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Substrate Independent Dyeing of Synthetic Textiles Treated with Low-Pressure Plasmas

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1. Introduction

The synthetic fibers are widely used in apparel and home furnishings due to their good physical and chemical properties. The synthetic fiber market is characterized by a trend towards ever-finer fibers. It is very difficult for these finer fibers to obtain very deep colours via the common dyeing processes. The increasing demand of polyester (PES) such as poly(ethylene terephthalate) (PET) in textile market for high performance applications in smart textiles, technical textiles, operation clothing etc. and more recently, for their potential applications as electronic textiles. It indicates that PET has the potential in research in the future due to the wide range of mechanical properties, relative high melting point and glass transition temperature, insensitivity to common solvents and moisture, chemical inertness. PET, an aliphatic-aromatic polymer composition and thermoplastic, shows a rather hydrophobic nature due to its rigid structure,

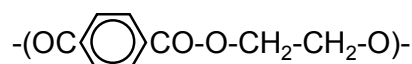$$-(OC\langle\bigcirc\rangle CO\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O)-$$

Fig. 1. Chemical structure of PET

The two carbonyl functions together with the aromatic ring provide the structural rigidity of the macromolecule; little flexibility arises due to the presence of the ethylene group in the repeating unit. The polar ester groups in the PET hold the PES into strong crystals. PET consists of a two-phase structure: crystalline (35 % in vol.) and non-crystalline (65 % in vol.). The most important phase in determining dyeability in the conventional dyeing process is the amorphous region. The PET becomes rubbery and swelling above its glass transition temperature. In this state the dye molecules are able to penetrate into the amorphous region and by cooling down the molecule can be trapped inside the PET macromolecules.

In recent years, consumers have shown an increasing preference for use of synthetic fibers blended with natural fibers to combine advantages of both materials. Due to the hydrophobic nature synthetics such as PES fibers are dyed at high temperatures around 130 °C and high pressure, this needs lot of energy and special equipment (Xu et al. 2002). Moreover, since polyesters are stronger than natural fibers, PES fabric blends containing wool, cotton etc. are very popular, since PES makes the fabrics more resilient and wrinkle free. Similar to PES, low priced polypropylene (PP) is frequently used in the technical

textiles, home textiles, the automobile industry and to lesser extent in apparel textiles due to their special characteristics such as resistance to chemicals, low density etc. The dyeing of PP is difficult and the fastness properties are not good due to the highly crystalline molecular structure. However, dyeing of PES blends is a problem due to damage/reduction in the strength of natural fibers (cellulose degradation etc.) at high dyeing temperatures. Due to the hydrophobic nature of PES, its compact structure and cristallinity dyeing is limited to water-insoluble dyes such as disperse dyes, vat dyes etc. (De Girogi et al., 2000). The low and finite water solubility of these dyes is also a critical factor in determining levelling properties and dyeing rate (Kulkarni et al., 1986). Conventional polyester dyeing processes additionally require dispersing agent, dye carriers, and surfactants to obtain dye solubility in water. Due to dye reduction and migration, the fastness to washing was found to be on the satisfactory level when dyeing with these dyes (Son et al., 2004). The rate of diffusion of these dyestuffs in the fiber is relatively low. Therefore, the rate of diffusion in the conventional PES dyeing commercially may be raised either by working at higher temperature in the region of 130 °C and/ or in the super atmospheric pressure in the presence of accelerating agent or carrier or surfactants or dyeing auxiliaries.

Recently, research on the use of different surface modification techniques such as low pressure plasma (LPP) and atmospheric pressure plasma (APP) in order to improve the dyeability of polyesters has grown in interest, since they are environmentally efficient. An increase in hydrophilicity and dyeability of knitted PES textiles after the plasma modification in an O_2/CF_4 mixture was obtained, as reported by Aubrecht et al. (2006). The dyeability with basic dye is enhanced on PET/cotton blends by in situ polymerization of acrylic acid and water (Öktem et al., 2002). Sarmadi et al., 1993 observed that the dyeability with basic dye (dye bath temperature 100 °C and 2 hours dyeing time) can further be improved by an increase in the time it is exposed to CF_4 cold plasma, and found K/S values between 0.50-1.51 for a 2% owf (on the weight of fabric) dark shade dyeing with hydrophobic basic dye. A higher color yield was obtained on acrylic acid grafted PET fiber induced by Ar plasma. Barani et al. (2010) compared the dyeability of PES microfiber fabrics using various pre- and post-treatments. They reported that alkali, sol-gel and oxygen plasma treatments are able to enhance the color strength. Continuous modification of PES was carried out using DBD (dielectric barrier discharge) plasma at atmospheric pressure with a Ar/O_2 ratio of 10:1 (Zhongfu et al., 2007). It was reported that the spectral value (K/S) dyed with blue disperse dyes was found to be increased by 50% in comparison with that of untreated samples due to the formation of –COOH groups during plasma treatment. The work of Ferrero et al. (2004) has shown that the fastness to washing with basic dye on PET by in situ polymerization of acrylic acid using low temperature plasma was found to be unsatisfactory probably because of an unstable bond between grafted acrylic acid and dye molecules. Anti-reflecting coating layers have been deposited with organo-silicon compounds using APP plasma, which enhanced the color intensity on PET surfaces as explained by Lee et al. (2001). Okuno et at. (1992) studied the correlation between the crystallinity and dyeability of PET fibers using non-film-forming gases by cold plasma. They found that plasma-treated samples significantly reduced the dyeability due to the etching of macromolecules in the dyeable amorphous phase. Recently, Addamo et al. (2006) reported that the color depth of air LPP plasma treated PET fibers is related to their topographical characteristics and to their chemical surface composition. They observed that the color strength with disperse dye at a dyeing temperature of 100 °C can be increased by decreasing the fraction of light reflected from the treated surfaces.

Moreover, much research has also been done in the environmentally friendly dyeing of PET with disperse dyes in supercritical CO_2 which has the advantage of reducing the need for additional chemicals and waste water (Okuno et al., 1992; Montero et al., 2003; Özcan et al., 2005). The scaling of the supercritical fluid dyeing experiment from laboratory size to industrial scale is far from being a straight-forward procedure because it requires very high pressures (260-300 bar) and high investment cost. At low pressure K/S value is decreased, which yields low dye solubility (Özcan et al., 2005). Moreover, conventional textile dyeing is dependent on the substrate materials due to their specific chemical nature. In a specific dyeing condition, dye molecules chemically and physically bind with the textile fibers and thus, the dyestuff class is also limited to the chemical groups present in the fiber due to dye-fiber interaction. For this reasons, substrate independent dyeing is of particular interest not only for textiles, but also for the materials industries where coloration is needed. Barranco et al. was adding dyestuff molecules downstream in a film-forming plasma in order to obtain dye molecule containing nanocomposite coatings (Barranco et al., 2006). There has been very little attention focused on the application of hydrophilic acid dyes on hydrophobic PET fabrics. Milling acid dyes, which have excellent color brightness and very good wet fastness, can easily be applied to plasma-treated polyester or their blends with natural fibers at low dyeing temperature of 80 °C within an hour dyeing time, where plasma modification is used as an alternative to the required pre-treatment of PET textiles (Hossain et al., 2007a).

While some efforts have been devoted to study dyeability of PES by plasma treatments, very few articles have been reported about the application of acid dyes to PES. In this research, an attempt was made to solve some limitations of PET dyeing using hydrophilic acid dye by modifying the surface with a novel nanoporous plasma polymer coating. Since the dyeing becomes independent from the substrate material, this approach enables the dyeing of all kinds of synthetic fibers or blend fabrics. Surface modification of fabrics induced by ammonia/acetylene and ammonia/ethylene plasmas was carried out in order 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 of the plasma polymer.

Nitrogenated amorphous hydrocarbon films (a-C:H:N films) were deposited on PET fabrics by cold plasma using a pilot-plant plasma reactor. Tightly woven and washed polyethylene terephthalate (PET) fabric (76 ends/in, 76 picks/in, 43.5 g/m²) from Sefar AG (Switzerland) was used in this study. The deposited-hydrophilic a-C:H:N films were characterized by contact angles (CAs). The mechanical stability of the plasma coating was examined by Abrasion & Pilling Tester. Dyeing of the plasma coating was examined by Datacolor Spectraflash, and the results of dyeing were compared for both plasmas (ammonia/acetylene and ammonia/ethylene), while a study was investigated to observe the influences of energy input in terms of power input per unit of gas flow W/F (J/cm³), film thickness, and gas ratio.

2. Plasma treatments

A gas discharge allows the acceleration of free electrons when driven by an external source (e.g. RF generator). As a consequence, highly reactive and activated molecular species such as chemical radicals, ions, metastables, electrons etc. can be created by ionization, fragmentation (dissociation), excitation, UV radiation, etching reactions etc. These species

chemically and physically react with the polymer surfaces, thus altering the surface properties and surface morphology in the topmost layers (Hossain, 2008).

The setup for RF excitation is well-established. In the case of a capacitively coupled RF discharge, two electrodes are mounted in a vacuum chamber as shown in Fig. 1. A process gas with a typical pressure of a few pascal is introduced while working in LPP conditions. When the RF voltage exceeds a certain value in the range of some hundred volts, depending on gas, pressure and reactor geometry, the discharge ignites. The energy coupling in RF plasmas via the electrons is well-defined enabling highly uniform discharges, a trait that is critical in treating irregularly shaped and large objects. RF plasmas are characterized by higher ionization efficiencies and can be sustained at lower gas pressures than DC discharges. Finally, in the case of RF discharge, the energy of the ions bombarding the sample is controlled by the (positive) plasma potential and the (negative) bias potential, which can be adjusted over a wide range of values.
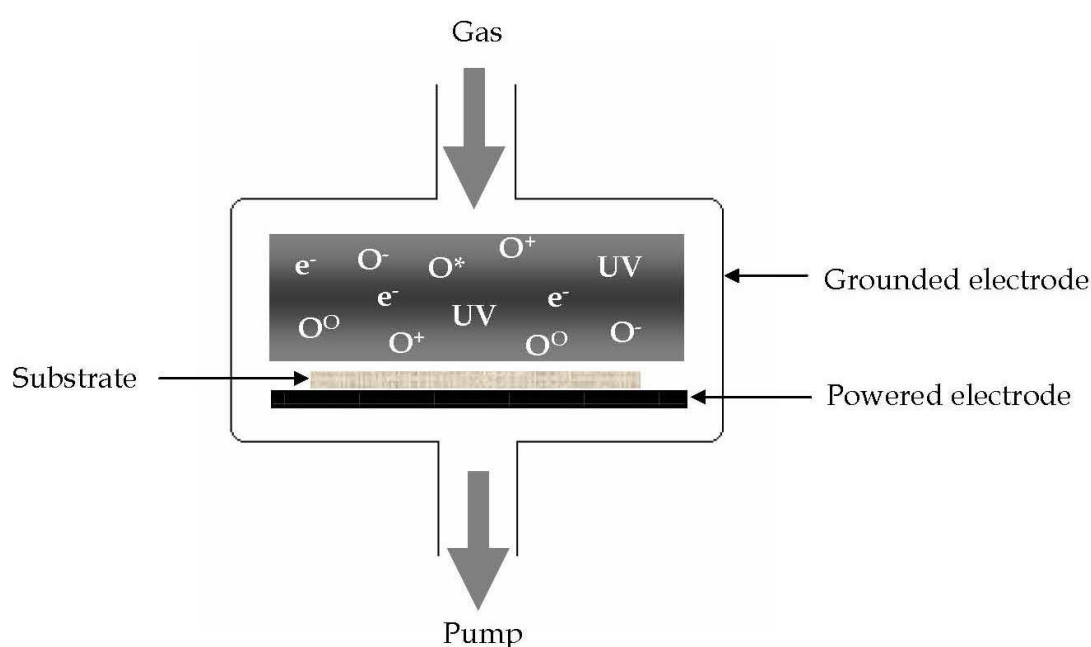
Fig. 2. RF plasma set up and illustration of active species present in oxygen plasma

Based on a wide range of applications and mechanism involved in plasma technology, plasma processes can be subdivided into two main categories:

- plasma modification referring to surface cleaning, activation, and surface etching >> non-film-forming plasma

Plasma activation generates radicals mainly by hydrogen abstraction from the polymer chain during collisions of reactive species with the polymer surfaces. Electrons, UV radiation or ion bombardment can generate radicals by C-C bond scission of the polymer. Non-polymer forming inorganic gases are used in this plasma activation process (Hossain et al., 2006a). Surface activation ranges from surface cleaning, radical formation and atom implantation to surface etching; it depends on different process parameters such as for example energy input. Surface cleaning is commonly used prior to other processing steps such as polymerization, metallization, dyeing, lamination etc. in order to increase the adhesion with textile surfaces.

- plasma modification referring to surface chemistry restructuring via deposition >> film-forming plasma, as described in the following section.

2.1 Deposition of plasma polymer films

In plasma depositions from the gas phase, which is commonly known as plasma polymerization or plasma enhanced chemical vapor deposition (PECVD), a very thin polymer layer (nm to μm) is deposited on the substrate surface. The layer is formed through polymerization of a monomer yielding film growth directly on the surface activated by the plasma (both in gas phase and surface reactions). In contrast to classic polymerization, plasma polymerization can use every monomer gas or vapor and is not limited to its reactivity. It is well known that plasma polymerization could be performed for almost any kind of monomer and it is mainly the elemental composition of the monomer, which is fed into the reaction that is important. The growth rate, mainly determined by gas flow rate and power input, varied depending on the monomer structure even if polymerized films showed similar characteristics (Morita et al., 1985).

In plasma polymerization, the monomer is fragmented under plasma conditions and builds up a plasma polymer. The plasma polymer does not contain regular repeating units; the chains are branched and randomly terminated with a high degree of crosslinking. Thus, it has a highly crosslinked and disordered structure without repeating units, as shown in Fig. 3. Structural preservation and gradients, with increasing degree of crosslinking over film thickness, can be controlled through process parameters, such as gas pressure, gas flow, and applied electric voltage, so that one can also construct so-called gradient layers. It is thus possible to obtain ultra-thin films with very useful properties for technological applications (Bismarck et al., 1999). A combination of polymerizable gases with non-polymerizable gases allows for the deposition of a variety of plasma polymer layers with many different functional groups possible. Thus, depending on the selection of the gas, monomer, process parameters, these thin coatings can be deposited with various physical and chemical characteristics. Consequently, functionalized surfaces with special properties can be obtained.
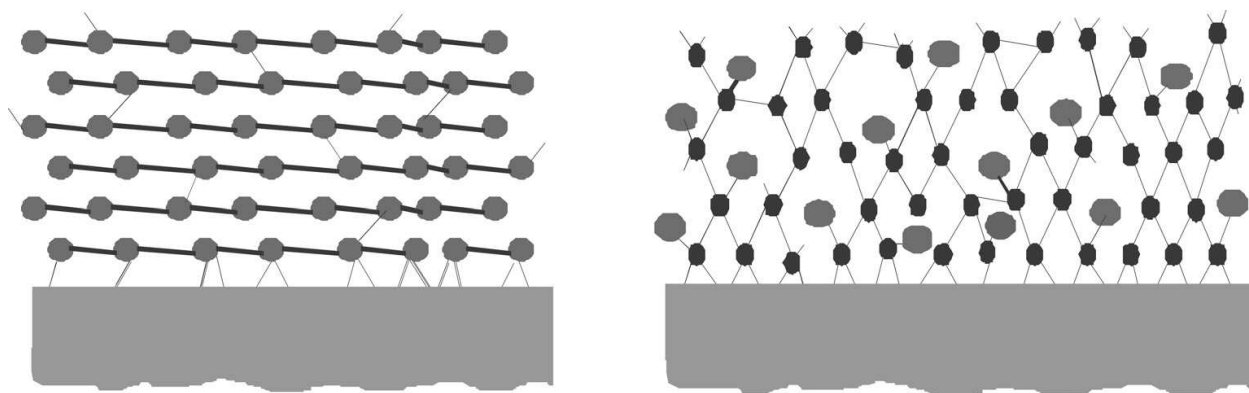

Fig. 3. Illustration of conventional polymer (left) and crosslinked plasma polymer (right)

The plasma treatments were carried out in a pilot-plant reactor, as shown in Fig. 4, in order to demonstrate the feasibility for industrial up-scaling. The reactor is described in more detail in the literature (Hossain et al., 2007b). The fabric samples were kept on the cylindrical electrode (65 cm width). The RF power (13.56 MHz) was connected to the electrode and the

glow discharges were carried out for the required power (500-750 W), gas flow (NH_3/monomer ratio = 0.71-4.0), and duration (10-60 min), while the pressure was kept at 10 Pa for all experiments.
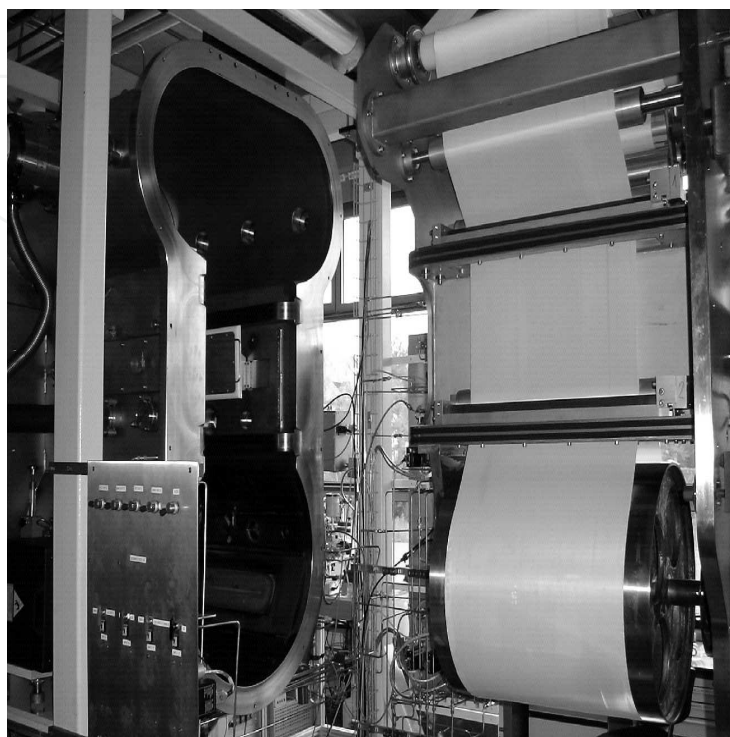

Fig. 4. Set-up of web coater

2.1.1 Nanoporous functionalized films

In this study, ammonia/acetylene and ammonia/ethylene gaseous discharges were performed in order to obtain nanoporous functionalized coatings. A RF plasma generator was used for the deposition of a-C:H:N films on PET textiles. In addition, since the plasma treatment is largely independent of the substrate material, this leads to the possibility to use a universal coating process instead of optimizing surface modification processes and plasma parameters for each different substrate material. However, special care should be taken in particular for textile substrates due to their 3-D structure and manufacturing residuals.

The structural modification of a-C:H films by the addition of nitrogen to the hydrocarbon precursor yielded hydrophilic functional sites (mainly amine functionalities) in a-C:H:N coatings (Hossain et al., 2007c). The a-C:H:N films become more graphitic and the density of voids increases with the incorporation of nitrogen and/or nitrogen functionalities in the coating (Cuong et al., 2005; Freire et al., 1995). As shown in Fig. 5, the AFM image indicates that the interconnected voids in the coating are below 25 nm. The dye molecules are thus small enough (about a few nanometer) to diffuse easily through the interconnected voids of the nanoporous structure into the plasma-polymer matrix and form dye-film bonds. Sufficiently large nanopores with a porosity of 10-20% strongly increase the specific surface area and provide a high functionality to attach molecules such as dyestuff.
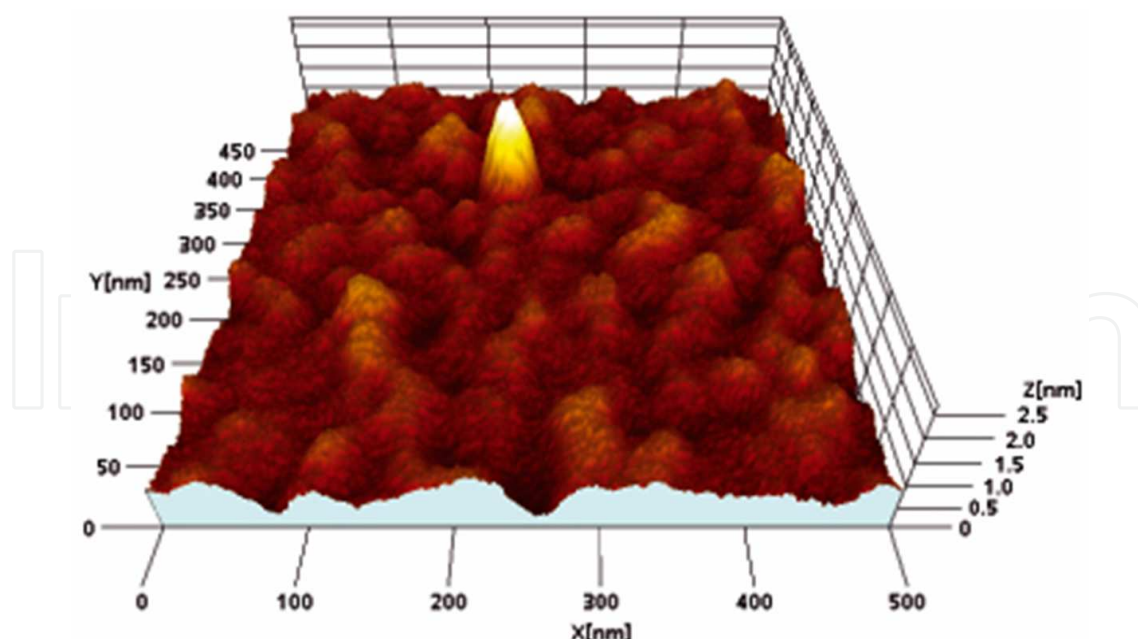
Fig. 5. 3-D AFM Imaging of a a-C:H:N plasma coating (W/F = 144 J/cm³, NH₃/C₂H₂ = 1.2)

Previously, we examined the mass deposition rates for a wide range of NH_3/hydrocarbon ratio (Hegemann et al., 2005). It was found that plasma deposition, in particular radical-promoted plasma polymerization, was governed by the composite parameter: power input per monomer flow W/F. At moderate energy input ($120 \leq W/F \leq 144$ J/cm³) a maximum in deposition rate can be achieved for a high NH_3/C_2H_2 ratio of 5:1, as can be seen in Fig. 6. Increasing the C_2H_2 content in the gas mixture leads to an increase of hydrocarbon radicals in the active plasma zone resulting in a gradual increase in a-C:H film character and enhanced deposition rates (Hegemann et al., 2005). Increasing the energy input yields more fragmentation and thus also more hydrocarbon radicals. However, modifications in film growth such as densification, degradation reactions of polymer chains, chemical and physical etching, and some temperature effects can be observed at higher specific energies (W/F > 144 J/cm³) yielding a reduced deposition rate due to the transition between film growth and erosion regime (Hossain et al., 2007a; Hegemann et al., 2005). Moreover, higher energy input avoids the formation of voids, with high crosslinking of the amorphous network, and raises film rigidity due to the hybridization state of carbon atoms in a-C:H:N system. The presence of clustered carbon atoms decreases in the amorphous network connectivity. As a consequence, at high energy input inhomogeneous porous coating causes declination of dye molecules penetration into the coating during plasma dyeing process (Hossain et al., 2007a). In addition, at very low flow rates the film growth is limited by the availability of monomer supply (Waldman et al., 1995). Commonly, in LPP plasma more energetic particles and long-living radicals are generated compared to APP plasma. As a consequence etching effects can play a major role in low pressure plasma. However, the application of ammonia/acetylene plasma is very beneficial in avoiding strong etching effects during plasma polymerization, while coherent etching yield the formation of voids within the growing films (Hegemann et al., 2007; Jang et al., 1992). It can be concluded that the optimum chemical modification can be attained at moderate energy input, and suitable NH_3/hydrocarbon ratio (around 1.0) to obtain accessible amine-functional groups within a-C:H:N coatings (Hossain et al., 2007b).
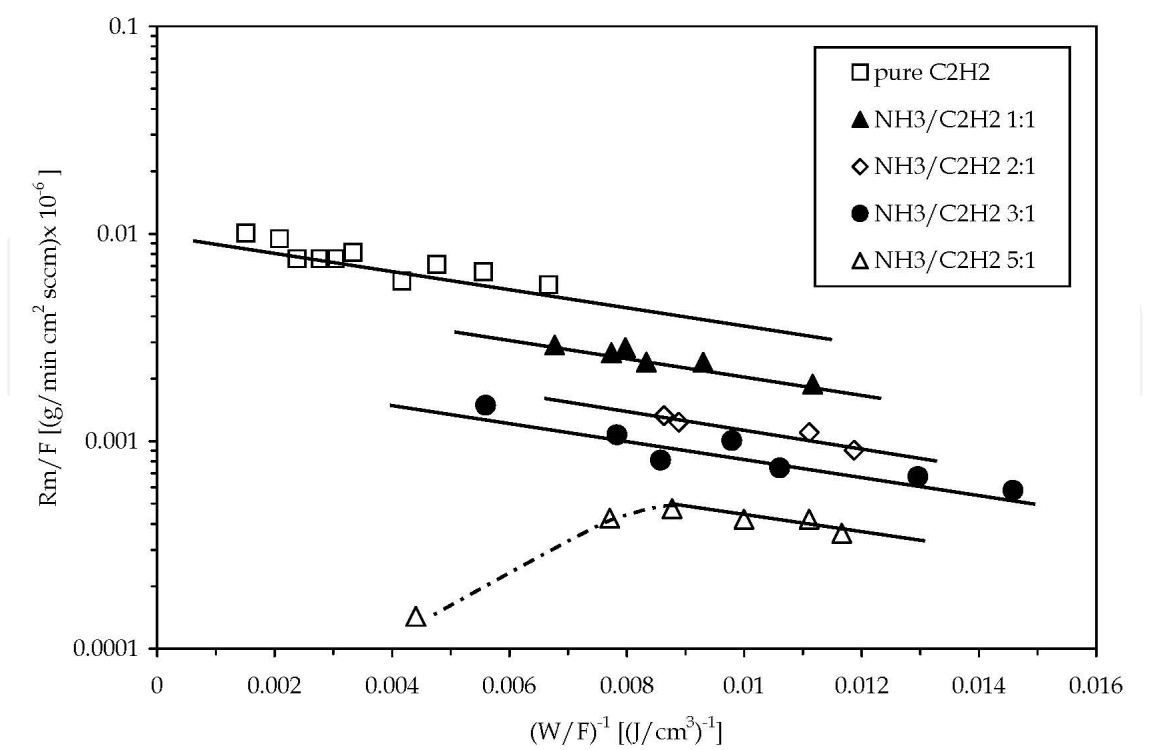
Fig. 6. Effect of energy input W/F (RF power/C_2H_2 flow) on the deposited film.

2.1.2 Wicking property improvement

The wicking property of plasma-coated fabrics was tested according to the water climbing time in the fabric at a certain height (strips size: 15 cm x 2 cm). The wicking times were recorded at fixed 2 cm water climbing height. Surface hydrophilicity was greatly enhanced, as shown in Fig. 7, due to the addition of polar functional groups (Hossain et al., 2007c). The
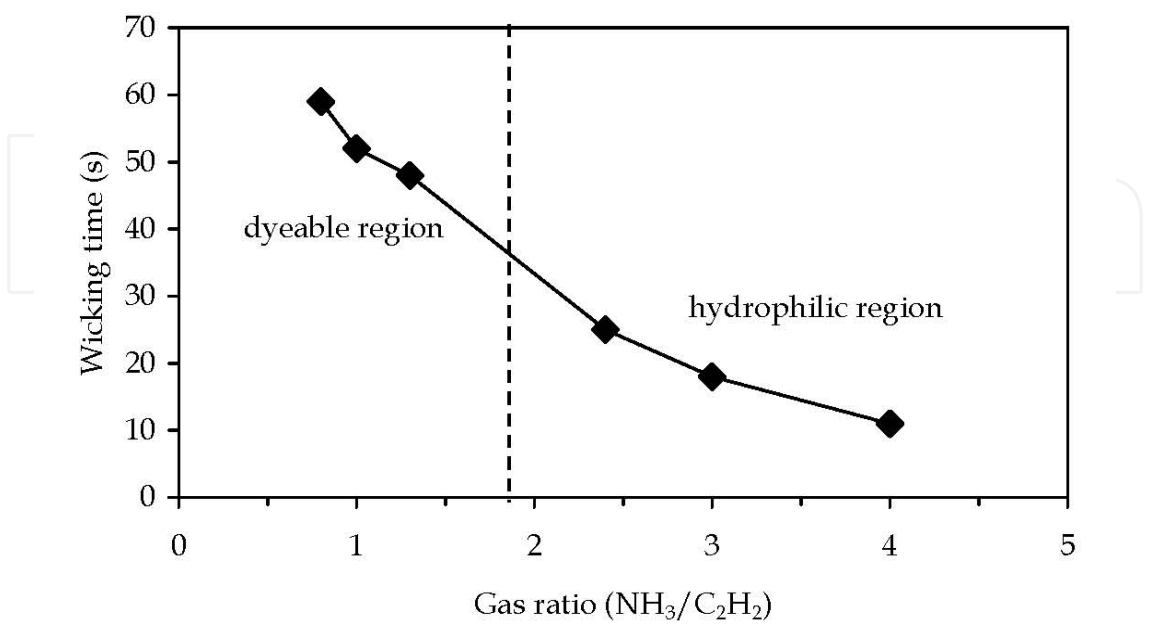

Fig. 7. Effect of gas ratio on wicking property of plasma-coated PET

wettability strongly depends on gas ratios rather than energy input etc. Higher NH_3/monomer ratios (> 2.50) were found to yield the lowest wicking times due to the formation of polar functionalities on the plasma polymer surface. Free radicals created on the plasma polymer produced polar oxygen functionalities, when the treated substrates were exposed to atmosphere, although no oxygen was used during plasma polymerization. On the other hand, higher gas ratios yield lower coloration, which is discussed in the following section.

3. Dyeing procedure

The dyeing of plasma treated samples was carried out in a laboratory-scale machine manufactured by Mathis, Switzerland (LABOMAT–8, Type BFA–8). Hydrophilic functional a-C:H:N films of the PET substrate were dyed with hydrophilic acid dyes (C.I. Acid Blue 127:1). The light-shade dyeing was performed using 0.5 % owf acid dye and 5 % owf sodium sulphate salt for exhaustion and the pH of the dye bath was adjusted to 4.5-5.0 by adding ammonium sulphate. The liquor to fabric ratio in dyeing was 1:100 and the following dyeing conditions were adopted: initial temperature 25 °C, followed by temperature gradient of 1.5 °C min^{-1} up to 80 °C, then the dye bath temperature was maintained at 80 °C for 60 min. After dyeing, the dyed fabrics were washed with soap (Ultravon W) at 60 °C for 30 min (L:R = 1:100), then rinsed with warm and cold water and dried at room temperature. Substrate independent plasma dyeing mechanism is described in the Fig. 8. Due to the presence of sulfonic acid groups (-SO$_3$H), acid dye is water-soluble which is transported to the coating on the fiber by the motion of dye-liquor or the textile or simultaneous movement of both in the exhaustion dyeing process. By adsorption process, dye molecule comes on the coated surface; it is then diffused into the nanoporous coating. The basic amino group of coating is decisive important for acid dyeing which can be protonated in the acid medium and becomes fiber-cation (ammonium group). On the other hand, dye-molecule dissociates in the Na$_2$SO$_4$/H$_2$O solution and which gives rise to dye anions, as a consequence they interact with the ammonium groups of the coated fiber mainly by the formation of ionic bonds. Secondary bonds such as dispersion, polar bonds and hydrogen bonds can also additionally be formed between fiber and dye. As a result, dye molecule is fixed in the plasma coating which is independent from the substrate materials.

i) Protonation and cation formation:

Film -NH$_2$ $\longrightarrow$ Film -NH$_3^+$

ii) Dissociation of dye molecules:

Dye -SO$_3$Na $\longrightarrow$ Dye -SO$_3^-$ + Na$^+$

iii) Film-dye bonding:

Film -NH$_3^+$ + Dye -SO$_3^-$ $\longrightarrow$ Film -NH$_3^+$ $^-$O$_3$S -Dye

Fig. 8. Film/dye interaction

CIELAB color values of the dyed fabrics were determined using a Datacolor Spectraflash interfaced to a PC. Each fabric was folded twice so as to give four thicknesses, and an

average of six readings was taken for each measurement. 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 color strength values (K/S values at 490 nm) of the fabrics were calculated from Kubelka-Munk equation (1), where K is the absorption coefficient, S is the scattering coefficient, and *R* is the decimal fraction of the dyed fabrics.

$$K/S = (1-R)^2/2R \tag{1}$$

3.1 Dyeing of plasma films

In order to obtain nanoporous thin films, different modifications were employed by varying the important plasma parameters such as discharge power and gas flow ratios. It was found that a gas ratio of NH_3/C_2H_4 around 0.70 - 1.0 and NH_3/C_2H_2 around 1.0 - 1.25 and a discharge power of around 500 - 600 W yield the optimum regarding amine functionalities (Hossain et al., 2007b). The amine functionalities were accessible by dye molecules. Fig. 9 demonstrated the dyeability of plasma-treated PET textiles with different coating thicknesses. The relative color strength value was increased gradually with the increase in coating thickness (i.e. plasma exposure time) (Hossain et al., 2007b; Balazs et al., 2007). It is noteworthy that with increasing plasma process time the penetration of reactive plasma species yielding plasma polymerization goes deeper into the textile structure, even in the inter-filament or inter-yarn spaces, resulting in better dyeability, i.e. number of amine-end groups. On the other hand, the reduced film thickness at very low flow rates led to a lower K/S value of the PET fabrics. Thus, dye molecules are able to penetrate into the nanoporous films and facilitate the dyeing of a-C:H:N thin films by forming chemical bonds mainly with amino groups within the plasma coatings (Hossain et al., 2009; Siow et al., 2006). Since the dyestuff used specifically binds with amine groups, dyeing can be used as a specific chemical tracer to
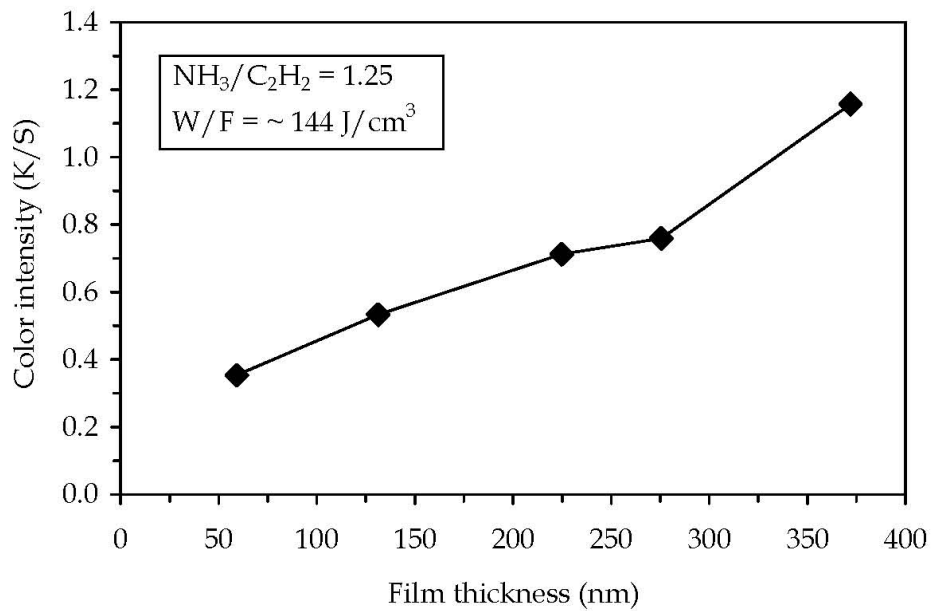

Fig. 9. Relative color strength values (K/S) depending on film thickness and exposure time (light-shade dyeing with 0.5% owf acid dyes).

detect the amount of amine groups inside the coatings. It should be mentioned that untreated PET textiles were not dyeable with acid dye, since they do not contain functional groups in their structure needed for ionic bond (dye-fiber interaction).

The gaseous mixture (suitable NH_3/C_2H_2 ratio ~ 1.25 and NH_3/C_2H_4 ratio ~ 1.0) helped to build up voids in the deposition resulting in a nanoporous plasma polymer coating which was accessible to dye molecules throughout the entire film volume (Freiere et al., 1995; Hammer et al., 2001). Higher ammonia flow to monomer gases indicates an increase nitrogen content, as can be seen in Fig. 10. Moreover, NH_3/C_2H_2 plasma yields a lower nitrogen content compared to NH_3/C_2H_4 plasma owing to an increased carbon content , which can be seen for equal gas ratios (ammonia/monomer = 1.25). The previous study also confirmed the chemical composition of the a-C:H:N deposited films discussing the XPS spectra elaborately (Hossain et al., 2007a). It can be assumed that higher NH_3/C_2H_4 produce more amides, cyanides, imines etc. within the coating rather than simple amine functional groups. Highly reactive ammonia, on the other hand, generates a high number of surface free radicals at higher nitrogen content (i.e. high NH_3/C_2H_2 = 2.70) as compared to a lower ratio (NH_3/C_2H_2 = 1.70). These reactive radicals contribute to form oxygen-containing polar functional groups by post-plasma reactions in the atmosphere. As a consequence, superhydrophilic coatings can be achieved with high ammonia content by incorporation of polar functional groups into the surface within a cross-linked hydrocarbon network. Likewise, the highest nitrogen content reveals the lowest color difference due to a lower number of amines (Table 1). The color difference was compared to non-plasma treated fabric. Thus, the dyeability of the plasma coatings was found to be low at a gas ratio > 2.50. Thus, coloration does not depend on the surface wettability, but on the density of amine-end group. The color intensity in different positions for each dyed sample was measured and the value was found to be almost identical and thus confirming a level dyeing.
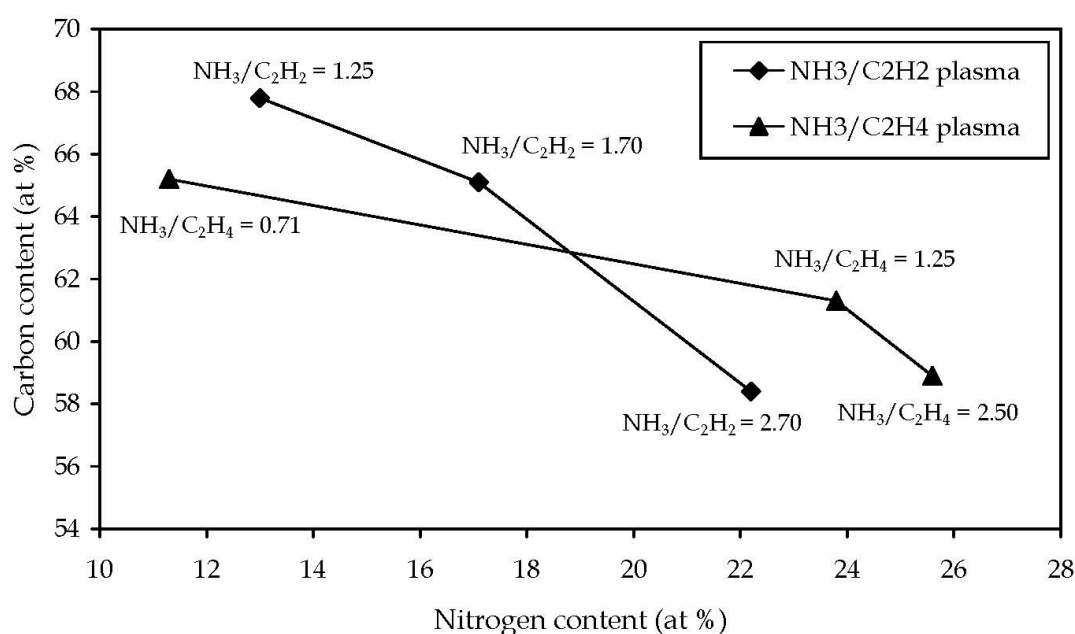

Fig. 10. Nitrogen and carbon contents of a-C:H:N films in different gas ratios

Power input (watt)	Film thickness (nm)	N-content in % $[N/(N+C)]$	Color difference (ΔE)
650	52	13	33.0
600	54	20	43.0
500	30	30	26.0

Table 1. Color difference of dyed a-C:H:N films at different plasma power, film thickness, and nitrogen concentration (NH_3/C_2H_4 plasma).

3.1.1 Rate of dye-uptake

Uptake of acid dyes onto the plasma coated fabric enhanced remarkably even in a very short dyeing time (5 min), as shown in Fig. 11. It is very interesting to see that the dye uptake remained similar from a short dyeing time (5 min) to a very long dyeing time (120 min), since no significant difference in dye uptake was found at longer time periods. The observed enhancement of dye uptake can be attributed to the deposition of nanoporous thin films which provide amine groups easily accessible to dye molecules within a short time. This demonstrates that the dye diffusion coefficients are quite high; in general these values are quite low when traditional dyeing processes are used (Banchero et al., 2005). In addition, since ultrathin films were dyed, the dye uptake reached to "dyeing equilibrium" very fast. Moreover, the uniform shade obtained certainly proved the regular distribution of dye molecules throughout the entire film thickness. The low internal diffusion time seems to be responsible for preventing non-uniformity problems along the film thickness. In fact, a high dye uptake rate represents a certain advantage since the total dyeing time can be shortened ten times over using plasma-enhanced dyeing, whereas, faster dye uptake kinetics is apt to cause non-uniform dye distribution in the final product when dyeing is done traditionally.
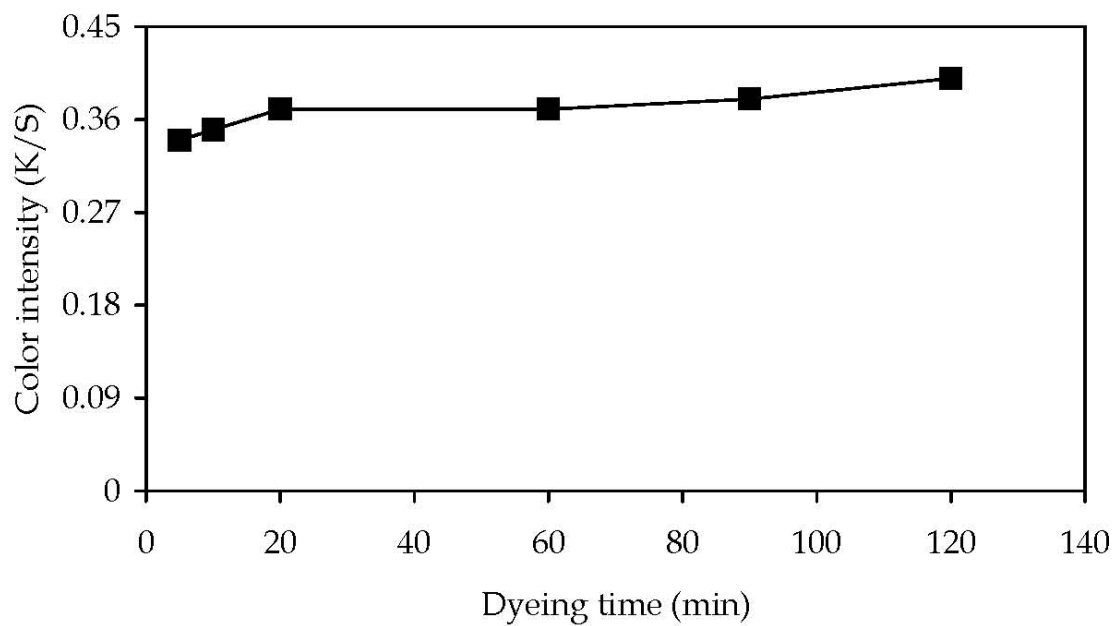

Fig. 11. Effect of dyeing time on dyeability (dyeing temperature 80 °C) (600 W, NH_3/C_2H_4 = 0.84, 20 min) and light-shade dyed PET (0.5% owf)

3.1.2 Temperature and pH effects

The dyeability was found to strongly depend on the dye bath temperature in the plasma dyeing process, as shown in Fig. 12; this is also a common phenomenon in traditional dyeing processes. Results show that the amount of dye absorbed on the coating decreases with decreasing dye-bath temperature. The low reduction in dyeability at lower temperature (< 80 °C) is probably due to dye aggregation and a low degree of adsorption. The differences, however, became very small especially at higher temperatures within the range of 80-120 °C. By increasing the temperature, dye uptake can be enhanced because of the increased solubility and mobility of dye molecules in water. There may be another reason for that, which is commonly seen in traditional synthetic dyeing processes: the enhanced color yield, which gradually increases with increasing temperature, can be attributed to a corresponding increase in the amount of accessible volume available for dye diffusion (Burkinshaw et al., 1995). The highest color yields were found to be at ~100 °C implying that the dye uptake reached the "saturation level" resulting in maximum acid-base intermolecular interaction between dyes and amine functionalities. At this level, the dye molecules occupied most of the incorporated amine functionalities in the film volume yielding maximum dyeability. Thus, substrates such as PES, PP, aramid, glass textiles etc. can be dyed at low temperatures similar to wool dyeing, since good coloration was obtained at levels as low as 80 °C.
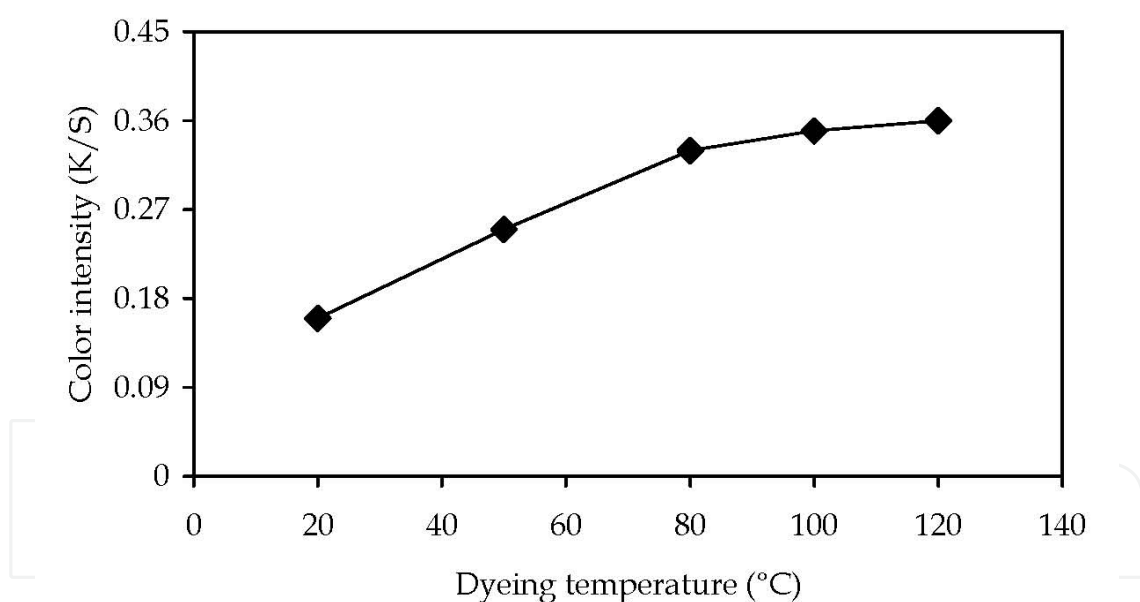

Fig. 12. Effect of dyeing temperature on dyeability (dyeing time 60 min)
(600 W, NH_3/C_2H_4 = 0.84, 20 min) and light-shade dyed PET (0.5% owf)

The pH value of the dye bath was found to be very important in order to achieve level dyeing and to increase dye affinity to the functionalized films. The optimum level dyeing and color strength were obtained at a pH in the range of 4.5-5. However, the color intensity was increased at pH 2.5-3.0 due to improved exhaustion, but uneven shade was observed. On the other hand, dyeability was reduced at pH 6.0-7.0 due to low substantivity or low affinity of dyes to the film resulting in weak dye-film interaction.
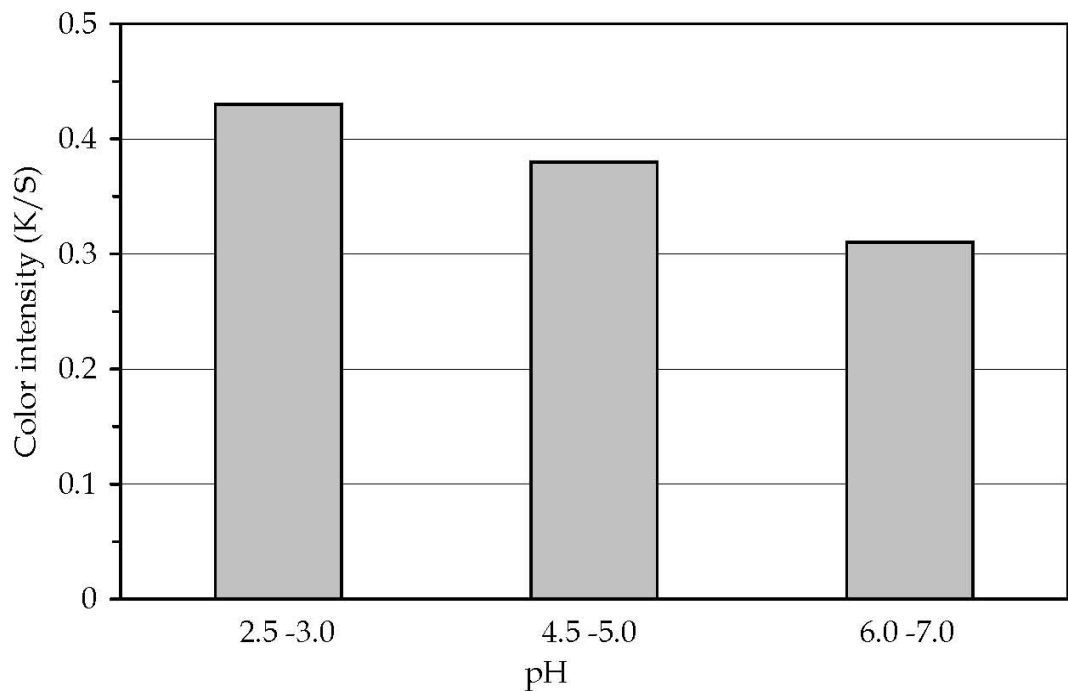
Fig. 13. Effect of dye bath pH on dyeability (dyeing time 60 min and dyeing temperature 80 °C) (600 W, NH_3/C_2H_4 = 0.84, 20 min) and light-shade dyed PET (0.5% owf).

3.1.3 Fastness properties

Table 2 shows summarized results of plasma-dyed PES that were assessed using an ISO test method (ISO 105-X12 for color fastness to rubbing and EN ISO 105-C06 for color fastness to washing). Under D65 illumination color changes, staining and rub were evaluated using grey scales: ISO-105-A02 grey scale for assessing change in color; ISO-105-A03 grey scale for staining and rub. All plasmas show almost comparable fastness properties after washing at 60 °C for ammonia/acetylene and ammonia/ethylene plasmas dyed PET. The acid dyeing

Gas ratio (vol.)	Wash fastness			Rub fastness	
	Color change	Staining (PET)	Staining (wool)	Dry	Wet
NH_3/C_2H_2 = 1.00	3	5	4	4-5	4-5
NH_3/C_2H_2 = 1.25	3	5	4	4	4
NH_3/C_2H_2 = 1.50	3	5	4	4	4-5
NH_3/C_2H_4 = 0.71	3	5	3-4	4	4-5
NH_3/C_2H_4 = 1.00	3	5	3-4	4	4-5
NH_3/C_2H_4 = 1.25	3	5	3-4	4	4-5

Table 2. Wash (at 60 °C) and rub fastness of a-C:H:N films deposited on PET fabrics

on a-C:H:N deposited plasma polymers exhibit acceptable fastness to laundering and rubbing. From these results, it is concluded that a nanoporous and functional plasma polymer enables permanent dye-fiber bonding with hydrophilic dyestuff. The coating was well adhered with the textile surface. No damages of the coating were detected after 60,000 rubbing cycles.

4. Commercialization

A considerable amount of basic research has been devoted mostly in laboratory scales to incorporate functional groups on the textile surfaces by plasma modification. Besides plasma parameters, the reactor geometry complicates the process scaling-up (Hegemann et al., 2007). Another fundamental problem at this moment is the lack of adapted plasma systems and the transfer of the laboratory findings into textile industry. Textilveredelung Grabher GmbH/Austria is using LPP plasma reactor (vol. 11 m³) in obtaining permanent hydrophilic and hydrophobic surface modification on textiles. The roll-to-roll system has a 15 m long plasma passage and is able to treat substrates up to 1.60 m in width (Fig. 14). Sefar AG/Switzerland is one of the pioneering companies in high-performance filtration solutions and uses the world largest APP systems, consisted of a high voltage power supply, for industrial applications (Fig. 15). The machine is installed inline textile processing and is capable of treating textiles, nonwovens, polymer webs etc. up to 4.0 m wide and materials speed up to 25 m/min (depending on the hydrophilization effect). The developed processes offer a range of cost-effective, and environmentally sound solutions to problems faced in screen printing. As a process gas He/Ar, and CO_2 etc. have been successfully used in their system at modifying textiles.

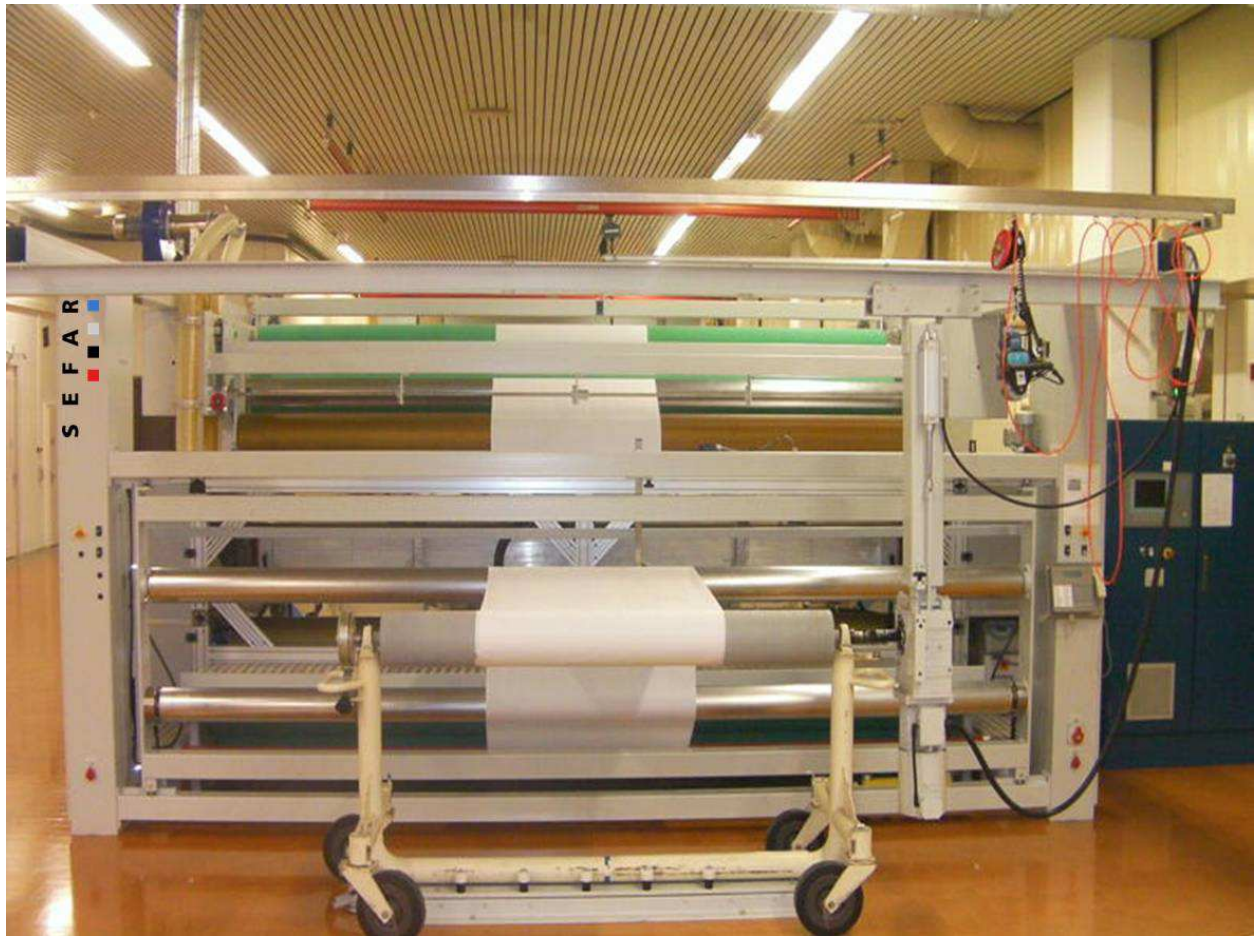Fig. 14. Industrial plasma reactor at Textilveredelung Grabher GmbH/Austria

Fig. 15. The continuous plasma system at Sefar AG/ Switzerland

They reported that an oxygen containing gaseous mixture (Ar/He with O_2 and ratio 20:1) was found to be more efficient compared to pure inert gases (Ar, He etc.) to remove organic contaminants by oxidizing polymer surfaces and to implant polar functional groups on the textile surfaces (Oyama et al., 1998). The use of gaseous mixtures facilitates cross-linking und better hydrophilicity. In this process, oxygen plasma causes reactions with surface contaminants resulting in their volatilization and removal of the degradation products as water vapor, CO, CO_2, H_2, etc. (Hossain et al., 2006b). Moreover, oxygenated functions such as –OH, -C=O, -COO, -COOR etc. are grafted onto the surface as can be seen in XPS analysis (Fig. 16). Thus, functionalized and activated surfaces can be obtained, which can be used for the subsequent wet processing such as lamination, coating, dyeability, printability etc. The grafted surfaces can also lead to covalent bonds suitable for further attachment of coatings, matrices etc. These new reactive sites can be used to improve adhesion and prevent delamination of the subsequent coatings, thus supporting the formation of abrasion resistant coatings.
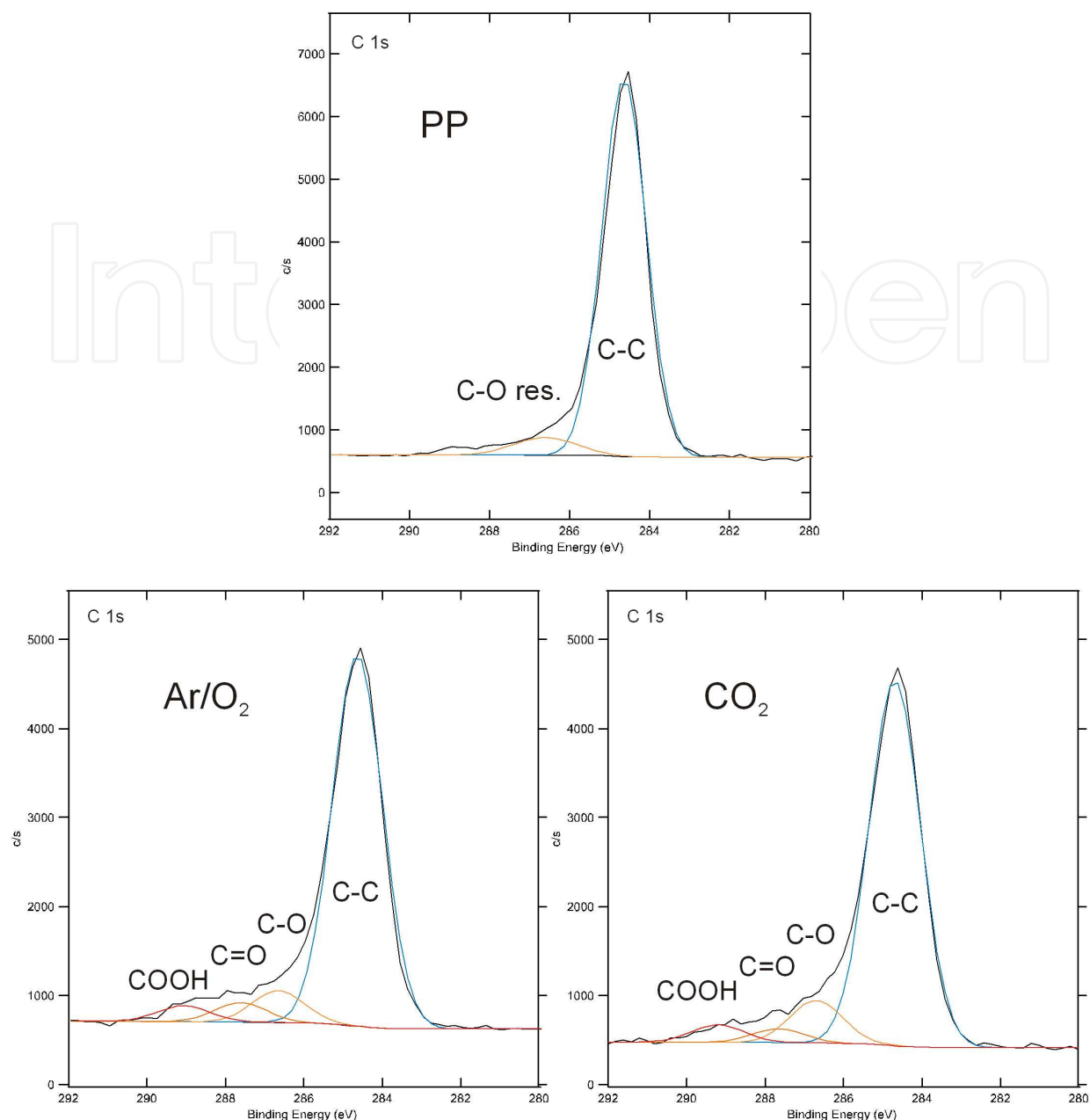
Fig. 16. XPS analysis of plasma-activated polypropylene (top: control, and bottom: Ar/O_2 and CO_2 plasmas)

4.1 Cost analysis

While plasma processing represents a dry, eco-friendly technology requiring a small amount of resources, it also has to prove its economic feasibility. Plasma activation processes without deposition of a film are state of the art in order to improve e.g. adhesion and can also be conducted using APP plasmas. Textile industry is thus using corona discharges operated in air for decades. However, the treatments are prone to aging effects (hydrophobic recovery) and show a limited uniformity. For more sophisticated applications such as the discussed (substrate independent) dyeing process, but also for the formation of permanent hydrophilic or hydrophobic surfaces, plasma polymerization processes are required. Thus, a large amount of research and development has been

done to explore both LPP and APP technologies. Nowadays, both systems are industrially available as mentioned above, which enable a comparison of special processes also regarding the costs.

Certainly, LPP offers more and different possibilities such as physical and chemical vapor deposition utilizing energetic particle interactions (sputtering, ion-induced etching, ion implantation, subplantation and densification). Moreover, LPP are able to penetrate deeper into complex material structures such as textiles. Finally, LPP processes are well established, reliable and robust. For plasma processes based on plasma-chemical reactions, however, it could be shown that both LPP and APP processes can be compared (Sawada et al., 1995). For instance, the incorporation of polar groups in ultrathin plasma polymer films might be examined yielding a permanent hydrophilic surface (Herbert et al., 2009). The deposition rate is mainly determined by the monomer flow rate due to a comparable energy input into the plasma phase. As reactive gases N_2, NH_3, H_2, O_2, CO_2, H_2O etc. might be added, again at a comparable flow rate. APP in addition requires a "filling gas" to reach atmospheric pressure, where helium (He) shows the best characteristics regarding plasma stability and energetic UV radiation (used for crosslinking). LPP on the other hand, requires (expensive) vacuum technology and the corresponding pumping system leading to the common assumption that APP may be advantageous. APP might be operated with a simple housing, but requires high flow rates of the filling gas in order to provide a sufficiently defined plasma atmosphere and to obtain a drift of the reactants to the surface, since convection processes have to be overcome.

Assuming that additional costs might be comparable in both technologies, i.e. personal costs, infrastructure, maintenance and (low) energy costs, a cost analysis can be performed on the basis of the investment and the running costs. While the investment is certainly higher for a LPP system, the running costs are actually higher for the APP system due to the high amount of required filling gas. Beside the already mentioned technological arguments, now also the costs can be estimated and compared for both plasma processes, which supports industry in selecting the best technology for their requirements.

For comparison, we selected a hydrophilic plasma treatment based on the deposition of an ultrathin (25 nm) plasma polymer film containing functional polar groups such as the one described in this chapter (LPP). For the comparable APP process, He at a flow rate of 100 slm is considered as filling gas. Both processes enable coating of 150 cm in width at a comparable process velocity in order to obtain the same amount of produced functional textiles per day. Fig. 17 displays the evolution of the costs with time. As it can be noticed, the break-even of the LPP system with the APP process is already reached after 14 months of operation due to the high running costs by He use. Even when recycling of He (recovery around 80%) can be considered causing increased investment costs, the break-even is reached after around 3 years. A similar analysis holds for the use of Ar or N_2 as filling gas as well as for hydrophobic treatments, again showing that LPP is beside many further advantages the more cost-efficient technology.

For the presented dyeing process thicker coatings might be required (see Fig. 9) which reduces the amount of functionalized textile per day and should be regarded for the cost analysis. Process optimization can still be expected. Also note that a 4 m wide plasma system as used by Sefar with APP might not be feasible using LPP. A well-based cost analysis, however, should be done by potential applicants giving good reasons for LPP systems as used by Textilveredelung Grabher.
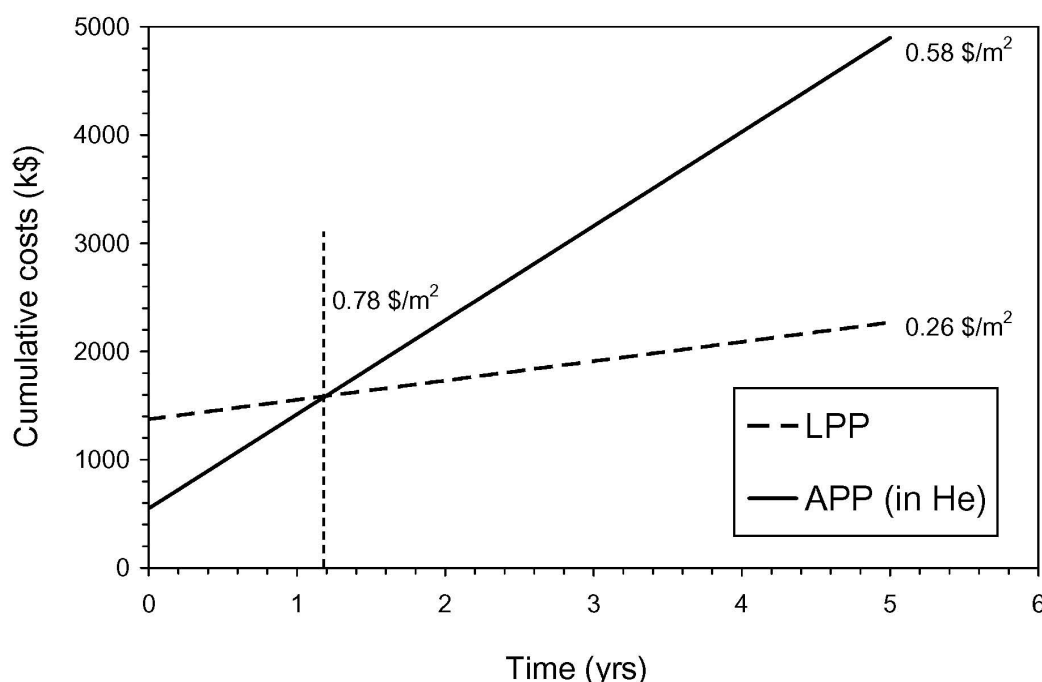
Fig. 17. Cost analysis for the comparison of LPP and APP processes for the permanent hydrophilization of textiles for 1.5 m in width and 5 km output per day showing the investment (at time zero) and the (constant) running costs. After 14 months both processes were producing 1500 km of functionalized textiles at a total cost of 0.78 $/m², which is further reducing with time.

5. Conclusion

This study investigated an alternative procedure to dye synthetic textiles, namely polyester, polypropylene etc., at low temperature using two different plasma polymerization methods, based on an original process of plasma deposition of nanoporous coatings. LPP discharge was performed for the modifications which avoid heat generation to the surface and additionally, it delivers high activation energy. The plasma modification alters the surface properties of textiles from hydrophobic to hydrophilic and to enable the dyeing of synthetics at low temperatures. Ammonia/hydrocarbon mixtures were investigated within a RF plasma using a web coater in order to deposit a-C:H:N coatings on PET textiles. Pure hydrocarbon discharges at low pressures can be used to deposit crosslinked a-C:H coatings. In particular, high deposition rates can be obtained with unsaturated hydrocarbon monomers such as acetylene and ethylene by producing the divalent radicals. Admixture of ammonia to the hydrocarbon discharge influenced the plasma polymerization mechanism depending mainly on gas ratio and energy input. Amine terminating groups, NH_2 and eventually NH, were embedded in hydrogenated carbon films (a-C:H films) using ammonia/hydrocarbon plasma. In addition, nitrogen incorporation in a-C:H films facilitated in forming crosslinked and branched plasma polymers. Thus, a nanoporous structure with a large specific surface area was achieved that contained functional groups inside the coating volume, which were accessible to e.g. acid dye molecules, thus facilitating substrate independent dyeing. It was found that dyeability is strongly influenced by both plasma parameters and fabric structure.

Besides plasma parameters the gas ratio plays a very important role in determining high color yields. Higher gas ratios were found to be less colored due to fewer amino functional groups, while they show higher hydrophilicity owing to the addition of polar functions on the surfaces during post plasma reactions. At gas ratios of around 1.25 for NH_3/C_2H_2 and 1.0 for NH_3/C_2H_4 crosslinked and branched a-C:H:N coatings were produced, which posed high number of accessible nitrogen functional groups, i.e. amino groups, resulting in high color intensity. Although their wetting properties were less pronounced as for higher ammonia content, dye molecules could easily enter the nanoporous film structure and chemically bound with the nitrogen functionalities. Thus, high K/S values per film thickness have been obtained. The uniformity of plasma polymers provides information about the even dyeing. Moreover, the plasma-deposited and dyed PET fabrics showed a good rubbing and washing fastness demonstrating the coating-functional permanency. The excellent abrasion resistance confirmed that the coating was permanently adhered to the substrate. Hence, the same dyeing principle can also be applied to all hydrophobic synthetic textiles and their blends with natural textiles which are difficult to dye.

A thorough cost analysis based on existing plasma processes were performed showing the ecological potential of plasma processes, in particular of low pressure plasma systems due to low running costs.

These findings demonstrate that plasma polymerization provides an eco-friendly multi-functionalized surface modification, since the use of chemicals; waste water etc. can be eliminated. Furthermore, since the coating thickness is in the nanometer range (<300 nm), the materials, architectural porosity, touch, and comfort etc. are not affected. The nanoporous plasma polymers can be effectively used as a foundation for multifunctional applications such as fiber-reinforced composites, superhydrophobicity, cell-adhesion etc. Thus, the developed nanoporous coatings that incorporate accessible functional groups are most promising candidates for technical textiles.

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Textile Dyeing

Edited by Prof. Peter Hauser

ISBN 978-953-307-565-5

Hard cover, 392 pages

Publisher InTech

Published online 14, December, 2011

Published in print edition December, 2011

The coloration of fibers and fabrics through dyeing is an integral part of textile manufacturing. This book discusses in detail several emerging topics on textile dyeing. "Textile Dyeing" will serve as an excellent addition to the libraries of both the novice and expert.

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