

Effect of PEGylated Chitosan on Plasma Etched PET Fabrics Surface Properties

Xuemei He,^{1,2} Qingqing Zhou,² Kongliang Xie¹

¹College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai 201620, People's Republic of China

²College of Textiles and Clothing, Yancheng Institute of Technology, Jiangsu 224003, China

Correspondence to: K. Xie (E-mail: kxie@dhu.edu.cn)

ABSTRACT: In this work, PEGylated chitosan derivatives were prepared and used to modified poly(ethylene terephthalate) (PET) fabrics. PET fabrics surface were etched by oxygen plasma before different concentrations PEGylated chitosan derivatives solution treatment. The effects of oxygen plasma and PEGylated chitosan derivatives on the surface properties of PET fabrics are investigated by Fourier transform infrared spectroscopy, scanning electron microscopy, and thermogravimetric analysis (TG) and differential scanning calorimetry (DSC). Surface wettability was monitored by water contact angle measurement and moisture regains. The results showed that the occurrence of oxygen-containing functional groups (i.e., C=O, C—O, and —OH) of the plasma-treated PET and the surface coarseness increased from those of the untreated one. There was a layer film formed on the surface of PET fabrics after PEGylated chitosan modification. The combination treatment of oxygen plasma with PEGylated chitosans lightly lowered the breaking strength and elongation of PET fabric. That moisture regains increased and the contact angle decreased implied the hydrophilicity enhancement for the PET fabrics. In addition, dyeing property of PEGylated chitosan derivative modified PET was improved. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 39693.

KEYWORDS: polyesters; polysaccharides; properties and characterization

Received 20 March 2013; accepted 23 June 2013

DOI: 10.1002/app.39693

INTRODUCTION

Poly(ethylene terephthalate) (PET) is widely used in the field of the fabrics industries because of its some excellent bulk properties, such as excellent mechanical properties, crease resistance, solvent resistance, high melting point, resistance to fatigue, and high tenacity as textile fiber. Unfortunately, it is also known for high hydrophobicity, low wettability, surface inertia, static electrification, and poor adhesion.^{1,2} To achieve better hydrophilic for more commercial applications, a desirable PET surface can be created using a variety of physical or chemical treatment methods, for example, chemical processes, graft polymerization, thermal, laser irradiation, plasma and irradiation treatments, coating, and so on.^{3–7} Among of them, chemical treatment is considering effective way to modify PET surface properties.

However, chemical treatments often use toxic reagent that have difficult-to-remove residues. To solve the problem, biopolymers, such as protein and polysaccharide, are used to modify the material properties.^{8,9} Chitosan has extraordinary chemical and biological properties including its biodegradability, biocompatibility, bioactivities nontoxicity, and anti-microbial properties. As a substitute for toxic functional chemical agent in textiles treat-

ments, it has been extensively used in fabrics dyeing and finishing, improving the dyeability of fabrics and imparting extra properties.^{10–12} Low solubility of chitosan in both water and organic solvents limited its further application in textile industry.¹³ Polyethylene glycol (PEG) is a neutral, water soluble, and nontoxic polymer, which has been used for pharmaceutical and biomedical applications. Some studies have investigated PEGylation of chitosan to improve its affinity to water and organic^{14–17}; therefore, recently, there are much of publications concerning chitosan modification through its hydroxyl or amino group by PEG.^{18,19} For example, Sugimoto et al. used reductive amination of PEGaldehyde in aqueous organic acid as a typical method for grafting PEG onto chitosan.²⁰

Surface plasma treatment has also been widely used to modify surface properties of PET fabrics, for example, enhancing hydrophobicity or hydrophilic, forming chemical groups, inducing grafting, and cross-linking surface macromolecules, increasing surface roughness for better adhesion.^{6,21–24} However, it also has the disadvantages of instability of plasm-treated surfaces and need for storage in special conditions to prevent reacting with atmosphere. Recently, the usefulness of combined plasma and chemical methods treatment strategy to functionalization of

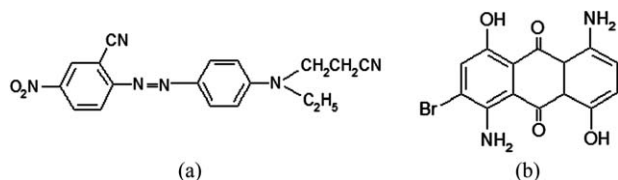


Figure 1. Chemical structures of disperse dyes: (a) disperse scarlet SE-GFL (C.I. Disperse Red 73); (b) disperse blue 2BLN (C.I. Disperse blue 56).

PET surfaces has attained a deal of attention. For example, Salem et al. used two-step modification process based on plasma treatment to improve coloration behavior of PET fabrics, namely, PET surface was treated by using low-temperature oxygen plasma to improve its wettability and reactivity and then poly (diallyldimethylammonium chloride) layers were applied by adsorption from its aqueous solution, which could increase the substantivity to acid dyes via complementary electrostatic attractions at neutral pH.²⁴ Bratskaya et al. studied the application of chitosan on oxygen plasma treated polypropylene surfaces to improve their wettability, dyeing behavior, and antimicrobial properties.²⁵ The aim of this study was to evaluate the physical and chemical properties of oxygen plasma and PEGylated chitosan treated PET fabrics and to investigate the effect of PEGylated chitosan on plasma-treated PET fabrics. First, oxygen plasma was applied to improve PET surface wettability and reactivity, followed that, the PET surface was modified by a functional PEGylated chitosan derivative allowing adjustment of the surface chemistry. The moisture regains and water contact angle of modified PET were measured and the dyeing properties of the surface modified PET was investigated with conventional dyeing by using disperse dyestuffs. The obtained color strength (*K/S* value) was examined by spectrophotometer.

EXPERIMENTAL

Materials and Characterization

PET plain weave fabrics with a density of 171 g/m² were supplied by Wujiang City Jin Cheng Textile Co. (China). Chitosan with 96.31% deacetylation (M_w 5.78 × 10⁵ Da) was provided by Zhejiang Jinke Bio. Co. Phthalic anhydride, succinic anhydride, PEG (MW 2000), *N,N*-dimethylformamide (DMF), cyanuric chloride, and acetone are of analytical grade and purchased from the Chemical Reagent Company of Guoyao. Two commercial disperse dyes (Figure 1) were used in this study kindly supplied from the Zhejiang Longsheng dye Chemical Co. (China).

To determine the chemical changes that may occur as a result of the chemical treatment of polyester fabrics, the PEGylated chitosan derivative treated as well as untreated polyester fabrics were subjected to Fourier transform infrared analysis (FTIR, Thermo Nicolet, USA) over the range 50–4000 cm⁻¹. The samples were ground to a very fine powder and mixed with a highly dried KBr powder (30 mg), then pressed to transparent disks. The morphology of the treated PET fabrics was characterized using a scanning electron microscope (SEM, FEI Quanta 200 scanning electron microscope, USA). Samples were coated an approximate layer thickness of 15 nm with gold, and the SEM images were taken at an accelerating voltage of 10 kV.

Thermal studies of untreated, plasma etching, and PEGylated chitosan modified PET were carried out using thermal analyzer (NETZSCH STA 449C, Germany) at a heating rate of 10°C/min under nitrogen atmosphere. The samples were heated from room temperature to 650°C. T_{max} was defined as the temperature at maximum weight loss rate.

Preparation of PEGylated Chitosan Derivative

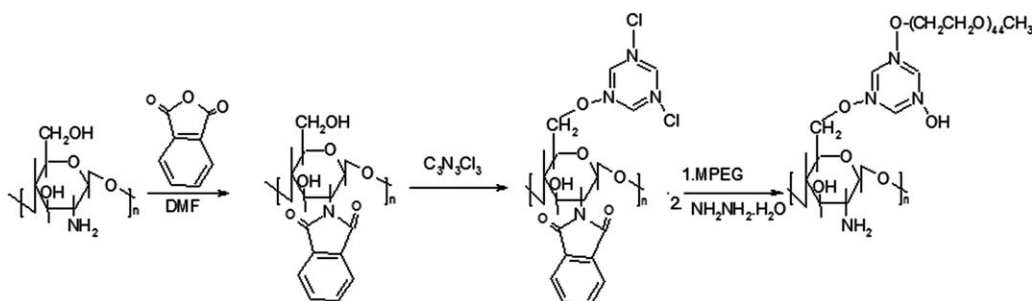
The preparation of PEGylated chitosan was performed by the method described by Makuška and Gorochoveva.¹⁶ Briefly, Chitosan was reacted with phthalic anhydride (5 mol equivalent to pyranose rings) in DMF at 100°C under vacuum for 6 h. The temperature was reduced to 60°C and left overnight. The product was reprecipitated in cold water. The precipitate was collected, washed with ethanol, and dried in vacuum to gain the *N*-phthaloylchitosan. A mixture of *N*-phthaloylchitosan (1 g, 3.76 mmol), trichlorotriazine (5.02 g, 27.2 mmol), and sodium carbonate (0.4 g, 3.76 mmol) in DMF (35 mL) was heated with stirring at 40°C for 20 h. The precipitate obtained by pouring the solution into 1 : 1 acetone/diethyl ether mixture (vol/vol) was collected by filtration, washed several times with water to remove residual Na₂CO₃, reprecipitated into acetone, washed by diethyl ether, and dried in an air to give the product 6-*O*-dichlorotriazine-2-*N*-phthaloylchitosan. Sample solution was prepared by dissolving polyethylene glycol (PEG2000) and 6-*O*-dichlorotriazine-2-*N*-phthaloylchitosan in DMF and then toluene were added. The mixture was refluxed for 8–15 h. The product was dialyzed by dialysis membrane. The obtained phthaloyl-protected grafted copolymer (1 g) was stirred in 10 mL of DMF and heated to 100°C under nitrogen. Hydrazine monohydrate was added and the reaction continued for 1 h to deprotect the phthaloyl group. The solution was allowed to cool to room temperature in precipitate, and then the precipitate was collected, washed thoroughly with ethanol, and dried. The preparation of PEGylated chitosan is shortly outlined in Scheme 1.

Oxygen Plasma Pretreatment on PET

Oxygen plasma treatment of PET surfaces was carried out in a plasma processor (HD-1A cold plasma modified equipment, Changzhou ShiThai Plasma Technology Development Co., China). The apparatus was equipped with a 2.4 GHz microwave source (maximum output power 500 W), which was connected by a quartz window to a vacuum chamber with dimensions of 350 mm × 350 mm × 350 mm (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, homogeneous plasma was formed in the chamber volume. The PET fabrics were treated using the following parameters: input power 100 W and time 2 min with oxygen at a flow rate of 0.2 L/min.

Modification of PET with PEGylated Chitosan

Oxygen plasma treated samples were immediately immersed in 0, 0.4%, 0.8%, 1%, and 1.2% (based on the volume of the 1% wt/vol acetic acid solution) aqueous PEGylated chitosan solutions for 2 h at room temperature, followed by washing with distilled water to accomplish pH neutralization. The PEGylated chitosan modified PET was air-dried at room temperature overnight before characterizations. The modified reaction



Scheme 1. Regioselective synthesis of PEGylated chitosan derivatives.

mechanism of PET fabrics with PEGylated chitosan was shown in Figure 2.

Dyeing Procedure with Disperse Dyes

The samples were dyed with disperse scarlet SE-GFL and disperse blue 2BLN, respectively. All dyeing were carried out in sealed, 300 cm³ stainless steel dye pots housed in a Roaches Pyrotec 2000 infra red dyeing machine. The dye bath was prepared such that a material to liquor ratio (L.R.) was 1 : 70 and the required dye concentration of 2% (based on the fabric weight). The samples were introduced into the dye bath at 60°C, then the temperature was gradually raised up to 90°C within 15 min, and then dyeing was continued for 60 min. The dyed samples were rinsed with cold water, then with hot water at about 60°C and finally were reduction cleared using with a solution containing 2 g dm⁻³ sodium hydrosulfite, 2 g dm⁻³ Pregel O, and 1.5 g dm⁻³ sodium carbonate at 70°C for 10 min at a liquor to-fabric ratio of 50 : 1. The samples are rinsed in cold water to remove unfixed dyes and finally air-dried.

Water Contact Angle Measurements

Contact angle measurements were carried out by DH-HV1351UM (Shanghai ZHongchen Digital Technology Equipment Co.). The surface wettability was evaluated from the value of the contact angle measured with a drop of distilled water on the surface of the samples. The volume of the drops was fixed to 5 μL. The measurements were carried out in air at room

temperature. The reported angle is an average of 5 measurements on different areas of each sample.

Moisture Regains

The moisture regain is the percent weight of moisture gain compared with the initial dry fabric weight. To determine the moisture regain properties, treated fabrics were kept in a conditioned room at a relative humidity of 65% ± 5% and temperature of 25°C ± 3°C for 24 h. The moisture regain value was calculated from the difference in weight of the initial dried fabric and conditioned fabrics.

Mechanical Measurements

The mechanical properties including tensile strength and strain at break were tested at room temperature. Tensile strength was determined using a tensile tester YG026A (Nantong Hongda Experiment instruments Co., China) in a standard procedure with 2 kgf maximum capacity load and 115 mm min⁻¹ speed and 20 cm × 5 cm the gauge length. The tensile resistance values are given as the mean of three samples measured. Stiffness was evaluated by YG (B) 022D automatically fabric stiffness tester (Wenzhou Darong Textile Instrument Co., China).

Color Measurement

Spectral reflectance factors (taken between 400 and 700 nm wavelengths in 20 nm increments) of the samples were measured using a Datacolor7000A reflectance spectrophotometer (Data color International, UK) interfaced to a computer. Each fabric sample was folded twice to give a total of four layers. Under illuminant D65 using the 10 standard observer, the relative color strength (K/S value) were automatically calculated from reflectance factors R of the dyed fabrics at the maximum absorbance wavelength by the software using the Kubelka-Munk eq. (1).

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

where K is the absorption coefficient of the substrate, S is the scattering coefficient of the substrate, and R is the reflectance of the dyed fabric at λ_{\max} .

RESULTS AND DISCUSSION

FTIR Analysis

Oxygen plasma treatment was carried out to improve the wettability of the originally hydrophobic PET surfaces and to provide required functionalities for further modification step with PEGylated chitosan derivatives. The chemical structure of

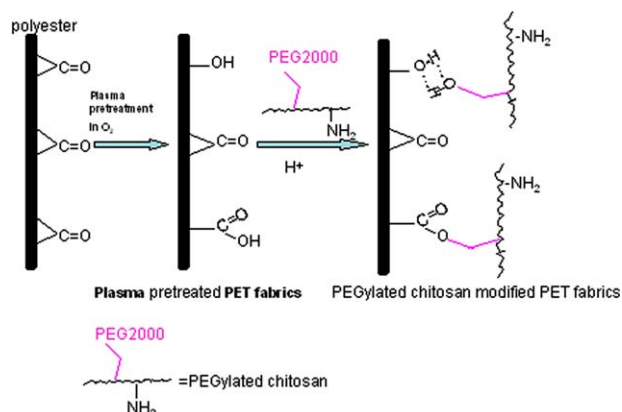


Figure 2. The modification reaction of PET fabrics with plasma and PEGylated chitosan. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

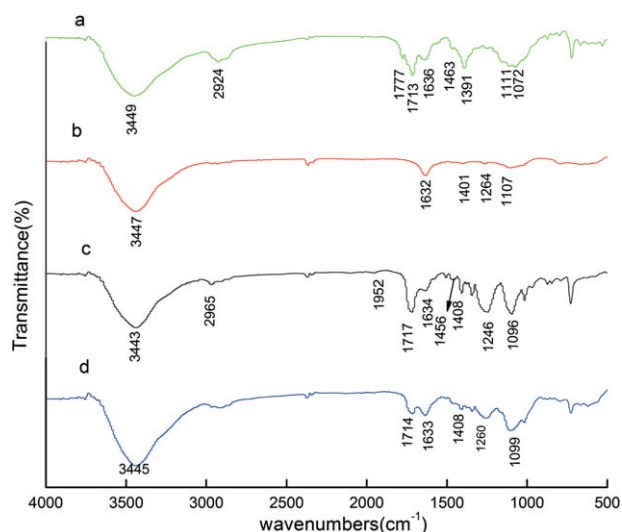


Figure 3. FTIR spectra of PEGylated chitosan derivatives and PET fabrics under different treatment conditions. (a) PEGylated chitosan derivatives; (b) plasma-treated PET; (c) untreated PET; (d) plasma and PEGylated chitosan treated PET. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

PEGylated chitosan derivative, the untreated sample, plasma etched PET, and treated fabrics with PEGylated chitosan were subjected to IR spectroscopic analysis, as shown in Figure 3. In Figure 3(a), there are characteristic absorption peak such as 1777 and 1713 cm^{-1} (carbonyl anhydride) and 720 cm^{-1} (arom) of phthalimido group on PEGylated chitosan derivatives.¹⁶ Distinctive absorption bands of PEG at 1111 cm^{-1} (C—O stretching and 2886 cm^{-1} (C—H stretching) were present in the spectra of PEGylated chitosan. This is consistent with the fact that PEG chains are long (MW 2000; about 44 ethylene oxide units). Absorption band at 1636 cm^{-1} and 3449 cm^{-1} was attributed to its amine ($-\text{NH}_2$) and hydroxyl ($-\text{OH}$) functional groups, both of these functional groups on PEGylated chitosan chains can serve as reaction sites for the adsorption of organic dyes. For untreated PET [Figure 3(c)], an absorption band was observed at 2965 cm^{-1} which is due to the C—H stretching as almost in all organic compounds. The characteristic absorption bands at 1717 cm^{-1} (C=O) and 1246 cm^{-1} (C—O) is assigned to the ester groups of PET. It is well known that excited oxygen atoms can react with the polymer chain to form oxygen-containing functional groups such as OH, CO, and COOH.^{26,27} After the plasma treatment, new peaks at 1632 cm^{-1} corresponding to C=O stretching vibration and at the region of 3200–3800 cm^{-1} corresponding to hydroxyl group ($-\text{OH}$) vibration appeared in Figure 3(b). The peak at 1717 cm^{-1} , 1507 cm^{-1} , and 1456 cm^{-1} for oxygen plasma treated PET significantly decreased. It is because a considerable proportion of PET molecules near the surface of treated PET are destroyed by plasma treatment, the peaks that are specific for PET must decrease. The results have been proved by Cheng in literature.²⁸ In Figure 3(d), the value corresponding to 1633 cm^{-1} is due to an increase in COOH and C=O bonds on spectra of PEGylated chitosan treated PET. Due to the PET fabric is covered by PEGylated chitosan derivatives, therefore, new char-

acteristic absorption bands at 1633 cm^{-1} (amide I, mainly (C=O) stretching) and 1562 cm^{-1} (amide II, mainly (NH) bending) were formed indicating the formation of amide groups onto the PET fabric surface. It can be confirmed that the combination the plasma and PEGylated chitosan treatment is an effective method to generate hydrophilic groups on the PET surfaces.

Surface Morphology

The surface morphologies of PET sample treated by oxygen plasma and PEGylated chitosan, respectively, were also observed by SEM in Figure 4. In Figure 4(a), the surface of untreated sample is seen a smooth morphology. It is very well known that the plasma treatment is slightly changing the morphology of the polymer surface and can depend on the gas composition,²⁹ pressure,³⁰ etc. Inagaki et al. found that O_2 plasma was high effective in etching of PET film but the lowest average roughness was found for O_2 plasma in comparison with plasma generated in other gases as Ar, H_2 , N_2 , and NH_3 in Ref. 29. From Figure 4(b), it has been observed that the change trend of treated PET fiber surface morphologies was coarse after oxygen plasma treatment. A coarse surface led to an increase in interfacial adhesion between the fiber and the polymer film.³¹ In Figure 4(c), surface chemical modification of PET fiber induced by the PEGylated chitosan was obvious that a layer of polymers were homogeneously distributed on the fiber surface. In all, SEM analyses showed obvious changes in surface topography as a consequence of the plasma-etching and PEGylated chitosan grafted deposition, and these changes in the topographical properties may occur during the contact between PET fibers and the dyeing bath.³²

Thermal Stability

The thermal stability of the prepared samples has been evaluated by thermogravimetric analysis in N_2 conditions. Figure 5 reports TG and DSC curves in N_2 atmosphere for the untreated PET, plasma etched PET, and PEGylated chitosan treated PET fabrics. In nitrogen, thermal degradation of untreated PET proceeded by three steps between 200 and 500 $^\circ\text{C}$ and led to the formation of a condensed aromatic residue that is 14.66% of initial mass.³³ Plasma etching PET showed a decrease in temperature with second T_{max} that shifted from 406.3 to 399.3 $^\circ\text{C}$ as compared with neat PET [see Figure 5(a)]. Plasma etched samples showed an intermediate degradation behavior between neat PET and PEGylated chitosan deposition PET. In Figure 5(b), despite the presence of a PEGylated chitosan derivatives layer, no remarkable effect in terms of degradation rate has been observed. This behavior may be due to the oxygen plasma treatment that can create reactive species onto the surface and catalyses the degradation process.³⁴ In Figure 5(a), untreated PET fiber had three thermal weight loss peak during 250–500 $^\circ\text{C}$, whereas oxygen plasma-treated PET fiber had four peaks in the period of 200–400 $^\circ\text{C}$ and 400–520 $^\circ\text{C}$, respectively, because of hydrolysis of the surface amorphous region and scission of surface macromolecular chains.³⁴ PEGylated chitosan modified PET fibers had three and four thermal weight loss peaks in the periods of 200–400 $^\circ\text{C}$, and 400–500 $^\circ\text{C}$, respectively. There was 16% weight loss over the range of 120–200 $^\circ\text{C}$, which coincided with the moisture-absorbing and moisture holding behaviors of

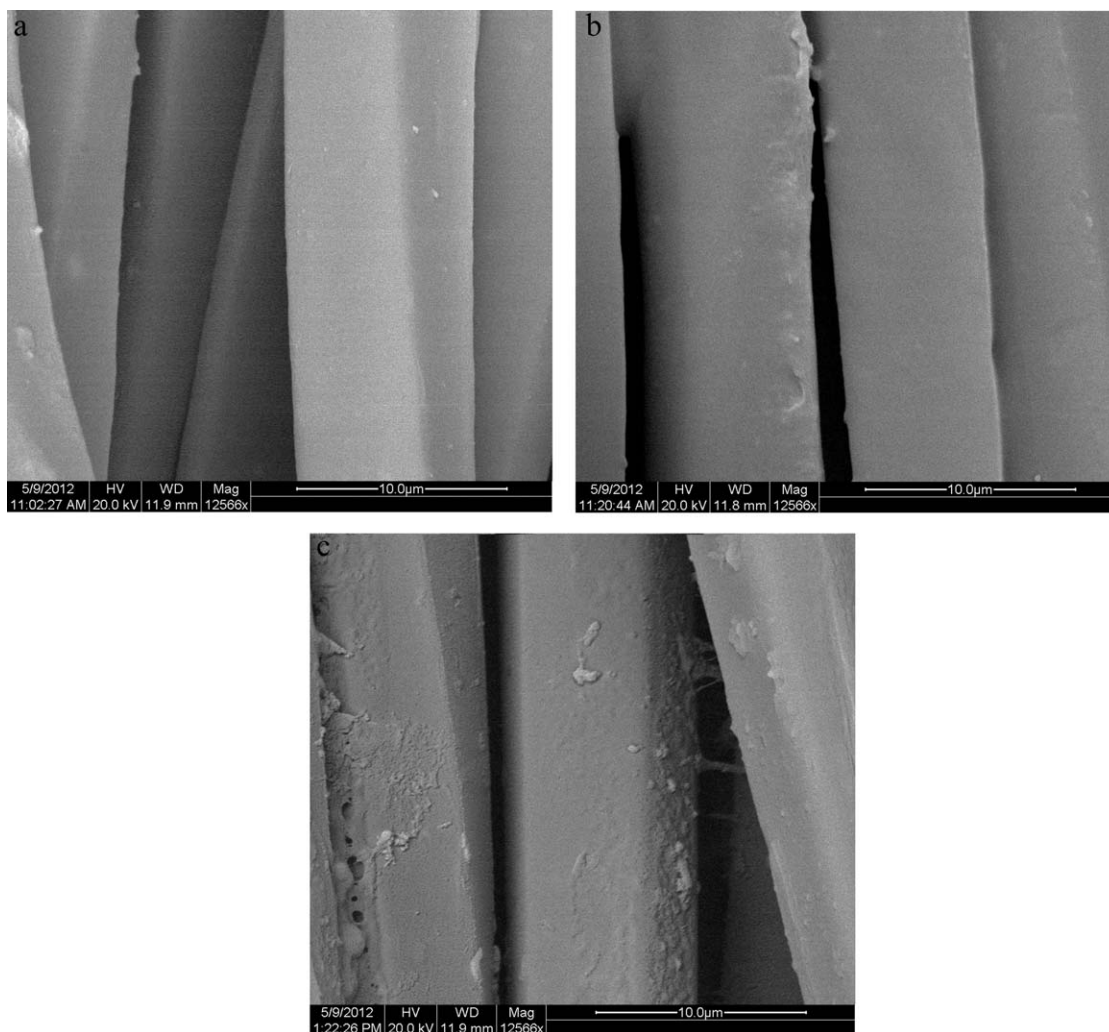


Figure 4. SEM of untreated and treated PET fabric samples: (a) untreated PET; (b) plasma etched PET; and (c) plasma and PEGylated chitosan modified PET.

PEGylated chitosan modification on the surface of PET fibers. Except for lower temperature thermal weight loss peak of water, PEGylated chitosan modification PET fibers had more weight

loss in the range of 200–500°C than plasma etched PET fibers, caused by the weak cross-linking effect induced by multiented reactive groups.

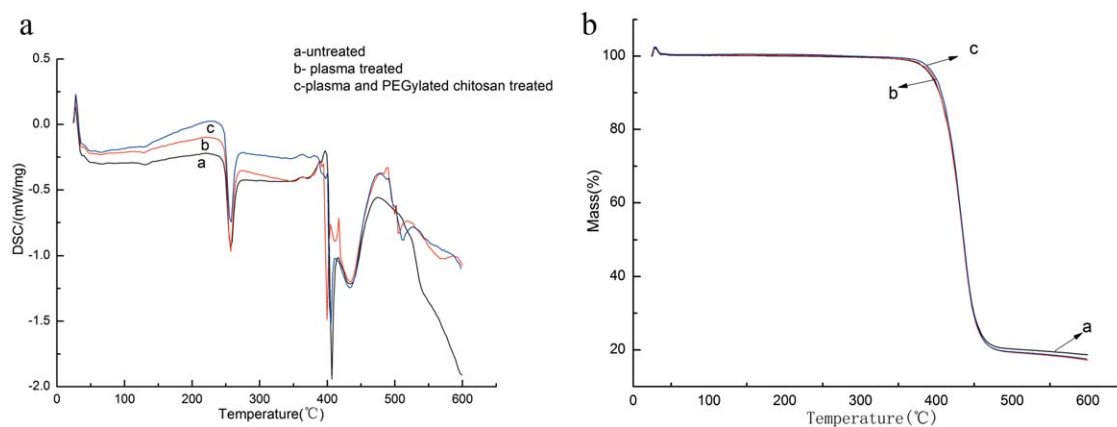


Figure 5. Thermal analysis of untreated and treated PET fabric samples: (a) DSC curves of untreated and treated PET fabric samples and (b) TG curves of untreated and treated PET fabric samples. (a') Untreated PET; (b') plasma etched PET; and (c') plasma etching and PEGylated chitosan modified PET. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Mechanical Properties of PET under Different Treated Conditions

Physical properties	Untreated	Plasma treated	1% PEGylated chitosan	Plasma and 1% PEGylated chitosan
Tensile strength (N)	520 ± 10.40	412 ± 8.24	480 ± 9.60	408 ± 8.16
Elongation at break (%)	20.80 ± 0.42	20.54 ± 0.41	18.50 ± 0.37	11.72 ± 0.23
Stiffness (mg mm)	178 ± 3.56	143.5 ± 2.87	132.5 ± 2.65	116 ± 2.32

Mechanical Properties

It is possible that the combination treatment of plasma with PEGylated chitosan derivatives has an influence on the mechanical properties (strength, elongation at break, and stiffness) of the PET fibers. Tensile strength, elongation at break, and stiffness of the untreated and the treated PET with different treatment conditions were shown in Table I. Both the tensile strength and the elongation at break of the plasma-treated PET fabrics obviously decreased from those of the untreated one. Reduction of the mechanical properties in terms of tensile strength and elongation at break of the plasma treatment PET was in agreement with the work reported by Shin et al.³⁵ who concluded that mechanical properties of polymeric are influenced mainly by energy from the plasma source not from the treatment time.

The mechanical properties of the plasma and PEGylated chitosan treated PET fabrics have remarkable reduction. Ferrante et al.³⁶ considered the reduction of the mechanical performances is related to the chemical modification of the external surface which includes reactions between PET and oxygen. Oxygen plasma treatment enhanced the cross-linking between PEGylated chitosan and PET fiber, which led to a decrease on mechanical properties.

Cioffi et al.³⁷ also proved that tensile tests on PET fibers showed that plasma treatment caused a decrease in average tensile strength compared with untreated fibers. After PEGylated chitosan treatment, the tensile strength of treated PET decreased because surface defects were introduced during the processing.³⁸ This result could be explained that PET fabrics are influenced by the surface etching, the quantity of the active polar groups, and free radical on the fibers surface. On the other hand, the stiffness of plasma etched PET and PEGylated chitosan modified PET decreased from the untreated samples, which implied PET fabrics become softer.

Wetting Properties

The wetting properties of the treated samples were studied by static contact angle and moisture regains. Figure 6 shows the variation in the contact angle and moisture regain of the PET under different treatment method. Contact angle measurement showed that plasma treatment has altered the surface wettability, as the contact angle decreased from 112°C for the untreated PET surface to 40°C for oxygen plasma treatment. Similar behavior was observed in literature⁶ for PET surface after oxygen plasma treatment. On the other hand, in order to analyze the treatment effectiveness, the surface moisture regain was also evaluated under different process. From Figure 6, after oxygen

plasma, moisture regains increase of 10 times from untreated sample. Compared with the untreated PET, moisture regains of plasma and 1% PEGylated chitosan modified PET increased. Some studies have proved that the introduction of the new oxygen-containing groups (such as —OH, CO, COOH, and COO—) in the polymer surface is the main reason for the increase in the hydrophilicity of the PET.^{7,18,20,39} The effect of various concentration PEGylated chitosan derivatives solution on the surface water contact angle of plasma etched PET fabrics was further studied. The results were shown in Figure 7. The water contact angle decreased with the PEGylated chitosan concentration increasing and gained the lowest water contact angle at 0.8% concentration where the water contact angle was about 65°C. It showed the hydrophilicity of PET fiber surface increased with the PEGylated chitosan concentration increasing. In the literature,³⁷ Cioffi et al. ever confirmed the oxygen plasma treatment could increase in interfacial adhesion, so, here, oxygen plasma pretreatment provides a more hydrophilic character, which was important for strengthen the cohesive effect between PEGylated chitosan derivative and PET fiber surface. The water contact angle degrades slowly as a consequence of the rearrangement of polar groups on surface of PEGylated chitosan derivatives modified PET fabrics. Due to the chain flexibility and extensive hydration of PEG, PET fabrics modified with this polymer occupy larger volumes in an aqueous environment, which should affect their diffusion behaviors in PET fibres.^{40,41} Further increase of PEGylated chitosan concentration caused an increase in water contact angle, so the suitable PEGylated chitosan concentration 0.8%.

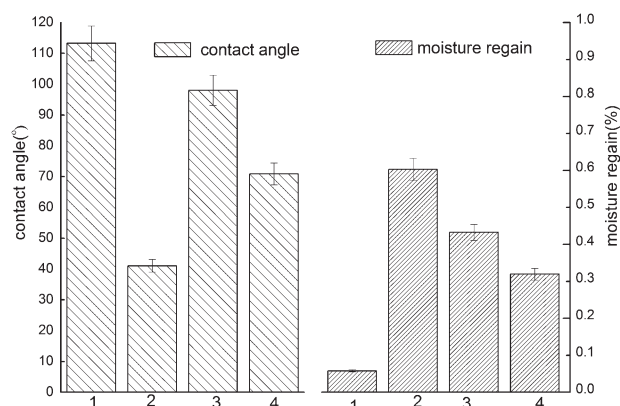


Figure 6. Water contact angle and moisture regains of PET fabrics under different treatment condition: 1, Untreated; 2, plasma treated; 3, plasma and 1% PEGylated chitosan; 4, 1% PEGylated chitosan.

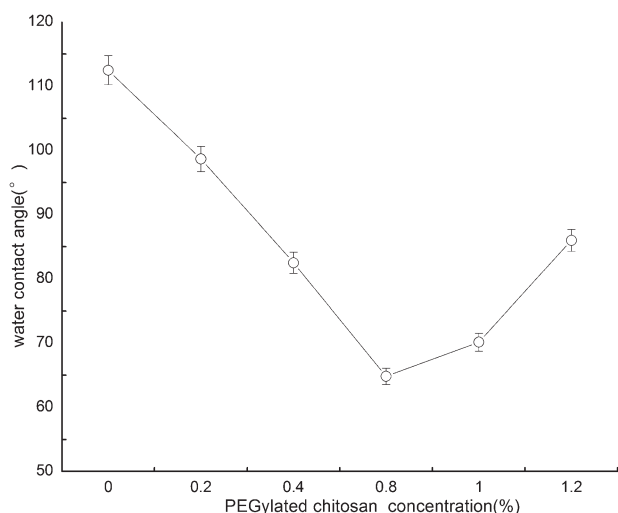


Figure 7. Water contact angle of plasma etching PET fabrics in different concentration PEGylated chitosan.

Dyeing Properties

Chemical treatment of polyester fibers with plasma and PEGylated chitosan treatment was expected to add new properties due to the introduction of functional groups in the main chain of the fiber structures. Figure 8 shows the dyeing properties of oxygen plasma etched and various concentration PEGylated chitosan deposited PET fabrics. It was obvious there was an increase upon dyeing color depth for oxygen plasma treated PET fabrics. The results were in agreement with the work reported by Raffaele-Addamo in literature.²³ This may be easily related to optical effects connected to the plasma-induced increase of surface roughness, which contributes to the increase of K/S values of dyed PET specimens by decreasing the fraction of light reflected from treated surfaces respect to smoother surfaces.²³

In comparison with untreated sample, it can be seen that the color depth increase with an increase in the concentration of PEGylated chitosan up to 0.8% and then slightly decreases by

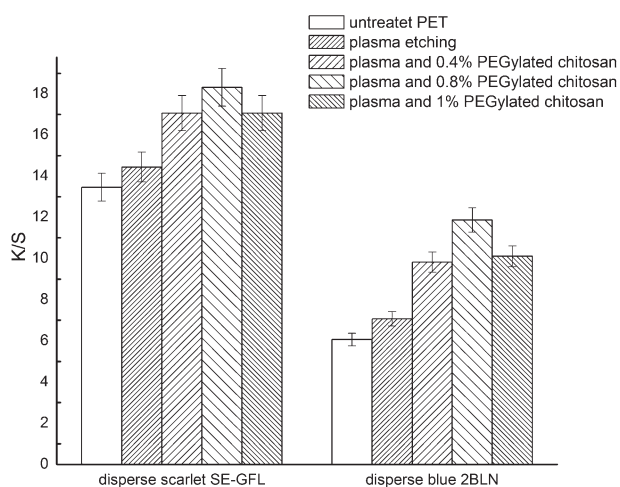


Figure 8. Color strength of PET fabrics treated with various concentrations of PEGylated chitosan.

using 1% (m/v) regardless of the colors of the disperse dyes. This additional increase in K/S value may be due to the formation of active groups such as $-\text{OH}$, $-\text{COOH}$, $-\text{NH}_2$ produced by plasma etching and PEGylated chitosan derivatives deposition on the surface of PET,³⁹ which was consistent with the reported results that the introduction of hydrophilic groups, induced by reactive plasmas, may increase the water swelling capability and the affinity of PET fibers for dyes containing polar groups²³ by Raffaele-Addamo et al. The PEGylated chitosan derivative induced various non-covalent interactions, including hydrogen bonding, p-p stacking, and van der Waals interactions between PET surface and dye molecules, which led to modified PET more easily for adsorption dye. So, increasing the dose level of PEGylated chitosan resulted in higher dye uptake and better dyeability towards disperse dyes.

CONCLUSIONS

In this work, the effects of oxygen plasma and PEGylated chitosan derivatives on the properties of PET samples have been studied. FTIR analysis showed that as a result of plasma treatment new chemical bonds were evolved and some original bonds were magnified which could contribute to crosslinks between PEGylated chitosan derivatives and PET chains. SEM images indicated that oxygen plasma treatment resulted in a rougher surface compared with untreated PET sample, whereas PEGylated chitosan derivative treatment led to the formation of a barrier layer films on the surface of PET. The application of both of these treatments resulted in a decrease of water contact angle and an increase of moisture regains, whereas oxygen plasma had a more significant effect, this made the modified PET fabrics more suitable for wearable compared with untreated sample. An increase in color depth upon dyeing was obtained after treating PET fabrics with PEGylated chitosan derivatives here.

ACKNOWLEDGMENTS

The authors thank to the faculty research foundation of Yan-cheng Institute Technology which provided financial support to this work (XKY2011019).

REFERENCES

- Santosa, W. L. F.; Moura, A. P.; Silva, E. A.; Cardozo-Filho, L.; Muniz, E. C.; Rubira, A. F. *Dyes Pigment.* **2007**, *75*, 378.
- Zohdy, M. H. *Radiat. Phys. Chem.* **2005**, *73*, 101.
- Jang, J.; Jeong, Y. *Dyes Pigment.* **2006**, *69*, 137.
- Shukla, S. R.; Harad, A. M.; Jawale, L. S. *Polym. Degrad. Stab.* **2009**, *94*, 604.
- Liu, Y. X.; He, T.; Gao, C. Y. *Colloids Surf. B* **2005**, *46*, 117.
- Wei, Q. F.; Liu, Y.; Hou, D. Y.; Huang, F. L. *J. Mater. Process. Technol.* **2007**, *194*, 89.
- Li, S. Y.; Wu, Z. K.; Tang, H. X.; Yang, J. *Appl. Surf. Sci.* **2012**, *258*, 4222.
- Li, W. D.; Ding, E. Y. *Surf. Rev. Lett.* **2006**, *13*, 819.

9. Noppakundilograt, S.; Buranagul, P.; Graisuwan, W.; Koopipat, C.; Kiatkamjornwong, S. *Carbohydr. Polym.* **2010**, *82*, 1124.
10. Fu, X. R.; Shen, Y.; Jiang, X.; Huang, D.; Yan, Y. Q. *Carbohydr. Polym.* **2011**, *85*, 221.
11. Glampedaki, P.; Jovic, D.; Warmoeskerken, M. G. *Prog. Org. Coat.* **2011**, *72*, 562.
12. Wang, B. L.; Wang, J. L.; Li, D. D.; Ren, K. F.; Ji, J. *Appl. Surf. Sci.* **2012**, *258*, 7801.
13. Mourya, V. K.; Inamdar, N. N. *React. Funct. Polym.* **2008**, *68*, 1013.
14. Ouchi, T.; Nishizawa, H.; Ohya, Y. *Polymer* **1998**, *39*, 5171.
15. Tanuma, H.; Saito, T.; Nishikawa, K.; Dong, T.; Yazawa, K.; Inoue, Y. *Carbohydr. Polym.* **2010**, *80*, 260.
16. Makuška, R.; Gorochovceva, N. *Carbohydr. Polym.* **2006**, *64*, 319.
17. Sanaee, Z.; Mohajerzadeh, S.; Zand, K.; Gard, F. S. *Vacuum* **2010**, *85*, 290.
18. Garcia-Fuentes, M.; Prego, C.; Torres, D.; Alonso, M. J. *Eur. J. Pharm. Sci.* **2005**, *25*, 133.
19. Ganji, F.; Abdekhodaie, M. J. *Carbohydr. Polym.* **2008**, *74*, 435.
20. Sugimoto, M.; Morimoto, M.; Sashiwa, H.; Saimoto, H. *Carbohydr. Polym.* **1998**, *36*, 49.
21. Han, M. H.; Jegal, J. P.; Park, K. W.; Choi, J. H.; Baik, H. K.; Noh, J. H.; Song, K. M.; Lim, Y. S. *Surf. Coat. Technol.* **2007**, *201*, 4948.
22. Vassallo, E.; Cremona, A.; Ghezzi, F.; Ricci, D. *Vacuum* **2010**, *84*, 902.
23. Raffaele-Addamo, A.; Selli, E.; Barni, R.; Riccardi, C.; Orsini, F.; Poletti, G.; Meda, L.; Massafra, M. R.; Marcandalli, B. *Appl. Surf. Sci.* **2006**, *252*, 2265.
24. Salem, T.; Uhlmann, S.; Nitschke, M.; Calvimontesa, A.; Hund, R. D.; Simon, F. *Prog. Org. Coat.* **2011**, *72*, 168.
25. Bratskaya, S.; Marinin, D.; Nitschke, M.; Dieter, P.; Schwarz, S.; Simon, F. *J. Adhes. Sci. Technol.* **2004**, *18*, 1173.
26. Svirachev, D. M.; Tabaliyov, N. A. *Bulg. J. Phys.* **2005**, *32*, 22.
27. Vesel, A.; Junkar, I.; Cvelbar, U.; Kovac, J.; Mozetic, M. *Surf. Interface Anal.* **2008**, *40*, 1444.
28. Cheng, C.; Liye, Z.; Zhan, R. J. *Surf. Coat. Technol.* **2006**, *200*, 6659.
29. Inagaki, N.; Narushim, K.; Tuchida, N.; Miyazaki, K. *J. Polym. Sci. Part B: Polym. Phys.* **2004**, *42*, 3727.
30. Tang, S.; Choi, H. *J. Phys. Chem. C* **2008**, *112*, 4712.
31. Vesel, A.; Mozetic, M.; Strnad, S. *Vacuum* **2011**, *85*, 1083.
32. Freure, C.; Chen, G.; Horton, J. H. *Surf. Sci.* **1999**, *437*, 231.
33. Samperia, F.; Puglisia, C.; Alicatab, R.; Montaudob, G. *Polym. Degrad. Stab.* **2004**, *83*, 3.
34. Carosio, F.; Alongi, J.; Frache, A. *Eur. Polym. J.* **2011**, *47*, 893.
35. Shin, G.; Lee, Y. H.; Lee, J. S.; Kim, Y. S.; Choi, W. S.; Park, H. J. *J. Agric. Food Chem.* **2002**, *50*, 4608.
36. Ferrante, D.; Iannace, S.; Monetta, T. *J. Mater. Sci.* **1999**, *34*, 175.
37. Cioffi, M. O. H.; Voorwald, H. J. C.; Hein, L. R. O.; Ambrosio, L. *Compos. Part A* **2005**, *36*, 615.
38. Lei, M. K.; Liu, Y.; Li, Y. P. *Appl. Surf. Sci.* **2011**, *257*, 7350.
39. Salem, T.; Pleul, D.; Nitschke, M.; Müller, M.; Simon, F. *Appl. Surf. Sci.* **2013**, *264*, 286.
40. Chun, B. C.; Cha, S. H.; Chung, Y. C.; Cho, J. W. *J. Appl. Polym. Sci.* **2002**, *83*, 27.
41. Shin, Y.; Son, K.; Yoo, D. I. *J. Appl. Polym. Sci.* **2007**, *103*, 3655.