

Tribology of self-lubricating high performance ATSP, PI, and PEEK-based polymer composites up to 300 °C

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Abstract: High-performance polymers (HPPs) are increasingly used in different industrial machinery components, particularly for rubbing parts that demand reliable and durable operation at extreme sliding conditions such as elevated temperature environments, where the use of conventional lubricants is not feasible. The current study investigates the role of environmental temperature on the tribological properties of three advanced HPPs, namely aromatic thermosetting copolyester (ATSP), polyimide (PI), and polyether ether ketone (PEEK) based polymer composites. Tribological experiments were carried out at different environmental temperatures from room temperature up to 300 °C, and under dry sliding conditions. Specific attention was given to the role of temperature on the development of transfer films and its subsequent effect on the tribological performance. The ATSP composite was recommended as the best performing material, based on the overall tribological performance at all examined operating temperatures.

Keywords: aromatic thermosetting copolyester (ATSP); polyimide (PI); polyether ether ketone (PEEK); high temperature tribology; transfer film

1 Introduction

High-performance polymers (HPPs) have been used as promising candidate materials for bearing and tribological components that demand operation with low friction and wear under extreme conditions such as cryogenic and elevated temperature environment, where the use of external lubrication is not feasible. The broad use of HPPs stems from their satisfactory properties such as high load bearing capacity, lightweight, low cost, self-lubricity, and good friction and wear properties [1–3]. Since unfilled polymers suffer from poor tribological performance (high friction and/or wear), they are typically blended with solid lubricants such as polytetrafluoroethylene (PTFE) and graphite flakes, and reinforcements such as carbon/glass fibers to improve their tribological and mechanical performance, respectively [4].

HPPs based on polyether ether ketone (PEEK), polyimide (PI), and aromatic thermosetting copolyester (ATSP) have been shown to provide self-lubrication and enhanced tribological performance by blending them with solid lubricants [5]. As solid lubricant, PTFE and graphite are shown to enhance the self-lubricity due to their capability to form transfer film on the surface of harder metallic counterpart [6]. The development of transfer film is shown to play an important role in the reduction of friction and wear at the sliding interface, which makes polymers an attractive selection for dry sliding components [5]. The transfer film formation depends on parameters such as sliding speed, normal load, temperature, surface roughness, polymer structure, and the type of filler in the polymer matrix [7, 8].

PEEK is a thermoplastic polymer with measured glass transition temperature (T_g) of 143 °C whose

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composites are widely used in many tribological applications [5]. For elevated service temperatures, a maximum operating temperature of 250 °C was reported [9]. PI-based composites are categorized among high operating temperature polymers with excellent friction and wear resistance under unlubricated conditions, particularly at elevated temperatures [10, 11]. ATSP is part of a newer family of HPPs (called Vitrimers; which is a thermoset that processes like a thermoplastic) that was invented in the mid-1990s [12]. Our studies demonstrated the superior tribological performance of ATSP, compared to PTFE and PEEK polymer coatings for a wide range of temperatures from −196 to 300 °C [13–18]. However, tribological studies in bulk form are scarce, and some studies investigated the performance of ATSP/PTFE composites under R-134A refrigerant environment and temperature of 60 °C for air-conditioning compressor applications [8, 19, 20].

The focus of the present study is to investigate the role of environmental temperature (room temperature (RT) up to 300 °C) on the tribological performance of commercially available high-performance polymer-based composites, namely PEEK bearing grade (HPV), a PI-based composite known as Vespel SP-211, and an ATSP-based polymer composite, which are shown to stand in the top of the polymer pyramid among the HPPs [1, 5]. The effect of temperature on the development of transfer film from polymer to steel counterpart was studied to examine its correlation with tribological performance.

2 Experimental

2.1 Materials and sample preparation

Three different polymer composite pins, namely ATSP-based, PI-based (Vespel SP-211), and PEEK bearing grade were used for tribological testing. ATSP resins were synthesized using crosslinkable aromatic copolyester oligomeric systems, namely CB and AB (forming CBAB oligomer system) with carboxylic acid and acetoxy functional end group, respectively. The oligomer synthesis was performed in a 2 L reactor through batch melt polymerization at temperature of 270 °C and under Argon gas atmosphere. Thereafter,

the oligomers were ground and sieved using a 90 μm sieve size. Detailed description of synthesis procedure can be found in Ref. [21]. To produce the ATSP-based bulk composites, the oligomers (CB and AB) were mixed with the desired graphite (Microfyne, Asbury Graphite Mills, Inc.) and PTFE (7A X, The Chemours Company FC, LLC) additives, with the weight ratios listed in Table 1. The mixture was then cured at 360 °C for 2 h and ground into smaller size particles that pass through 125 μm sieve. The ground compound was then compressed in compression molding at a temperature of 360 °C under 5,000 psi pressure for 2 h, and then naturally cooled down to RT to obtain the final condensed ATSP bulk composite plate.

Thereafter, the sample was machined into cylindrical pins with a diameter of 6.35 mm for tribological testing. The Vespel and PEEK polymer composites were commercially available and were purchased from the vendors in stock shapes and machined into 6.35 mm diameter pins. Vespel SP-211 is a PI-based polymer that is blended with graphite and PTFE to improve its friction and wear properties. PEEK bearing grade is blended with graphite and PTFE to improve the tribological properties, and carbon fiber to enhance the dimensional stability [22]. Note that the exact weight percentage of the PEEK and PI additives were not provided by the vendor. 416 stainless steel (416SS) disks were machined with dimension of 50.8 mm in diameter and 6.35 mm in thickness to use as the counterpart. The root-mean square surface roughness (R_q) of 0.215 μm was obtained through surface grinding.

2.2 Experimental procedure

The tribological experiments were performed under dry sliding conditions and using a flat-pin-on-disk configuration. The experiments were conducted at

Table 1 Description of blended polymer materials.

Materials	Composition	Vendor
ATSP	CBAB + 30% graphite + 10% PTFE	ATSP Innovations
Vespel SP-211 (PI)	Vespel [®] (polyimide) + 25% PTFE/graphite	DuPont
PEEK bearing grade (HPV)	PEEK + 30% carbon fiber/graphite/PTFE	Boedeker plastics

environmental temperatures ranging from RT to 300 °C, as shown in Table 2. The PEEK composite was tested only at 25 and 150 °C as the maximum operating temperature is below 300 °C. For each test, a constant normal load of 130 N equivalent to a nominal contact pressure of 4 MPa was applied from the pin side. The disk was unidirectionally rotating against the pin at 1 m/s (530 rpm) sliding speed for 1 h duration equivalent to sliding distance of 3,600 m. The *in-situ* friction and normal forces were recorded by a two-axis transducer to calculate the *in-situ* coefficient of friction (COF) during the experiment. The experiments with each material were repeated at least three times to assess the reproducibility. The samples were ultrasonically cleaned by immersing them in isopropyl alcohol for 10 min before the experiments. Thereafter, the samples were rinsed with isopropyl alcohol and dried by blowing warm air. The same procedure was followed after each test and the tested coupons were used for characterization.

The mass of each polymer pin was measured before and after each experiment using a scale with a precision of 0.01 mg to calculate the wear rate according to Eq. (1):

$$k = \frac{\Delta m}{F_N d} \quad (1)$$

where k is the wear rate (mg/(N·m)), Δm is the polymer mass loss (mg), F_N is the applied normal load (N), and d is the total sliding distance (m). The worn and unworn surfaces of the polymers were examined using scanning electron microscopy (SEM) to depict the surface changes and associated wear mechanisms by the tribological testing. Energy-dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), optical microscopy, and profilometric scans

Table 2 Details of blended polymers and experimental conditions.

Polymer composites	Temperature (°C)	Contact pressure (MPa (load, N))	Speed* (m/s (rpm))
ATSP	25, 150, 300	4 (130)	1 (530)
PI			
PEEK	25, 150		

*The linear speed was calculated considering the average wear tracks diameter as 18 mm.

were performed on the tested surfaces of the steel disks to evaluate formation and variation of polymer transfer films with temperature. Differential scanning calorimetry (DSC) measurements were performed to determine the T_g of each polymer using a TA Instrument 2910 MDSC V4.4 E.

3 Results and discussion

3.1 DSC analysis

To measure the T_g of each polymer, the prepared specimens were heated at a heating rate of 10 °C/min under nitrogen gas flow from 25 to 400 °C. Figure 1 shows the DSC heating curves of each polymer composite. The DSC curve of PI shows no T_g or melting temperature (T_m) due to the thermosetting nature of the polymer. For ATSP polymer composite, there exists an endothermic peak at 332 °C corresponding to T_m , and a shoulder at 307 °C corresponding to the T_g . The PEEK DSC curve shows a double melting behavior with lower endothermic peak at 212 °C and a higher endothermic peak at 341 °C. Such behavior could be ascribed to annealing effect and partial recrystallization and melting at heating between T_g and T_m [23]. For PEEK, the T_g was measured as 155 °C.

3.2 Friction and wear

Figure 2(a) shows the evolution of unfiltered *in-situ* COF as a function of sliding distance for the pin-on-disk experiments of blended HPPs at temperatures of 25, 150, and 300 °C. For all polymers, the *in-situ* COF started with an initial running-in behavior and eventually reached a steady-state period. For RT

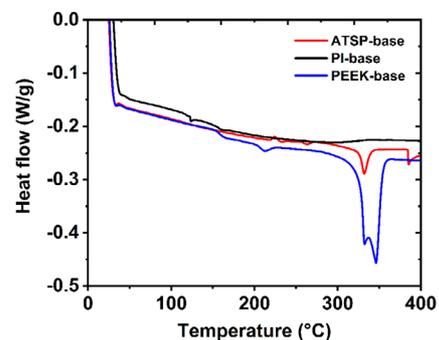


Fig. 1 DSC scans of ATSP-, PI-, and PEEK-based polymer composites.

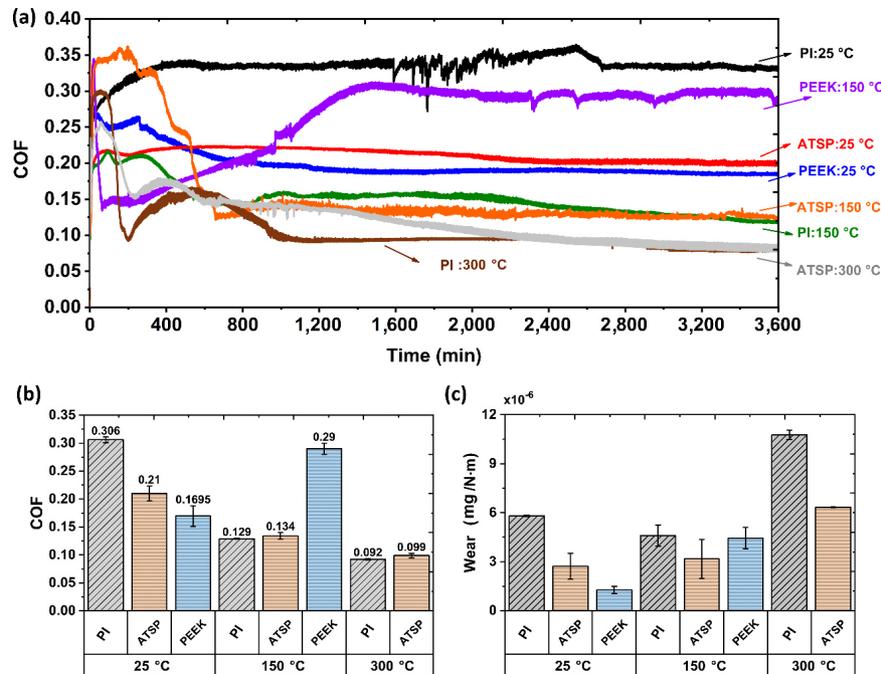


Fig. 2 (a) *In-situ* COF vs. time for all polymer composites; (b) variation of average COF at steady-state; and (c) average calculated wear. Error bars designate ± 1 standard deviation.

experiments, both PEEK and ATSP composites showed the most stable friction after the running-in period. Unlike PEEK and ATSP, PI showed a transient period between two steady-state stages where instabilities in the COF occurred. These instabilities and variations in the COF caused the squeaking noise at the interface, which is undesirable in industrial applications. This behavior could be attributed to the inability of the material to form a transfer film on the counterpart, and therefore the pin continued to wear off due to the plowing of the asperities from the steel disk surface. When the temperature increased to 150 °C, ATSP and PI showed the most stable friction with a decreasing trend, while the COF of PEEK composite followed an increasing trend and needed the longest time to reach steady-state behavior.

Figure 2(b) summarizes the variation of the average COF with temperature. The COF is calculated for the steady-state period, and the error bars in the figure designate the \pm one standard deviation. When the temperature increased from RT to 150 °C, the COF of ATSP- and PI-based composites reduced by 36% and 58%, respectively, while it had an adverse effect on the COF of PEEK-based composite by increasing it by 71%. For ATSP and PI, the COF followed a decreasing

trend with temperature and compared with RT, the COF reduced by 53% and 70% at 300 °C, respectively. Among all tested samples, the highest COF was obtained for PI (0.31) for experiments at RT followed by PEEK (0.29) at 150 °C, and the lowest COF occurred at 300 °C for both ATSP (0.099) and PI (0.092) polymer composites. The high friction of PI at RT could be attributed to its inability to form a uniform transfer film on the counterpart, as it will be discussed later.

The variations in COF with temperature could be attributed to several different reasons, such as the changes in real contact area due to changes in polymer elastic modulus, the changes in the interfacial shear strength, and the extent and uniformity of transferred polymer to the counterpart. Although the increase of temperature facilitates easier sliding at the interface due to lower shear strength of the softened polymer and reduces friction, lower elastic modulus on the other hand could increase the real contact area and therefore increases the COF. Thus, different trends for friction could be obtained depending on which factor is more dominant. For example, as shown in Fig. 2(b), it can be postulated that the decrease of interfacial shear strength was the dominant factor for PI and ATSP base composites, while the increase

in real contact area could be the dominant factor for PEEK-based composite. This can be explained by the difference in T_g of the polymers. According to Fig. 1, PEEK T_g was measured as 155 °C, similar to that in Ref. [24], while the T_g for the ATSP with oligomers CBAB was 307 °C, and the SP grades of Vespel had no T_g . Therefore, for the experiments at 150 °C, PEEK was exposed to temperatures in the vicinity of its T_g and softened more than the other two polymer composites. Similar behavior was observed in Ref. [25] where during temperature ramping from RT to 240 °C, a significant increase in COF was observed due to reduction in storage modulus at temperatures above T_g up to 180 °C.

Figure 2(c) summarizes the variation of average wear rate of the tested polymers at different temperatures. The wear rates were calculated from the mass loss measurements shown in Table 3 and using Eq. (1). A similar trend for all tested polymers is the increase of wear from room to elevated temperatures. However, the rate of increase in wear is lower for ATSP composite, compared with PEEK and PI composites. Compared with RT, the wear of ATSP and PI at 300 °C increased by 57% and 85%, respectively, and for PEEK the wear increased by 71% at 150 °C. In general, PEEK showed the lowest wear for RT experiments, while ATSP showed minimal wear at elevated temperatures. Note that although the wear rate of PEEK and PI composites are relatively the same at 150 °C, the increased rate of wear, compared to RT is significantly higher for PEEK compared with PI. The increase of PEEK wear at elevated temperature could be attributed to the softening of the polymer and the corresponding reduction in storage modulus at 150 °C (near T_g), which enabled the removal of PEEK material by the hard asperities of the steel counterpart. Overall, ATSP composite could be considered as the best performing polymer considering

Table 3 Average mass loss measurement for each polymer composite pin at different temperatures.

Materials (pin)	Temperature (°C)		
	25	150	300
	Mass loss (mg)		
ATSP	1.20	1.45	2.88
Vespel SP-211 (PI)	2.82	2.24	5.23
PEEK bearing grade (HPV)	0.60	1.88	—

the tribological performance (friction and wear) for this wide range of operating temperatures from 25 to 300 °C, making it an attractive solution for oil-less engineering applications.

3.3 Transfer film analysis

Introducing solid lubricants such as PTFE and graphite into polymer matrices is an effective way for friction and wear reduction through the formation of transfer films on the counterface [5, 26, 27]. During sliding, when the interfacial adhesion between the asperities of the tribo-pairs exceeds the cohesive strength of the softer material (typically polymers), the material will begin to transfer to the counterpart in the form of a thin transfer film [28]. The formation of such transfer film is also observed in this study and is visually depicted in Figs. 3(a)–3(c) using optical microscopy images of the wear tracks on the steel disks.

The optical images of the RT experiments indicate the formation of a uniform and continuous transfer film on the disk surface after testing of ATSP and PEEK composite pins, which enabled the protection of the softer polymer against harder asperities of the steel disk. However, the transfer polymer from PI composite pin showed a patchy and non-continuous

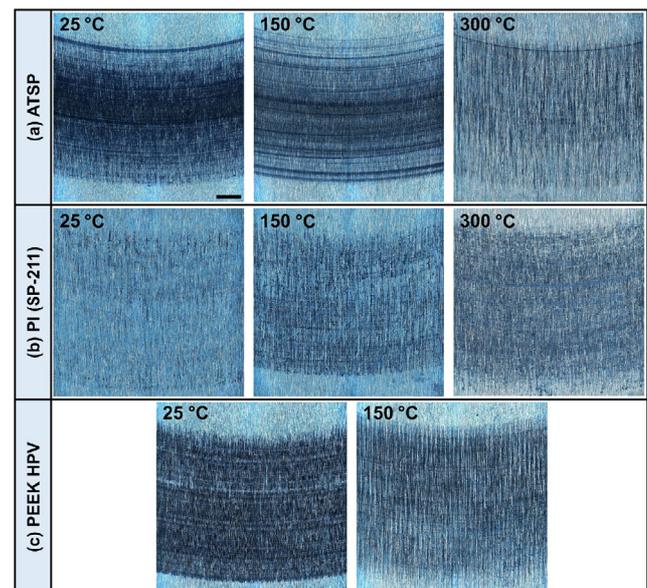


Fig. 3 Optical microscopy images of the steel disks after experiments at different temperatures with (a) ATSP-based; (b) PI-based; and (c) PEEK-based polymer composites (scale bar is 1 mm for all images).

characteristic (i.e., transfer layer) and did not properly adhere to the counterface, which caused higher wear of PI compared to other polymer composites, as shown in Fig. 2(c). This behavior could be attributed to lower concentration of PTFE in the composition of PI, as will be shown in the EDS analysis of the pins' surfaces. The effectiveness of graphite in formation of transfer film is shown to be for temperatures greater than 100 °C, and its wear rate is shown to increase with temperature [29], and thus, it formed a non-uniform layer at RT. Increasing the temperature helped to develop a uniform and continuous transfer film after testing with ATSP and PI, which helped to reduce the friction. As shown in Fig. 2(a), the experiments at elevated temperatures took longer time to reach steady-state condition, compared with RT experiments, indicating a longer time to form the uniform transfer film on the counterface. Therefore, the increased wear rate at elevated temperatures could be attributed to continuous high material wear by the harder metallic counterpart asperities until a stable and uniform film was formed.

Figures 4(a)–4(c) show the SEM images and corresponding EDS mapping of the steel disk surfaces

after testing with ATSP, PI, and PEEK composites at RT. The formation of transfer film from the polymer pins to the disk is clearly discernible from the SEM images, revealed by darker areas on the surface. However, the extent and uniformity of the transferred films are not the same among the polymers. Figure 4(a) shows the transfer material from ATSP pin to the steel surface showing a continuous and uniform transfer film. PI on the other hand formed irregular transfer layer, and only small patches were developed on the asperity crevices at RT, as shown in Fig. 4(b). The obtained SEM image of the steel surface after testing with PEEK (shown in Fig. 4(d)) indicates the evidence of continuous transfer film, but with lower area coverage compared with ATSP. The EDS analysis of the developed film on the steel surface shows that the dark areas on the wear track of the SEM images correspond to carbon elements, which are the dominant element in the structure of the polymer.

To find the composition of the transferred films on the disks, XPS was utilized, and the results are shown in Fig. 5. The high-resolution C 1s spectra of the transferred films from PEEK-based, PI-based, and ATSP-based polymer composites after experiments at

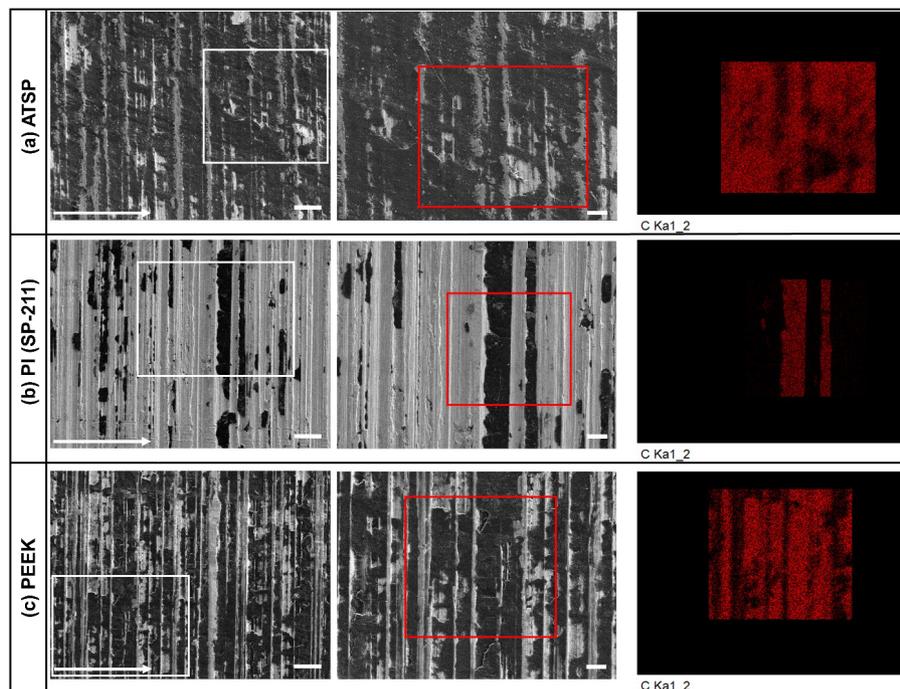


Fig. 4 SEM images and corresponding EDS analysis of the steel surface showing the formation of transfer film by sliding of (a) ATSP; (b) PI; and (c) PEEK at RT (scale bar is 25 μm for low magnification (left) and 10 μm for high magnification (middle and right) images. The arrows show the sliding direction.

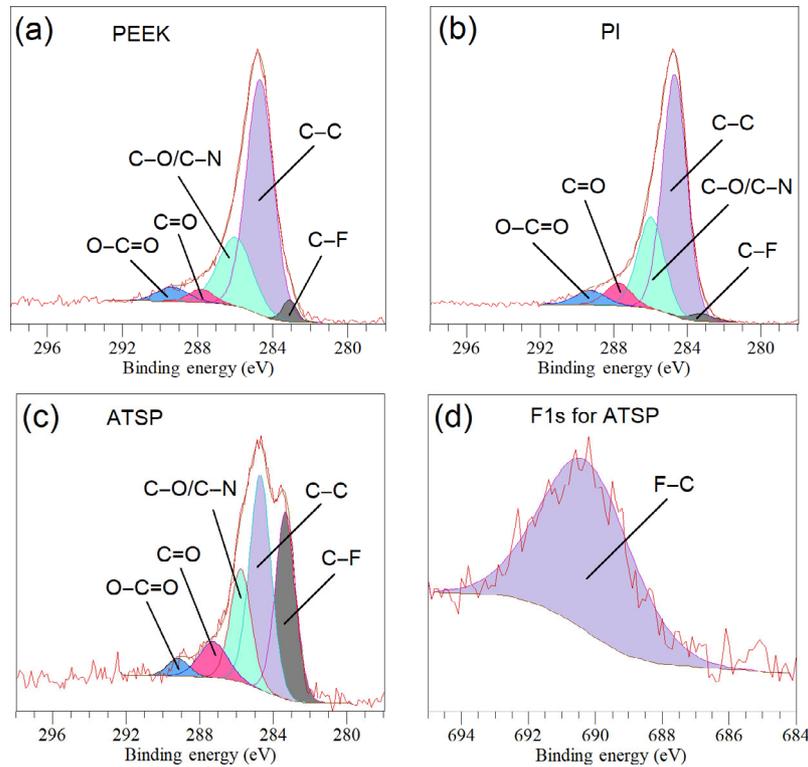


Fig. 5 High-resolution C 1s peak of transferred film on the steel disks from (a) PEEK-based; (b) PI-based; and (c) ATSP-based polymer composites after RT experiments. (d) High-resolution F 1s peak for ATSP-based polymer.

RT were investigated with an Omicron XPS system equipped with the Argus detector at X-ray voltage of 15,000 and X-ray power of 225 W. We used the CN10 charge neutralizer to avoid charging the samples and increase the resolution. Aperture 3 with a rectangular analysis area was selected to maximize the accuracy of the elemental analyses.

As shown in Fig. 5, the high-resolution C 1s spectra of all the transferred films presented five common peaks at ~283.3, 284.8, 286, 587.7, and 289.3 eV, representing the C–F, C–C/C=C, C–O/C–N, C=O, and O–C=O groups, respectively. Compared to the transferred films from PEEK-based and PI-based pins, the C 1s spectrum of the film generated by the ATSP-based pin showed an intense shoulder peak at 289.3 eV, which originated by carbon atoms bonded to fluorine atoms by single bonds. This is while the same peaks formed by the PEEK-based and PI-based films that were fairly weak. This is why only the F 1s spectrum of the ATSP-based film was deconvoluted, which was comprised of only C–F component. Therefore, it can be concluded that (i) the concentration of PTFE was higher in the transferred

film from ATSP-based polymer pin; and (ii) fluorine only covalently bonded with carbon through a single bond, representing no bond formation between PTFE and ATSP during curing process and/or side reaction at the interface during sliding. Thus, the XPS spectra show the presence of higher percentage of PTFE in the case of the ATSP-based film at the sliding regions that helped to reduce friction and wear, compared to PI-based pin.

The elemental compositions for the samples are also provided in Table 4. In agreement with the results of the depicted spectra, the transferred film from ATSP-based pin possessed higher F content, compared to the other polymers. Expectedly, the film from PEEK contained higher oxygen content (~20.7%).

Table 4 Elemental analysis obtained from high-resolution spectra in XPS for the transferred film from each polymer after RT experiments.

Polymer composites	C (at%)	N (at%)	O (at%)	F (at%)
ATSP	68.5	4.4	19.2	7.9
PI	82.3	2.2	14.3	1.2
PEEK	74.6	3.2	20.7	1.5

Figures 6(a)–6(c) show representative profilometric line scans across the wear track on the surface of the steel disks after testing with ATSP, PI, and PEEK composites, respectively. The scans were measured using a Dektak (Bruker) stylus profiler. From Fig. 6(a), a continuous transfer of material from ATSP is evident for experiments at RT and 150 °C, with transferred layer thickness of approximately 0.4 and 0.15 μm , respectively. For the experiment at 300 °C, the thickness of the transferred film was less than the stylus resolution, and therefore it could not be measured. Figure 6(b) shows similar line scans for experiments with PI. All the scans show no change on the surface topography outside and inside the wear track due to the inability of the material to form a transfer film at RT, and inability of the stylus to measure the extremely thin transferred film at the temperatures of 150 and 300 °C. In the case of PEEK bearing grade, the profile at RT (Fig. 6(c)) shows a uniform and continuous transferred layer with thickness of 0.5 μm . However, the scan at 150 °C shows the development of partial and non-continuous film. The formation of such discontinuous film and deterioration of the mechanical

properties, namely elastic modulus at 150 °C, could be the reason for higher friction and wear for PEEK.

3.4 SEM/EDS analysis of the worn surfaces

Figures 7(a)–7(c) show the SEM/EDS analyses that were performed on the surface of each polymer composite pin surface. The analyses were performed in a JEOL JSM-7500F FE-SEM to provide a qualitative screening of PTFE additive distribution inside the polymer matrices. The EDS mappings on all polymers demonstrate the presence of fluorine elements (indicated by cyan color) originating from the PTFE powders. The EDS maps show excellent distribution of the PTFE powders in the polymer matrix but with different intensities for each polymer. The ATSP contains the largest concentration of PTFE followed by PI and PEEK.

The SEM images of the untested and worn surfaces of the polymeric samples were also used to study the wear mechanisms associated with the experiments at different temperatures. A sputter coater machine was used to coat the samples with a 4 nm layer of Pt/Pd to obtain the SEM images. Figures 8(a)–8(d) show the

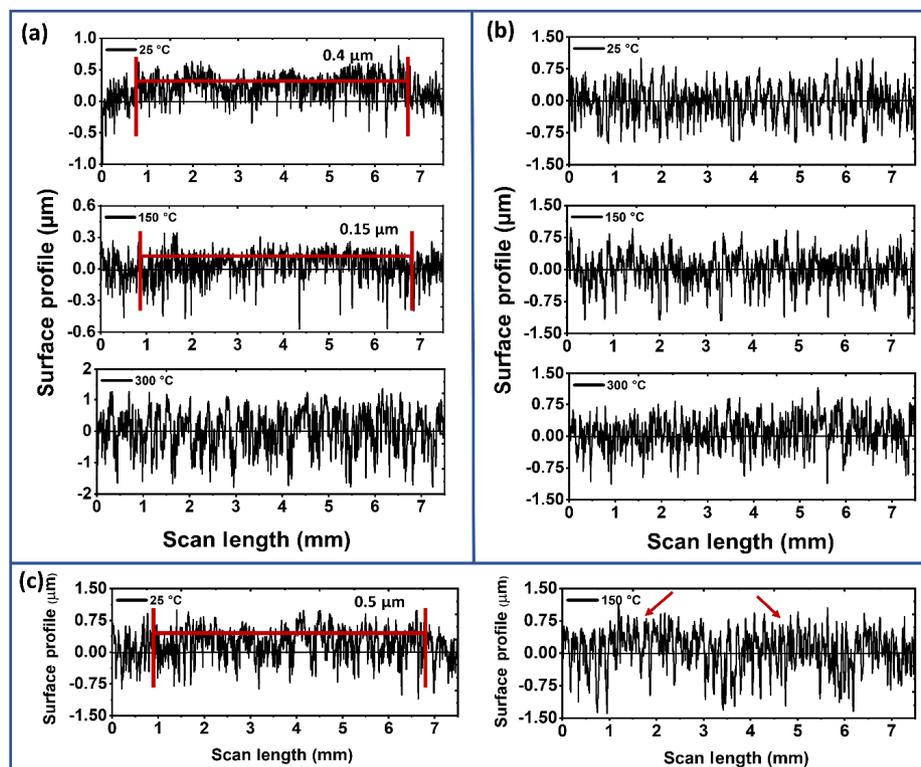


Fig. 6 Profilometric measurements on the surface of steel disks after experiments at different temperatures with (a) ATSP; (b) PI; and (c) PEEK bearing grade polymers. Red lines represent the wear scar.

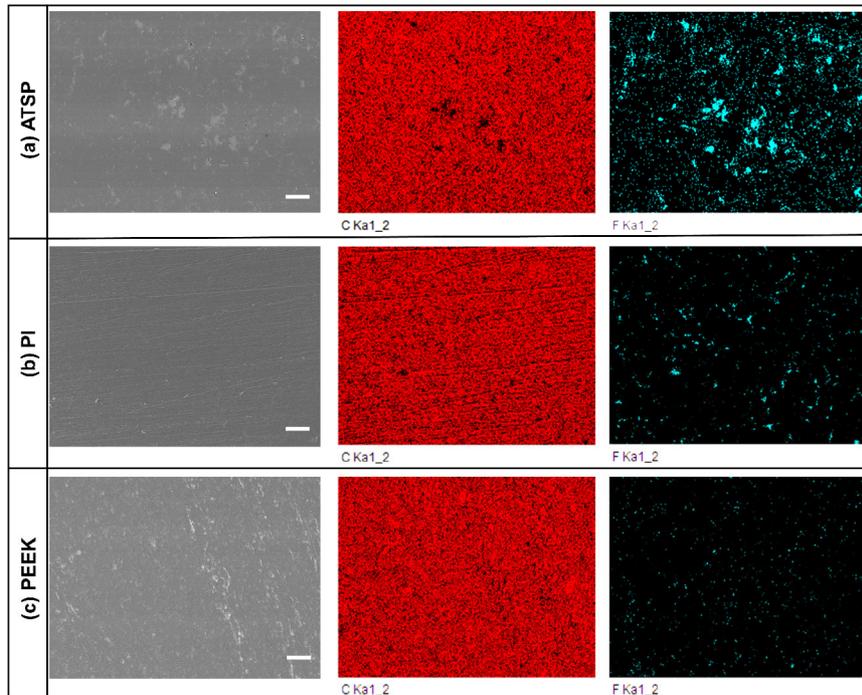


Fig. 7 SEM and EDS mapping of (a) ATSP-base; (b) PI-base; and (c) PEEK-base polymer composite pins surfaces.

SEM images of the untested and tested surfaces of ATSP composite pins at different temperatures. The surface texture of the untested ATSP is depicted in Fig. 8(a) showing a rough topography after machining. The SEM images of the worn surfaces after experiments in Figs. 8(b)–8(d) indicate that the dominant wear

mechanism at all temperatures is polishing and removal of top asperities and initial irregularities in the topography of the surface.

Figure 9(a) shows the SEM image of the untested PI composite pin surface. In general, the surface features a smoother topography compared to ATSP and

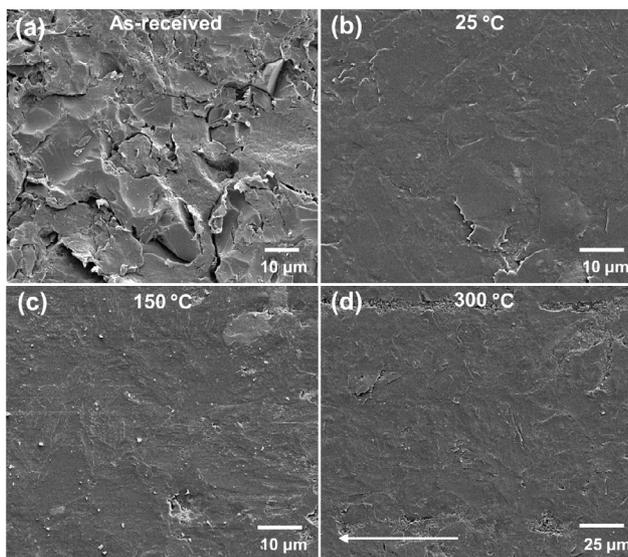


Fig. 8 SEM images of ATSP composite pins. (a) Untested surface; and tested surfaces at temperatures of (b) 25 °C, (c) 150 °C, and (d) 300 °C. The arrow in (d) shows the sliding direction for all cases.

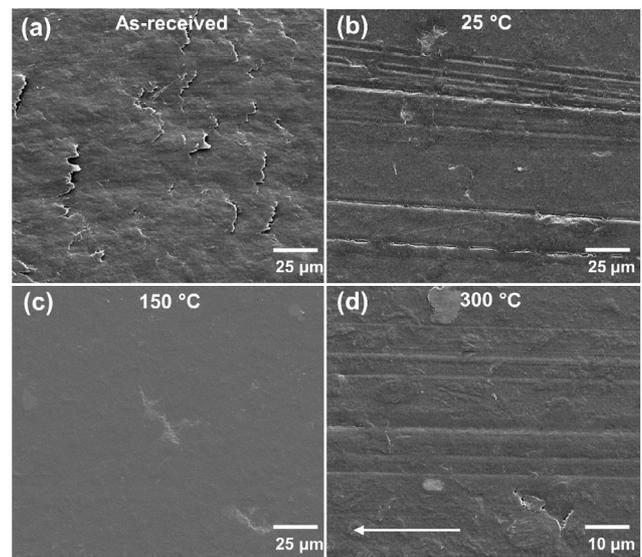


Fig. 9 SEM images of PI composite pins. (a) Untested surface; and tested surfaces at temperatures of (b) 25 °C, (c) 150 °C, and (d) 300 °C. The arrow in (d) shows the sliding direction for all cases.

contains directional shallow grooves from machining. As shown in Figs. 9(b)–9(d), the removal and polishing of the initial irregularities and grooves are characteristics of the worn surface of the PI composite pins after sliding at all temperatures causing the surface to become smoother than the as-received one. However, as shown in Fig. 9(a), sliding at RT caused severe micro-cuttings and scratches on the surface, implying harsh sliding conditions at the interface, which contributed to high friction and wear at RT.

The SEM image of the untested surface of PEEK composite pin is shown in Fig. 10(a). The surface features a rough topography and contains machining marks, tracks and scrapes from machining. However, similar to the other polymer composites, the surface became smoother upon sliding at both RT and 150 °C. The SEM image after the RT experiment in Fig. 10(b) shows the exposed carbon fibers on the worn surface (shown with dashed arrows), which were embedded in the matrix in different orientations. Since PEEK is less wear resistant than carbon fibers, it can easily wear out, and therefore the majority of the load will be carried out by the fibers, which gives the composite

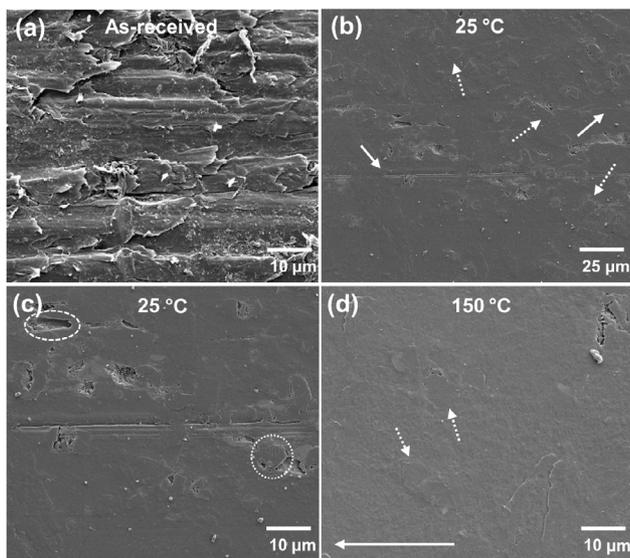


Fig. 10 SEM images of PEEK composite pins. (a) Untested surface; and tested surfaces at temperatures of (b) 25 °C at low magnification, (c) 25 °C at high magnification, and (d) 150 °C. The solid arrows in (b) show the abrasive marks and dashed arrows show the embedded carbon fibers. The dashed circles in (c) show the interfacial cracking and pitting. The solid white arrow in (d) shows the sliding direction.

high strength and wear resistance. Due to different modulus between carbon fiber and PEEK matrix, the stress concentration can be generated at the matrix/fiber interface, which contributes to debonding at the interface or detachment of fiber from the matrix [30]. From Fig. 10(c), some regions show pitting marks that could be from detachment of fibers and interfacial cracking (marked with the dashed circle). Note that the detached fibers serve as third-body abrasive particles and therefore generate abrasive marks on the surface, as shown with the solid white arrow in Fig. 10(b). Signs of plastic deformation and continuous grinding of carbon fibers are extra surface features once the polymer was slid at higher temperature (Fig. 10(d)).

The comparison of wear mechanisms among the polymers revealed that ATSP composite was the least affected polymer when the temperature changed from RT to 300 °C and the surface experienced only mild burnishing at all temperatures resulting in desirable friction and wear properties. The PI composite wear mechanism changed from severe micro-cutting and abrasive wear at RT, to burnishing effect at elevated temperatures resulting in lower friction at elevated temperatures. The PEEK composite wear mechanism on the other hand showed plastic deformation of the surface at elevated temperatures, indicating the deterioration of mechanical properties at 150 °C that resulted in high COF, compared with RT. Therefore, based on the overall tribological performance (i.e., friction and wear), the ATSP composite is recommended as the best performing polymer with excellent performance over a wide range of operating temperatures from RT up to 300 °C.

4 Conclusions

The tribological behavior of three high-performance polymer composites, namely ATSP-based, PI-based, and PEEK-based polymer composites, were experimentally investigated under dry sliding conditions and different temperatures of 25, 150, and 300 °C. Variation of the COF and wear as well as evolution of transfer film on the counterface with temperature were investigated, and the following conclusions could be made.

1) For ATSP and PI composites, the COF followed a decreasing trend with increase of temperature from 25 to 300 °C: It was reduced by 53% and 70% at 300 °C, compared with RT. The COF of PEEK composite increased by 71% when the temperature raised to 150 °C due to formation of a discontinuous film and deterioration of mechanical properties.

2) The transfer film was found to play significant role in the tribological performance at all temperatures. ATSP developed a uniform and continuous transfer film at all temperatures, whereas PI could not develop a transfer film and form patchy transfer layer at RT, resulting in high friction and wear. The increase in temperature helped to develop a uniform and continuous transfer film, leading to a decrease in the COF. PEEK could not maintain its uniform developed transfer film at RT once the temperature was raised to 150 °C. In addition, due to proximity of the tested temperature to T_g (155 °C), the significant softening of PEEK, as well as lower extent of transfer film resulted in higher COF and wear, compared with RT.

3) For all polymer composites, the wear followed an increasing trend with temperature due to the inability of the polymers to develop the transfer film at the early stage of sliding period, and therefore the material was worn out faster until a stable film was formed on the counterface. The dominant wear mechanism for all polymers was polishing of the surface, as shown by SEM analysis. In addition, severe micro-cuttings and scratches formed on the PI surface at RT, which caused higher friction and wear.

4) Based on the overall tribological performance at all operating temperatures, the ATSP composite is recommended as the best performing polymer for use in oil-less engineering applications that demand reliable operation in a wide range of temperatures.

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References

- [1] Friedrich K. Polymer composites for tribological applications. *AIEPR* **1**: 3–39 (2018)
- [2] Lan P, Nunez E E, Polycarpou A A. Advanced polymeric coatings and their applications: Green tribology. *Encyclopedia of Renewable and Sustainable Materials* **4**: 345–358 (2020)
- [3] Nunez E E, Bashandeh K, Polycarpou A A. Thermal and mechanical properties of polymer coatings. In *Polymer Coatings: Technologies and Applications*. Sanjay M R, Parameswaranpillai J, Siengchin S, Ed. Boca Raton: CRC Press, 2020: 157–175.
- [4] Friedrich K, Zhang Z, Schlarb A K. Effects of various fillers on the sliding wear of polymer composites. *Compos Sci Technol* **65**: 2329–2343 (2005)
- [5] Nunez E E, Gheisari R, Polycarpou A A. Tribology review of blended bulk polymers and their coatings for high-load bearing applications. *Tribol Int* **129**: 92–111 (2019)
- [6] Nunez E E, Yeo S M, Polychronopoulou K, Polycarpou A A. Tribological study of high bearing blended polymer-based coatings for air-conditioning and refrigeration compressors. *Surf Coat Tech* **205**: 2994–3005 (2011)
- [7] Chang L, Zhang Z, Ye L, Friedrich K. Tribological properties of high temperature resistant polymer composites with fine particles. *Tribol Int* **40**: 1170–1178 (2007)
- [8] Nunez E E, Polycarpou A A. The effect of surface roughness on the transfer of polymer films under unlubricated testing conditions. *Wear* **326–327**: 74–83 (2015)

- [9] Tharajak J, Palathai T, Sombatsompop N. Recommendations for h-BN loading and service temperature to achieve low friction coefficient and wear rate for thermal-sprayed PEEK coatings. *Surf Coat Tech* **321**: 477–483 (2017)
- [10] Yanming W, Tingmei W, Qihua W. Effect of molecular weight on tribological properties of thermosetting polyimide under high temperature. *Tribol Int* **78**: 47–59 (2014)
- [11] Roy A, Mu L, Shi Y. Tribological properties of polyimide-graphene composite coatings at elevated temperatures. *Prog Org Coat* **142**:105602 (2020)
- [12] Frich D, Goranov K, Schneggenburger L, Economy J. Novel high-temperature aromatic copolyester thermosets: Synthesis, characterization, and physical properties. *Macromolecules* **29**: 7734–7739 (1996)
- [13] Lan P, Meyer J L, Economy J, Polycarpou A A. Unlubricated tribological performance of aromatic thermosetting polyester (ATSP) coatings under different temperature conditions. *Tribol Lett* **61**: 10 (2016)
- [14] Lan P, Meyer J L, Vaezian B, Polycarpou A A. Advanced polymeric coatings for tilting pad bearings with application in the oil and gas industry. *Wear* **354–355**: 10–20 (2016)
- [15] Lan P, Gheisari R, Meyer J L, Polycarpou A A. Tribological performance of aromatic thermosetting polyester (ATSP) coatings under cryogenic conditions. *Wear* **398–399**: 47–55 (2018)
- [16] Bashandeh K, Lan P, Meyer J L, Polycarpou A A. Tribological performance of graphene and PTFE solid lubricants for polymer coatings at elevated temperatures. *Tribol Lett* **67**: 1–14 (2019)
- [17] Bashandeh K, Lan P, Polycarpou A A. Tribological performance improvement of polyamide against steel using polymer coating. *Tribol T* **62**: 1051–1062 (2019)
- [18] Bashandeh K, Tsigkis V, Lan P, Polycarpou A A. Extreme environment tribological study of advanced bearing polymers for space applications. *Tribol Int* **153**: 106634 (2021)
- [19] Demas N G, Zhang J, Polycarpou A A, Economy J. Tribological characterization of aromatic thermosetting copolyester-PTFE blends in air conditioning compressor environment. *Tribol Lett* **29**: 253–258 (2008)
- [20] Zhang J, Demas N G, Polycarpou A A, Economy J. A new family of low wear, low coefficient of friction polymer blend based on polytetrafluoroethylene and an aromatic thermosetting polyester. *Polym Advan Technol* **19**: 1105–1112 (2008)
- [21] Economy J, Polycarpou A, Meyer J. Polymer coating system for improved tribological performance. U.S. Patent 9 534 138, Jan. 2017.
- [22] Cannaday M L, Polycarpou A A. Tribology of unfilled and filled polymeric surfaces in refrigerant environment for compressor applications. *Tribol Lett* **19**: 249–262 (2005)
- [23] Ostberg G M K, Seferis J C. Annealing effects on the crystallinity of polyetheretherketone (PEEK) and its carbon fiber composite. *J Appl Polym Sci* **33**: 29–39 (1987)
- [24] Davim J P, Cardoso R. Effect of the reinforcement (carbon or glass fibres) on friction and wear behaviour of the PEEK against steel surface at long dry sliding. *Wear* **266**: 795–799 (2009)
- [25] Lin L, Pei X Q, Bennewitz R, Schlarb A K. Tribological response of PEEK to temperature induced by frictional and external heating. *Tribol Lett* **67**: 1–9 (2019)
- [26] Berman D, Erdemir A, Sumant A V. Graphene: A new emerging lubricant. *Mater Today* **17**: 31–42 (2014)
- [27] Kasar A K, Menezes P L. Synthesis and recent advances in tribological applications of graphene. *Int J Adv Manuf Tech* **97**: 3999–4019 (2018)
- [28] Bahadur S. The development of transfer layers and their role in polymer tribology. *Wear* **245**: 92–99 (2000)
- [29] Low M B J. The effect of the transfer film on the friction and wear of dry bearing materials for a power plant application. *Wear* **52**: 347–363 (1979)
- [30] Zhang G, Chang L, Schlarb A K. The roles of nano-SiO₂ particles on the tribological behavior of short carbon fiber reinforced PEEK. *Compos Sci Technol* **69**: 1029–1035 (2009)



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