RESPONSE SURFACE METHODOLOGY APPLIED IN THE STUDY ON THE INFLUENCE OF THERMOFIXATION ON POLYAMIDE FABRICS

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Abstract – The effects of thermofixation on physicochemical properties of polyamide 6.6 knit were studied applying response surface methodology (RSM). Besides presented a higher value of shrinkage (3.33 %), dyestuff and energy consumptions obtained by the applied mathematical model were, respectively, 0.227 g kg^{-1} and 7.46×10^5 J kg^{-1} lower than other process, demonstrating that RSM can be applied in the prediction of the ideal parameters in the polyamide 6.6 thermofixation process.
Keywords: polyamide 6.6; response surface methodology; thermofixation; dyestuff absorption; energy consumption.

Introduction

Polymers of significant importance nowadays, polyamides (PA) are extremely versatile, being used in the most diverse applications ranging from fabrics for lingerie and the beach line up to membranes for reinforcement in concrete or even in nanofiber bundles [1].

PA 6.6, fiber approached in this study, is a polymer obtained through polymerization by condensation between hexanedioic and hexane-1,6-diamine and has a basic structure of macromolecular chains composed of groups of six carbon atoms linked together through amidic bonds, with carboxylic and amino group at its end. Thus, the aim of this paper was investigating the best thermofixation conditions of PA 6.6 knit, also assessing the environmental impacts of energy and dyestuff consumption on the dyeing process of PA 6.6.

Experimental

Acetic acid 98% and ammonium sulphate 98%, supplied by Labsynth; leveling agent, sequestering and nonionic detergent supplied by Golden Technology; Direct Blue-86 (DB86) supplied by Archroma. All chemicals were used with no previous purification. The experiments were executed in knit with gramature of 325 g m^{-2} and with of 0.90 m (tubular), 156/132 dTex PA 6.6 (88%) and 70 Den elastane (12%) yarns.

A total of 11 samples measuring 20 cm x 20 cm each, with a 15 cm square designed inside it, were thermofixed by dried air (DH-B Thermofixation/Vaporization – Mathis) applying a 2^2 factorial planning assisted by central composite and rotational design. Was verified the influences of the Temperature (T) and Time (t) on Shrinkage (*S*), being the S calculated by Eq. 1.

$$S\ (\%) = \left(1 - \left(\frac{W_F}{W_O}\right)\right) \times 100 \quad (1)$$

Where: S = Shrinkage; W_F = final width; W_O = initial width (15 cm)

Table 1 displays the independent variables (T and t) that were varied at two levels, with alphas, operating limits in order to obtain the best dependent variable (*S*) conditions.

Table 1 - Dependent and independent variables and its levels

Variable	$-\sqrt{2}$	-1	0	$+1$	$+\sqrt{2}$
T (ºC)	132	140	160	180	188
t (s)	9	15	30	45	51

After the thermofixation, the samples were washed in a 10:1 liquor ratio bath (Suzuki Wash Machine) containing 1.0 g L^{-1} of dispersant and 1.0 g L^{-1} of detergent, during 20 min at 90ºC, according to formulation and process recommended by chemicals supplier (Golden Technology). The samples were dried at standard conditions of temperature (21 ± 1 ºC) and moisture (60 ± 10 %) during 24h. The final measurement was performed on three different points of the side, as demonstrated in Fig. 1, to calculate the values of 'W_F'.

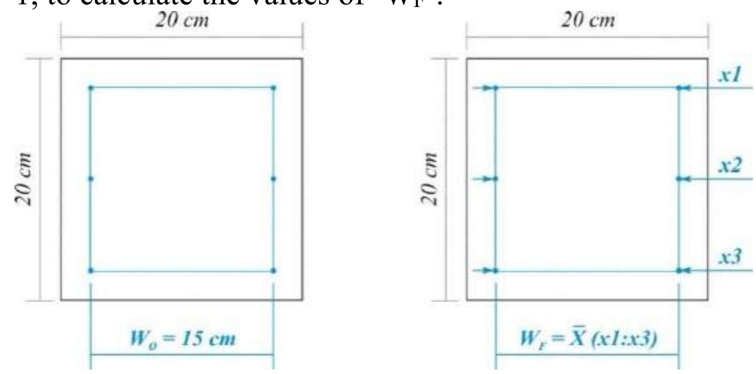

Figure 1 - Measurement of samples

The factors and their corresponding values were varied at five levels ($-\sqrt{2}$; – 1; 0; + 1; + $\sqrt{2}$). The levels of the investigated independent variables were chosen by considering the preliminary tests on the effect of individual variables on thermofixation process and operating limits in order to obtain the best conditions of shrinkage. The model fit was assessed by analysis of variance (ANOVA) and the optimization was assessed by quadratic regression adjusted value (R^2 adjusted) and RSM (Statistica 13®).

Results and Discussion

Table 2 presents the results of the experimental planning applied, with all combinations of independent variables and their respective responses.

Table 2 - Interaction of independent variables and their responses

n	x1	T (ºC)	x2	t (s)	W_O	W_F	S (y)
1	-1	150	-1	30		13.90	7.333
2	-1	150	1	60		14.10	6.000
3	1	170	-1	30		14.40	4.000
4	1	170	1	60		14.50	3.333
5	$-\sqrt{2}$	146	0	45		13.70	8.667
6	$\sqrt{2}$	174	0	45	15.0	14.60	2.667
7	0	160	$-\sqrt{2}$	24		14.10	6.000
8	0	160	$\sqrt{2}$	66		14.30	4.667
9 (C)	0	160	0	45		14.20	5.333
10 (C)	0	160	0	45		14.30	4.667
11 (C)	0	160	0	45		14.30	4.667

The model shown in Eq. 2, which fitted to the experimental data, was analyzed by ANOVA and by multiple regression, described in Table 3.

$$S = -122.7887 - 1.2088T + 0.00305T^2 - 0.2657t + 0.0006t^2 + 0.0011Tt \quad (2)$$

Table 3 - ANOVA and multiple regression

RESULTS	Statistic	ANOVA			
		df	SS	F_{Calc}	F_{Tab}
Regression	-	2	26.2279	57.808	2.8
Residual	-	8	1.88725	-	
R multiple	0.967				
R^2	0.935		-		
R^2 adjusted	0.919				

The variance values were higher than 90% and the R^2 adjusted value was close enough to the unit. These values indicate that the model can predict 91.9% of the experimental data with at a 95% of interval confidence level. The presented F_{Calc} value was twenty-fold higher than F_{Tab}, demonstrating that the model is adequate to use on the prediction of S values under the studied conditions.

RSM analysis

The optimization is carried out by model fitting in combination with RSM, where the studied factors coexists from the analysis of each surface if an optimal condition for each factor is obtained. The Fig. 2 (a) demonstrated that the best values of S, nearby 2 (red dash line), would be possible applying process conditions T = 180 ºC and t = 45 s (white/black dash lines). The critical values obtained by the model with 95% of interval confidence presented similar values, being T = 189.72 ºC and t = 44.47 s. However, analyzing the contour plot (Figure 2b), it was observed that S values lower than 3 can be obtained at certain conditions of T and t, such 178 ºC and 30 s respectively.

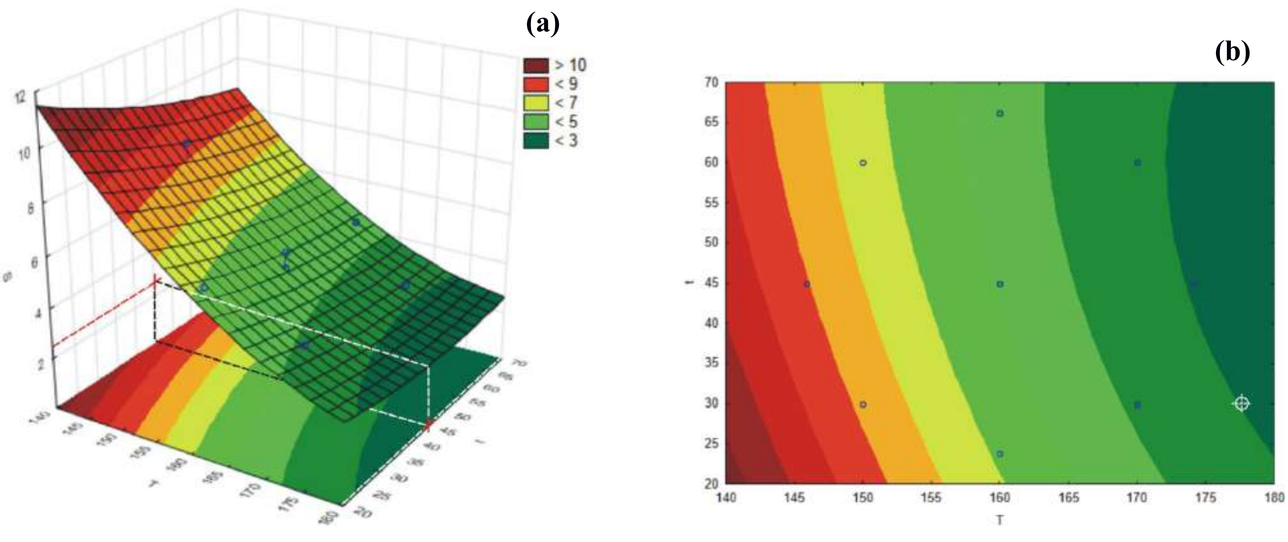

Figure 2 - 3D RSM (a) and 2D RSM (b) with interaction of the independent variables

Dyeing analysis

Usually, the dyeing of PA 6.6 is done with acid dyestuffs that react with aminics groups present in the fiber (50.0 mmoL kg^{-1}). Thermofixation process increase the alignment of polymeric chains, minimizing this number down to 35.0 mmoL kg^{-1} [2]. It means that a higher amount of dyestuff would be necessary in order to obtain the same color. Thus, were done 2 more thermofixation samples, which parameters are described in the Table 4, with procedure executed as same the initial samples.

Table 4 - Optimized thermofixation parameters

Code	Sample	T (ºC)	t (s)	W_O	W_F	S (%)
1	Lower S value in Matrix (6)	174	60	15	14.6	2.667
2	Optimized value 1 (3D RSM)	190	45	15	14.7	2.200
3	Optimized value 2 (2D RSM)	178	30	15	14.5	3.133

As the values of *S* were very close each other, the samples were dyed (Mathis Alt-1) with Direct Blue 86 (DB86), at standard intensity of 1.5% on weight of fabric (owf). DB86, a phthalocyanine dyestuff is commonly used in the dyeing of polyamide in order to evaluate problems of equalization and levelling, because of the complexity of its structure [3]. In addition, phthalocyanine dyestuffs generate effluent which presenting a very difficult of treatment and high acute toxicity [4]. The dyeing procedure and chemicals were applied under conditions of time and temperature suggested by the dyestuff's supplier (Archroma).

After dried at standard conditions, the color strength ($K\ S^{-1}$) values were assessed using Konica Minolta CM 3600d, under illuminant D_{65}, 10º, at 490 nm (Table 5). The $K\ S^{-1}$ was calculated by the Kubelka-Munk equation (Eq. 3), as follow [5].

$$K\ S^{-1} = \frac{(1-R)^2}{2R} \quad (3)$$

Table 5 - $K\ S^{-1}$ values of the optimized values of thermofixation

Code	T (ºC)	t (s)	S	$K\ S^{-1}$
1	174	60	2.667	12.98
2	190	45	2.200	12.80
3	**178**	**30**	**3.133**	**13.13**

It can be observed that $K\ S^{-1}$ value obtained with the optimized parameters in the sample 3 was higher than the others, so that the amount of dye used to obtain the darkest color would be less than that the amount used in the other samples, based on the DB86 color strength equation (Eq. 4) performed at 5 levels experiments.

$$\%DB86 = exp\left(\frac{K\ S^{-1} - 12.453}{1.9074}\right) \quad (4)$$

In a dyeing of 1 kg of PA 6.6 thermofixed with Sample 1 parameters it would be necessary to increase 1.08 g of dyestuff to dye the same 1 kg thermofixed with Sample 3 parameters. To dye a same amount of knit thermofixed with the Sample 2 parameters, would be necessary 2.27 g more dyestuff in order to obtain same value of $K\ S^{-1}$ obtained in the dyeing of the 1 kg with PA 6.6 thermofixed with Sample 3 parameters.

An FT-IR analysis (Jasco 6300 FT-IR) of two samples, one without thermofixation and other thermofixed with Sample 2 parameters, was done. In the amine terminal (3295 cm^{-1}) does not occur any change. However, alterations can be observed in the amide groups (1634 cm^{-1}) and in the carboxylic groups (1539 cm^{-1}). The difference in both amide and carboxylic groups was promoted by the increase of the intramolecular hydrogen bonds, result of a polymeric chamber alignment by the thermofixation.

Energy consumption

The width (1.8 m), weight (325 g m^{-2}) and yield (1,71 m kg^{-1}) of the substrate were used to calculate the amount of electrical energy (Q_E) spent for each sample processed (Eq. 5). Adopting substrate thermofixation applied in an industrial Stenter Machine with 10 fields, 435 kW of total installed potency and applying the Eq. 6 [6], the amount of needed electrical energy was calculated. The results are described in Table 6.

$$Q_E = I_P \times \frac{Y}{S_S} \times 6.00 \times 10^4 \quad (5)$$

Where Q_E = consumption of electrical energy in 'J kg^{-1}'; I_P = installed potency in 'kW'; Y = yield in 'm kg^{-1}'; S_S = stenter speed in 'm min^{-1}'.

Table 6. Spend of electrical energy

Code	I_P (kW)	t (s)	Stenter Speed (m m^{-1})	J kg^{-1}
1		60	30	1.49×10^6
2	435	45	40	1.12×10^6
3		**30**	**60**	**7.44×10^5**

The Sample 3 also presented lower electrical energy consumption than Samples 1 and 2, being 7.46×10^5 J kg^{-1} and 3.76×10^5 J kg^{-1}, respectively.

Conclusions

The RSM demonstrate be useful in the prediction of the ideal parameters in the thermofixation process of PA. Despite the Sample 3 present a higher shrinkage value, it did not exceed 1% against the other values. Besides, its parameters presented lowest consumption of energy, being 7.46×10^5 J kg^{-1} and 3.76×10^5 J kg^{-1} against Sample 1 and 2, respectively.

The amount of dyestuff necessary to obtain the color strength studied and presented by the parameters of Sample 3, also was lower than the values presented by Samples 1 and 2; being 1.08 g kg^{-1} and 2.27 g kg^{-1}, respectively.

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