Effect of Radiation on the Friction-Wear Properties of Polyetherketone with a Cardo Group

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ABSTRACT: We studied the effect of radiation on the friction-wear properties of polyetherketone with a cardo group (PEK-C) with a MM-200 model friction and wear tester. We found that radiation could improve the friction-wear properties of PEK-C to a certain degree. The friction coefficient and wear rate of PEK-C decreased as the radiation dose increased from 5×10^4 to 1×10^7 Gy. Scanning electron microscopy results revealed that the size of wear debris of unirradiated PEK-C was larger than that of irradiated PEK-C. The worn surface of unirradiated PEK-C showed plough marks, whereas the worn surface of irradiated PEK-C did not show plough marks; its surface was quite smooth. With the frictional couple of a carbon steel ring and an irradiated PEK-C block, a relatively uniform and coherent transfer film was formed on the ring surface. It was inferred that the transfer film contributed largely to the decreased friction coefficient and wear rate of the irradiated PEK-C. An IR spectrum showed that no significant chemical change took place when the PEK-C sample was irradiated. Thermal analysis results showed that radiation changed the thermal properties of PEK-C, therefore, its friction-wear properties changed at the same time. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 962–967, 2001

Key words: polyetherketone with a cardo group (PEK-C); radiation; friction wear; surface analysis

INTRODUCTION

With the development of advanced materials used in space, further demands for good mechanical and physical properties, especially antiradiation properties, have been made of polymer materials. Haruvy[1] pointed out that various radiation sources, such as fast electrons, fast protons, ultraviolet rays, γ rays, and energetic heavy particles, exist in cosmic space. According to the approximate computations of scientists, the maximum dose of radiation at the surface of a material mounted on a space system is 2500 Mrad/year. Therefore, for good applications of polymer materials in space, we need to carry out systematic research into the effect of radiation on the basic properties and tribological properties of polymers and provide a theoretical basis for the application of polymers in space.

In a search of the literature,[2–5] we have discovered that the effect of radiation on the tribological properties of polymers has received scant attention. Generally, polymers with comparatively simple structures, such as polytetrafluoroethylene (PTFE) and polyethylene (PE), have been studied. In this article, we present the effect of radiation on the tribological properties of polyetherketone with a cardo group (PEK-C), which

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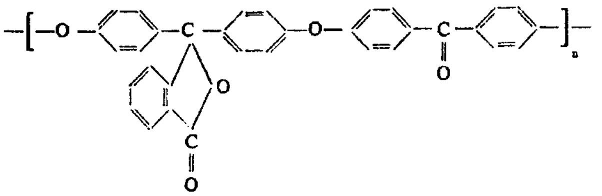


Figure 1 Structural formula of PEK-C.

has a comparatively complex structure, and investigate the friction-wear mechanism of irradiated PEK-C.

EXPERIMENTAL

PEK-C (shown in Fig. 1) was produced by the Changchun Institute of Applied Chemistry, Chinese Academy of Sciences (Changchun, China). To produce samples for testing, we heated PEK-C powder at a rate of 5°C $\min^{-1}$ from room temperature to a maximum temperature of 320°C, with the pressure held at 10 MPa for 30 min, and then cooled the powder to room temperature.

Electron beam radiation was carried out in N_2 gas with an electron accelerator at the Lanzhou Institute of Modern Physics of the Chinese Academy of Science. Radiation was performed at ambient temperature.

The friction and wear tests were conducted on a MM-200 model friction and wear tester (Xuanhua, China) at room temperature (20–25°C) under ambient atmosphere. The contact schematic diagram of the frictional couple is shown in Figure 2. Before each test, the plain carbon steel (AISI 1045 steel ring) and PEK-C block were polished with no. 900 water-abrasive paper (the irradiated PEK-C block was not polished with the paper, whereas the PEK-C block before irradiation was). Then, the surfaces of the steel ring and PEK-C block were cleaned with cotton dipped in acetone and then dried in air. In this work, three to five 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 worn surfaces of PEK-C were observed with a JEM-1200EX scanning electron microscope (JEOL Corp., Japan), and transfer films of PEK-C formed on the surface of the steel ring were observed with an EMP-810 electron probe microanalysis (Shimadzu Corp., Japan). IR spectra were recorded with a Bio-Rad FTS165 Fourier transform infrared spectrometer (USA) that was connected to reflection accessories and an IR microscope. Electron spin resonance (ESR) measurements were carried out at room temperature with a ER200D-SRC ESR spectrometer (Bruker, Switzerland). A Perkin-Elmer TGA7 (USA) was used for the characterization of the thermal properties of the materials.

RESULTS AND DISCUSSION

Figure 3 shows the effect of the radiation dose on the friction-wear properties of PEK-C. The friction coefficient and wear rate of PEK-C decreased with an increasing radiation dose. When the radiation dose exceeded 5×10^6 Gy, the wear rate of the irradiated sample decreased sharply to one-sixth the wear rate of an unirradiated sample. When the radiation dose was 1×10^7 Gy, the wear rate was only one-eighth the wear rate of an unirradiated sample. The main reason for the decreased friction coefficient and wear rate of irradiated PEK-C may be the degradation of the samples after they were irradiated. Li et al.[6] pointed out that PEK-C may form tribenzene free radicals by decarboxylation after irradiation. Because the main chain of PEK-C is led into a huge phenolphthalein side radical, its rigidity is relatively great. When a degradation reaction occurs, its rigidity decreases, its flexibility increases, and it acquires a low and steady friction coefficient. We think that the main reason for the marked decrease of the wear rate may be the formation of a low molecular weight substance on the surface of the sample, and the low molecular weight substance may play a dominant role in the lubrica-

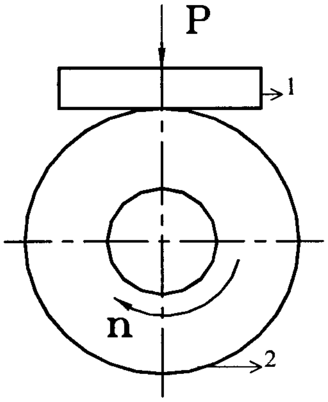


Figure 2 Contact schematic diagram for the friction couple: (1) sample and (2) rotating ring (P = load).

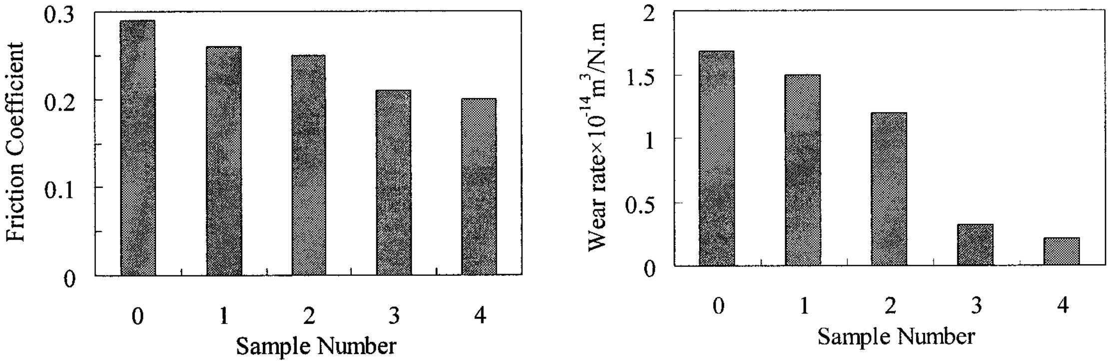


Figure 3 Effect of irradiation on the friction-wear properties of PEK-C (sliding was performed under ambient conditions over a period of 120 min at a sliding speed of 0.42 m/s and a load of 196*N* at room temperature) with radiation doses of (0) 0, (1) 5 × 10^4, (2) 5 × 10^5, (3) 5 × 10^6, and (4) 1 × 10^7 Gy.

tion of the sample. Furthermore, with an increased radiation dose, this effect became more and more obvious. When the dose was relatively low, that is, 5 × 10^4 Gy, the friction coefficient decreased from 0.29 to 0.26, and the wear rate decreased from 1.68 to 1.50 (× 10^{-14} $m^3/N \cdot m$). The friction coefficient and wear rate were accompanied by a slight decrease. However, when the dose was relatively high, that is, 5 ×10^6 Gy, the friction coefficient decreased from 0.29 to 0.21, and the wear rate decreased from 1.68 to 0.32 (× 10^{-14} $m^3/N \cdot m$). The friction coefficient and wear rate were accompanied by a sharp decrease.

Figure 4 shows the scanning electron micrographs of the worn surface of unirradiated and irradiated PEK-C. There are obvious plough marks on the wear scar of the unirradiated PEK-C block. Also, there are microcracks on some parts of the wear scar. However, there are no obvious plough marks on the wear scar of the irradiated PEK-C block, and the worn surface is relatively smooth. Microcracks appear in some parts of the wear scar. Irradiated degradation may have occurred in these parts.

Figure 5 shows scanning electron micrographs of the wear debris of unirradiated and irradiated PEK-C. The size of the wear debris of the normal PEK-C is larger than that of the irradiated PEK-C. This shows that the antiwear of PEK-C improves with irradiation. The aforementioned investigation and analysis results are consistent with the results of the friction and wear tests. There may be different wear types for the two samples in this situation, and further study is needed.

The transfer films formed on the steel ring surfaces by the plain carbon steel ring being run against unirradiated PEK-C and irradiated PEK-C are shown in Figure 6. No obvious transfer film was formed on the counterpart steel

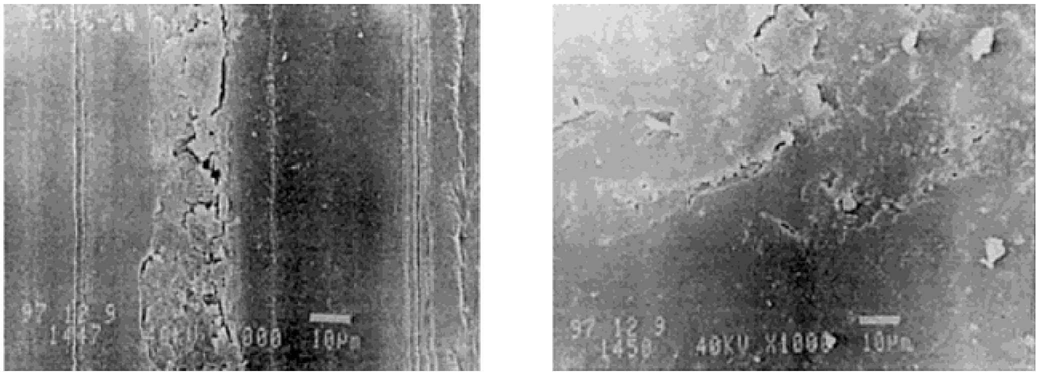


Figure 4 Scanning electron microscopy morphologies of worn surfaces of PEK-C before (left) and after (right) radiation (R = 5 × 10^6 Gy).

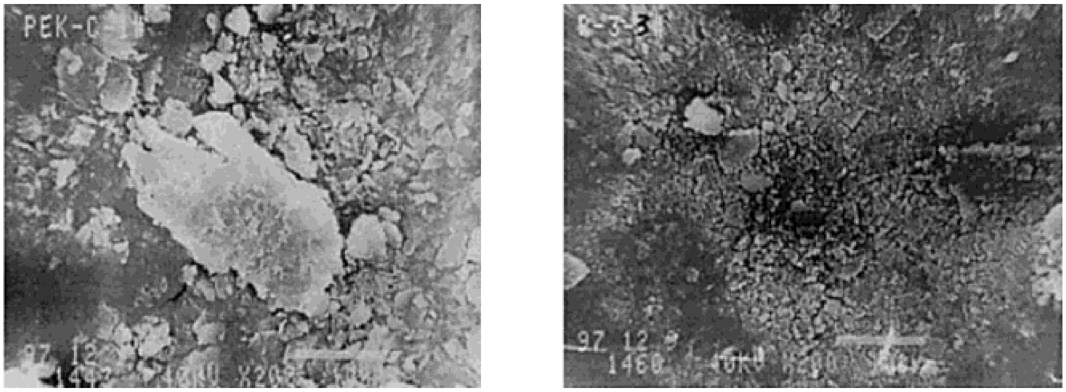


Figure 5 Scanning electron microscopy morphologies of wear debris of PEK-C before (left) and after (right) radiation ($R = 5 \times 10^6$ Gy).

ring by the steel ring being run against the normal PEK-C block, whereas a relatively uniform and coherent transfer film was formed by the steel ring being run against the irradiated PEK-C block. There exists an obvious difference in the morphologies of the counterpart steel ring surfaces of normal PEK-C and irradiated PEK-C. The counterpart surface of irradiated

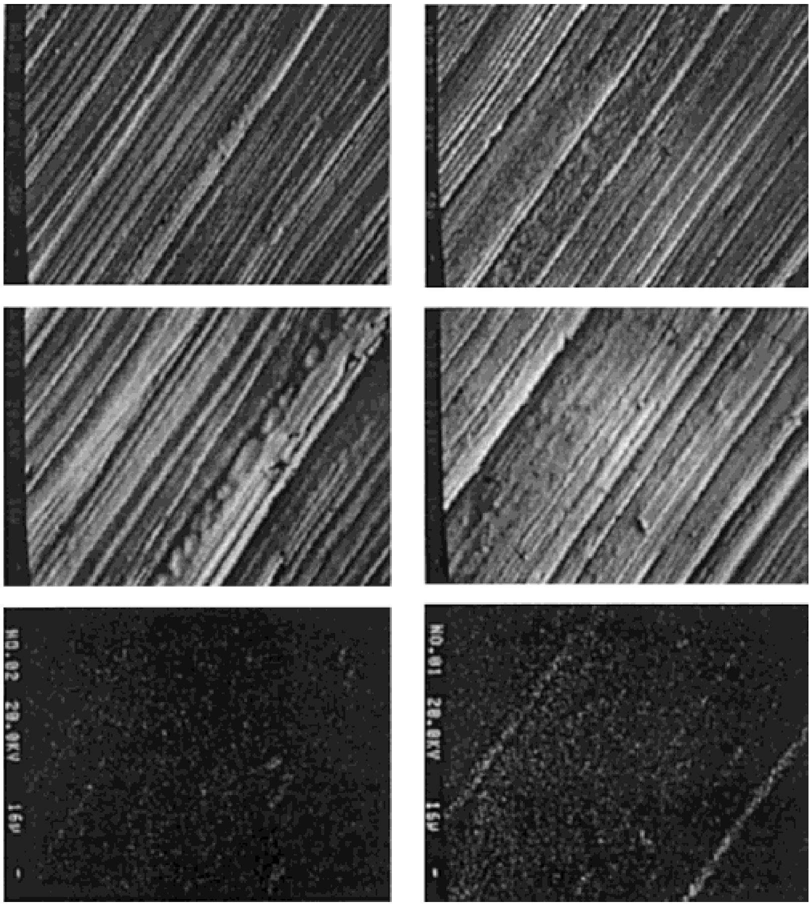


Figure 6 Scanning electron microscopy images of the worn surface of the counterpart ring (top, 200×; middle, 600×) and C element surface distribution map (bottom) of PEK-C before (left) and after (right) radiation.

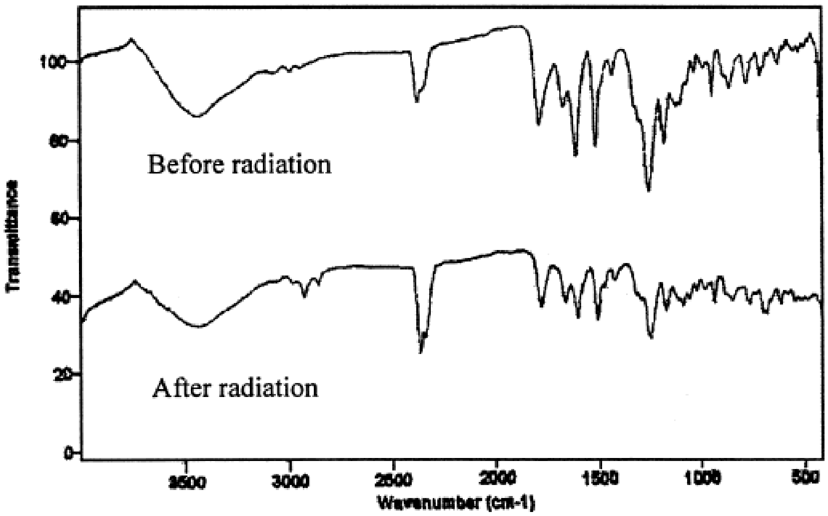


Figure 7 IR spectra of PEK-C before and after radiation ($R = 1 \times 10^7$ Gy).

PEK-C was smoother than that of normal PEK-C.

From the morphology of the surface distribution of the C element, the transfer of C on the surface of the steel ring for irradiated PEK-C was much greater than for normal PEK-C, thereby greatly reducing the wear of irradiated PEK-C. In a word, it was just the transfer film that was responsible for the improved tribological properties of the irradiated PEK-C. That is, with the formation of the relatively uniform and coherent transfer film, subsequent sliding occurred between the surface of the irradiated PEK-C block and the transfer film. Consequently, a lower wear rate and a lower friction coefficient were reached.

Figure 7 shows the IR spectra of PEK-C before and after radiation. The two spectra are very similar. There may be two causes producing this ending. First, the radiation-resistant property of PEK-C is very strong, so the degree of radiation degradation is relatively slight. Second, absorption peaks such as carboxyl group and benzene on the molecular chain existed after partial degradation, so we can hardly determine the difference from IR spectra.

Figure 8 shows ESR spectra of PEK-C after irradiation. We captured free-radical signals from the spectra. By analyzing the structural formula of PEK-C, we have concluded that PEK-C may form tribenzene free radicals by decarboxylation after it is irradiated. This result is consistent with the literature.

Figure 9 shows thermogravimetric analysis (TGA) curves of PEK-C before and after radiation. In the TGA curves of the two samples, we see notable difference. The initial temperatures of sharp decomposition for the two samples were different (505.6°C for unirradiated PEK-C and 536.2°C for irradiated PEK-C). In addition, the temperatures of complete decomposition for the two samples were different (710°C for unirradiated PEK-C and 660°C for irradiated PEK-C). The thermal property of PEK-C changed after irradiation, so the radiation caused the changes in the friction-wear property of PEK-C at the same time.

CONCLUSION

1. The friction-wear property of PEK-C improved after it was irradiated. The friction

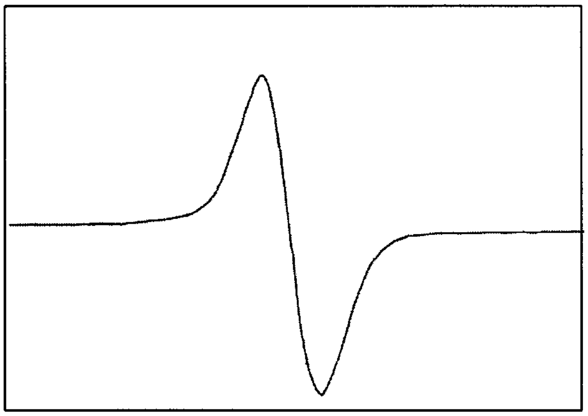
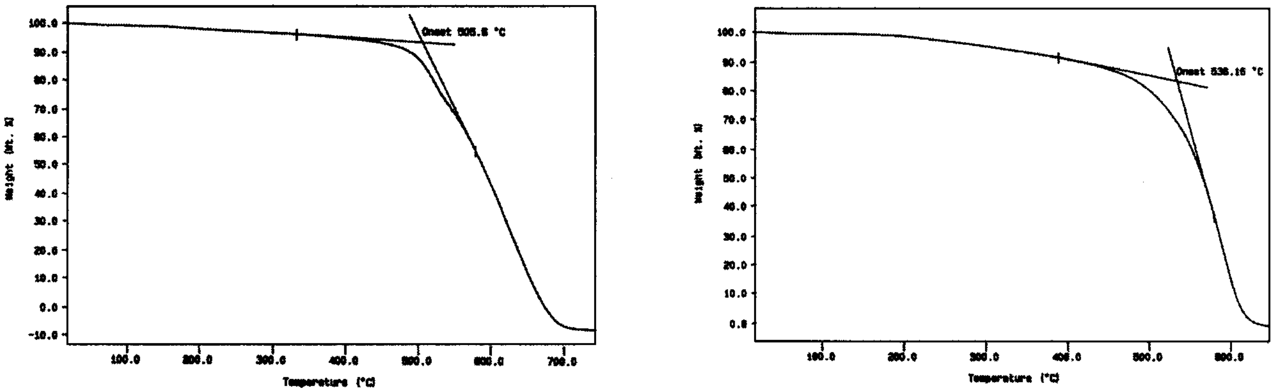


Figure 8 ESR spectra of PEK-C after radiation ($R = 1 \times 10^7$ Gy).



Before radiation

After radiation

Figure 9 TGA curves of PEK-C before and after radiation ($R = 1 \times 10^7$ Gy).

coefficient and wear rate of PEK-C both decreased with an increasing radiation dose. When the dose exceeded 5×10^6 Gy, the wear rate of PEK-C decreased sharply. The main reason for the significant decrease in the wear rate may be the formation of a small molecular substance on the surface of the sample, and this low molecular weight substance may play a dominant role in the lubrication of the sample.

2. Obvious plough marks appeared on the wear scar of the unirradiated PEK-C block. However, there were no obvious plough marks on the wear scar of the irradiated PEK-C block, and the worn surface was relatively smooth. In addition, the size of the wear debris of the normal PEK-C was larger than that of the irradiated PEK-C. With the frictional couple of the carbon steel ring and irradiated PEK-C block, a relatively uniform and coherent transfer film was formed on the ring surface. The transfer film contributed largely to the decreased friction coefficient and wear rate of the irradiated PEK-C.
3. The thermal properties of PEK-C changed after it was irradiated, so radiation caused the changes in the friction-wear properties of PEK-C at the same time.

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