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Morphological Changes and Dye Uptake of Poly(ethylene terephthalate) and 2,5-cellulose Diacetate Immersed in Supercritical Carbon Dioxide

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ABSTRACT

The dyeing process of poly(ethylene terephthalate) (PET) and 2,5-cellulose diacetate (CA) fibers at 40–100°C using supercritical carbon dioxide (CO_2SCF) as solvent system has been kinetically investigated in relation to the morphological modifications induced by the CO_2SCF treatment in these fibers, determined through DSC, X-ray diffraction, SEM analysis and shrinkage measurements. A comparison between the effects of annealing both polymer fibers in CO_2SCF and in hot air evidenced that CO_2SCF has a plastifying action towards PET by lowering its T_g value to 0–5°C and thus favoring the dyeing process at low temperature. Such effect was not observed with CA. © *1998 Elsevier Science Ltd. All rights reserved*

Keywords: poly(ethylene terephthalate), 2,5-cellulose diacetate, supercritical carbon dioxide, morphological changes, dye uptake.

1. INTRODUCTION

It is well known that chemical and solvent treatment of polyester fibers and films have a marked effect on the dyeing and colour properties of these

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substrates [1, 2]. Indeed, low molecular weight interactive penetrants produce physical modifications in solid polymers [3, 4] including reversible swelling, crystallization and glassy to rubbery state transition. These effects have also been investigated in relation to the dyeing and penetration properties of disperse dyes into cellulose triacetate or cellulose diacetate [5, 6].

In this paper, we report some studies on the morphological modifications and the dyeing process of poly(ethylene terephthalate) and cellulose diacetate fibers using supercritical carbon dioxide as solvent system. This represents a new, ecologically acceptable method for dyeing fibers, which may substitute conventional dyeing techniques producing hazardous waste waters.

Supercritical fluids are characterized by a very high solute diffusivity and a lower viscosity with respect to common liquid solvents. Consequently, in supercritical fluids all transport processes are facilitated, thus becoming much faster. For its peculiar properties, the most commonly employed supercritical fluid is carbon dioxide ($T_c = 31.3°C$, $P_c = 72.9\,atm$), which is neither toxic, nor flammable, and can be easily obtained with a higher purity grade at relatively low cost.

Supercritical carbon dioxide (CO_2SCF) has been recently demonstrated to have a very high solubility in many polymers, similar to that of organic solvents exhibiting a swelling action. Moreover, it is able to induce a decrease in the glass transition temperature (T_g) of polymers [7], such as poly(methyl methacrylate) and its blends with poly(vinylidene fluoride). These properties of CO_2SCF suggest its use as temporary plasticizer in order to facilitate the uptake of additives [8], flavoring agents and dyes in several polymers.

In the present work, the plasticizing action of CO_2SCF on poly(ethylene terephthalate) has been verified by DSC analysis and by determining its thermal return after CO_2SCF treatment, in comparison with the thermal return observed after heating the polymer in air.

2. EXPERIMENTAL

2.1 Materials

Three different samples of poly(ethylene terephthalate) (PET) were employed, i.e. (i) PET, in the form of industrial yarns ($PET_{cr,or}$), supplied by Montefibre (Mw = 10 500; linear density = 75.6 den, tenacity = $3.66\,g\,den^{-1}$), was a semi-crystalline thermofixed polymer, (ii) PET cold drawn filaments in an unoriented amorphous phase ($PET_{am,un}$) were produced by a standard plant for the industrial production of yarns (Mw = 10 500); they were extruded at 280°C and quenched by means of a cold air stream. From these samples, an oriented amorphous phase (iii) ($PET_{am,or}$) was obtained, by stretching at 20°C, with a deformation of 450%. The diameter of the cold drawn filaments was 20 μm.

2,5-Cellulose diacetate (CA) industrial yarns were produced by Novaceta (linear density = 75 den, tenacity = 1.11 g den^{-1}). All fabrics were employed as orthogonal textures. They were dyed with CI Disperse Blue 56 C.I. 63285, purchased from Ciba Geigy.

2.2 Treatment with CO_2SCF and dyeing procedure

The polymeric samples were treated with CO_2SCF in a 300 ml reactor, which could be heated up to 100°C. The samples were placed on a stainless steel net inside the vessel, which was heated up to the desired temperature value. CO_2 was then introduced in the liquid phase from a cylinder (SIAD), and isothermically compressed to the working pressure.

Dyeing was carried out in the same reactor at a pressure in the range 100–250 bar, by dissolving the dye in CO_2SCF without auxiliary chemicals. The polymer samples (about 5 g of fiber or fabric) and dye (1.5 wt.% respect to the polymer) were placed in the vessel. CO_2SCF was then introduced and the dye uptake was carried out at 40–90°C.

The standard contact time was 30 min in both types of treatment.

2.3 Dye uptake

The dye concentration in the PET fabrics was determined by reflectance analysis at 635 nm (minimum reflectance of the dye), according to the Kubelka-Munk (KM) equation [9]. The KM factor was first calibrated using a series of fabrics dyed in water baths containing different concentrations of the dye.

The dye uptake in CA fabrics was determined by measuring the absorbance at $\lambda = 626.5$ nm (maximum absorbance) of acetone solutions, obtained by dissolving dyed CA samples in this solvent.

2.4 Differential scanning calorimetry (DSC)

A Perkin–Elmer DSC-4 Thermal Analysis Data Station System was used. Samples of about 7 mg, placed in a DSC pan, were heated from −10°C to 290°C at a scanning rate of 20°C min^{-1}, under a constant flow of dry nitrogen.

The crystallinity index X_c was calculated as $\Delta H_m / \Delta H_m^0$, i.e. as the ratio between the measured melting enthalpy of the polymer and the melting enthalpy of the completely crystallized polymer. $\Delta H_m^0 = 23.76\,\mathrm{cal\,g^{-1}}$ was assumed for PET [10].

2.5 Shrinkage measurements

The shrinkage S of the oriented PET yarns was determined either after heat treatment in air at 100–190°C for 30 min, or after treatment in CO_2SCF at 250 bar at 40–100°C for 30 min. The following formula was employed:

$$S = \frac{l_0 - l}{l_0} \times 100$$

where l_0 and l represent the yarn lengths before and after the treatment, respectively. They were measured after maintaining the samples at 20°C and 65% relative humidity for 2 h.

2.6 Structural and morphological characterization

X-ray diffractions were measured with a 500D Siemens Wide Angle X-ray Diffractometer (WAXD), using a Ni-filtered Cu K_α radiation. The apparent crystal sizes in the directions perpendicular to the (100), (010) and (105) crystal planes of PET were determined according to the Sherrer equation [11].

For Scanning Electron Microscopy (SEM) analysis, the fibrous materials were shadowed with gold and then examined with a Philips model 515 scanning electron microscope, operated at 10–15 kV.

2.7 Water bath dyeing procedure

An Ahiba apparatus was used for dyeing in water baths. The liquor ratio was 1:40 and the weight of the dyes was always 1.5 wt.% of the polymer sample. The dyeing process of the PET and CA samples started at 60 and 40°C, respectively. The temperature was then raised to 125°C (for PET), or to 90°C (for CA), and maintained at this value for 1 h.

2.8 Light and wet-washing fastness

For the determination of colour 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). Wet-washing fastness was determined according to UNI 7638 (ISO 105-C 01/03/04).

3. RESULTS AND DISCUSSION

3.1 Morphological changes induced in PET by CO_2SCF

It is well known that PET, when quenched from the melt, gives rise to a metastable amorphous phase, which can be converted by heating into the stable crystalline phase [12]. PET filaments in the isotropic amorphous phase ($PET_{am,un}$) may be stretched at temperatures below their glass transition temperature (T_g), to give an anisotropic amorphous phase ($PET_{am,or}$). The thermal behavior of such cold filaments, analyzed by DSC, evidenced only the melting endothermic peak [13], the typical exothermic peak of co-crystallization being unobservable.

The diffusion of the CO_2SCF molecules into PET induces a great enhancement of segmental mobility of the polymer chains in the amorphous phase. This induces a considerable lowering of the glass transition temperature of PET, when it is immersed in CO_2SCF. Under these conditions, however, the T_g value of the polymer cannot be directly measured. Analogous drastic modifications of T_g have been reported to occur after treating PET with a water–acetone system [14].

As a consequence of this T_g decrease, the diffusion of dyes could efficiently occur at temperatures well below those employed in the conventional dyeing procedures in water baths. Also, the crystallization of PET could take place at temperatures below that required for inducing its crystallization by annealing in hot air.

In order to investigate these points, $PET_{cr,or}$, $PET_{am,or}$ and $PET_{am,un}$ samples, which had been treated with CO_2SCF under various temperature and pressure conditions, were first examined by SEM and by WAXD. The first type of analysis showed that the surface morphology of these fibers did not significantly change after both types of treatment. On the other hand, WAXD analysis evidenced the presence of crystallinity in $PET_{am,un}$ and $PET_{am,or}$ samples after treatment in CO_2SCF at low temperature, while the crystallinity of the $PET_{cr,or}$ did not significantly change: only a little decrease in the broadening of the (100), (010) and (105) plan diffractions was observed, leading to the conclusion, according to Sherrer [11], that the dimensions and the order of crystallites slightly increased after CO_2SCF treatment.

Previous authors have reported that the first DSC melting thermogram of PET is influenced by its thermal and crystallization history [15, 16]. In particular, DCS curves generally have different shapes, if PET had previously been annealed at temperatures below its melting point and above the cold crystallization temperature. In this case, a new endothermic peak appears in the thermogram, which has been attributed to the fusion of bundle crystals

[9] formed during the annealing treatment. Moreover, an increase in the annealing temperature (T_{ann}) causes a progressive shift of the maximum of this endothermic peak to higher temperature. In particular, the greater is the temperature difference $\Delta T = T_{ann} - T_g$, the higher is the temperature at which this endothermic peak appears in the thermogram.

We verified also that the CO_2SCF treatment induces the formation of a network of crystallites in $PET_{am,un}$, as evidenced by the presence of a secondary endothermic peak in the DSC curves, as shown in Fig. 1. As was observed with $PET_{am,un}$ samples which had been treated in hot air, and also after the CO_2SCF treatment, the secondary endothermic peak shifts to higher temperature in the DSC scans of samples treated at progressively higher temperature in CO_2SCF. By plotting the temperature values corresponding to the maxima of the secondary endothermic peaks, T_{ms}, against the corresponding treatment temperatures, T_{tr}, linear correlations were obtained for both types of treatment (as shown in Fig. 2).

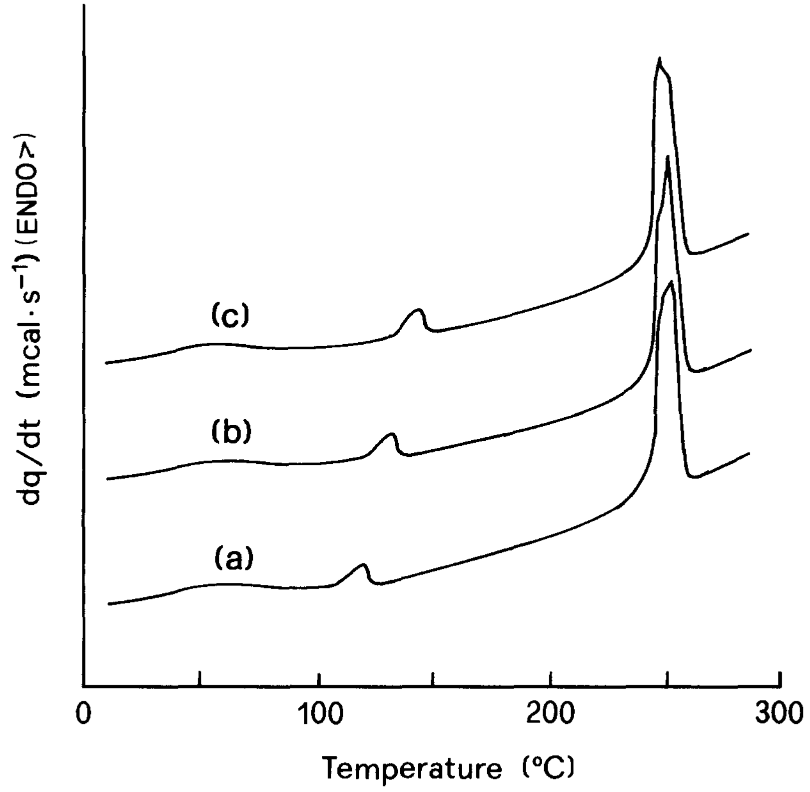

Fig. 1. DSC scannings of $PET_{am,un}$ annealed in CO_2SCF for 30 min at (a) 40°C, (b) 60°C and (c) 80°C.

Table 1 gives the corresponding data, together with the crystallinity values X_{cs} evaluated from the integration of the secondary endothermic peaks. It is worth noting that these latter do not show a definite trend with annealing conditions, i.e. the amount of bundle crystals formed by annealing does not seem to vary under different experimental conditions.

The observed correlation between T_{ms} and T_{tr} for both types of annealing treatment (in CO_2SCF and in hot air) confirms that the T_g value of the polymer in CO_2SCF should be lower than its T_g value in air (77°C). In fact, a

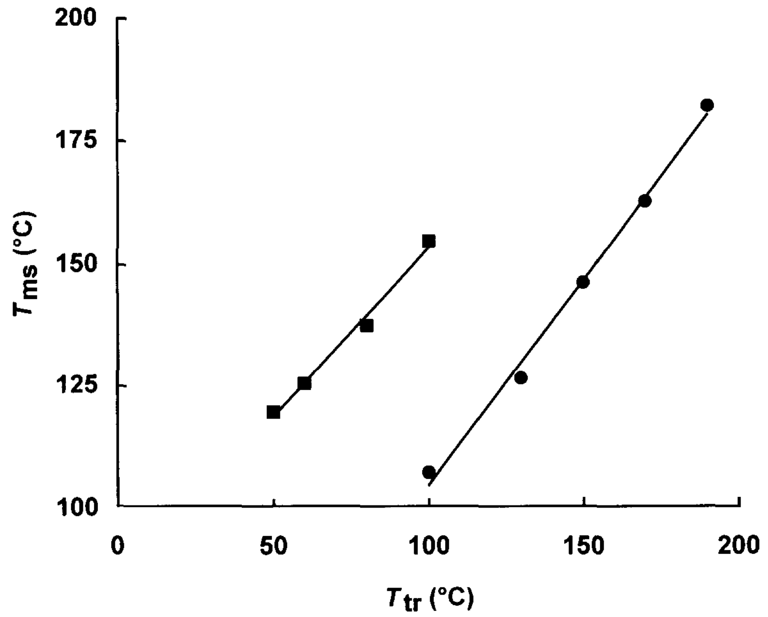

Fig. 2. Trends of the maximum temperature of the secondary endothermic peaks (T_{ms}) vs treatment temperature (T_{tr}) in (●) hot air and (■) CO_2SCF.

TABLE 1

Thermal Behaviour of PET: Melting Temperature (T_{ms}) and Crystallinity ($X_{cs} = \Delta H_{ms}/\Delta H^0_m$) Relative to the Secondary Endothermic Peak of $PET_{am,un}$ Samples Treated for 30 min in Hot Air or in CO_2SCF at Different Temperatures (T_{tr})

Hot air			*CO_2SCF*		
T_{tr} *(°C)*	T_{ms} *(°C)*	X_{cs}	T_{tr} *(°C)*	T_{ms} *(°C)*	X_{cs}
100	107	0.016	40	114	0.008
130	126	0.028	50	119	0.019
150	146	0.027	60	125	0.018
170	160	0.027	80	137	0.014
190	181	0.026	100	154	0.026

treatment at relatively low temperature in this solvent system causes the same shift of the secondary endothermic peak in the DSC curves as a treatment in hot air at much higher temperature.

Moreover, the percent shrinkage detected after having treated both industrial or cold drawn PET yarns in hot air or in CO_2SCF was also found to be linearly correlated to the corresponding treatment temperature T_{tr} in the ranges 100–190°C and 40–100°C for the two types of treatment, respectively. The results obtained in the case of $PET_{am,un}$ samples are shown in Fig. 3. In this case the linear plots S vs T_{tr} have almost the same slope for both types of treatment.

Thus, from the linear correlations of Figs 2 and 3, under the assumption that the $\Delta T = T_{ann} - T_g$ values do not depend on the type of treatment, the T_g value of PET in CO_2SCF can be estimated to be around 0–5°C, by comparing the treatment temperatures in hot air and in CO_2SCF yielding the same annealing effect in the DSC scans and in the percent shrinkage of the samples.

3.2 Dyeing of PET in CO_2SCF

Kinetic measurements of the dye diffusion in PET fibers immersed in CO_2SCF were carried out at different temperatures in the range 40–90°C. Dyeing of CO_2SCF-treated $PET_{cr,or}$ at low temperature was achieved also employing a series of different disperse dyes.

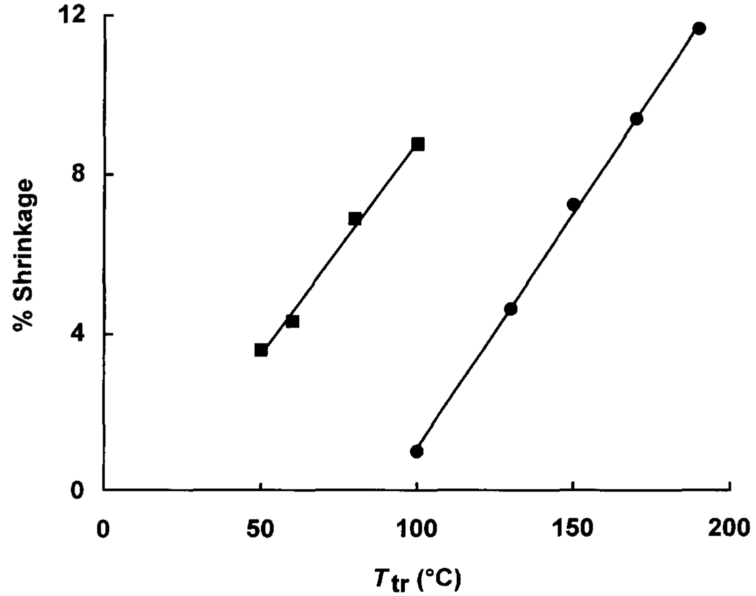

Fig. 3. Percent shrinkage (S) vs treatment temperatures (T_{tr}) in (●) hot air and (■) CO_2SCF.

As already observed, in the presence of CO_2SCF, the T_g of the amorphous fraction of the PET fiber becomes lower. Consequently, the dyeing properties of this modified fiber are markedly different from those of PET in water baths, the T_g value of PET in air being higher in some cases than the temperature of the CO_2SCF dyeing treatment. Under these conditions, the CO_2 system plays a role of plastifying agent in lowering the T_g value of the fiber below the temperature of treatment in CO_2SCF.

Thus, the improvement of the transport properties of the dye into the polymer employing the CO_2SCF solvent system is due both to an increase of solubility of the dye in the specific solvent, respect to water baths, and to an increase of the molecular mobility of the polymeric material, which changes its state from glassy to rubbery. These effects act in a synergetic way in promoting the dye uptake.

The kinetic results relative to the dyeing process in CO_2SCF are shown in Fig. 4(A), each dye uptake value having been obtained by dyeing a different PET sample. From the relation $C_t = k\sqrt{t}$, C_t being the dye concentration in the polymer at time t [17], the diffusion constants k at different temperatures were evaluated from the slopes of the corresponding linear plots of Fig. 4(A).

The fact that PET fibers immersed in CO_2SCF are always in the rubbery state (dyeing temperature > glass transition temperature of PET immersed in CO_2SCF) is confirmed by the linearity of the plot $\ln k$ vs $1/T$ in the range 40–100°C (Fig. 5). A transition from the glassy state to the rubbery state of the polymer should have been evidenced by a change in the slope of such Arrhenius plot. The activation energy for the diffusion process of the dye in the rubbery polymer can thus be estimated as $57.6 \pm 2.1\ \mathrm{kJ\,mol^{-1}}$.

Upon the release of pressure occurring at the end of the treatment in the supercritical fluid, adsorbed CO_2 rapidly diffuses out of the polymer; its plasticizing action thus ends, inducing an abrupt decrease of the dye diffusivity in the polymer, which returns to its original glassy state, so entrapping the dye in its free volume. Indeed, light as well as wet-washing fastness at 60°C of PET fibers dyed in CO_2SCF at 40°C (but also at 60, 80 and 100°C) were found to be almost identical to those of PET dyed at 125°C in a water bath.

3.3 2,5-Cellulose diacetate (CA)

For the examined CA fiber a T_g value of 74°C was determined, which is in agreement with its degree of substitution, as well as with its humidity content (6%), the CA hydroplastic material having a T_g value of 180°C, when anhydrous.

Preliminary investigations on the effects induced in CA by the CO_2SCF treatment did not evidence any change in its thermal behavior, crystallinity and shrinkage properties. We thus conclude that CO_2SCF does not exert any plasticizing action towards CA. This effect can be obtained with CA, using liquids having a higher affinity for hydroxyls rather than for acetyl groups. Indeed, the interactions between CA and plasticizing liquid media, such as

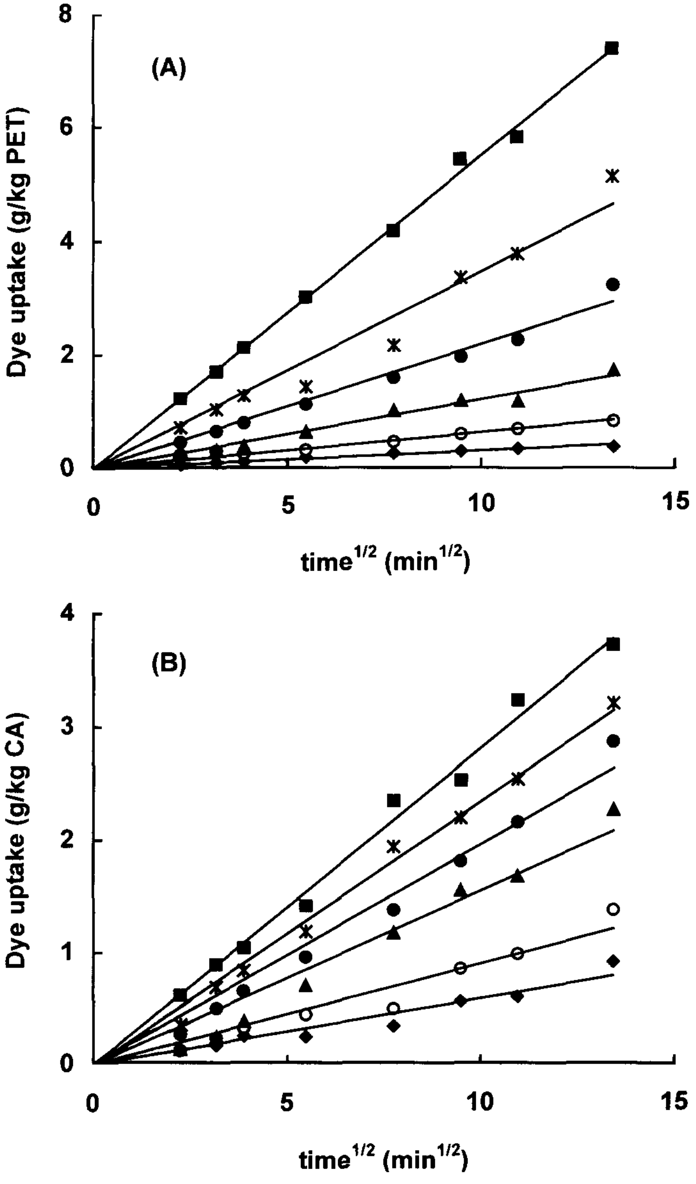

Fig. 4. Dye uptake in (A) PET and (B) CA vs the square root of dyeing time in CO_2SCF at (◆) 40°C, (○) 50°C, (▲) 60°C, (●) 70°C, (*) 80°C and (■) 90°C.

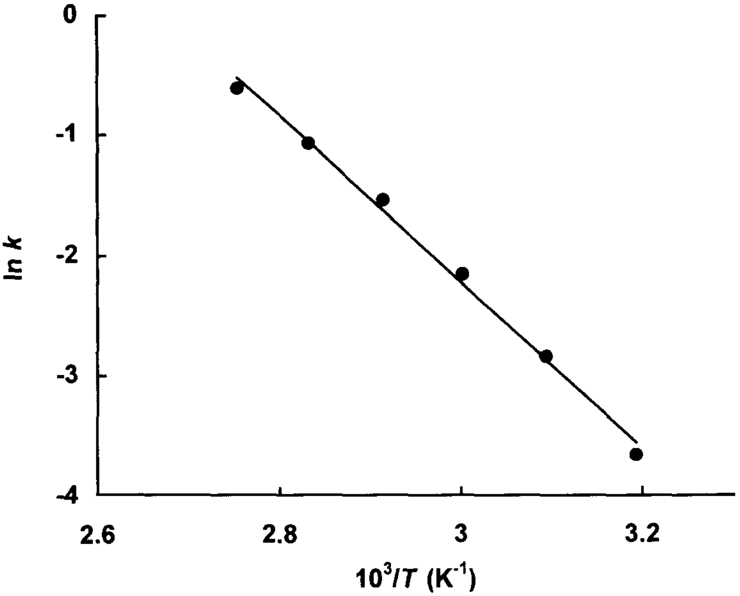

Fig. 5. Arrhenius plot of the diffusion constants of the dye in PET.

ethylene glycol, glycerine and water have been reported to induce a reduction of T_g [18].

Also, the dye uptake in CA was not accelerated, when the dyeing process was carried out in CO_2SCF employing both a dry or wet fibrous material. The kinetic results obtained in the present study are reported in Fig. 4(B). The corresponding diffusion constants *k*, obtained from the slopes of the plots of dye uptake at different temperatures vs the square root of the dyeing time, exhibit the Arrhenius plot reported in Fig. 6, consisting in two straight lines with different slope. This provides information about the mechanism of dye uptake in CA, evidencing that the glass transition temperature of CA in CO_2SCF is close to its T_g value in air, i.e. it falls within the temperature range of the dye uptake kinetic investigation. The activation energy values obtained from the two slopes of the Arrhenius plot of Fig. 6 (42 ± 4 and $19.8 \pm 0.6\,\mathrm{kJ\,mol^{-1}}$) thus refer to the diffusion process of low molecular weight compounds (e.g. dyes) in glassy and rubbery CA, respectively.

This evidences that it is much more convenient to carry out the dyeing process of CA in supercritical fluids when this polymer is in the rubbery state, because the diffusion of the dye in the polymer under these conditions should be substantially faster than in the glassy state.

Finally, the light as well as the wet-washing fastness at 60°C of CA dyed in CO_2SCF were also found to be equal to that of CA dyed in a water bath at 80–90°C.

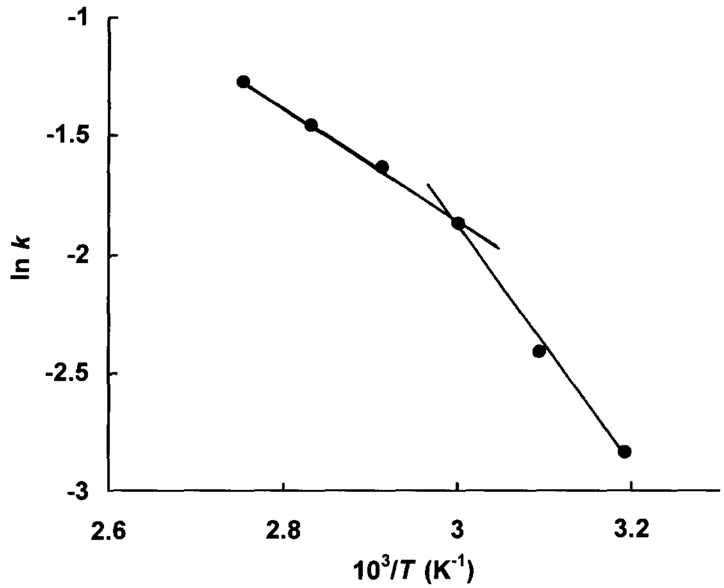

Fig. 6. Arrhenius plot of the diffusion constants of the dye in CA.

4. CONCLUSIONS

Supercritical carbon dioxide plays a role of plastifying agent by lowering the T_g value of PET. As a consequence, the diffusion of disperse dyes within the polymer can occur at temperatures well below those required for dyeing in water baths, and the rate of dye uptake is very high. Moreover, in CO_2SCF the crystallization process of PET starts at lower temperature with respect to that required for crystallization by annealing (i.e. thermosetting) in hot air.

In contrast, the T_g of cellulose diacetate in CO_2SCF is about 74°C, i.e. not markedly different from that measured before the treatment in the supercritical fluid. Thus, the dyeing process in CO_2SCF must be carried out in this case at the same temperature employed in water baths (80–90°C).

If supercritical fluids have a plasticizing action on polymers, as is the case of PET, dyeing in these solvent systems avoids the use of large amounts of dispersing agents and surfactants employed in conventional processes, thus avoiding pollution problems. Moreover, the process does not need the step of drying the textiles, and is very suitable for some special industrial treatments of fibers, allowing the fibers to be dyed [19], impregnated with UV-stabilizers and perfumeries [20], thermoset and textured at low temperature (40–80°C).

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