Effect of temperature and atmosphere on the tribological behavior of a polyether ether ketone composite

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Abstract: Polyether ether ketone (PEEK) is a high-performance thermoplastic, which is often selected for high-temperature tribological applications under chemically aggressive environments. The present work investigates the tribological behavior of a high-performance PEEK composite under conditions that are often found inside hermetic compressors. Therefore, an AMTI tribometer equipped with a hermetic chamber and a heating system was used to conduct sliding tests of PEEK cylinders on AISI 304 stainless steel polished discs ($S_q < 10$ nm) with reciprocating movement and a normal force of 175 N. The tribological behavior of the PEEK/AISI 304 stainless steel system was investigated as a function of ambient temperature (30 °C and 80 °C) and atmosphere (atmospheric air and tetrafluoroethane). Wear and surface roughness analyses were performed with white light interferometry and optical microscopy. Raman spectroscopy was used to investigate transfer films on the counter body surface. Temperature was observed to have a strong influence on the tribological behavior of the samples tested under atmospheric air, with a 25% decrease in the friction coefficient associated with a 100% increase in the wear rate. However, the friction measured from the samples tested under a tetrafluoroethane atmosphere showed no significant temperature dependence.

Keywords: solid lubricant; thermoplastics; environment; temperature

1 Introduction

Over the recent decades, the refrigerant industry has introduced several different refrigerant fluids—a change that is generally driven by environmental issues [1–7]. More recently, the refrigerant industry has shown interest in oil-less compressors [8, 9]. This new generation of products, in addition to having environmental benefits, attains new levels of efficiency and allows for the development of innovative refrigerators [10]. In this context, solid lubricant polymeric materials are a promising alternative to reduce the friction and wear in these lubricant-free systems. However, the harsh

operating conditions of hermetic compressors require the use of high-performance polymers. Compounds based on polyether ether ketone (PEEK) are certainly some of the most promising materials in current polymer tribology [11].

Few studies regarding the tribological behavior of polymeric materials under dry conditions and refrigerant atmospheres are available [2–7]. Cannaday and Polycarpou [3] found that a tetrafluoroethane atmosphere resulted in tribological properties that were slightly superior to those reported in atmospheric air for several polymeric materials and composites. Moreover, McCook et al. [12] reported that neat PEEK showed a lower friction coefficient and less wear under dry and vacuum environments. However, the effect of the ambient temperature on these systems remains unclear.

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The main goal of the present work is to investigate the impact of the ambient temperature and refrigerant atmospheres on the tribological behavior of a wear-resistant, solid-lubricated PEEK composite. Thus, a harsh cylinder-on-disc configuration and reciprocating movement were chosen as test conditions. White light interferometry, optical imaging, and Raman spectroscopy provide further insights into possible interactions between polymer composites and their test environments.

2 Materials and methods

A commercially available 10% PTFE, 10% graphite, and 10% carbon fiber (CF)-filled PEEK composite was selected for its superior self-lubrication and wear characteristics [11]. The material was provided as an 11-mm-thick injection-molded plate, which was machined into 8 mm rods and then sliced into cylinders of 4 mm height. Discs (30 mm in diameter) of AISI 304 stainless steel were chosen as the counter body material. Table 1 presents the nominal mechanical properties of the selected materials.

The tribological behavior of the PEEK/AISI 304 stainless steel pair was investigated as a function of ambient temperature (30 °C and 80 °C) and atmosphere (atmospheric air and tetrafluoroethane).

The surface of the AISI 304 stainless steel discs was prepared by sanding with 600- and 1000-mesh abrasive sand paper, followed by polishing with a 1 μm -diameter diamond abrasive. After this surface finishing step, the discs were subjected to ultrasonic cleaning in ethanol for 15 min. A white-light interferometer (Zygo New View 7200) was used to evaluate the resulting topography. A Gaussian filter (800 μm) was applied during surface roughness analysis to remove waviness from the sample surfaces.

Dry tribological tests were conducted in a servo hydraulic AMTI tribometer equipped with a hermetic chamber, a heating system, a 2-channel load cell, and closed-loop actuator controls (load and displacement). This apparatus was configured in a cylinder-on-plate mode (Fig. 1) with linear reciprocating movement under a constant normal load of 175 N. Each test was performed for 2 h at a frequency of 2 Hz and a stroke of 10 mm. Before the initiation of each tribological test

Table 1 Mechanical properties of PEEK composite and AISI 304 stainless steel.

Material	Young modulus (GPa)	Poisson coefficient	Hardness (MPa)	Tensile strength at yield (MPa)
PEEK	11	0.40	–	150
AISI 304	193	0.29	1265	215

Fig. 1 Cylinder-on-plate configuration. Red arrow indicates normal force. Green arrows indicate the sliding movement of PEEK cylinders.

under the tetrafluoroethane atmosphere, the refrigerant gas was purged three times using a mechanical vacuum pump to eliminate atmospheric contaminants.

The polymer wear rates were calculated using geometric wear volume measurements obtained from white-light interferometry. The results were constructed from an average of at least three tests under each condition. The wear tracks were analyzed using white-light interferometry, optical microscopy (Olympus BX60), and Raman spectroscopy (Renishaw 2000, equipped with a 514 nm argon laser) to obtain further information regarding wear mechanisms and tribo-layer formation.

3 Results and discussion

Figure 2 presents typical axonometric projections from virgin and worn polymeric cylinders. The geometric data show that the fiber-reinforced composites did not undergo long-range plastic deformation during the sliding test. Therefore, the enlargement of the apparent contact area in the worn cylinders (Fig. 2(b)) is attributed exclusively to material removal, i.e., volumetric wear. Moreover, because of the contact area enlargement, the initial maximum Hertzian pressure of 210 MPa dropped to nominal pressures of approximately 40 MPa.

Fig. 2 Geometry of PEEK cylinder before (a) and after (b) wear test at 30 °C in a tetrafluoroethane atmosphere. Red arrow indicates the sliding direction.

The maximum Hertzian pressure ($p_{\max}$) of the cylinder's on-plane contacts is given by the expression:

$$p_{\max} = \left(\frac{E'F}{\pi lR} \right)^{1/2} \quad (1)$$

$$\frac{1}{E'} = \frac{(1-\nu_1^2)}{E_1} + \frac{(1-\nu_2^2)}{E_2} \quad (2)$$

where F is the applied load, and l and R are the cylinder length and radius, respectively. E and ν represent the Young's Modulus and the Poisson coefficient, whereas the indices 1 and 2 represent the polymeric cylinder and the metallic counter body, respectively. The nominal pressure is given by the applied load divided by the apparent contact area (worn area in Fig. 2(b)).

The resulting average wear rates experienced by the polymeric composites are summarized in Fig. 3. Atmospheric air and tetrafluoroethane showed no representative effect on the polymer wear rates. Cannaday and Polycarpou [3] reported that PEEK and PEEK composites showed a slight wear rate reduction when tested in a tetrafluoroethane atmosphere. However, the temperature drove the increase in wear rates

Fig. 3 Wear rate of PEEK cylinders during sliding tests against AISI 304 stainless steel discs.

from $1.7 \times 10^{-6} \text{ mm}^3/(\text{N}\cdot\text{m})$ at 30 °C to approximately $3.5 \times 10^{-6} \text{ mm}^3/(\text{N}\cdot\text{m})$ at 80 °C. At high temperatures, the cohesive properties of the polymeric matrix were significantly reduced, thus enhancing the polymer abrasive wear [13–15].

Figure 4 presents typical axonometric projections from virgin and as-worn counter body surfaces. Grooves aligned in the sliding direction on the metallic surfaces were formed during the tribological tests.

The resulting average root mean square roughness (R_q) values measured on the virgin and worn counter body surfaces are summarized in Fig. 5. Sliding tests increased the counter body surface roughness by approximately 600%. It is clear that the tribological tests drastically changed the topography of the counter bodies. However, the resulting roughness after the tribological tests seemed to be independent of evaluated temperatures and atmospheres.

Moreover, profile analyses on wear tracks were performed to evaluate the nature of the grooves displayed in Fig. 4. As exemplified in Fig. 6, peaks and valleys were defined from the mean height of the virgin region, and their areas were calculated. Six profiles were evaluated for each tested condition. From the results, no statistically relevant difference was observed between the total area of the peaks and valleys. In other words, representative volumetric changes did not occur on the metallic surfaces. Therefore, it is possible to attribute groove formation to a microploughing abrasive mechanism [16]. Because successive plowing leads to microfatigue wear mechanisms [16], one can consider these grooves to have been mainly produced in the earlier stages of tribological contact, when the nominal contact pressure was close to 210 MPa, which is about the yield stress of AISI 304 stainless steel (215 MPa). However, previous work [17] has revealed that even

Fig. 4 Topography of AISI 304 stainless steel disc before (a) and after (b) wear test at 30 °C and atmospheric air. Red arrow indicates sliding direction.

Fig. 5 Wear tracks root mean square roughness (R_q) extracted from profiles transverse to the sliding direction. Average R_q from virgin regions is also displayed.

Fig. 6 Topography profile (transverse to sliding direction) extracted from wear track boundary of counter body tested under atmospheric air at 80 °C. Green and red areas show wear track peaks and valleys, respectively, in relation to the mean height from the virgin region.

under nominal contact pressures below the yield stress of the metallic material, the polymeric portion is still able to plow metallic polished surfaces.

Figure 7 presents typical results from image analyses of worn samples. Micrographs of PEEK wear regions revealed grooves aligned in the direction of sliding, typical of microploughing wear mechanisms, and shear-induced plastic flow regions on the boundary of the worn surfaces, attributed to smearing [11, 14, 16]. Additionally, as the cylinders wear out, one could observe carbon fibers protruding from the active surface. Contact between these spots and the metallic surface produces elevated pressures and temperatures, which could plow the counter body surface and result

Fig. 7 Optical micrographs of polymer (a) and counter body (b) worn regions from samples tested under atmospheric air at 80 °C. Red arrows indicate sliding direction. Blue arrows indicate regions of shear-induced plastic flow (a) and material deposition (b).

in the grooves shown in Fig. 4 [17–19]. Subsequently, abraded metallic surfaces filled with sharp asperities were able to plow the polymer surface and wear out the carbon fiber edges. However, although the topographical analyses did not show evidence of significant material deposition on the wear tracks, micrographs from the counter body surface revealed the formation of a tribo-layer. According to Ref. [17], the grooves plowed into polished counter bodies enhance the establishment of a tribo-layer. Note that free carbon fibers were not observed on the counter body surface.

Raman spectroscopy analyses (Fig. 8) performed on the observed tribo-layers revealed D ($\sim 1,360\text{ cm}^{-1}$) and G ($\sim 1,580\text{ cm}^{-1}$) bands, which are common to graphite-based structures [20, 21]. The low band intensities obtained from the samples, tested at 30°C , indicate that the tribo-layer formed under these test conditions is thinner than the one formed at higher temperatures. This behavior is in agreement with Sheiretov et al. [2] who reported that higher temperatures enhance the formation of uniform tribo-layers. Furthermore, the higher intensity ratio between the D and G bands (I_D/I_G) from samples tested under atmospheric air at 80°C (0.97 vs. 0.70 from tetrafluoroethane at 80°C) indicates greater disorder in its graphite structure [20, 21]. The origin of these graphite-based tribo-layers remains unclear because it can be attributed to different carbon sources, such as (i) graphite fillers from polymer compositions; (ii) degraded polymers (PEEK and PTFE); and (iii) degraded carbon fibers.

Fig. 8 Wear track Raman spectra. Raman spectrum of virgin AISI 304 stainless steel is also shown.

Figure 9(a) shows the evolution of the friction coefficient during the sliding tests, whereas Fig. 9(b) shows their average steady-state values. Three tests were performed for each condition, and an average friction coefficient was calculated from each average value within the steady-state regime.

During the running-in regime, samples tested in atmospheric air exhibited friction coefficients 25% higher than those of samples tested in the tetrafluoroethane atmosphere. However, once the steady-state regime was established, the samples tested in atmospheric air and at high temperatures exhibited the lowest friction coefficients, with values of approximately 0.34. At low temperatures, the friction coefficients slightly changed from running-in to steady-state regimes, and the samples tested under the tetrafluoroethane atmosphere showed no significant temperature dependence, with steady state friction coefficients varying around 0.38.

The observed friction behavior results from dissipated energy, attributed to the adhesive interfacial forces and plowing process on the polymeric and counter body surfaces. The adhesive interfacial forces are often affected by the formation of tribo-layers, the establishment of which has long been recognized as the reason for the gradual transition from the running-in to steady-state regime [13, 14, 17].

According to Yen et al. [22], “the presence of vapors, such as water, is required for graphite to lubricate.” Thus, the water vapor present in atmospheric air reduces the bonding energy between the hexagonal planes of the graphite structures present in the formed graphite-based tribo-layer. This behavior agrees with

Fig. 9 Friction behaviour (a) and steady state friction coefficients (b) of PEEK composites sliding against AISI 304 stainless steel discs.

the lower steady-state friction coefficient observed in the samples tested in atmospheric air at 80 °C. Moreover, according to McCook et al. [12], the relative humidity present in atmospheric air increases the friction coefficient of the PEEK matrix running against the metallic surfaces. Therefore, it is reasonable to assume that during running-in and steady-state regimes at low temperatures, the adhesive interfacial forces are governed by interactions between the PEEK matrix and the metallic surface, rather than the tribo-layer. In other words, the tribo-layers during running-in regimes and steady-state regimes at low temperatures were not thick enough to be effective.

4 Conclusions

1. PEEK composite wear rates were drastically affected by the test temperature, but no significant atmospheric dependence was detected.
2. Sliding tests wore AISI 304 stainless steel counter bodies under all testing conditions, resulting in an increased surface roughness (R_q) but no volumetric losses.
3. Graphite-based tribo-layers were observed on counter body surfaces after the sliding tests.
4. Higher test temperatures enhanced the formation of tribo-layers, and the presence of humid atmospheric air resulted in graphite structures with greater disorder, and consequently lower friction coefficients.
5. Without an effective tribo-layer, the presence of humidity in atmospheric air enhanced the system's friction coefficient.
6. The friction of samples tested in a dry tetrafluoroethane atmosphere showed no significant temperature dependence.

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