Surface modification of polytetrafluoroethylene film using single liquid electrode atmospheric-pressure glow discharge*

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(Received 15 October 2010; revised manuscript received 18 February 2011)

Polytetrafluoroethylene films are treated by room temperature helium atmospheric pressure plasma plumes, which are generated with a home-made single liquid electrode plasma device. After plasma treatment, the water contact angle of polytetrafluoroethylene film drops from 114° to 46° and the surface free energy increases from 22.0 mJ/m^2 to 59.1 mJ/m^2. The optical emission spectrum indicates that there are reactive species such as O_2^+, O and He in the plasma plume. After plasma treatment, a highly crosslinking structure is formed on the film surface and the oxygen element is incorporated into the film surface in the forms of –C–O–C–, –C=O, and –O–C=O groups. Over a period of 10 days, the contact angle of the treated film is recovered by only about 10°, which indicates that the plasma surface modification is stable with time.

Keywords: single liquid electrode, atmospheric pressure glow discharge, wettability, ageing effect

PACS: 52.77.Bn, 68.08.Bc, 82.35.Gh **DOI:** 10.1088/1674-1056/20/6/065206

1. Introduction

Polytetrafluoroethylene (PTFE, $-[CF_2–CF_2]_n-$) has become one of the most attractive polymers for biomedical industry due to its excellent flexibility, thermal stability, fire and chemical resistance and low friction coefficient. In practical applications, PTFE has usually been manufactured into medical implants, artificial blood vessels, filters and oxygenating devices, thereby bringing great benefits to the patients.[1–3] On the other hand, it is well known that the surface wettability of the biomedical materials has great influence on the cell adhesion and the protein adsorption. The hemocompatibility and affinity of hydrophilic surfaces are usually better than those of hydrophobic surfaces.[3,4] Unfortunately, as the surface free energy is low, PTFE surface is hydrophobic. Therefore, there is a great need to improve the wettability of PTFE surface. During the past 10 years, many surface modification methods have been employed to improve the wettability of PTFE surface, including chemical etching,[5] UV-lasers,[6] electron and ion beams irradiation,[7,8] and plasma modification.[9,10] Plasma modification is one of the new surface modification methods. It usually involves the covalent grafting of reactive functional groups onto the substrate surface for specific needs. Plasma modification has apparent advantages: first, it can affect only a few nanometer depth of the substrate surface but has no influence on its bulk properties, second, it is a clean technology and does not cause any environmental pollution.[11–14]

In recent years, as a new kind of plasma surface modification method, atmospheric pressure glow discharge (APGD), which will be detailed here, has attracted much attention. Besides the advantages mentioned above, the APGD has some other attractive features: first, it is operated without vacuum equipment, thereby simplifying operation and reducing cost largely, second, it allows short treatment time and room temperature operation environ-

*Project supported by the State Key Program of National Natural Science Foundation of China (Grant No. 10735090) and the Young Scientist Fund of the National Natural Science Foundation of China (Grant No. 11005151).

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ment, third, it can attain a high plasma stability.[15] During the past few years, many researchers have concentrated on using APGD plasma plumes to improve the surface properties of various polymers, such as wettability,[16−18] biocompatibility,[19−22] printability,[23,24] and adhesion.[25]

However, there is an inherent drawback about plasma modification, i.e. the ageing effect. It has been observed that with time passing, the chemical compositions and properties of the plasma treated polymer surfaces often undergo substantial changes, which will restrict their industrial applications greatly. Siow *et al.*[26] have pointed out that there are two principle mechanisms about the ageing effect: the post-plasma oxidation, which is initiated by the reaction between remaining radicals and in-diffusing atmospheric oxygen and the surface adaptation, also known as surface restructuring, which is dependent on the interfacial energy difference between the polymer and its environment. In the surface adaptation process, some of the polymer chains can be moved from the surface into the bulk, which will lead to a great decrease in the surface density of functional groups. However, so far, there have not been the detailed study results of the chemical reactions involved in the ageing process.[27] How to suppress the ageing effect of the plasma treated samples is quite important and has great influence on their applications.

In this paper, we aim to improve the wettability of PTFE films and restrict its ageing effect. We treat the PTFE film surface by helium APGD plasma plumes, which are generated with a home-made single liquid electrode discharge device. So far, the single liquid electrode APGD has been presented here for the first time. The optical emission spectroscopy (OES) is used to detect the reactive species in the plasma plume. The wettability and the surface free energy of PTFE films are detected using contact angle measurements. The surface characteristics of PTFE films are detected complementarily by scanning electron microscope (SEM) and X-ray photoelectron spectroscopy (XPS).

2. Experimental details

2.1. Material preparation

The materials of plasma treatment were the commercial 50-μm PTFE films. The PTFE films were cut into 8 mm×8 mm pieces. All the samples were washed ultrasonically in acetone, absolute ethyl alcohol and distilled water successively for 10 minutes. Then the films were dried at room temperature and kept under vacuum prior to use.

2.2. Plasma procedure

The schematic diagram of the atmospheric plasma device is shown in Fig. 1. A similar novel APGD plasma device was described by Chen *et al.*[28−30] The quartz tube (inner diameter: 8 mm, length: 200 mm, thick: 1 mm) acted as a gas feeding tube as well as the dielectric layer. The potassium chloride solution (KCl, 0.1 mol/L, conductivity: 0.12 S/cm) in the outer layer of the quartz tube acted as the only electrode. There were two reasons for using solution electrode: first, the solution electrode was in a tight contact with the quartz tube, which made the electric field distribution more uniform and the plasma plume more homogeneous, second, the liquid electrode could serve as a coolant of the whole discharge system and lower the temperature during the discharge. According to Chen *et al.*'s results, the conductivity of the liquid electrode had great influence on the plasma discharge and as conductivity decreased, it was more difficult for the discharge to occur. Therefore, in our experiment, the electrode conductivity was fixed at 0.12 S/cm, a relatively high value. The electrode was connected to an AC power with a maximum peak voltage of 30 kV and an adjustable frequency from 8 kHz to 30 kHz. The plasma plume was generated in ambient air with the working gas of helium (He). The gas velocity was controlled by the flow meter. The ambient temperature and the relative humidity were

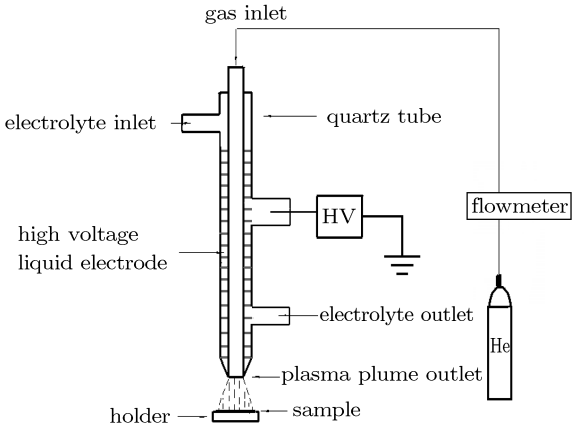


Fig. 1. Schematic diagram of the atmospheric plasma device.

controlled at 22 °C and 30% respectively. The PTFE samples were stick to the sample holder and treated by the plasma plumes directly. The distance between the sample holder and the orifice of the tube was fixed at 10 mm and the treatment time was varied from 5 s to 30 s. During the treatment, the discharge power was varied from 0 W to 72 W at a frequency of 13 kHz. After plasma treatment, the PTFE samples were stored in room air prior to various measurements.

2.3. Measurement procedures

The static contact angles of PTFE films were measured immediately after plasma treatment by dropping the de-ionized water and α-bromonaphthalene on the surface and using the sessile drop method. The measurements were performed at room temperature by using the JY-82A contact angle meter (Chengde Dingsheng Testing Machine Co., Ltd, China). The volume of each drop was fixed at 5 μL by a micro-syringe and each contact angle value was the average of 5 measurements. The surface free energy of PTFE samples and its polar and dispersive components were calculated with the measured contact angles of the two liquids using the Owens-Wendt method.[31−33] The optical emission spectrum of APGD plume was investigated by Stellarnet EPP-2000C (USA) in a wide wavelength range of 190 nm–850 nm. The SEM investigation was operated in a usual way by HITACHI S-4200 (Japan) instrument and the PTFE samples were sputter-coated with a thin layer of gold prior to measurement. The X-ray photoelectron spectroscopic data were obtained using an ESCALab250 electron spectrometer from Thermo Scientific Corporation with monochromatic 150-W AlKα radiation. The base pressure was about 6.5×10^{-8} Pa. The binding energies were referenced to the C1s line at 284.8 eV from alkyl or adventitious carbon by the software of Advantage 4.15. Elemental composition was inferred from the photoelectron peak areas using the respective photoionization cross section calculated by Scofield.[34]

3. Results and discussion

The water contact angles of the PTFE samples treated at different treatment time are shown in Fig. 2. It can be found that under three different discharge powers, the water contact angel drops largely with the increase of treatment time from 0 to 15 seconds, while with the further increase of the treatment time, the contact angle changes slightly. Thus, it seems that the treatment time of 15 seconds is suitable for PTFE surface modification.

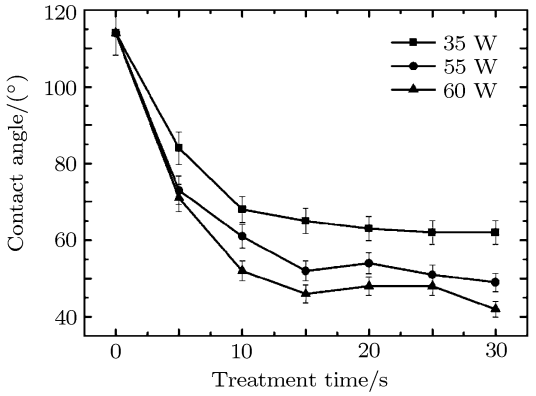


Fig. 2. Water contact angles of PTFE films each as a function of treatment time for different discharge powers.

The water contact angles of the plasma treated PTFE samples at different discharge powers are shown in Fig. 3. For each of the PTFE samples, the dispersion of the contact angle from different regions is below 5°, which indicates that the plasma treatment is uniform. According to Fig. 3, with the increase of the discharge power from 0 W to 60 W, the contact angle drops largely from 114° to 46°, reducing about 60%, which shows that the wettability of PTFE film is improved apparently. On the other hand, with the further increase of the discharge power from 62 W to 72 W, it is noticed that the water contact angles of the treated samples raise gradually to around 63°. By analysing the discharge mode of the plasma plume, it is noticed that when the discharge power is increased to a critical point (about 65 W), the glow discharge changes into filamentary style and the plasma plume

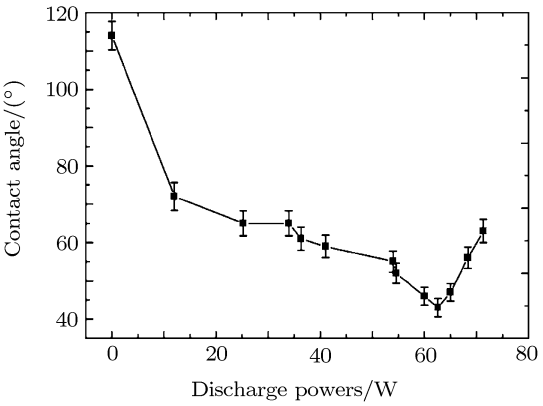


Fig. 3. Water contact angles of the plasma treated PTFE films at different discharge powers for 15-s treatment.

turns unstable. This phenomenon was in accordant with Chen *et al.*'s research results. It is speculated that the discharge mode transition can reduce the modification effect of the plasma plume. Based on the above factors, the discharge power around 60 W is ideal for PTFE surface modification.

Referring to the Owen and Wendt approach, the surface free energy (γ) consists of two components ($\gamma = \gamma^{\rm p} + \gamma^{\rm d}$), one ($\gamma^{\rm p}$) is attributed to the polar interaction and the other ($\gamma^{\rm d}$) is ascribed to the dispersive force. The relationship between the surface energy and the contact angle can be described by the Owen–Wendt equation

$$\gamma_{\rm l}(1+\cos\theta) = 2(\gamma_{\rm s}^{\rm d}\gamma_{\rm l}^{\rm d})^{1/2} + 2(\gamma_{\rm s}^{\rm p}\gamma_{\rm l}^{\rm p})^{1/2}, \qquad (1)$$

where $\gamma_{\rm l}$, $\gamma_{\rm l}^{\rm p}$, and $\gamma_{\rm l}^{\rm d}$ are the surface free energy and its polar and dispersive components of the reference liquids respectively, which are listed in Table 1; $\gamma_{\rm s}$, $\gamma_{\rm s}^{\rm p}$ and $\gamma_{\rm s}^{\rm d}$ are the surface free energy and its polar and dispersive components of the PTFE sample respectively. By measuring the contact angles of two reference liquids on the sample surface, we can calculate the surface free energies of PTFE samples before and after plasma treatment. According to Table 2, it can be seen that after plasma treatment at a discharge power of 60 W for 15 seconds, the surface free energy of the PTFE film increases from 22.0 mJ/m^2 to 59.1 mJ/m^2. Both the polar component and the dispersive component increase and the fraction of polar component in total surface free energy increases apparently (from 8.8% to 36.2%). It indicates that after the plasma treatment, a mass of polar groups forms on the PTFE surface, which leads to the great increase of the surface polarity.

Table 1. Surface free energy and its dispersion and polar components of reference liquids.

Liquids	$\gamma_{\rm l}^{\rm d}$	$\gamma_{\rm l}^{\rm p}$	$\gamma_{\rm l}$
Water	21.8	51	72.8
α-bromonaphthalene	44.6	0	44.6

Table 2. Water contact angle and surface free energy of the untreated and the treated PTFE sample at a discharge power of 60 W for 15-s treatment.

Sample	Surface free energy/(mJ/m^2)					
	Contact angle/(°)	$\gamma^{\rm d}$	$\gamma^{\rm p}$	γ	$(\gamma^{\rm d}/\gamma)$/%	$(\gamma^{\rm p}/\gamma)$/%
Untreated	114	20.1	1.9	22.0	91.2	8.8
He plasma treated	46	37.7	21.4	59.1	63.8	36.2

The optical emission spectrum of the He APGD plasma plume at a discharge power of 60 W is shown in Fig. 4. It can be found that the spectrum is very rich in emission features and most atomic and molecular lines can be identified by referring to Refs. [29] and [35]–[37] and NIST Atomic Spectrum Database Lines Form.[38] The spectrum is dominated by excited nitrogen (N_2: 338, 357, and 316 nm; N_2^+: 392 nm), oxygen (O_2^+: 428 nm, O: 298 nm) and helium (He 2^3P–3^3D at 588 nm, 2^1P–3^1D at 667 nm and 2^1P–3^1S at 707 nm) species. The presence of nitrogen and oxygen lines in the spectrum can be attributed to the ambient air environment. During the discharge, a small quantity of nitrogen and oxygen from room air can be activated and take part in the modification process. The presence of reactive oxygen (O_2^+, O) is related to the formation of hydrophilic groups and has great influence on the wettability improvement of PTFE samples. In the plasma plume, the formation of O_2^+ can be due to the Penning oxidation ($He^+ + O_2 \rightarrow O_2^+ + He$ and $He^* + O_2 \rightarrow O_2^+ + He + e^-$) and the presence of atomic oxygen can be attributed to the collision between oxygen molecule and energetic electron ($e^- + O_2 \rightarrow O + O + e^-$).[36,37]

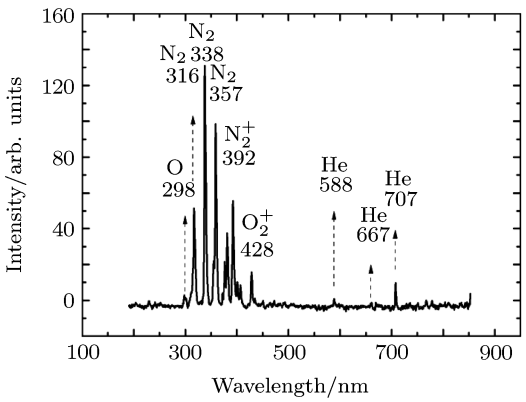


Fig. 4. Emission spectrum of the plasma plumes with 0.2 m^3/h He and at a discharge power of 60 W.

The surface chemical composition change of the treated PTFE sample is analysed by XPS test. The

full XPS spectra and the atomic percentage ratios of the plasma treated PTFE sample at a discharge power of 60 W for 15 seconds are shown in Fig. 5 and Table 3, respectively. According to the molecular structure of PTFE (–[CF_2–CF_2]$_n$–), before plasma treatment, there should be only the C_{1s} peak at 291.7 eV and the F_{1s} peak at 689.6 eV, while after plasma treatment, an apparent O_{1s} peak at 532.1 eV and a weak N_{1s} peak at 401.6 eV are present in the XPS spectra. After plasma treatment for 15 seconds, The F/C ratio drops from 2 to 1.18 and the O/C ratio increases from 0 to 0.33, which indicates that the defluorination and oxidation process are quite efficient and some oxygenic functional groups are incorporated into the treated PTFE surface.

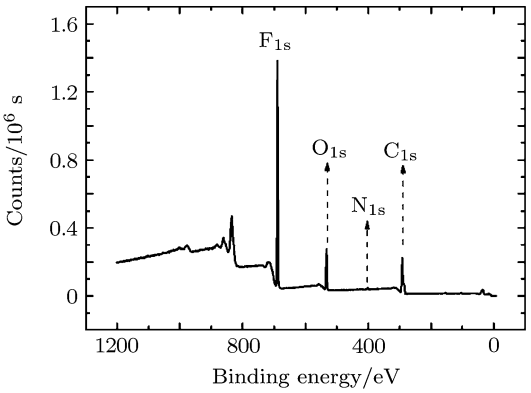


Fig. 5. The XPS survey spectra of the plasma treated PTFE sample at a discharge power of 60 W for 15-s treatment.

Table 3. Surface compositions of the untreated and treated PTFE samples, measured by XPS.

Sample	Atomic percentage/%				Elemental rations		
	F	C	O	N	F/C	O/C	N/C
Untreated	66.67	33.33	–	–	2	–	–
He plasma treated	46.61	39.54	12.89	0.96	1.18	0.33	0.02

To gather further information about the defluorination and oxidization process, the high resolution spectra of C_{1s} peak are shown in Fig. 6. By fitting this curve, we can decompose the spectrum into six components, i.e., the peaks at 294.3, 291.8, 289.3, 288.6, 286.8, and 285.0 eV. In the spectrum, the peak at 291.8 eV corresponds to –CF_2, which is the main component of the PTFE sample. The peak at 285.0 eV corresponds to –C–H and –C–C– bonds arising from plasma treatment or residues of Mg Kα radiation.[39] The peaks at 294.3, 286.8, 288.6 and 289.3 eV are speculated to correspond to –CF_3, –C–O–C–, –C=O, and –O–C=O bond.[40,41] Therefore, we speculate that the hydrophilic oxygenic polar functional groups, such as –C–O–C–, –C=O, and –O–C=O are incorporated into the PTFE surface after plasma treatment and they are responsible for the surface polarity and wettability improvement largely.

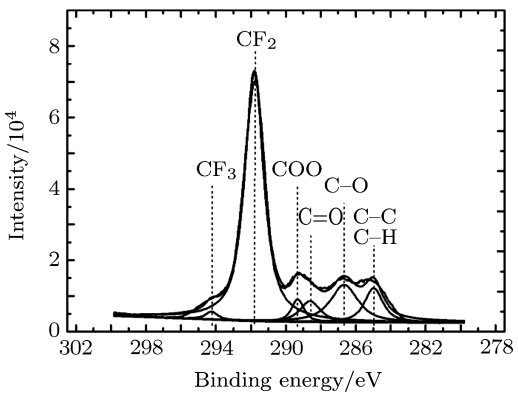


Fig. 6. High resolution C_{1s} spectrum of plasma treated PTFE film.

Figure 7 shows the SEM images of the untreated (Figs. 7(a) and 7(b)) and plasma treated PTFE samples at a discharge power of 60 W for 15-s treatment (Figs. 7(c) and 7(d)). It can be found that the untreated PTFE surface is flat, while some micropores on a scale of about 300 nm exist on the surface. After plasma treatment, the micropores are reduced greatly and some connected channels are found across the surface. It is speculated the occurrence of connected channels can be attributed to the etching effect of plasma plumes. Combining the optical spectrum and the XPS results, in the plasma process, the energetic ions, electrons, excited atoms and molecules, as well as the UV rays in the plasma plume can affect the film surface, causing permanent damage on the PTFE surface, mainly in the form of the backbone chain scission. Meanwhile, the electronic excitation can lead to the formation of free radicals such as –C–O–C–, –C=O, and –O–C=O. The free radicals may cross-link the polymer chains. Continuously cross-linking can form the three-dimensional networks of cross-linked molecular chains on the treated PTFE surface.[42–44] Therefore, some connected channels form on the surface and the micropores of the PTFE film surface are greatly reduced.

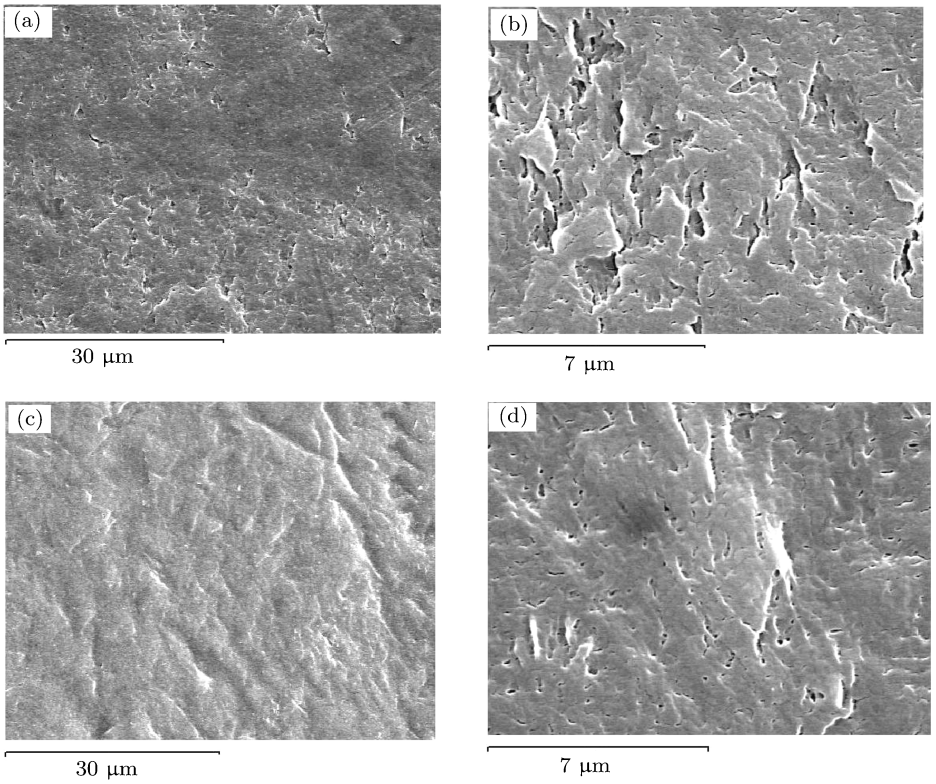


Fig. 7. The SEM images of PTFE films: (a) untreated, 1000 ×, (b) untreated, 5000 ×, (c) He plasma treated at 60 W, 15 s, 1000×, (d) He plasma treated at 60 W, 15 s, 5000×.

The ageing behaviour of the treated PTFE samples is shown in Fig. 8. It can be found that with time passing, the hydrophobicity recovery of the plasma treated PTFE samples is rather low, only about 10° over a period of ten days. Moreover, it is found that the plasma treated surfaces tends to recover mostly in the first one day. Compared with other results in this field,[45−47] the surface modification by single liquid electrode APGD plasma plumes is relatively stable with time. It is speculated that the highly cross-linking structure of the plasma treated PTFE sample is the key factor for the weak hydrophobic recovery. Siow has indicated that the surface restructuring motion is one of the two main processes for ageing behaviour, which can lead to a great decrease in the surface density of functional group. After APGD plasma treatment, the highly cross-linking structure on the surface can restrict the ability of the free radicals on the surface to engage in the restructuring motion, so that the free radicals density on the surface can be maintained at a relatively high value and the hydrophobic recovery behaviour can be restricted largely. On the other hand, it is found that the PTFE samples treated at three different discharge powers almost have the same recovery degrees. It is speculated that when the discharge power increases to a certain value, the cross-linking degree of the plasma treated PTFE sample arrives at a fixed value, which does not change with the further increase of the discharge power.

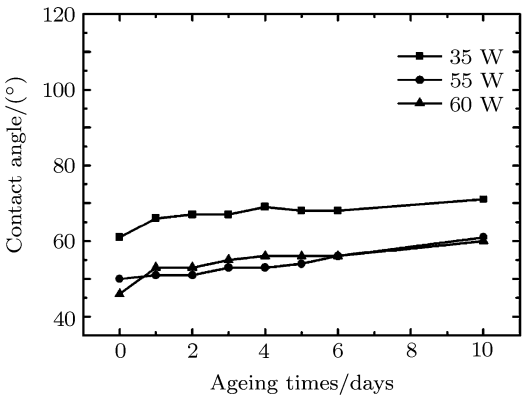


Fig. 8. Water contact angles of PTFE films each as a function of ageing time at different discharge powers.

4. Conclusion

We treat PTFE films by helium APGD plasma plumes which are generated with the home-made single liquid electrode plasma discharge device. After plasma treatment at a discharge power of 60 W for 15 seconds, the water contact angle drops from 114°

to 46°, and the surface free energy increases from 22.0 mJ/m^2 to 59.1 mJ/m^2. The optical emission spectrum shows that there exist reactive species such as O_2^+, O and He in the plasma plume. In the plasma treatment process, the reactive species and energetic electrons influence the PTFE surface, breaking the original chemical chains and reconstructing new chemical bonds, which leads to the formation of highly cross-linked structure on the PTFE surface. After plasma treatment for 15 seconds, the F atomic percentage drops and the O atomic percentage increases apparently, indicating that the defluorination and oxidation are very high efficient. The oxygen element is incorporated into the treated PTFE surface in the forms of –C–O–C–, –C=O, and –O–C=O. The ageing survey results show that in a period of 10 days, the contact angle of the plasma treated PTFE film has only 10° recovery, indicating that the wettability improvement of PTFE film by plasma treatment is stable with time. It is expected that the high cross-linking structure on the treated PTFE surface can reduce the reptation motion and then reduce the hydrophobic recovery of the treated samples.

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