

Friction and Wear Behavior of Proton-Implanted Phenolphthalein Poly(ether sulfone)

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ABSTRACT: Blocks of phenolphthalein poly(ether sulfone) (PES-C) were implanted with 110 keV protons in four doses: 1×10^{14} , 5×10^{14} , 2.5×10^{15} , and 1.25×10^{16} ions/cm². The structures of the pristine and implanted PES-C blocks were characterized by FTIR-ATR and X-ray photoelectron spectroscopy (XPS), whereas their friction and wear behavior were investigated with an M-2000 friction and wear tester at room temperature in an ambient atmosphere. The results revealed that with an increased implantation dose, it took more time for the friction coefficient to become smaller and level off when the dose did not exceed 10^{16} ions/cm². At the highest dose, 1.25×10^{16} ions/cm², the friction coefficient started smaller but increased quickly and leveled off at a higher number. In addition, the wear rate first increased and then decreased. When the dose exceeded

10^{16} ions/cm², the wear rate of the sample showed an obvious decrease. The FTIR-ATR spectra showed that partial degradation took place on the surface of PES-C after proton implantation, and when the dose reached or exceeded 2.5×10^{15} ions/cm², a new broad peak between 1600 and 1800 cm⁻¹ appeared, showing that a carbon-rich structure had formed on the sample surface. XPS analyses justified the FTIR-ATR results, including the formation of amorphous carbon and the partial degradation, which was responsible for the variety of friction and wear behaviors of PES-C.

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Key words: poly(ether sulfone); surfaces; structure; infrared spectroscopy; XPS

INTRODUCTION

Polymers have a great potential in many important applications because of their unique properties, such as low density, versatile electronic properties, outstanding processability, and low manufacturing cost. However, the use of polymers is still limited because of their inherent softness and unexpected dielectric properties. To improve the properties of polymers, ion implantation and other plasma- or radiation-based techniques are being increasingly employed as surface treatments to modify the surface characteristics of many polymers^{1–3} and have been shown to be very effective in improving such surface properties of polymers as surface electrical properties, hardness, and wear resistance.^{4–6} In the last few years many fundamental studies^{7–9} have explained these changes on the basis of the crosslinking effect that originates from the ionization effects of ion bombardment. In fact, accord-

ing to the stopping power laws, ionization is the preferred energy loss mechanism of light and energetic ions, whereas in heavier and less energetic ions, nuclear collision has a more important role. This means that light-ion bombardment will produce a higher crosslinking rate and harder surfaces, whereas heavy-ion bombardment will lead to breakage of the polymer chains and, as a consequence, softer surfaces.

In this article, the effects of proton implantation on both the friction and wear properties of phenolphthalein poly(ether sulfone) found in this investigation are reported and the modification mechanisms are discussed. It was expected that this investigation would be helpful for improving the friction and wear properties of PES-C and expanding its application in engineering.

EXPERIMENTAL

The phenolphthalein poly(ether sulfone) (PES-C) used (shown in Fig. 1) was produced by Xuzhou Engineering Plastics Co. (Xuzhou, China). To produce samples for testing, PES-C powder was heated in a mold at a rate of 5°C/min from room temperature to a maximum temperature of 340°C, with the pressure held at 30 MPa for 40 min, and then the block was cooled to room temperature.

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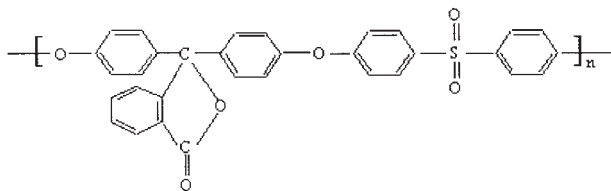


Figure 1 Structural formula of PES-C.

Proton implantation was performed on a 200 keV implanter in the Institute of Modern Physics, Chinese Academy of Sciences (Lanzhou, China). The blocks of PES-C (numbered 0#–4#) were implanted with 110 keV ions of hydrogen to doses of 0, 1×10^{14} , 5×10^{14} , 2.5×10^{15} , and 1.25×10^{16} ions/cm², respectively.

Friction and wear tests were conducted on an M-2000 friction and wear tester (Xuanhua, China) at a sliding speed of 0.432 m/s and a load of 100N over 90 min. The ambient temperature was around 20°C, and the relative humidity was 40% ± 5%. The contact schematic diagram of the friction couple is shown in Figure 2. Before each test, the steel ring and the block were cleaned with cotton dipped in acetone. In this work, three samples were tested under each condition; the friction coefficient and the wear rate values are the averages of the results of three replicated tests.

Finally, the chemical composition and structure of PES-C before and after implantation were investigated using X-ray photoelectron spectroscopy (XPS) and FTIR-ATR. XPS analyses were conducted on a PHI-5702 electron spectrometer using an AlK α line excitation source with the reference of C1s at 284.80 eV. The FTIR spectra of the implanted and the pristine PES-C samples were recorded on a Nexus 870 infrared spectrometer using an ATR accessory. The wear scars of PES-C were observed with a JSM-5600LV scanning electron microscope (Japan)

RESULTS AND DISCUSSION

Figure 3 shows the variety of friction coefficients of both the pristine and the implanted PES-C as a func-

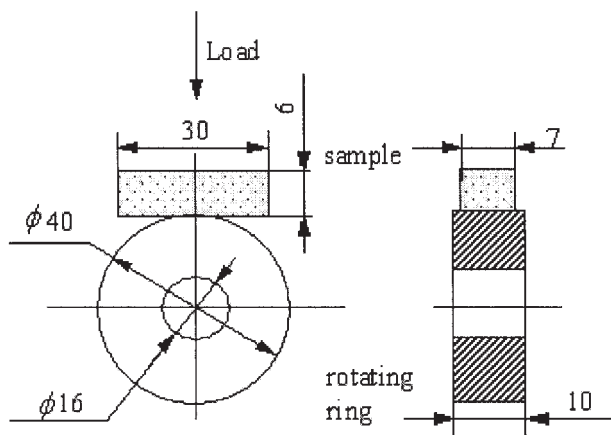


Figure 2 Contact schematic diagram of the friction couple.

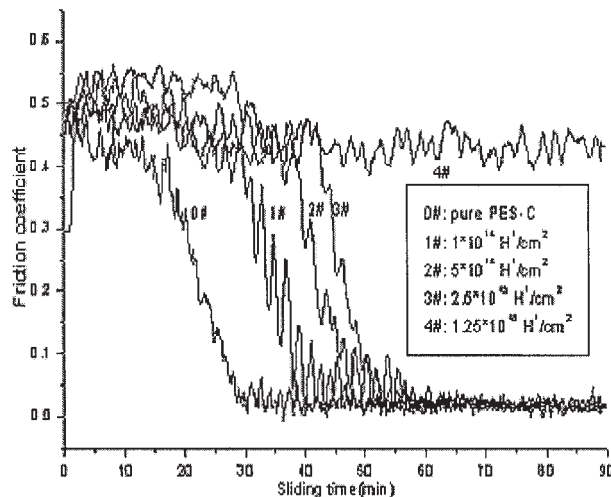


Figure 3 Friction coefficient of PES-C against steel ring for: 0#, unimplanted; 1#, 1×10^{14} ; 2#, 5×10^{14} ; 3#, 2.5×10^{15} ; 4#, 1.25×10^{16} ions/cm² proton-implanted PES-C (load: 100N; sliding velocity: 0.432 m/s; time: 90 min).

tion of sliding time. It can be clearly seen that the friction coefficients had a transition from a higher value to a lower one and leveled off when the implantation dose was lower than 10^{16} ions/cm². But the transition point was different. For the pure PES-C, it took about 30 min before the friction coefficient decreased to a steady value, whereas about 60 min was needed for the 2.5×10^{15} ions/cm²-implanted sample. When the dose reached 1.25×10^{16} ions/cm², the variety of friction coefficients was found to be different from those of the other samples: the initial friction coefficient was smaller but increased quickly and leveled off at about 0.42 until the experiment ended.

According to the results reported in the literature, the variety of friction coefficients for ion-implanted

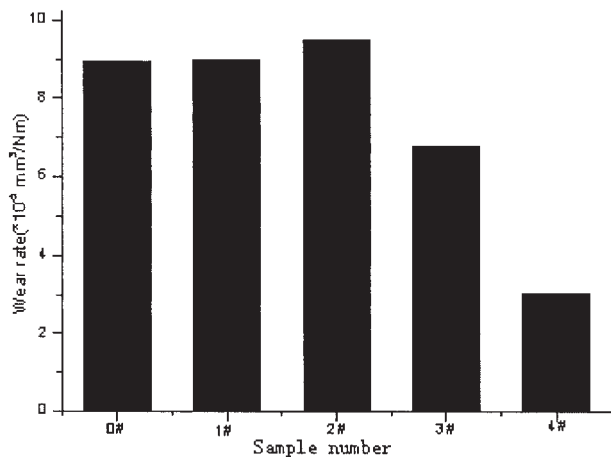


Figure 4 Wear rate of PES-C against steel ring for: 0#, unimplanted; 1#, 1×10^{14} ; 2#, 5×10^{14} ; 3#, 2.5×10^{15} ; 4#, 1.25×10^{16} ions/cm² proton implanted PES-C (load: 100N; sliding velocity: 0.432 m/s; time: 90 min).

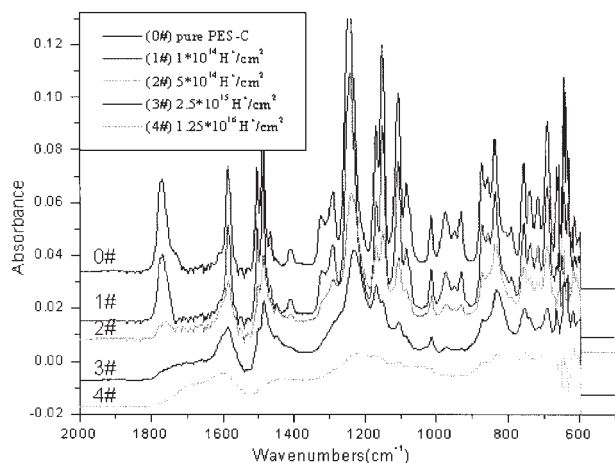


Figure 5 FTIR-ATR spectra of PES-C before and after proton implantation.

polymers is somewhat difficult to interpret. Some researchers found an increased friction coefficient after ion implantation.^{10–12} Others found the opposite results.^{13–15} Crosslinking by ion implantation was proposed as a probable reason for the increase in the friction coefficient, and the formation of a carbonated layer might play a role in the reduction of the friction

coefficient. However, in our experiments, the variation in the friction coefficient was not steady and the friction coefficient did increase before it reduced to a steady value, the reasons for which are discussed below.

Figure 4 shows the effect of implantation dose on the wear rate of PES-C. From Figure 4, it can be seen that the variation in the wear rate was not monotone but first showed an increase and then a decrease. When the implantation dose did not exceed 10^{15} ions/cm², the wear rate increased with increasing dose. But when the dose exceeded 10^{15} ions/cm², the wear rate decreased. In our experimental scale, when the dose reached 1.25×10^{16} ions/cm², the wear rate decreased from 8.94×10^{-5} mm³/N m for the pristine sample to 3.03×10^{-5} mm³/N m for the implanted sample with the maximum dose.

Figure 5 shows the FTIR-ATR spectra of PES-C before and after proton implantation between 2000 and 500 cm⁻¹. It is clear that the intensity of the bands at 1770 cm⁻¹ (ν C=O), 1242 cm⁻¹ (δ asC—O—C), 1150 cm⁻¹ (ν sO=S=O), and 1488 cm⁻¹ (ν C=C) was reduced, indicating the molecular chain of PES-C was destroyed to some extent.^{16–18} And the reduction at 1770 cm⁻¹ and 1242 cm⁻¹ may attributed to the scission of the side chain in PES-C, whereas the reduction

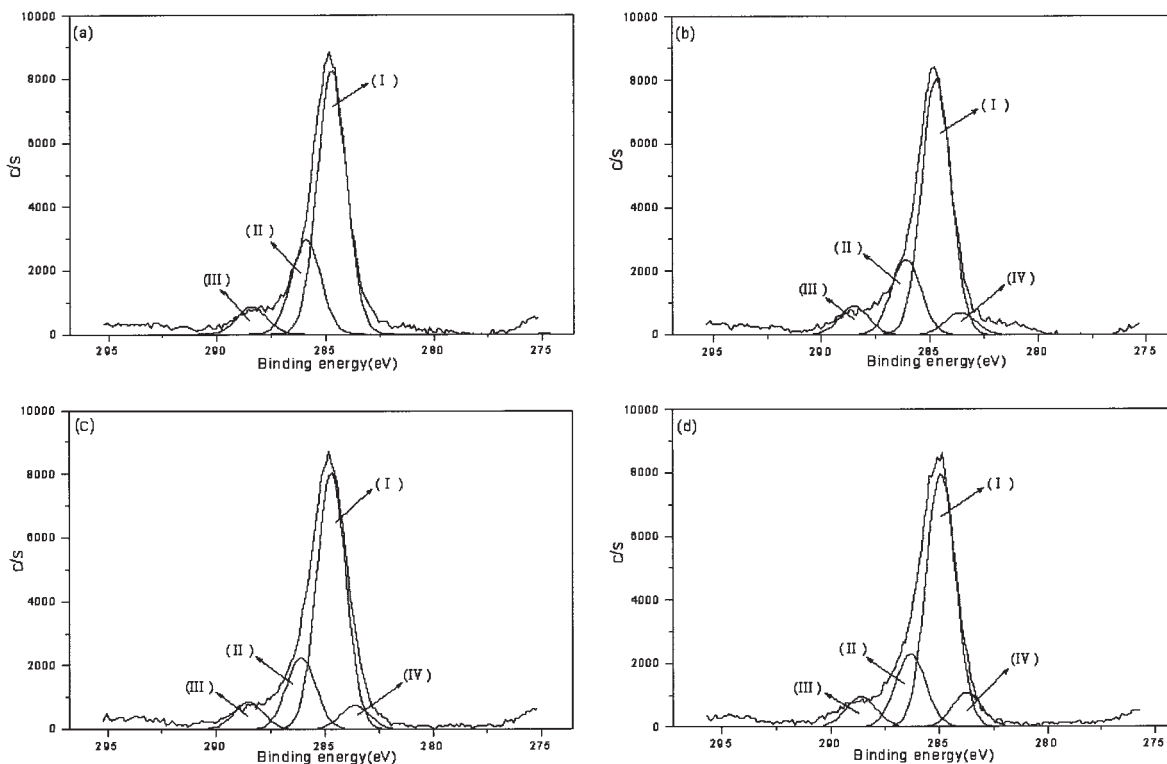


Figure 6 Curve fitting of C1s implanted with protons at various doses: (a) 0; (b) 5×10^{14} ; (c) 2.5×10^{15} ; (d) 1.25×10^{16} ions/cm².

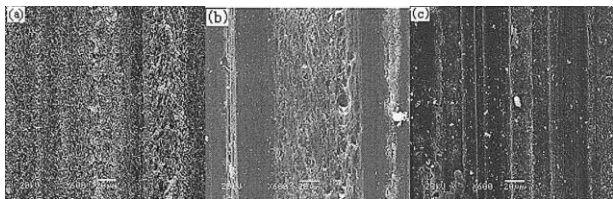


Figure 7 Scanning electron microscopy morphologies of worn surfaces of (a) 5×10^{14} ions/cm² implanted PES-C.; (b) unimplanted; (c) 1.25×10^{16} ions/cm² implanted PES-C.

at 1150 cm^{-1} may be a result of the destruction of the main chain, as $\text{O}=\text{S}=\text{O}$ bonds only existed in the main chain. In addition, the destruction of some phenyl was shown by the reduction in 1488 cm^{-1} ($\nu\text{C}=\text{C}$). In addition, when the dose reached or exceeded 2.5×10^{15} ions/cm², a broad peak between 1600 and 1800 cm^{-1} appeared, indicating the formation of carbon-rich structures on the surface of the sample,¹⁷ which was responsible for the variation in the friction and wear behavior of PES-C.

XPS analyses were conducted for the unimplanted and implanted specimens with different doses. And the C1s curve of the pristine and implanted PES-C was deconvoluted to several peaks [Fig. 6(a)–(d), labeled I–IV, respectively]. The C1s band before proton implantation [Fig. 6(a)] can be analyzed in three main components: carbon atoms not attached to O or S atoms (component I, at 284.8 eV), carbon atoms in the C–O or C–S groups (component II, at 286.1 eV), and carbon atoms in the carbonyl groups (component III, at 288.5 eV). After implantation [Fig. 6(b)–(d)], a low-intensity component (component IV, at 283.6 eV) appeared, which could be assigned to an amorphous carbon moiety.¹⁹ This means that proton implantation induced the formation of carbonization in PES-C. In addition, it can be seen from Figure 6(a)–(d) that the relative content of C–O or C–S (component II) and C=O (component III) decreased with increasing implantation dose, indicating the partial degradation of PES-C after proton implantation.^{20,21} In other words, the XPS results, including formation of amorphous carbon and partial degradation, agreed with the FTIR–ATR results.

From the above results, it can be concluded that with an increase in implantation dose a carbon-rich structure might form, prolonging the time for the friction coefficient to decrease to a steady value or even to increase to a higher steady value at a dose of 1.25×10^{16} ions/cm². In addition, the wear resistance of PES-C was improved at higher doses. Yet at a relatively lower dose, the increase in the interface temperature during the wear process might soften the PES-C surface [Fig. 7(a)] and result in higher wear rates. However, the adhesive wear of the pristine sample may have induced plastic ruffles and ripples on the wear surfaces [Fig. 7(b)], with a resulting wear rate

that was lower than that of the less- H^+ -implanted PES-C,¹⁰ although for the 1.25×10^{16} ions/cm²-implanted PES-C, the wear scar was covered with fatigue cracks and plastic deformation layers [Fig. 7(c)], which is consistent with increased wear resistance.

CONCLUSIONS

1. Proton implantation affects the friction and wear properties of PES-C differently. With the increase in implantation dose, it took more time for the friction coefficient to decrease to a steady value or even to increase to a higher steady value at a dose of 1.25×10^{16} ions/cm². But the wear rate first showed an increase and then a decrease. At a higher dose, the wear rate showed an obvious decrease.
2. The proton implantation-induced structural changes resulted in variation in tribological behavior, that is, partial degradation and a carbon-rich structure, which shifted the wear mechanism from adhesive wear, in the pristine sample, to fatigue wear, in the implanted sample at higher doses.

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