ELSEVIER

Dyes and Pigments 45 (2000) 75–79

DYES and PIGMENTS

Dyeing polyester fibres with disperse dyes in supercritical CO_2

M. Rita De Giorgi *, Enzo Cadoni, Debora Maricca, Alessandra Piras

Dipartimento di Scienze Chimiche, Università di Cagliari, Complesso Universitario di Monserrato, 09042 Monserrato (CA), Italy

Received 15 November 1999; received in revised form 11 January 2000; accepted 18 January 2000

Abstract

The isothermal sorption of a series of thiadiazolyl azo dyes to be used as disperse dyes for polyester fibres has been carried out using supercritical CO_2 as the dyeing medium. The experiments were recorded at temperatures from 80 to 120°C and pressures from 2500 to 4000 psi. The results obtained in supercritical CO_2 were compared with those of traditional dyeing in water. The study showed that the disperse dyes used generally exhibited high substantivity towards PET fibres and excellent fastness and, that the extent of dye absorbed by the fibre in supercritical fluid, at 80°C and 3500 psi, was similar to that obtained in aqueous medium at 120°C in the presence of dispersing agents. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Supercritical dyeing; Supercritical carbon dioxide; Polyethylene terephthalate; Thiodiazolyl azo dyes; Disperse dyes

---

1. Introduction

In the past decade, supercritical fluids have been used in many different applications ranging from classical extraction [1,2] to sophisticated industrial processes which can only be justified by the high economic value of the final products. Many applications in the area of polymer processing involve impregnation with organic molecules using supercritical fluid, such as impregnation with pharmaceutical products, the production of advanced optical components and supercritical dyeing [3–8]. The use of supercritical fluids as a solvent in the dyeing process has attracted considerable attention in recent years. The advantages of the fluid are both economic and ecological.

In this context, one of the most frequently used supercritical fluids is carbon dioxide. Besides the advantage of having a low critical temperature, this particular supercritical fluid is also available at low cost and in high purity. On account of its solvating ability towards non-polar or slightly polar organic molecules in the supercritical phase, CO_2 can be used to transport disperse dyes to polyester fibres, without having to use the traditional aqueous medium, thus avoiding pollution problems. Since polyester fibres typically have a very compact structure and high crystallinity, the choice of dyes for them is limited to the disperse dye range.

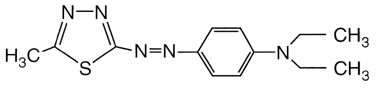
The fastness properties of a series of thiadiazolyl azo dyes, applied as disperse dyes on polyester fibres according to the traditional method, have been explored previously using a chemometric approach [9–11] that aimed at establishing quantitative structure–activity relationships (QSAR).

---

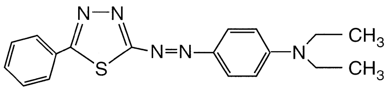
* Corresponding author. Fax: + 39-070-6754388.
E-mail address: degiorgi@vaxcal.unica.it (M.R. De Giorgi).

PII: S0143-7208(00)00011-5

Because of its remarkable substantivity and fastness characteristics, a small set of representative dyes of formula (I) was applied to polyester using supercritical CO_2 as dyeing medium [11]. The aim of this work was to find the optimum conditions of the dyeing process in supercritical CO_2 for the application of the thiadiazolyl disperse dye to PET.

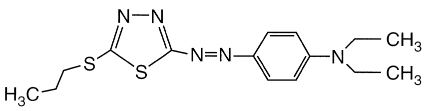


N,N-diethyl-4-[2-(5-methyl-1,3,4-thiadiazol-2-yl)diazenyl]-aniline (dye 1)



N,N-diethyl-4-[2-(5-phenyl-1,3,4-thiadiazol-2-yl)diazenyl]-aniline (dye 2)

I



N,N-diethyl-4-{2-[5-(propylsulfanyl)-1,3,4-thiadiazol-2-yl]-diazenyl}aniline (dye 3)

The experiments were carried out at different pressures and temperatures. The results obtained in supercritical CO_2 were compared to those obtained using traditional aqueous dyeing in the presence of dispersing agents.

2. Experimental

2.1. Intermediates

2-Amino-5-phenyl-1,3,4-thiadiazole was prepared [12] by treating 0.043 mol of thiosemicarbazide and 0.043 mol of benzoyl chloride dissolved in 100 cm^3 of anhydrous acetone with 5.0g $NaHCO_3$.

The reaction mixture was stirred for 3–4 h and refluxed for 1 h. By cyclizing the *N*-benzoylthiosemicarbazide with H_2SO_4 and H_2O at 120°C for 40 min, 2-amino-5-phenyl-1,3,4-thiadiazole was obtained. The crude product was separated by adding aqueous ammonia to the reaction mixture and the desired compound crystallised from ethanol–water.

2-Amino-5-propylsulfonyl-1,3,4-thiadiazole was prepared [13] by adding 0.07 mol of propyl iodide to 0.07 mol of 2-amino-1,3,4-thiadiazole dissolved in alcoholic KOH. The mixture was refluxed for two hours, concentrated in a vacuum and diluted with water. The collected product was recrystallised from benzene.

2-Amino-5-methyl-1,3,4-thiadiazole was a commercial product (Aldrich).

2.2. Dye synthesis

N,N-diethyl-4-[2-(5-methyl-1,3,4-thiadiazol-2-yl)-diazenyl]aniline [9], *N,N*-diethyl-4-[2-(5-phenyl-1,3,4-thiadiazol-2-yl)diazenyl]aniline [10], and *N,N*-diethyl-4-{2-[5-(propylsulfanyl)-1,3,4-thiadiazol-2-yl]diazenyl}aniline, were synthesised by diazotization of the corresponding amine with nitrosylsulphuric acid and subsequent coupling with the chosen coupling agent. The nitrosylsulphuric acid, which was prepared by adding 0.76 g of sodium nitrite to 5 cm^3 of sulphuric acid, was cooled to 0°C, and 0.01 mol of the various amines were added portionwise with stirring. Ten cm^3 of a propionic:acetic acid mixture (1:4) were then added to the diazonium salt while keeping the temperature at 0–5°C for 2 h.

The ensuing clear diazonium solution was added, with stirring at 5°C, to a solution of 0.01 mol of the chosen coupling agent, and dissolved in 20 cm^3 of a 1:4 mixture of propionic–acetic acid, at pH 4, by the portionwise addition of sodium acetate. After a short time, the reaction mixture was poured into iced water and filtered. The resulting dyes were washed with water on the filter, dried and recrystallized from ethanol (dyes **1** and **2**) and methanol–water (dye **3**). Since to our knowledge, dye **3** is an unknown compound, we report some few physical and spectroscopic data here.

^1H NMR spectra were recorded on a Varian VXR-300 spectrometer. GC/MS analyses were performed at 70 eV using a Hewlett-Packard 5989 A mass spectrometer, using the DIP (direct insertion probe) method. *N,N*-diethyl-4-{2-[5-(propylsulfanyl)-1,3,4-thiadiazol-2-yl]diazenyl}aniline: crystallisation solvent methanol:water (1:1), mp 107–109°C.

^{1}H NMR ($CDCl_3$) δ: 1.21 (t, 3H, $SCH_2CH_2\mathit{CH}_3$), 1.40 (t, 6H, $N(CH_2\mathit{CH}_3)_2$), 2.01 (m, 2H, $SCH_2\mathit{CH}_2CH_3$), 3.54 (t, 2H, $S\mathit{CH}_2CH_2CH_3$), 3.80 (q, 4H, $N(\mathit{CH}_2CH_3)_2$), 7.12 (d, 1H, ArH), 8.00 (d, 1H, ArH).

EI–MS: $m/e = 335$ (83%, M^+), 320 (20%, $M^+ - CH_3$), 293 (5%, $M^+ - C_3H_6$), 278 (4%, $M^+ - CH_3 - C_3H_6$), 206 (47%), 191 (56%), 173 (10%), 148 (100%, $C_6H_4N(CH_2CH_3)_2^+$), 133 (35%), 119 (24%), 105 (27%), 91 (22%), 79 (20%), 43 (58%)

2.3. Dyeing of polyester

Supercritical CO_2 dyeings were performed using an SFE 400 supplied by SUPELCO, equipped with a 50 cm^3 internal volume vessel. The operating pressure could be set up to 6000 psi, managed in 100 psi increments. The oven temperature range (30–200°C) was controlled at 10°C increments.

The polyester fabrics (1 g) were suspended on a stainless steel net inside the vessel and the solid, pure dye was placed on the bottom of the vessel. A ratio of 1.5% dye omf was used. When the system reached the desired temperature and pressure, the fluid was let into the vessel. After 30 min under constant conditions, the system was expanded to atmospheric pressure and the dry samples were removed. Dyeings in aqueous medium were produced also in which polyester samples were dyed in a thermostatted bath (Linitest) using a 40:1 liquor ratio, at 120°C for 1 h (1.5% omf pure dye, 0.25% omf Na_2SO_4, 0.5% omf Dispersogen-A, 40% omf Lenol-O); Dispersogen-A and Lenol-O were Hoechst auxiliary products.

2.4. Fastness assessment

Wet fastness was determined according to UNI 7638 (ISO 105-C 01/03/04). For the determination of fastness to artificial light, a Xenotest Hanau 150S (Heraeus) apparatus was employed, equipped with a 1500 W xenon arc lamp, according to UNI 7639 (ISO 105-B02).

3. Results and discussion

To optimise the dyeing process in the case of supercritical CO_2, a study of dye absorption by the fibre at different pressures (2500–4000 psi) and temperatures (80, 100, 120°C), was carried out. The dye concentration absorbed on the fibre was measured spectrophotometrically after hot extraction of the dye with *N,N*-dimethylformamide. Fig. 1 shows the influence of pressure on the dye concentration on the fibre at a constant temperature of 80°C. Table 1 shows the concentrations of the three synthesised dyes at different pressures and at 100°C.

The results show that the concentration of dye absorbed by the fibre increased initially on increasing the pressure to 3500 psi, but was practically constant between 3500 and 4000 psi. Similar results were obtained when the study was carried out at 100 and 120°C.

The data reported in Fig. 1 and Table 1 show a difference in dye uptake at low pressures. In the

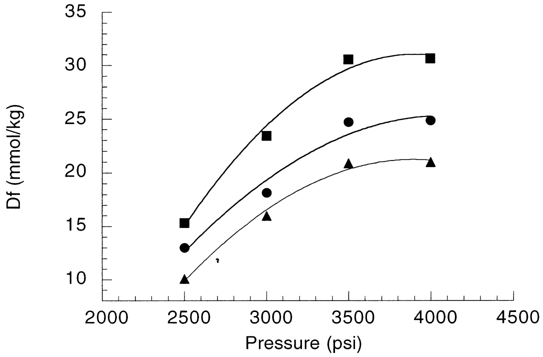


Fig. 1. Variations in dye uptake (D_f) by the fibre as a function of pressure at constant temperature (80°C).

Table 1
Variation in dye uptake by the fibre as a function of pressure at constant temperature (100°C)

Pressure (psi)	Dye **1** (mmol/kg)	Dye **2** (mmol/kg)	Dye **3** (mmol/kg)
2500	12.05 ± 0.06	13.98 ± 0.75	16.32 ± 0.43
3000	16.99 ± 0.04	19.13 ± 0.09	24.41 ± 0.71
3500	20.87 ± 0.09	24.67 ± 0.73	30.52 ± 0.98
4000	20.95 ± 0.05	24.82 ± 1.01	30.60 ± 1.05

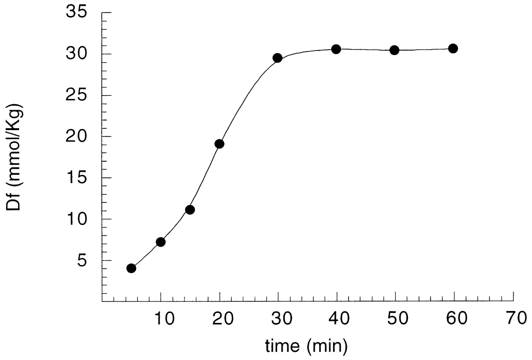


Fig. 2. Equilibrium sorption isotherm of dye **3** on polyester at 3500 psi and 80°C.

Table 2
Dye uptake on polyester samples in supercitical fluid and in water

Dye	D_f[a] (mmol/kg)	D_f[b] (mmol/kg)	Dyeing colour
1	20.87 ± 0.09	20.36 ± 0.12	Red-orange
2	24.67 ± 1.02	24.55 ± 1.16	Violet
3	30.42 ± 0.98	30.63 ± 1.05	Red

[a] Supercritical CO_2, 80°C, 3500 psi, 30 min.
[b] Water, 120°C, Lenol-O, Dispersogen-A, 1 h.

2500–3000 psi pressure range, the extent of adsorption at 100°C was higher than that found at 80°C, and the same adsorption at both temperatures was also obtained in the 3500–4000 psi range, probably because the fibre reaches saturation. Future dyeings were therefore carried out at 3500 psi and 80°C.

To determine the optimum duration of dyeing, the sorption isotherm of dye was determined at 80°C and 3500 psi. Fig. 2 shows the equilibrium sorption isotherm of dye **3**. The values shown are the arithmetical averages of three measurements made at the same temperature and pressure. Saturation of the fibre at 80°C and 3500 psi was achieved after dyeing for 30–40 min.

The dyeings in supercritical CO_2 were compared with traditional dyeings produced in aqueous medium in the presence of dispersing agents at 120°C. The results are reported in Table 2.

Polyester fibres are more difficult to dye because of the low dye sorption rates at temperatures below their glass transition (T_g); adequate rates are achieved when the dyeing temperature exceeds T_g, because of increased motion of the chain segments.

An alternative method of speeding up the rate of dyeing is to add low MW, carriers [14,15] which reduce the glass transition temperature of the fibre.

The fact that the dyeing of polyester in supercritical CO_2 can be carried out at lower than 120°C suggests that the fluid causes a change in the structure of the polymer, allowing the dye to migrate in the non-crystalline regions of the fibre. Supercritical CO_2 is know to reduce the glass transition temperature T_g of many polymers considerably, resulting in an increased mass transfer rate inside the polymeric matrix [16,17].

This study has shown that the extent of dye absorbed by the fibre in supercritical fluid at 80°C and 3500 psi is similar to that obtained in aqueous medium at 120°C (Table 2) and that the samples dyed using the two methods provide the same depth of shade.

Data on fastness to washing perspiration and light (Table 3) of the dyeing carried out in supercritical fluid, were identical to those obtained for dyeings obtained in aqueous medium at 120°C.

Table 3
Fastness values on PET obtained in supercritical CO_2 and in water

Dye	Dyeing in supercritical CO_2 (80°C, 3500 psi, 30 min)					Dyeing in water (120°C, dispersing agents, 1 h)				
	Washing		Perspiration		Light	Washing		Perspiration		Light
	40°C	60°C	Acid	Alkali		40°C	60°C	Acid	Alkali	
1	5	5	5	5	5	5	5	5	5	5
2	5	5	5	5	6	5	5	5	5	6
3	5	5	5	5	6	5	5	5	5	6

This study has shown that azo disperse dyes, with the thiadiazol group, exhibit high substantivity towards and excellent fastness on polyester fibres.

From these results, it can be concluded that the thiadiazolyl azo dyes used, when applied to polyester fibres from supercritical fluid gave dyeings that were similar to those obtained in aqueous medium. The study has shown that it is possible to obtain the same dyeing results using CO_2 as with aqueous dyeing in 30 min at 80°C, i.e. slightly above the T_g of the polymeric substrate, without the use of dispersing agents.

Acknowledgements

This work was supported by MURST and CNR, Rome.

References

[1] Reverchon E, Schiraldi A, Fantozzi P, Fluidi supercritici: applicazioni agroalimentari. CNR Raisa, 1993.

[2] De Giorgi MR, Cadoni E, Medda E, Alessi P, Cortesi A, In: Proceedings 5th Conference on Supercritical Fluids, Garda, Italy, 1999. p. 273.

[3] Alessi P, Cortesi A, Kikic I, In: Proceedings 5th Meeting on Supercritical Fluids, Nice, France, 1998. p. 373.

[4] West BL, Kazarian SG, Vincent MF, Brantley NH, Eckert CA. J Appl Polym Sci 1998;69:911.

[5] Saus W, Knittel D, Shollmeyer E. Textile Res J 1993;63:153.

[6] Knittel D, Schollmeyer E. Textile Res J 1995;63:1092.

[7] Knittel D, Schollmeyer E, Benken R, Buschmann HJ, Saus W. German Patent. DE 4200352, 1992; World Patent WO 93/14259, 1993.

[8] De Giorgi MR, Cadoni E, Poma G. In: Proceedings 5th Meeting on Supercritical Fluids, Nice, 1998. p. 393.

[9] De Giorgi MR, Carpignano R, Viscardi G. Melliand Textilber 1993;74:108.

[10] De Giorgi MR, Carpignano R, Cerniani A, Cesare F. Ann Chim 1995;85:543.

[11] De Giorgi MR, Carpignano R, Cerniani A. Dyes and Pigments 1998;37:187.

[12] Ohta M, Higashijima T. Pharm Soc Japan 1952;72:376.

[13] Pala J. Il Farmaco 1958;13:660.

[14] Arcoria A, Cerniani A, De Giorgi MR, Longo ML, Toscano MR. Dyes and Pigments 1989;11:269.

[15] Arcoria A, De Giorgi MR, Fatuzzo F, Longo ML. Dyes and Pigments 1993;21:67.

[16] Bach E, Cleve E, Schollmeyer, E. In: Von Rohr, Treep Ch, editors. High pressure chemical engineering Elsevier Science, 1996. p. 581.

[17] Beltrame PL, Castelli A, Selli E, Villani L, Mossa A, Seves A, Testa G. Dyes and Pigments 1998;39:35.