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FULL PAPER

Coloration Technology

Investigation into the aqueous and supercritical carbon dioxide dyeing of polyester and cellulose acetate: The influence of temperature and carriers on fabric coloration and dye levelling

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Abstract

This paper investigated the effect of temperature and time on the dyeing of polyester and cellulose diacetate and demonstrated the benefits of supercritical carbon dioxide (SC-CO_2) dyeing. It was evident that the SC-CO_2 medium enabled effective coloration of polyester at lower temperatures, ca. 100°C, and lower dyeing times in comparison with aqueous dyeing, and also reduced the necessity for water. By contrast, the comparable aqueous disperse dyeing of polyester needed to be at 120°C to achieve full coloration. Energy costs are important in textile dyeing and lowering the dyeing temperature is one approach to minimising energy consumption. In this study, we demonstrated for the first time the beneficial effect of a range of dyebath carriers/accelerants in lowering the SC-CO_2 dyeing time and temperature for polyester, while still achieving effective coloration. The beneficial effect of salicylic acid carrier was similarly observed in the SC-CO_2 dyeing of cellulose acetate, where the dyeing temperature could be reduced from 85 to 60°C and dyeing time similarly reduced. The recycling of textiles is an ongoing challenge for the textile industry. In this study, we have further explored the use of the SC-CO_2 fluid as a medium for reprocessing of discarded dyed polyester and the potential reuse of the "locked-in" colourant. It was evident that the p-Vanillin accelerated the SC-CO_2 colour mixing of the blue and yellow dyed polyester fabrics and could assist in producing new colours in "first life and second life" polyester at lower processing temperatures.

1 | INTRODUCTION

The textiles industry is regarded as one of the most polluting manufacturing sectors in the world and has been challenged to reduce its ecological impacts.[1,2] Up to 25% of the total energy used in fibre to fabric manufacture can be attributed to the dyeing and finishing of textiles where high temperatures are common.[3,4] In addition, for cotton, the water consumed in processing may vary from 10 000 to 300 000 litres per 1000 kg of finished product,[5] coupled to estimates that up to ca. 1000-2000 tons of unfixed dyes may be discharged in dyehouse effluent.[6] Therefore, the development of "waterless" textile processing (dyeing, scouring and bleaching) offers the potential for revolutionising traditional textile "wet" processing.[7–12] In our previous paper[13] we discussed the use of supercritical carbon dioxide (SC-CO_2) dyeing of cellulose acetate and polyester and the technical and commercial advantages of SC-CO_2 dyeing of polyester. With polyester (polyethylene terephthalate) dominating the global fibre market in 2020 with 52% (57.1 million tonnes) of the total fibre usage[14] and the recycling of polyester increasingly being embedded within a sustainable textile framework, it is evident that this waterless processing offers an obvious opportunity for establishing "green" twenty-first century textile manufacturing.

In the early development of the coloration of polyester it was recognised that dyeing at high temperature (ca. 120°C) in pressurised dyeing vessels was the preferred process; however, most dyehouses at that time were equipped with traditional atmospheric, water-based equipment limited to at the boil dyeing. Therefore, to mitigate this immediate technical problem and obvious need for longer term investment, an alternative approach was developed where organic "carriers/accelerants" were incorporated into the aqueous disperse dyebaths to allow coloration at 98-100°C[15–21] and enabled a gradual transition to new "High Temperature" (HT) processing equipment. This transition to HT vessels was further encouraged by the recognition that the early carriers could be toxic, smelly and adversely affect dye fastness.[22–25] Nevertheless, the use of carriers has continued to the present day with the current carriers available offering better safety and dye fastness but still with an ongoing environmental impact.

A recurring discussion in the literature over the past 60 years has been the nature of the beneficial action of these carriers/accelerants in aqueous disperse dyeing, with the focus on the observed increased rate of dyeing and diffusion of the disperse dye and the reduction in dye penetration and migration times. A range of potential mechanisms have been proposed regarding the action of carriers on synthetic fibres, but mainly focus on[16,18–28]:

1. Lowering the dry and wet glass transition temperature, T_g, in the amorphous regions of the polyethylene terephthalate polymer fibre coupled to accelerated dyeing and dye diffusion at lower temperature. The reduction in wet T_g is particularly relevant in the aqueous medium, where water also has a plasticising action on the hydrophobic fibre;
2. Swelling of the fibre, hence facilitating quicker dye penetration;
3. Increasing dye solubility and disaggregation of the dye molecules.

Typically, carriers have been based on phenols, such as o-phenyl phenol; aromatic esters, such as butyl benzoate; phenyl ethers, such as diphenyl ether; chlorinated aromatics, such as dichlorobenzene and trichlorobenzene; and creosotic acid esters.[23–25] However, their usage is continuing to evolve with the use of "greener", bio-based carriers, such as vanillin, recently reported.[29–31] Therefore, in recognising the continuing use of carriers in aqueous dyeing and their ongoing rationalisation based on safety and environmental considerations, in this study we compare the effect of dyeing temperature and time on the coloration of polyester in aqueous and SC-CO_2 media and the potential role of carriers in beneficially accelerating the SC-CO_2 dyeing process. In addition, to the benefit of lower energy costs in the SC-CO_2 coloration process, the use of carriers was also examined with a view to improving the recycling of dyed "waste" polyester fabrics.

2 | EXPERIMENTAL

2.1 | Materials

The polyester plain woven fabric, 191 g/m^2, was supplied by Denby Dale Clothing Ltd, and the cellulose diacetate woven satin fabric, 100 g/m^2, was supplied by Whaleys.

The soaping agent Eriopon LAN was supplied by Town End. The Corangar Red PE-3469, Corangar Blue PE-3648, Corangar Blue PE-3618 and Corangar Yellow PE-3205 dyes were generously supplied by Colourtex, and were manufactured specifically for the SC-CO_2 dyeing range with no dispersing agents. The analogous Corangar Red PE-3469, Blue PE-3648 and Yellow PE-3205 SC-CO_2 dyes were also supplied as the comparable industrial disperse dyes by Colourtex.

2.2 | Lab-scale SC-CO_2 dyeing of polyester fabric with Corangar dyes

Polyester woven fabric (10 g) was dyed with 0.5, 1 and 2% on weight of fabric (owf) Corangar Red PE-3469, Blue PE-3648 and Yellow PE-3205, respectively, in a DyeCoo Textiles Systems SC-CO_2 Lab Dyeing machine, where each dyeing tube was filled with the fabric, the dye, eight steel balls and carbon dioxide (147-212 g, depending on dyeing temperature, with the pressure constant). The pressurised dyeing vessel was introduced into an oil bath and the dyebath temperature raised to 120°C over 30 minutes. The dyebath was maintained at 120°C for 15-90 minutes and was then cooled to 50°C before opening the vessel to atmosphere and releasing the pressure. After dyeing, the dyed polyester fabrics were reduction cleared at 60°C for 20 minutes with an aqueous solution containing 2 g/L sodium dithionite, 2 g/L sodium hydroxide and 2 g/L Eriopon LAN in order to remove any surface-deposited dye, rinsed in water and then finally air dried.

2.3 | Lab-scale aqueous dyeing of polyester fabric with disperse dyes

The analogous commercially manufactured disperse dyes (Colourtex Disperse Dyes) were used as received and the 0.5, 1 and 2% owf dye dispersions used to dye the polyester woven fabric at between 80 and 120°C for 15-90 minutes in a Roaches Pyrotec 2000 dyeing machine. The fabric to liquor ratio was 1:10 and the dyebath pH was adjusted to 4 using an acetic acid/sodium acetate (2 g/L) buffer. The aqueous dyeing temperature was raised from 20 to 120°C at a rate of 2°C/min and maintained at 120°C for 15-90 minutes. The dyeing vessel was then cooled to 50°C and the fabric rinsed in water. After dyeing, the dyed polyester fabrics were reduction cleared at 60°C for 20 minutes with an aqueous solution containing 2 g/L sodium dithionite, 2 g/L sodium hydroxide and 2 g/L Eriopon LAN, to remove any surface-deposited dye, rinsed in water and then finally air dried.

2.4 | Lab-scale SC-CO_2 dyeing of polyester and cellulose acetate fabric with Corangar dyes and carriers/accelerants

Polyester woven fabric (10 g) was dyed with 2% owf Corangar Red PE-3469, Blue PE-3648 and Yellow PE-3205, respectively, in a DyeCoo Textiles Systems SC-CO_2 Lab Dyeing machine, where each dyeing tube was filled with the fabric, eight steel balls, the dye, 5-10% owf of either butyl benzoate, benzoic acid, salicylic acid, o-Vanillin or p-Vanillin and carbon dioxide (147-212 g, depending on dyeing temperature, with the pressure constant). The pressurised dyeing vessel was introduced into an oil bath and the dyebath temperature raised to 90-100°C in 20 minutes. The dyebath was maintained at 90-100°C for 15-90 minutes and was then cooled to 50°C before opening the vessel to atmosphere and releasing the pressure. After SC-CO_2 dyeing, the dyed polyester fabrics were reduction cleared at 60°C for 20 minutes with an aqueous solution containing 2 g/L sodium dithionite, 2 g/L sodium hydroxide and 2 g/L Eriopon LAN in order to remove any surface-deposited dye, rinsed in water and then finally air dried.

Cellulose acetate woven fabric (10 g) was dyed with 2% owf Corangar Red PE-3469, Blue PE-3648 and Yellow PE-3205, respectively, in a DyeCoo Textiles Systems SC-CO_2 Lab Dyeing machine, where each dyeing tube was filled with the fabric, eight steel balls, dye, 5-10% owf of salicylic acid and carbon dioxide (229 g, with the pressure constant). The pressurised dyeing vessel was introduced into an oil bath and the dyebath temperature raised to 60-85°C in 20 minutes. The dyebath was maintained at 60-85°C for 15-90 minutes and was then cooled to 50°C before opening the vessel to atmosphere and releasing the pressure.

After dyeing, the dyed cellulose acetate fabrics were immersed in the aqueous Eriopon LAN soaping agent solution (1% wt/wt) for 15 minutes at 100°C, with a liquor ratio of 20:1, to remove any unfixed dye. After the soaping process, the fabrics were then thoroughly rinsed in excess water (100:1) and air dried.

2.5 | "Superlevelling" of SC-CO_2 Corangar dyes on polyester fabric in SC-CO_2 medium

Two polyester fabrics (5 g each) dyed with 1% owf Corangar Yellow PE-3205 and 1% owf Corangar Blue PE-3648, respectively, were treated together in the DyeCoo Textile Systems SC-CO_2 Lab Dyeing machine, where each dyeing tube was filled with carbon dioxide (either 147 or 163 g, with the pressure constant) and eight steel balls. The pressurised dyeing vessel was introduced into a heated oil bath and the temperature raised to 90-100°C in 20 minutes. The dyebath was maintained at 90-100°C for 15-90 minutes and was then cooled to 50°C before opening the vessel to atmosphere and releasing the pressure. After dyeing, the dyed polyester fabrics were reduction cleared at 60°C for 20 minutes with an aqueous solution containing 2 g/L sodium dithionite, 2 g/L sodium hydroxide and 2 g/L Eriopon LAN in order to remove any surface-deposited dye, rinsed in water and then finally air dried.

2.6 | Colour assessment

The colour strength, *K/S*, at λ_{max} of the dyed fabrics was measured on a Datacolor Spectroflash SF600 PLUS-CT instrument. The CIELab colour coordinates (L^*, a^*, b^*, C^* and h) were calculated from the reflectance data for

10° observer and illuminant D65. The K/S value was calculated using the Kubelka–Munk equation, Equation 1:

$$K/S = (1-R)^2/2R \tag{1}$$

where K is the absorption coefficient, S is the scattering coefficient and R is the reflectance at the wavelength of maximum absorption.

The K/S data presented was the mean of two or three dyeings with a typical standard error of ±0.7%.

The colour difference (ΔE) values between the yellow and blue fabrics in the levelling study were measured using a Datacolor Spectroflash SF600 PLUS-CT instrument.

2.7 | Colour wash fastness tests

The colour wash fastness analysis of the dyed polyester and cellulose diacetate fabrics was performed using the ISO 105 C06: A1M test method with standard ECE detergent, with phosphates, at 40 C for 45 minutes with 10 steel balls. After wash testing the greyscale colour change rating between the unwashed dyed and washed fabrics was determined visually in a light box and the staining of adjacent multi-fibre strip fabric was similarly rated in a D65 standard lighting colour matching cabinet.

2.8 | Light fastness

The light fastness analysis was performed according to the ISO EN 105 BO2:2014 light fastness test. Samples of the dyed fabrics (5 cm × 1 cm) and blue wool reference standards were mounted on non-optically brightened white card. The left-hand quarter of the mounted specimens were masked and the samples exposed to xenon arc light using a James Heal TruFade xenon arc light fastness tester. Samples exposure continued until blue wool standard 6 had faded to a greyscale rating of 4 when the greyscale colour change of the samples and blue wool reference standards were determined.

3 | RESULTS AND DISCUSSION

3.1 | Aqueous and SC-CO_2 dyeing of polyester

In this study we evaluated the dyeing of polyester fabric both in aqueous and SC-CO_2 media with a view to establishing the relative dye exhaustion and coloration opportunities for the SC-CO_2 dyeing technology, particularly in the light of the ongoing commercial challenge of managing energy costs. In highlighting the attractiveness of SC-CO_2 processing in terms of being a "waterless" dyeing process requiring no water, it is also worth highlighting the additional benefit that the textile material emerges dry after opening the dyeing machine to atmosphere and requires no mechanical or thermal treatment to remove water bound to the textile. In industrial-scale dyeing machines, the post-reduction clearing and scouring processes to remove any surface dye or oligomer are similarly performed using SC-CO_2 fluid and the process remains waterless. However, in this study, a lab-scale dyeing vessel was used that does not have a "rinsing" facility and the post-dyeing reduction clearing and scouring were undertaken in aqueous media. Nevertheless, the dyeing process is still "waterless".

Table 1 and Figure 1 illustrate the effect of dyebath temperature on the exhaustion and fibre penetration behaviour of the Corangar Red PE-3469 in the SC-CO_2 dyeing medium and its equivalent aqueous disperse dyeing. With the traditional aqueous disperse dyeing the limiting effect of the glass transition temperature, fibre swelling, water plasticisation and accessibility of the amorphous regions in the polyester fibre was obvious and only at 120°C did the dye effectively colour the polyester polymer within an acceptable dyeing timeframe.[26,27] By contrast, the SC-CO_2 solvent dyeing allowed the dissolved colourant to penetrate more effectively at a lower temperature, requiring at least 100°C to achieve the equivalent colour strength of the conventional (90 minutes, 120°C) aqueous disperse dyed fabric. Previously, it was similarly demonstrated for the dyeing of polyester with the natural dye curcumin that raising the dyeing temperature and dyeing time of the SC-CO_2 dyeing process significantly improved the dye exhaustion and colour strength of the final dyed polyester fabric.[32]

Table 2 similarly shows that the dyeing of the Corangar Blue PE-3648 and its equivalent aqueous disperse dye on polyester fabric followed the same behaviour observed with the Corangar Red dye. With the SC-CO_2 solvent coloration, a dyeing temperature of only 100°C was required to achieve the equivalent colour strength of the conventional aqueous disperse dyeing, which offered the potential for energy savings with this single dye application. It can also be observed that at 120°C a higher colour strength can be achieved with the SC-CO_2 dyeing that may be due to better dye penetration into the polyester or increased disaggregation of the exhausted dye molecules in the fibre resulting in increased tinctorial intensity. However, at present the nature of this effect in SC-CO_2 is uncertain.

In textile dyeing processes, the nature of the individual colourant and the behaviour of the associated

TABLE 1 Effect of aqueous and $SC\text{-}CO_2$ dyeing at 80-120°C on colour strength (*K/S*) of polyester fabric treated with 2% owf Corangar Red PE-3469 and equivalent aqueous disperse dye.

Aqueous dyeing			$SC\text{-}CO_2$ dyeing	
Time, min	*K/S*	Dyeing temperature (°C)	Time, min	*K/S*
60	0.3	80	60	5.0
90	0.3		90	5.8
60	0.9	90	60	10.6
90	0.9		90	12.2
15	1.5	100	15	13.5
30	1.9		30	16.3
60	3.2		60	19.2
90	3.2		90	20.0
15	10.1	120	15	21.7
30	19.3		30	22.6
60	19.2		60	22.8
90	20.3		90	22.4

Abbreviation: $SC\text{-}CO_2$, supercritical carbon dioxide.

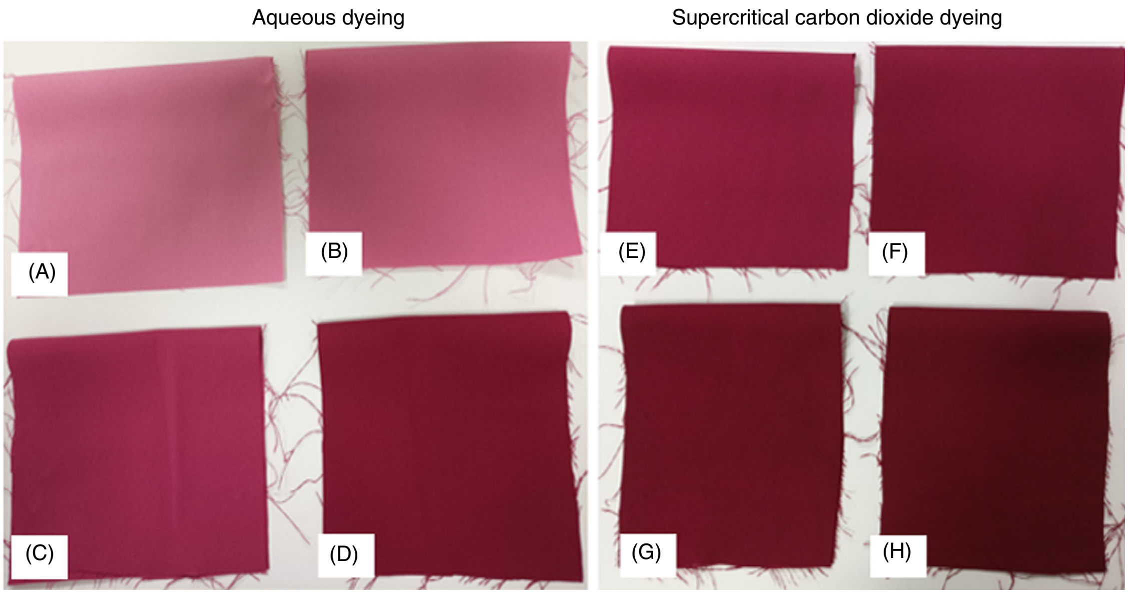

FIGURE 1 Photograph of polyester fabrics dyed with 2% owf Corangar Red PE-3469 in $SC\text{-}CO_2$ and equivalent aqueous disperse dyeing illustrating the effect of dyeing temperature and time on colour. A and B, Aqueous dyeing at 100°C for 30 and 90 minutes, respectively. E and F, $SC\text{-}CO_2$ dyeing at 100°C for 30 and 90 minutes, respectively. C and D, Aqueous dyeing at 120°C for 30 and 90 minutes, respectively. G and H, $SC\text{-}CO_2$ dyeing at 120°C for 30 and 90 minutes, respectively. $SC\text{-}CO_2$, supercritical carbon dioxide.

dyebath auxiliaries can influence the overall dye exhaustion, penetration and final colour. Similarly, it is apparent in $SC\text{-}CO_2$ solvent dyeing that the structure of the specific colourant can influence dyeing behaviour (Tables 1–3). It is evident that good exhaustion occurred at 90°C in $SC\text{-}CO_2$ with the Corangar Yellow PE-3205 and produced coloured fabrics comparable with aqueous dyeing at 120°C. By contrast, with the red and blue colourants it was necessary to dye in $SC\text{-}CO_2$ at a minimum of 100°C to achieve comparable colour strength similar to fabrics dyed in water at 120°C. This better coloration effect at lower temperature may be related to the stereochemical structure/size of the colourant or potentially the improved penetration/disaggregation of the exhausted dye molecules in the fibre. However, at present the nature of this effect in $SC\text{-}CO_2$ is uncertain. Unfortunately, the structures of the commercial dyes used in this study are confidential, but it has been reported in the literature that the structure of disperse dyes can influence the diffusion coefficients and aqueous dyeing times of

TABLE 2 Effect of aqueous and $SC\text{-}CO_2$ dyeing at 80-120°C on colour strength (*K/S*) of polyester fabric treated with 2% owf Corangar Blue PE-3648 and equivalent aqueous disperse dye.

Aqueous dyeing			SC-CO_2 dyeing	
Time, min	*K/S*	Dyeing temperature (°C)	Time, min	*K/S*
60	0.5	80	60	5.4
90	0.6		90	6.5
60	1.3	90	60	12.0
90	1.4		90	13.4
15	3.9	100	15	13.3
30	3.6		30	17.5
60	4.2		60	20.5
90	7.1		90	21.2
15	20.9	120	15	22.6
30	20.8		30	22.6
60	20.9		60	23.2
90	20.9		90	22.9

Abbreviation: SC-CO_2, supercritical carbon dioxide.

TABLE 3 Effect of aqueous and $SC\text{-}CO_2$ dyeing at 80-120°C on colour strength (*K/S*) of polyester fabric treated with 2% owf Corangar Yellow PE-3205 and equivalent aqueous disperse dye.

Aqueous dyeing			SC-CO_2 dyeing	
Time, min	*K/S*	Dyeing temperature (°C)	Time, min	*K/S*
60	0.4	80	60	13.9
90	0.5		90	15.4
60	1.3	90	60	19.6
90	1.5		90	20.3
15	3.8	100	15	18.1
30	3.9		30	20.7
60	4.5		60	20.8
90	7.6		90	19.5
15	20.6	120	15	20.3
30	21.3		30	20.7
60	21.6		60	21.3
90	21.8		90	20.7

Abbreviation: SC-CO_2, supercritical carbon dioxide.

disperse dyes in polyester and cellulose acetate.[33–36] In terms of commercial coloration, it is important to ensure that when dyeing with SC-CO_2 trichromatic mixtures, the exhaustion and migration of the individual dyes (red, blue and yellow, respectively) are comparable and the build-up of the shade consistent and uniform during dye exhaustion up until the final specified colour.

3.2 | Carrier dyeing of polyester

Despite the ability of carriers to facilitate accelerated exhaustion and levelling of disperse dyes in polyester dyeing, over the past 30 years perceived issues with the health/safety of carriers and increasing awareness of their environmental impact has seen a decline in their commercial use.[24] Nevertheless, their use persists, with more eco-friendly, bio-based alternative carriers continuing to be evaluated and show promise.[29–31]

In this study we assess for the first time the potential of carriers/accelerants (Figure 2) in the SC-CO_2 dyeing of polyester and cellulose acetate and whether they can be coupled with the waterless coloration technology to provide energy savings through lower dyeing temperatures, in addition to the recognised reduced water usage. To benchmark the effect of the carriers, colour strength "targets" have been set that relate to the maximum *K*/*S* values achieved in the aqueous and SC-CO_2 dyeings at

FIGURE 2 Chemical structures of potential carriers used in supercritical carbon dioxide dyeing.

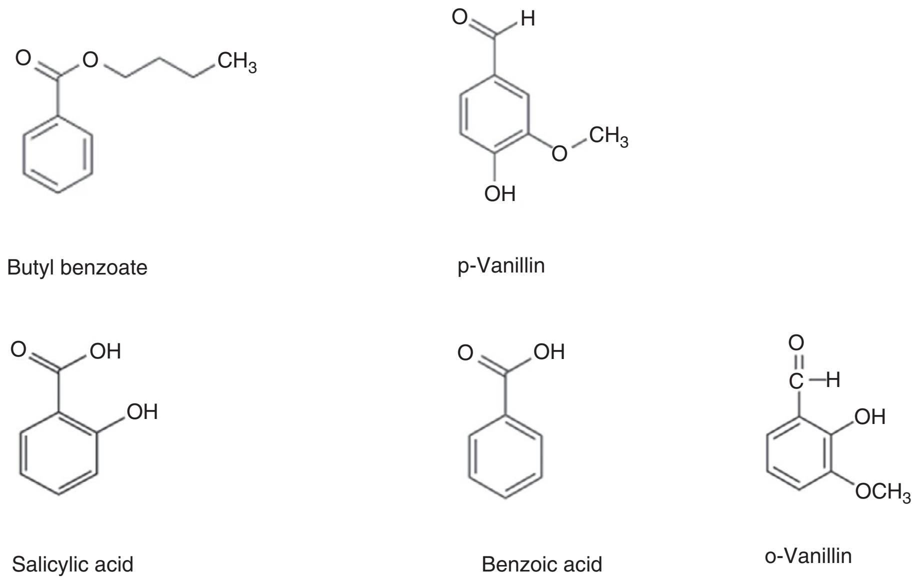

TABLE 4 Effect of potential carriers on dye exhaustion of 2% owf Corangar Red PE-3469 in SC-CO_2 dyeing of polyester fabric.

SC-CO_2 dyeing conditions		Fabric colour strength (*K/S*)			
Temperature (°C)	**Time, min**	**SC-CO_2 alone**	**Butyl benzoate[a]**	**Benzoic acid[a]**	**p-Vanillin[a]**
90	15	5.3	4.8	8.5 (7.7)[b]	10.5 (8.0)[b]
	30	7.9	7.0	11.3 (11.0)[b]	16.2 (12.8)[b]
	60	10.6	10.8	14.3 (16.1)[b]	18.2 (15.7)[b]
	90	12.2	12.4	16.0 (16.0)[b]	19.5 (17.5)[b]
100	15	13.5	13.3	18.6 (14.8)[b]	16.9
	30	16.3	16.1	20.6 (17.8)[b]	19.3
	60	19.2	19.6	22.1 (21.1)[b]	20.6
	90	20.0	20.7	21.7 (21.5)[b]	20.9
Aqueous dyeing @120°C, target *K/S* ca. 20.3		SC-CO_2 dyeing @120°C, target *K/S* ca. 22.6			

Abbreviation: SC-CO_2, supercritical carbon dioxide.
[a]Carrier addition, 10% owf.
[b]Carrier addition, 5% owf.

120°C. The effectiveness of the carrier in lowering the SC-CO_2 dyeing temperature is gauged by referencing the observed carrier-assisted dyed fabric *K/S* to that "target" dyeing at 120°C.

Table 4 indicates that a commonly used aqueous carrier, butyl benzoate, offers no improvement over the control SC-CO_2 Corangar Red PE-3469 dyeing at either 90 or 100°C. However, by contrast, the addition of 10% owf benzoic acid or p-Vanillin, respectively, into the SC-CO_2 dyebaths resulted in increased colour strength for both dyed polyester fabrics at the lower temperatures. Unfortunately, the effect of lowering the carrier/accelerant application level to 5% owf was to similarly reduce the colour strength benefit, therefore further applications were maintained at 10% owf Further assessment of the effect of benzoic acid and p-Vanillin on the low temperature Corangar Blue PE-3648 dyeing of polyester again showed the increased colour strength of the carrier-treated fabrics, with the effect being better at 10% o.wf. (Table 5). In addition, the effect of substituting o-Vanillin for p-Vanillin was to reduce the colour strength benefit and further evaluations were therefore limited to p-Vanillin.

In looking to identify further potential carriers, salicylic acid (5% and 10% owf, respectively) was also incorporated into the Corangar Yellow PE-3205 SC-CO_2 dyeing of polyester fabric and surprisingly was found to have little effect on increasing the colour strength of the dyed fabric at both 90 and 100°C. While the common feature in all the carrier/accelerant structures was the aromatic functionalities, it has also been reported that the

TABLE 5 Effect of potential carriers on dye exhaustion of 2% owf Corangar Blue PE-3648 in SC-CO_2 dyeing of polyester fabric.

SC-CO_2 dyeing conditions		Fabric colour strength (*K/S*)			
Temperature (°C)	Time, min	SC-CO_2	Benzoic acid[a]	p-Vanillin[a]	o-Vanillin[a]
90	15	6.0	10.9	10.5 (8.5)[b]	9.6
	30	12.1	15.1	16.1 (12.1)[b]	12.4
	60	12.0	18.7	18.2 (15.9)[b]	16.1
	90	13.4	18.1	19.5 (17.3)[b]	16.1
100	15	13.4	19.1	20.7	16.1
	30	17.5	20.9	20.4	20.1
	60	20.5	21.6	22.2	21.5
	90	21.2	21.9	21.1	21.4
Aqueous dyeing @120°C, target *K/S* ca. 20.9		SC-CO_2 dyeing @120°C, target *K/S* ca. 22.8			

Abbreviation: SC-CO_2, supercritical carbon dioxide.
[a]Carrier addition, 10% owf.
[b]Carrier addition, 5% owf.

TABLE 6 Colour strength (*K/S*) and fastness of 2% owf Corangar Red PE-3469, Corangar Blue PE-3648 and Corangar Yellow PE-3205 SC-CO_2 dyed[c] polyester fabrics.

Corangar dye, 2% owf	*K/S* before	*K/S* after	Wash fastness[b]	Cross-staining						Light fastness
				Wool	Acrylic	PET	Nylon	Cotton	CA	
Red PE-3469	20.0	20.0	5	5	5	5	5	5	5	6
Red PE-3469[a]	22.1	21.5	4-5	5	5	5	4	5	4-5	5
Blue PE-3648	21.2	20.7	4-5	5	5	3-4	3-4	5	3-4	5
Blue PE-3648[a]	22.6	20.9	4	5	5	3-4	3	5	3-4	4
Yellow PE-3205	21.0	21.0	5	5	5	5	5	5	5	3
Yellow PE-3205[a]	21.7	20.3	4-5	5	5	5	5	5	5	3

Abbreviations: CA, cellulose acetate; PET, polyester; SC-CO_2, supercritical carbon dioxide.
[a]10% owf salicylic acid.
[b]ISO 105 C06.
[c]Dyed at 100°C for 90 min.

structure of the dye and its interaction with the carrier can influence the aqueous,[25,33,34] and most likely the SC-CO_2, dyeing.

One of the recognised deficiencies for carriers used in aqueous disperse dyeing of polyester was the effect of residual carrier in the fibre reducing the wash and light fastness of the dyed fabrics.[23,24] In this study it was evident that the residual carrier in the polyester fibre did affect the ISO 105 CO6 wash fastness, marginally reducing some of the greyscale ratings by 0.5 (Table 6). Similarly, with the light fastness assessment there was a small reduction in stability in the blue and red Corangar-dyed polyester fabrics exposed to simulated sunlight. Therefore, while it is evident that some of the carrier is in the fibre, it is uncertain if there is any unexhausted carrier powder present in the dyeing vessel at the end of the dyeing process. Visual inspection of the dyeing tubes after the 100-120°C dyeing indicated that little or no dye was evident in the vessel and that high exhaustion had occurred, leading to acceptable coloration. Similarly, with carrier-assisted dyeings where strong coloration had occurred, little carrier powder or dye powder was evident in the dyeing tubes at the end of the coloration process. Where dye poor exhaustion at lower dyeing temperatures had occurred, the washings from the dyeing vessels indicated some colourant, and most likely carrier, was present in the dyeing vessel.

3.3 | Carrier dyeing of cellulose acetate

Examination of Table 7 indicates that the effect of the salicylic acid was to clearly accelerate the dyeing of the

TABLE 7 Effect of 10% owf salicylic acid "carrier" on the $SC-CO_2$ dyeing of cellulose acetate fabric.

$SC-CO_2$ dyeing conditions			Fabric colour strength (K/S)	
$SC-CO_2$ dye, 2% owf	**Temperature**	**Time, min**	**No carrier addition**	**Salicylic acid[a] addition**
Corangar Yellow PE-3205	60°C	15	10.8	19.8
		30	13.7	23.6
		60	16.6	28.7
		90	18.5	27.3
Corangar Yellow PE-3205	85°C dyeing (commercial)	90	24.3	
Corangar Blue PE-3648	60°C	15	1.4	2.5
		30	1.7	2.3
		60	2.2	4.5
		90	1.9	4.6
Corangar Blue PE-3648	85°C dyeing (commercial)	90	8.3	
Corangar Red PE-3469	60°C	60	11.5	28.4
		90	15.5	31.2
Corangar Red PE-3469	85°C dyeing (commercial)	90	27.1	

Abbreviation: $SC-CO_2$, supercritical carbon dioxide.
[a]Carrier addition, 10% owf.

cellulose diacetate fabric with Corangar Yellow PE-3205 at 60°C relative to the typical commercial $SC-CO_2$ dyeing conditions at 85°C. In addition, the higher colour strength of the fabric dyed with the salicylic acid addition at 60°C was also evident and surprising in that it exceeded the colour strength achieved under the comparable $SC-CO_2$ dyeing at 85°C. This increase in colour strength could be due to the salicylic acid facilitating better dye penetration into the cellulose acetate fibre or improving the disaggregation of the dyes in the fibre, leading to a higher tinctorial strength colourant. It is known that carriers can disaggregate disperse dyes in the fibre, as well as in aqueous solution, and potentially can affect the dye crystal structure in the fibre, leading to higher colour strength.[35] However, at present, the nature of this effect in $SC-CO_2$ is uncertain.

The salicylic acid also accelerated the exhaustion of the Corangar Red PE-3469 relative to the control dyeings at 60°C (Table 7). Similarly, an increase in the final colour strength of the red dyed fabric relative to the standard dyeing at 85°C was observed and again probably reflects the interaction of the dye with the salicylic acid carrier, potentially lowering dye aggregation in the fibre or improving dye penetration. However, at present, the nature of this effect in $SC-CO_2$ is uncertain.

While the effect of salicylic acid was also to accelerate the dyeing of the Corangar Blue PE-3648 on the cellulose diacetate, the effect was not as great as that observed with the Corangar Yellow PE-3205 or Corangar Red PE-3469. This relatively lower increase in colour strength was probably related to the individual dye structure and the associated reduced interaction of the salicylic acid accelerant in facilitating increased exhaustion of the Corangar Blue into the cellulose diacetate fibre at 60°C.[34] This disparity between the colourant exhaustion levels at lower temperatures appears to be dye specific but will require that trichromatic mixtures are compatible in lower temperature dyeings and deliver the expected specified colour.

The effect of residual salicylic acid accelerant in the polyester fibre was to reduce the ISO 105 CO6 wash fastness of the Corangar dyes by a 0.5 greyscale value (Table 6). Similarly, with the cellulosic diacetate-dyed fabrics, the accelerant had an adverse effect on wash fastness (Table 8); however, the fastness reduction was slightly greater with cellulose diacetate, due to the structure/higher glass transition temperature of dyed polyester polymer restricting dye loss. It was also evident that the salicylic acid dyebath addition had little effect on the light fastness for the Corangar red and blue dyes (Table 8).

3.4 | Carrier dyeing for recycling polyester

Previously, the superlevelling dyeing properties of the $SC-CO_2$ medium have been highlighted and how this phenomenon could be utilised in the recycling of waste dyed polyester garments and fabric explored.[13] In this study, we extended the concept and assessed the effect of

TABLE 8 Colour strength (*K/S*) and fastness ratings of 2% owf Corangar Red PE-3469, Corangar Blue PE-3648 and Corangar Yellow PE-3205 SC-CO_2 dyed cellulose diacetate fabrics (dyed at 60 and 85°C, with and without salicylic acid carrier).

Corangar dye, 2% owf	*K/S* before	*K/S* after	Wash fastness[a]	Cross-staining						Light fastness[b]
				Wool	Acrylic	PET	Nylon	Cotton	CA	
Red PE-3469[c]	14.0	11.3	4	5	5	5	4-5	5	4-5	4
Red PE-3469[c,d]	31.2	22.8	3-4	5	5	4-5	4	5	4	4-5
Red PE-3469[e]	27.1	25.5	4-5	4-5	5	4-5	3-4	5	3-4	4
Blue PE-3648[c]	1.9	1.8	4	5	5	3-4	3	5	3	2
Blue PE-3648[c,d]	4.6	3.6	3	5	5	3-4	3	5	3	2-3
Blue PE-3648[e]	8.3	7.8	4-5	4	2-3	3-4	2-3	4	3	2
Yellow PE-3205[c]	18.7	14.8	4	3	5	5	4	5	4	4-5
Yellow PE-3205[c,d]	27.3	22.5	3-4	3	5	5	4	5	4	4-5
Yellow PE-3205[e]	24.3	20.8	4-5	2-3	5	4	3-4	5	3-4	4-5

Abbreviations: CA, cellulose acetate; PET, polyester; SC-CO_2, supercritical carbon dioxide.
[a]ISO 105 CO6.
[b]ISO EN 105 BO2:20.
[c]SC-CO_2 dyeing at 60°C.
[d]10% owf salicylic acid.
[e]SC-CO_2 dyeing at 85°C.

TABLE 9 Effect of SC-CO_2 levelling temperature and time on the colour difference (ΔE) between 2% owf Corangar Yellow PE-3205 and 2% owf Corangar Blue PE-3648 dyed polyester fabrics during colour homogenisation of “waste” fabrics in the presence of p-Vanillin carrier.

Levelling temperature (°C)	Levelling time, min	ΔE	
		No carrier addition	p-Vanillin[a]
100	15	43.7	32.3
	30	30.7	19.3
	60	20.8	11.7
	90	14.5	6.1
120	15	14.7	8.5
	30	5.3	5.9
	60	3.2	2.0
	90	1.2	1.0

Abbreviation: SC-CO_2, supercritical carbon dioxide.
[a]Carrier addition, 10% owf.

incorporating the p-Vanillin accelerant into the levelling of yellow and blue dyed polyester fabric at 100 and 120°C with the aim of producing “homogenised” coloured materials at lower processing temperatures. Table 9 confirms that the levelling of the Corangar solvent dyes between the yellow and blue dyed polyester fabrics was accelerated by the p-Vanillin accelerant. However, colour levelling was still best achieved at 120°C over 90 minutes, when the final ΔE was neither perceptible visually, nor objectively.

In developing this concept of colour levelling using the first life dyes in the polyester “waste” material, recent studies have highlighted the need for better characterising dye solubility in the SC-CO_2 medium and associated exhaustion/levelling profiles of the SC-CO_2 disperse/solvent dyes within a commercial context.[37,38] By establishing this fundamental database, the ability to accurately predict fabric colour derived from coloured mixtures may become as routine as predictive coloration in commercial aqueous dyeing.

4 | CONCLUSIONS

In this study we have demonstrated the influence of temperature on the exhaustion of non-polar dyes into polyester fabric in aqueous and SC-CO_2 media. It was apparent that solvent dyeing in SC-CO_2 fluid facilitated easier transfer of the dye from the dyebath at lower temperatures into the polyester fibre relative to the comparable aqueous dyeing. Nevertheless, aqueous disperse dyeing of the polyester fabric under commercial dyeing conditions at 120°C still enabled efficient coloration, comparable with that observed with the waterless SC-CO_2 dyeing.

The use of carriers in the "accelerated" aqueous dyeing of polyester, below 120-130°C, has long been recognised and practised. In this study, we demonstrated for the first time the use of accelerants in the coloration of polyester in the SC-CO_2 medium and how the dyeing temperature can be effectively reduced to 90-100°C for some dyes. The probable presence of residual carrier in the resultant coloured polyester fibre marginally reduced the colour fastness of the dyed fabric to washing and light.

Similarly, the use of salicylic acid accelerant in the dyeing of cellulose diacetate enabled dyeing at lower temperature, 60°C; however, the magnitude of the accelerant effect was dependent on the nature of the Corangar SC-CO_2 dye. The observed increase in the colour strength of the carrier-assisted Corangar dyed fabric may be due to greater disaggregation of the dye in the fibre, although the exact nature of this effect at present is uncertain. The probable presence of residual carrier in the coloured cellulose diacetate fibre marginally reduced the colour fastness of the dyed fabric to washing.

In recognising the effect of the carriers was achieved at relatively high application levels, ca. 10% owf, it is probable that the lower dyeing temperature benefit would not be sufficiently attractive to change the existing robust and auxiliary-free SC-CO_2 dyeing process. Therefore, the application of carriers in SC-CO_2 dyeing, with residual material potentially being left in the fabrics, which may also affect fastness properties, would most likely preclude their commercial use.

The superlevelling nature of SC-CO_2 processing has been previously proposed as a potential route to homogenising the colour in mixed dyed polyester waste fabric and providing a viable waterless circular manufacturing and recycling/remanufacturing framework offering savings on energy costs, integrated simpler processing and associated efficient recycling. This colour homogenisation has been further investigated by incorporating p-Vanillin accelerant into the SC-CO_2 fluid and it has been demonstrated the additive accelerates the dye levelling process at 100-120°C between the yellow and blue disperse dyed fabrics.

In conclusion, this study has demonstrated the obvious applicability of SC-CO_2 dyeing for polyester and cellulose diacetate. Further, it has demonstrated for the first time the benefits of carriers/accelerants within this processing medium for dyeing. However, similar to their application in aqueous media, there will be a debate about the commercial use of carriers in SC-CO_2 dyeing based on their added cost, environmental impact and potential adverse effects on fastness.

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