Investigation on the Effects and Mechanisms of PTFE Surface Modification by Low Pressure Plasma*

LIU Hongxia (刘红霞), LIU Yun (刘云)

Department of Environmental Engineering, Xi'an Jiaotong University, Xi'an 710049, China

Abstract Using argon as the work gas, the effects and mechanisms of poly(tetrafluoroethylene) (PTFE) film surface modification were investigated in a low pressure plasma reactor. Results show that higher hydrophilicity with little degradation, in terms of the scanning electron microscopy (SEM), was obtained after treatment, especially when the sample was placed in the post-discharge area. More polar functional groups and higher surface free energy, especially the polar component, formed on the PTFE surface were responsible for the modification. For the relatively high purity radicals and rare discharge particles in the post-discharge area, the etching was restrained and the introducing reactions were enhanced, and thus, a better modification occurred there.

Keywords: low pressure plasma, poly(tetrafluoroethylene), surface modification

PACS: 52.40.Hf

DOI: 10.1088/1009-0630/14/8/09

1 Introduction

The surface modification of commercial polymers is very important from a practical point of view, especially for medical applications. Different surface modification strategies have been developed [1-5], where various plasma-based approaches are noteworthy for their merits, such as speediness, simplicity, reliability, elimination of pollution, and cost effectiveness [6-8]. The most important characteristic is the action only takes place on a thin surface layer, that is, in the range of several hundred to several thousand angstroms, while the bulk of the treated substance remains unchanged so that the modified material retains its original mechanical properties.

Plasma containing high energy reactive species such as electrons, ions, and radicals, can initiate cleaning, etching, cross-linking, grafting and other chemical reactions (e.g., substitution, and formation of functional groups) [9,10] on a polymer surface. When the process is performed in the active discharge area, where a mixed atmosphere is constituted by all reactive species, all reactions as above mentioned may occur simultaneously on the polymer surface. From the viewpoint of chemistry, surface modification with plasma is mainly fulfilled by radical introducing reactions, and the others like electrons and ions, although able to improve the surface hydrophilicity to a certain extent, reduce surface smoothness [11-14]. This is highly disadvantageous for polymers’ application in the medical field [15]. If we can isolate the radicals from other reactive particles, the radical introducing reactions would be accelerated, and then better modifications would result.

In plasma, all reactive species (electrons, positive and negative ions and radicals) would disappear in the processes of electron-positive ion recombination and atom recombination. But radicals are extremely long-lived for the lower rate constant of their recombination reactions [16]. Therefore, an atmosphere of relatively high purity radicals could be expected. If so, effective modification with few etching actions initiated by discharged particles will be realized in such a region.

Poly(tetrafluoroethylene) (PTFE), a kind of fluorine-containing polymer, possesses excellent hydrophobic surfaces (the surface energy of PTFE is 18.6 mJ/m²). Its hydrophobicity is a result of the low polarizability of the C-F bonds [17] and hampers its applications in many cases. Given that, many investigators have studied the surface modification of PTFE through various methods [6,7,18-21]. Their results showed that the substitution of hydrophilic groups such as hydroxyl and carbonyl groups for fluorine atoms is an essential reaction in the surface modification of PTFE. Based on this finding, we investigated the modification effects on PTFE surface at different positions in a remote plasma reactor under various treatment conditions. For a thorough understanding of the changes in the surface properties, the double Langmuir electron probe and electron spin resonance (ESR) were applied to verify the distribution of electrons, ions and radicals firstly, and then, surface free energy calculation as well as X-ray photoelectron spectroscopy (XPS) analysis were conducted.

*supported by National Natural Science Foundation of China (No. 21077084), and the Foundational Research Fund of Xi’an Jiaotong University (No. 08143023)
LIU Hongxia et al.: Investigation on the Effects and Mechanisms of PTFE Surface Modification

2 Experimental setup

2.1 Plasma generator

The experimental arrangement used is shown schematically in Fig. 1. The reactor consists of a gas inlet, reaction chamber, gas exhaust, power supply and matching network (SY-500 W power supply and SP-II matcher). The reaction chamber is a cylindrical Pyrex glass tube (45 mm in diameter, 1000 mm in length), and an induction coil of nine turns for the energy input of rf power (13.56 MHz frequency) is attached to the Pyrex glass tube at a distance of 50 mm from the tube threshold. Argon, with a purity of more than 99.99%, was used as the work gas.

Fig.1 Schematic view of experimental arrangement: (1) gas bottle; (2) valve; (3) mass flowmeter; (4) inductance oil; (5) matching system; (6) rf generator; (7) sample; (8) reaction chamber; (9) vacuum gauge; (10) electromagnetism valve; (11) vacuum pump

Fig.2 Double Langmuir electron probe testing system

ESR is the most efficacious measuring method for radicals [23,24]. In this experiment, clean and real wool acted as the receptacle of the radicals [25]. The wool was placed at different distances from the center of the induction coil to be treated. The treated wool was maintained at room temperature for 24 h, and then the concentration of radicals was determined using an ESR spectrometer (model ESP-500, made by BRUKER Company.). The measurement conditions adopted were as follows: room temperature, a microwave frequency of 9.8 GHz, a microwave power of 3.177 mW, a modulation amplitude of 0.2 mT, a modulation frequency of 100 kHz, a time constant of 163.84 ms, and a scan time of 163.84 ms.

2.2 Argon plasma diagnosis

The double Langmuir electron probe was employed to perform the argon plasma diagnosis. The leader of this electron probe was connected with the plasma reactor, and its location in the reactor was adjustable, as shown in Fig. 2. The measured Volt-Ampere characteristics of the electrical probe were used to determine the electron and ion concentrations [22].

Fig.2 Double Langmuir electron probe testing system

Prior to the experiments, the PTFE film (20 µm thickness) was cut to dimensions of 25 mm × 50 mm as specimens, washed with acetone in an ultrasonic washer and then dried at room temperature under vacuum. During the experiments, the PTFE samples were positioned on a glass plate downstream from the argon plasma active discharge zone at intervals of 20 cm. The treatments were carried out within 20~100 W of rf power at a 13.56 MHz frequency for 10~120 s, and the gas flow was adjusted to 20~100 cm³/min by a mass flow controller.

The static contact angles of water on the treated PTFE sheet surfaces were measured at 20°C using a contact angle meter with a goniometer (Model JY-82). Twice-distilled water was used for the contact angle measurement. To lessen the effect of gravity, the volume of each drop was regulated to about 0.2 cc by a microsyringe. The average value of the angles of both sides of each drop was counted as one measurement. Three completely repeated experiments were performed at the same position. Each sheet was measured at 6 different points and the contact angle was determined by their average value with a standard deviation of 1°.

To evaluate the surface hydrophilicity expeditiously, the surface conglutination work (W_a) of PTFE sheet was calculated by the Young-Dupre equation [26]:

\[ W_a = \delta_{LG} (1 + \cos \theta), \]

where \( \delta_{LG} \) is the interfacial surface tension between water and sheet at 20°C (\( \delta_{LG} = 72.8 \times 10^{-3} \text{N·m}^{-1} \)), and \( \theta \) is the contact angle of the water.

2.4 Surface free energy calculation

The liquids used in measuring the contact angle of the sheet are shown in Table 1. According to YAMAIISHI [27], the surface free energy (\( \gamma_L \)) of the liquid can be divided into three components: the dispersion force (\( \gamma^d_L \)), dipole force (\( \gamma^p_L \)), and hydrogen bonding force (\( \gamma^h_L \)). This procedure leads an extension of Fowkes’ equation to the Young equation. The surface free energy (\( \gamma_S \)) and three components (\( \gamma^d_S \), \( \gamma^p_S \) and \( \gamma^h_S \)) of PTFE sheet can be calculated by solving the system of equations as follows:

\[
\begin{align*}
\gamma_L(1 + \cos \theta_s) &= 2\left( \sqrt{\frac{\gamma^{d}_{L}}{\gamma^{d}_{S}}} \gamma^{d}_{S} + \sqrt{\frac{\gamma^{p}_{L}}{\gamma^{p}_{S}}} \gamma^{p}_{S} + \sqrt{\frac{\gamma^{h}_{L}}{\gamma^{h}_{S}}} \gamma^{h}_{S} \right), \\
\gamma_L(1 + \cos \theta_j) &= 2\left( \sqrt{\frac{\gamma^{d}_{L}}{\gamma^{d}_{S}}} \gamma^{d}_{S} + \sqrt{\frac{\gamma^{p}_{L}}{\gamma^{p}_{S}}} \gamma^{p}_{S} + \sqrt{\frac{\gamma^{h}_{L}}{\gamma^{h}_{S}}} \gamma^{h}_{S} \right), \\
\gamma_L(1 + \cos \theta_k) &= 2\left( \sqrt{\frac{\gamma^{d}_{L}}{\gamma^{d}_{S}}} \gamma^{d}_{S} + \sqrt{\frac{\gamma^{p}_{L}}{\gamma^{p}_{S}}} \gamma^{p}_{S} + \sqrt{\frac{\gamma^{h}_{L}}{\gamma^{h}_{S}}} \gamma^{h}_{S} \right), \\
\gamma_S &= \gamma^d_S + \gamma^p_S + \gamma^h_S,
\end{align*}
\]
where subscripts $L_i$, $L_j$ and $L_k$ stand for the three standard liquids used, respectively; S for the solid to be measured; superscripts d, p and h for the dispersion, polar and hydrogen bond forces of the surface free energy, respectively.

<table>
<thead>
<tr>
<th>NO.</th>
<th>Liquids</th>
<th>$\gamma_L$</th>
<th>$\gamma^d_L$</th>
<th>$\gamma^p_L$</th>
<th>$\gamma^h_L$</th>
</tr>
</thead>
<tbody>
<tr>
<td>i</td>
<td>Water</td>
<td>72.8</td>
<td>29.1</td>
<td>1.3</td>
<td>42.4</td>
</tr>
<tr>
<td>j</td>
<td>Tetrabromoethane</td>
<td>47.5</td>
<td>44.3</td>
<td>3.2</td>
<td>0.0</td>
</tr>
<tr>
<td>k</td>
<td>n-Hexadecane</td>
<td>27.6</td>
<td>27.6</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

2.5 SEM analysis

Surface morphology of the PTFE sheets before and after treatment was examined using scanning electron microscopy (SEM) in a JEOL instrument (Model JSM-5800, Japan) after sputter coating with gold under vacuum. The magnification was 5000 times.

2.6 XPS analysis

Changes in the surface chemical composition and structure of PTFE sheets were studied by XPS in a PHI-5400 ESCA system (Perkin-Elmer, US) using a Mg-K$_\alpha$ ($h_\nu = 1253.6$ eV) radiation with a pass energy of 235 eV at a 15° angle of incidence. The background pressure in the analytical chamber was $5 \times 10^{-8}$ Pa. O/C and F/C atomic ratios at the PTFE sheet surface were estimated from the relative intensity of the O$_{1s}$ core level against the C$_{1s}$ core within an experimental error of ±0.01.

3 Results and discussion

3.1 Distribution of reactive species in the whole argon plasma reactor

Fig. 3 shows the radicals’ spectra of ESR analysis and the distribution of reactive species in the whole argon plasma. As seen in Fig. 3(a), uniform spectra and different intensities of ESR occurred at about the 3505 G on each sample treated at different distances from the active discharge zone. It indicated that congener carbon radicals were produced in the whole plasma reactor and their concentration was influenced by the sample position, but changed little within 40 cm, as shown in Fig. 3(b). Fig. 3(b) also shows the changes in the concentration of electrons and ions. It was reduced rapidly with the increased distance at the same rf power and approximated to 0 at 40 cm. This result means electrons, ions and radicals can be separated effectively at the position 40 cm from the center of the induction coil, at which position a relatively high purity of radicals is obtained.

Here, we must explain what the term radical means in this paper since it is the key point of this study. As argon is an inert gas, the long-lived metastable argon atoms are the only species that might exist in the downstream region of plasma (except atomic oxygen, nitrogen, and OH radicals from imperfect vacuum conditions)\cite{11,14,28}. So, the term radical used in this paper just represents the long-lived metastable argon atom.

3.2 Surface hydrophilicity

The hydrophilicity was evaluated by surface conglutination work ($W_a$) of PTFE sheet. The $W_a$ of the argon plasma direct- and post-discharge treated PTFE sheets were investigated as functions of the sample position as well as the rf power, treatment time and argon flow. The $W_a$ shows a strong dependence on these variables. Fig. 4 shows the typical effect of the sample position on the $W_a$.

![Fig. 3](color online)

Fig. 3 (a) ESR and (b) distribution of electrons, ions and radicals in a flowing afterglow Ar plasma (plasma conditions: 90 W; 3 min and 20 cm$^3$/min; pressure at 22 Pa) (color online)

Under special treatment conditions, as shown in Fig. 4, the $W_a$ reach values of $97.1 \times 10^{-3}$ N·m$^{-1}$, $106.8 \times 10^{-3}$ N·m$^{-1}$, $110.5 \times 10^{-3}$ N·m$^{-1}$, $101.5 \times 10^{-3}$ N·m$^{-1}$ and $98.3 \times 10^{-3}$ N·m$^{-1}$ at sample positions 0 cm, 20 cm, 40 cm, 60 cm, 80 cm, respectively. This result indicates that argon plasma post-discharge (i.e., at a sample position of 40 cm) is the best way to obtain the hydrophilic modification of PTFE for an atmosphere composed by the relatively high purity of radicals and rare discharge articles. So, we will next only discuss the hydrophilic changes under different rf powers, treatment times and gas flows at the direct- and post-discharge zone in order to make a comparison.

Fig. 4 Effect of sample position on surface conglutination work of PTFE (plasma conditions: 100 W; 30 s and 30 cm$^3$/min; pressure: 28 Pa)

From Fig. 5, the $W_a$ increases sharply with the rf power increasing up to 20 W, then, the trend slows down, and the peak values occur at about 40 W. Subsequently, the $W_a$ decreases tardily and increases again after 80 W. The ionization degree of argon gas and the energy of reactive species are both augmented rapidly with the initial increase in the rf power, and hence, the intensity of the interreactions between PTFE surfaces and plasma reactive species is enhanced. However, little change between 20 W and 80 W as well as rapid increasing after 80 W are not well understood, but it could be as follows.

Fig. 5 Effect of plasma treatment power on surface conglutination work of PTFE (plasma conditions: 30 s and 30 cm$^3$/min; pressure: 28 Pa)

Between 20 W and 80 W, the changes in the ion density and energy approximately tend to stabilize, and the system seems to reach a balanced state. During this course, the modified reactions keep at a certain extent. But when the rf power is above 80 W, the ionization degree may have a jump so that the concentration of reactive species increases largely; as a result, the modification of the PTFE surface is improved again. Of course, this still needs further study in the future.

In Fig. 6, large increases in the $W_a$ are observed within a very short time (10 s), and subsequently, the values reduce gradually with an increasing plasma treatment time. Plasma density is one of the important parameters in initiating chemical reactions on the polymer surface because of a higher density can promote the probability of reactive species action on a surface [14,28,29]. In this case, when the rf power and gas flow are fixed, the ion density in argon plasma reaches the saturation fleetly at the beginning of the discharge, so the modification effect reaches the crest quickly. But a treatment time longer than 10 s with the same plasma density would cause extra degradation on the PTFE surface, which leads to the surface hydrophilicity regression. The same conclusion was also drawn in other studies [30]. We believe that the optimum plasma treatment time is 10 s for the maximum improvement on surface hydrophilicity.

Fig. 6 Effect of plasma treatment time on surface conglutination work of PTFE (plasma conditions: 100 W and 30 cm$^3$/min; pressure: 28 Pa)

The effect of the argon flow on the $W_a$ is shown in Fig. 7, where the plots are changeful. At the beginning of the gas flow increase, the plasma density climbs up quickly, while the energy of the system received keeps constant since the rf power and time are fixed. So, the probability of reactive species action on the surface is enhanced largely, and a sharp increase in the $W_a$ occurs. But this phenomenon ends soon. When the flow is above 30 cm$^3$/min, an unexpected situation, namely, a sudden drop in the $W_a$ happens. This may be due to the falling vacuum degree in the whole plasma, caused by a rising gas flow, which has great influence on the degree of modification. Surprisingly, further raising the gas flow to more than 40 cm$^3$/min, we found that the $W_a$
began to increase again, gradually at first and rapidly at above 80 cm$^3$/min. Considering the importance of the plasma density during surface modification as mentioned above, we venture a speculation that, when the gas flow is higher than 40 cm$^3$/min, the influence on surface modification by the increased plasma density is greater than by the reduced vacuum degree, especially beyond 80 cm$^3$/min. In any case, when the gas flow changes while other conditions are fixed, surface modification is the outcome of the combined effects of the energy, the amount of reactive species as well as the vacuum degree of the system. Thorough investigations would be carried out in our next work for these intricate processes. In addition, it can be clearly seen from the plots in Figs. 5~7 that argon plasma post-discharge treatment can create higher surface hydrophilicity than that of direct-discharge. Compared with Fig. 3(b), it can be concluded that the reason for the better surface modification by plasma post-discharge is the enhanced reactions with PTFE surface by relatively high purity radicals at 40 cm.

3.3 Surface morphology

As the distribution plots show in Fig. 3(b), great etching on the PTFE surface by heavy collisions of the charged species is unavoidable. The etching can cause large molecular chain rupture and removal, and degrade the PTFE sheets. However, it would be weakened at 40 cm. To confirm this speculation, we investigated the surface morphology of original and treated PTFE sheets with SEM. Fig. 8 shows typical pictures. Clearly, the surface morphology of argon plasma post-discharge treated sheet is similar to the original, and the direct-discharge treated one is with some lumps.

3.4 Surface free energy

The surface free energy and its components of PTFE samples are listed in Table 2. It indicates that the surface free energy ($\gamma_S$) of the PTFE sheet is increased after modification by argon plasma treatment. Compared with the original sample, $\gamma_S$ increases more than twofold for plasma direct-discharge and post-discharge treated PTFE sheets. With further investigation of the components of surface free energy, we find that the polar force, which is constituted by the dipole force ($\gamma_p^S$) and hydrogen bonding force ($\gamma_h^S$), is the main factor affecting $\gamma_S$. Before and after argon plasma treatment, the polar force ($\gamma_p^S + \gamma_h^S$) increases from 0.1% to about 45.8% and 51.3%, respectively. Therefore, $\gamma_p^S$ is the main contributor to the increase in the polar force. The dispersion force ($\gamma_d^S$) decreases from 99.1% to about 54.2% and 48.7%, respectively. Accordingly, it can be concluded that the improvement of surface hydrophilicity largely lies in the increase in the polar force ($\gamma_p^S + \gamma_h^S$), especially $\gamma_p^S$.

3.5 XPS analysis

XPS analysis was used to characterize the surface chemical composition of PTFE sheets and the results are given in Table 3. From Table 3, it can be seen that
Table 2. Surface free energy results of the treated PTFE samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface free energy (×10⁻⁵ N/cm)</th>
<th>(\gamma_S)</th>
<th>(\gamma_D)</th>
<th>(\gamma_S)</th>
<th>(\gamma_D/\gamma_S) (%)</th>
<th>((\gamma_D+\gamma_S)/\gamma_S) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original PTFE</td>
<td></td>
<td>21.4</td>
<td>21.2</td>
<td>0.2</td>
<td>99.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Plasma direct-discharge treated PTFE (0 cm)</td>
<td></td>
<td>41.7</td>
<td>22.6</td>
<td>16.8</td>
<td>54.2</td>
<td>45.8</td>
</tr>
<tr>
<td>Plasma post-discharge treated PTFE (40 cm)</td>
<td></td>
<td>47.2</td>
<td>23.0</td>
<td>18.2</td>
<td>48.7</td>
<td>51.3</td>
</tr>
</tbody>
</table>

*Plasma condition: 100 W; 30 s and 30 cm³/min; pressure: 28 Pa

Table 3. Surface composition of PTFE samples measured by XPS

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface treatment conditions</th>
<th>Elemental ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>rf power Treatment time Argon flow</td>
<td>F/C</td>
</tr>
<tr>
<td></td>
<td>(W) (s) (cm³/min)</td>
<td></td>
</tr>
<tr>
<td>Original PTFE</td>
<td>3.27</td>
<td>0.02</td>
</tr>
<tr>
<td>Plasma direct-discharge treated PTFE (0 cm)</td>
<td>100</td>
<td>30</td>
</tr>
<tr>
<td>Plasma post-discharge treated PTFE (40 cm)</td>
<td>100</td>
<td>30</td>
</tr>
</tbody>
</table>

*Plasma condition: 100 W; 30 s and 30 cm³/min; pressure: 28 Pa

For further investigations on O1s, separate spectra were carried out. Good O1s spectra for the decomposition are shown by the dotted lines in Fig. 9. It is reasonable to assign the peak lying at the binding energy of 532.3∼532.4 eV to the C=O group, and the peak lying at the binding energy of 533.6∼533.7 eV to the C-O group [31]. Compared with the original PTFE, the spectral intensity and peak areas in the O1s spectra of treated PTFE are augmented. This indicates that some oxygen-containing functional groups (such as C=O and C-O) are introduced onto the PTFE surface. Furthermore, the C=O and C-O peaks show stronger and wider peaks with argon plasma post-discharge treatment than with argon plasma direct-discharge treatment. This is consistent with the changes in surface free energy and surface hydrophilicity as already shown in Figs. 4∼7, and Table 2, that is, when the amount of introduced oxygen moieties is larger, the enhancement of surface free energy and hydrophilicity of the samples is greater.

In conclusion, from the XPS survey spectra, it can be seen that the defluorination from PTFE is the key factor in surface modification by argon plasma. Argon plasma post-discharge has a higher capability for de-
fluorination than the direct-charge because of the relatively high purity argon radicals. Thus, the surface polarity and hydrophilicity of argon plasma post-discharge treated PTFE increase more than those of argon plasma direct-discharge treated PTFE.

4 Conclusions

The effects and mechanisms of PTFE film surface modification by low pressure argon plasma have been investigated. The hydrophilic improvement depends on the plasma rf power, exposure time and gas flow, and higher hydrophilicity with little degradation is consistently obtained in the plasma post-discharge area. As shown by the surface free energy calculation and X-ray photoelectron spectroscopy (XPS) analysis, the modification can be attributed to the formation of polar functional groups and the higher surface free energy on the PTFE surface. For the relatively high purity radicals and rare discharge particles in the post-discharge area, the etching action and the introducing reactions on the PTFE surface are limited and enhanced, respectively, and thus, better modification occurs consequently.

References

12 Chen J R, Yan J L, Zhang Y Z. 2004, Composite Interfaces, 11: 123
31 Briggs D. Translated by Chao L L, Deng Z W. 2001, Surface Analysis of Polymers by XPS and Static SIMS. Chemical Industry Press, Beijing, p.69

(Manuscript received 17 December 2010)
(Manuscript accepted 13 December 2011)
E-mail address of LIU Hongxia: hxlui72@mail.xjtu.edu.cn