

# Enhancement of the hydrophobicity of silk fabrics by SF<sub>6</sub> plasma

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## Abstract

Hydrophobic properties are of interest in fabric and textile manufacture. We have used radio-frequency inductively coupled SF<sub>6</sub> plasma to modify the surface of Thai silk fabrics for the enhancement of the hydrophobic property. The water contact angle of fabrics increased from 0° up to 145° after SF<sub>6</sub> plasma treatment. The measured water absorption time was found to depend upon the treatment time and RF power, for SF<sub>6</sub> pressures lower than 0.05 Torr. At higher SF<sub>6</sub> pressures, all samples achieved absorption times in excess of 200 min, regardless of the treatment time and RF power. The morphology changes of fabrics after plasma treatment were characterized by scanning electron microscopy and atomic force microscopy. After plasma treatment, the RMS surface roughness of the fibres increased from about 10 to 30 nm. From X-ray photoelectron microscopy analysis, we found that the hydrophobicity of the fabrics is the highest when the fluorine/carbon ratio at the surface increases. A small decrease of the oxygen/carbon ratio was also observed on the fabrics that showed the longest absorption times.

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## 1. Introduction

The finishing process in textile industry is an ever evolving field where enhancing special fabric properties are constantly sought. The desirable qualities are shrink resistance, flame retardance, anti-bacterial properties, hydrophilicity, and hydrophobicity among others [1,2]. Dip-coating and padding with chemicals are the most commonly used processes to achieve these goals. However, these chemical methods are not always environmentally friendly. Chemical treatments may also produce changes in the mechanical properties of the fabric which makes them less comfortable to wear. Plasma treatment is a rapid, and environmentally amenable method to achieve surface modifications without significant effects in the bulk of the fabric fibres. Indeed, the plasma process can be used to modify surface of fabric to a skin depth in the nanometer scale [3]. Another attractive aspect of plasma-based surface treatments results from the effects of using different gases

[4] to produce the plasma. The use of dry treatments shorten the processing times. Thus, plasma treatment is an innovative method which could replace wet chemical application to modify the surface properties of polymers and textile materials. The plasma driven processes of inducing physical and chemical surface changes such as etching, grafting, implantation, polymerization, and crosslinking take place simultaneously. Several research groups have investigated enhancement in hydrophobicity of fabrics and polymers using plasmas of perfluorocarbons such as tetrafluoromethane (CF<sub>4</sub>) [5], hexafluoropropylene (C<sub>3</sub>F<sub>6</sub>) [6], and hexafluoroethane (C<sub>2</sub>F<sub>6</sub>) [7]. Li and Jinjin [6] confirmed the presence of –CF, –CF<sub>2</sub> and –CF<sub>3</sub> groups on fabric surface treated with C<sub>3</sub>F<sub>6</sub> plasma. Sun and Stylios [7] found that C<sub>2</sub>F<sub>6</sub> can produce polymers as result of the plasma treatment on the treated wool and cotton. Iriyama and Yasuda [8] reported that plasma treatment of CF<sub>4</sub> and C<sub>3</sub>F<sub>6</sub> does not yield good durability. They attributed this to the formation of short polymer segments dangling on the treated surface. Kim et al. [9] reported that the CH<sub>4</sub> plasma polymerization deposited a very smooth hydrocarbon layer exposing –CH<sub>2</sub> and –CH<sub>3</sub> groups leading to increased hydrophobicity. In this work, the sulphur hexafluoride (SF<sub>6</sub>)

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was used as the fluorine source for producing fluorination on the sample surface for hydrophobicity improvement.  $\text{SF}_6$  is used as a dielectric medium in high voltage applications, and is one of the gases used in microelectronics and solar cell industries, in particular as etching gas in the plasma cleaning process of vacuum chambers [10]. It has been suggested that  $\text{SF}_6$  does not undergo polymerization because the  $\text{CF}_x/\text{F}$  ratio is essentially zero in the plasma [11]. This work focuses on the surface modification of fabrics by radio-frequency inductively coupled plasma. We have chosen Thai silk fabrics to study the improvement of its hydrophobicity properties by treating with  $\text{SF}_6$  plasma. Thai silk is one of the most valuable fabrics in the world market. The  $\text{SF}_6$  pressure, the RF power and the treatment time were varied to find the optimum conditions for improvement of the hydrophobicity of Thai silk. We also investigated the correlation between the fabric hydrophobicity and the surface roughness, and the fluorine content.

## 2. Experimental

A schematic of the radio-frequency plasma generation and treatment is shown in Fig. 1. The main components of the system are the reactor chamber, the RF generator, the impedance matching network, and the gas supply system. The reactor is a cylindrical chamber of stainless steel. The top stainless steel plate has a circular opening of 20 cm in diameter where a quartz window is mounted. A flat coil (7 turns) is mounted directly on top of the quartz window to induce the plasma at 13.56 MHz. A base pressure at  $2 \times 10^{-5}$  Torr was achieved using a turbo molecular pump backed by a rotary vane pump. After the base pressure was reached,  $\text{SF}_6$  gas is allowed to enter the chamber via mass flow controller. Prior to the exposure to the plasma, fragments of Thai silk ( $112 \text{ g/m}^2$ ) were cleaned with dilute detergent, repeatedly washed with distilled

water and dried in air atmosphere. The fabric samples were cut to the size of  $12 \text{ cm} \times 12 \text{ cm}$  and were held stretched in a horizontal plane with the aid of a holding ring providing a treatment area of  $115 \text{ cm}^2$ . The silk samples were placed at a distance of 2 cm away from the quartz plate that separates the planar coil antenna from the chamber. The samples were exposed to the plasma at varying  $\text{SF}_6$  pressures of 0.005, 0.05, 0.5, and 1 Torr. The operating RF power was adjusted to 25, 50, and 75 W. The treatment time was at 1 or 5 min. The water contact angle of treated fabrics was measured using a Tantaq CAM-PLUS contact angle meter. The water absorption time was obtained using a  $40 \mu\text{l}$  water droplet until it was completely absorbed by the fabric. An average of at least six measurements was taken as the absorption time for each plasma condition. The maximum absorption time was limited at 210 min due to evaporation of the water. X-ray photoelectron spectroscopy experiments (Kratos Analytical model AMICUS) were performed on freshly-treated fabrics using Mg  $\text{K}\alpha$  radiation (1253.6 eV) to verify the changes in surface chemical composition of the treated fabrics. The morphology changes in the surface of fabrics were observed by scanning electron microscopy (SEM model JEOL JSM-6400). The surface roughness was also measured from the atomic force microscopy images (AFM model NanoScope IV), operated in tapping mode.

## 3. Results and discussion

Fig. 2 (a) and (b) shows the equilibrium contact angle and a water droplet resting on treated silk fabrics. According to Young's equation, the interfacial tensions (Gas/Liquid), (Gas/Solid) and (Solid/Liquid) are balanced resulting in an equilibrium contact angle. The measured contact angle of the plasma treated fabrics was about  $140 \pm 5^\circ$ , while the

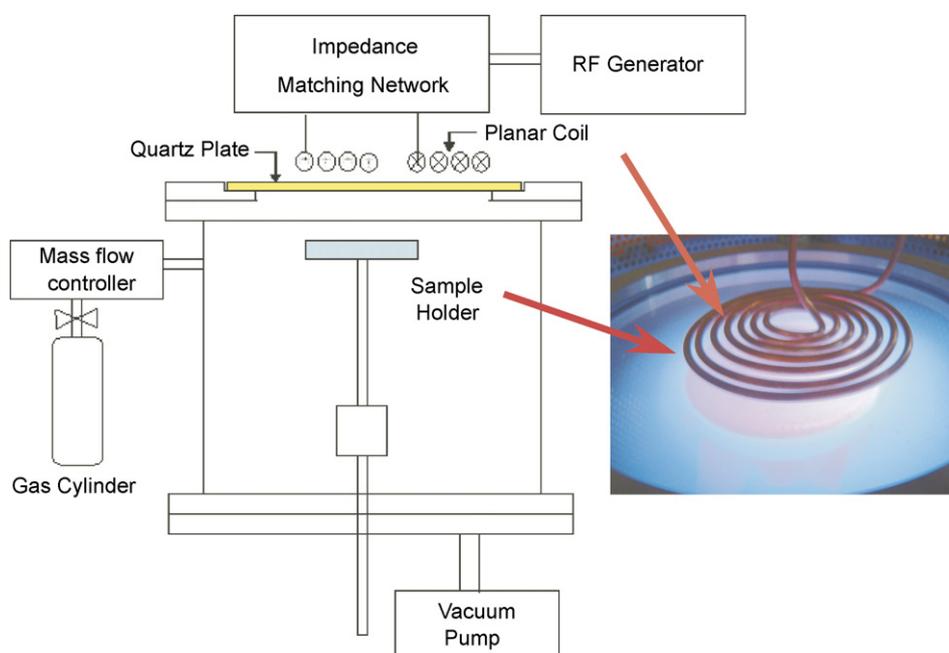


Fig. 1. Diagram of the radio-frequency (RF) inductively coupled  $\text{SF}_6$  plasma reactor.

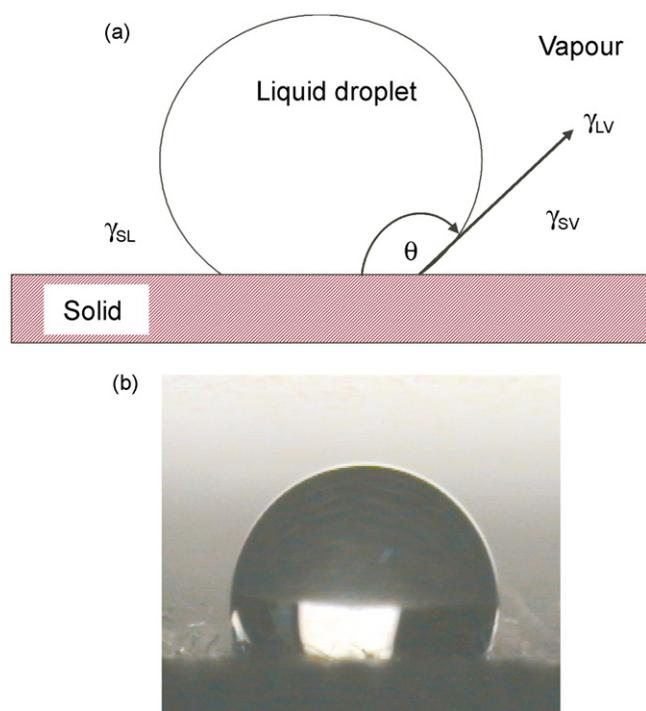


Fig. 2. (a) Equilibrium contact angle.  $\gamma_{LV}$  is surface tension of the liquid in equilibrium with its saturated vapor.  $\gamma_{SV}$  is surface tension of the solid in equilibrium with the saturated vapor of the liquid, and  $\gamma_{SL}$  is the interfacial tension between the solid and the liquid. (b) A water droplet resting on treated silk fabric.

untreated fabrics absorb water immediately leading to a contact angle of nearly zero degree. Clearly the plasma treatment greatly enhanced hydrophobicity of the fabrics. We observed that the contact angle of the treated fabric which varies in the 135–145° range, is not very sensitive to the different plasma conditions. Moreover, it is difficult to compare the hydrophobicity of fabrics as a function of plasma conditions by only using contact angle data due to high errors of these measurements associated with roughness and irregularity of the surfaces. However, the measured contact angles can be used to obtain the change in surface energy or the work of adhesion, defined as the work required to separate a unit area of interface between a liquid and a solid. The contact angle and the surface energy is related by  $W_a = \gamma_{LV}(1 + \cos \theta)$ , where the surface tension ( $\gamma_{LV}$ ) of water in the air equals to 0.073 N/m. After plasma treatment, the work of adhesion decreases from 146 to 17 dynes/cm indicating more ability of fabric surface to repel water. The variation of water absorption times with the SF<sub>6</sub> pressure, the RF power and the exposure time are shown in Fig. 3. Fig. 3(a) and (b) shows the hydrophobicity of silk after plasma treatment for 1 and 5 min, respectively. The absorption time increased from 0 to beyond our limiting time (210 min) with optimal plasma treatment conditions. Also increasing the exposure time from 1 to 5 min causes an increase on the absorption time. This increase in the absorption time is evident on the data at RF power of less than 50 W for SF<sub>6</sub> pressures higher than 0.05 Torr. The SF<sub>6</sub> plasma fired at pressure higher than 0.05 Torr were more effective in increasing absorption time. This is due to a large concentration of fluorinating species

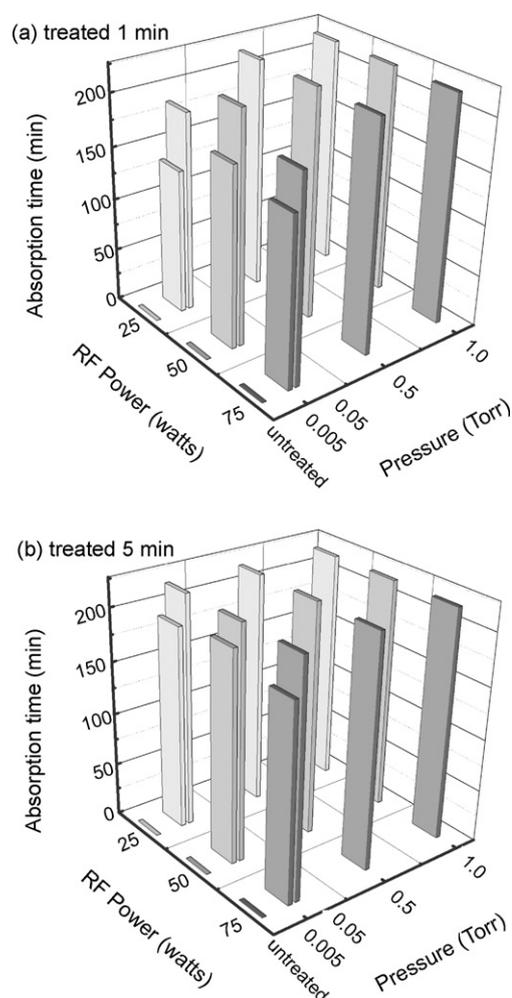


Fig. 3. Water droplet absorption time as a function of RF power and pressure (a) on silk treated for 1 min and (b) on silk treated for 5 min.

and their shorter mean free path, increasing the rate of ionization and fluorination reactions. The efficiency of fluorination also depends on the RF power used. This is due to increasing of the density of the charged species as the RF power is increased, in this case from 25 to 50 W. The optimum power for the treatment was found to be 50 W. We also noted that the treatment with higher RF power (75 W) or treatment times longer than 5 min result in some degree of discoloration of the fabric as well as the reduction in the water absorption time. In general, for longer treatment times, other surface modifications may also occur to some degree. The dye damage (discoloration) is due to reaction of radicals to double bonds causing bleaching. In addition changes were seen on the fibre surface morphology. These changes are believed to be due to etching of the fibres [12–15]. The bombardment by energetic ions causes some hydrophobic groups, i.e.  $-\text{CF}$ ,  $-\text{CF}_2$  and  $-\text{CF}_3$ , previously attached to the fibre surface to be removed. Dai [16] showed that increasing RF power for their plasma produced more ions resulting in increasing of the etching rate, whereas the density of the total reactive species remains the same. The changes in chemical modification of silk surface were obtained by X-ray photoelectron spectroscopy. Fig. 4 shows the XPS survey spectra of silk treated with different

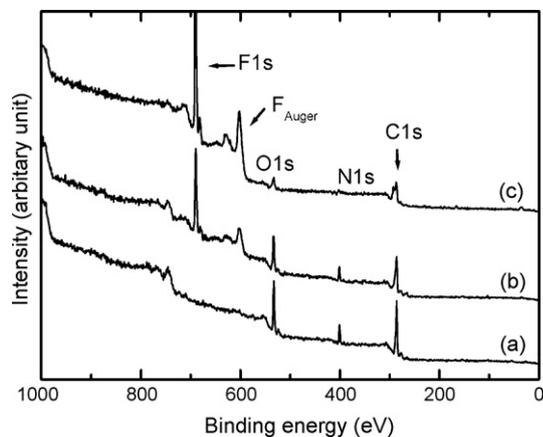


Fig. 4. XPS survey spectra for untreated and SF<sub>6</sub> plasma treated silk. (a) untreated silk, (b) silk treated at the pressure of 0.05 Torr, the RF power of 25 W, and the treatment time of 1 min, and (c) silk treated at the pressure of 0.5 Torr, the RF power of 50 W, and the treatment time of 5 min.

plasma conditions. The spectrum for untreated silk is also included in Fig. 4 for comparison. Clearly the F1s peak is only visible on the samples after treating with SF<sub>6</sub> plasma. The intensity of F1s peak increases as SF<sub>6</sub> plasma pressure, RF power and exposure time are increased. Concomitant with the increase of the F1s signature, the bands for C1s, O1s and N1s decrease. Silk is mainly composed of a protein called fibroin which has a  $\beta$ -sheet secondary structure supported by multiple hydrogen bonds [17] as shown in Fig. 5. There is no difference in XPS survey spectrum between Thai silk and different types of silk due to the same chemical composition in the structure of silk [14,17]. According to the structure of silk, there are three different types of carbon atoms, i.e. the carbon 1s XPS spectra of untreated silk exhibit three distinct peaks corresponding to three different binding energies as shown in Fig. 6 (a). First, the binding energy at 284.7 eV was assigned to carbon atoms bound only to carbon and hydrogen (C – C – H), C1. Second, the peak C2 at 286.4 eV corresponds to C – O or C – N groups. Finally, the peak C3 at 288.4 eV arises from C = O groups. Fig. 6(b) shows the XPS spectra of silk treated for 1 min at the SF<sub>6</sub> pressure of 0.05 Torr and the RF power of 25 W. On the SF<sub>6</sub> plasma treated silk, the XPS data shows distinct signals at 289.1 and 291 eV. These signals are assigned to CF and CF<sub>2</sub>

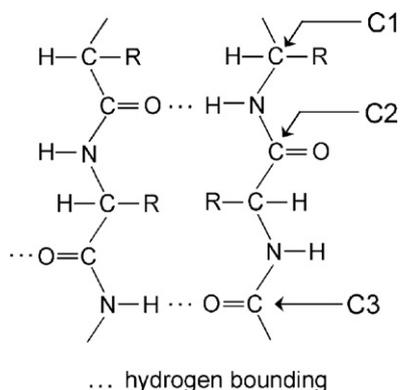


Fig. 5. The structure of fibroin polymer in silk fabric.

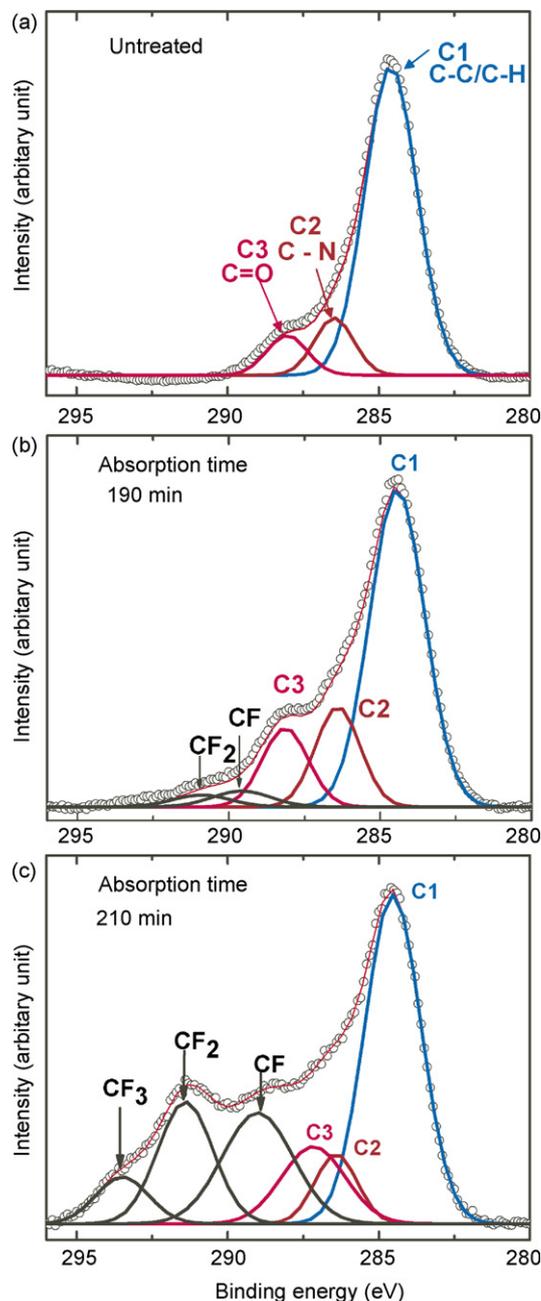


Fig. 6. (C1s) XPS spectra of fabric surface. (a) untreated silk, (b) silk treated at the pressure of 0.05 Torr, the RF power of 25 W, and the treatment time of 1 min, and (c) silk treated at the pressure of 0.5 Torr, the RF power of 50 W, and the treatment time of 5 min.

moieties, respectively, in addition the signals from pristine silk are still evident on the spectra of the treated samples. Generally, more intense treatment resulted in greater fraction of fluorine. The spectra show more pronounced changes for silk treated at higher SF<sub>6</sub> pressures, higher RF powers and higher treatment time as shown in Fig. 6(c). An additional peak becomes apparent at a binding energy of 293.5 eV. This peak is attributed to CF<sub>3</sub> groups. We did not detect sulfur signals on the XPS spectra. Thus, it must be concluded that only F radicals are responsible for the observed surface chemical changes. The mechanism of fluorination begins when SF<sub>6</sub> gas decomposes in the plasma and liberates F atoms and SF<sub>x</sub> radicals. Several

radical reactions are known for sulfur fluorides [18]. The most relevant reactions to our experiment are;



From XPS analysis, only the  $\text{F}^\bullet$  active species graft to the fabric surface to form  $-\text{C}-\text{F}-$  groups after H, O and N atoms bound to C were abstracted by energetic species present in the plasma (ions, radicals, electrons and photons)



where R represents the chemical backbone of the fabrics.

Thus, we use fluorine/carbon (F/C) ratio as a measurement of the degree of surface chemical modification. The correlation between the  $\text{SF}_6$  pressure and F/C atomic ratios of silk treated for different times, while keeping the RF power at 50 W is shown in Fig. 7 (a). The F/C atomic ratio of fabrics increases from about 0.25 at a pressure of 0.005 Torr to above 0.4 at pressures higher than 0.05 Torr. The results also show that the F/C atomic ratios slightly increase as treatment time increases but significantly increase when the  $\text{SF}_6$  pressure increases.

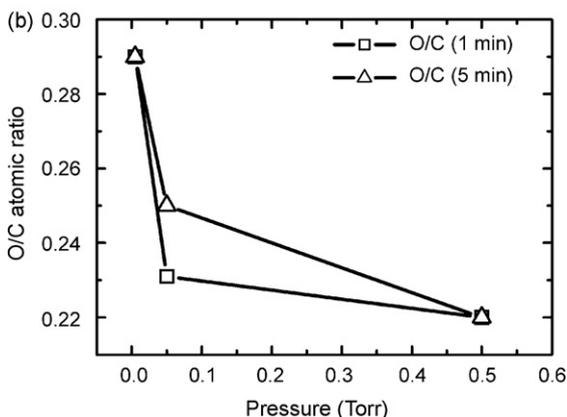
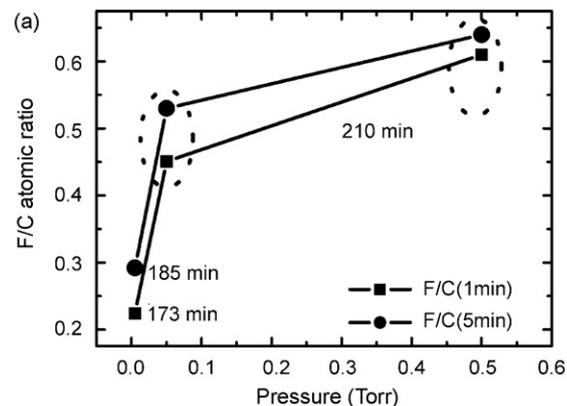


Fig. 7. F/C and O/C atomic ratios of silk samples treated at different  $\text{SF}_6$  plasma pressures (0.005, 0.05 and 0.5 Torr) for 1 and 5 min with RF power of 50 W.

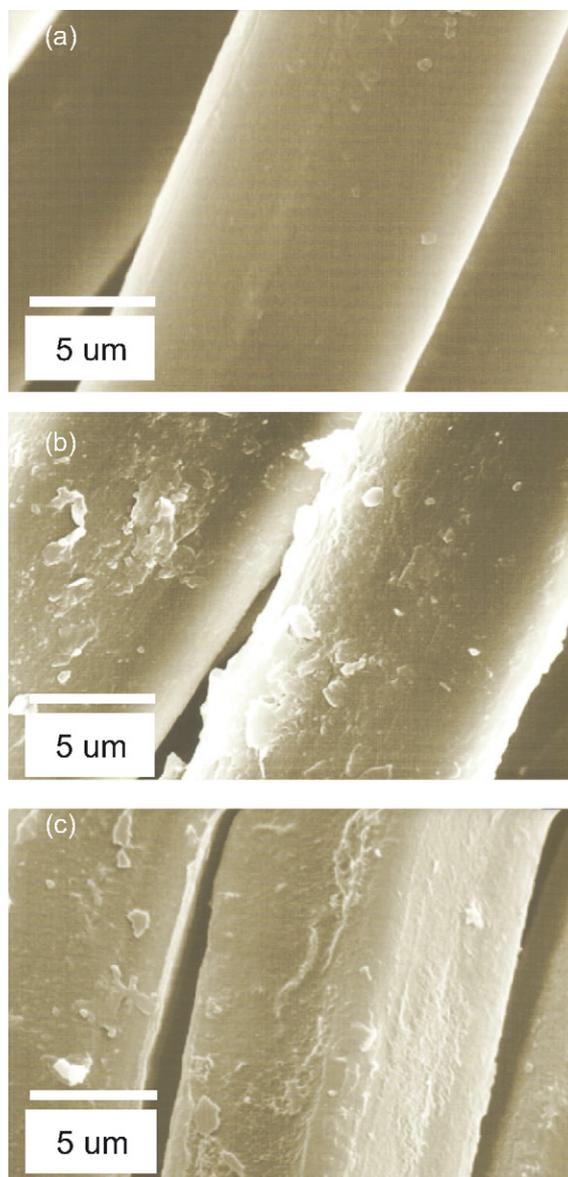


Fig. 8. SEM micrographs of silk fabrics with magnification of 3000. (a) Before treatment, (b) after treatment with 0.05 Torr of  $\text{SF}_6$ , and RF power of 25 W for 1 min and (c) after treatment with 0.5 Torr of  $\text{SF}_6$ , and RF power of 50 W for 5 min

Fig. 7(b) shows the correlation between  $\text{SF}_6$  pressure and O/C atomic ratios of silk operated at the same plasma conditions. The O/C atomic ratio slightly decreases from 0.29 to 0.22–0.25 as pressure increases from 0.005 Torr to above 0.05 Torr, evidencing the oxygen abstraction reactions.

Concomitant with the chemical changes described in the previous paragraph, a small mass-loss was observed upon  $\text{SF}_6$  plasma treatment of the silk. The mass loss depends on the pressure during plasma exposure reaching ca. 2.0% at 0.5 Torr of  $\text{SF}_6$ . We ruled out outgassing as the source of the mass loss by vacuum treatment and heating the samples before obtaining their weights before treating with  $\text{SF}_6$  plasma. Therefore, it must be concluded that etching or ablation of the fibres is the main culprit for this effect. Roughening of the fibres was also evident. The changes in surface morphology of fabrics were

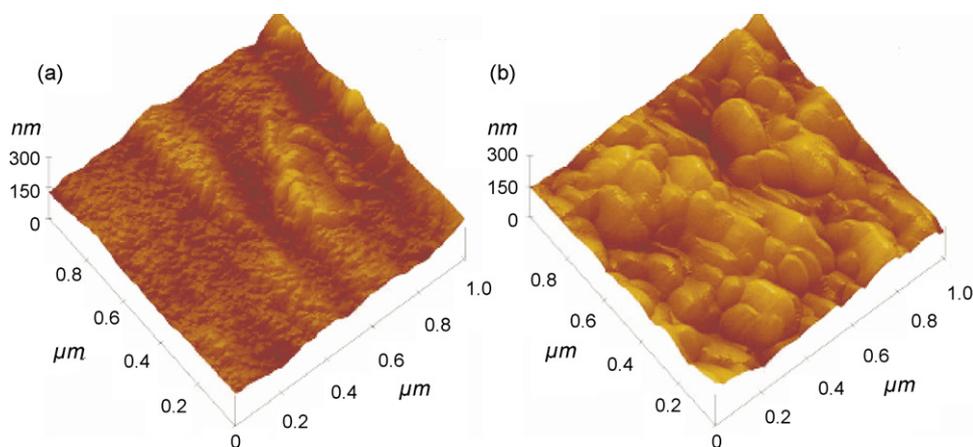


Fig. 9. AFM images  $2 \times 2 \mu\text{m}$  of silk fabrics. (a) before plasma treatment and (b) after plasma treatment at a  $\text{SF}_6$  pressure of 0.5 Torr, and RF power of 50 W for 5 min

observed by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The images in Fig. 8 (a)–(c) show that the untreated fibres were smooth, in clear contrast with the silk treated with  $\text{SF}_6$  plasma. The morphology of the treated fabrics is similar for all plasma conditions used in our study. This observation was confirmed quantitatively by the root-mean-square (RMS) surface roughness obtained from analysis of AFM images. As seen in Fig. 9 showing AFM images of untreated and treated silk, the main result of our surface observations was found to be an increase of the RMS roughness from 10 to 30 nm upon plasma treatment. Presumably, the increased roughness of treated fabrics is due to both of etching process by high energy species generated in  $\text{SF}_6$  plasma and deposition of materials on the sample surface. The lack of correlation between RMS roughness and the plasma treatment conditions is in qualitative agreement with the work of Jiang et al. [19] and Gogolides et al. [10] in which the rms roughness is not a clear function of plasma parameters and the abundance of C – F bonds on the treated samples. Indeed, the roughening effect induced by the plasma treatment has been observed before and it is common to treatments with a variety of gases, including Ar,  $\text{O}_2$ ,  $\text{N}_2$ , He, Air and  $\text{CH}_4$ . Although the surface roughness can increase the hydrophobicity of certain surfaces by the so called “Lotus effect”. Our samples became hydrophobic mainly due to the replacement of hydrophilic species by fluorine containing moieties. After fluorination of the fibres, a smaller number of hydrogen bonds between water molecules and surface groups can be formed, thus reducing the hydrophilicity.

#### 4. Conclusions

In this study, we established that the hydrophobicity improvement of Thai silk fabrics can be achieved via treatment with  $\text{SF}_6$  plasma. The main reaction for the enhancement of hydrophobicity is surface fluorination of the fabric confirmed by X-ray photoelectron analysis. Suitable operating conditions for obtaining high water absorption times are  $\text{SF}_6$  pressures higher than 0.05 Torr and RF power of 50 W for treatment times in the 1–5 min range. The F/C atomic ratio increases

when the  $\text{SF}_6$  pressure increases. The water absorption times of the fabrics are the highest when the fluorine/carbon ratio at the surface increases. A small decrease of the oxygen/carbon ratio was also observed on the fabrics that showed the longest absorption times.

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