Sliding performance of polymer composites in liquid hydrogen and liquid nitrogen

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Outstanding features favour the application of polymers and polymer composites in low-temperature technology. The booming hydrogen technology is a challenge for these materials, which are considered as seals and bearings in cryogenic pumps. In the present study, three types of thermoplastics, i.e., polyetheretherketone (PEEK), polyetherimide (PEI) and polyamide 6,6 (PA6,6), and one epoxy were considered as matrix materials. Micron-sized fillers, i.e., short carbon fibres, graphite flakes, and PTFE powders, were incorporated into these polymers together with nano-sized TiO_2 particles. Optimised compositions of each matrix were selected from our previous works at room temperature in order to be studied at very low temperature conditions. In particular, frictional tests were carried out with polymer composite pins against polished steel surfaces under constant load over a certain distance in liquid hydrogen and liquid nitrogen. Afterwards, worn surfaces were analysed by using scanning electron microscopy (SEM). It was found out that the tribological properties in liquid hydrogen are dominated by the matrix materials, in particular thermoplastics perform generally slightly better than thermosetting resins.
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1. Introduction

Outstanding features favour the application of polymers and polymer composites in low-temperature technology. The high specific strength and stiffness, the high fatigue life, the low thermal conductivity, the electrical insulation capability and special features of thermal expansion behaviour are some of the advantages for their cryogenic use. Liquid hydrogen is considered to be the new generation of clean and renewable energy source instead of gasoline in the transportation business. Lightweight pressure vessels for storage and transportation of liquefied gases became increasingly interesting for ground and air vehicles recently. Many automobile and related companies are examining the new generation hydrogen vessels, e.g., for cars, buses, and aircrafts [1, 2]. The booming hydrogen technology is a great challenge for the materials science community to prove that their materials are able to operate at the required low temperature and medium conditions [3, 4]. Polytetrafluoroethylene (PTFE)-based and other polymer-based materials were successfully demonstrated in rockets and other space applications, where they were commonly used in cryogenic machines as axial or radial shaft seals and piston seals in cryogenic pumps, piston-type low-temperature air-driven

engines and radial roller bearings [5–9]. However, for space applications, the lifetime is usually limited to only a few minutes, whereas propulsion units for aircraft, ground and air vehicles with hydrogen engines have to work for more than 40,000 h. Therefore, the long-term behaviour of such materials at related temperatures and media has to be investigated in more detail, which is very important to the safety in hydrogen technology.

Regarding the friction and wear properties of polymers and composites at low temperatures, not much research has been undertaken so far. In the early 1960s, most research on friction and wear at low temperatures was done in connection with space applications by NASA Lewis Research Centre *et al.* [9]. PTFE and its composites were successfully used for space rockets. In the last two decades, more research on this topic was attributed to the application of superconducting magnetic winding systems. Iwasa *et al.* [10–13] built both a 'pin-on-disk' rotational and a linear friction apparatus to produce and observe frictional sliding between several metal/insulator pairs at 4.2 K in liquid helium, which are the service condition for magnet application. This investigation has been used for selecting proper materials of low slip heat as insulator for the
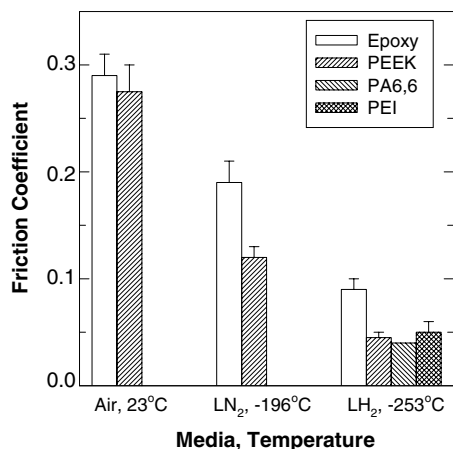
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Figure 1 Summary of friction coefficient of different matrix composites in liquid hydrogen and liquid nitrogen (LH$_2$ indicates liquid hydrogen, and LN$_2$ for liquid nitrogen).
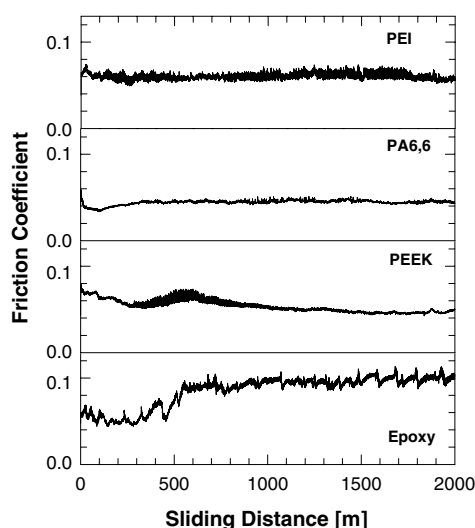

Figure 2 Dependence of friction coefficient on sliding distance of all four kinds of materials in liquid hydrogen.

superconducting winding system. A further investigation has been performed by Lipski *et al.* [14] to measure the linear coefficient of friction of several good radiation resistant insulators in a vacuum and 77 K environment. Nishijima *et al.* [15] compared the friction and wear characteristics of copper slid against a traditional G-10 composite (glass fibre reinforced epoxy) at 77 K. However, the low-temperature friction and wear behaviour of polymers and composites has not been studied extensively. Most recently, a series of 'Cryotribometers,' allowing various methods of cooling and load application as well as different input energies, were built at the Federal Institute for Materials Research and Testing (BAM), Berlin, in order to evaluate the friction and wear behaviour of materials at temperatures down to 4.2 K [16–19]. Their research concentrated on the lubrication and friction of suitable material combinations for sliding seals, injection valves and regulating valves, which will be used in liquid hydrogen pumps and other hydrogen driven engines.

In the present study, three types of thermoplastics and one epoxy resin, all modified with different types of fillers, were tested with regard to their frictional be-

haviour against steel at various temperatures and media, using the hydrogen laboratory facilities of BAM. Worn surfaces were analysed by scanning electron microscopy (SEM), and possible wear mechanisms were discussed.

2. Experimental details
2.1. Materials
For the matrix materials, three types of thermoplastics, i.e., PEEK (Victrex, 450G), PEI (Ultem 1000), and PA6,6 (DuPont, Zytel 110), were applied. An epoxy resin (Dow DER 331) cured by a polyamine hardener (Dow HY 2954) was also considered.

In order to improve the friction and wear behaviour of polymeric materials, one of the traditional concepts is to reduce their adhesion to the counterpart material and to enhance their hardness, stiffness and compressive strength [20, 21]. Internal lubricants such as PTFE and graphite flakes are frequently incorporated. Short carbon fibres (CF) are able to increase the creep resistance and the compressive strength of the polymer matrix system used. Inorganic nanoparticles are also promising for new processing routes of wear resistant materials. Therefore, all these fillers were considered. Optimised compositions of each matrix were selected from our previous works at room temperature [22–24]. Details of the compositions applied in the present study are given in Table I. Pitch-based short carbon fibres (Kureha M-2007S), PTFE powders (Dyneon 9207) and graphite flakes (Superior 9039) were selected as traditional fillers, which were all micron-sized. The average diameter of short carbon fibres was approximately 14.5 μm, with an average fibre length of about 90 μm. The particle size of PTFE amounted to 4 μm, whereas that of the graphite flakes was around 20 μm. TiO$_2$ (Kronos 2310) with an average diameter of 300 nm was also applied as an additional nano-size filler.

All three thermoplastic composites were compounded using a Berstorff twin-screw-extruder (screw diameter $=$ 25 mm, screw aspect ratio $L/D=44$), and finally manufactured using an Arburg All-rounder injection-moulding machine [22]. Wear test specimens were cut from 80 $\times$ 80 $\times$ 4 mm^3 injected plates. The epoxy composites were prepared by mechanical mixing using a commercially available laboratory mixing device [23, 24]. The mixture was then filled into 10 mm thick moulds for curing. Test specimens were machined from the cured composite plates.

TABLE I Details of polymer composites considered in the present study[a]

Matrix	Short carbon fibre (vol%)	Graphite (vol%)	PTFE (vol%)	TiO$_2$ (300 nm) (vol%)
Epoxy	15	15	0	5
PEEK	15	5	5	0
PA	15	5	0	5
PEI	5	15	0	5

[a]Optimised compositions selected from previous works of each matrix at room temperature [22–24].

2.2. Wear test

Wear specimens were finally cut to a length of 12 mm and a cross section (≈apparent contact area) of 4×4 mm^2. Unlubricated sliding wear tests were carried out on a pin-on-disc apparatus designed and constructed at the BAM, Berlin [16–19]. A hardened and polished carbon steel disc (German Standard 100Cr6) with a radius of 16.5 mm and an initial surface roughness of Ra = 50 nm served as counterpart. The sliding speed and the contact load were kept constant at 0.2 m/s and 50 N, respectively, and the total sliding distance was 2000 m for all measurements. The friction coefficient was monitored as a ratio of the tangential force to the normal contact load applied. Liquid nitrogen and liquid hydrogen served as cryogenic media, in which specimens and counterparts were submerged during the whole sliding period. Only two specimens were tested for each measurement due to the expense of the liquid hydrogen. A scanning electron microscope (SEM, Jeol-5400) was applied to analyse the worn surfaces, after they were coated with a thin gold layer.

3. Results and discussions

Fig. 1 summarizes the results of the friction coefficient of various polymer matrix composites as a function of various temperatures and media. It was found that the friction coefficients of all composites were reduced with a reduction in testing temperature. The possible reasons may be due to: (1) the increase of stiffness of the polymer composites at low temperatures [25, 26]; and (2) the liquid lubricating effect of the cryogenic media (either liquid nitrogen or liquid hydrogen) between the two contact partners. The first effect can reduce the deformation of the polymer composite pins when being in contact with the metal counterpart under a certain load, which, in turn, can reduce the real contact area of the two counterparts. The second effect can probably form a thin liquid (or even partly gaseous) lubricating film between the two counterparts [16], thus contributing to a reduction of the shear stresses during sliding. Besides these interpretations, it can be found from Fig. 1 that the friction coefficient seems to be dominated by the polymer matrix, in which the thermoplastics i.e., PEEK, PEI, and PA6,6, generally perform better than
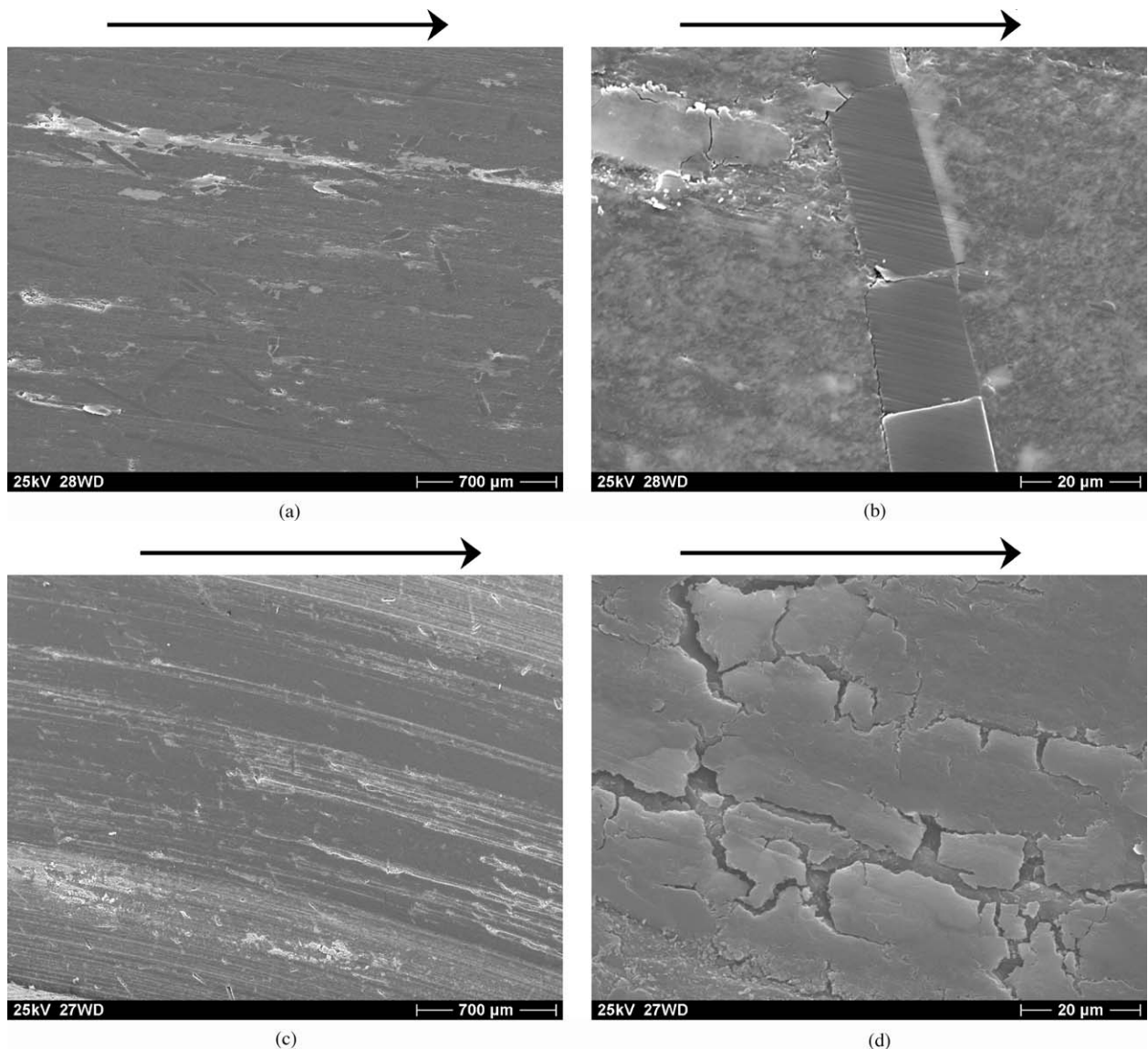

Figure 3 (a, b) SEM worn surfaces of epoxy matrix composite at room temperature, (c, d, e) in liquid nitrogen ($-196°$C) and (f, g) in liquid hydrogen ($-253°$C). The arrow lines indicate the sliding directions. (*Continued*)
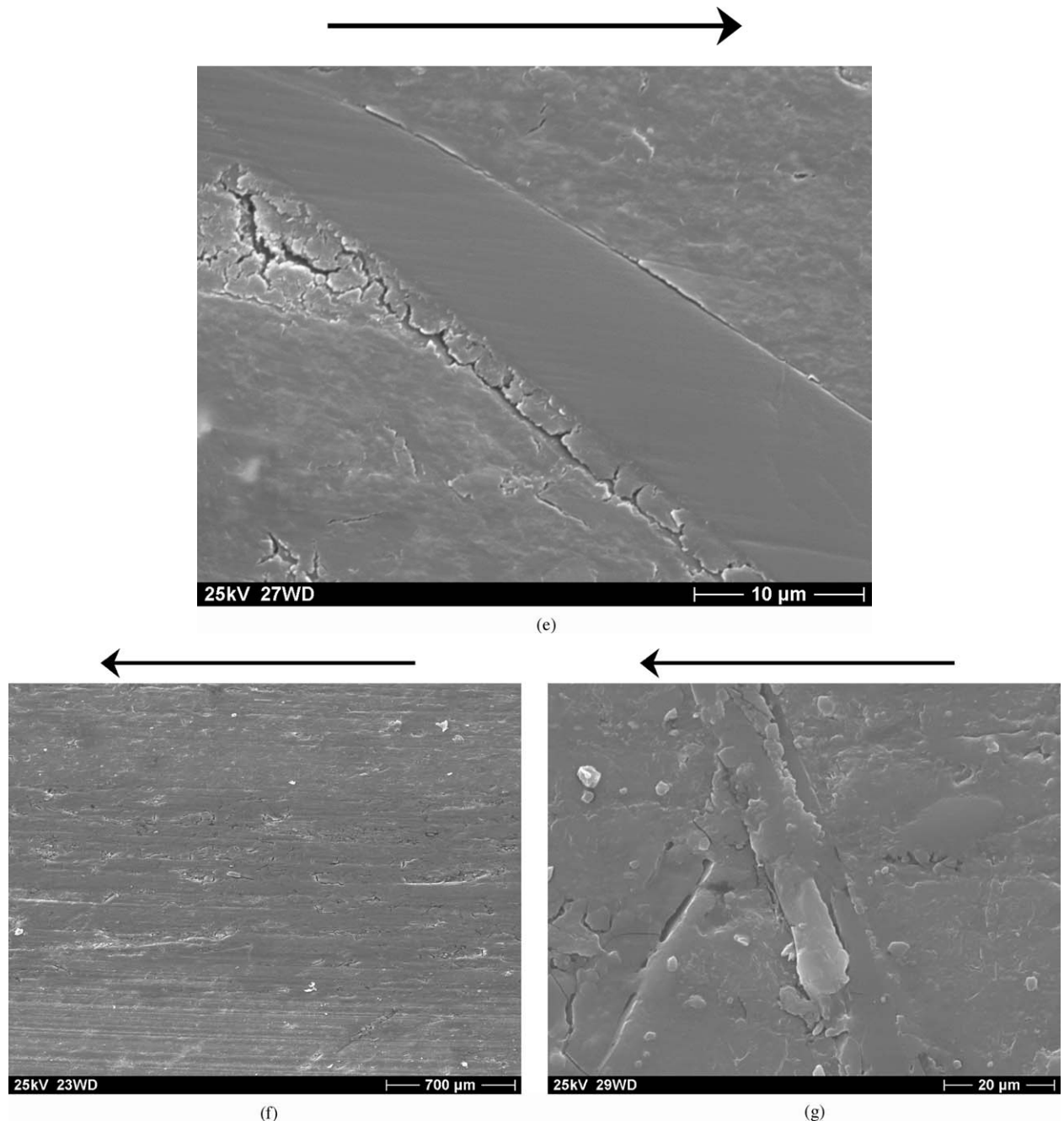
(e)

(f)

(g)

Figure 3 (*Continued*).

the thermosetting resin, in spite of similar filler types and amounts. The reason for this is probably due to the fact that thermoplastics still maintain a better toughness in comparison to thermosetting resins, even though it is generally reduced at lower temperatures in both cases. Details can be also recognized later from the SEM analyses of the worn surfaces.

Fig. 2 plots the dependencies of the friction coefficient on the sliding distance of all four kinds of materials, when being measured in liquid hydrogen. At the beginning of the tests, all the friction coefficients started on a similar scale ($\mu \approx 0.06$), which can be explained by the fact that the liquid medium between the counterparts acted as an initial lubricating agent. After a while, however, it can be assumed that also the specific properties of the polymer composite materials, due to some wear phenomena occurring, would come into play. In this case, the dependence of the friction coefficient on the sliding distance was slightly different for the thermoplastic matrix composites, compared to the thermosetting one. Generally the friction coefficients did not exhibit any increase during the whole sliding distance for the thermoplastic composites, which was even reduced for PEEK and PA6,6. Conversely, the epoxy composite displayed a considerable increase of the friction coefficient from 0.06 to around 0.1 after sliding of about 500 meters. The frictional curve was also accompanied with serrated vibrations in case of the epoxy system. An increased roughening caused by the surface damage may be the reason of this phenomenon.

Figs 3–6 present SEM observations of the worn surfaces of different matrix composites subjected to sliding conditions in the two cryogenic media at their liquefaction points. The arrow lines indicate the sliding directions. It is well known that the fibre thinning, cracking and peeling-off are dominant mechanisms
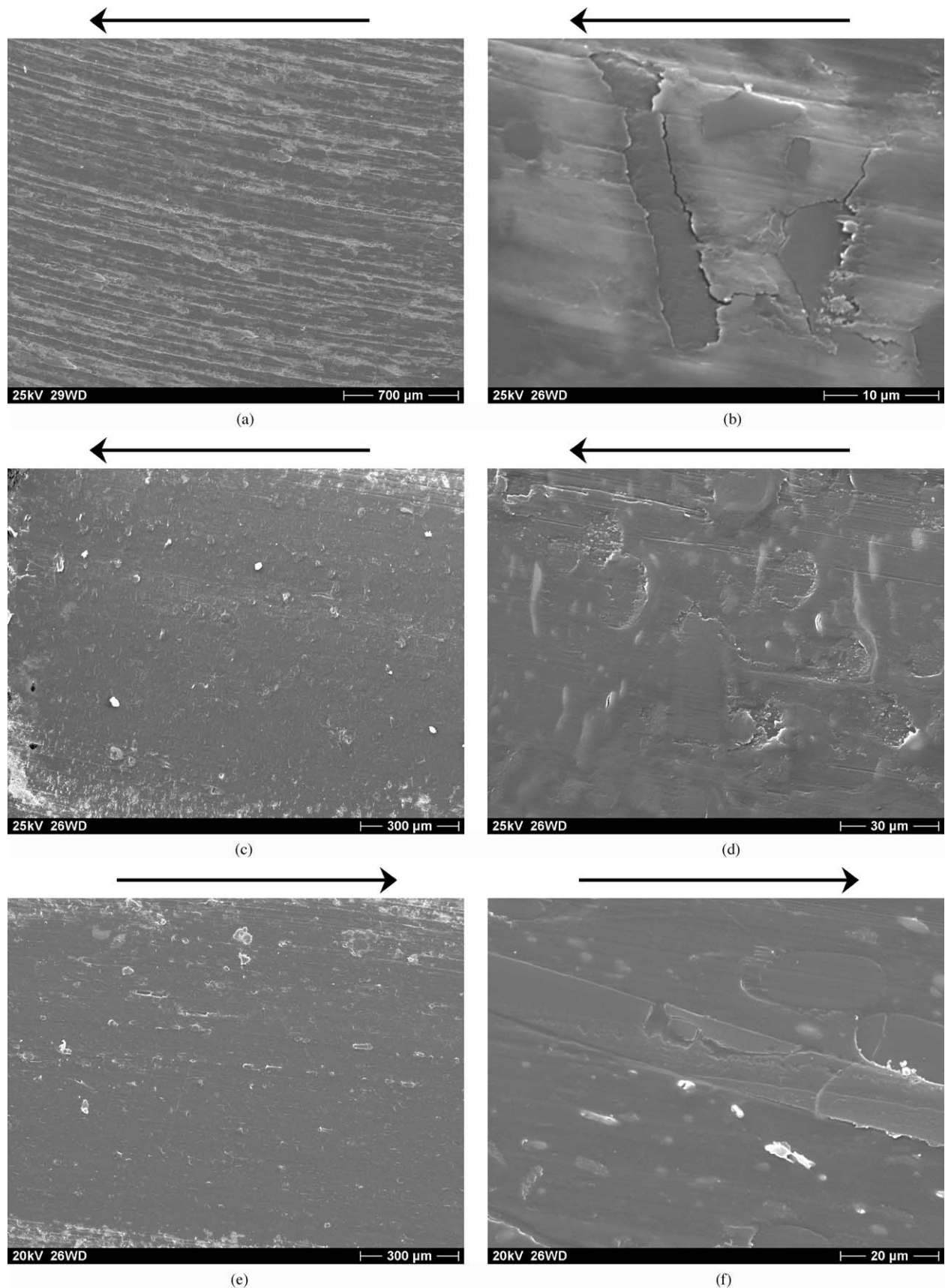
Figure 4 (a, b) SEM worn surfaces of PEEK matrix composite at room temperature, (c, d) in liquid nitrogen ($-196°$C) and (e, f) in liquid hydrogen ($-253°$C). The arrow lines indicate the sliding directions.

which govern the wear process of short carbon fibre reinforced polymer composites [20]. Incorporating nano-size TiO_2, the epoxy matrix composite displayed better wear resistance, for which relatively smooth worn surfaces could be recognized [23], as also shown

in Figs 3a and b for dry sliding conditions at room temperature of this study. One fact is, that less fibre matrix debonding and matrix damage took place. In addition, nanoscale wear scratches can be observed on the short carbon fibres in Fig. 3b, in which a rolling effect of the
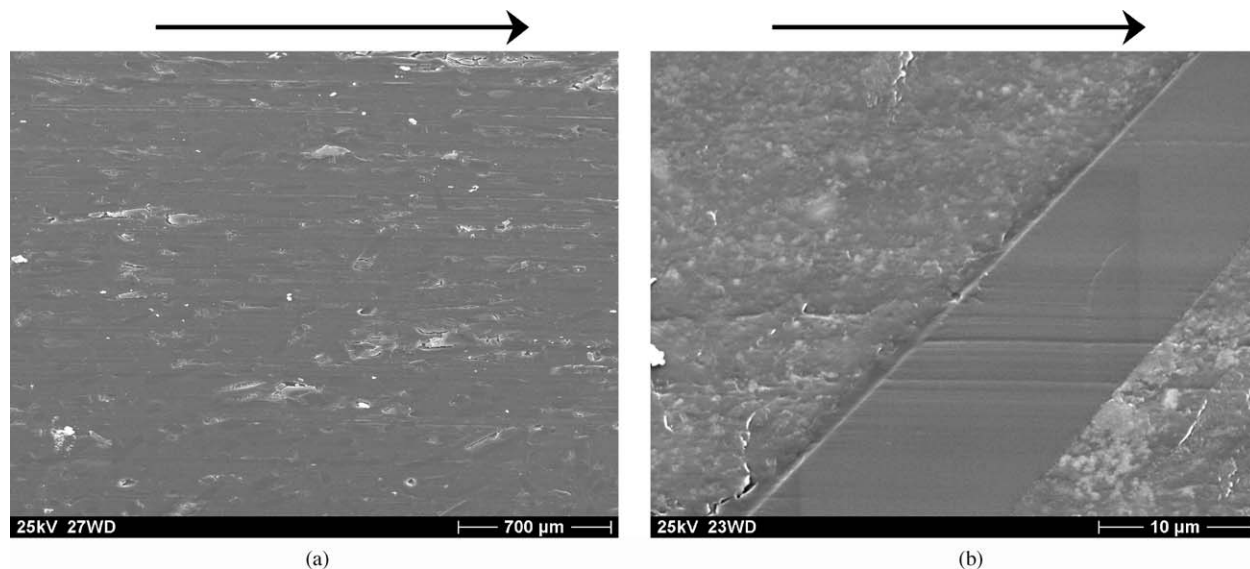
Figure 5 (a, b) SEM worn surfaces of PEI matrix composite in liquid hydrogen (−253°C). The arrow lines indicate the sliding directions.
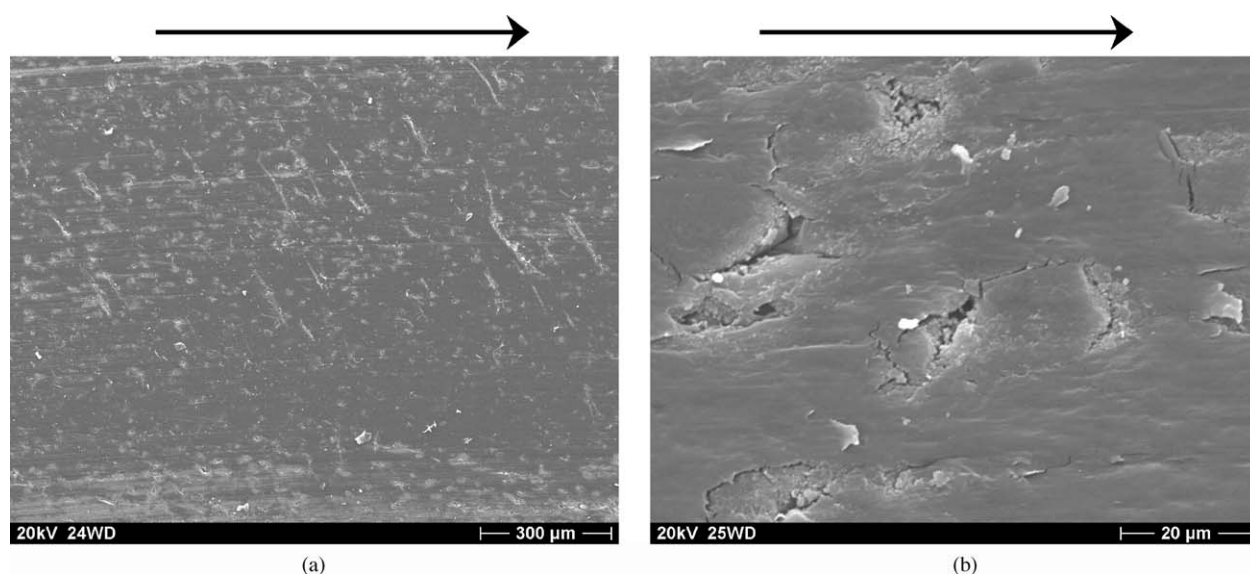

Figure 6 (a, b) SEM worn surfaces of PA6,6 matrix composite in liquid hydrogen (−253°C). The arrow lines indicate the sliding directions.

nanoparticles, acting on a nanoscale level, may be of help to protect the worn surface of the composites from more severe wear mechanisms [23, 24]. When this material was tested in cryogenic media (liquid nitrogen or hydrogen), however, much more matrix damage could be observed on the worn surfaces (Fig. 3c–g), which seems to be a result of the embrittlement of the epoxy at low temperatures. The friction coefficient was reduced compared to that at room temperature, mainly due to the liquid lubricating effect of the cryogenic media.

Concerning the PEEK matrix composite, the worn surfaces at room temperature (Fig. 4a and b) seem to be not as smooth as those of the epoxy composites, which may be due to a stronger adhesion effect of the PEEK matrix. However, in both liquid nitrogen (Fig. 4c and d) and hydrogen (Fig. 4e and f), the worn surfaces of the PEEK composites look much smoother than that of the epoxy resin. Only very few fibre matrix debonding and matrix damage events can be found. PEEK still maintains a much better toughness, so that the wear resistance of its composites is definitely better than that of the epoxy one in the cryogenic media.

In the cases of the other two thermoplastic matrix composites (PEI and PA6,6), PEI composites exhibited smoother worn surfaces (Fig. 5a and b) in liquid hydrogen. Even the PA6,6 matrix composite gave the lowest friction coefficient in liquid hydrogen for all composites considered. However, the worn surface analyses (Fig. 6a and b) indicated that the wear property of PA6,6 may be not as good as that of other two thermoplastic composites, e.g., PEEK and PEI. The relatively poor mechanical properties of PA6,6 at cryogenic temperatures might be the reason [25].

4. Conclusions

Based on this work devoted to investigating the sliding performance of different polymer matrix composites in liquid hydrogen and liquid nitrogen at their liquefaction points, the following conclusions can be drawn:

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- In liquid hydrogen media, the tribological property is dominated by matrix materials, in which thermoplastics perform generally slightly better than thermosetting.
- PA6,6 matrix composite displayed the lowest friction coefficient in liquid hydrogen. However, the worn surface analyses indicated that the wear property of PA6,6 may not be as good as that of other thermoplastics, e.g., PEEK and PEI, probably due to the relatively poor cryogenic properties of PA6,6.

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