EFFECTS OF POLYTETRAFLUOROETHYLENE MICRO POWDER ON FRICTION NOISE OF MODIFIED FLUORORUBBER

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Water-lubricated rubber compound bearings have been widely applied in ships and vessels for its good water-lubrication and wear-resistant properties. However, stick-slip induced noise such as squeal easily occurs when propulsion shafting starts, stops or operates slower than a noise-generation critical speed. This study employed copper ring sliding against fluororubber to simulate the working condition of rubber bearing and proposed a low-noise fluororubber composite. The fluororubber was modified by PTFE micro powder. Raw fluororubber mechanically mixed with PTFE micro powder then cured. Composites with five PTFE-contents were prepared. Mechanical and friction properties including modulus, vibration acceleration level, volume wear rate and coefficient of friction (COF) were investigated. The PTFE powder remarkably influenced the mechanical properties of the composites as a result. Vibration acceleration levels of different composites under two sliding speeds were tested, which characterized the friction noise of composites. The modulus increased and noise-generation critical speed decreased with the augmentation of PTFE. The experiment showed that fluororubber composite with 10 wt% PTFE performed the best low-noise properties, in which no squeals occurred and total vibration acceleration level was lowest under the sliding speed of 0.025 m/s.

Keywords: PTFE, fluororubber, friction-noise

1. Introduction

When the rotation speed of the propulsion shafting is insufficient to form the hydrodynamic lubrication of the water film, the shafting is directly contact with the bearing to generate dry friction. The large load generated by the weight of the propeller and the shafting causes asperities of the rubber surface and the surface of the metal sleeve to stick when relative static or relative movement speed is low. As the shafting rotates, the stick joint is sheared and the surface is cut. The asperities slide back to the original state with a slight displacement, and after the stick occurs again, an alternating movement of stick and slip is formed, causing self-excited vibration, resulting in squeal. In general, the stick-slip effect has a critical relative velocity, which disappears when the shafting speed is greater than the critical speed [1].

In the process of propeller starting and stopping, there is always a speed lower than the critical speed. Therefore, it is difficult to avoid the squeal due to the stick-slip effect when the rubber is used as the bearing material. Through in-depth study of the stick-slip effect, it is found that the modulus of rubber has a direct relationship with it. Usually, the modulus of rubber is relatively low, and it is easy to generate self-excited vibration [2]. Increasing the modulus reduces the critical speed at which noise is generated, or reduces the probability and tendency of noise to occur. However, the modulus cannot be increased indefinitely. When the high-modulus bearing material sticks to the shaft, the asperities are not easily
deformed and will be cut or sheared, which makes it more wearable [3]. Therefore, in order to obtain better friction and wear and noise reduction performance, it is necessary to properly design the modulus and study the characteristics of the material.

Fluororubber is a material with stable properties and easy adjustment of modulus. The main types are FKM23, FKM26 and FKM246. Among them, the FKM26 can easily increase the hardness to 80 (shore A) with carbon black reinforced. In this paper, on the basis of carbon black reinforcement, PTFE micro powder with reduced self-lubricating effect is added, and a larger filling ratio range is set. The influence of PTFE micro powder on the mechanical and frictional wear properties of fluororubber is studied as comprehensively as possible, which aims to further improve the modulus of the fluororubber and explore the optimization effect of PTFE on the frictional noise of the fluororubber.

2.  Methods

2.1  Raw materials and reagents


2.2  Preparation of modified materials

Vulcanization is a process in which a rubber crosslinks a macromolecule through a crosslinking agent or a crosslinking initiator under conditions of three factors of temperature, pressure, and time, which causes the rubber to change from a plastic state to an elastic state. For fluororubbers, phenolic vulcanizing agents can achieve C-O bond with high thermal stability compared to conventional organic peroxide vulcanizing agents (such as DCP-TAIC systems) and bis-amine vulcanizing agents (such as 3# vulcanizing agents), so that fluororubber has better heat resistance and permanent compression resistance [4]. Such phenolic vulcanizing agents are suitable for the needs of bearing materials. Therefore, this study employed bisphenol AF-BPP curing system. The rubber reinforcement system used N550 fast-pressing furnace black, which gives the rubber compound excellent wear resistance, heat resistance and thermal conductivity. The formulation of modified fluororubber was 100 parts of fluororubber, 6 parts of calcium hydroxide, 3 parts of light magnesium oxide, 30 parts of N550, 0.5 parts of BPP, and 2 parts of bisphenol AF. The PTFE modified fluororubber formulation is shown in Table 1. After pre-tests, it was found that the modified fluororubber was difficult to process when the PTFE content is more than 30 wt%, and the vulcanization is prone to bubbles, the highest ratio is set to 30 wt%. There is less research on the proportion of fillings below 10 wt%, so subdividing the formulations smaller than this ratio to make the regular exploration more complete.

<table>
<thead>
<tr>
<th>Sample</th>
<th>PTFE micro powder filling ratio/wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>F00</td>
<td>0</td>
</tr>
<tr>
<td>F03</td>
<td>3</td>
</tr>
<tr>
<td>F05</td>
<td>5</td>
</tr>
<tr>
<td>F08</td>
<td>8</td>
</tr>
<tr>
<td>F10</td>
<td>10</td>
</tr>
<tr>
<td>F20</td>
<td>20</td>
</tr>
<tr>
<td>F30</td>
<td>30</td>
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</tbody>
</table>
The fluororubber and the auxiliary agents were mixed into the mixer for 30 minutes, and the temperature was controlled below 60 °C. Took out the large mixture of rubber, and passed it on the open mill for 5 times, divided it into 7 parts on average, cooled it, and then added it to the roll of the open mill. Added the different quantity PTFE micro-powder according to the ratio in Table 1. Refining, punching the triangle package, thinning to white powder is not visible, then thinning 10 times, to obtain PTFE modified fluororubber film, thickness of 2 ~ 3 mm, then leaving it at room temperature for 24 h.

Fluororubber should be vulcanized in a two-stage vulcanization to prevent reversal of cure and promote the stability of the vulcanizate. First, the raw rubber was added to the mould of the corresponding standard test sample, and a vulcanization was carried out using a small flat vulcanizing machine under the conditions of 170 °C, 10 min, and 15 MPa. Then, a vulcanized sample was taken out and placed in an oven for two-stage vulcanization at atmospheric pressure. The condition is 230 °C for 24 h, and finally a vulcanized rubber sample was obtained.

2.3 Tests and characterization

According to GB/T 528-2009, GB/T 529-2008 and GB/T 7757-2009, the mechanical properties of vulcanized rubber such as tensile, tear and modulus were tested using a mechanical testing machine. The raw rubber compound was added into a mould of 150 mm×110 mm×2 mm, and a rectangular film is obtained by vulcanization, and at least 5 type 1 dumbbell-shaped samples were cut out by using a cutter for the tensile test. At least 5 rectangular specimens were cut for the tear test; the raw rubber compound was added to a cylindrical mould of φ 29.0 mm × 12.5 mm, and the compressed cylindrical specimen was obtained by vulcanization. The standard sample is clamped to the mechanical testing machine fixture (stretching, tearing), or placed between the testing machine compression test steel plates, and the preset program is run for testing.

The friction and wear performance was mainly determined by the unit loading force and the wear volume rate of the unit to the length of the grinding. The parameters and items of the test mainly include: volume wear rate and coefficient of friction (COF). The raw fluororubber compound was added to a mold of a size of 19.05 mm × 12.32 mm × 12.32 mm, and a standard friction and wear sample was obtained by vulcanization. The sample was loaded into an MRH-3A friction-wear test machine and loaded onto a metal ring. The material of the polished metal ring is tin-bronze alloy, and the size is φ 49.2 mm×13.6 mm (Figure 1). The test speed was 1100 r/min, the loading force was 66 N, and the test time was 120 min.

![Figure 1: Sketch of block-ring friction-wear test.](image)

The COF is obtained by the following formula:

\[
\mu = \frac{F_f}{F_n}
\]

where \(\mu\) is the COF. \(F_f\) is the friction force, measured by the friction-wear test machine. \(F_n\) is the loading force. The value of COF is directly calculated by the test machine program.
Material wear resistance is characterized by volumetric wear rate \([5, 6]\):

\[
w = \frac{\Delta V}{F_n \times L}
\]

(2)

where \(w\) is the volume wear rate, \(\Delta V\) is the volume reduction of the standard sample after wear, using one analytical balance to measure the difference in quality before and after wear. The density is calculated \((V = \Delta m/\rho)\), the material density was measured by a rubber density meter; \(F_n\) is the loading force, \(L\) is the sliding length.

Two acceleration sensors were installed near the metal ring rotor of the friction-wear test machine. The speed was set to 2 categories: 10 r/min (about 0.025 m/s), 39 r/min (about 0.1 m/s), the tangential acceleration time domain data of the metal ring and the friction and wear sample were obtained by vibration test and analysis system, and the frequency domain data was extracted by Fourier transform of the time domain data, and then the time was drawn. The domain spectrum and the frequency domain spectrum were used to compare and analyze the noise reduction performance of the material.

3. Results and discussions

3.1 Mechanical performances

Table 2 shows that as the PTFE content increases, the tensile strength \((TS)\) and elongation at break \((E_b)\) of the modified fluororubber gradually decrease, and the tear strength \((T_s)\) increases remarkably.

The addition of PTFE significantly increases the modulus \((E_c)\) of the fluororubber, but the hardness do not change significantly. The modified fluororubber with 30 wt\% PTFE content increases by 300% compared to without PTFE. PTFE causes a significant decrease in tensile strength and elongation at break. Compared to fluororubber without PTFE, the tensile strength of the modified fluororubber is reduced by 15% with the PTFE content of 3 wt\%. The tensile strength is reduced by 40% with the PTFE content of 30 wt\%. Unmodified PTFE is incompatible with the rubber matrix, and its presence destroys the continuity of the fluororubber matrix, resulting in reduced strength and easier breakage. The tear strength gradually increases with the increase of PTFE content. The possible reason is that PTFE micropowder absorbs a part of the impact and delays the cracking of the rubber matrix, thus optimizing the tearing performance.

<table>
<thead>
<tr>
<th>Sample</th>
<th>F00</th>
<th>F03</th>
<th>F05</th>
<th>F08</th>
<th>F10</th>
<th>F20</th>
<th>F30</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTFE content/wt%</td>
<td>0</td>
<td>3</td>
<td>5</td>
<td>8</td>
<td>10</td>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td>(E_c/\text{MPa})</td>
<td>7.54</td>
<td>9.56</td>
<td>10.45</td>
<td>12.11</td>
<td>15.19</td>
<td>22.91</td>
<td>30.15</td>
</tr>
<tr>
<td>(TS/\text{MPa})</td>
<td>14.50</td>
<td>12.30</td>
<td>11.80</td>
<td>11.34</td>
<td>11.15</td>
<td>9.81</td>
<td>8.67</td>
</tr>
<tr>
<td>(E_b/%)</td>
<td>99.52</td>
<td>84.12</td>
<td>80.52</td>
<td>78.46</td>
<td>76.85</td>
<td>73.62</td>
<td>71.84</td>
</tr>
<tr>
<td>(T_s/(\text{kN} \cdot \text{m}^{-1}))</td>
<td>8.75</td>
<td>9.43</td>
<td>9.42</td>
<td>10.08</td>
<td>10.87</td>
<td>12.09</td>
<td>15.47</td>
</tr>
</tbody>
</table>

3.2 Tribological performances

Figure 2 shows the relationship between volume wear rate and COF of modified fluororubber as a function of PTFE content. It can be seen from Figure 2 that with the increase of the amount of PTFE added, the volume wear rate and COF of the modified fluororubber show a trend of decreasing first and then increasing, but the two are not synchronized. The F05 sample with a PTFE content of 5 wt\% exhibits the best wear resistance, and the volume wear rate is reduced by about 11% compared to the PTFE rubber without PTFE. The F10 sample with a PTFE content of 10 wt\% has the lowest COF. In addition, when the PTFE content is increased to more than 10 wt\%, the wear resistance of the rubber compound is not
as good as that of the fluororubber without PTFE modification, and the friction coefficient gradually exceeds that of the unmodified fluororubber.

![Figure 2: Variation of volume wear rate and coefficient of friction with PTFE content for modified fluororubber.](image)

PTFE is a non-polar compound, which has poor bonding with rubber. The PTFE micro powder is easy to fall off the rubber during the friction. The PTFE itself is not wear-resistant, and the polymer molecules are easily peeled off and act as a lubricant to achieve self-lubrication. At the same time, the change of the mechanical properties of PTFE on the rubber itself will affect the tribological behavior of the matrix, resulting in a change in the microscopic wear mechanism, thereby affecting the wear resistance. The macroscopic wear resistance of PTFE modified fluororubber should be a comprehensive reflection of the above two aspects. When the content of PTFE is less than 5 wt%, the lubricity is dominant, so the wear rate decreases with the increase of PTFE. When the PTFE content is more than 5 wt%, the wear resistance caused by the addition of PTFE affects the mechanical properties of rubber is dominant, so the volume wear rate increases with PTFE content increasing.

### 3.3 Friction noise

Noise monitoring was carried out on the modified fluororubber friction-wear test with different PTFE content. Under low speed, all the materials showed squeal, and the squeal disappeared as the rotating speed increased. Figure 3 shows the frequency domain spectrum of the self-vibration acceleration level of the test machine at 7 r/min and 39 r/min and the F00, F03, F05, F08, F10, F20 and F30 samples at two speeds.

It can be seen from the figure that in the unloaded states, the idling noise of 39 r/min in the frequency band below 10500 Hz is greater than 10 r/min. Obviously, this is caused by the rotating motor of the testing machine, and the rotating speed is high so that the noise is large. At a low speed of 10 r/min, the modified fluororubber (ie, F00–F08) samples with a PTFE content of less than 10 wt% will produce frictional squeal, and the F00 without PTFE is the most typical. There is a strong line spectrum in the wide frequency band, and the line spectrum with the highest amplitude is 2726 Hz, which is the main frequency of the frictional squeal, and the rest of the line spectrum is its harmonic frequency (fn = 2726n, n=1, 2, 3, 4...). The highest vibration acceleration level is 124 dB. With the addition of PTFE, the F03, F05 and F08 materials still squeal at 10 r/min, and the spectrum still shows strong line spectrum characteristics, but the highest acceleration level is reduced to 100–105 dB. After the PTFE content increased over 10 wt%, the F10, F20, and F30 materials disappeared at 10 r/min. When all the 7 samples are raised to 39 r/min, there is no squeal. Compared with the idling noise at two speeds, the vibration of F10, F20 and F30 materials is basically the same at 10 r/min and 39 r/min, and the material has no abnormal friction noise at both speeds, showing good noise reduction performance.
Based on the above test results, the friction noise of the modified fluororubber is improved by the PTFE micro powder. There are two main reasons for the improvement of frictional noise by PTFE micro powder. First, the addition of PTFE increases the modulus of the fluororubber matrix, and is less prone to stick-slip effects [7], reducing the critical speed of the stick-slip motion. Second, with the filling of PTFE micro powder, PTFE occupies more space when the friction surfaces are in contact with each other, and the hardness of PTFE itself (50~55, Shore D) is much higher than that of rubber, and it is chemically inert, so that the effective contact area of the stick-slip of the copper ring is smaller. The vibration absorption of the rubber matrix is reflected to reduce the friction noise.

4. Conclusion

The mechanical properties, wear resistance and friction noise of fluororubber are changed after the addition of PTFE micropowder. The addition of PTFE significantly increases the modulus of the fluororubber, but the hardness do not change significantly. The modified fluororubber with 30 wt% PTFE content increases by 300% compared to PTFE. As the PTFE content increases, the tensile strength of the cured rubber decreased but the tear strength increases; the volume wear rate and the friction coefficient decrease first and then increase, but the two are not synchronized. The friction and wear properties of the modified fluororubber with PTFE content below 8 wt% are improved, the volume wear rate and friction
coefficient are smaller than that of unmodified fluororubber. PTFE modified fluororubber of 5 wt% content has the best wear resistance. The PTFE modified fluororubber of 10 wt% content has the lowest friction coefficient.

When the modified fluororubber ground by the copper ring, the frictional squeal will occur due to the stick-slip effect at low speed, the squeal disappears after the rotation speed is higher than the "critical speed". PTFE improves the noise reduction performance by increasing the modulus of the modified fluororubber and affecting the stick-slip effect of the material during friction. As the PTFE content increases, the friction noise gradually decrease. The 30 wt% PTFE modified fluororubber has the lowest friction noise and the lowest critical speed.

REFERENCES


