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Change in Surface Microstructure and Properties of PTFE after Solar Radiation and its Mechanism

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Abstract: A series of solar radiation tests for the polytetrafluoroethylene (PTFE) bulk and film samples were carried out using Q-SUN XE-3-HSC type Solar Radiation Simulator, with the test parameters as follows: radiation intensity is 1 120 W/m², temperature is 55 °C and humidity is 70% RH. Surface morphology, composition and microstructure of the PTFE samples before and after radiation tests were characterized contrastively. Effect of solar radiation on the tribology and wetting properties of PTFE were also studied by tribometer and contact angle tester, respectively. The results show that, for radiated PTFE, surface roughness, the relative content of C element, the friction coefficients and the contact angle with water increased in varying degrees. In conclusion, the obvious change in PTFE samples can be mainly attributed to break of (CF_x)-C bonds after bombardment of high energy UV photons, which causes the loss of F-rich groups, oxidation, crosslinking and restructuring of active unsaturated groups.

Key words: solar radiation; PTFE; microstructure; tribological properties; wetting properties

1 Introduction

A solar radiation is the main energy source of the earth's surface. At the same time, its heat and photochemical effect may induce important change in structure and properties of equipments and materials working in outdoor environment, some polymer materials even can be degraded completely by continuous strong solar radiation^[1]. Consequently, an in-depth study about the effect of solar radiation on typical engineering materials and its damage mechanism has important significance.

Polytetrafluoroethylene (PTFE), with the condensed structural formula of “-[-CF₂-CF₂-]_n”, is a polymer aggregated by tetrafluoroethylene, which has been widely used in petrochemical, machinery manufacture and defence industries for its excellent chemical stability, thermal stability,

electrical insulation, self-lubricity and hydrophobicity properties. But the radiation-resistant property of PTFE is relatively poor (about 104 Rad). Degradation, crosslinking and other change in properties or structure would occur after solar radiation^[2]. Accordingly, many researchers introduce radiation methods, such as ion beam, electron beam, high-energy ray, ultraviolet radiation, to modify or inarch the surface of PTFE materials^[3-5]. But the related research about the influence of solar radiation on the structure and properties of PTFE is still rare.

In this paper, changes in microstructure, lubricating property and wetting property of PTFE under the action of continuous solar radiation were studied using a solar radiation test chamber, with the purpose to provide reference for the serving and storing of PTFE-related materials in direct sunlight environment.

2 Experimental

PTFE with purity of 99.99% was bought from The First Plastic Factory of Beijing. A sort of samples was PTFE circular disks of $\Phi 50$ mm×8 mm, which were used for performance testing. The other sort of samples was PTFE film of 2 mm×2 mm×0.08 mm, which were used for microstructure characterization.

According to related Standards for Solar Radia-

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tion Tests, such as MIL-STD-810D/E505 of USA, DEFSTAN 00353-03 of Europe and GJB150.7A-2009 of China, the experimental scheme is designed as follows: all of the discal and filmy samples were divided into 4 groups, one group was as-obtained PTFE, the other three groups were radiated by simulated sunlight for 4, 8 and 12 days, respectively. The test equipment is Q-SUN XE-3-HSC type Solar Radiation Simulator, its schematic diagram is shown in Fig.1. The radiation source is made up of 3 parallel-fixed Xe lamps, their energy and spectrum distribution are shown in Table 1. The test parameters were as follows, radiation intensity was $1\ 120\ \text{W/m}^2$, test temperature was $55\ ^\circ\text{C}$ and the humidity was 70% RH, respectively.

Table 1 Spectrum and energy distribution of the solar radiation test chamber

Characteristic	Range of the spectrum			
	Ultraviolet light	Visible light	Infrared ray	
Wavelength/nm	280-320	320-400	400-780	780-3 000
Intensity/(W/m ²)	5	63	560	492

The effect of solar radiation on micro morphology of PTFE was observed by XTL361 type stereoscopic microscope and Dimension Icon type atomic force microscope (AFM). The spectral reflection factors of PTFE before and after solar radiation were tested by X-Rite Color-Eye 7000A spectrophotometer, respectively.

Changes in composition and microstructure of PTFE before and after solar radiation were characterized by ESCALab220i-XL X-ray photoelectron spectrometer (XPS) and IR-408 type Fourier transform

infrared spectrometer (FT-IR).

Wetting property of PTFE samples in distilled water was tested by Powereach JC2000C1 type contact angle meter, and the change of contact angle after radiation was calculated using Profile Image Method.

Tribological properties of PTFE samples after solar radiation for different time were tested by MSTS-1 type ball-on-disk tribometer. 9Cr18 steel balls with diameter of 9.525 mm were selected as the upper samples, the normal load is 9 N, the rotating speed is 200 r/min, and the wearing time is 30 min. Wear scars of PTFE samples were observed by LEXTOLS4000 3D type laser scanning confocal microscopy.

3 Results and discussion

3.1 Change in microstructure of PTFE after solar radiation

The optical micrograph of original and solar radiated (12 days) PTFE samples is shown in Fig.2 (a), (b), respectively. The surface of original sample with uniform texture is smooth and clean, and shows milk-white color. After continuous solar radiation for 12 Days, the color of PTFE becomes dark slightly, the contrast grade of different areas is different, and there are some granular material appeared at local areas. As shown in Fig.2 (c), (d), transparency of the original PTFE film is relatively high, during the wavelength of 360-750 nm, the spectral reflection factor is about 13.7%-23.2%, and the average reflectivity is 17.7%. After 12 days' radiation, spectral reflection factor of the radiated PTFE film increased notably (63.3%-79.9%), the average value is about 73.1%. According to existing

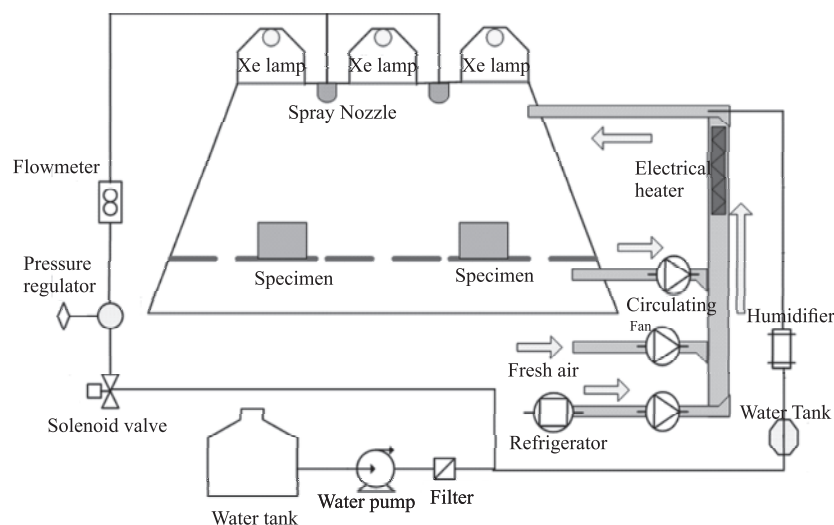


Fig.1 The schematic diagram of Q-SUN XE-3-HSC type solar radiation simulator

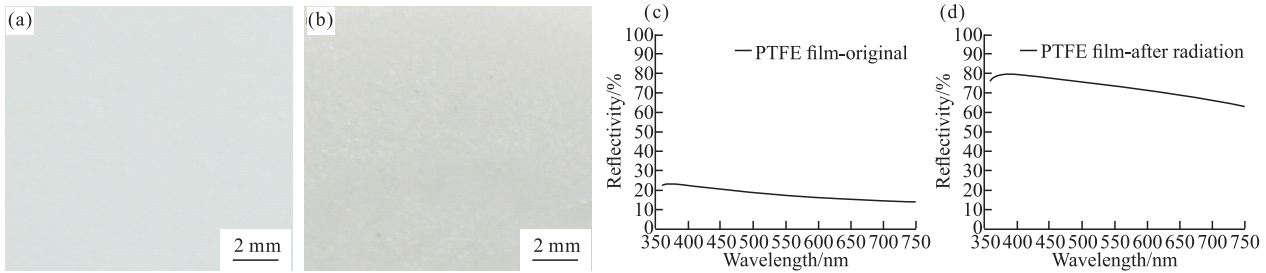


Fig.2 Surface appearance and spectral reflectivity of PTFE samples before and after solar radiation: (a), (c) original PTFE samples; (b), (d) radiated PTFE samples

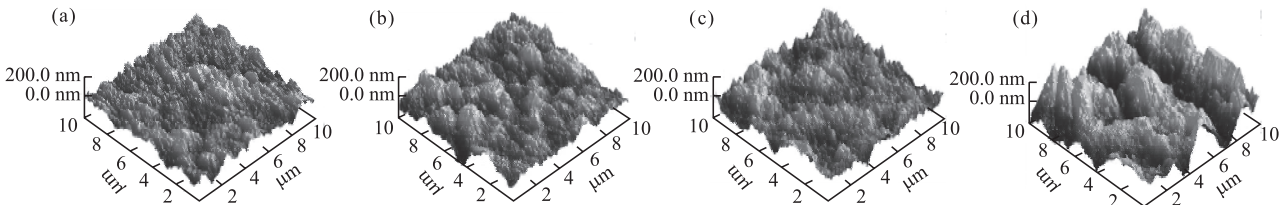


Fig.3 AFM morphologies of PTFE samples after solar radiation for different time: (a) original; (b) 4 days; (c) 8 days; (d) 12 days

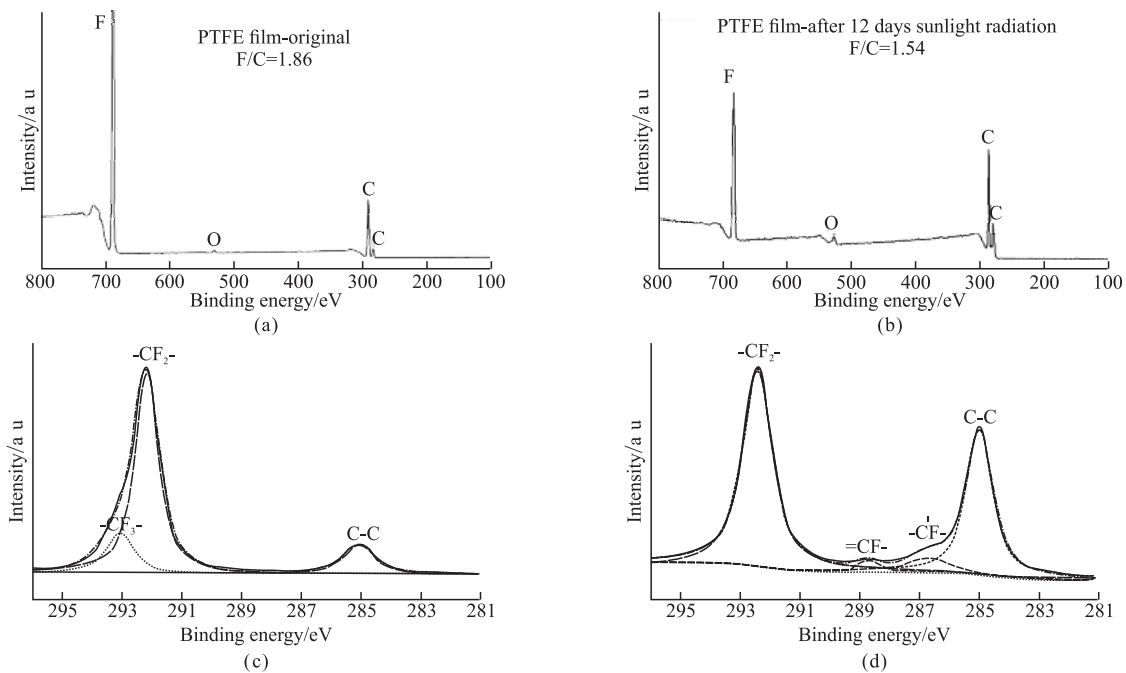


Fig.4 XPS spectrums of PTFE samples before(a,c) and after (b,d) solar radiation : (a,b)survey scan spectra; (c,d) fitted C1s spectra

studies and flight experiment results, photodarkening effect of PTFE materials would occur after ultraviolet (UV) irradiation [6]. So, change of surface appearance and spectral reflectivity the PTFE film samples can be mainly attributed to the UV components of the spectrum of Solar Radiation Simulator.

As shown in Fig.3, the microstructure of PTFE samples after solar radiation for different time was characterized by AFM. The original PTFE has a relatively smooth surface, with roughness of about 30.3 nm. The whole surface is covered by cluster structures with size ranging from nanometer to sub-micron. After 4 days radiation, surface roughness of the sample increased evidently ($R_a=36.3$ nm), most of the surface is

covered by dome-like outburst structures. After 8 days solar radiation, surface roughness increased slightly again, the whole surface disintegrated into bulge and bottomland areas, the bulge structures congregated by aculeated peaks. After 12 days radiation, surface roughness of the samples increased notably, the average value of R_a is as high as 81 nm. Bulge structures showed continuous mountain-like profile, and grooves of about sub-micron in depth formed at bottomland areas.

Based on analysis of the AFM morphologies, it can be summarized that the local areas of PTFE were corroded selectively by solar radiation. Surface roughness increased gradually with the increase of

radiation time, and finally formed continuous large area bulges and bottomlands on the surface layer.

XPS survey scan spectrums and the C1s spectra of PTFE samples before and after 12 days radiation are shown in Fig.4. No matter original and radiated samples, the surface composition of PTFE samples is made up of F, C elements and a little O. After solar radiation, the ratio of element content for F/C decreased from 1.86 to 1.54, some F element lost and the content of C increased, O element also increased slightly. As shown in Fig.4 (c) and (d), the fitted component peaks of original PTFE are at the binding energies of 293.1, 292.2 and 285.1 eV, corresponding with the local structures of $-\text{CF}_3$, $-\text{CF}_2$ -, and $-\text{C}-\text{C}$ -, respectively. In contrast, after solar radiation, the intensity and location of previously existing peaks changed observably, the peak correspond with $-\text{CF}_3$ disappeared, the intensity of $-\text{C}-\text{C}$ - peak increased, and some new peaks which can be assigned to $=\text{CF}$ - appeared.

Fig.5 (a) and (b) are the FT-IR absorption spectra of PTFE samples before and after radiation. It is illustrated there are symmetrical and dissymmetrical stretching vibration bands of C-F bonds at $1\ 202.5\ \text{cm}^{-1}$ and $1\ 143.39\ \text{cm}^{-1}$ in FT-IR spectra of original PTFE. The peaks at 719.73 , 637.39 and $554.73\ \text{cm}^{-1}$ correspond to amorphous ribbon of local areas, which shows that the original PTFE sample exhibiting the characteristic spectrum of bulk PTFE, and some materials aggregated as amorphous state [7]. After solar radiation for 12 days, some cuspidal absorption peaks appeared at $1\ 205.12$, $1\ 146.09$ and $635.54\ \text{cm}^{-1}$, and the integrated intensity of the peak corresponding to amorphous ribbon ($635.54\ \text{cm}^{-1}$) increased evidently. Furthermore, some immethodical peaks of new complex structures appeared around $1\ 540.45\ \text{cm}^{-1}$. It can be seen that, after solar irradiation, the degree of amorphization of PTFE increased, and PTFE generated some new structures.

The test results obtained by XPS and FT-IR can

be explained as follows, the ideal molecular structure of PTFE is double helix chain, the outer layer and the inner layer are made up of F atoms and carbon chain, respectively, and the bonding force of C—C bonds are C—F about 346.94 and 484.88 kJ/mol, respectively. F atoms of the outer layer can protect the inner carbon chain well, so PTFE itself has good chemical stability^[8]. However, the original PTFE is not entirely aggregated of idea monomers of $[-\text{CF}_2-\text{CF}_2-]_n$ -. Besides $-\text{CF}_2$ - structure, there were also some fluorocarbon groups (CF_x -) and amorphous structure, which existed in the form of terminal group ($-\text{CF}_3$) or groups lacking of F ($-\overset{|}{\text{C}}-\cdot$, $-\overset{|}{\text{C}}\text{F}$), and the bonding force between these groups and principal carbon chains is weak. There are partial ultraviolet light in the spectrum of irradiation source (Xe lamp). The bonds between $(\text{CF}_x)-\text{C}$ structures may be broken by high-energy ultraviolet photons. If the (CF_x) - groups are lack of F, it will lead to rupture of long chains of PTFE surface. And if (CF_x) -group are rich in F, it will result in loss of F element in the form of volatile products. In addition, some new complex structure also formed resulting from cross-linking, restructuring and oxidation (C-O bonding) of cracked active unsaturated groups^[9,10].

3.2 Effect of solar radiation on tribological properties of PTFE

Fig.6 shows the friction coefficient curves (under the test condition of 9 N and 200 r/min) of original and radiated PTFE samples. It can be seen that, the original PTFE shows good solid lubricating properties, the friction coefficients in starting period are about 0.1. After a transitory running-in period of about 100 seconds (S), the friction coefficient stabilized at about 0.075, and the fluctuation of friction coefficients was mild. After 4 days solar radiation, the friction coefficients in stable period rose to about 0.085, and the fluctuation range also increased. After 8 days solar radiation, the change of average friction coefficient

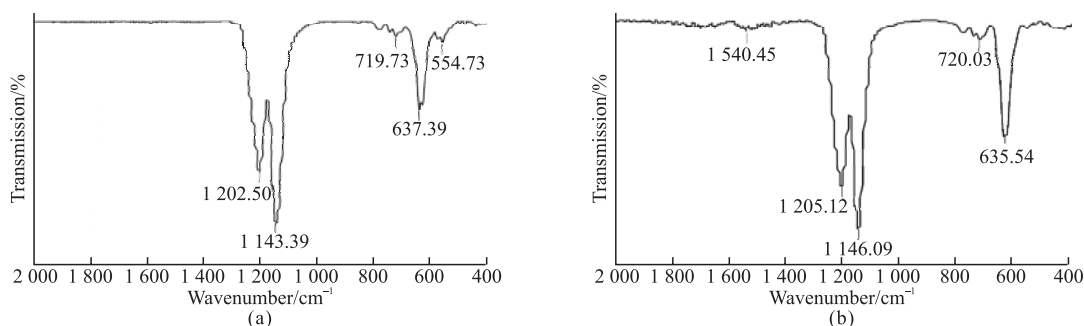


Fig.5 FT-IR absorption spectra of original PTFE before (a)and after (b) solar radiation

was little, but the fluctuation of friction coefficients increased notably. After 12 days solar radiation, the friction in starting period was relatively stable, and the friction coefficients remained nearby 0.075. But after running for 400 S, the fluctuation of friction coefficients increased dramatically, the average value of friction coefficients increased to 0.1, and the maximum value of friction coefficients had exceeded 0.15.

Fig.7 shows the laser scanning confocal micrographs of above-mentioned samples after wearing for 30 min. As can be seen, wearing of all of the four samples is mild. There are many grooves around the center of wear scars, which are parallel to the sliding direction. And some material accumulated at both sides of the wear scars. As for the original sample, the grooves on wear scar are relatively deep and dense, but the worn surface is clean and smooth. As for the samples after radiation, the grooves are relatively shallow and sparse. The worn surfaces are more smooth at macro level, but some granular and flake peeling materials accumulated at local area, the size and amount of accumulations also increased gradually with the increase of irradiation time.

“-CF₂-” units in PTFE molecule arranged in a zigzag shape spiral chain with large molecular weight. Under the influence of friction heat, the material near

contact area softened, some PTFE macromolecule were pulled out of crystalline zone and formed transfer film on the counter part surface by Coulomb force and Vander Waals force gradually. The helix structure of PTFE is apt to slip, and thus showing solid lubricating properties.

Changes in tribological properties of PTFE after solar radiation can be mainly attributed to the following reason: lubricating properties of PTFE declined because loss of F element and F-rich groups, and the average friction coefficient increased. Stationarity of friction decreased because of increasing of surface roughness, and fluctuation of friction coefficients also increased. Some long-chain structures were destroyed because of rupture of carbon bonds, brittleness and anti-scuffing properties of surface materials increased, and so spalling materials accumulated at worn surface after long period solar radiation^[11,12].

3.3 Effect of solar radiation on wetting properties of PTFE

Fig.8 shows the contact angles of PTFE samples with medium of distilled water. The original PTFE exhibits good hydrophobicity with contact angle of 97.13°. After solar radiation for 4, 8 and 12 days, the contact angles of PTFE samples with water increased to 97.91°, 100.8° and 103.1°, respectively.

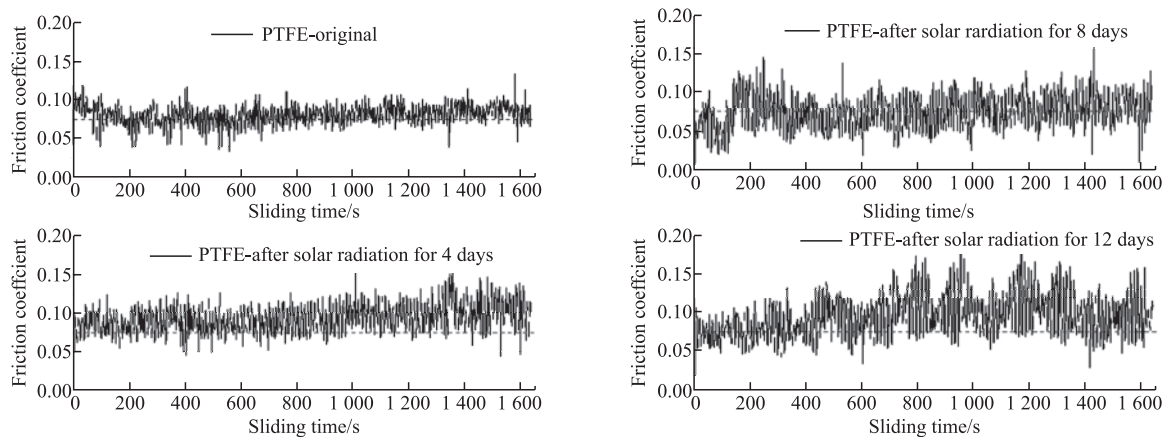


Fig.6 Friction coefficient curves of PTFE after radiated for different time

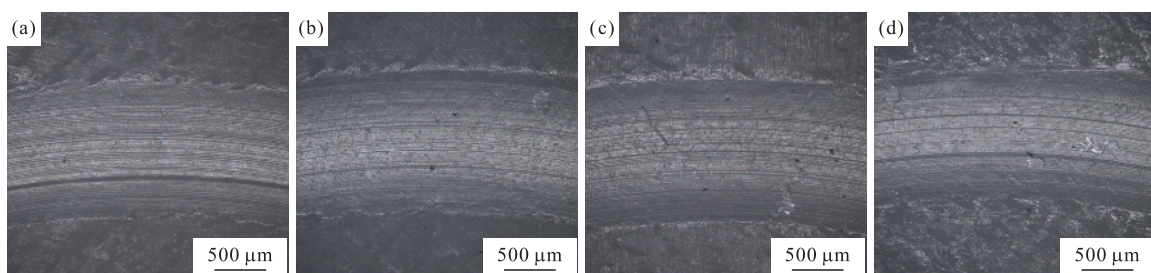


Fig.7 Morphologies of worn surfaces of PTFE samples after solar radiation for different time (a)original, (b)4 days, (c)8 days, (d)12 days

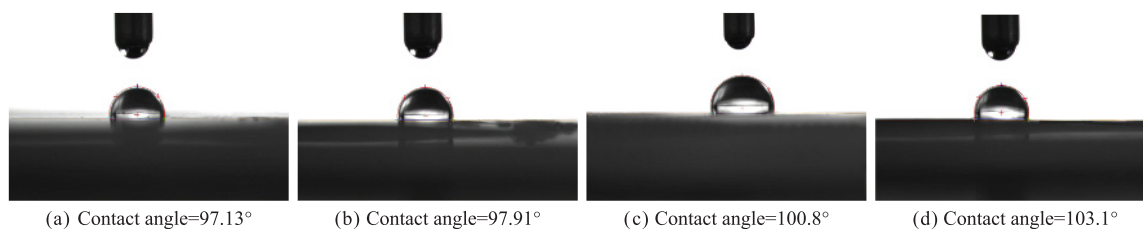


Fig.8 Contact angles of PTFE samples after solar radiation for different time: (a) original; (b) 4 days; (c) 8 days; (d) 12 days

After solar radiation, contact angle and hydrophobicity of PTFE samples increased gradually with the increase of radiation time, which is mainly related with change of content of F-rich groups ($-\text{CF}_2-$, $-\text{CF}_3$) and surface roughness^[13].

On the one hand, the F-rich groups and C-F bonds in the outer layer of PTFE molecular are hydrophobic, while the inner layer carbon chains are hydrophilic. After solar radiation, both F-rich groups and F element of sample surface decreased, the hydrophobicity of radiated PTFE should be weakened, and the contact angle should be reduced^[14].

On the other hand, hydrophobicity of materials is also related with its surface roughness (R_a). According to Wenzel model, liquid can saturate the notches of rough solid surface completely, resulting in the apparent contact area is less than the actual liquid-solid contact area. The ratio of actual contact area to apparent contact area is defined as roughness factor R (the larger R , corresponding to rougher surface). And $\cos\theta = R \times \cos\theta_0$, θ is the apparent contact angle of rough surface, θ_0 is the actual contact angle. Correspondingly, the modified Young Equation is $R \times (\gamma_{sg} - \gamma_{sl}) = \gamma_{lg} \times \cos\theta$, where γ_{sg} , γ_{sl} , γ_{lg} are interface tension of solid/gas, solid/liquid and liquid/gas interfaces, respectively. It can be seen from the equation, when the actual contact angle θ_0 is less than 90° (for hydrophilic material), the greater the roughness factor R is, the smaller the apparent contact angle is, and so the surface is more wettable. When the actual contact angle θ_0 is more than 90° (for hydrophobic material), surface roughening will increase the contact angle, which further increase the hydrophobicity of material surface^[15,16]. PTFE itself is hydrophobic material (θ_0 is more than 90°), micro-roughness increased significantly after solar radiation, the contact angle of PTFE with water should increase after solar radiation.

Based on comprehensive analysis of the effect of changes in chemical groups and surface roughness on contact angle of PTFE, the increase of hydrophobicity after solar radiation can be mainly attributed to increase

in surface roughness.

4 Conclusions

a) After continuous solar radiation, microstructure and composition of PTFE were changed, mainly including: surface roughness and the degree of amorphization increased, content of F element decreased, and C content increased. Besides structural units of “ $-\text{CF}_2-$ ”, some new complex cross-linked structures also appeared after solar radiation. The change in PTFE samples can be mainly attributed to break of $(\text{CF}_x)\text{-C}$ bonds after bombardment of high energy UV photons, which causes the loss of F-rich groups, oxidation, crosslinking and restructuring of carbon chains, and so local areas of samples were etched selectively.

b) Due to defluorination of F-rich groups, increase of surface roughness and brittleness, and also rupture of some carbon chains, the average value and fluctuation of friction coefficients of PTFE sample increased after solar radiation, and some spalling and accumulation of materials appeared at local areas.

c) Surface roughness of PTFE increased after solar radiation, notches of rough solid surface were saturated by liquid medium, so that the contact angle of hydrophobic PTFE increased, its hydrophobicity further enhanced.

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