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# Wear and friction performance of PTFE filled epoxy composites with a high concentration of SiO<sub>2</sub> particles

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## ABSTRACT

In this work, the tribological performance of PTFE filled SiO<sub>2</sub> particles–epoxy composites is investigated. Under a load of 60 N (~140 MPa contact pressure), the optimum content of PTFE lies between 10 and 15 wt%, which yields an ultralow coefficient of friction (CoF) in conjunction with a low wear rate of the composite when dry sliding against bearing steel balls within 1000 m. With 12.5 wt% PTFE in the composite, a CoF around 0.095 and a wear rate as low as  $8.4 \times 10^{-7} \text{ mm}^3/\text{Nm}$  were measured up to a sliding distance of around 2000 m. After 2000 m, eventually the gradual accumulation of the fractured SiO<sub>2</sub> particles and back-transferred steel on the worn composite surface leads to a significant increase of CoF. In the steady-state of sliding, smearing of the PTFE particles along the worn surface was observed together with fracturing of the SiO<sub>2</sub> particles and cracking of the epoxy matrix. Successive EDS mapping shows the formation and evolution of a PTFE-containing third-body tribolayer on the worn surface of the composite. The thickness of the tribolayer was measured about 20–30 nm on the surface of SiO<sub>2</sub> particles after sliding for more than 700 m.

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## 1. Introduction

PTFE is one of the most commonly used solid lubricants, which exhibits an ultra-low coefficient of friction (CoF) due to the smooth profile of rigid rod-like PTFE molecules and easy shear of PTFE lamellae. Its poor mechanical strength, excessive viscoelastic deformation and high wear rate hamper its use as lubricant component of composite tribo-materials [1,2]. Epoxy is a commonly available thermoset polymer after curing, which has a high mechanical strength and thermal and chemical resistance as the binding phase of polymer based composites. In addition, fine epoxy powders facilitate the production of well-mixed composites. As a kind of reinforcement, fairly cheap and available SiO<sub>2</sub> particles possess a high hardness and compressive strength (~1 GPa). Raju et al. [3] found that the addition of 10 wt% SiO<sub>2</sub> could evidently enhance the mechanical properties and the abrasive wear performance of a glass fiber reinforced epoxy composite. However, the fiber reinforcement in the form of fiber bundles in a composite fabric liner may be subject to fracture, de-

bonding and pull out from the matrix, leading to third-body abrasion [4].

Considerable work has been done on improving the tribological performance of PTFE filled composites, whilst most of them focus on the effect of nano-particle reinforcements [5–10]. Other research on the tribological performance of micro-size reinforcements mainly covers the loading range between 0 and 25 wt% [11,12]. Since the wear resistance is to a certain extent related to the hardness of the materials [13], polymer composites filled with higher concentrations of hard reinforcements could yield low wear rates, as was shown by Friedrich et al. [14] and Sawyer et al. [15]. It is tempting to synthesize a composite material with a high concentration of reinforcements that offers a low wear rate and also holds a low-CoF sliding state when sliding against a proper counterpart. In this work, epoxy-based composites filled with PTFE and 48–63 wt% SiO<sub>2</sub> particles are synthesized. The influence of different PTFE contents in the composites on the tribological performance is studied in order to find the optimum PTFE content and the wear mechanism is revealed. This study contributes to a better understanding of the formation of the third-body tribolayer on the worn composite surface, especially on SiO<sub>2</sub> particles, and its influence on the tribological performance of the composite. An additional aim of this study is to reveal the load-bearing capacity of the composite, which benefits the optimization of the design of self-lubricating composite liner.

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## 2. Experimental

### 2.1. PTFE/SiO<sub>2</sub>/epoxy composite

The epoxy- and SiO<sub>2</sub>-containing powder, *Epomet F*, was purchased from Buehler GmbH. The powder is mainly composed of about 31 ± 2 wt% epoxy resin (tetrabromobisphenol-A epoxy, CAS: 26265-08-7) and 65 ± 2 wt% SiO<sub>2</sub> particles. It also contains 1–2 wt% 2,4,6-tris(dimethylaminomethyl)phenol, ~1 wt% antimony oxide (Sb<sub>2</sub>O<sub>3</sub>) particles (for flame retardant property) and less than 1 wt% carbon black (pigment). The size of the SiO<sub>2</sub> particles ranges between 20 and 100 μm, and that of the Sb<sub>2</sub>O<sub>3</sub> lies between 10 and 30 μm, as measured with light microscopy. The density of *Epomet F* powder is about 2.09 g/cm<sup>3</sup>, according to the datasheet from the manufacturer. The PTFE powder, *Zonyl MP 1000* fluoro-additive from DuPont, comprises of loose agglomerates with sizes up to 150 μm (the size of the primary particles is about 12 μm). The density of molded PTFE is around 2.2 g/cm<sup>3</sup>, while the density of the loosely agglomerated PTFE particles is only about 0.5 g/cm<sup>3</sup>. In order to minimize the agglomeration of the PTFE particles in the composite, the PTFE powder was sieved through a 71 μm sieve with a sieve shaker (Retsch AS 200).

The two dry powders were mixed for 3 min in a clean glass container. Thereafter, the glass container with the pre-mixed powders was vibrated in a shaker for 40 min. The powder mixture was then transferred to a mounting press (Buehler Metaserv Pneumet II) for curing. It was cured at about 160 °C for 20 min under 0.41 MPa pressure and cooled down with water afterwards. The molded samples, about 7 mm thick and ø30 mm in diameter, were then polished to about 6.5 mm thick with silicon carbide abrasive papers up to 4000 grade. The surface of the polished composite was rinsed with distilled water before tribo-tests.

The PTFE/SiO<sub>2</sub>/epoxy composite is referred as “Epomet–PTFE composite”, with the content of PTFE ranging from 0 to 30 wt%. For conciseness, the Epomet–PTFE composites are named according to the content of PTFE as ‘Epomet–PTFE-xx’, where xx denotes the weight percentage of the PTFE powder. The measured Vickers hardness and compressive strength of the Epomet–PTFE composites are listed in Table 1. The mechanical properties of the composites are inversely proportional to the PTFE content.

### 2.2. Tribological tests

A systematic study of the friction and wear behavior of the Epomet–PTFE composites was carried out using a ball-on-disk tribometer (CSM Instruments, Switzerland) under dry sliding conditions. For the details of the set-up reference is made to our previous publication [4]. The counterpart used in the tribo-tests was ø13 mm 100Cr6 bearing steel balls. The nominal surface roughness (Ra) of these commercial balls is 50 nm (G28 grade). The hardness and Young's modulus of the 100Cr6 steel are about 780 HV and 210 GPa, respectively.

During tribological tests the counterpart ball was stationary. The normal load used was 60 N (or otherwise specified) and the sliding velocity was 2 cm/s. The diameter of the wear track of the composites is ø22 mm. All tests were performed at room temperature (22 ± 2 °C)

**Table 1**  
Mechanical properties of the Epomet–PTFE composites.

| Composites      | Hardness [HV] | Compressive strength [MPa] |
|-----------------|---------------|----------------------------|
| Epomet–PTFE0    | 90 ± 20       | 232 ± 6                    |
| Epomet–PTFE7.5  | 62 ± 14       | 184 ± 5                    |
| Epomet–PTFE12.5 | 55 ± 16       | 146 ± 7                    |
| Epomet–PTFE20   | 34 ± 9        | 107 ± 3                    |
| Epomet–PTFE30   | 20 ± 7        | 51 ± 4                     |

and the relative humidity of 35 ± 2% maintained with feedback controlled flux of dry air or water vapor into the protection box, depending on the ambient humidity. For the Epomet–PTFE-15, the initial maximum Hertzian contact pressure was near 700 MPa with a contact area of 0.13 mm<sup>2</sup>, assuming that its Young's modulus is around 40 GPa. The sliding distance was 1000 m in most tests, while the longest test was set to 20,000 m sliding distance. Before the tribo-tests, the counterpart balls were cleaned with acetone and dried with clean compressed air.

Confocal microscopy (Nanofocus μSurf) was used to measure the profile of the worn surface of the Epomet–PTFE composites and the wear scar of the counterpart balls, for the assessment of the wear volume by a Matlab code with a margin of error of ± 5%. In order to have reliable statistics, average wear volume of the Epomet–PTFE composites was obtained with at least two tribo-tests, each test yielding four confocal microscopy measurements. After the tribo-tests, the morphology of the worn surface of the Epomet–PTFE composites and the wear scars of the steel counterparts were observed using light microscopy and scanning electron microscopy (SEM, Philips XL-30 FEG ESEM) operating at 3.5 kV acceleration voltage. Energy dispersive spectroscopy (EDS) was used to analyze the elemental composition of the worn surfaces. An Au layer (few nm thick) was applied on the surface of the Epomet–PTFE composite to avoid charging. To obtain the average elemental composition on the worn surface of the composites, at least three EDS area scans were executed in the middle of the worn surface with the size of the scanning areas about 465 × 350 μm<sup>2</sup>. When studying the third-body tribolayer formed on the worn surfaces, at least 8 EDS scans of area ~2.7 × 2 μm<sup>2</sup> were performed on the worn SiO<sub>2</sub> particles.

To classify the tribological performance of the Epomet–PTFE composites, the results were compared with those of other commercial bearing materials. The comparative tribo-tests were carried out under identical test conditions as aforementioned, except a lower load (40 N) was used in these tests to avoid triggering the stop condition of exceeding the maximum tangential force of the tribometer. The involved polymer-based commercial bearing materials are as follows: TX liner from SKF, Vyncolit X620/1 black and CF8131 from Sumitomo Bakelite.

### 2.3. Estimation of tribo-layer thickness

Based on the measured weight percentage (wt%) of each element on the SiO<sub>2</sub> particles with EDS, the thickness of the PTFE-containing third-body tribolayer can be estimated. The reference values of the elemental composition of SiO<sub>2</sub>, PTFE and epoxy are calibrated with the EDS quantitative results performed on each individual component. The calculation of material composition on the worn SiO<sub>2</sub> particles is based on the calibrated values. The equations used for the calculation are shown as following:

$$PTFE\_C\% \times x + epoxy\_C\% \times z = total\_C\% \quad (1)$$

$$PTFE\_F\% \times x = total\_F\% \quad (2)$$

$$SiO_2\_Si^i\% \times y = total\_Si^i\% \quad (3)$$

where the terms like *PTFE\_C%* denote the wt% of C in PTFE measured with EDS, *x*, *y* and *z* indicate the wt% of the PTFE, SiO<sub>2</sub> and epoxy, respectively on the worn SiO<sub>2</sub> particles within the detection depth of EDS. The calculated wt% of the PTFE, SiO<sub>2</sub> and epoxy can be further converted into volumetric fraction (vol%), based on their nominal densities. It should be noted that *Fe\_L* peak and *F* peak partly overlap. Therefore, the contribution from back transferred *Fe* is removed before calculating the PTFE content on

the worn SiO<sub>2</sub> surface and averagely on the worn composite surface, according to EDS results obtained at 15 kV.

### 3. Results and discussion

#### 3.1. Friction and wear

The CoF curves of the Epomet–PTFE composites are shown in Fig. 1. It is found that the Epomet–PTFE composites with PTFE content not less than 10 wt% exhibit fairly low CoF values (< 0.11) within a sliding distance of 1000 m. In particular in the case of the Epomet–PTFE-12.5, a low CoF (~0.095) with small fluctuations is attained. It is noteworthy that the CoF of a pure Epomet sample (without PTFE) rapidly increases from around 0.3 to a steady-state value of about 0.8 at normal load of 20 N (not shown here), which suggests that the little amount of Sb<sub>2</sub>O<sub>3</sub> and carbon black gives negligible lubrication to the sliding system. In the case of the Epomet–PTFE-7.5, the CoF starts to increase after sliding for 400 m until it reaches about 0.3 that triggers the stop condition of the maximum tangential force of the tribo-meter. Rather large fluctuations in CoF value are observed after sliding for 650 m. As regards the Epomet–PTFE-10, it is found that the average CoF was quite low (< 0.1) within the sliding distance of 1000 m. However, large fluctuations in CoF are also seen after sliding for more than 400 m and a slight increase of the average CoF is observed after sliding for 900 m. When the PTFE content is too high (20 wt% or higher), large fluctuations in the CoF curves are also found after sliding for 600 m. In this work, 10 wt% PTFE is considered as the lower threshold, below which a low CoF value within the sliding distance of 1000 m cannot be reached.

The wear rate of the Epomet–PTFE composites with various PTFE contents within a sliding distance of 1000 m is shown in Fig. 2. Under 60 N load (~140 MPa contact pressure in the steady-state), there is also a higher threshold of the PTFE content above which the wear rate of the Epomet–PTFE composites increases dramatically. For instance, the wear rate of the Epomet–PTFE composites with not more than 15 wt% PTFE is in the order of 1 × 10<sup>-6</sup> mm<sup>3</sup>/Nm, whereas that of the Epomet–PTFE composites with PTFE content not less than 20 wt% is measured to be two orders of magnitude

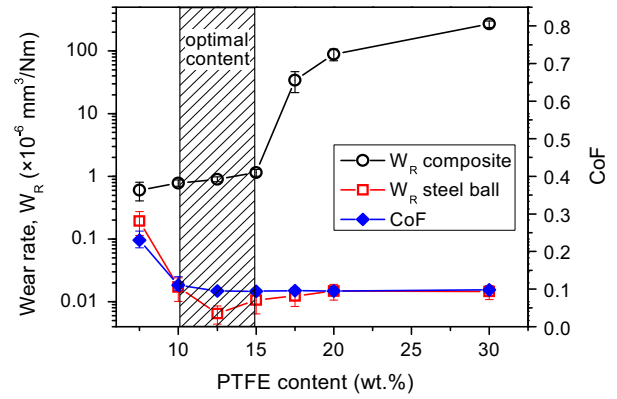


Fig. 2. Wear rates of the Epomet–PTFE composites with various PTFE contents and of the ø13 mm 100Cr6 steel counterpart ball, after sliding for 1000 m at 60 N normal load and 2 cm/s sliding velocity. Error bars are plotted for the wear rate of the composites, and some of the error bars are too small to be seen on a logarithm scale. The average CoF values of the composites are also displayed.

higher. As for the Epomet–PTFE-17.5, the wear rate was measured to be around 1.8 × 10<sup>-5</sup>, 4.3 × 10<sup>-5</sup> and 3.4 × 10<sup>-5</sup> mm<sup>3</sup>/Nm in three tests. This implies that 17.5 wt% PTFE is still above the threshold value. A wear rate as low as about 8.4 × 10<sup>-7</sup> mm<sup>3</sup>/Nm (wear volume around 5.2 × 10<sup>-2</sup> mm<sup>3</sup>) is achieved for the Epomet–PTFE-12.5 after sliding for 1000 m. This is the advantage of having a high concentration of SiO<sub>2</sub> particles in the Epomet–PTFE composites.

The wear rate of the steel counterpart balls was measured with confocal microscopy, and the result is also illustrated in Fig. 2. It is shown that the wear rate of the steel balls is below 2 × 10<sup>-8</sup> mm<sup>3</sup>/Nm when sliding against the Epomet–PTFE composites with the PTFE content not less than 10 wt%. However, in the case of sliding against the Epomet–PTFE-7.5, the wear rate of the steel ball is about one order of magnitude higher, in accordance with the measured high friction force. It is noteworthy that the wear rate of the Epomet–PTFE-7.5 is about 7 × 10<sup>-7</sup> mm<sup>3</sup>/Nm, which is comparable with the wear rate of the counterpart steel ball. This result suggests that without enough PTFE in the composite, the steel counterpart has a high abrasive wear due to the high concentration of SiO<sub>2</sub> particles.

From the friction and wear results, it is concluded that the Epomet–PTFE composites with 10–15 wt% PTFE content (and 59–55 wt% SiO<sub>2</sub> particles) deliver the best tribo-performance under a load of 60 N within the sliding distance of 1000 m, namely low CoF and low wear rates of both the composite and the counterpart ball. This result fits in the overall estimated optimum PTFE content (10–20 vol%) in the PTFE–polymers composite [16] and with the Epoxy, ZnO and PTFE nanocomposites [7]. Although the high content of SiO<sub>2</sub> particles can enhance the load-bearing capacity and wear resistance of the Epomet–PTFE composite, one may argue its possible negative effect on the wear of the counterpart ball and stability of the wear performance over long working lifetime. To check this issue, a tribo-test of extreme long sliding distance was done with the Epomet–PTFE-30 (46 wt% SiO<sub>2</sub>) at a contact pressure close to a real application of plane bearings. As shown in Fig. 3, it is found that when sliding at 10 N load (~48 MPa contact pressure in the steady-state), the Epomet–PTFE-30 could hold a low CoF state as long as 20,000 m sliding distance against an Al<sub>2</sub>O<sub>3</sub> ball, whilst against the steel ball it could hold the same low CoF state over 6000 m sliding distance. In the beginning of tests the CoF increases slightly up to a sliding distance of 1000–1200 m and thereafter decreases to reach the steady-state of low friction at the sliding distance of about 2000 m. In particular, the CoF values are comparable when sliding against two different counterparts. It is noteworthy that there is no depletion of PTFE during such a long sliding test as indicated by the

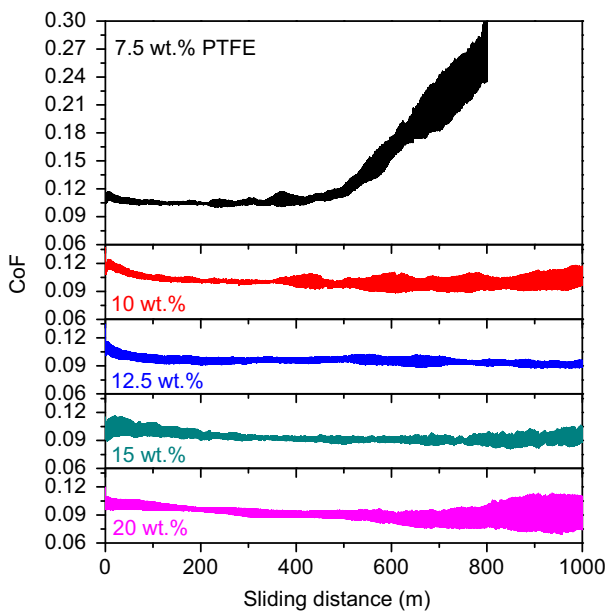


Fig. 1. CoF curve of the Epomet–PTFE composites with various PTFE contents, sliding against ø13 mm 100Cr6 steel counterpart ball at 60 N normal load and 2 cm/s speed.

stable CoF curve, but rather a steady state of friction reflecting the bulk property of the composite. The wear rate of the Epomet-PTFE-30 in the latter case is measured to be around  $1.0 \times 10^{-6} \text{ mm}^3/\text{Nm}$  after 1000 m. Therefore, this composite has a potential as a self-lubricating liner in sliding bearings that adds up to maintenance free operation.

### 3.2. Wear of Epomet-PTFE composites

To investigate the wear mechanism, the worn surfaces of the Epomet-PTFE composites were characterized first with light microscopy. Fig. 4 shows the wear evolution of the Epomet-PTFE-15 sliding against the steel ball. On the polished surface (Fig. 4a), it is seen that agglomerated PTFE particles (dark color) and SiO<sub>2</sub> particles (gray color with sharp boundary) are embedded in the epoxy matrix

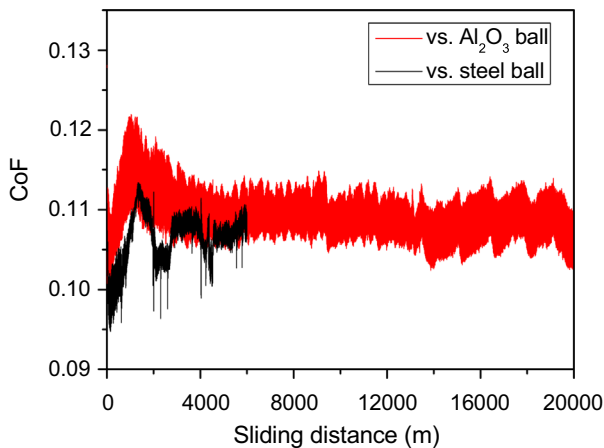


Fig. 3. CoF curves of the Epomet-PTFE-30 sliding against  $\phi 13$  mm 100Cr6 steel and Al<sub>2</sub>O<sub>3</sub> counterpart balls (both Ra $\sim$ 50 nm), at 10 N normal load and 2 cm/s speed.

(whitish color). Most of PTFE particles and SiO<sub>2</sub> particles are separately dispersed in epoxy in the composites with low to moderate content of PTFE, while some of PTFE particles are connected with neighboring SiO<sub>2</sub> particles. The size of the PTFE particles is around 10–50  $\mu\text{m}$ , and the SiO<sub>2</sub> particles are 20–100  $\mu\text{m}$  in size. There are hardly SiO<sub>2</sub> particles entrapped by PTFE phase. After sliding over 400 m (Fig. 4b), cracks in the SiO<sub>2</sub> particles are observed (highlighted with dashed ellipses). Some parts of the epoxy matrix are probably covered with a PTFE layer and thus become darker, while the microstructure of the worn surface bears a strong resemblance to the originally polished surface, indicating a minor wear. In Fig. 4c, it is found that more cracked SiO<sub>2</sub> particles appear after sliding for 700 m. After sliding for 1000 m, parallel scratches are evidently observed. The morphology of the SiO<sub>2</sub> particles in the middle of the worn surface is almost unchanged, indicating little wear of the composite after sliding for 1000 m. The average wear depth in the middle part of the worn surface is around 2.5  $\mu\text{m}$ .

The wear evolution of the Epomet-PTFE-7.5 was also investigated as shown in Fig. 5. Similar to the previous case, cracks in the SiO<sub>2</sub> particles and parallel scratches are also found on the worn surface after 400 m (Fig. 5b). However, after 650 m, the morphology of the worn surface has been significantly changed (Fig. 5c). The worn surface becomes rougher (measured with confocal microscopy) and shows a wavy morphology at some locations (marked with a circle in the figure). EDS quantitative results indicate that the wavy-shaped material consists mainly of fractured SiO<sub>2</sub> and back-transferred steel (adds up to approximately  $75 \pm 8 \text{ wt}\%$ ), while the rest are PTFE and epoxy. The occurrence of wavy morphology is attributed to the gradual accumulation of the fractured SiO<sub>2</sub> and back-transferred steel on the worn surface of the composite, which leads to an increased CoF. It should be noted that in the case of the Epomet-PTFE-12.5, after sliding more than 2000 m and showing an increase of CoF, the amount of Si and Fe wt% on the worn composite surface increases, while the F wt% on the worn composite remains almost the same value. It is thus

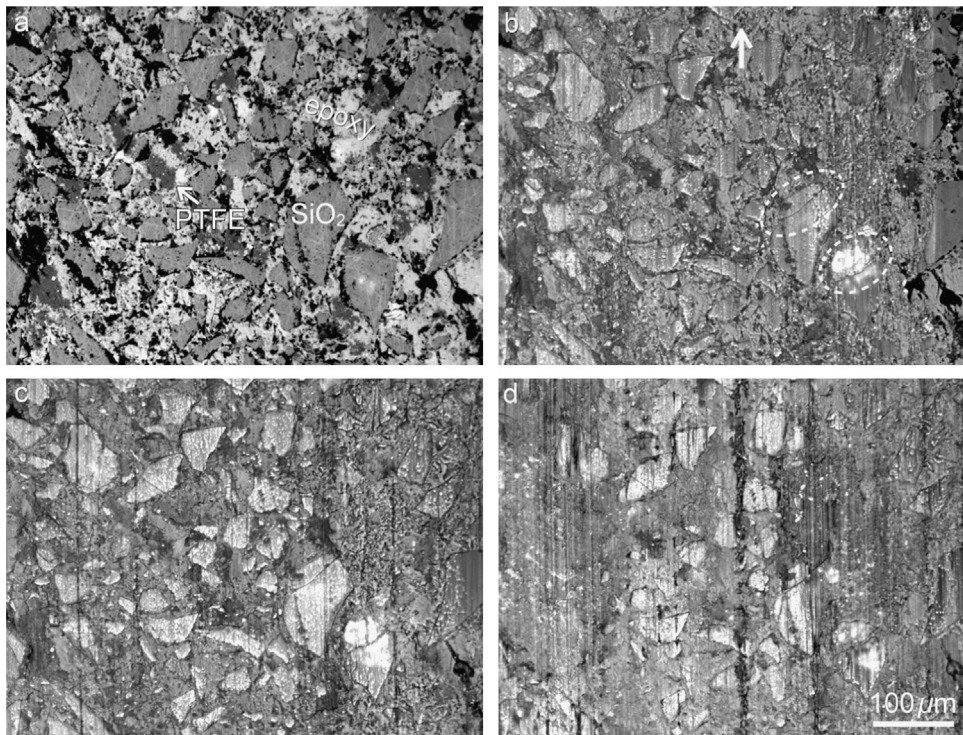
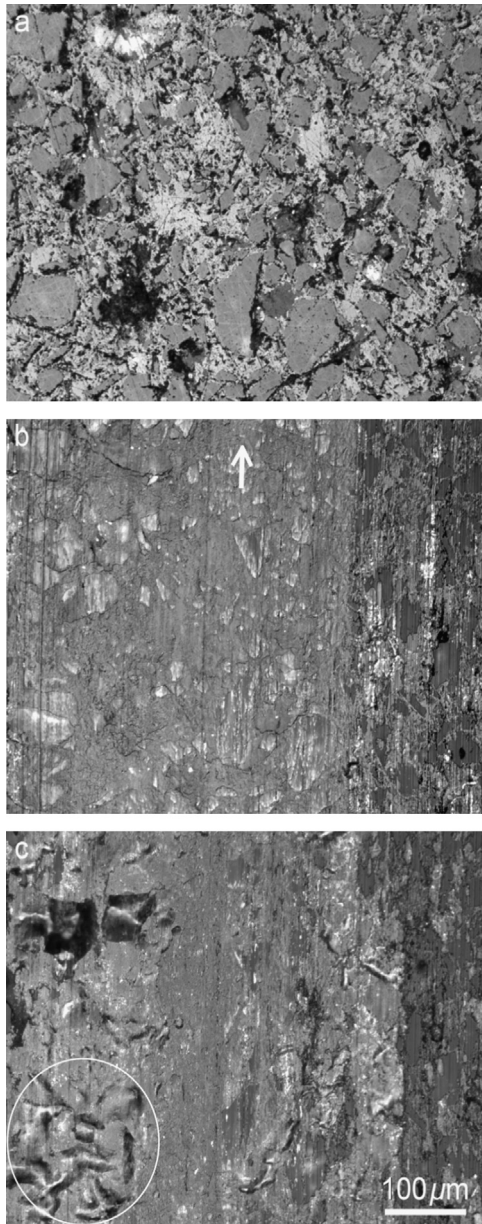


Fig. 4. Light micrographs showing the wear evolution of the same area on a worn surface ( $\phi 22$  mm) formed on the Epomet-PTFE-15 sample, sliding against  $\phi 13$  mm 100Cr6 steel ball at 60 N load and 2 cm/s speed for different distances: (a) 0 m (original surface), (b) 400 m, (c) 700 m and (d) 1000 m. The arrow points to the relative sliding direction of the counterpart steel ball and the dashed ellipses indicate the fractured SiO<sub>2</sub> particles.



**Fig. 5.** Light micrographs showing the wear evolution of the same area on a worn surface ( $\phi 22$  mm) on the Epomet-PTFE-7.5 sample, sliding against the  $\phi 13$  mm 100Cr6 steel ball at 60 N load and 2 cm/s speed, after various sliding distances: (a) 0 m (original surface), (b) 400 m and (c) 650 m. The arrow indicates the relative sliding direction of the counterpart steel ball.

concluded that the increase of CoF is not due to the depletion of PTFE at the sliding interface, but is attributed to the gradual accumulation of the fractured  $\text{SiO}_2$  and back-transferred steel on the worn composite surface.

As to the Epomet-PTFE-20, excessive PTFE content results in some large PTFE agglomerates or PTFE network, seen on the originally polished surface (Fig. 6a). This could lead to the formation of softer regions that worn off easily under a high load. After sliding for 400 m (Fig. 6b), only a few cracks in the  $\text{SiO}_2$  particles and some parallel scratches are seen on the worn surface. However, the morphology of a worn surface is completely changed after sliding for 1000 m due to the massive wear of the composite (Fig. 6c). The well-mixed thick third-body layer is observed on the worn surface. The average wear depth in the middle of the worn surface is around  $23 \mu\text{m}$ , while the largest wear depth in some locations of the worn surface reaches about  $70\text{--}100 \mu\text{m}$ . It is estimated that in the



**Fig. 6.** Light micrographs showing the wear evolution of the same area on a worn surface ( $\phi 22$  mm) on the Epomet-PTFE-20 sample, sliding against the  $\phi 13$  mm 100Cr6 steel ball at 60 N load and 2 cm/s speed, after various sliding distances: (a) 0 m (original surface), (b) 400 m and (c) 1000 m. The arrow indicates the relative sliding direction of the counterpart steel ball.

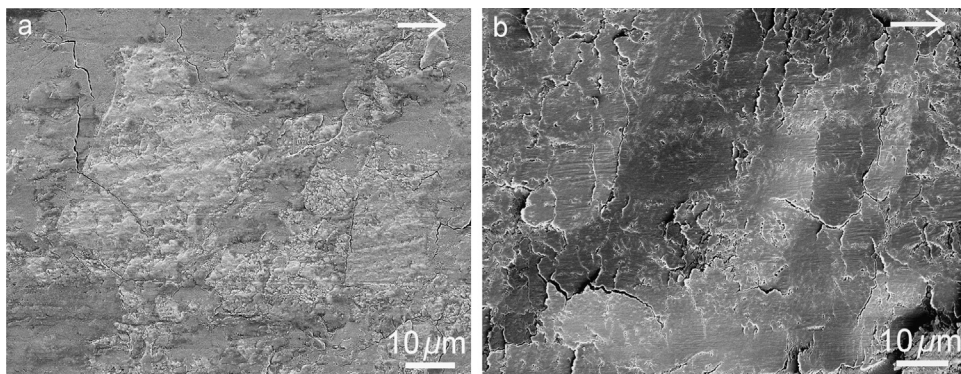
Epomet-PTFE-20, there are about 40, 19 and 41 vol% of the epoxy, PTFE and  $\text{SiO}_2$ , respectively. The large volume fraction of PTFE could weaken the mechanical properties and the binding functionality of the epoxy matrix to the  $\text{SiO}_2$  particles. That is so, especially in the PTFE aggregated regions, which is a drawback of having a low volume fraction of the epoxy matrix (too high  $\text{SiO}_2$  concentration) when sliding under a high contact pressure. After sliding over a certain distance under 60 N load, de-bonding and cracking of the epoxy matrix could occur, which further deteriorates the binding functionality of the epoxy matrix. Then, the weakly bonded regions are peeled off from the bulk, leaving some craters in these regions. These craters could propagate along the worn surface, eventually they lead to a massive wear of the composite. Although a fairly low CoF is measured in this case, a massive wear of the composite is not acceptable for the application of bearing liner. It is important to note that when sliding under a low load (10 N), not only the Epomet-

PTFE-20 but also the Epomet-PTFE-30 does not show large craters and a massive wear of the composite after sliding longer than 10,000 m. This implies the potential use of the Epomet-PTFE-20 and Epomet-PTFE-30 under mediate contact sliding conditions.

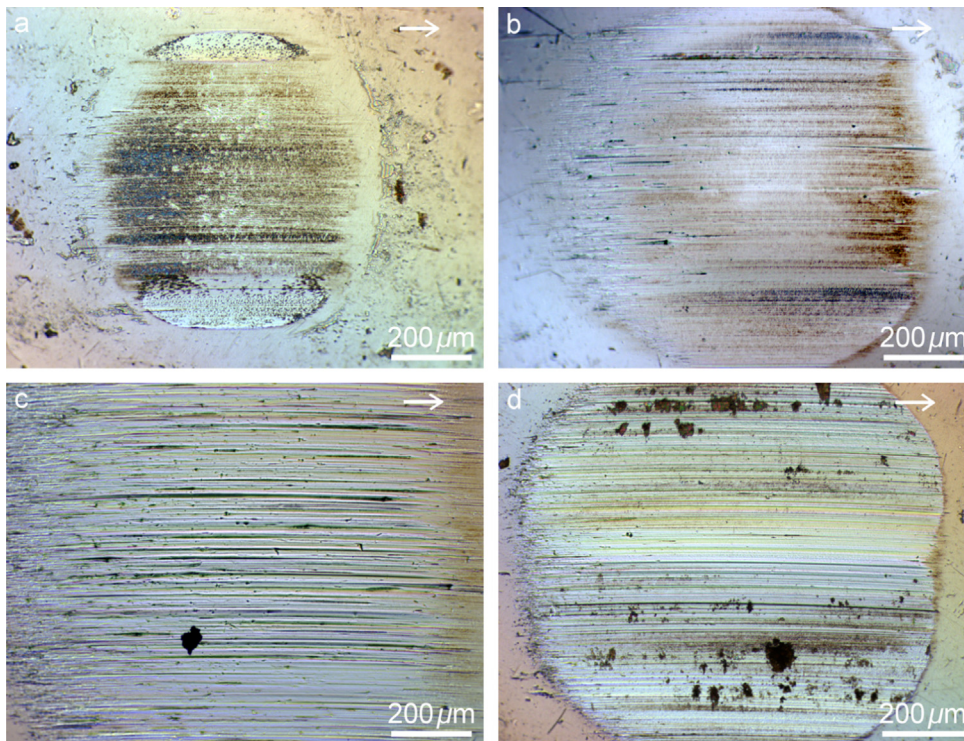
In order to have a clearer understanding of the wavy morphology and micro-cracks formation, the worn surfaces of various Epomet-PTFE composites after sliding for 500 m were further studied with SEM. On the worn surface of Epomet-PTFE-15, the edges of most SiO<sub>2</sub> particles are clearly distinguishable (Fig. 7a). The worn surface is quite smooth, except a few micro-cracks in the SiO<sub>2</sub> particles. The cracks are not only found in SiO<sub>2</sub> but also extended into epoxy matrix. With a careful observation, a trace of polymer on the surfaces of the worn SiO<sub>2</sub> particles is observed. On the worn surface of the Epomet-PTFE-7.5 (Fig. 7b), the wavy morphology consists of lots of continuous and fractured flakes. There is no trace of SiO<sub>2</sub> particles on the worn surface, which are covered with the continuous and fractured flakes. This indicates

that the wavy morphology is a thick tribo-layer formed during sliding.

It is concluded that the PTFE content in the composites plays an important role in the tribo-performance of the Epomet-PTFE composites. After a long sliding distance (> 500 m), completely different morphologies of the worn surfaces are observed, due to the different PTFE contents in the composites. Whilst insufficient PTFE leads to a rough worn surface and a high CoF, too much PTFE gives rise to a massive wear of the composite. With an optimum PTFE content, the least morphological changes are found on the worn surface within 1000 m sliding distance, showing a low CoF as well as a low wear rate of the composite. The low wear rate of the composite in this case enables the tracing of its wear evolution and helps to understand its wear mechanism better. The wear mechanism of the Epomet-PTFE-15 in the steady-state includes smearing/transfer of the PTFE particles along the worn surface, fracturing and cracking of the SiO<sub>2</sub> particles and cracking of the



**Fig. 7.** SEM micrographs of the worn Epomet-PTFE composites sliding against  $\phi 13$  mm 100Cr6 steel ball at 60 N load and 2 cm/s speed: (a) smooth worn surface of the Epomet-PTFE-15 with cracking of SiO<sub>2</sub> particles; (b) the worn surface of the Epomet-PTFE-7.5 exhibiting a wavy morphology and lots of transverse micro-cracks. The arrows indicate the relative sliding direction of the counterpart balls.



**Fig. 8.** Light micrographs showing the wear scar of the  $\phi 13$  mm 100Cr6 steel balls sliding against the Epomet-PTFE composites, at 60 N load and 2 cm/s speed, after various sliding distances: (a) against the Epomet-PTFE-15 for 200 m, (b) against the Epomet-PTFE-15 for 1000 m (c) against the Epomet-PTFE-20 for 1000 m and (d) against the Epomet-PTFE-7.5 for 650 m. The arrows indicate the relative sliding directions of the Epomet-PTFE composites.

epoxy matrix. However, eventually the gradual accumulation of the fractured  $\text{SiO}_2$  and back-transferred steel on the worn composite surface leads to a significant increase of CoF.

### 3.3. Wear of the steel balls

The wear scars of the steel balls were characterized with light microscopy and confocal microscopy. Sliding against the Epomet–PTFE-15 for 200 m, the wear scar of the steel ball is covered with a thick polymer layer (as shown in Fig. 8a). Similarly thick polymer layers are also found on the wear scars when sliding against the Epomet–PTFE-7.5 and Epomet–PTFE-20 for 200 m. The polymer layer, or more specifically the transfer film, which probably composed of epoxy and PTFE, could alleviate the direct contact and scratching between the steel and  $\text{SiO}_2$  particles. This favors a stable sliding condition, which is associated with the low CoF ( $< 0.12$ ) in the first 200 m sliding distance for all the Epomet–PTFE composites, as shown in Fig. 1a.

However, after sliding over a longer distance ( $> 650$  m), different morphologies are shown on the wear scars against the Epomet–PTFE composites with various PTFE contents. In the case of the Epomet–PTFE-15, an evident and continuous transfer film is found on the wear scar after sliding for 1000 m (Fig. 8b), comparable to the transfer film formed after sliding 200 m (Fig. 8a). However, in the case of the Epomet–PTFE-20, hardly any visible transfer film is observed on the wear scar after sliding for 1000 m (Fig. 8c), but many parallel scratches. As to the Epomet–PTFE-7.5, the wear scar after sliding for 650 m is found to be severely worn and partly covered with a very thin transfer film (Fig. 8d). Some large polymer flakes (or wear debris) are seen on the wear scar as well, which could be related with the fractured polymer flakes found on the corresponding worn surface of the composite. Therefore, insufficient PTFE in the composite not only leads to the roughening of the worn surface and a high CoF, but also causes a considerable wear on the steel ball counterpart.

The wear evolution of the steel balls is investigated in detail with confocal microscopy, as shown in Fig. 9. In the case of the steel ball sliding against the Epomet–PTFE-15 (Fig. 9b middle panel), the steel ball only wears little after sliding for the first 200 m. The middle part is even higher than that of the original surface, indicating the formation of a transfer film ( $1\text{--}2\ \mu\text{m}$ ) on the wear scar. After sliding for 400 and 700 m, wear is observed on both sides of the wear scar (corresponding to the inner and outer edges of the worn surface of the composite), while the middle part is still slightly higher than the original surface. After sliding for 1000 m, an increased wear of the ball at the two sides and in the middle part is found. This could be associated with the much thinner transfer film observed after sliding for 1000 m (Fig. 8b).

As to the steel ball sliding against the Epomet–PTFE-7.5, a much larger wear of the ball is measured (Fig. 9b top panel). Similar to the former case, the wear of the ball on two sides is larger than that of the middle part after sliding for 400 m. This is attributed to the fact that the wear debris is prone to be pushed towards the two edges (shoulders) of the worn surface of the composite. The wear debris contains many fractured  $\text{SiO}_2$  particles, which could severely scratch the two sides of the wear scar. When concave regions are formed on the two sides, more wear debris is collected in these regions, accelerating the wear process. Therefore, it is anticipated that abrasive wear of the steel ball starts from two sides, and gradually propagates towards the center. The profile of the steel ball after sliding for 650 m in this case agrees well with this hypothesis.

The wear evolution of the steel ball sliding against the Epomet–PTFE-20 (Fig. 9b bottom panel) is quite similar with that of the ball sliding against the Epomet–PTFE-15. However, less wear at the two sides is observed. This may suggest that the wear debris

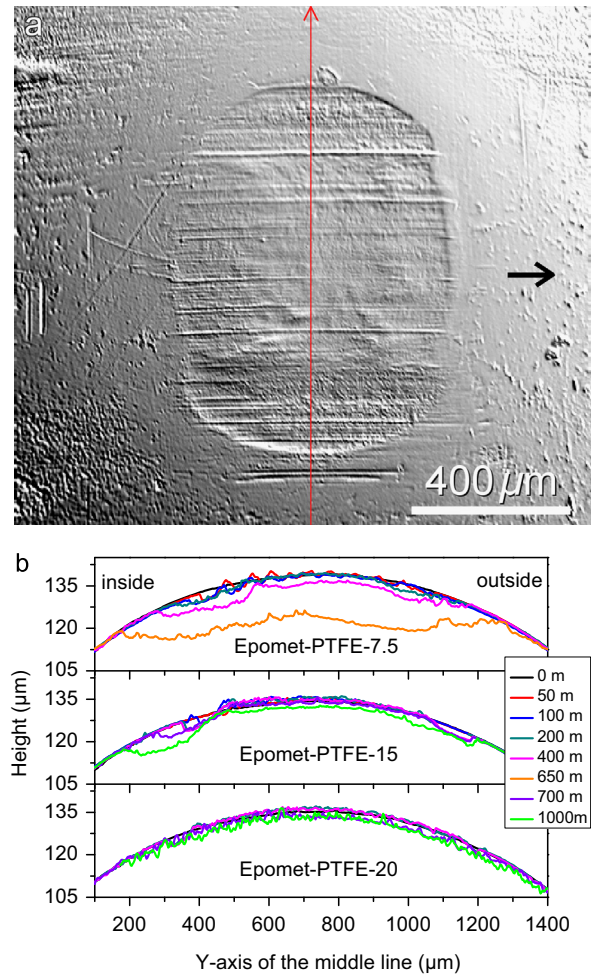


Fig. 9. (a) Typical confocal image of a wear scar with the black arrow pointing to the sliding direction of Epomet–PTFE composite discs. (b) The middle-line profiles (as indicated by the red line shown in (a)) of the wear scars of the steel balls at different sliding distances against the Epomet–PTFE composites at 60 N load and 2 cm/s speed.

generated in this case is not as abrasive as it is for sliding against the Epomet–PTFE-15. This is probably due to a higher content of PTFE in the debris.

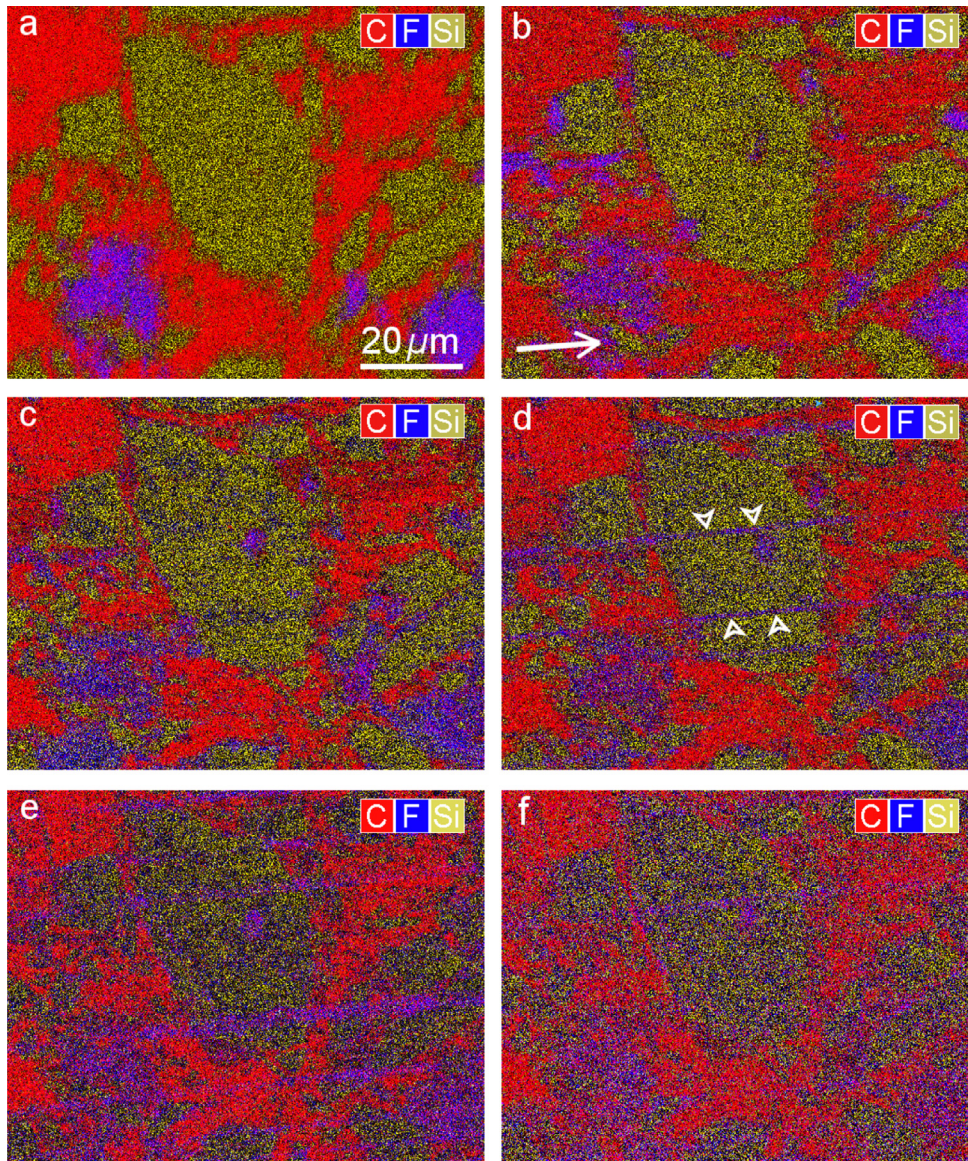
It is concluded that a thick transfer film on the wear scar favors a sliding condition with a low CoF. After a long sliding distance, insufficient PTFE ( $\leq 7.5$  wt%) could cause a considerable wear of the steel ball, while too much PTFE ( $\geq 20$  wt%) does not necessarily lead to a thick transfer film as expected. This is probably due to the instability of the transfer film accompanied with the massive wear of the composite.

### 3.4. EDS analysis of PTFE-containing tribolayer

Given that the Epomet–PTFE composites with PTFE content between 10 and 15 wt% show a very slight microstructural change within 1000 m sliding distance under 60 N load, it is feasible to trace the evolution of chemical elements on the worn composites surface and study the formation of third-body tribolayers in the steady-state with EDS analysis.

The evolution of the elemental change of the worn surface of the Epomet–PTFE-12.5 with sliding distance is illustrated with EDS mapping, as shown in Fig. 10. On the as-polished surface, quiet clear boundaries are seen among the C, F and Si concentrated regions. After sliding for only 10 m, slight spreading of F over C and Si concentrated regions is observed. With increasing sliding distance, it is seen that





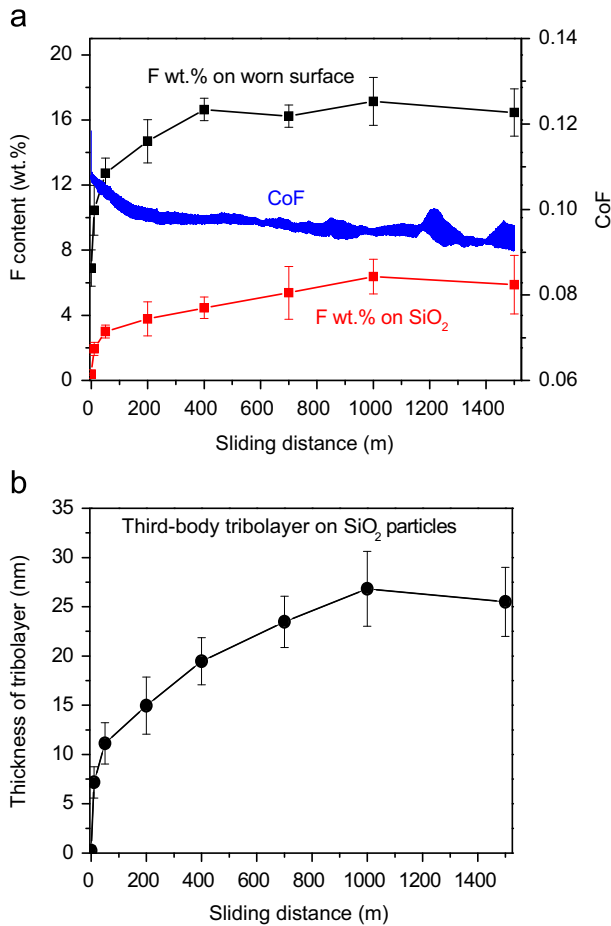
**Fig. 10.** EDS elemental mapping: the worn surface of the Epomet-PTFE-12.5 sliding for (a) 0 m, (b) 10 m (c) 50 m, (d) 200 m, (e) 700 m, and (f) 1000 m against the steel ball, under 60 N normal load and 2 cm/s sliding speed. The arrow indicates the relative sliding direction of the steel ball.

more and more *F* is spread onto *C* and *Si* regions, indicating the gradual build-up of PTFE-containing tribolayer on the worn surface. It is found that the tribolayer on the  $\text{SiO}_2$  particles mainly contains PTFE. In Fig. 10d, several parallel *F*-concentrated lines are clearly observed on the worn  $\text{SiO}_2$  particle (marked with arrows), which gradually spreads over the particle with increasing sliding distances (see Fig. 10e and f). These *F*-concentrated lines are the PTFE-containing third-body that is accumulated through the scratch grooves on the wear scar of the steel ball. After sliding more than 1000 m, a fairly homogeneous distribution of *F* on the worn surface is observed (Fig. 10f). Apart from that, slightly more epoxy on the worn  $\text{SiO}_2$  particles is seen, which is associated with more epoxy debris generated after a longer sliding distance. In short, the EDS mapping results show that a layer of PTFE-containing third-body tribolayer gradually builds up on the worn surface of the composite, covering the epoxy matrix and  $\text{SiO}_2$  particles.

To determine the amount of PTFE-containing third-body tribolayer, EDS quantitative analysis was carried out on the worn surface, as well as on the worn  $\text{SiO}_2$  particles (for the sake of convenient and accurate measurement with a background of foreign composition-Si, O). For measuring the average PTFE content on the worn surfaces, three different areas with size about  $465 \times 350 \mu\text{m}^2$  are chosen on a

worn surface (about  $700 \mu\text{m}$  wide), each of which covers at least 30  $\text{SiO}_2$  particles. Fig. 11a shows that the weight percentage of *F* significantly increases within the first 400 m sliding, especially within the first 50 m. It suggests a faster building-up of the PTFE-containing third-body tribolayer in the initial stage. It should be noted that the contribution of  $\text{Fe}_L$  peak to *F* peak is removed in the quantitative analysis, according to the EDS results obtained at 15 kV. After 400 m, the average weight percentage of *F* measured on the worn surface stabilizes, which could be correlated with the steady-state of the corresponding CoF curve.

To further quantify the thickness of PTFE-containing tribolayer, EDS quantitative analysis was deliberately performed on the worn  $\text{SiO}_2$  particles, averaged with 8 different scanning areas ( $2.7 \times 2 \mu\text{m}^2$ ). The evolution of the average *F* wt% on the  $\text{SiO}_2$  particles is shown in Fig. 11a. Similar with the previous EDS results, a significant increase of *F* wt% on the  $\text{SiO}_2$  particles is found in the first 50 m. From 50 m to 1000 m, it gradually increases, reaching a more or less steady state after 1000 m. In comparison with the CoF curve of the Epomet-PTFE-12.5, it can be seen that the trend of CoF reduction is inversely proportional to the increase in PTFE content or the thickness of the tribolayer formed.



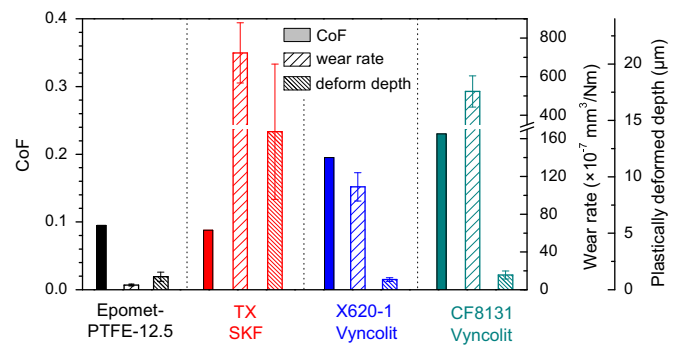
**Fig. 11.** (a) The measured average F content (wt%) with EDS on the worn surface and on the SiO<sub>2</sub> particles of the Epomet-PTFE-12.5 sliding against  $\phi 13$  mm 100Cr6 steel ball versus sliding distances under 60 N normal load and 2 cm/s sliding speed. The corresponding CoF curve is also presented. (b) Average thickness of third-body tribolayer formed on SiO<sub>2</sub> particles, estimated from the EDS results.

Based on the measured weight percentage of each element on the SiO<sub>2</sub> particles, the thickness of the PTFE-containing third-body tribolayer can be estimated. The calculation of the volume percentage of epoxy and PTFE on the SiO<sub>2</sub> particles is elaborated in the experimental part, in which it is assumed that the third-body tribolayer only contains epoxy and PTFE. However, to estimate the thickness of the PTFE-containing third-body tribolayer on the SiO<sub>2</sub> surface, the approximate detection depth of EDS must be known first. The following equation has been shown to give a good practical estimate of X-ray interaction with actual samples [17]:

$$R = \frac{0.064(E_o^{1.68} - E_c^{1.68})}{\rho}$$

where  $R$  is the detection depth (spatial resolution) in  $\mu\text{m}$ ,  $E_o$  is the accelerating voltage in kV,  $E_c$  is the critical excitation energy in kV and  $\rho$  is the mean specimen density in  $\text{g}/\text{cm}^3$ .

The estimated detection depth of EDS into SiO<sub>2</sub> with 3.5 kV accelerating voltage is about 180 nm. To validate, another estimation was carried out with the simulation of the electron trajectory using the “Win X-Ray” software [18], which gives a detection depth of the X-ray also around 180 nm in this case. Therefore, the detection depth of EDS in this case is assumed to be 180 nm. It is also assumed that the third-body tribolayer has a uniform thickness on the SiO<sub>2</sub> surface and the shape of the detecting volume of EDS is simplified as a cuboid instead of a pear shape, so that the volume percentage can be directly converted to thickness percentage. The result is presented in Fig. 11b. It shows a non-linear increase of the average thickness of the third-



**Fig. 12.** CoF, wear rate and plastically deformed depth of the Epomet-PTFE-12.5 composite compared with other commercial bearing liner materials. All the samples are tested with the same setup and at identical condition (against the steel ball, 40 N normal load, 2 cm/s sliding speed and 1000 m distance). The plastically deformed depth refers to the wear depth measured after 5 m sliding under the same condition.

body tribolayer, reaching about 20–30 nm after sliding over more than 700 m. The maximum thickness of the PTFE-containing third-body is probably between 25 and 35 nm in the steady-state in this case. It has also to be noted that the worn surface of SiO<sub>2</sub> is a bit rough, which means an inhomogeneous distribution and non-uniform thickness of the third-body on the SiO<sub>2</sub> surface.

It is also noteworthy that the increase of the  $F$  wt% on the SiO<sub>2</sub> surface is less than the average increase of the  $F$  wt% on the worn surface. This suggests a larger increase of the  $F$  wt% on the epoxy surface than that on the SiO<sub>2</sub> surface. The area fraction of epoxy and SiO<sub>2</sub> on the composite surface is similar, around 1:1.05 according to the composition. This result implies that there is a thicker layer of the PTFE-containing third-body formed on the epoxy matrix. For instance, after sliding for 700 m, the increase of the  $F$  wt% is about 6 wt% on the SiO<sub>2</sub> surface while around 9 wt% in average on the worn surface, which means an increase about 12 wt% on the surface of epoxy matrix. Therefore, the thickness of the PTFE-containing third-body tribolayer on the epoxy matrix is estimated to be about 40–60 nm after sliding for more than 700 m.

### 3.5. Performance-comparison with other commercial liner materials

It has been shown that the Epomet-PTFE composites possess a very high load-bearing capacity and good wear resistance. To classify the performance of the composites, a comparison was made between the Epomet-PTFE-12.5 and other polymer-based commercial bearing materials tested at identical condition, the result of which is shown in Fig. 12. The composition of the commercial bearing materials is listed in Table 2.

It is seen that the Epomet-PTFE-12.5 not only shows a fairly low CoF, but also exhibits a much lower wear rate than the other commercial materials. The plastic deformation of the Epomet-PTFE-12.5 and Vyncolit samples are fairly low, but the wear rates of the Vyncolit samples after 1000 m sliding are much higher than that of the Epomet-PTFE-12.5. This suggests that a lower plastic deformation (or a higher hardness) does not necessarily lead to a lower wear rate. It is noteworthy that the commercial liner materials tested in this work are fiber-reinforced polymer composites. The long-fiber reinforced polymer composites are generally anisotropic, although various weaving directions of the fibers could alleviate this effect. Short fiber reinforced polymer composites are less anisotropic, yielding better performance than the long-fiber reinforced polymer composites. In the particle-reinforced composite, a homogeneous distribution of each component and isotropic properties could be achieved with well-mixed small particles. This could be partly responsible for the better performance of the Epomet-PTFE-12.5.

**Table 2**  
Composition of the commercial bearing materials.

| Composites      | Matrix         | Reinforcements               | Lubricants        |
|-----------------|----------------|------------------------------|-------------------|
| Vyncolit X620/1 | Phenolic resin | Short glass fibers (27–35%)  | Graphite (24–28%) |
| Vyncolit CF8131 | Phenolic resin | Short carbon fibers (25–35%) | Graphite (15–25%) |
| TX liner        | Phenolic resin | Long PET fibers              | Long PTFE fibers  |

#### 4. Conclusion

Epomet–PTFE composites with a high concentration of SiO<sub>2</sub> particles were synthesized and investigated. Insufficient PTFE in the composite could lead to the undulations on the worn surface, as well as very large wear of the steel ball. Excessive PTFE can cause the agglomeration of PTFE particles and weaken the mechanical properties of the composites. The tribo-results show that within 1000 m sliding distance the Epomet–PTFE composites with optimum contents of PTFE exhibit a good tribological performance under 60 N load. For instance, a low CoF (~0.095) in combination with a low wear rate ( $\sim 8.4 \times 10^{-7}$  mm<sup>3</sup>/Nm, including plastic deformation) is achieved for the Epomet–PTFE-12.5, indicating a high load capacity and very good wear resistance of the Epomet–PTFE composites. Tribo-tests of long sliding distance confirm that the composite holds a low CoF and a low wear rate of steady state from the bulk rather than a behavior of PTFE coating, implying its potential use as a self-lubricating liner material.

The microstructural change on the wear surface of the composite enables us to trace the evolution of chemical elements and to study the formation of third-body tribolayers. A gradual build-up of PTFE-containing third-body tribolayer is revealed with a series of EDS mapping. The EDS results suggest that the average thickness of the tribolayer in the steady-state is about 20–30 nm on the worn SiO<sub>2</sub> surface and 40–60 nm on the worn epoxy surface after sliding for more than 700 m. The thickness of the PTFE-containing third-body on the SiO<sub>2</sub> surface increases with the sliding distance, until a stationary value is reached after sliding for about 1000 m.

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