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Anthraquinone and Azo Dyes in Dyeing Processes of PET Films and PET Knitted Fabrics Using Supercritical CO_2 Medium

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Summary: Dyeing processes using supercritical fluid present advantages over the conventional dyeing process using aqueous medium. Previous works from our group on polymeric fibers such as *N*,*N*-dimethylacrylamide (DMAAm) modified poly(ethylene terephthalate), PET, showed higher sorption of disperse dyes in supercritical medium. Furthermore, recent studies showed that the association of UV radiation and DMAAm treatment leads to a better incorporation of dyes in modified PET soaked in aqueous medium. In this work, modified and non-modified PET knitted fabrics (KF) were dyed in supercritical CO_2 medium. Azo and anthraquinone dyes were used in order to compare the extent of incorporated dye in PET films and PET KF in supercritical CO_2. The dyeing process variables were studied by factorial design and by a response surface methodology (RSM) technique. The anthraquinone dye presented a better incorporation in PET than the azo dye. The UV light exposure and the dyeing times inputs showed positive main effects in the incorporation of dyes in PET films and PET KF. From the RSM data, DMAAm and UV light modified PET KF presented 7.43 mg of incorporated azo dye by g of PET if the optimized dyeing conditions, time: 135 min and pressure: 212 bar would be used. In the respective optimized dyeing conditions for the anthraquinone dye, time 150 min and pressure 229 bar, the incorporated dye would be 22.9 mg of dye by g of PET.

Keywords: disperse anthraquinone dye; disperse azo dye; PET; supercritical CO_2

Introduction

The supercritical fluid technology has increased in the last ten years in Brazil.[1] The dyeing of PET fibers using supercritical fluid presents several advantages in comparison to the conventional aqueous dyeing process. The dyeing in supercritical fluids does not produce liquid effluents, therefore it decreases the dyeing costs. Dry dyeing has no costs regarding drying stages. The CO_2 can return to the initial step and the remaining dye can be recycled. Recent data in literature indicate that the supercritical CO_2 dissolves a small quantity of disperse dye,[2–7] working as a carrier in order to diffuse itself into the polymeric matrix, resulting in a material which is homogeneously dyed and presents good fastness properties.[8,9] Supercritical CO_2 decreases the T_g of PET,[10] changes the free volume and swells the material, changing the mass transfer properties of the dye to the polymeric matrix.[11,12] Supercritical CO_2 can remove residual monomers and solvents from the polymer production process.[10] The dyeing of PET with disperse dyes has been the main target of the researchers which study the dyeing technology in supercritical medium.[2,4–6,8–10,12–16] This occurs due to the fact that PET possesses a crystalline structure which

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hinders the dye incorporation. Liman et al.[17] have shown that the diffusion of organic molecules in PET films were influenced by the degree of crystallinity of PET sample. The industrial PET dyeing presents several disadvantages in comparison to the dyeing of other textile fibers.[4–6,9,16,18–20] In aqueous medium, the dyeing of PET is carried out at pressures above the atmosphere pressure and at temperatures of approximately 130 °C. The bath ratio is high due to the low water absorption of PET and to the low solubility of disperse dyes in water. In addition, several dyeing carriers are necessary. The determination of the mass transfer coefficients,[10,14,15] partition coefficient at equilibrium,[11,16] solubility of dyes in supercritical CO_2 medium,[2–7] relation between the structure and the solubility of dyes are some of the recently investigated parameters that might aid workers that tend to utilize the PET dyeing with disperse dyes technology. Studies on the performance of different disperse dyes in PET can be useful in order to select the best dyes in supercritical medium. Our group has studied the dyeing of *N*,*N*-dimethylacrylamide (DMAAm) and UV light modified PET films and PET KFs dyed with CI Disperse Blue 79 and CI Disperse Red 60. This work compares the performance of these dyes in supercritical CO_2 medium in the dyeing of DMAAm modified PET films and PET kintted fabrics (PET KF) and DMAAm and UV light modified PET KF.

Experimental

Materials

Commercial PET films and PET knitted fabrics (PET KF), supplied by Seda Têxtil Ltda., Brazil, were used. Dyes, Navy Blue Dianix ER-FS 200 (CI Disperse Blue 79) and Red Dianix E-FB (CI Disperse Red 60) were supplied by DyStar. Modifier, *N*,*N*-dimethylacrylamide was supplied by Fluka. The structures of the dyes, modifier and PET can be visualized in Figure 1.

Methods

Pre-treatment of PET Films and PET KF

UV Light Radiation

The PET KF were washed with water for 6 h and then dried at 40 °C. Non-modified KF PET was placed in a UV light cabin with a high pressure light bulb of mercury vapor of 250 W from Empalux, Brazil. The emission peaks of the light bulb are at 254, 263, 297, 303 and 365 nm.[21] The samples were placed at a fixed distance of 5.5 cm from the light source during 60 min. The UV light cabin was closed and without ventilation, which induces the heating of

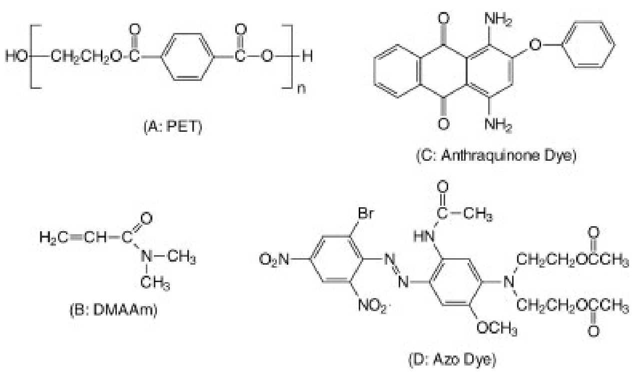

Figure 1.
Structures of poly(ethylene terephtalate) (A); *N*,*N*-dimethylacrylamide (B); anthraquinone dye (CI Disperse Red 60) (Red Dianix E-FB) (C); and azo dye (CI Disperse Blue 79) (Navy Blue Dianix ER-FS 200) (D).

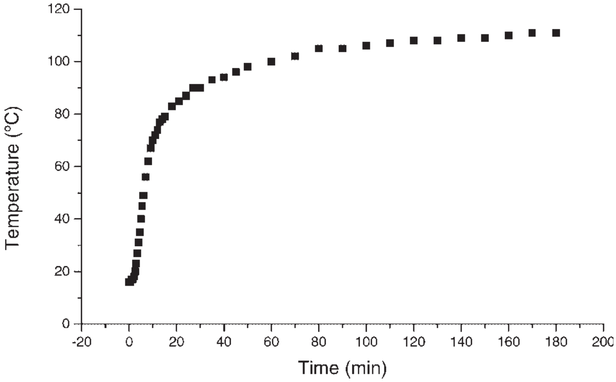

Figure 2.
Heating curve within the UV light treatment cabin.

the sample. Figure 2 shows the heating curve within the UV light treatment cabin.

DMAAm Treatment

Non-modified materials (just washed and dried PET films and KF PET) and the PET KF after being submitted to the UV exposure were immersed in DMAAm during 15 min at 85 °C. The PET KF that was treated by UV exposure and then immersed in DMAAm will be mentioned in this work as UV light → DMAAm modified KF PET.

Dyeing of PET Films and PET KF

The non-modified PET (films and KF), the DMAAm and UV light → DMAAm modified KF PET were dyed regarding to the 2^6 factorial design (Table 1) and to the star design (Table 2), the latter in accordance with the response surface methodology (RSM). The dyeing was made using the equipment described elsewhere.[22] In the dyeing experiments, it was used the conc. of 3 wt.-% of dye in relation to the polymeric.

The 2^6 factorial design, illustrated in Table 1 (inferior and superior levels) and in Table 3 (design matrix), was utilized for the dyeing in supercritical CO_2 of non-modified and DMAAm modified PET films and PET KF.

In the star design, illustrated in Table 2 (different levels) and in Table 4 (matrix design), the inputs pressure and time of dyeing in supercritical CO_2 were used to obtain the optimal conditions of dyeing on UV light → DMAAm modified PET KF.

UV-VIS Spectroscopy

The dyes were extracted from the dyed PET (films and KF) with *N*,*N*-dimethylformamide (DMF). The amount of extracted dye was determined by UV-VIS spectroscopy at 520 nm for the anthraquinone dye (CI Disperse Red 60) and 578 nm for the azo dye (CI Disperse Blue 79).

Table 1.
Variables and levels utilized in the dyeing of DMAAm modified PET films and PET KF.

Numeric variables	Level (1)	Level (−1)
A = Time (min)	180	30
B = Pressure (Kgf/cm^2)	250	140
C = Temperature (°C)	65	50
Categorical variables	Level (2)	Level (1)
D = PET form	Knitted fabric	Film
E = Dye specie	Anthraquinone	Azo
F = DMAAm treatment	Non-modified	DMAAm modified

Table 2.
Variables and levels utilized in the dyeing of UV light → DMAAm modified PET KF in supercritical CO_2.

Variables	Levels				
	1.4142	1	0	−1	−1.4142
X_1 = Pressure (bar)	235	200	175	150	140
X_2 = Dyeing time (min)	205	180	120	60	35

Determination of Dyes Size

The sizes of dyes were calculated by the AM1[24] semi-empiric method through determination of the electronic structures, using the Gamess[25] software.

Results and Discussion

Dyeing of DMAAm Modified PET Films and PET KF

The 2^6 factorial design described in Table 1 was used in order to evaluate the influence of those six variables in the incorporation of dyes in DMMAm modified PET films and PET KFs. In developing the whole factorial, 64 runs were performed and the amount of dye incorporated in each run, as M_d/M_p, is shown in Table 3. After the results presented in Table 3, it was possible to calculate the main and the interaction effects. Figure 3 presents the half normal probability plot from 2^6 factorial design presented in Table 1 and 3.

The analysis of Figure 3 allows us to verify that the main effects of the A, C, D, E, F inputs and the interaction effects A × F, C × D, D × E and A × B × C × D × E were significant. The other effects were disregarded due to the lack of physical meaning. Table 5 presents the values of significant effects.

After Table 5 it is possible to observe that the dyeing time has greater main effect than the other inputs, followed by the temperature dyeing. The type of dye (azo or anthraquinone) presents a significant positive main effect, demonstrating that the anthraquinone dye (level 2 of the categorical input E) presents itself as a more efficient dye than the azo dye (level 1 of the categorical input E). The type of PET (film

Table 3.
Codified variables and dye mass (M_d)/polymer mass (M_p) ratio for non-modified and modified PET films and PET KF dyed with azo and anthraquinone dyes.

Experiments	Variables[a)]						Response M_d/M_p
	A	B	C	D	E	F	mg · g^{-1}
1	−1	−1	−1	D1	E1	F1	0.02
2	1	−1	−1	D1	E1	F1	0.08
3	−1	1	−1	D1	E1	F1	0.01
4	1	1	−1	D1	E1	F1	0.10
5	−1	−1	1	D1	E1	F1	0.07
6	1	−1	1	D1	E1	F1	0.27
7	−1	1	1	D1	E1	F1	0.01
8	1	1	1	D1	E1	F1	0.23
9	−1	−1	−1	D2	E1	F1	0.11
10	1	−1	−1	D2	E1	F1	0.70
11	−1	1	−1	D2	E1	F1	0.35
12	1	1	−1	D2	E1	F1	0.56
13	−1	−1	1	D2	E1	F1	0.19
14	1	−1	1	D2	E1	F1	0.42
15	−1	1	1	D2	E1	F1	0.52
16	1	1	1	D2	E1	F1	2.53
17	−1	−1	−1	D1	E2	F1	0.13
18	1	−1	−1	D1	E2	F1	0.92
19	−1	1	1	D1	E2	F1	1.06
20	1	1	1	D1	E2	F1	0.80
21	−1	−1	−1	D1	E2	F1	0.39
22	1	−1	−1	D1	E2	F1	0.94
23	−1	1	1	D1	E2	F1	0.48
24	1	1	1	D1	E2	F1	2.06
25	−1	−1	−1	D2	E2	F1	0.08
26	1	−1	−1	D2	E2	F1	0.67
27	−1	1	1	D2	E2	F1	0.03
28	1	1	1	D2	E2	F1	0.52
29	−1	−1	−1	D2	E2	F1	1.50
30	1	−1	−1	D2	E2	F1	0.85
31	−1	1	1	D2	E2	F1	3.04
32	1	1	1	D2	E2	F1	1.58
33	−1	−1	−1	D1	E1	F2	0.10
34	1	−1	−1	D1	E1	F2	0.18
35	−1	1	−1	D1	E1	F2	0.02
36	1	1	−1	D1	E1	F2	0.22
37	−1	−1	1	D1	E1	F2	0.15
38	1	−1	1	D1	E1	F2	0.90
39	−1	1	1	D1	E1	F2	0.08
40	1	1	1	D1	E1	F2	0.20
41	−1	−1	−1	D2	E1	F2	0.40
42	1	−1	−1	D2	E1	F2	2.11
43	−1	1	−1	D2	E1	F2	0.91
44	1	1	−1	D2	E1	F2	0.65
45	−1	−1	1	D2	E1	F2	1.02
46	1	−1	1	D2	E1	F2	2.66
47	−1	1	1	D2	E1	F2	1.89
48	1	1	1	D2	E1	F2	2.71
49	−1	−1	−1	D1	E2	F2	0.29
50	1	−1	−1	D1	E2	F2	1.94
51	−1	1	1	D1	E2	F2	0.33
52	1	1	1	D1	E2	F2	1.58
53	−1	−1	−1	D1	E2	F2	1.20
54	1	−1	−1	D1	E2	F2	1.73
55	−1	1	1	D1	E2	F2	1.05

(*continued*)

Table 3. *(Continued)*

Experiments	Variables[a]						Response M_d/M_p
	A	B	C	D	E	F	mg · g^{-1}
56	1	1	1	D1	E2	F2	2.92
57	−1	−1	−1	D2	E2	F2	0.14
58	1	−1	−1	D2	E2	F2	1.37
59	−1	1	1	D2	E2	F2	0.40
60	1	1	1	D2	E2	F2	1.33
61	−1	−1	−1	D2	E2	F2	0.14
62	1	−1	−1	D2	E2	F2	3.63
63	−1	1	1	D2	E2	F2	1.47
64	1	1	1	D2	E2	F2	1.88

[a] Variables: A, time; B, pressure; C, temperature; D, PET form (D1 = film and D2 = knitted fabric); E, dye specie (E1 = azo and E2 = anthraquinone); F, DMAAm treatment (F1 = non-modified sample and F2 = modified with DMAAm).

or KF) presents a significant positive main effect, which means that the PET KF (level 2 of the categorical input D) is a material which absorbs the dyes in an easier way than the films (level 1 of the categorical input D). The advantage of the PET KF in comparison to the PET films in dye incorporation is related to the higher surface area of KF when compared to the 100 μm thick PET films.

The form and the size of the azo and anthraquinone dyes were calculated by the AM1[24] semi-empiric method of determination of the electronic structures, using the Gamess[25] software. The azo and anthraquinone dyes presented a structure similar to an ellipsoid. The calculated longitudinal diameters of them are 18 and 13 Å, respectively, and the transversal diameters are 9 and 7 Å.

Lee et al.[4] considered the supercritical CO_2 as a liquid and used a model for expanded liquid in order to calculate the molar fraction of the CI Disperse Blue 79 (azo dye) in supercritical CO_2 at temperatures of 323.7 to 413.7 K and between pressures of 100 to 300 bar. Those authors calculated that at a temperature of 353.7 K the molar fraction of the azo dye varies from 0.177×10^{-6} to 7.515×10^{-6} when the pressure varies between 101.9 and 301.3 bar. In another work, Lee et al.[5] calculated that the CI Disperse Red 60 (anthraquinone dye) presents a molar fraction in supercritical CO_2, at a temperature of 353.7 K, that varies from 0.778×10^{-6} to 29.531×10^{-6}, when the pressure varies from 102.9 to 305.7 bar. After the studies of Lee et al.[4,5] it was possible to observe that, in the studied ranges, the anthraquinone dye would be around fourfold more soluble in CO_2 than the azo dye.

The data of the dyes size obtained by calculation and the data published by Lee et al.[4,5] can be used to explain the absorption performance of such dyes in PET film and in PET KF as well. The higher efficiency of the anthraquinone dye in the dyeing of PET films and PET KF can be attributed to its smaller size and also to its higher solubility in supercritical CO_2 in comparison to the azo dye. After Table 5 it

Table 4.
Star design results for the UV light → DMAAm modified PET KF.

Experiments	Variables		Response M_d/M_p	
	X_1 = pressure	X_2 = dyeing time	Anthraquinone dye	Azo dye
	bar	min	mg · g^{-1}	mg · g^{-1}
1	−1	−1	1.82	5.07
2	1	−1	3.69	1.23
3	−1	1	0.89	3.04
4	1	1	22.13	6.84
5	0	0	8.59	3.91
6	0	0	9.33	2.17
7	0	0	10.79	3.17
8	−1.4142	0	1.33	3.23
9	0	1.4142	8.00	5.44
10	1.4142	0	8.90	7.19
11	0	−1.4142	2.25	0.48

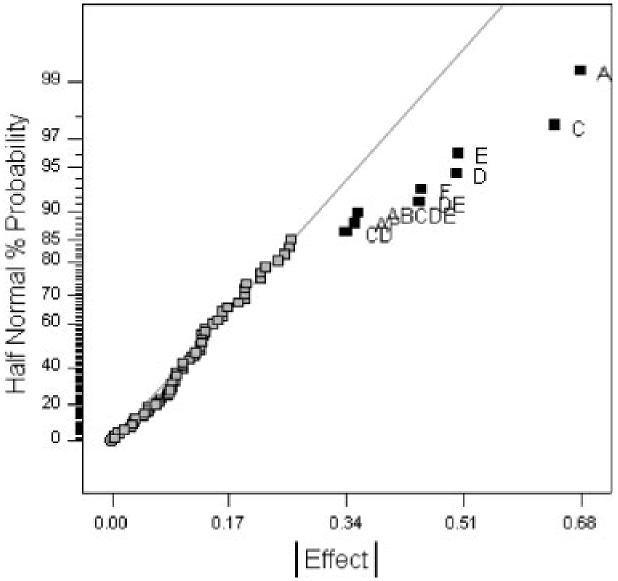

Figure 3.
Half normal % probability for the effects of the 2^6 complete factorial design variables presented in Table 1 and 3.

was possible to observe that the input F (treatment with DAAm) presents a positive main effect in relation to the incorporation of the dyes. Therefore, the DMAAm (level 2 of the input F) modified PET films and PET KF incorporate more dye than the PET films and PET KFs which were not treated with DMMAm (level 1 of the input F). These results are in accordance with the previously obtained results.[18]

Dyeing of UV Light → DMAAm Modified PET KF

The UV light → DMAAm modified PET PET KFs were dyed with azo and anthraquinone dyes, in supercritical CO_2 medium. A star design, in which the time and pressure of dyeing inputs, was utilized in order to optimize the conditions for dye incorporation into PET KF in supercritical CO_2. The whole design is constituted of 11 runs and the different used levels were presented in Table 2. The PET KF treatment was made with exposure to UV light for 1 h followed by DMAAm immersion at 85 °C for 15 min. The dyeing temperature was maintained at 90 °C, above the T_g of the materials. Table 4 presents the respective value of incorporated dye (as M_d/M_p) in the PET KF for each run of star design.

In the response surface methodology (RSM), a polynomial function is used to describe the relationship between the

Table 5.
Main and interaction effects of the A, B, C, D and F inputs of the 2^6 factorial design described in Table 1 and 3.

Variables			Main effect
A = Time			0.68
C = Temperature			0.64
D = PET form			0.50
E = Dye specie			0.50
F = DMAAm treatment			0.45
	Interaction effect		
A × F	C × D	D × E	A × B × C × D × E
0.35	0.34	−0.44	−0.36

response (Y) and the independent inputs (or X_1 and X_2-Table 4). In general, when working with two independent variables, the equation has a general form $Y = \xi_0 + \xi_1 X_1 + \xi_2 X_2 - \xi_3 (X_1)^2 - \xi_4 (X_2)^2 + \xi_5 X_1 X_2$.[26] However, after analysis of the significance, some models parameters (ξ_i) could be rejected.

The data of the M_d/M_p response column of Table 4 for the azo dye were adjusted to the quadratic model

$$Y = \xi_0 + \xi_1 X_1 + \xi_2 X_2 - \xi_3 (X_1)^2 - \xi_4 (X_2)^2 + \xi_5 X_1 X_2 \qquad (1)$$

and the response column for the anthraquinone dye was adjusted to a linear model

$$Y = \xi_0 + \xi_1 X_1 + \xi_2 X_2 + \xi_5 X_1 X_2 \qquad (2)$$

The model Equation (1) and (2) were chosen in such a way that only the parameters considered as significant after T-test were joined. The T-test is performed by dividing the parameter by the standard deviation associated to that parameter. As the value of the parameter is the half of the respective effect,[26] the values of main and interaction effects were used to obtain the values of parameters of models. Table 4 presents the ξ_i parameters for both models [Equation (1) and (2)].

The data in Table 4 demonstrates that, considering the anthraquinone dye, the pressure effect prevails over the time effect, and that there is a strong interaction effect between these variables. On the other hand, the effect of dyeing time for the azo dye (1.79) prevails over the pressure effect that present value close to the standard error.

Table 6.
ξ_i parameters in codified variables for $Y = \xi_0 + \xi_1 X_1 + \xi_2 X_2 + \xi_5 X_1 X_2$ and $Y = \xi_0 + \xi_1 X_1 + \xi_2 X_2 - \xi_3 (X1)^2 - \xi_4 (X_2)^2 + \xi_5 X_1 X_2$ adjusted to the response columns in Table 4.

Paremeters ξ_i	ξ_0	ξ_1	ξ_2	ξ_3	ξ_4	ξ_5
Anthraquinone dye	7.1	4.2	3.21	-	-	4.84
T-Test	7.6	3.9	2.9	-	-	3.1
Azo dye	3.08	0.7	1.3	1.1	−0.1	1.91
T-Test	4.5	1.7	3.1	2.1	0.1	3.2

Table 7 presents the ANOVA for M_d/M_p response adjusted to Equation (1) for azo dye and Figure 4 presents the obtained response surface.

The results in Table 7 demonstrate that the proposed model does not present significant lack of adjustment ($P_{\text{lack of fit}} = 0.3091 > 0.05$) at a confidence level of 95%. The value of $P = 0.0398 < 0.05$ for the regression demonstrates that at least one of the parameters of the model that is significant, at a confidence level of 95%. The value of $R = SQ_R/SQ_T$ demonstrates that 85.0% of the results can be explained by the model.

Table 8 presents the ANOVA data for the adjusted model of the anthraquinone dye [Equation (2)].

The results in Table 8 demonstrate that the proposed model does not present significant lack of adjustment ($P_{\text{lack of fit}} = 0.0913 > 0.05$) at a confidence interval of 95%. The value of $P = 0.0047 < 0.05$ for the regression demonstrates that at least one of the parameters of the model is significant, at a confidence interval of 95%. The value of $R = SQ_R/SQ_T$ demonstrates that 82.7% of the results can be explained by the model. The response surface obtained is presented in Figure 5.

Table 7.
ANOVA for the response surface model $Y = \xi_0 + \xi_1 X_1 + \xi_2 X_2 - \xi_3 (X_1)^2 - \xi_4 (X_2)^2 + \xi_5 X_1 X_2$ applied to the M_d/M_p response of the azo dye described in Table 2 and 4.

Source	Graus de liberdade	Sum of squares	Mean squares	F Test	P
Regression	5	39.65	7.93	5.68	0.0398
Residual error	5	6.98	1.40		
Lack of fit	3	5.45	1.82	2.38	0.3091
Pure error	2	1.53	0.76		
Total	10	46.63			

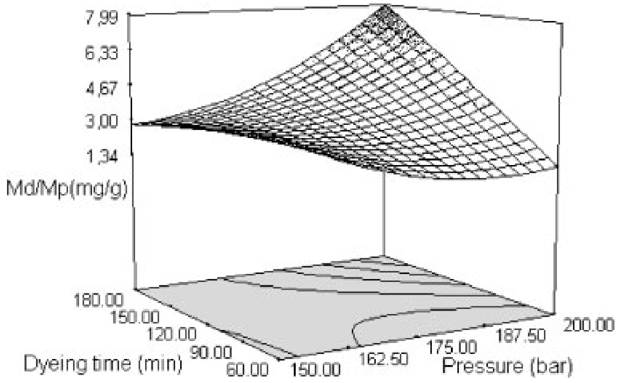

Figure 4.
Response surface for the model $Y = \xi_0 + \xi_1 X_1 + \xi_2 X_2 - \xi_3 (X_1)^2 - \xi_4 (X_2)^2 + \xi_5 X_1 X_2$ applied to the M_d/M_p response (azo dye) presented in Table 4.

The optimization of the models enabled the calculation of the optimum point for the dyeing. The obtained value would be 7.43 $mg \cdot g^{-1}$ if a time of 135 min and pressure of 212 bar were used for incorporated azo dyeing of the PET KF. For anthraquinone, the maximum in dye incorporation would be of 22.9 $mg \cdot g^{-1}$ at a time of 150 min and pressure of 229 bar.

The maximum value in M_d/M_p obtained from the models at CO_2 supercritical optimized conditions for the anthraquinone dye (22.9 $mg \cdot g^{-1}$) is greater than the respective maximum value obtained for the azo dye (7.43 $mg \cdot g^{-1}$), at the investigated range levels. This difference can be attributed to the size difference between the dyes, as previously discussed, and also to the solubility in supercritical CO_2 difference between both dyes, as demonstrated by Lee et al.[4,5] Joung and Yoo[6] also demonstrated that the anthraquinone dyes are more soluble in supercritical CO_2 than the azo dyes.

Results previously obtained[27] on the dyeing in aqueous medium for UV light → DMAAm modified PET KF presented maximum incorporation of 6.04 $mg \cdot g^{-1}$ for the anthraquinone dye and 5.15 $mg \cdot g^{-1}$ for the azo dye. By comparison these results to the ones obtained for the dyeing process in supercritical CO_2 (Table 4) it is possible to observe that the maximum values obtained for the dyeing in supercritical medium are above the ones obtained for the dyeing in water. Even though the characteristics of each dyeing process are different (aqueous medium vs. supercritical medium), the potential of the dyeing in supercritical CO_2 of UV light → DMAAm modified PET KFs is evident.

Park and Bae[28] calculated the concentration of CI Disperse Red 60 at equilibrium in PET fibers, for the PET-CO_2-dye system for temperatures of 333.2 to 413.2 K, at a pressure range from 150 to 300 bar. They obtained saturation values of the dye in the fiber of 16.8974 $mg \cdot g^{-1}$, at a

Table 8.
ANOVA for the response surface model $Y = \xi_0 + \xi_1 X_1 + \xi_2 X_2 + \xi_4 X_1 X_2$ applied to the M_d/M_p response of the anthraquinone dye described in Table 2 and 4.

Source	Degree of freedom	Sum of squares	Mean of squares	F Test	P
Regression	3	318.92	106.31	11.16	0.0047
Residual error	7	66.71	9.53		
Lack of fit	5	64.20	12.84	10.25	0.0913
Pure error	2	2.51	1.25		
Total	10	385.63			

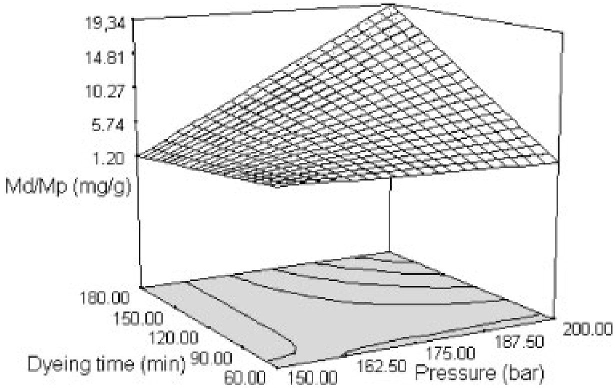

Figure 5.
Response surface for the model $Y = \xi_0 + \xi_1X_1 + \xi_2X_2 + \xi_4X_1X_2$ applied to the M_d/M_p response (anthraquinone dye) described in Table 4.

pressure of 200 bar and 373.2 K, after 240 min of dyeing. After the response surface in Figure 5 the value of 22.5 mg of anthraquinone dye incorporated into the PET KF at 200 bar, 358 K and 204 min of dyeing could be obtained, which demonstrates the efficiency of the UV light → DMAAm pre-treatment on the incorporation of dyes in PET PET KFs when using supercritical CO_2 medium.

As published before by one of us,[18] the pre-treatment with DMAAm diminishes the contact angle and, therefore, an increase of superficial tension, promotes the swelling of the polymer and increases the roughness of the surface. The UV light treatment before the DMAAm sorption promotes a significant increase of the sorption of the dye process by the PET KF for both dyes. This fact is related to the even greater increase of the superficial tension of the material in comparison to the UV light → DMAAm modified material and to the DMAAm[27] modified material.

It is possible to observe by the UV light → DMAAm treatment that the anthraquinone dye reaches much higher levels of dye incorporation (M_d/M_p) than the azo dye. This demonstrates that the CI Disperse Red 60 is potentially more efficient than the CI Disperse Red 79 for the dyeing of UV light → DMAAm modified PET KF.

Conclusion

PET knitted fabrics (PET KF) submitted to the dyeing process in supercritical CO_2 presented better performance in anthraquinone dye incorporation than the azo dye. This better performance can be related to the smaller size and higher solubility of the anthraquinone dye in supercritical CO_2. The statistic models used were efficient in order to optimize the parameters of dyeing process of modified PET KF in supercritical CO_2. The exposure to the UV light and dyeing time inputs presented positive main effects in relation to the incorporation of dyes in PET films and PET KF. Besides the advantages in relation to the environmental impact, the dyeing in supercritical CO2 is more efficient when compared to the dyeing in aqueous medium.

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