Effect of temperature on tribological performance of polyetheretherketone-polybenzimidazole blend

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\textbf{ABSTRACT}

Polyetheretherketone (PEEK) is one of the most commonly used High Performance Polymers (HPP) although its high temperature performance is poor. In this study, polybenzimidazole (PBI), a HPP with one of the highest glass transition temperatures currently available, is blended to PEEK to form a 50:50 blend (TU60). Tribological performance of the blend (TU60) was investigated by rubbing it against steel at temperatures up to 280 °C. Results obtained are compared to those from neat PEEK and neat PBI. All three polymers were thermally stable during the duration of tests. However chemical analyses on polymeric transfer layers on steel surfaces and polymer debris suggest polymer degradation. The degradation observed is shear-assisted, possibly promoted by shear heating. Indeed the estimated interfacial temperature based on Jaeger model was above the melting point of PEEK in some cases. TU60 outperforms PEEK in all test conditions and PBI at 280 °C. TU60 formed transfer layers on steel similar to that of PEEK. When contact temperature is closed to the melting point of PEEK, PEEK in some cases. TU60 outperforms PEEK in all test conditions and PBI at 280 °C. TU60 formed transfer layers on steel similar to that of PEEK. When contact temperature is closed to the melting point of PEEK, PEEK in the TU60 creates a low strength transfer layer which acts as an interfacial lubricant. This reduces friction which in turn reduces PBI degradation in TU60 at high temperature. This work provides a strategy for creating interfacial layers to improve polymer tribological performance while maintaining the integrity of the polymer.

1. Introduction

Thermoplastic materials and their composites have potential in replacing metal components in various tribological applications. Their main advantages are their light weight, easy fabrication, corrosion and chemical resistance [1]. However, their mechanical properties are often poor at high temperature. As a result, while some of them possess good tribological properties, they may degrade due to frictional heating and may lead to early failure of components. The development of high performance polymers (HPPs) with high glass transition temperature ($T_g$) and high thermal stability, many of which have extensively been investigated in tribology [2–4], started in the late 1950's mainly for the aerospace industry. One of the most used HPPs is polyetheretherketone (PEEK). PEEK is a semi-crystalline thermoplastic with good mechanical properties and its composites have been used for various engineering applications [1,5]. PEEK has a $T_g$ of 143 °C, a melting temperature ($T_m$) of 343 °C and a working temperature of up to 200 °C [6]. When it is subjected to temperature above its $T_g$, its mechanical properties deteriorate [7]. By increasing the crystallinity of PEEK, its tribological and mechanical properties improved compared to its amorphous counterpart [8,9]. The overall mechanical properties of PEEK could also be improved by the addition of fillers such as carbon fibres [10], glass fibres [11], silica [12], various oxides [13] or polymer lubricants [14,15]. While solid fillers improve thermal resistance of PEEK, they can be abrasive to the countersurface [16]. Another approach to increase $T_g$ of PEEK is by blending it with another polymer of higher $T_g$. This method can be very economical and effective. A 50:50 blend of poly(aryletherketone) (PAEK) ($T_g$ 152 °C) with polyetherimide (PEI) ($T_g$ 215 °C) showed a single $T_g$ at 186 °C, suggesting the formation of a miscible blend with increased thermal stability [17]. The resulting blend, however, showed higher wear rate and no improvement in friction compared to neat PEEK at room temperature [18,19]. This was attributed to a change in wear mechanism from plastic grooving of neat PAEK to fatigue failure with the addition to PEI. Hanchi and Eiss [20] investigated the effect of temperature on the tribological performance of PEEK-PEI blend and showed that the frictional and wear behaviour of the blend was better than that of neat PEEK up to the blend's $T_g$, above which the blend exhibited rapid wear. Chen et al. [21,22] investigated the tribological behaviour of PEEK-PEI-PES (polyarylethersulfone) and PEEK-PEI-PPS (polyphenylene sulfonide) plastics alloys and observed an increase in wear rates and no improvement in friction compared to that of neat PEEK. These studies show that blending PEEK with a high

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Such promise is fulfilled by Polybenzimidazole (PBI) [23], an amorphous HPP with a Tg of 427 °C and retains its mechanical properties up to 435 °C. It is thermally stable up to 500 °C after which end-group reactions and cross-linking occurs [24]. Compare to other HPPs, PBI has high modulus, hardness and scratch resistance [25]. Sharma et al. [3] and Jean-Fulcrand et al. [26] showed that PBI outperformed other HPPs at elevated temperature (up to 280 °C). PBI has been added to other polymers to improve thermal stability and mechanical properties of the latter. Blends of PBI with PEI [27], PA (polylarylate) [28], PEEK [29] and PS (polysulphone) [30] were previously investigated. These are immiscible [27,28,30] or miscible blends [29], with hydrogen bonds formed between the N-H group of the PBI and the carbonyl group for PEI [27] and PA [28]; and the sulfonate group for PS [30]. When the blend is miscible, PBI improves the thermal stability of the least performing polymer by increasing its Tg [27].

In many engineering systems, polymer-metal rubbing contacts are common. During rubbing, polymeric materials may be transferred onto metal countersurfaces. The morphology of the transfer materials is dependent on the structure of the polymer. Linear flexible polymers, such as polytetrafluoroethylene (PTFE) and ultra high molecular weight polyethylene (UHMWPE), tend to form a thin uniform transfer layer [16]. On the contrary, PEEK, PBI and PEI, which have rigid backbones, form “patchy” transfer layers [4,32]. The effect of temperature on transfer layer formation has previously been investigated. For PEI, the morphology of transfer layer changed from patchy to thin and drawn as test temperature increased from 25 °C to 100 °C [33]. Note the test and contact temperatures may be different. An increase in contact temperature with higher applied load had an impact on the transfer layer formation of PBI [26]. Compositions of the transfer layers may be heterogeneous. Onodera [34] studied the transfer film formation of PTFE-PEEK blend on an aluminium disc using X-ray Photoelectron Spectroscopy (XPS) and showed that the surface of the transfer layer was mainly PTFE, with PEEK underneath. While the formation of transfer layers is believed to influence the behaviour of the polymer-metal contacts [35,36], their link remains unclear. Previous studies showed no correlation between transfer layer coverage and wear of the polymer [32,37].

To guide polymer blend design for tribological application, a better understanding on the role of individual constituents of a blend in controlling the blend’s tribological performance is necessary. Blending of PBI with PEEK has been shown very recently to improve the retention of storage modulus above PEEK’s Tg [29]. PBI has also shown good tribological performances under a wide range of temperature [3,38]. This suggests PBI is a promising candidate for improving PEEK tribological performance at high temperature. In this study, we investigate if such promise is fulfilled. Neat PBI requires high processing temperatures. For this reason, a successful development of PEEK-PBI blend would broaden PBI’s application as a filler. The high temperature tribological performance of a PEEK-PBI blend was examined and compared to that of neat PEEK and neat PBI. The nature and chemistry of materials transferred were scrutinized to shed light on the roles of PEEK and PBI to the performance of the blend. The knowledge obtained provide guidance on how polymer blend could be designed to optimize its high temperature tribological performance.

### 2. Materials and methods

#### 2.1. Materials

PEEK, PBI and PEEK-PBI blend (TU60) discs were provided by Hoeribiger America Inc. PEEK discs were made from a Victrex 450G injection molded bar stock. PBI and TU60 discs were made by compression moulding using Celazole U-60 (PBI Performance Products, Inc.) and TU-60 (Vicrex) respectively. TU60 contains 50% PEEK and 50% PBI by weight. The discs had a diameter of 46 mm and a thickness of 5 mm. AISI 52100 bearing steel balls of 6 mm diameter were supplied by Victor P.E. Inc. and TU-60 (Victrex) respectively. TU60 contains 50% PEEK and 50% PBI by weight. The discs had a diameter of 46 mm and a thickness of 5 mm. AISI 52100 bearing steel balls of 6 mm diameter were supplied by PCS instruments. Mechanical and thermal properties of polymer and steel samples are listed in Table 1. PBI and TU60 were dried in an oven at 150 °C for at least 2 days [39]. Before used, polymer samples were dipped in isopropanol and dried using a dry cloth. Toluene (Fisher Chemical, ≥ 99.5%). Steel balls were cleaned using toluene in a sonication bath for 15 min, followed by sonication in isopropanol for another 5 min and were dried using a dry cloth. Toluene (Fisher Chemical, ≥ 99.5%) and isopropanol were used as received.

Table 1. Material properties of ball and disc samples.

| Material | Tg (°C) | Tm (°C) | Thermal conductivity (W/mK) | Heat deflection temperature (°C) | Hardness Shore D | Young’s modulus (MPa) | Compressive yield strength (MPa) | Surface Roughness, Ra (μm) |
|----------|---------|---------|-----------------------------|----------------------------------|------------------|---------------------|-----------------------------|--------------------------|
| PBI      | 436     | N/A     | 0.3 a                       | 435°                             | 95               | 5.9 b               | 400 a                      | 1.41 ± 0.43               |
| PEEK     | 150     | 345     | 0.41 b                      | 262°                             | 90               | 4.9 b               | 207 a                      | 1.27 ± 0.18               |
| PEEK-PBI (TU60) blend | 150 | 345 | 0.25 a | 152° | 85 b | 3.5 b | 125 b | 0.79 ± 0.15 |
| Steel    | N/A     | 1424    | 46                           | N/A                              |                  |                     |                             | < 10 × 10⁻³           |

* a Data obtained with white light interferometry.
* b Data from Victrex.
* c Data from PBI Performance Products.

Tg, HPPs does not always result in blends with good high temperature tribological performance.

Table 1. Material properties of ball and disc samples.
was calculated by dividing the measured frictional force to the load. The rubbing distance was monitored by thermocouples located below and above the disc. The temperature at which the frictional force was measured by the amount of wear acquired with a scan size of 100 × 100 µm² at a resolution of 512 pixels × 512 pixels and a scanning rate of 1 Hz. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

The deformation mode of the polymer can be examined by the amount of elastic recovery of the polymer wear track at the end of the test. Assume that the width of the wear track on the polymer disc is the same as the width of the steel ball wear scar during rubbing. We define the ratio $ER$ as the ratio between the width of the wear scar and the width of the wear track after the test based on images taken with white light interferometry. If the contact is plastic, $ER$ should be close to one due to permanent deformation. If the contact is mostly elastic, the ratio should be above one because the wear track would show elastic recovery, resulting in smaller width [42].

### 2.4. Microstructure and composition analysis

Analysis were carried out on polymer discs that have not been subjected to elevated temperature (referred as pristine samples), polymer wear tracks, polymer outside of the wear tracks (referred as unsheared samples), polymer debris attached to steel balls, and steel ball wear scars. Transfer layers in this study refer to polymeric materials transferred of any morphology that remains on steel ball wear scar after friction tests. The transfer layers formed at the PEEK-steel, PBI-steel, and TU60-steel contacts are referred as PEEK transfer layers, PBI transfer layers and TU60 transfer layers respectively. Since results in this work suggest that speed-temperature superposition applies to our materials systems, only results obtained from polymer-steel contacts with a sliding speed of 0.5 m s⁻¹ are presented.

Worn steel ball and polymer disc surfaces were examined using the backscattered electron (BSE) mode of a scanning electron microscope (SEM) at 10 kV (Hitachi S-3400 N, Hitachi High-Technologies, Japan). The energy dispersive X-ray (EDX) mode of the SEM, X-ray Photoelectron Spectroscopy (XPS, Thermo Scientific K-Alpha™ X-ray photoelectron spectrometer) and Fourier transform infrared (FTIR) Spectroscopy (Perkin Elmer Multiscope Infrared Microscope coupled to a Spectrum One FTIR) were used to obtain chemical information of polymer discs and steel balls before and after friction tests. The depth resolutions for EDX and FTIR are 1 µm and for XPS 20 nm. FTIR spectra were obtained from 100 scans between 700 to 4000 cm⁻¹ at a wavenumber resolution of 4 cm⁻¹. For polymer disc, reflectance spectra were corrected using the Kramers-Kronig correction to remove the effect of dispersion of the signal within the bulk. The resulting spectra were baseline corrected and normalised by assigning the minimum and

### Table 2

**FTIR band assignment.**

| Polymers | Wavenumber (cm⁻¹) | Peak assignment |
|----------|-------------------|-----------------|
| PBI      | 3415 & 3145       | N-H stretching  |
|          | 1640              | C=C/C=N stretching |
|          | 1500–1400         | Ring vibration characteristics of conjugation between benzene and imidazole rings |
|          | 1280              | imidazole ring vibration mode |
|          | 1250–1050         | C-H from imidazole |
|          | 1000–700          | C-H bending of out-of-plane of benzene rings |
| PEEK     | 1653              | C=O stretching |
|          | 1593, 1500, &1485 & 1410 | Ring vibration characteristics from benzene |
|          | 1305              | (C-C(=O)-C) bending |
|          | 1277 & 1190       | C-O-C stretching |
|          | 1215, 1155 & 1010 | C-H bending in-plane deformation |
|          | 863-765           | C-H bending out-of-plane deformation |

![Figure 1](image-url) **Fig. 1.** DSC traces (a) and FTIR spectra (b) of cleaned PEEK, PBI and TU60 discs. Results have been shifted vertically for clarity. DSC measurements were performed using a thermal analyzer (TA Instrument Q2000) in nitrogen atmosphere. The samples were first heated from room temperature to 470 °C at a heating rate of 20 °C/min to erase their anterior thermal history. They were equilibrated at 470 °C for 1 min and then cooled to room temperature. A second heating was performed up to 470 °C at the same heating rate. Three traces were obtained for each samples and results were reproducible. Inserts in (a) are atomic force microscopy (Raman-AFM Alpha300 RA, WITec, Germany) topographic images taken in AC mode using POINTPROBE-PLUS silicon SPM sensor tips (Nanosensors, Switzerland). Images were acquired with a scan size of 100 × 100 µm² at a resolution of 512 pixels × 512 pixels and a scanning rate of 1 Hz. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

During rubbing, both the steel ball and the polymer disc were worn. The worn surfaces on steel balls (wear scars) and polymer discs (wear tracks) were observed using optical microscopy (Hirox RH-2000 with a MXB-2500REZ objective) and white light interferometry (Wyko NT9300, Veeco Metrology, USA). Wear volume of steel balls and polymer discs were obtained from these images [41].

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For XPS, samples were mounted using conductive carbon tape and an Argon flood gun was used to avoid sample charging. XPS spectra were recorded at an operating pressure of $2 \times 10^{-5}$ mbar and at 20 eV pass energy for core level spectra (C 1s, O 1s, N 1s and Fe 2p) with an X-ray spot size of 200 μm [2]. Advantage software package from Thermo Scientific was used to analyse the spectra. All spectra were corrected to a saturated hydrocarbon peak (C 1s = 285.00 eV). The samples analysed were tested at 190 °C. XPS analysis focused mainly on O 1s spectra [43] as it is the most informative for polymer and iron degradation. N 1s spectra [43] is also discussed if necessary. Assignments of characteristics peaks of interest in XPS spectra are in Table 3.

3. Results and discussion

3.1. Friction response of PEEK, PBI and their blend

Frictional responses from PEEK-steel, PBI-steel and TU60-steel contacts are compared in the following section. At 100 °C for all three contacts, friction coefficient $\mu$ first decreases steadily as sliding speed $U$ increases, $\mu$ then stabilises (Fig. 2 (a)). This trend has previously been observed with various polymers [45,46] and was attributed to frictional heating at high sliding speed. Polymer may soften if the contact temperature approaches the Tg, which is connected to plastic deformation due to stick-slip [16], are observed on PEEK wear tracks formed below Tg, (see Fig. 5 (a)). At 190 °C, i.e. above PEEK Tg, the amount of PEEK wear increases with speed at all $U$, it is higher than its $\mu$ at 100 °C. The friction of PEEK-steel and TU60-steel contacts is controlled by PEEK, as suggested by results at 100 °C. At 190 °C, which is above Tg of PEEK, friction of both contacts is likely to be controlled by viscous dissipation of PEEK. Since TU60 has a higher stiffness and only contains 50% PEEK, the amount of viscous PEEK in the contact is likely to be less in TU60-steel contacts than in PEEK-steel contacts, resulting in lower friction. PBI-steel contacts have the lowest $\mu$.

At 280 °C, all three polymer-steel contacts give relatively constant friction coefficients with the speeds tested (Fig. 2 (c)). PBI-steel contacts and PEEK-steel contacts possess similar $\mu$ at 280 °C to their counterparts at 190 °C. On the other hand, $\mu$ of TU60-steel contacts reduces substantially and is the lowest of the three polymer-steel contacts at this temperature. The contact temperature rise of TU60-steel contacts in these tests is estimated to range from 3 to 28 °C (see Fig. 3 (c)). This leads to a contact temperature close to $T_m$ of PEEK and thus results in a drastic reduction in strength of PEEK in TU60. Past research explained the benefit of adding a softer polymer to a hard polymer matrix [50,51]. The softer material forms a low shear strength film at the contact, which covers the harder material and acts as a lubricant, hence reduces friction. This friction reduction mechanism applied in this study only if the contact temperature is close to $T_m$ of one of the phases, which in the case of TU60, the $T_m$ of PEEK.

3.2. Wear

PEEK experiences the highest material loss in this study (see open squares, Fig. 4(a–c)). The amount of PEEK wear increases with speed at 100 °C. This is due to a reduction in strength as contact temperature rises with sliding speed (see Fig. 3 (a)). At 190 °C, i.e. above PEEK $T_m$, the amount of PEEK wear increases substantially over the entire speed range. At 280 °C, PEEK wears so severely that tests were only conducted up to $U = 0.75$ m s$^{-1}$. The increase in PEEK wear is coupled with a transition in wear mechanisms with temperature. "Fish-scale" features, which are connected to plastic deformation due to stick-slip [16], are observed on PEEK wear tracks formed below $T_m$ (see Fig. 5 (a)). At 190 °C and above, PEEK wear track is deeper (see Fig. 5(d–f)). A significant amount of debris are generated, some of which adhered quite strongly around the steel ball wear scars (see Fig. 5(d–f)). Steel balls when rubbed against PEEK shows negligible wear (see open squares, Fig. 4(d–f); and Fig. 5(d–f)). PEEK has an ER between 1 to 1.25.

At 190 °C, the relationship between $\mu$ and $U$ for PBI resembles that at 100 °C but shifted to the left to lower $U$ (Fig. 2 (b)), suggesting a speed-temperature dependence of friction of polymers, i.e. a high temperature, low speed phenomenon can be replicated at lower temperature with higher speed. This shift in friction with temperature is related to viscoelastic properties of polymers and was previously explained by McLaren [49]. The speed-temperature dependence is also observed for TU60-steel contacts, such that $\mu$ is constant and is similar to the plateau value observed at 100 °C. While $\mu$ of PEEK-steel contacts is also constant with $U$, it is higher than its $\mu$ at 100 °C. The friction of PEEK-steel and TU60-steel contacts is controlled by PEEK, as suggested by results at 100 °C. At 190 °C, which is above Tg of PEEK, friction of both contacts is likely to be controlled by viscous dissipation of PEEK. Since TU60 has a higher stiffness and only contains 50% PEEK, the amount of viscous PEEK in the contact is likely to be less in TU60-steel contacts than in PEEK-steel contacts, resulting in lower friction. PBI-steel contacts have the lowest $\mu$.

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Table 3 peak assignments for Fig. 11.

| Peak positions (eV) | PEEK      | PBI       | Iron oxide |
|---------------------|-----------|-----------|------------|
| 398.6               | inside [44] (pink) |amide [44] (blue) |           |
| 400.4               |           |           |            |
| 530.8               | C = O bond (orange) |-OH (green)-OH from water  (green) |           |
| 531.6               |           |           |            |
| 532.3               | C = O from ester/carboxylic groups |           |            |
| 532.9               | C-O-C group (purple) |           |            |
| 534.2               | C-O from ester/carboxylic groups |           |            |
| 533.2               | C-O from polymer/water bond (purple) |           |            |
| 529.8               | $\alpha$-Fe$_2$O$_3$ (red) |           |            |
| 531.4               | $\alpha$-FeOOH (black) |           |            |

Fig. 2. Coefficient of friction against sliding speed of PEEK, PBI and TU60 at (a) 100, (b) 190 and (c) 280 °C.
suggesting that it experiences mainly plastic deformation (see Fig. 7 (a)). As the strength of PEEK reduces with increasing temperature, the contact area in PEEK-steel increases (see Fig. 5 (d–f)), despite negligible steel ball wear (see Fig. 4(d–f)).

The amount of PBI wear is the least of the three polymers and is relatively independent from both temperature and sliding speed (see solid squares, Fig. 4(a–c)). This is not surprising as PBI has the highest strength of the three polymers tested in this work and the maximum estimated contact temperature (∼320 °C) is below its Tg. PBI wear tracks show grooves due to micro-cutting (see Fig. 5 (m–o)). As the temperature increases, wear tracks get deeper (see Fig. 6(d–f)) and cracks grow under plastic deformation (Fig. 5(n)).

The deformation mode of TU60 changes with temperature, being elasto-plastic deformation at 100 and 190 °C and plastic at 280 °C (see Fig. 7(c)). The wear volume of the TU60 increases with sliding speed and are similar to that of PEEK at 100 °C (see Fig. 4(a)). Grooves, similar to those in PBI wear tracks, run along the TU60 wear tracks (see Fig. 5 (g)). Part of the wear tracks are covered by patches with rolled up edges (Fig. 5 (g) and Fig. 8(k)). At higher temperatures, the wear volume of TU60 is relatively constant with speed and is lower than the wear volume at 100 °C (Fig. 4(a–c)). At 190 °C, patches that cover part of the tracks appear wrinkly (Fig. 5(h) and Fig. 8(j)). At 280 °C, these patches look melted and spread, covering most of the track. The underlying grooves are barely visible (Fig. 5(i) and Fig. 8(i)). Since PEEK and PBI are separate phases in TU60 (see Fig. 8(l)) and the former has lower Tg, these melted patches are likely to be PEEK which have soften, and formed a film during rubbing. As the contact temperature increases, these PEEK patches cover more of the wear tracks (see Fig. 8(i–k)) due to reduced PEEK strength. The line profile taken from a phase image (Fig. 8 (d)), which shows how phase changes as the AFM tip moved from PBI and PEEK phases (see white line, Fig. 8 (h)), shows PEEK and PBI give two distinct phase angles in pristine TU60 (Fig. 8 (d)). More fluctuations are shown in the phase line profile with TU60 tested at 100 °C. Further increase in test temperature reduces the phase difference between apparently PEEK and PBI phases in TU60 wear tracks (Fig. 8 (a)), confirming that PEEK is covering most of the tracks at high temperatures (Fig. 5(i)). TU60 wears less than PEEK discs at high temperatures (see Fig. 7). This is because while PEEK in TU60 is softened, PBI maintains the mechanical integrity of the blend and withstands the applied load. Thus the actual area that supports the applied stress is smaller than the nominal area. As a result, the local stress can be higher, giving rise to slightly higher wear of the steel balls in TU60-steel contacts (Fig. 4 (e–f)) as compared to PBI-steel contacts even though friction for the former is lower than the latter (see Fig. 2). The effect of test temperatures on TU60-steel contacts (see Fig. 4 (b,c)) is similar to that of PBI-steel contacts. In addition, the wear track profiles change from more PEEK-like to PBI-like as temperature increases. This supports that PBI in TU60 governs the deformation and wear process of TU60 at 280 °C.
3.3. Polymeric materials transfer on steel

Transfer of polymeric materials to steel balls occurs in two forms: (1) polymeric debris, and (2) transfer layer in the wear scar. In all cases, debris formation is encouraged by increased test temperature (Fig. 5). As expected, the amount of debris is related to the strength of the materials, with PEEK having the most and PBI the least.

Heterogeneous transfer layers are found on steel ball wear scars for all three polymers. The effect of sliding speed is only observed with PEEK at test temperature of 100 °C since the contact temperature transit from below to above its T_g as speed increases (see Fig. 3(a)), giving rise to thicker layer. Line profiles of transfer layers created with the three temperatures are shown in Fig. 9. PEEK has the thickest transfer layers while both TU60 and PBI give thinner films.

PEEK transfer layer becomes thicker as temperature increases (Fig. 9(a)). At high speed or high temperature, transfer layers fully cover steel ball wear scars. PBI transfer layer has a thickness of up to 0.5 μm, and is relatively independent of temperature (Fig. 9(b)). It also does not cover the wear scar fully. TU60 transfer layers have similar morphology to those of PBI transfer layers at 100 and 190 °C. At 280 °C its thickness increases even though the film remains non-uniform (Fig. 9(c)). Based on friction and wear results in sections 3.1 and 3.2, TU60 transfer layer is mainly PEEK or PEEK-related (see section 3.4.3 for chemistry of transfer layers). It is thinner than PEEK transfer layers due to lower amount of PEEK at the TU60-steel interface.

3.4. Transfer layer characterisation

For a cleaned steel ball, results from EDX shows that in terms of atomic percentage, it contains 76% iron and 24% carbon (Fig. 10). The large amount of carbon on the ball is likely due to isopropanol used in the cleaning process. XPS analysis (Fig. 11) shows on the cleaned steel ball iron oxide, α-Fe_2O_3 (529.8 eV, red solid line), water (531.6 eV, green dotted line) and solvent residue (532.6 eV, light green dashed line).

EDX analysis of pristine samples of the three studied polymers confirms their molecular compositions. All XPS spectra (Fig. 11) and FTIR spectra (Fig. 12) of unsheared samples show signatures typical of the polymers. Thus the exposure of high temperature up to 280 °C alone is insufficient to degrade PEEK, PBI and TU60 within the duration of the test.

3.4.1. PEEK-steel contacts

FTIR spectra of PEEK wear tracks (Fig. 12(a–c)) is similar to that of pristine PEEK in all test conditions. Since PEEK suffers severe wear (see Fig. 4, section 3.2), this may be due to constant removal of sheared PEEK, exposing new PEEK. The removed PEEK leads to debris accumulations around the contact.
EDX analysis shows PEEK transfer layers and accumulations around a PEEK-steel contact contain about 45% carbon and 45% iron; and 70–80% carbon and 10–20% iron respectively (Fig. 10). When examined with XPS, no peak related to iron oxide is observed ((Fig. 11 (a)). Since EDX and XPS have different penetration depths (1 μm and 20 nm respectively), these results support observations in Fig. 5(d–f) and Fig. 9 (a) that thick PEEK transfer layer form on steel wear scars and block XPS iron oxide signals from the underlying steel ball surfaces. The lack of iron oxide signals from the XPS analysis also suggests that no debris is embedded in the transfer layer.

In general, XPS and FTIR spectra of the PEEK transfer layers on the steel wear scar resemble shifted and broadened unsheared PEEK spectra. New peaks also appear. Focusing on the FTIR spectra (Fig. 12(a–c)), broad absorption peaks in the hydroxyl region (at 2800–3800 cm\(^{-1}\) with a maximum at ∼3290 cm\(^{-1}\)), and in the carbonyl region (from 1650 to 1800 cm\(^{-1}\)) appear and become more prominent with increasing temperature. The broad carbonyl peaks indicate that multiple carbonyl species, such as aldehydes, carboxylic acids and esters, are present. Furthermore, intensities of peaks at 1160 and 1190 cm\(^{-1}\), representative of the ether group, increase with respect to the phenyl peak at 1593 cm\(^{-1}\). XPS spectrum of the transfer layer (Fig. 11 (a)) shows an increase in peak intensity in the carbonyl region (orange and blue) as well as in the ether, ester, and carboxylic region (purple and grey). These observations suggest that PEEK transfer layers has undergone some oxidative degradation [52]. FTIR spectra of transfer layers also show broadening of the aromatic hydrogen bond...
Fig. 11. XPS of O 1s spectrum of pristine, wear track, wear scar for (a) PEEK, (b) PBI, (c) TU60 and steel at 190 °C and TU60 wear scar at 280 °C. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Fig. 12. FTIR spectra of unsheared, wear track, wear scar and debris of PEEK (a–c), TU60 (d–f) and PBI (g–i) at 100, 190 and 280 °C.
peaks (1498 and 1602 cm\(^{-1}\)) and the formation of aliphatic groups, with their prominence increases with temperature. This suggests chain scission of the phenyl rings has occurred. The degradation products of the cracked phenyl rings give new non-aromatic hydrogen carbons peaks at 3067, 2853 and 2922 cm\(^{-1}\) and from 1365-1465 cm\(^{-1}\) [53]. These findings are surprising because it suggests that the degradation of PEKK at a PEEK-steel contact is associated with UV-photodegradation [53–55] as well as thermal degradation.

FTIR spectra of polymer debris adhered to the steel ball are similar to those of the PEEK transfer layers, with even more broadening of peaks. This indicates that polymer debris undergoes more oxidative degradation than the PEEK transfer layer. The level of chain scission is more significant in the debris. Since the exposure to high temperature alone is not sufficient to cause polymer degradation in this study, our results suggest that polymer debris has been sheared more substantially than the transfer layer. This is possibly due to its strong adhesion with steel. Once formed around the contact, these debris would stay and be sheared throughout the course of the test, resulting in highly oxidized debris.

FTIR spectra of PEEK transfer layers show sharper and more intense peaks at 965, 866 and 848 cm\(^{-1}\) (the aromatic C-H out-of-plane bending modes) as compared to unsheared PEEK and are less defined in the transfer film at 280 °C. These peaks can be due to increased crystallinity [56, 57] or chain alignment [58, 59]. The same FTIR spectral features are observed in polymer debris at 100 °C only.

3.4.2. PBI-steel contact

EDX analysis (Fig. 10) of PBI transfer layers from PBI-steel contacts shows a relatively constant level of carbon ( ~ 15%) across the entire contact area. This is lower than the initial level of carbon on cleaned steel balls and that of PEEK transfer layer in PEEK-steel contacts. The result is in agreement with the morphology of thin PBI transfer layers shown in Fig. 9 (b). In this case, the underlying steel surface is exposed. The effect of rubbing on the chemistry of the steel surface is examined by comparing the amount of oxygen to iron (O:Fe) in the steel ball wear scar. Pristine steel has an O:Fe ratio of 0.33 whereas α-FeOOH has a O:Fe ratio of 1.5. O:Fe ratio varies spatially in the wear scar. The region at the leading edge of the wear scar (blue box, Fig. 10) shows high level of iron (~68%) and low level of oxygen (~16%) with O:Fe = ~0.23. At the centre and the trailing edge of the contact (red and black boxes respectively), O:Fe increases significantly, reaching 1.7 and 1.15 respectively. The increase in O:Fe in these locations suggests that rubbing steel ball against PBI disc promotes oxide formation, as the contact temperature increases at the centre and trailing edge (heat drag) of the wear scar due to frictional heating [59]. The O:Fe ratio at the centre of the contact is above that of α-FeOOH, suggests a different oxide such as α-FeOOH, is formed. This observation is supported by XPS spectrum of the PBI transfer layer (Fig. 11 (b)) showing a significant increase in signals from water (green, 531.6 eV), and α-FeOOH (black, 531.4 eV) [60] as compared to that of α-FeOOH (red, 529.8 eV). α-FeOOH oxide has previously been observed on PBI wear scar [26]. It was attributed to hydrolysis of the more stable α-FeOOH promoted by rubbing. These oxides and hydroxides are formed underneath the transfer layer or are debris embedded into the transfer layer. XPS spectrum of PBI wear track (Fig. 11 (b)) also contains strong signals from water (green dotted, 531.6 eV). Signals from α-FeOOH (black, 531.4 eV) and α-FeOOH (red, 530 eV), likely from dislodged debris from the steel ball, are also observed.

Similarly to PEEK, XPS and FTIR spectra taken from PBI wear tracks, PBI transfer layer on steel ball scars and PBI debris show shear-assisted PBI degradation. At 100 °C, rubbing causes changes in the imidazole regions. The peak intensity of the imide group (530.8 eV) and the hydroxyl peak at 531.6 eV (orange and green dotted lines respectively in Fig. 11 (b)). This is confirmed by a broad C=O stretching at 1680 cm\(^{-1}\) in their FTIR spectra (see Fig. 12 (g-i)). The O-H stretch between 2700-3300 cm\(^{-1}\) is more intense in spectra taken from the wear track, at higher temperatures, and from polymer debris. The results suggest the formation of carboxyl and carboxylic groups such as quinone, di-carboxylic acid [61]. This thermo-oxidative degradation path has previously been observed by Musto [27].

Increasing the test temperature affects the degradation process of PBI debris. The carbonyl peaks at 530.8 eV (orange) and at 1680 cm\(^{-1}\) in XPS and FTIR spectra respectively becomes broader as temperature increases. A new peak at 2222 cm\(^{-1}\), which is characteristics of nitrite groups, appears on the FTIR spectra of transfer layers and polymer debris tested at 280 °C. This is the consequence of a more vigorous degradation mechanism. Since PBI is thermally stable in the temperature tested, observed degradation is mostly promoted by shear, aided by high temperature.

3.4.3. TU60-steel contacts

EDX of the unsheared TU60 shows 90% carbon and 9% oxygen (Fig. 10) which corresponds to a 50:50 wt % PEEK/PBI composition. The XPS spectrum of unsheared TU60 contains carboxyl (orange), hydroxyl (green) and ether (purple) groups from PEEK and PBI. FTIR spectra of unsheared TU60 resemble those of unsheared PEEK at all three test temperatures. Peaks corresponding to PBI, at 1438 and 1484 cm\(^{-1}\) from benzimidazole group, between 1000 – 1100 cm\(^{-1}\) from the C-H stretch of imidazole, and between 3000-3500 cm\(^{-1}\) from the N-H stretch of imidazole can also be found (see Fig. 12 (d-f)). No sign of oxidative degradation such as peaks from hydroxyl (3000-3600 cm\(^{-1}\)) or carbonyl groups (1650 cm\(^{-1}\)) is observed, confirming the thermal stability of unsheared TU60 under such temperature.

After rubbing, FTIR spectra of TU60 wear tracks show changes in PBI characteristic peaks (region at 3000-3400, 1400-1500 and 1050-1250 cm\(^{-1}\)). At 100 °C, the intensity of these peaks increases with respect to those of unsheared TU60. However, they decrease at 190 °C, and then increases again at 280 °C. These results can be understood in relation to the T\(_{g}\) of PEEK. Recall T\(_{g}\) and T\(_{m}\) of PEEK are 150 °C and 345 °C. Below T\(_{g}\), the softer PEEK is removed from the wear track during rubbing, giving rise to stronger signals for PBI. At 190 °C, the PEEK phase has softened and is smeared over the majority of the wear track (see also and Fig. 8 (b, f and i)), results in weakened PBI signals. At 280 °C, where contact temperature might reach T\(_{m}\) of PEEK, the PEEK layer covering the track (see Fig. 8 (a, e and i)) might be thinner than that at 190 °C due to its low shear strength, giving rising to stronger PBI signals.

TU60 transfer layer contains 45–63% carbon (see Fig. 10) based on EDX analysis. This is similar to those formed by PEEK-steel contacts. Despite that, XPS spectra of steel ball wear scar from TU60-steel contacts show signals from α-FeOOH. This is not observed in the TU60 wear track nor in the transfer layers formed in PEEK-steel contact. This suggests that the TU60 transfer layer in this case is probably patchy, exposing the underlying iron oxide surface. At 100 °C, FTIR spectrum of the TU60 transfer layer resembles to that of PEEK transfer layers tested at 100 °C, suggesting both transfer layers have undergone similar degradation processes, with limited oxidative degradation nor chain scission. TU60 transfer layer spectrum however has stronger signal in the region 2800-4000 cm\(^{-1}\). It also shows broadening and increased complexity of the peaks in the region 1050–1750 cm\(^{-1}\). This is due to features from PEEK degradation superimposed with peaks from PBI. Similar observations are seen when comparing spectra from TU60 transfer layers and TU60 wear tracks except the intensity in the 2800-
4000 cm$^{-1}$ region for the former is lower than the latter, possibly suggesting less PBI content in the transfer layer. PEEK and TU60 debris have similar spectra, confirming that TU60 debris are mainly composed of PEEK and have experienced similar degradation process as PEEK debris. Nonetheless, PBI features for example, at 3150 and 3400 cm$^{-1}$ from the N-H stretch of imidazole, are present in TU60 debris. It is broad and very intense in the region 2800-4000 cm$^{-1}$, implying considerable degradation of the debris.

The phenomena described at 100 °C also applies generally to 190 and 280 °C. The FTIR spectra of TU60 and PEEK transfer layers are similar, with the PBI signal becoming less distinguishable at high temperatures. Spectra of TU60 transfer layers at high temperatures have less defined peaks than at 100 °C. In addition, the formation of peaks related to chain scission (2800-3100 cm$^{-1}$) are now visible suggesting more degradation at high temperatures. Unlike the PBI transfer layer, no degradation of PBI in a nitrile group (2222 cm$^{-1}$) is observed, indicating that PEEK improves the thermo-oxidative stability of PBI in TU60. The increase in similarities of the TU60 and PEEK transfer layers at 280 °C, supports the formation of a very soft PEEK layer acting as a lubricant inside the contact. This layer of PEEK fully covers the PBI inclusion in TU60. TU60 debris spectrum shows more degradation than that of the transfer layer.

FTIR spectrum from TU60 transfer layers obtained at 190 °C is very different from those from 100 and 280 °C. It resembles that of PEEK debris formed at 280 °C. Multiple tests have been conducted to ensure that this is indeed the case. It is currently unclear the reason causing this observation. Perhaps, it is related to the test temperature and contact temperature relative to $T_m$ and $T_g$ of PEEK. The PEEK phase at 190 °C may experience higher shear stress than that at 280 °C, causing more degradation. Note the XPS spectra of TU60 transfer layers formed at 190 and 280 °C are similar. More work is needed to understand this fully.

As the blend is rubbed at higher temperature, XPS spectrum of TU60 transfer layer becomes broader (Fig. 11 (c)) in the C=O and C-O regions at 530.8 (orange) and 533 eV (purple). This suggests that different types of C-O and C=O bonds have been created at 532.3 (blue) and 534.2 eV (grey), and can be attributed to carboxylic, aldehyde or ester groups. It is in agreement with the FTIR data which also see an increase in peak intensity at 1210–1310, 1700 and 3000-3500 cm$^{-1}$, confirming the formation of various carbonyl and hydroxyl species (Fig. 12 (d–f)).

The results from XPS and the FTIR show that TU60 transfer layer, while composed of both PEEK and PBI, is predominantly PEEK. In all cases, debris show more degradation than the transfer layers.

In summary, the three pristine polymers show good thermal stability over the range of test temperatures for an hour (which is the duration of tests). Any observed degradation after the polymers has been rubbed against steel is shear-assisted and it is most significant over the range of test temperatures for an hour (which is the duration of tests). Any observed degradation after the polymers has been rubbed against steel is shear-assisted and it is most significant on the transfer layers and debris. An increase in test temperature intensifies polymer degradation processes. During rubbing, PEEK undergoes chain scission and oxidative degradation with the formation of various carbonyl groups. PBI also shows sign of degradation under shear, forming carbodiimide and various carbonyl groups. Similar to PEEK, high temperature promotes PBI degradation and nitrile components are observed. TU60 transfer layers and debris show mostly signals from PEEK. The blend follows PEEK degradation mechanism. Interestingly, PBI degradation in TU60 is delayed, if not minimized, with no formation of nitrile groups at high temperature.

4. Conclusion

Polymer blend is frequently formulated to improve properties of its constituents. Polyetheretherketone (PEEK) is one of the most commonly used high performance polymers (HPPs) despite its poor high temperature performance. Polybenzimidazole (PBI) possesses extremely high $T_g$ and high high temperature performance. Processing neat PBI however requires very high temperature. Thus, a PEEK-PBI blend (TU60) can potentially improve properties of PEEK while widen the application of PEEK. In this study, tribological performance of a PEEK-PBI blend, TU60, hence the effectiveness of PBI reinforcement, was evaluated with polymer-steel contacts at test temperatures up to 280 °C. The results were compared to performance of neat PEEK and neat PBI.

Our results show that this strategy is only effectiveness at test temperature above PEEK $T_g$. At 280 °C, where the contact temperature is likely to be close to PEEK’s $T_m$, TU60 even outperforms PBI in friction reduction in the expense of a slight increase in wear. Chemical analysis (XPS, FTIR, and EDX) of polymeric materials transferred to steel in TU60-steel contacts show they are mainly PEEK-related. Unlike PEEK transfer layer, TU60 transfer layer is not continuous. TU60 transfer materials exhibit signs that they have undergone thermal degradation, and in some cases, also UV degradation, similar to those observed in PEEK transfer layers in PEEK-steel contacts. Degradation is only observed when mechanical shear was applied. The PEEK characteristics of the TU60 transfer materials and its degree of degradation increases with temperature.

Interestingly, while high temperature PBI degradation gives rise to nitrile formation in neat PBI transfer materials, this is reduced in TU60 transfer materials. Our observations suggest that at high temperature, the reinforcement provided by PBI maintains TU60 integrity. Combined with PEEK low $T_g$, this allows the PEEK constituents in the blend to soften, creating a PEEK-based transfer layer on steel. At 280 °C, the estimated contact temperature reaches the melting point of PEEK. While the PBI constituents limit the amount of soft (possibly molten) PEEK, and hence limit wear of TU60, the latter is likely to have very low shear strength and thus acts as a lubricant. This results in TU60 having lower friction coefficient than PBI when rubbed against steel. The reduced friction may be responsible for reduced PBI degradation in TU60. The strategy employed here of reinforcing PEEK with PBI has proven to be very effective and can potentially be applied to other low $T_g$ HPPs.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.triboint.2018.08.001.

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