



Surface physical–morphological and chemical changes leading to performance enhancement of atmospheric pressure plasma treated polyester fabrics for inkjet printing

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ABSTRACT

Without any preprocessing, polyester fabric has lower ability to hold on water due to the smooth morphology and chemistry property of polyester fibers. Therefore, patterns directly printed with pigment inks have poor color yields and easily bleed. In this paper, atmospheric pressure plasma was used to pretreat polyester fabric in order to provide an active surface for the inkjet printing. The results showed that surface-modified polyester fabrics could obtain the effects of features with enhanced color yields and excellent pattern sharpness. SEM images indicated that the rough surface of plasma treated fibers could provide more capacities for the fabric to capture inks and also facilitate the penetration of colorant particles into the polyester fabric. XPS analysis revealed that air + 50%Ar plasma introduced more oxygen-containing groups onto the fabric surface than air plasma. Although AFM images indicated that etching effects generated by air plasma treatments were more evident, the air/Ar plasma treated sample has higher *K/S* value and better color performance. These studies have also shown that the chemical modification of plasma appears to be relatively more significant for improving the effect of inkjet printing.

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1. Introduction

Inkjet printing is becoming increasingly important and popular for the printing of textiles; it eliminates the setup expense associated with screen preparation and can potentially enable cost-effective short-run for production. Inkjet printing furthermore allows visual effects such as tonal gradients and infinite pattern to repeat sizes that cannot be practically achieved with a screen printing process [1,2]. Due to its special characteristics such as superior strength and resilience, polyester fabric is often used as inkjet printing substrate. Nevertheless, patterns which are directly printed on polyester fabrics with pigment inks have poor color yields and bleed easily. Therefore, pretreatment of fabric must be done before printing to obtain better inkjet printing effects. Compared with traditional methods, plasma treatment has the following advantages: it only modifies the outermost thin layer of the surface, while the bulk properties will be kept untouched; lower chemical consumption and higher security; no waste water

produced; less burden on environment and totally fit to the definition of ecological textile manufacturing [3].

Some research has been performed on plasma surface modification at atmospheric pressure. Wakida et al. treated wool and polyethylene terephthalate (PET) fabrics with low-temperature plasma of helium/argon under atmospheric pressure to improve the samples wettability [4]. Shenton et al. made comparisons of treating effect between atmospheric plasma and vacuum [5]. McCord et al. modified nylon and polypropylene fabrics with atmospheric pressure plasmas [6]. Cai et al. used air/He and air/O₂ atmospheric plasma to desize PVA on cotton [7]. Hwang et al. investigated the effect of plasma treatment on surface characteristics of polyethylene terephthalate films using helium and oxygenated-helium atmospheric plasmas [8]. Matthews et al. made some investigation into etching mechanism of PET films and PVA desizing mechanism treated in He and O₂/He atmospheric plasmas [9,10]. Gawish et al. introduced glycidyl methacrylate onto nonwoven polypropylene surface initiated by atmospheric oxygenated-helium plasma to obtain novel antistatic, antimicrobial, and insect-repelling fabrics [11]. However, there are few literatures about surface modification with atmospheric plasma to improve the inkjet printing effects of fabrics.

In our previous work, oxygen plasma treatment was applied to silk fabric for pigment inkjet printing. Fang et al. showed that

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images of inkjet printed on treated silk fabrics exhibited deeper and more vivid color compared with untreated silk fabrics [12]. This paper describes the surface physical–morphological and chemical effects of atmospheric pressure plasma treatment for pigment inkjet printing on polyester fabric. Scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and other analytical skills were used to characterize the influence of plasma treatment on surface morphology and hydrophilicity of the polyester fabric. The relationship between anti-bleeding performance and the property of holding inks of polyester fabric was also investigated.

2. Experimental

2.1. Materials

Chemically untreated white polyester plain weave fabric (100%) of 62 g/m² and cyan pigment-based ink (Nanocolorants and Digital Printing R&D Centre of Jiangnan University) were used in this study.

2.2. Plasma treatments

ST/RI pulse plasma surface modification equipment (Shanghai Textile Research Institute, China) was used in this study. The experimental facility (shown in Fig. 1) has an active exposure area of approximately 25 cm × 25 cm between two copper electrodes. Each copper electrode is embedded in a glass dielectric barrier with a thickness of 6 mm. The device is powered by a range of 0–500 W power supply operating in the frequency of 1 kHz.

As schematically shown in this figure, the sample was directly put into the reactor. The plasma system was first evacuated and then filled with the gas up to the atmospheric pressure. The entire dielectric barrier discharge was performed at two different gas compositions, namely pure air and air + 50% argon (purity 99.99%). The samples were treated at a total power of 300 W, dielectrics space 3 mm for 180 s. After plasma treatment had been finished, samples were then removed and carefully handled in order to avoid possible surface contamination on the fabrics.

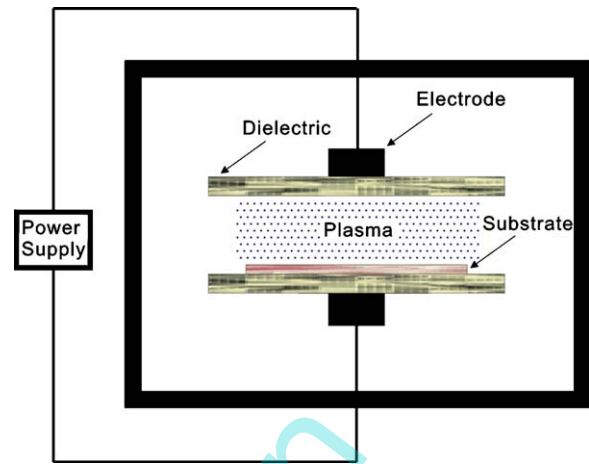


Fig. 1. Schematic view of experimental setup.

2.3. Inkjet printing procedure

Fabrics were inkjet printed by Mimaki JV4-180 digital printer (Mimaki Company of Japan) with usual ink supply and subsequently baked at 120 °C for 3 min with Minni thermo-350 baker (Roaches Company of England).

2.4. Surface characterization

2.4.1. AFM observation

Atomic force microscopy (AFM) provides new tools for examining nanostructures [13]. The AFM used in this study was CSPM4000 produced by Benyuan Company. The vertical resolution of the machine is 0.1 nm, while the horizontal resolution is 0.2 nm. The scanning mode used was contact mode in this study, and the scanning range was set at a size of 5.0 μm × 5.0 μm. All samples were scanned at room temperature in atmosphere.

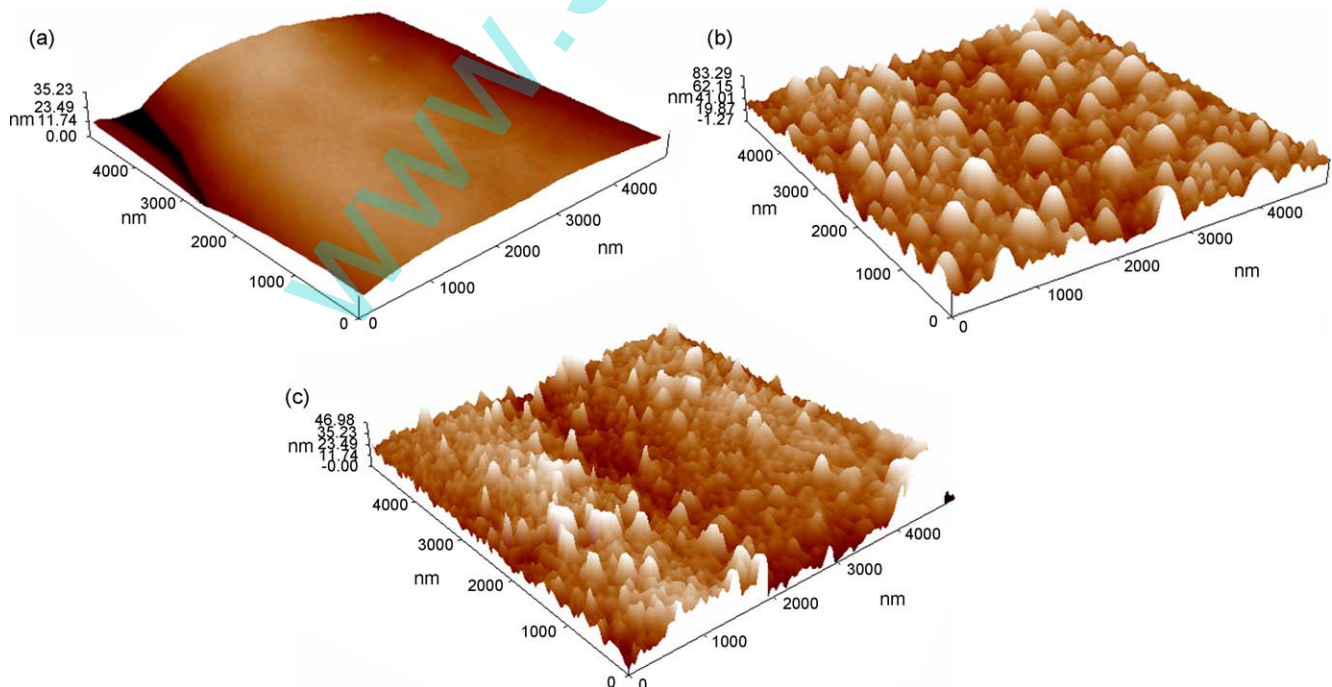


Fig. 2. AFM images of untreated (a), air plasma treated (b) and air + 50%Ar plasma treated (c) fibers.

2.4.2. X-ray photoelectron spectroscopy

Surface chemical composition of polyester fabric was analyzed on a RBD upgraded PHI-5000C ESCA system (PerkinElmer) with Mg K α radiation ($h\nu = 1253.6$ eV). X-ray anode was run at 250 W and the high voltage was kept at 14.0 kV with a detection angle at 54°. The sample was directly pressed to a self-supported disk (10 mm \times 10 mm) and mounted on a sample holder before transfer into the analyzer chamber. The spectra were normalized with respect to the C–C peak positioned at 284.6 eV. All measurements were performed shortly after plasma treatment.

2.4.3. Wettability analysis

The water absorption time was obtained using distilled water droplet until it was completely absorbed by the fabric. An average of at least six measurements was taken for each condition. The measurements were performed with DSA-100 drop shape analyzer (Krüss Co. Ltd., Germany) to evaluate the effects of plasma treatment on fabric wettability.

2.5. Anti-bleeding performance effect

A DZ3-video focus-exchanged microscope (Union Optical Co. Ltd of Japan) with zoom ratio of 14 and total magnification of 30–5880 (with 1/2 CCD and 19" monitor) was used to measure the

Table 1

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

Samples	Chemical composition		Atomic ratios
	C 1s (%)	O 1s (%)	O/C
Untreated	81.05	16.68	0.21
Air plasma treated	73.90	22.85	0.31
Air/Ar plasma treated	68.65	28.52	0.42

anti-bleeding performance of the treated and untreated inkjet printing fabrics at 75 multiple.

2.6. Color values of inkjet printed fabrics

X-Rite Premier 8400 color measurement system (X-Rite Company of America) was used to measure the K/S , L and C values of samples with illuminant D₆₅ and visual angle 10°.

2.7. Coloration of fibers by pigment

The fiber surface morphology was observed using a scanning electron microscopy (JSM-5610) which is the best known and most widely used tool for surface analysis. The polyester fabric

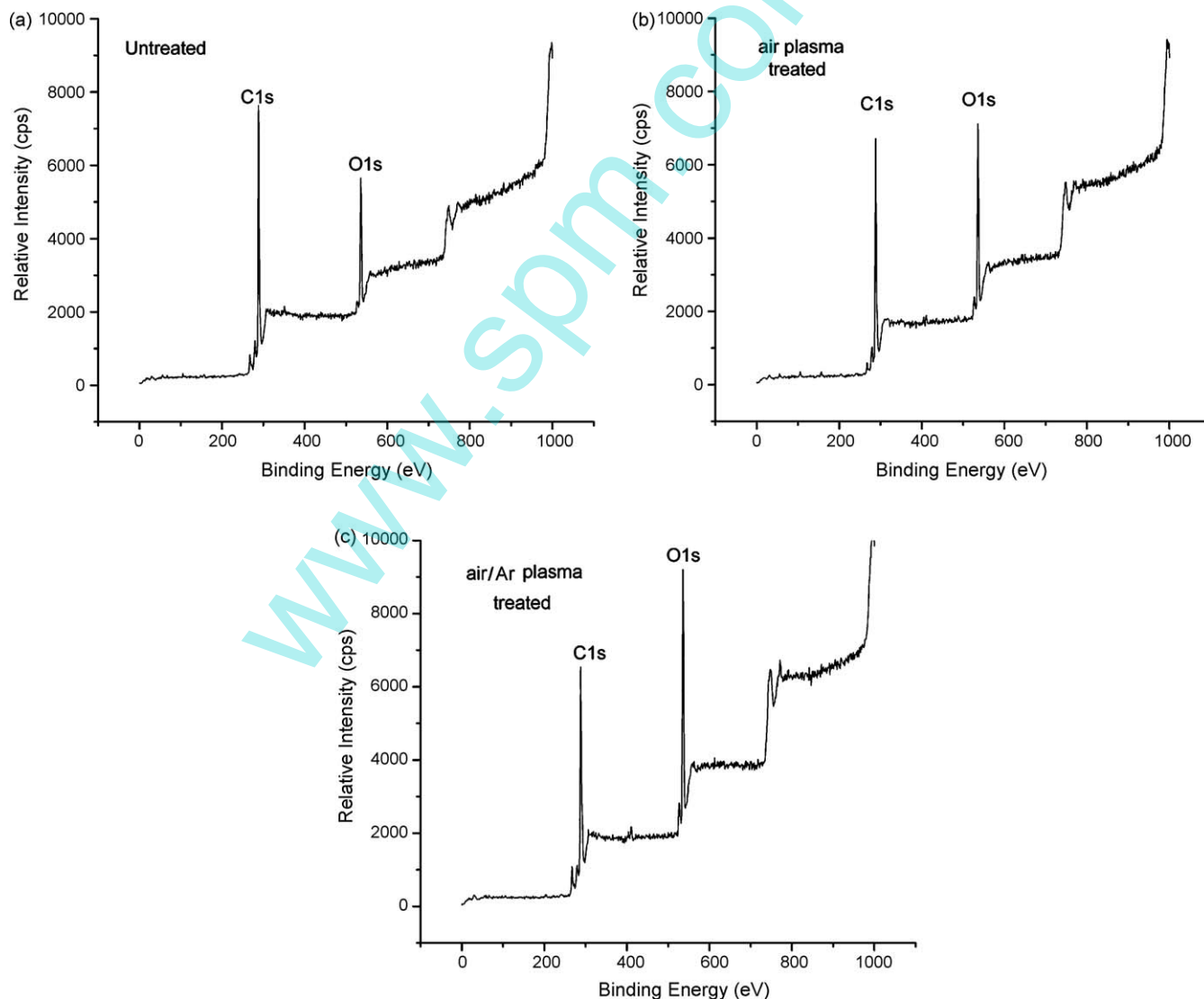


Fig. 3. XPS overall scans of untreated (a), air plasma treated (b) and air + 50%Ar plasma treated (c) polyester fabric.

specimens were inspected at 2400 magnification to examine the pigmentation on untreated and plasma treated fibers. All the samples were coated with gold before SEM testing, and all images were obtained at ambient conditions immediately after plasma treatment. Fastness to washing and rubbing were assessed according to ISO 105-C06:1997 and ISO 105-X12:1993.

3. Results and discussion

3.1. Surface morphology

The AFM images of $5.0 \mu\text{m} \times 5.0 \mu\text{m}$ in Fig. 2 reveal the surface structures of the polyester fibers. The series of images show the change in surface morphology of the polyester fibers before and after plasma treatments. As can be seen in Fig. 2(a), the untreated fiber has a relatively smooth surface. However, after atmospheric pressure air and air/Ar plasma treatment, the fibril structure is not visible any more and an increased number of pit-like structures are formed on the fiber surfaces as shown in Fig. 2(b) and (c). This is the result from the etching effect of the plasma treatments. 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]. It is interesting to note that the roughness of the sample treated with pure air plasma is more prominent and symmetrical than air + 50%Ar plasma treated by compared Fig. 2(b) with (c). As is well known, the argon plasma has only a slight effect on the morphology of the polyester fiber [15]. The mix of argon weakened the etching effect of plasma.

3.2. Surface chemistry

The surface chemical composition and XPS spectra of untreated and plasma treated polyester fabric surface are shown in Table 1 and Fig. 3. Fig. 3(a), (b) and (c) are the overall scans of untreated, air and air + 50%Ar plasma treated polyester surface, respectively. It can be observed that the oxygen peaks intensified for both treated samples. The surface oxygen concentration of the air/Ar plasma

treated sample was most pronounced among the three groups. The O/C ratio of air/Ar treated sample significantly increased to 0.1 and 0.2 respectively compared with the air plasma treated and untreated sample. These results suggest that the oxygen-containing polar groups were introduced to the polyester surface when treated by plasma.

In order to investigate what chemical functional groups were incorporated into the surface of polymer, deconvolution analysis of C 1s peaks was performed. The C 1s XPS spectra of original and treated polyester fabrics are presented in Fig. 4. As well documented in literatures, the spectrum of the original polyester contains three peaks at 284.60 eV, 286.10 eV, and 288.75 eV, which may be respectively assigned to C–C/C–H, C–O (and/or C–OH) and O=C–O (and/or COOH) [16–19]. The scan of the air and air/Ar plasma treated surface contains extra C=O peak at 288.10 eV, comparing with that of the untreated surface.

According to the content variation of each chemical component shown in Table 2, the C–C component significantly decreased after both air and air/Ar plasma treatment, and at the same time, most of the oxygen-containing polar groups such as C=O, C–OH and COOH increased on the surface of treated polyester fibers. This result indicates that some of the C–C bonds in polyester fiber surface may be broken by the plasma treatment, and then the broken C–C bonds will recombine with oxygen atoms produced by plasma to form the oxygen-containing polar groups as reported in literatures [20,21].

It is known that the argon plasma does not allow incorporation of new chemical species into the polymer chains [16]. Despite this, air/Ar plasma treated surface was found to get much more oxygen-containing polar groups than the surface treated by air plasma. This phenomenon can be explained as that argon has lower breakdown potential than air. The blending of it can make the discharging more symmetrical, which can lead to ampler plasma ionization [22].

3.3. Wettability analysis

Fig. 5 shows the snap shots of the distilled water droplets spreading on untreated and air/Ar plasma treated polyester fabrics.

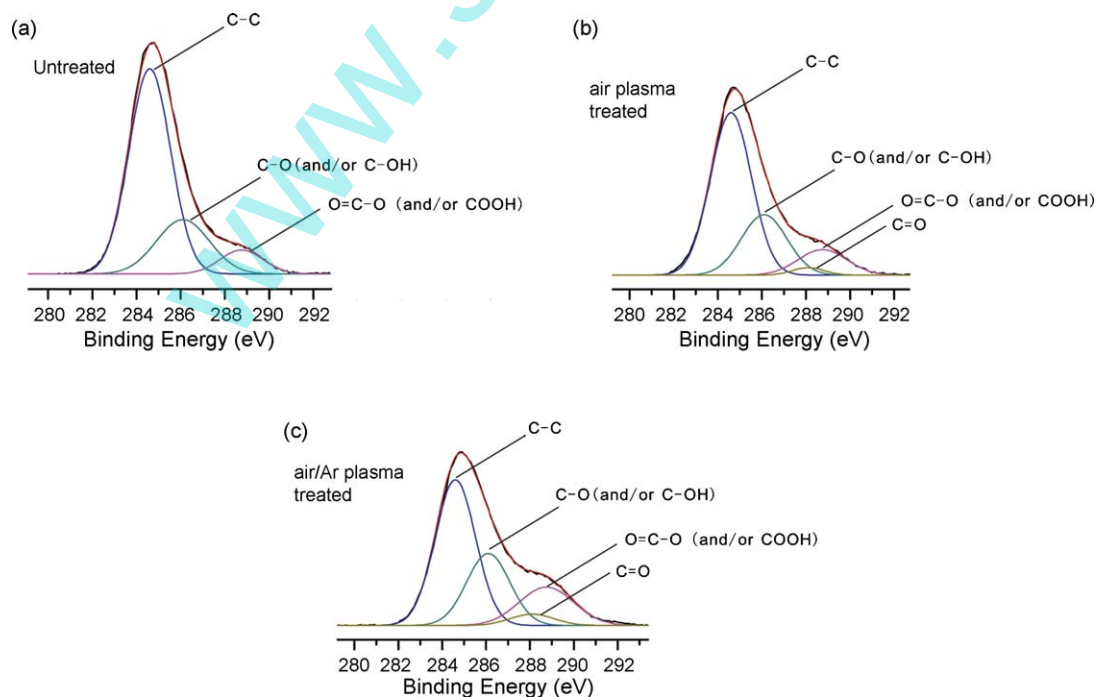


Fig. 4. High-resolution XPS analysis of C 1s peaks of untreated (a), air plasma treated (b) and air + 50%Ar plasma treated (c) polyester fibers.

Table 2
Percent peak area of XPS C 1s core level spectra of polyester fabrics.

Binding energy (eV)	Untreated (%)	Air plasma treated (%)	Air/Ar plasma treated (%)	Possible functional groups
284.6	68.7	61.1	50.9	C–C/C–H
286.1	23.1	25.3	26.8	C–O (and/or C–OH)
288.1	0	2.2	4.3	C=O
288.75	8.2	11.4	18.0	O=C–O (and/or COOH)

As can be seen from Fig. 5(a), it was difficult for the droplet to be absorbed on untreated polyester substrate even after 90 s. Nevertheless, Fig. 5(b)–(f) shows that it only needs 457 ms for air/Ar plasma treated (and 503 ms for air plasma treated) fabrics to absorb the droplet. The effect can be attributed to that plasma treatment not only brought etching effect to the surface of polyester fiber, but also introduced polar groups (–OH, –COOH, –C=O, –NH₂) into the surface layer [23,24]. Both of the foregoing actions could enhance the hydrophilicity of the polyester fabrics.

3.4. Anti-bleeding performance

Fig. 6 presents the anti-bleeding performance of untreated and plasma treated polyester fabrics. As shown in Fig. 6(a) and (c), the bleeding phenomenon of untreated polyester fabric was severe along the weft and warp edge of inkjet printed fabrics. The anti-bleeding performance of the treated sample was dramatically

improved with excellent sharpness after air/Ar plasma treatment as seen in Fig. 6(b) and (d). It was due to the hydrophilic improvement of the fabric, consequently expediting the absorption speed and increasing the holding ability of inks.

3.5. The effects of plasma on color

The color measurement results of treated and untreated fabrics are listed in Table 3. It shows that *K/S* values of inkjet printing samples increased after plasma treatment and *L* value decreased a little and *C* value increased. That means the chroma and saturation of the sample increased and the luminance decreased. On one hand, the etching and the polar groups on the surface of the fabrics induced by plasma improved the anti-bleeding performance of the polyester fabric, which increased the amount of ink colorant stayed on per area of the fabric. On the other hand, the etching action of plasma increased the surface roughness of fabrics [12]. It also

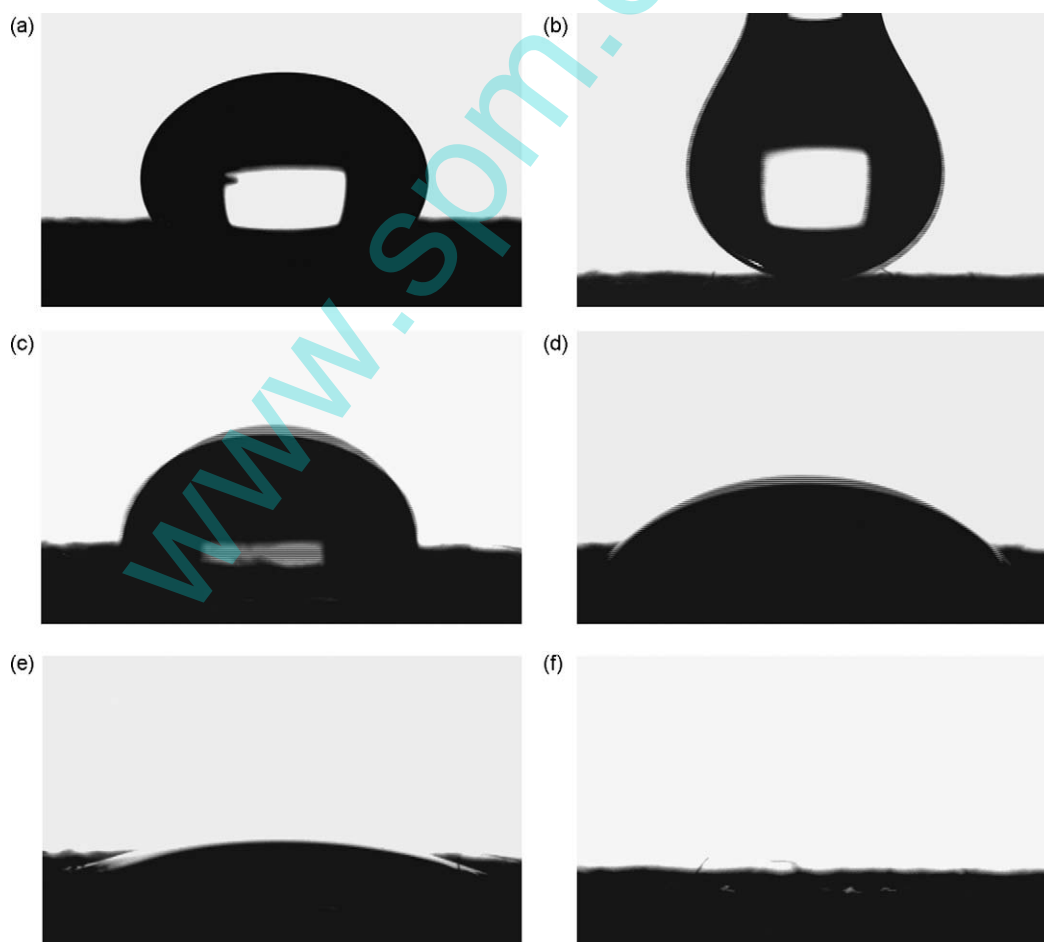


Fig. 5. Views of drop shapes: 90 s after being dropped on untreated polyester substrate (a), 0 s (b), 117 ms (c), 217 ms (d), 317 ms (e) and 457 ms (f) after being dropped on air/Ar plasma treated substrates.

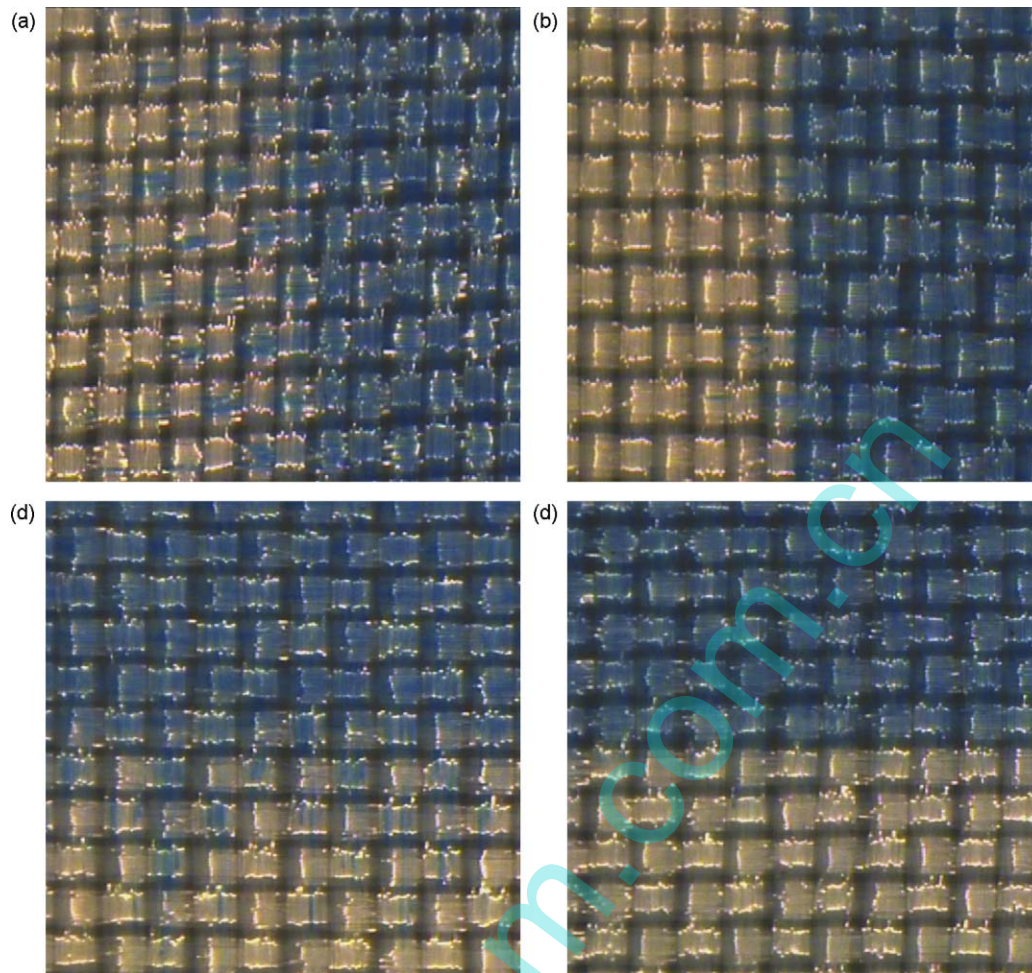


Fig. 6. Images of polyester fabrics which were taken by DZ3-video focus-exchanged microscope at 75 multiple after inkjet printing with pigment inks. (a) Weft untreated; (b) weft air/Ar plasma treated; (c) warp untreated; (d) warp air plasma treated.

contributed to the increase of K/S values of inkjet printed specimens by decreasing the fraction of light reflected from treated rough surfaces compared with untreated smooth surfaces. It is interesting that the sample treated by air plasma has better color performance than air/Ar plasma treated sample by comparing the K/S value. Even though air plasma brought more sufficient etching effect, the more oxygen-containing groups introduced by air/Ar plasma played more important role in improving the inkjet printing effect.

3.6. Pigmentation analysis

The SEM images were observed to comprehend the pigmentation on fibers as shown in Fig. 7 with a magnification of 2400 times. As can be seen in Fig. 7(a), because of the smooth surface of untreated polyester fiber, the pigment particles were difficult to be fixated on it and spread freely on the fiber surface even into the

gaps between two fibers. This result could explain the bleeding phenomenon observed by video focus-exchanged microscope. Forming a striking contrast to that, the pigment particles were evenly distributed on the surface of polyester fibers as shown in Fig. 7(b). This indicated that the rough surface of plasma treated fibers could provide more capacities for the fabric to capture inks and also facilitate the penetration of colorant particles into the polyester fabric [25–27].

3.7. Color fastness test

Fastness to washing (staining and alteration) and rubbing (dry and wet) of printed polyester fabrics are given in Table 4. The results show that there was almost no difference on both fastnesses between untreated and air/Ar plasma treated samples. This result indicates that plasma treatment has no effect on the color fastness of inkjet printed polyester fabrics.

Table 3
Color measurement results of untreated and plasma treated fabrics.

Samples	K/S	L	C
Untreated	2.57	59.84	36.84
Air plasma treated	3.58	58.46	39.06
Air/Ar plasma treated	3.82	58.03	39.43

Table 4
Color fastness measurement results of treated and untreated fabrics.

Sample	Rubbing fastness		Washing fastness	
	Dry	Wet	Staining	Alteration
Untreated	3	2–3	4–5	4
Air/Ar plasma treated	3	2–3	4–5	4

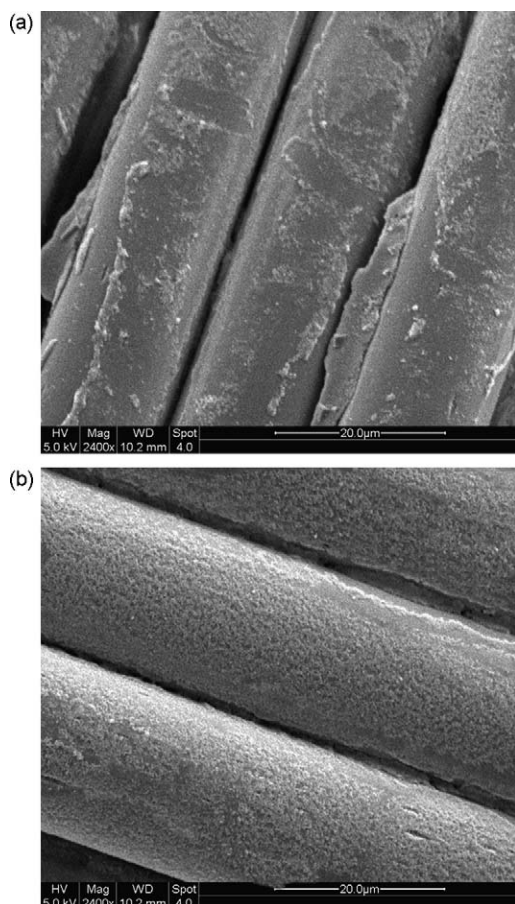


Fig. 7. SEM images of the pigmentation on untreated (a) and air/Ar plasma treated (b) fibers.

4. Conclusion

Atmospheric pressure plasma has been found to be very effective in the treatment of polyester fabric for pigment inkjet printing. The results show that plasma treated polyester fabrics have much better anti-bleeding performance than untreated samples. Images of inkjet printed on polyester fabrics treated with plasma exhibit deeper and vivid color compared with untreated fabrics. Although more remarkable and symmetrical grooves were generated on the surfaces of polyester fiber treated by air plasma as revealed by AFM images, XPS indicated that air + 50%Ar plasma introduced more oxygen-containing groups

which led to rather better wettability of polyester fabric than air plasma treated. Overall, the air/Ar plasma treated sample has better inkjet printing performance than pure air plasma treated. Under these circumstances, there is a good possibility that the chemical modification of atmospheric pressure plasma plays a relatively more important role in enhancing the inkjet printing effects of polyester fabric.

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