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Dyeing of Cotton in Supercritical Carbon Dioxide

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ABSTRACT

The dyeing of cellulosic fibers with disperse and natural dyes was attempted using supercritical carbon dioxide (CO_2*SCF) as solvent system. The dye uptake was strongly increased if cotton was pretreated with polyethylene glycol (PEG), a known plasticizing agent of cellulose, while reasonable wet-washing and light fastness properties were achieved if PEG-treated cotton was dyed in *CO_2*SCF with disperse dyes included in benzamide crystals. This might be a consequence of partial occlusion of cellulose pores by benzamide, forming hydrogen bonds with cotton and PEG. © 1998 Elsevier Science Ltd. All rights reserved*

Keywords: cotton, supercritical carbon dioxide, dyeing, fastness.

INTRODUCTION

Supercritical carbon dioxide (CO_2SCF) has been recently employed as solvent system in the dyeing and finishing processes of synthetic fibers [1–3]. However, only disperse dyes or other non-ionic compounds able to penetrate

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lipophilic polymeric materials, when dissolved in CO_2SCF, can be used in these treatments.

The supermolecular structure of polymers has been shown to undergo marked variations after immersion in CO_2SCF. In particular, a recent study [4] evidenced that poly(ethylene terephthalate) (PET) undergoes significant morphological changes, when immersed in CO_2SCF, and consequently its glass transition temperature T_g becomes much lower in CO_2SCF than in air. Moreover, the CO_2SCF treatment was observed to produce the same modifications in the polymer structure that can be obtained by annealing in air at much higher temperature.

The present study concerns the dyeing of cellulosic fibers in CO_2SCF. The application of such process to these fibers presents some serious difficulties. It is well known, in fact, that cotton can be dyed in aqueous baths with direct, reactive and vat dyes, which are insoluble in CO_2SCF. Moreover, CO_2SCF is known to extract water from the hydroplastic cotton [5]; the T_g value of the dried fiber can consequently increase up to 220°C, thus greatly extending the temperature range in which the polymer is in the glassy, hardly dyeable state.

EXPERIMENTAL

Materials

A commercial bleached, unfinished cotton fabric of plain cloth (110 gm^{-2}) was employed in the form of $12 \times 4\,\mathrm{cm}$ samples. Polyethylene glycols with number average molecular weight of 200, 400 and 600 (PEG 200, PEG 400 and PEG 600, respectively) were Fluka products. Benzamide (RP grade) was purchased from Aldrich.

The following commercially available (Aldrich) disperse dyes were employed: C.I. Disperse Blue 3, C.I. Disperse Red 13, and C.I. Disperse Blue 56. Natural dyes comprised *Lycopene*, C.I. Natural Yellow 27 (a carotenoid dye), obtained from tomato food extraction by CO_2SCF, and *Calendula officinalis*, C.I. Natural Yellow 27 (a mixture of carotenoid dyes *Lycopene* and *Rubixanthin*), obtained from CO_2SCF extraction of *Calendula officinalis* flowers.

Dyeing procedure

The fabric samples were treated in water solutions containing 8 wt.% polyethylene glycol via padding, and then dried at room temperature. They were dyed in CO_2SCF in a 300 ml vessel, heatable up to 100°C, according to the previously reported procedure [4]. Dyeing in CO_2SCF was carried out at 98°C for 30 min under a 200–250 bar pressure.

When benzamide was employed in the dyeing process, dyes were dissolved in fused benzamide (melting temperature: 131°C). After cooling down to room temperature, benzamide crystals containing 10 wt.% dyes were placed inside the vessel together with the cotton sample, prior to liquid CO_2 inlet.

Characterization of dyed samples

The dye uptake, determined as already reported [4] by reflectance analysis according to the Kubelka–Munk (KM) equation [6], was expressed in terms of the KM factor.

Colour fastness to artificial light was determined using a Xenotest Hanau 150S (Heraeus), according to UNI 7639 (ISO 105-B02). The determination of wet-washing fastness was carried out according to UNI 7638 (ISO 105-C04).

Differential scanning calorimetry (DSC) was carried out as reported previously [4, 7], employing a Perkin–Elmer DSC-4 Thermal Analysis Data Station System.

RESULTS AND DISCUSSION

Native cellulose consists of linear macromolecules formed by β-anhydroglucose units linked together by glucosidic bonds. Cellulose chains in the solid state are able to form intra and inter-molecular hydrogen bonds, leading to an organized chain structure [8]. In the case of cellulose, however, the folded chains model, compatible with a structure similar to that proposed for synthetic polymers, has not been confirmed by experimental results [9]. Thus a native cellulosic fiber, such as cotton, can be regarded as a highly crystalline fiber, in which amorphous regions are formed by the most extended stiff chains. Dye molecules cannot penetrate the highly ordered crystalline regions of native cellulose and their adsorption can only take place in the amorphous regions, which are highly ordered as well.

According to the pore model [10, 11], which is able to adequately describe the diffusion of dye molecules in cotton dyed in aqueous baths, cotton can be regarded as a network of interconnecting channels or pores. Water and dye molecules diffuse through this network and are simultaneously adsorbed on the surface of pores. Thus cotton swells when immersed in aqueous solutions, its T_g, value becomes lower and interactions between polar dye molecules and polymer chains occur.

Our preliminary attempts of dyeing cotton with a disperse dye in CO_2SCF, following the same procedure [4] employed for PET and 2,5-cellulose diacetate were unsuccessful, owing to the poor affinity and poor interaction between disperse dyes and cotton. Moreover, cotton immersed in CO_2SCF undergoes dehydration, and it is consequently in the glassy state up to relatively high temperature. In these condition, the pore model prevails relative to the free volume model typical of the easily dyeable PET.

Thus, in order to achieve efficient dyeing in CO_2SCF, cotton should be pre–treated by means of a plasticizing agent of cellulose, able to induce its transition to the rubbery state.

The interactions between cellulose materials and plasticizing liquid media, such as water, glycerine and ethylene glycol, have been extensively studied [12]. However, such well known plasticizing molecules should not be effective in CO_2SCF, being removed from the fibrous material by the supercritical fluid itself.

On the other hand, polyethylene glycol and polypropylene glycol have been widely employed [13–16] to increase the affinity of cellulose for disperse dyes in transfer printing. In particular, polyethylene glycols (PEG) are water soluble polymers, which are used in large amounts in the cosmetic, pharmaceutical and food industries because of their physiological compatibility.

The effect of PEG pre-treatment of cotton fabrics in the CO_2SCF dyeing process was thus investigated. Cotton samples were first immersed in aqueous solutions containing different amounts of PEG 200, PEG 400 or PEG 600. The best results, in terms of highest dye uptake, were found in the case of cotton samples pre-treated with 8 wt.% PEG 400 or PEG 600 solutions. The resulting colour strength was 5.5 times greater with respect to that of the fabric dyed without pre-treatment (see Table 1), but, unfortunately, the washing fastness index at 40°C of such treated cotton was very low.

These results may be explained by taking into account that PEG is able to form hydrogen bonds with the cellulose chains. This prevents the complete deswelling of the fibers during the CO_2SCF treatment, thus maintaining the

TABLE 1
Dye Uptake, Expressed as Kubelka–Munk Factor, Wet-Washing Fastness at 40°C and Light Fastness of Cotton Dyed in CO_2SCF

Cotton	*Dye*	*Kubelka–Munk factor*	*Wet-washing fastness*	*Light fastness*
Untreated	C.I. Disperse Blue 56	0.7	1	< 1
Treated with PEG 400	C.I. Disperse Blue 56	3.9	1–2	< 1
	C.I. Natural Yellow 27	2.2	1	< 1
Treated with PEG 400 and benzamide	C.I. Disperse Blue 56	4.2	4	4-5
	C.I. Disperse Blue 3	3.5	3–4	4
	C.I. Disperse Red 13	3.2	3–4	4
	C.I. Natural Yellow 27	2.8	3	1

cotton the more accessible to dyeing. In the CO_2SCF process the dyes dissolved in the fluid are able to diffuse into the channels or pores of cotton. At the end of the treatment, however, when CO_2 is evacuated, no dye fixation can be achieved, neither a specific binding to the fiber pores being possible, nor the entrapment of the dye in the free volume of the polymer. Thus, the dyes migrate out of the polymer in the undissolved state through the polymer pores and washing fastness is consequently very low.

In order to avoid these undesired effects. benzamide, which is soluble in CO_2SCF and is a good solvent for disperse dyes, was employed as synergistic agent in a subsequent series of experiments. The dyeing of PEG-pretreated cotton samples was thus carried out in CO_2SCF, using dyes included in benzamide crystals. A higher dye fixation in the fiber was observed to occur, while satisfactory light and wet-washing fastness were obtained, according to the results reported in Table 1.

In order to understand how this could be achieved, DCS analyses were carried out. It was first verified that, if benzamide was added to PEG, an endothermic peak appeared in the thermogram at a temperature (*ca* 90°C) well below the melting point of pure benzamide (131°C), indicating that strong interactions occur between the two components of the mixture. Moreover, the melting point of pure PEG (around 22°C) was not observable in the thermogram of a cotton pre-treated with PEG, nor was the melting point of benzamide in the thermogram of a cotton sample treated in CO_2SCF in the presence of benzamide. Thus both PEG and benzamide strongly interact with cotton. In particular, benzamide is able to form hydrogen bonds with cotton and PEG, thus favouring dye entrapment through the partial occlusion of cellulose pores.

Finally, PEG-treated cotton was dyed also with CO_2SCF-soluble carotenoid dyes. Also in this case, the use of benzamide was demonstrated to increase the wet-washing fastness of dyed cotton, as shown in Table 1. The light fastness of these dyed samples was in any case very poor, as it is usually when carotenoid dyes are employed.

CONCLUSIONS

Good results of dye uptake, light and wet-washing fastness can be obtained when cotton is pre-treated with PEG and dyed in CO_2SCF in the presence of benzamide. The excess of PEG and benzamide can then be easily removed by washing the dyed samples in hot water. The CO_2SCF dyeing process of cotton presents several benefits, being easy and flexible and requiring low energy costs. Moreover, carbon dioxide is non-toxic as are PEG and benzamide, and can be obtained from natural sources and can be easily recycled.

It is also worth noting that a pre-treatment with PEG can be used to increase the affinity of cotton for disperse dyes also in the dyeing of cotton/polyester fabrics by means of the CO_2SCF process, which might thus have a wider application (e.g. for dyeing articles of clothing).

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