

## TRIBOLOGICAL BEHAVIOUR OF GRAPHITE FILLED POLYIMIDE COMPOSITES IN HYDROGEN ENVIRONMENT

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### Abstract

*The tribological behaviour of graphite filled polyimide composites against steel (AISI 52100) was investigated in air, vacuum and hydrogen environments. Composites consist of two polyimides filled with different types and amount of graphite. Friction and wear measurements were performed at 0.2m/s and 3.1MPa at ambient temperature. Worn surfaces and morphology of the material transfer on the steel counter-face were investigated by optical microscopy and SEM analyses. Results reveal that the polyimide structure has an important influence on the friction behaviour of graphite filled composites in hydrogen environment.*

### 1. Introduction

Hydrogen as an environmentally friendly energy carrier plays a key role in future energy supply and transport systems. However, the broad extension of hydrogen technology requires extremely high reliability and safety in all areas, not only in storage and piping, but also for common applications such as automobiles and stationary fuel cells. Particularly, components like seals and valves are critical parts. Problems are caused by hydrogen embrittlement, removal of protective oxide layers, and extreme low temperatures in case of liquid hydrogen. Polymers composites are widely used as dry sliding materials in friction assemblies. 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.

High performance polymer composites have been intensively investigated for tribological applications in air, but rarely in hydrogen [1-4]. Polyimide (PI) materials, in particular Vespel SP1 and SP2 from Dupont, have been studied in both air and vacuum over a wide temperature range [5-10]. They have generally good tribological properties under vacuum conditions and at high temperature in air due to the formation of a transfer film on the counter-face. In contrast, graphite is a well know lubricant in ambient and moist atmosphere but loses its lubricity in vacuum environment [11-13].

In this study, the tribological behaviour of sintered polyimide composites filled with different types and amounts of graphite is investigated in air, vacuum and hydrogen environments.

## 2. Experimental

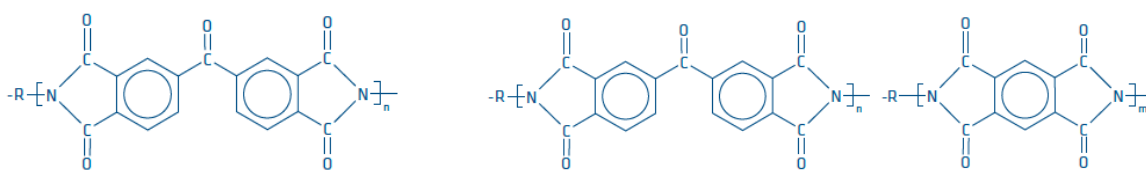
### 2.1 Test set-up and parameters

The polymer samples were arranged in a pin-on-disc configuration consisting of 2 flat pins continuously sliding in the same track of a rotating disc. Polymer composites were cut into pins (4x4x12 mm<sup>3</sup>) for friction measurements. Steel discs (AISI 52100) with a roughness of Ra = 0.075 and Ra = 0.22 μm and an outside diameter of 55 mm were used as counter-face. Sliding velocity was 0.2 m/s and normal load 50 N (3.1 MPa).

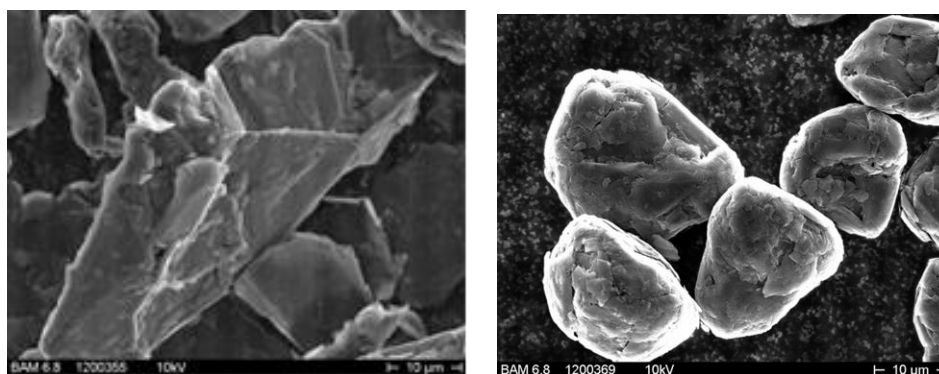
Tribological tests were performed at room temperature in air, in vacuum (5•10<sup>-3</sup> Pa) and in hydrogen gas. Friction was recorded over time and wear of composites was determined by weight.

### 2.2 Materials

Composite materials were sintered by hot compression molding by Ensinger Sintimid GmbH. Special compositions were produced with two PI matrices (Fig. 1) and two types of graphite (Fig. 2): synthetic (Gs, density = 2.25 g/cm<sup>3</sup>; grain size: d50 = 27 μm) and natural (Gn, density = 2.27 g/cm<sup>3</sup>, grain size: d50 = 17 μm). The natural graphite has predominantly a round shape whereas synthetic graphite possesses a plate-like geometry (see Fig. 2). Material compositions are presented in table 1.



**Figure 1.** PI1 (BTDA based ) and PI2 (co-polyimide based on BTDA and PMDA)



**Figure 2.** SEM images of graphite particle: left synthetic (Gs), right natural (Gn)

name	matrix	composition in wt%
PI	PI1	-
PI15Gs	PI1	15% synthetic graphite
PI15Gn	PI1	15% natural graphite
PI40Gs	PI1	40% synthetic graphite
PI40Gn	PI1	40% natural graphite
PI215Gs	PI2	15% synthetic graphite
PI215Gn	PI2	15% natural graphite

**Table 1.** Materials composition and denomination

### 3. Results

Figure 3 shows the friction coefficient of PI1 and PI2 composites in air, hydrogen and vacuum environment. The type of graphite varied in both polyimides, while the influence of the amount of graphite was investigated only in PI1.

Results show that the type of graphite (natural or synthetic) doesn't significantly affect the friction behaviour in PI1 or PI2, but the matrix and the counterface roughness have an influence in all environments.

Against a smooth steel disc, the friction of PI1 is extremely high (0.8) in air, but adding 15 wt% of graphite is sufficient to reduce friction to 0.4. Generally, the addition of graphite in PI1 reduces friction but this improvement is moderate when the amount of graphite further increases. In H<sub>2</sub> atmosphere, friction is lower than in air for pure PI1 and 15 wt% graphite filled PI1, or similar for the composites with 40 wt% graphite. In vacuum conditions, the friction behaviour of PI1 and its composites are much lower than in air or hydrogen. The friction coefficient of 15 wt% filled PI1 is similar to the one of pure PI1 (0.15). Increasing the amount of graphite to 40 wt% has a negative effect in vacuum conditions, leading to friction value of 0.2.

Further tests were performed with a rougher steel disc. Compared to the smooth surface, the friction of PI1 composites increases slightly in air and vacuum but decreases in H<sub>2</sub>. With regards to PI2, a different frictional profile is observed. While the friction of PI2 composites is similar to PI1 composites in vacuum, PI2 composites are characterized by a lower friction coefficient in air and in hydrogen environment.

The wear behaviour of polyimide materials is presented in Figure 4. Adding 15%wt graphite to PI reduces wear in air and in H<sub>2</sub> atmosphere, but increasing graphite content to 40 wt% leads to an extremely high wear rate in vacuum environment. Comparing the two types of graphite, wear rate is slightly higher with the composite containing natural graphite in air and hydrogen environment. Concerning the polyimide matrix, a small improvement may be attributed to PI2 matrix, but the influence on the wear rate is rather marginal.

Surface analyses of the pin composites and the counter-face were performed after the tests. Optical microscopy images of the disc indicate that a transfer film is hardly present when pure PI1 run against steel disc in air or in H<sub>2</sub> environment at normal pressure (Fig. 5), but some polymer lumps are visible on the disc. On the contrary, PI1 transfers on the counter-face in vacuum. PI1 composites with 15%wt graphite present a smooth transfer film at the surface of the disc, while a compact transfer with wear debris are observed with the composite filled with 40%wt graphite. SEM images reveal that transfer films are discontinuous. Against PI2 composites, the transfer on the steel disc is thinner than against PI1 composites in all conditions.

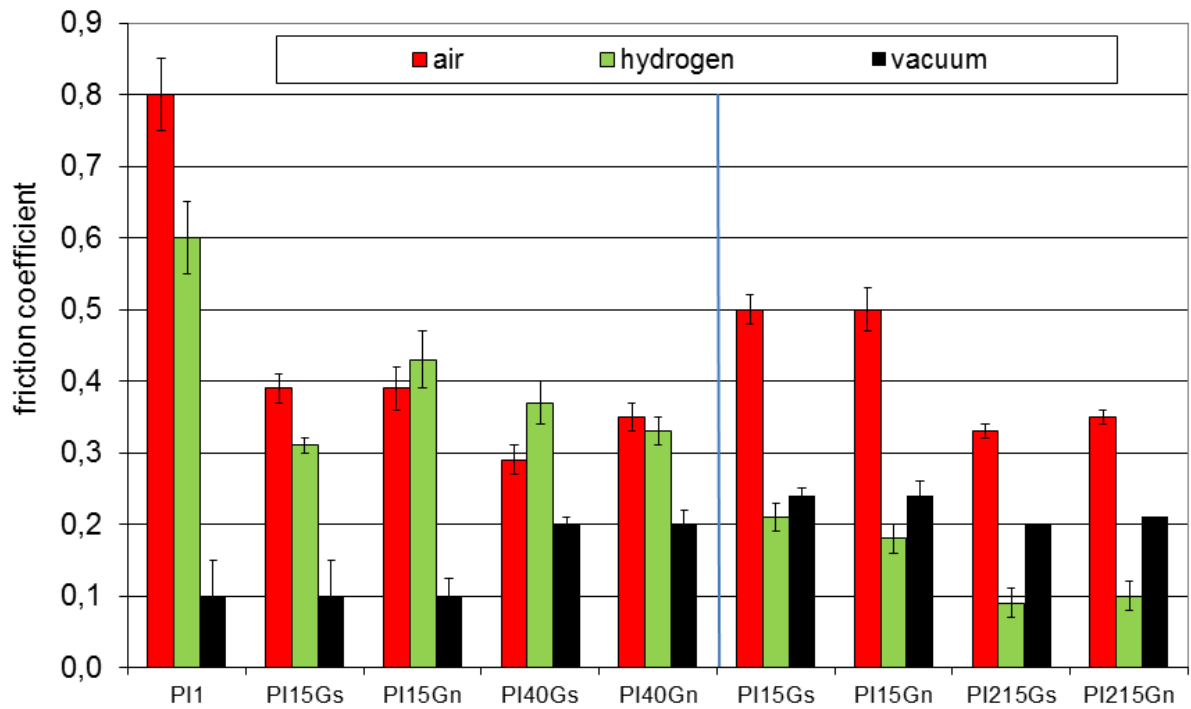


Figure 3. Friction coefficient of PI composites in air, vacuum and hydrogen environments; against steel (left Ra = 0.075, right Ra = 0.22 μm)

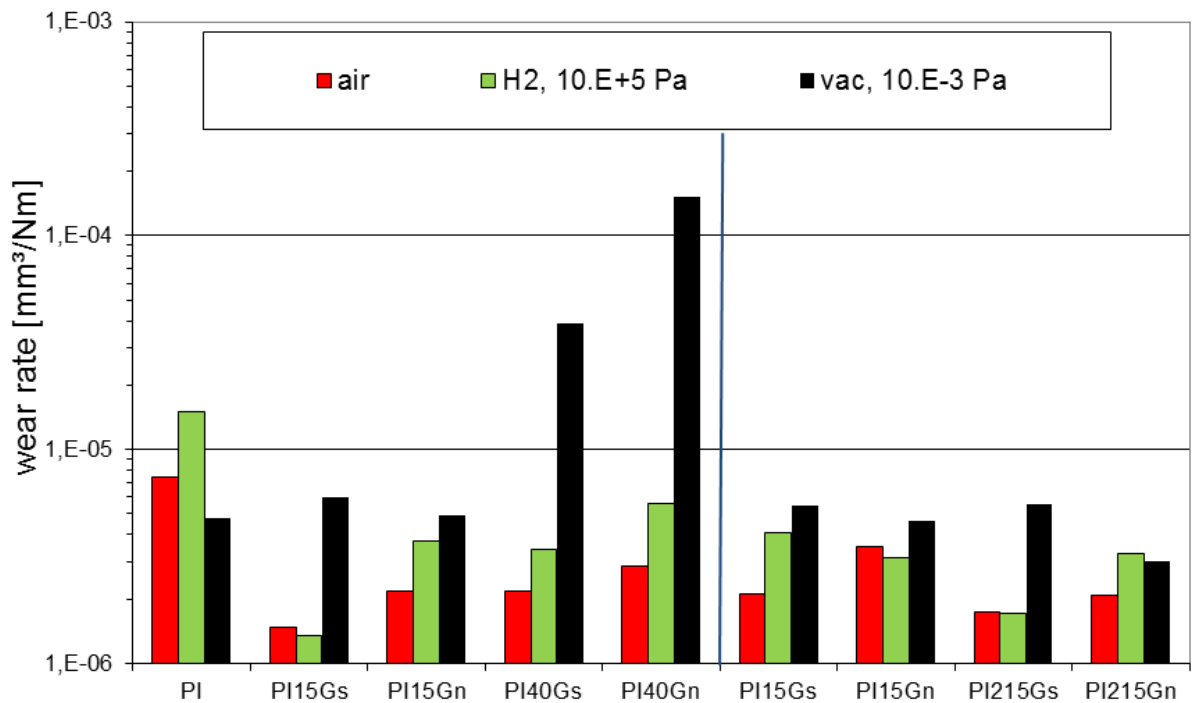
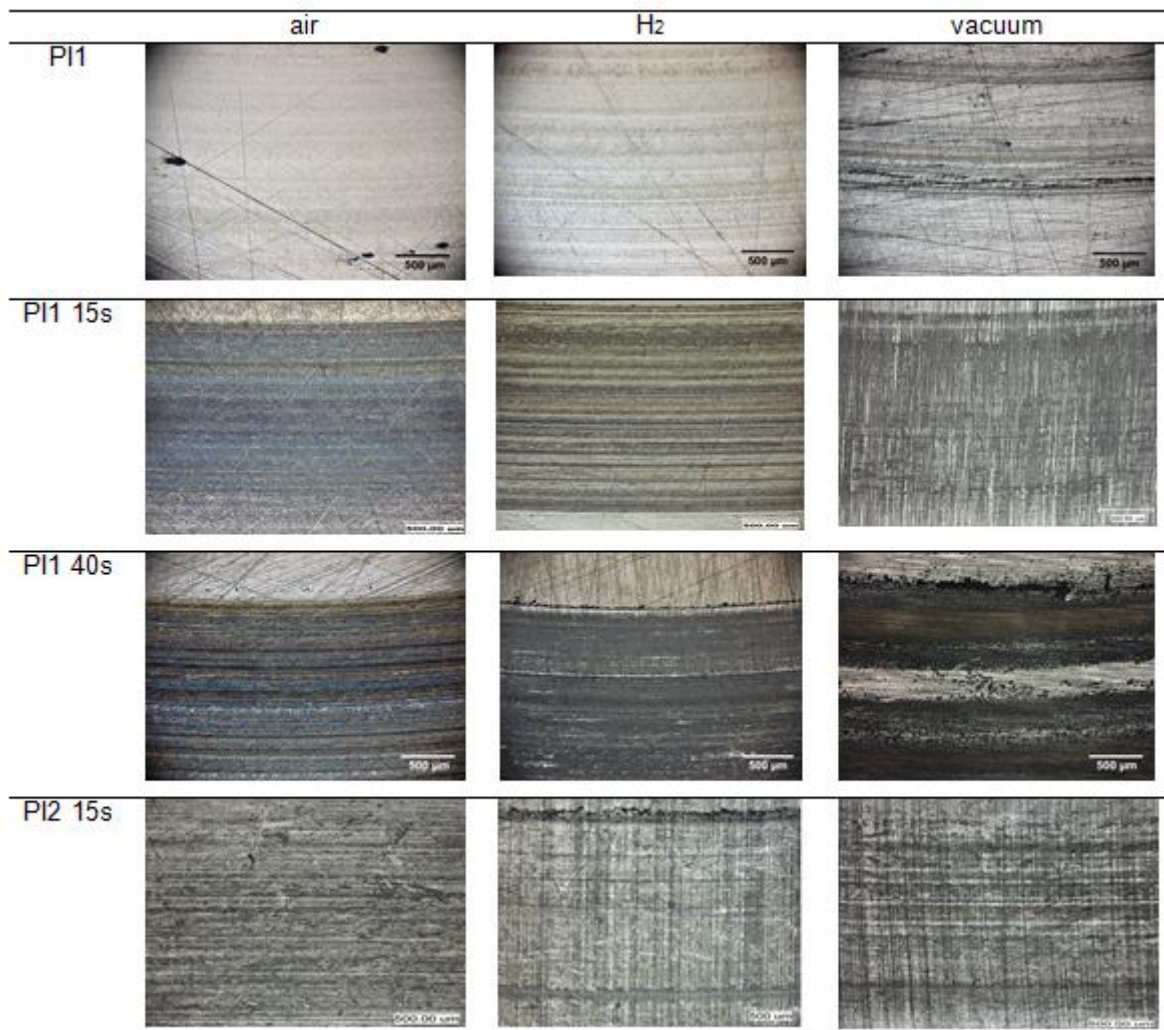


Figure 4. Wear rate of PI composites in air, vacuum and hydrogen environments; against steel (left Ra = 0.075, right Ra = 0.22 μm)



**Figure 5.** Optical microscopy images of the transfer on to the steel disc after tests in air, vacuum and hydrogen environment

Some worn surfaces of polymer composites are presented in Fig. 6. PI15s composite is characterized by light abrasive marks and graphite particles are still well embedded in the polymer matrix, while graphite is clearly seen on the surface of PI40s after tests in all environments. On the other hand, the surface of PI215s and PI215n are more deformed. Particularly after hydrogen and vacuum conditions, graphite is more present at the surface and deep wear furrows are observed on both composites.

Fig. 7 shows the SEM morphologies of worn surfaces. The worn surfaces of the PI115s are characterized by cracks perpendicular to sliding direction, which indicates that fatigue and adhesion are the dominant wear mechanism. The worn surfaces of PI215s that ran against a rougher counterface were relatively smooth under all test conditions with large amount of graphite present at the surface.



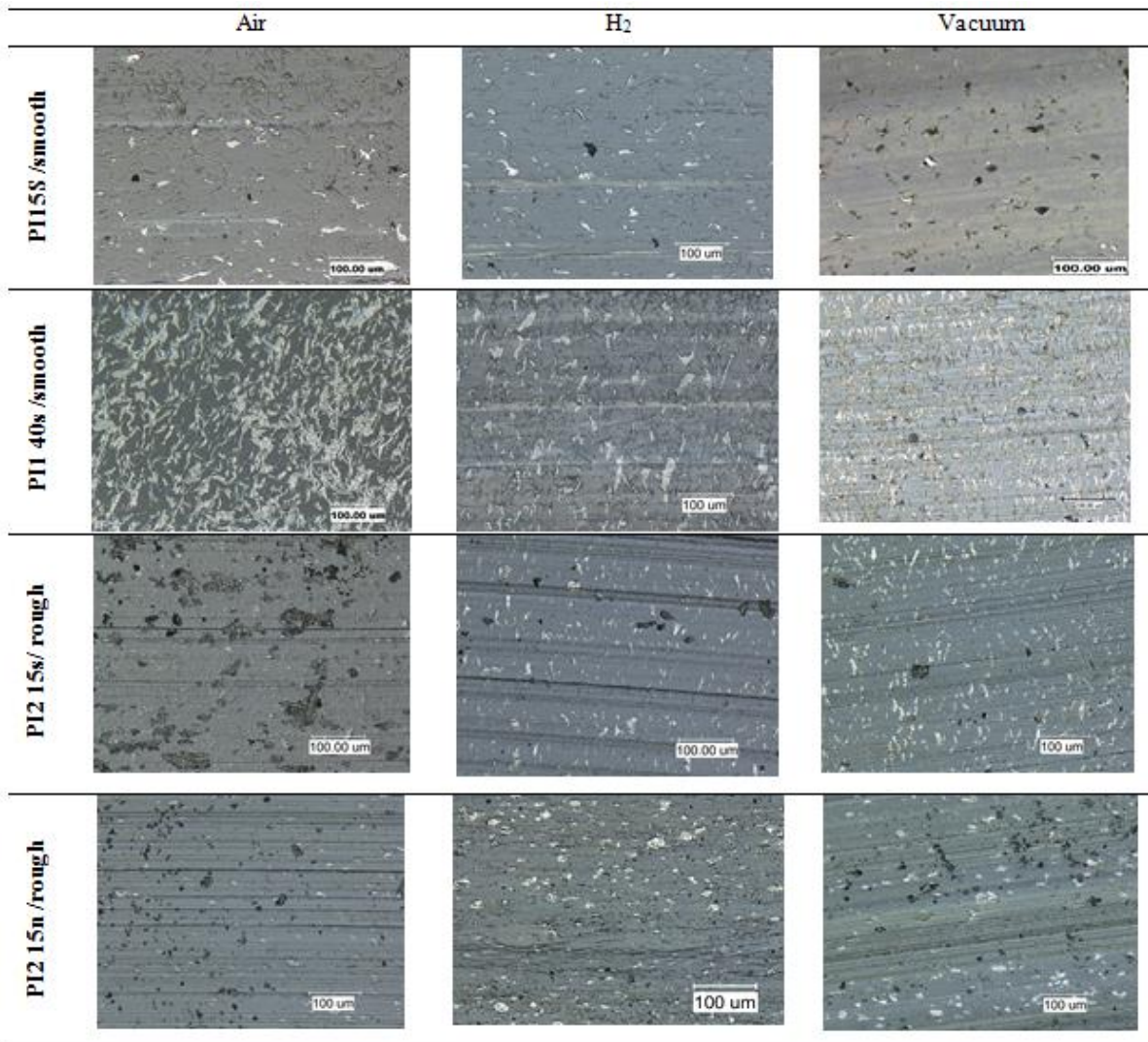


Figure 6. Optical microscopy images of pin after tests in air, vacuum and hydrogen environment

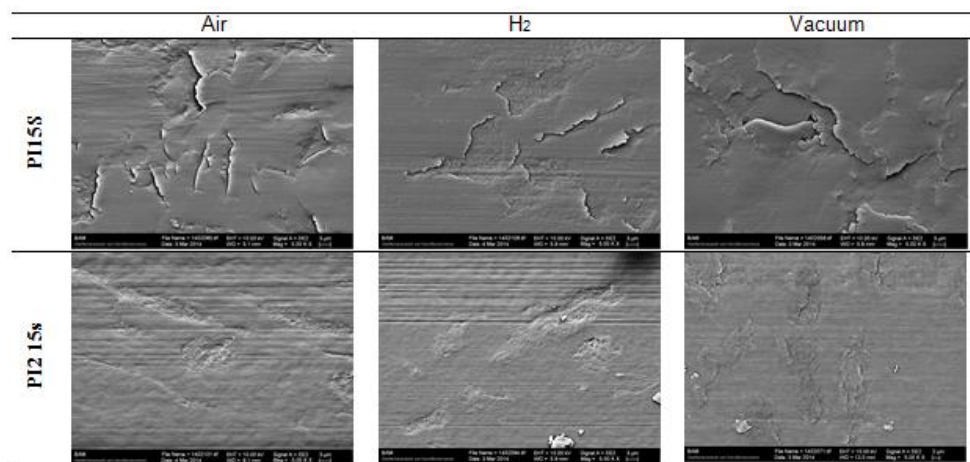


Figure 7. SEM of PI15s and PI215s composites after tests in air, vacuum and hydrogen environment

#### 4. Discussion

As observed in other works [5, 6], the friction of pure polyimide is high in moist air at ambient temperature. This is due to the fact that in moist environment hydrogen bonds are formed between water and the carbonyl group of PI [2, 3]. This restricts the molecular mobility of PI, preventing polymer transfer in humid air. In the absence of water vapour, PI chains are more flexible and can easily be oriented in sliding direction. The formation of a thin transfer film under vacuum condition leads to friction reduction. In hydrogen environment at normal pressure ( $10^5\text{Pa}$ ), friction is slightly lower and more stable than in air. This may be due to the fact that the tribometer is evacuated before introducing  $\text{H}_2$ , which certainly removed the absorbed water layer present at the surface of the polymer. The relatively high friction level (0.6) suggests, however, that  $\text{H}_2$  molecules also hinder the mobility of the polyimide chain, similar to  $\text{H}_2\text{O}$ .

The wear rate of pure PI is not significantly influenced by the environment (Fig. 4). Hydrogen bonding contributes to wear resistance in humid air, while in the absence of water vapour, a thin transfer film hinders direct contact between polymer and metal, preventing wear. The addition of graphite filler has a beneficial effect in air and  $\text{H}_2$  atmosphere reducing friction and wear rate compared to pure polyimide. As shown in Fig. 5, graphite transfers on to the disc.  $\text{H}_2\text{O}$  vapor and  $\text{H}_2$  molecules saturate the dangling bonds of graphite present at the interface, which forms an effective lubricating “third body” layer.

Under vacuum conditions, PI1 shows low friction due to orientation of polymer chain as seen above. However, it is well known that graphite loses its lubricity in vacuum, but 15%wt graphite doesn't influence the friction and wear of PI matrix. A thin transfer film is present at the surface of the disc which allows lubrication. This can be attributed to water desorption of PI matrix in vacuum, which can be sufficient to saturate graphite dangling bonds at the interface. With a higher filler content, dusting of graphite leads to higher friction and severe wear that is clearly visible on the surface of the disc. Against a rougher disc, more graphite is present at the interface, which reduces friction in hydrogen but increases it in vacuum conditions.

As shown in Fig. 3, different polyimide structures lead to different results. Friction of PI2 is lower in humid air than for PI1 composites. With a PMDA based structure, PI2 has a lower content of polar groups and water absorption. This decreases interchain attractive forces and reduces H-bonds, leading to certain flexibility of the molecules, which is confirmed by the lower glass transition of PI2 ( $T_g = 260^\circ\text{C}$ ) compared to PI1 ( $T_g = 360^\circ\text{C}$ ). PI2 molecules can therefore more easily be oriented and transfer at the surface of the disc.

In hydrogen environment, a low and stable friction is obtained with PI2 composites. A very thin and homogenous transfer is seen at the surface of the disc. Surface analysis of the polymer pins indicated more graphite at the surface of PI2 after test in  $\text{H}_2$  compared to PI1 composites and compared to the pin surfaces after test in air. Hydrogen adsorbs on this graphite rich surface to produce effective lubrication.

In this study, the type of graphite (synthetic or natural) does not influence the friction behaviour of filled PI composites, but the wear rate is slightly higher in air and  $\text{H}_2$  with the composites containing natural graphite, which has a lower mechanical strength.

## 5 Conclusion

The tribological performances of sintered polyimide composites filled with different amounts and type of graphite were investigated in air, hydrogen and vacuum environment at 0.2 m/s and 3.1 MPa. Experimental results indicate that the polyimide structure has a major influence on friction behavior in air and hydrogen, while graphite type has an effect on wear behaviour. The best performance in hydrogen environment was obtained with graphite filled PI2, which is a co-polyimide based on BTDA and PMDA.

## 6. Acknowledgments

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## 7. References

- [1] G. Theiler *et al.*, Tribological behaviour of PTFE-composites against steel at cryogenic temperature. *Tribology intern.* 35 (2002) 7, 449-458
- [2] G. Theiler *et al.*, "Polymer Composites for Tribological Applications in Hydrogen Environment", *Proc. 2nd Int. Conf. on Hydrogen Safety, San Sebastian, Spain, 11-13 Sept. 2007*
- [3] Y. Sawae *et al.*, "Wear Characteristics of PTFE and PTFE Based Composites in Gaseous Hydrogen". *Proc. World Tribology Congress 2009, Kyoto, Japan*, B1-125
- [4] Nakashima K., Yamaguti A, Kurono Y, Sawae Y, Murakami T, Sugimura J.: "Effect of high-pressure hydrogen exposure on wear of polytetrafluoroethylen sliding against stainless steel". *Proc. Institution of Mech. Engineers, part J-J. of Eng. Tribol.*, Vol. 224 (J3) (2010), 285-292
- [5] D.H. Buckley, Friction and wear characteristics of polyimide and filled polyimide compositions in vacuum. Nasa Technical Note TN D-3261, 1966
- [6] Fusaro R.L. Effect of atmosphere and temperature on wear, friction and transfer of polyimide films. *ASLE Trans* 1978; 21(2):125-33
- [7] P. Samyn *et al.*, "Tribological behavior of pure and graphite-filled polyimides under atmospheric conditions", *Polymer Eng. Sci.* 43(8) (2003) 1477-1487
- [8] P. Samyn *et al.*, The lubricity of graphite flake inclusions in sintered polyimides affected by chemical reactions at high temperatures, *Carbon* 46(2008) 1072-1084
- [9] A. Merstallinger *et al.*, Self-lubricating composites for medium temperatures in space based on polyimide sintimid. *Proc. 11<sup>th</sup> ESMAT Symposium Lucerne, Switzerland*, 21-23 Sept. 2005
- [10] Friedrich K. Sliding wear performance of different polyimide formulations. *Tribol. Int.* 1989, 22(1) 25-31
- [11] H. Zaidi *et al.*, Behaviour of graphite in friction under various environments, *Surface science* 251/252 (1991) 778-78
- [12] M. Brendlé *et al.*, Triboreactions of graphite with moisture – a new model of triboreactor for integrating friction and wear, *Wear* 254 (2003) 818-826
- [13] J.K. Lancaster *et al.*, Influence of environment and pressures on the transition to dusting wear of graphite, *J. Appl. Phys. D* 14 (4) 14 (1981) 747-762.