

# Improving the Colorfastness of Poly(ethylene terephthalate) Fabrics with the Natural Dye of *Caesalpinia sappan* L. Wood Extract and the Effect of Chitosan and Low-Temperature Plasma

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**ABSTRACT:** The effect of a low-temperature plasma and/or chitosan pretreatment as a mordant on the dyeing of poly(ethylene terephthalate) fabrics with an aqueous extract of *Caesalpinia sappan* L. wood, which showed a remarkably high coloring property in a natural dyeing system, was investigated. After dyeing, scanning electron microscopy, add-on, color measurements, and fastness to washing tests were performed. Dyeing with the *C. sappan* L. extract led to fair-to-good fastness properties in conventional natural dyeing. The results clearly show that the pretreatment with

chitosan and/or plasma is better than a metal mordant in terms of the dye uptake and reduction in the dyeing time, that the proposed pretreatment coloration reaction could be carried out without the need for repetitive dye steps, and that it prevents the excessive use of dye chemicals, thereby resulting in a more ecofriendly process. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 160–166, 2008

**Key words:** dyes/pigments; fibers; morphology; polyesters; stiffness

## INTRODUCTION

Lately, there has been increasing interest in the dyeing of fabrics with natural dyes because of their health-oriented and environmentally friendly properties as well as their apparently low toxicity and allergenicity. However, dyeing fabrics with natural dyes often leads to problems related to the washing or light fastness of the dyed materials and the color reproducibility of the dyeing process. Most attempts at overcoming these problems have involved the use of metallic salts as mordants.

*Caesalpinia sappan* L. (the class of Leguminosae) is an indecuous tree distributed in China and Taiwan, and its heartwood has traditionally been used as an analgesic and as a therapy for thrombosis or tumor.<sup>1</sup> Moreover, several neoflavonoid compounds have been isolated from the wood of *C. sappan* L.,<sup>2,3</sup> and many experiments regarding the biological activities of these compounds, such as their inhibi-

tory activity in the central nervous system and anti-hypercholesteremic activity, have been reported.<sup>4–7</sup> In this study, brazilin, which is the main component of *C. sappan* L., as shown in Figure 1, and is colored intensely red by alkalis, was examined for its possible use in the dyeing of poly(ethylene terephthalate) (PET) fabrics.

As most of the polymers used for improving color performance, such as metal mordants, carriers, and other functional dyeing additives, are synthetic materials, their biocompatibility, nontoxicity, dyeability, and bioactivity are much more limited than those of natural polymers such as chitin, chitosan, and their derivatives. Chitosan, which is produced by the deacetylation of chitin, is an amino polysaccharide that is a useful natural biopolymer resource and can provide ionic conductivity when dissolved in acetic acid. Because of its inherent polyamino group in the molecular structure, chitosan has an extremely high affinity for a wide range of dye classes, such as disperse, direct, reactive, acid, vat, sulfur, and naphthol dyes, with basic dyes being the only exception. The diffusion mechanism of chitosan is similar to that of cellulose. It has been previously reported, for example, that the pretreatment of fabrics with a chitosan solution leads to an increase in the bonding of the dyestuff to the fabrics and intensifies their colorization because the binding is due to the presence of protons from an acetic acid solution.<sup>8–10</sup>

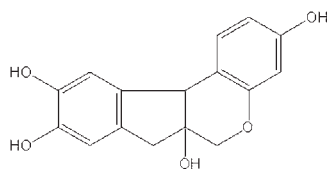
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**Figure 1** Structure of brazilin.

The industrial use of the low-temperature plasma treatment was commonly developed by the microelectronics industry, and recently, the gas plasma process has been extensively used to enhance the physicochemical affinity of polymer surfaces and improve their color depth because plasma processes are used to modify the polymer surfaces. This process is also used to improve the physicochemical properties of polymer surfaces by, for example, enhancing their adhesion characteristics, increasing their wettability, deepening their coloration, and rendering wool fabrics shrink-proof, resulting in a more consistent interface with biological mobility. Previously, we reported that an oxygen or argon plasma treatment induces a change in the surface structure of PET fabrics and influences their dyeing and soft handling properties. Furthermore, we investigated the effectiveness of the chitosan pretreatment condition compared with the dyeing process alone.<sup>11,12</sup>

This study focused on improving the coloration of PET fabrics with a chitosan and/or low-temperature plasma pretreatment instead of a metal mordant in natural coloration systems. The results (obtained without the pretreatment) are compared with those obtained with the same dyes after the treatment of the fabrics with the mordant, chitosan, and/or plasma. These results reflect a reduction in the needed concentrations of these toxic and environmentally harmful metal media. Furthermore, the method explored herein is expected to be an efficient dyeing method that eliminates the need for repetitive dye steps and also prevents the excessive use of dye chemicals.

## EXPERIMENTAL

### Fabrics and reagents

A commercial polyester fabric (KS K 0905, FITI, Seoul, Korea) and the wood of *C. sappan* L. were used for dyeing. Table I and Figure 1 show the characteristics of PET and the chemical structure of brazilin (C<sub>16</sub>H<sub>14</sub>O<sub>5</sub>), which is known as the major dyeing component of the wood of *C. sappan* L. Chitosan powder (supplied by Taehoon-Bio Co., Uljin, Korea) with a weight-average molecular weight of 31,000 and degree of deacetylation of approximately 95% was used. Aluminum potassium sulfate [AlK

(SO<sub>4</sub>)<sub>2</sub>·24H<sub>2</sub>O] was used as the metal mordant. Oxygen gas with a purity higher than 99.99% was used as the processing carrier gas. All other commercially available solvents and reagents were general-purpose grade and were used as received without further purification.

### Plasma apparatus and treatment

A capacitively coupled glow-discharge etching system with a 13.56-MHz radio frequency generator (maximum power of 650 W) was used for the O<sub>2</sub> low-temperature plasma. The experimental apparatus used for the plasma treatment was constructed as previously reported.<sup>13</sup> The characteristics of the plasma device were as follows: reactor capacity, 0.3 m<sup>3</sup> (130 L); electrode mode, parallel-plate internal electrode; reactor type, cylindrical chamber; electrode size, 175 mm × 550 mm × 3 mm; and vacuum pump, 200 L/min.

The PET fabrics were cut into 10 cm × 25 cm × 108 μm samples and then subjected to plasma treatment. Before the plasma treatment, these PET samples were conditioned in a desiccator, vacuum-compressed in silica gel for 24 h or more, and then dried *in vacuo* at 40°C for 12 h. The activation of the PET surface was conducted for 20 min at a gas pressure of 0.5 Torr with a generating power of 300 W while a constant gas flow was maintained through the reactor. After this, the sample was taken out of the reactor and used immediately for dyeing to prevent the reaction of its surface radicals with oxygen or water vapor in the air. In general, it is suggested that plasma-treated fabrics and films should be used immediately because their surfaces are very sensitive to the environmental conditions.

### Chitosan treatment

The aqueous chitosan solutions (10 g/L) were prepared by the dissolution of the appropriate quantity of the polysaccharide in 1 L of water in an acetic acid solution. The dissolution of the chitosan was performed at room temperature through stirring with a magnetic stirrer for over 24 h, and then the solution was immediately used for dyeing to prevent molecular degradation by contact with air. PET fabrics were sufficiently immersed in this chitosan/acetic acid solution for 2 h. After the solution was

**TABLE I**  
Characteristics of Obtained PET

Weave	Fabric count (ends × picks/5 cm)	Yarn no.	Thickness	Weight
Plain	210 × 191	75D × 75D	0.108 mm	67 ± 3 g/m <sup>2</sup>

allowed to thoroughly penetrate the fabrics, it was padded onto PET with a mangle with a 40% wet pickup, cured in an oven for 3 min at 110°C, and dried at room temperature overnight. This was followed by rinsing of the fabrics several times with distilled water until the pH was 7.0 and then complete drying.

#### Aluminum mordant treatment

The natural dyes used for PET conventionally require some chemicals in the form of metal salts to produce an affinity between the fabrics and the pigments, which are known as mordants. An accurately weighed PET sample was treated with aluminum metal salts, and only premordanting with metal salts was carried out before dyeing. The mordant was dissolved in water to obtain a liquor ratio of 1 : 80 (1% owf), and the temperature of this solution was adjusted to 30°C. The PET sample was introduced into the mordant solution and then subjected to further heating. The temperature of the dye bath was raised to 60°C, and it was held at this temperature with mechanical shaking for 30 min. The sample was then rinsed thoroughly with tap water and dried at room temperature.

#### Dyeing

Well-dried stems from the wood of *C. sappan* L. were squashed and retted in distilled water for 24 h and allowed to boil in a beaker kept over a water/MeOH (1 : 4 v/v) bath for quick extraction in 1 h, while the material to liquor ratio was kept at 1 : 10. The procedure was repeated with a mixture of 1750 mL of aqueous MeOH and the previous residual solution for another 1 h, and then it was cooled to room temperature. The solution was filtered for further use.

Dyeing was done with an IR dyeing machine (KSL-24 Perfect, Korea Science Co., Daegu, Korea). The PET fabrics pretreated with the chitosan or low-temperature plasma and the untreated, as-received fabrics were dyed with the previously prepared dye extract while the liquor ratio was kept at 1 : 40. The dye solution was prepared by the addition of 40 mL of the dye extract solution to 1000 mL of water (1 : 40). The temperature of the bath was raised from 30 to 60°C for 30 min after the prepared fabric was dipped in the dye bath, and then it was maintained at this level for another 1 h. The dyed samples were rinsed with tap water and allowed to dry at room temperature for 24 h.

#### Color measurement

To determine the color depth, the color yield of the untreated samples and those treated with chitosan and/or plasma was colorimetrically evaluated by

surface light reflectance measurement with a CCM (X-Rite 8200, X-Rite Co., AC/LLC United States). The viewing conditions were the illuminant D65, a 10° standard observer system, and the wavelength range of 400–800 nm. Each sample was measured five times at different portions of the sample, and the average reflectance was recorded. The color depth (i.e.,  $K/S$ , where  $K$  and  $S$  are the coefficients of light absorption and light scattering, respectively) at the maximum absorption wavelength was assessed by the Kubelka–Munk equation:

$$K/S = (1 - R)^2/2R$$

where  $R$  is the reflectance of the dyed fabric at the maximum absorption wavelength.

The color difference ( $\Delta E$ ) values, based on whiteness ( $L^*$ ), redness ( $a^*$ ), and yellowness ( $b^*$ ), were determined with the modified CIELAB formula equation as follows: CIELAB formula equation as follows which is a rectangular coordinate system with axes of  $L^*$ ,  $a^*$ , and  $b^*$

$$L^* = 116(Y/Y_0)^{1/3} - 16$$

$$a^* = 500[(X/X_0)^{1/3} - (Y/Y_0)^{1/3}]$$

$$b^* = 200[(Y/Y_0)^{1/3} - (Z/Z_0)^{1/3}]$$

where  $X/X_0$ ,  $Y/Y_0$ , and  $Z/Z_0$  are greater than 0.01;  $X$ ,  $Y$ , and  $Z$  are the tristimulus values of the sample, and  $X_0$ ,  $Y_0$ , and  $Z_0$  are the tristimulus values of the specific reference white considered ( $Y_0 = 1$ ). Moreover,

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]$$

where

$$\Delta L^* = L_T^* - L_S^*$$

$$\Delta a^* = a_T^* - a_S^*$$

$$\Delta b^* = b_T^* - b_S^*$$

$L^*$ : Lightness of batch,  $L_S^*$ : Lightness of standard,  $a^*$ : Redness-greenness of batch,  $a_S^*$ : Redness-greenness of standard,  $b^*$ : Yellowness-blueness of batch,  $b_S^*$ : Yellowness-blueness of standard.

#### Scanning electron microscopy (SEM)

To examine the morphologies of the plasma- and/or chitosan-treated PET samples, they were ion sputter-coated (VPS 020, Ulvac Vacuum Co., Ltd., Osaka, Japan) with a layer of white gold (400 Å) for 120 s and observed through an SEM S-4100 (Hitachi Co.,

Ltd., Tokyo, Japan) operating at an acceleration voltage of 15 kV. All images were taken at a magnification of 5000 $\times$ .

### Color fastness

The color fastness to washing tests were carried out according to KS K 0903 (based on ISO 105-A05). The samples were estimated against the standard gray scale for color change and stain.

## RESULTS AND DISCUSSION

### Weight loss of PET fabrics by plasma

The use of glow-discharge plasma could be ideal for selective and surface-specific modification. To enhance the modification of hydrophobic PET, the surfaces were exposed to low-temperature plasma under oxygen gas. Several factors, such as the plasma power and contact time, were controlled to obtain the optimum plasma conditions. The conditioned weights at 65% relative humidity and 21 $^{\circ}$ C were measured before and after the plasma treatment to determine the weight loss. The weight percentage changes were calculated from the weight change in the fabrics after the plasma treatment, and the weight loss was calculated with the following formula: Weight loss (wt %) =  $[(W_0 - W_1)/W_0] \times 100$ , where  $W_0$  and  $W_1$  represent the weights of the PET fabric before and after the low-temperature plasma treatment at 0.5 Torr for 20 min, respectively.

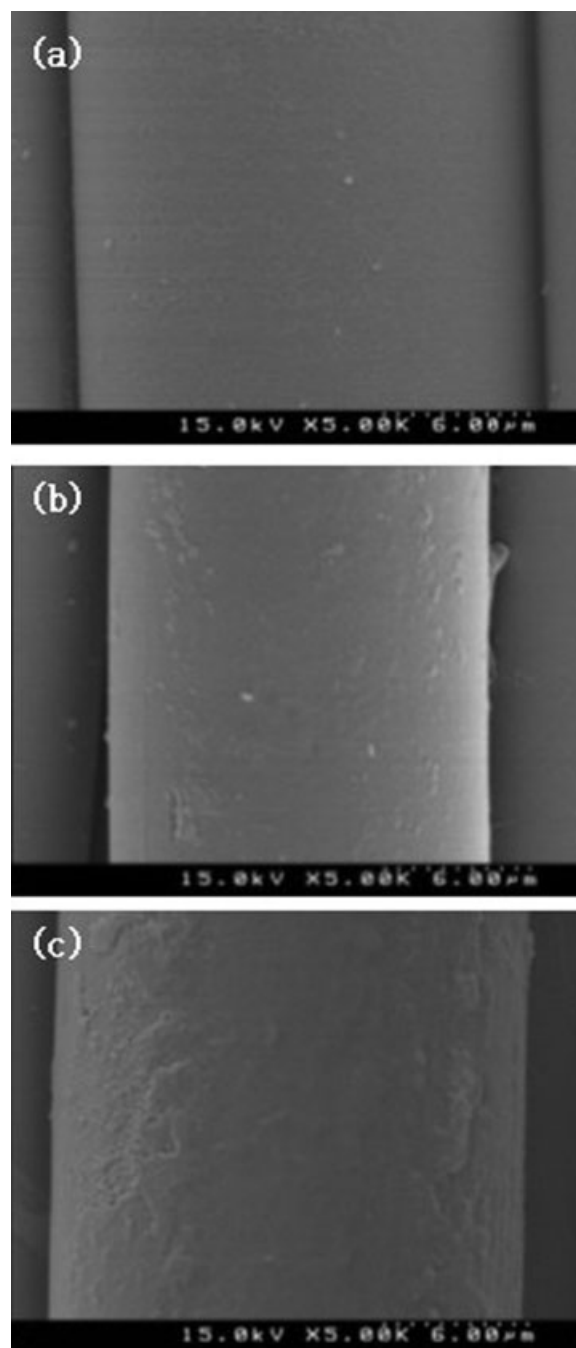
The weight loss of the PET surface was found to be about 1.4%, as shown in Table II. It was supposed that the weight loss would be dependent on the discharge conditions, such as the discharge power and contact time, as well as the surface characteristics of PET, such as its dense, tight, hydrophobic properties. However, the exposure of the PET surface to the O<sub>2</sub> low-temperature plasma was expected to make it hydrophilic.

### Surface characterization of PET by SEM

Figure 2 shows the SEM images of PET treated with the plasma at 300 W for 20 min [Fig. 2(a)], chitosan in a 1% aqueous acetic solution [Fig. 2(b)] and both the plasma and chitosan [Fig. 2(c)]. As shown in Figure 2(a), the physically plasma-etched sample had a

**TABLE II**  
Weight Loss of PET Fabrics Treated by Low-Temperature Plasma

Plasma condition	Weight (g)		Weight loss (%)
	Before	After	
Maximum power = 300 W Conduct time = 20 min Treatment temperature = 30 $^{\circ}$ C	1.17	1.59	1.4



**Figure 2** SEM images of PET fabrics: (a) fabric plasma-treated at 300 W for 20 min, (b) fabric chitosan-treated with a 1% aqueous acetic solution, and (c) plasma- and chitosan-treated fabric.

comparably smooth surface. It is supposed that the effective surface area is increased and provides more possibilities for adhesion relations between the PET fabric and the chitosan, and this indicates that the O<sub>2</sub> low-temperature plasma treatment acts primarily on the microstructure of the surface in the beginning. Moreover, the image of the chitosan-treated sample in Figure 2(b) indicates that some of the chitosan adhered thinly. However, the structure of the

plasma-pretreated and chitosan-coated sample showed an indication of distinct chitosan adhesion. These results can be regarded as indicating that there is a tendency for the physicochemical bonding between the free amino groups of the chitosan molecules and hydrophilic groups of the PET to be increased by the plasma etching.

### Add-on of chitosan

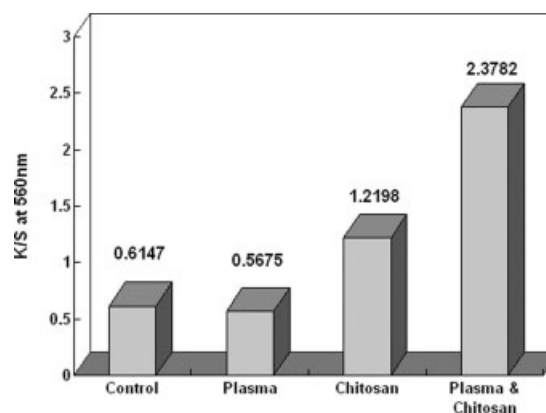
Chitosan is a cationic, unbranched, long-chain polymer whose structure is analogous to that of cellulose in which the hydroxyl groups on C<sub>2</sub> have been substituted by either acetyl amino or amino groups. The application of chitosan to fabrics is known to be associated with problems such as weak binding, uneven distribution, and low permeability. In an attempt to overcome these problems, chitosan has been occasionally applied in the form of a mixture with a surfactant. However, using chitosan to treat fabrics offers the possibility of producing deeper and more vivid colors without an increase in the concentration of the dye used, thereby producing more environmentally friendly fabrics. Essentially, PET shows no affinity for most natural dyes, whereas the chitosan-treated samples showed a greater dye uptake because of the bonding of the amino groups to the PET surfaces. To confirm the adhesion between the PET fabrics and chitosan, the samples were dried completely until the weight loss was stabilized, and then their conditioned weights were measured before and after the treatment of the samples. The add-on rates were obtained with the following equation:

$$\text{Add-on(\%)} = \{(W_1 - W_0)/W_1\} \times 100$$

where  $W_0$  and  $W_1$  represent the weights of the untreated and chitosan-treated PET, respectively. From this result, the add-on rates of the chitosan-treated PET fabrics were calculated to be about 0.64%.

### Color estimation

In typical dyeing systems, certain additives such as metal salts and surfactants can either speed up or slow down the process of dye uptake. Harry<sup>14</sup> suggested that the sorption of dyes by chitosan is exothermic, whereas an increase in temperature leads to an increase in dye sorption but diminishes the total sorption capacity. However, problems such as the low exhaustion of the dyes and the fastness of the dyed fabrics with natural dyes have been overcome with metallic salts as mordants, which are traditionally used for the development of color depth.



**Figure 3**  $K/S$  values of the PET fabrics dyed with *C. sappan* L. under various treatment conditions.

It is well known that PET fabrics dyed with natural dyes have a very low  $K/S$  value and fastness. Figure 3 shows that the dyed samples obtained with different treatment approaches gave rise to different depths of PET coloration. The  $K/S$  value of the dyed PET fabrics was mostly increased by the pretreatment with chitosan and/or plasma. The  $K/S$  value of the plasma-treated PET fabrics slightly decreased compared to that of the control. This seems to be caused by the hydrophobic functional groups of PET and plasma factors such as the contact time, surface area, and generating power. Also, it is interesting to treat plasma with chitosan because it could contribute to the effect of the O<sub>2</sub> low-temperature plasma treatment in a reaction with the ligands of chitosan. Therefore, the  $K/S$  value was increased, and this demonstrated the effect of the plasma and chitosan treatment on the dyeing process. Furthermore, the treatment with chitosan resulted in a high  $K/S$  value in all cases, and the  $K/S$  value of the sample treated with both the plasma and chitosan was increased more than twofold compared to that of the samples treated with only the plasma or chitosan. This result might be due to the higher affinity of brazilin for the pretreated PET fabrics. The  $K/S$  values of the chitosan-treated PET fabrics were higher than those of the mordant-treated PET. This may be due to the easier formation of coordination between the amino groups ( $-NH_2$ ) of chitosan and the hydroxyl groups of brazilin. Therefore, it can be inferred that even though the  $K/S$  values were not sufficiently high, the treatment with the plasma and chitosan was very effective in improving the dye uptake of the PET fabrics.

The discharged colorant of the aqueous extract obtained from the stems in hot water showed a reddish or dark orange color. The effect of the treatment condition on the colorimetric  $L^*$ ,  $a^*$ ,  $b^*$ , and  $\Delta E$  values for PET is shown in Table III. The plasma

pretreatment resulted in a higher value of  $L^*$  corresponding to lighter shades, whereas the PET fabrics subjected to chitosan treatment showed lower  $L^*$  values signifying deeper shades. The enhanced color depth of the dyed fabrics afforded by the pretreatment with chitosan is reflected in the lower  $L^*$  value of the pretreated dyed fabric, as shown in the corresponding colorimetric data (Table III). It is also obvious from Table III that the pretreatment yielded a color that was redder than that obtained without the pretreatment. The  $L^*$ ,  $a^*$ ,  $b^*$ , and  $\Delta E$  values of the as-received, untreated PET fabric were 73.89, 5.17, 10.80, and 17.92, respectively. However, the  $\Delta E$  values of the fabrics pretreated with chitosan- and plasma-treated PET fabrics were slightly decreased compared to those of the nonpretreated samples. In the case of the chitosan- and plasma-pretreated sample,  $\Delta E$  was considerably higher with a  $K/S$  value of 44.67. Obviously, the amino groups of chitosan created additional dye sites on the PET fabrics, and this was accompanied by an increase in the dye uptake. Above all, it is certain that the red color was deeper than that of the received PET in all cases, unless the fabrics were subjected to the  $O_2$  low-temperature plasma treatment. Also, when the fabrics were treated with chitosan, the redness of the dyed samples changed from yellow-red to reddish. When the chitosan-treated samples were treated with plasma etching, the  $L^*$ ,  $a^*$ ,  $b^*$ , and  $\Delta E$  values were 48.00, 20.47, 2.18, and 44.67, respectively. At this time, as mentioned previously, the  $\Delta E$  value was more than twice as high as that of the as-received PET. From these results, it was concluded that  $K/S$  exhibits a tendency similar to that of  $\Delta E$ .

### Color fastness

Color fastness is an important property that is correlated to the color quality of commercial products. To determine whether the pretreatment provided increased dye durability and dye uptake, the dyed PET fabrics were subjected to a washing test using a standard gray scale for the evaluation of their color change. Table IV lists the effects of the different dyeing systems on the color fastness to washing of the PET fabrics pretreated with plasma and/or chitosan and then dyed with the solution of the *C. sappan* L.

**TABLE III**  
Color Values of the PET Fabrics Dyed with *C. sappan* L. Extract Under the Various Treatment Conditions

Experiment	$L^*$	$a^*$	$b^*$	$\Delta E$
Dye	73.89	5.17	10.80	17.92
Plasma + dye	75.10	4.03	9.95	16.16
Chitosan + dye	63.28	13.19	4.53	14.70
Plasma + chitosan + dye	48.00	20.47	2.18	44.67

**TABLE IV**  
Color Fastness of the PET Fabrics Against Washing

Experiment	Color change	Stain
Dye	2	3-4
Plasma + dye	3	4
Chitosan + dye	2	3-4
Plasma + chitosan + dye	3	3-4

extract. It was expected that the PET fabrics pretreated with the plasma and/or chitosan would have superior color fastness to washing. However, contrary to our expectations, the results do not show any significant overall change in the color fastness compared with that of the untreated fabrics. This result suggests that the pretreatment with the mordant does not directly affect the adsorption of the dye into the PET fabrics and that the mordanting of the PET fabrics with the metallic salt,  $AlK(SO_4)_2$ , affected the substrates more than the chitosan and/or plasma treatment with respect to the washing fastness of the *C. sappan* L. extract when the mordanting and dyeing were done at 60°C. Therefore, from the data presented in Table IV, it is evident that, in general, the washing fastness of the fabrics pretreated with plasma and/or chitosan before dyeing was not lower than that of the fabrics untreated before the dyeing procedures, and this indicated that the brazilin in the *C. sappan* L. extract was bound to the free amino groups during the chitosan pretreatment. As shown in Table IV, the washing fastness of the PET fabrics was similar to that of the untreated samples. It was concluded that although the dyed PET fabrics had reasonable  $K/S$  values, most of the dye extract was separated from the dyed materials during the washing.

### CONCLUSIONS

A study was made of the dye uptake by PET fabrics subjected to chitosan and/or  $O_2$  low-temperature plasma as a premordant in which the fabric was processed by a padding, plasma-etching, and immersion procedure. The dye uptake of the chitosan-treated PET fabrics was increased, and the  $\Delta E$  value for the brazilin dyestuff and PET fabrics was also improved. With respect to the surface modification by the plasma, the morphology observed by SEM revealed that the sample treated for 20 min was not significantly changed. However, when this sample was treated with chitosan and/or plasma, its  $K/S$  value was increased. In particular, in the case of the chitosan- and plasma-treated PET, significantly higher values were obtained. The color fastness to washing was generally not sufficient, with the

results for the treated samples being similar to those of the untreated ones.

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