Effect of Various Inorganic Fillers on the Friction and Wear Behaviors of Polyphenylene Sulfide

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ABSTRACT: The friction and wear behaviors of polyphenylene sulfide (PPS) filled with various particulate inorganic fillers were studied. The fillers were Ag_2S, NiS, PbSe, and PbTe in varying proportions. Friction wear tests were performed in a pin-on-disc configuration at a sliding speed of 1.0 m s^{-1} and a load of 19.6 N. The pins were made of PPS-based composites and the discs of hardened tool steel. X-ray photoelectron spectroscopy (XPS) was used to study the interface of the transfer film and its steel substrate for the possible chemical changes occurring during sliding. It was found that Ag_2S and NiS as the fillers decreased the wear rate of PPS very effectively, while PbSe and PbTe increased it dramatically. XPS analysis revealed that chemical reactions occurred during sliding between the fillers and the counterface metal iron in the cases of Ag_2S and NiS, while there was no such chemical reaction when PbSe or PbTe was used as the filler. The chemical reactions in the cases of Ag_2S and NiS contributed to enhancing the adhesion of transfer film to the counterface, and thus led to reduced wear. These observations led to the conclusion that the fillers that reduced wear had to be chemically active to the counterface metal. The Gibbs free energy criterion was suggested to test this hypothesis. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 1643–1650, 1998

Key words: polyphenylene sulfide; composite; friction and wear behaviors; XPS; criterion

INTRODUCTION

Polymers and polymer-based composites have been widely used in friction and wear applications, and many of these composites are made by adding inorganic compounds to the polymer. The inorganic compounds affect the friction and wear behaviors in peculiar ways because some compounds increased wear while others decreased it. Briscoe et al.[1] showed that the addition of CuO and Pb_3O_4 produced a marked reduction in the wear of high-density polyethylene (HDPE) and PTFE. Tanaka[2] reported that ZrO_2 and TiO_2 were

very effective in reducing the wear of PTFE. Bahadur et al.[3–7] found that wear was considerably reduced with the addition of CuO and CuS to PTFE, CuS, CuF_2, CaO, PbS, and Ag_2S to nylon 11, and CuO, CuS, and CuF_2 to polyetheretherketone (PEEK). Contrary to the above observations, it was found that wear rate increased when the fillers such as BaF_2, CaF_2, ZnF_2, SnF_2, ZnS, SnS, ZnO, and SnO were added to some polymers.[8]

Although a lot of work has been done on the effect of inorganic fillers on the friction and wear behaviors of polymer-based composites, the mechanisms for filler action have not been well understood. Evans and Lancaster[9] suggested that the wear resistance of polymers in the presence of fillers was increased because hard fillers supported the bulk of the load and modify the count-

erface. However, such an explanation was not universally valid because there was no direct relationship between the hardness of fillers and their ability to resist wear.[10] Another explanation is based on the hypothesis that fillers enhanced the adhesion of transfer film to the counterface. As in the case of PTFE composite, it was reported that some inorganic fillers reduced the wear by increasing adhesion between the transfer film and its substrate.[11] The adhesion between the transfer film and the counterface is related to mechanical and/or chemical actions. The mechanical action involves interlocking of the transfer film into the asperities of the counterface. Fillers may abrade the counterface, depending upon their hardness and shape, and thus modify the interlocking characteristics of the transfer film.[12] The chemical action hypothesis is much more involved. Sviridyonok et al.[13] indicated that for highly polar polymers, such as polyamides and poly (methyl methacrylate), the formation and the interaction of free radicals generated during the sliding process controlled the transfer wear process. Buckley et al.[14] studied unfilled and filled PTFE in sliding, and concluded that the higher temperatures and stresses in the contact region facilitated the adhesion of PTFE to the metal counterface by thermal degradation and the formation of fluoride ions. Bahadur and coworkers[15–17] reported that decomposition of the fillers occurred during sliding in the case of fillers that reduced wear, while no such decomposition was involved for the fillers that increased wear. They subsequently concluded that the effectiveness of the fillers in reducing wear depended upon their ability to decompose during sliding. The decomposed products reacted with the counterface metal and thereby enhanced the adhesion of the transfer film to the counterface. However, this supposition is disputable in consideration of the fact that some inorganic fillers with very high decomposition/melting temperatures such as CuO could not decompose even under severe friction conditions. This indicates that further work is needed with respect to these issues.

As a high-temperature thermoplastic polymer, PPS has the potential for applications in load-bearing sliding contacts, because it has excellent dimensional stability, and good mechanical and tribological properties. However, little work has been done on the effect of inorganic fillers on its friction and wear behaviors, especially on the action mechanisms of the fillers. In this article, the effect of some inorganic fillers on the friction and wear behaviors of PPS is studied with emphasis on the mechanisms that account for the different friction and wear behaviors of the composites.

EXPERIMENTAL DETAILS

Commercial PPS powders (trade name PW-28 powder), supplied by the Phillips 66 Company, were used as the matrix material for the composites, while analytically pure inorganic powders of Ag_2S, NiS, PbSe, and PbTe were used as the fillers. These compounds were selected because of the following considerations. First, a lot of copper compounds have been found to be effective in increasing the wear resistance of various polymer composites, while Ag and Ni are next to Cu in the periodic table of the elements. Second, some lead compounds have also been found to reduce the wear of polymers, while sulfur compounds affected the wear of polymers in an intricate manner. That is, some of them reduced wear while others increased it. Se and Te are in the same column of the periodic table as S and, thus, are also expected to have similar properties. In view of the above aspects, Ag_2S, NiS, PbSe, and PbTe were selected to see if the periodic table could provide some guidance in the selection of fillers for wear reduction.

The fillers were in the form of fine powder with particle sizes of about 200 μm. The fillers in varying proportions from 10 to 30 vol % were used, analogous to the work of Bahadur and Gong.[17]

Prior to compression molding, PPS powder was dried at 250°C for 8 h. The polymer and the filler were mixed mechanically and compressed in a mold to a pressure of 56 MPa. The mixture was then heated to 310°C at a rate of 5°C min^{-1}, held there for half an hour. Because the pressure was reduced because of the melting of PPS, the pressure was raised to 28 MPa again at this time. Finally, the mold was cooled to room temperature in air. The size of the molded slabs was 35 × 30 × 6 mm. Rectangular pins, 5 × 6 mm in cross-section and 25 mm long, were cut out of the molded slabs. These pins were used as the specimens for friction and wear tests. Before testing, the composite pins were abraded against a 320 grade emery paper, which was mounted on a rotating flat disc surface. This preparation ensured a good contact between the pin and the disc surface during sliding.

The tool steel (composition 0.9% C and 1.6% Mn) discs 5 mm thick and 75 mm in diameter were used as the counterface. They were oil hard-

ened and tempered to a hardness of 58 HRc. The discs were ground and later polished by abrasion against 320 grade emery paper to provide an initial surface roughness of 0.10 μm Ra. Both the pins and the discs were cleaned with soap and water, flushed with acetone, prior to the friction and wear tests.

Sliding friction and wear tests were performed in a pin-on-disc configuration at a sliding speed of 1.0 m s^{-1} and under a load 19.6 N. The composite pin was held in a specimen holder on a loading arm that had two strain gauges to record the friction force. Wear loss was measured by weighing the pin to an accuracy of 10^{-8} kg and was converted into volume loss by accounting for the density of the tested composite. The steady-state wear rates were calculated by the regression method from the slopes of the linear parts of wear loss versus sliding distance curves, and the correlation coefficients were above 0.99. The coefficient of friction was also measured at the same intervals as the wear loss. Three replicate tests were performed for each composite sample and the average values of wear loss were used in this work. The coefficients of variation among the corresponding wear and coefficients of friction values were within 15%.

XPS analysis was used to analyze the possible chemical reactions occurring at the sliding interface during sliding. This was performed in an AEI ES 200 electron spectrometer where the excitation source was Mg Kα radiation (hν = 1253.6 eV). The spectrometer was calibrated to give Cu (2p$_{3/2}$) at 932.6 eV and Au (4f$_{7/2}$) at 84.0 eV. The positions of the XPS peaks were determined with reference to the contaminated carbon peak C(1s) at 284.8 eV. The binding energies were measured to an accuracy of $\pm$0.3 eV.

RESULTS

Friction and Wear Behaviors

The friction and wear tests were performed on PPS and its composites with Ag$_2$S, NiS, PbSe, and PbTe. The results of friction and wear tests are listed in Table I. It is seen that the wear rate of unfilled PPS is much higher than that of Ag$_2$S-PPS and NiS-PPS. On the contrary, the addition of PbSe and PbTe to PPS caused a considerable increase in the wear rate of the composites. At the same time, the filler proportion exhibited great effect on the wear rate of the composites,

while had slight effect on the friction coefficient. For example, the steady-state wear rate of Ag$_2$S–PPS decreased from 0.1898 mm^3 km^{-1} to 0.0452 mm^3 km^{-1} (a reduction in wear rate by a factor of 2.1 and 8, respectively, compared with unfilled PPS) when Ag$_2$S proportion in the composite increased from 10 to 30 vol %. This indicates that Ag$_2$S as a filler was beneficial in modifying the wear behaviors of PPS.

Similar results were obtained with NiS as the filler, with the only difference that the reduction in wear rate was smaller (0.182 mm^3 km^{-1} to 0.072 mm^3 km^{-1}, a decrease by a factor of 2.2 and 5.5, respectively, compared with unfilled PPS) when NiS proportion changed from 10 to 30 vol %.

Contrary to the above, PbSe and PbTe increased the wear rates of PPS considerably. With 30 vol % PbSe, the steady-state wear rate of PPS increased by a factor of 8 and with 30 vol % PbTe by a factor of 19. Meanwhile, the wear rates increased with increasing filler proportions with respect to PbSe–PPS and PbTe–PPS. This shows that PbSe and PbTe were not suitable to be used as fillers for PPS.

On the other hand, irrespective of the Ag$_2$S proportion in PPS, the coefficient of friction started with a low value but increased continuously during the transient state and finally reached a higher steady-state value. The variation of the coefficient of friction with filler content for PPS–PbSe and PPS–PbTe composites was similar to that of NiS composites. However, the effect of filler addition to PPS on the friction coefficient was not so obvious as in the case of wear rate. This indicates that wear and the coefficient of friction do not necessarily change simultaneously with the use of fillers.

XPS Analysis of Transfer Films

The transfer films of four composites, PPS filled with 30 vol % Ag$_2$S, NiS, PbSe, and PbTe, were analyzed by XPS. The maximum filler proportion of 30 vol % was used because of the maximum likelihood for the detection of chemical action, if any. All the samples used in XPS analysis were from the steady wear state corresponding to 20 km sliding distance. To detect the possible chemical changes close to the interface between the transfer film and its steel substrate, the top layer of the transfer film was gently removed with a razor blade. The species were identified with reference of the data in XPS handbook,[18] with the exception that the data related to PPS and Ag$_2$S

Table I The Friction and Wear Properties of PPS and Its Composites

PPS and Its Composites	Filler Content (wt %)	Friction Coefficient	Steady-State Wear Rate (mm³ km⁻¹)	Factor of Decrease
Unfilled PPS	0	0.37–0.43	0.3969	—
PPS–Ag$_2$S	10	0.38–0.45	0.1898	2.1
	20	0.39–0.47	0.0735	5.4
	30	0.39–0.48	0.0452	8.8
PPS–NiS	10	0.38–0.46	0.1824	2.2
	20	0.41–0.49	0.0923	4.3
	30	0.41–0.50	0.0720	5.5
PPS–PbSe	10	0.36–0.44	1.7861	−4.5
	20	0.38–0.45	2.3020	−5.8
	30	0.39–0.47	3.1752	−8
PPS–PbTe	10	0.37–0.44	4.4850	−11.3
	20	0.38–0.46	5.5566	−14
	30	0.39–0.49	7.5411	−19

were based on our own XPS analysis results, because these data are not available in the handbook. The XPS analytical results for the species in PPS and Ag$_2$S are shown in Table II. The binding energies of these species have been used to identify the corresponding species of the filled composites.

The species of the transfer film of PPS filled with 30 vol % Ag$_2$S are summarized in Table III. It was deduced that some chemical reactions occurred during sliding of Ag$_2$S–PPS pin against tool steel disc. These include the reactions of the counterface metal Fe with the filler Ag$_2$S and with the oxygen in air. Fe$_2$O$_3$ is the product of oxidation reaction of the counterface Fe with atmospheric O$_2$, and FeS and FeSO$_4$ are the products of reaction among the counterface Fe, filler Ag$_2$S, and O$_2$ in atmospheric air. The latter would produce elemental Ag. Because of the closeness of binding energies in the Ag (3d) spectrum, it is difficult to tell elemental Ag from the Ag in Ag$_2$S. However,

elemental Ag was most likely present as a result of the chemical reaction between Ag$_2$S and Fe. This is rational because the reactions between the inorganic sulfide compounds and Fe in earlier studies of the transfer films have identified the presence of elemental metals in the sulfide compound (see refs. 4–6).

The XPS species of the transfer film of PPS filled with 30 vol % NiS are shown in Table IV. The results here are similar to those obtained in the case of PPS filled with Ag$_2$S: pure Ni, the product of chemical reaction between the filler NiS and the counterface Fe, and the oxidation reaction between the counterface Fe and the O$_2$ in air giving Fe$_2$O$_3$.

The XPS species of the transfer film of PPS filled with 30 vol % PbSe are given in Table V. The thing in common with the above XPS results is the oxidation reaction between the counterface Fe and the O$_2$ in air since Fe$_2$O$_3$ was detected. However, unlike the case of Ag$_2$S or NiS, no compound such as FeSe$_2$ [binding energy: 54.9 eV for Se (3d) in FeSe$_2$], or pure element such as Pb [binding energy: 136.6 eV for Pb (4f) in elemental Pb], produced from chemical reaction between the filler and the counterface metal was detected. This reduces the likelihood of chemical reaction between the filler PbSe and the counterface Fe during sliding.

The XPS results for PPS filled with 30 vol % PbTe were similar to those of the PPS filled with 30 vol % PbSe, as shown in Table VI. No product of chemical reaction between the filler and the

Table II Identified Species in the XPS Spectra of PPS and Ag$_3$S Filler

	Binding Energies of Peaks (eV)		
Species	C (1s)	S (2p)	Ag (3d)
Contaminated C	284.8		
C in PPS	284.8		
S in PPS		163.7	
Ag$_2$S		161.1	368.1

Table III   Identified Species in the XPS Spectra of the Transfer Film of PPS + 30 vol % Ag$_2$S

Species	Binding Energies of Peaks (eV)				
	C (1s)	O (1s)	S (2p)	Fe (2p)	Ag (3d)
Contaminated C	284.8				
C in PPS	284.8				
S in PPS			163.7		
Fe$_2$O$_3$		530.2		710.9	
FeSO$_4$		532.4	168.8	712.1	
FeS			161.6	712.2	
Fe				707.0	
Ag$_2$S			161.1		368.1
Ag					368.3

counterface metal was detected either. There was still Fe$_2$O$_3$ from the chemical reaction between the counterface Fe and the O$_2$ in air. This indicates that no chemical reaction occurred between the filler and the counterface metal during sliding.

It should be pointed out that no chemical reaction between the S in PPS and the counterface Fe was detected in the cases of PPS filled with PbSe or PbTe. The decomposition of the fillers during compression molding is not expected because the fillers had melting temperatures much higher than the molding temperature. This conclusion is consistent with the earlier observations made on other polymer-filler systems (see refs. 4 and 8). Therefore, FeS and FeSO$_4$ detected in the transfer films of the composites with Ag$_2$S and NiS fillers are essentially the products of chemical reaction between the fillers and the counterface metal.

DISCUSSION

Tribochemical Actions of Fillers

The tribochemical actions of the fillers are important for adhesion between the transfer film and the counterface. As described above, the fillers Ag$_2$S and NiS reacted chemically with the counterface Fe and generated FeS and FeSO$_4$, accompanied by the formation of elemental Ag and Ni also. This reaction provided chemical bonding at discrete spots between the transfer film and its substrate in addition to mechanical bonding. The nascent metal, Ag or Ni, produced by such chemical reaction on the exposed tips of the filler is reactive and is thus likely to provide additional bonding with the counterface. Because of these enhanced bonding mechanisms, the transfer film

Table IV   Identified Species in the XPS Spectra of the Transfer Film of PPS + 30 vol % NiS

Species	Binding Energies of Peaks (eV)				
	C (1s)	O (1s)	S (2p)	Fe (2p)	Ni (2p)
Contaminated C	284.8				
C in PPS	284.8				
S in PPS			163.7		
Fe$_2$O$_3$		530.2		710.9	
FeSO$_4$		532.4	168.8	712.1	
FeS			161.6	712.2	
Fe				707.0	
NiS			161.1		855.1
Ni					852.7

Table V Identified Species in the XPS Spectra of the Transfer Film of PPS + 30 vol % PbSe

Species	Binding Energies of Peaks (eV)					
	C (1s)	O (1s)	S (2p)	Fe (2p)	Pb (4f)	Se (3d)
Contaminated C	284.8					
C in PPS	284.8					
S in PPS			163.7			
Fe_2O_3		530.2		710.9		
Fe				707.0		
PbSe					137.4	53.4

adheres strongly to the counterface. It is, thus, not easily peeled off during the repetitive sliding motion so that the contribution to wear from this source is reduced. In addition to this, the continued presence of transfer film provides better protection to the polymer pin against the abrasive effect of the counterface so that the abrasive wear is virtually eliminated.

Unlike the above cases, when PbSe and PbTe was used as the fillers, no chemical reaction between the filler and the counterface was detected. No such chemical reaction was plausible, as has been justified in the next section using the concept of Gibbs free energy. Thus, in this case the mechanisms for chemical bonding, as discussed above for the Ag_2S and NiS fillers, were not available.

Gibbs Free Energy Criterion for Filler Selection

From earlier studies of Bahadur et al. (see refs. 4–8, 15, and 16) as well as the results presented in this article, it was concluded that chemical reactions between the fillers and the counterface Fe are the key in terms of the effectiveness of fillers in reducing the wear of polymers. it was also hypothesized that the compound and the elemental metal generated from chemical reaction between the filler and the counterface metal promoted the bonding between the transfer film and the counterface. Therefore, it can be deduced that the chemical activity between the filler and the counterface metal should be an important criterion in selecting the filler for wear reduction. Subsequently, it is proposed that the Gibbs free energy change criterion could be applied for the selection of filler for wear reduction. The Gibbs free energy change[19] provides a thermodynamic basis to determine whether or not a chemical reaction is possible. If the Gibbs free energy change for possible chemical reaction between the filler and the counterface metal is negative, a reaction is feasible. On the other hand, if the Gibbs free energy change is positive for the contemplated chemical reaction, then this chemical reaction is not feasible.

The above hypothesis was tested on the fillers for which XPS analysis results were available in the literature. This has been presented in Table

Table VI Identified Species in the XPS Spectra of the Transfer Film of PPS + 30 vol % PbTe

Species	Binding Energies of Peaks (eV)					
	C (1s)	O (1s)	S (2p)	Fe (2p)	Pb (4f)	Te (3d)
Contaminated C	284.8					
C in PPS	284.8					
S in PPS			163.7			
Fe_2O_2		530.2		710.9		
Fe				707.0		
PbTe					137.4	572.0

Table VII   Gibbs Free Energy Changes (ΔG) in Chemical Reactions between the Fillers and the Counterface Metal Fe

Polymer	Filler	Wear	ΔG (kJ/mol)	Chemical Reaction Equation	XPS Results	Reference
PPS	Ag_2S	Down	−59.7	$Ag_2S + Fe = FeS + 2Ag$	Ag, FeS, Fe_2O_3,	This article
			−780.1	$Ag_2S + Fe + 2O_2 = FeSO_4 + 2Ag$	$FeSO_4$	
PPS	NiS	Down	−20.9	$NiS + Fe = FeS + Ni$	Ni, FeS, Fe_2O_3,	This article
			−741.3	$NiS + Fe + 2O_2 = FeSO_4 + Ni$	$FeSO_4$	
PPS	PbSe	Up	+26.4	$PbSe + Fe = FeS + Pb$	Fe_2O_3	This article
PPS	PbTe	Up	+6.7	$PbTe + F = FeTe + Pb$	Fe_2O_3	This article
PEEK	CuO	Down	−353.1	$CuO + 2Fe = Fe_2O_3 + 3Cu$	Cu, Fe_2O_3, $Cu(HO)_2$	4,6
			−212.73	$Cu + H_2O = Cu(OH)_2$		
Nylon 11	CuO	Down	−402.0	$6CuO + 2Fe = 3Cu_2O + Fe_2O_3$	Cu, Cu_2O, $Cu(OH)_2$,	5,15,16
			−212.7	$CuO + H_2O = Cu(HO)_2$	Fe_2O_3	
Nylon 11	CuS	Down	−767.2	$CuS + Fe + 2O_2 = FeSO_4 + Cu$	Cu, Fe_2O_3, $FeSO_4$	15
PEEK	CuS	Down	−46.8	$CuS + Fe = FeS + Cu$		
			−1141.6	$2FeS + 5O_2 = 2SO_2 + Fe_2O_3$		
Nylon 11	CuF_2	Down	−168.6	$CuF_2 + Fe = FeF_2 + Cu$	Cu, FeF_2, Fe_2O_3	7
Nylon 11	ZnS	Up	+100.9	$ZnS + Fe = FeF_2 + Zn$	FeO, Fe_2O_3	8
			−272.0	$Fe + 0.5O_2 = FeO$		
PES	ZnO	Up	+219.3	$3ZnO + Fe = 2Fe_2O_3 + 3Zn$	Fe_2O_3	8
PES	CaF_2	Up	+507.0	$CaF_2 + Fe = FeF_2 + Ca$	Fe_2O_3	8

Gibbs free energy data are from ref. 19 at standard conditions (298.15 K, 0.1 MPa).

VII. Equations representing the possible chemical reactions between the filler and Fe (in the counterface) were written to provide the reaction product detected in XPS studies. For example, for the Ag_2S filler, the Gibbs free energy change (ΔG) was calculated by substituting the values of the free energy on both sides of the equation and subtracting the summation of the values on the left side of the equation from the summation of the values on the right side. Table VII shows that in all the cases where fillers reduced wear, ΔG is negative, while in cases where wear increased, ΔG is positive. For the four fillers used in this article, ΔG values are negative for the Ag_2S and NiS fillers and are positive for the PbSe and PbTe fillers.

It should be stated that the negative ΔG does not guarantee that the postulated chemical reaction will definitely occur, but simply indicates that such a reaction is feasible because the kinetics of reaction is also important. If the reaction is too slow, it does not practically occur. It is also conceivable that some fillers that do not chemically react with the counterface could still reduce wear because the conditions could be favorable to produce wear debris that would promote the development of transfer film by its entrapment in the crevices of the asperities.

CONCLUSIONS

1. The wear rate of PPS decreased in cases of the Ag_2S and NiS fillers and increased when the fillers PbSe and PbTe were used.
2. The optimal filler proportion for maximum reduction in wear was 20−30 vol % in cases of both Ag_2S and NiS fillers.
3. When Ag_2S and NiS were used as the fillers, XPS analysis revealed a chemical reaction between the filler and the counterface Fe. No such chemical action was detected in cases of PbSe and PbTe fillers.
4. The Gibbs free energy change criterion for the selection of fillers for wear reduction was proposed. If the change is negative for a contemplated chemical reaction between the filler and the counterface metal, the chemical reaction is possible, and vice versa.

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