POLYMER COMPOSITES FOR TRIBOLOGICAL APPLICATIONS IN HYDROGEN ENVIRONMENT

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ABSTRACT

In the development of hydrogen technology, special attention is paid to the technical problems of hydrogen storage. One possible way is cryogenic storage in liquid form. Generally cryotechnical machines need components with interacting surfaces in relative motion such as bearings, seals or valves, which are subjected to extreme conditions. Materials of such systems have to be resistant to friction-caused mechanical deformation at the surface, low temperatures and hydrogen environment. Since materials failure can cause uncontrolled escape of hydrogen, new material requirements are involved for these tribo-systems, in particular regarding operability and reliability. In the past few years several projects dealing with the influence of hydrogen on the tribological properties of friction couples were conducted at the Federal Institute for Materials Research and Testing, (BAM), Berlin. This paper reports some investigations carried out with polymer composites. Friction and wear were measured for continuous sliding and analyses of the worn surfaces were performed after the experiments. Tests were performed at room temperature in hydrogen as well as in liquid hydrogen.

INTRODUCTION

Hydrogen as an environmentally friendly energy carrier plays a central role in future energy supply and transport systems. In the development of hydrogen technology it is necessary to have a large number of materials for safe, reliable, and enduring service. In respect of reliable operation in hydrogen environment, components with moving parts like bearings, or valves are critical. Problems are caused by hydrogen embrittlement, removal of protective oxide layers, and extreme low temperatures in the case of liquid hydrogen.

Polymers and polymer composites are widely used as dry sliding materials in friction assemblies, where external supply of lubricants is impossible or not recommended. The field of application of self-lubricating materials in tribological systems is considerably extending. Over the years, composite materials have replaced many traditional metallic materials for sliding components. These offer not only light weight and corrosion resistance but also excellent tribological properties.

In hydrogen technology, fibre reinforced polymer composites are prime candidates. They are used in lightweight pressure vessels for storage and transportation of liquefied gases. However, tribological experimental data of materials in hydrogen and at low temperatures are hardly available due to cost and safety reasons. The hydrogen laboratory of BAM is equipped with special facilities for investigating friction and wear behaviour of materials in liquid and gaseous hydrogen environment.

This paper reports some investigations carried out with 12 composites in hydrogen environment. The influence of the hydrogen medium on the tribological properties of friction couples was investigated with experiments at room temperature and at -253°C.

EXPERIMENT

Materials

12 polymer composites were selected according to their good tribological properties at room temperature; most of the materials were chosen in collaboration with the Institute for Composite Materials (IVW, Kaiserslautern). An overview of the compositions is given in table 1. For the tribological experiments, AISI 52 100 steel discs were used as counterface. It is the most frequently used steel for bearing applications.

Table 1: Material compositions (vol %)

Name	Matrix		Fibers	Fillers and lubricants
A	PEEK	polyetheretherketone	10% CF	10% PTFE + 10% MoS_2
B	PI	polyimid		15% MoS_2
C	PEEK	polyetheretherketone	13% CF	10% PTFE
D	PTFE	polytetrafluoroethylene	18,2% CF	13,5% PEEK
E	PTFE	polytetrafluoroethylene	16,7% CF	9,2% bronze
F	PTFE	polytetrafluoroethylene		20% PPS
G	PA6.6	polyamide		30% PTFE
H	PEEK	polyetheretherketone	10% CF	10% PTFE + 10% graphite
I	PEEK	polyetheretherketone	15% CF	5% PTFE + 5% graphite
J	EP	epoxy	15% CF	5% TiO_2 + 15% graphite
K	PEI	polyetherimide	5% CF	5% TiO_2 + 15% graphite
L	PA	polyamide	15% CF	5% TiO_2 + 5% graphite

Experiments

Tribological tests were carried out at room temperature in air and hydrogen gas as well as in liquid hydrogen as shown in table 2. The BAM tribometers CT2 and CT3 used in this study are described in detail in [1]. Both cryotribometers are thermally insulated by vacuum superinsulation and cooled directly by a bath of liquid cryogen (CT2, Figure 1) or by a heat exchanger (CT3). Each experiment was repeated two or three times. The test parameters are indicated in table 3.

Table 2: Environmental medium

Medium	Air	Helium	Hydrogen	Hydrogen
Temperature	~ 20°C	~ 20°C	~ 20°C	-253°C
Abbreviation	RT, air	RT, He	RT, H_2	LH_2

Table 3: Test parameters

	Friction measurement flat pins	Wear measurement spherical pins
Normal load, F_N	50 N (3.12 MPa)	16 N (1 MPa)
Sliding speed, v	0.2 m/s	0.2 m/s
Sliding distance, s	2000 m	2000 m

The samples were arranged in pin-on-disc configuration consisting of a fixed 2-pins holder continuously sliding against a rotating disc. Polymer composites were cut into pins (4x4x12 mm^3) for friction measurements. In order to reduce the time of the running-in period, specimens were pre-worn with grinding paper (Grid 800) against the disc counterpart and then carefully cleaned with ethanol. With this method, the roughness of the specimens before testing was always the same, and the parallel alignment of the two mating surfaces could be guaranteed. Spherical pins (3 mm radius) were used for wear measurement. The diameter of the wear scar was measured after the experiments and the wear volume was calculated. Steel discs with an inside diameter of 25 mm and an outside diameter of 42 mm were also cleaned with ethanol before service.

After the experiments transfer films and the surface of the pins were examined with optical and Scanning Electron Microscopy (SEM). Energy dispersive X-ray (EDX) and X-ray Photo Electron Spectroscopy (XPS) analyses were performed to examine the surface composition of the transfer film and to determine possible chemical reactions at the contact surfaces.

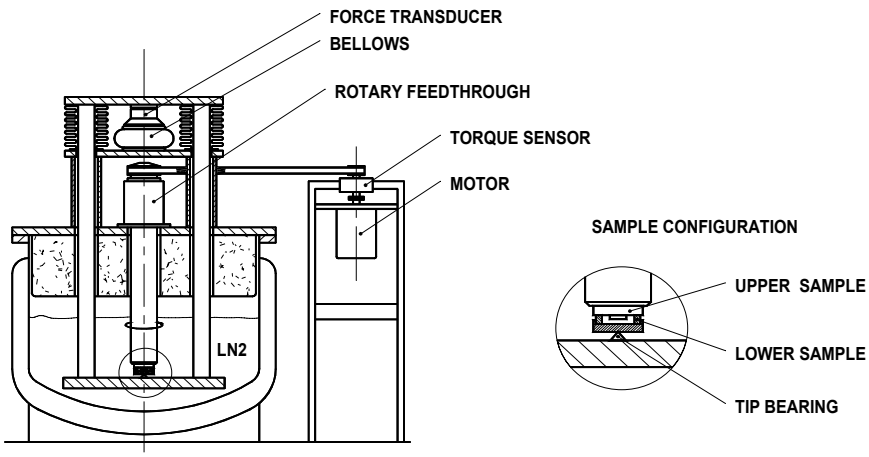


Figure 1 Tribometer for tests in liquid cryogens (CT2) [1]

RESULTS AND DISCUSSION

Influence of the hydrogen environment

Friction measurements of selected composites were carried out at RT in hydrogen and compared with experiments at RT in air and in helium. Figure 2 indicates that the friction coefficient is much smaller in hydrogen than in air for all the composites and also smaller than in helium environment for most of them. This suggests that hydrogen has a certain influence on the performance of these friction couples.

One possible explanation is due to the thermal properties of the medium, which plays an important role in transporting the friction heat from the contact area, in particular for tribological system with polymer components. Indeed, the thermal conductivity at RT of hydrogen (170.10^{-3} W/mK) is higher than those of helium and air (resp.143.10^{-3} W/mK and 24.10^{-3} W/mK). This corresponds to a lower friction in hydrogen environment. The similar results in hydrogen and helium for the composite E, that contains bronze particles, can be due to the higher thermal conductivity of this material compared to the other ones.

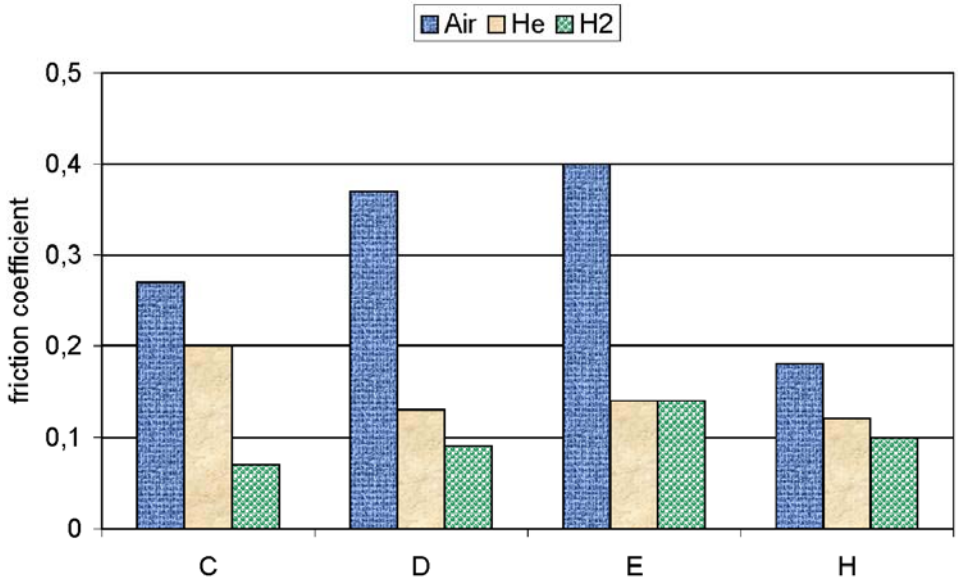


Figure 2 Friction coefficient of polymer composites at RT in air, in H_2 and He

Wear measurements with spherical pins indicate a smaller wear in liquid hydrogen than at RT in air or in hydrogen (Fig.3). As explained in [2], this is due at first to the low temperature properties of polymeric materials, in particular by the increase of stiffness below the glass transition. Secondly, cryogenic fluids remove the friction heat produced during the test and therefore act as efficient coolant.

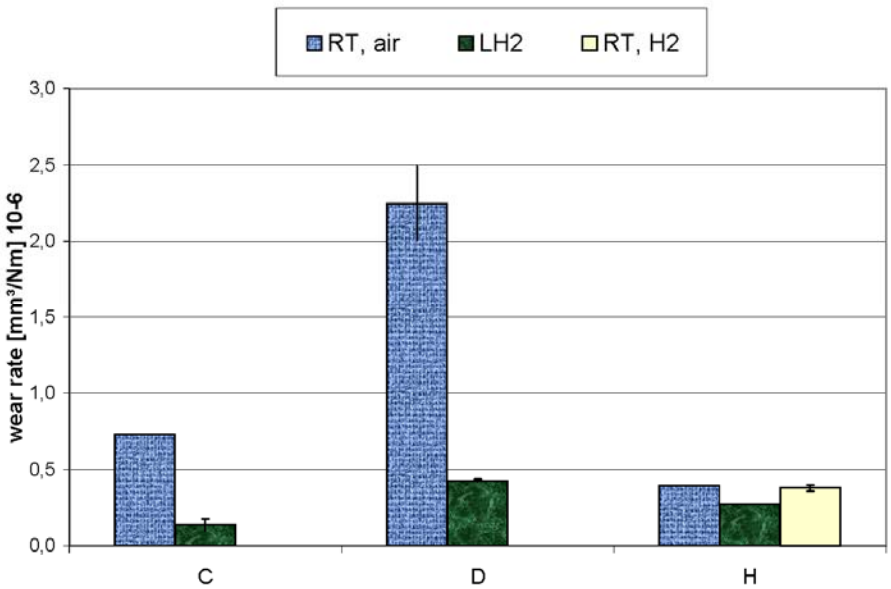
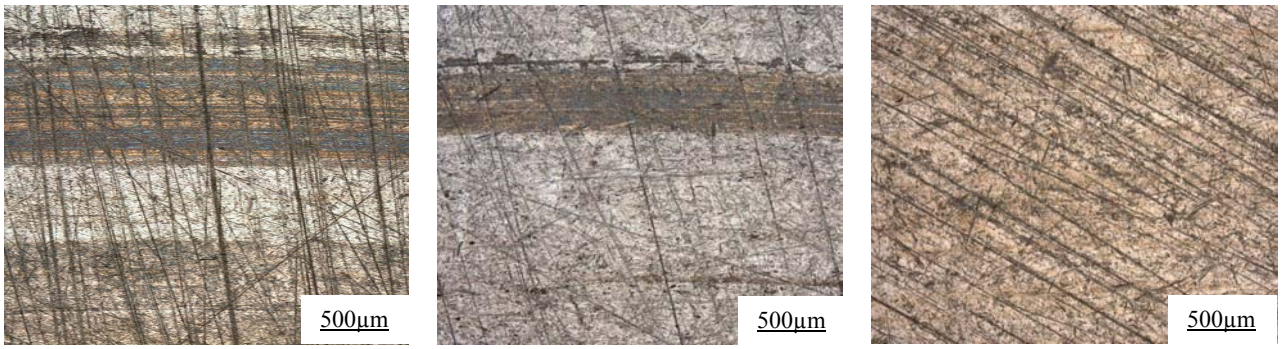


Figure 3 Wear rate of polymer composites against steel discs at RT in air and in LH_2

Optical microscopy images of the steel disc after the experiments with material H indicate as well a much thinner transfer film in LH_2 compared to RT in air (Fig. 4). At RT in hydrogen, the transfer film is thinner than in air but much thicker than in LH_2.



a) b) c)

Figure 4 Optical microscopy images of the polymer (H) transfer film on the steel disc
a) at RT in air, b) in H_2, and c) in LH_2

EDX analyses of the polymer pins were performed after the experiments at RT in air, H_2 and He. Figure 5 indicates the presence of iron at the surface of the pin, much more pronounced in air than in H_2 or He for material D, whereas for material C (Fig. 6), the iron is significantly present in air as well as in He. Therefore, it is suggested that the hydrogen environment prevents the iron from the disc from transferring onto the polymer pin, leading to a lower coefficient of friction.

Previous XPS analyses with material E have shown that the reduction effect of hydrogen can promote the formation of iron fluorides at the surface of the steel discs [2], whereas, in the presence of oxygen, the formation of metal-oxygen-polymer complex promotes the polymer adhesion to the steel disc [3]. Surface analyses of the disc indicate that the transfer film developed after the experiments in hydrogen at RT is not as homogenous as after the experiments at RT in air (Fig. 7). This confirms the lack of adhesion of the transfer film in hydrogen environment.

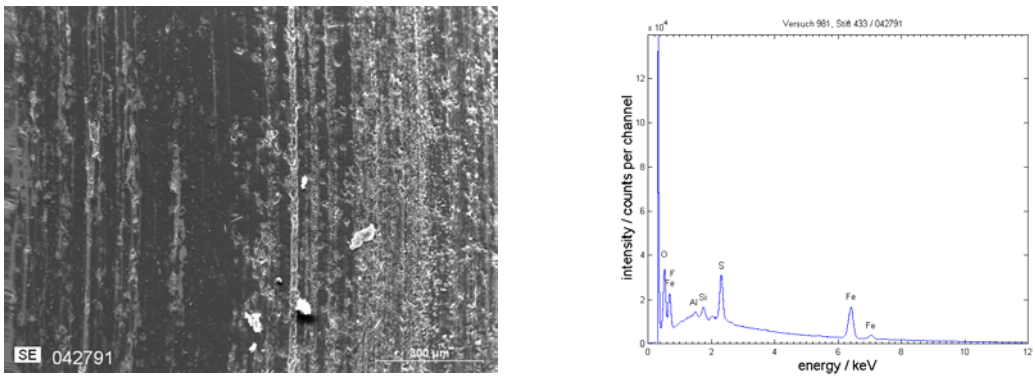
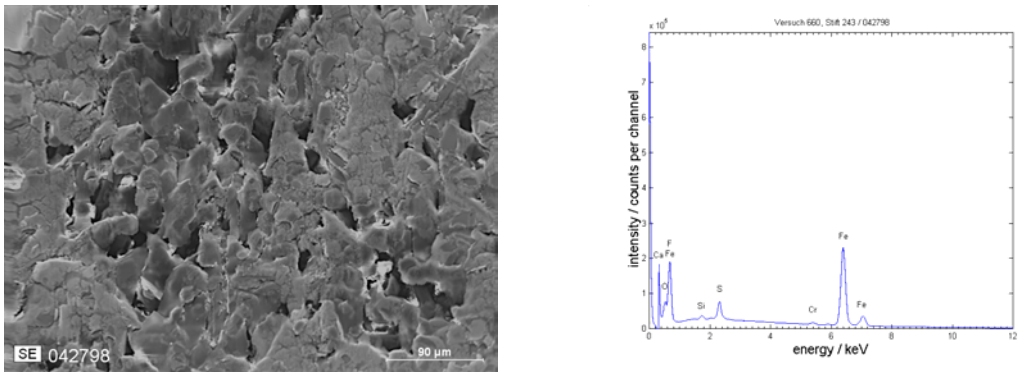


Figure 6 EDX images of a polymer composite (C) after tests at RT in He

a)



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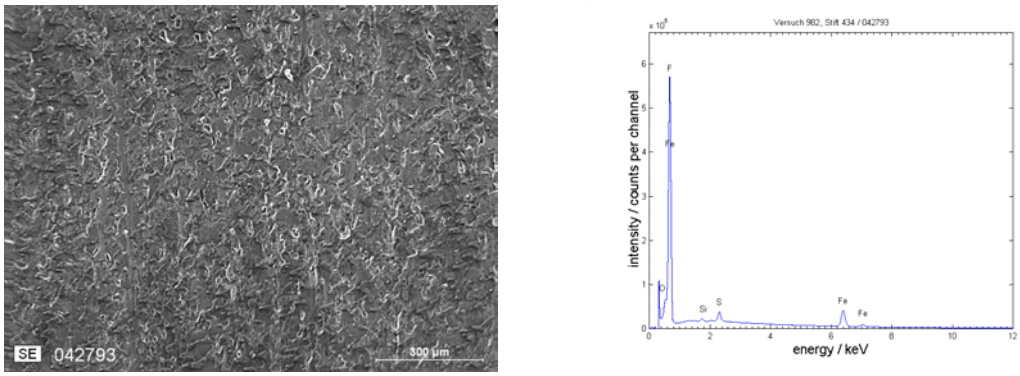

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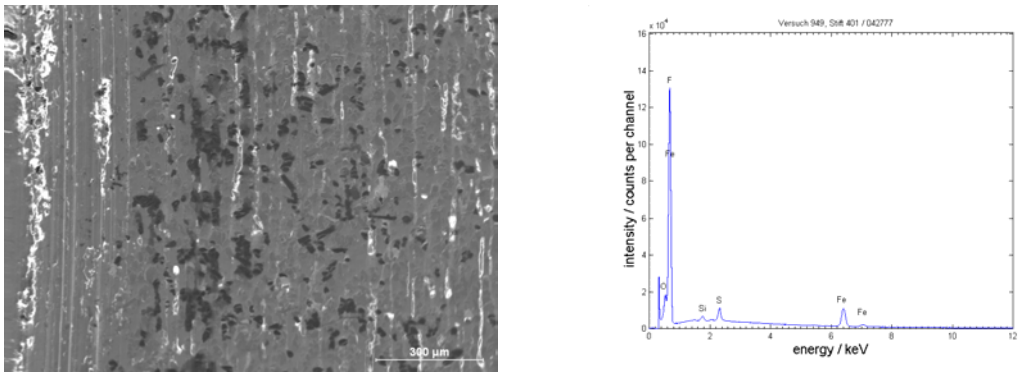
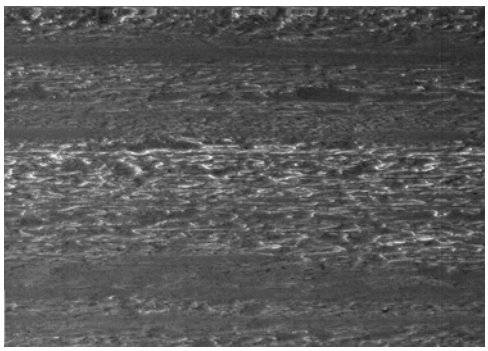


Figure 5 EDX images of a polymer composite (D) after tests at RT in a) air, b) He and c) H_2

a)



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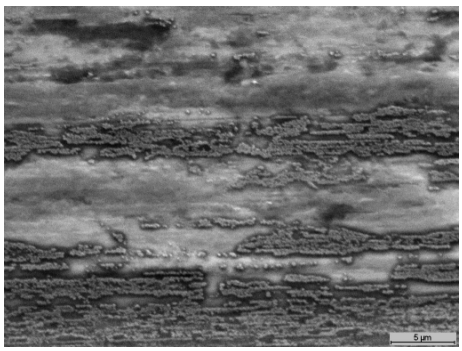

Figure 7 SEM images of the transfer film formed with the PTFE composite (E) on the steel disc after experiments at RT a) in air and b) in hydrogen

Influence of the composition

The friction coefficient of the twelve polymer composites are presented in Figure 8 and Figure 9, respectively at room temperature in air and in liquid hydrogen.

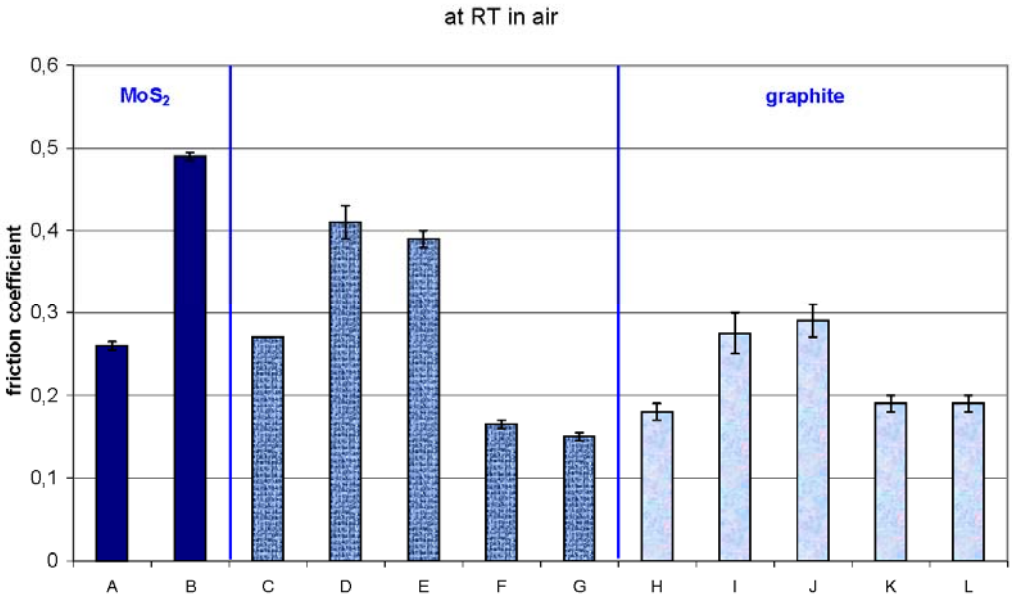

Figure 8 Friction coefficient of polymer composites against steel discs at room temperature in air

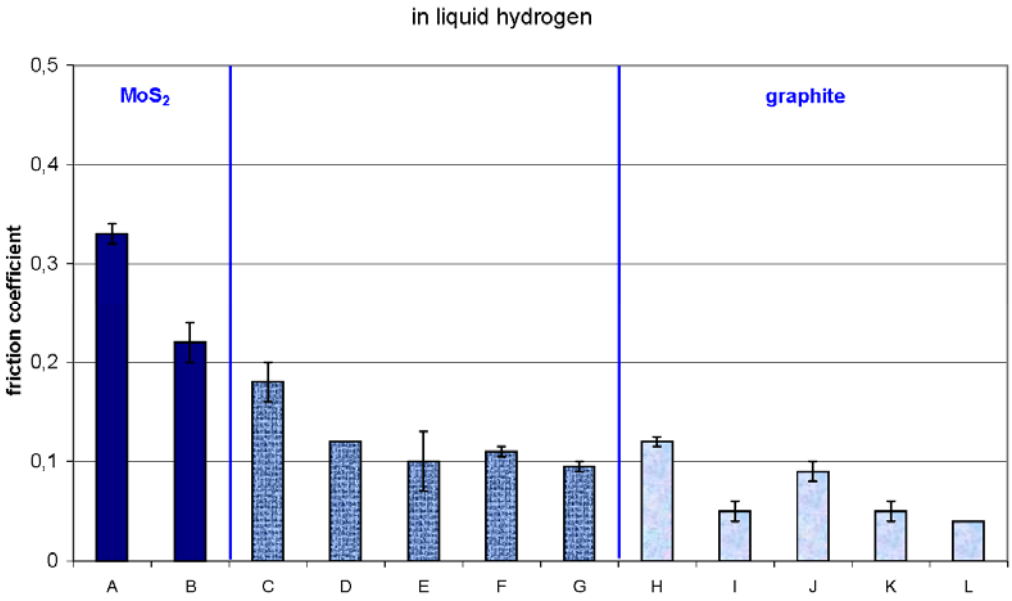

Figure 9 Friction coefficient of polymer composites against steel discs in liquid hydrogen

At RT in air, the friction coefficient varies from 0.15 to 0.5. There is not a direct relation between low friction and a particular matrix or solid lubricant. PTFE matrix composites can have a low friction, for example with the addition of PPS (material F), but also a rather high friction when filled with CF and PEEK (material D).

In liquid hydrogen (Fig.9), the friction coefficient is significantly lower than at RT in air for almost all the composites. Nine composites have indeed a friction equal or lower than 0.12. As seen previously [2, 4], this is not a hydrodynamic effect of the liquid hydrogen, since the viscosity of LH_2 is too low to establish a hydrodynamic film of sufficient thickness to separate the polymer pin from the steel disc. It has been shown that the thermal properties of the hydrogen can explain the better tribological behaviour of the polymer composites.

Furthermore, the type of solid lubricant seems to have an influence on the friction behaviour in hydrogen. Composites with MoS_2 have higher values whereas polymers filled with graphite give the lowest ones. This is in accordance with the lubricating properties of the solid lubricants themselves [5, 6].

The characteristic feature of MoS_2 is its highly anisotropic crystal layer structure. The weak interlamellar bonding results in low shear strength during sliding which produces a low coefficient of friction. It is well known, however, that the humidity of the atmosphere has a significant effect on the friction. Contaminants such as water or oxygen can modify the easy shear between the basal planes. Hydrogen environment seems to affect MoS_2 in the same way as water.

In contrast, graphite is not inherently a good lubricant, but it becomes one when certain contaminants are intercalated between the carbon layers, preventing the π-electron and interlayer bonding. That is why graphite shows low friction in the presence of moisture. In our experiments, the friction coefficient is much lower in hydrogen environment than in air. This indicates also that tribochemical reactions can occur between hydrogen and graphite layer as observed in [5], eventually leading to hydrocarbon chains which would decrease the shear strength at the friction contact. Donnet et al showed for carbon-film running in hydrogen that at least one monolayer of hydrogen covers the wear track between two consecutive passes [7]. It is suggested that the hydrogen atmosphere acts as an infinite lubricant reservoir responsible for the passivation of the surface bonds.

CONCLUSIONS

Based on the tribological experiments performed with several polymer composites in hydrogen environment, the following conclusions can be drawn:

- Hydrogen has a beneficial effect on the friction behavior of polymer composites. H_2 seems to prevent the iron from transferring onto the pin.

- Furthermore, the polymer transfer onto the steel disc is lower in hydrogen environment. This could be due to the lower polymer adhesion in H_2 atmosphere. It is also suggested that H_2 could act as an infinite lubricating reservoir.

- In LH_2, the wear rate is lower than at RT in hydrogen. This is mainly due to the low temperature properties of the polymer and to the capability of the cryogenic fluid to remove the friction heat.

- The polymer matrix doesn't have a significant influence on the tribological performance of the composite in hydrogen. The choice of the solid lubricant is, however, more important. MoS_2 filled composites have to be avoided in hydrogen environment. On the contrary, graphite

containing materials have the best performance in hydrogen. Probably, there are chemical reactions between H_2 and graphite.

From a tribological point of view, polymer composites are suitable and reliable in hydrogen environment, which seems to have a beneficial effect. However, it is recommended to use graphite containing materials which give the best performance.

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