

Influence of counterface and environment on the tribological behaviour of polymer materials

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ABSTRACT

This paper focuses on the influence of the counterface materials on the sliding behaviour of polymer materials in hydrogen. Polyimide (PI), polyetheretherketone (PEEK) and Polytetrafluoroethylene (PTFE) materials were investigated against hardened 52100 martensitic bearing steel and 304 austenitic stainless steel with similar roughness ($R_a = 0.2 \mu\text{m}$). Results indicate that the friction and wear of PI and PEEK materials depend on the counterface material. This effect wasn't observed for PTFE composites. While the tribological performance of polyimide is better against 52100 in hydrogen, improved sliding behaviour of PEEK materials is observed with 304 counterface, particularly at higher sliding speed. Surface analyses of the transfer film reveal that the influence of the counterface is primarily related to the chemical nature of the steel for PI and to the thermal conductivity of the disc for PEEK materials.

1. Introduction

The development of hydrogen technologies is a key strategy to sustainably reduce CO₂ emissions in industry and transport. Power-to-Gas is a challenging solution, in which hydrogen can be used in mobility, industry, heat supply and electricity generation applications.

With regards to infrastructure, components such as coupling, sealing, bearing or valve systems with tribological issues are critical parts. It is therefore necessary to pursue researches on material compatibility in hydrogen. During the last decade, only few working groups have been studying the friction and wear of polymer materials in hydrogen environment [1–8].

One of the ongoing studies at BAM deals with the sliding performance of polymer materials in hydrogen. Up to now, experiments were performed against bearing steel 52100. In particular, the effect of fillers and temperature have been reported in previous publications [6,7].

It is well known that the tribological performance of polymers strongly depends on the counterface characteristics. Most studies on polymer-metal sliding reported on the influence of the roughness [9–12]. Studies reporting the influence of counterface material on the friction and wear of polymers are less frequent [13–17], although it is generally recognized that the counterface material plays a significant role in the tribological characteristics of polymers, due to its thermal conductivity, chemistry or surface energy.

The effect of counterface material in hydrogen has rarely been studied. Only few papers reported on the influence of the mating materials on the friction behaviour of polymers materials [3]. In his investigation, Morita studied several polymers sliding against hardened bearing steel, austenitic stainless steel and cobalt-based alloy. Tests revealed that friction and wear depend on the counterface materials.

Therefore, the present study focuses on the influence of the counterface materials on the sliding behaviour of polymer materials in hydrogen. At first, the performance of unfilled polymers in hydrogen are compared to air and additionally to vacuum condition for polyimide that is known to be sensitive to humidity [18]. Secondly, some results with polymer composites are presented to assess the influence of solid lubricants on the sliding behaviour of these polymers in hydrogen. Overall, a special attention is taken to the transfer film formation related to hydrogen and counterface material.

2. Materials and experiments

The materials investigated in this study are based on polyimide (PI, TECASINT), Polyetheretherketone (PEEK, Victrex™) and Polytetrafluoroethylene (PTFE, Dyneon™). The choice of the composites was made according to promising results in previous projects and for comparative purpose. Table 1 gives details of the composition. PEEK materials were prepared by injection molding, PI and PTFE materials via

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Table 1
Material compositions.

	vol%	Density [kg/m ³]
PI	100% PI	1.34
PEEK	100% PEEK	1.30
PEEK Gr	9% Graphite	1.39
PEEK CF/PTFE/Gr	10% CF (short carbon fibers), 10% PTFE, 10% Graphite	1.53
PEEK CF/PTFE/MoS ₂	10% CF (short carbon fibers), 10% PTFE, 10% MoS ₂	1.86
PTFE CF/PEEK	12% CF 14% PEEK	1.97

a sinter process. The polymer samples with a contact area of $4 \times 4 \text{ mm}^2$ were arranged in a pin-on-disc configuration continuously sliding against a rotating steel disc. The counterfaces are hardened 52100 martensitic bearing steel and 304 austenitic stainless steel. The relevant material properties are given in Table 2. The discs were cleaned with ethanol before test. Sliding velocity was set to $v = 0.2 \text{ m/s}$ or 1 m/s and normal force to 50 N (3 MPa contact pressure). Experiments were conducted in air, high vacuum, and high purity hydrogen gas (99.999% H₂) at room temperature in a tribometer (CT2) described in Ref. [19]. Before hydrogen testing, the cryogenic chamber was purged 3 times with high purity N₂ to eliminate any environmental contamination.

The wear of the composites was determined by the total weight loss after 5000 m sliding. At least two and up to 10 experimental values were available to calculate the average friction coefficient and wear rate. After the experiments, worn surfaces and morphology of the material transfer on the steel counterface were investigated by optical microscopy, SEM, and ATR-IR analyses.

3. Results and discussion

3.1. Friction and wear results

Fig. 1 shows the evolution of the friction of PI in air, vacuum and hydrogen against 52100 and 304 steel discs. In air, the influence of the counterface material is low: sliding is smoother against the bearing steel, but the coefficient of friction reaches similar values (0.5 and 0.47) against 52100 and 304, respectively.

In vacuum and hydrogen environment, the friction coefficient is much lower than it is in air independently of the steel disc. Against 304, the coefficient of friction of PI is quite unstable and reaches a similar value (0.16) after 5000 m sliding distance in vacuum and hydrogen. Against 52100, the friction is significantly lower in hydrogen (0.05) than in vacuum (0.2), despite the present of some peaks.

Concerning the wear rate, the performance of PI is independent of the steel material in air and in vacuum as indicated in Fig. 2. In hydrogen, however, lower wear rate is obtained with the martensitic steel compared to the stainless steel 304.

An example of the friction progression of pure PEEK sliding against 52100 and 304 steel discs is shown in Fig. 3. In air, the friction is slightly lower against the stainless steel than against the 52100 disc. The influence of the environment is not significant in contact with 52100 discs, but lower friction is observed in hydrogen atmosphere when PEEK slides against 304. In this case, the average coefficient of friction is 0.25 instead of 0.47 with 52100 disc (Fig. 4), but the friction coefficient

Table 2
Counterface materials.

		52100	304
Tensile strength	N/mm ²	1680	~600
Elastic Modulus	N/mm ²	212,000	193,000
Hardness	HV740	HV740	HV170
Roughness, Ra	μm	0.2	0.2
Thermal conductivity	W/mK	46.6	16.2

varies from 0.05 to 0.4 against 304. Two different friction behaviours are observed as shown in Fig. 3. Since several tests gave such discrepancies, further experiments were performed at higher velocity to verify if a possible friction transition could appear at $v = 0.2 \text{ m/s}$. Fig. 5 shows the friction progression at 1 m/s in hydrogen. Under this condition, the friction coefficient reaches a steady state value of 0.07 against 304 steel but increases significantly against 52100.

Wear values presented in Fig. 6 indicate better performances of PEEK against 304 discs compared to 52100 in air and in hydrogen, particularly at higher sliding speed. Surprisingly, higher sliding speed results in significant lower wear when PEEK slides against steel 304.

The average friction coefficients and wear rates of several composites are given in Fig. 7. While the variation of the test results is significant for unfilled polymers (Figs. 3 and 4), the repeatability of the measurements is good for composite materials. Friction coefficient and wear values are lower than pure PEEK in hydrogen. Overall, the tribological behaviour is improved for PEEK composites against 304 steel discs, except for graphite filled PEEK, which shows higher friction against 304, but lower wear values. The counterface material doesn't seem to influence the performance of PTFE composite in hydrogen.

3.2. Surface analyses and discussion

Fig. 8.1a and b shows the surface of the counterfaces after tests against PI in hydrogen environment. Transfer film is observed at the surface of the 52100 while only separate polymer debris are present on the 304 disc.

The friction mechanism of PI has been explained in our previous study with 52100 [5]: It was shown that in moist air, H-bonds between water molecules and the carbonyl groups of PI restrict the molecular mobility of PI, preventing orientation and polymer transfer. In this case, transfer is induced by mechanical shearing of the polymer by the rough disc, which gives high friction. In dry atmosphere, i.e. in vacuum and hydrogen, the PI chains are more flexible and can easily be oriented in sliding direction to form a transfer film, reducing friction drastically (Fig. 1a). Further, it was shown that the low friction of PI in H₂ is associated with tribological induced reactions with the fresh metal surface, producing a homogeneous transfer on the disc [Fig. 8.1a]. The abrupt jumps of friction that appear periodically with the 52100 disc are associated to the removal of polymer debris at the friction contact.

By comparing the test results, the friction coefficient and wear rate of PI are similar against both counterfaces in air and in vacuum, respectively. In hydrogen, the friction reaches the same level as in vacuum against 304 but doesn't decrease further as it does against 52100. Fig. 8.1b shows only polymer wear debris spread over the surface of the 304 disc, in particular along the steel grooves, but no homogenous transfer film is formed.

The surface of the polymer pins after tests in hydrogen against 52100 and 304 discs indicate that ploughing wear is predominant in both cases (Fig. 8.2a and b). The worn surface formed against the martensitic steel is however smoother indicating that the wear mechanism is governed by mild abrasion. This is obviously due to the presence of a transfer film on the counterface, that protects the pin from wearing further.

Against 304 disc, ploughing marks are observed on the worn PI along with polymer debris. These are back transferred wear particles from the disc to the polymer surface. The transferred polymer debris is carried away from the steel surface, which increases the wear rate [20].

Infrared spectra of PI transfer after hydrogen tests are given in Fig. 9. By comparing the intensity of an imide absorption peak (C=O) normalized to the intensity of the C=C, no chemical structure changes are observed after tests against 304 in hydrogen environment. This indicates that no triboreactions appear in hydrogen contrarily to 52100. This confirms that at the 52100 surface, chemical interactions occur between metal atoms and polyimide, enhancing the adhesion of transfer to the disc as mentioned in Ref. [5]. This also suggests that the chrome oxide layer of the stainless steel prevents any reactions and thereby

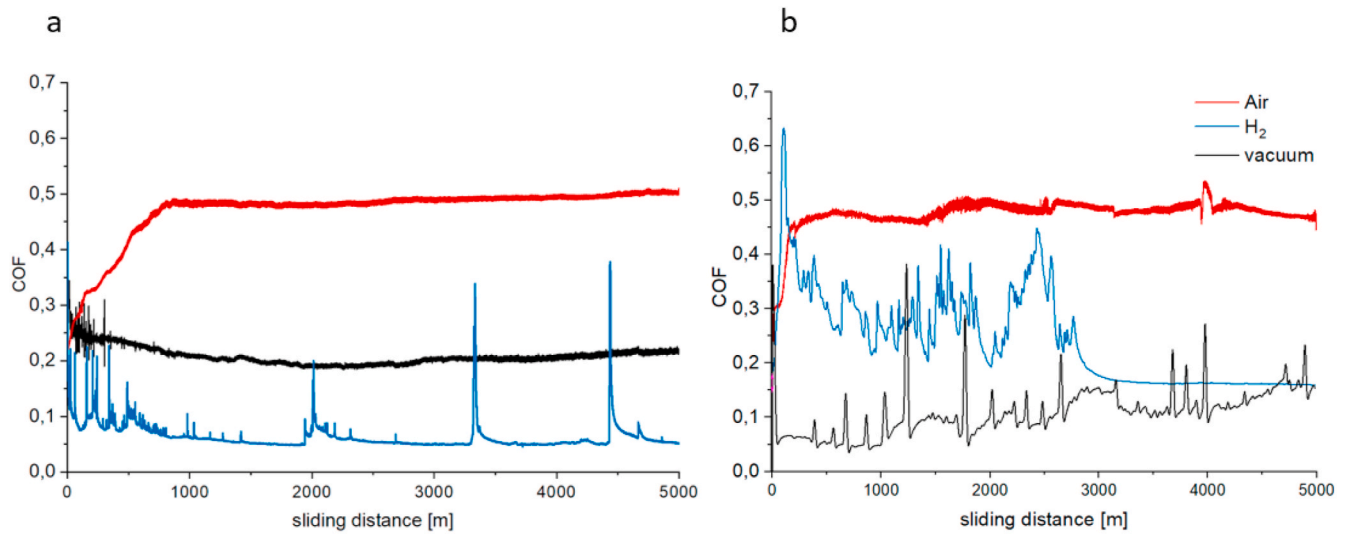


Fig. 1. Friction of PI against a) 52100 and b) 304 at $v = 0.2$ m/s and 50 N.

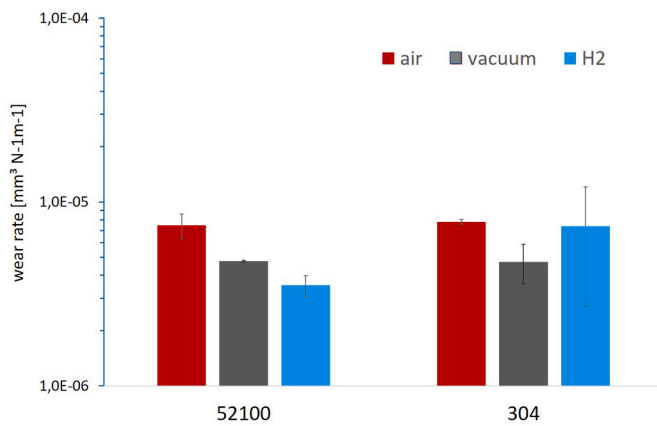


Fig. 2. Wear rate of PI against 52100 a) and 304 b) at $v = 0.2$ m/s, 50 N.

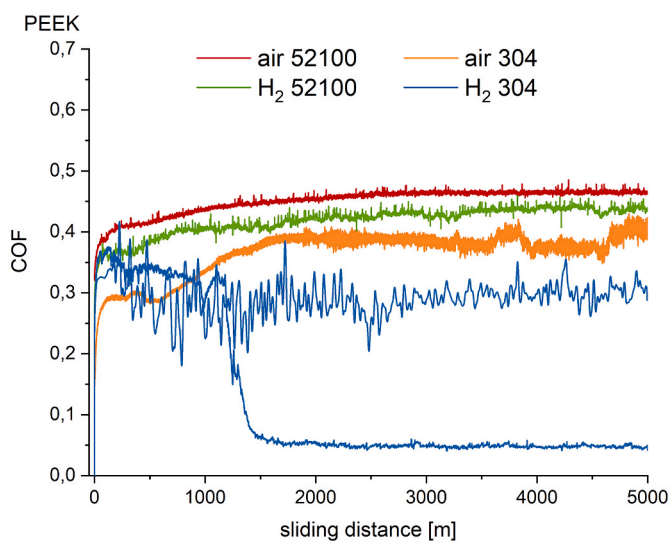


Fig. 3. Friction progression of PEEK against 52100 and 304 in air and hydrogen at $v = 0.2$ m/s.

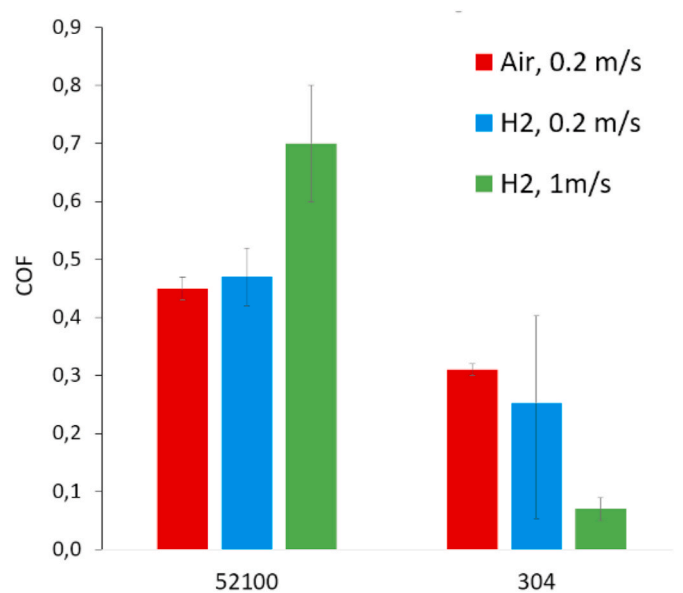


Fig. 4. Average coefficient of friction of PEEK against 52100 and 304 in air and hydrogen.

adhesion of the transfer film is hindered.

Since friction and wear of PI are independent of the counterface material in air and vacuum, it follows that the effect in hydrogen environment is related to the chemical nature of the steel rather than the thermal conductivity and/or hardness properties of the disc. The low thermal conductivity of 304 isn't an important factor in the test conditions, certainly due to the high glass transition temperature of PI (above 330 °C).

Concerning PEEK, the friction coefficient and wear rate are lower against stainless steel in air and in hydrogen. Optical microscopy images of the discs after experiments in air (Fig. 10) show lumpy polymer particles on the 52100. These are matrix particles related to adhesive wear of pure polymer. Thin black and brown transfer is observed on the 304 counterface. As mentioned in Ref. [21], thin PEEK films can form by shearing of debris under localized heating. The lower thermal conductivity of the 304 may induce softening of PEEK, which has a transition temperature at 140 °C, producing this transfer film due to the decrease of interfacial shear strength.

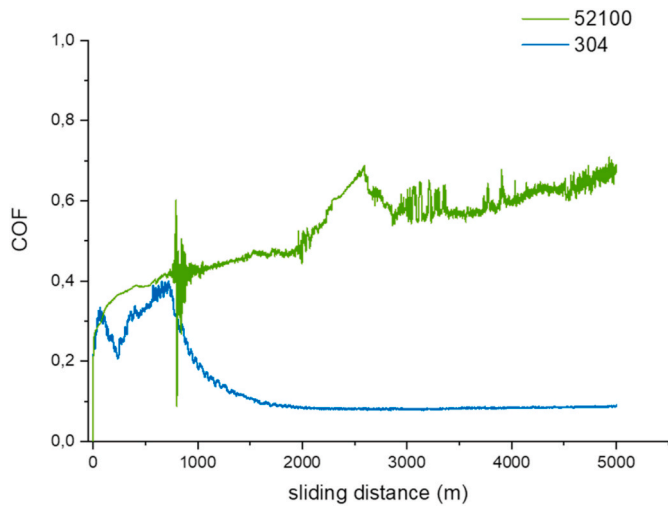


Fig. 5. Friction progression of PEEK against 52100 and 304 in hydrogen at $v = 1$ m/s.

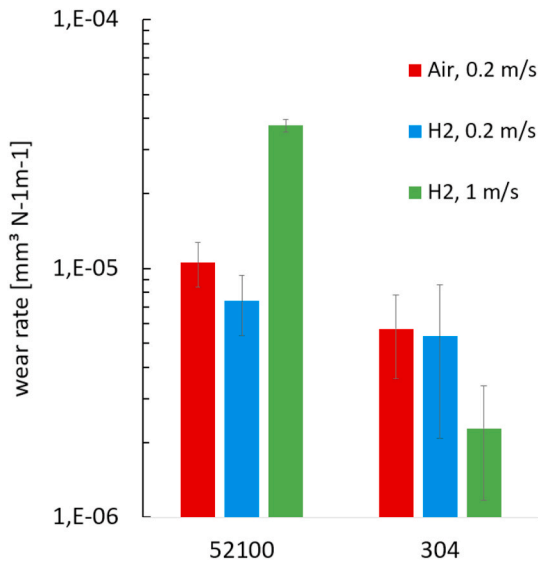


Fig. 6. Average wear rate of PEEK against 52,100 and 304 in air and hydrogen.

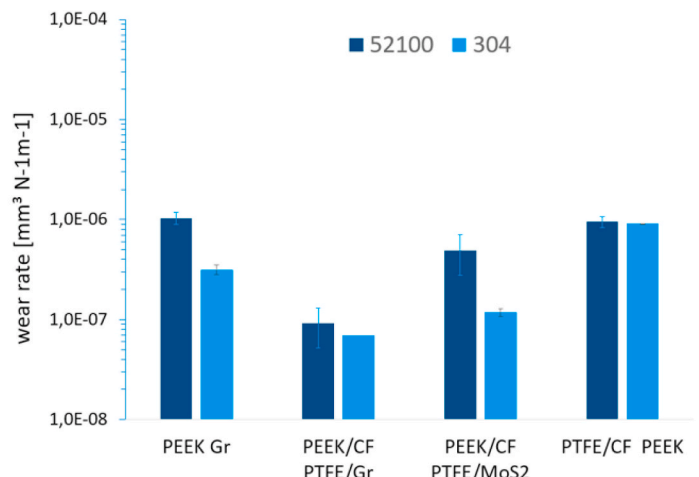
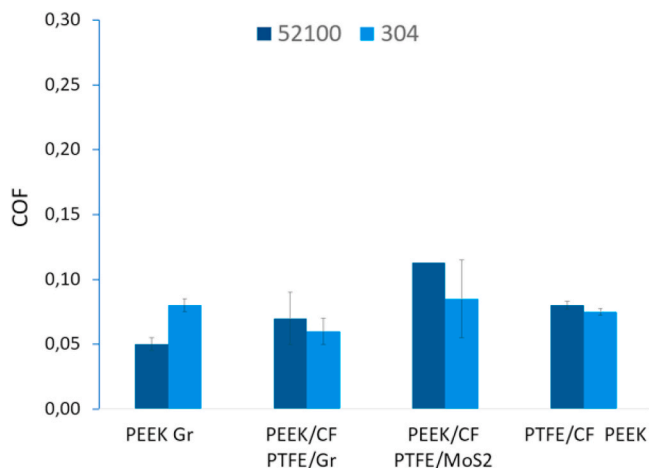


Fig. 7. Average coefficient of friction and wear of PEEK composites in hydrogen at $v = 0.2$ m/s.

While the friction coefficient against 52100 is relatively constant at 0.4, two friction mechanisms appear against 304 in hydrogen. Surface analyses of 304 counterface after experiments in hydrogen are shown in Fig. 11. High friction is associated with partial transfer and isolated polymer debris on the disc, while the formation of a homogenous transfer film gives rise to low friction in hydrogen environment. In both cases, tests were performed in the same tribometer, with the same pin configuration and parameters.

FT-IR analyses of the PEEK transfer film after tests in hydrogen are given in Fig. 12. Spectra have been separated for visibility purpose. No peak variation could be observed between high and low friction in hydrogen. This indicates that no chemical reactions appear with PEEK in hydrogen, but that the transfer film formed is mainly due to softening of the polymer.

One possible explanation for these two phenomena may be a friction transition at $PV = 0.6$ MPa m/s, where P is the contact pressure [MPa] and V the sliding velocity [m/s]. Experiments performed at higher velocity support this assumption. Surfaces of the discs after tests at 1 m/s are shown in Fig. 13.1a–1b. The low friction of PEEK against 304 is associated with a homogenous transfer film (Fig. 13.1b). The worn pin surface is covered by black transfer and characterised by material flow and deformation, indicating softening of the polymer (Fig. 13.2b).

Against 52100 discs, filaments of PEEK debris, which have been rolled during tests, are observed on the discs (Fig. 13.1b) and on the surface of the worn pin. Rod-like debris have been detected at similar PV conditions in air by [22]. These rolled debris are also seen on the surface of the worn pins, which presents further mild abrasive wear (Fig. 13.2a).

It is therefore suggested that 304 disc improves the sliding performance of PEEK compared to 52100 primarily due to the low thermal conductivity of the disc, promoting softening of PEEK and transfer film formation.

As shown in Fig. 7, friction and wear values of composites are more stable compared to unfilled polymers. This is obviously due to the presence of solid lubricants (such as graphite, MoS₂ and PTFE) that promotes the formation of transfer film. As seen in Fig. 14d, the transfer film formed with PTFE composite is similar on both counterfaces, which corresponds to comparable friction and wear results. Due to its unique band structure, PTFE can easily transfer on both steel discs. Concerning PEEK composites, transfer film is also observed on both discs, but 304 steel seems to promote a thinner layer than 52100 disc does (Fig. 14 a, b, c).

SEM analyses of the transfer layer after tests in hydrogen against PEEK/CF/PTFE/MoS₂ emphasize the discrepancies between the two steel discs (Fig. 15). As for unfilled PEEK, the transfer film on 52100 consists mainly of large polymer debris (Fig. 15a), while fine stretched polymer transfer is seen on 304 (Fig. 15b). This may explain why the

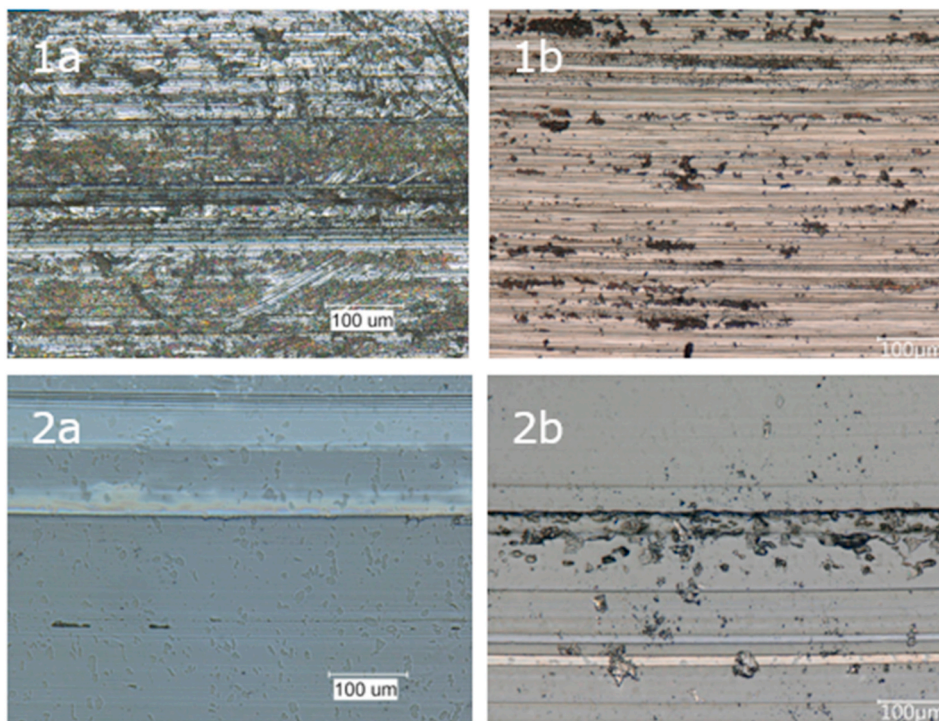


Fig. 8. Optical microscopy images of the discs (1) and PI pins (2) after tests performed in hydrogen at $v = 0.2$ m/s and 50 N against (a) 52100 and (b) 304.

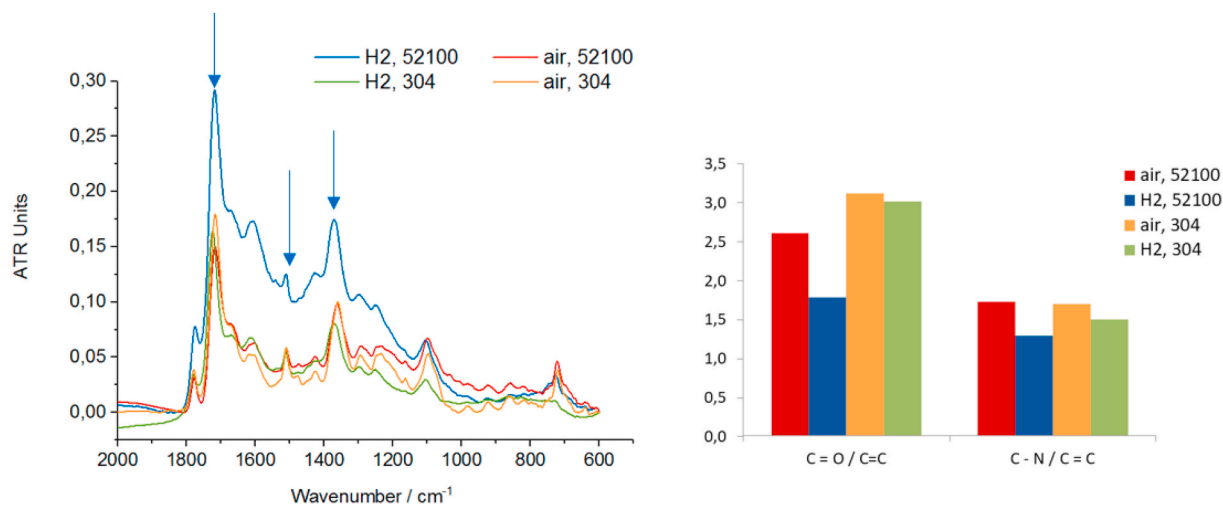


Fig. 9. FT-IR spectra of PI transfer film against 52100 and 304 in air and in hydrogen at $v = 0.2$ m/s, 50 N.

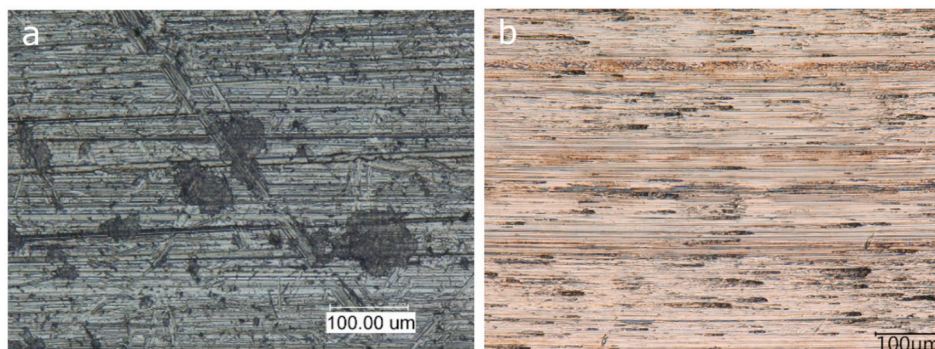


Fig. 10. Optical microscopy images of the steel disc after tests against PEEK performed in air against a) 52100 and b) 304.

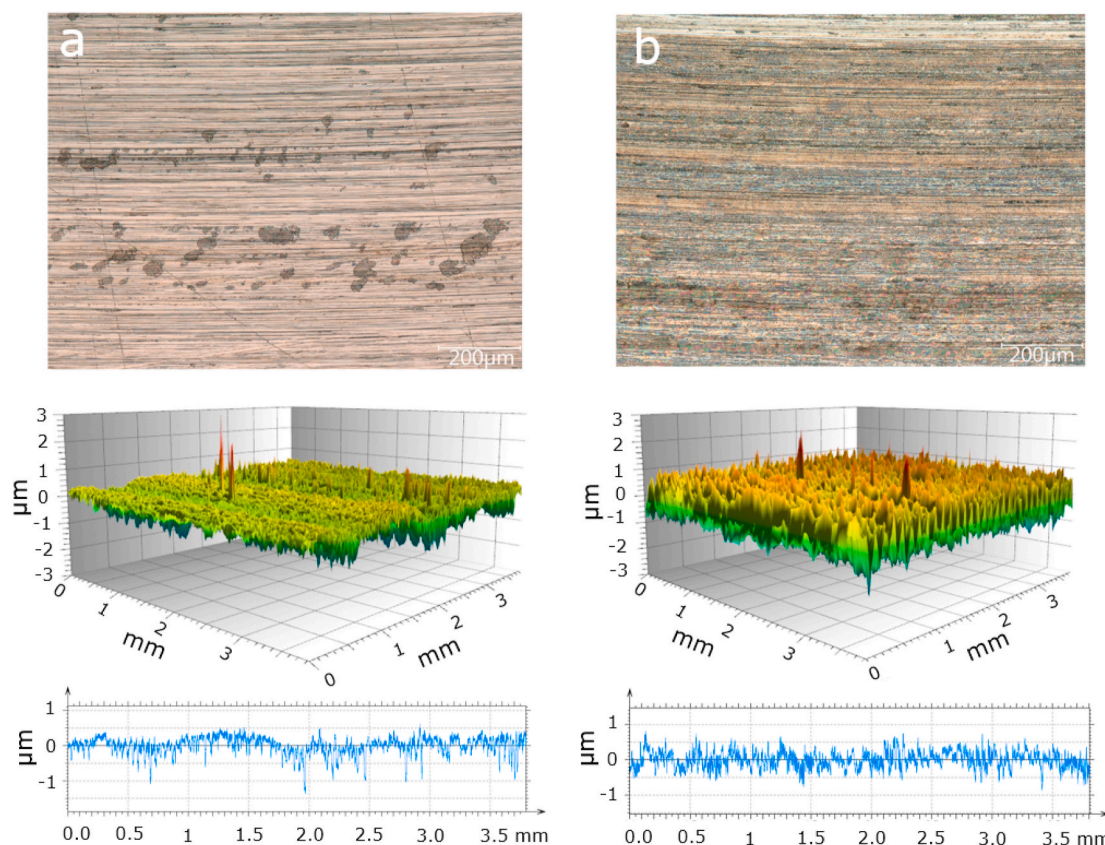


Fig. 11. Optical microscopy images and topography of the 304 steel disc after tests performed in hydrogen with PEEK a) high friction, b) low friction, at $v = 0.2$ m/s, 50 N.

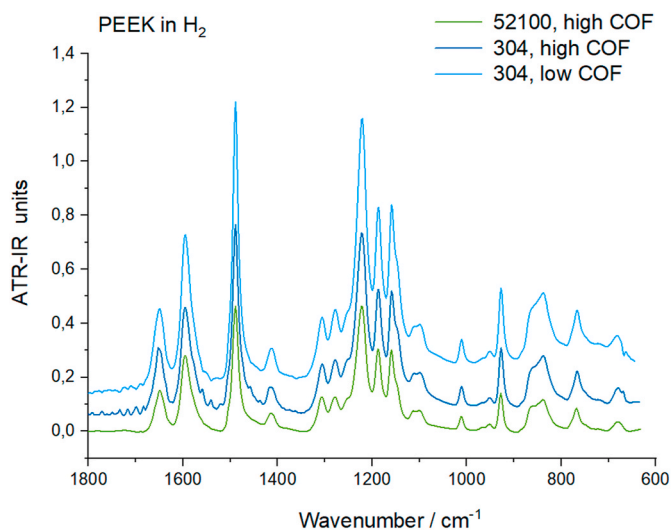


Fig. 12. FT-IR spectra of PEEK against 52100 and 304 in hydrogen at $v = 0.2$ m/s, 50 N.

friction and wear rate are higher against 52100 disc. It is noticeable that MoS_2 is mainly detected within the polymer matrix, whereas PTFE is spread all over the counterface.

As mentioned before, the performance of PEEK composites in hydrogen is improved against 304 steel discs, except for PEEK Gr which shows a high friction coefficient against 52100 on both discs. Jacobs et al. [17] found that Martensitic 52100 is particularly disadvantageous in air when the compound contains chemically active fillers like CF,

MoS_2 or graphite, while austenitic stainless steel produces far lower composite wear. He suggested that 52100 tends to tribo-corrosion in the sliding contact preventing the formation of stable transfer films. This process can be promoted by catalytically active fillers. In hydrogen environment, however, no tribo-corrosion should appear, therefore transfer film is seen on both discs. But the transfer film is thicker on the bearing steel. A content of some ppm of water in the environment may be enough to induce some corrosion. The influence of traces of water in hydrogen on the tribological performance of materials was also proven by other authors [23–24].

4. Conclusions

This paper focuses on the influence of the counterface materials on the sliding behaviour of polymer materials in hydrogen. PI, PEEK and PTFE materials were tested against hardened 52100 martensitic bearing steel and 304 austenitic stainless steel in high purity hydrogen environment (99.999% H_2). The following conclusions can be drawn:

- In comparison to air, unfilled polymers have better performance in hydrogen environment against both counterfaces, especially PI that is environment sensitive;
- The tribological performance of polyimide in hydrogen is better against 52100 than against 304. The influence of the counterface in hydrogen environment is related to the chemical nature of the steel, 52100 disc promotes chemical reactions that enhance the transfer film adhesion.
- Improved sliding behaviour of unfilled PEEK is observed with 304 counterface compared to 52100, particularly at higher sliding speed. This is due to the low thermal conductivity of the disc, that promotes softening of PEEK and transfer film formation.

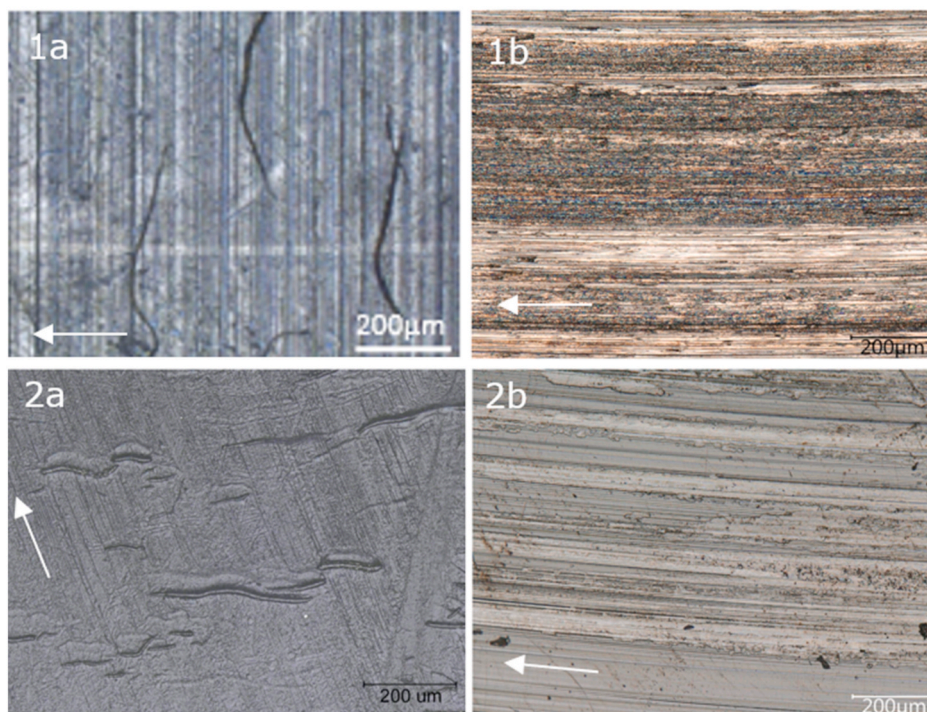


Fig. 13. Optical microscopy images of the discs (1) and pins (2) after tests performed in hydrogen with PEEK at $v = 1$ m/s and 50 N against (a) 52100 and (b) 304.

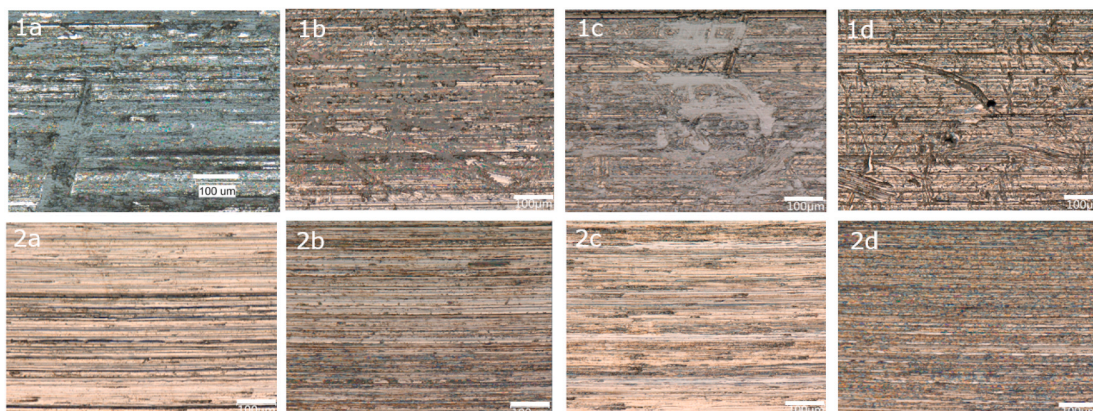


Fig. 14. Topography of the counterface 52100 (1) and 304 (2) after tests performed in hydrogen against a) PEEK Gr b) PEEK CF/PTFE/Gr c) PEEK CF/PTFE/MoS₂ d) PTFE PEEK/CF.

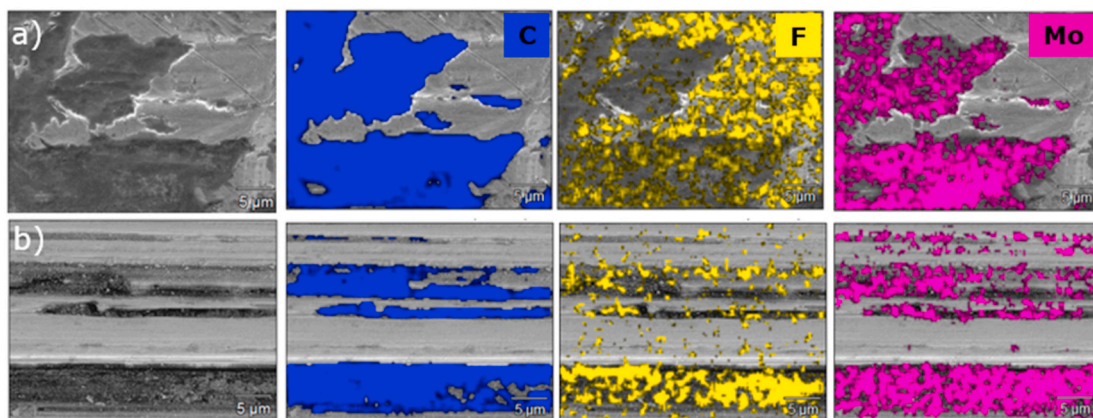


Fig. 15. SEM and EDX analyses of the transfer film of PEEK CF/Gr/MoS₂ after tests against a) 52100 and b) 304.

- Similarly, the tribological behaviour of PEEK composites in hydrogen is improved against 304 steel discs, although the influence of the counterface material is less pronounced than with unfilled PEEK due to the presence of solid lubricants-rich transfer on both discs.
- The influence of the counterface material wasn't observed for PTFE material that transfers on both discs.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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