost parallel each other.

Some hard-to-dye textiles such as aramid, PE, and PP textiles were also dyed with cosolvent or without cosolvent in the presence of supercritical CO₂. Figure 4 shows that Kevlar knit fabric with intrinsic yellow color could be dyed with R60. As temperature

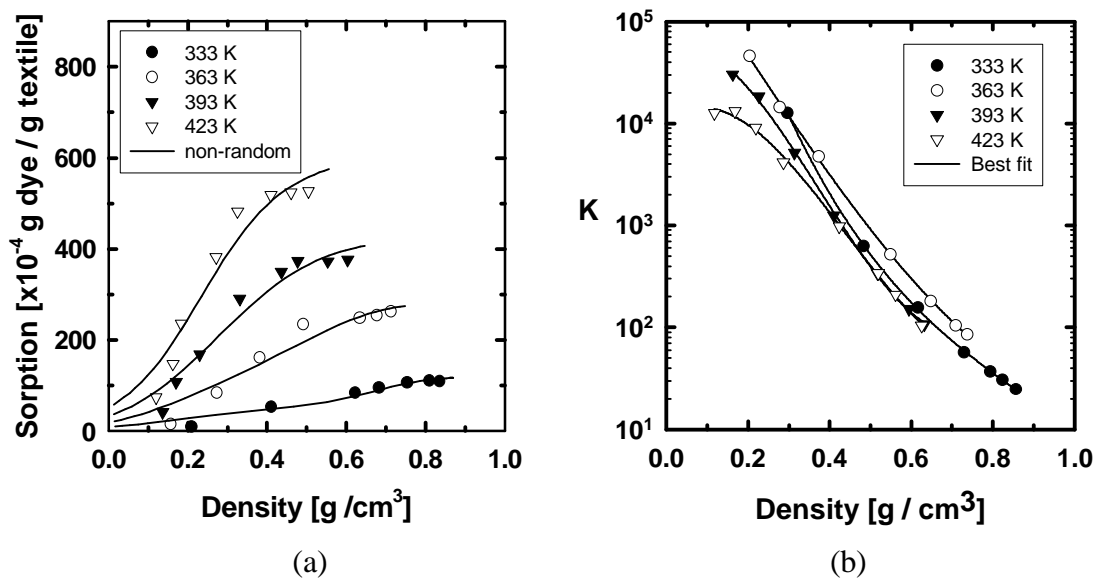


Figure 3 : (a) Experimental sorption of O30 in PET textile and (b) Distribution coefficient of B60

between PET and supercritical CO₂.

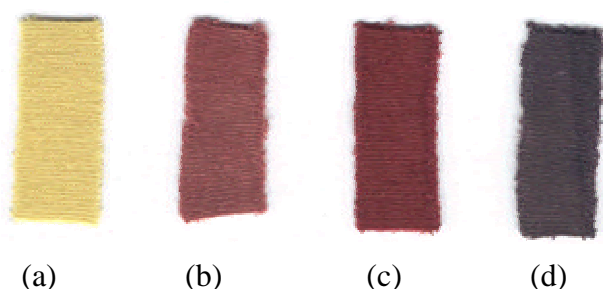


Figure 4 : Kevlar knit fabric dyed with disperse dyes at 34.5 MPa. (a) Original sample, (b) dyed with R60 at 120°C, (c) dyed with R60 at 200°C, (d) dyed with a mixture of Red 60 and Blue 60 at 200°C (co-solvent added)

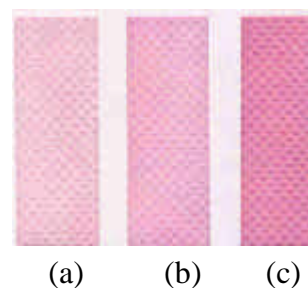


Figure 5 : PP fabric dyed with R60 in supercritical CO₂ at 120°C and (a) 10.1 MPa, (b) 20.3 MPa and (c) 30.4 MPa. (no co-solvent added)

increased, the color got richer ((b) and (c)). Since Kevlar is yellow, it was dyed with a mixture of red and blue to get black color (d). PP spun-bonded fabric was originally white. It was dyed with R60 at 120°C and three different pressures. As the pressure increases, its color got deeper (Figure 5).

The dye fastness test was done on PET fiber and PET microfiber samples (Table 1). Both fibers showed almost the same level of dye fastness that is generally recognized as very good. Though a microfiber is finer than a regular fiber, its color was almost the same as the regular one. This means that, in both cases, the dye molecules deeply penetrated into the fiber. The microfiber is thinner than the fiber but its textile fabric is twice as thick as the normal fiber, making a similar dye fastness.

CONCLUSIONS

Sorption of Y54 and O30 dyes in PET and PTT textile in the presence of supercritical carbon dioxide increased monotonically with pressure at the same temperature and increased with temperature at the same pressure. The increasing rate was reduced with increasing pressure. A non-random Langmuir sorption model was derived from high-pressure equilibrium correlation predicted the sorption fairly well. The logarithm of the equilibrium distribution coefficients decreased linearly with density for all temperatures. Kevlar, PP, and PE fibers were not dyed successfully using supercritical carbon dioxide. Some special co-solvents promoted the dye sorption.

ACKNOWLEDGMENT

This research has been supported by the R&D Management Center for Energy and Resources (96-E-ID02-P-19). We thank LG Chemical Co., Ltd. for the disperse dyes and Texland Co. and Toray Saehan Co., Ltd. for Kevlar and PP textile samples.

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Table 1 : Tests of dye fastness for PET fiber and PET microfiber.

Fastness	PET Fiber	PET Microfiber	Standard Test Methods
Wash Fastness Fading Staining of cotton Staining of polyester	 4~5 4~5 4~5	 4~5 4~5 4	KS K 0430 A-3(1996)
Abrasion Fastness Dry condition Wet condition	 5 5	 4~5 5	KS K 0650 (1990)
Sublimation Fastness Fading Staining of cotton Staining of polyester	 4~5 3 2	 4~5 3 2	KS K 0179 (1980) (180±2? *30sec)
Water Fastness Fading Staining of cotton Staining of polyester	 4~5 4~5 5	 4~5 4~5 5	KS K 0645 (1998)
Sweat Fastness Fading Staining of cotton Staining of polyester	(Acid/Base) 4~5/4~5 5/5 5/5	(Acid/Base) 4~5/4~5 5/5 5/5	KS K 0715 (1997)
Sunlight Fastness Fading	4~5	4~5	AATCC 16E 63? 20 hour (1993) Xenon-arc lamp continuous light