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Hydrophobicity Improvement of PET Fabrics after SF$_6$ Plasma Treatment

We have used plasma assisted surface fluorination of polyethylene terephthalate (PET) fabrics to increase the water repellency of the fabrics. Treatment at different operating conditions for the radio-frequency inductively coupled in a SF$_6$ atmosphere resulted in improved hydrophobicity. The water repellency of treated fabrics was characterized by water contact angle and absorption time measurement. The measured contact angle of optimum-treated fabrics was 140 degrees, and the absorption time was 210 min. The morphology changes in the surface of PET were obtained by scanning electron microscopy and atomic force microscopy. The rms surface roughness of PET was increased from 28 nm to 45 nm after plasma treatment. The changes in chemical composition were observed in X-ray photoelectron spectra (XPS) analysis. We found that the F/C atom ratios obtaining by XPS analysis on PET were correlated to the pressure, the RF power, and the treatment time. An increase in the F/C atom ratios seems to contribute to the absorption time.

1 Introduction

The textile industry is continuously evolving to improve several interesting properties of fibers and fabrics. Wettability, easy of printing, dyeing, water or soil repellence, and chemical resistance are some examples (Chi-Ming, 1994, Vohrer et al., 1998). Hydrophobicity or water repellency is one of the most desirable properties for fabric manufacture. It has been reported that the plasma process has advantages comparing to direct chemical modification because it is rapid, clean, gas-dependent, non-aqueous and environmentally friendly method (Yip et al., 2002). Thus, plasma treatment is an attractive method especially for final step of fabric finishing.

Poly(ethylene terephthalate) (PET) fabrics have excellent wear resistance, and also offer slight water repellency (Jie-Rong et al., 1999). We have chosen this type of fabrics to study further improvements of its hydrophobicity property by varying the operating conditions of radio-frequency (RF) inductively coupled plasma (Konuma, 2005 and Paosawatyanyong, 2004). This technique allows the surface modification of fabric

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to the depth on the order of nanometers without changing its bulk properties. Thus, surface dependent properties can be changed without compromising the mechanical strength. Possible chemical reactions on the surface after initiating ions, electrons, free radicals, and active species are such as polymerization, grafting, crosslinking, and implantation. Previous research used fluorine-based gases for surface fluorination on polymer films and fabrics (Jie-Rong et al., 1999, Rangel et al., 2003 and Selli et al., 2001). Normally, plasma treatments of perfluorocarbons such as tetrafluoromethane (CF$_4$), hexafluoropropane (C$_3$F$_6$), etc. are used to enhance the hydrophobicity of fabric surfaces (McCord, 2003). In this work, sulphur hexafluoride SF$_6$ was used as a fluorine source for surface fluorination of fabric because it is a nontoxic gas compared with other fluorine-based gases (RoBler et al., 2005). It has been reported that none of these gases polymerized in the plasma (Strobel et al., 1987). However, SF$_6$ is one of the gases used as an etching agent in plasma cleaning process and in microelectronic process (Jiang et al., 2003). Therefore, studies to determine whether the effect of fluorination or the effect of etching of SF$_6$ plasma is dominant to improve water repellency are of interest. We also present quantitative data showing that the water repellency correlates well with the chemical composition changes introduced by fluorination.

2 Materials and Methods

Polyethylene terephthalate (74.8 g/m^2) fabrics were cleaned with dilute detergent, repeatedly washed with distilled water and dried in air atmosphere. A schematic of the radio-frequency (13.56 MHz) plasma generation and treatment is shown in Fig. 1. The sample was located at a distance of 4 cm away from the planar coil antenna above a quartz plate. The chamber was evacuated to a base chamber pressure of 2×10^{-5} Torr before SF$_6$ was allowed into the chamber via mass flow controller. RF power is inductively coupled through the quartz window. The SF$_6$ plasma was generated at RF powers of 25, 50 and 75 W. The operating conditions were set at pressure of 0.005, 0.05 and 0.5 Torr, and the treatment time was 15 s, 1 min and 5 min.

The water contact angle measurement has been known as a simple method to determine the degree of hydrophobicity. As shown in Fig. 2, when the water drop is in equilibrium, according to the Young's equation, the interfacial tensions (Gas/Liq-

uid), (Gas/Solid) and (Solid/Liquid) are balanced resulting in an equilibrium contact angle θ. We performed the contact angle measurements using a Tantac CAM-PLUS contact angle meter. A 4 µl water droplet was gently dripped on the surface
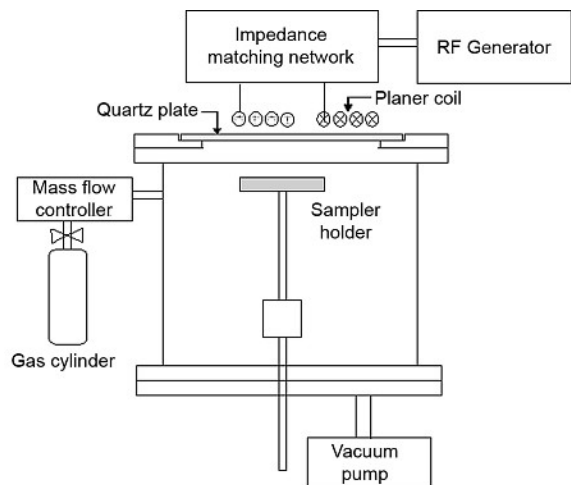

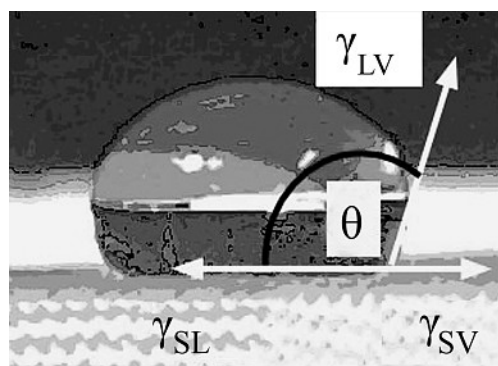*Fig. 1. Diagram of the radio-frequency (RF) inductively coupled SF$_6$ plasma reactor*

Fig. 2. Equilibrium contact angle. γ$_{LV}$ is surface tension of the liquid in equilibrium with its saturated vapor. γ$_{SV}$ is surface tension of the solid in equilibrium with the saturated vapor of the liquid, and γ$_{SL}$ is the interfacial tension between the solid and the liquid (Chi-Ming, 1994)

of fabric using a microsyringe, and the measurement was performed by directly reading of the angle on the scale. The absorption time, i.e. the time required for a water droplet with a specific size to be completely absorbed by the fabric, was obtained by taking the average value from several droplets (each of which was 40 µl in volume). The maximum absorption time was limited at 210 min to avoid possible evaporation of the water droplet.

X-ray photoelectron spectroscopy experiments (Kratos Analytical model AMICUS) were performed on freshly-treated fabrics using Mg K α 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 quantitatively measured by atomic force microscopy (AFM model NanoScope IV) used in tapping mode.

3 Results

It was clearly evident that the plasma treatment greatly enhanced hydrophobicity of the fabrics. The measured contact angle of the treated fabrics was about 140 ± 5 degrees, while that of the untreated fabrics was about 20 ± 5 degrees resulting in an eight times decrease of surface energy (Chi-Ming, 1994). The measured contact angle of treated fabrics, varying from 130 to 140 degrees, is not sensitive to the different plasma conditions. Morever, due to high errors of contact angle measurement associated with roughness and irregularity of the surfaces, absorption time was chosen as an alternative index to represent the fabric hydrophobicity. The variation of water absorption times with SF$_6$ pressure, RF power and exposure time are shown in Fig. 3. Fig. 3A to C show the hydrophobicity of PET after plasma treatment for 15 s, 1 min and 5 min, respectively. The absorption time was increased from 10 s to about 200 min after optimal plasma treatment. After an exposure to the fluorinating plasma for more than 1 min, SF$_6$ plasmas were effective independent of the operating pressure so all samples showed roughly the same absorption time when compared with the data for 15 s. In general, the longer the treatment time, the greater amount of active species bombard the fabric surface.
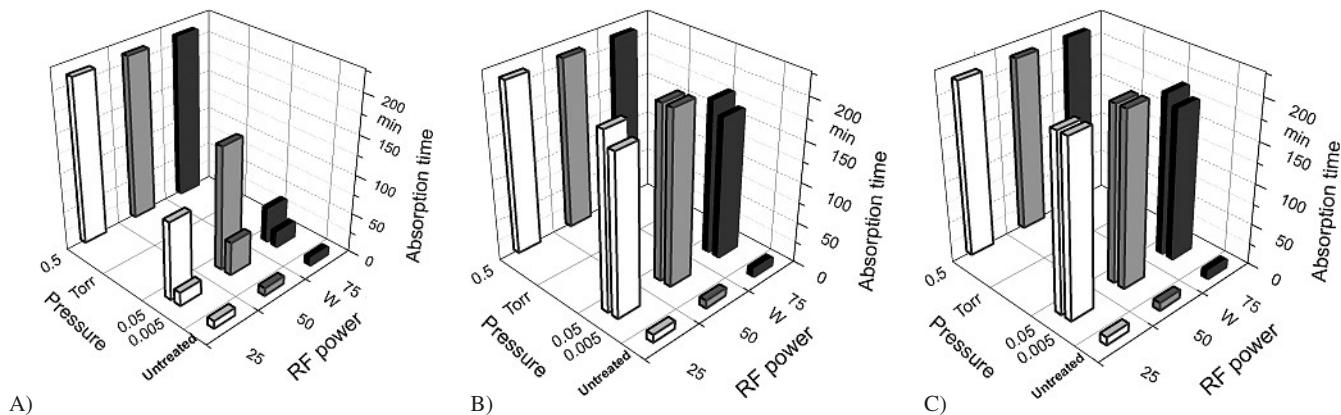

A)   B)   C)

Fig. 3. Absorption time of a 40 µl water droplet on PET samples as a function of pressure, RF power and (A) 15 s, (B) 1 min, (C) 5 min treatment time
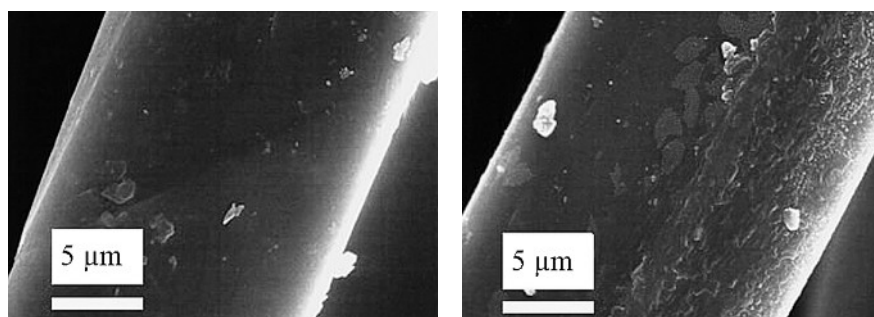
Fig. 4. SEM micrographs of PET fabrics with magnification of 5000. (A) before plasma treatment (B) after plasma treatment at the pressure of 0.5 Torr, the RF power of 50 W, and the treatment time of 5 min
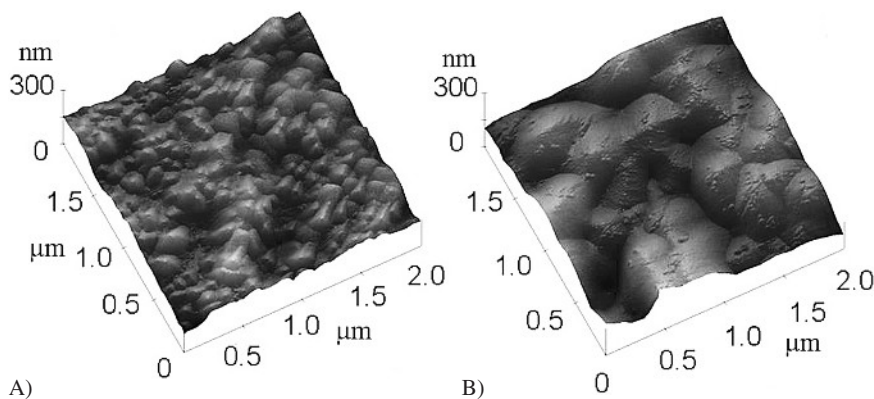

Fig. 5. AFM images 2 × 2 μm of PET fabrics. (A) before plasma treatment (B) after plasma treatment at the pressure of 0.5 Torr, the RF power of 50 W, and the treatment time of 5 min

For example, when PET fabrics were exposed to SF_6 plasma for 15 s, the SF_6 plasmas operated at pressures of more than 0.5 Torr were effective in increasing absorption time; however, plasma treatment at a pressure of less than 0.5 Torr was ineffective. This could be due to the shorter mean free paths of active species inducing more ionization and fluoronation reactions at higher pressure. Also the absorption time for 15 s treatment depended strongly on the RF power at low SF_6 pressure of 0.005 Torr and 0.05 Torr, and the optimum power for the treatment was found to be 50 W. Similar results were found for 1 min treatment at SF_6 pressure of 0.005 Torr. This is due to increasing of the density of the charged species as the RF power is increased. However, we noted that the treatment with higher RF power (75 watts) or the treatment time longer than 5 min resulted in some degree of discoloration of the fabric as well as the reduction in the absorption time. These changes are believed to be due to etching of the fibers (Selli et al., 2001).

The decreasing of absorption time at higher RF power than 75 W can be explained by the non-uniformity of plasma below the planar coil as well.

SEM images in Fig. 4 show the overall morphology of both untreated and plasma-treated fabrics. It can be clearly seen that the SF_6 plasma roughened the surface of treated fabrics.

This observation was confirmed quantitatively by the root-mean-square (rms) surface roughness obtained by AFM analysis (surface topography shown in Fig. 5). It was found that the roughness of PET increased from 28 nm to 45 nm after plasma treatment. We did not observe a clear trend of the rms roughness with plasma conditions. We found that the measured rms roughness depended on the location of the AFM tip probe on the fibre surface. Our results are agreed with Jiang et al. and Gogolides et al. in which the rms roughness is not a clear func-

tion of plasma parameters and the intensity of C–F bond groups (Jiang et al., 2003, Gogolides et al., 2004). It is not obvious that the surface roughness induced by plasma treatment is sufficient to contributed to improve hydrophobicity by the well known "Lotus effect". The roughening of some surfaces of plants could contribute to improved hydrophobicity (Neinhuis et al., 1997, Wagner et al., 2003). Essentially droplets can achieve a smaller contact area by being supported on top of the sharp features of the surface minimizing the interaction energy.

It has been reported that the structured surface of many water-repellent leafs consists of the height of the elevations ranging from 5 to 100 microns and the distance between the elevations ranging from 5 to 200 microns (Wagner et al., 2003). It was reported that the aspect ratios (height/distance) were smaller than one. Comparing with our results in Fig. 5B, the height and distance between the nanoprotuberance created by plasma etching are in the range of 50 to 200 nm and 200 to 500 nm, respectively, while the diameter of the water droplet is in the order of cm. Due to extremely different order in the height and the distance (Hsish et al., 2005) compared with the size of water drops, it is clearly seen that the Lotus effect is not the main reason for the improved hydrophobicity of our sample fabrics.
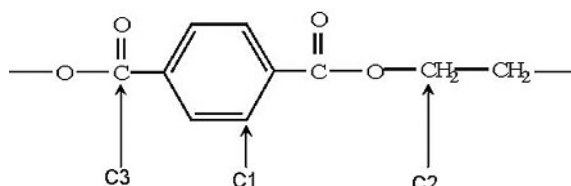

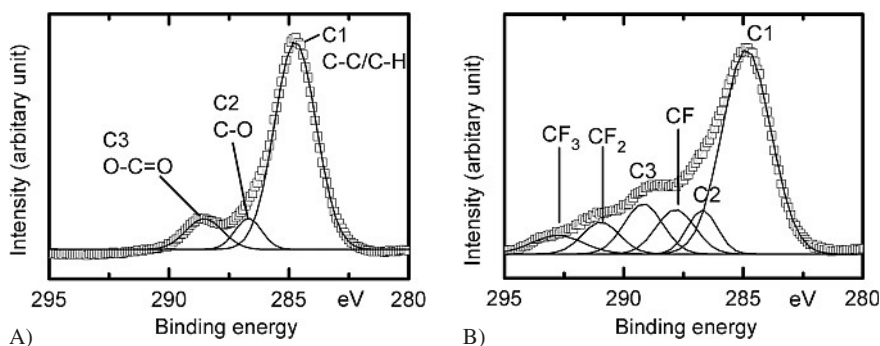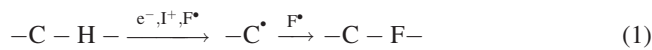*Fig. 6. Binding energies of the C1s core level in PET*

Fig. 7. C (1 s) XPS spectra of PET fabric surface. (A) untreated fabric, (B) treated fabric

According to the structure of PET as shown in Fig. 6, there are three different types of carbon atoms which consequently correspond to three distinct peaks in XPS spectra. These peaks could be clearly seen from the XPS signal of the untreated fabric shown in Fig. 7A. The assignment of the signals is as follows; C1 (at 284.7 eV) corresponding to carbon bonding in aromatic ring (C–C/C–H), C2 (at 286.6 eV) assigned to methylene carbons singly bonded to oxygen atom (C–O), and C3 (at 288.5 eV) corresponding to carbon atoms in ester group (O–C=O) (Selli et al., 2001, Poletti et al., 2003, Gupta et al., 2000, and Beamson and Briggs, 1992). While all of these peaks remained evident, three additional peaks at 289.1, 291 and 293 eV were detected after the treatment. These peaks have been assigned with CF, CF_2 and CF_3 moieties, respectively (Selli et al., 2001, Poletti et al., 2003, Gupta et al., 2000, and Beamson and Briggs, 1992). These additional peaks appear in Fig. 7B overlapping with some of the signals seen for the untreated fabric. This result indicated the interaction between the SF_6 plasma and PET yielded some substitutions of H and O atoms by F atoms.

Besides the alteration of carbon bonding in PET structure, the XPS analyses also revealed the amount of fluorine depended upon conditions of the treatment. Generally, with higher RF power or higher pressure for longer time resulted in greater fraction of fluorine. Some reactive routes that explain clearly the chemical reactions that take place during the plasma fluorination can be described. Eq. 1 and Eq. 2 are examples of the reactions of hydrogen abstracting from carbon atom and fluorine attachment to carbon atom occurring in aromatic ring and methylene, respectively, where is $C^•$ is a radical of carbon atom and $F^•$ is a radial of fluorine atom.

$$-C-H-\xrightarrow{e^-,I^+,F^•} -C^• \xrightarrow{F^•} -C-F- \qquad (1)$$

$$-CH_2-CH_2-\xrightarrow{e^-,I^+,F^•} -CH^•CH_2 \xrightarrow{F^•} -CFH-CH_2- \quad (2)$$

It should be noted that the fraction of oxygen in the samples was also affected by the plasma treatment. That is, there is oxygen abstracting from carbon atoms as well as hydrogen abstracting during the plasma fluorination. The higher amount of fluorine is embedded to the fabric, the lower fraction of oxygen is observed. This is an important result of our experiments, and it is directly related to a decrease of the hydrophilic character of the fabric.

Fig. 8 shows the F/C atomic ratios as a function of generated RF power for 15 s, 1 min and 5 min treatment time, while keeping the SF_6 pressure constant. The O/C atomic ratio of fabrics decreases from 0.7 to about 0.3 after plasma treatment.

The results also show that the F/C atomic ratios were at maximum at the optimum RF power of 50 W in which correspond to the higher absorption time as shown in Fig. 3. In general, an increase of RF power leads to an increase of the density of the charged species resulting to more fluorine bonded to PET surface. However, in some cases the decrease of F/C atomic ratios of samples treated at RF power higher than 75 W is due to the presence of non-uniformity of the plasma, which led to less fluorine bonded to the sample surface. We note that the absorption time in this case was related to the amounts of fluorine bonded to the PET surface.

The F/C and O/C atomic ratios determined by XPS analysis on PET samples plasma treated at different SF_6 plasma pressure (0.005 Torr, 0.05 Torr and 0.5 Torr) for 1 min and 5 min with the optimum RF power of 50 W are shown in Fig. 9.
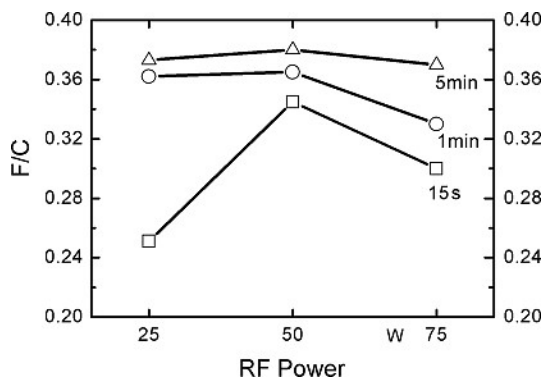

Fig. 8. F/C atomic ratios of PET samples treated at different RF power for 15 s, 1 min and 5 min with the SF_6 pressure of 0.005 Torr
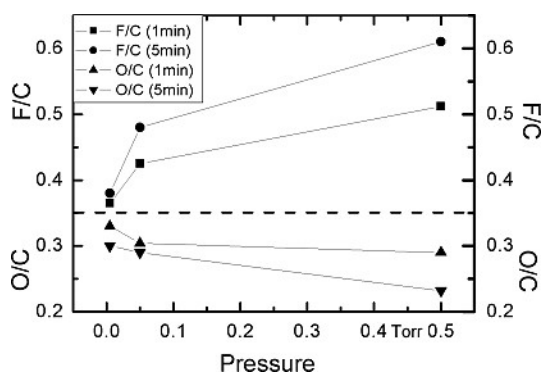

Fig. 9. F/C and O/C atomic ratios of PET samples treated at different SF_6 plasma pressure (0.005 Torr, 0.05 Torr and 0.5 Torr) for 1 min and 5 min with the RF power of 50 W

The F/C atom ratios increase whereas the O/C atom ratios decrease with an increasing of SF_6 plasma pressure. We did not see the difference in the absorption time for this data set in Fig. 9 because of having limitation of maximum absorption time. However, we believe that the amounts of fluorine bonded to fabric surface influenced the water repellence properties.

4 Discussion

The increased roughness of plasma-treated fabrics is probably due to bombarding and etching process from high energy species generated in plasma. Previous work that used plasma treatment for the enhancement of hydrophilicity and hydrophobicity of fabrics, with gases such as Ar, He, Air, SF_6, and CH_4 roughen fabric surface (Jie-Rong et al., 1999, Rangel et al., 2003, Selli et al., 2001, Poletti et al., 2003, and Gupta et al. 2000) as a side effect. This suggests that the increase on the roughness is not unique to SF_6 based plasma. After the plasma treatment, the roughening PET fibers in the fabric can be clearly observed. It should be noted that the rms surface roughness of all samples in this work is in the same order of magnitude as the values reported by Gupta et al. (2000) and Poletti et al. (2003). We concluded that the main reason for the enhancement of PET hydrophobicity is the surface fluorination by fluorine-based gases plasma, and is not from the change in roughness of the sample. Also, the height and distance between the nanoprotuberance created by plasma etching are much smaller than the size of the water drop used in the experiment. This was also confirmed by the presence of fluorine detected in the XPS spectra of the plasma-treated samples. When the data for the absorption time was considered together with the results from XPS analyses, it was found that the absorption time has strong correlation with the amount of fluorine bonded to PET surface. According to the Fig. 3 and Fig. 8, the higher the F/C atomic ratio leads to longer absorption times or the improved hydrophobicity of the fabric. On the other hand, the amount of fluorine atoms bonded to PET structure can be controlled by conditions of the plasma treatment.

5 Conclusions

We have successfully increased the hydrophobicity of PET fabrics via an SF_6 plasma assisted treatment. A correlation between the water absorption time and the plasma conditions has been found in our plasma system. For the short time treatment, the absorption time was correlated strongly to the SF_6 pressure and the RF power. The F/C atom ratios obtaining by XPS analysis on PET increase for samples that show greater absorption time. The increase of the F/C ratio can be attributed to the predominant surface fluorination.

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