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Friction and Wear of Fiber Reinforced Polyimide Composites in Electron or Proton Irradiation

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ABSTRACT: The polyimide (PI) composites reinforced with carbon fibers, glass fibers, and aramid fibers were fabricated by means of a hot-press molding technique and irradiated by electron or proton for a certain time. The friction and wear behavior after irradiation, sliding against GCr15 steel balls, were evaluated in a ground-based simulation facility using ball-on-disk tribosystem. The change of the chemical composition of the radiated surface was examined by X-ray photoelectron spectroscopy. The worn morphologies and radiated surfaces of the materials were observed by scanning electron microscope to reveal the wear mechanism. Experimental analysis indicated that the chemical composition of the materials changed and an irradiated layer was formed at the surface. This irradiation layer had an important effect on the friction and wear behavior of the PI composites. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40774.

KEYWORDS: composites; fibers; friction; polyimides; wear and lubrication

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INTRODUCTION

Polyimide (PI) composites reinforced with fibers are widely used in space vehicles and system as structural materials, thermal and irradiation resistance coatings, as well as tribological components such as bearing, slip-rings, and gears duo to its extraordinary performance.[1] Irradiation and wear resistance of the components made of PI composites must be considered to run safely and reliably in the launch environment and space environment.[2–6] In the geosynchronous orbit, high energy electrons and protons are the main radiation factors which can cause the chemical structure of the polymer surfaces change through breakage, crosslink, and degradation of polymer bonds.[7–11] In the past study, many researchers used different fibers to enhance the mechanical and tribological properties of PI.[12–19] Some researchers studied the effect of the radiation factors on the chemical and physical change of the polymer materials.[20–24] In our group, Liu studied the effects of proton and electron irradiation on the structural and tribological properties of PI filled with lubricants.[25]

In the present research, carbon fibers (CF), glass fibers (GF), and aramid fibers (AF) were used for reinforcing PI prepared by hot pressing. For comparison, pure PI was also radiated by electron or proton. The aim of this study was to analyze the effect of electron or proton irradiation on the friction and wear behavior of the PI composites.

EXPERIMENTAL

Materials

PI YS-20 grade powder of particles size <75 μm was supplied by Shanghai Synthetic Resin Institute (Shanghai, China). The specific density is stated to be 1.4 g/cm^3. The composites were fabricated by means of hot press molding technique, which is the most common technique for the sintering of PI composites. A fixed volume content of the fibers of 15 vol % was chosen according to Ref. 26. The mixtures were compressed and heated up to 380°C in a mold with intermittent deflation. The pressure was held at 20 MPa for 60 min to allow full compression sintering. At the end of each run of compression sintering, the processed specimens were cooled in air in a stove and cut into preset sizes for testing.

The CF used were supplied by Nantong Senyou Carbon Fiber Co., Ltd., China. The length of CF was in the range of 20–50 μm and the diameter was about 7 μm. The GF of 10 μm in diameter and 10 : 1 aspect ratio were purchased from Nanjing Institute of Glass Fiber Research and Design, China. The AF were supplied by Shanghai Ruiyan Trading Co., Ltd., China. The length of the AF was ranged between 75 and 125 μm and the diameter was about 25 μm.

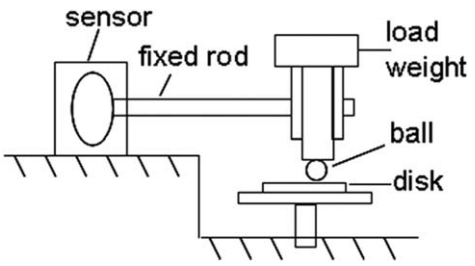

Figure 1. The contact schematic diagram for the friction couple.

Radiation Condition

Electron and proton irradiation were carried out in a ground-based simulation facility in Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences. The irradiation were performed under vacuum environment (proton irradiation: $\sim 10^{-3}$ Pa; electron irradiation: $\sim 10^{-4}$ Pa) at a accelerative voltage of 25 kV, and the flux of proton and electron were determined to be 2.5×10^{14} cm^{-2} s^{-1}. The time of proton and electron irradiation were fixed at 15 min.

Testing Procedure

Friction and wear behavior of the PI composites after irradiation sliding against stainless steel ball were evaluated on a ball-on-disk tribometer at room temperature and at a sliding speed of 0.1256 m/s and a load of 1 N. The contact schematic diagram of the friction couple is shown in Figure 1. The GCrl5 steel ball, as counterpart, was 3.175 mm in diameter. The chemical composition was C 0.95–1.05 wt %, Si 0.15–0.35 wt %, Mn 0.25–0.45 wt %, P $\leq$ 0.025 wt %, S $\leq$ 0.025 wt %, Cr 1.40–1.65 wt %, and Fe balance, with a bulk hardness of HRC65 $\pm$ 5. Before each test, the steel ball and the block were cleaned with cotton dipped in acetone. The wear tests of the samples were processed under electron and proton irradiation. Then, the wear volume was computed from cross-sectional worn area multiplied by the circumference of wear track and calculated from the following relationship:

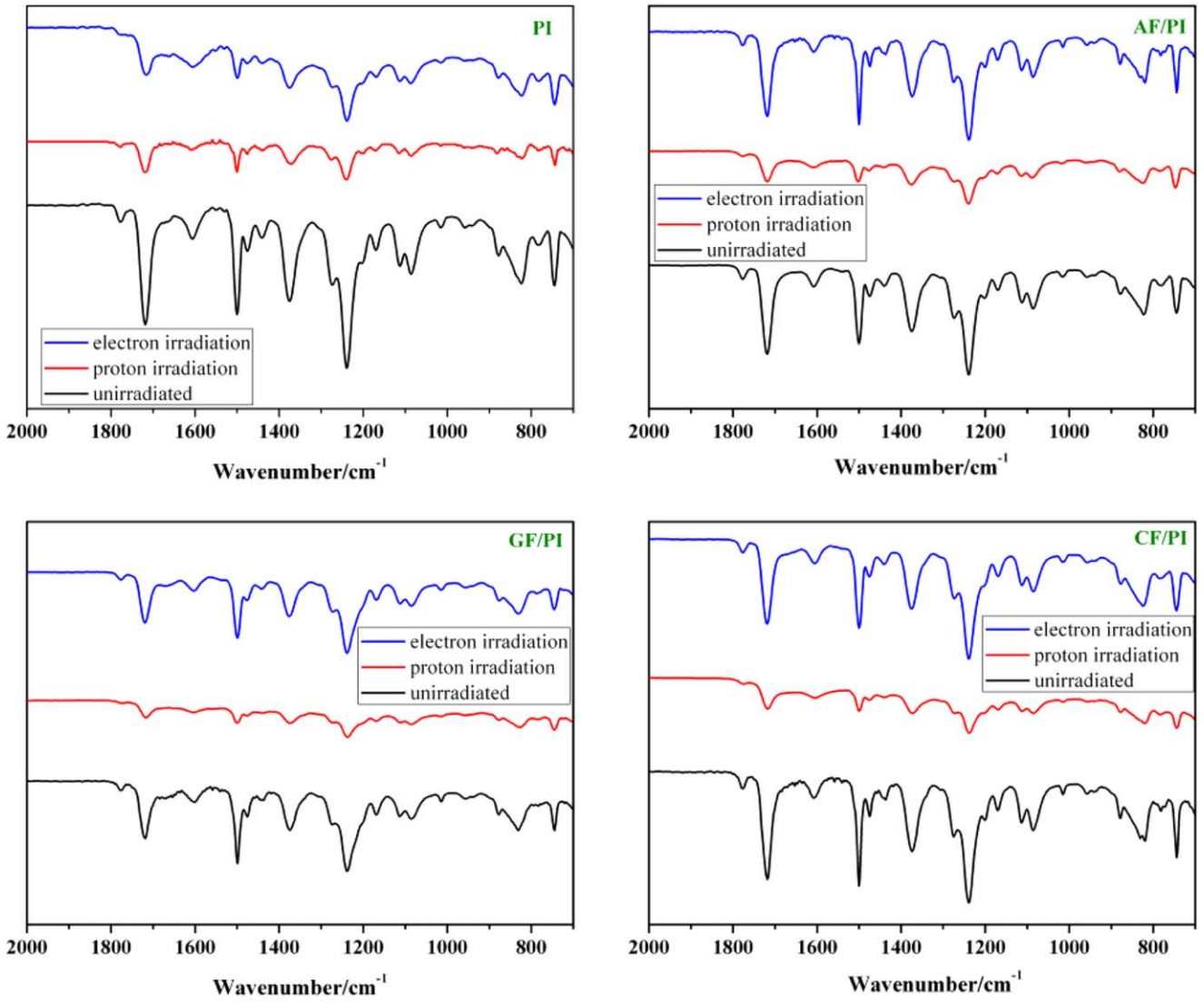

Figure 2. The FTIR-ATR spectra of the specimens before and after electron or proton irradiation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

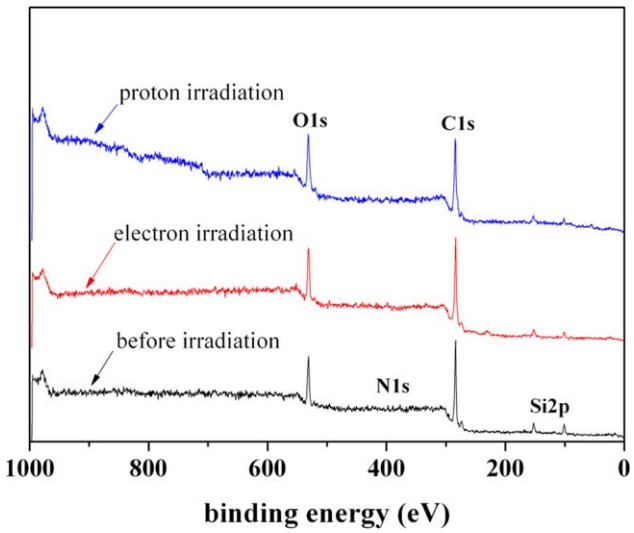

Figure 3. XPS spectra of PI before and after electron or proton irradiation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$\Delta V = \left[\frac{\pi(R/2)^2}{180}\arcsin\frac{b}{R} - \frac{b\sqrt{(R/2)^2-(b/2)^2}}{2}\right]\pi d \quad (1)$$

where ΔV is the wear volume loss (mm^3), R is the diameter of the ball (3.175 mm), b is the width of the wear trace (mm), and d is the diameter of the disk (12 mm). The specific wear rate K (mm^3/N m) was calculated from the volume loss using the following equation:

$$K = \frac{\Delta V}{PL} \quad (2)$$

where P is the load (N), L is the rotating distance (m). In this work, the average of three replicate tests results is reported. The coefficient of friction, which was the average value in the steady stage, was continuously recorded by an on-line data acquisition system attached to the tester. All the friction and wear tests are carried out at 20–25°C.

Table I. The Relative Atomic Concentration in Surface of the Specimens Before and After Electron or Proton Irradiation

Sample	Element	Un-irradiated	Proton irradiation	Electron irradiation
PI	C	76.98	78.85	77.61
	N	2.13	3.8	1.77
	O	20.89	17.35	19.63
AF/PI	C	70.65	76.5	73.56
	N	2.55	2.43	4.8
	O	20.43	15.95	18.92
CF/PI	C	75.24	81.95	76.07
	N	2.24	4.57	5.1
	O	17.83	11.44	17.01
GF/PI	C	66.79	72.53	70.33
	N	2.11	2.87	4.97
	O	19.55	17.52	20.9

Characterization

Before and after irradiation, the chemical group changes on the surface of the samples were characterized by Fourier transform infrared spectroscopy (FTIR) spectra which record with a Nexus 870 infrared spectrometer using an attenuated total-reflection (ATR) accessory in the wave number range 4000–700 cm^{-1}. The composites samples were transferred in air to a VG Scientific ESCA LAB 210 spectrometer for analysis of the surface elemental compositions by X-ray photoelectron spectroscopy (XPS). The XPS analysis was carried out using unmonochromated Mg Ka X-radiation using Al/Mg dual anode at 20 kV under 300 W and the base pressure in the sample chamber was about 10^{-7} Pa. The morphologies of worn surface were examined on a JEM-5600LV scanning electron microscope (SEM, JEOL, Japan). In order to increase the resolution for the SEM observation, the tested polymeric samples were plated with gold coating to render them electrically conductive.

RESULTS AND DISCUSSION

Changes in Surface Chemical Composition

Figure 2 shows the FTIR-ATR spectra of the specimens before and after 15 min electron or proton irradiation. It is obviously seen that the intensities of these characteristic peaks at 1717 cm^{-1} (C═O), 1491 cm^{-1} (C═C), 1372 cm^{-1} (C—N—C), 1230 cm^{-1} (C—O—C) are reduced after irradiation, indicating that the imide and aromatic structures in PI molecules were partly destroyed.[27,28] The PI molecules may be destroyed due to the high energy collision or radical group degradation caused by electron and protonated effect. It can be speculated that some complex chemical reactions occurred during the irradiation. So, electron or proton irradiation can result in larger degradation of PI matrix and change of the chemical composition which can be further confirmed by XPS characterization (Figure 3). The information of the intensity change of C and O is important to verify radiated mechanism. The relative

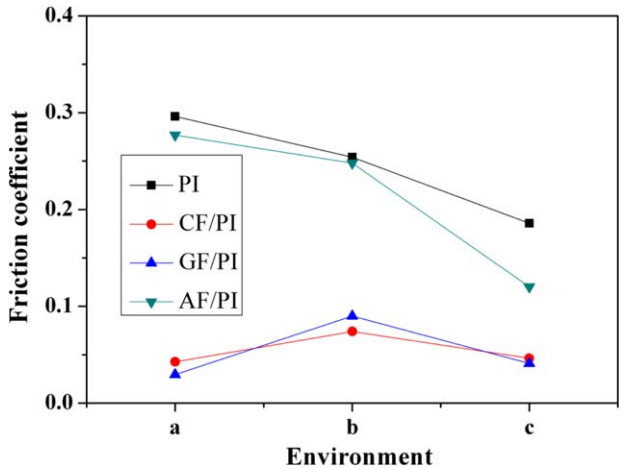

Figure 4. The steady friction coefficient of the specimens under different environment. (a) Un-irradiated, (b) after electron irradiation, (c) after proton irradiation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

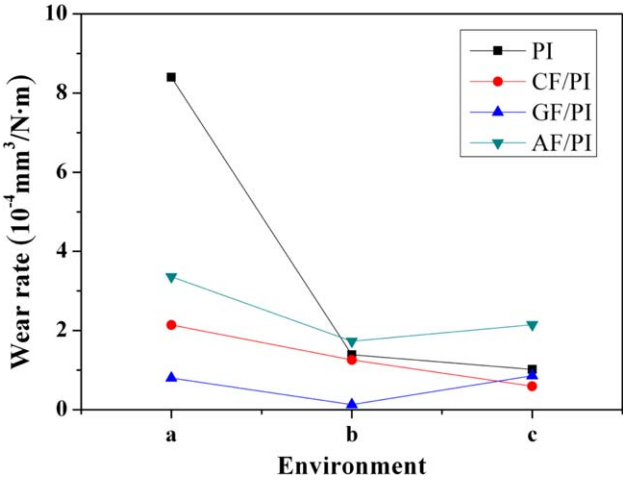

Figure 5. Wear rate of the specimens under different environment. (a) Un-irradiated, (b) after electron irradiation, (c) after proton irradiation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

concentration of C, N, and O listed in Table I were calculated by integral area in fine spectra, while the peak of Si (Si2s: 151.0 eV, Si2p: 99.3 eV) was not contained because of contamination. Take the example of pure PI (Figure 3, Table I), the surface concentration of C element increased from 76.98% to 77.61% (after electron irradiation) and 78.85% (after proton irradiation). For the O element, the concentration decreased from 20.89% to 19.63% and 17.35%, respectively. As a result, carbon-rich layer is formed at the PI surface. The same conclusion can be acquired from fiber/PI composites (Table I).

Friction and Wear Behavior

Figure 4 shows the change of steady friction coefficient of the fibers/PI composites before and after irradiation. It can be seen that inorganic fibers filled PI composites exhibit lower friction coefficient in the range from 0.02 to 0.1 than neat PI or AF/PI in the range from 0.1 to 0.3. For CF/PI or GF/PI, the friction coefficient increases after electron irradiation, then reduces after proton irradiation. This might be attributed to the occurrence of breakage and degradation of PI molecules caused by electron irradiation. The irradiated PI matrix is easily worn off as a result of low mechanical strength and poor wear resistance. The inorganic fibers with high strength and excellent wear resistance are exposed at the worn surfaces of the composites, which can carry the most parts of load applied on the sliding surface. Proton irradiation leads to formation of graphite-like-structure at the surface,[28] which helps decrease the friction coefficient. However, the friction coefficient of the organic fibers filled PI composites or pure PI always decreases after electron or proton irradiation. Because AF, with poor irradiation resistance in the same level with PI matrix, were also degraded after electron irradiation. A low molecular weight substance[10] as a lubrication is formed at the sample surface, which results in the decrease of friction coefficient. The same results can be obtained after proton irradiation. The carbon-rich layer formed by proton irradiation plays a role as lubricant so that the friction coefficients of PI and AF/PI composites decrease.

Figure 5 shows the wear rates of the composites under different environment. Apparently, the wear resistance of un-irradiated PI depending on itself is greatly improved due to the reinforcement of different fibers. The GF/PI exhibits the lowest wear rate, while organic AF have the less reinforcement effect than inorganic fibers (CF and GF). After electron irradiation, the wear rates of all materials decreases to the same level (below 3 $\times$ 10^{-4} mm^3/N m), which is ascribed to the formation of the radiated layer as a solid lubricant. The radiated layer caused by electron determines the level of the wear rate value of the PI composites. So, the electron irradiation has an important effect on the wear behavior of the PI-based composites. Compared to those of un-irradiated composites, the wear rates of PI composites decline after proton irradiation because of the formation of carbon-rich layer in the process of radiation. Based on this study, the friction and wear behavior depended on the material itself as well as radiated environment. Electron and proton irradiation can alter the chemical composition and change the surface structure of the PI composites, which further affected the friction and wear behavior of the materials.

The morphologies of the worn surface of PI composites sliding against GCr15 steel under different environment are shown in Figure 6. The un-irradiated surface of the PI shows the same morphology with the worn surface [Figure 6 (a1)]. Only some debris remaining on the two sides of the wear trace were

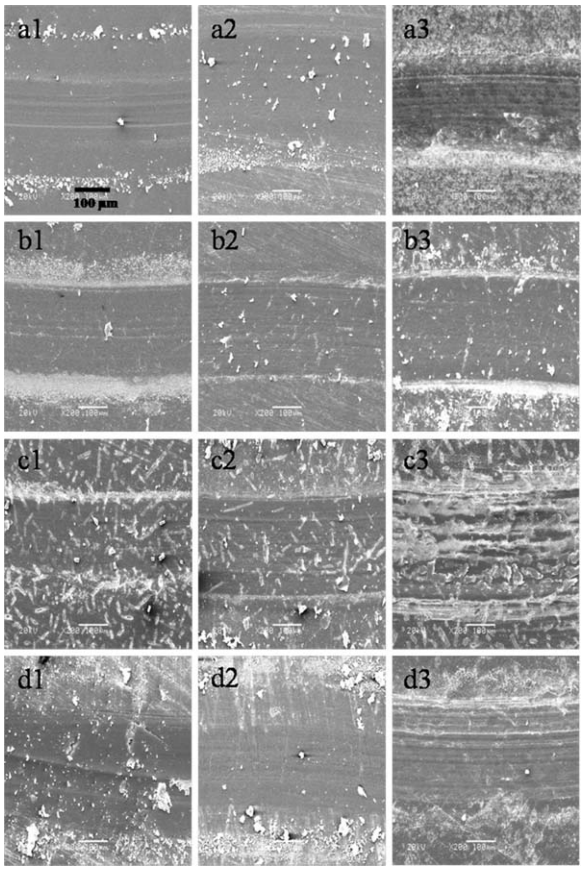

Figure 6. SEM micrographs of the worn surfaces of the composites. (a) PI, (b) CF/PI, (c) GF/PI, (d) AF/PI; (1) un-irradiated, (2) after electron irradiation, (3) after proton irradiation.

formed during the wear process because of the repeated shear. Slightly adhesive wear is the main wear mechanism. For fibers reinforced PI composites, fibers, gradually exposed on the worn surface, carried the applied load and protected the polymer from severe damage when polymer matrix were worn off during the process of wear [Figure 6(b1,c1)]. It can be seen from Figure 6(a2) that electron irradiation had no obvious effect on the surface of the PI composites. The wear mechanism is similar with un-irradiated materials. However, the morphologies of the PI composites are greatly changed after proton irradiation, which has an important role on the wear behavior and wear mechanism. The carbon-rich layer, as solid lubricant, is formed after proton irradiation confirmed by XPS analysis (Table I). The irradiation and worn surfaces are relatively rough and soft [Figure 6(a3–d3)], which indicates that adhesive wear and third-body wear take the dominant wear mechanism.

CONCLUSIONS

A comparative investigation on the effect of the electron or proton irradiation on the friction and wear of the different fibers reinforced PI composites was carried out in this work. The results obtained are as follows:

a. The electron or proton irradiation altered the chemical composition and changed the structure of PI composite surfaces. Irradiation destroyed chemical structure and then induced the increase of carbon content at the sample surface.
b. The friction coefficients of PI and AF/PI composites decreased after electron irradiation, while those of CF/PI and GF/PI composites showed some increase. Compared to un-irradiated samples, the wear rates of electron irradiated samples reduced.
c. Proton irradiation was helpful to reduce the friction coefficients of PI and AF/PI composites. The wear rates of PI, CF/PI, and AF/PI composites declined after proton irradiation, while GF/PI composite were an exception.
d. For CF/PI and GF/PI composites, the wear mechanism of the composites changed from adhesive wear before irradiation to third-body wear after irradiation.

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