Inkjet Printing Effects of Pigment Inks on Silk Fabrics Surface-Modified with O_2 Plasma

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ABSTRACT: Without any preprocessing, silk fabric has lower ability to hold on water due to the smooth morphology of silk fibers. Therefore, patterns directly printed with pigment inks have poor color yields and easily bleed. Plasma surface-treatment of silk fabric was carried out in an oxygen atmosphere under different experimental conditions. The samples were printed with magenta pigment ink after treatment. The results showed that the optimum treatment conditions we obtained were exposure time of 10 min at a working pressure of 50 Pa and a working power around 80 W. At such conditions, surface-modified silk fabrics could obtain the effects of features with enhanced color yields and excellent pattern sharpness. Atomic force microscope images indicated that low-temperature oxygen plasma initiated modifications to the surface of silk fiber with more grooves. Dynamic contact angle analysis showed that the hydrophilicity of silk fiber was remarkably improved after pretreatment with plasma. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 2949–2955, 2008

Key words: plasma; silk fabric; surface modification; inkjet printing; color performance

INTRODUCTION

Fabric inkjet printing has demonstrated super properties over the customary textile printing methods (e.g., roller printing, screen printing, transfer printing, etc.) because of excellent pattern quality, considerably little pollution, and especially rapid response to the frequent shift of cloth fashion. Inks for fabric printing are usually classified into two categories of dye and pigment inks. Pigment inks show more environmental advantages and have shorter processes than dye inks because the final products printed can be achieved by simple heat curing of the printed fabrics without steaming and washing.[1–5] However, the sharpness of the inkjet printing images is a main factor in controlling quality of the final products. To improve the inkjet printing sharpness of fabrics, preprocessing of fabric must be done before printing. Traditional preprocessing was sizing process with thickener, such as sodium alginate to modify the surface of fabrics. This process is very long and complicated, with huge energy and water consumption. At the same time, toxic substance and waste water would be produced during process. In recent years, people have paid great attention to environmental deterioration and ecology balance, especially to the problem of water shortage and environmental pollution.[6–12]

The plasma technique, as one of the environmental friendly processes, has been widely used to modify the surface properties of polymers and textile materials over the past decade. 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.[13]

About the research on surface modification by low-temperature plasma, some work has already been done. Nowadays, researches of using it to modify the surface properties of textile materials are focusing on these aspects: wool antifelting, textile preprocessing, synthetic fiber improving dyeing property, and textile functional finishing.[14–20]

Kan et al. used low-temperature nitrogen plasma to improve the antifelting performance of wool fabrics.[14,15] Bae et al. published some of the studies directed at employing low-temperature oxygen plasma to desize PVA on cotton fabric.[16] Wen et al. used antistatic reagent and oxygen plasma to modify PET fabric to obtain durable antistatic effect.[17] Raffaele-Addamo studied the influences of low-temperature nitrogen and oxygen plasma on the PET fabric and found that plasma treatment reduced the dyeing time, increased the adsorption of dyestuff, and also increased the K/S values of dyed PET specimens by

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decreasing the fraction of light reflected from treated surfaces.[18]

Chaivan et al. modified the surface of silk with SF_6 low-temperature plasma to make the surface highly hydrophobic.[19] Tsafack and Levalois-Grützmacher introduced acrylate monomer containing phosphorus into cotton fabric surface, which initiated by low-temperature argon plasma treatment to make the fabric with flame-retardant property.[20]

About plasma surface modification performed under atmospheric pressure, several research works have been done. Wakida et al. treated wool and poly (ethylene terephthalate) fabrics with low-temperature plasma of helium/argon under atmospheric pressure to improve the samples' wettability.[21] Shenton et al. made comparisons of treating effect between vacuum and atmospheric plasma.[22] McCord et al. modified nylon and polypropylene fabrics with atmospheric pressure plasmas.[23] Cai et al. used air/He and air/O_2 atmospheric plasma to desize PVA on cotton.[24] Hwang et al. investigated the effect of plasma treatment on surface characteristics of polyethylene terephthalate films using helium and oxygenated-helium atmospheric plasmas.[25] Matthews et al. made some investigation into etching mechanism of PET films and PVA desizing mechanism treated in He and O_2/He atmospheric plasmas.[26,27] 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.[28] However, there are few literatures about the influence of treatment with low-temperature plasma on inkjet printing of fabrics.

In this article, we presented a study of the effects of low-temperature oxygen plasma treatment for pigment inkjet printing on silk fabric. Samples were analyzed using atomic force microscopy (AFM) and dynamic contact angle (DCA) to determine the influence of plasma treatment on surface morphology and hydrophilicity of the silk fabric. The relationship of antibleeding performance of silk fabric with its hydrophilicity and the property of holding water was also investigated.

EXPERIMENTAL

Raw materials

Silk fabric (47.8g/m^2, Wu-jiang silk mill of China) and light magenta pigment-based ink (Nanocolorants and Digital printing research center of Jiangnan University).

Plasma treatment

HD-1A capacitive coupled radio frequency glow discharge plasma facility (Shi-tai Plasma Company, China) was used in this study. It has an active exposure area of ~ 20 × 38 cm^2 between two copper electrodes with 23-cm gap separation. Each copper electrode is embedded in a glass dielectric barrier. The device is powered by a range between 0 and 500 W power supply operating in the frequency of 13.56 MHz. The input RF power is full forward and nil reflected. The temperature remains at room temperature for the entire glow-discharge period.

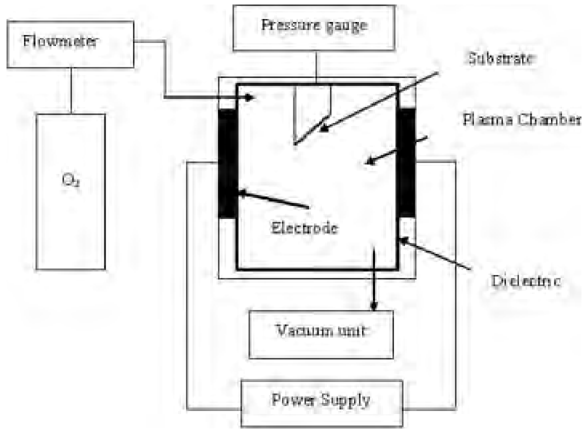

Figure 1 Schematic view of experimental setup.

The experimental setup was schematically shown in Figure 1. The sample (24 cm × 7 cm) was suspended in the middle of plasma chamber, then vacuum pump was set to 10 Pa. Pure oxygen with flow rate set at 0.1 L/min was introduced into the chamber for gas washing and lasted 30 s. Gas flow rate was regulated after gas washing until the treatment pressure reached the preset stable value, then the glow discharge was initiated, and continued for a period of time. After plasma treatment had reached the predetermined time, power was turned off. The vacuum chamber was vented, samples were then removed, and handled carefully to avoid possible surface contamination to the fabrics.

Inkjet printing process

Plasma-treated fabric → Inkjet Printing → Baking (150°C × 3 min)

Measurements

Surface morphology

Surface morphology of the treated and untreated samples was studied by using a CSMP4000 atom force microscope (Benyuan Company of Chinese Academy of Sciences). It uses a probe that has a nanosize tip mounted on a flexible cantilever. The tip is scanned slowly across the surface of a specimen. The force between the atoms on the surface of the scanned material and those on the scanning tip cause the tip to deflect. This deflection can be recorded by using a laser focused on the top of the cantilever and reflected onto photodetectors. The photodetector signals are used to map the surface characteristics of specimens with resolutions down to the nanoscales. Atomic force microscopy provides high resolution images of surfaces even if they are nonconducting. In this study, scanning is carried out in contact mode, scanning range is set at a size of 1.0 μm × 1.0 μm and scanning frequency is 1.5 Hz. All images are obtained at ambient conditions immediately after plasma treatment.

Dynamic contact angles

The wettability of samples is characterized by CDCD-100F dynamic contact angle measurement equipment (Camtel, England). The dynamic testing based on the Wilhelmy principle[29] that a solid is dipped into a liquid, the liquid will ascend (hydrophilic) or descend (hydrophobic) along the vertical side of the solid. The Wilhelm method measures the pull force or the push force, and the wetting force to measure contact angles. If the dimensions of a sample are $w \times t$ (width × thickness) and it is submerged to a height h, then the forces (F) acting on the sample can be expressed as:

$$F = \text{Weight} - \text{Upthrust} + \text{Interfacial tension} = (\rho_p lwt)g - (\rho_L hwt) + 2(wt)\sigma\cos\theta \quad (1)$$

where ρ_p is the density of sample, ρ_L is the density of liquid used, and l is the length of the sample.

Before making any measurements, the balance is tared (zeroed) which eliminates the weight term. So the equation can be rewritten as:

$$F = -(\rho_L hwt) + 2(wt)\sigma\cos\theta \quad (2)$$

Extrapolation to zero depth eliminates the buoyancy effect (Upthrust, Fb), that is using forces at zero immersion to calculate advancing and receding angles. The relationship between F and θ becomes:

$$F = 2(wt)\sigma\cos\theta \quad (3)$$

The measurements of this study are performed at room temperature and 65% relative humidity with distillate water immediately after plasma treatment. Measurement velocity is 0.3 mm/s.

Antibleeding performance

DZ3-video focus-exchanged microscope (Union Optical, Japan) zoom ratio of 14, total magnification of 30× to 5880× (with 1/2 CCD and 19 in. monitor) was used to measure the antibleeding performance of the treated and untreated inkjet printing fabrics at 75×.

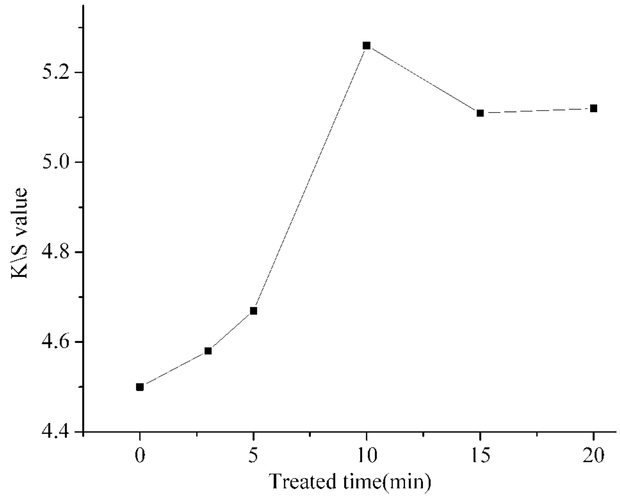

Figure 2 K/S values of silk fabrics treated by O_2 plasma for various time. The samples were treated at a pressure 50 Pa and power 80 W.

Color

X-Rite Premier 8400 (http://www.xrite.com/documents/literature/en/L10-191_Benchtop_en.pdf) computer color measurement system was used to measure the K/S, L, and C values, which was produced by X-Rite company of America. Illuminant was D_{65} and visual angle was 10°.

RESULTS AND DISCUSSIONS

The effects of treatment time on *K/S* values of inkjet printing

To study the influence of treating time, plasma treatments were carried out at 3, 5, 10,15, and 20 min durations with gas pressure and working power fixed at 50 Pa, 80 W, respectively. The results were summarized in Figure 2.

Figure 2 shows that K/S value had been increased with an increase of plasma exposure time. This could be attributed to the increasing number of plasma created polar groups and roughness on the surface, due to etching and other chemical changes of the surface.[10] It was interesting that when the fabric was treated for more than 10 min, the K/S value remained unchanged. It is generally agreed that a large number of active particles will be generated during plasma treatment, such as electrons, ions, free radicals, photons, excited atom/molecules, but the high-speed electron was really contributing.[30] At fixed input power, the dissociative reaction rate increased and led to further increasing of high-speed electron before the exposure time reached 10 min, and may be the electron number would not change any more when treating time exceeded 10 min which led to saturation of plasma effect on surface of silk fabric.

The effects of power on *K/S* values

By keeping pressure at 50 Pa and treatment time at 10 min, several power conditions (50, 60, 70, 80, and 90 W) were used to find out the effect of input electrical power to the plasma. The results were shown in Figure 3. It showed that *K/S* value increased with an increase of the input power to the plasma. Higher input power increased the number of high-speed electrons in the plasma, and improved the plasma treatment effect,[31] which led to the increased *K/S* value of the fabrics. The present work aimed to improve the antibleeding performance of silk fabric. On the basis of the above purpose, we found that when the fabric was treated with 80 W, it could satisfy the antibleeding performance of inkjet printing. For energy saving and practical need, 80 W was the optimum treatment power.

The effects of working pressure on *K/S* values

The relationship between pressure and *K/S* value was studied under constant power (80 W) and time (10 min), and the results were shown in Figure 4. *K/S* value reached to its maximum value when working pressure was set at 50 Pa. It could be explained by the fact that the number of active particle was very low at low working pressure, and increasing the pressure increased the plasma effect. However, the total energy of plasma was constant at fixed input power, and the mean energy of every active particle was reduced when pressure was very high, which led to the shrinkage of the electron mean free path. Electrons could not accumulate enough energy to dissociate when collided with each other. The amount of real dissociative electron decreased and caused the decreasing of plasma effect.[30] From Figures 2–4, it would be known that the optimum modifications to silk fabrics were the plasma treatment at 80 W and 50 Pa for 10 min.

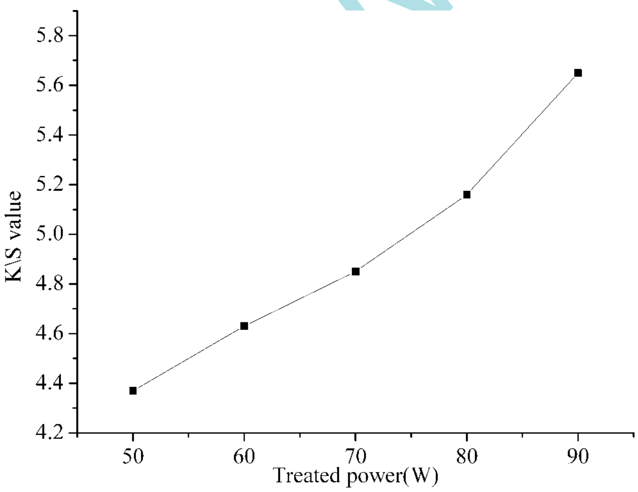

Figure 3 *K/S* values of silk fabrics treated by O_2 plasma for various powers. The samples were treated at a pressure 50 Pa for 10 min.

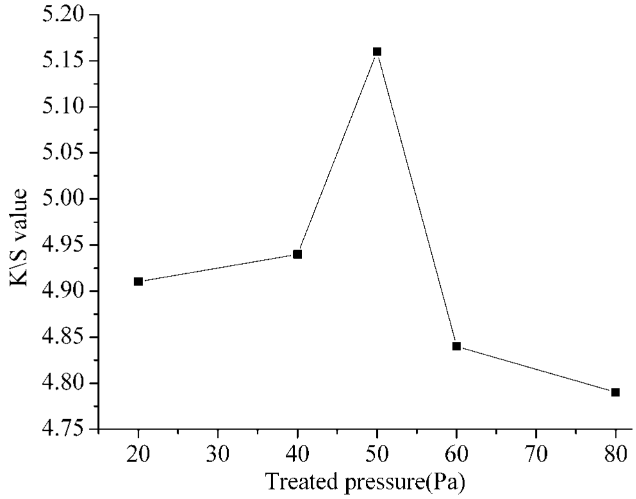

Figure 4 *K/S* values of silk fabrics treated by O_2 plasma for various pressure. The samples were treated at a power 80 W for 10 min.

AFM analysis of surface morphology

Figure 5 displayed some of the AFM images obtained in a systematic investigation on the morphological change of different treated and untreated silk fibers. As shown in Figure 5(a), the original surface of untreated silk fiber was characterized by the presence of smooth pattern, and only little protrusion appeared, which was due to the own property of natural fibers. Figure 5(b,c,d) pointed out that oxygen plasma etched the surface and thus one had to expect grooving of silk fiber after plasma treatment. However, it was interesting that there was almost no distinct difference to fiber's surface morphology if treating time exceeded 10 min, which suggested that saturation of etching effect had reached. It was generally agreed that when natural and synthetic fibers were treated with low-temperature oxygen plasma, the following reaction may happen on the surface of fiber.[32]

$$RH + O^{\bullet} \rightarrow R_1H + R_2O^{\bullet} \text{ or } RH + O^{\bullet} \rightarrow R^{\bullet} + OH^{\bullet}$$
$$R^{\bullet} + O^{\bullet} \rightarrow RO^{\bullet}$$
$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet}$$
$$ROO^{\bullet} + R_1H \rightarrow ROOH + R_1^{\bullet}$$
$$ROOH \rightarrow RO^{\bullet} + OH^{\bullet}$$

As the reaction continues, the physical etching effects of oxygen plasma would eventually lead to the

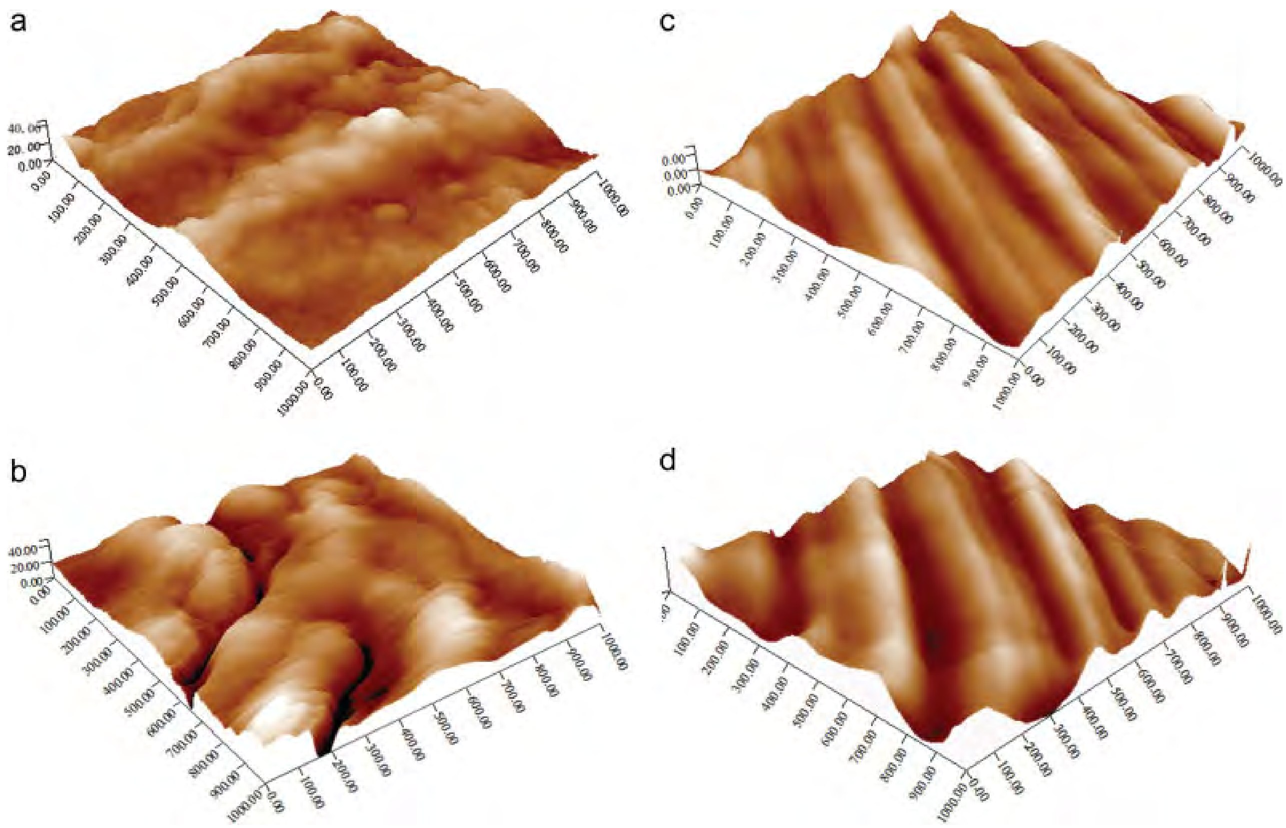

Figure 5 Three-dimensional views of contact mode AFM images of silk fiber surface: (a) untreated fiber surface, (b) 5-min treated surface, (c) 10-min treated surface, (d) 15-min treated surface. The samples were treated at a pressure 50 Pa and power 80 W. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

increasing of the surface roughness of fibers. This is what should have been argued from the beginning, etching is eminent and thus analysis should be based on the fact that oxygen plasma etches the surface, hence, K/S values should be related to this effect.

Wettability analysis of treated fibers

The wettability measurement results were depicted in Figure 6. On the basis of this graph, it could be observed that all samples treated with plasma had a substantial improvement in their wettability when compared with the untreated one. Both advanced contact angle and retrograde contact angle were decreased after treatment for 1 min. The advanced contact angle was ulteriorly decreased with an increase of treated time. This suggested that the hydrophilicity of the silk fiber had been enhanced remarkably. The effect must be attributed to that plasma treatment not only brought etching effects to the surface of silk fiber, but also introduced polar groups (—OH, —COOH, —C═O, —NH_2) into the surface layer.[33,34] Both of the foregoing action could improve the hydrophilicity of the silk fiber.

Antibleeding performance effect

Figure 7 shows the antibleeding performance of untreated and treated silk fabrics. As shown in Figure 7(a), the bleeding performance of untreated silk fabric was severe along the edge of inkjet printing. The antibleeding performance of the treated sample was dramatically improved with excellent sharpness after plasma treatment. It is due to the etching and

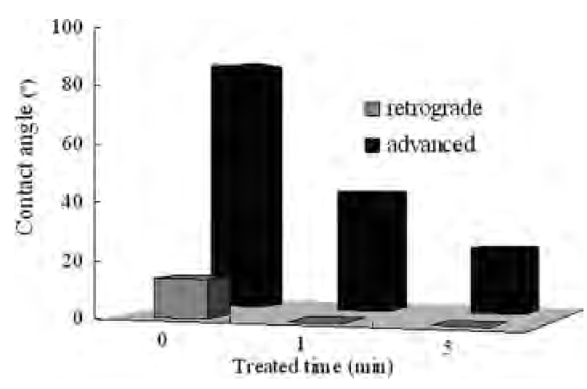

Figure 6 Dynamic contact angle of treated and untreated samples. The samples were treated at a pressure 50 Pa and power 80 W.

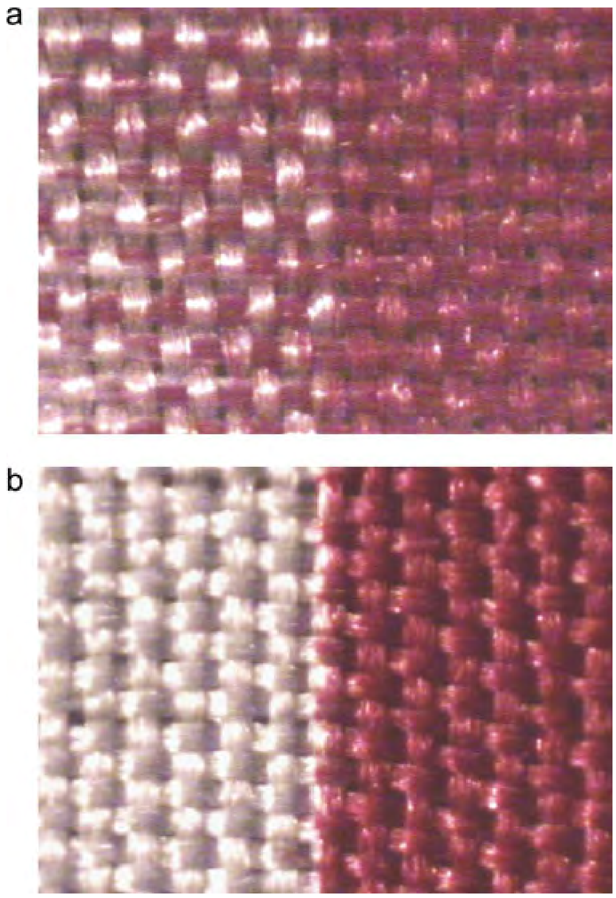

Figure 7 Antibleeding images of silk fabric which were taken after inkjet printing by DZ3-video focus-exchanged microscope at ×75: (a) untreated, (b) treated. The sample was treated at a pressure 50 Pa and power 80 W for 10 min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the polar groups introduced onto the surface layer of the fabric which improved the hydropilicity of the fabric, consequently expedited the absorption speed of the ink. In addition, by studying the AFM image of the fiber, we found that plasma treatment produced more grooves on the surface of the fiber. These grooves had ability of holding more inks on the surface of the fabric. The aforementioned function led to excellent sharpness of inkjet printing.

The effects of oxygen plasma on color

The color measurement results of treated and untreated fabrics were listed in Table I. It showed that *K/S* values increased after plasma treatment, L value decreased a little and C value increased. On one hand, the etching and the polar groups on the surface of the fabrics induced by plasma improved the antibleeding performance of the silk 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. It also 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.

TABLE I
Color Measurement Results of Treated and Untreated Fabrics

Sample	*K/S*	*L*	*C*
Untreated	4.50	50.589	47.004
Treated	5.16	49.895	49.654

The sample was treated at a pressure 50 Pa and power of 80 W for 10 min.

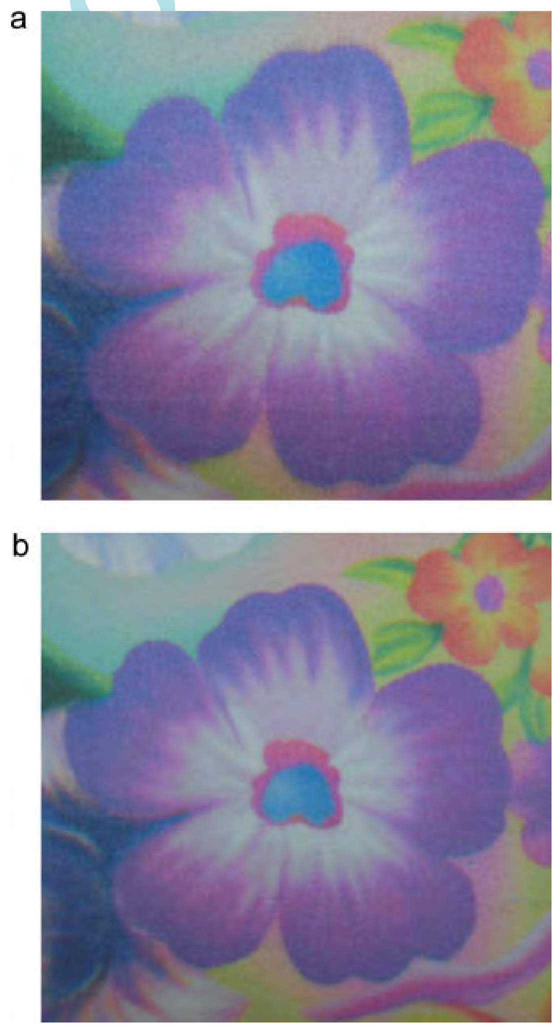

Figure 8 Real inkjet printing images of silk fabrics: (a) untreated, (b) Treated. The sample was treated at a pressure 50 Pa and power 80 W for 10 min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Real inkjet printed images

Figure 8 showed the real inkjet printing images of untreated and treated silk fabrics. From the images, we saw that the treated sample had excellent sharpness along the edge of inkjet printing while the untreated one was degraded. In comparison with the untreated fabric, the color of the treated sample turned deeper and vivider.

It also should be pointed out that some hydroxyl group can be introduced onto fabrics' surface following oxygen plasma treatment. The pigment ink that we used is composed of several ingredients, such as pigment particle, dispersant, polylols, and deionized water. The dispersant is adsorbed onto the surface of pigment particle, which contains some carboxyl groups, and these carboxyl groups can interact with the hydroxy groups through hydrogen bonding. This effect also contributes to the deeper and vivider color performance.

CONCLUSIONS

This work indicated that the sharpness improvement of pigment inkjet printing on silk fabric was achieved by low-temperature O_2 plasma. The results showed that plasma-treated silk fabrics had much better antibleeding performance than untreated samples. Images of inkjet printed on silk fabrics treated with low-temperature oxygen plasma exhibited deeper and vivider color compared with untreated silk fabrics. The optimum treatment conditions obtained were exposure time of 10 min at a working pressure of 50 Pa and a working power of 80 W. As revealed by AFM images more grooves were induced on the surface of silk fiber by O_2 plasma treatment. DCA measurement results demonstrated that plasma treatment remarkably enhanced the hydrophilicity of silk fiber. Both of the above changes of silk fibers resulted in the improvement of antibleeding performance of silk fabrics. Therefore, low-temperature oxygen plasma offers an attractive prospect to the application of inkjet printing of fabrics with pigment inks.

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