

# Poly(ethylene terephthalate) Films Modified with *N,N*-Dimethylacrylamide: Incorporation of Disperse Dye

W. L. F. SANTOS,<sup>1</sup> M. F. PORTO,<sup>1</sup> E. C. MUNIZ,<sup>1</sup> L. OLENKA,<sup>2</sup> M. L. BAESSO,<sup>2</sup> A. C. BENTO,<sup>2</sup> A. F. RUBIRA<sup>1</sup>

<sup>1</sup>Departamento de Química, Universidade Estadual de Maringá, Av. Colombo, 5790, 87020-900, Maringá, PR, Brasil

<sup>2</sup>Departamento de Física, Universidade Estadual de Maringá, Av. Colombo, 5790, 87020-900, Maringá, PR, Brasil

Received 23 June 1999; accepted 4 October 1999

**ABSTRACT:** Poly(ethylene terephthalate), PET, can be modified with *N,N*-dimethylacrylamide to obtain a better incorporation of disperse dye (Disperse Blue 79). Minimal variations in the decomposition at 10% level, melting, and glass transition temperatures, show that the thermal stability of modified PET films does not change when compared to nonmodified PET. The atomic force images show nanopeaks formation on the surface due to the modification. Modified PET films show a decrease in the contact angle and then, an increase in the superficial tension measurements, when compared to the value of  $37 \pm 1$  dynes  $\cdot$  cm<sup>-1</sup> (nonmodified), with values lying in the range of  $42\text{--}46 \pm 0.5$  dynes  $\cdot$  cm<sup>-1</sup>. The data obtained by photoacoustic spectroscopy (PAS) for dyed PET films show a dye peak at 580 nm. The data analysis of the peak area show that PET films modified with *N,N*-dimethylacrylamide for 15 min at 85°C, dyed for 6 h at 85°C with a dye concentration of 0.333 g/L, incorporate three times more dye than the nonmodified films dyed in the same conditions. By the data obtained from PAS, it was possible to calculate the depth profile of dyeing with values around 54  $\mu$ m. Factorial analyses show that the dyeing time was the most important variable. The major amount of incorporated dye was obtained by the following combination of variables: temperature and time of modifier treatment were, respectively, 72.5°C and 15 min; time and temperature of dyeing were, respectively, 90°C and 195 min for a dye concentration of 0.133 g/L. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 269–282, 2000

**Key words:** poly(ethylene terephthalate); *N,N*-dimethylacrylamide, photoacoustic spectroscopy, disperse dye

## INTRODUCTION

Poly(ethylene terephthalate), PET, is largely used in industries, due to its excellent mechanical, electrical, and optical properties, such as, dimensional and hydrolytic stability, transparency, and flexibility.<sup>1,2</sup>

Woven fibers of PET represent the biggest percentage among synthetic fibers in the market,<sup>3</sup> and are used pure or mixed with cellulose, in the

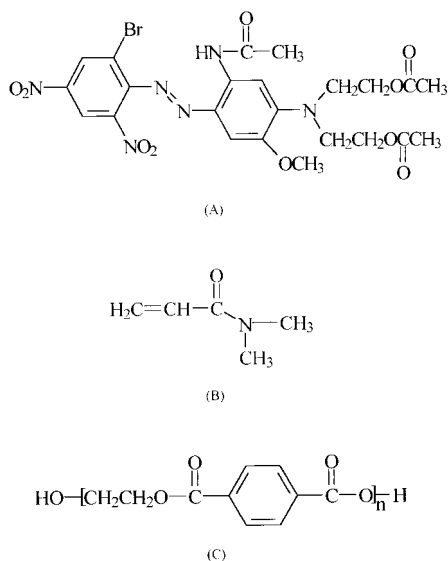
making of different articles, like curtains, caps, and others. These articles demand, due to their utilization, that dyes are added to the material to have a better appearance.

Among synthetic fibers, PET has the most compact and crystalline<sup>4</sup> structure, except for some kinds of polyester, of low commercial use. These fibers are dyed with disperse dyes, insoluble in water (5–30 mg/L), which are applied with dispersing agents to achieve stable dispersions.<sup>4</sup>

In the sorting process, not only the fiber crystallization,<sup>5</sup> but also the absence of long-range electrostatic forces, such as ion–ion, or ion–dipole makes the dye incorporation difficult in the PET.

Correspondence to: A. F. Rubira.

*Journal of Applied Polymer Science*, Vol. 77, 269–282 (2000)  
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**Figure 1** (A) Dye: CI Disperse Blue 79, (B) modifier: *N,N*-dimethylacrylamide, (C) polymer: poly(ethylene terephthalate).

Several authors<sup>4–10</sup> have studied the effects of modifying agents and dyeing conditions with dispersed dyes in PET films and fibers.

According to Stinson and Obendorf,<sup>8</sup> nonmodified PET absorbs only 0.4% of the water, and does not swell in the water. This lack of interaction between PET and the aqueous dyebath requires either the use of high-temperature/high pressure systems in the dyeing with disperse dyes, to achieve industrially acceptable dyeing rates, or the use of low molecular weight organic compounds, called carriers (phenols, amines, aromatic hydrocarbons, esters, etc.), which are rapidly absorbed and accelerate the dyeing rate.<sup>4</sup>

Needles and Walker,<sup>5</sup> using disperse dye as a probe to investigate the structure of PET, showed that even though the surface of PET was very crystalline, the interior regions are less crystalline.

Bendak and El-Marsafi,<sup>6,7</sup> showed that the treatment of the fiber with organic solvents such as dimethylformamide, ethylamine, or aqueous NaOH solution decreases the crystalline appearance of the surface, making the dye incorporation easier.

Fité,<sup>4</sup> proposed a dyeing method with the disperse dye dissolved in organic solvents such as methyl chloride. This gives microdispersed dye in small water concentrations that is maintained as stable through sonication and upon adding phosphoglycerides to create a supramolecular structure. This structure, constituted of one or more concen-

tric layers, consists of liposomes that encapsulate the solvent and the solubilized disperse dye. This method allows the dyeing of PET at low temperatures.

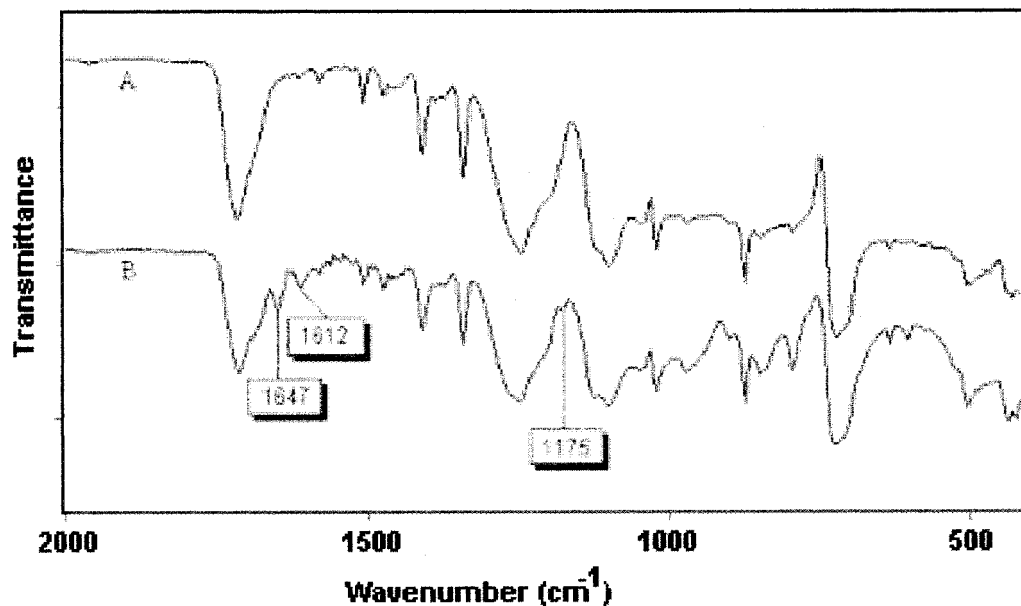
Saligram and collaborators,<sup>9</sup> report a dyeing using sonication to form and break small bubbles, resulting in a temperature and pressure increase at a microscopic level. This cavitation causes agitation that makes the dyeing better at low temperatures, achieving levels comparable to dyeing at ebullition using carriers.

Knittel and collaborators<sup>10</sup> showed that synthetic fibers like PET can be dyed using carbon dioxide in a supercritical state as solvent, avoiding water pollution and the need of drying, allowing excellent firmness levels.

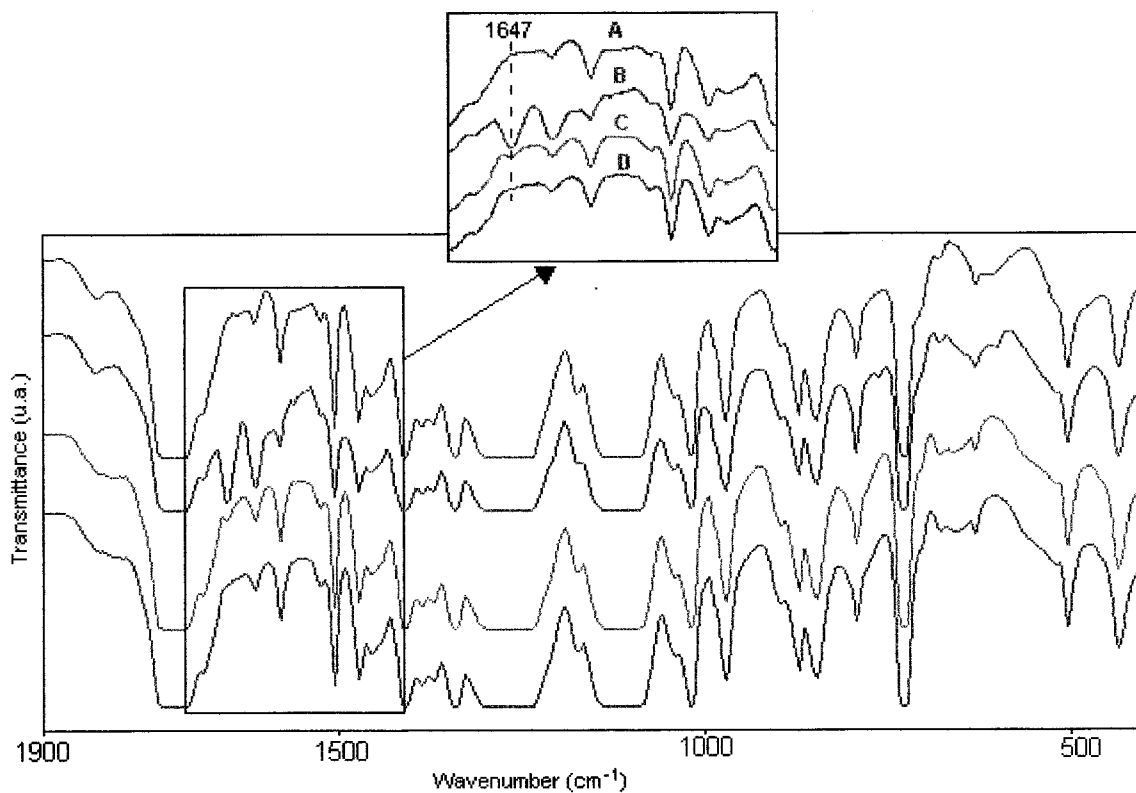
*N,N*-dimethylacrylamide has been used in the biomaterials area, due to its hydrophilic character, in the obtention of polymeric materials compatible to blood and tissue. The grafting of the *N,N*-dimethylacrylamide monomer in polymeric substrates like poly(dimethylsiloxane), to be applied as a catheter,<sup>11</sup> and the obtention of selective semipermeable amphiphilic membranes,<sup>12</sup> used to determine the diffusional characteristics of glucose, insulin, and albumin, are applications

**Table I** Codified Variables of Each Experiment of the Complete Factorial Design 2<sup>3</sup> Added to the Points (9, 10, 11, 12, 14, 15, 16), Corresponding the Star Design: X<sub>1</sub> = Treatment Temperature, X<sub>2</sub> = Dyeing Time, X<sub>3</sub> = Dyeing Temperature

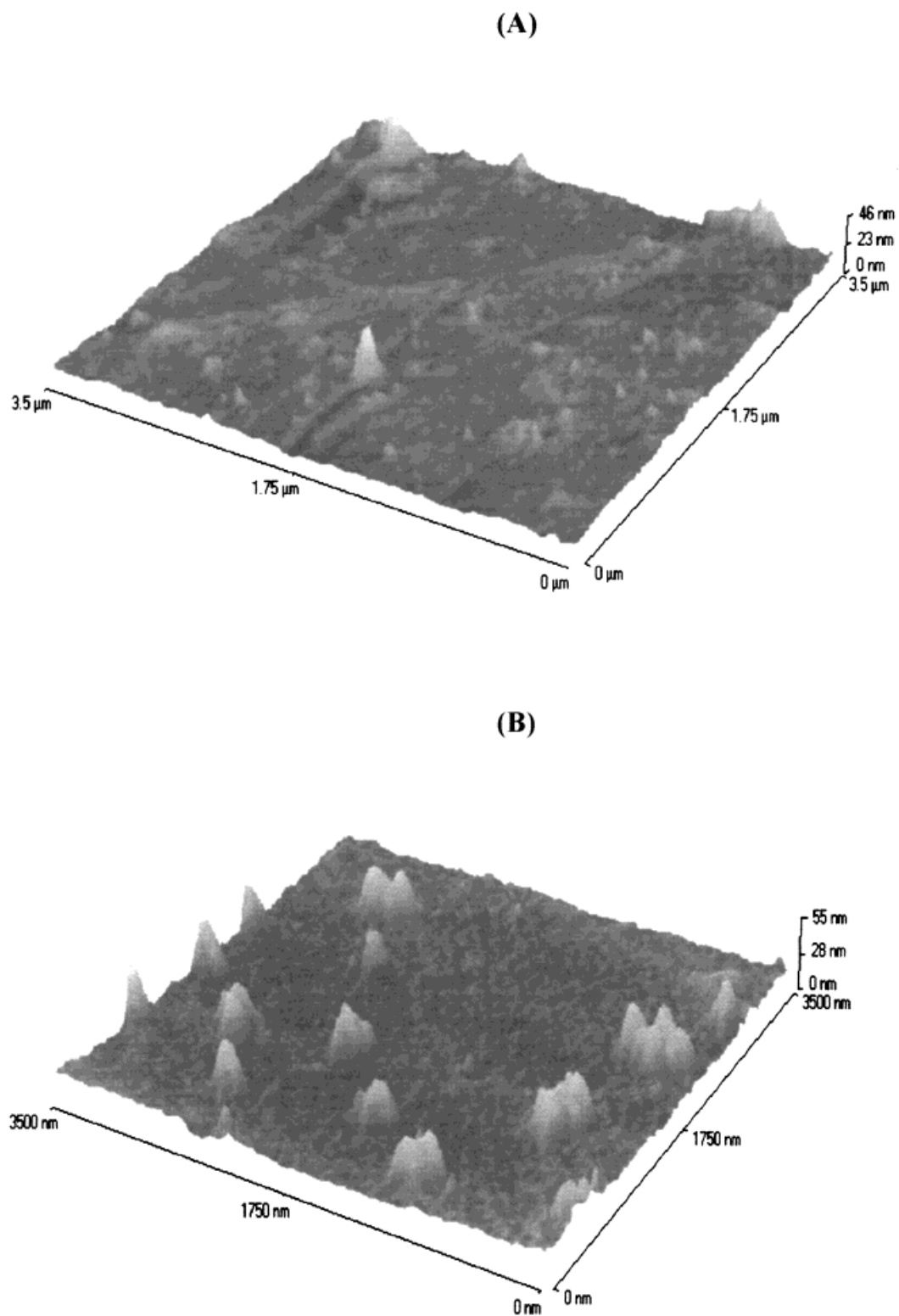
Test	X <sub>1</sub> = Treatment Temperature	X <sub>2</sub> = Dyeing Time	X <sub>3</sub> = Dyeing Temperature
1	-1	-1	-1
2	-1	+1	-1
3	-1	-1	+1
4	-1	+1	+1
5	+1	-1	-1
6	+1	+1	-1
7	+1	-1	+1
8	+1	+1	+1
9	0	0	0
10	0	0	0
11	-2 <sup>1/2</sup>	0	0
12	+2 <sup>1/2</sup>	0	0
13	0	-2 <sup>1/2</sup>	0
14	0	+2 <sup>1/2</sup>	0
15	0	0	-2 <sup>1/2</sup>
16	0	0	+2 <sup>1/2</sup>



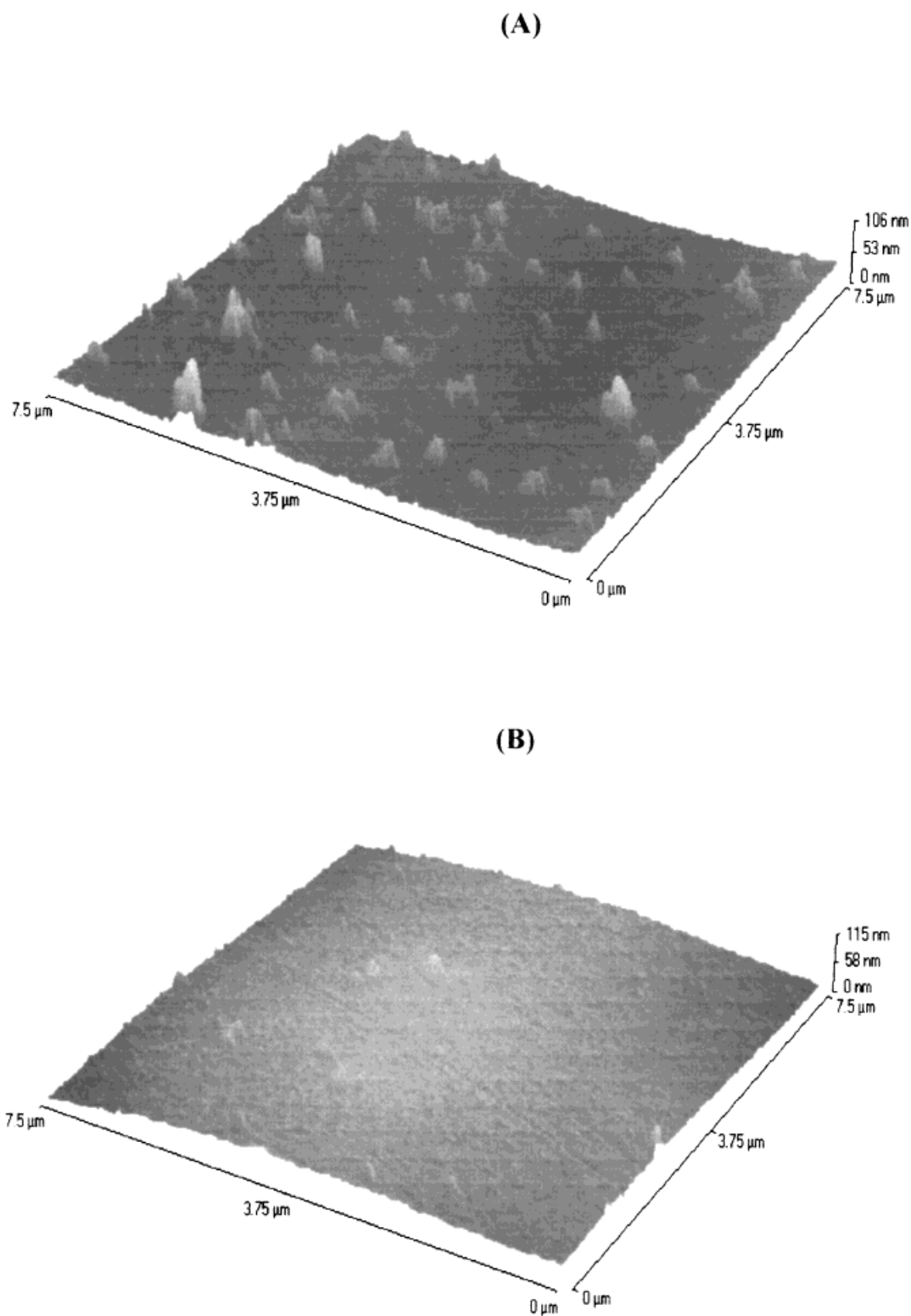
**Figure 2** FTIR-ATR spectrum in nonmodified PET (A) and *N,N*-dimethylacrylamide modified (B) PET samples.



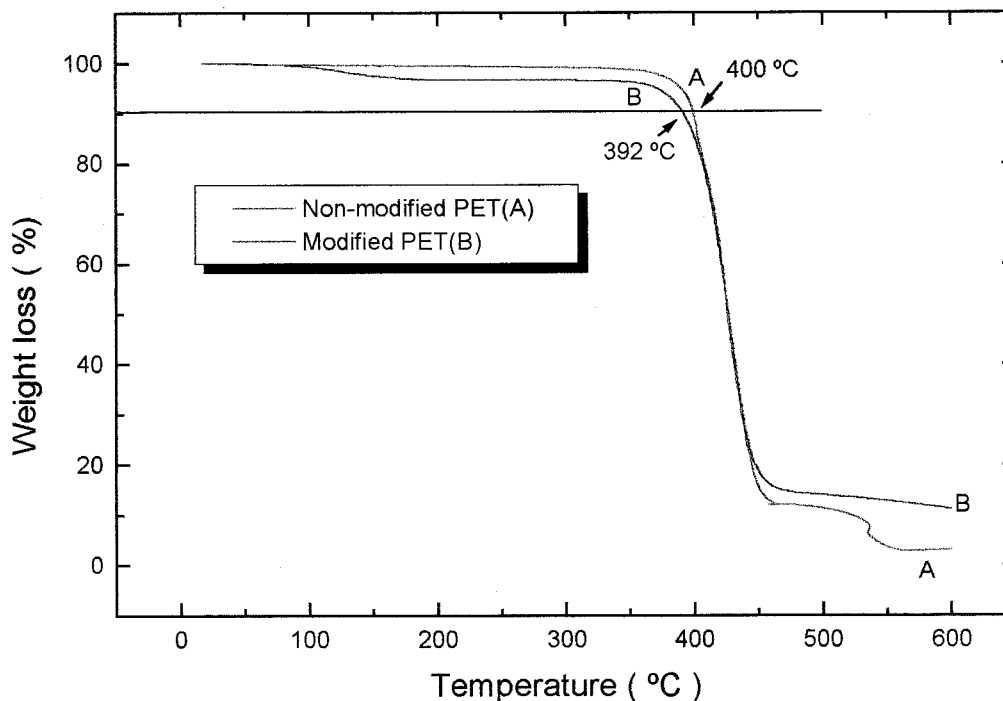
**Figure 3** FTIR spectrum of the samples: (A) nonmodified PET, (B) *N,N*-dimethylacrylamide PET, (C) PET sample exposed to water under agitation at 90°C for 1 h, and (D) PET sample exposed to water under agitation at 90°C for 6 h.



**Figure 4** Atomic force images of *N,N*-dimethylacrylamide modified PET films: (A) 15 min, 60°C; (B) 15 min, 85°C.



**Figure 5** Atomic force images of *N,N*-dimethylacrylamide modified PET films: (A) 15 min, 85°C, (B) 2 h, 85°C.



**Figure 6** TGA curves for virgin PET samples (A) and *N,N*-dimethylacrylamide-modified PET (B). Decomposition temperature of 10%. Heating from 20–600° with 20° min<sup>-1</sup> tax. Nitrogen flow: 20 mL · min<sup>-1</sup>.

indicating that the *N,N*-dimethylacrilamide is not harmful to human body.

Photoacoustic spectroscopy (PAS) studies the interaction between radiation and matter, through the photoacoustic effect that is produced by a moduled radiation incident on the sample, placed inside a closed cell. The PAS is a nondestructive technique, and is effective in the study of optical and thermal properties of materials.<sup>13</sup> It may be used to monitor dyes in textile fibers,<sup>14</sup> with the advantage that the dye penetration depth in the textile substrate can be calculated.<sup>15</sup>

In this work we have used *N,N*-dimethylacrylamide as a compatibilizing agent between PET and the disperse dye. By using a factorial design, the variables of time and temperature of dyeing, as well as time and temperature of treatment and also concentration of dye, were investigated. The photoacoustic technique has been used to monitor the optical absorption bands as a function of the preparation parameters.

## EXPERIMENTAL

### Materials

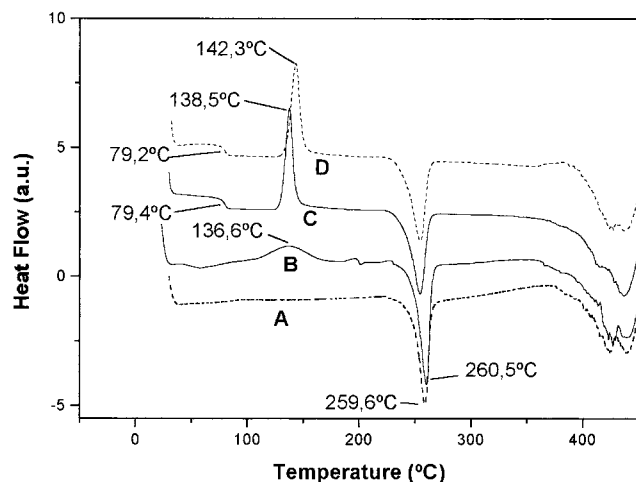
The commercial dye used was Samaron HGS(Dy Star)<sup>®</sup> (Disperse Blue 79) (C<sub>23</sub>H<sub>25</sub>BrN<sub>6</sub>O<sub>9</sub>). The

solvent (modifier) was *N,N*-dimethylacrylamide (C<sub>5</sub>H<sub>9</sub>NO) (Aldrich). The PET substrate used was a Mylar commercial type film tipo B (100 μm). Figure 1 shows the structure of the polymer, dye, and modifier.

### Procedures

PET films were immersed in *N,N*-dimethylacrylamide modifier solvent, under agitation and temperature control. A complete factorial design, in two levels, using two variables was realized: temperature [85(+1) and 60°C(-1)] and immersion time [15 min (-1) and 2 h(+1)]. The film samples used in the complete factorial 2<sup>2</sup> design were weighted before and after the modification to evaluate the amount of incorporated modifier. The samples used in the complete factorial design were also used for contact angle measurements.

After the modification with *N,N*-dimethylacrylamide, the washed and dried films were immersed in a dispersion of Samaron HGS(Dy Star) (CI Disperse Blue 79) dye, also under agitation and temperature control. A fractional factorial design, in two levels [2<sup>(5-2)</sup>], was initially realized to screen five variables: (1) temperature of modifier solvent treatment [85(+1) and 60°C(-1)]; (2) immersion time [15 min (-1) and 2 hs(+1)]; (3)



**Figure 7** DSC curves of the PET samples (obtained by heating of 25–450°C with 10°C min<sup>-1</sup> tax. Nitrogen flow: 20 mL/min: (A) nonmodified PET, (B) *N,N*-dimethyl-acrylamide modified PET. Curves C and D were obtained after the heating of the film at 280°C, maintenance of the film at this temperature for 10 min, and cooling by immersion liquid nitrogen. (C) Nonmodified PET, (D) *N,N*-dimethylacrylamide modified PET.

dyeing temperature [85(+1) and 60°C(-1)]; (4) dyeing time [30min (-1) and 6 h(+1)]; and (5) dye concentration [0.133(-1) and 0.333 g · L<sup>-1</sup>(+1)]. The dye concentration values correspond to 2 and 5%, respectively, of dye on the weight of the film, which is associated to a fixed relation of mass of film:bath volume corresponding to [(1:150) (g/mL)], guaranteeing the referred concentrations above. Afterwards, a complete factorial design, in two levels, using only the more important three variables was realized: treatment temperature [85(+1) and 60°C(-1)], dyeing temperature [85(+1) and 60°C(-1)], and dyeing time [30 min(-1) and 6 h(+1)]. A central point with two repetitions and an ampliation of six points called star design<sup>16</sup> was added to the complete factorial design. Table I shows the codified variables of the

**Table II** Enthalpy of Fusion for Nonmodified PET Films and Films with the Incorporation of Modifier at Different Times and Temperatures

	Modified PET			
	Nonmodified PET	15 min/ 60°C	15 min/ 85°C	120 min/ 85°C
$\Delta H_{\text{fusion}}$	45J/g	38J/g	38J/g	39J/g

**Table III** Contact Angle Superficial Tension of Nonmodified and *N,N*-Dimethylacrylamide Modified PET Samples at Different Times and Temperatures

Samples	Time	Temperature	Contact Angle	Superficial Tension (dynes/cm)
Nonmodified Sample	—	—	83°	37 ± 0.5
1	15 min	60°C	76°	42 ± 0.5
2	15 min	85°C	71°	45 ± 0.5
3	2 h	60°C	72°	44 ± 0.5
4	2 h	85°C	68°	46 ± 0.5

complete factorial design (2<sup>3</sup>) added the runs denoted as 9, 10, 11, 12, 13, 14, 15, and 16, correspondent to the star factorial design. The star factorial design was realized so as to amplify the number of variable levels, allowing the calculation of response surfaces by the RSM technique.<sup>16</sup>

To determine the depth profile of the dye in the PET films, these were treated for 15 min at 85 °C with the *N,N*-dimethylacrylamide modifier and dyed in only one face with 2% of dye at different time and temperature conditions.

### Measurements

Differential scanning calorimetry measurements were performed to determine the glass transition temperature of PET, before and after modification. Thermogravimetric analysis of pure and *N,N*-dimethylacrylamide modified PET films were performed to verify the thermal stability of the polymer. The measurements were made with Shimadzu equipment, model 50S. IR-ATR spectrum of pure and *N,N*-dimethylacrylamide-modified samples in the infrared region were obtained with FTIR Bomem equipment. Atomic force microscopy measurements were carried out to verify modifications of the surface of the polymer, using

**Table IV** Main Effect and Interaction Effect of the Variables Involved in the Design Described in Table III

Variables	Main Effect	Interaction Effect
Time	1.5	—
Temperature	2.5	—
Time × temperature	—	-0.5

**Table V** Mass Variation of PET after the Incorporation of Modifier. Variables: Time and Temperature

Test	Time	Temperature	$M_b$ (g)	$M_a$ (g)	$\Delta M$ (mg)	(%)
1	15 min	60°C	0.1747	0.1755	0.8	0.5
2	15 min	85°C	0.2025	0.2075	5.0	2.5
3	2 h	60°C	0.1645	0.1688	4.3	2.6
4	2 h	85°C	0.1782	0.1916	13.4	7.5

$M_b$  = Mass of film before incorporation;  $M_a$  = Mass of film after incorporation.

a Topometrix-Discover TMX 2010. Contact angle measurements were made on modified and non-modified PET films to verify alterations in the superficial tension. The contact angle measurements were obtained by a TANTEC model CAM-Micro.

To quantify the dye incorporation in the fiber, measurements in the 200 to 800 nm region were made using a photoacoustic spectrometer, equipped with a 1000-Watt Xenon lamp, from the Oriel Corporation (model 68820).

The depth profiles of the dye in *N,N*-dimethylacrylamide-modified and dyed PET films were determined through photoacoustic technique, using a scanning frequency of 4–100 Hz.

## RESULTS AND DISCUSSION

Spectral analysis in the infrared regions of modified PET films shows peaks of the modifier at 1647, 1612, and 1175  $\text{cm}^{-1}$  (Fig. 2), which were respectively attributed to: carbonyl stretching, C=C stretching and C—N stretching of the modifier.<sup>17</sup> This indicate the *N,N*-dymethylacrylamide incorporation in PET. These peaks indicate the absence of a chemical interaction between the modifier and PET, as already observed by Ershov and collaborators<sup>18</sup> in the study of the interaction between polyester fiber and acrylic copolymers.

Figure 3 shows the IR-ATR spectrum of the nonmodified film, modified film, modified film and exposed to water washing for 1 h, and modified film and exposed to water washing for 6 h. It can be observed from Figure 3 that after the exposition of the film to water at 90°C for 6 h, peaks of modifier are still present.

The swelling of the polymer with modifier, and the formation of peaks on the surface can be observed by analysis of atomic force images presented on Figure 4. When the treatment is carried out at 85°C, a size increase of the peaks can be

observed when compared to treatment at 6°C, as shown in Figure 4. The 2-h treatment leads to a coalescence of the peaks and a swelling of the surface as a whole when compared to 15-min treatment (Fig. 5).

The decomposition temperature at a 10% level, determined by thermogravimetric analysis, for PET and modified PET, was 400 and 392°C, respectively. This is evidence that the treatment does not alter the thermal stability of the polymer (Fig. 6). Figure 6(B) shows a weight loss of 2.5% around 136°C, which was attributed to the modifier loss.

Differential scanning calorimetry of pure and *N,N*-dimethylacrylamide-modified PET films shows that the PET melting temperature (258°C) and the glass transition temperature (70°C), are not dependent of treatment conditions (Fig. 7). A better defined glass transition temperature was observed in the spectrum of modified PET films. This can be attributed to the increase of the amorphous/crystalline ratio of the material after incorporation of the modifier. The melting values of PET before and after incorporation of the modifier (Table II) are evidence that this amorphous/crystalline ratio increases.

Olenka,<sup>19</sup> after verifying the alterations in thermal diffusivity of PET films, due to the *N,N*-dimethylacrilamide modification and Samaron HGS dyeing, made X-ray spectroscopic measurements to monitor alterations in the cristallinity of

**Table VI** Main Effect and Interaction Effect of the Variables of the Factorial Design Described in Table V

Variables	Main effect	Interaction effect
Time	3.7	—
Temperature	3.7	—
Time $\times$ temperature	—	1.5



**Table VII** Codified Variables and Photoacoustic Signal of the Fractional Factorial Design ( $2^{5-2}$ )

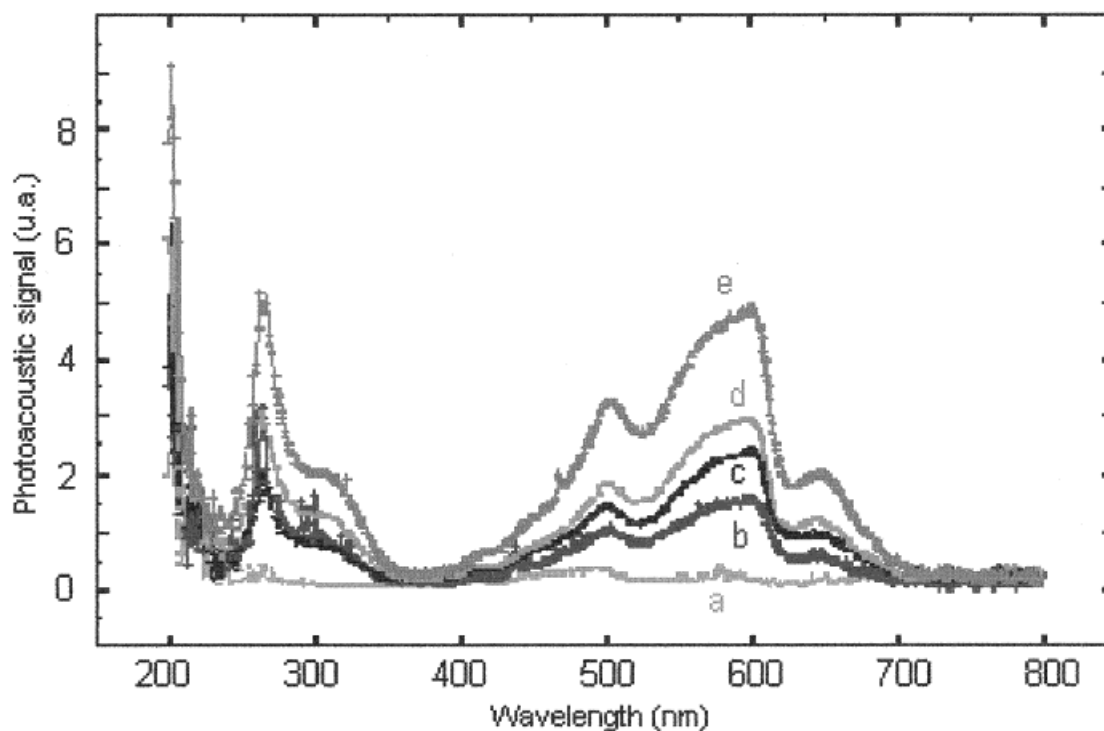
Test	Treatment Temperature	Dyeing Temperature	Treatment Time	Dyeing Time	Dye Concentration	Response
1	-1	-1	-1	-1	+1	20.2
2	+1	-1	-1	+1	-1	41.1
3	-1	+1	-1	+1	-1	35.2
4	+1	+1	-1	-1	+1	34.7
5	-1	-1	+1	+1	+1	22.7
6	+1	-1	+1	-1	-1	39.4
7	-1	+1	+1	-1	-1	17.4
8	+1	+1	+1	+1	+1	85.3

Treatment temperature ( $^{\circ}\text{C}$ ) [85(+), 60(-)]; dyeing temperature ( $^{\circ}\text{C}$ ) [85(+), 60(-)]; treatment time (min) [120(+), 15(-)]; Dyeing time(min)[360(+),30(-)]; dye concentration (g/l) [0.133(+), 0.333(-)]. The response column corresponds to the area under the curve of the photoacoustic signal (u.a.) in function of the wavelength (nm), in 500–700 nm range.

the material during the treatment and dyeing processes. In this work, it is shown that after modification with *N,N*-dimethylacrilamide, the cristallinity of PET increases. In addition, it is observed that the samples treated at  $60^{\circ}\text{C}$  exhibit an increase of cristallinity during the dyeing, whereas the samples treated at  $85^{\circ}\text{C}$  exhibit a decrease of cristallinity during the dyeing.

The melting heat data, associated to the results obtained by Olenka,<sup>19</sup> show that there has been an increase of the cilia number and other isolated ordered chains to short-range order that are not observed by DSC, but observable by X-ray.<sup>20</sup>

The modified PET DSC curve (Fig. 7) shows an exothermic transition around  $136^{\circ}\text{C}$  [Fig. 7(B)].



**Figure 8** Photoacoustic spectrum of PET films. Virgin film (A), nonmodified film dyed at  $85^{\circ}\text{C}$  for 6 h with a dye concentration of 0.333 g/L (B) and *N,N*-dimethylacrylamide-modified PET film for 15 min at  $85^{\circ}\text{C}$  and dyed at  $85^{\circ}\text{C}$  with 0.333 g/L of dye at different times (C = 30 min; D = 2 h; E = 6 h), width 5 nm.

**Table VIII Main Effect of the Variables Involved in the Factorial Design Shown in Table VII**

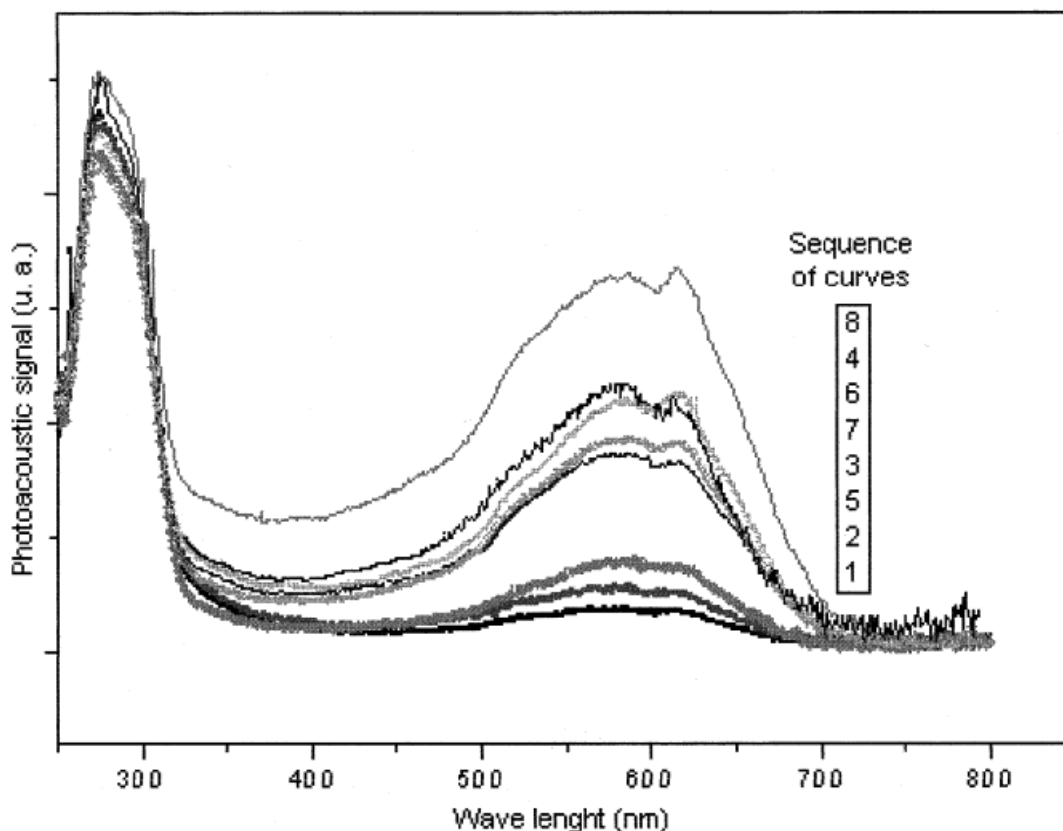
Variables	Main Effect
Treatment temperature	26.3
Dyeing temperature	12.3
Treatment time	8.4
Dyeing time	18.1
Dye concentration	7.5

This transition matches the weight loss of about 2.5% in the TGA curve [Fig. 6(B)], which was attributed to the modifier loss at this temperature, although that temperature is close to the PET crystalline transition peak.

In Table III, the contact angle and superficial tension values for PET are collected. A decrease of the contact angle and, therefore, an increase of the superficial tension of modified films, can be observed. This result matches the AFM data, where the alteration of the film surface due to the

modifier treatment was observed. On Table IV, the main effect and interaction effect of the variables involved in the design described in Table III are mentioned. It can be visualized on Table IV that the influence of the temperature is more important than the influence of time on the PET superficial tension.

The weight variation of PET film due to the incorporation of the modifier is shown in Table V. The results show a weight increase of 2.5% for the films treated for 15 min at 85°C. An increase of 7.5% for the films treated for 2 h at 85°C was verified. Table VI shows that the main effect of the variables, at the studied levels, is the same regarding the modifier incorporation, and that the main effect of the time is maximum when the temperature of treatment is maintained at the higher level (+1), and vice versa. The results are compatible to the results obtained by contact angle measurements, because *N,N*-dimethylacrylamide is mainly responsible for the superficial tension alteration of the modified PET in relation to the nonmodified PET. Even though the 2 h and



**Figure 9** Photoacoustic signal correspondent to the complete factorial planning ( $2^3$ ). The numbers correspond to the numbers in Table IX, width 30 nm.

**Table IX Codified Variables and Photoacoustic Signal of the Complete Factorial Design (2<sup>3</sup>) Added the Points (9, 10, 11, 12, 13, 14, 15, 16), Corresponding to the Star Ampliation**

Test	X <sub>1</sub> = Treatment Temperature	X <sub>2</sub> = Dyeing Time	X <sub>3</sub> = Dyeing Temperature	Response
1	-1	-1	-1	5.7
2	+1	-1	-1	8.7
3	-1	+1	-1	31.1
4	+1	+1	-1	41.1
5	-1	-1	+1	13.9
6	+1	-1	+1	40.0
7	-1	+1	+1	35.2
8	+1	+1	+1	61.1
9	0	0	0	18.0
10	0	0	0	18.4
11	-(2 <sup>1/2</sup> )	0	0	16.8
12	+(2 <sup>1/2</sup> )	0	0	37.7
13	0	-(2 <sup>1/2</sup> )	0	0.0
14	0	+(2 <sup>1/2</sup> )	0	25.6
15	0	0	-(2 <sup>1/2</sup> )	7.5
16	0	0	+(2 <sup>1/2</sup> )	64.1

Treatment Temperature (°C) [85(+1),60(-1)]; dyeing time(min) [360(+1),30(-1)]; dyeing temperature (°C)[85(+1),60(-1)]. The response column corresponds to the area under the curve of the photoacoustic signal (u.a.) in function of the wavelength (nm), in 500–700 nm range.

85°C conditions show an increase of 7.5% in the amount of incorporated modifier, against only 2.5% of the 15 min and 85°C conditions, the result does not reflect the dye incorporation in the material after dyeing, as the fractional design shows (Table VII).

Photoacoustic spectrum, that shows the dye incorporation in PET films under different treatment and dyeing conditions, is shown on Figure 8. The photoacoustic spectroscopy curves of dyed PET show a peak of 580 nm that was attributed to the dye, because the nonmodified PET curve does not show any peak in this region. Analysis of the area, or height, of the peak, evidence that the *N,N*-dimethylacrylamide incorporation helps the dye incorporation: films treated for 15 min at 85°C and dyed for 6 h at 85°C with 5% of dye (Fig. 8, curve e) incorporates three times more dyes than the dyed nonmodified film under the same condition (Fig. 8, curve b).

The results of the dye incorporation from the factorial design are shown in Table VII. The main effect, calculated for each variable, shows a higher influence of the treatment temperature, dyeing time, and dyeing temperature variables (in decreasing order) in relation to other variables, obtained from the fractional design described in Table VIII.

To better evaluating the main effect and interaction effects of treatment temperature, dyeing

time, and dyeing temperature variables, a complete factorial design was performed, keeping the treatment time fixed at 15 min, and maintaining the dye percentage constant at 2%. Figure 9 shows the photoacoustic spectrum corresponding to the complete factorial design, and the Table IX shows the relative area concerning the curves presented in Figure 9, in the 500–700 nm range, which correspond to the amount of incorporated dye in modified PET films.

Table X shows the main effects and interaction effects of the variables involved in the factorial design described in Table IX. It can be observed in Table X, that among all the analyzed variables, the dyeing time variable present the highest in-

**Table X Main Effect and Interaction Effect of the Variables of the Complete Factorial Design Described in Table IX**

Variables	Main Effect	
A = Treatment temperature	16.25	
B = Dyeing time	25.75	
C = Dyeing temperature	15.75	
Interaction effect		
AB	AC	BC
1.75	9.75	-3,75

**Table XI Multiple Linear Regression Adjustment of the Second-Order Response Surface Model, Based on the Square Minimal Method  $y = \xi_0 + \xi_1x_1 + \xi_2x_2 + \xi_3x_3 + \xi_{11}(x_1)^2 + \xi_{22}(x_2)^2 + \xi_{33}(x_3)^2 + \xi_{12}x_1x_2 + \xi_{13}x_1x_3 + \xi_{23}x_2x_3$  [Eq. (1).], Applied to the Design Described on Table IX**

Fit Polynomial Coefficients									
$\xi_0$	$\xi_1$	$\xi_2$	$\xi_3$	$\xi_{11}$	$\xi_{22}$	$\xi_{33}$	$\xi_{12}$	$\xi_{13}$	$\xi_{23}$
17.88	7.88	11.36	11.96	4.82	-2.38	9.12	0.85	4.87	-1.93
Variance analysis									
Source	Sum of square	Degrees of Freedom	Mean Square	Test $F$					
Regression	5001.8040	9	555.7560	7.7749					
Residual	428.8848	6	71.4808						
Lack of adjustment	428.8048	5	85.7610	1072.0140					
Pure error	0.800	1	0.0800						
Total correlation	5430.6890	15							
				% explained variance = 92.1026					
				% explainable variance = 99.9985					

fluence in the dye incorporation in modified PET films. A strong interaction effect between the treatment temperature and dyeing temperature variables can also be observed. The main effect of the dyeing temperature variable is maximum when the treatment temperature is maintained at a high level, and vice versa.

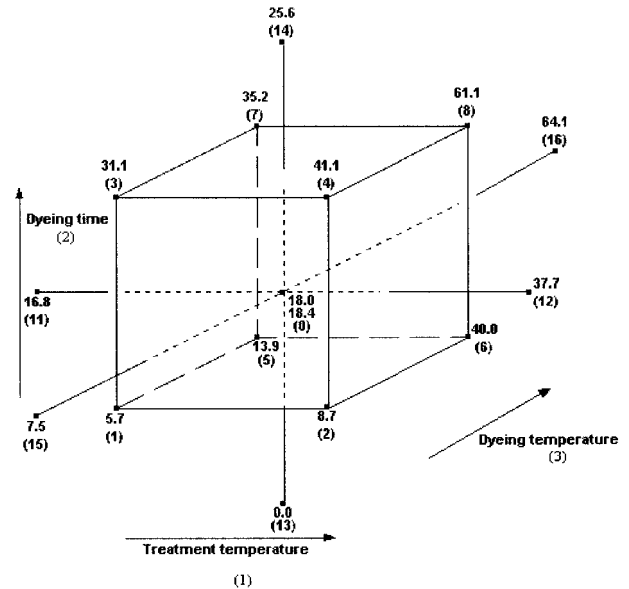
To calculate a response surface for the problem through the star factorial design, the following second-order response surface model was proposed:

$$y = \xi_0 + \xi_1x_1 + \xi_2x_2 + \xi_3x_3 + \xi_{11}(x_1)^2 + \xi_{22}(x_2)^2 + \xi_{33}(x_3)^2 + \xi_{12}x_1x_2 + \xi_{13}x_1x_3 + \xi_{23}x_2x_3 \quad (1)$$

Concerning the star factorial design, the best fit of the eq. (1) is achieved when the values for  $\xi_i$ ,  $\xi_{ii}$ , and  $\xi_i$  parameters described in Table XI are used.

The model does not show lack of significant adjustment, observed in Table XI because the mean square/mean square residual ratio is 7.78, which is a lot bigger than,  $F(9,6) = 4.10$  (95% confidence interval). However, the surface response represented by eq. (1), using the values described in Table XI, does not show a maximum in the studied region. From Figure 10 it can be observed that the best results occur at high temperatures of dyeing (85–90°C), average to high temperatures of treatment (72–85°C), and average to high times of dyeing (3–6 h). The best point (64.1 u.a.) occurs at the dyeing temperature of

90°C, treatment temperature of 72.5°C and dyeing time of 3 h and 15 min. The second best condition (61.1 u.a.) occurs at the dyeing temperature of 85°C, treatment temperature of 85°C, and dyeing temperature of 6 h. Preliminary tests made with the fiber around the best star design



**Figure 10** Star planning involving the treatment temperature, dyeing temperature, and dyeing time variables. The values referred in the points (●) correspond to the area above the photoacoustic signal by wavelength curve, in the 500–700 nm range.

points show that the results obtained with the film can be extrapolated to the fiber, only if there is an increase of the dye percentage in relation to the weight of the material, keeping constant the dye weight and PET exposed surface.

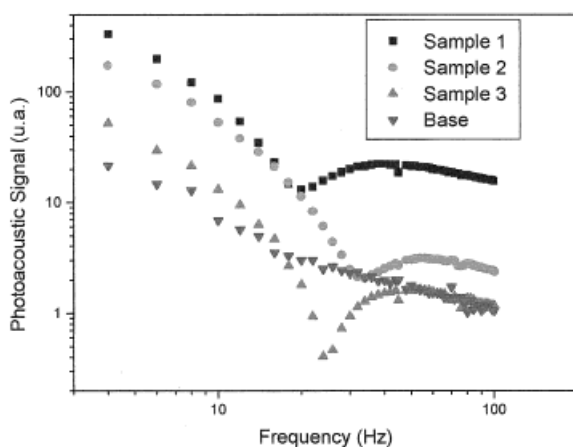
The photoacoustic technique allows a sensitive and a precise identification of many singular properties of the material. As it penetrates the samples, the incident radiation is attenuated. The frequency modulation,  $\omega$ , determines the light depth penetration. The thermal diffusion length,  $\mu_s$ , decreases with increasing frequency modulation  $\omega$ . The relation:<sup>18</sup>

$$\mu_s = \sqrt{\frac{2\alpha}{\omega}}, \quad (2)$$

where  $\alpha$  is the thermal conductivity, shows that as the frequency modulation is higher, the thermal diffusion width is smaller.

With a scanning frequency in the 4–100-Hz range, it is possible to observe that there is a different frequency for each sample when the polymer is dyed and treated differently. We can observe that the nondyed sample does not show this transition frequency (Fig. 11). Using this transition frequency and the thermal diffusivity values calculated by Olenka,<sup>19</sup> the dye depth profile in the PET film sample was calculated and the values are presented in Table XII.

The depth profile shows that for the dyeing time of 30 min, we are close to a limit saturation value, because the dye values (30 min and 6 h) seem to be inside the error margin observed in the



**Figure 11** Photoacoustic signal in function of the light frequency modulation: Base: PET film; samples 1, 2, and 3: correspond to samples 1, 2, and 3 of Table XII.

**Table XII** Depth Profile of the Samples Treated for 15 min at 85°C and Dyed in Only One Face

Samples	$\alpha \times 10^3$ cm <sup>2</sup> /seg	Transition Frequency (Hz)	Dye Width ( $\mu$ m)
1	1.86	20	54.4
2	2.53	34	48.7
3	1.52	24	44.9

Sample 1: dyeing temperature = 85°C, dyeing time = 6 h.  
Sample 2: dyeing temperature = 85°C, dyeing time = 30 min.  
Sample 3: dyeing temperature = 60°C, dyeing time = 30 min.

transition frequency. However, it was observed that the amount of incorporated dye is significantly different in the 30 min and in 6 h condition, as it can be visualized in Table IX. The relative area concerning the curve of photoacoustic signal, in the 500–700 nm range, for a dyeing time of 30 min, with treatment and dyeing temperatures maintained at 85°C (point 6) is 40.0. For the same treatment and dyeing temperatures, but using 6 h as the dyeing time (point 8) the answer is 61.1, i.e., 1.7 times larger.

## CONCLUSION

Poly(ethylene terephthalate), can be modified with *N,N*-dimethylacrylamide to obtain a better incorporation of disperse dye. The time variable can be reduced from 6 h (for the nonmodified film) to 30 min (modified film) without compromising the dyeing intensity.

The number of experiments made in this system using five variables (fractional design) can be optimized in a complete factorial design by the use of only three more important variables: treatment temperature, dyeing time, and dyeing temperature.

Photoacoustic spectroscopy was an adequate technique to monitor the dyeing of PET films and to characterize the dye depth profile.

## REFERENCES

1. Farrow, G.; Hill, E. S.; Weinle, P. L. In *Encyclopedia of Polymer Science and Technology*; Bikales, N. G., Ed.; John Wiley & Sons: New York, 1969, p. 1, vol. 11.
2. Hanthorne, J. M.; Heffelfinger, C. J. In *Encyclopedia of Polymer Science and Technology*; Bikales,

- N. G., Ed.; John Wiley & Sons: New York, 1969, p. 42, vol. 11.
3. Shashin, M. M. *Polym Testing* 1995, 14, 243.
  4. Fité, F. J. C. *Textile Res J* 1995, 65, 362.
  5. Needles, H. L.; Walker, C. *J Appl Polym Sci* 1991, 47, 249.
  6. Bendak, A.; Elmarsafi, S. *Ann Chim* 1991, 81, 141.
  7. Bendak, A.; Elmarsafi, S. *Ann Chim* 1992, 82, 603.
  8. Stinson, R. M.; Obendorf, S. K. *J Appl Polym Sci* 1996, 62, 2121.
  9. Saligram, A. N.; Shukla, S. R.; Mathur, M. *J Soc Dyers Colourists* 1993, 109, 263.
  10. Knittel, D.; Saus, W.; Schollmeyer, E. *Indian J Fibre Textile Res* 1997, 22, 184.
  11. Almeida, A. T.; Queirós, A. A. A.; Barrak, E. R.; Higa, O. Z. *Proceedings of the 13 CBECIMAT, Curitiba-PR*, 1998, p. 4054.
  12. Shamlou, S.; Kennedy, J. P.; Levy, R. P. *J Biomed Mater Res* 1997, 35, 157.
  13. Olenka, L.; Neto, A. M.; Baesso, M. L.; Miranda, M. L. C.; Bento, A. C.; Santos, W. L. F.; Rubira, A. F. *Proceedings of the XXII Encontro Nacional da Matéria Condensada, São Lourenço-MG*, 1999, p. 232.
  14. Eickmeier, A.; Schollmeyer, E. *Angew Makromol Chem* 1993, 205, 203.
  15. Olenka, L.; Silva, E. N.; Neto, A. M.; Baesso, M. L.; Miranda, M. L. C.; Bento, A. C.; Santos, W. L. F.; Rubira, A. F. *Proceedings of the XXII Encontro Nacional da Matéria Condensada, São Lourenço-MG*, 1999, p. 386.
  16. Box, G. E. P.; Draper, N. R. *Empirical Model-Building and Response Surfaces*; John Wiley & Sons: New York, 1987.
  17. Pouchert, C. J. *The Aldrich Library of Infrared Spectra*; Aldrich Company Inc.: Milwaukee, WI, 1981, p. 435, 3rd ed.
  18. Ershov, A. A.; Tsailingol'd, V. L.; Lopatina, O. P.; Gandurin, L. I.; Kozlova, O. K. *Zhur Priklad Khimii* 1991, 64, 613.
  19. Olenka, L. *Master Dissertation presented to Programa de Mestrado em Física/UEM* (1999).
  20. Koenig, J. L. *Spectroscopy of Polymers*; ACS Professional Reference Book: Washington, DC, 1992, p. 107.