Effect of surface treatment of silk fabrics with plasma on inkjet printing

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Abstract

Inkjet printing of silk fabrics usually uses acid and reactive dye inks. Silk fabrics should be pretreated with sizes before inkjet printing. After inkjet printing silk fabrics need steamed and washed with a large amount of water to remove unfixed dyes. It is not only a long process but also results in a large mount of waste water. Inkjet printing of silk fabrics with pigment inks seems simple and good but bleeding of the printed pattern occurs. This is related to the surface structure of silk fabrics. In order to improve the surface structure of silk fabrics low temperature plasma was used to treat silk fabrics in the atmosphere of oxygen. The surface structure of plasma treated silk fabrics was characterized by AFM (atom force microscopy). And the plasma treated fabrics were printed with a magenta pigment-based ink. The results show that silk fabrics treated with 80 watt power at 50 Pa pressure for 10min had higher color yield and excellent sharpness of pattern. AFM images indicated that plasma treatment produced more grooves on the surface of silk fibers than those untreated. Dynamic contact angle test showed that the hydrophilic property of silk fiber was improved after plasma treatment.

Introduction

Fabric inkjet printing has demonstrated super advantages over the customary textile printing methods (e.g., roller printing, screen printing, transfer printing, etc.), such as excellent pattern quality, environment friendly, and especially rapid response to the frequent shift of fabric fashion. Inks for fabric printing are usually classified into two categories as dye and pigment inks. Pigment inks show more environmental benefits and have shorter processes than dye inks because the final products printed can be achieved by simple heat curing without steaming and washing[1–5]. And more important is that pigment inks are suitable for inkjet printing on all kinds of fiber fabrics. However, the sharpness of the inkjet printing images on some kinds of fiber fabrics is a main factor in controlling quality of the final products. In order to improve the inkjet printing sharpness of images, pre-processing of fabric must be done before printing. Traditional pre-processing was sizing process with thickener, such as sodium alginate to modify the surface of fabric. 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 attentions to environmental deterioration and ecology balance, especially the problem of water shortage and environmental pollution[6-12].

The plasma technique, as one of environmental friendly process, has been widely used to modify the surface properties of polymers and textile materials over the past decade. Compared with traditional methods, plasma treatment have the following advantages: it only modifies the outmost thin layer of the fiber 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 textile ecological manufacturing[13].

About the research on surface modification by low temperature plasma, many works have already been done. Nowadays, researches of using it to modify the surface properties of textile materials are focusing on these aspects: wool anti-felting; textile pre-processing; synthetic fiber improving dyeing property; textile functional finishing[14-20].

Among plasma surface modification that performed under atmospheric pressure, there were also lots of research work have been done. T. Wakida treated wool and poly(ethylene terephthalate) fabrics with low temperature plasma of helium/argon under atmospheric pressure to improve fabric wettability[21]. M. J. Shenton et al made comparisons of treating effect between vacuum and atmospheric plasma[22]. M. G. McCord modified nylon and polypropylene fabrics with atmospheric pressure plasmas[23]. Z. Cai et al. used air/He and air/ O_2 atmospheric plasma to desize PVA on cotton[24]. Y. J. Hwang et al investigated the effect of plasma treatment on surface characteristics of polyethylene terephthalate films using helium and oxygenated-helium atmospheric plasmas[25]. S. R. 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]. S. M. 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 paper 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 anti-bleeding 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), Light magenta pigment-based ink (Nanocolorants and Digital Printing R&D Centre of Jiangnan University).

Plasma treatment

HD-1A capacitive coupled radio frequency glow discharge plasma facility (Changzhou Shi-tai Plasma Company of China) was used in this study. It has an active exposure area of approximately

20×38cm between two copper electrodes with 23cm gap separation. Each copper electrode is embedded in a glass dielectric barrier. The device is powered by a range between 0-500W power supply operating in the frequency of 13.56MHz. The input RF power is full forward and nil reflected. The temperature remains at room temperature for the entire glow-discharge period.

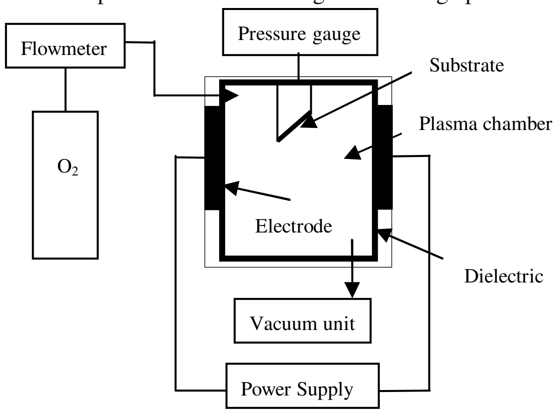


Figure 1. *Schematic view of experimental set-up*

The experimental setup was schematically shown in Figure 1. The sample (24×7cm) was suspended in the middle of plasma chamber, then vacuum pump 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 to the preset stable value, the glow discharge was initiated, and continued for a period of time. After plasma treatment had reached to the predetermined time, turned off power. The vacuum chamber was vented, samples were then removed and handled carefully in order to avoid possible surface contamination to the fabrics.

Inkjet printing process

Plasma treated fabrics → Inkjet Printing with pigment inks → Curing (150 °C×3min)

Measurements

Surface morphology

Surface morphology of the treated and untreated samples was analyzed by using a CSMP4000 atomic 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. AFM provides high resolution images of surfaces even if they are non-conducting. In this study, scanning is carried out in contact mode, scanning range is set at a size of 1.0μm×1.0μm and scanning frequency is 1.5Hz. 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 (Cammel Ltd Company of England). The dynamic testing based on the Wilhelmy principle[29]. When 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 or push force and the wetting force, then calculate contact angles.

Anti-bleeding performance

A DZ3-video focus-exchanged microscope (Union Optical CO.LTD of Japan) with zoom ratio of 14 and total magnification of 30 to 5880 (with 1/2 CCD and 19" monitor) was used to observe the anti-bleeding performance of the treated and untreated inkjet printing fabrics at 75 multiples.

Color

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 D_{65} and visual angle 10°.

Results and discussions

The effects of Treatment time on K/S values of inkjet printing

Table 1 shows the influence of plasma treating time on the K/S values of inkjet printed fabrics with a pressure and working power fixed at 50 Pa, 80 W, respectively.

Table 1 K/S values of silk fabrics treated by O_2 plasma for various time [a]

Time(min)	0	3	5	10	15	20
K/S value	4.50	4.58	4.67	5.16	5.11	5.12

[a] *The samples were treated at a pressure 50 Pa, a power 80 W.*

Table 1 shows that K/S value 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, particles, excited atom/molecules, but the high-speed electron was the really contributing particle[31]. At fixed input power the dissociative reaction rate increased and led to further increasing of high-speed electron before the exposure time reached to 10 min, and may be the electron number wouldn’t 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 90W) were used to find out the effect of input electrical power to the plasma. The results were listed in Table 2.

Table 2 K/S values of silk fabrics treated by O_2 plasma for various power [a]

Power(W)	50	60	70	80	90
K/S value	4.37	4.63	4.85	5.16	5.65

[a] *The samples were treated at a pressure 50 Pa for 10 min.*

It shows that K/S value increased with an increase of the input power to the plasma. Higher input power increased the number of high-speed electron in plasma, and would improve plasma treatment effect[30], which led to the increase K/S value of fabrics. The present work aimed to improve the anti-bleeding performance of silk fabric. Based on the above purpose, we found that when the fabric was treated with 80 W, it could satisfy the anti-bleeding 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

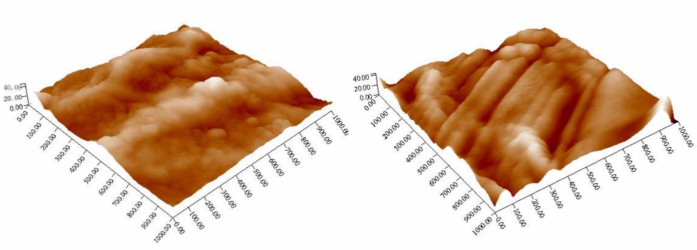
Table 3 K/S values of silk fabrics treated by O_2 plasma for various pressure [a]

Power(W)	50	60	70	80	90
K/S value	4.37	4.63	4.85	5.16	5.65

[a] The samples were treated at a power 80 W for 10 min.

The relationship between pressure and K/S value was studied under constant power (80 W) and time (10 min), and the results were showed in Table 3. 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 little at low working pressure, increasing pressure increased 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. Electron couldn't accumulate enough energy to dissociate when collided with each other. The amount of real dissociative electron decreased and caused the decreasing of plasma effect[31]. From Tables 1 to 3, it would be known that the optimum modifications to silk fabrics were the plasma treatment at 80 W and 50 Pa for 10 min.

AFM analysis of Surface morphology



(a) Untreated surface *(b) 5 min treated surface*

Figure 2. *3D views of contact mode AFM images of silk fiber surface [a]*

[a] The sample was treated at a pressure 50 Pa, power 80 W for 5 min.

Figure 2. displayed some of the AFM images obtained in a systematic investigation on the morphological change of untreated and treated silk fibers. As shown in Figure 2. (a), the original surface of untreated silk fiber was characterized by the presence of smooth pattern, and only little protrusion appeared, which due to the own property of natural fibers. Figure 2. (b) pointed out that oxygen plasma etched the surface and thus one had to expect grooving of silk fiber after plasma treatment. It was generally agreed that when natural and synthetic fibers were treated with low temperature oxygen plasma, the following reaction may happen on fiber surfaces[32].

$$RH + O\bullet \rightarrow R_1H + R_2O\bullet \text{ or } RH + O\bullet \rightarrow R\bullet + OH\bullet \quad (1)$$

$$R\bullet + O\bullet \rightarrow RO\bullet \quad (2)$$

$$R\bullet + O_2 \rightarrow ROO\bullet \quad (3)$$

$$ROO\bullet + R_1H \rightarrow ROOH + R_1\bullet \quad (4)$$

$$ROOH \rightarrow RO\bullet + OH\bullet \quad (5)$$

As the reaction continues, the physical etching effects of oxygen plasma would eventually lead to the 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, results of K/S value should be related to this effect.

Wettability analysis of treated fibers

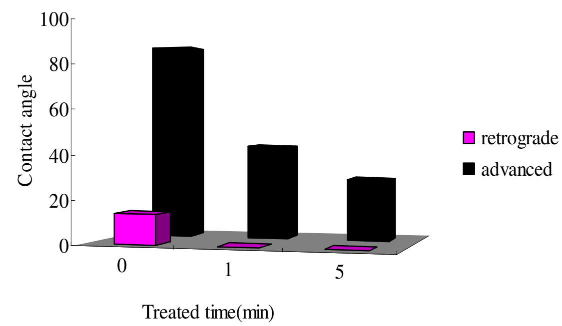
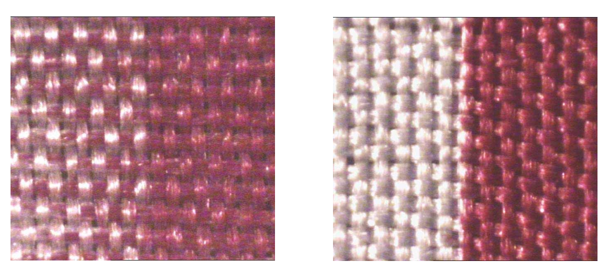


Figure 3. *dynamic contact angle of treated and untreated samples [a]*

[a] The sample was treated at a pressure 50 Pa, power 80 W.

The wettability measurement results were depicted in Figure 3. Based on 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 treated 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 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.

Anti-bleeding performance effect



(a) Untreated *(b) Treated*

Figure 4. *Anti-bleeding images of silk fabric which were taken after inkjet printing by DZ3-video focus-exchanged microscope at 75 multiples. [a]*

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

Figure 4. showed the anti-bleeding performance of untreated and treated silk fabrics. As shown in Figure 4. (a), the bleeding performance of untreated silk fabric was severe along the edge of inkjet printing. The anti-bleeding performance of the treated sample was dramatically improved with excellent sharpness after plasma treatment. It is due to the etching and 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 study the AFM image of the fiber, plasma treatment produced more grooves on the surface of the fiber. These grooves had ability of holding more inks on surface of the fabric. The above mentioned 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 4. It shows that K/S values increased after plasma treatment, L value decreased a little and and C value increased. 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 silk fabric which increased the amount of ink colorant stayed on per area of 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 4 color measurement results of treated and untreated fabrics [a]

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

[a] The sample was treated at a pressure 50 Pa, power 80 W for 10 min.

Real inkjet printed images

(a) Untreated *(b) Treated*

Figure 5. *The real inkjet printed images of silk fabrics. [a]*

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

Figure 5. shows the real inkjet printing images of untreated and treated silk fabrics. From both the images we saw that the treated sample with 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.

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 anti-bleeding performance than untreated samples. Images 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 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 anti-bleeding 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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