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Surface structural changes, surface energy and antiwear properties of polytetrafluoroethylene induced by proton irradiation

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ABSTRACT

In this work, the polytetrafluoroethylene (PTFE) surface was modified with 25 keV proton beam irradiation in vacuum condition. Multiple characterization techniques including X-ray photoelectron spectroscopy, Raman spectroscopy and infrared spectroscopy were employed for research on microstructure changes in the PTFE surface. The changes in the surface energy and antiwear properties of PTFE were evaluated using contact angle analysis and a ball-on-disk tribometer, respectively. Experimental results showed that the surface energy of PTFE obviously increased from 13.17 mJ/m^2 to 33.73 mJ/m^2 and the wear rate decreased from 8.9×10^{-3} mm^3/Nm to 5.8×10^{-4} mm^3/Nm after proton irradiation for 15 min. Moreover, TRIM simulation indicated that the H$^+$ ions cannot penetrate through the PTFE block and only stop at a depth of about 730 nm from the material surface. Proton irradiation has been proved to be a simple, rapid and effective measure for the surface modification of PTFE with distinctly improved surface energy and antiwear properties, and the possible reaction mechanism taking place in PTFE was also discussed in this paper.

1. Introduction

Polytetrafluoroethylene (PTFE), one of the most promising polymer base materials, has been widely used in spacecraft design, chemical processing, biotechnology industries, automotive and semiconductor due to its attractive physical and chemical properties, such as low frictional coefficient ($\mu < 0.2$), low dielectric ($k = 2.0–2.1$), good thermal stability, and excellent chemical stability [1–3]. Thereby PTFE could be particularly suitable for solid lubricant material, especially for dry friction without any oils or other liquids because of its remarkable performance. However, the reality is that some mechanical components made of PTFE usually have relatively high wear rate during the using process [4,5], and it could hardly adhere to any solids and liquids (except to similar perfluorinated hydrocarbons) mainly due to its low surface energy [4]. Therefore, the PTFE surface should be modified to prolong the fatigue life of materials, and it is very important to expand the application range in various mechanical parts.

So far, many techniques have been developed to target specific parts of the modified PTFE, such as incorporation of various fillers into the polymer material [6–12] and surface modification using charged particle irradiation [13–16]. Judging from current experimental results, the combination of fillers and polymer material could affect the main body properties of the polymer [11,12]. But the ion irradiation technique could only modify the uppermost surface of polymers and avoid a prejudicial effect specifically against the main body character of polymers, which has attracted great research interest. Francois et al. have obtained a further decreased surface energy for the PTFE material by the irradiations of electron and atomic oxygen [16]. The heavy ion or synchrotron irradiation techniques were also used for the surface treatment of the PTFE [17,18]. Proton irradiation is known as one of powerful technologies for the surface treatment of the polymer materials [19]. In the past decade, proton irradiation has received more and more attentions because the accelerated protons have a more precise location and irradiation dose during the treatment process [20,21]. Now proton irradiation has become a useful technology that creates advanced materials [22,23]. At present, to the author's knowledge, there is no research that uses proton irradiation to modify the PTFE material, which makes an important research work.

In this paper, 25 keV H$^+$ beam irradiation was employed for the surface modification of PTFE material. The surface energy and the antiwear properties before and after proton irradiation were evaluated by contact angle (CA) analysis and a ball-on-disk tribometer. The structural changes in the PTFE surface were characterized by attenuated total reflectance infrared spectroscopy (ATR-FTIR), laser micro-Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). Possible reaction mechanism was proposed for the chemical reaction taking place in the PTFE surface induced by proton irradiation, which could be used to explain the structural changes in the PTFE surface and improved antiwear properties. Moreover, proton irradiation as a kind of unique surface modification

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technique is very useful in polymer science, such as creating advanced materials used for space or medical applications.

2. Experimental section

2.1. Materials

PTFE polymer specimens for testing were fabricated with the powder of PTFE purchased by Daikin Fluorochemicals Co., Ltd using a cold press molding technique according to our previous report [24]. The molding PTFE specimen was cut into 18 × 18 × 2 mm^3 blocks, which were polished carefully to have a roughness of about 0.2 μm. Before irradiation and friction tests, all the samples were cleaned using ultrasonic acetone. The roughness was determined using a three-dimensional non-contact surface mapping profiler (MicroXAM, ADE Corporation Inc.).

2.2. H^+ ion irradiation

The H^+ irradiations were performed in the vacuum chamber, described in our previous report [25]. Fig. 1 showed the schematic diagram of proton irradiation equipment. The 25 keV H^+ irradiations were performed by means of ECR (electron cyclotron resonance) microwave plasma technology in high vacuum environment. The proton flux was determined to be about 2.5×10^{14} ions/$cm^2 \cdot s$ and the irradiation time was controlled as 0 min, 15 min and 60 min, respectively. The interactions between the incident ions and PTFE material were simulated using the TRIM code being part of the SRIM program package on the basis of quantum mechanical Monte Carlo simulation [26,27], and the stopping and range of ions were obtained.

2.3. Infrared spectroscopy

The infrared spectroscopic measurements were carried out on a Nexus 870 infrared spectrometer (Nicolet, America) using an attenuated total reflection accessory.

2.4. Laser micro-Raman spectroscopy

The changes in the surface structure of the PTFE were measured by a laser micro-Raman microscope (LabRam HR800, Japan) at an excitation wavelength of 633 nm.

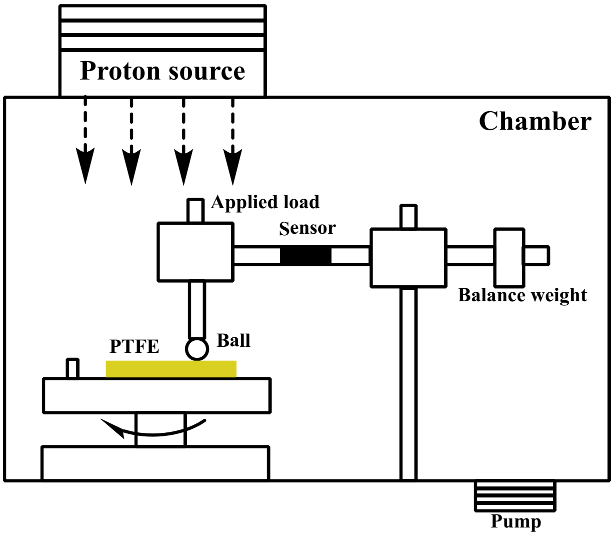

Fig. 1. The schematic diagram of proton irradiation equipment.

2.5. X-ray photoelectron spectroscopy

To compare the changes in chemical composition at the surface of the samples before and after irradiation, XPS analyses were carried out on an ESCALAB 250Xi X-ray photoelectron spectroscopy instrument (ThermoFisher, America). All spectra were acquired using Al-Kα X-ray source (1391 eV) with a binding energy range of 0–1400 eV. Survey scans were used to determine the chemical composition of the elements present at the PTFE surface. Narrow-region photoelectron spectra were used to analyze the characteristic peak of C1s, O1s, and F1s. All binding energies were referenced to the C1s hydrocarbon peak at 284.6 eV.

2.6. Contact angle measurements

Contact angle analysis is an easy, quick and direct means of measuring the surface energy of PTFE with distilled water and diiodomethane [28]. The contact angle tests were carried out using the static sessile drop method with a DSA-100 optical contact-angle meter (Kruss Company Ltd., Germany) at room temperature. 5 μL double distilled water or diiodomethane was deposited onto the original and irradiated PTFE surface, and the contact angle between the droplet and surface was then measured with a Sony Digital Camera (Sony Ltd., Japan). For each specimen, liquid droplets were dropped onto five different locations of the sample surface. The method of Owens–Wendt–Rabel–Kaelble (Eq. (1)) was selected for the calculation of the total surface energy and its polar and dispersive components [29].

$$\gamma_L \cdot (1 + \cos\theta) = 2 \cdot \left(\sqrt{\gamma_S^D \cdot \gamma_L^D} + \sqrt{\gamma_S^P \cdot \gamma_L^P} \right) \tag{1}$$

where γ_L is the liquid surface tension, γ_L^D is the dispersive component of the liquid, γ_L^P is the polar component of the liquid, γ_S^D is the dispersive component of the solid, γ_S^P is the polar component of the solid, and θ is the contact angle between the droplet and solid surface.

2.7. Antiwear properties

The wear properties before and after proton irradiation were investigated using a ball-on-disk tribometer in the irradiation chamber. The GCr15 counterpart ball, a diameter of 3.175 mm, slid on the PTFE disk under a load of 1 N for 1800 s in high vacuum (3×10^{-4} Pa) at room temperature. The rotated speed of PTFE disk was 0.13 m/s and the rotatory diameter was 12 mm. The wear rate calculated according to the formula (Fig. 2) described in our previous report [25] was used to evaluate the antiwear performance of PTFE. The debris on the counterpart steel ball was observed by a JEM-5600LV scanning electron microscope (JEOL, Japan).

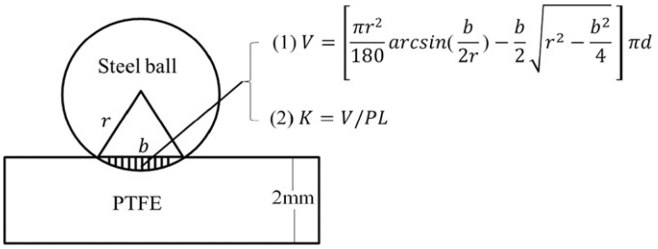

Fig. 2. Calculation formula of the wear rate.