

Effect of Proton Implantation on the Tribological Properties of Phenolphthalein Poly(ether sulfone)

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ABSTRACT: Phenolphthalein poly(ether sulfone) (PES-C) was implanted with 110 keV protons in four doses of 1×10^{14} , 5×10^{14} , 2.5×10^{15} , and 1.25×10^{16} ions cm^{-2} . The friction and wear properties of both implanted and unimplanted PES-C were investigated with a THT07–135 high-temperature tribometer against a steel ball. Results revealed that the friction coefficient and wear rate both decreased with increasing doses: especially when the dose reached 1.25×10^{16} ions cm^{-2} , its wear rate decreased nearly two orders of magnitude. Scanning electron microscopy results revealed that the size of wear debris of unimplanted PES-C was greater than that of the implanted one. The worn surface of unimplanted PES-C showed plastic deformation, plastic flow, and adhesiveness, whereas the worn surface of the implanted one showed only some mild nicks. The carbon element distribution map revealed that much more carbon

element transferred to the counterpart steel ball friction against the implanted PES-C. The IR spectrum showed that partial degradation might occur when PES-C was implanted with protons. Measurement of hardness revealed an increase with increasing doses. The reason for the increase might be the formation of carbon-rich structures on the surface of the sample. From the above, conclusions can be drawn that the wear mechanisms of unimplanted samples were mainly related to adhesion, plastic deformation, and plastic flow, whereas that of implanted samples was mainly attributed to mild “three-body” wear. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1043–1048, 2004

Key words: phenolphthalein poly(ether sulfone) (PES-C); surfaces; hardness; wear; crosslinking

INTRODUCTION

Polymers have been widely used across most industrial sectors because of their excellent physical and chemical properties, coupled with their outstanding processability and the resulting cost-effectiveness. However, use of polymers is still limited because of their inherent softness and dielectric properties. Recent studies have shown that ion implantation of such polymers as polyimide (PI), polycarbonate (PC), polyethylene (PE), polystyrene (PS), and polytetrafluoroethylene (PTFE) can improve surface hardness, wear, and other surface-sensitive properties,^{1–5} and it is assumed that the improvement of surface hardness and wear resistance is mainly related to the crosslinking of polymers. However, as is known, when polymers are bombarded with ion beams, chain scission and crosslinking occur simultaneously. Differences exist in the proportion of each part, which depends on the structure of the polymers and other experimental parameters. Because of the complexity, it is still a chal-

lenge to study the effects of ion bombardment on the structure and the resulting properties of polymers.

Phenolphthalein poly(ether sulfone) (PES-C) is a newly developed high-performance engineering thermoplastic. It has been used widely as the matrix of polymer composites because of its excellent mechanical and thermal properties. In this work, the effects of proton implantation, on both friction and wear properties of PES-C and the impact of implantation dose, have been investigated. It is expected that this investigation would be helpful to improve the friction and wear properties of PES-C and expand its application in engineering.

EXPERIMENTAL

Phenolphthalein poly(ether sulfone) (PES-C; structural formula shown in Fig. 1) was produced by Xuzhou Engineering Plastics Co. (Xuzhou, China). To produce samples for testing, PES-C powder was heated at a rate of 5°C min^{-1} from room temperature to a maximum temperature of 320°C , with the pressure held at 20 MPa for 40 min, and then cooled to room temperature.

Proton implantation was performed on a 200 keV implanter in the Institute of Modern Physics, Chinese Academy of Sciences (Lanzhou, China). The blocks of

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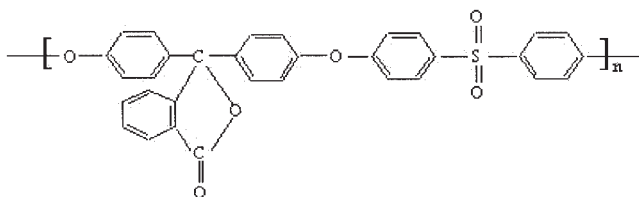


Figure 1 Structural formula of PES-C.

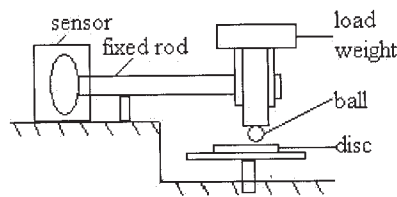


Figure 2 Contact schematic diagram for the friction couple.

PES-C (numbered as S0-S4) were implanted with 110 keV ions of hydrogen at doses of 0 , 1×10^{14} , 5×10^{14} , 2.5×10^{15} , and 1.25×10^{16} ions cm^{-2} , respectively. The implantation resulted in a color change of the PES-C blocks with increasing dose, from light brown to bright black at a dose of 1.25×10^{16} ions cm^{-2} .

Friction and wear tests were conducted on a THT07-135 high-temperature tribometer at room temperature under ambient atmosphere. The contact schematic diagram of the frictional couple is shown in Figure 2. Before each test, the steel ball and the block were cleaned with cotton dipped in acetone. In this work, three samples were tested under each condition; the friction coefficient and wear rate were the average values of three replicated test results.

Finally, the morphologies of the wear debris and transfer film of PES-C formed on the counterpart steel ball were observed with a JSM-5600LV scanning electrical microscope (JEOL, Tokyo, Japan). The wear scars of PES-C were observed with an optical microscope. To characterize the component changes on the surface of PES-C, an IF S66V/S infrared spectrometer was used. The specimens for FTIR experiments were pre-

pared by the KBr tableting method, with experiments conducted in the transmitting mode. Changes of surface hardness were characterized with an MH-5-VM hardness meter at a load of 25 g and a loading time of 5 s.

RESULTS AND DISCUSSION

Figure 3 shows the effect of the implantation doses on the friction coefficient of PES-C. It can be clearly seen that the initial friction coefficient of the samples decreased with increasing dose. When the dose exceeded 10^{15} ions cm^{-2} , it reduced to half the value for the pristine sample when the sliding distance was equal to or lower than 0.02 km. On the other hand, the friction coefficients of all the samples increased with the sliding distance. When it exceeded 0.1 km, the friction coefficients of S0-S3 became closer in value and leveled off, whereas that of S4 was always lower until the test ended.

Although it is known that ion implantation can be used to improve the wear properties of many polymers effectively, the friction data are somewhat diffi-

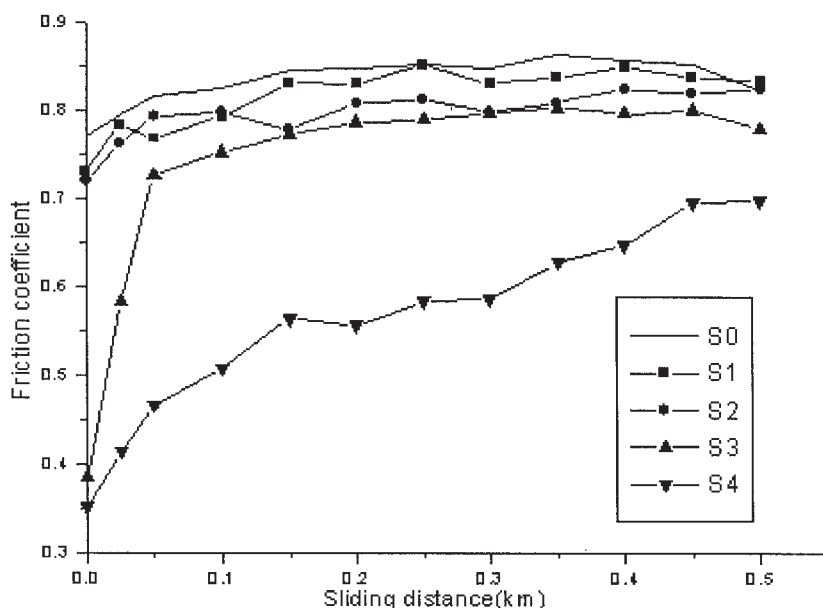


Figure 3 Friction coefficient as a function of sliding distances of S0: unimplanted; S1: 1×10^{14} ; S2: 5×10^{14} ; S3: 2.5×10^{15} ; S4: 1.25×10^{16} ions cm^{-2} proton implanted PES-C against steel ball under 1N at room temperature.

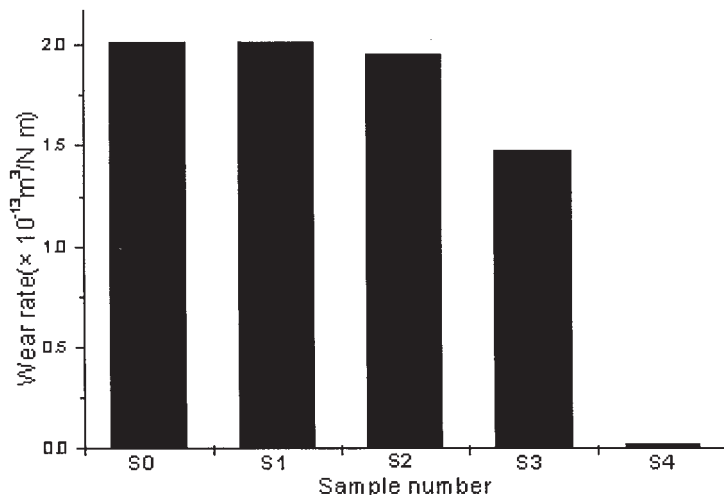


Figure 4 Wear rate of PES-C against steel ball under 1N after 0.5 km sliding for S0: unimplanted; S1: 1×10^{14} ; S2: 5×10^{14} ; S3: 2.5×10^{15} ; S4: 1.25×10^{16} ions cm^{-2} proton implanted PES-C.

cult to interpret. Generally, friction values of the implanted polymers are higher than those of unimplanted ones.⁶⁻⁸ This is not always true, for instance, under our testing conditions, because proton implantations reduced the friction coefficient of PES-C with increasing doses. Others also have found the reduction of friction coefficient after ion implantation.⁹⁻¹¹

Figure 4 shows the wear rate of PES-C sliding against a steel ball under 1N load for sliding distances of 0.5 km, as measured by a profilometer. Results indicate that, with increasing implantation dose, the wear rate of PES-C tended to decrease. A lower dose, however, seemed to have little effect on the wear rate. Only when the dose reached 10^{15} ions cm^{-2} did the reduction become obvious. Especially for S4, with a

dose of 1.25×10^{16} ions cm^{-2} , wear rate decreased from 2.014×10^{-13} to 2.762×10^{-15} $\text{m}^3/\text{N m}$, a decrease of nearly two orders of magnitude.

As can be seen from the above, the friction coefficient and wear rate of PES-C both decreased with increasing doses. The main reason for the reduction of friction coefficient may be related to the reduction of shear strength attributed to the break of chemical bonds of PES-C during the process of ion implantation, which is favored by the structure of PES-C. When implanted by high dose of ions, PES-C may form tribenzene free radicals by decarboxylation, and the radicals react further, thus contributing to the degradation of the polymer. After degradation, the rigidity of PES-C decreased and its flexibility increased, which

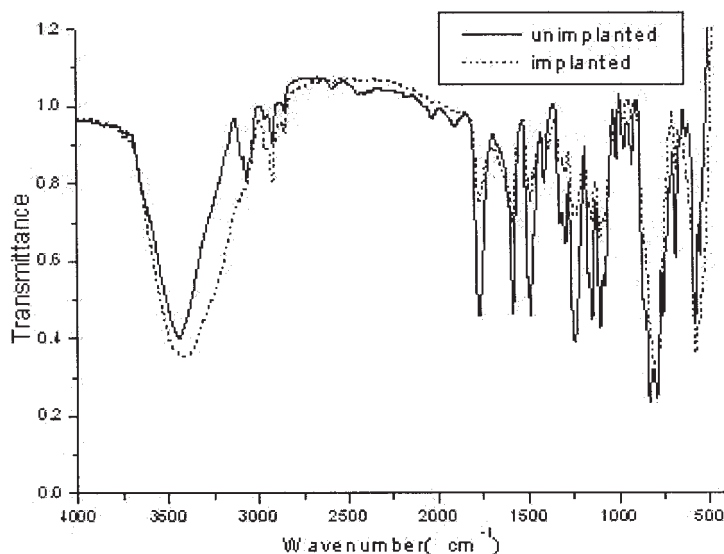


Figure 5 Infrared spectra of the samples before and after implantation (1.25×10^{16} ions cm^{-2}).



Figure 6 SEM micrographs of the wear debris of PES-C before and after proton implantation: (a) before implantation; (b) after implantation (1.25×10^{16} ions cm^{-2}).

led to a lower friction coefficient. The marked decrease of the wear rate may also result from the formation of low molecular weight material, which may play a dominant role in the lubrication of the sample in a short period,¹² after which other factors govern the decrease of wear rate, as discussed below.

Figure 5 shows the infrared spectra of PES-C before and after implantation. It can be seen that the C—H stretching vibration at 3066.69 cm^{-1} “disappeared” after implantation. However, it may actually be covered by the absorption peak centered at 3415.85 cm^{-1} , which corresponds to the O—H stretching vibration of

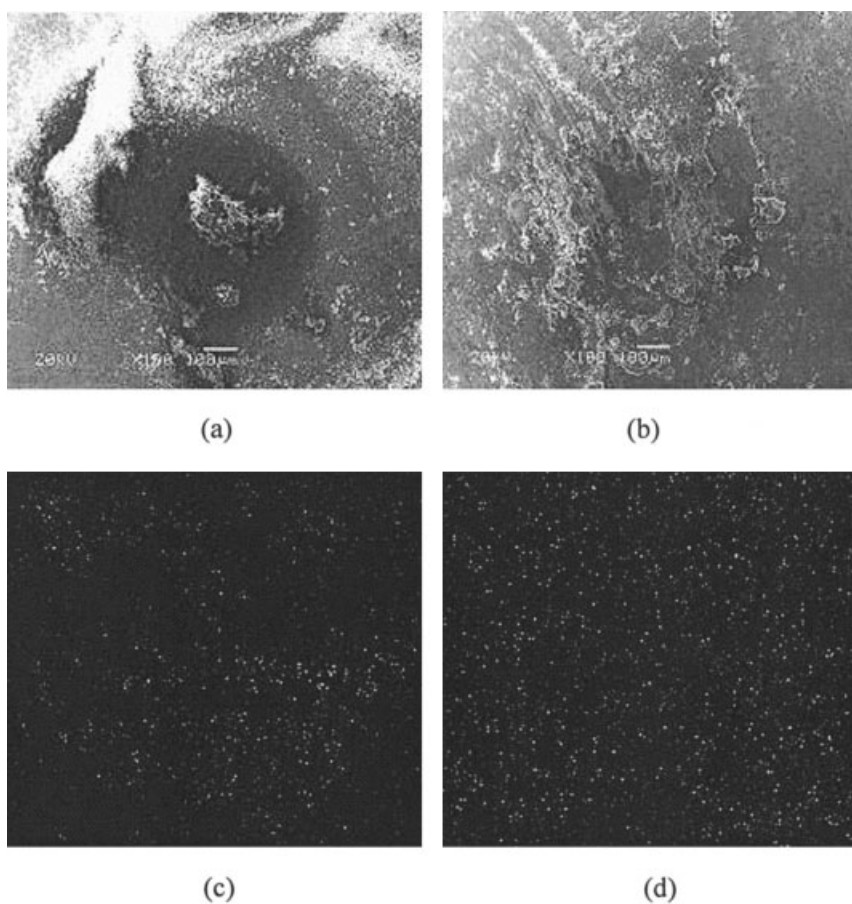


Figure 7 SEM micrographs of the transfer film on the counterpart steel ball: (a) unimplanted samples; (b) implanted samples (1.25×10^{16} ions cm^{-2}); (c) the C element distribution corresponding to (a); (d) the C element distribution corresponding to (b).

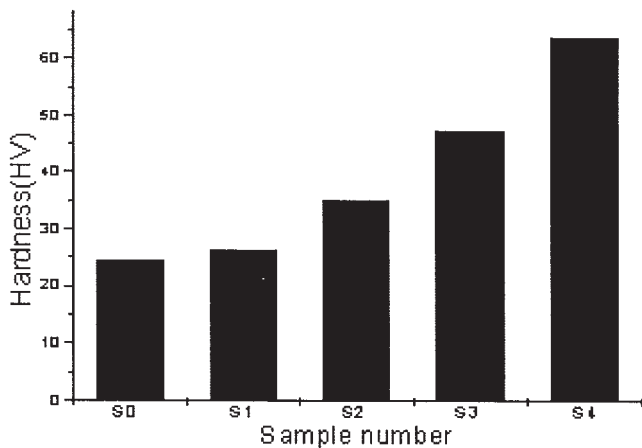


Figure 8 Hardness change of samples with different implantation doses.

the absorbed H₂O on the surface of the sample. Moreover, the absorbed H₂O may play a role in the reduction of friction coefficient and wear rate of implanted PES-C in a short period. The intensity of bands in the range of 2000–1000 cm⁻¹ also obviously decreased. The reason may be the partial degradation of the molecular chain of PES-C in the surface zone. In a

word, the IR spectra indicate the partial degradation of PES-C to some extent.

Figure 6 shows the wear debris of PES-C before and after implantation. It is clear that the size of the debris after implantation became smaller and less than that of the normal PES-C. This was consistent with the variety of the wear rate, and it reflected the fact that the wear resistance of PES-C was improved by proton implantation.

Figure 7 shows the morphologies of the transfer film formed on the counterpart steel ball and the C element distribution of the counterpart. From the micrographs, we can see that wear debris accumulated on the steel ball against the unimplanted sample, but the C element distribution map did not reveal a coherent transfer film on it, in contrast to that against the implanted sample. The SEM micrograph, of the steel ball against the implanted sample, however, revealed some detachment of the transferred PES-C [Fig. 7(b)]. The reason may be the mild abrasiveness of the wear debris that was harder than the matrix of PES-C (Fig. 8). The hardening of the sample surface might result from the formation of carbon-rich structures on the surface of the sample,¹³ as evidenced by the newly created weak band at 1503.73 and 1608.10 cm⁻¹ in the IR spectrum (Fig. 5) of the implanted samples.¹⁴ The

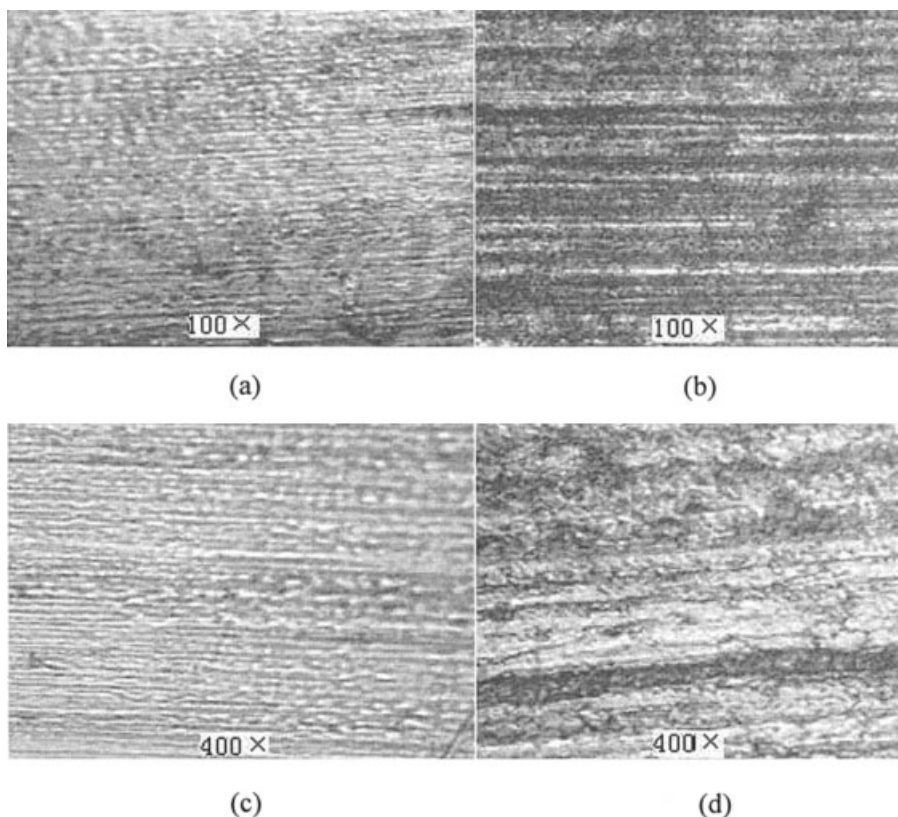


Figure 9 Optical micrographs of the wear scar of PES-C before and after implantation (1.25×10^{16} ions cm⁻²): (a) unimplanted ($\times 100$); (b) implanted ($\times 100$); (c) unimplanted ($\times 400$); (d) implanted ($\times 400$).

improvement of surface hardness also explains the reduction of the wear volume. This is in agreement with Rabinowicz's model for abrasive wear,¹⁵ which indicates that the wear volume per unit distance of sliding is inversely proportional to the hardness of the materials.

Figure 9 shows the optical micrographs of the wear scar of PES-C before and after implantation. In the wear scar of the unimplanted sample, there is clear evidence of plastic deformation and plastic flow; also, adhesiveness occurs in some parts. These phenomena showed that the main wear mechanisms, of unimplanted PES-C, were plastic deformation, plastic flow, and adhesiveness. In contrast, there was little plastic deformation and plastic flow in the wear scar of the implanted PES-C. However, mild nicks covered the worn surface of the latter, which may be caused by a small amount of debris of the implanted PES-C. As noted above, the transferred PES-C decreased the abrasive effect. In addition, there was much less wear debris for the implanted PES-C, so the wear rate of the implanted sample was very low in spite of the mild "three-body" wear mechanism.

CONCLUSIONS

1. The friction and wear properties of PES-C improved after proton implantation. The friction coefficient and wear rate of PES-C both decreased with increasing implantation dose. When the dose reached 1.25×10^{16} ions cm^{-2} , the wear rate of PES-C decreased sharply. The main reason for the significant decrease may be the formation of carbon-rich structures on the

surface of the sample, caused by proton implantation, as well as the small molecular substances formed on the sample surface whose role may be restricted within a short period.

2. The main wear mechanisms of the unimplanted PES-C were plastic deformation, plastic flow, and adhesiveness, whereas that of the implanted ones was mainly mild "three-body" wear. In spite of the mild abrasiveness, the low wear rate of the implanted samples is understandable considering the less wear debris and the transferred PES-C on the counterpart steel ball.

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