DETERMINATION OF THE SOLUBILITIES OF DISPERSED RED DIANIX DYE IN SUPERCRITICAL CO_2 BY A STATIC METHOD AND MODELING

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ABSTRACT – The search for new materials has received a lot of attention in the last years. Poly (ethylene terephtalate) - PET - is a polymer formed by the poly-condensation of ethylene glycol and terephtalitic acid. This polymer when melted is highly viscous and can be extruded into films and fibers. Its surface has been subjected to many modifications aiming at several different applications. Supercritical carbon dioxide dyeing of textile films is a particular case of impregnation with a lot of potential advantages, due to the CO_2 high diffusivity and solvatation power. In this work, the behavior of the PET-dyes-scCO_2 system under supercritical conditions (pressure and temperature) is analyzed. Many polymers swell in supercritical carbon dioxide leading to a high rate of CO_2 permeation. One of the advantages of the dyeing process with supercritical carbon dioxide is the recovery of CO_2, while the conventional dyeing process causes environmental impacts due to its liquid effluent that contains dye residues and dispersants. The objective of this work is to investigate the influence of the incorporating conditions of the dispersed red dianix dye on films of PET. The behavior of the PET-dye-scCO_2 system was studied by carrying out dyeing assays in different temperature conditions (60º and 70ºC), and different pressures (15, 18, 21MPa), for several periods of time (min), using the batch method with dyeing time control. To verify which of the factors were more important in this dyeing process, an experimental planning with two parameters at different levels was made using the SAS statistical software. A model for the diffusivity as a function of temperature and pressure was obtained from the experimental data.

Key words: Poly (ethylene terephtalate), Red-dianix dye, Supercritical Carbon Dioxide.

INTRODUCTION

Poly (ethylene terephtalate)-PET- is largely used in industries due to its mechanical, electrical and optical properties, such as hydrolytic and dimensional stability, transparency and flexibility [1,2].

According to Stinson and Obendorf [3], non-modified PET absorbs only 0,4% of water, and does not swell in water. This lack of interaction between PET and the aqueous dye bath requires either the use of high temperature, high pressure systems or the use of carriers (phenols, amines, aromatic hydrocarbons, esters, etc), which are rapidly absorbed and increase the dyeing rate [4]. However, the conventional methods of humid dyeing cause environmental problems due to the inevitably excessive water consumption and the consequent discharge of chemical additives to the environment [5]. The dyeing of PET films using supercritical CO_2 has become an alternative of countless advantages, from the environmental point of view, since it does not have effluents [6].

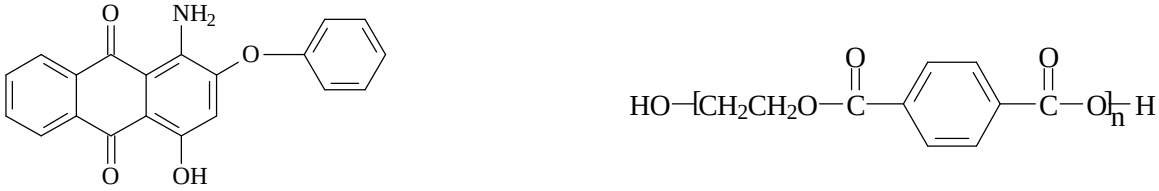
The supercritical fluids present densities similar to liquids and compressibility close to gases. One of the most frequently used supercritical fluids is carbon dioxide. On account of its solvating ability towards non-polar or slightly polar organic molecules in the supercritical phase, CO_2 can be used to transport disperse dyes to the polymer matrix. Due to these properties, supercritical fluids have been used in the impregnation of dyes in textile materials [7, 8, 9, 10].

Earlier studies [11, 12] have shown that the supercritical CO_2-aided dye incorporation process in non-modified and N, N-dimethylacrylamide modified poly (ethylene terephtalate) films is a feasible technique with countless advantages compared with the conventional method.

The objective of this study was the investigation of supercritical CO_2-aided disperse red dianix dye incorporation process in non-modified PET films. By using factorial design, the variables of temperature and pressure of dyeing were investigated, using the statistical SAS® software. A model for the diffusivity as a function of temperature and pressure was obtained from the experimental data.

I – MATERIALS AND METHODS

Samples of poly (ethylene terephtalate) films – PET – were used. The commercial dye used was dispersed red dianix dye E-FB (Dy Star)®. The N, N-dimethylformamide (Aldrich) solvent was used in the dye extraction process of the samples. Figure 1 shows the polymer and dye structures.



(A) (B)

Figure 1- (A): CI Disperse red 60 dianix (E-FB) and (B): poly (ethylene terephtalate).

Before starting the experiments an experimental design was made and the parameters involved in supercritical CO_2-aided dye sorption on the PET fibers were: pressure (P) in three levels (15, 18, and 21 MPa) and temperature (T) in two levels (60ºC, and 70ºC), in accordance with Table 1. It is important to point out that in some cases equilibrium has been achieved before the factorial time was completed. This design was preferred because relatively few experimental combinations of the variables are adequate to estimate complex response functions

Table 1 – Experimental design

Variable	**Level**		
Temperature (ºC)	60		70
Pressure (MPa)	15	18	21

Supercritical CO_2 dyeing were performed using an SFE, as it is shown in Figure 2, equipped with a 60cm^3 internal volume vessel. The poly (ethylene terephtalate) films were suspended on individual supports inside the vessel and the solid dye was placed on the bottom of the vessel. In the dyeing experiments, it was used 2 wt.% of dye in relation to the mass film. Afterwards, the temperature of bath was adjusted to the requested value, CO_2 was pressured and the pressure was pre-determined by experimental planning. The PET film was impregnated by the dye at several times, maintaining the static system. After this operation, the exit valve, situated on the bottom vessel was opened. This procedure was adopted in order to avoid the deposition of the dye over the PET film.

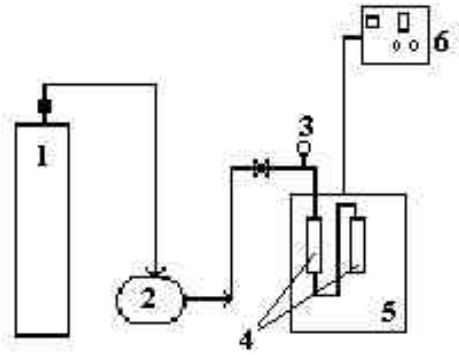


Figure 2- Experimental set – (1) cylinder of CO_2; (2) compressor; (3) manometer; (4) dyeing cells (5) thermostatic bath (6) control of temperature and agitation.

After being submitted to the dyeing procedures in $scCO_2$, the concentration-absorbed dye by the film was spectrophotometrically measured, after the hot extraction of the dye with N, N-dimethylformamide at 80°C for 30 minutes, under constant agitation.

II – RESULTS AND DISCUSSION

The experimental results can be separated into three major portions: a) the measurement of dye sorption on the PET films in supercritical carbon dioxide at several contact times, b) determination of equilibrium solubilities with effective mass transfer coefficient, and c) prediction of the effective mass transfer coefficient.

To optimize the dyeing process in the case of supercritical CO_2-aided, a study of the dye absorption by the film at different pressures (15, 18, 21 MPa) and temperatures (60ºC, 70ºC), was carried out. The statistical analysis of the variables used in the process with $scCO_2$-aided has shown that the regression coefficients of parameters such as temperature ($p=0.0319$) was significant. However, the pressure ($p=0.2443$) was statistically insignificant.

Figures 3 and 4 show the pressure and temperature influence of the dye sorption on the PET films. This solubility analysis shows a similar behavior, in other words, there is a maximum sorption of the dye on PET films, as a function of the time variable. However, the results show that the concentration of absorbed dye by the PET film was practically constant between 15 MPa and 18 MPa, but decreased at the pressure of 21 MPa. The decrease in CO_2 solubility and absorption at long times is attributed to an increase of PET crystallinity. These results are consistent with the data from other systems in which a semicrystalline polymer is annealed by plasticization with CO_2, allowing polymer chains to reorient to a more thermodynamically favorable conformation, forming crystallites [13, 14]. These researchers have observed maximal in the time-dependent sorption studies of CO_2 in PET film.

The fact that the dyeing of Poly (ethylene terephthalate) films in supercritical CO_2 can be carried out at pressures lower than 21 MPa suggests that the fluid causes a change in structure of the polymer, allowing the dye to migrate in the non-crystalline regions of the film. Supercritical CO_2 is known to reduce the glass transition temperature T_g of many polymers considerably, resulting in an enlarged mass transfer rate inside the polymeric matrix [8].

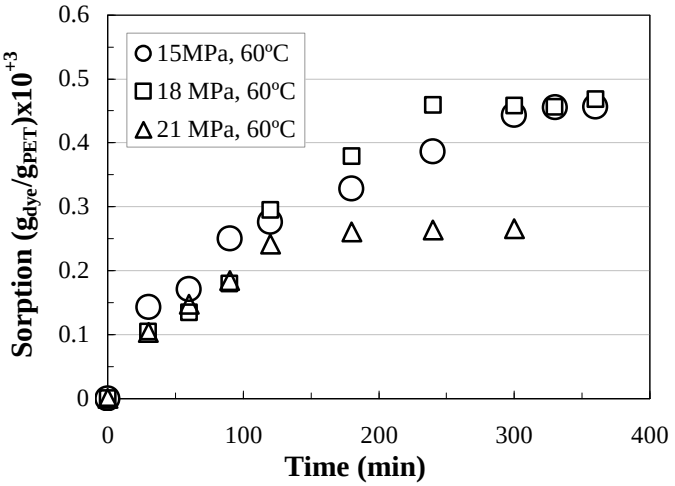


Figure 3 – The dye sorption on the PET film as a function time at the pressure of 15, 18, 21 MPa and 60ºC.

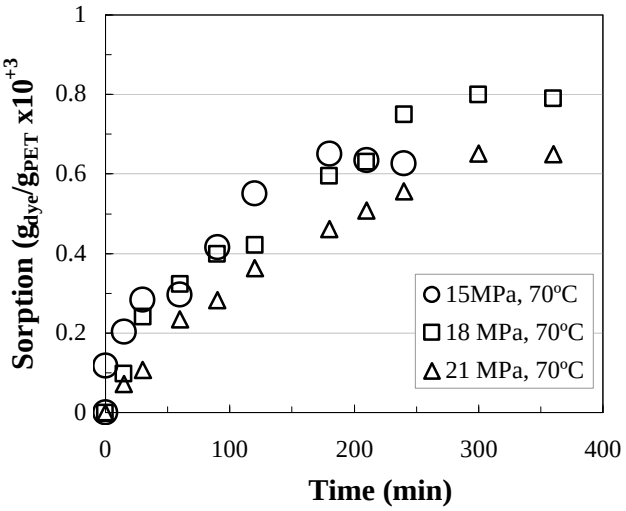


Figure 4 – The dye sorption on the PET film as a function time at the pressure of 15, 18, 21 MPa and 70ºC.

In order to describe the mass transfer of disperse dyes in a polymer matrix, it is important to have a good knowledge of the transport mechanism of the solvent. The question is if the supercritical CO_2 just “opens the way” for the diffusing dye or if the dye molecules diffuse within the solid fluid [15]. In this work we suppose that the $scCO_2$ transports disperse dyes in PET films. Under a diffusion-controlled assumption, the dye absorption rate on the PET film in $scCO_2$-aided can be represented by the following equation [16]:

$$\frac{dy}{dt} = k_o\left(y_s^{eq} - y_s\right) \quad (1)$$

Where y_s^{eq} is the equilibrium concentration (g_{dye}/g_{PET}),

And k_0 is an effective mass transfer coefficient (g_{dye}/g_{PET}) min^{-1}

Integration of equation (1) yields:

$$\ln\left(y_s^{eq} - y_s\right) = k_0 t + k_1 \quad (2)$$

Where k_1 is integration constant.

Diffusion-controlled assumption was valid, the values of $\ln\left(y_s^{eq} - y_s\right)$ varied linearly with contact time. Each effective mass transfer coefficient k_0 was determined by fitting the experimental values to equation (2). This effective mass transfer coefficient was compared with k_0 adjusted by equation (3) and presented in Table 2.

$$k_0 = aP + bT + cPT \quad (3)$$

Where a and b=linear coefficients

c=cross-product coefficient

The coefficients a, b, and c were adjusted by non-linear regression analysis using MATLAB® software. The coefficients values were $a=1.689\times10^{-6}$, $b=-0.152\times10^{-6}$, and $c=-0.0085\times10^{-6}$.

Table 2 – Calculate and adjusted effective mass transfer coefficient

	Temperature (60ºC)		**Temperature (70ºC)**	
	$k_0(g_{dye}/g_{PET})min^{-1}$		**$k_0(g_{dye}/g_{PET})min^{-1}$**	
Pressure (MPa)	Calculate	Adjusted (*)	Calculate	Adjusted (*)
15	0.0072×10^{-3}	0.0086×10^{-3}	0.0076×10^{-3}	0.0058×10^{-3}
18	0.0096×10^{-3}	0.0121×10^{-3}	0.0099×10^{-3}	0.0090×10^{-3}
21	0.0189×10^{-3}	0.0156×10^{-3}	0.0103×10^{-3}	0.0123×10^{-3}

Standard error= 2.7×10^{-8}

In order to verify if the adjusted effective mass transfer coefficient was consistent, a validation test under the following conditions was made: P=19 MPa and T=65ºC. While the calculated effective mass transfer coefficient was $k_0=0.0122\times10^{-3}(g_{dye}/g_{PET})$ min^{-1}, the adjusted effective mass transfer coefficient was of $k_0=0.0117\times10^{-3}(g_{dye}/g_{PET})$ min^{-1} with AAD (%) = 4.1%. Where AAD (%) = $\sum_{i=1}^{N}\left(\frac{k_{0(calc.)} - k_{0(adj.)}}{k_{0(calc.)}}\right)\times100$

CONCLUSION

Experimental data of disperse red dianix dye on PET films at 60ºC and 70ºC and pressures of 15 MPa, 18 MPa and 21 MPa in $scCO_2$-aided was measured. It showed that the pressure 15 MPa was sufficient to obtain the greatest sorption values. Over the investigated conditions, the equilibrium concentration was 0.460; 0.459; 0.261 (g_{dye}/g_{PET}) at 60ºC and 0.655; 0.790; 0.651 (g_{dye}/g_{PET}) at 70ºC. The effective mass transfer coefficients k_0 were determinated taking into account the diffusion-controlled dominant. The magnitudes of the effective mass transfer coefficients k_0 follow this order of pressure: 15 MPa < 18 MPa < 21 MPa in both temperatures. The equation adjusted matches reasonably the k_0 data.

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