

# Ammonia/Acetylene Plasma Deposition: An Alternative Approach to the Dyeing of Poly(ethylene terephthalate) Fabrics at Low Temperatures

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**ABSTRACT:** It has long been recognized that dyes other than disperse dyes would play a much larger industrial role if they could be applied to poly(ethylene terephthalate) (PET) fabrics at low temperatures. This research is related to a new process for the dyeing of hydrophobic PET with hydrophilic acid dyestuffs. The process is based on low-pressure plasma polymerization using an ammonia/acetylene gaseous mixture, which provides a nanoporous plasma coating containing accessible amine groups. Surface functionalization and crosslinking have been analyzed with X-ray photoelectron spectroscopy. The color strength (absorption coefficient/scattering coefficient) of

dyed PET is evidently improved by the attachment of dye molecules to the plasma polymer coating. The dyeability strongly depends on the plasma exposure time, gaseous mixture, and energy input. The permanency of the bond between the dye molecules and the plasma film can be characterized as the fastness property of dyed PET. The stability of the plasma coating has been examined with an abrasion and pilling tester. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 2545–2552, 2009

**Key words:** dyes/pigments; functionalization of polymers; thin films; plasma polymerization; polyesters

## INTRODUCTION

Poly(ethylene terephthalate) (PET) fabrics, a type of polyester fabric, possess excellent physical and chemical properties.<sup>1</sup> In addition to their common uses in textiles and clothing, they have great importance in technical textiles, home textiles, the automobile industry, and medical textiles.

It is well known that polyesters are dyed with disperse dyes at high temperatures (~ 130°C; sublimation becomes a more critical factor) in a closed system because of their hydrophobic nature.<sup>2</sup> The selection of dyestuffs is also limited to disperse dyes for polyesters because of their compact structure and high crystallinity.<sup>3</sup> The low and finite water solubility of these dyes is considered a critical factor in determining the leveling properties and the dyeing rate.<sup>4</sup> High-temperature dyeing leads to difficulties

for polyester/natural blends, causing damage to the natural fibers during the dyeing process. Because of dye reduction and migration, the washing fastness has been found to be satisfactory for dyeing with this dye class.<sup>5</sup> Moreover, although textile dyestuffs rarely cause allergic reactions, nevertheless, they are the most frequent textile allergens. A significant number of dyes (two-thirds of all allergic dyes) that are potentially injurious to health belong to the class of dispersion dyes.<sup>6</sup> The disperse dyes with an allergy-releasing effect are predominantly yellow, orange, red, and blue dyes, which can also be hidden as mixtures in black textiles. Synthetic fibers bind less firmly with certain types of dyes. This can lead, particularly in damp environments, to an increased migration of dyes from synthetic fiber fabrics, which might result in a contact allergy.<sup>7</sup>

In this context, an alternative dyeing method at low temperatures (or with alternative dyes) for polyesters is of growing interest. There has been very little attention focused on the application of hydrophilic acid dyes to hydrophobic PET fabrics. Acid dyes, which show excellent color brightness and good wet fastness, can easily be applied to plasma-activated polyesters at a low temperature (~ 80°C) within an hour of dyeing time; plasma modification

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is used as an alternative to the required pretreatment of PET textiles. Many authors have investigated the dyeability of plasma-treated polyesters. Sarmadi and Kwon<sup>8</sup> observed that the dyeability with a basic dye (at a dye-bath temperature of 100°C and with a dyeing time of 2 h) can be improved by an increase in the time of exposure to CF<sub>4</sub> cold plasma, and they found absorption coefficient (*K*)/scattering coefficient (*S*) values (where *K/S* is the color strength) between 0.50 and 1.51 for 2% owf dark-shade dyeing with a hydrophobic basic dye.<sup>8</sup> Beside plasma activation by non-film-forming gases, the applicability of plasma polymerization to textiles has recently been reviewed.<sup>9</sup> The dyeability with a basic dye is enhanced on PET/cotton blends by *in situ* polymerization of acrylic acid and water, as investigated by Öktem et al.<sup>10</sup> The work of Ferrero et al.<sup>11</sup> has shown that the colorfastness to washing with a basic dye on PET by *in situ* polymerization of acrylic acid with low-temperature plasma is unsatisfactory, probably because of unstable bonds between grafted acrylic acid and dye molecules. Antireflecting coating layers have been deposited with organosilicon compounds with atmospheric plasma, which enhances the color intensity on PET surfaces, as explained by Lee et al.<sup>12</sup> Okuno et al.<sup>13</sup> studied the correlation between the crystallinity and dyeability of PET fibers by using nonpolymerizable gases with low-temperature plasma. They found that plasma-treated samples significantly reduced the dyeability because of the etching of macromolecules constituting the dyeable amorphous phase. Recently, Raffaele-Addamo et al.<sup>14</sup> reported that the color depth of air radio frequency plasma-treated PET fibers is related to their topographical characteristics and to their chemical surface composition. They observed that the *K/S* value with a disperse dye at a dyeing temperature of 100°C can be increased by a reduction of the fraction of light reflected from treated surfaces. Moreover, much research has also been carried out about the environmentally friendly dyeing of PET with disperse dyes in supercritical CO<sub>2</sub>, which provides the advantage of reducing the need for additional chemicals and wastewater.<sup>3,15,16</sup> The scaling of the supercritical fluid dyeing experiment from a laboratory size to an industrial scale is far from a straightforward procedure because it requires high pressures (260–300 bar). At low pressures, the *K/S* value is decreased, and this yields low dye solubility.<sup>16</sup>

In this research, an attempt was made to solve some limitations of PET dyeing with a hydrophilic acid dye by modification of the surface with a novel nanoporous plasma polymer coating. The dye molecules were attached to the functional plasma film, and no dyeing of the PET fibers occurred. Because the dyeing thus becomes independent of the substrate material, this approach enables the dyeing of

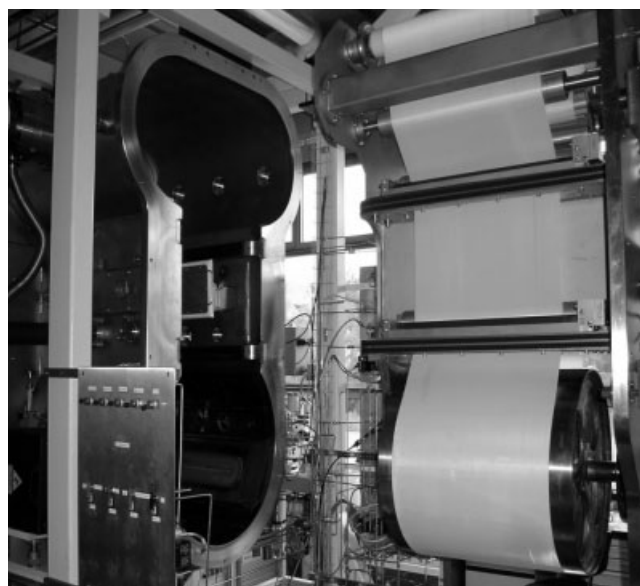


Figure 1 Setup of the web coater.

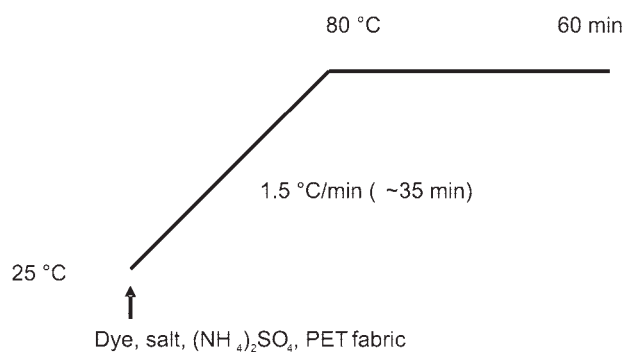
all kinds of synthetic fibers. Surface modification of fabrics, induced by NH<sub>3</sub>/C<sub>2</sub>H<sub>2</sub> discharges, was carried out to incorporate amine end-functional groups into the hydrocarbon plasma polymer and consequently provide accessible functional groups for the diffusion of hydrophilic acid dye molecules into the nanoporous structure.

## EXPERIMENTAL

### Materials and plasma treatments

Tightly woven and washed PET fabric (76 ends/in., 76 picks/in., and 43.5 g/m<sup>2</sup>) from Sefar, Inc. (Heiden, Switzerland), was used in this study. The gases Ar, O<sub>2</sub>, and NH<sub>3</sub> (purity = 99.99 vol %), used in the plasma treatments, were supplied by Carbagas (Gümligen, Switzerland).

The semicontinuous web coater (plasma reactor) used is shown in Figure 1. The fabric samples (maximum width of 65 cm) were continuously transported around the internal cylindrical electrode (drum with a diameter of 59 cm) by take-up rollers driven by a motor. Plasma polymerization was enabled around the drum by 13.56-MHz RF excitation (Cesar 1312, Dressler, Munich, Germany). V/I probe measurements (model 1640, ENI) indicated a power absorption of ~ 80% within the plasma under rather symmetric conditions, that is, low bias voltages. Principally, a second RF electrode mounted in a separated process chamber within the web coater could be used for the plasma pretreatment to enable a one-step process. A pumping system consisting of a rotary pump (Alcatel CIT, Velizy, Cedex, France) and a turbo molecular pump (diffusion pump; DCU 600, Pfeiffer Vacuum GmbH, Asslar, Germany) maintained a base



**Figure 2** Dyeing procedure of the plasma-treated PET.

pressure of  $10^{-3}$  Pa. The working pressure and desired gas flow were monitored and adjusted with an adaptive pressure controller (VAT, Zürich, Switzerland) and a 647B multigas controller (MKS Instruments, Munich, Germany), respectively. The chamber containing the fabric samples placed around the drum was cleaned and etched with Ar/O<sub>2</sub> plasma (400 W, 10 Pa, 1 min) before the deposition. To obtain amine-incorporated functionalized coatings suited for acid dyeing, the plasma process parameters (power, gas flow, and exposure time) were extensively investigated with a process gaseous mixture of NH<sub>3</sub> and C<sub>2</sub>H<sub>2</sub> at a pressure of 10 Pa. A gas shower in the reaction chamber at four positions around the drum enabled a homogeneous treatment along the width and length of the fabrics. After the treatment, the samples were kept in a conditioned room ( $20 \pm 2^\circ\text{C}$ ,  $65 \pm 2\%$  relative humidity) ready for dyeing and further experiments. The chemical characterization of the plasma-polymerized coatings was performed with an X-ray photoelectron spectroscopy (XPS) analyzer (PHI 5600 Multi-Technique system, PerkinElmer, Schwerzenbach, Switzerland), whereas the film thickness on Si wafers was measured by surface profilometry (HRP-75, KLA Tencor, Dresden, Germany). The topographical changes of the plasma-coated surfaces were characterized on Si wafers (100) by atomic force microscopy (AFM; Solver Pro, NT-MDT, Moscow, Russia) in noncontact mode operation. The plasma process parameters and the various fastness properties of dyed PET are also discussed later in this work. The degree of hydrophilicity induced by the plasma treatment was measured on the basis of static contact angle measurements with a G10 (Krüss GmbH, Hamburg, Germany), which was also used for an aging study.

### Dyeing procedure

The dyeing of the plasma-treated samples was carried out in a laboratory-scale machine (Labomat-8, Type BFA-8) manufactured by Mathis (Zürich, Switzerland). Plasma-treated fabrics were dyed with C.I. Acid Blue

(127 : 1). The light-shade dyeing was performed with 0.5% owf acid dye and 5% owf sodium sulfate salt for exhaustion, whereas the pH of the dye bath was adjusted to 4.5–5 by the addition of ammonium sulfate. The liquor-to-fabric ratio in dyeing was 1 : 50, and the following dyeing conditions were adopted: the initial temperature of 25°C was followed by a temperature gradient of 1.5°C/min up to 80°C, and then the dye bath temperature was maintained at 80°C for 60 min. The dyeing method is shown in Figure 2. However, the total dyeing time could be noticeably reduced because the dye molecules did not have to penetrate the polyester structure but only had to penetrate the nanoscaled coating, showing fast saturation.<sup>17</sup> After dyeing, the dyed fabrics were washed with soap (Ultravon W) at 60°C for 30 min (liquor-to-fabric ratio = 1 : 100), then rinsed with cold, hot, and cold water, and finally dried at room temperature.

### Color measurement

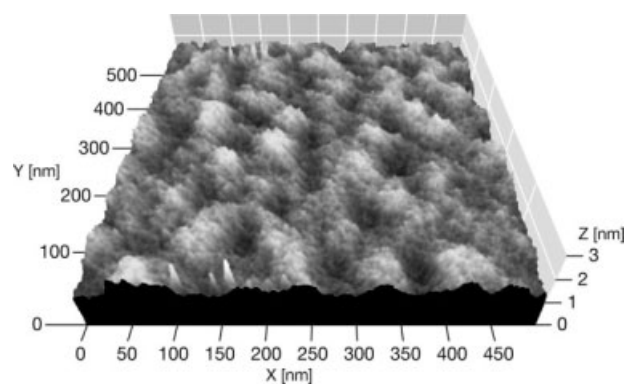
The color coordinators ( $L^*$ ,  $a^*$ ,  $b^*$ ,  $C^*$ , and  $h^\circ$ ) were measured with a Datacolor Spectraflash (Datacolor AG, Switzerland). The reflectance [ $R$  (%)] value of the dyed fabrics was measured over the wavelength range of 360–750 nm. The illuminant type was D65, and the observer angle was 10°. The  $K/S$  values at 490 nm for the fabrics were calculated with the Kubelka–Munk equation:

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

## RESULTS AND DISCUSSION

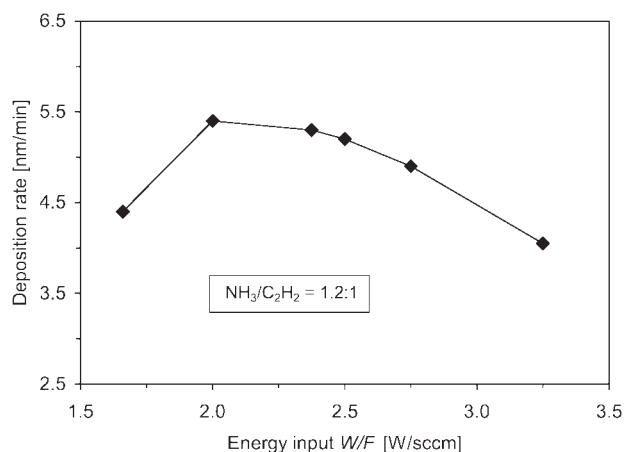
### Surface modification of PET by plasma polymerization

The structural modification of amorphous hydrogenated Carbon (a-C) : H films by the addition of nitrogen to the hydrocarbon precursor yields hydrophilic functional sites (mainly amine functionalities) within a-C : H : N coatings.<sup>18</sup> The a-C : H : N films become



**Figure 3** AFM image of the a-C : H : N plasma coating ( $W/F \approx 2.4$  W/sccm,  $\text{NH}_3/\text{C}_2\text{H}_2 = 1.2$ ).





**Figure 4** Effect of  $W/F$  (RF power/ $C_2H_2$  flow) on the deposited plasma film.

more graphitic, and the density of voids can increase with the incorporation of nitrogen and/or nitrogen functionalities into the coating.<sup>19,20</sup> As shown in Figure 3, the AFM image indicates that the apparent voids in the coating are below 25 nm. The (dissolved) dye molecules, a few nanometers in size, are small enough to diffuse easily through the interconnected voids of the nanoporous structure into the plasma polymer and form dye–film bonds.<sup>17</sup> Sufficiently large nanopores strongly increase the specific surface area and provide high functionality to attach molecules such as dye-stuff. Moreover, the gaseous mixture of ammonia and acetylene ensures a textured surface rather than a smooth one.<sup>18</sup> Previously, we examined the mass deposition rates for a wide range of  $NH_3/C_2H_2$  ratios.<sup>21</sup> It was found that plasma deposition, particularly in radically promoted plasma polymerization, is governed by the composite parameter power input per monomer flow or energy input ( $W/F$ ). At moderate  $W/F$  values ( $2.0 \text{ W/sccm} \leq W/F \leq 2.4 \text{ W/sccm}$ ), a maximum in the deposition rate can be achieved, as shown in Figure 4. Increasing the  $C_2H_2$  content in the gas mixture leads to an increase in the number of hydrocarbon radicals in the active plasma zone, resulting in a gradual increase in the a-C : H film character and enhanced deposition rates.<sup>21</sup> Increasing  $W/F$  yields more fragmentation and thus also more hydrocarbon radicals. However, modifications in film growth such as densification, degradation reactions of polymer chains, and chemical and physical etching and some temperature effects can be observed at higher specific energies ( $W/F > 2.4 \text{ W/sccm}$ ), yielding a reduced deposition rate due to the transition between film growth and erosion.<sup>9,17,21</sup> Moreover, a higher  $W/F$  value prevents the formation of voids through high crosslinking of the amorphous network. As a result, at higher  $W/F$  values, reduced dye molecule penetration into the coating can be observed during the dyeing process.<sup>17</sup> At very low flow rates, the film growth is

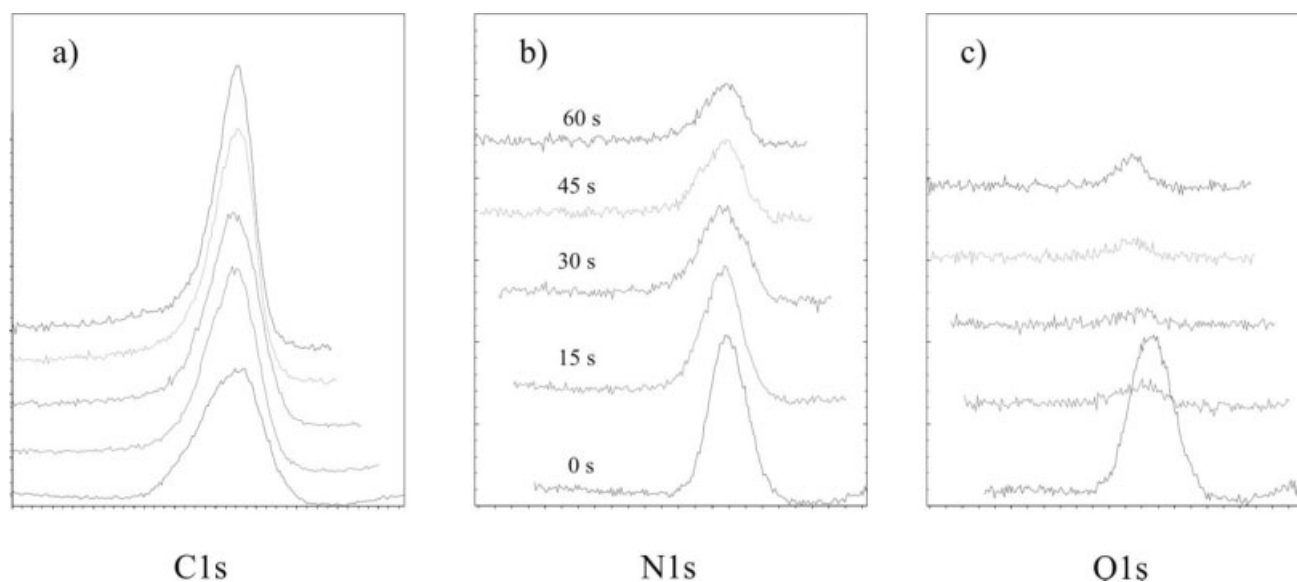
limited by the availability of the monomer supply.<sup>22</sup> Commonly, in low-pressure plasmas, more energetic particles and long-living radicals are generated in comparison with atmospheric-pressure plasma. As a result, etching effects can play a major role at low pressures. However, within ammonia/acetylene discharges, the etching conditions can be effectively controlled during plasma polymerization to produce the formation of voids within the growing films.<sup>23</sup> It can be concluded that the optimum chemical modification is attained at a moderate  $W/F$  value and a suitable  $NH_3/C_2H_2$  ratio ( $\sim 1.0$ ), leading to accessible amine-functional groups within a-C : H : N coatings.<sup>24</sup> With the web coater at Empa, it has been demonstrated that these plasma coatings can be deposited from reel to reel with a width of 65 cm. Upscaling to industrial reactors is facilitated by the use of the power input into the plasma zone per monomer flow ( $W/F$ ) as a similarity parameter.<sup>25,26</sup>

### XPS analysis

To observe the incorporation of nitrogen into the a-C : H : N films, we performed Ar sputtering at five different time frames (0, 15, 30, 45, and 60 s), and C1s, N1s, and O1s peaks were recorded [Figs. 5(a–c)]. It can be seen from the C1s peak that the carbon network (C–C, C–H, C=N, C–N, C=O, COO, etc.) increases with the increase in the sputtering time.<sup>24</sup> In contrast, the opposite phenomenon was observed for the N1s peak, with the incorporation of nitrogen (N–C, N=C, N–O, etc.) decreasing as the sputtering time was increased (from 22 to 10 atom %). Because the deposition conditions were kept constant during plasma polymerization (yielding the same film chemistry, which was proved for different deposition times), preferential sputtering effects of weaker nitrogen groups during XPS measurements within a crosslinked hydrocarbon matrix can be assumed. In general, nitrogen is considered to be a replacement of carbon in the plasma film, yielding nanostructured (porous) crosslinked surfaces. This analysis is in good agreement with the results of other groups.<sup>20,22</sup> Surface oxidation is obtained, most likely because of the incorporation of, for example, C=O, COO, and N–O groups during postplasma reactions in contact with the atmosphere before the XPS analysis.<sup>24</sup> As these hydrophilic groups stay on the topmost layer of the surface, after a short sputtering time, the detected oxygen functionalities are below 2 atom %, as shown in Figure 5(c), indicating less oxidation within the nanoporous structure and thus fewer radical sites left after plasma polymerization.

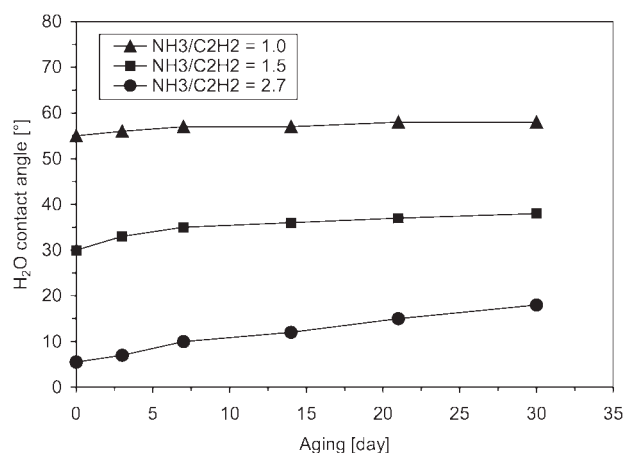
### Contact angle

The static contact angles were measured on glass substrates and PET fabrics with a deionized water



**Figure 5** C1s, N1s, and O1s spectra in the a-C : H : N films for different sputtering times: 0, 15, 30, 45, and 60 s ( $W/F \approx 2.4$  W/sccm,  $\text{NH}_3/\text{C}_2\text{H}_2 = 1.2$ ).

droplet of 7  $\mu\text{L}$  at an ambient temperature of 20°C and at 65% relative humidity. The untreated PET showed a hydrophobic nature with a contact angle of  $\sim 80^\circ$  because of the textured surface and some manufacturing residuals. The wettability of PET fabrics was improved remarkably by the plasma coatings: the water drop on the surface disappeared immediately in all cases, and this showed complete wetting due to capillary effects. To obtain an effective contact angle on textile structures, a more sophisticated analysis can be performed.<sup>27,28</sup> To analyze the surface hydrophilic effect under the different treatment conditions, the static contact angles were also measured on glass substrates. Figure 6 shows the contact angle as a function of aging for different gas ratios. It is evident that at a  $\text{NH}_3/\text{C}_2\text{H}_2$

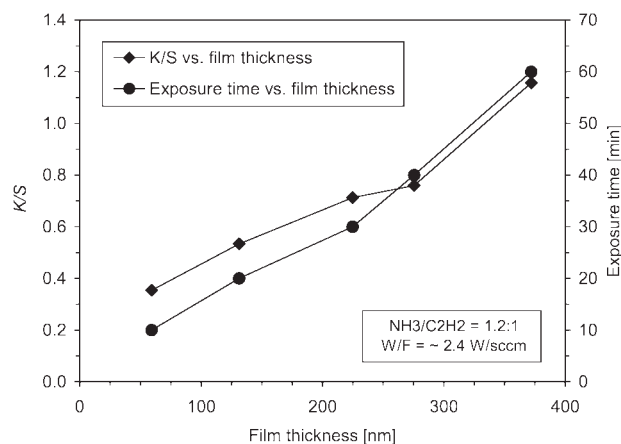


**Figure 6** Water contact angle (static) on plasma-treated glass substrates with aging for different  $W/F$  values (RF power/ $\text{C}_2\text{H}_2$  flow).

gas ratio greater than 2.7, there is a large decrease in the contact angle below  $20^\circ$  even after 30 days of aging. As discussed previously, the optimum plasma deposition was obtained at the moderate  $W/F$  value of  $\sim 2.4$  W/sccm and at a gas ratio of around 1.0, leading to stable nanoporous a-C : H : N coatings; this is supported by the observation of higher  $K/S$  values. The contact angles were found to be increased under these conditions, but they were still below  $60^\circ$  (Fig. 6), showing the hydrocarbon nature of these plasma coatings due to increased monomer fragmentation accompanied by an increase in the deposition rate. After 2 weeks of storage, the contact angles of these coatings tended to saturate as the surface reorientation and reorganization stabilized (lower number of polar functionalities at the film surface). On the other hand, at a gas ratio greater than 2.7, the high number of polar functionalities resulted in a slow gradual increase in the contact angle with storage times up to 30 days because of restructuring on the modified amorphous surfaces or simply hydrocarbon adsorption from the environment. On the other hand, several groups like our group have reported stronger and faster reorganization observations for PET films and PET fibers by nonpolymerizable RF plasma (e.g.,  $\text{Ar}/\text{O}_2$ ).<sup>27,29,30</sup> Hence, contact-angle measurements proved the permanence of the plasma polymer coatings, whereas no direct dependence on the incorporated functional groups, that is, the dyeability, was observed.

### Surface dyeability

Plasma polymerization significantly influences surface charges on the substrate because of the addition



**Figure 7** Relative  $K/S$  values depending on film thickness and exposure time (light-shade dyeing with 0.5% owf acid dyes).

of reactive functionalities to the modified surfaces. The positively charged amine end groups are incorporated into the plasma-deposited film; therefore, an anionic dye is used to dye the film. It is important to note that the dyeability is independent of the substrate material because only the plasma surface film is dyed without changes in the properties of the bulk textile. The dissolved dyes, adsorbed onto the thin film, then easily diffuse, as these dye molecules are small in size (a few nanometers), into the water-filled pores. They are able to form an ionic bond with the amine end groups. In this case, the dyeing principle is similar to that for natural fiber dyeing.

Dyeability was markedly improved with a relative  $K/S$  value up to 1.2 for 0.5% owf light-shade dyeing. This value strongly depended on the plasma-deposited film, whereas the  $K/S$  value of the untreated PET could be given as approximately zero, as no dyeing was possible. As shown in Figure 7, the dye uptake increased almost linearly with the increase in the film thickness.<sup>12</sup> These results also indicate that the error for the  $K/S$  measurements can be assumed to be smaller ( $\pm 0.1$ ) in comparison with conventional dyeing of PET fibers, probably because of the principle difference in the dyeing mechanism. The gaseous mixture (suitable  $\text{NH}_3/\text{C}_2\text{H}_2$  ratio  $\sim 1.0$ ) helped to build up voids in the deposition, resulting in a nano-

porous plasma polymer coating that was accessible to dye molecules throughout the entire film volume.<sup>20,31</sup> In contrast, the dyeability of the plasma coatings was found to be low at a gas ratio greater than 2.7 because of the lower number of amines (stronger fragmentation and plasma–surface interaction) and less nanoporous character (densification). Thus, coloration depended not on the surface wettability but on the density of the amine end group. Depending on the nanoporous character, a high specific surface area was provided, improving the dyeability. The color intensity at different positions for each dyed sample was measured, and the values were found to be almost identical and thus confirmed level dyeing. This additionally indicated the homogeneous distribution of functional groups all over the plasma polymer, as also seen in the XPS analysis.

The relative  $K/S$  value was increased gradually with an increase in the plasma exposure time, as can be seen in Figure 7. It is noteworthy that with increasing plasma process time, the penetration of reactive plasma species yielding plasma polymerization into the textile structure was enhanced, even in the interfilament or inter yarn spaces, resulting in better dyeability, that is, a higher number of amine groups. The deposited film thickness was directly proportional to the treatment time. On the other hand, the reduced film thickness at very low flow rates led to a lower  $K/S$  value of the PET fabrics. This result is consistent with the results of Okuno et al.<sup>13</sup> It was found that the a-C : H : N coatings showed excellent stability and adhesion to the fabric surface with an abrasion and pilling tester (NU-Martindale, James H. Heal, England). No damage to the film and fibers on the surface of the plasma-treated and dyed PET was detected after 60,000 cycles (tested according to SN 198514). Recently, we proved a reduced yellowness index with ammonia/ethylene mixtures instead.<sup>18</sup>

The change in color was also investigated on the basis of the CIELAB color space in terms of colorimetric data ( $L^*$ ,  $a^*$ ,  $b^*$ ,  $C^*$ , and  $h^\circ$ ) at different exposure times and with the same  $W/F$  value at a constant pressure. Table I shows that the changes in

**TABLE I**  
Effect of Plasma Exposure Time on Light-Shade Dyed PET with 0.5% owf Acid Dyes

Power (W)	Plasma parameter				Color coordinate (D65/10)				
	Pressure (Pa)	Time (min)	$\text{C}_2\text{H}_2$ (sccm)	$\text{NH}_3$ (sccm)	$L^*$	$a^*$	$b^*$	$C^*$	$h^\circ$
475	10	10	200	250	65.95	-11.08	-5.45	12.35	206.21
475	10	20	200	250	61.78	-11.79	-2.67	12.09	192.75
475	10	30	200	250	60.08	-10.62	2.12	10.83	168.69
475	10	40	200	250	57.20	-11.95	3.10	12.00	185.27
475	10	60	200	250	55.38	-9.02	7.57	11.78	140.00

**TABLE II**  
Colorfastness Properties of Plasma-Treated Dyed PET Fabrics

Exposure time (min)	Color change	Staining		Rub	
		Cotton	Wool	Dry	Wet
10	3-4	4	3-4	4	3
20	3	4	3	4	3
30	3-4	3-4	3-4	4	3
40	3	3-4	3	4	3
60	4	4	4	4-5	3

$W/F \approx 2.4 \text{ W/sccm}$ ;  $\text{NH}_3/\text{C}_2\text{H}_2 = 1.2$ .

the  $L^*$  values were closely related to the changes in the  $h^\circ$  values. Although a decrease in the  $L^*$  and  $h^\circ$  values of the dyed samples correlated with increasing exposure time, no significant change in  $C^*$  was observed. A similar trend was reported for aramid fabrics with C.I. Disperse Blue 56 by sputter etching.<sup>32</sup> Although only slight changes were noticed for the red/green component  $a^*$ , the blue/yellow component  $b^*$  increased rapidly in the color value with an increase in the plasma exposure time. This implies that the yellowness index increased with the film thickness because of more unsaturated bonds on the surface; this is one disadvantage of using acetylene ( $\text{HC}\equiv\text{CH}$ ) as a film-forming monomer.

In conclusion, the color depth of plasma-treated PET fabrics can be improved markedly, depending on the film thickness and the amine functionalities inside the deposited film. Moreover, the depth of the shade of the dyed fabrics is influenced by the surface morphology,<sup>17,18</sup> and in contrast, a dark shade is difficult to obtain because of the smooth surface of synthetic fibers. The plasma modification enhances the surface roughness and adhesion of PET, leading to lower light reflection [ $R$  (%)] due to interference and scattering effects, as a result of the higher  $K/S$  value.<sup>32-34</sup>

### Fastness properties

The washing colorfastness of the dyed samples was assessed with the ISO test method. Under D65 illumination, color changes, staining, and rubbing were evaluated with gray scales: the ISO-105-A02 gray scale for assessing changes in color and the ISO-105-A03 gray scale for staining and rubbing. Table II shows that acid dyeing on plasma-treated samples displayed acceptable fastness properties to laundering and rubbing. It can further be seen that no significant difference in the two fastness properties could be detected. This finding demonstrates that a permanent ionic bond was obtained between the dye molecules and amine end groups in the functionalized coating.

### CONCLUSIONS

Amine-incorporated functional coatings were deposited onto PET fabrics with low-pressure RF plasma polymerization. The plasma treatment significantly improved the dyeability and colorfastness properties of dyed PET with an acid dyestuff. With the incorporation of nitrogen into the a-C : H : N films, the film morphology could be influenced to obtain a nanoporous structure. The acid dye molecules were found to diffuse into the amine-functionalized nanoporous film and formed ionic bonds with amine end groups. The dye uptake was strongly correlated with the plasma process time, that is, with the deposited film thickness, and this indicated that only the plasma coating on the PET fibers was dyed, not the PET fibers themselves. The  $K/S$  values could be controlled by the adjustment of the film thickness during plasma polymerization. Moreover,  $W/F$  and the gas ratio, which have a strong influence on film growth and film structure, should be considered to obtain higher  $K/S$  values. The film growth was strongly influenced by  $W/F$ . A moderate  $W/F$  value (between 2.0 and 2.4 W/sccm) gave the optimum film deposition with respect to the dye uptake and thus functional group density. Because  $K/S$  values are enhanced with the number of incorporated accessible amine groups, the surface hydrophilicity does not strongly influence the dyeability. It is obvious that the entire dyeing process is independent of the substrate material because merely the functional film is dyed. Hence, the same dyeing principle can also be applied to all hydrophobic synthetic textiles, as we have already proved for PP, CA, aramid, and so forth. This study has thus explored a new method for dyeing hydrophobic polyesters at low temperatures. This ecological modification reduces the need for additional chemicals, wastewater, and so forth, and there is a corresponding reduction in the cost of the effluent treatment. Having diversified dyestuff molecules that are small in size will be useful for dyeing plasma-coated fabrics and will facilitate the application of these findings in industry.

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