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Comparison of Dye Diffusion in Poly(ethylene terephthalate) Films in the Presence of a Supercritical or Aqueous Solvent

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Impregnation of polymers with supercritical CO_2 appears to be a promising technique in the area of polymer processing. The main aim of this paper is to measure the diffusion coefficients of a solute (a dyestuff) permeating a poly(ethylene terephthalate) (PET) film in a supercritical impregnating system at different working conditions and to compare the results with similar data obtained with the same solute in the same material but in a traditional aqueous system. The experimental technique used is that of the "film roll method" for the experiments conducted in the supercritical system and has already been tested in a previous work. For the aqueous system, the sorption kinetics of the dyestuff on plane PET sheets has been measured. The results confirm the high gain in the rate of diffusion obtained with the supercritical impregnating system, related to the high plasticizing power of supercritical CO_2 toward synthetic polymers. Interesting considerations come also from the comparison of the data obtained by operating with supercritical CO_2 at different working pressures and temperatures and in the presence of a proper modifier (ethanol).

1. Introduction

It is known that the glass transition temperature of many polymers in the presence of supercritical CO_2 (scCO_2) is considerably reduced, this resulting in an increased mass-transfer rate inside the polymeric matrix. Many applications in the area of polymer processing with supercritical fluids involve impregnation with organic molecules using CO_2 as a solvent. For example, the production of advanced optical components,[1] impregnation with pharmaceutical products,[2] and supercritical fluid dyeing[3] are some of the most interesting applications.

In the present paper some experimental data of diffusion coefficients of a disperse dyestuff in a PET film are measured in the presence of both a supercritical and an aqueous solvent. The main aim of this work is to compare directly the diffusion coefficients of the same dyestuff measured on the same polymeric substrate in the presence of these two different solvents in order to underline the great advantage in mass-transfer rate gained using a supercritical fluid. Other interesting considerations can be deduced from the comparison of the diffusion coefficient values measured in the presence of scCO_2 at different working conditions and in the presence of a proper modifier.

2. Experimental Techniques

Two different techniques were used for measuring diffusion coefficients in supercritical or aqueous solvents.

2.1. Determination of the Diffusion Coefficient in a Supercritical Solvent. Dye diffusion in PET films using scCO_2 as an impregnating medium has already been studied using the "film roll method" in a previous work.[4] The film roll method consents to measure the dyestuff distribution profile inside the polymer and was used by other researchers in water impregnating systems to evaluate diffusion coefficients of nonionic dyes in synthetic polymers.[5−8] It has been extended and properly adapted to a scCO_2 impregnating system.

A strip of a PET film 12 μm thick is wrapped tightly around a stainless steel tube, producing a roll of thin layers; a flap of film is allowed to protrude from the outer layer of the roll in order to be completely immersed in the dyeing medium. During the dyeing process, this flap reaches dye saturation and provides the dye concentration value in the polymer (C_0) at the polymer−bath interface. The film roll is then introduced in a heated autoclave provided with a magnetic stirrer and is dyed at constant temperature and pressure. A dyestuff, Disperse Red 324, already used in the literature for similar experiments on PET fibers,[9] was chosen for these experiments. The working conditions range from 150 to 250 bar and from 100 to 120 °C; the amount of the dyestuff inside the autoclave is in large excess compared to the solubility in scCO_2 at similar working conditions.[9] The same literature source gives a value of the dye solubility in a PET fiber; considering the total weight of the film roll, the amount of dyestuff in the autoclave is also in large excess with respect to the maximum quantity absorbable from the polymer if it was completely saturated. As a consequence of these facts, with the temperature and pressure being constant during the entire dyeing period, the dyestuff concentration is constant and the bath can be considered "infinite".

Some of the experiments have been conducted in the presence of ethanol as a modifier. The proper amount of modifier is introduced into the autoclave before pressurization. The molar percentage of ethanol ranges from 8.5 to 10% (referred to as the molar content of CO_2 in the autoclave at the set working conditions).

Figure 1 shows a simplified scheme of the experimental apparatus used for impregnating the PET films. It

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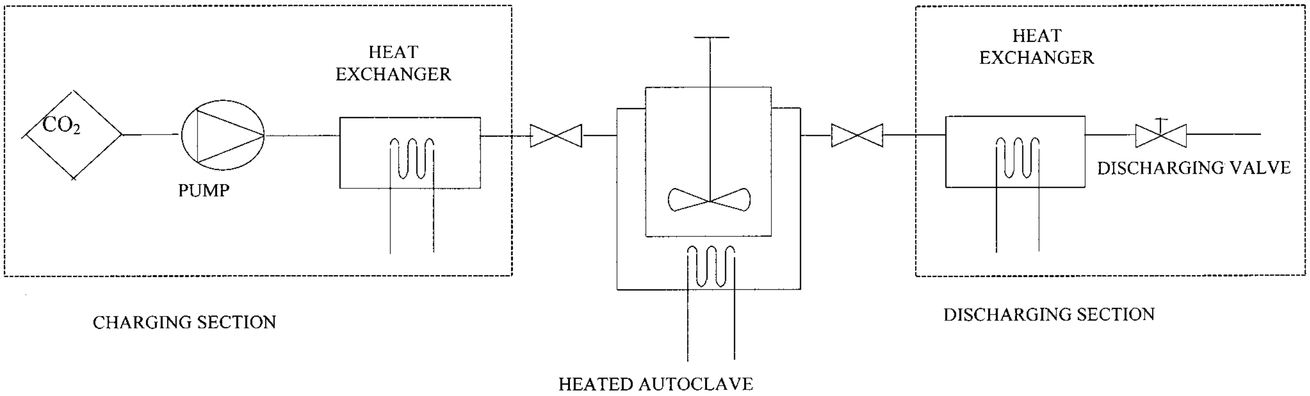

Figure 1. Experimental apparatus.

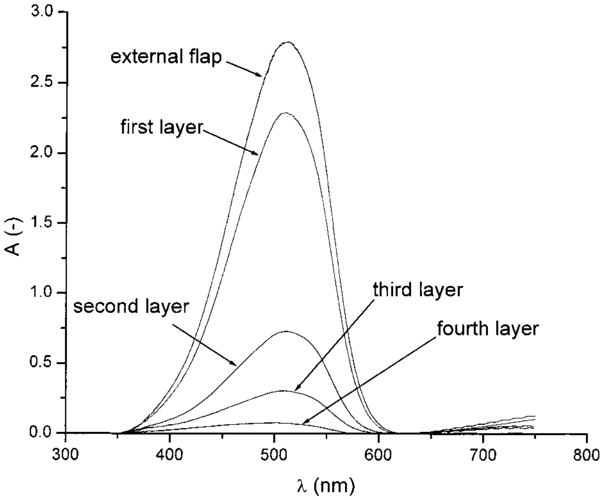

Figure 2. Spectrum of the dye in different PET layers (experimental conditions: $T = 100$ °C, $P = 250$ bar, dyeing period = 1 h).

is a batch system where liquid CO_2 is pumped into the autoclave, while a heat exchanger provides the proper working temperature to the fluid. After the working pressure is reached, the PET film is dyed under continuous and constant stirring for periods ranging from 1 to 8 h, depending on the experiments. At the end of the dyeing process, the fluid is discharged through a system of valves, where another heat exchanger prevents clogging due to excessive cooling related to CO_2 expansion. A more detailed scheme of the experimental apparatus and further information concerning the experimental technique can be found elsewhere.[4]

After impregnation, the film is unrolled and cut into sections representing the successive layers. The external layers of the roll sometimes presented some dye deposition on their surface that was removed by rinsing the samples in acetone. It was verified that the use of acetone did not involve any extraction of the dye sorbed inside the polymer even after a few minutes of contact. The dye concentration in each layer is determined, via a spectrophotometer, from the intensity of the light absorbance A in the UV–vis spectral band. The absorbance measured in each layer, then, consents to obtain the dimensionless dye distribution profiles, C/C_0, along the radius, x, of the film roll because

$$C/C_0 = A/A_0 \tag{1}$$

where A_0 and C_0 are respectively the absorbance and the dye concentration, in the flap of film and A and C the values measured in a generic layer of the roll. Figure 2 reports, as an example, the spectrum of the dye in different PET layers for one of the experiments. The light absorbance measured at the maximum absorption wavelength of Disperse Red 324 in the polymer (510 nm) in some samples exceeded the upper limit of the instrument ($A \sim 4$). To solve the problem, the light absorbance in each layer and in the flap was measured at a wavelength of 570 nm, where $A < 1.5$. A few samples have been treated in benzyl alcohol at 130 °C for 2 h in order to extract the dye sorbed inside the polymer: the linear relationship between light absorbance and dyestuff concentration has been verified.

Figures 3 and 4 report the dimensionless concentration profiles at different operative conditions: Figure 4, in particular, shows the curves obtained by adding a modifier. The coordinate x is the radial penetration into the roll, where $x = 0$ is assumed at the outer surface of the roll. The comparison of parts a and b of Figure 2

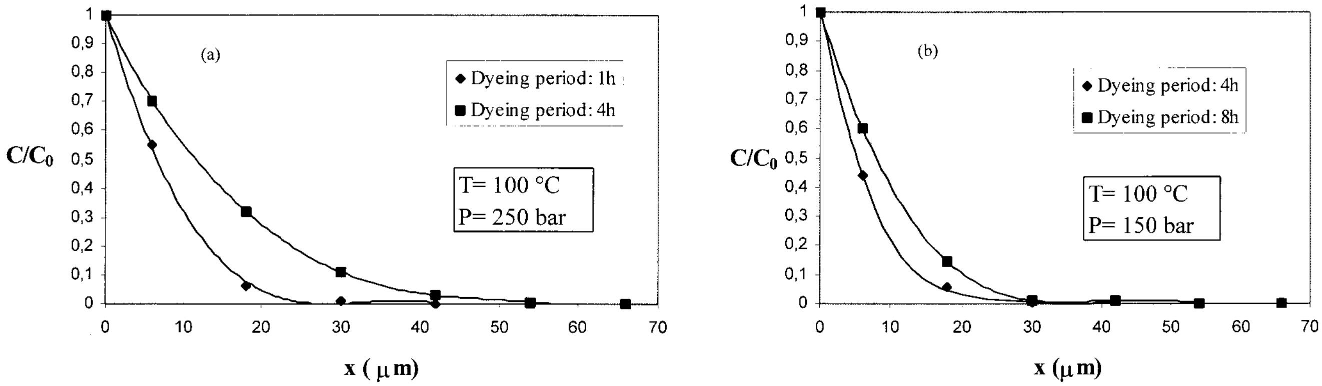

Figure 3. Dimensionless concentration profiles vs radial penetration (experiments without a modifier).

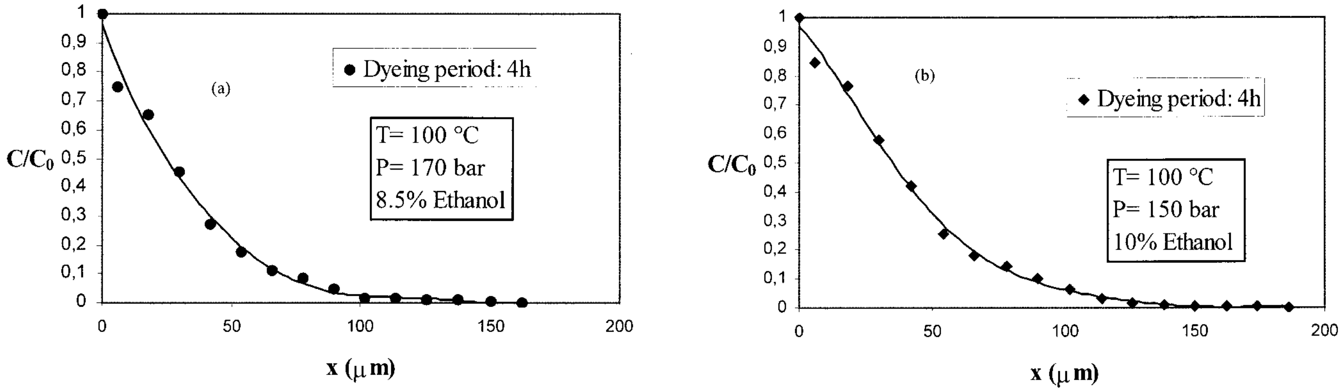

Figure 4. Dimensionless concentration profiles vs radial penetration (experiments with a modifier).

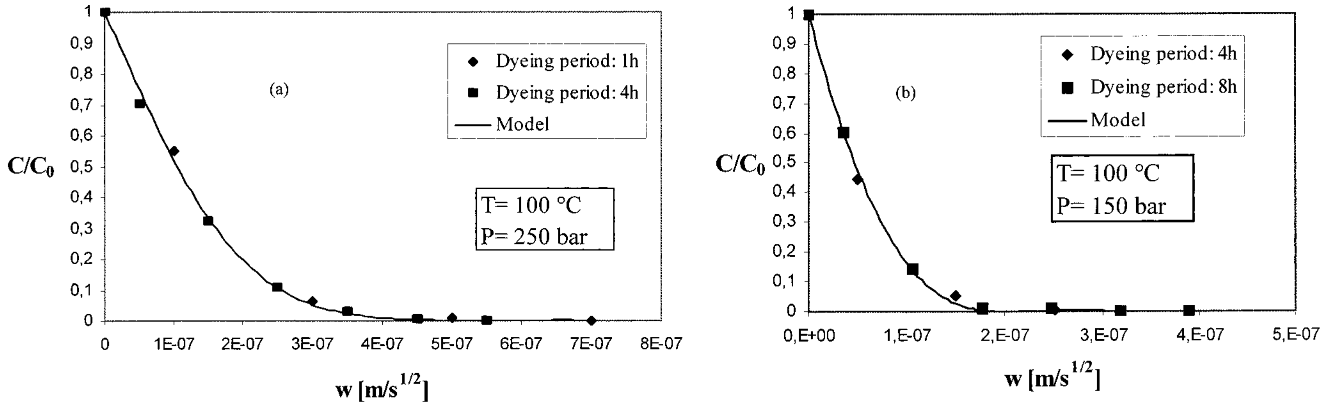

Figure 5. Dimensionless concentration vs *w* (experiments without a modifier): experimental data and model 4.

shows clearly how the working conditions can affect the penetration depth of the dyestuff inside the roll. The comparison of Figures 2b and 3b, instead, shows the influence of the presence of a modifier at the same working conditions of pressure and temperature.

Experimental data are fitted with a proper model in order to determine the value of the diffusion coefficient. At the working conditions performed in the present experiments, the PET film is certainly above its glass transition temperature[10,11] and mass-transfer phenomena can be described by Fick's law of diffusion. With the film roll thickness being low compared to its diameter, the polymer can be considered as a monodimensional slab and the equation describing the one-component diffusion in a nonstationary monodimensional homogeneous system[12] can be used, where D is the diffusion coefficient:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \tag{2}$$

If the slab can be considered semi-infinite (the dyestuff never reaches the inner layers of the film during the dyeing period) and the concentration C_0 constant with time, the following boundary conditions can be written:

$$t = 0 \qquad x > 0 \qquad C = 0 \tag{3.1}$$

$$t \geq 0 \qquad x = 0 \qquad C = C_0 \tag{3.2}$$

$$t \geq 0 \qquad x \rightarrow \infty \qquad C = 0 \tag{3.3}$$

More detailed considerations concerning the model's hypothesis can be found elsewhere.[4]

The solution of eq 2 that satisfies the conditions of eqs 3.1–3.3 has been derived by Crank[12] and has the expression

$$\frac{C}{C_0} = \operatorname{erfc}\left(\frac{w}{D^{1/2}}\right) \tag{4}$$

where the variable w is defined as follows:

$$w = x/2t^{1/2} \tag{5}$$

The value of the diffusion coefficient D can be obtained by fitting the experimental data with eq 4 as shown in Figures 5 and 6. Table 1 reports the results at different working conditions. Table 2, then, shows the value of absorbance A_0 in the external flap for each experiment. As stated previously, the absorbances have been evaluated at a wavelength of 570 nm.

The first datum in Table 1 has been measured to provide a comparison with literature data. Schnitzler and Eggers[9] found a value of 1.07×10^{-13} m^2/s at 120 °C and 300 bar. Because the experimental apparatus used in this work is not able to operate at 300 bar, a direct comparison cannot be done. Anyway, considering a 50 bar gap and the fact that Schnitzler and Eggers used PET fibers instead of a film, this datum is in good agreement with the literature.

2.2. Determination of the Diffusion Coefficient in an Aqueous Solvent. According to the literature,[13] diffusion coefficient values of disperse dyes in hydrophobic polymers, dyed in water systems, are from 1 to 3 orders of magnitude lower than those obtained in a scCO$_2$ impregnating system. This difference is a direct consequence of the plasticizing effect of scCO$_2$ on PET and gives a reason for the great reduction in dyeing time

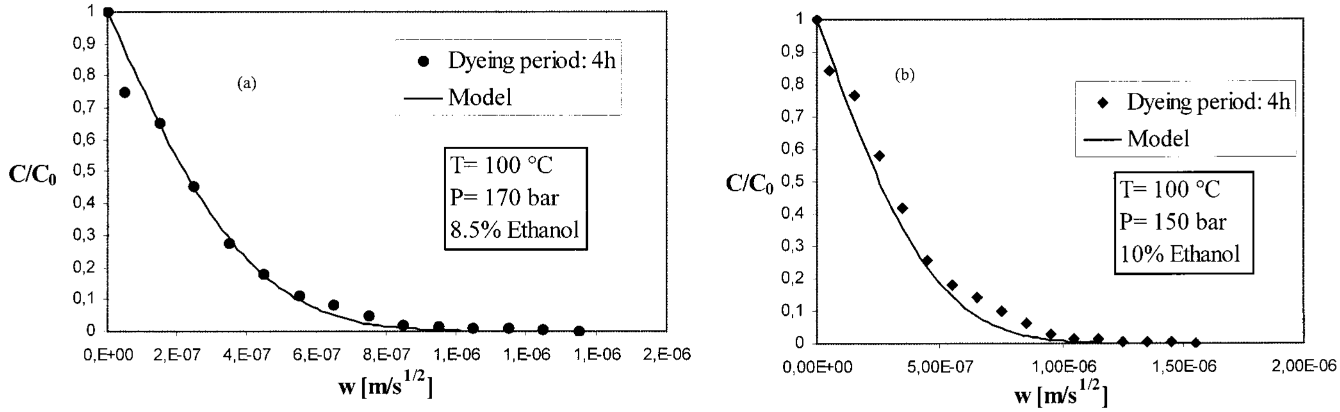

Figure 6. Dimensionless concentration vs *w* (experiments with a modifier): experimental data and model 4.

Table 1. Diffusion Coefficients of Disperse Red 324 in PET in scCO$_2$ at Different Working Conditions

T (°C)	P (bar)	ethanol (%)	D (m^2/s)
120	250		7.1×10^{-14}
100	250		1.2×10^{-14}
100	200		9.0×10^{-15}
100	150		2.4×10^{-15}
100	150	10	7.1×10^{-14}
100	170	8.5	5.5×10^{-14}

Table 2. Absorbance Values in the External Flap of the Film at Different Working Conditions

T (°C)	P (bar)	ethanol (%)	dyeing period (h)	A_0
120	250		1	1.36
120	250		4	1.44
100	250		1	0.76
100	250		4	0.73
100	200		2	0.87
100	200		4	0.89
100	150		4	0.56
100	150		8	0.59
100	150	10	4	1.17
100	170	8.5	4	1.27

in scCO$_2$ dyeing processes. To verify this assertion, experiments have been performed in a water system with the same dye as that previously used in the scCO$_2$ system.

A different technique has been used for the aqueous solvent with the same PET film. Instead of the concentration profiles being evaluated along the radius of a roll, the diffusion coefficient has been measured from the sorption kinetics of the dyestuff on plane sheets of the PET film. Plane sheets of the same PET film as that used for the experiments in scCO$_2$ have been dyed in a well-stirred aqueous bath at constant temperature and dye concentration for different impregnating periods. The dyeing vessel consisted of a glass flask surmounted by a condenser; a heating magnetic stirrer provided perfect mixing of the bath. The amount of dyestuff was of 0.8 g in a water volume of approximately 300 mL in order to ensure saturation of the dyeing suspension. All samples have been dyed at the boiling point of the solution in order to guarantee concentration constancy of the dyestuff. The samples consisted of 10 plane sheets whose dimensions are 3.5 × 6 cm; they have all been introduced at the same time in the dyeing system but have been extracted after different dyeing periods.

The total amount of dyestuff in each sample, M_t, has been measured again spectrophotometrically:

$$M_t/M_\infty = A_t/A_\infty \tag{6}$$

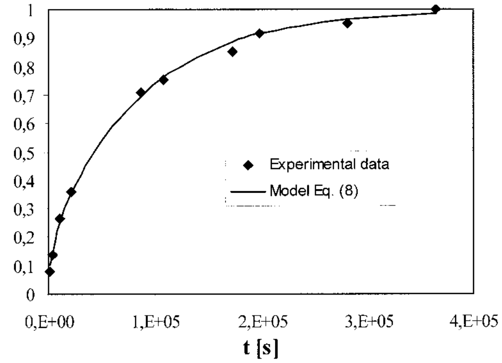

Figure 7. Sorption kinetic curve of the dyestuff in the polymer in the presence of an aqueous solvent.

where M_t and A_t are respectively the total dye amount and the absorbance of a sample extracted after a dyeing time of t; M_∞ and A_∞ are, then, the total dye amount and the absorbance after an infinite dyeing time. Equation 6 allows one to obtain the sorption kinetic curve of the dyestuff on the polymer (Figure 7). Dye saturation of the polymer is assumed to occur after a dyeing time of 3.6×10^5 s when the last sample is extracted from the bath: the absorbance of the last sample is assumed to be proportional to M_∞.

The model used to evaluate the diffusion coefficient is the same as the model described by eq 2, where the boundary conditions for a sheet of thickness $2l$ are

$$t = 0 \qquad -l < x < l \qquad C = 0 \tag{7.1}$$

$$t \geq 0 \qquad x = -l \qquad C = C_0 \tag{7.2}$$

$$t \geq 0 \qquad x = l \qquad C = C_0 \tag{7.3}$$

Solving eq 2 with the conditions of eqs 7.1–7.3 gives the concentration profile C inside the polymer; the total mass balance to the plane sheet then gives[12]

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\{-D(2n+1)^2\pi^2 t/4l^2\} \tag{8}$$

For small times, eq 8 can be simplified[12] and becomes similar to the solution for a semi-infinite medium:

$$\frac{M_t}{M_\infty} = 2\sqrt{\frac{Dt}{\pi l^2}} \tag{9}$$

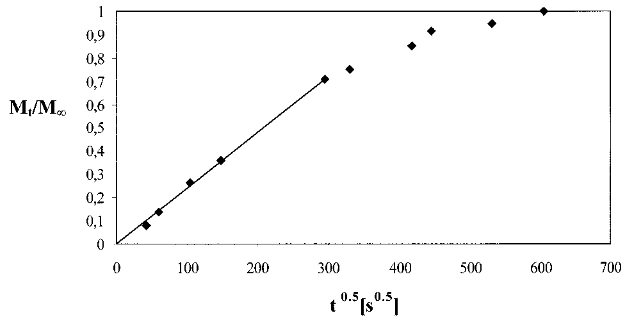

Figure 8. Experimental sorption data vs the square root of dyeing time (aqueous system).

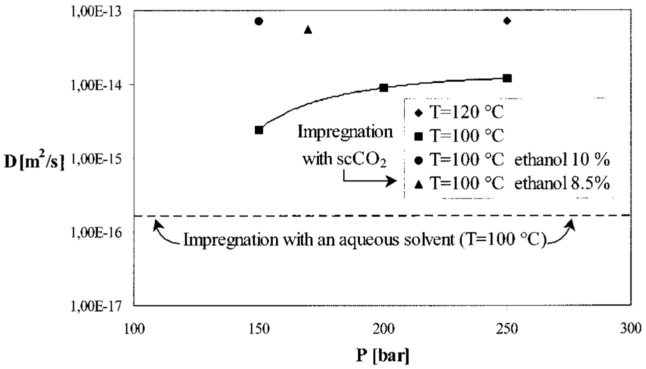

Figure 9. Diffusion coefficient values of Disperse Red 324 in PET in supercritical and aqueous solvents.

where M_t/M_∞ is directly proportional to the square root of time. Plotting experimental data versus the square root of time results in a linear dependence only for the first five samples (corresponding to a dyeing period of 8.6×10^4 s). From the slope of the line reported in Figure 8 and through eq 9, a diffusion coefficient of 1.7×10^{-16} m²/s can be estimated. Substituting this value of D in eq 8 gives the curve reported in Figure 7.

3. Discussion of the Results

A comparison of traditional and supercritical PET dyeing has already been done in the literature[14] concerning the quality of the dyed product. PET fibers dyed in the presence of $scCO_2$ exhibit high fastness and the same extent of dye absorbed as that obtained in the aqueous system. The main aim of the present work is a direct comparison of traditional and supercritical PET dyeing through the measurement of the diffusion rate of the same dyestuff because experimental data of the same molecule in both systems are not easily available from the literature. Figure 9 shows all experimental data reported in Table 1 for Disperse Red 324 in PET in a $scCO_2$ atmosphere, compared to the diffusion coefficient of the same dyestuff in the same material but in a traditional water system. The comparison gives interesting information concerning the plasticizing effect of $scCO_2$ on PET and confirms the high difference between the diffusion rates in the two solvents: depending on the working conditions the rate of diffusion of a dye in PET can be from 1 to almost 3 orders of magnitude faster in a $scCO_2$ than in an aqueous system. The reason for this behavior is related to the great reduction in the glass transition temperature and the swelling power that CO_2 shows toward hydrophobic polymers. $ScCO_2$, then, confers a greater mobility to the polymeric chains, allowing faster penetration of a solute. On the contrary, the traditional dyeing of PET in a water system must be performed at temperatures higher than 100 °C or in the presence of proper carrier molecules in order to swell the polymeric matrix.

Other interesting information can be drawn by comparing data in Table 1 (or in Figure 9) for the $scCO_2$ system. For the data obtained in the absence of a modifier, Figure 9 underlines the influence of pressure on the data obtained at 100 °C: increasing the pressure results in a great increase in the diffusion coefficient. The effect of temperature is even stronger: a 20 °C increase in temperature accelerates the rate of diffusion more than a 100 bar increase in pressure. The variation of the diffusion coefficient with temperature and pressure is related to the plasticizing power of $scCO_2$. It is known from the literature[10,11,15] that, at the same working temperature, increasing pressure results in a greater density of CO_2 and a consequent higher plasticizing effect that causes a decrease of the glass transition temperature of the polymer. At the same working pressure (250 bar), then, an increase in the temperature causes a further increase in the polymeric chains' mobility and the dyestuff can easily penetrate the substrate.

As stated in many recent publications,[16−21] also the crystallization of the amorphous regions of PET can take place at these working conditions. It is a reasonable assumption that the dye diffusion takes place in the amorphous regions of the polymer because the dyestuff is not soluble in the crystalline domains.[18] If CO_2 can change the degree of crystallinity of the PET samples during the impregnation process, this would affect the total amount of sorbed dye and the simple diffusion model described in eq 2 should take into account also the kinetics of crystallization. To understand the extent of these possible changes in the morphology of PET samples, differential scanning calorimetry analysis has been performed on samples before and after treatment in $scCO_2$. A 36% average crystallinity was measured for both samples; therefore, the kinetics of crystallization was negligible in our experiments. On the other hand, according to the literature, all relevant variations in polymer crystallinity have been observed in samples that were originally amorphous or low-crystalline (6.1% crystallinity[16] or 8% crystallinity[18]).

Figure 9 shows also the effect of the presence of a modifier (ethanol) on the rate of diffusion. It appears to be greater than that of temperature. In particular, adding a 10% amount of ethanol to the system at 150 bar and 100 °C results in the same diffusion coefficient as that at 250 bar and 120 °C without a modifier. This is a really interesting result because the presence of a modifier allows one to obtain almost the same results in impregnation at lower temperature and pressure.

It would be interesting to understand how the presence of a modifier can affect the mechanism of diffusion. It is known that the presence of a modifier increases the solubility of solutes in a supercritical fluid,[22] but it is not well-known how it can influence the rate of diffusion inside the polymer. In the present paper, data of Disperse Red 324's solubility in $scCO_2$ have not been evaluated, but the absorbance values, A_0, measured at the polymer−bath interface are proportional to the dye concentration both in the polymer (C_0) and in the supercritical fluid (the second assumption is valid if the equilibrium isotherm between the dye concentration in $scCO_2$ and in the polymer is supposed to be linear). A_0 values in the presence of the modifier are approximately double those values at similar working pressures without a modifier (see Table 2). That confirms the influence of the modifier on the dye solubility in $scCO_2$.

The other point is that the diffusion coefficient is greatly increased by the presence of ethanol. Two possible explanations concerning the effect of a modifier on the polymer phase can be found in the literature. One is related to the possibility that the presence of a modifier may increase the swelling of the PET film,[23] resulting in a faster rate of diffusion. The action of CO_2, defined elsewhere[24] as a “molecular lubricant” because it enhances the dye mobility inside the polymeric matrix, can be amplified by the presence of a modifier. The other explanation is connected with the high solubility of the modifier in the polymer. It is known that the partition coefficient of a modifier between the polymer and fluid phase may be high.[25] As a consequence of this fact, the high concentration of the modifier inside the polymer could alter its chemical nature, promoting a higher sorption of the dye. In both cases the presence of the modifier in the polymer during the impregnation phase could involve that some amount would probably be trapped inside the PET films at the end of the process. This possibility should not be forgotten in the choice of the proper modifier, in particular with the aim of a textile application.

4. Conclusions

Experimental diffusion coefficients have been measured for the same dyestuff in the same PET film using both an aqueous and a supercritical impregnating medium. The results confirm the great gain in the rate of diffusion obtained with the supercritical system that is one of the main advantages of this new dyeing technique.

Interesting considerations can be drawn also from the comparison of the diffusion coefficients measured using $scCO_2$ at different working conditions. The most important results are those obtained adding a modifier. The great increase in the rate of diffusion would consent to operate at lower values of temperature and pressure with the same results as higher temperatures and pressures. This appears to be a great advantage because one of the main obstacles to this new technique is the high working pressure that must be achieved to obtain good dyeing results.

Notation

A = intensity of the light absorbance in a generic layer of the film roll
A_0 = intensity of the light absorbance in the flap of film
A_t = intensity of the light absorbance in a film plane sheet after a dyeing time t
A_∞ = intensity of the light absorbance in a film plane sheet after an infinite dyeing time
C = dye concentration in the polymer [g/m^3]
C_0 = saturation dye concentration in the polymer [g/m^3]
D = diffusion coefficient of the dye in the polymer [m^2/s]
l = semithickness of the film plane sheet [m]
M_∞ = total dye amount in a film plane sheet after an infinite dyeing time [g]
M_t = total dye amount in a film plane sheet after a dyeing time t [g]
n = index defined in eqs 8 and 10
P = pressure [bar]
T = temperature [°C]
t = time [s]
w = variable defined in eq 5 [m/s$^{1/2}$]
x = generic coordinate along the direction of diffusion [m]

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