The Correlation of Wear Behaviors and Microstructures of Graphite–PTFE Composites Studied by Positron Annihilation

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SYNOPSIS

The correlation between the wear behaviors of graphite–polytetrafluoroethylene (PTFE) composites and their macro- and microscopic structural changes was studied in a wide graphite volume content range of 0 to 50%. It was found that the macroscopic structure of graphite–PTFE composites changes from the state of PTFE-wrap-graphite to the state of detachment between PTFE and graphite powder along with an increase of graphite volume content. The sudden change occurred at the point of graphite volume content of about 40%. In this article the positron annihilation lifetime spectrum was used to detect the properties of microscopic imperfections. The results indicated that the changes of microimperfects of graphite–PTFE composites in size and in concentration are also related to the increase of graphite volume content while the crystallinity of PTFE shows a tendency to increase. The wear behaviors of graphite–PTFE composites corresponded to the physical properties of imperfects in a macro- and microscopic sense and were reflected fairly well by the interfacial properties between crystal and amorphous regions in PTFE. The positron annihilation technique is a useful tool for the study of tribological behaviors of polymers. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The positron annihilation technique (PAT) is an advanced method for detecting the microstructure of condensed matter. When positrons are injected into molecular solids, a high fraction form positronium (Ps).[1] This is not the case for metals. The formation probability and annihilation characteristics of positronium in molecular crystals depend on the chemical and physical properties of solids.[2] In simple van der Waals solids, to which category polymers belong, the interaction between positronium and the rest of the system has been commonly described in terms of the free volume theory,[3] as first formulated by Ferrell[4] and later further developed by Brandt, Berko, and Walker.[3] According to the free volume theory, the rate of positron annihilation, in the absence of chemical interactions between positronium

and matter, is a function only of the effective free volume and thus a function of the overlap of positronium and electron wave function of the lattice.[5,6] In other words, as the size of the free volume sites increases, the overlap is reduced and so is the annihilation rate. Since the macroscopic properties of materials are relevant to their microstructure, the detection of microscopic defects is one of the interesting topics in material science.[2-8]

Understanding of the correlation between the wear behaviors of polymers and their microscopic properties is important from both scientific and practical standpoints, since polymers are being used more and more in engineering applications. As important tribomaterials, PTFE and its composites have been widely applied in industry and scientific research.

The transfer of bulky PTFE to the counterface often results from the dry sliding of ductile polymers.[9] The adhesion of PTFE transfer film to the counterface has been thought for a long time to play an important role in controlling the wear rate of

PTFE. This is generally true for measurements at low speed, low load, and room temperature. Experimental results of Gong[10,11] and his co-workers showed that the chemical properties of the counterface do not affect the wear behavior of PTFE and its composites, because detachment of the transfer film does not occur from the interface between the first layer of the transfer film and the substrate, but from the middle of the film at some distance from the interface. These results indicate that the wear behaviors of PTFE and its composites are restricted to their microstructure at the harsh terms. The effects of deformation on the microstructure of PTFE bulk studied by positron annihilation were reported by Wang et al.[12] They found that positron annihilation lifetime is a sensitive means to probe the microstructural change of polymers during deformation. However, less applications of the positron annihilation technique in the study of wear behaviors of polymers have been reported. In this article the correlation between wear behaviors of graphite–PTFE composites and their microstructural changes studied by the positron annihilation technique has been investigated. It is expected that the results could be helpful for the microscopic design of tribomaterials.

EXPERIMENTAL

The wear behaviors of graphite–PTFE composites were measured on an Optimol SRV wear tester with the contact of ball on disc. The rider ball was made of GCr15 bearing steel (SAE 52100) with a diameter of 10 mm. Specimens of graphite–PTFE composites were formed to plates with a thickness of about 8 mm. The friction tests were carried out at a load of 200 N, an amplitude of 1.5 mm, a frequency of 20 Hz, and a test duration of 5 min at room temperature (20°C). The wear volume of each specimen was calculated according to longitudinal sectional drawings measured by a profilometer.

PTFE used in this work was commercial powder with a grit size of 5 μm, whereas the grit size of graphite powder was 1 μm. The average molecular weight of PTFE was about 2.5×10^7 measured on a Perkin-Elmer-7 differential scanning calorimeter according to the method used by Takeshi Suwa et al.[13]

Positron annihilation lifetime measurements were carried out by using a fast–slow coincident positron annihilation lifetime spectrometer system, which has a resolution of 270 ps. A 10 μCi ^{22}Na positron source was used in the tests at room temper-

ature of 20°C. The counting rate of the instrument was about 260 counts per second (cps), and 5×10^6 counts were collected for each spectrum.

RESULTS

Wear Behaviors of Graphite–PTFE Composites

The wear rates of PTFE and its composites along with the increase of graphite volume content from 0 to 50% are shown in Figure 1. The wear rate of graphite–PTFE composites decreases at first with the increase of graphite content from 0 to 20%, and then increases in the range of 20% to 40%. Finally, the wear rate increases acutely when graphite volume content is above 40%. The highest wear rate was observed at 50% graphite–PTFE composite, while the lowest wear rate was produced by 20% graphite–PTFE composite. No wear of ball was found in the tests. The result indicate that the effective filler volume content should be less than 40% for the polymer-based composites. The same result was also observed in a study of the wear behaviors of MoS_2–PTFE composites. These same phenomena should be attributed to the changes of macroscopic structure of polymer composites. To explain the phenomena, a simple method for determining the porosities of polymer composites was adopted in this study. It is well known that the polymer composites may be porous materials because of the addition of filler when the filler volume content is more than a certain value. If the pores in polymer composites are big enough and linked together, a proper solvent
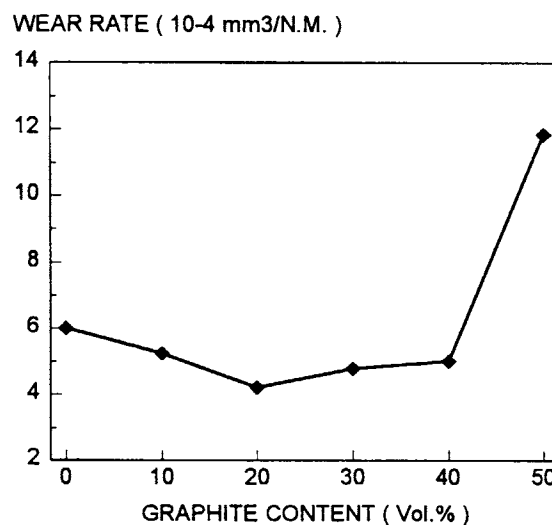
WEAR RATE (10-4 mm3/N.M.)

Figure 1   The relationship between the wear rate and graphite content.

can penetrate the matrix of the polymer composites, and the capacity for solvent detected by the macroscopic method shows the porosity of the polymer composites. In this study the penetrating solvent was ethanol. This is because ethanol possesses wettability for PTFE and graphite. The porosities of graphite–PTFE composites with various graphite volume contents measured by this method are shown in Figure 2.

No adsorption of specimens occurred when graphite volume content was below 30%. The penetration of ethanol occurred when the graphite volume content in composites above 40%. This result indicated that a sudden change of the macrostructure of polymer composites occurred at the point of graphite volume content of 40%. This sudden change also corresponded to a sudden decrease of electric resistance value measured in qualitative of polymer-based composites. When graphite volume content was more than 40%, the graphite–PTFE composites changed into a conductor from semiconductor or insulator (for pure PTFE). These test results indicate that when the graphite volume content in matrix is less than 30%, the structure of graphite–PTFE composites is the state of PTFE-wrap-graphite and PTFE-wrap-pore; when the graphite volume content is more than 40%, its structure changes into the form of detachment between PTFE and graphite powder. This is because the specimens were prepared by compression molding. For the two-phase coincident system, there exist three combination forms: the powder A–wrap–powder B (volume content of B is from 0 to 40%); the detachment between powder A and powder B (B content from 40 to 60%); and the powder B–wrap–powder A (B content from 60 to 100%).

Microstructures of Graphite–PTFE Composites Studied by Positron Annihilation

Unlike metals, polymers as the molecular solid always contain a large fraction of imperfect sites, such as impurities, defects, voids, and grain boundaries. Many of these sites serve as free volumes for positronium formation. Furthermore, the average electron density of molecular solids is lower than that of metals, so the ortho-positronium lifetime is easily distinguishable from that of the positron. In this work, each positron annihilation lifetime and intensity spectrum of composites was resolved into four positron components using the computer program PATFIT-88.[14] As a general rule,[5] each lifetime component is inversely related to the electron density of the materials under study. The shortest lifetime
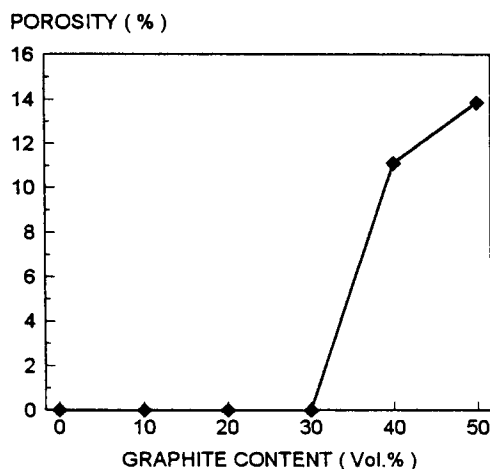

Figure 2 The porosity of graphite–PTFE composites.

τ_1 is mainly due to para-positronium (singlet positronium) annihilation and positron annihilation in the bulk of the crystalline regions.[15] The second lifetime τ_2 on the order of 0.4 ns is due to positron-molecule and positronium–molecule complexes and free positron annihilation in the crystalline regions.[5,16] Any lifetime longer than 0.5 ns is usually interpreted as ortho-positronium annihilation. For a system containing various defects, one can find two ortho-positronium lifetimes, a shorter lifetime τ_3 ($\sim$ 1 ns) and a longer lifetime ($>$ 2 ns) due to annihilation in the bulk and at the site of imperfections,[5,15,17] respectively. To each lifetime component there corresponds a certain probability, called the intensity, I, which is quoted as a percent. Intensities, particularly of the long-lived components, often designated as I_3 and I_4, are related to the chemical and physical properties of molecules under study.

The lifetime τ_2 and intensity I_2 spectra of graphite–PTFE composites are shown in Figure 3. The regulation showing in lifetime spectrum τ_2 is inversely corresponding to its intensity spectrum I_2. According to the interpretation of lifetime τ_2 and intensity I_2,[5,16] it can be seen that graphite as an electron donor makes the electron density of PTFE in the crystalline regions and the interface[18] between PTFE and graphite increase, and hence the lifetime τ_2 decrease. The interaction between PTFE and graphite reflects on their interface by electron transfer. The increase of lifetime τ_2 along with the increase of graphite volume content from 40% to 50% is due to the detachment between PTFE and graphite powder since the weakness of their interaction. Figure 4 shows the lifetime τ_3 and intensity I_3 spectra of graphite–PTFE composites.
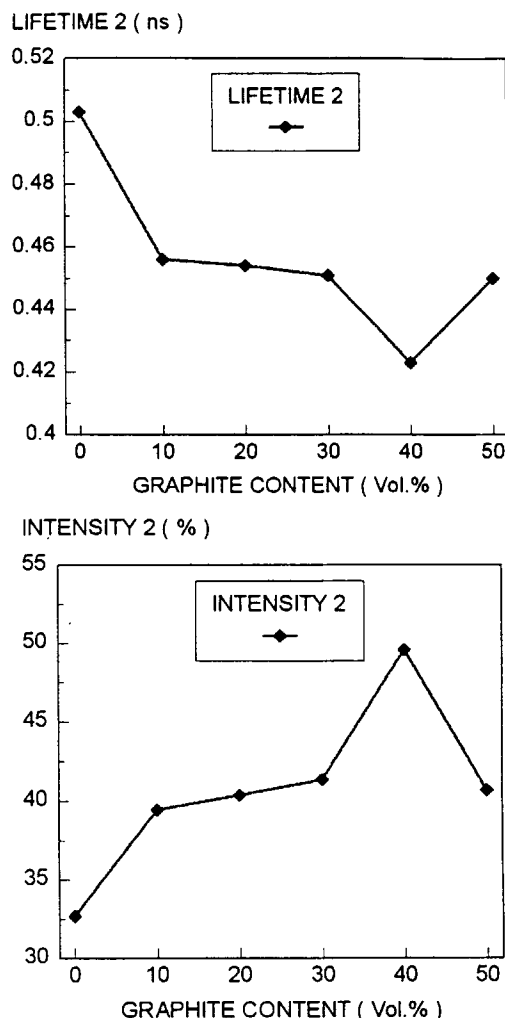
LIFETIME 2 (ns)

GRAPHITE CONTENT (Vol.%)

INTENSITY 2 (%)

GRAPHITE CONTENT (Vol.%)

Figure 3   Lifetime τ_2 and intensity I_2 spectra of graphite-PTFE composites.

According to the viewpoint of some researchers,[15] τ_3 and I_3 result from the pick-off annihilation of ortho-positronium trapped at the crystal–amorphous interface in polymers. It can be seen that the intensity I_3 linearly decreases with the increase of graphite volume content. This indicates that the free volume concentration on the interface between the crystal and amorphous regions of PTFE decreases as the graphite volume content increases, and the size of free volume which is related to lifetime τ_3 does not change obviously when the graphite volume content is less than 40%. A sudden increase of free volume size occurs at a volume content of graphite at 50%. This may be why the combinating state of the two powders has changed from PTFE-wrap-graphite to the detachment form. The decreasing concentration of free volume indicates that both the volume content of PTFE in composite is decreased and the

PTFE is oriented on the interface between PTFE and graphite powder. The orienting tendency causes the free volume size stretch.

Figure 5 shows the spectra of the longest lifetime component τ_4 and its intensity I_4. The longest lifetime τ_4 is attributed to ortho-positronium pick-off annihilation in the free volume of amorphous regions,[17] and the ortho-positronium intensity I_4 is directly proportional to the concentration of free volume. The result in Figure 5 indicates that the imperfect's size is getting bigger, while its concentration is becoming lower when the volume content of graphite increases. This phenomenon can be explained based on the preparation process of the graphite–PTFE composite. As the PTFE composites were prepared, the molding pressure resulted in a relative slippage between graphite–PTFE–graphite, and then PTFE powder extruded by graphite powder was oriented partly to some extent. Along with the increase of graphite volume content, the action of extrusion was getting bigger. In this case, the lifetime τ_4 decreased and I_4 increased, respectively.

DISCUSSION

The addition of graphite in the PTFE matrix caused many changes in the macro- and microstructure of graphite–PTFE composites. In a macroscopic sense, the state of PTFE-wrap-graphite gradually turned into the form of detachment between PTFE and graphite powder when the graphite volume content was above 40%. In this case, as a adhesive phase, PTFE was extremely affected by the filled volume content of graphite and became discontinuous. So, as tribomaterials, the maximum volume content for PTFE composites filled with graphite should be less than 40%. This rule is true for most polymer-based composites filled with inorganic powder. In a microscopic sense, for the interface between PTFE and graphite powder, the greater the content of graphite powder, the more the electronic density in interface regions increased, and the strength of the interaction between them was a function of their contacting surface area. When preparing the PTFE composites by the method of compression molding, a relative slippage between PTFE and graphite powder caused the ductile PTFE oriented along the direction of relative sliding; thus the crystallinity of PTFE increased, and the size of free volume also increased. All of these changes would influence the wear behaviors of graphite–PTFE composites. It was also found from this study on the microstructure of graphite–PTFE composites by positron annihilation
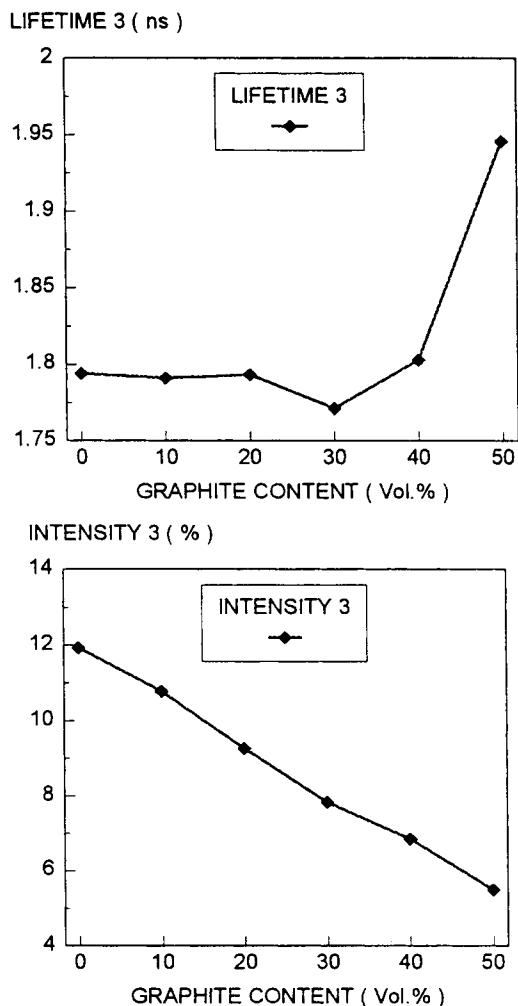
LIFETIME 3 (ns)

INTENSITY 3 (%)

Figure 4 Lifetime τ_3 and intensity I_3 spectra of graphite-PTFE composites.

that the *ortho*-positronium lifetime τ_3 spectrum fit fairly well to the curve of their wear rate. This discovery might indicate that the wear behavior of polymer composites was controlled by the interfacial properties between crystal and amorphous regions in polymer. For symmetrical polymer molecules, there exists a linear relationship between lifetime of *ortho*-positronium τ_3 and free volume size,[19] expressed as $\tau_3 = 7.80V + 1.29$, where τ_3 is expressed in nanoseconds and the cavity size V is expressed in cubic nanometers. Results indicated that the macroscopic wear behaviors of graphite-PTFE composites could be correlated to their microscopic free volume sizes in the interface between crystal and amorphous regions in PTFE. Although the wear behavior of material affected by many factors is a complex issue, it may be simplified by detecting the free volume properties.

CONCLUSIONS

The graphite-PTFE composites become porous materials when the volume content of graphite is above 40%, since the state of PTFE-wrap-graphite gradually changes into the form of detachment between PTFE and graphite powder as the volume content of graphite increases. The changes of microimperfects (expressed as free volume) of graphite-PTFE composites in size and in concentration are related to increased graphite volume content. With increasing graphite volume content, the crystallinity of PTFE shows an increasing tendency, and the electron density of PTFE in the crystal regions and in the interface between PTFE and graphite powder increases also. The wear behaviors of poly-
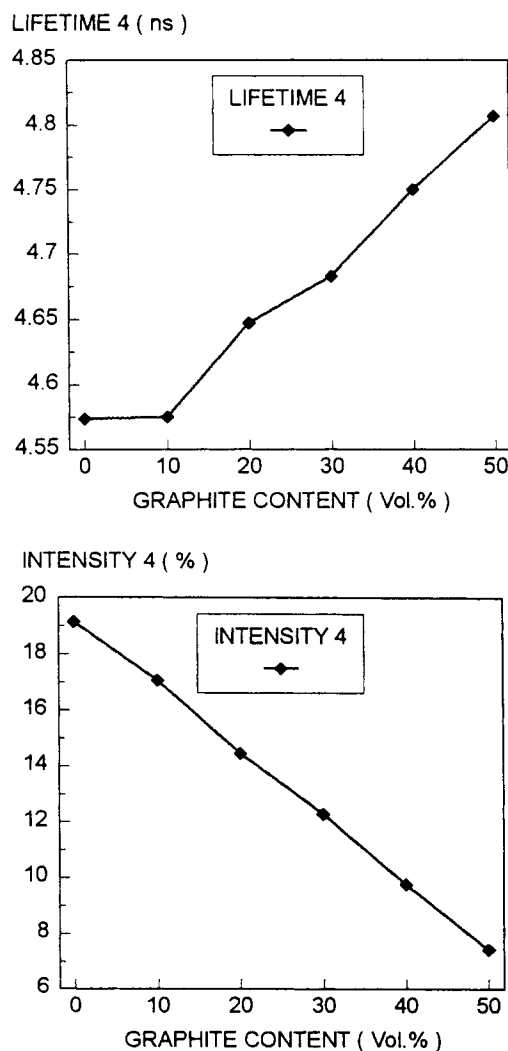
LIFETIME 4 (ns)

INTENSITY 4 (%)

Figure 5 Lifetime τ_4 and intensity I_4 spectra of graphite-PTFE composites.

mer composites are reflected from both macro- and microimperfects. For the graphite–PTFE composites, the interfacial properties between crystal and amorphous regions in PTFE are important factors for the wear behaviors of the composites. The positron annihilation lifetime is an effective means to study the correlation between the wear behaviors of polymer-based composites and their microimperfections.

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