

Using atmospheric pressure plasma for enhancing the deposition of printing paste on cotton fabric for digital ink-jet printing

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Abstract Atmospheric pressure plasma (APP) treatment was applied as a pretreatment process to enhance the deposition of printing paste in order to improve the final colour properties of digital ink-jet printed cotton fabrics. Three printing pastes containing natural polymers, i.e. (1) sodium alginate, (2) chitosan and (3) sodium alginate-chitosan mixture, were prepared separately. After APP treatment, cotton fabric was padded with different printing pastes prior to digital ink-jet printing. Experimental results showed that APP pretreatment could increase the colour yield of the digital ink-jet printed cotton fabric significantly even after washing. In addition, other properties such as colour fastness to crocking, colour fastness to laundering, outline sharpness and anti-bacterial properties were also improved when compared with those of the control cotton fabric printed without APP pretreatment. However, the influence of printing paste on the colour properties of the digital ink-jet printed cotton fabrics depended very much on the composition of the printing paste. The scanning electron microscope images evidenced that the APP treatment could enhance the deposition of printing paste on the cotton fabric surface as proved qualitatively by both the contact angle and

wetting time measurement as well as quantitatively by both the X-ray photoelectron spectroscopy and carboxyl group/nitrogen content analysis.

Keywords Atmospheric pressure plasma · Cotton · Surface modification · Chitosan · Sodium alginate · Digital ink-jet printing

Introduction

Application of digital ink-jet printing in textile areas has increased recently because this technique offers production benefits such as speed, flexibility, creativity in design patterns and cleanliness in production for cotton products (Gupta 2001; van Parys 2002; Tyler 2005). In the conventional printing of cotton fabric, reactive dyes are applied along with alkali and other chemicals in the form of a printing paste. Due to the requirement of specific ink purity and conductivity for digital ink-jet printing (Le 1998; Aston et al. 1997; Schulz 2002; Zhou and Li 2002), none of the conventional printing chemicals can be directly incorporated into the ink formulation. As a result, a printing paste should be prepared and applied to cotton fabrics before conducting digital ink-jet printing.

Currently, sodium alginate is an important thickener commonly used for preparing the printing paste for digital ink-jet printing due to its solubility and excellent stability even after high-temperature

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fixation treatments (Tyler 2005). Similar to sodium alginate, chitosan is also widely used as a novel biomaterial which is biocompatible, biodegradable and non-toxic (Qin 2004). Previous research has reported that chitosan can be applied to textile printing for improving colour yield, colour fastness and anti-bacterial function (Qin 2004; Ye et al. 2005; Lim and Hudson 2004; Jovic et al. 2005; Choi et al. 2005). Therefore, chitosan may be used as a chemical for preparing the printing paste for digital ink-jet printing of cotton fabric. The effectiveness of depositing the printing paste on the fabric surface will definitely affect the final colour properties of digital ink-jet printed cotton fabric.

Recently, plasma treatment has proved to be an effective pretreatment for improving the deposition process by altering the surface properties of materials without inducing much change in its bulk properties (De Geyter et al. 2008; Kan and Yuen 2009; Morent et al. 2008; Zhang and Fang 2009). In our previous research (Yuen and Kan 2007), it was confirmed that low-temperature plasma treatment could enhance the printing of cotton fabric using sodium alginate as the printing paste. However, the low-temperature plasma system used was operated in vacuum condition with yellowness being induced in the plasma-treated fabric which is not flexible enough to be integrated into the continuous and open system normally used for fabric processing.

Nowadays, atmospheric pressure plasma (APP) provides the requisite flexibility and possibility for continuous and open process (Wang and Qiu 2007; Shenton and Stevens 2001). The use of APP as a pretreatment process for digital ink-jet printing of cotton fabric and its effect on the colour properties of cotton fabric deposited with different printing pastes, i.e. sodium alginate, chitosan and sodium alginate-chitosan mixture, have been studied in this paper. Analytical methods such as scanning electron microscopy, X-ray photoelectron spectroscopy and functional groups determination have been used for characterising the surface properties of the APP-treated cotton fabric.

Experimental

Fabric

Hundred percent singed, desized, scoured and bleached plain weave cotton fabric of 136 g/m² with

50 ends/cm (yarn count: 15 tex) and 30 picks/cm (yarn count: 15 tex) was used in this study. Commercially pretreated cotton fabric used specifically for digital ink-jet printing with the same fabric specifications was adopted as the control fabric (the control fabric was pretreated with the printing paste containing sodium alginate, sodium carbonate and urea but the exact composition was not known due to commercial reasons). The size of the fabric samples was 20 cm × 20 cm. All samples were conditioned at 21 ± 1 °C with a relative humidity of 65 ± 2% for 24 h before being used.

Plasma pretreatment

Plasma pretreatment of cotton fabric was carried out by an atmospheric pressure plasma jet (APPJ) apparatus (Surfx Technologies, USA). The APPJ produced a stable discharge at atmospheric pressure with the radio frequency of 13.56 MHz. The pretreatment was carried out using a rectangular jet nozzle which covered an active area of 25.4 mm × 1 mm. The nozzle was mounted vertically above the fabric and the plasma pretreatment was set up as shown in Fig. 1. The distance between the nozzle and fabric surface was set at 6 mm and the plasma pretreatment time was 3 s. Helium with a flow rate of 15 l/min and oxygen with a flow rate of 0.3 l/min were used as carrier and reactive gases respectively. Five pieces of fabrics were pretreated with the plasma. After plasma pretreatment, the fabrics were conditioned at 21 ± 1 °C with a relative humidity of 65 ± 2% for 24 h before being used for further processing.

Preparation of printing paste with sodium alginate

A stock sodium alginate was prepared by dissolving 50 g sodium alginate (Pfaltz and Bauer, USA) in

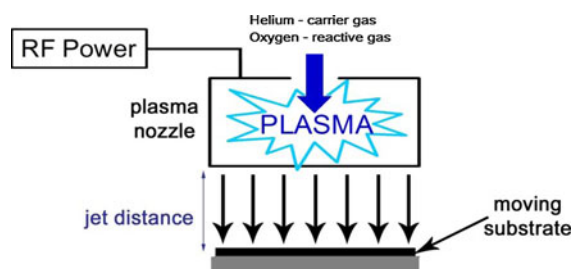


Fig. 1 Schematic diagram of plasma pretreatment

950 ml of deionised water. The amount of sodium alginate used in the printing paste was measured directly from the stock sodium alginate. The printing paste was prepared by well mixing 150 g stock sodium alginate, 8 g sodium bicarbonate (BDH, UK) and 10 g urea (BDH, UK), together with deionised water, making up a total weight of 400 g (Yuen et al. 2004).

Preparation of printing paste with chitosan

Chitosan in solid form was supplied by Sigma Co. (USA) and a stock chitosan solution was prepared by dissolving 5 g of chitosan completely into 500 ml of 10% acetic acid with constant stirring. The stock solution was then filtered to remove any suspended impurities. The amount of chitosan used in the printing paste was measured directly from the stock chitosan solution. The printing paste containing chitosan was prepared by well mixing 40 g stock chitosan, 8 g sodium bicarbonate (BDH, UK) and 10 g urea (BDH, UK), together with deionised water making up a total weight of 400 g (Choi et al. 2005).

Preparation of printing paste with sodium alginate-chitosan mixture

Sodium alginate itself can achieve good printing property, but its anti-bacterial property is not good when compared with chitosan (Yuen et al. 2007). Mixing of sodium alginate with chitosan may enhance both printing property and anti-bacterial function. The printing paste containing sodium alginate and chitosan mixture was prepared by well mixing 150 g stock sodium alginate, 10 g stock chitosan, 8 g sodium bicarbonate (BDH, UK) and 10 g urea (BDH, UK), together with deionised water making up a weight of 400 g.

Fabric pretreatment with printing paste

The well mixed printing paste was padded onto the cotton fabric using a padding machine (T.K.HOMO Mixer, Model: HV-M, Japan) with an even pressure of 2.6 kg/m² and a constant padding speed of 2.5 rpm until a pick-up of 80% was achieved. The treated fabrics were dried in an oven at 80 °C and then conditioned at 21 ± 1 °C with a relative humidity of 65 ± 2% for 24 h before conducting digital ink-jet printing.

Printing procedure

The digital ink-jet printer used was Mimaki Tx2-1600 (Mimaki Engineering Co., Ltd, Japan) with a piezo-electric drop-on-demand print head. A commercially available reactive ink of magenta colour with vinyl-sulphone reacting system (Yuen et al. 2005) was used without further purification. With the use of the built-in software of the digital ink-jet printer, a square pattern of size 100 mm × 100 mm was generated with a resolution of 360 dpi for easy comparison. After printing, the fabrics were air-dried and then treated with superheated steam at 110 °C for 5 min for colour fixation. The steamed fabric samples were finally washed in a 10 g/l non-ionic detergent solution (Kieralon OL, BASF) until all the unreacted dyes and chemicals were removed from the fabric surface.

Colour yield measurement

The printed fabrics were conditioned at 21 ± 1 °C and 65 ± 2% relative humidity before colour yield measurement with a Macbeth Colour Eye 7000A Spectrophotometer. The spectrophotometer was set to exclude specular reflection and a large aperture (D65 and 10° observer). The fabric was folded two times to ensure opacity and then measured twice in both the warp and weft directions in order to obtain average results. The colour yield expressed as a K/S value with different wavelength ranging from 400 to 700 nm within the visible spectrum and measured at 20 nm interval was calculated according to Eq. 1 and then summed up as K/S Sum value. The higher the K/S Sum value, the more the dye-uptake will be, resulting in better colour yield.

$$\frac{K}{S} = \frac{(1 - R)^2}{2R} \quad (1)$$

where K = absorption coefficient (depending on the concentration of the colorant); S = scattering coefficient (caused by the dyed substrate); and R = reflectance of the coloured sample.

In order to determine the durability of the printed colour, the printed fabrics were washed twice with simulated domestic washing according to the AATCC Test method 135 under the condition of normal washing cycle at 27 ± 3 °C followed by tumble drying process. After each washing, the fabrics were conditioned and the colour yield was measured.

Surface morphology

The surface morphology of fabrics was investigated by scanning electron microscope (SEM) (JEOL, Model No: JSM-6335F, Japan) with a magnification of 10,000 \times .

X-ray photoelectron spectroscopy (XPS) analysis

The chemical composition of fibre surface was investigated by X-ray photoelectron spectrometer (XPS; SKL-12, China) modified with a VG CLAM 4 multi-channel hemispherical analyser. X-ray source was a dual anode source generated from VG (type XR3E2) but with a non-monochromatic Mg K α radiation (1,253.6 eV) at 10 kV and 15 mA. The analysis was carried out under an ultra high vacuum (8×10^{-8} Pa). The peak positions relative to hydrocarbon peak at 285.0 eV were corrected for charging so that the relative intensities of C_{1s} (285.0 eV) and O_{1s} (533.0 eV) peaks could be determined.

Contact angle and wetting time measurement

A contact angle goniometer—Model 200-F1 (Rame-Hart, USA) was incorporated in an image capturing system to measure the contact angle of fabric samples. A micrometer syringe (GILMONT instrument, Barnant Company, USA) was used for placing a glycerol solution (86–88%) droplet of 5 μ l onto the fabric surface. The time required for the droplet to be completely absorbed into the fabric surface was taken as the wetting time. For each specimen, 6 measurements were taken.

Determination of carboxyl group and nitrogen content

In order to study the chemical effect of the printing paste on the cotton fabric, the carboxyl group and nitrogen content of the fabrics were evaluated. Since the printed area contained the reactive dye, thus the unprinted portion of the fabrics was examined so as to eliminate the influence of the dye. The amount of carboxyl group present in the fabric specimens was determined by titration method (Fras et al. 2002). 1.0 g air-dried sample was weighed and put into a 200 ml glass-stopper flask. 100 ml of calcium acetate solution (A.R grade) were added. The flask was shaken

overnight, and then the suspension of fibre was filtered. 50 ml of filtrate was pipetted into a beaker and the murexide was added as a colour indicator. The pH value of the filtrate was adjusted to 12 by the addition of 0.1 M sodium hydroxide solution. The decrease in concentration of calcium acetate solution after contacting with the fibres was determined by the titration with 0.1 M EDTA solution as a titrant and the end point was determined colorimetrically. The carboxyl group content of the cellulose sample was obtained according to Eq. 2 (Fras et al. 2002):

$$\text{COOH (mmol/kg)} = \frac{(V_a - V_b) \times C \times f \times 1,000}{m} \quad (2)$$

where V_a is the consumption of titrating reagent (EDTA) for the sample [ml], V_b is the consumption of titrating reagent (EDTA) for the blank value [ml], C is the concentration of the titrating reagent [mol/l], f is the factor of the titrating reagent (Bird et al. 1961), and m represents the weight of sample [g]. All the values obtained were mean value of 4 parallel measurements.

Nitrogen content of fabrics was determined by Kjeldahl method. 2 g of fabric was weighed and then placed in a Kjeldahl digestion flask containing 0.7 g mercury oxide, 15 g potassium sulphate and 25 ml concentrated sulphuric acid. After a thorough digestion of the fabric samples, the mixture was diluted with 200 ml of deionised water followed by reaction with 25 ml potassium sulphide solution (40 g/l). The mixture was then neutralized with 90 ml of concentrated sodium hydroxide solution (450 g/l) immediately before distillation. The generated ammonia was obtained from a collecting flask which contained exactly 50 ml of 0.05 N sulphuric acid. This solution was then titrated with 0.05 N sodium hydroxide solution. The nitrogen contents were calculated according to Eq. 3:

$$\text{Nitrogen content (\%)} = \left[\frac{(A - B)N \times 0.01401}{C} \right] \times 100 \quad (3)$$

where A is the volume of standard NaOH solution (ml); B is the volume of standard NaOH required to neutralise sulphuric acid in the collecting flask (ml); N is the normality of the NaOH solution; C is the

weight of the sample used in grams and 0.01401 is the milliequivalent weight of nitrogen.

Colour fastness tests

The colour fastness of the digital ink-jet printed fabrics was assessed by the AATCC Test Method 61 (colour fastness to laundering) and AATCC Test Method 8 (colour fastness to crocking).

Outline sharpness measurement

In order to compare the outline sharpness of the prints, the width of the printed pattern in both the warp and weft directions was measured using an optical light microscope (Nikon Optiplot-pol, USA) with a magnification of 400.

Anti-bacterial effect

The anti-bacterial effects of the digital ink-jet printed fabrics were quantitatively evaluated by the AATCC Test Method 100. The quantitative anti-bacterial evaluation was given by Eq. 4:

$$R(\%) = \left[\frac{(B - A)}{B} \right] \times 100 \quad (4)$$

where R = percentage reduction; A = number of bacteria recovered from the inoculated treated test specimen swatches in a jar incubated over the desired contact period, and B = number of bacteria recovered from the inoculated treated test specimen swatches in the jar immediately after inoculation.

Results and discussion

Colour yield measurement

Table 1 shows that colour yield of different digital ink-jet printed fabric samples. In the case of fabrics pretreated with plasma, their K/S Sum values were higher than those of the corresponding fabrics without plasma pretreatment. The K/S Sum values obtained were in the following order: SA-plasma > SA/Ch-plasma > SA > Ch-plasma > Control > SA/Ch > Ch.

In the case of printing paste with sodium alginate, urea was used to swell cotton fibres during the

Table 1 K/S sum values of digital ink-jet printed cotton fabrics

Sample ^a	Non-ionic detergent washing ^b	One simulated domestic washing cycle	Two simulated domestic cycles
Control	90.3	81.3	73.1
SA	95.7	94.2	94.0
SA-plasma	117.4	116.2	116.0
SA/Ch	89.3	88.5	88.0
SA/Ch-plasma	99.8	98.8	98.5
Ch	81.5	80.7	80.3
Ch-plasma	93.9	93.0	92.8

^a The following notations are adopted in labelling different fabric samples: *control* commercially available fabric with unknown printing paste content, *SA* fabric padded with printing paste of sodium alginate, *SA-plasma* fabric pretreated with plasma followed by padding with printing paste of sodium alginate, *SA/Ch* fabric padded with printing paste of sodium alginate and chitosan mixture, *SA/Ch-plasma* fabric pretreated with plasma followed by padding with printing paste of sodium alginate and chitosan mixture, *Ch* fabric padded with printing paste of chitosan, and *Ch-plasma* fabric pretreated with plasma followed by padding with printing paste of chitosan

^b “Non-ionic detergent washing” fabric samples referred to the printed fabrics washed with non-ionic detergent right after digital ink-jet printing

superheated steaming process so that the dye could penetrate into the fibres rapidly (Achwal 2002; Chen et al. 2002). Urea acted like a moisture-absorbing agent in the printing paste to increase moisture regain during steaming, thereby accelerating the migration of dyes from the printing paste to the cotton fibres leading to the increased colour yield (Achwal 2002; Chen et al. 2002). On the other hand, pretreatment with plasma using oxygen gas could increase the amount of hydrophilic groups such as $-C=O$, $C=O$, $O-C-O$ and $O-C=O$ on the cellulosic fibre surface (Morent et al. 2008; Wong et al. 1999; Inbakumar et al. 2010; Lam et al. 2011). The increased amount of hydrophilic groups could further enhance dye absorption and increase colour yield finally.

For the printing paste containing sodium alginate-chitosan mixture (SA/Ch), about 98.9% of the final colour yield was achieved when compared with the control fabric as shown in Table 1. The slightly reduced colour yield of SA/Ch fabric samples might be due to the neutralisation effect caused by mixing the chitosan solution with sodium bicarbonate in the printing paste (Yuen et al. 2007). The neutralisation

effect might reduce the amount of sodium bicarbonate present in the printing paste and generate a neutralisation product, i.e. water. Therefore, the decreased amount of sodium bicarbonate might reduce the fixation of reactive dyes inside the fibre while the increased amount of water might impose the risk of reactive dye hydrolysis, thereby reducing the colour yield. On the other hand, the application of plasma pretreatment would etch the cotton fibre surface resulting in the formation of cracks (Wong et al. 1999; Inbakumar et al. 2010). After depositing the printing paste, the cracks so formed were filled up with the printing paste. This would bring more dyes into close contact with the fibre during the dye fixation process and thus increase dye uptake. In addition, hydrophilic groups formed on the fibre surface after oxygen plasma pretreatment (Wong et al. 1999; Inbakumar et al. 2010) would also enhance the spread of the printing paste so that more dye would be brought into close contact with the fibre leading to an increase in colour yield.

As for the printing paste with chitosan alone, it was noted that the Ch fabric sample without plasma pretreatment achieved about 90% of colour yield when compared with the control fabric. This might be due to the neutralisation effect that occurred during the mixing of chitosan solution with sodium bicarbonate (Yuen et al. 2007). Since 40 g of stock chitosan was used, thus more acetic acid was required in the printing paste. The increased quantity of acetic acid would help increase the relative acidity of the printing paste. It was believed that acetic acid would react with the sodium bicarbonate thereby reducing the amount of sodium bicarbonate present in the printing paste for reactive dye fixation. After comparing the colour yield of SA/Ch and Ch fabric

samples, it was concluded that neutralisation effect did occur causing a drop in both colour yield values. However, neutralisation effect imposed on SA/Ch fabric sample was smaller when compared with the Ch sample because they contained different amounts of acetic acid. Meanwhile, the reactive dyes of vinylsulphone type had a tendency to deactivate in the presence of urea. Under the superheated steaming condition, thermal decomposition of urea might occur to form biuret and ammonia followed by the conversion of the reactive vinylsulphone into inactive aminoethylsulphone leading to a reduction in colour yield.

Table 1 also shows the colour yield of digital ink-jet printed cotton fabrics subject to different washing treatment. As for the control fabric, the colour yield decreased progressively with simulated domestic washing cycles but there was no significant change in the colour yield for other samples after two consecutive simulated domestic washing cycles. Therefore, it was confirmed that the printing paste used in this study could achieve a good stability and durability of colour. Hence, the colour fastness to both crocking and laundering would be improved.

Scanning electron microscopy (SEM)

Figures 2, 3, 4 and 5 show the fibre surfaces of different fabric samples. Figure 2a shows the SEM image of the untreated cotton fabric with wrinkle texture, although smooth fibre surface was observed. Figure 2b shows the SEM image of the plasma pretreated cotton fibre surface. After plasma pretreatment, cracks and grooves were observed along the fibre axis particularly in the wrinkle portion making the fibre surface become roughened. The change in

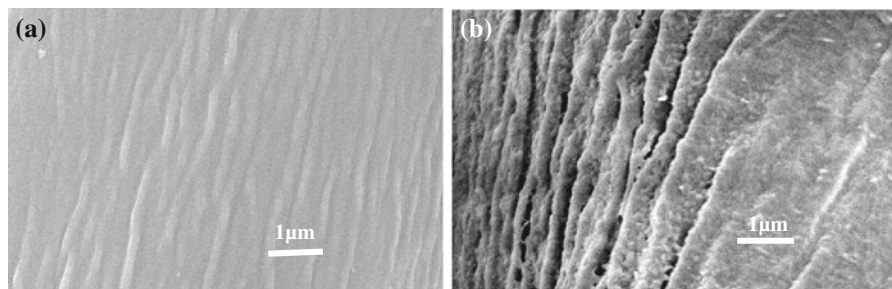


Fig. 2 **a** Untreated fabric; **b** plasma pre-treated fabric

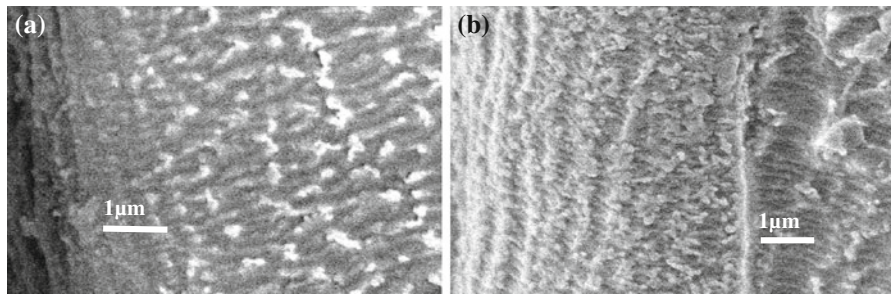


Fig. 3 **a** SA fabric; **b** SA-plasma fabric

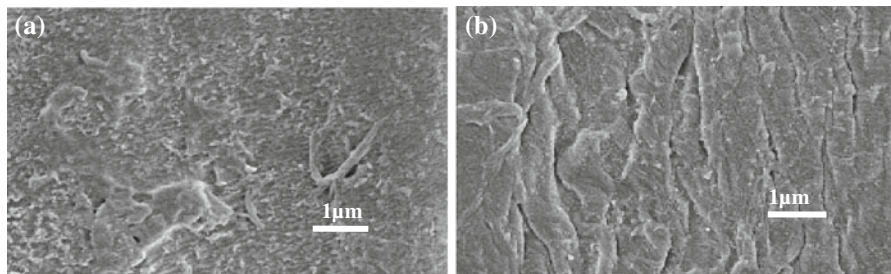


Fig. 4 **a** SA/Ch fabric; **b** SA/Ch-plasma fabric

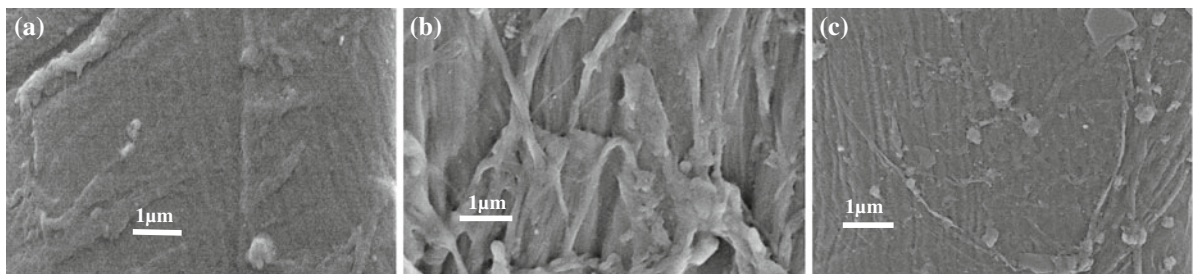


Fig. 5 **a** Ch fabric; **b** Ch-plasma fabric; **c** Ch-plasma fabric after two washing cycles

cotton fibre surface appearance was properly due to the localised ablation of the surface layer by oxygen plasma causing a surface damage. The presence of cracks and grooves on the fibre surface indicated the predominant etching effect of oxygen plasma on the fibre surface. The differential etching of crystalline and amorphous regions might be the cause of the roughness resulting in the development of cracks and grooves found along the fibre axis (Wong et al. 1999).

Figure 3a shows the SEM image of cotton fibre surface padded only with sodium alginate printing paste but without plasma pretreatment. It was

observed that the printing paste clearly adhered to the fibre surface like a film. At the same time, the fibre surface was much rougher than that of the untreated fabric. Figure 3b shows the surface of plasma pretreated cotton fibre padded only with sodium alginate printing paste. The cracks formed on the fibre surface after plasma pretreatment were filled up completely with the printing paste. In addition, the formation of cracks on the fibre surface would increase the surface area and facilitate more dye to approach the fibre surface increasing thereby the colour yield.

As for the treatment with sodium alginate-chitosan mixture printing paste shown in Fig. 4a, a rough and clod surface was noted. The formation of rough and clod surface was due to the mixing of sodium alginate and chitosan on the fibre surface. With regards to the plasma-pretreated sample shown in Fig. 4b, the sodium alginate-chitosan mixture printing paste was distributed evenly along the fibre axis to form clods.

Figure 5a shows the surface appearance of cotton fabric treated with chitosan printing paste only (Ch). When compared, the wrinkled texture present in the untreated cotton fibre surface as shown in Fig. 2a was diminished probably due to the deposition of chitosan resulting in a more uniform surface texture. However, a clod surface texture was noted after plasma pretreatment as shown in Fig. 5b. As the plasma pretreatment with oxygen could introduce more hydrophilic functional groups to the fibre surface, thus more chitosan could adhere to the fibre surface. When comparing Fig. 4a with Fig. 5a and Fig. 4b with Fig. 5b, it was observed that more printing paste was deposited on the fibre surface with the help of plasma pretreatment.

After one simulated domestic washing cycle, the surface of fabric samples was examined again. It was noted that both the SA and SA-plasma fabric samples had similar surface morphology as shown in Fig. 2a, b, respectively. This means that the printing paste could be removed completely from the fibre surface during washing. As for the fabric samples containing chitosan with and without plasma pretreatment, some clod structures were still observed after two washing cycles as shown in Fig. 5c. When compared, the plasma-pretreated fabric sample had more clods than the one without plasma pretreatment. In the non-plasma-pretreated cotton fabric, there were no carboxyl groups and probably only a few aldehyde groups present on the surface of sample. They were most likely present as impurities/contaminants (Fras et al. 2005). This suggested that chitosan deposition on the non-plasma-pretreated cotton fabric was predominantly driven by physical interactions such as Van der Waals' forces or hydrogen bonding. After plasma pretreatment, aldehyde and carboxyl groups would be introduced to the cotton fibre. As a result, the interaction between chitosan and cotton fibre might be due to the combination of electrostatic and electrodynamic interactions (ionic and covalent bonds) with the additional hydrogen bonding (Fras

Zemljic et al. 2009). In addition, a large amount of water imbibed into the plasma-pretreated cotton fabric may imply that there was an increase in accessibility for chitosan to deposit at the fibrous materials (Fras Zemljic et al. 2009). Nevertheless, the fabric samples treated with chitosan, i.e. SA/Ch, SA/Ch-plasma, Ch and Ch-plasma, still retained some chitosan on the fibre surface after simulating domestic washing. The retention of chitosan would assist in maintaining the colour yield and also exhibited anti-bacterial function to the cotton fabric.

XPS surface chemical analysis

Table 2 shows the elemental composition of both the untreated and plasma-pretreated samples as well as the O/C peak ratios, which are important for reflecting the degree of surface modification. The increase in O/C ratio of the sample after oxygen plasma treatment was significant. The decrease in C_{1s} and increase in O_{1s} revealed that some of the carbon bonds present on the fabric surface had been broken by plasma pretreatment. Carbon radicals formed by the abstraction of hydrogen atoms from the polymer chains might then combine with oxygen atoms generated in plasma gas or air by means of electron impact dissociation (Wang et al. 2005), thereby forming the oxygen-containing polar groups such as –C=O, C=O, O–C–O and O–C=O on the cellulosic fibre surface (Morent et al. 2008; Wong et al. 1999; Inbakumar et al. 2010). Hence, the cotton fibre surface may be activated by oxygen plasma, thereby promoting higher wettability and potential adhesion between the printing paste and the plasma pretreated cotton surface.



Surface contact angle and wetting time analysis

Table 3 shows the results of surface contact angle and wetting time of both the untreated and plasma-

Table 2 Surface elemental analysis and atomic ratios

Sample	Element concentration (%)		Atomic ratio (O/C)
	C _{1s}	O _{1s}	
Untreated cotton fabric	66.28	33.72	0.51
Plasma-pretreated cotton fabric	54.65	45.35	0.83

Table 3 Surface contact angle and wetting time of untreated and plasma-pretreated cotton fabric (measured within 5% tolerance limit)

Sample	Untreated cotton fabric	Plasma-pretreated cotton fabric
Contact angle (°)	 98	 58
Wetting time (s)	6.3	4.5

pretreated cotton. Lower contact angle value and shorter wetting time were obtained for plasma-pretreated fabric when compared with the untreated fabric. The change in contact angles and wetting times of the oxygen plasma-treated fabrics may be explained by the alteration of morphology and chemical composition of the surface of the plasma-pretreated fabric. This indicated that there was an increase in the surface energy of oxygen plasma-pretreated fabric when compared with the untreated fabric. Changes in surface morphology might also lead to wettability change. It was believed that plasma oxidation reactions would generate oxygen-containing hydrophilic functional groups, such as $-C=O$, $C=O$, $O-C-O$ and $O-C=O$, attached to the polymer surface (Morent et al. 2008; Wong et al. 1999; Inbakumar et al. 2010; Sun and

Stylios 2005). Therefore, the reduced contact angle and increased wettability of the plasma-pretreated sample might be attributed to oxygen-containing surfaces induced by oxygen plasma treatment. As a result, the adhesion between the printing paste and cotton fibre surfaces would be enhanced (Shahidi et al. 2010; Shateri Khalil-Abad et al. 2009; Fras Zemljic et al. 2009).

Carboxyl group and nitrogen content

Generally speaking, carboxyl group ($-COOH$) cannot not be detected in the pure and undamaged cotton because there is only hydroxyl group ($-OH$) available in the cellulose. However, the presence of carboxyl group may implicate some chemical changes occurred to cotton fabric samples. Table 4 shows the amount of carboxyl group present in different cotton fabric samples. It was expected that all the cotton fabric samples might contain undetectable amount of carboxyl groups but actually it was not the real case. In the untreated cotton fabric, trace amount of carboxyl group was detected because the cotton fabric was oxidized after various pretreatment processes such as singeing, desizing, scouring and bleaching.

Some carboxyl groups were detected for both the control and SA fabrics but after simulated domestic

Table 4 Carboxyl group and nitrogen content of digital ink-jet printed cotton fabric

Sample	Non-ionic detergent washing ^a		One simulated domestic washing cycle		Two simulated domestic washing cycles	
	Carboxyl group (mmol/kg)	Nitrogen content (%)	Carboxyl group (mmol/kg)	Nitrogen content (%)	Carboxyl group (mmol/kg)	Nitrogen content (%)
Untreated ^b	8.20	ND	8.20	ND	8.20	ND
Control ^c	12.17	0.2	11.73	ND	11.72	ND
SA	13.39	0.2	11.72	ND	11.70	ND
SA-plasma	14.06	0.5	13.36	ND	13.35	n.d.
SA/Ch	12.78	4.9	12.14	3.9	12.10	3.1
SA/Ch-plasma	13.41	6.3	12.74	5.0	12.70	4.0
Ch	12.16	19.4	12.14	15.5	12.00	12.4
Ch-plasma	13.38	25.3	13.32	20.2	13.30	16.2

ND non-detectable

^a “Non-ionic detergent washing” fabric samples referred to the printed fabrics washed with non-ionic detergent right after digital ink-jet printing

^b “Untreated” fabric sample referred to the cotton fabric without plasma pretreatment

^c Commercially available fabric with unknown printing paste content

washing cycles, the amount of carboxyl group detected was reduced to a steady level. Although sodium alginate residues, which contain some carboxyl groups, were completely removed, carboxyl group was still detected because the cotton fabrics used had been subjected to various pretreatment processes such as desizing, scouring and bleaching prior to padding of printing paste (Fras Zemljic et al. 2008). Similar observation was noted for all the sodium alginate containing samples. It was also seen that the SA-plasma treated fabric sample had a higher amount of carboxyl group when compared with the SA fabric sample.

After simulated domestic washing cycles, the SA/Ch fabric samples retained more carboxyl groups than the SA fabric sample because the use of acetic acid for dissolving the chitosan will cause acid hydrolysis to the cotton fibre leading to the formation of carboxyl group inside the fibre. When compared, the SA/Ch-plasma fabric sample obtained more carboxyl group than the SA/Ch fabric sample. Although no sodium alginate was used to prepare the Ch and Ch-plasma printing paste, a larger amount of carboxyl group was still found due to the acid hydrolysis of cotton. In Table 4, it was obvious that plasma pretreatment with oxygen could introduce more carboxyl groups to the fabric when compared with the untreated fabric (Morent et al. 2008; Wong et al. 1999; Inbakumar et al. 2010; Lam et al. 2011).

Pure cotton fibres are mainly composed of cellulose or carbohydrates containing undetectable amount of nitrogen. Hence, the nitrogen content found in cotton fabric can be used as a reference to indicate the presence of chitosan in the cotton fabric samples. In the case of the control, SA and SA-plasma fabric samples, only a tiny amount of nitrogen content was found in them before the non-ionic detergent washing process. However, the nitrogen content decreased to an undetectable level after one simulated domestic washing cycle. The existence of nitrogen content may be contributed by (1) the urea residues present in the printing paste and (2) the decomposition products of urea to form biuret and ammonia, which could be easily removed by the subsequent washing process. As for the fabric samples containing chitosan, a higher nitrogen content was observed. Although there was a gradual decrease in the nitrogen content during the washing process, a certain amount of nitrogen content was still detected. The existence of nitrogen

content was contributed mainly by the presence of chitosan in the fibre. When compared with the SA/Ch fabric sample, it was obvious that the Ch fabric sample contained more chitosan particles which were employed to prepare the printing paste for producing the Ch fabric sample. In the case of the SA/Ch-plasma and Ch-plasma fabric samples, plasma pretreatment could further increase the chitosan adsorption because the deposition of chitosan on the non-plasma-pretreated cotton fabric was predominantly driven by physical interactions such as Van der Waals' forces or hydrogen bonding. After plasma pretreatment, both aldehyde and carboxyl groups would be generated inside the cotton fibre to enhance the interaction between chitosan and cotton fibres due to the electrostatic and electrodynamic interactions (ionic and covalent bonds) associated with the additional hydrogen bonding (Fras Zemljic et al. 2009).

Colour fastness tests

Table 5 shows the results of colour fastness to crocking and laundering. All the fabric samples pretreated with different printing paste showed good colour fastness to dry and wet crocking when compared with the control fabric. As for the fabric sample pretreated with different printing paste, their colour fastness to laundering was confirmed to be at an acceptable level as the overall results of colour

Table 5 Results of colour fastness to crocking and laundering

Fabric samples	Crocking		Laundering	
	Dry	Wet	Colour change	Staining ^a
Control	3–4	3	4	4
SA	4	3–4	4–5	4–5
SA-plasma	4–5	4	4–5	4–5
SA/Ch	4–5	4	4–5	4–5
SA/Ch-plasma	5	4–5	4–5	4–5
Ch	4–5	4	4–5	4–5
Ch-plasma	4–5	4–5	4–5	4–5

^a Fibres in the multi-fibre fabric included six fibres namely wool, acrylic, polyester, nylon, cotton and acetate. The number indicates the grey scale rating in which the higher the grey scale rating, the better the colour fastness will be, i.e. 5 is the best rating while 1 is the worst rating. The staining result reports the worst rating in the fibre among the six fibres in multi-fibre fabric

change and staining were around 4–5 which was slightly better than the control fabric. The improved grey scale rating indicated that the printing paste used could facilitate better penetration of reactive dye during the digital ink-jet printing process so that sufficient colour fastness could be obtained with no significant bleeding of reactive dye being observed.

The improvement in grey scale rating might be due to the presence of primary amino groups contained in chitosan. Most probably after the amino groups deposited in the fibres, they might create a cationic surface which would attract more reactive dye anions with opposite charges (Chiou et al. 2004). Although the hydrolysed reactive dyes might attach to the chitosan molecules without fixation, yet they could still be easily removed by repeated laundering. The improved colour fastness indicated that reactive dyes of the printing ink adhered more firmly to the fabric. Cracks and grooves generated by plasma pretreatment would enhance the adhesion of the printing paste at the fibre surface. At the same time, the hydrophilic groups induced by plasma pretreatment could chemically improve the deposition of printing paste on the fibre surface. More printing paste coated on the fibre surface would result in more reactive dyes being taken-up during the digital ink-jet printing process, thereby greatly improving the grey scale rating of colour fastness.

Outline sharpness measurement

Outline sharpness of the digital ink-jet printed pattern was measured by the optical analysis method. The measurement was conducted in both the warp and weft directions with the results being shown in Table 6. Obviously, digital ink-jet printed patterns in the warp direction were wider than those in the weft direction for both the control and plasma-pretreated fabrics. This might be due to the differential wicking effect caused by the warp and weft yarns. Patterns printed on the plasma-pretreated cotton fabrics were narrower than those of the untreated fabric in both the warp and weft directions. This could be attributed to the reduced spread of reactive inks caused by the strong fibre and dye attraction, i.e. formation of covalent bonds between hydroxyl groups of fibre and reactive dye present in the printing ink. This indicated that plasma pretreatment could enhance the outline sharpness of ink-jet prints. In addition, when chitosan was added in the printing paste, the patterns became

Table 6 Outline sharpness of digital ink-jet printed fabrics with different printing paste conditions (measured within 5% tolerance limit)

Sample	Sharpness with different printing paste	
	Warp (mm) ^a	Weft (mm) ^a
Control	102	102
SA	101.5	101
SA-plasma	101	100.5
SA/Ch	101	100.5
SA/Ch-plasma	100.5	100
Ch	101	100.5
Ch-plasma	100.5	100

^a Widths of printed patterns were measured in mm in both warp and weft directions

narrower. The phenomenon might be due to the introduction of cationic groups ($-\text{NH}_3^+$) present in chitosan resulting in a strong ionic attraction between cationic cotton and anionic reactive inks.

Table 6 shows that all the SA, SA/Ch and Ch printing pastes had better outline sharpness than the control fabric, although the difference was rather small. Among different printing pastes, the Ch and SA/Ch samples achieved better outline sharpness than the SA sample. Since plasma pretreatment could enhance the adhesion of film coating, thus more SA, SA/Ch and Ch printing pastes could be placed effectively on the fibre surface as shown in Figs. 3a, 4a and 5a. The deposited printing paste could retain the printed pattern in correct position resulting in good outline sharpness.

Anti-bacterial effect

AATCC Test Method 100 was used to determine anti-bacterial property of digital ink-jet printed fabrics pretreated with different printing pastes. Table 7 shows the concentration of *Staphylococcus aureus* bacteria determined from the fabrics with different printing pastes for 0 h and 48 h respectively.

The results shown in Table 7 indicated that chitosan had a good anti-bacterial effect as all the bacteria could be completely killed by the chitosan present in the pretreated cotton fabric. Sodium alginate used alone to pretreat the SA and SA-plasma samples could reduce bacteria to the extent of greater than 70%, but its performance was not as good as chitosan. When compared, the control fabric did not exhibit any anti-

Table 7 Anti-bacterial evaluation of digital ink-jet printed fabrics pretreated with different printing paste (measured within 5% tolerance limit)

Sample	Bacteria concentration		
	0 h	48 h	% of bacterial removal (-ve)/increase (+ve)
Control	1.30×10^8	2.30×10^8	+172.4
SA	1.95×10^8	5.66×10^7	-70.97
SA-plasma	2.40×10^8	6.95×10^7	-71.04
SA/Ch	2.44×10^8	0	-100
SA/Ch-plasma	2.72×10^8	0	-100
Ch	9.33×10^7	0	-100
Ch-plasma	8.10×10^7	0	-100

bacterial effect as reflected by the large growth of bacteria. Although plasma pretreatment could enhance the deposition of SA/Ch and Ch printing paste, as shown in Figs. 4a and 5a, yet it did not have any significant anti-bacterial effect on the digital ink-jet printed fabric. On one hand, chitosan itself could achieve significant anti-bacterial properties, but on the other hand, it could provide other functional effects like colour-related properties. Although chitosan exhibits excellent anti-bacterial property when used in the printing paste, it was not necessary to use 100% chitosan because small amount of chitosan could demonstrate similar effect as 100% chitosan (Shin et al. 2001; Fras Zemljic et al. 2009). As a result, the use of sodium alginate-chitosan mixture could provide the same anti-bacterial effect with the best printing properties.

Conclusion

The surface of cotton fabric was modified physically and chemically by plasma treatment leading to a better deposition of digital ink-jet printing paste containing (1) sodium alginate, (2) chitosan and (3) sodium alginate-chitosan mixture on the fabric surface. After digital ink-jet printing process, the colour yield of the printed cotton fabric samples was measured using K/S Sum value. It was revealed that the SA printing paste had the best colour yield with or without plasma pretreatment. In terms of other colour-related properties such as colour fastness and outline

sharpness, the SA printing paste was not the best one while the SA/Ch and Ch printing pastes achieved better result. SA/Ch not only provided the desirable colour fastness and outline sharpness but it also achieved the colour yield similar to the control fabric. 100% chitosan present in the printing paste could provide excellent anti-bacterial properties for the digital ink-jet printed fabric. On the other hand, sodium alginate alone could also reduce the growth of bacteria but the effect was not significant. When sodium alginate-chitosan mixture was used in the printing paste, similar anti-bacterial effect and better printing properties could be achieved when compared with 100% chitosan. SEM images showed that cracks were formed along the fibre axis and at fibre surface as a result of plasma pretreatment. The cracks were filled up with the printing paste in order to help increase the dye uptake of fabric. On the other hand, plasma pretreatment could generate hydrophilic groups at the cotton fibre surface, thereby enhancing the deposition of printing paste to improve colour yield.

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