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Surface modification of polyester fabrics by atmospheric-pressure air/He plasma for color strength and adhesion enhancement

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ABSTRACT

Surface properties of water-based pigmented inks for ink-jet printed polyester fabrics were modified with atmospheric-pressure air/He plasma to improve the color strength and pigment adhesion of the treated surfaces. The influence of various parameters, including the surface morphology, chemical compositions, surface energy and dynamic contact angles of the control and plasma treated samples was studied. Color strength and edge definition were used to evaluate the ink-jet printing performance of fabrics. The change in pigment adhesion to polyester fibers was analyzed by SEM (scanning electron microscopy). AFM (Atomic force microscope) and XPS (X-ray photoelectron spectroscopy) analyses indicated the increase in surface roughness and the oxygen-containing polar groups(C=O, C—OH and COOH) reinforced the fixation of pigments on the fiber surface. The result from this study suggested that the improved pigment color yield was clearly affected by alteration of pigment adhesion enhanced by plasma surface modification. Polyester fabrics exhibited better surface property and ink-jet printing performance after the air/He mixture plasma treatment comparing with those after air plasma treatment.

1. Introduction

Nowadays, digital ink-jet printing rapidly grows with favorable acceptance and has found an increasing number of applications in today's textile printing. The technique offers benefits such as high-quality printed pattern, little pollution and fast response of garment customization [1,2]. Pigment-based inks are often used as inkjet printing media since they have no selection on fabrics. However, patterns directly printed on polyester fabrics often have low color strength and blurred edge definition [3]. Therefore, pre-processing of printing substrate must be done to acquire better performance of inkjet printing. Compared to traditional methods for producing high-quality color reproduction, the advantages of plasma surface modification are: be particularly suitable for textile processing because most textile materials are heat sensitive polymers; no production of waste water; higher security and lower chemical consumption; environmentally friendly and matching the definition of ecological textile manufacturing [4].

Recently, plasma has been widely employed to modify surfaces of textile fabrics for functional finishing and improving dyeing behaviors. Pandiyaraj et al. [5] modified polypropylene films using various gaseous plasma treatments to increase its surface energy. Shahidi et al. [6] studied dyeing properties of polypropylene fabrics treated with dielectric barrier discharge plasma. They increased the K/S (Kubelka-Munk coefficient) values of the dyed fabrics of which the tensile strength has not been changed. Zhang and Elabid [7] used atmospheric pressure plasma with fine and uniform filament discharge operated at 20 kHz to improve the low temperature dyeability of PET (polyethylene terephthalate) fabric. Pransilp and Kiatkamjornwong [8] studied the influences of oxygen, nitrogen and SF_6 gas plasma on color reproduction and color adhesion of the treated cotton fabric surface printed with water-based pigmented inkjet ink.

In our previous work, the effects of exposure time and aging of surface properties on the polyester fabrics printed by the pigmented jet inks were investigated [9,10]. Nevertheless, there are few literatures about the influence of atmospheric plasma on pigmental adhesion properties of polyester fibers. In this paper, the polyester fabrics were surface modified with atmospheric-pressure air/He plasma to improve ink absorption of water-based pigmented inkjet inks and color reproduction of the treated surfaces. An in-depth study of the influence of various parameters, including the surface morphology, chemical compositions, surface energy and dynamic contact angles of the plasma treated samples was carried out. AFM and XPS were used to characterize the influence of

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plasma treatment on surface morphology and chemical components of the specimens. The pigment adhesion on polyester fibers was also investigated by SEM.

2. Experimental

2.1. Raw materials

The fabric specimens were 100% polyester plain weave fabric (58 g/m^2, Wuxi bleaching and dyeing plant, Wuxi, China) without chemical processing. Pigment-based ink (NDC, Key Laboratory for Eco-Textiles Ministry of Education, Wuxi, Jiangnan University) was used in all ink-jet printing experiments.

2.2. Plasma treatments

All surface modification in this study was carried out in a DBD (dielectric barrier discharge) plasma reactor (ST/RI, Shanghai Textile Research Institute, Shanghai, China). As schematically shown in Fig. 1, the experimental equipment has an approximately 25 cm × 25 cm active exposure area of between two copper electrodes, both of which is embedded in a 6 mm thick glass dielectric barrier. The plasma system was first evacuated and then filled with the gas up to the atmospheric pressure. The entire DBD was performed at a mixed ambience of atmospheric air and 10% helium and lasted for a period of time. The facility is conducted by a range of 0–500 W power supply operating in the frequency of 1 kHz. The samples directly put into the reactor were treated at a total power of 300 W, dielectrics space 3 mm for 120 s.

2.3. Inkjet printing procedure

The modified and control fabrics were digitally printed using an ink-jet printer (JV4-180, Mimaki Company, Nagano, Japan) and subsequently baked at 120 °C for 3 min with baker (Minni thermo-350, Roaches Company, West Yorkshire, England).

2.4. Measurements

Morphological and topographical modifications of the polyester fiber surface, resulting from plasma treatment, were investigated using an AFM (CSPM4000, Benyuan Company, Guangzhou, China). The vertical resolution of the machine is 0.1 nm, while the horizontal resolution is 0.2 nm. Squares of 5.0 μm side were scanned in contact mode and all AFM images were collected at room temperature in atmosphere.

Surface chemical composition of fabric surface was determined by XPS (PHI-5000C ESCA, Perkin Elmer, Waltham, United States), using Mg Kα radiation ($h\nu = 1253.6$ eV) operated at 14.0 kV and 250W with a detection angle at 54°. The spectra were in reference to the C—C peak positioned at 284.6 eV.

The contact angles were investigated through the Wilhelmy plate technique by dynamic contact angle measurement equipment (CDCD-100F, Camtel Ltd Company, England). The Wilhelm method measures the pull force or the push force and the wetting force, to measure the contact angles [11]. The experiments were performed at room temperature and 65% relative humidity shortly after the plasma modification. Measurement velocity is 0.3 mm/s. Ethanediol and distilled water were selected as the probe liquid. Five different positions were measured and the average values were calculated. The data for the test liquid surface tension and surface tension components at 20 °C was given in Table 1 [12,13].

Table 1
Test liquids and their surface tension components.

Liquids	Temperature (°C)	Surface tension data (mN/m)		
		γ_L	γ_L^d	γ_L^p
Distilled water (H_2O)	20	72.8	21.8	51.0
Ethylene glycol ($C_2H_6O_2$)	20	48.0	29.0	19.0

Surface energy of the substrate can be counted from the contact angle values determined in previous study. Some calculation equations are listed as follow [12]. The total surface energy can be deemed as consisted of two parts, the Lifshitz-vander Waals and the acid-base component. The former indicates the dipole–dipole (Keesom), induction (Debye) and dispersion forces, and latter represents the H-bonding or acid-base interactions. Hence, for a solid phase S, the total surface energy can be expressed as:

$$\gamma_s = \gamma_s^p + \gamma_s^d \qquad (1)$$

According to Fowkes, the total interaction between solid phase S and liquid phase L can be expressed as:

$$\gamma_{SL} = [(\gamma_S^d)^{1/2} - (\gamma_L^d)^{1/2}]^2 + [(\gamma_S^p)^{1/2} - (\gamma_L^p)^{1/2}]^2 \qquad (2)$$

Young's equation correlates the contact angle to the three interfacial tensions:

$$\cos\theta = \frac{\gamma_S - \gamma_{SL}}{\gamma_L} \qquad (3)$$

By rearranging Eqs. (2) and (3), the relationship between contact angle and surface energy can be expressed as:

$$\gamma_L(1 + \cos\theta) = 2(\gamma_S^p \gamma_L^p)^{1/2} + 2(\gamma_S^d \gamma_L^d)^{1/2} \qquad (4)$$

Where θ is the contact angle, γ_S, γ_S^d, γ_S^p represent total surface energy, dispersion component, and polar component of the fabric, respectively. γ_L, γ_L^d and γ_L^p represent total surface tension, dispersion component, and polar component of the liquids, respectively. From Eq. (4), using two liquids, water and glycol, we can calculate the γ_S^d, γ_S^p and γ_S for the tested fabric.

Surface morphology of the control and plasma treated fiber was investigated using SEM (JSM-5610, Japan Electron Optics Laboratory, Tokyo, Japan). The polyester fiber samples were observed at 2400 magnification to inspect the pigment adhesion on fibers.

2.5. Printing performance

Edge definition, K/S, L and C values were measured to evaluate the anti-bleeding performance and color strength of samples. A digital camera (IXY DIGITAL 50, Canon, Tokyo, Japan) and color measurement system (X-Rite Premier 8400, X-Rite Company, Michigan, United States) were employed in this study.

3. Results and discussion

3.1. Surface morphology

Surface morphology of the polyester fiber can be revealed in Fig. 2. The AFM images of 5.0 μm × 5.0 μm show the topographical modifications of specimens before and after plasma treatments. As seen in Fig. 2(a), a relatively smooth surface of the untreated fiber is clearly observed. However, after the atmospheric-pressure plasma processing, the original structure was changed. As illustrated in Fig. 2(b) and (c), the fibril structure is not visible and replaced by a number of pit-like structures formed on the fiber surface. This is due to the sputtering etching effect of the plasma modification. According to literatures, the main species in the plasma which are responsible for the etching effect are positive ions and photons, with ability of breaking primary chemical bonds and inducing cross-linking [14].

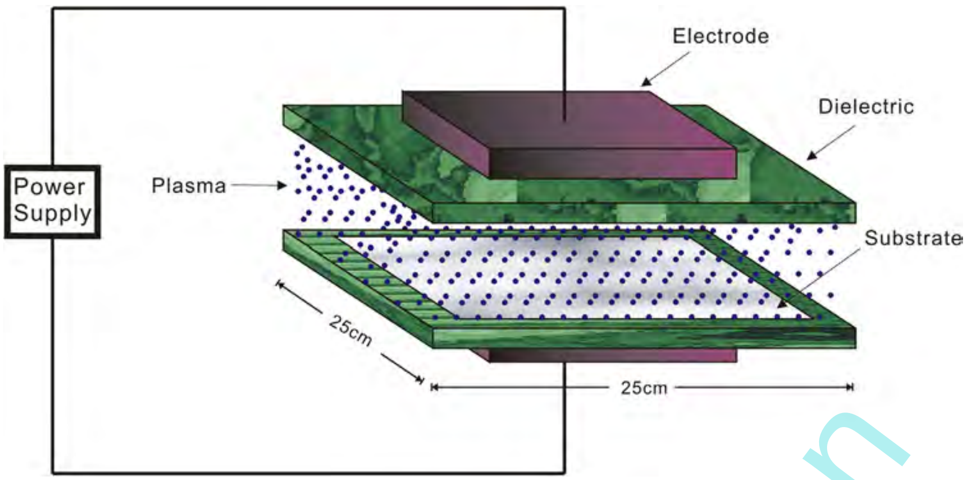

Fig. 1. Schematic view of experimental set-up.

Table 2
Relative chemical composition and atomic ratios of polyester fabrics determined by XPS.

Samples	Chemical composition		Atomic ratios
	C1 s (%)	O1 s (%)	O/C
Untreated	81.77	15.23	0.19
Air plasma treated	71.45	25.36	0.35
Air/He plasma treated	69.38	27.55	0.40

The sample was treated by a power 300 W for 120 s.

3.2. Surface chemistry

The surface chemical composition which is shown in Table 2 reveals the chemical nature of the polyester surface before and after plasma modification. The oxygen concentration increased over 10%, while the carbon containing reduced similar percentage. Compared with the control sample, the O/C ratio of plasma modified sample significantly increased 0.16 and 0.21, respectively. It can be expected that the oxygen-containing polar groups were incorporate into the polyester surface when processed by plasma.

In order to identify what chemical groups have been introduced onto polyester fabric surface, deconvolution analysis of C1s peaks has been executed. Each component was characterized by the position on the energy scale (fixed to a certain value), the intensity and the width (determined by the fit procedure, respectively). The results are shown in Fig. 3. As reported in literatures, the spectrum of the original polyester contains three peaks at 284.60 eV, 286.10 eV, 288.10 eV and 288.75 eV, which may be respectively assigned to C—C/C—H, C—O (and/or C—OH), C═O and O—C—O (and/or COOH) [15–17]. The content variation of each chemical composition which can be seen in Table 3 indicated that the sub-peak at 284.6 eV evidently decreased after plasma modification while the sub-peaks at 286.1 eV and 288.75 eV appears to have a large increase. It was generally agreed that when natural and synthetic fibers were processed by plasma, the following chemical reactions may occur on the fiber surface [18].

$$RH \rightarrow R^{\bullet} + H^{\bullet};$$

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet};$$

$$ROO^{\bullet} + R_1H \rightarrow ROOH + R_1{}^{\bullet};$$

$$R^{\bullet} + O^{\bullet} \rightarrow RO^{\bullet};$$

$$RO^{\bullet} + R_1H \rightarrow R^{\bullet} + R_1OH;$$

$$RO^{\bullet} + H^{\bullet} \rightarrow ROH.$$

This result implied that many C—C bonds in polyester fiber surface was broken by the plasma treatment, subsequently the fractured C—C bonds will recombine with oxygen atoms such as C═O, C—OH and COOH generated in plasma to form the oxygen-containing polar groups as reported in literatures [19]. The experimental data indicate that the air/He mixture plasma was more effective than air plasma at the same treatment time. A similar result was found in our previous research when air/Ar was used as discharge gas [20]. Different from former researches, this phenomenon can be explained as that the breakdown voltage of helium is far lower than that of air under the same condition [21]. The mixture of helium reinforced the discharge of plasma and made the modification more sufficient.

3.3. Contact angles

The influence of plasma surface modification on hydrophilicity was investigated by dynamic contact angle measurement. As shown in Table 4, the distilled water and glycol contact angle values of control fabric was 85° and 72°, respectively. This result is not only attributed to the surface chemical properties of specimen but also the surface roughness of the fibril structures [22]. However, the water and glycol contact angles obviously decreased to 29° and 18° after the plasma processing. The results implied that the wettability of the fabric had been significantly improved by the surface modification. It is speculated that the air/He plasma introduced polar groups into the fiber surface while etching the polyester fiber. In addition, the effects will be further verified in surface energy study.

3.4. Surface energy

Plugging the contact angle values into equation 4, the total surface energy (γ_S), dispersion component (γ_S^d) and polar component (γ_S^p) of the fabrics can be calculated.

It is clearly seen in Table 5 that the total surface energy dramatically increased after plasma modification. Moreover, the polar component is also markedly altered compared to the dispersion component. The increase of surface energy is usually ascribed to the polar component since plasma introduced oxygen containing polar groups onto the material surface. The consequence is also approved the result of XPS analysis.

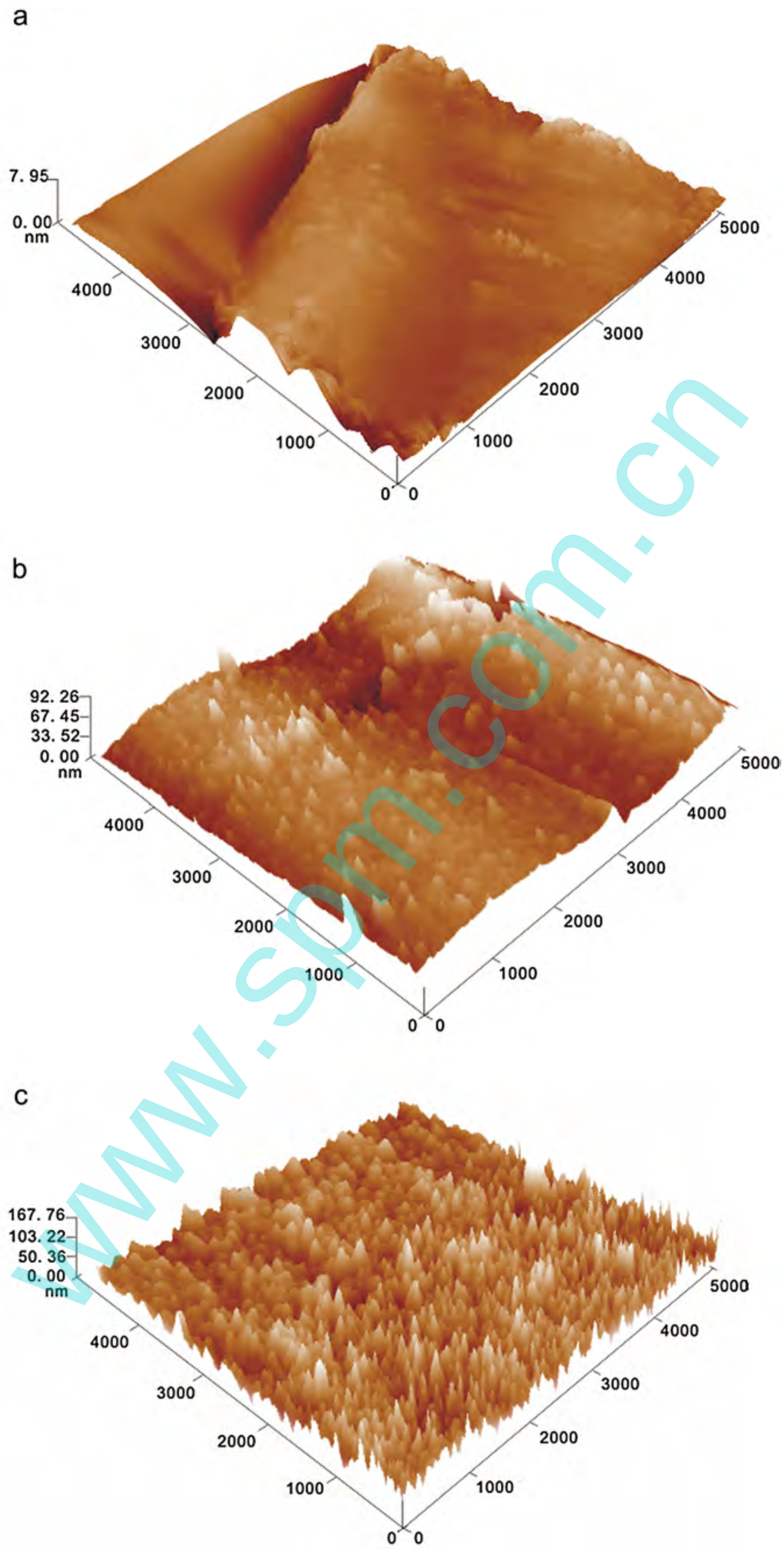

Fig. 2. AFM images of the polyester fibers, (a) untreated; (b) air plasma treated; (c) air/He plasma treated. The samples were treated at a power of 300 W for 120 s.

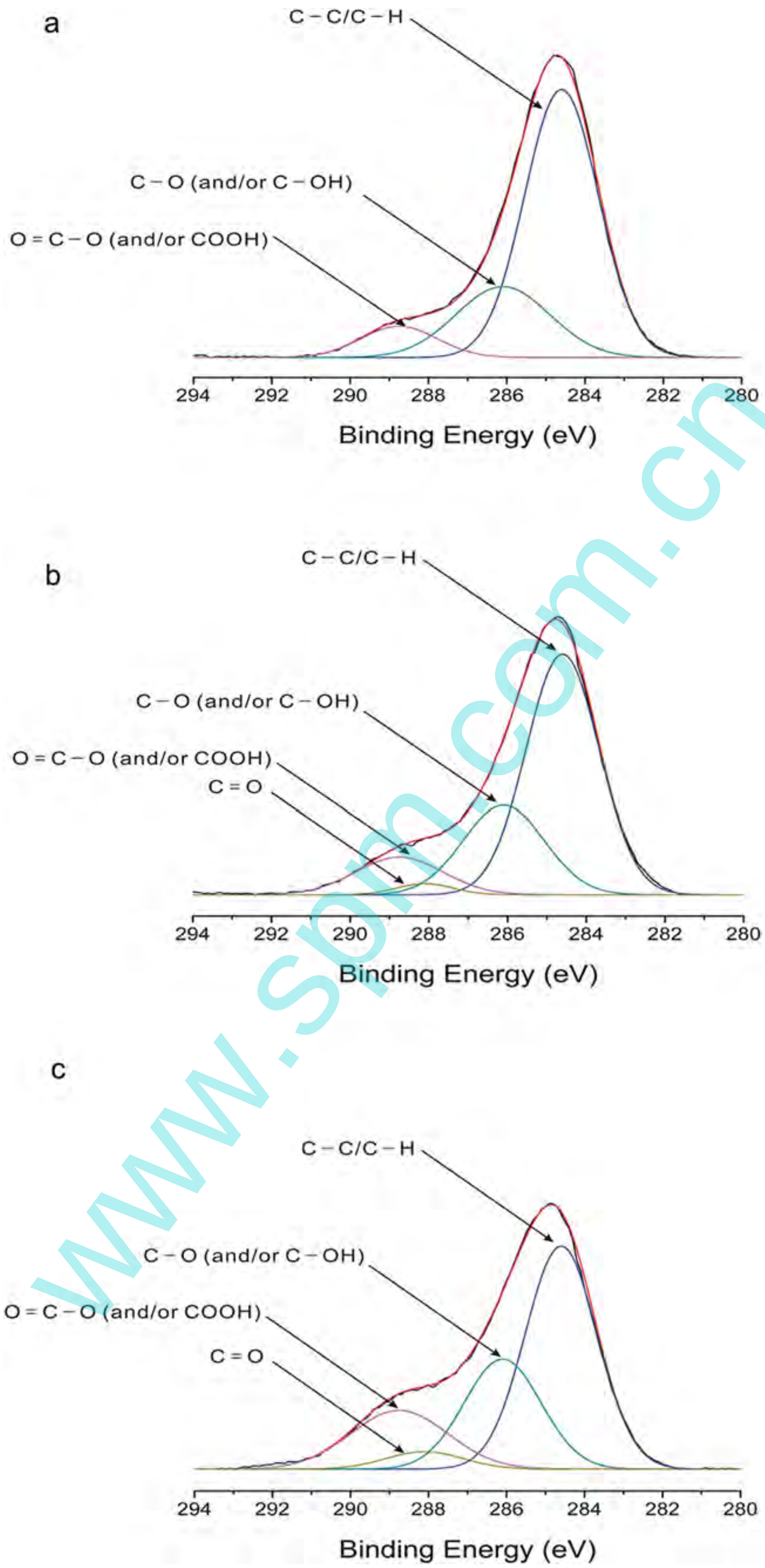

Fig. 3. XPS spectra of polyester fabrics, (a) untreated; (b) air plasma treated; (c) air/He plasma treated. The samples were treated at a power of 300 W for 120 s.

Table 3
Results of deconvolution of C1s peaks for polyester fabrics.

Binding energy (eV)	Untreated (%)	Air plasma treated (%)	Air/He plasma treated (%)	Possible functional groups
284.6	70.6	55.7	51.9	C—C
286.1	15.4	21.6	23.2	C—O (and/or C—OH)
288.1	0	2.5	3.1	C═O
288.75	14.0	20.2	21.8	O═C—O (and/or COOH)

The sample was treated by a power 300 W for 120 s.

Table 4
Contact angle of liquids measured on the polyester fabrics.

Liquids	Contact angle (°)	
	θ_1 (Untreated)	θ_2 (air/He plasma treated)
Distilled water	85 ± 2	29 ± 2
Glycol	72 ± 2	18 ± 2

The sample was treated by a power 300 W for 120 s.

Table 5
Surface energy results of untreated and plasma treated fabrics.

Samples	γ_S(mN/m)	γ_S^d(mN/m)	γ_S^p(mN/m)
Untreated	22.68	12.05	10.63
Air/He plasma treated	71.99	4.13	67.86

The sample was treated by a power 300 W for 120 s.

3.5. *Pigment adhesion*

In order to investigate the pigment adhesion on polyester fibers, the scanning electron microscopy was also employed to observe the surface fixation of pigments with a magnification of 2400 times. As presented in Fig. 4(a), because of the original chemical properties and smooth surface of polyester fibers, the pigment particles were difficult to be fixated on them and disorderly move on the fiber surface even into the gaps between two fibers. This result could directly explain the bleeding phenomenon examined by video focus-exchanged microscope. By contrast, an even distribution of pigment particles on the treated fibers can be seen in Fig. 4(b). This indicated that the hydrophilicity and rough surface of plasma modified fibers could offer more capacities for the fabric to capture inks and also facilitate the penetration of colorant particles into the polyester fabric [23,24].

3.6. *Color strength*

Digital inkjet printing was carried out to evaluate the effect of the plasma modification on printing performance. Color blocks and lines were printed with magenta and cyan ink on the substrates and images captured by digital camera. It is clearly seen in Fig. 5(a) that the bleeding phenomena is very serious along both weft and warp edge. As can be imagined, the actual printing pattern must be indistinct under this circumstance. Compared to that, the edge definition was observed to be much more legible in Fig. 5(b). This is due to the fact that the anti-bleeding property of the sample has been dramatically improved after plasma processing.

The K/S values which are considered as representations of color strength on the inkjet printing samples are shown in Table 6. The observably increased K/S values symbolize an enhancement of the chroma of the plasma modified fabrics. This result can also be supported by the previous study. It is considered that the improvement of the anti-bleeding property increased the amount of ink colorants stayed on per area of the fabric.

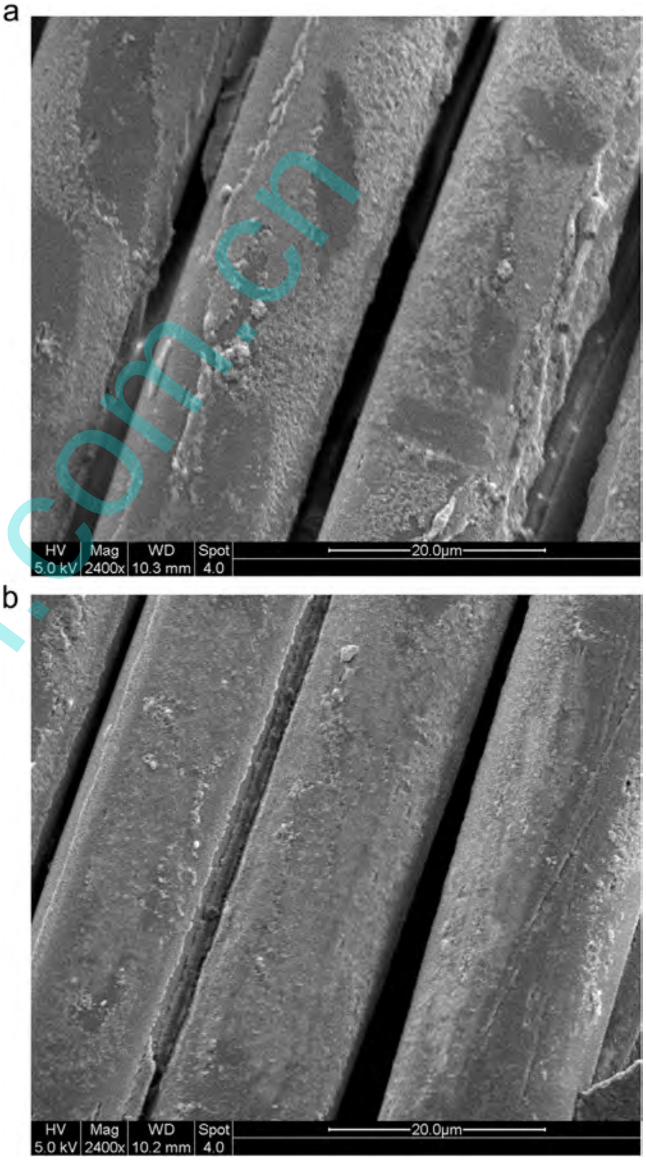

Fig. 4. SEM images of the pigment fixation on (a) untreated and (b) air/He plasma treated fibers.

Table 6
Color measurement results of untreated and plasma treated fabrics.

Samples	K/S		L		C	
	magenta	cyan	magenta	cyan	magenta	cyan
Untreated	3.09	2.27	56.72	51.75	46.27	39.18
Air/He plasma treated	3.71	2.64	52.33	48.32	49.36	42.23

The sample was treated by a power 300 W for 120 s.

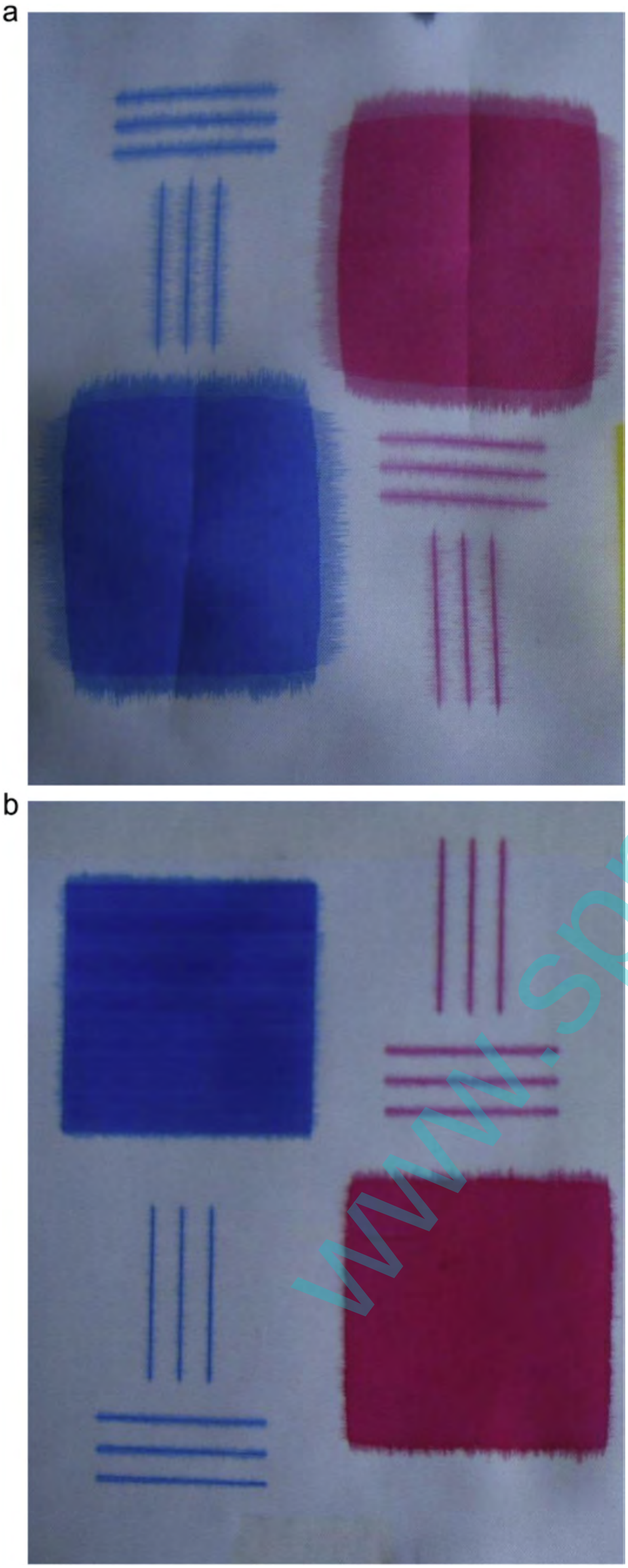

Fig. 5. Anti-bleeding performance of (a) untreated and (b) air/He plasma treated polyester fabrics.

4. Conclusions

The ink absorption of water-based pigmented inkjet inks and color reproduction of polyester fabrics can be improved by surface modification of atmospheric-pressure air and air/He mixture plasma. AFM investigation shows a number of pit-like structures formed on the fiber surface, indicating that the surface morphology of polyester fiber had been changed by plasma. XPS analysis reveals some oxygen-containing polar groups such as C=O, C—OH and COOH generated by plasma were implanted onto fiber surface. As a consequent, the wettability of the fabric had been significantly improved which has been identified by contact angle and surface energy study. Furthermore, the performance of ink jet printing of polyester fabrics was found to be preferable according to the higher color strength and clearer edge definition. SEM observations indicated that the improved pigment color yield was clearly contributed by the alteration of pigment adhesion. Given the above, plasma surface modification has been found to be an effective way to enhance the pigmental adhesion properties and ink-jet printing performance of polyester fabrics. The air/He mixture plasma was more effective than air plasma at the same treatment time.

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References

[1] L.P. Yeo, B.K. LokQ, M.P. Nguyen, C.W. Lu, Y.C. Lam, Selective surface modification of PET substrate for inkjet printing, Int. J. Adv. Manuf. Technol. 71 (2014) 1749–1755.
[2] A. Soleimani-Gorgani, F. Najafi, Z. Karami, Modification of cotton fabric with a dendrimer to improve ink-jet printing process, Carbohydr. Polym. 131 (2015) 168–176.
[3] H.M. El-Hennawi, A.A. Shahin, M. Rekaby, A.A. Ragheb, Ink jet printing of bio-treated linen, polyester fabrics and their blend, Carbohydr. Polym. 118 (2015) 235–241.
[4] X. Li, J. Lin, Y. Qiu, Influence of He/O_2 atmospheric pressure plasma jet treatment on subsequent wet desizing of polyacrylate on PET fabrics, Appl. Surf. Sci. 258 (2012) 2332–2338.
[5] K.N. Pandiyaraj, R.R. Deshmukh, A. Arunkumar, M.C. Ramkumar, I. Ruzybayev, S.I. Shah, P.G. Su, M.H. Periayah, A.S. Halim, Evaluation of mechanism of non-thermal plasma effect on the surface of polypropylene films for enhancement of adhesive and hemo compatible properties, Appl. Surf. Sci. 347 (2015) 336–346.
[6] S. Shahidi, M. Ghoranneviss, R. Ilali, M. Karami, M. Miladi, Dyeing properties of the atmospheric pressure plasma-treated polypropylene fabric subjected to butane tetra carboxylic acid, J. Text. Inst. 107 (2016) 636–644.
[7] A.E.A. Elabid, J. Zhang, J.J. Shi, Y. Guo, K. Ding, J. Zhang, Improving the low temperature dyeability of polyethylene terephthalate fabric with dispersive dyes by atmospheric pressure plasma discharge, Appl. Surf. Sci. 375 (2016) 26–34.
[8] P. Pransilp, M. Pruettiphap, W. Bhanthumnavin, B. Paosawatyanyong, S. Kiatkamjornwong, Surface modification of cotton fabrics by gas plasmas for colorstrength and adhesion by inkjet ink printing, Appl. Surf. Sci. 364 (2016) 208–220.
[9] K. Fang, C. Zhang, Surface physical-morphological and chemical changes leading to performance enhancement of atmospheric pressure plasma treated polyester fabrics for inkjet printing, Appl. Surf. Sci. 255 (2009) 7564.
[10] C. Zhang, K. Fang, Aging of surface properties of polyester fabrics treated with atmospheric pressure plasma for inkjet printing, Surf. Eng. 28 (2012) 306–310.
[11] S. Ganesan, Simulations of impinging droplets with surfactant-dependent dynamic contact angle, J. Comput. Phys. 301 (2015) 178–200.
[12] B. Janczuk, T. Bialopiotrowicz, A. Zdziennicka, Some remarks on the components of the liquid surface free energy, J. Colloid Interface Sci. 211 (1999) 96–103.
[13] Q. Zhao, Y. Liu, E.W. Abel, Effect of temperature on the surface free energy of amorphous carbon films, J. Colloid Interface Sci. 280 (2004) 174–183.
[14] D. Rapp, P. Englander-Golden, Cross sections for dissociative ionization of molecules by electron impact, J. Chem. Phys. 42 (1965) 1464–1479.
[15] T. Jacobs, R. Morent, N. De Geyter, T. Desmet, P. Dubruel, C. Leys, Effect of humid air exposure between successive helium plasma treatments on PET foils, Surf. Coat. Technol. 205 (2010) 2256–2261.
[16] S. NazariPour, S. Ghugare, R. Wiens, K. Gough, S. Liu, Controlled in situ formation of polyacrylamide hydrogel on PET surface via SI-ARGET-ATRP for wound dressings, Appl. Surf. Sci. 349 (2015) 695–704.

[17] A. Berendjchi, R. Khajavi, A.A. Yousefi, M.E. Yazdanshenas, Surface characteristics of coated polyester fabric withreduced graphene oxide and polypyrrole, Appl. Surf. Sci. 367 (2016) 36–42.

[18] Chen Jie-rong, Application of Low Temperature Plasma Technologyon Textile Industry, China Textile Press, Beijing, 2005, pp. 12.

[19] Z. Sanaee, S. Mohajerzadeh, K. Zand, F.S. Gard, H. Pajouhi, Minimizing permeability of PET substrates using oxygen plasma treatment, Appl. Surf. Sci. 257 (2011) 2218–2225.

[20] C. Zhang, K. Fang, Surface modification of polyester fabrics for inkjet printing with atmospheric-pressure air/Ar plasma, Surf. Coat. Technol. 203 (2009) 2058–2063.

[21] S. Yue, X. Liu, Z. Shi, Experimental study on breakdown voltage between parallel plates in high-pressure helium, Acta Phys. Sin.-Chin. Ed. 64 (2015) 105101.

[22] X. Yan, L. Yang, Y. An, Surface roughness and hydrophilicity enhancement of polyolefin-based membranes by three kinds of plasma methods, Surf. Interface Anal. 47 (2015) 545–553.

[23] H. Krump, I. Hudec, M. Jasso, E. Dayss, A.S. Luyt, Physical–morphological and chemical changes leading to an increase in adhesion between plasma treated polyester fibres and a rubber matrix, Appl. Surf. Sci. 252 (2006) 4264–4278.

[24] A. Raffaele-Addamo, E. Selli, R. Barni, C. Riccardi, F. Orsini, G. Poletti, L. Meda, M.R. Massafra, B. Marcandalli, Cold plasma-induced modification of the dyeing properties of poly(ethylene terephthalate) fibers, Appl. Surf. Sci. 252 (2006) 2265–2275.