Influence of fillers on the low amplitude oscillating wear behaviour of polyamide 11

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Abstract

The oscillating wear failure of the materials is frequently observed in various tribo-applications such as bearings, gears, bushes, palliatives, bolted and riveted joints and seals, etc. where oscillations of small amplitude or vibrations are inevitable. In general, the oscillating wear performance of the materials depends on the amplitude of oscillation, its frequency and duration, load, contact geometry, environment, etc. A vast literature is available reporting on the influence of fillers and fibres on the adhesive (unidirectional) and abrasive wear behaviour of polyamides (PAs) but not much on their oscillating wear behaviour.

For the present study, PA 11 and its three composites containing short glass fibres (GF) and metallic powdery fillers such as bronze and copper were selected for the investigations. Experiments were carried out on the SRV Optimol instrument in pin on disc configuration, under various loads at room temperature. It was observed that the GF reinforcement greatly improved the friction and wear performance of PA 11. Incorporation of bronze and copper powders in GF reinforced composite further improved the friction and wear behaviour of PA 11. Copper proved to be beneficial filler than the bronze in this context. Worn surface studies were also done to investigate the wear mechanisms. The SEM and EDAX studies on the copper-containing composite indicated that the film transfer on the disc was very thin, uniform and coherent. It showed evidence of Cu transfer on the disc, which was thought responsible for strong adherence of the film to the mild steel disc resulting in the best friction and wear behaviour of the composite.

Keywords: Glass fibres; Polyamides; SEM

1. Introduction

Reinforcement in polymers with fibres (short, long or continuous) of various types such as glass, carbon, aramid, etc. is essential to enhance the strength properties of virgin polymers. Such reinforcements have proved performing varying roles in various wear modes. The extent of its influence, however, depends on the types of fibres, their combinations, amount and quality of fibre-resin bonding and types of wear modes in which component is used. In sliding wear mode, for example, it improves the wear resistance significantly though not necessarily the friction coefficient. In the case of abrasive wear mode most of the time, deterioration in wear performance is observed [1-3]. Almost equal number of papers has reported both the trends (improvement or deterioration) in the erosive wear mode due to reinforcement in the polymers. In the case of fretting or low amplitude oscillating wear mode the number of papers, however, are inadequate to establish a general trend in this respect. The influence of fibres or fillers is very much unpredictable in this wear mode and needs to be addressed more thoroughly.

Low amplitude oscillating wear is generally a threat to the tribo-component, which undergoes either small amplitude displacements or vibrations intentionally or unintentionally. The typical examples are: bolted or riveted joints, gripped components, seals, palliatives, flanges, bearing liners, etc. Since the polymers and composites especially fibre reinforced polymers (FRPs) form an important class of tribo-materials, it becomes more imperative to examine the influence of fillers/fibres on the fretting wear (better known as more general name, low amplitude oscillating wear). In fact, in certain situations, where vibrations are inevitable resistance to such wear damage becomes an important criteria for material selection.

In the literature not much is reported on the fretting wear of FRPs. Friedrich [4] studied the influence of glass fabric on the fretting-fatigue behaviour of polyester and found that the fabric improved the wear behaviour of the polyester.
which was thought due to the improvement in the fracture toughness. Rehbein and Wallaschek [5] reported the significant reduction in the wear rate of PTFE due to the inclusion of short carbon fibres (CF). Inclusion of PTFE and CF in PI worked very well in this aspect. Bijwe and co-workers [6-8] also reported on the positive contribution of short GF; solid lubricants and CF in reducing the fretting wear of polyetheretherketone (PEEK) and polyetherimide (PEI). In the case of PEEK, increasing amount of PTFE (0-30%) proved to be very much beneficial for eliminating stick-slip behaviour of PEEK and improving its friction and wear behaviour and PV limit very significantly [9]. Among various metallic and non-metallic coatings applied, Chivers and Gordelier [10] reported the best behaviour by epoxy + graphite coating for palliatives rather than PI + graphite. Bijwe and Sharma [6] reported the beneficial effect of MoS2 on the fretting wear behaviour of PI.

However, the detrimental influence of fibres or solid lubricants has also been reported in many cases. For example, Sharma [11] noticed the detrimental effect of graphite on the fretting wear behaviour of PI. Bijwe et al. [12] reported improvement in the wear performance of PEI due to glass fabric reinforcement of plain weave but deterioration due to other two selected weaves. Bill [13] studied the fretting wear behaviour of Ti-6Al-V alloy coated with PI and composites of PI filled with 60% graphite fluoride and 75% MoS2. He found that the fillers deteriorated the fretting wear behaviour of the PI coating although the PI coatings improved the fretting wear performance of the original alloy. Kang and Eiss [14] investigated the influence of polysiloxane on the fretting wear behaviour of PI coatings and observed the increase in wear rate due to the inclusion of polysiloxane at particular humidity level.

While studying the reciprocating wear behaviour of 0-50 vol. % graphite and MoS2 filled PTFE composites, Yan et al. [15,16] noticed the drastic deterioration in the wear behaviour of the composite beyond 40vol.%, which was preceded by an initial improvement up to 20vol.%. Thus, the literature survey reveals that the incorporation of fibres and fillers led to improvement, deterioration or mixed trends in the fretting wear behaviour of polymers.

Interestingly, most of the available literature pertains to the fretting wear of polymides, epoxy and their composites. Though polyamides are very important engineering tribo-materials, not much is reported on the fretting wear of this class of polymers or composites. Guo and Jiu [17] studied the fretting wear behaviour of PA 1010 and noticed the fibrillar debris around the fretting zone owing to its higher ductility and higher frictional heating during fretting. Renicke et al. [18] reported on the positive influence of inclusion of 15% PTFE in the composite of PA 46 + 30% short GF. Since neat polymer was not studied, the influence due to the inclusion of GF reinforcement could not be addressed. Byett and Allen [19] studied reciprocating wear behaviour of PA 66 and composites with PTFE and silicon oil, UHMWPE, GF and reported that in all the cases the reinforcement enhanced the wear behaviour of the neat polymers. Thus the literature indicates that the papers on the influence of fibres and fillers on the fretting wear of PAs were not available. Hence, it was proposed to investigate the influence of short GF and metallic fillers on the low amplitude oscillation wear of polyamide 11 (PA 11). PA 11 was selected for these studies because of its very good abrasive and erosive wear performance in the author’s laboratory [20,21]. Moreover, the same fillers selected in the studies presented here have shown detrimental effect on the abrasive wear performance of PA 11 [22] while the beneficial effect in adhesive wear mode [23]. Hence, it was thought interesting to investigate the influence of fillers on the low amplitude oscillating wear performance of PA 11.

2. Experimental

2.1. Selection of materials

Polyamide 11 (chemical structure of -NH-(CH2)10-CO-) was selected as a base matrix to fabricate the composites. PA 11 in granular form was procured from Elf Ato Chem, France. The short glass fibres (ø1.5 mm length and ø0.8 (μm diameter), bronze (20-110 (μm) and copper powders (20-70 (μm) were procured from Twiga Fibreglass Ltd., India, Wolstenholme Bronze Powders Ltd., UK and Central Drug House Ltd., India, respectively. Composites based on the PA 11 (Table 1) with the short glass fibres and the metal powders were processed by extrusion on twin-screw extruder followed by injection moulding. Test pins (10 mm x 10 mm x 4 mm) were cut for tribo-evaluation from the injection moulded test specimens for tensile strength measurement. The mechanical properties are compiled in Table 2.

**Table 1** Details of the compositions of PA 11

<table>
<thead>
<tr>
<th>Material</th>
<th>Short GF (wt.%)</th>
<th>Bronze powder (wt.%)</th>
<th>Copper powder (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A0</td>
<td>20</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>A0G</td>
<td>20</td>
<td>6</td>
<td>-</td>
</tr>
<tr>
<td>A0GC</td>
<td>20</td>
<td>-</td>
<td>6</td>
</tr>
</tbody>
</table>

**Table 2** Details of the mechanical properties of the selected materials

<table>
<thead>
<tr>
<th>Property</th>
<th>A0</th>
<th>A0G</th>
<th>A0GC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength (MPa) (ASTM D 638)</td>
<td>36</td>
<td>38</td>
<td>43.5</td>
</tr>
<tr>
<td>Tensile elongation (%) (ASTM D 638)</td>
<td>16</td>
<td>16</td>
<td>6</td>
</tr>
<tr>
<td>Hardness (Shore D value)</td>
<td>80</td>
<td>82</td>
<td>82</td>
</tr>
<tr>
<td>Flexural strength (MPa) (ASTM D 790)</td>
<td>29</td>
<td>40</td>
<td>40</td>
</tr>
</tbody>
</table>
2.2. Oscillating wear studies

Oscillating wear studies were carried out on a pin-on-disc configuration on SRV Optimol tester whose schematic is given in Fig. 1. Polymer pin (10 mm x 6 mm x 4 mm) fretted against a smooth (Ra 0.2 (μm) mild steel disc (diameter 24 mm and thickness 8 mm). Before starting the experiment the pin was fretted against 1200 grade silicon carbide (SiC) abrasive paper (grit size 5 (μm) fixed on the mild steel disc under low load for uniform contact. The pin was then cleaned with the brush to remove the wear debris and weighed. The operating parameters were as follows:

- Loads (N): 50, 100, 150, 200
- Frequency of oscillation (Hz): 50
- Stroke length (peak to peak distance) (mm): 1
- Duration of oscillation (h): 1
- Temperature (°C): 25
- Atmosphere: Ambient
- Humidity (%): 80-85

The distance between the two peaks of sinusoidal stroke profile [24].

The specific wear rate \( K_0 \) was calculated from the following equation:

\[
K_0 = \frac{\Delta V}{L a f t}
\]  

where \( \Delta V \) is the volume loss (m³), \( L \) is the load (N), \( A \) the amplitude (m), \( f \) the frequency (Hz) and \( t \) is the oscillating time (s).

3. Results and discussion

The peak friction coefficient \( (f_a)_{peak} \) and steady-state friction coefficient \( (f_a)_{steady} \) as a function of load are shown in Figs. 2a and b, respectively, while the specific wear rate as a function of load is plotted in Fig. 3. Fig. 4 shows the micrographs of the worn surfaces of the counterfaces, while Figs. 5 and 6 are for that of composites.

Inclusion of glass fibres in PA 11 has improved hardness, tensile strength and flexural strength at the cost of deterioration in the elongation to break. Inclusion of 6 wt.% bronze and 6 wt.% Cu in PA 11 + GF composite showed further increase in tensile strength but deterioration in the elongation to break. Highest flexural strength was shown by AC composite indicating better compatibility of Cu powder with PA 11 than the bronze powder.

As seen from Fig. 2, \( f_a \) and \( f_a \) of PA 11 was almost in the range of 0.41 irrespective of the load. GF reinforcement and inclusion of metal fillers decreased the friction coefficient drastically. With increase in load, it showed continuous decrease for all the composites. The friction coefficient was in the following order \( A_g > A_{gb} > A_{gc} \). Moreover, the specific wear rates of the materials revealed the positive influence of fillers. The wear rates were in the order \( 10^{-13} \) m³/Nm for the composites while for PA 11 it was in the range \( 10^{-14} \) m³/Nm. The relative wear resistances (RWR) of the composites (the ratio of wear rate of unfilled polymer to that of composite) are shown in Table 3. Incorporation of 20 wt.% short GF \( (A_g) \) improved the relative wear resistance by more than four times while the addition
of bronze and copper powders to AG further enhanced it by approximately 6 and 13 times, respectively, depending upon the applied pressure.

The important difference between the fretting and sliding wear is due to the fact that the wear partners in the fretting wear have an overlap ratio near or equal to 1 and consequently wear debris cannot easily escape from the tribo-contact. The facilitation of wear process by the entrapped debris in the interphase is an additional type of wear mechanism. The third body interphase formed due to the generation and preservation of debris in the contact zone is responsible to separate the two surfaces. The kinematics of the contact zone is governed by the nature of third body interphase, which continuously gets sheared between the two surfaces and hence, the frictional force developed depends on the mobility of the interphase and on the nature of wear debris in it. In the case of FRP, the debris generates from polymer, metal counterpart, fibre and fillers, if any. The nature of polymeric wear debris is very crucial. Since the temperature of the contact zone is significantly higher than that in the case of unidirectional sliding, the rheology of polymeric or fibrous debris is one of the very important decisive factors in controlling friction and wear performance of a composite. Though the third body abrasion is dominant in the case of wear of metal pair, it has less weightage when polymer composite frets against a metal. In this case transfer of polymer/fibre on the counterpart in the form of thin film or particles takes place to an appreciable extent, which depends on the material, fillers and operating conditions.

In the selected composites, A0 showed highest wear rate while AGC showed the lowest. The disc surfaces worn against these composites are shown in the micrographs in Fig. 4. Micrographs 4a and b are for the disc worn against unfilled PA 11 while 4c and d are for the disc fretted against composite AGC. The disc surface (4a) shows the transfer of PA 11 film, which is non-uniform and patchy. Micrograph 4b shows an enlarged view where from patches of the transferred film are removed. Magnified view of the patch shows the process of detachment or peeling off of a film, which contributes to the wear of material. The transferred film that is adhered to the surface firmly, resists easy peeling off, which inhibits further transfer from the polymer pin and thus resists the wear. In the case of PA 11, since the adherence of film was poor,

Table 3

<table>
<thead>
<tr>
<th>Material</th>
<th>Relative wear resistance at 100 N</th>
<th>150 N</th>
<th>200 N</th>
<th>250 N</th>
</tr>
</thead>
<tbody>
<tr>
<td>A0</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td>A1</td>
<td>3.9</td>
<td>4.3</td>
<td>3.6</td>
<td>4.3</td>
</tr>
<tr>
<td>AGB</td>
<td>6.4</td>
<td>11.6</td>
<td>6.3</td>
<td>5.2</td>
</tr>
<tr>
<td>AGC</td>
<td>12.8</td>
<td>11.6</td>
<td>7.8</td>
<td>11.4</td>
</tr>
</tbody>
</table>
wear of PA 11 was high. In the case of composite of PA 11, which contained GF and Cu, transfer film on the disc was very coherent, thin and strongly adhered to the disc (micrograph 4c). EDAX of the same surface in terms of Cu dot mapping is shown in the micrograph 4d. It seems that the filler Cu, which was responsible for binding the film of PA to the disc firmly, had chemically reacted with the mild steel counterpart and formed an inter-metallic compound, which enhanced the adhesion between the transfer film and the metallic counterpart as observed by Bahadur and Tabor [25] during sliding wear studies of PA 11 composite reinforced with carbon fibres and CuO filler. This led to the lowest wear of this composite.

Micrographs in Fig. 5 show worn surfaces of PA 11 (5a), PA 11 + GF (5b) and PA 11 + GF + bronze (5c). Micrograph 5a shows the marks of micro-ploughing and evidence of third body abrasion. The material shows severe plastic deformation and indication of extrusion of material in the form of elongated sheets. The high wear of the material is supported from its surface topography. Micrograph 5b, on the other hand, hardly shows any marks of such ploughing. The surface shows embedded worn tips of glass fibres, which resisted the excessive plastic deformation of the polymer surface. The surface shows the indication of material softening. The fibre tips hinder the transfer of polymer on the disc leading to low wear. The surface in the crater of the composite AGB (5C) indicates the back transfer of the powdery debris from the third body interphase on the softened polymer matrix. The bed of powdery wear debris could be due to bronze, steel and glass fibres. Such features have been reported in the case of fretting wear of polymer composites by many authors for their selected systems [4,12].

Micrographs in Fig. 6 illustrate the effect of load on the surface topography of the composites. Micrographs 6a and b are for surface of PA 11 worn under 100 and 250 N, respectively. The extent of damage to the surface is higher at high load. The micrograph 6b shows the wear debris removal process clearly. Because of the continuous periodic motion, the molecular chains undergo tensile shearing. The
chains get elongated in the front edge and do not get detached at first instance. Due to reciprocating motion, when the stress is applied in the reverse direction chains suffer from a compulsive relaxation, which results in the deterioration of the intermolecular forces. The compulsive relaxation damages the strength of the chains excessively. During consecutive cycle, the same process repeats and the rolling of chains starts. The additional mechanisms such as thermal and mechanical fatigue also contribute in the process. These loose rolls attached to the surface of the polymer make the patterns similar to beach marks. Such rolls are responsible for high friction because of their inability to bring out efficient load transfer. The shearing of such partly adhering chains causes high friction coefficient. Once detached they are responsible for high wear.

If the polymer contains a secondary filler particle, this process of chain elongation, forced relaxation and detachment when reached the elongation limit, would be hindered and both friction and wear would be less. Exactly the same was observed in the case of composite as seen in micrographs 6c-e. The surface appearance of the worn composites is different. Micrographs 6c and d are for AG at 100 and 250 N, respectively, showing more damage to the surface and fibres due to high load. As seen in the micrograph 6c, few long fibres along with the microcut and peeled off fibres from the original position can be seen. The cavities are filled with their pulverised fibrous debris (6c). Few fibre tips embedded in the surface can also be seen. In the micrograph 6d, noticeable feature is about the accumulated pieces of fibres in the central contact zone. These are transferred to the pin surface from the interphase. Another noticeable feature is the thick back transferred patches of molten polymer from the disc. These secondary plateaus cannot withstand the load and show microcracking and result in showing high wear. Micrograph 6e shows the crater of AGC, which has shown the best wear behaviour. The fibrous debris appeared to be covered with the very thin polymeric films, which resists further abrasion mechanism leading to low friction and wear. The back transferred thin film is because of the strong adherence of the primary transferred film to the disc as shown in the micrograph 6c. Thus the difference between the friction and wear behaviour of A0, AG, AGB and AGC is because of the absence and presence of fillers and their nature.
4. Conclusions

From the present studies it was concluded that the short GF reinforcement improved the friction and wear properties of PA 11 significantly. Further incorporation of metallic powders, viz. bronze and copper improved the friction and wear behaviour of PA + GF composite significantly. The coherent thin film formation had significant influence on the friction and wear behaviour of PA 11. Copper was found to be the best effective filler in reducing the friction and wear rate of PA 11 as compared to the bronze powder because the copper atoms enhanced the adhesion between the transfer film and the mild steel counterface thereby reducing both the friction and wear of PA 11.
References


