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Effect of atmospheric-pressure air/He plasma on the surface properties related to ink-jet printing polyester fabric

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ABSTRACT

Pigment inkjet printing shows more environmental advantages and can potentially enable cost-effective short-run for production. However, patterns directly printed with pigment inks have poor color yields and easily bleed. In the present study, polyester fabrics were surface modified with atmospheric-pressure air/He plasma. The effect of plasma treatment on various fabric properties such as the surface morphology, chemical compositions, surface energy and dynamic contact angles was investigated. Color strength and edge definition were used to evaluate the ink-jet printing performance of samples. The changing of the surface fixation of pigments on polyester fibers was also analyzed by scanning electron microscopy (SEM). Atomic force microscope(AFM) and X-ray photoelectron spectroscopy (XPS) analyses indicated the increase in surface roughness and the oxygen-containing polar groups reinforced the fixation of pigments on the fiber surface. This work explores a novel approach for the atmospheric-pressure plasma, which can provide its important application in enhancing the surface properties and ink-jet printing performance of fabrics.

1. Introduction

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 [1,2]. Therefore, preprocessing of printing substrate must be done to acquire better performance of inkjet printing.

Chemicals solutions such as cationic reagents and thickeners are often used as conventional approach to size the fabrics [3–5]. This wet pretreatment which involves several steps is very complicated, with high energy and water consumption. In the mean time, waste water and harmful substances which results in serious environmental issues would be generated.

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 [6–8].

The atmospheric pressure plasma has been reported to be effective to increases the dyeing rate of fabric [9]. In that case, the effect of plasma modification on the chemical property of ink-jet printing fabric deserves special attention.

Therefore, in this study, 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 investigated. AFM and XPS were used to characterize the influence of plasma treatment on surface morphology and chemical components of the specimens. The surface fixation of pigments on polyester fibers was also investigated by SEM. Color strength and edge definition were used to evaluate the ink-jet printing performance of samples.

2. Experimental

2.1. Raw materials

The fabric specimens were 100% polyester plain weave fabric (65 g/m^2) without chemical processing. Pigment-based ink without any binder (Key Laboratory for Eco-Textiles Ministry of Education, Jiangnan University) was used in all ink-jet printing experiments.

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The average particle size of the pigment is about 180 ± 10 nm.

2.2. Plasma treatments

All surface modification in this study was carried out in ST/RI dielectric barrier discharge (DBD) plasma reactor manufactured by Shanghai Textile Research Institute, China. As schematically shown in Fig. 1, the main chamber which is made of stainless steel has a dimension of 40 cm × 40 cm × 40 cm. There is 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. A rotary vane pump is attached to the gas outlet and the pressure in the chamber is maintained by a set of valves. The system was evacuated to 50 Pa before plasma treatment. Then the gas was admitted up to a pressure of 100 kPa. The entire DBD was performed at a mixed ambience of atmospheric air and 10% helium and lasted for 90s. The facility is conducted by a range of 0–500W 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.

2.3. Inkjet printing procedure

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

2.4. Measurments

Morphological and topographical modifications of the polyester fiber surface, resulting from plasma treatment, were investigated using a CSPM4000 AFM produced by Benyuan Company. The vertical resolution of the machine is 0.1 nm, while the horizontal resolution is 0.2 nm. Squares of 3.0 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 X-ray photoelectron spectroscopy (XPS), which is performed in a PHI-5000C ESCA (Perkin Elmer) system, using Mg Kα radiation (hν = 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 using a CDCD-100 F produced by Camtel Ltd Company of England. The Wilhelm method measures the pull force or the push force and the wetting force, to measure the contact angles [10]. 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 as mentioned in literature [11,12].

Surface energy of the substrate can be counted from the contact angle values determined in previous study. Some calculation equations are listed as follow [11]. 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:

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

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

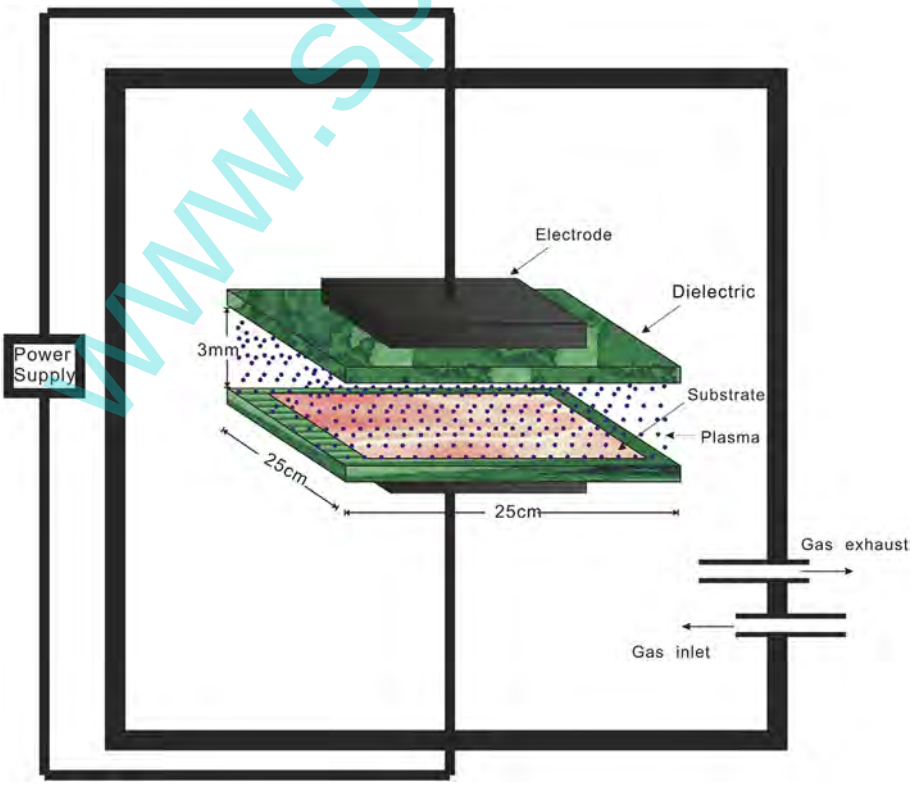

Fig. 1. Schematic view of experimental set-up.

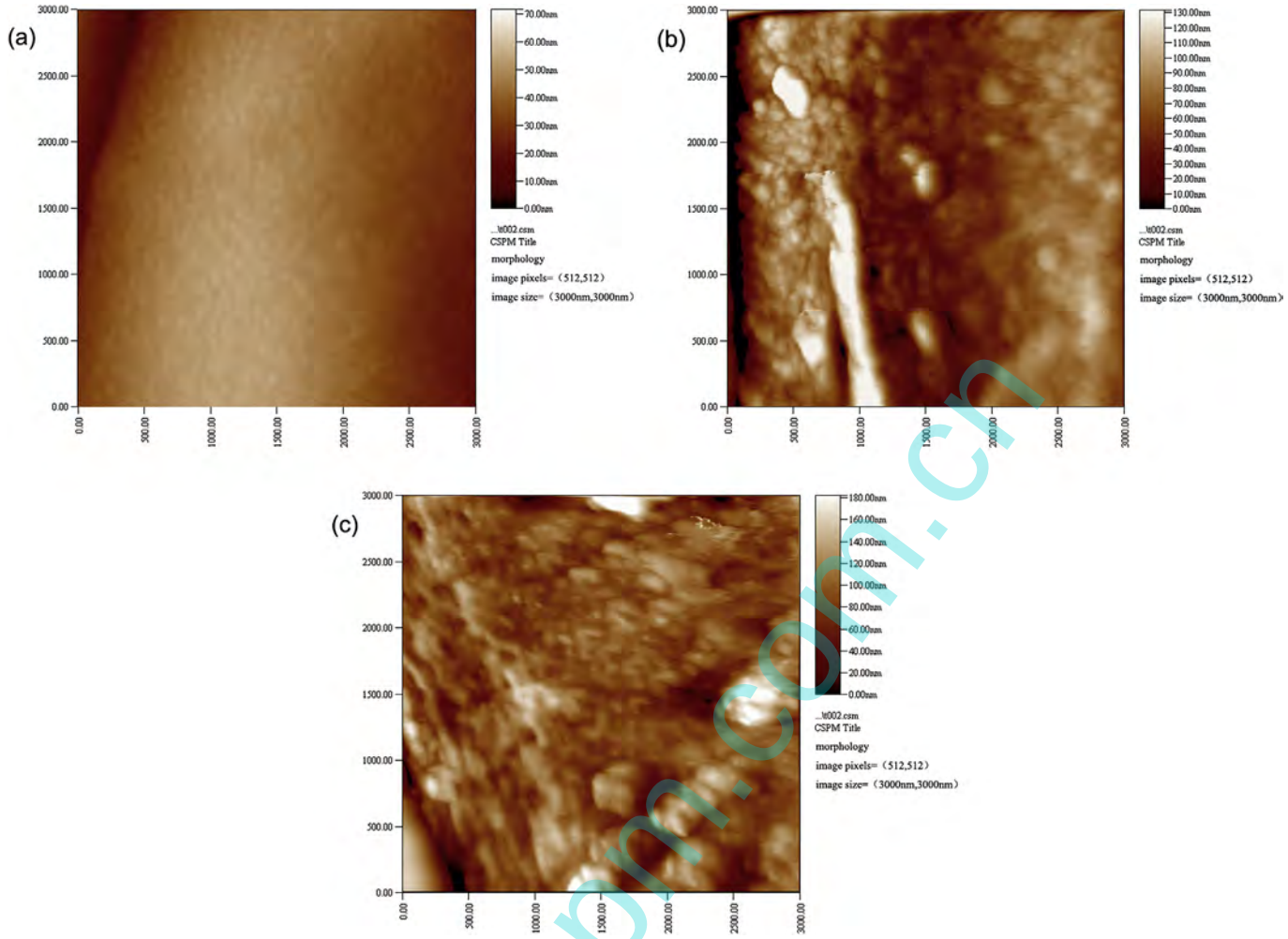

Fig. 2. AFM images of the polyester fibers, (a) untreated; (b) air plasma treated; (c) air/He plasma treated. The samples were treated at a power of 300W for 90 s.

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

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

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

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

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

Where θ is the contact angle, $\gamma_S, \gamma_S^d, \gamma_S^p$, 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 a JSM-5610 scanning electron microscopy. The polyester fiber samples were observed at 2400 magnification to inspect the surface fixation of pigment 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 DZ3-video focus-exchanged microscope (Union Optical CO.LTD of Japan) and X-Rite Premier 8400 color measurement system (X-Rite Company of America) were employed in this study. The color strength values (K/S values) of the fabrics were calculated from Kubelka-Munk equation (5), where K and S refers absorption and scattering coefficient, and R is the decimal fraction of the dyed fabrics.

$$K/S = (1-R)^2 \Big/ 2R \quad (5)$$

Table 1
Relative chemical composition and atomic ratios of polyester fabrics determined by XPS.

Samples	Chemical composition		Atomic ratios
	C1s (%)	O1s (%)	O/C
Control	81.58	15.42	0.19
Air plasma treated	71.39	25.43	0.36
Air/He plasma treated	69.64	27.34	0.39

The sample was treated by a power 300W for 90s.

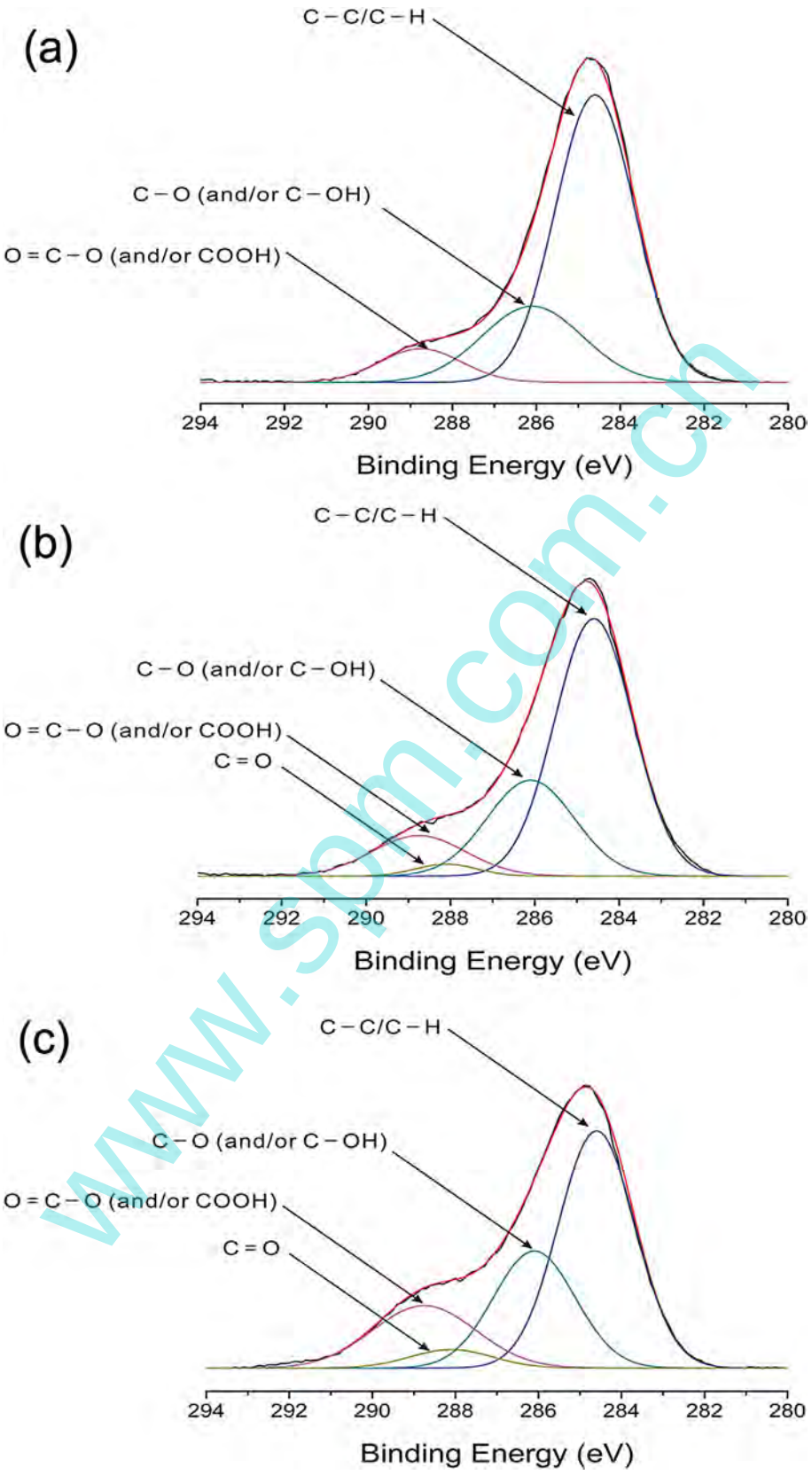

Fig. 3. XPS spectra of polyester fabrics, (a) untreated; (b) air plasma treated; (c) air/He plasma treated. The samples were treated at a power of 300W for 90 s.

Table 2
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	71.0	56.2	53.8	C–C
286.1	15.6	21.3	21.7	C–O (and/or C–OH)
288.1	0	2.4	2.8	C = O
288.75	13.4	20.1	21.7	O = C–O (and/or COOH)

The sample was treated by a power 300W for 90s.

Table 3
Contact angle of liquids measured on the polyester fabrics.

Liquids	Contact angle(°)	
	θ_1 (Untreated)	θ_2 (air/He plasma treated)
Distilled water	85.32	28.56
Glycol	72.17	17.92

The sample was treated by a power 300W for 90s.

Table 4
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 300W for 90s.

3. Results and discussion

3.1. Surface morphology

Surface morphology of the polyester fiber can be revealed in Fig. 2. The AFM images of 3.0 μm × 3.0 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 literature, 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 [13].

3.2. Surface chemistry

The surface chemical composition which is shown in Table 1 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 0.17 and 0.20, 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. The results are shown in Fig. 3. As reported in literature, the spectrum of the original polyester contains three peaks at 284.60eV, 286.10eV, 288.10 eV and 288.75eV, 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) [14–16]. The content variation of each chemical composition which can be seen in Table 2 indicated that the sub-peak at 284.6eV evidently decreased after plasma modification while the sub-peaks at 286.1eV and 288.75eV appears to have a large increase. 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 literature [17,18].

The experimental data indicate that the air/He 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 [19]. 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 [20]. 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 3, the distilled water and glycol contact angle values of control fabric was about 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 [21]. However, the water and glycol contact angles obviously decreased to about 28° and 18° after the plasma processing. The results implied that the wettability of the fabric had been significantly improved by the

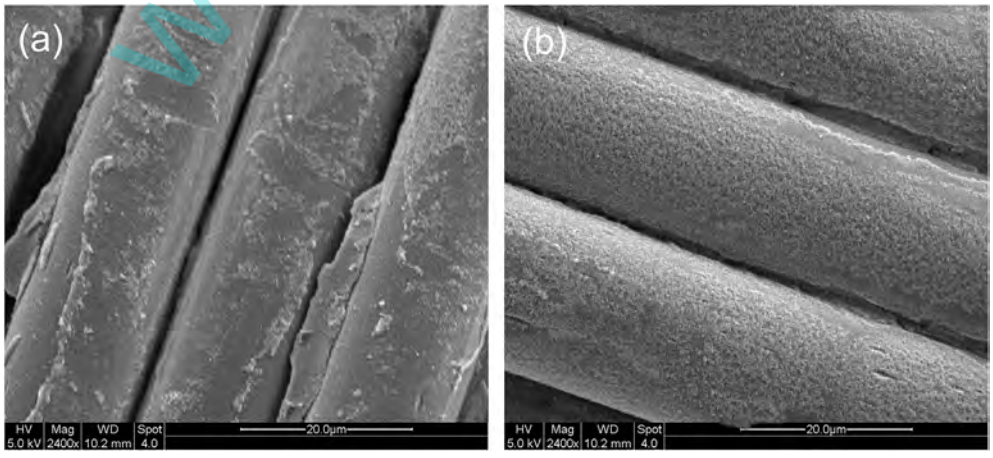

Fig. 4. SEM images of the pigmentation on (a) untreated and (b) air/He plasma treated fibers. The samples were treated at a power of 300W for 90 s.

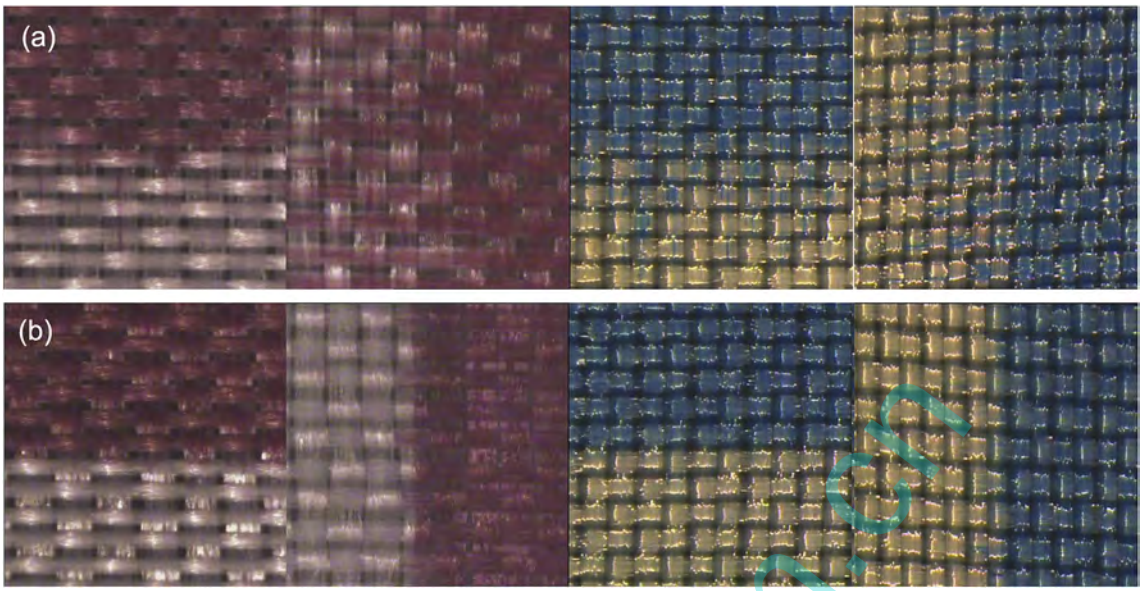

Fig. 5. Anti-bleeding performance of (a) untreated and (b) air/He plasma treated polyester fabrics. The samples were ink-jet printed with magenta and cyan inks.

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 4 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.

3.5. Surface fixation of pigments

In order to investigate the surface fixation of pigments on polyester fibers, the scanning electron microscopy was also employed to observe the pigmentation 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 adhere to 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 [22–24].

Table 5
Color measurement results of untreated and plasma treated fabrics.

Samples	K/S		L		C	
	magenta	cyan	magenta	cyan	magenta	cyan
Untreated	3.52	2.62	56.43	50.82	45.37	39.23
Air/He plasma treated	4.33	3.45	52.02	47.19	51.07	43.37

The sample was treated by a power 300W for 90s.

3.6. Color strength

Digital inkjet printing was carried out to evaluate the effect of the plasma modification on printing performance. Color block were printed with magenta and cyan ink and images of 2.0 mm × 2.0 mm area on the fiber surfaces were observed. 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 5. 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 pigment adhesion study. It is considered that the improvement of the anti-bleeding property increased the amount of ink colorant stayed on per area of the fabric. In addition, the increased color strength was also explained by the alteration of surface morphology of treated substrate which can reduce the spectra reflectance [25].

4. Conclusions

In this paper, the surface properties related to ink-jet printing performance of the polyester fabrics control and surface modified with atmospheric-pressure plasma was studied. AFM investigation shows that 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 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. The performance of ink-jet printing

of polyester fabrics was indicated to be preferable according to the higher color strength and clearer edge definition. That result can also be explained by the improvement of the pigment adhesion on fibers analyzed by SEM. Therefore, Atmospheric-pressure plasma has been explored as a novel approach for the atmospheric-pressure plasma, which can provide its important application in enhancing the surface properties and ink-jet printing performance of fabrics. Moreover, the air/He plasma was more effective than air plasma at the same treatment time.

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