MAXIMUM ATTAINABLE COLORATION OF POLYESTER IN SUPERCRITICAL CARBON DIOXIDE

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Polyester textile (PET) was dyed in supercritical carbon dioxide, using four different dyes: Disperse Orange 3, Disperse Orange 13, Solvent Blue 14 and Solvent Blue 35. The saturation dye uptake was investigated and was found to increase with dyeing temperature (95 to 115 ºC) and with density of the carbon dioxide (400 to 550 kg/m^3). The distribution coefficients of the dyes decreased with temperature and density. The saturation dye uptake was in the same order as in conventional aqueous dyeing of PET.

INTRODUCTION

In current textile dyeing processes, large amounts of water are polluted with dye, salts and other chemicals. The disposal and purification of the wastewater is an increasing environmental and economical burden. The use of supercritical carbon dioxide (scCO$_2$) as dye solvent, instead of water, solves this problem: Both the solvent and the residual dye can be recycled and no salt or other chemicals are needed. An additional advantage of working in scCO$_2$ is that diffusion is faster in a supercritical fluid than in a liquid. Furthermore, after the dyeing process, there is no need for an energy consuming drying step. An overview of the state of the art of textile dyeing in scCO$_2$ is given by Bach et al. [1].

The dyes that are used in scCO$_2$ are generally non polar, mostly azoic or anthraquinone derivatives. They can have reactive groups for the formation of covalent bonds with natural (polar) textiles such as cotton, silk and wool. For non polar textiles like polyester (poly ethylene terephtalate; PET), reactive groups are not necessary. Dye molecules diffuse from the scCO$_2$ into the polymer matrix where they are adsorbed.

This work focuses on PET dyeing. Four dyes are investigated, the structures are given in figure 1.

The dyeing is facilitated by the sorption of scCO$_2$ into the PET:

- The mobility of the polymer chain segments is increased by the CO$_2$ and therefore the diffusivity of penetrating dye molecules is enhanced.
- Also the polymer is swollen by the CO$_2$ – sorption, increasing the free volume in the PET. The degree of swelling increases with temperature and density of the scCO$_2$ [2].

It is expected that the ability of PET to absorb dye molecules is positively affected by the free volume and therefore by an increase in temperature and/or density of the scCO$_2$. To test this, we have measured the maximum (saturation) dye uptake of PET for different dyeing temperatures and –densities.

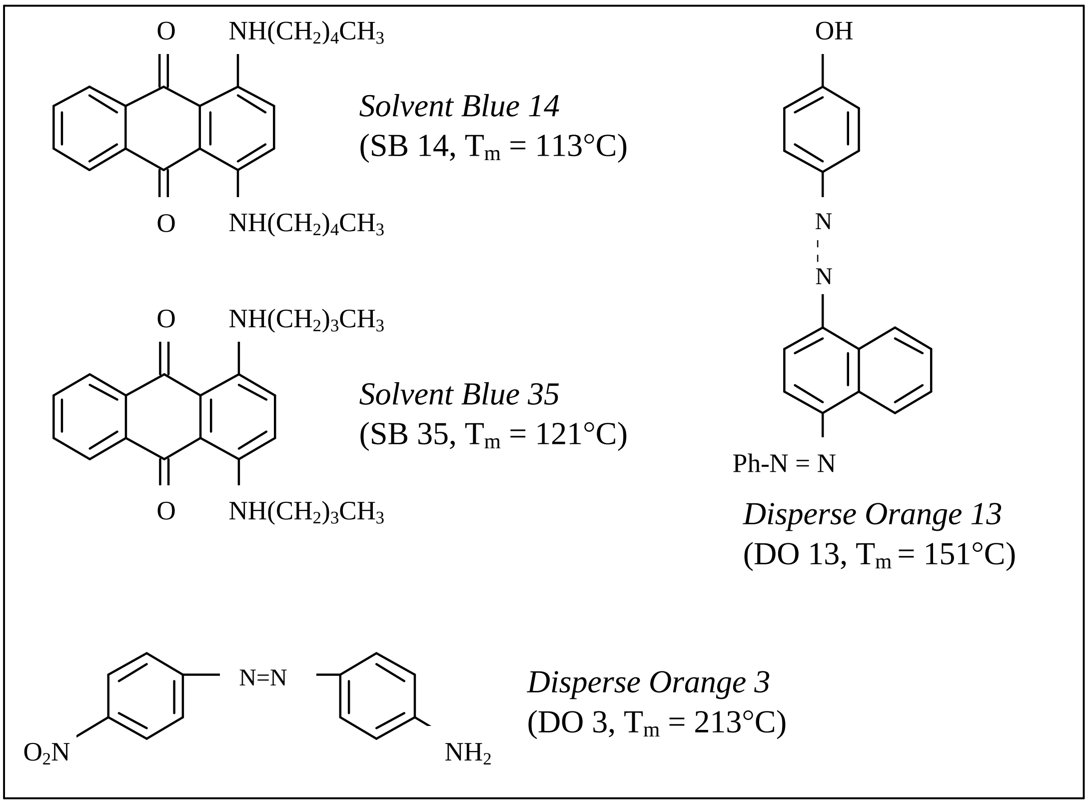

Figure 1 : Structures and melting points T_m of the four dyes used in this work.

Another factor that is studied here is the distribution coefficient (K), the ratio of the dye concentrations in the PET (C_{PET}) and in the CO_2 (C_{CO2}):

$$K = \frac{C_{PET}\,(mg/g)}{C_{CO2}\,(mg/g)} \tag{1}$$

Since the experiments determine saturation concentrations of PET, the values of C_{CO2} are the solubilities of the dyes in the CO_2 and the values of K are the saturation distribution coefficients. The solubilities C_{CO2} are calculated by fitting the empirical equation of Jouyban [3] to literature data, for DO 3 [4] and for DO 13 [5]. The K-values are determined here for DO 3 and DO 13, for different temperatures and $scCO_2$ – densities.

EXPERIMENTAL SECTION

materials

The polyester was knitted and free of spinning oil, with threads of 12 µm and a weight of 120 g/m^2. The dyes were purchased from Sigma-Aldrich and did not contain additives such as dispersing agents. The purities were, according to the supplier: SB 14: 97 %; SB 35: 98 %; DO 3: 90 %; DO 13: 90 %. The CO_2 was purchased from HoekLoos and had a purity of 99.97 %.

Dyeing equipment

The experiments were conducted in a 40 liter pressure vessel with a rotating perforated drum inside that contained the textile cloth. For these experiments the amount of textile was 10 g. The dye was put in a porous stainless steel cylinder that was fixed inside the drum. The dye was used in excess; after each experiment residual dye was found in the cylinder.

A simplified scheme of the experimental set-up is given in figure 2. The system was pressurized in 10 minutes, with a air-driven reciprocating pump. The dyeing vessel was heated with a steam jacket. During the heating, the $scCO_2$ reached the desired pressure and temperature in 30 minutes. The $scCO_2$ was circulated through the vessel by a centrifugal pump, to intensify mixing.

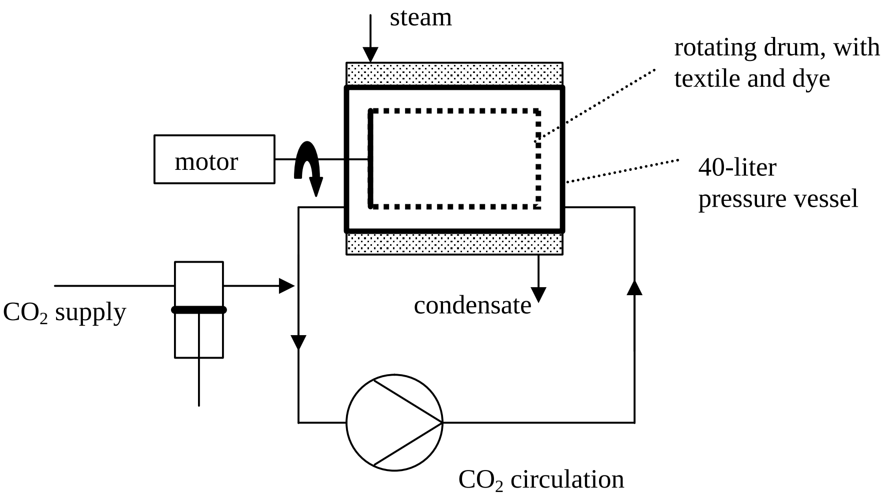

Figure 2 : Experimental dyeing machine

analyses

For the determination of the amount of dye sorbed by the PET, the dyed material was washed with cold acetone to remove any unfixed dye. The PET was then subjected to a Soxhlet-extraction with dimethylformamide (DMF). After all dye had been removed, the dye concentration in the DMF was determined with a UV/VIS spectrophotometer.

RESULTS AND DISCUSSION

Dyeing experiments were carried out at two $scCO_2$-densities (400 and 550 kg/m^3) and three temperatures (95, 105 and 115°C). For the investigated dyes, experimental conditions and corresponding dye uptake values are given in table 1.

In all of the experiments with SB 14 and SB 35, melting of the dye powder was observed, although the atmospheric melting temperatures (see figure 1) are 113 and 120°C respectively. The lowering of melting temperatures of dyes due to the presence of $scCO_2$ has been observed earlier by Von Schnitzler [6]. In the experiments where melting occurred, the polyester cloth was covered with blue stains that could not be washed off with acetone. The dye uptake values for SB 14 and SB 35 are left out of consideration from here on.

Table 1 : Dye uptake in polyester at different dyeing conditions, for Disperse Orange 3 and 13 (DO3 and DO13), Solvent Blue 14 and 35 (SB 14 and SB 35).

Density (kg/m^3)	temperature (°C)	time (hour)	Dye uptake in weight percentages			
			DO 3	DO 13	SB 14	SB 35
400	95	3	1.61	1.50	1.59	1.38
	95	5	1.60	1.51	1.61	1.41
	105	3	1.79	1.69	2.08	1.92
	115	3	1.93	1.85	2.57	1.78
550	95	3	1.94	1.84	not measured	
	95	5	1.95	1.82		
	105	3	2.19	2.08		
	115	3	2.29	2.22		

Saturation dye uptake

In the experiments with DO 3 and DO 13 no melting of dye powder was observed and the cloth was dyed evenly. To check whether the concentrations of DO 3 and DO 13 in the polyester after 3 hours of dyeing can be regarded as saturation values, the experiments done at 95°C were repeated at the same conditions but with a dyeing time of 5 hours. From the table it is clear that for 95°C the increase in coloration above 3 hours is negligible; the distribution of dye over the supercritical and the polymer phase has reached an equilibrium. Since such an equilibrium is established faster at a higher temperature, it can be stated that all the dye uptake values for DO 3 and DO 13 in table 1 are in fact saturation values.

The results for DO 3 and DO 13 are graphically presented in figure 3. It can be seen that dye uptake increases with:

- increasing temperature at constant $scCO_2$ – density and
- increasing density at constant temperature.

This effect is attributed to the increased swelling of the polymer phase at higher temperature and higher $scCO_2$ – density.

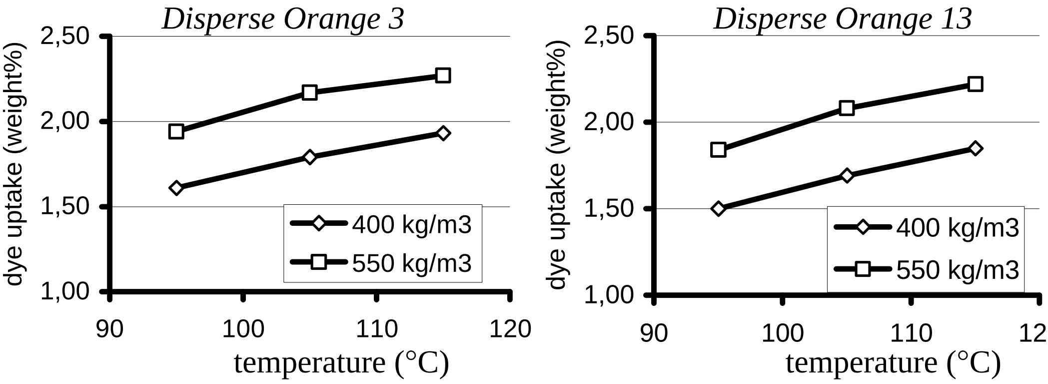

Figure 3 : Saturation dye uptake of polyester cloth as a function of temperature and $scCO_2$ - density for two disperse dyes.

Distribution coefficient

To investigate the influence of temperature and the density of the $scCO_2$ on the distribution coefficient, the concentrations of DO 3 and DO 13 from table 1 are substituted in Eq. 1, together with the solubilities of the dyes in $scCO_2$. Table 2 shows the measured concentrations in the PET, the calculated concentrations in the $scCO_2$ and the resulting distribution coefficients K. A decrease in K with temperature and $scCO_2$ – density is observed.

Table 2 : Distribution coefficients of two disperse dyes at different dyeing conditions.

density (kg/m^3)	temperature (°C)	Disperse Orange 3			Disperse Orange 13		
		C_{PET} (mg/g)	C_{CO2} (mg/g)	K	C_{PET} (mg/g)	C_{CO2} (mg/g)	K
400	95	16.1	0.00933	1725	15.0	0.0104	1442
	105	17.9	0.0123	1455	16.9	0.0123	1374
	115	19.3	0.0188	1027	18.5	0.0143	1294
550	95	19.4	0.0416	466	18.4	0.0416	445
	105	21.9	0.0824	266	20.8	0.0601	346
	115	22.9	0.184	124	22.2	0.0807	275

The decrease in K with temperature is also observed when PET is dyed in water [7]. To compare the supercritical dyeing process with the aqueous process, saturation dye uptake values from the experiments are read from figure 3 for 100°C and compared to dye uptake values in water at 100°C, the latter being taken from literature [8,9]. Table 3 shows that the saturation uptake values in $scCO_2$ and water are in the same order. Because the PET that was used in the aqueous experiments was possibly different from the PET used in this work, further conclusions can not be drawn from table 3.

Table 3 : Comparison between dye uptake in water and in $scCO_2$.

dye	saturation dye uptake (weight%)	
	in water (100°C)	in $scCO_2$ (100ºC)
DO3	1.3 [ref.8]	2.1
DO13	2.0 [ref. 8,9]*	1.9

* Both references give the same dye uptake for PET dyed in water.

CONCLUSIONS

The maximum attainable dye uptake of polyester in supercritical carbon dioxide lies between 1 and 3 weight percent and increases with temperature (95 to 115 ºC) and with the density of the CO_2 (400 to 550 kg/m^3). The distribution coefficient of the dye lies between 100 and 1700 and decreases with temperature and density.

Solvent Blue 14 and Solvent Blue 35 show a significant lowering of the melting point in the presence of supercritical CO_2 and these dyes are therefore not suited for dyeing at temperatures equal to and above 95°. Disperse Orange 3 and Disperse Orange 13 can be used in supercritical CO_2 up to at least 115°C.

When the dye uptake of PET in CO_2 is compared to that in water, it can be concluded that the supercritical process can accomplish a depth of coloration in the same order as in water.

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