USING AGEING EFFECT FOR HYDROPHOBIC MODIFICATION OF COTTON FABRIC WITH ATMOSPHERIC PRESSURE PLASMA

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A hydrophobic modification of cotton fabric was demonstrated with atmospheric pressure plasma treatment with oxygen as the reactive gas. Oxygen plasma was determined to be capable of inducing hydrophobic modification of cotton fabric surface by utilizing the ageing effect. Upon ageing, the surface polarity was reversed and hydrophobic aliphatic hydrocarbons were formed, which was confirmed by Fourier Transform Infrared Spectroscopy. Surface hydrophobicity was quantified by the wetting area measurement. Wetted area of plasma-modified cotton was found to be strongly dependent on plasma-induced surface structures and the chemical composition on the fiber surface. Scanning electron microscopy revealed that physical morphological alteration was also a crucial factor that contributed to surface hydrophobicity. This work seeks to determine a controlled hydrophobic modification of textile materials through optimization of plasma process based on the Orthogonal Array Testing Strategy (OATS). Optimum process conditions were determined based on reduction of wetted area of plasma-modified cotton fabrics. Finally, hydrophobicity of plasma-modified cotton fabric was compared with conventional water repellency treatment.

Keywords: Atmospheric pressure plasma; Cotton fabric; Hydrophobicity; Orthogonal optimization

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INTRODUCTION

Depletion of non-renewable resources is leading to a resurgence of interest in plant-derived materials in various segments of the textile industry. Cellulosic fiber possesses attractive inherent bulk properties, but surface modifications are used for diversifying its end uses (Allan et al. 2002; Baltazar et al. 2007; Canal et al. 2009; Karahan and Özdoğan 2008; Termerman and Leys 2005; Tsafack and Levalois-Grùtzmacher 2007). Plasma is an eco-friendly surface modification technique that serves as an alternative to conventional wet processing of textiles. Atmospheric pressure plasma (APP) generates a low-temperature plasma flux suitable for modifying heat-sensitive materials. This category of plasma has recently attracted growing interest owing to its outstanding properties; it is a potential technique for dry treatment of textile materials (Matthews et al. 2004; Ren et al. 2008; Zhang and Fang 2009).

Wettability of a surface is governed by the combination of surface roughness and chemical composition. Hydrophobic surfaces offering liquid repellence are exploitable for diverse applications. Conventionally, fluorinated chemicals are employed for deposition of hydrophobic coatings on hydrophilic substrates, in order to impart hydrophobicity to the surface. However, during the deposition process, volatile organic compounds and residual fluorinated monomers or other chemicals will be generated, which are hazardous to human health and the environment. In this study, oxygen (O_2), being a non-toxic gas, was used to study the possibility of hydrophobic modification of cotton substrate with plasma. Oxygen plasma is capable of inducing hydrophobic modification of cotton fabrics, using the ageing effect. Upon ageing, surface polarity is reversed by formation of hydrophobic aliphatic hydrocarbons on the polymer surface, which thereafter shows a gradual hydrophobic recovery and decreases the surface free energy with the passage of time (Occhiello et al. 1992; Dellavolpe et al. 1994; Morra et al. 1989; Munro and McBriar 1988; Morra et al. 1990; Rashida et al. 2004).

Therefore, in this study, we seek to determine a method for controlled hydrophobic modification of cotton textile materials by atmospheric pressure plasma treatment using oxygen, together with an ageing effect, through optimization of the plasma process. To control the degree of modification of the cotton substrate, the Orthogonal Array Testing Strategy (OATS) experimental design technique was employed, and the surface hydrophobicity was quantified by the wetted area measurement (Taguchi 1995). OATS analysis is a useful and simple technique for analyzing process variables involved in a production process. Previous studies (Sui et al. 1994; Yeung et al. 1997; Lam and Cheng 1998) have shown that it can provide a simple and convenient way to determine the optimum condition and level of importance of different variables in a production process. The optimum process condition was obtained based on reduction of wetted area of plasma-modified fabrics. Finally, hydrophobicity of plasma-modified cotton fabric was compared with conventional water-repellency treatment by using standard evaluation methods.

EXPERIMENTAL

Materials

Plain woven cotton fabric of 129 g/m^2 with thickness of 0.031 mm was used as the substrate. The fabric was washed with 2% non-ionic detergent at pH 7 and temperature 60^oC for 30 minutes, and then rinsed in deionized water for 15 minutes. The cleaned fabric was conditioned under standard conditions of 65±2% relative humidity and 21 ± 1^oC for at least 24 hours prior to all experiments.

Atmospheric Pressure Plasma (APP) Treatment

APP treatment was imparted by an atmospheric pressure plasma jet (APPJ, Surfx Technologies LLC, Los Angeles) with a rectangular nozzle. The substrate was moved at a constant speed of 2 mm/s for exposure to the afterglow plasma generated at a radio frequency of 13.56 kHz. Helium (He) was used as the inert carrier gas. Oxygen (O_2) was the reactive gas. A schematic diagram of the experimental setup is shown in Fig. 1, and the APP treatment was conducted under standard conditions of 65±2% relative humidity and 21 ± 1^oC.

The optimum condition of hydrophobic modification of the substrate with APP treatment was determined through Orthogonal Array Testing Strategy (OATS) (Ye et al. 1987; Yin and Jillie 1987). The flow rate of the carrier gas, He, was fixed at 15 L/min.

The other four plasma variables, treatment time (*T*), ignition power (*P*), reactive gas (oxygen) concentration (*O*), and jet distance (*d*), were optimized based on selected values of variables (Table 1).

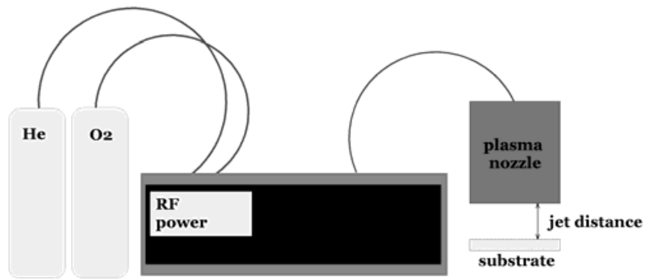

Fig. 1. Schematic diagram of He-O_2 plasma treatment on cotton fabric

Table 1. Variables and Levels Used in OATS

level	*T* (s/mm)	*P* (W)	*O* (%)	*D* (mm)
I	3	120	0.5	3
II	5	140	1	5
III	7	160	1.5	7

Ageing Effect

After atmospheric pressure plasma treatment, cotton fabrics were put into a BHT-free plastic bag in order to maintain a good storage environment (i.e. 65±2% relative humidity and 21±1^{o}C) and prevent contamination. The plastic bag with fabrics was stored inside a desiccator (silica gel) for 168 hours (one week) for ageing. After ageing, the fabrics were conditioned under standard condition of 65±2% relative humidity and 21±1^{o}C for at least 24 hours prior to further experiments.

Water Repellency Treatment

A commercial fluorocarbon-based water repellency finishing agent was used for treating cotton fabric for comparison purposes. 30g/L commercial water repellency finishing agent was prepared and was padded onto the fabric at a pressure of 2.6 kg/m^2 and padding speed of 2.5 rpm for wet-pick-up of 80%. The padded cotton fabric was completely dried in an oven at 80°C and was then cured at 150°C for 3 minutes. The treated fabric was conditioned under standard conditions of 65±2% relative humidity and 21±1°C for at least 24 hours prior to further evaluation.

Scanning Electron Microscopy (SEM)

Surface topographical modification of plasma-modified cotton fabric was analyzed with a scanning electron microscope (SEM, Model JSM-6490, JEOL Ltd., Japan).

Contact Angle Goniometry

The change of surface wettability of plasma-modified fabrics was characterized by static contact angle goniometry using the sessile drop technique with a micro-litre dispenser (GS-1200, Gilmont, Barnant Company, US). The contact angle, defined as the tangential angle at the three-phase contact point, was evaluated based on the image captured by a digital microscope (AM413T- DinoLite Pro, ANMO Electronics Corp., Taiwan). Distilled water (72.8 mN/m) with drop size 3μL was used as the probe liquid. Reported contact angle values were the average of 10 measurements for each sample.

Mass Loss Measurement

To quantify the degree of etching by plasma, the etching rate was calculated based on mass loss (Gao et al. 2009). The mass of fabric samples was weighed with an electronic semi-micro balance (CPA225, Sartorius AG, Germany). Mass loss ΔM was calculated as $(M_p - M_o)/M_o$, where M_p and M_o are mass of the plasma-modified sample and the original samples, respectively. The etching rate E (nm/s) was derived from the mass loss based on density of the cotton fabric, and it represented the changes of fabric thickness per unit treatment time.

Wetted Area Measurement

Wettability modification of the plasma-modified cotton fabric was characterized by the wetted area measurement (Wardman and Abdrabbo 2010). All experiments were carried out in a conditioned room at a temperature of 21±1°C and relative humidity 65±2%. For the wetted area measurement, a Methylene Blue liquid with concentration of 0.1g/L was used, and the drop size was 10μL approximately. The wetted area was defined as the area within the liquid boundary after complete drying in the conditioned room. Recorded wetted area was the average of 3 measurements of individual samples. The wetting behavior was quantified through the variation of the wetted area with a dye liquid expressed as reduction of wetted area $\Delta A = (A_p - A_o)/A_o$, where A_p is the wetted area of plasma-modified samples and A_o represents wetted area of the control sample.

Water Repellency Evaluation

Water repellency of cotton fabric was evaluated by AATCC test method 22-2005.

Fourier Transform Infrared Spectroscopy (FTIR-ATR)

The surface chemical composition was investigated by a Fourier transform infrared spectrophotometer (FTIR, Spectrum 100, PerkinElmer Inc., United States) equipped with a horizontal attenuated total internal reflectance (HATR) accessory, used to analyze the surface chemical composition of plasma-treated fabrics. ZnSe was used as the ATR crystal. Each spectrum was an average of 128 scans at a resolution of 4 cm^{-1}. Semi-quantitative analysis of the surface chemical modification was based on the peak height of the second order derivative spectra recorded.

RESULTS AND DISCUSSION

Hydrophobic Modification of Cotton Substrate

Wetting behavior of liquids over the fabric surface is a complex phenomenon affected by surface morphology, surface roughness, and surface chemical composition of the substrate. Surface characteristics of the plasma-modified substrate depend strongly on the nature of plasma gas and the etching condition. In this study, cotton fabrics modified with oxygen plasma with ageing effect were found to be hydrophobic.

With respect to the contact angle goniometry, the water contact angle (*WCA*) of original cotton fabric was determined to be 62.28°. Droplets of distilled water balled up on the fabric surface modified by oxygen plasma. In general, water contact angles of modified cotton fabrics were boosted by almost 100% (Table 2). In parallel, the wetted area measurement revealed a rise in hydrophobicity of modified fabrics (Table 2). The wetted area of the original fabric (A_o) was found to be 310mm^2. The wetted area of modified fabrics (A_p) using O_2 was reduced significantly.

Table 2. Contact Angle, Wetted Area and Etching Rate of Oxygen Plasma-Modified Cotton Fabrics

Run \ Control	*WCA*	Δ*WCA*(%)	A_p	Etching rate, *E* (nm/s)
Control	62.28	N/A	310 (= A_o)	N/A
1	125.51	101.5	242 (↓21.9%)	-7.40
2	124.62	100.1	82 (↓73.5%)	-21.91
3	124.50	99.9	271 (↓12.6%)	-4.54
4	123.69	98.6	211 (↓31.9%)	-1.92
5	127.42	104.6	35 (↓88.7%)	-9.85
6	128.48	106.3	151 (↓51.3%)	-11.41
7	130.55	109.6	97 (↓68.7%)	-0.99
8	129.96	108.7	277 (↓10.6%)	-2.09
9	132.95	113.5	10 (↓96.8%)	-12.05

(i) WCA (^{o}) represents water contact angles;
(ii) ΔWCA (%) represents the percentage change of water contact angle with respect to the control fabric;
(iii) A_o (mm^2) represents wetted area of control fabric;
(iv) A_p (mm^2) represents wetted area of modified fabrics; and
(v) Negative value of etching rate represents reduction of fabric thickness after etching.

FTIR analysis was employed to determine the surface chemistry of the oxygen plasma-modified fabrics. In general, oxygen is used as the reactive gas for hydrophilic modification of hydrophobic surfaces. However, oxygen plasma was considered capable of inducing hydrophobic modification of cotton fabric surface, by using the ageing effect. Firstly, there was an increment of O-H stretching at 2400-2270 cm^{-1} (Fig. 2), indicating formation of carboxylic acids via oxidation of primary hydroxyl sites (Vaideki et al. 2007). Upon ageing, the surface polarity was reversed. The evolved volatile low molecular weight hydrolyzed fragments (LMWHFs) are mobile moieties. The thermodynamic reorientation towards the bulk and sublimation in the open system of these polar moieties converted the cotton surface to be hydrophobic (Morra et al. 1989; Munro and McBriar 1988; Morra et al. 1990; Rashida et al. 2004). The residual radicals continuously reacting with the ambient environment upon storage were another factor contributing to transformation of surface polarity, and hence reducing the wettability (Molina et al. 2002; Nakamatsu et al. 1999; Wertheimer et al. 1999). Ageing of the modified fabric was determined by FTIR (Fig. 3), the increment of peaks at 2990-2850 cm^{-1} (-CH_3 and –CH_2-) and 2850-2700 cm^{-1} (-CH_3 attached to O) (Vaideki et al. 2007) indicating that formation of aliphatic hydrocarbons led to surface hydrophobicity of the modified cotton fabrics. During the plasma treatment, hydrogen gas in the ambient environment may be changed to reactive hydrogen species such as H^+ and H_2^+ under conditions of electrical initiation. The reactive hydrogen has a high level of reactivity. When these reactive species bombard the fiber surface, a free radical may be formed by eliminating an atom from a saturated compound, as shown in Scheme 1(a). However, it was postulated that the free radical on the polymer chain combines together as shown in Scheme 1(b) (Kan et al. 2004).

-C-C-H + H^+ → -C-C• + H_2^+ (Scheme 1a)

2 -C-C• → -C-C–C-C- (Scheme 1b)

As a result, carbon-carbon cross-linkages will be formed as aliphatic hydrocarbon on the fiber surface. These may impart hydrophobicity and hinder diffusion through the surface. Therefore, with the ageing effect, wetted area of oxygen plasma-modified cotton fabrics (Table 3) was reduced significantly after conditioning under relative humidity of 65 ±2% and 21 ±1°C for 168 hours.

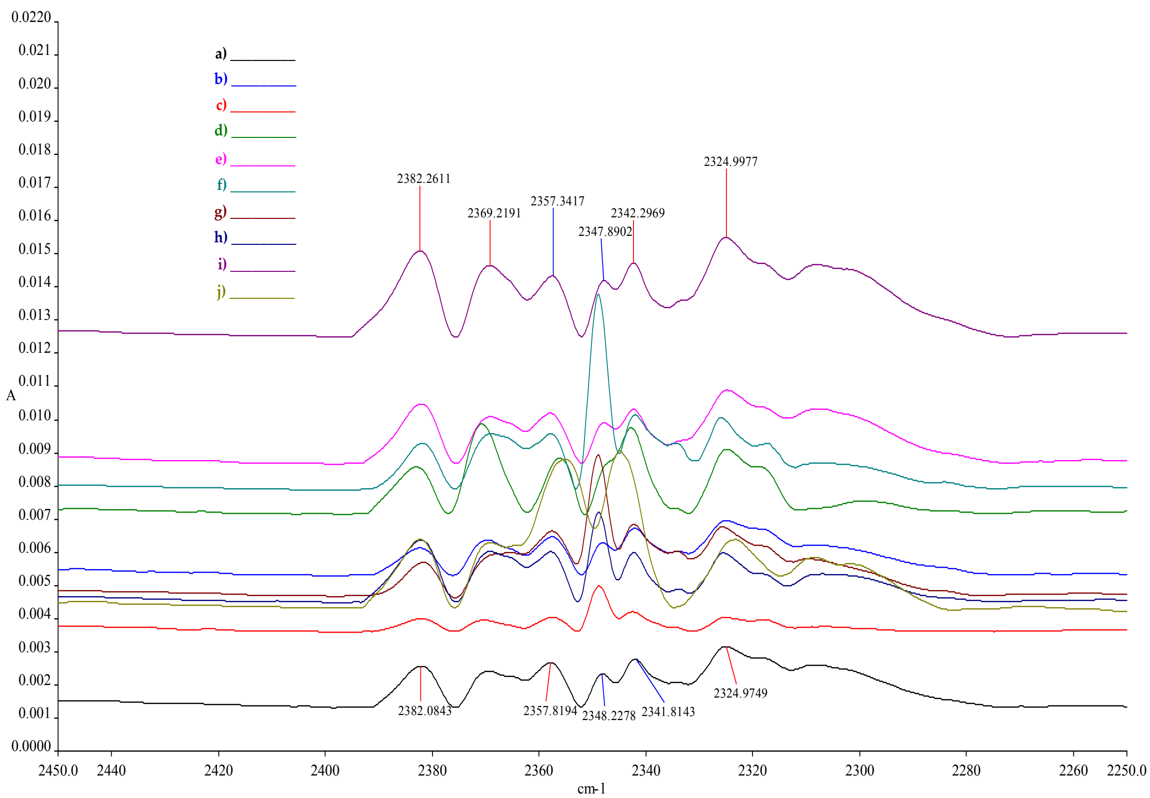

Fig. 2. FTIR spectra of oxygen plasma- modified cotton fabrics in the region of 2400-2280 cm^{-1}. Spectrum (a) represents the control fabric, while spectra (b)-(j) represent the optimisation runs 1-9, respectively.

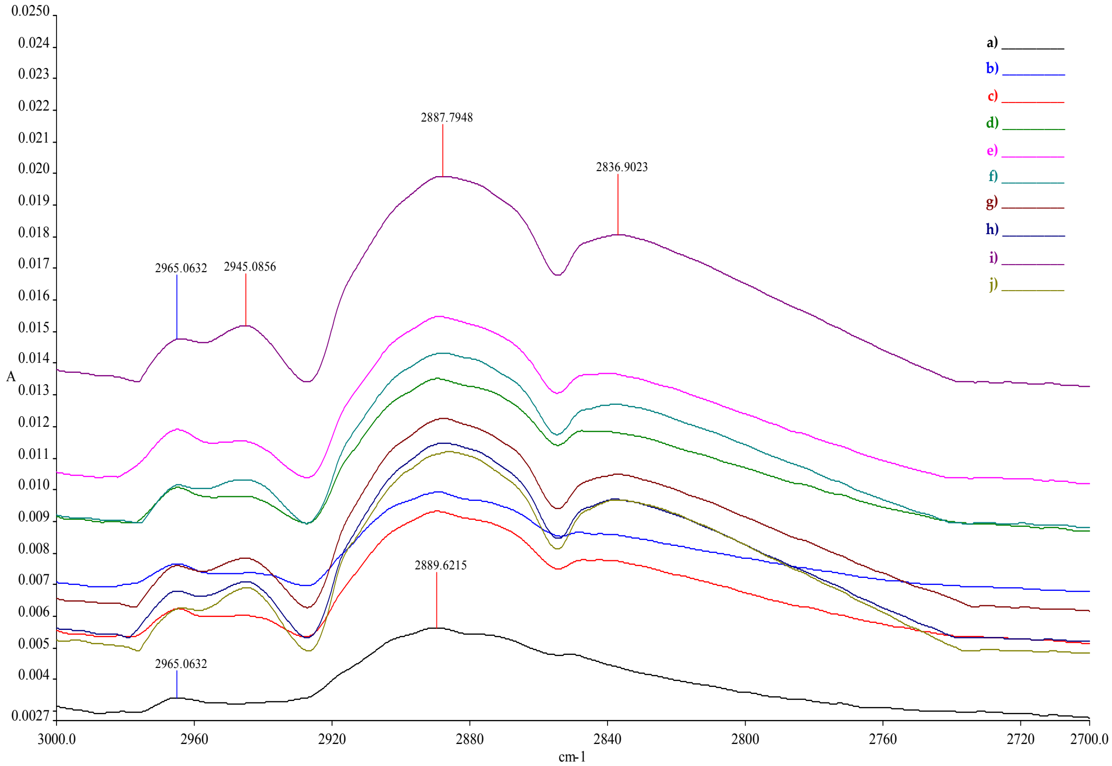

Fig. 3. FTIR spectra of oxygen plasma-modified cotton fabrics in the region of 3000-2700 cm^{-1}. Spectrum (a) represents the control fabric, while spectra (b)-(j) represent the optimisation runs 1-9, respectively.

On the other hand, surface etching is also proposed to be the prime factor contributing to the surface hydrophobicity. Original cotton fibers are ribbon-like, with micro-ridges and grooves on the surface, as shown in Fig. 4. In accordance with SEM images shown in Fig. 5, surface roughening was observed after plasma treatment. In addition, reduction of fabric thickness was found to be in nano-scale, with the depth of etching limited within 100 nm (Table 2). Surface roughening together with the ageing effect may introduce surface hydrophobicity to cotton fabrics (Rashida et al. 2004; Liu et al. 2008; Lee and Michielsen 2006).

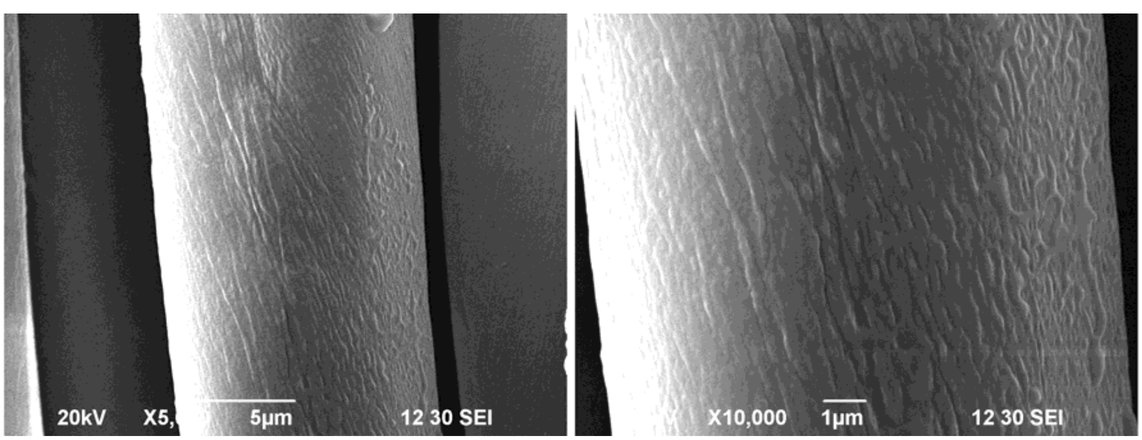

Fig. 4. SEM micrographs of original cotton fibres captured at magnification of 5,000x and 10,000x

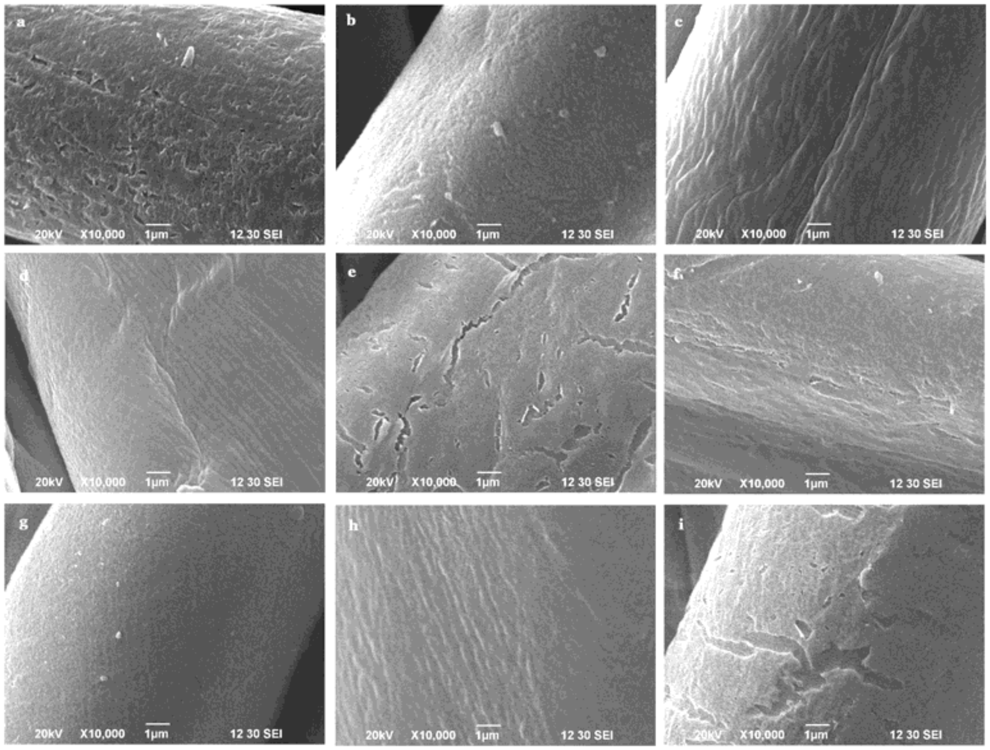

Fig. 5. SEM micrographs illustrate surface morphology of cotton fibres exposed to O_2 atmospheric pressure plasma (magnification 10,000x). Micrographs (a)-(i) represent optimisation runs 1-9, respectively.

Micro-structures forming extensive network of channels on cotton fiber surface assist horizontal wicking of liquids. When cotton fabric was exposed to oxygen plasma, ridges on the fibers were removed in most of the experimental runs, except those modified at a jet distance of 7 mm, namely, runs 3, 4, and 8. The modified fiber appeared to be similar to a duck feather (Lu et al. 2008). The reduction of surface roughness reduced horizontal wicking of the dye liquid. It was observed that some dye liquid was retained at the point of first contact, without spreading. In such cases (namely, runs 1, 5, and 9), close proximity to the jet nozzle (3 mm) eroded the fiber surface severely, developing micro-pits, as illustrated in Fig. 5. Dye liquid diffused in a radial direction through the pits. As a result, the dye liquid was localized within a small area. Macroscopically, wetted area of the modified cotton fabric was reduced. Inhibition of horizontal wicking by both reduction and increment of surface roughness introduced surface hydrophobicity on plasma-modified cotton fabrics.

Physical ablation is the predominant reaction which induces a distinctive surface morphology of the substrate. Helium carrier gas participated in ablation, while oxygen gas reacted chemically with the substrate, resulting in surface oxidation and hydrolysis of cellulosic fibers, providing an etching effect. Oxygen plasma generates a great deal of volatile low molecular weight hydrolyzed fragments which are easily removed from the substrate surface via sublimation in an open system. Simultaneously, thermal degradation induced by oxygen was severe, with respect to thermal conductivity λ of the gases. λ of oxygen is higher than that of air (Table 3).

Table 3. General Physical Properties of Oxygen (O_2) (Lide 2010-2011, Medard 2009)

Gas	Oxygen	Air
Thermal conductivity (λ) (mW/mK at 300K)	26.3	23.94 (at 0°C)
Density (ρ) (kg/m^3 under 1.0130 bar at 21°C)	1.325	1.200

Optimum Condition Analysis by Orthogonal Array Testing Strategy (OATS)

OATS, used for process optimization, is useful for design of experiments and is widely employed by scientists, researchers, and engineers (Tauguchi 1995). A complete set of factorial experiments was applied to the system to condense the expenditure in terms of tests and time. The four plasma variables investigated were treatment time (*T*), ignition power (*P*), reactive gas concentration (*O*), and jet distance (*d*), within the selected range (Table 1). A fractional factorial experimental design of the four factors (at three levels for each system) was generated accordingly for plasma hydrophobic modification of the cotton fabric. In the design, the correlations among parameters were assumed to be negligible. Detailed arrangement of experiments is shown in Table 4, and the total number of experimental trials was 9 runs.

Table 4. The OATS Analysis for Optimum Condition

	Variables				
Run	*T*	*P*	*O*	*d*	ΔA
1	I	I	I	I	-0.22
2	I	II	II	II	-0.74
3	I	III	III	III	-0.13
4	II	I	II	III	-0.32
5	II	II	III	I	-0.89
6	II	III	I	II	-0.51
7	III	I	III	II	-0.69
8	III	II	I	III	-0.11
9	III	III	II	I	-0.97
$\Sigma\Delta A_I$	-1.09	-1.23	-0.84	**-2.08**	
$\Sigma\Delta A_{II}$	-1.72	**-1.74**	**-2.03**	-1.94	
$\Sigma\Delta A_{III}$	**-1.77**	-1.61	-1.71	-0.56	
ΔA_i	*0.68*	*0.51*	*1.19*	*1.52*	sd = 0.16

(i) ΔA represents the changes of wetted area with respect to the control fabric, negative value represents reduction in wetted area;
(ii) Figure in **bold** exhibits the greatest reduction in ΔA among all values shown in the levels of different variables used while the *Italic* shows the level of importance of each variable.

When oxygen plasma treatment was used for surface hydrophobic modification of cotton fabrics with use of the ageing effect, both surface morphology and surface chemical composition are attributes of hydrophobicity of a modified substrate. The changes of wetted area, ΔA, as an indicator of the wetting behavior, are tabulated by plasma treatment conditions in Table 4. The optimum condition acquired in this study was: *T* = 7 s/mm, *P* = 140 W, *O* = 1%, and *d* = 3 mm. Statistical trend analysis, as shown in Fig. 6, reveals that the significance of dominating factors in controlling surface hydrophobicity was in the order of $d > O > T > P$.

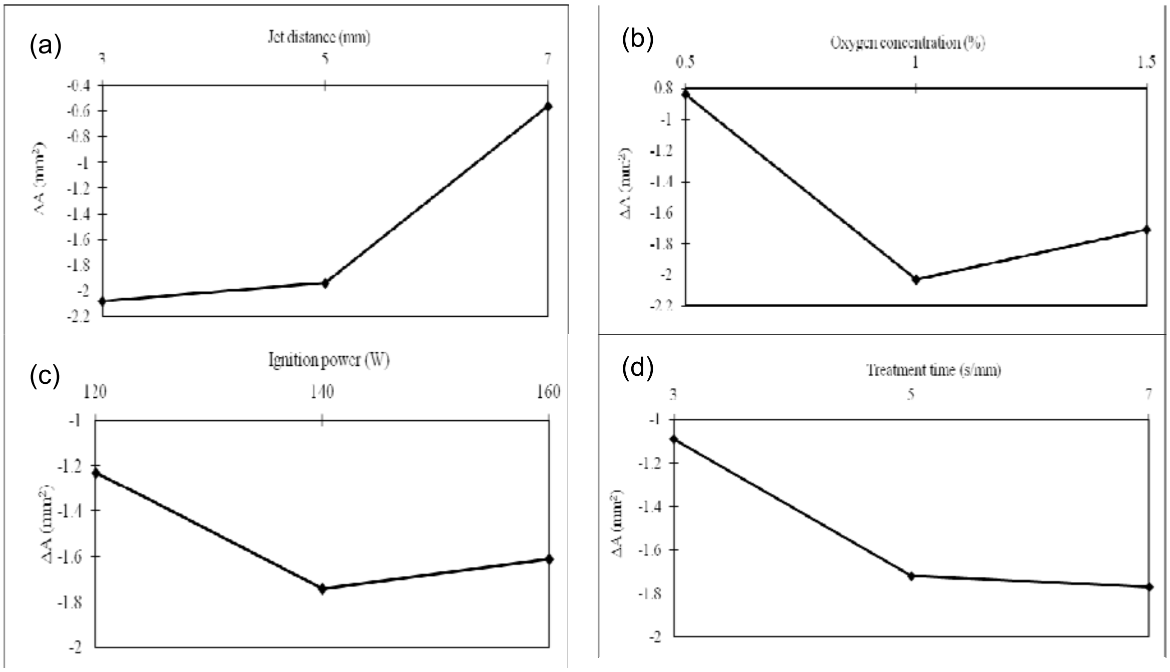

Fig. 6. Statistical trend analysis of reduction of wetted area after O_2 atmospheric pressure plasma treatment with different parameters: (a) jet distance (d), (b) concentration of O_2 (O), (c) ignition power (P), and (d) treatment time (s/mm).

Jet distance (d)

To begin with, the surface hydrophobicity was most sensitive to *d*, jet distance. The impact of jet distance on hydrophobic modification was greatly affected by density of the plasma gas. In accordance with Table 3, density of oxygen is similar to air, which is not able to occupy the entire space between the substrate and the plasma nozzle. As a result, oxygen is found to be sensitive to change of jet distance in hydrophobic modification, as illustrated in Fig. 6a. At 7 mm jet distance, there was only 20% reduction of wetted area (Fig. 6a). The plasma modification effect was reduced with an increase of jet distance (Fig. 6a). The reduction of wetted area induced by jet distance of 3 mm was the largest, while 7 mm caused the least reduction.

APPJ is a downstream treatment. Jet distance is the perpendicular distance between the plasma nozzle and the substrate located below it, as shown in Fig. 1. In general, an appropriate proximity between the plasma source and the substrate affect efficacy of active species in etching of a surface. In APP treatment, active plasma species experience a severe collision with air molecules when travelling towards the substrate surface. Velocity and energy content decrease with respect to time and distance transported. 3 mm jet distance essentially reduced the side effect of ambient collision with air, reserving most of the energy for physical ablation of substrate fibers.

With regard to SEM micrographs shown in Figs. 5a, 5e, and 5i, it can be said that the hydrophobicity is related to the change of surface structure. The micro-voids formed on the fiber surface facilitate penetration of dye into the fiber, leading to localization of wetted area of dye on the modified fabric. Physical observations are compiled and shown, along with FTIR analysis, in Table 5. Chain scission and sublimation of volatile low molecular weight oxidized fragments were determined to be most severe at 3 mm, which resulted in the high peak area when compared with other jet distances. Further increasing jet distance reduces efficacy of the two reactions. A small jet distance of 3 mm is the most effective proximity for O_2 plasma hydrophobic modification of cotton substrate.

Table 5. Correlation between Jet Distance and Hydrophobisation Evaluated by FTIR Analysis

	OC ($A \cdot cm^{-1}$)*
Control	0.2413
3mm	1.3821
5mm	1.3353
7mm	1.1699

*The peak area in the range of 3000-2300cm^{-1}; OC ($A \cdot cm^{-1}$) represents the aliphatic hydrocarbons (Vaideki et al. 2007).

Oxygen concentration (O)

The reactive concentration of oxygen, *O*, is the second crucial factor that affects the degree of hydrophobic modification. Oxygen plasma is chemically oxidative and is promising to induce surface hydrophilisation. In general, a higher degree of hydrophilisation is more prone to ageing of the oxygen plasma-modified surface (Molina et al. 2002; Nakamatsu et al. 1999; Werthimer et al. 1999). Manipulation of the degree of hydrophilisation of the substrate controls the hydrophobic modification of the aged cotton substrates. 1% O_2 led to the highest hydrophobicity of the plasma-modified cotton substrate with respect to the greatest degree of hydrophilisation. The reduction of ΔA changed with concentration of oxygen (Fig. 6b). The reversal of surface polarity was confirmed by the FTIR analysis, as shown in Table 6.

Table 6. Correlation between Oxygen Concentration and Hydrophobisation Evaluated by FTIR Analysis

	OC ($A \cdot cm^{-1}$)*
Control	0.2413
0.5%	0.6480
1%	0.6802
1.5%	0.6704

*The peak area in the range of 3000-2300 cm^{-1}; *OC* ($A \cdot cm^{-1}$) represents the aliphatic hydrocarbons (Vaideki et al. 2007).

0.5% O_2 attained the least hydrophobicity of the modified cotton substrate, and induced physical ablation predominantly with the least surface oxidation. The amount of hydrophilic groups available for ageing sequentially was found to be the least. The reduction of ΔA induced by 0.5% O_2 was not very dramatic. Though 1.5% O_2 did not induce as much oxidation as that using 1% O_2, surface morphological modification was proposed to be attributed to the significant increase in hydrophobicity of the modified fabric. Figures 5, 5c, 5e, and 5g show that the cotton fibers attained micro-ridges and grooves after treatment with 1.5% O_2 plasma. A smooth surface with hydrophobic hydrocarbons on the modified substrate surface was manifested as hydrophobic modification. A moderate oxygen concentration was most effective for O_2 plasma hydrophobic modification of cotton substrate.

Ignition power (P)

Ignition power was found to be the least effective parameter influencing hydrophobic modification of cotton fabric. Generally speaking, increasing ignition power promotes electrical discharge and hence excitation of plasma gases. In Table 7, the degree of oxidation increases with ignition power. However, the etching rate did not follow the same trend. There was a sudden drop of etching rate at high ignition, 160W. Oxidation and thermal degradation were the two surface reactions caused by O_2 plasma that led to deviations from the conventional postulation. Thermal conductivity λ of O_2 of 26.3mW/mK was higher than that of air (Table 3).

Table 7. Correlation between Ignition Power and Hydrophobisation Evaluated by FTIR Analysis and Etching Rate

	OC ($A\cdot cm^{-1}$)*	*E* (nm/s)**
Control	0.2413	N/A
120W	1.0582	-3.44
140W	1.2977	-11.28
160W	1.5314	-9.33

*The peak area in the range of 3000-2300 cm^{-1}, *OC* ($A\cdot cm^{-1}$) represents the aliphatic hydrocarbons (Vaideki et al. 2007);
** The etching rate, *E* (nm/s), represents changes of fabric thickness per unit treatment time.

The higher is the ignition power, the more profound is thermal degradation of the substrate, with respect to the higher concentration of O-containing species in the plasma; i.e. thermal degradation became more prominent with increase of ignition power. At 160 W, thermal degradation caused melting of micro- and nano-bumps formed by physical ablation. As a result, thermal degradation overwhelmed ablation, leading to deduction of surface roughness. The statistical trend analysis indicated that a moderate ignition power of 140W induced the highest degree of hydrophobic modification, as shown in Fig. 6c.

Treatment time (t)

Treatment time is also an essential parameter for controlling hydrophobic modification of cotton fabric with plasma modification. The statistical trend analysis illustrated in Fig. 6d reveals that the degree of hydrophobic modification increased with treatment time. Time is required to accumulate sufficient amount of active species on the substrate for the reaction. 3s/mm treatment time induced only a low level of oxidation. Increasing treatment time to 5s/mm and 7s/mm progressively promoted oxidation of cotton fibers, as shown in Table 8. 7s/mm induced the greatest reduction of wetted area, exhibiting the best hydrophobic modification of cotton fabric among the 3 durations of treatment employed.

Table 8. Correlation between Treatment Time and Hydrophobisation Evaluated by FTIR Analysis

	OC (A·cm^{-1})*
Control	0.2413
3s/mm	0.5292
5s/mm	1.4074
7s/mm	1.9507

*The peak area in the range of 3000-2300 cm^{-1}, *OC* (A·cm^{-1}) represents the aliphatic hydrocarbons (Vaideki et al. 2007).

Verifying the Optimum Condition

In order to verify the optimal condition for hydrophobic modification of cotton fabric using oxygen plasma, the postulated condition of plasma treatment was used in actual experimental trials. Oxygen plasma excited by 140 W radio frequency with 1% O_2 concentration for 7 s/mm at 3 mm jet distance yielded the highest surface hydrophobicity. The reduction of ΔA was found to be -0.98, which is the smallest ΔA value among the 9 runs. Therefore, the optimum condition obtained can improve hydrophobicity of cotton fabric. Surface voids induced by O_2 (Fig. 7) were determined to be the prime factor affecting dye penetration, leading to the apparently high hydrophobicity of cotton substrate. Meanwhile, Table 9 shows water repellency ratings of the control fabric and plasma-treated cotton fabrics. The oxygen plasma-modified cotton fabric achieved a rating similar to commercial water repellent agents. Since plasma treatment is a dry treatment, oxygen plasma treatment can provide an alternative way for imparting hydrophobicity in cotton fiber in an environmentally friendly manner.

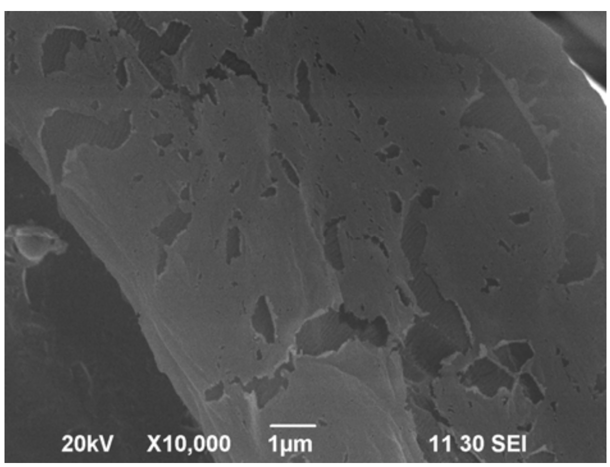

Fig. 7. Surface morphology of cotton fibres modified under optimal condition (operation parameters: 3mm, 1% O_2, 7s/mm and 140W) at 10,000x

Table 9. Water Repellency Rating

Sample	Rating
Control	0
O_2-plasma treated (under optimum condition)	90
Water repellent agent finished	90

CONCLUSIONS

1. Hydrophobic modification of hydrophilic cotton fabric through atmospheric pressure plasma using oxygen as the reactive gas together with an ageing effect was conducted. Surface roughening was proposed to be the prime factor contributed to the reduction of wetted area over the plasma-modified fabric surface. The roughening was found to be in nano-scale. In addition, the formation of aliphatic hydrocarbon on the fiber surface may impart hydrophobicity and hinder diffusion through the surface.
2. The OATS method was used for optimizing the plasma treatment, and it was noted that sensitivity of individual parameters for plasma hydrophobic modification was, in decreasing order, jet distance, oxygen concentration, treatment time, and ignition power. Parameter dependence and operational conditions for achieving optimal hydrophobic modification were identified. A short jet distance, moderate O_2 concentration, long treatment duration, and moderate ignition power were found essential for hydrophobic modification of the hydrophilic substrate. The optimal condition was determined as jet distance = 3 mm, oxygen concentration = 1% O_2, treatment time = 7 s/mm, and ignition power = 140 W.
3. In order to verify the optimal conditions for hydrophobic modification of cotton fabric using O_2 plasma, the postulated condition of plasma treatment was used in actual experimental trials. The reduction of ΔA was found to be -0.98, which was the smallest ΔA value among the 9 runs. Therefore, the optimum conditions obtained could improve hydrophobicity of cotton fabric.
4. Meanwhile, water repellency ratings of the control fabric and plasma-treated cotton fabrics showed that oxygen plasma-modified cotton fabric achieved a rating similar to commercial water repellent agents. Since plasma treatment is a dry treatment, oxygen plasma treatment could provide an alternative way of imparting hydrophobicity to cotton fibers in an environmentally friendly manner.

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