Applied Surface Science 256 (2010) 5888–5897

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Mechanical strength and hydrophobicity of cotton fabric after SF_6 plasma treatment

K. Kamlangkla[a], B. Paosawatyanyong[b], V. Pavarajarn[c], Jose H. Hodak[d], Satreerat K. Hodak[b,*]

[a] Nanoscience and Nanotechnology Program, Center of Innovative Nanotechnology, Chulalongkorn University, Bangkok 10330, Thailand
[b] Department of Physics, Faculty of Science, Chulalongkorn University, and ThEP Center, Commission on Higher Education, Bangkok 10330, Thailand
[c] Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand
[d] Department of Physics, Faculty of Science, Mahidol University, Bangkok 10400, Thailand

ARTICLE INFO

Article history:
Received 19 September 2009
Received in revised form 13 March 2010
Accepted 15 March 2010
Available online 23 March 2010

PACS:
52.77.Dq

Keywords:
Cotton
Plasma processing
Mechanical properties

ABSTRACT

Surface treatments to tailor fabric properties are in high demand by the modern garment industry. We studied the effect of radio-frequency inductively coupled SF_6 plasma on the surface characteristics of cotton fabric. The duration of the treatment and the SF_6 pressure were varied systematically. We measured the hydrophobicity of treated cotton as a function of storage time and washing cycles. We used the weight loss (%) along with the etching rate, the tensile strength, the morphology changes and the hydrophobicity of the fabric as observables after treatments with different plasma conditions. The weight loss remains below 1% but it significantly increases when the treatment time is longer than 5 min. Substantial changes in the surface morphology of the fiber are concomitant with the increased etching rate and increased weight loss with measurable consequences in their mechanical characteristics. The measured water absorption time reaches the maximum of 210 min when the SF_6 pressure is higher than 0.3 Torr. The water contact angle (149°) and the absorption time (210 min) of cotton treated with extreme conditions appear to be durable as long as the fabric is not washed. X-ray photoelectron spectroscopy analysis reveals that the water absorption time of the fabric follows the same increasing trend as the fluorine/carbon ratio at the fabric surface and atom density of fluorine measured by Ar actinometer.

1. Introduction

The finishing process in textile industry is an important step to improve the quality of the textiles. Both chemical and physical methods are commonly used to obtain the surface modifications in order to achieve various desired characteristics. Recently, the coating with nanoparticles has been developed for textile modification to enhance or to provide special properties [1,2]. However, widespread use of nanoparticles has not yet been fully tested for carcinogenic potential [3]. The conventional chemical treatment is done by soaking fabrics in solutions of chemicals, followed by drying and curing. These treatments use a large amount of chemicals and reagents that could affect adversely the environment. Also these treatments may make the fabric less durable or less comfortable to wear. Alternative techniques have been investigated over the past decades to reduce amount of chemicals on fabric surface.

Low temperature plasma processing have been extensively used in research and textile industry for investigating the surface characteristic changes of polymer materials and fabrics by various gases [4–6]. Compared to the conventional chemical methods, plasma treatments are rapid, operating in low pressure gas phase, and reducing waste generation. One crucial advantage of plasma based surface conditioning is that chemical changes are only effective to a skin depth in the nanometer scale without significantly affecting the bulk properties of fabric fibers [7]. Furthermore, various types of modifications are readily selected by the choice of the gas used to generate the plasma. The plasma driven physical and chemical surface processes can simultaneously produce etching, grafting, polymerization (cross-linking), deposition, and implantation. Therefore, plasma treatment is an alternative method that could replace many wet chemical routes which require a number of steps in the textile modification process. Many research groups have investigated on different types of plasmas and the extent of the change in physical and chemical properties of fabrics while seeking desirable qualities such as shrink resistance [8], anti-bacterial properties [9], flame retardancy [10], hydrophilicity [11], and hydrophobicity [5,6]. Plasmas of perfluorocarbons such as tetrafluoromethane (CF_4) [12], hexafluoropropylene (C_3F_6) [13],

* Corresponding author. Department of Physics, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand. Tel.: +66 086 554 5524; fax: +66 02 253 1150.
E-mail address: Satreerat.H@Chula.ac.th (S.K. Hodak).

0169-4332/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.apsusc.2010.03.070

and hexafluoroethane (C_2F_6) [14] can be used to produce -CF, -CF_2 and -CF_3 functional groups on fabric surface which lead to enhancement of the hydrophobicity of polymer and textile materials. In this work, we use sulphur hexafluoride (SF_6) as the fluorine source for hydrophobicity improvement because it is a readily available and inexpensive fluoro-containing gas which are important factors towards any viable industrial process. SF_6 is commonly used with flurocarbon gases in many industrial processes such as etching gas in plasma cleaning processes [15] and as dielectric medium in high voltage applications. It has been shown that SF_6 does not undergo undesirable polymerization reactions in the plasma [16]. Therefore, this simpler system which does not use fluorocarbon gases avoids polymer depositions and allows one to simplify analysis of the experiments by observing fluorination and etching of the cotton fabrics [15]. There have been previous studies of the use of SF_6 in plasma treatment of fabrics. It was shown that SF_6 treated thai silk and PET have enhanced hydrophobicity [17,18]. Nevertheless, not many research groups have been aware of the degrading consequences in the plasma-treated fabrics. Indeed, there are measurable changes in the mechanical properties of the treated fabrics. We have chosen cotton fabric to study the effect of SF_6 plasma on the mechanical and hydrophobic properties because cotton is widely used and naturally hydrophilic. Our goal was to find the conditions that yield the maximum hydrophobicity without significantly degrading the tensile strength for the fabric. The percentage weight loss, the tensile strength and surface morphology of treated cotton as a function of the treatment time and plasma pressure were also evaluated in order to establish the optimum conditions. The hydrophobicity of treated cotton as a function of storage time and washing cycles was also measured.

2. Experimental details

The fabric used in this study was 100% cotton fabric (120 g/m^2). The density of warp and weft was 50 ends/cm and 25 picks/cm, respectively, and the yarn count for warp and weft directions was 38 cm/g and 42 cm/g, respectively. Fragments of cotton were cleaned with dilute detergent, repeatedly washed with distilled water and dried in air atmosphere. The fabric samples were cut to the size of 14 cm × 17 cm. Then, they were heated in an oven at 80 °C for 24 h in order to remove the moisture in fabric. The sample was held horizontally stretched with the aid of a holding rectangle providing a treatment area of 225 cm^2. A schematic representation of the radio-frequency (13.56 MHz) inductively coupled plasma reactor (RF-ICP) is shown in Fig. 1. The main components of the system

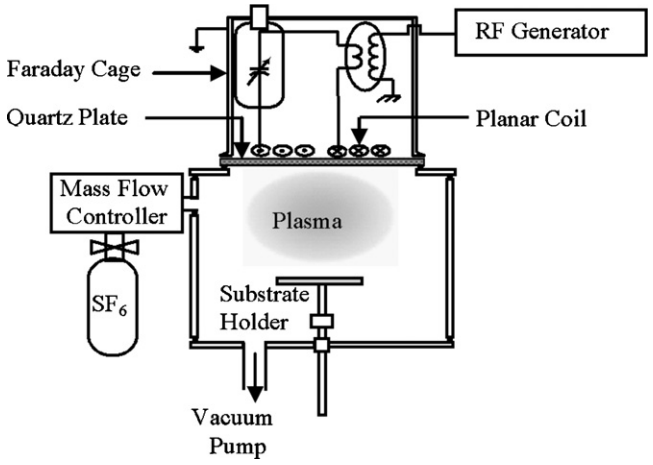

Fig. 1. Diagram of the radio-frequency (RF) inductively coupled SF_6 plasma reactor.

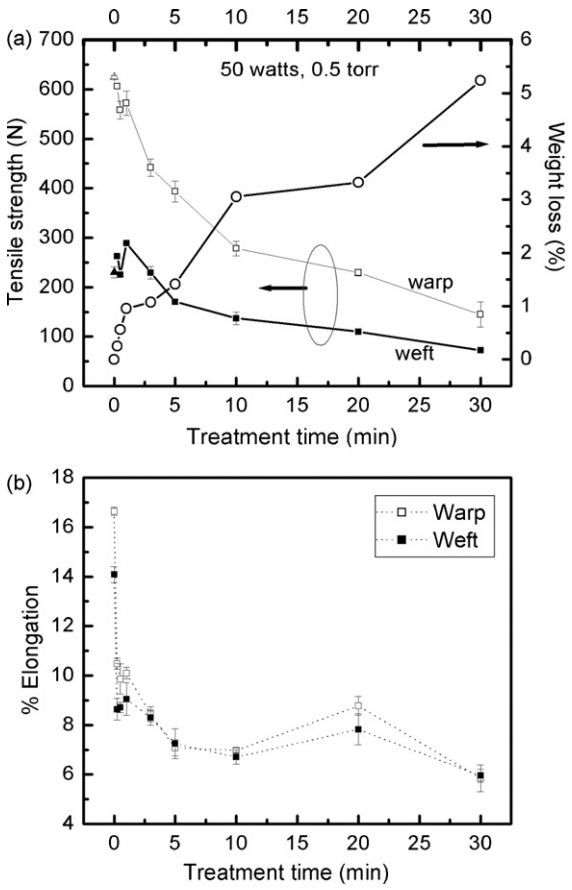

Fig. 2. (a) The weight loss, tensile strength and (b) elongation at break of fabric versus the treatment time.

consist of the cylindrical chamber of stainless steel, the RF generator, the impedance matching network, the spiral shaped antenna, and the gas supply system. The details of the reactor were described elsewhere [18]. The advantage of this RF-ICP plasma system using a planar coil is that it can produce high density and uniform plasma over a large area of fabric surface [19]. The plasma system here used in the range of 25–75 W RF power has an electron temperature during the glow discharge in the range of 2.5–4 eV with plasma density in the range of 10^{10} to 10^{12} cm^{-3} [20]. The sample was positioned parallel to the planar coil 2 cm away from the quartz window separating the chamber from the flat coil antenna. The total distance between the sample and the antenna is 4 cm. In our system, the sample was grounded and no bias was applied to the sample. To carry out the treatment the chamber was evacuated down to a pressure of 2×10^{-5} Torr using a turbo molecular pump backed by a rotary vane pump. The sample was maintained at this pressure for 30 min to allow for outgassing of any remaining moisture. Then, the chamber was filled with the desired pressure of SF_6. The samples were exposed to plasma for various treatment times in the 15 s to 30 min range with a fixed SF_6 pressure of 0.5 Torr and an RF power of 50 W. In another series of experiments, SF_6 pressures were adjusted in the 0.005–0.5 Torr range while a treatment time was fixed to 5 min. The weight of the sample was taken immediately after the plasma treatment. The weight loss of fabrics was determined from the weight difference of the initial weight of the fabric (W_i) and the weight of the fabric after exposing it to plasma (W_f) as follows:

$$\text{weight loss } (\%) = \frac{W_i - W_f}{W_i} \times 100 \quad (1)$$

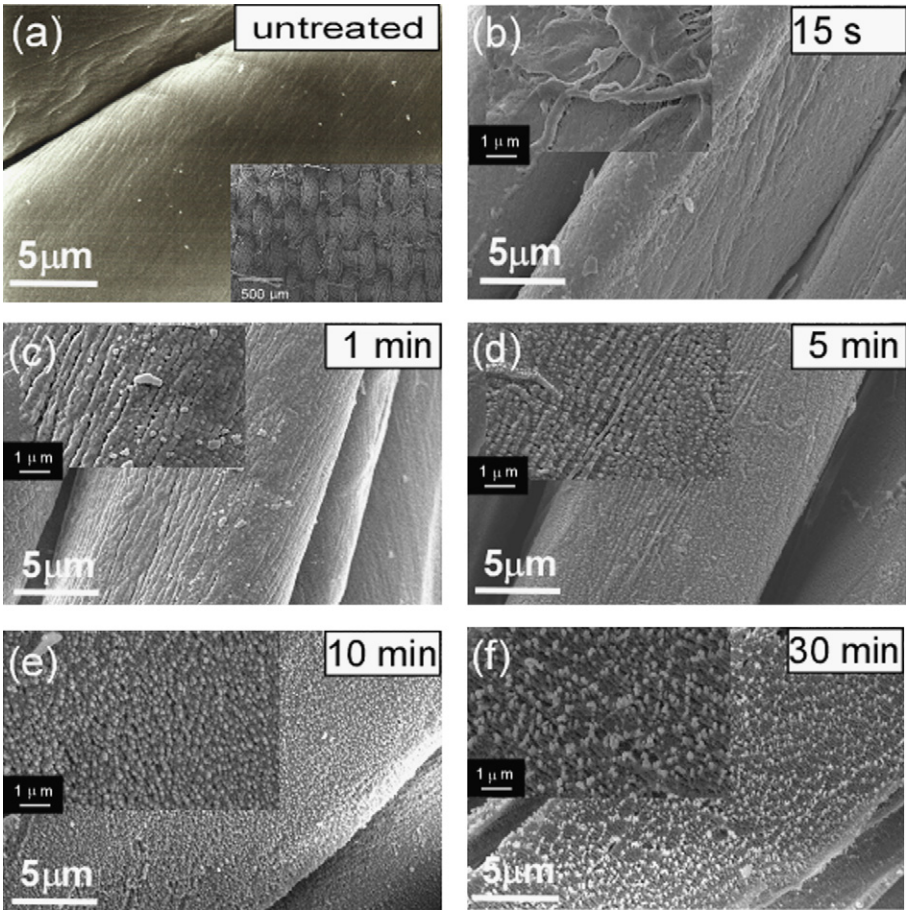

Fig. 3. SEM micrographs of cotton fabric with magnification of 5000 and 15,000. (a) Before treatment, (b) after treatment with 0.5 Torr of SF_6, and RF power of 50 W for 15 s (c) 1 min (d) 5 min (e) 10 min (f) 30 min.

The maximum force that the fabric can support before rupture is the tensile strength. The tensile strength was measured by a Lloyd's tensile tester (Lloyd LR 5K) on 5 cm × 15 cm specimens. Four measurements were taken on warp and weft directions and were averaged separately. The morphology changes of the treated fabric surface were observed by scanning electron microscopy (SEM model JEOL JSM-6400) and atomic force microscopy (AFM model Veeco Nanoscope IV). The water contact angle of treated fabrics was measured using a Tantac CAM-PLUS contact angle meter. The water absorption time was obtained by placing a 40 μl water droplet on the flat fabric surface and measuring the time required for it to be completely absorbed by the fabric. At least six measurements were averaged for each plasma treatment condition used in this work. The water droplets were laid on a circle 3 cm in radius, centered in the fabric sample. The upper limit in the absorption time was at 210 min due to the reduction of volume caused by the evaporation of the water droplet. Washing fastness tests on fresh treated fabrics were carried out using a Gyrowash (James H. Heal Co. Ltd.) according to ISO 105-C01 method [21]. Due to the surface irregularity of cotton fabric, plasma etching rate was quantified on a 120 kDa polymethyl-methacrylate (PMMA) flat film. The PMMA (Aldrich) was cast from 0.06 g/ml choloroform solution onto flat glass substrates using spin coating at a speed of 2000 rev/min. Freshly treated fabric samples were used to perform X-ray photoelectron spectroscopy experiments using Mg K_α radiation (1253.6 eV) (Kratos Analytical model AMICUS) in order to determine the changes in surface chemical composition of the treated fabrics. In situ diagnostics of the SF_6 plasma during cotton processing were carried out using the optical emission actinometry by means of a CCD spectrometer (HR4000 Ocean Optics).

3. Results and discussion

3.1. The variation of mechanical properties and morphology of cotton with exposure time to SF_6 plasma

As a result of the chemical and physical modifications produced by the plasma, the mechanical resistance of the fabrics changes. Material is also etched out from the surface of the fibers. Thus, it is important to correlate the percentage weight loss (%) with tensile strength. Results of SF_6 plasma exposure for varying times under a constant RF power of 50 W on the mechanical properties of cotton are shown in Fig. 2. The tensile strength in warp direction is higher than that in the weft direction but they follow nearly the same decreasing trend with increasing in exposure time as shown in Fig. 2a. The weight loss increased concomitantly with the reduction in tensile strength, with two clearly different loss rates. In a first stage, the combined release of moisture and etching occur leading to a pronounced outgassing which lasts ca. 1 min under our experimental conditions. The second stage, the weight loss passes through an inflection point as outgassing become dominated by a slower trend due to etching only (all the physisorbed gas and water already desorbed). The warp yarns in a fabric are stronger than the weft yarns because they are tightly stretched lengthwise. Generally, the tensile strength in warp direction is commonly used to quantify the mechanical resistance of the fabric. However, we observed a small enhancement of tensile strength in both directions for the cotton treated for moderate exposure times. This may be the result of higher fiber-to-fiber friction and thus yarn-to-yarn friction. For exposure times shorter than 1 min, the tensile strength of treated cotton is nearly constant where the initial weight loss

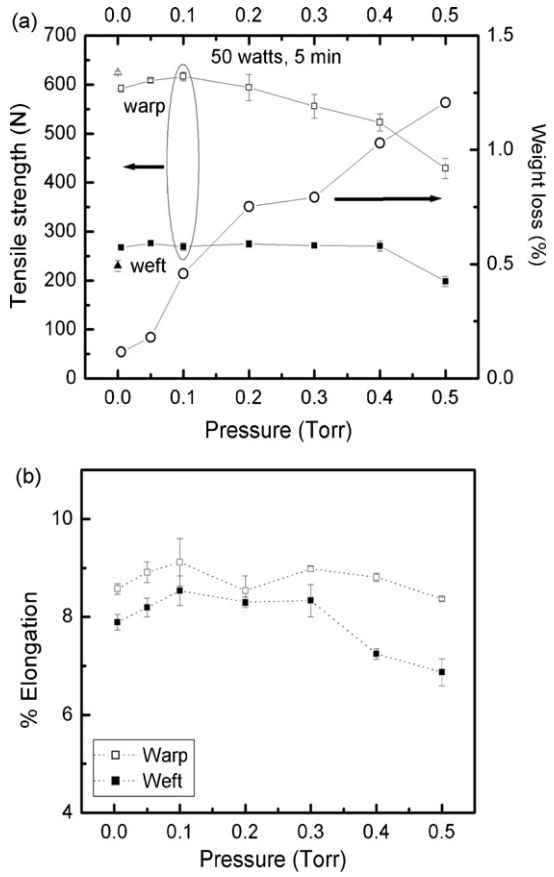

Fig. 4. (a) The weight loss, tensile strength and (b) elongation at break of fabric versus the SF_6 pressure.

process is observed. Indeed, we assign this stage to outgassing of strongly bound water molecules and other gases trapped in the fabric. The weight loss is found to be more than 1% when fabrics were exposed to plasma for more than 5 min. The results of treatment times longer than 10 min are due to a clearly different process. The measured weight loss reached 5.2% for 30 min of plasma exposure and it continues to rise for longer treatments. The percent elongation at break, calculated from the ratio of the change in the length (ΔL) of the sample to its original length (L), is plotted in Fig. 2b. These results were obtained for an SF_6 pressure of 0.5 Torr. The percent elongation at break, determining the strain on a sample when it breaks, decreases from 14% for weft direction and 17% for warp direction of untreated cotton to the values between 6% and 11%. This reduction continues for longer plasma exposure times. It is noteworthy that a small increase in percent elongation in both directions occurs for the cotton treated for exposure time of ca. 20 min. In Fig. 3, SEM images show the surface roughness of both untreated (Fig. 3a) and plasma-treated fabrics (Fig. 3b–f). The features of cotton textiles were also shown in Fig. 3a. The untreated cotton fibers were smooth, in clear contrast with the treated fibers having a granular appearance on the surface. We do not observe much difference in surface morphology of fabrics exposed to plasma for 15 s to 1 min, further supporting the hypothesis that during this stage, outgassing of adsorbed molecules is the sole source of the weight loss with the heavier loss occurring on the second stage being driven by etching the fibers which leads to the observed changes in mechanical properties and fiber morphology. Thus, for longer treatment times, the bombardment by energetic ions causes increased removal of surface materials. The roughening increases the surface area which leads to faster etching and outgassing. The etching process by bombarding high energy species creates grooves along the fibers. When the etching process continues for times longer than 5 min, the grooves become wider. The granular structure was developed at treatment times longer than ca. 10 min.

3.2. The effects of the SF_6 plasma pressure

We further investigated the effect of SF_6 pressure to the surface modification of cotton fabrics. These samples were exposed to varying SF_6 pressures in the 0.005–0.5 Torr range. Fig. 4a shows that the tensile strength of the samples treated in 0.005–0.3 Torr range remains constant for warp and weft directions at about 550 N

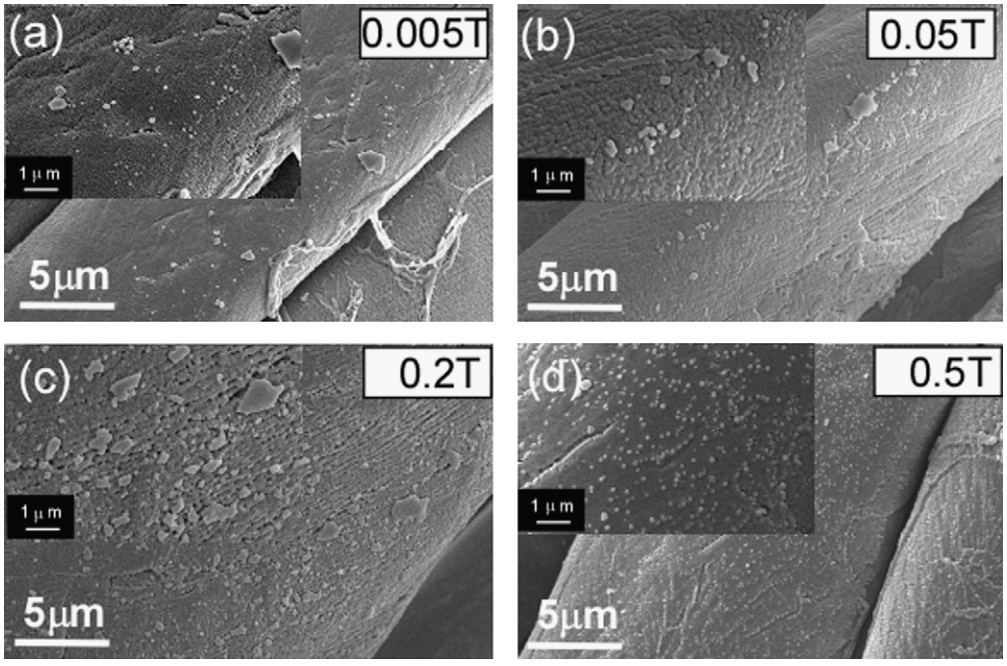

Fig. 5. SEM micrographs of cotton fabric with magnification of 5000 and 15,000. (a) After treatment for 5 min with 0.005 Torr of SF_6 (b) 0.05 Torr (c) 0.2 Torr (d) 0.5 Torr.

Table 1
Water contact angle (°) of cotton fabrics treated by SF_6 plasma for various exposure time at a fixed pressure of 0.5 Torr.

Contact angle (±5°) vs. exposure time	Storage time (week)					Washing cycle (time)				
	Con.	1	2	3	4	Con.	1	2	3	5
Untreated	0	0	0	0	0	0	0	0	0	0
15 s	145	0	0	0	0	145	0	0	0	0
30 s	145	113	108	105	102	145	0	0	0	0
1 min	146	126	123	120	117	146	0	0	0	0
3 min	147	138	135	130	126	147	0	0	0	0
5 min	148	141	139	137	135	148	20	10	0	0
10 min	149	148	147	145	142	149	85	75	50	10
30 min	149	148	147	146	145	149	120	110	100	80

Table 2
Water droplet absorption time of cotton fabrics treated by SF_6 plasma for various exposure time at a fixed pressure of 0.5 Torr.

Absorption time (min) vs. exposure time	Storage time (week)					Washing cycle (time)				
	Con.	1	2	3	4	Con.	1	2	3	5
Untreated	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
15 s	60	<0.5	<0.5	<0.5	<0.5	60	<0.5	<0.5	<0.5	<0.5
30 s	90	5	1	<0.5	<0.5	90	<0.5	<0.5	<0.5	<0.5
1 min	>210	15	10	5	2	>210	<0.5	<0.5	<0.5	<0.5
3 min	>210	60	40	35	25	>210	<0.5	<0.5	<0.5	<0.5
5 min	>210	>210	60	50	45	>210	1	<1	<0.5	<0.5
10 min	>210	>210	>210	180	180	>210	60	30	2	0.5
30 min	>210	>210	>210	>210	>210	>210	120	90	60	30

and 280 N, respectively. For these short treatments (<5 min) the weight loss slowly increases from 0.1% to 1.0% corresponding to the first stage described in the previous section. Fig. 4b shows the elongation at break after 5 min treatments with RF power of 50 W. The percent elongation at break for most samples was between 7% and 9% with the lowest values obtained at the highest pressure studied. Fig. 5 shows that no significant surface morphology changes were observed for 5 min treatments in this range of SF_6 pressure. Although, our experiments reveal only minor changes of the surface morphology observed by scanning electron microscopy for different pressure used, the etching mechanism are expected to be strongly dependent on plasma pressure especially at short treatment time [22]. Nevertheless, we have carried out the atomic force microscopy experiments on both cotton fibers and polymer flat films to have a clearer idea about plasma effects in the next section. The higher plasma density causes larger flux of bombarding ions which in turn cause proportionally faster etching of the fibers. Competing effects of chemical bonding of reactive species and the bombardment by energetic ions are expected to occur during plasma treatment. Therefore, the chemical modifications caused by plasma treatment maybe partially reverted as molecular fragments from degradation of glucose units are etched away. We believe that this is the origin of the dramatic increase in surface roughening of the fabric after extended plasma treatment. Other works reported the effect of plasma treatments based on different types of gas on tensile strength of fabrics. Yip et al. found that the tensile strength of O_2 and Ar plasma-treated nylon fabrics is not directly related to the exposure time [4]. The tensile strength decreased slightly for a short time, increased for an intermediate time and decreased after a longer time. They suggested that a shorter exposure time favors polymerization while a longer exposure time favors etching. Hwang et al. reported that the surface morphology changes of fabrics which result in increased fiber-to-fiber friction after exposing to He atmospheric pressure plasma play a major role in enhancing the tensile strength [23]. McCord et al. found that the tensile strength of nylon fabrics increased after processing with helium and helium/oxygen atmospheric pressure plasma without noticeable surface morphology changes [24]. We found that the exposure time to long treatments causes more marked changes via the etching effect even if low pressure plasma is used.

3.3. Hydrophobic properties and plasma etching rate

Tables 1 and 2 show the enhancement of hydrophobic properties quantified by the water droplet contact angle and absorption time of cotton by various exposure times from 15 s to 30 min at a fixed SF_6 pressure of 0.5 Torr. Tables 3 and 4 contains the results in hydrophobic characteristics of cotton after plasma treatments with various SF_6 pressures from 0.005 Torr to 0.5 Torr with a fixed exposure time of 5 min. The measured contact angle of the fresh-plasma-treated fabrics was about $145 \pm 5^\circ$, while the untreated cotton absorb water immediately leading to a contact angle of nearly 0°. We observed that the contact angle of the treated fabric, which varied in the 138–149° range, was not strongly sensitive to

Table 3
Water contact angle (°) of cotton fabrics treated by SF_6 plasma for various pressure at a fixed exposure time of 5 min.

Contact angle (±5°) vs. pressure (Torr)	Storage time (week)					Washing cycle (time)				
	Con.	1	2	3	4	Con.	1	2	3	5
Untreated	0	0	0	0	0	0	0	0	0	0
0.005 Torr	138	0	0	0	0	138	0	0	0	0
0.05 Torr	140	111	108	105	95	140	0	0	0	0
0.1 Torr	144	113	110	109	105	144	0	0	0	0
0.2 Torr	145	116	115	113	111	145	0	0	0	0
0.3 Torr	147	119	118	117	115	147	0	0	0	0
0.4 Torr	148	136	134	132	131	148	0	0	0	0
0.5 Torr	148	141	139	137	135	148	20	10	0	0

Table 4
Water droplet absorption time of cotton fabrics treated by SF_6 plasma for various pressure at a fixed exposure time of 5 min.

Absorption time (min) vs. pressure (Torr)	Storage time (week)					Washing cycle (time)				
	Con.	1	2	3	4	Con.	1	2	3	5
Untreated	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
0.005 Torr	47	<0.5	<0.5	<0.5	<0.5	47	<0.5	<0.5	<0.5	<0.5
0.05 Torr	61	5	3	2	0.5	61	<0.5	<0.5	<0.5	<0.5
0.1 Torr	120	30	20	10	5	120	<0.5	<0.5	<0.5	<0.5
0.2 Torr	150	35	30	20	15	150	<0.5	<0.5	<0.5	<0.5
0.3 Torr	>210	40	35	30	22	>210	<0.5	<0.5	<0.5	<0.5
0.4 Torr	>210	60	50	45	30	>210	<0.5	<0.5	<0.5	<0.5
0.5 Torr	>210	>210	60	50	45	>210	1	<1	<0.5	<0.5

the different plasma conditions. However, it is difficult to compare the hydrophobicity of fabrics as a function of plasma conditions by only using contact angle data due to large errors of these measurements associated with roughness and irregularity of the surfaces. Thus we use the water absorption times as a robust measurement of hydrophobicity. Longer exposure times cause a corresponding increase in the absorption time from 0 to beyond our limiting time (210 min). The SF_6 plasma fired at pressures higher than 0.3 Torr was more effective in increasing absorption time. This is due to a larger concentration of fluorinating species and their shorter mean free path, increasing the rates of ionization radical formation and fluorination reactions. We further checked the durability in terms of aging and washing fastness. After keeping the samples at 20 °C and the relative humidity of 65% for 1–4 weeks, the contact angles of cotton treated for longer time than 30 s decreased by less than 30% but remained higher than 100° (see Table 1). Surprisingly, after exposure to SF_6 plasma for 30 min, the contact angle of treated cotton was still close to 100° (see Table 1) and the absorption time was 30 min after washing up to five cycles (see Table 2). When the exposure time is less than 5 min, after one washing cycle the fabrics became hydrophilic. The best hydrophobic durability was obtained in the cotton fabric treated for 30 min in which the contact angle was close to 100° after five washing cycles. As seen in Table 3, with the increase of SF_6 pressure, the contact angle and absorption time slowly increased. The cotton samples treated at higher pressure than 0.1 Torr still exhibited the contact angles larger than 100° during 4 weeks of aging. After three washing cycles, the contact angle of cotton treated for 5 min in the highest SF_6 pressure used of 0.5 Torr was not measurable and the absorption time reduced to values (< 0.5 min) comparable to those for untreated cotton (see Table 4). It seems that the hydrophobicity of cotton treated with extreme conditions appears to be durable as long as the fabric is not washed. Similar results have found by other groups [13,25]. Li et al. have found that the fluorine/carbon (F/C) ratios decreased after washing treated cotton [13]. Selli et al. have reported that the F/C ratio in poly(ethylene terephthalate) sample treated under RF power of 20 W significantly decreased from 0.32 to 0.14 after 30 days storing where as the O/C ratio did not change with aging [25]. They observed a slightly decrease in F/C for the PET samples treated at higher RF power along with unchanging hydrophobicity. It was suggested that the surface interactions on various types of fabrics might be different due to the nature of the fabrics and different generated functional groups [13].

We measured the root mean square (RMS) surface roughness from atomic force microscopy images of individual fibers. The surface topography of untreated and treated cotton fibers with different plasma conditions are shown in Fig. 6a–f, respectively. The RMS roughness of cotton increased from 5 nm to 8–20 nm after plasma treatment. With the increase in treatment time from 1 min to more than 5 min, the RMS seems slightly increased. We found that RMS decreases with the increase in SF_6 pressure. The surface roughness is involved in the so-called lotus effect of certain plant leaves in which the summits on the leaf surface support a water droplet. The surface of the hydrophobic natural plant leaves consists of an array of needles that range from 5 to 100 μm in length with separations ranging from 5 to 200 μm [26]. Our results in Fig. 6b–f show that the height and the distance between the granuli created by plasma etching are in the range of 50–200 nm and 200–500 nm, respectively, roughly three orders of magnitude smaller than those found in water repellent plant leaves. These surface irregularities are incommensurate with the site of macroscopic water droplets. Therefore, in our case we believe that it is unlikely that the roughening makes any contribution to the improved hydrophobicity that we observe for our treated samples. By way of comparison of the flat surface morphology and the etching rate in our process, we exposed a polymethyl-methacrylate (PMMA) film to SF_6 plasma with the same conditions as cotton. We note that even PMMA does not have the same chemical composition as cellulose, a fraction loss of the film could be a crude approximation for determining the plasma etching rate of cotton fabric. The molecular weight of the PMMA used (120 kDa) was chosen for sake of comparison with the work by others [27]. Fig. 6g–l shows AFM images of untreated and treated PMMA films under the same SF_6 plasma conditions as cotton. The decrease in RMS of treated cotton with the increase in SF_6 pressure is in clear contrast with the results found for PMMA. The inconsistency is most likely due to the difference of flatness between PMMA and cotton surface. We found that process of plasma etching at higher conditions (see Fig. 6i and j) creates the granuli on the surface causing the increase of the Rms roughness from 0.29 nm to 2.55 nm and 4.27 nm, respectively. Some fraction of the film was scraped away to obtain the thickness of each film before and after plasma etching using the atomic force microscopy (AFM) measurements. An initial thickness of PMMA polymeric film was found to be 1–4 μm depending on the number of layers deposited. After an exposure to SF_6 plasma, the thickness was reduced from which we extracted the average etching rate shown in Fig. 7a–c. In these experiments, we varied the exposure time, the RF power and the SF_6 pressure. The etching rate of the film treated for 1 min was only 23 nm/min while the etching rate after 5 min was on the order of 100 nm/min. We conclude that < 1 min is the time (with fixed RF power of 50 W and fixed pressure of 0.5 Torr) where no changes in surface morphology of cotton and PMMA films were seen. At high RF power (50–100 W) and high pressure (0.4–0.5 Torr), a high etching rate of ~100 nm/min was obtained. Since the sample holder is connected to ground, the sample is subjected to plasma potential only. This could be due to some capacitive coupling with the antenna resulting in high energy ion bombardment.

3.4. Chemical modifications

The changes in chemical composition of the cotton surface were readily observed by X-ray photoelectron spectroscopy. Fig. 8 shows XPS survey spectra of untreated cotton and cotton treated at different plasma conditions. The samples exhibit the F1s signal after processing with plasma, with intensities rising as the SF_6 pres-

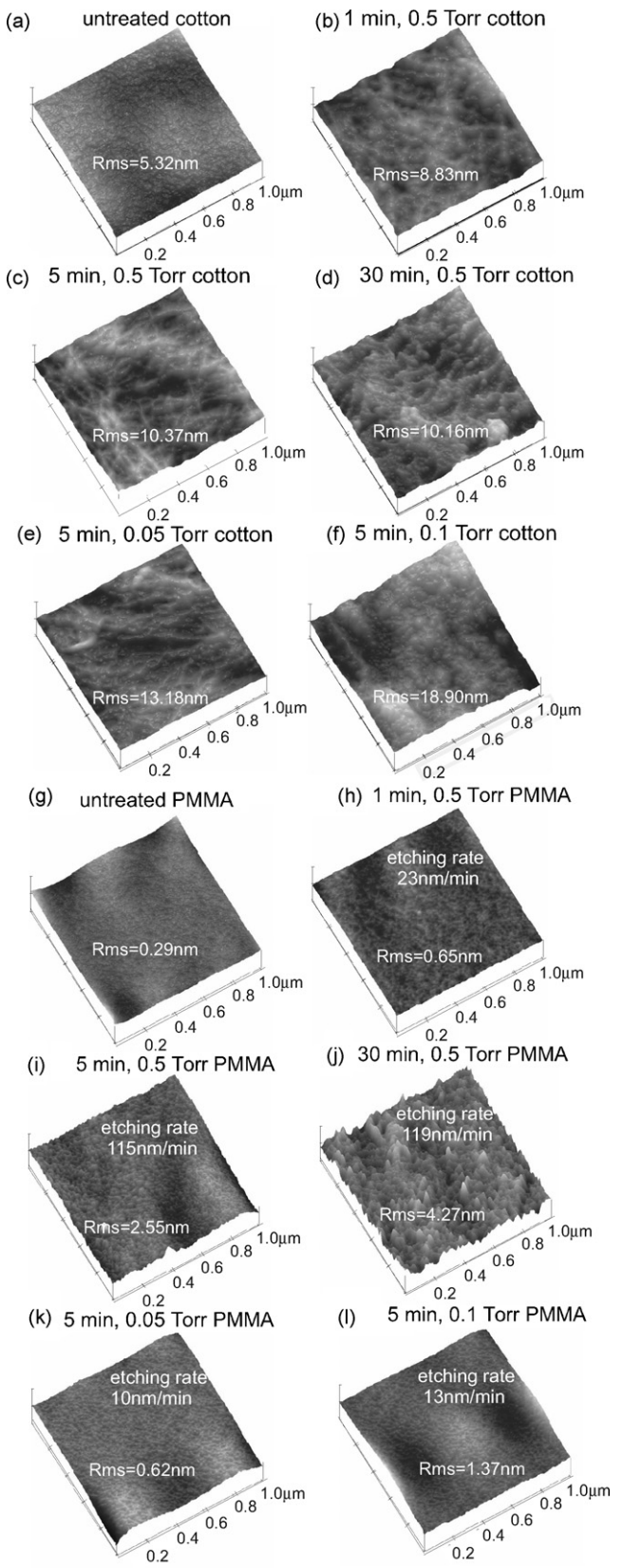

Fig. 6. AFM images 1 μm × 1 μm of cotton fibers and PMMA films. (a) Untreated cotton; (b) 1 min with 0.5 Torr (cotton); (c) 5 min with 0.5 Torr (cotton); (d) 30 min with 0.5 Torr (cotton); (e) 5 min with 0.05 Torr (cotton); (f) 5 min with 0.1 Torr (cotton); (g) untreated PMMA film; (h) 1 min with 0.5 Torr (PMMA film); (i) 5 min with 0.5 Torr (PMMA film); (j) 30 min with 0.5 Torr (PMMA film); (k) 5 min with 0.05 Torr (PMMA film); (l) 5 min with 0.1 Torr (PMMA film).

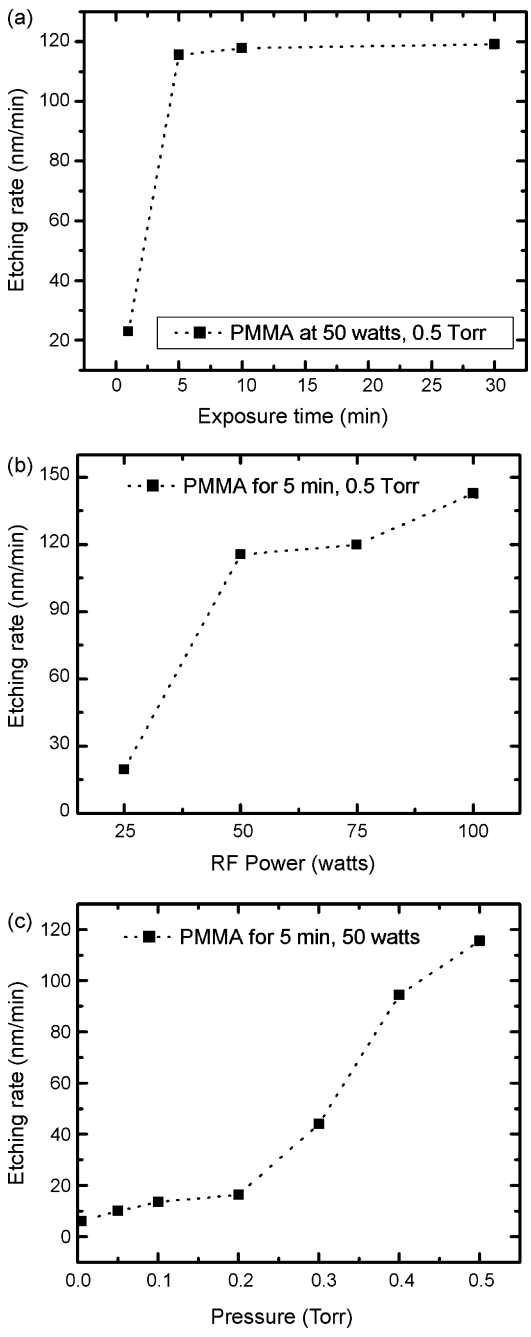

Fig. 7. Etching rate of PMMA films versus (a) exposure time; (b) RF power and (c) SF_6 pressure.

sure and exposure time increased. In contrast, the peak area for C1s and O1s signals decreased with increasing pressure and exposure times. The structure of cellulose consists of glucose molecules linked together as shown in Fig. 9a. In this structure, there are three different types of carbon atoms, i.e. the C1s XPS spectra of untreated cotton should exhibit three distinct peaks corresponding to three different binding energies [28] as shown in Fig. 9a. The signal with binding energy at 284.7 eV (C1) in our data was assigned to carbon atom bound to a carbon atom or a hydrogen atom (C–C/C–H), the peak at 286.2 eV (C2) corresponds to C–OH groups and the peak at 287.2 eV (C3) arises from O–C–O groups. Fig. 9b shows the XPS spectra of cotton treated for 1 min at a SF_6 pressure of 0.005 Torr and RF power of 50 W. On the treated cotton, the XPS data shows distinct signals at 289.1 eV which is assigned to the CF moiety. The

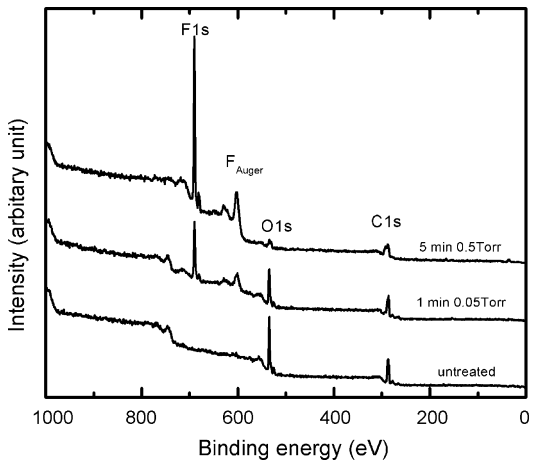

Fig. 8. The XPS spectra for untreated and SF_6 plasma-treated cotton.

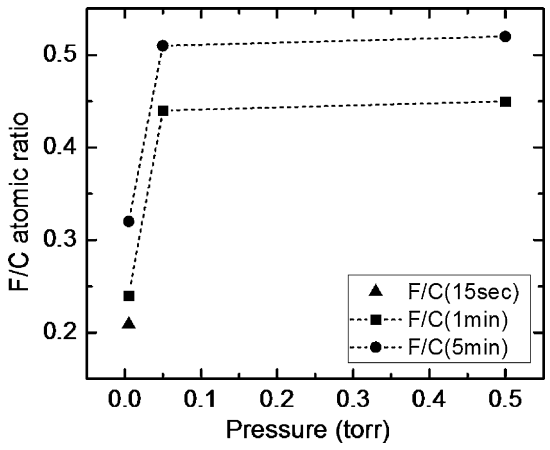

Fig. 10. F/C atomic ratios of cotton treated at different treatment time and pressures (0.005, 0.05 and 0.5 Torr).

signals from pristine cotton are still evident on the spectra of the treated samples consistent with incomplete surface fluorination. In general, more pronounced changes are observed for cotton treated with high SF_6 pressure of longer exposure times (Fig. 9c and d). In particular, additional peaks become apparent at a binding energies of 291 eV and 293.5 eV. These signals are attributed to CF_2 and CF_3 groups, respectively. In summary, more intense treatments produce a greater fraction of fluorine bonds as evidenced by the increasing of total integrated areas of CF, CF_2 and CF_3 peaks.

From XPS spectra, we conclude that only F radicals are responsible for the surface chemical changes. The mechanism of fluorination relevant to our experiment is concerned with the chemistry of SF_6 discharges consisting of ionizations, dissociations, attachments, detachments, and recombinations of charged and neutral species [29,18,30]. The XPS chemical analysis revealed that only the $F^{\bullet}$ is the active species that graft onto the fabric surface producing C–F bonds after abstraction of H and O atoms by other plasma species (ions, radicals, electrons and photons) [18]. We found that the water absorption time of the fabrics reaches the highest (210 min) when the F/C ratio at the surface reaches 0.5, along with a small decrease of the O/C ratio. The calculation is based on the integrated area under the assigned C1s and F1s deconvolution peaks with sensitive factors for XPS transition. Fig. 10 shows the F/C atomic ratios of cotton treated for different treatment time and pressures. The F/C atomic ratios slightly increase with treatment time but significantly increase with SF_6 pressure. Thus, the most important factor in enhancement of the hydrophobicity of treated cotton is the pressure. Our results agreed with the previous work on silk [18]. The number of hydrogen bonds between water molecules and surface groups of treated cotton are smaller causing the hydrophobicity [18].

We estimated the yield of fluorine species using an Ar actinometer by introducing 5% of Argon in the chamber atmosphere and monitoring the optical emission of F and Ar. To convert the emission intensities to atom density of fluorine or fluorine concentration

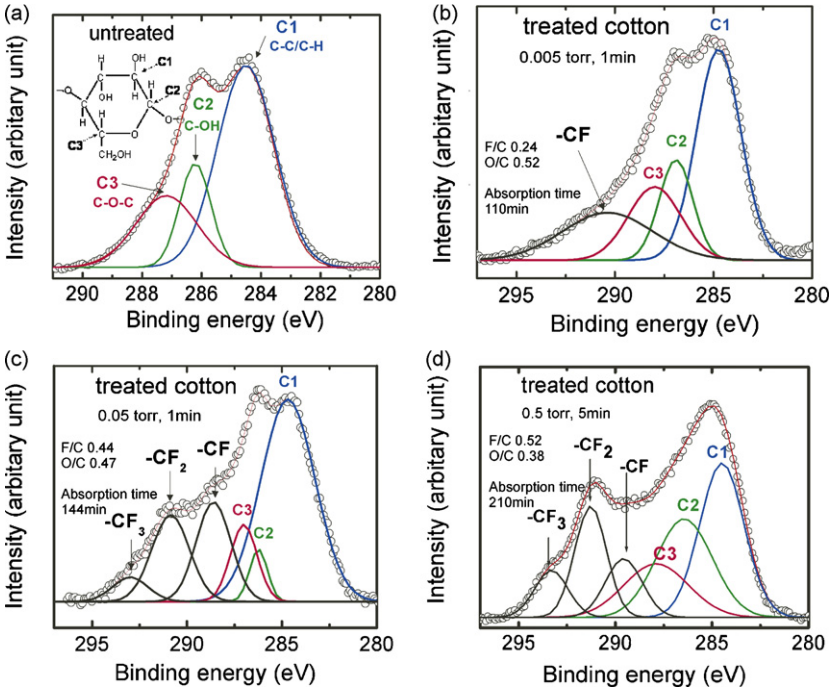

Fig. 9. C1s XPS spectra of fabric surface. (a) Untreated cotton and the molecular structure of cellulose; (b) cotton treated at the pressure of 0.005 Torr for 1 min; (c) cotton treated at the pressure of 0.05 Torr for 1 min; (d) cotton treated at the pressure of 0.5 Torr for 5 min.

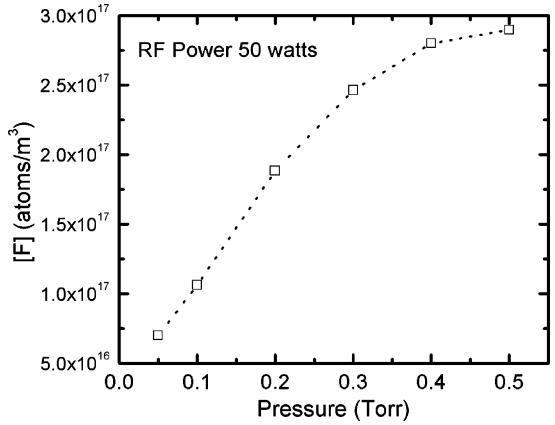

Fig. 11. Fluorine atom density as a function of SF_6 pressure at the fixed RF power of 50 W.

using a known Ar concentration, we used Eq. (2)[15];

$$[F] = \frac{2[Ar]I_F}{I_{Ar}} \quad (2)$$

where I_F is the intensity of the 704 nm F emission line, I_{Ar} is the intensity of the 750 nm Ar emission line [31], [Ar] is a known concentration of the actinometer and 2 is a proportionality constant. Fig. 11 show the fluorine concentration as a function of pressure. The F atom density increased with increasing SF_6 pressure, which is consistent with the increased etching rates observed at higher SF_6 pressures.

3.5. Weight losses due to surface damages

A mass spectrometry study on piranoses and disacharides showed that inductively coupled plasma induced fragmentation primarily leads to loss of formaldehyde (CH_2O) and water as shown in Fig. 12[32]. Formaldehyde arises from the loss of C6 consistent with our results of loss of C1 signal upon treatment. Water is produced from dehydration at position 1,2 in the glucose ring leading to the formation of (a double bond) 1,2-dehydroglucose. Both chemical changes lead to a smaller surface density of OH groups and therefore they render the surface less hydrophilic. Further fragmentation occurs leading to the loss of CH_2O. Carbon dioxide and numerous charged fragments with 2–5 carbon atoms are also observed. It has been proposed that the glycosyl bond is easily broken in the plasma [32]. The loss of an entire terminal piranose ring also give rise to small charged fragments and molecules by decomposition. A crucial characteristic of the plasma induced (ionization-fragmentation) processes in pyronoses is that the large energy of the plasma species causes pronounced fragmentation as evidenced by the low abundance the molecular ion. In the case of pyrolysis of cellulose and other glucanes, other fragments have been identified but in the main losses as acetic acid, formic acid, H_2O and glycolaldehyde [33]. Most likely pyrolysis will significantly alter the appearance of the fabrics and their mechanical properties. We believe that only mild modification occurs without pyrolysis setting in during our plasma treatment. Since the final appearance of the fabrics is nearly identical to that before plasma exposure.

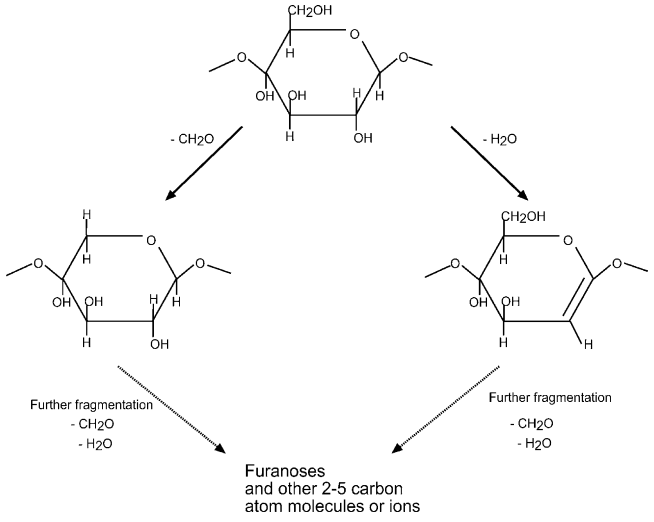

Fig. 12. Main fragmentation losses.

4. Conclusions

The etching effect is strongly related to changes in physical property change such as the weight loss and tensile strength. The tensile strength of fabrics decreases as the treatment time and SF_6 pressure increases resulting from etching process. The exposure time plays an important role in the change of mechanical properties of fabric with the SF_6 pressure having secondary effects. In conclusions, we did not observe dramatically surface morphology changes from SEM images for the cotton owning the weight loss less than 1%. A two-stage weight loss was observed which was attributed to desorption and fragmentation of surface molecule respectively. Overall good and durable hydrophobic properties on cotton can be achieved only for the longer treatments used but the mechanical strength of the fabrics are compromised to a significant extent. We found that the optimal plasma conditions to enhance hydrophobicity without losing tensile strength and weight of fabric is in the pressure range of 0.005–0.3 Torr or the treatment time less than 1 min, but with less hydrophobic durability in terms of aging and washing cycles. The main reaction for the enhancement of hydrophobicity by means of contact angle and water absorption time is surface fluorination of the fabric confirmed by X-ray photoelectron analysis.

Acknowledgements

The authors are grateful to National Research Council of Thailand (NCRT), Commission on Higher Education, and The 90th Anniversary of Chulalongkorn University Fund (Ratchadaphiseksomphot Endowment Fund) for the financial support. We thank Mr. Pichitpol Charoensuppayanan from the Faculty of Fashion and Textile Design, Rajamangala University of Technology Phra Nakhon for the help of tensile strength measurement. We thank Mr. Sirawat Seaning for assistance with AFM measurement. We also thank Dr. Jose H. Hodak for valuable discussions about plasma induced fragmentation.

References

[1] M. Yu, G. Gu, W.D. Meng, F.L. Qing, Appl. Surf. Sci. 253 (2007) 3669–3673.
[2] H.Y. Yang, S.K. Zhu, N.J. Pan, Appl. Polym. Sci. 92 (2003) 3201–3210.
[3] A. Nel, T. Xia, L. Madler, N. Li, Science 311 (2006) 622–627.
[4] J. Yip, K. Chan, M. Sin, K.S. Lau, J. Mater. Process. Technol. 123 (2002) 5–12.
[5] C-M. Chan, Polymer Surface Modification and Characterization, Hanser, Munich, Germany, 1994.
[6] U. Vohrer, M. Muller, C. Oehr, Surf. Coat. Technol. 98 (1998) 1128–1131.
[7] H.U. Poll, U. Schladitz, S. Schreiter, Surf. Coat. Technol. 489 (2001) 142–144.
[8] A. Hesse, H. Thomas, H. Hocker, Textile Res. J. 65 (6) (1995) 355–361.
[9] W. Zhang, Y. Luo, H. Wang, J. Jiang, S. Pu, P.K. Chu, Acta Biomater. 4 (6) (2008) 2028–2036.
[10] M.J. Tsafack, J. Levallois-Grutzmacher, Surf. Coat. Technol. 201 (2006) 2599–2610.
[11] M.M. Hossain, A.S. Herrmann, D. Hegemann, Textile Res. J. 65 (6) (2006) 299–307.
[12] S. Sigurdsson, R. Shishoo, J. Appl. Polym. Sci. 66 (1997) 1591–1601.
[13] S. Li, D. Jinjin, Appl. Surf. Sci. 253 (2007) 5051–5055.
[14] D. Sun, G.K. Stylios, J. Mater. Process. Technol. 173 (2006) 172–177.

[15] E. Gogolides, C. Boukouras, G. Kokkoris, O. Brani, A. Tserepi, V. Constantoudis, Micro. Electron. Eng. 73–74 (2004) 312–318.
[16] M. Strobel, S. Corn, C.S. Lyons, G.A. Korba, J. Polym. Sci. 25 (1987) 1295–1307.
[17] B. Paosawatyanyong, T. Supasai, V. Pavarajarn, S.K. Hodak, Int. Polym. Process. 13 (2008) 135–139.
[18] S.K. Hodak, T. Supasai, B. Paosawatyanyong, K. Kamlangkla, V. Pavarajarn, Appl. Surf. Sci. 254 (2008) 4744–4749.
[19] T. Munsat, W.M. Hooke, S.P. Bozemann, S. Washburn, Appl. Phys. Lett. 66 (17) (1995) 2180–2182.
[20] B. Paosawatyanyong, J. Sci. Res. Chula. Univ. 29 (2) (2004) 199–212.
[21] Textile test for colour fastness to washing, International Standard ISO 105-C01, 1989.
[22] G. Poletti, F. Orsini, A.R. Addamo, C. Riccardi, E. Selli, Appl. Surf. Sci. 219 (2003) 311–316.
[23] Y.J. Hwang, M.G. McCord, Textile Res. J. 75 (11) (2005) 771–778.
[24] M. McCord, Y. Hwang, P. Hauser, Y. Qui, J. Cuomo, O. Hankins, M. Bourham, L. Canup, Textile Res. J. 72 (6) (2002) 491–498.
[25] E. Selli, G. Mazzone, C. Oliva, F. Martini, C. Riccardi, R. Barni, B. Marcandalli, M.R. Massafra, J. Mater. Chem. 11 (2001) 1985–1991.
[26] P. Wagner, R. Furstner, W. Barthlott, C. Neinhuis, J. Exp. Bot. 54 (385) (2003) 1295–1303.
[27] G. Kokkoris, N. Vourdas, E. Gogolides, Plasma Process. Polym. 5 (2008) 825–833.
[28] M.G. McCord, Y.J. Hwang, Y. Qiu, L.K. Hughes, M.A. Bourham, J. Appl. Polym. Sci. 88 (2003) 2038–2047.
[29] F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, Wiley, New York, 1988.
[30] G. Kokkoris, A. Panagiotopoulos, A. Goodyear, M. Cooke, E. Gogolides, J. Phys. D: Appl. Phys. 42 (2009) 055209.
[31] National Institute of Standard and Technology, NIST Atomic Spectra Database, 2003. Available from: http://www.physics.nist.gov/cgi-bin/ASD/line1.pl.
[32] V.F. Taylor, R.E. March, H.P. Longerich, C.J. Stadey, Int. J. Mass Spectrom. 243 (2003) 71–84.
[33] R.J. Evans, D. Wang, F.A. Agblevor, H.L. Chum, S.D. Baldwin, Carbohydr. Res. 281 (1996) 219–235.