Friction and Wear Behaviour of Graphite Filled Polymer Composites in Hydrogen Environment

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(Manuscript received 18 December 2013; accepted 29 June 2014; published 15 April 2015)
(Presented at Technical Session in the 5th World Tribology Congress TORINO September 2013)

High performance polymer composites have been intensively investigated for tribological applications in air, but rarely in hydrogen environment. Author’s previous benchmark of composites in liquid hydrogen (LH2) showed that graphite filled polymers have beneficial friction behaviour in this extreme condition. Therefore, further investigations have been undertaken in hydrogen environment. This paper presents first results obtained with polyimide composites filled with different types (natural, synthetic) and amounts of graphite in air, vacuum and hydrogen environments. A particular attention is taken to the influence of hydrogen on graphite as well as on the polymer matrix.

Keywords: polymer composites, polyimide, graphite, friction, wear, hydrogen environment, vacuum

1. Introduction

Ensuring a sustainable energy supply is currently one of the most important issues for industry and research institutes. Hydrogen, as an energy carrier independent of the primary energy, is thought to play a key role in future energy systems. However, the broad extension of hydrogen technology requires extremely high reliability and safety in all areas for common applications as automobiles and stationary fuel cells. Particularly components containing tribosystems are critical parts.

Polymers and polymer 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 environment. Author’s previous benchmark of composites in liquid hydrogen (LH2) showed that graphite filled polymers have beneficial friction behaviour [1]. In order to better understand the influence of hydrogen on graphite and on the matrix, deeper investigations are necessary.

Polyimide materials (PI) have been extensively investigated in different environments over a wide temperature range [2-8]. They have good tribological properties under vacuum conditions and at high temperature in air due to the formation of a transfer film on the counterface. PI composites are used as seals, valve components, bearings and bushings in high demanding applications.

In contrast, graphite is a well know lubricant in ambient and moist atmosphere but loses its lubricity in vacuum environment.

This paper presents first results obtained with polyimide composites filled with different types (natural, synthetic) and amounts of graphite in air, vacuum and hydrogen environments.

2. Experimental methods

2.1. Materials

PI materials were produced by hot compression molding by Ensinger Sintimid GmbH. The matrix used in this project is a benzophenone tetracarboxylic dianhydride (BTDA) based polyimide resin (Fig. 1).

![BTDA based polyimide](image)
Special compositions were produced with synthetic (Gs, density = 2.25 g/cm³; grain size: d50 = 27 µm, d90 = 53 µm) and natural (Gn, density = 2.27 g/cm³, grain size: d50 = 17 µm, d90 = 25 µm) graphite in order to study the influence of graphite type. As seen in Figs. 2 and 3, the natural graphite has predominantly a round shape whereas synthetic graphite possesses a plate-like geometry. Material compositions are presented in Table 1.

Table 1: Materials composition and denomination

<table>
<thead>
<tr>
<th>name</th>
<th>matrix</th>
<th>Composition in mass%</th>
</tr>
</thead>
<tbody>
<tr>
<td>PI</td>
<td>PI</td>
<td>-</td>
</tr>
<tr>
<td>PI15Gs</td>
<td>PI</td>
<td>15% synthetic graphite</td>
</tr>
<tr>
<td>PI15Gn</td>
<td>PI</td>
<td>15% natural graphite</td>
</tr>
<tr>
<td>PI40Gs</td>
<td>PI</td>
<td>40% synthetic graphite</td>
</tr>
<tr>
<td>PI40Gn</td>
<td>PI</td>
<td>40% natural graphite</td>
</tr>
</tbody>
</table>

2.2. Equipment and test parameters

Tribological tests were performed in two tribometers, as detailed in Table 2 and Table 3.

Table 2: Environmental media

<table>
<thead>
<tr>
<th>Media</th>
<th>tribometer</th>
<th>temperature</th>
<th>pressures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>VT1, CT2</td>
<td>20°C</td>
<td>10⁵ Pa</td>
</tr>
<tr>
<td>Vacuum</td>
<td>VT1</td>
<td>20°C</td>
<td>10⁻³ Pa</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>VT1</td>
<td>20°C</td>
<td>10⁵ Pa</td>
</tr>
<tr>
<td>(H₂)</td>
<td>CT2</td>
<td>20°C</td>
<td>10⁵ Pa</td>
</tr>
</tbody>
</table>

Table 3: Test parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal load, $F_N$</td>
<td>50 N (3.12 MPa)</td>
</tr>
<tr>
<td>Sliding speed, $v$</td>
<td>0.2 m/s</td>
</tr>
<tr>
<td>Sliding distance, $s$</td>
<td>5000 m</td>
</tr>
</tbody>
</table>

Fig. 2 SEM of synthetic (left) and natural (right) graphite powder

Fig. 3 Optical microscopy images of PI + 15% Gs (left) and PI + 15% Gn (right)
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(VT1 and CT2) described in [9-11]. Experiments were conducted at room temperature in air (at 45% humidity), in vacuum $(10^{-3} \text{ Pa})$ and in hydrogen gas at $10^3 \text{ Pa}$ and at $10^5 \text{ Pa}$. Before hydrogen experiments the tribometer was evacuated to $10^{-3} \text{ Pa}$. Tests parameters are presented in Tables 2 and 3.

The samples were arranged in a pin-on-disc configuration consisting of a fixed 2-pins holder continuously sliding against a rotating disc. Polymer composite samples were cut into pins $(4 \times 4 \times 12 \text{ mm}^3)$ for friction measurements. Steel discs (AISI 52100) with a roughness of $\text{Ra} = 0.08 \mu\text{m}$ and an outside diameter of $55 \text{ mm}$ were used as counter-face. Pins and steel samples were cleaned with ethanol before testing. Wear of composites was determined by weight.

3. Results

Figure 4 shows the friction coefficient of PI composites in various environments. The addition of graphite improves the friction of PI in all environments. In air, the friction of PI is extremely high ($0.8$), but adding $15 \text{ mass}\%$ of graphite is sufficient to reduce the friction to $0.4$.

In vacuum environment, friction decreases considerably for all composites. This improvement is however moderate when the amount of graphite increases.

In $10^3 \text{ Pa} \ H_2$, where both contacting surfaces are contaminated with $H_2$ molecules, the friction decreases compared to vacuum condition for both composites containing graphite.

In $H_2$ atmosphere, friction is lower than in air for pure PI and $15 \text{ mass}\%$ graphite filled PI, but increases slightly for the composite with $40 \text{ mass}\%$ graphite. Figure 5 shows that friction behaviour of the composite with $15 \text{ mass}\%$ graphite is more stable in $H_2$ than in air.

The wear behaviour of PI materials is presented in Figure 6. Comparing to friction, the wear rate of pure and graphite filled PI are not significantly affected by the environment. Adding graphite to PI reduces wear in air and in $H_2$ atmosphere. In contrast, increasing graphite content causes higher wear rate in vacuum conditions.

The type of graphite does not influence significantly the friction behaviour of graphite filled PI composites in air, $H_2$ or vacuum environment, but the wear rate is slightly higher with the composite containing natural graphite.

Surface analyses were performed after tests. Optical microscopy images of the disc indicate that no transfer film is present when pure PI runs against steel disc in air or in $H_2$ environment at normal pressure (Fig. 7). On the contrary, PI transfers on the counter-face in vacuum and $H_2$ at $10^3 \text{ Pa}$. With the addition of graphite, a smooth transfer film is observed at the surface of the disc. Worn surfaces of polymer composites (Fig. 8) indicated graphite-rich surfaces of the PI40s in all environments, while graphite particles are still well embedded in the polymer matrix in PI15s after tests in air and $H_2$. 

Fig. 4 Friction coefficient of PI composites against steel in various environments

Fig. 5 Friction behaviour of 15 mass% graphite (Gs) filled polyimide against steel

Fig. 6 Wear rate of PI composites against steel in various environments
Fig. 7 Optical microscopy images of the discs after tests against:

- PI in a) air, b) in \( \text{H}_2 \) at \( 10^5 \) Pa, c) in \( \text{H}_2 \) at \( 10^3 \) Pa and d) in vacuum
- PI15Gs in e) air, f) in \( \text{H}_2 \) at \( 10^5 \) Pa, g) in \( \text{H}_2 \) at \( 10^3 \) Pa and h) in vacuum
- PI40Gs in i) air, j) in \( \text{H}_2 \) at \( 10^5 \) Pa, k) in \( \text{H}_2 \) at \( 10^3 \) Pa and l) in vacuum
4. Discussion

As observed in other works, the friction of pure polyimide is very 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 at ambient temperature. This is not the case in vacuum, where the PI chains are more flexible and can easily be oriented in sliding direction, reducing drastically friction.

In hydrogen environment at normal pressure (10^5 Pa), the results and surface analyses are rather similar to the one obtained in air. This suggests that H₂ molecules can hinder the mobility of the polyimide chains similarly to H₂O. The dissociation of H₂ molecules may produce also strong H-bonds as in moist environment. By reducing the hydrogen pressure to 10^3 Pa H₂, friction of pure PI decreases drastically, which is associated with polymer transfer on to the disc similarly to vacuum condition.

As observed in Fig. 6, the wear rate of pure PI decreases slightly at lower pressures. Cross-links of polyimide in humid air contribute to wear resistance, but in vacuum condition, polymer transfer protects the composite against abrasive steel asperities.

The addition of graphite has a beneficial effect in air and H₂ atmosphere reducing friction and wear rate compared to pure polyimide. In these conditions, H₂O vapor and H₂ molecules saturate the dangling bonds of graphite present at the interface, which forms an effective lubricating “third body” layer.

In this study, the type of graphite does not influence the friction behaviour of filled PI composites in air, H₂ or vacuum environment, but the wear rate is slightly higher with the composites containing natural graphite, which has a lower mechanical strength.

Results in vacuum conditions indicate that the polyimide matrix has a major influence on the friction (lower friction in vacuum than in air), via polymer transfer on the counterface, whereas graphite have a larger contribution to wear of PI composites.

However, it is noticeable that comparing to vacuum conditions, only 10^3 Pa H₂ is sufficient to have a significant effect on the friction and wear of the 40 wt% graphite filled composites. In this test condition, H₂ seems to influence mainly graphite, substantially present in the composites and therefore at the interface (Fig. 8), resulting in lower friction to the detriment of wear resistance.

5. Conclusion

Results obtained up-to-now reveal that graphite has a beneficial effect on the friction and wear behaviour of polyimides composites both in air and in H₂ atmosphere. Furthermore, H₂ molecules seem to act similarly to water vapor on both graphite and on polyimides, having a
positive and negative effect respectively.

Since the lubricity of both graphite and polyimides depend not only on the environments, but also on the test conditions, experiments will follow at higher p.v. conditions. Further experiments along with surface analyses will be carried out also with various graphite and polymers in order to characterize deeply the influence of H₂ environment on the tribological behaviour of graphite filled composites.

Acknowledgments

The authors are grateful to the Germany Research Association (DFG) for the financial support of the study (Gr1002/9).

References


