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# One-bath One-dye Class Dyeing of PES/Cotton Blends after Corona and Chitosan Treatment

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**Abstract:** In this work, the effects of corona discharge (CD) and chitosan treatment on the dyeability of polyester/cotton blends with direct and reactive dyes were studied. The surface chemical changes of polyester and cotton were analyzed using X-ray Photoelectron Spectroscopy (XPS). The correlation between chemical changes, wettability, and dyeability after CD and/or chitosan treatment has been established. Color intensity of both single components and PES/cotton blend increased proportionally with increasing chitosan concentration. The results obtained open the possibility for a new method for dyeing of polyester/cotton blends in a single bath using one dye-class that is commonly used for dyeing of textile material of cellulosic origin.

**Keywords:** Dyeing blend, Direct dye, Reactive dye, Corona discharge, Chitosan

## Introduction

Polyester/cotton blends are the most popular ones in the clothing industry due to complementary properties of fibers. With this blend, it is reasonable to think of the cotton as being the fiber which contributes most to the comfort of the final textile product and polyester as the component which contributes most to its performance - in particular, its strength and easy-care properties. Since polyster (PES) fiber has properties opposite to those of natural fibers with respect to chemical composition (no active sites or groups), supramolecular structure (difficult dye-penetration and diffusion), and wetting behavior (extremely hydrophobic), these factors are inhibiting the use of most available textile dyes, except the disperse dyestuffs. Moreover, due to the high glass transition temperature of poly(ethylene terephthalate) (75-90 °C), the diffusion rate of disperse dyestuff molecules into the standard PES fibers at normal dyeing temperatures (95-100 °C) is very low. Hence, the dyeing of single PES and PES blends can be carried out either in autoclaves at high temperature (HT-dyeing at 130 °C) or at normal dyeing temperatures with the addition of plasticizers, so-called carriers. As a result, dyeing conditions typically used for other types of substrates are not applicable. On the other hand, hydrophilic cellulosic fibers (i.e. cotton) readily swell in water, facilitating dye penetration into fiber, the factors that enable the use of different dye classes and dyeing at normal temperatures.

Currently established dyeing methods for PES/cotton blends require using two classes of dyes, disperse dyes for PES and direct, reactive, or vat dyes for cotton. When both components in blend are to be dyed, either the one-bath or two-bath method is used, usually at high temperature. A special case is thermosol method, which can be also applied on the one-bath or two-bath principle. With adequate regulation of processing parameters both one-bath and two-bath methods give satisfactory dyeing quality but also have some disadvantages, such as: long dyeing time, high energy consumption, compatibility problems between different dye classes in the dyebath, low stability of reactive dyes to subsequent reduction clearing of the polyester, etc.

Several approaches have been used to enhance the single PES and PES/cotton blend dyeing processes with the aim to avoid the use of high-temperature or carriers. The effects of preheating under dry and wet conditions on modification of amorphous polyester structure and on sorption and condition of dye in fiber micro-voids were studied [1]. The efficiency of carrier pre-treatment, as a substitute for conventional dyeing under atmospheric pressure, was proved by twice as much dye uptake on pre-treated samples, compared to the untreated samples [2]. Furthermore, the performance of new, so called readily- or easily-dyeable PES fibers is being studied. These PES fibers have a modified structure with higher flexibility of molecular chains, which results in higher hydrophilicity and facilitates disperse dye penetration, consequently reducing the dyeing temperature [3].

Another important approach to enhance dyeability of PES/cotton blends involved synthesis of dyes with new coloristic properties for one-bath-one-stage dyeing process. The synthesis of azo disperse dyes for dyeing of PES/cotton blends, having fluorosulfonyl group and hydrolyzing under alkaline conditions, has been recently reported [4]. In one-bath dyeing, after adding alkali (20 g/*l* $Na_2CO_3$) for fixation of reactive dye at

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80 °C, hydrolysis of residual disperse dye occurs, which is then removed by rinsing, resulting in improved fastness properties. For the one-bath-one-stage dyeing process under neutral conditions and at 130 °C, selected disperse and bis-3-carboxypyridinium-s-triazine reactive dyes have been especially promoted during last two decades [5,6].

With the aim to find further possibilities for achieving one-bath-one-stage dyeing process by avoiding the use of separate dye class for each component in the PES/cotton blend, the application of novel synthesized dyes having, under certain conditions, substantivity both for polyester and cotton has been studied [7]. These are the so called reactive disperse dyes with sulfatoethylsulfonyl group which at pH 5 have characteristics of disperse dyes and are predominantly distributed on PES fiber. Under these conditions the dye uptake on cotton is negligible, but it increases rapidly after addition of alkali, whereas the sulfatoethylsulfonyl group converts to reactive vinylsulfonyl group capable of reaction with cotton.

Another approach involves modification and control of PES fiber surface properties. The need to control surface characteristics of PES derives from specific requirements for given application (wettability, hydrophilicity, dyeability, oligomer content, adhesion properties, antibacterial activity, biocompatibility, etc.) and with this in mind several treatments, such as alkaline hydrolysis [8-13], enzymatic hydrolysis [14,15], plasma treatment [16-23], and chitosan treatment [24] are currently being intensively studied. It has been reported that after corona discharge treatment in air, the hydrophilicity and adhesion properties [25,26], as well as activation energy of dyeing of the PES fabrics are improved [27]. When applied to cotton, corona discharge enhances hydrophilicity, and ionization, and can be used as an alternative method in preparation of cotton for dyeing and printing [28].

Recently, quite a new approach is suggested for dyeing of PES/cotton blend consisting of pre-treatment with biopolymer chitosan and subsequent dyeing with direct dyes [29]. The main goal of this approach is to avoid the use of disperse dyes for PES/cotton blend dyeing. In the present work, similar idea has been adopted, which additionally involves corona discharge pre-treatment of PES/cotton blend with the aim to enhance dyeability of both components. In order to assess the feasibility of one-bath one dye-class dyeing method proposed, polyester, cotton, and PES/cotton blend woven fabrics were treated with corona discharge (CD) and/or chitosan solutions of different concentrations, and subsequently dyed with direct or reactive dye. In order to characterize the extent of surface modification of both PES and cotton, the effects of various CD treatment times on the wettability were assessed and the surface chemical changes were quantified by XPS. The quality of PES/cotton blend dyeing was assessed on the basis of color intensity, the degree of reactive dye fixation, and color fastness obtained.

## Experimental

### Materials

All fabrics used for the experiment (Table 1) were kindly supplied by Mak a.d. (Bulgaria). Chitosan was used as obtained (without further purification) from Primex (Norway). It had the following properties: degree of deacetylation 96 %, viscosity 102 cP (1 % w/v chitosan solution), solubility 99.9%, dry matter content 85 %, and ash content 0.1 %.

Direct dye Sirius Red F3B (Bayer, Germany) (Direct Red 80; C.I. 35780; molecular weight: 1373.1 g/mole) and reactive dye Ostazin Red H3B (Chemapol, Czech Republic) (Reactive Red 3; C.I. 18159; molecular weight: 774.048 g/mole) were used for dyeing. Their structures are shown in Figure 1. The dyes were used as received without further purification.

### Surface Modification

Fabric samples (55×35 cm) were treated in a corona discharge equipment Corona - Plus TYP TF-415 (Vetaphone, Denmark) equipped with PF9 ceramic electrode. The treatment power was maintained constant (800 W) and the distance between the electrode and the silicone covered roller was 3-4 mm. The samples were treated on both sides, always passing twice through the discharge area in each treatment cycle. Treatments were done with 3 and 5 cycles, with the roller rotation speed maintained at 4 and 10 min$^{-1}$, so the corresponding resident times were 40, 60, 80, and 130 s.

For chitosan treatment, the solutions were freshly prepared by dissolving specified quantities of chitosan (1, 5, and 10 g/*l*) in distilled water containing acetic acid (3 g/*l*). The fabric samples (of which some were previously treated with 40 s corona discharge) were treated in these solutions for 20 min with permanent agitation. After the treatment the samples were squeezed on a laboratory padder and dried at room temperature, rinsed with distilled water, and dried again. The

**Table 1.** Characteristics of textile fabrics used

| Fabric | Material | Weave | Weight of unit area (g·m$^{-2}$) | Fabric density (threads·cm$^{-1}$) | | Linear yarn density (tex) | |
|---|---|---|---|---|---|---|---|
| | | | | Warp | Weft | Warp | Weft |
| PES | 100 % PES | Plain | 149.5 | 23.6 | 18 | 17.8×2 | 17.8×2 |
| Cotton | 100 % Cotton | Twill 2/1 S | 206.7 | 43 | 22 | 15×2 | 15×2 |
| PES/cotton | 50 % PES/<br>50 % Cotton | Twill 2/1 Z | 172.5 | 36.9 | 26 | 15×2<br>(PES/cotton 50/50) | 20×1<br>(PES/cotton 50/50) |

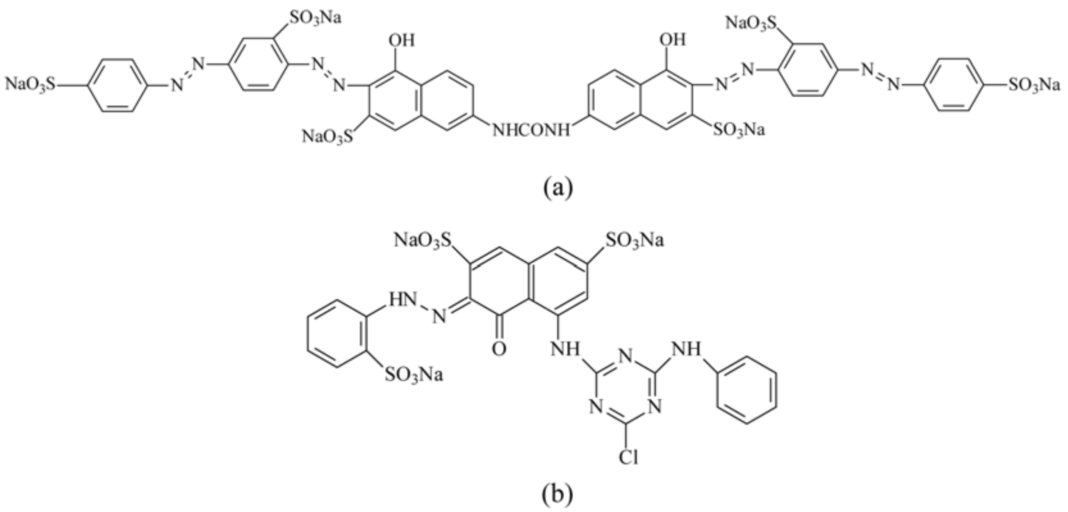


**Figure 1.** Dye structure of (a) C.I. Direct Red 80 and (b) C.I. Reactive Red 3.

**Table 2.** Sample labels and treatment parameters

| Designation | Treatment |
|---|---|
| 0P | Untreated PES fabric |
| 1P | PES fabric treated with CD for 40 s |
| 2P | PES fabric treated with chitosan solution 1 g/*l* |
| 3P | PES fabric treated with chitosan solution 5 g/*l* |
| 4P | PES fabric treated with chitosan solution 10 g/*l* |
| 5P | 1P + chitosan 1 g/*l* |
| 6P | 1P + chitosan 5 g/*l* |
| 7P | 1P + chitosan 10 g/*l* |
| 0C | Untreated cotton fabric |
| 1C | Cotton fabric treated with CD for 40 s |
| 2C | Cotton fabric treated with chitosan solution 1 g/*l* |
| 3C | Cotton fabric treated with chitosan solution 5 g/*l* |
| 4C | Cotton fabric treated with chitosan solution 10 g/*l* |
| 5C | 1C + chitosan 1 g/*l* |
| 6C | 1C + chitosan 5 g/*l* |
| 7C | 1C + chitosan 10 g/*l* |
| 0M | Untreated PES/cotton blend fabric |
| 1M | PES/cotton blend fabric treated with CD for 40 s |
| 2M | PES/cotton blend fabric treated with chitosan solution 1 g/*l* |
| 3M | PES/cotton blend fabric treated with chitosan solution 5 g/*l* |
| 4M | PES/cotton blend fabric treated with chitosan solution 10 g/*l* |
| 5M | 1 M + chitosan 1 g/*l* |
| 6M | 1 M + chitosan 5 g/*l* |
| 7M | 1 M + chitosan 10 g//*l* |

sample labelling and corresponding treatment parameters are given in Table 2.

### XPS Analysis

X-ray photoelectron spectroscopy (XPS) was used to investigate the surface chemical changes after corona discharge (CD) treatment of textile fabrics. The fabric samples were analyzed using an ESCA-LAB MKII spectrometer (VG Scientific, USA) with Mg $K_\alpha$ monochromatic radiation source (1253.6 eV) and using 300 W power. Spectra were obtained with a monochromator and take-off angle of 0 °, working with residual vacuum of $10^{-6}$ Pa. The survey spectra, to determine elemental concentrations of the surface layer (C and O in Tables 3 and 4) were taken in the range of 0-1100 eV (with 0.3 eV increments). Carbon spectra (C 1s) of high resolution were taken in the range of 280-300 eV (with 0.1 eV increments) from which the chemical state of carbon was determined (C1 to C4). The curve fitting was made using Spectrum NT software. All binding energies were calculated with respect to the reference value of carbon (C 1s) photoelectron signal at 285 eV [30]. The curve peak positions on C 1s deconvoluted spectra were fixed at 284.6 eV for C1 (C-H or C-C), 286.4 eV for C2 (C-O), 288.1 eV for C3 (C=O or O-C-O), and 288.9 eV for C4 (COOH) [31-34]. The chemical shifts of peaks were from 1.58 -5.52 eV for PES and 1.87 -5.13 eV for cotton.

### Wettability

The wettability data were obtained using AATCC Test Method 39-1980. In order to determine wetting time, one drop of water was placed from a distance of 1 cm onto a tensioned fabric sample. The time (s) required for water mirror to disappear from the surface was taken as wetting time. The results are the average of at least 5 measurements.

### Dyeing

In order to assess dye behavior towards each component, PES and cotton samples were dyed in a single dyebath

**Table 3.** Surface elemental composition from XPS survey spectra and relative amounts of differently bonded carbons estimated from high resolution C 1s XPS spectra for PES

| Sample | Surface composition (at.%) | | Atomic ratio | Carbon components (at.%) | | | |
|---|---|---|---|---|---|---|---|
| | C | O | O/C | C1 | C2 | C3 | C4 |
| Untreated | 76.1 | 23.9 | 0.31 | 67.01 | 20.35 | 12.64 | 0 |
| CD treated | 72.1 | 27.9 | 0.39 | 40.24 | 39.22 | 15.34 | 5.20 |
| Theoretical values for PES | 71.4 | 28.6 | 0.40 | 60 | 20 | 20 | 0 |

**Table 4.** Surface elemental composition from XPS survey spectra and relative amounts of differently bonded carbons estimated from high resolution C 1s XPS spectra for cotton

| Sample | Surface composition (at.%) | | Atomic ratio | Carbon components (at.%) | | | |
|---|---|---|---|---|---|---|---|
| | C | O | O/C | C1 | C2 | C3 | C4 |
| Untreated | 66.6 | 33.4 | 0.50 | 64.32 | 35.68 | 0 | 0 |
| CD treated | 54.0 | 46.0 | 0.84 | 32.66 | 48.49 | 14.40 | 4.45 |
| Theoretical values for cellulose | 54.5 | 45.5 | 0.83 | 0 | 83 | 17 | 0 |

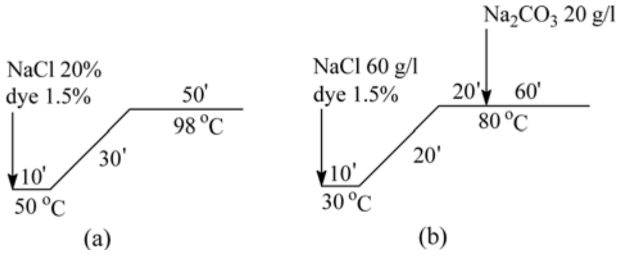


**Figure 2.** Dyeing profiles with (a) C.I. Directed Red 80 and (b) C.I. Reactive Red 3.

simultaneously. The dyeing of PES/cotton blend fabric was performed under the same conditions for the reason of comparison. When dyeing single component fabrics in the same solution their mass ratio was 50:50 and total mass 4 g, the same as the mass of PES/cotton blend sample. The dyeing was performed in an Ahiba (Switzerland) dyeing apparatus with vertical fabric movement in 180 m*l* dyebath volume according to the dyeing profiles shown in Figure 2. The chemicals used were of laboratory grade.

After dyeing, the samples were rinsed with warm and cold distilled water and dried. The reflectance values *R* were measured using a reflectance spectrophotometer Spectraflash SF600X (Datacolor, USA). In order to determine the degree of dye fixation *F*, samples dyed with reactive dye were treated in soap solution (95 °C, 10 min) and reflectance *R* is measured again. Color intensity *K/S* was calculated at maximum absorption wavelengths (540 nm for Direct Red 80 and 550 nm for Reactive Red 3) using Kubelka-Munk equation (1):

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

Fixation degree *F* was calculated using equation (2):

$$F = \frac{(K/S)_T}{(K/S)_0} \cdot 100 \qquad (2)$$

where subscript *T* refers to the fabric treated with soap solution and subscript 0 to untreated fabric. Washing and rubbing fastnesses were determined on dyed samples according to ISO 105-C06:1994 and ISO 105-X12:2001 standard, respectively.

## Results and Discussion

### Surface Chemical Analysis

XPS analysis was performed on untreated and CD treated PES and cotton fabric samples. Surface elemental concentrations and O/C ratios were calculated from the survey spectra. Relative amounts of carbon with different numbers of oxygen bonds were estimated from high resolution C 1s carbon spectra, shown in Figure 3 for PES fabric (0P and 1P) and in Figure 4 for cotton fabric (0C and 1C).

The surface elemental composition and relative amounts of differently bonded carbons, as well as their ratios for PES and cotton fabric are given in Tables 3 and 4.

Results for elemental composition of untreated PES correspond well to previously reported values [35]. After CD treatment significant changes in chemical constitution of PES fabric appear, such as increasing of oxygen content and reducing of carbon content in the surface layer. O/C ratio of CD treated fabric is about 25 % higher compared to the untreated one and almost reaches the theoretical value for PES. The relative amount of each type of carbon is also modified after CD treatment. This can be observed in peak intensity changes in Figure 3, where carbon C1 and C2 peaks have similar areas for CD treated sample, indicating that the sample contains almost the same amounts of C1 and C2 carbons, though the original content (before CD treatment) of C1 carbon was more than 3 times that of carbon C2 (Table 3). Non-oxidized carbon fraction (C1) in treated sample is less by 40 %, but contents of carbon with one (C2) and two (C3) oxygen bonds were dramatically increased amounting

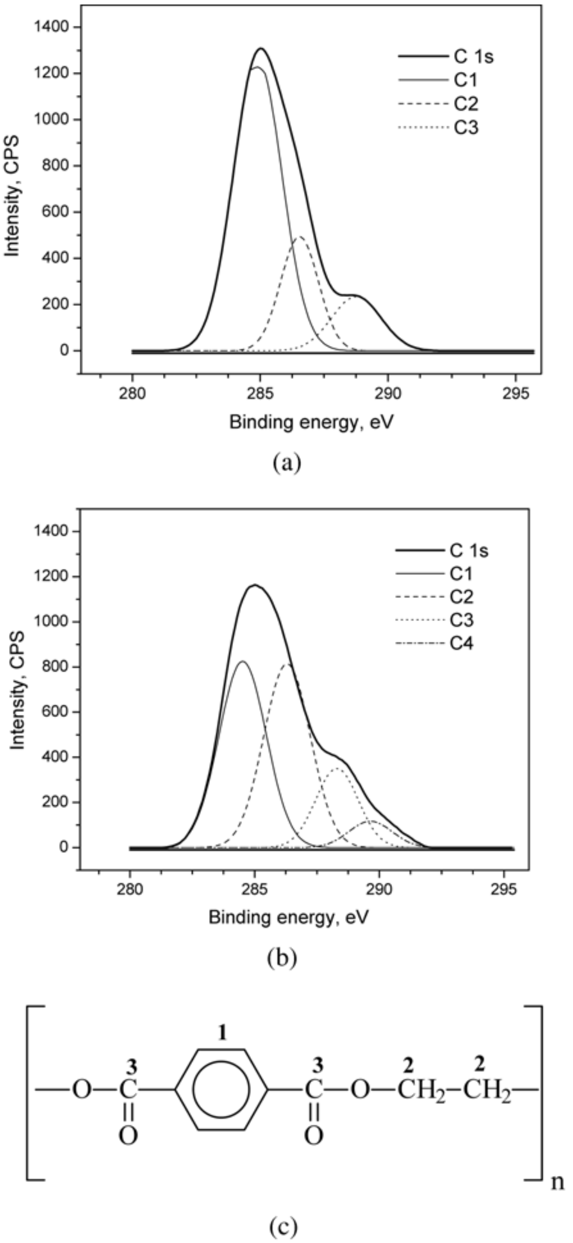


**Figure 3.** Deconvoluted XPS C 1s spectra of (a) untreated and (b) CD treated PES fabric, and (c) the structure of the repeating PES unit with labelled carbon atoms.

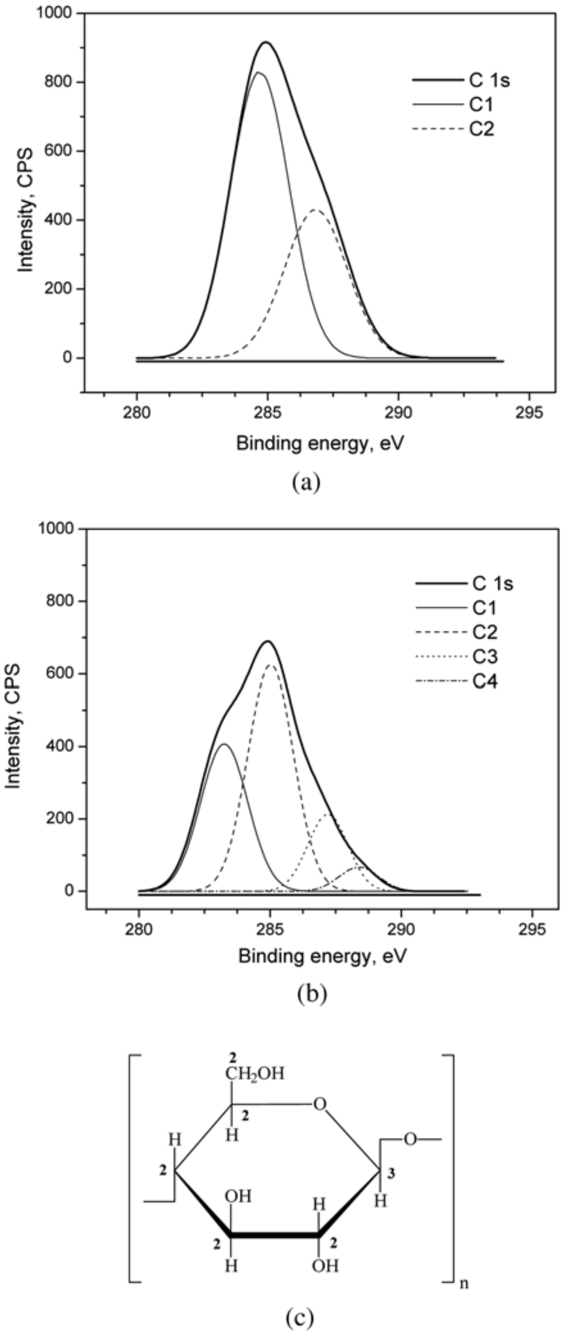
100 % and 24 %, respectively. A carbon with a new functional group with oxygen (C4) is formed on CD treated sample.

The significant decrease of C1 relative amount indicates that carbon atoms from aromatic rings in PES greatly participated in oxidation. This oxidation could be initiated and subsequently notably accelerated by physical effects formed in corona discharge [36]. In general, interactive action of physical effects and chemical reactions can enhance surface modification processes occurring in every surface treatment based on plasma discharge. Energy reach particles, e.g. ions, electrons, photons, charged radicals, etc., which exist in plasma, can bombard exposed material surface resulting in strong degradation of surface layer. Plasma constituents of higher energy level (for example UV photons) can destroy chemical bonds on the surface and initiate many reactions between the active plasma species and the sample surface, thus inducing efficient surface modification [37,38].

Various oxidation processes take place on the surface during CD plasma treatment of polyester, but most probably the oxidation of C-H groups to alcohol occurs, where hydrogen atoms are replaced with hydroxyl groups. These processes form phenols from aromatic species or convert -O-$CH_2$- segments to -O-(CHOH)- or -O-(CHOOH)- groups increasing C2 and C3 contents, forming C4 carbon and increasing oxygen concentration on the surface layer. Physical bombardment can induce breaking of polymer chains producing shorter polymer fragments resulting in degradation of the treated polymer material. Chain cleavage is probably produced at -O-$CH_2$- and -O-(C=O)- molecular sites, because ester group is considered a weak point in polymer backbone, while cleavage of aromatic rings seems very unlikely [39]. Molecule fragments produced from chain cleavage are very reactive and can react with atmospheric gases contributing also to polar groups increase on the polymer surface (post plasma reactions) [19].

Significant chemical modifications also happen on CD treated cotton fabric with a reduction of carbon content by 20 % and increase of oxygen content by approximately 40 %, resulting in O/C ratio increase by 68 % on original value and reaching the values of pure cellulose (Table 4). Relative amounts of differently bonded carbons were obtained from high resolution XPS spectra peaks for total carbon (C 1s). In spite of the fact that cellulose does not contain carbon atoms without neighbouring oxygen (C1 in Table 4) and expectation to show two component C 1s XPS spectrum with C2 and C3 carbon components in 5:1 ratio (Figure 4(c)), a significant amount of C1 carbon was detected in the original sample, suggesting that cellulose surface did not consist of pure cellulose. Results for carbon components C1:C2=64.32:35.68 and O/C atomic ratio are in compliance with previous studies [33], because even in "pure" cellulose material still exists a spectral intensity of C1 carbon component, contributing typically with 10-20 % of intensity of C 1s XPS [40] and indicating hydrocarbon contamination or some modification of polymer. It was reported recently that it was difficult to completely remove waxes containing carbon C1 and therefore it could be taken as a marker for the presence of such substances [41].

Carbon C1 content in CD treated cotton fabric is reduced to the half of the original value and carbon C2 content is increased by 36 %. These changes are noticeable in Figure 4 as a great change of C1 and C2 carbon peak areas. Carbons C3 and C4 also appear as indications of newly formed functional groups with oxygen, their peaks being evident in



(a)

(b)

(c)

**Figure 4.** Deconvoluted XPS C 1s spectra of (a) untreated and (b) CD treated cotton, and the structure of (c) the cellulose repeating unit with labelled carbon atoms.

Figure 4(b). Chemical composition of the treated sample suggests that the main chemical change occurs on C1 carbon by removing non-cellulosic cotton components and increasing oxygen polar group content due to oxidative chemical changes on the surface. These changes are expected to increase surface free energy, wettability, substantivity for dyes and other hydrophilic substances.

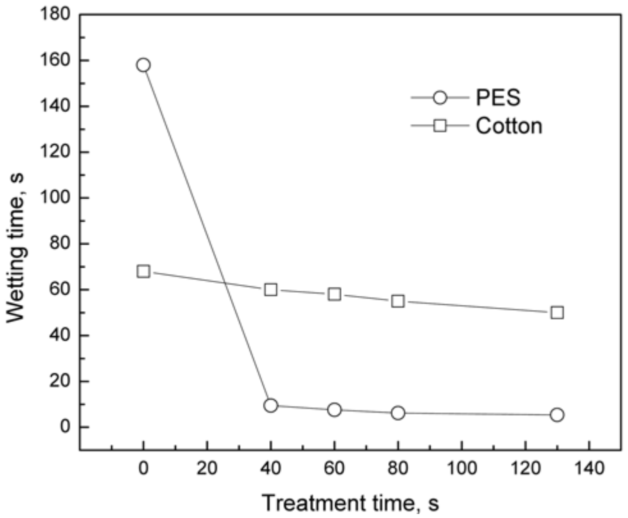


**Figure 5.** Wettability of PES and cotton fabric vs. CD treatment time.

## Wetting Properties

Wetting and absorption of liquids are of essential importance in the industrial processes such as dyeing and finishing, as well as for functional properties of textile in use and maintenance. Modification of fiber surface composition in textiles can change the entire surface wetting behavior.

The surface hydrophilicity of untreated and CD treated samples was evaluated by measuring water drop absorption time. CD treated PES samples showed remarkable increase of hydrophilicity, with absorption time always under 10 s, compared to 158 s of untreated PES fabric (Figure 5).

Absorption times on various points of a sample were approximate, indicating a high uniformity of treatment which is the consequence of high discharge power applied. Wettability is highly improved after a short CD treatment (40 s), giving evidence of the existence of new hydrophilic groups on fiber surface. This finding corresponds the previously published results reporting that short resident times can reduce contact angle by more than 20 $^{o}$ [38]. A dramatic increase of PES fabric hydrophilicity could be attributed to hydrophilic groups formed on the fiber surface. As already described, due to oxidation reactions induced by CD treatment, the number of oxygen containing functional groups (-OH, -C=O and -COOH) is significantly increased, increasing the surface free energy and wettability. The wettability of CD treated cotton fabric samples is slightly enhanced in almost linear manner with the treatment time (Figure 5).

Obviously, there is a CD treatment time after which the saturation of the effects appears, i.e. longer treatment does not produce significant changes. Anyhow, longer resident times and higher discharge power are considered necessary because longer durability of treatment is achieved both on synthetic and natural textile materials.

**Dyeing Properties**

The effect of different pre-treatments on color intensity is shown in Figures 6-8 for Direct Red 80 and Figures 9-11 for Reactive Red 3. CD treated samples of PES (1P) and cotton fabrics (1C), which were dyed simultaneously, show enhanced dyeing properties with color intensity on PES higher by 67 % for Direct Red 80 and 7 % for Reactive Red 3, and on cotton higher by 30 % for Direct Red 80 and 6.3 % for Reactive Red 3. Anyway, the obtained color intensities on PES even after CD treatment remain very low (*K/S* less than

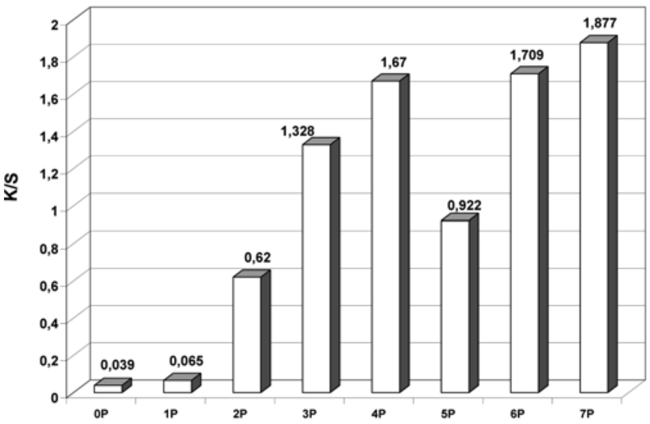


**Figure 6.** Color intensity of C.I. Direct Red 80 on PES fabric.

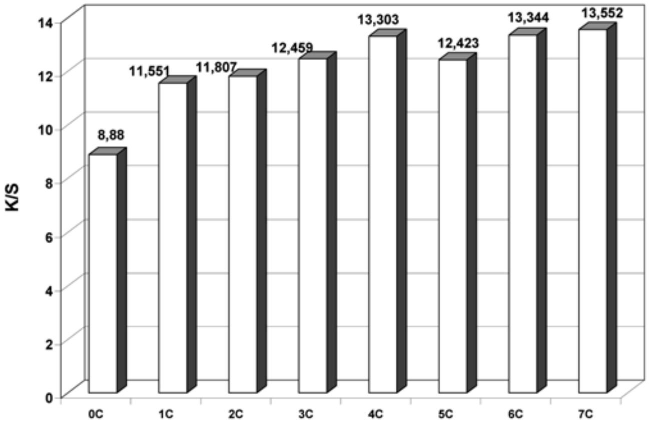


**Figure 7.** Color intensity of C.I. Direct Red 80 on cotton fabric.

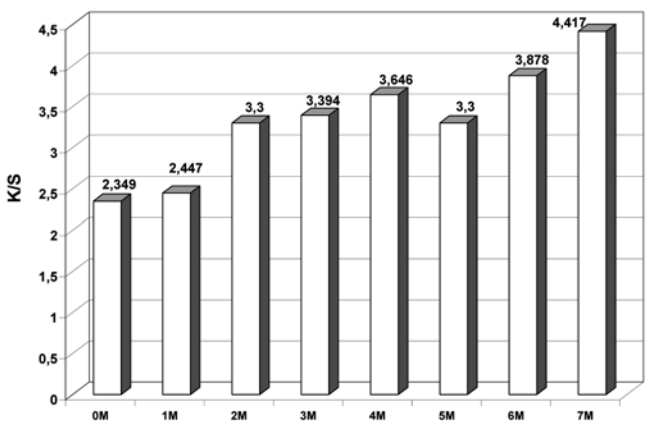


**Figure 8.** Color intensity of C.I. Direct Red 80 on PES/cotton blend fabric.

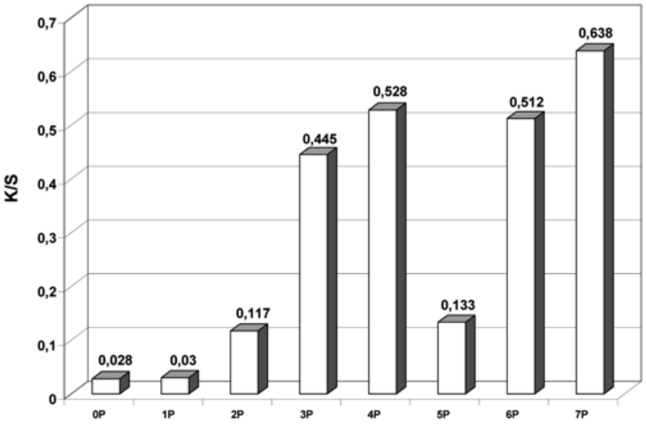


**Figure 9.** Color intensity of C.I. Reactive Red 3 on PES fabric.

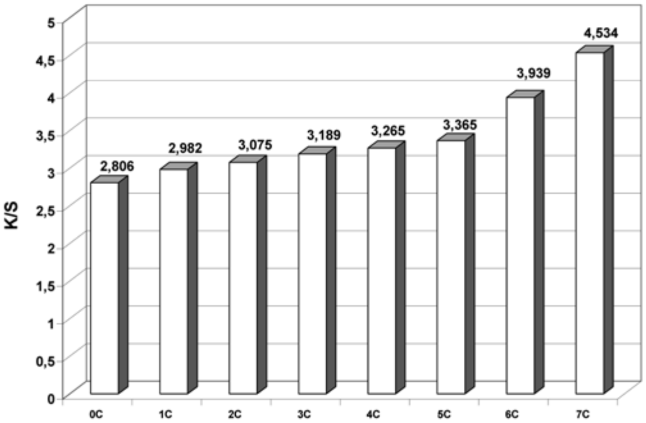


**Figure 10.** Color intensity of C.I. Reactive Red 3 on cotton fabric.

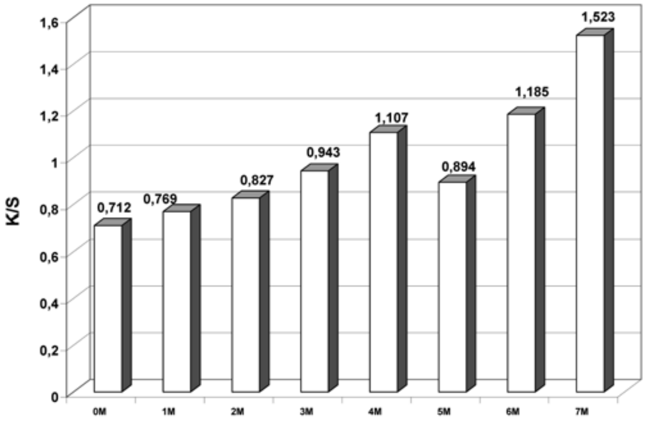


**Figure 11.** Color intensity of C.I. Reactive Red 3 on PES/cotton blend fabric.

0.1), which is considered unsatisfactory from the technical point of view. Similar result has been obtained on CD treated PES/cotton blend fabric (1M), with obviously higher *K/S* value as the consequence of the contribution of cotton component. Hence, the competitive dyeing power of CD treated polyester could be only slightly improved, even though favourable physical and chemical modifications of fiber surface occurred, as confirmed through XPS analysis and wetting measurements.

When PES fabric was treated with chitosan (2P, 3P and 4P), the samples showed remarkable enhancement in dyeability with both direct and reactive dye. Color intensity (*K/S*) after dyeing was higher 15-40 times for direct and 3-18 times for reactive dye compared to untreated fabric, depending on chitosan concentration applied. Since color intensity increased proportionally with the concentration of chitosan solution, the observed effect can be attributed to chitosan deposition on polyester [42]. Most important observation is that *K/S* values reached satisfactory level, especially with higher chitosan concentrations applied. The percentage increase of color intensity on chitosan treated cotton fabric (2C, 3C and 4C) is 33-50 % for direct and 9.6-16.5 % for reactive dye, again clearly depending on chitosan concentration increase.

In case of PES/cotton blend fabric treated with chitosan (2M, 3M and 4M), the enhanced dyeability of each component contributes to overall color intensity increase for direct dye by 40-55 % and reactive dye by 16-55 %.

Chitosan treated samples have higher binding capacity for direct and reactive dyes as a consequence of hydroxyl and amino group reactivity, which is in compliance with reported fact that chitosan, depending on experimental conditions, exhibits a significant adsorption of anionic dyes [43]. It has been previously confirmed that chitosan can successfully be used as a pre-treatment agent for improvement of dye exhaustion in leather dyeing by anionic and reactive dyes [44,45]. The enhanced substantivity of anionic and reactive dyes was attributed to the presence of primary amino groups, which, at certain pH values, form ionic bonds with anionic dyes, and covalent bonds with reactive dyes. In cotton treatment, chitosan has been used as an agent for subsequent after-treatment of dyed cotton textiles for covering undyed spots of unmatured cotton fibers [46] and for enhancing

**Table 5.** Color fastness (C.I. Direct Red 80 and C.I. Reactive Red 3) and fixation degree (C.I. Reactive Red 3) for differently treated samples (labelling-see Table 2)

| Sample | C.I. Direct Red 80 | | | C.I. Reactive Red 3 | | | |
|---|---|---|---|---|---|---|---|
| | Fastness | | | Fastness | | | Fixation degree *F* |
| | Washing | Rubbing - dry | Rubbing - wet | Washing | Rubbing - dry | Rubbing - wet | |
| 0P | 3-4 | 4-5 | 4-5 | 3-4 | 4-5 | 4-5 | 0.78 |
| 1P | 3-4 | 4-5 | 4-5 | 3-4 | 4-5 | 4-5 | 0.77 |
| 2P | 3-4 | 4-5 | 4-5 | 3-4 | 4-5 | 4-5 | 0.78 |
| 3P | 4 | 4-5 | 4-5 | 4 | 4-5 | 4-5 | 0.77 |
| 4P | 3-4 | 4-5 | 4-5 | 3-4 | 4-5 | 4-5 | 0.80 |
| 5P | 3-4 | 4-5 | 4-5 | 3-4 | 4-5 | 4-5 | 0.81 |
| 6P | 3-4 | 4-5 | 4-5 | 4 | 4-5 | 4-5 | 0.80 |
| 7P | 3-4 | 4-5 | 4-5 | 4 | 4-5 | 4-5 | 0.76 |
| 0C | 4 | 5 | 4-5 | 4 | 5 | 4-5 | 0.83 |
| 1C | 4 | 5 | 4-5 | 4 | 5 | 4-5 | 0.81 |
| 2C | 4 | 5 | 4-5 | 4 | 5 | 4-5 | 0.82 |
| 3C | 4 | 5 | 4-5 | 4 | 5 | 4-5 | 0.81 |
| 4C | 3-4 | 4-5 | 4-5 | 4 | 4-5 | 4-5 | 0.80 |
| 5C | 4 | 5 | 4-5 | 4 | 5 | 4-5 | 0.80 |
| 6C | 4 | 5 | 4-5 | 4 | 4-5 | 4-5 | 0.79 |
| 7C | 3-4 | 4-5 | 4-5 | 4 | 4-5 | 4-5 | 0.78 |
| 0M | 3-4 | 5 | 4-5 | 3-4 | 5 | 4-5 | 0.83 |
| 1M | 3-4 | 5 | 4-5 | 3-4 | 5 | 4-5 | 0.81 |
| 2M | 3 | 5 | 4-5 | 3 | 5 | 4-5 | 0.82 |
| 3M | 3 | 5 | 4-5 | 3 | 5 | 4-5 | 0.81 |
| 4M | 3-4 | 5 | 4-5 | 3-4 | 5 | 4-5 | 0.80 |
| 5M | 3 | 5 | 4-5 | 3 | 5 | 4-5 | 0.81 |
| 6M | 3 | 5 | 4 | 3 | 5 | 4 | 0.79 |
| 7M | 3 | 5 | 4 | 3 | 5 | 4 | 0.78 |

dyeing of cotton with lac natural dyes in acidic medium [47]. The reaction kinetics of the reactive dye Procion Yellow RS with chitosan amino groups was also studied, giving rise to the conclusion that dichlorotriazine dyes react with chitosan amino groups in acid and alkaline solutions and with hydroxyl groups in alkaline solutions [48].

The interaction of chitosan with dyes has been extensively studied for ecological purposes. Chitosan and chitin have potential as effective and inexpensive adsorbents of reactive dyes, metal ions and organic compounds from industrial waste waters, because amino and hydroxyl groups can serve as coordination and electrostatic interaction sites [49-51]. The adsorption of a reactive dye (Reactive Red 189) from water solutions on cross linked chitosan beads was also studied [52,53]. On the basis of pH influence on the adsorption of reactive dye the authors suggested two possible interaction mechanisms between the reactive dyes and chitosan: the electrostatic interaction between protonised amino groups ($-NH_3^+$) and dye anion, and the chemical reaction between reactive groups (-Cl in reactive dye) and amino ($-NH_2$) or hydroxyl (-OH) groups in chitosan. In our experiment, the most encouraging results have been obtained with samples to which a combined treatment was performed by CD (first step) and chitosan solution (second step) (Samples numbered 5, 6, and 7). In case of PES/cotton sample dyeing with any of the dyes used, when using the highest chitosan concentration the color intensities are doubled compared both to untreated sample (7 M vs. 0 M) and CD treated sample (7 M vs. 1 M). Color intensity was again uniformly increased with chitosan concentration, but the most important observation is that the color intensities were noticeably higher compared to samples treated with CD or chitosan only. Obviously, significantly higher chitosan quantities were adsorbed on samples previously activated with CD treatment bringing to the conclusion that prior modification with the aim of increasing the polar group contents on the fiber surface improves subsequent chitosan treatment efficiency.

The fixation degree (*F*) of reactive dyes (Table 5) has standard values expected for reactive dyes having monochlorotriazine reactive group. On samples treated with CD and/or chitosan small fluctuations were noticed and a relationship between pre-treatment and fixation degree could not be established. However, higher fixation degree produces lower dye concentrations in waste waters, which is additional benefit to the increased color intensity. Higher dye fixation is the consequence of the reaction between chitosan hydroxyl group and reactive centre of dyes. It is well known that monochlorotriazine reactive group of reactive dyes can react with cellulose hydroxyl group (Cell-OH) after the adjustment of alkaline pH with $Na_2CO_3$. Also, in alkaline solution, a deprotonizing of chitosan hydroxyl group occurs [54]:

$$-CH_2OH + OH^- -CH_2O^- + H_2O$$

so chitosan hydroxyl group can bind reactive dye covalently in alkaline conditions in the same manner as cellulose hydroxyl group in the regular dyeing process.

The dyed samples were tested to washing and rubbing fastness in order to check the quality of dyeing (Table 5). The values obtained were within the standard level required for washing fastness. However, the rubbing fastness of the samples with highest chitosan concentration was reduced by one degree, due to not sufficiently durable chitosan deposition in the surface layer of the treated material.

## Conclusion

This study showed the feasibility of one-bath one-dye class dyeing of PES/cotton blend with direct (Direct Red 80) or reactive (Reactive Red 3) dye after pre-treatment with corona discharge (CD) and chitosan. It has been confirmed that corona discharge treatment enhances hydrophilicity of cotton and PES fibers due to surface modification of the material and formation of C-O, C=O, and COOH groups. Increased hydrophilicity of PES and cotton induced only slightly increased color intensity (*K/S*) with both dyes investigated. Nevertheless, subsequent treatment with biopolymer chitosan noticeably enhanced the color intensity obtained, especially with PES fiber. The dyeability improved proportionally with the concentration of chitosan treatment solutions. However, the highest values of color intensity were obtained for the PES/cotton fabric subjected to the combined CD and chitosan treatment, suggesting that CD pre-treatment enhances efficiency of chitosan application. The improvement in color intensity (compared to untreated PES/cotton fabric) of 88 % for direct dye and 114 % for reactive dye has been obtained. Satisfactory values of dye fastness and fixation degree of reactive dye were obtained.

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