

Plasma-assisted Surface Modification of Polyester Fabric for Developing Halochromic Properties

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Abstract: In the field of textiles, introducing pH-sensitive dyes onto fibrous materials is a promising approach for the development of flexible sensor. In this study, poly(ethylene terephthalate) (PET) textile surface with halochromic properties was fabricated by plasma-assisted sol-gel coating, followed by immobilization of two different azo pH-indicator dyes; namely Brilliant yellow and Congo red by conventional printing technique of fabrics. 3-aminopropyltriethoxysilane (APTES) was used as a coupling agent for attaching the pH-sensitive dyes through its terminal amines. The surface immobilization of APTES on PET fabric was conducted by the pad-dry-cure method. Moreover, the influence of oxygen plasma pre-treatment and the method of post-treatment either by oxygen plasma or by thermal treatment on the stability of sol-gel based matrix was investigated. The morphology and chemistry of 3-aminopropyltriethoxysilane coated PET surfaces were examined by using surface sensitive methods including electrokinetic and time-dependent contact angle measurements as well as X-ray photoelectron spectroscopy (XPS). In addition, fastness tests of the printed fabrics and color strength were carried out to assess the effectiveness of the fabric surface modification. Results indicate that sol-gel matrix exhibited a more stability by thermal post-treatment at 150 C for 5 min. Also, the results revealed that the printed fabrics with halochromic properties demonstrated sufficient stability against leaching by washing. The current work opens up a novel opportunity to develop flexible sensors based on fibrous materials, which have the potential to be employed in variable industrial applications.

Keywords: Halochromic properties, Surface modification, Sol-gel, Electrokinetics, XPS

Introduction

In recent years, the field of pH-responsive textiles has been stimulated growing academic and commercial interest due to their broadening applicability in various applications [1]. For example, Jovic *et al.* prepared poly-NiPAAm/chitosan hydrogel particles of the submicron scale for developing of cotton fabric with dual sensitivity and responsiveness to pH and temperature changes to provide new and interesting features [2]. Van der Schueren *et al.* studied dyeing of cotton and nylon fabrics with standard water soluble pH-indicator dyes that develop pH-sensitive flexible textile sensors to provide an indication of the environment's pH by an easy visual colour observation [3]. Osti *et al.* recorded a considerable decrease in cases of skin maceration through therapy and pain control by using pH-responsive wound dressing [4].

Within the group of pH-responsive textiles, a growing interest is recognized with halochromic textiles. These textiles can change their colour due to a change of pH [5]. A colour-changing textile sensor systems show high flexibility, which is the major benefit over the usually used sensor systems [3,6]. In literature, most halochromic textiles obtained so far are from cellulosic fabrics, which is considered as an excellent carrier for pH-sensitive dyes [7]. On the other hand, tailoring PET fabric surfaces with halochromic properties represents one of the outstanding challenges.

Poly(ethylene terephthalate) (PET) is the most broadly

used textile material in the textile industries. PET fabrics display required properties, such as dimensional stability, high tensile strength as well as chemicals and environmental resistance [8]. These notable characteristics make it an excellent candidate for a wide range of applications, for example, domestic textiles, technical textiles, the automotive and medical textiles industry [9]. Unfortunately, the polyester fabric does not exhibit reactive functionalities, such as -NH₂, -COOH, and/or -OH groups needed for various interactions, which renders the molecule of PET has partial reactivity, poor adhesion, and hydrophobic properties. These deficiencies in functional properties of PET fabrics have constrained their further uses in different industrial fields such as packaging, adhesives, biomedical and printing technologies.

To obtain polyester fabrics with halochromic properties, it is often required to incorporate certain functional groups onto its surface. Especially, -NH₂ groups with their associated reactivity and polarity can be valuable in the attachment of a various pH indicator dyes, which typically have anchoring groups able to react with -NH₂ groups. To this end, significant efforts have been expended to tailor the surface properties of PET by the introduction of nitrogen-containing functionalities for changing the chemical and physical nature of the polyester to adjust its surface for a wide range of applications.

With this regards, there has been growing interest to discover an approach for introducing amine functionalities on PET surfaces. For example, Hegemann *et al.*, deposited nanoscale ultrathin films (<80 nm) on PET textile materials by ammonia/ethylene plasma modifications [10], Glampedaki

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et al. created primary amine groups on PET surfaces using ethylenediamine [11], Narushima *et al.* discussed reasons for differences in attachment of nitrogen functional groups by ammonia plasma processing on polyester surfaces [12]. Xu *et al.* treated PET fabrics with 3-aminopropyltriethoxysilane (APTES) to improve its anti-static properties [13].

Among the new methods, the sol-gel technology can be considered as one of the most important developments in material science in the recent years [14]. It can be used for modification of various textile substrates, which allows the possibility to modify surface properties to a certain degree, and to combine different properties such as antibacterial, UV protection, and wrinkle-free [15]. The product of the sol-gel process is the so-called nanosols, which is a liquid dispersion of low viscosity. The application of nanosols can be carried out in the field of fibrous materials by conventional procedures used for textile finishing. Probably the simplest method is pad-dry-cure. Curing procedures may include the thermal treatment, a plasma treatment, lasers, IR or UV radiation [16-19].

In the case of PET, chemical bonding to the nanosols coating is directly not possible [20]. In this case, the fabric surface has to be activated in order to introduce reactive groups, to achieve sufficient adhesion between the nanosols coating and the fabric surface [20]. Low-temperature plasma (LTP) treatments can be used to increase material wetting behaviour and adhesion properties. The physical and/or chemical modification of the first few molecular layers of the surface may result from the interaction of the plasma-generated excited species with a substrate interface, at the same time maintaining the properties of the bulk [21]. The plasma may also induce a crosslinking process [22], but to the best of our knowledge, little information is found about effects of the plasma post-treatment on the textile surface coating.

The aim of this study is to endow PET fabric surfaces with a pH-sensitive layer containing Brilliant yellow or Congo red dyestuffs by plasma-assisted sol-gel process, in which oxygen gas was employed as plasma process gas to improve PET reactivity and as a curing source of applied coatings. In addition, elucidation of the effects of using either oxygen plasma as the curing environment or the thermal curing on the formation and stability of sol-gel coatings on PET surface. The effect of treatments on the surface properties of the polyester fabric will be evaluated using a combination of different surface-sensitive characterization methods such as dynamic wetting measurements, X-ray photoelectron spectroscopy (XPS) and streaming potential measurements. Furthermore, the influence of the surface treatment of PET was studied with traditional printing technique by using Brilliant yellow and Congo red dyes and the obtained colour strength (K/S value) evaluated spectrophotometrically. The colour fastness properties to washing were also studied.

Experimental

Materials

Commercial PET 100 % plain weave fabric of (165 g/m²) used as the substrate for modification throughout this study was supplied by private sector Co., Egypt. To remove any residual impurities from fabric such as weaving and finishing oils, fabrics were treated before use with an aqueous solution containing 0.5 g/l non-ionic detergent Tissocyl CSB (Zschimmer & Schwarz, Burgstädt, Germany) and 1 g/l sodium carbonate. The liquor-to-fabric ratio of the aqueous solution was kept at 50:1 for 60 min at 70 °C. The fabrics were then thoroughly rinsed and allowed to air dried at room temperature until constant weight before use in the experimentation. The samples used for the modification procedures were 4×4 cm² in size and 0.3 mm in thickness. 3-aminopropyltriethoxysilane (Sigma-Aldrich), ammonium hydroxide solution (NH₄OH; 28-30 wt.%) (Acros organics), ethanol 95 % (VWR chemicals), Brilliant yellow (Figure 1(a), Aldrich), Congo red (Figure 1(b), Sigma), citric acid (Sigma), defoamer (Contripon AT, Zschimmer & Schwarz, Germany), guar gum (sigma-Aldrich), urea (Sigma-Aldrich), and mild oxidizing agent (Ludigol, BTC Speciality Chemical). Oxygen (99.95 %) were used as process gases for plasma treatments of PET fabric samples and purchased from Messer Griesheim, Germany. Nanopure water (>18.0 MΩ) purified using the Millipore Milli-Q gradient system, was used in all experiments.

Oxygen Plasma Treatment

The oxygen plasma treatment of PET surfaces was carried out in a plasma processor 440 (Technics Plasma, Kirchheim, Germany). The apparatus was equipped with a 2.4 GHz microwave source (maximum output power 600 W), which

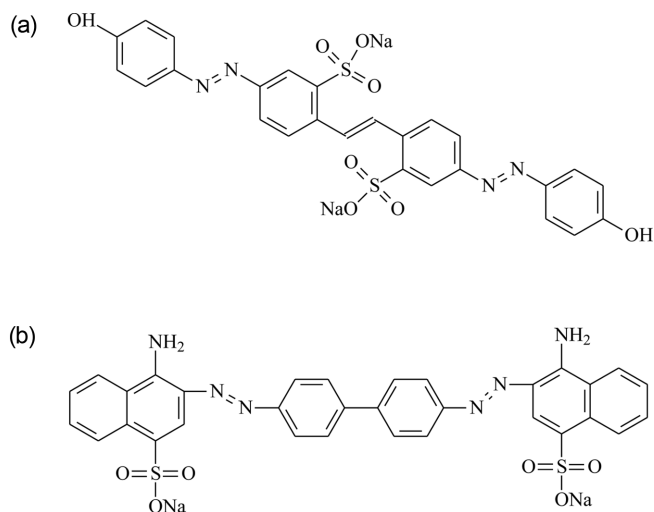


Figure 1. Structures of used pH-indicator dyes (a) Brilliant yellow, and (b) Congo red.

was connected by a quartz window to a vacuum chamber with dimensions of $350 \times 350 \times 350 \text{ mm}^3$ (base pressure 0.02 mbar). The process gas was introduced into the chamber via a gas-flow control system. After switching on the microwave source, homogenous plasma was formed in the chamber volume. The samples were treated under 0.14 mbar of pressure for 15 s, oxygen gas flow 10 sccm and the power was maintained at a constant level 600 W. These pre-treatment conditions were selected as optimal on the basis of our previous investigation [16].

Preparation of APTES Sol

Silica sol was prepared by using 3-propylaminotriethoxysilane (APTES) as a precursor, ammonium hydroxide (NH_4OH ; 28-30 wt.%) as a catalyst, ethanol as a solvent, and water. APTES, water, ethanol, and ammonium hydroxide solution were mixed in the molar ratios as shown in Table 1 and stirred overnight at room temperature.

Coating of PET Fabric with APTES Sol

Immediately following the oxygen plasma pre-treatment, the fabric samples were immersed in the prepared sol for 10 min at room temperature. Then air dried and post-treated either thermally in a convection oven or by low-temperature plasma under conditions as listed in Table 2. The thermal post-treatment conditions were chosen as these are commonly cited for PET coatings [23-26]. The samples obtained were thoroughly washed with distilled water in order to remove weakly adsorbed APTES and then dried again at room temperature.

X-ray Photoelectron Spectroscopy (XPS)

XPS measurements were carried out by means of an Axis Ultra X-ray photoelectron spectrometer (Kratos Analytical, Manchester, UK). The spectrometer was equipped with a monochromatic Al $K\alpha$ ($h\nu=1486.6 \text{ eV}$) X-ray source of 300 W at 15 kV. The kinetic energy of the photoelectrons was determined with a hemispherical analyser set to pass

energy of 160 eV for wide-scan spectra and 20 eV for the high-resolution element spectra. During all measurements, electrostatic charging of the sample was avoided by means of a low-energy electron source working in combination with a magnetic immersion lens. Later, all recorded peaks were shifted by the same amount that was necessary to set the C 1s peak to 284.76 eV for the carbon of the PET's phenyl ring [27]. Quantitative elemental compositions were determined from peak areas using experimentally determined sensitivity factors and the spectrometer transmission function. Spectrum background was subtracted according to Shirley [28]. The high-resolution spectra were deconvoluted by means the spectra deconvolution software (Kratos Analytical, Manchester, UK). Free parameters of component peaks were binding energy values, height, full width at half-maximum, and Gaussian-Lorentzian ratio.

Kinetics Measurements of Wetting

The wetting properties of the PET fabric surface before and after surface functionalization were estimated by means of dynamic wetting measurements, which were carried out with a FibroDAT 1122HS dynamic contact angle tester (Fibro System, Sweden) equipped with a high-speed video camera according to the sessile drop method. A microliter syringe was used to place a deionized water droplet (Millipore water having a surface tension of $\gamma_{lv}=72.8 \text{ mN/m}$ at 23°C) of a $10 \mu\text{l}$ volume on the fabric surface under investigation by a short stroke from an electromagnet [29]. The strength of stroke was minimized to avoid oscillation effects. The data were collected after the water droplet stabilized on the surface. The instrument was located in a temperature-controlled laboratory maintained at $23 \pm 1^\circ\text{C}$. The initial contact angle of water and the absorption time (i.e. time recorded until the drop had completely penetrated into the PET fabric surface) were used to evaluate the wettability of PET fabrics before and after plasma treatment. The contact angle and the absorption time of water droplets shown for each sample are averages of five single measurements [29].

Streaming Potential Measurements

Electrokinetic measurements were carried out to determine the electrokinetic potential (ζ) of the PET surface as a function of the pH values of the electrolyte solution using the streaming potential method. The streaming potential is generated when a liquid is forced to flow directly through a channel formed between two sample surfaces separated by a narrow slit. The streaming potential was determined using EKA electrokinetic analyzer from Anton Paar (Graz, Austria). The pH values were adjusted with $0.1 \text{ mol}\cdot\text{l}^{-1}$ HCl or $0.1 \text{ mol}\cdot\text{l}^{-1}$ KOH. To prevent a significant change in the ionic strength by adding HCl and KOH, all measurements were carried out in $10^{-3} \text{ mol}\cdot\text{l}^{-1}$ KCl, which is known as an inert electrolyte. The zeta potential values were calculated

Table 1. The molar ratios of used silica sol

Molar ratios			
APTES	H ₂ O	C ₂ H ₅ OH	NH ₄ OH
1	100	150	10

Table 2. Conditions for thermal and low-temperature plasma post-treatments

Thermal post-treatment		Low-temperature plasma post-treatment	
Curing temperature ($^\circ\text{C}$)	Curing time (min)	Power (w)	Time (min)
110	30	600	1
150	5	600	5

from the measured streaming potentials by the use of the Smoluchowski equation [30].

Printing Procedure

The printing pastes with the anionic dyes BY and CR dyes was formulated according to the following recipe:

Ingredients	By weight (%)
Dye	1
Guar gum	1.5
Urea	10
Ludigol	0.5
Citric acid	0.5
Contripon AT	0.2
Water	86.3

The aforementioned formulated printing pastes of the pH-indicator dyes were applied to the untreated and treated PET fabrics by using a conventional flat screen printing method [31]. After printing, the printed fabric samples were dried in the air followed by steaming at 100 °C for 20 min. Then, the printed fabric samples were rinsed with cold water and soaped using 3 g/l of non-ionic detergent (Tissocyl CSB) at 60 °C for 15 min at a liquor-to-fabric ratio of 50:1. Afterward, the samples are rinsed in cold water to remove unfixed dyes and finally air-dried.

Colour Strength Measurements of Printed Fabrics

The PET fabrics printed under different conditions of treatments were individually tested for their colour strength (K/S). The K/S values are a function of the spectral reflectance of a given wavelength and are defined as the ratio between light absorption (K) and scattering (S) characteristics of the sample. The colour strength K/S values of the printed fabrics were instrumentally determined from reflectance measurements with the following Kubelka-Munk equation [32,33].

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

where (β) is the degree of remission= $R/100$. Reflectance (R) obtained from a software calculation is expressed as a percent value. (S) is the scattering coefficient and (K) is the absorption coefficient of the printed fabrics. The K/S_{\max} value corresponded to the largest value of K/S over the scanned wavelength is commonly used to describe the color strength of a dye-substrate system [34]. Therefore, the increase of the K/S_{\max} value can be used as a characteristic for different surface modification approaches applied to PET.

On the other hand, the halochromic behavior of the printed PET fabrics was evaluated by immersing them into aqueous pH-baths. Sodium hydroxide and hydrochloric acid were

used to adjust the pH of the aqueous pH baths. The absorbance of Kubelka-Munk as a function of pH at acidic and alkaline peak maximum were presented, thus showing the pH range in which visual color changes occur.

The colorimetric measurement by reflectance was carried out in ACS imaging system CS-5 Chroma Sensor colorimeter (standard illuminant D65; 10° standard observer). The reflectance of the printed fabrics was measured over the wavelength range of 400-700 nm. In the process, the unprinted fabrics were used as a reference. Each fabric sample was folded twice, and three scans were performed at different places on the fabric surface. The average value was recorded.

Color Fastness Properties

The colour fastness properties of the printed fabrics to washing and crocking were assessed by DIN EN 20105-C01:1992 and DIN EN ISO 105-X12:2002, respectively.

Results and Discussion

Effect of Oxygen Plasma Pre-treatment

The pre-treatment of PET fabric surface is essential to incorporate an access to graft APTES to surface sites. Influence of oxygen plasma pre-treatment on APTES coating formation was investigated by the use of electrokinetic measurements. Figure 2 shows that in comparison with the untreated PET fabric surface, dramatic changes in PET fabric surface properties after oxygen plasma pre-treatment were noticed using streaming potential measurements. The isoelectric point ($IEP = pH|_{\zeta=0}$, where ζ is the zeta potential) for the untreated and plasma pre-treated PET fabric lies at pH 4.2 and 3 respectively.

Figure 2 also shows the determined zeta potential values

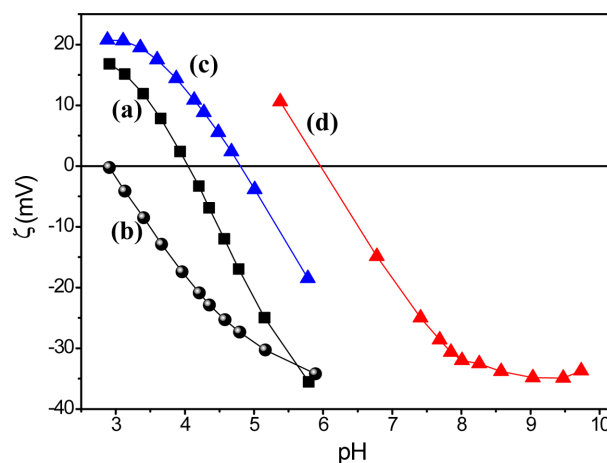


Figure 2. Zeta potential for untreated PET fabric (a), oxygen plasma pre-treated PET fabric (b), APTES coated PET fabric without oxygen plasma pre-treatment (c) and APTES coated PET fabric after oxygen plasma pre-treatment (d) as a function of pH (in 1 mM KCl).

(ζ) for APTES coating formation without oxygen plasma pre-treatment and after oxygen plasma pre-treatment. The IEP for APTES coated PET fabric without oxygen plasma pre-treatment was at pH 5. While, after APTES deposition on the oxygen plasma pre-treated PET fabric surface the IEP shifted to pH 6.

The linear shape of the function $\zeta = \zeta(\text{pH})$ of the untreated polyester fabric surface over the studied pH range is typical for non-polar substrate surfaces without dissociating surface groups. Hence, the adsorption of the potential-determining ions OH^- and H^+ control the charge formation of the untreated PET fabric surface.

After oxygen plasma pre-treatment, IEP shifted to lower pH values is attributed to the participation of Brønsted acidic groups to the interfacial charge incorporated by the oxygen plasma pre-treatment. Thus, the IEP shift is mainly obtained by the existence of negatively charged carboxylate groups ($\text{O}=\text{C}-\text{O}^-$), which are taking part to the overall surface charge [22,35]. The dissociated carboxylic acid groups incorporated by oxygen plasma pre-treatment can be used as reactive sites for successive functionalization with APTES.

The alteration of the interfacial charge at the polyester fabric surfaces was noticed after APTES coating formation, which results in a notable shift of the IEP to a higher pH value in comparison with both the untreated and oxygen plasma pre-treated PET fabrics. These changes into the surface region of PET fabric surface could be regarded to the additional contribution of Brønsted basic groups.

Even without oxygen plasma pre-treatment, the IEP value is shifted towards pH 5 (IEP for the untreated PET around pH 4.2). After oxygen plasma pre-treatment, the shift increases giving IEP for APTES coated PET fabric at pH 6. Oxygen plasma pre-treatment enhance the formation of polar groups on the PET fabric surface, therefore improving the formation of siloxane bonds and then leads to enhancement of adhesion with the nanosol coating.

In comparison with the untreated PET fabric surface, XPS results show that the [O]:[C] of the oxygen plasma pre-treated PET surfaces display a high content of the introduced oxygen-containing functional groups (Table 3).

The materials wettability can be assessed by wetting experiments that are commonly investigated using the static contact angle [36]. However, the static contact angle

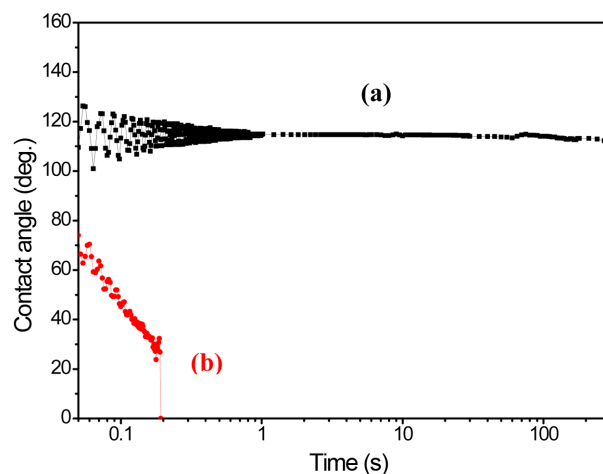


Figure 3. Evolution of water time-dependent contact angle on untreated PET fabric (a) and oxygen plasma pre-treated PET fabric (b). The error of each measurement is $\pm 4^\circ$.

measurements cannot be used to evaluate the wetting behavior of textile fabrics (heterogeneous structures), owing to the penetration ability of water through the pores of fabrics by capillary forces [37]. For this reason, the effectiveness of plasma treatment regarding wettability was evaluated by the time-dependent contact angle measurements. Figure 3 shows time-dependent variations in the contact angle of $10 \mu\text{l}$ water droplet placed on the surface of the polyester fabric before and after oxygen plasma at different treatment time.

In the first few seconds of measurements, it was clear that the contact angle is not stable due to the oscillation effects of a water droplet applied to the surface. In Figure 3 the time-dependent contact angles of water show that an obvious change between the untreated and oxygen plasma pre-treated polyester fabric surfaces. For the untreated polyester fabric, the contact angle after stabilization of water droplet is about 118° and the water droplet spreading is hindered, indicating that the polyester fabric surface is hydrophobic. This wetting behavior as observed in the electrokinetic experiments clarifies the preferential adsorption of OH^- ion. In addition, the polyester fiber chemical structure lacks polar groups as well as the hydrophobic processing agents that are

Table 3. The elemental surface composition and atomic ratios determined by XPS

Sample	C (at.%)	O (at.%)	N (at.%)	Si (at.%)	[O]:[C]	[N]:[C]	[Si]:[C]
Untreated PET	74.18	20.72	0	5.1	0.28	0	0.07
Oxygen plasma pre-treated PET	61.04	35.93	0	3.03	0.59	0	0.05
Plasma post-treatment of APTES coated PET for 5 min	51.32	30.69	4.52	13.46	0.60	0.09	0.26
Thermal post-treatment of APTES coated PET at 150°C for 5 min	62.86	24.39	5.43	7.32	0.39	0.09	0.12

used during the fabric production.

On the contrary, it was observed that a remarkable increase in wettability of the oxygen plasma pre-treated PET fabrics. The introduction of oxygen-containing polar groups such as carboxylic acid groups could be the reason behind the decrease in water absorption time (Figure 3).

Effect of Different Post-treatments on APTES Layer

In this work, we tried to obtain stronger adhesion between the polyester fabric surface and APTES coated layer through the formation of a network on PET fabric surface. Toward this aim, different post-treatments were evaluated. In the present study, the effects of plasma post-treatments and conventional thermal curing were compared. The effectiveness of surface modification with APTES layer was estimated through electrokinetic measurements, time-dependent contact angle measurement and XPS results.

Following APTES deposition on the plasma pre-treated PET fabric surface, APTES coated layer was subjected to plasma post-treatments for 1 and 5 min, the samples obtained were thoroughly washed to remove weakly adhered APTES. Figure 4 shows the effects of plasma post-treatments in terms of IEP in comparison with APTES deposited on the plasma pre-treated fabric surface without curing process. Regardless the post-treatment time, zeta potential vs. pH plot showed a shift of IEP to higher pH from (pH 6 to 6.5). On the other hand, IEP was not influenced by the duration of plasma post-treatment.

These findings may be due to the plasma post-treatment slightly enhances the bonding between the PET fabric surface and APTES layer. We hypothesize that there is some oxygen radicals intermediate produced during oxygen plasma post-treatment as shown in Figure 5. These radicals are subsequently coupled and form a network structure as

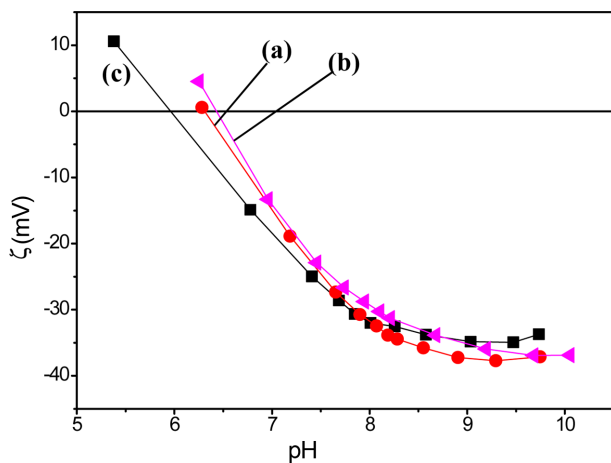


Figure 4. Effect of plasma post-treatments for 1 min (a) and 5 min (b) on IEP of the APTES coated PET fabric surfaces with regard to APTES coated PET after oxygen plasma pre-treatment without post-treatment (c).

the curing proceeds.

Figure 6, which summarizes results on the wetting behavior of APTES coated PET fabric depending on plasma post-treatment conditions, shows that the time-dependent contact angle slightly increased after attachment of APTES layer by plasma post-treatment for 5 min in comparison with oxygen pre-treated PET fabric. Most likely, the hydrophilic nature of APTES layer may be due to oxygen plasma post-treatment creates an amount of polar groups on APTES layer

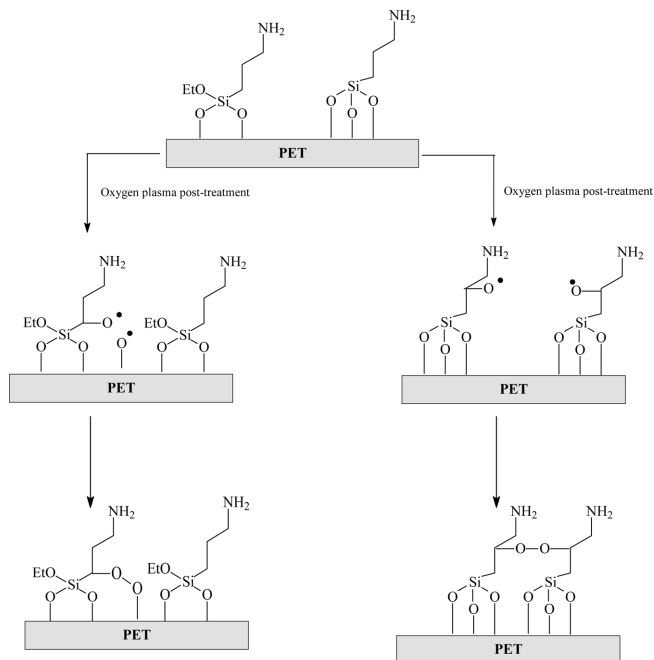


Figure 5. Schematic representation of oxygen radicals intermediates formation and their coupling during plasma post-treatment.

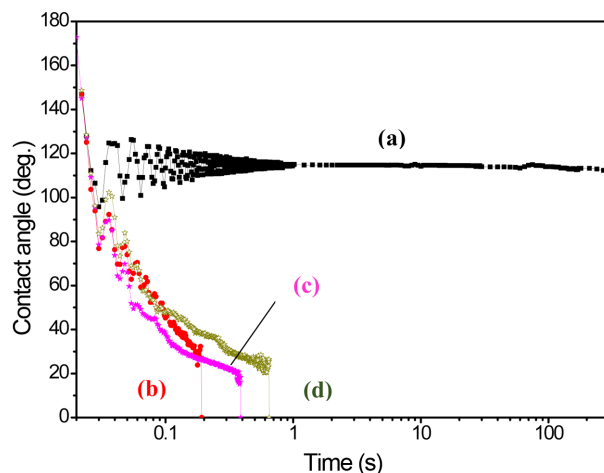


Figure 6. Evolution of water time-dependent contact angle on untreated PET fabric (a), oxygen plasma pre-treated PET fabric (b), oxygen plasma post-treated APTES-PET fabric for 1 min (c), and oxygen plasma post-treated APTES-PET fabric for 5 min (d). The error of each measurement is $\pm 4^\circ$.

Table 4. Color wash fastness properties of PET fabrics printed with Brilliant yellow (BY) and Congo red (CR) dyes

Fabric	Washing fastness					
	Brilliant yellow dye			Congo red dye		
	Staining on		Alteration	Staining on		Alteration
Cotton	Wool	Cotton		Wool		
Untreated PET fabric	1	1	1	1	1	1
APTES coated PET fabric	4	4	3-4	4	4	3-4
APTES coated PET fabric @ pH=4 for BY and pH=3 for CR	3-4	3-4	3	3-4	3-4	3
APTES coated PET fabric @ pH=8 for BY and pH=6 for CR	3-4	3-4	3	3-4	3-4	3

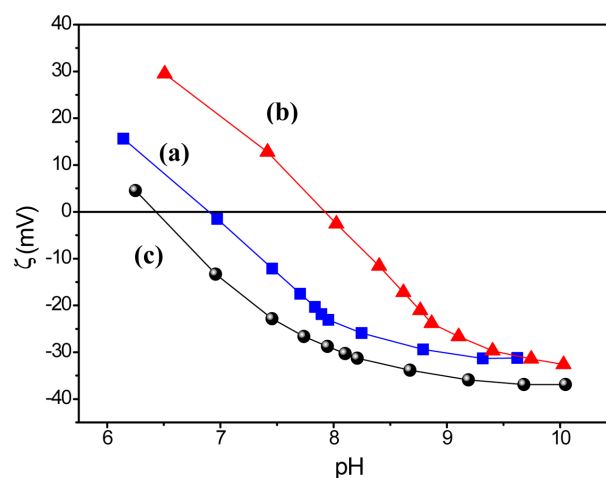
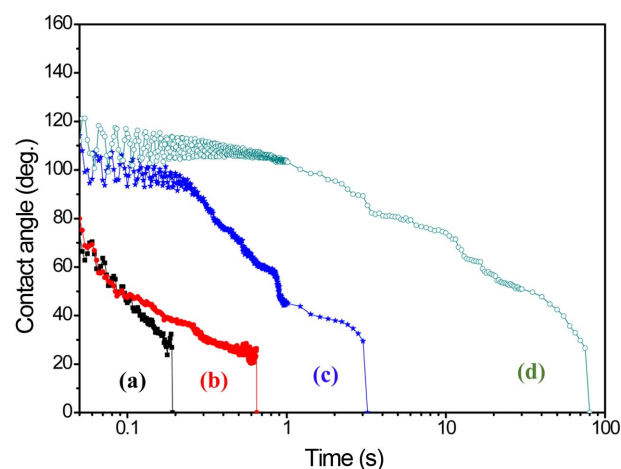
coated on PET fabric surface. Suggesting that part of the formed polar groups may be cross-linked through the formation of -O-O- bonds, while the remaining part keeps the hydrophilic character of APTES coated PET fabric surface. This idea is illustrated in Figure 5.

XPS results (Table 3) obtained after the plasma post-treatment for 5 min indicated that the [N]:[C] atomic ratio increases from 0 to 0.09 and the [Si]:[C] atomic ratio increases from 0.05 to 0.26. The increase in nitrogen and silicon contents confirm the successful attachment of APTES to the surface of plasma pre-treated polyester fabric. On the other hand, compared to the plasma pre-treated polyester fabric, the XPS results of the APTES coated layer post-treated by plasma for 5 min show nearly the same [O]:[C] atomic ratio about 0.60, this in a good agreement with the results of wettability measurements.

In comparison the influence of plasma post-treatment with thermal post-treatments at 110 °C for 30 min and 150 °C for 5 min on IEP (Figure 7), it was found that the IEP shift from pH 6.5 to 7 and 8 respectively. This IEP shift could be attributed to the treatment of APTES layer deposited on PET fabric surface at 110 °C for 30 min and 150 °C for 5 min, which gives more stable Si-O-Si bonds than that obtained by plasma post-treatment.

Prior to the first measurement by the streaming potential method, a rinsing process is required, which can completely displace weakly bonded APTES. It can be concluded that to promote condensation and Si-O-Si bond formation the oven-drying is necessary. Consequently, it can be considered that thermal treatment of deposited APTES layer at 150 °C, and treatment time 5 min as a favorable condition for the development of stable APTES coatings.

Figure 8 shows a clear difference between the oxygen plasma pre-treated PET fabrics, plasma post-treated APTES-PET fabric for 5 min and the thermally post-treated APTES-PET fabrics for different conditions. The thermally post-treated APTES coated PET fabric at 150 °C for 5 min treatment resulted in the production of the more hydrophobic surface. The noticed differences in the time-dependent contact angle can be understood on the basis of the different

**Figure 7.** Effect of thermal post-treatments at 110 °C for 30 min (a) and 150 °C for 5 min (b) on IEP of the APTES coated PET fabric surfaces with regard to plasma post-treatment for 5 min (c).**Figure 8.** Evolution of water time-dependent contact angle on oxygen plasma pre-treated PET fabric (a), oxygen plasma post-treated APTES-PET fabric for 5 min (b), thermal post-treatment (120 °C for 30 min) APTES-PET fabric (c) and thermal post-treatment (150 °C for 5 min) APTES-PET fabric (d). The error of each measurement is $\pm 4^\circ$.

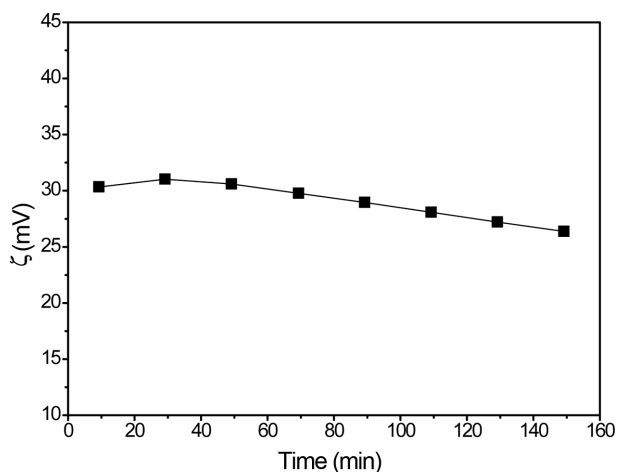


Figure 9. Time evolution of zeta potential for thermal post-treatment (150 °C for 5 min) APTES-PET fabric.

chemistry of the polyester fabric surface. This is consistent with the results of XPS analysis Table 3.

Time-dependent Zeta potential

Figure 9 shows the evolution of zeta potential as a function of time for APTES coated PET fabric post-treated at 150 °C for 5 min. the absolute value of zeta potential decreased from an initial value ζ_0 until attaining a constant

value ζ_c . This deviation in zeta potential could be explained by water adsorption on the surface of the fiber that produces a shift of the shear plane of the electrochemical double layer into the electrolyte solution.

Surface Morphology

Figures 10(a) and 10(b) illustrate SEM images of untreated PET and oxygen plasma pre-treated PET fabric surfaces, respectively. It is obvious that both surfaces are relatively smooth in addition to the existence of some contaminants. It is worth noting that, no significant differences was observed after plasma pre-treatment, indicating that there was no etching occurred to the fabric surface as a result of plasma modification.

It can be seen that the APTES layer is adhered to the plasma pre-treated PET fabric surface (Figure 10(c)). Moreover, the authors observed that the PET surface is not fully covered by the APTES layer in the case of plasma post-treatment. But, in the case of thermal post-treatment at 150 °C for 5 min (Figure 10(d)) APTES layer on the surface in more pronounced. The increased amount of deposition of APTES on/and between fibers is apparent in Figure 10(d). This may be due to a through rinse will remove APTES deposition adhered by plasma post-treatment. However, APTES deposited and fixed by thermal post-treatment is more difficult to be removed by rinsing.

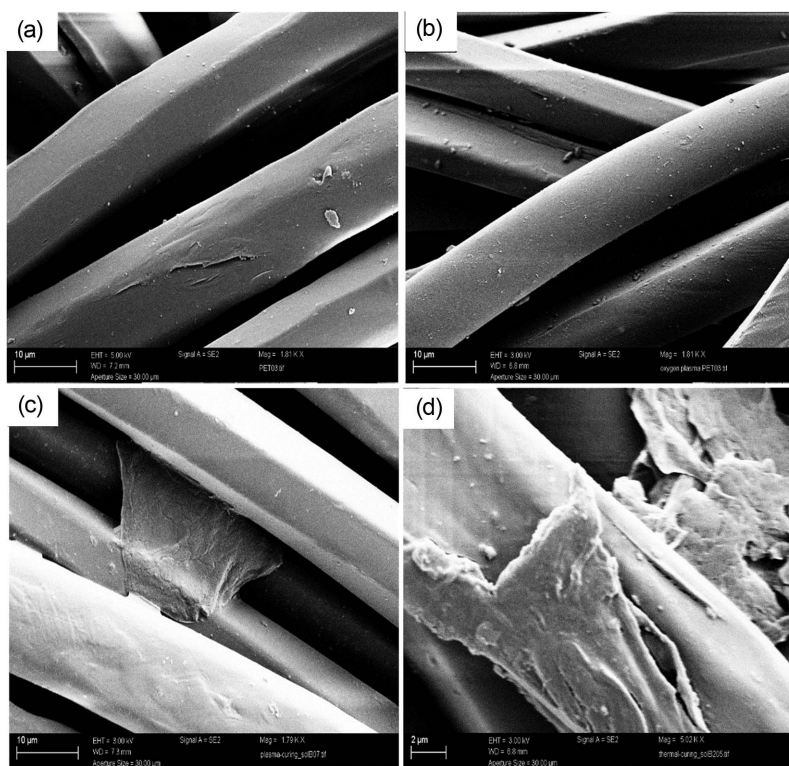


Figure 10. SEM images of the untreated PET fabric (a), oxygen plasma pre-treated (600 W, 15 s) PET fabric (b), APTES-PET fabric post-treated by oxygen plasma for 5 min after rinsing (c), and APTES- PET fabric thermally post-treated at 150 °C for 5 min after rinsing (d).

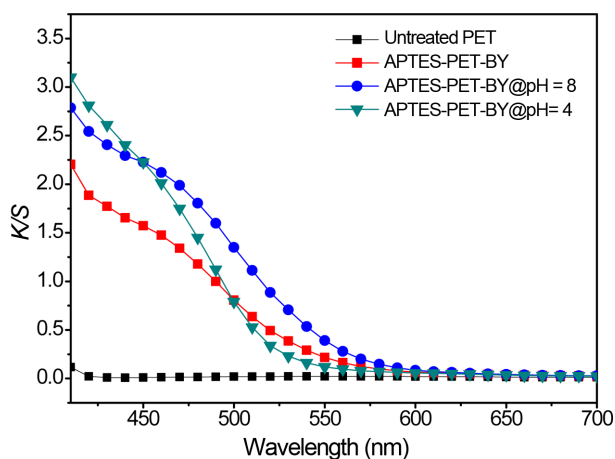


Figure 11. Color build-up K/S on untreated and APTES coated PET fabrics printed with brilliant yellow dye as a function of pH (from pH 4 to 8).

Application of Brilliant Yellow Dye onto APTES Coated PET Fabrics and Evaluation of Its Halochromic Properties

Using of a flexible material as an alternative for rigid material in pH sensors is recognized as promising step in order to attain an increased flexibility of the sensor systems. In the present work, a halochromic functionality can be incorporated into PET fabrics using printing of indicator dyes. Figure 11 shows the color build-up of PET printed with brilliant yellow, the color build-up was visualized using K/S curves. The results displayed that the printed APTES coated PET with brilliant yellow exhibited values higher than that of the untreated PET fabric. Furthermore, it was observed that the λ_{\max} for K/S curves increases gradually from 450 to 475 nm with increasing the pH from 4 to 8. This gradual changes in color strength values could be regarded to the molecular changes with changing pH values. The expected acid-base equilibrium of BY has stated previously [38]. The PET fabrics printed with brilliant yellow dye was proved to be as successful pH sensors, due to its color change with the pH variation.

Application of Congo Red Dye onto APTES Coated PET Fabrics and Evaluation of Its Halochromic Properties

Generally, azo dyes are considered as an important dyestuff class, in addition, several pH-indicators are azo dyes. As an example for anionic azo dye, Congo red (CR) is commonly used in paper, textiles, plastic and rubber industries. In correspondence with the literature, CR shows the maximum wavelength at 500 nm [39]. Figure 12 shows the Kubelka-Munk spectra of CR on APTES coated PET fabric from pH 3 to 6. It is to be noted that, by immobilizing CR on treated fabric, the color changed from blue (pH 3) to red (pH 6). Moreover, it was observed that the λ_{\max} for K/S curves increases gradually from 500 to 520 nm with increasing the pH from 3 to 6 and an extra shoulder appears around

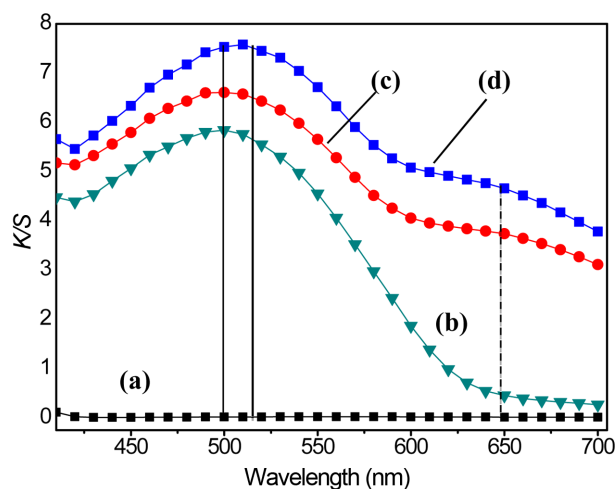


Figure 12. Color build-up K/S on (a) untreated PET fabric printed with Congo red, (b) APTES-PET-CR, (c) APTES-PET-CR @pH=3, and (d) APTES-PET-CR @pH=6.

650 nm. The halochromism of CR is most probably based on a tautomerism.

Color Fastness

Color fastness properties of the printed APTES-PET fabrics with either brilliant yellow or Congo red dyes has been used to measure the resistance to washing down. Color fastness is used as a tool for measuring the durability of surface modification.

The gray scales were used to assess the color fastness of the samples visually. It ranges from 1-5, where 1 for a severe shade change and 5 for no shade change and with half points in between. As shown in Table 4, for the color fastness towards washing, PET fabrics printed with the Brilliant yellow and Congo red displayed a very good washing fastness towards washing irrespective of pH.

Conclusion

It has been demonstrated that plasma-assisted sol-gel coating process can be used to produce PET fabrics with halochromic properties. By using this process, 3-aminopropyltriethoxysilane (APTES) layer attached to the PET fabric surface. Subsequently, two different azo pH-indicator dyes namely Brilliant yellow and Congo red successfully immobilized onto PET fabric surface. This has implications for the ability of the APTES layer to function as a coupling agent for the attachment of pH-sensitive dyes via the $-NH_2$ group. Different surface sensitive techniques were conducted to monitor the attachment of the APTES layer onto PET fabric surfaces such as XPS and electrokinetic measurements. The XPS results show that the oxygen plasma pre-treated PET surfaces possess a high amount of introduced oxygen-containing functional groups, in addition,

the time-dependent contact angles of water display an obvious difference between the untreated and oxygen plasma pre-treated polyester fabric surfaces. It is observed that the APTES coatings deposited on the PET fabric surface at 110 °C for 30 min and 150 °C for 5 min gave a more stable coating than that obtained by plasma post-treatment. In addition, the thermally post-treated APTES coated PET fabric at 150 °C for 5 min treatment resulted in the production of the more hydrophobic surface. Also, the results revealed that the printed fabrics with halochromic properties demonstrated sufficient stability against leaching by washing. It is viewed that the current work can be considered as new opportunity to develop flexible sensors based on textiles which have the potential to be used as a tool for pH sensing.

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