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Tribological behaviors of the polyphenyl ester-polytetrafluoroethylene composites filled with whisker

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ABSTRACT

To develop high performance sealing material for Stirling engine, the blend composites of polyphenyl ester-polytetrafluoroethylene were prepared by cool-pressing and hot-sintering. The effect of potassium titanate whisker (PTW) and calcium sulfate whisker (CSW) on the tribological properties of the POB-PTFE composites was investigated. The results showed that POB-PTFE composites could be used as the matrix of seal material in Stirling engine. The creep and shear resistance of the POB-PTFE composites are improved by the addition of PTW, the friction coefficient of the composites did not be changed with the variation of load, meanwhile the wear resistance remain relatively stable. The friction coefficient of the composites did not vary with the variation of velocity when the content of PTW is less than 5% either. The POB-PTFE composites filled with PTW is an optimized sealing material for Stirling engine, but the composites filled with CSW is inadequate to cope with the special requirements for heavy load and high sliding velocity.

Keywords: tribological behaviors, whisker, POB-PTFE composites, sealing material, Stirling engine

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INTRODUCTION

Stirling engine is a kind of closed heat regenerative cycle machine that it's external heating and high-pressure hydrogen or helium gas as working medium, its dynamic performance and reliability is closely related to the dynamic sealing technology [1,2]. It usually requires that the dynamic sealing material have excellent self-lubrication, namely, small friction coefficient, while requiring excellent abrasion resistance, heat resistance and dimensional stability. Therefore, the excellent performance of the sealing material is a key to solve the Stirling engine work efficiency and service life.

B. Brushan [3] contrasted analysis of the polytetrafluoroethylene (PTFE), polyimide (PI), aromatic polyester, polyphenylene sulfide (PPS), phenolic resin and other high-temperature reciprocating sliding tribological properties of polymer composites. The analysis result indicated PTFE is the best basis of Stirling dynamic seal material, through the use of filler for filling modification, can obviously improve the friction and wear properties of PTFE. In recent years, in view of the modified polymer material, the researchers conducted using nanoparticles [4-6], micro fiber [7-9], and different types of high temperature resistant polymer [10,11] modified PTFE material related to the tribological behavior and mechanism of research, this provides more research ideas to solve the sealing problem of Stirling engine.

POB as tribological modification of PTFE material can significantly improve the creep properties and wear resistance of PTFE, but it usually accompanied by lower mechanical properties, such as compression strength, tensile strength, and so on. It is unfavorable to meet the high bearing capacity of Stirling engine sealing material. Research shows that, with high length to diameter ratio of inorganic whisker and POB filled PTFE material together, show good coordination lubrication and reduce friction effect, which will provide effective technology to solve the Stirling engine sealing material [13].

The technical requirements of Stirling engine on the seals are under the pressure of 20MPa, below the speed of 2.5m/s, below the temperature of 200℃, hydrogen or helium gas environment, and to realize the long life of oil-free reciprocating seal. Usually, the actual runtime by load, speed, temperature of seals are constantly changing, so it needs in-depth analysis of the impact rule of these factors on tribological behavior of the sealing material, and scientifically design and preparation of high performance sealing materials to meet the requirements of the actual working condition. Therefore, this paper is to study the tribological performance of PTFE and POB blending composites based on bolt on disc friction and wear testing machine, to study the environment temperature and the influence of content of PTFE composites POB tribological behavior. Using PTW and CSW filled POB-PTFE composites, using the type reciprocating friction and wear testing machine to investigate the effect of whisker content on mechanical properties and tribological behavior of the composites, the effect of load and sliding velocity on the influence law of friction and wear performance, to develop high performance sealing material for Stirling engine.

EXPERIMENTAL SECTION

Material and Physical measurements

The material of PTFE adopted is Japan daikin company production suspension PTFE resin, brand M18F, average particle size 25μm, bulk density 0.33g/cm^3. POB is the production of Chengguang Research Institute of Chemical Industry, size -400 mesh, and molecular weight 9000~70000. PTW is six potassium titanate whisker, produced by Shanghai whisker composites material manufacturing co., LTD., size -400 mesh, and diameter 0.5~2μm, length to diameter ratio 5~20, surface treatment by silane coupling agent KH550. Calcium sulphate whisker is producted by Hefei Jiankun chemical co., LTD., apparent density 0.3g/cm^3, diameter 1~6μm, length to diameter ratio is greater than or equal to 30, tensile strength 20.5GPa, surface treatment by silane coupling agent KH550.

Weighed PTFE, POB and whisker respectively, mixed using mechanical high-speed mixer, sieved into the corresponding mold and suppressed. The pressing pressure was 45~50MPa, holding 1min, after unloading pressure stripper, removed samples after the flash, sintered in the air sintering furnace. The sintering temperature was 375~380℃, heating rate was 0.5~1.0℃/min, the sintering time was 60 min, along with the furnace to cool naturally.

Experimental method

Sanding the sample using 400# metallographic sandpaper to the same surface roughness, and then ultrasonic cleaning 30min in acetone, keep at 60℃ in the oven for drying process, using precision balance to weigh the samples. The same steps above will be done again after the test, so as to calculate the quality of wear and tear, and the corresponding calculated through the test material density and wear volume. Using JMS-5600LV scanning electron microscope (SEM) directly to observe the morphology of PTW and CSW whisker.

Usually, Stirling engine's reciprocating stroke is 40~50mm, in order to accurately simulate the actual working condition, this research use RFT-Ⅲ reciprocating friction and wear testing machine to evaluate POB-PTFE composites' friction and wear performance filled with PTW and CSW, the sample size is Φ4mm×10mm, test under the environment of the atmosphere, reciprocating amplitude is 50mm, test time is 60min, steel friction pair is 30GrMoSi, size is 70mm×14mm×10mm, ion nitriding treatment on the surface, roughness is Ra0.8 ~1.6. Whisker content was 2%, 5% and 8% (weight ratio), in order to close to the Stirling engine seal actual working condition, this research adopts the test load respectively 7MPa, 16MPa and 28MPa, sliding speed 0.25m/s, 0.50m/s and 1.0m/s.

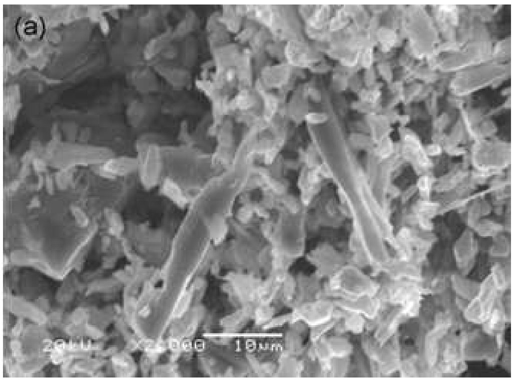
Because the RFT-Ⅲ testing machine does not evaluate the tribological behavior of materials under different temperature conditions, therefore, this study used THT07-135 type high temperature bolt disc friction and wear tester for the preparation of the POB-PTFE composites to analyze the friction and wear performance under different temperature, the sample size is Φ25×8mm, atmosphere environment, rotation diameter is 12mm, test time is 30min, friction pair is CGr15 steel ball, dual diameter is Φ3mm. POB content in the composites was 0%, 5%, 10%, 5%, 20% and 25% respectively, and the load is respectively 2N, 5N and 8N, sliding speed is respectively 0.13m/s, 0.26m/s and 0.57 m/s. Due to the change of the friction coefficient under different conditions is very important to design and choose Stirling sealing material, therefore, this section is only focus on study the effect of load and sliding velocity on the friction coefficient.

CMT5205 electronic universal testing machine was used to evaluate the compression stress-strain properties of the composites, the sample size is 19.1×12.3×12.3mm, the compression rate is 2.0mm/min, the main analysis of the compression strain is 0~5% compression pressure changes.

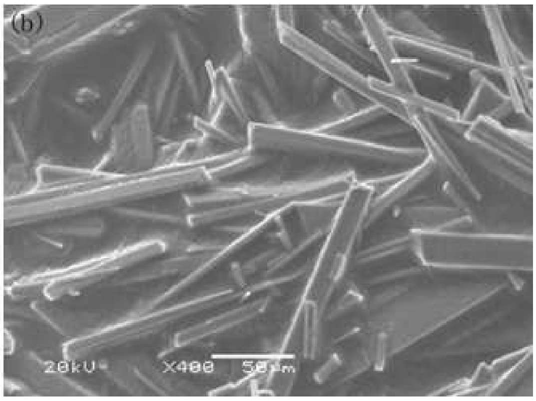
RESULTS AND DISCUSSION

Microstructure of PTW and CSW

In order to improve the tribological properties of polymer materials, the usual solution is to reduce the surface of the polymer in dual adhesive ability, it mainly includes the add can rise to coordination the lubrication effect of filler material, such as adding a low friction coefficient solid lubricant, graphite (Gr) and molybdenum disulphide (MOS2), etc. In addition, hard metal or inorganic materials are filled to improve the hardness of polymer, compression strength and rigidity, including with a range of length to diameter ratio of fiber, such as aramid (AF), glass fiber (GF) and carbon fiber (CF) to improve the creep properties of the polymer, but also can improve the heat resistance performance of materials, to resist plastic deformation caused by frictional heat [14,15]. Studies [16-19] have found that not all the adding material can improve the wear resistance performance of polymer materials, some filler in the process of friction produce chemical reaction, generate new reactants, can effectively improve the binding ability of transfer film on the surface of the friction pair, and for not improve polymer filler is due to abrasion in the surface of the dual form discrete transfer film. Therefore, scientific design and selection has better ability to resist creep of filling materials, for further research on Stirling sealing material is of great importance.



(a) Potassium titanate



(b) Calcium sulfate

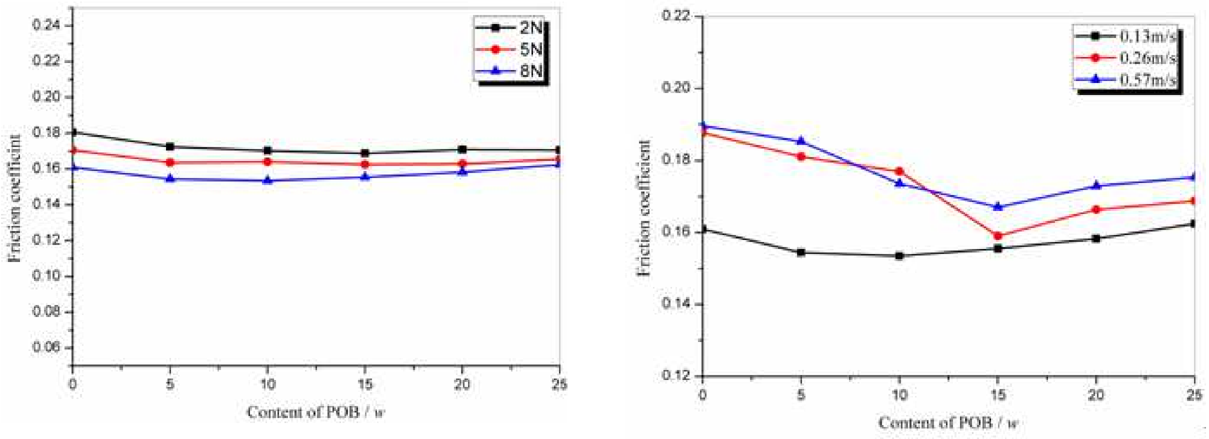
Fig. 1 SEM pictures of the two different whiskers in microstructure

This research adopted PTW and CSW, its microstructure is shown in figure 1. It shows that the two kinds of whisker are rod-shaped fiber structure, and with different length to diameter ratio, the PTW whisker, the average is 0.5~3μm in diameter, length to diameter ratio is 5~20. As can be seen from the figure 1(a), PTW whisker distribution of fiber length to diameter ratio is larger and disordered fiber mixed and disorderly state. It can be seen in Figure 1(b) that CSW whisker in the absence of force, under the condition of the fiber diameter is uniform, and whisker distribution of length to diameter ratio is good. For Stirling system dynamic sealing material, excellent abrasion resistance and long service life is need in working process. Therefore, in addition to the sealing material has excellent tribological performance, at the same time it required to add the filler to improve the creep resistance of PTFE material and compression strength, so the whisker has a certain length to diameter ratio is the ideal choice.

Tribological performance of PTFE filled with POB

In order to intensify the tribological behavior of POB-PTFE composites by whisker filled, it is necessary first to carry out the influence law of POB content on the tribological properties of PTFE. Early research [12] has shown that, POB adding can significantly improve the wear resistance of PTFE.

Figure 2 shows the influence of POB content on the friction coefficient of PTFE under the condition of different load and sliding speed, by using THT07-135 type high temperature bolt disc friction and wear tester. As see from figure 2(a), when the sliding velocity is 0.13m/s, along with the increase of POB content, the friction coefficient remain relatively stable. As the load increases gradually, the friction coefficient of PTFE composites reduced slightly, from 0.18 to 0.15. It can be seen that when the POB content is higher, the friction coefficient increase with load, the lower amplitude decreases. Studies have shown that high levels of POB filled PTFE composites, when the load changes, the relatively stable friction coefficient, which can be used as substrate material for Stirling engine sealing.



(a) Friction coefficient *vs.* load **(b) Friction coefficient *vs.* sliding velocity**

Fig. 2 Friction coefficient of PTFE composites with the variation of POB content

Figure 2(b) shows the load of 8N, the friction coefficient of PTFE composites under different sliding speed along with the change of content of POB. It can be seen that at low speed (0.13m/s), along with the increase of POB content, the friction coefficient is relatively stable; When the sliding velocity is higher (0.26m/s, 0.57m/s), along with the increase of POB content, the friction coefficient increase gradually after the performance to gradually reduce. When the POB content is 15%, the friction coefficient is relative to a minimum. The excellent performance of Stirling dynamic sealing material need a stable friction coefficient when pressure and velocity changes. So it is necessary to further improve the tribological performance of POB-PTFE composites through whisker filling.

Figure 3 shows the friction and wear properties of POB-PTFE composites at room temperature, 100℃ and 200℃ respectively. It can be seen that with the increase of ambient temperature, the friction coefficient keeps relatively stable, between 0.17 and 0.18. It indicates that POB modified PTFE composites' friction coefficient is not a larger impact, along with the change of environmental temperature, and as Stirling sealers, environmental temperature change and the friction temperature rise will not affect the sealers frictional power consumption, it is very important for efficient function and long-term reliability. In addition, from the change rule of wear volume in the picture, it is observed that volume wear is maximum when the environment temperature is 100℃. Therefore, by using inorganic whisker temperature resistance and high temperature wear resistance of polymer material is an effective technology to solve the sealing material high temperature wear failure.

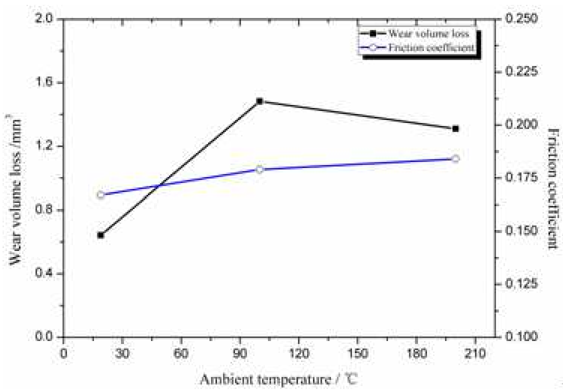


Fig. 3 Tribological properties of POB-PTFE composites under different temperatures

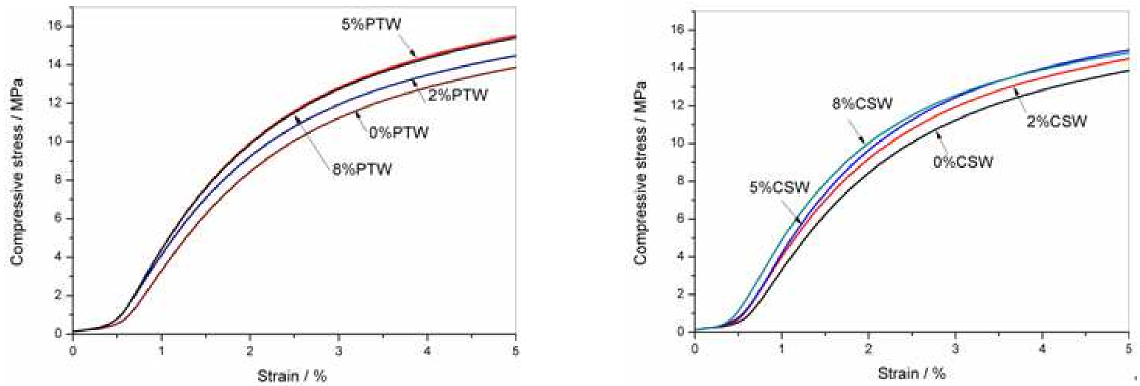
Tab.1 Compressive stress of PTW, CSW filled POB-PTFE composites

Content of Whisker / %	PTW	CSW
0	13.88	13.88
2	14.49	14.48
5	15.53	14.96
8	15.41	14.82

Compression stress-strain behavior of whisker filled POB-PTFE composites

Usually Stirling dynamic seal need to meet the operation condition of the gas pressure difference from 5 to 22MPa and serving for a long time, so the compression stress-strain behavior of material is very important to choose high performance sealing materials. Figure 4 shows the compressive stress-strain curve of PTW and CSW whisker filled POB-PTFE composites. It can be seen that when the compression strain is 5%, the compressive stress of the composite are lower than 20MPa. When the engine at low gas pressure difference (8MPa) or less, the sealing material in the elastic stage, when the gas pressure differential at high (>8MPa), sealing material is plastic. Studies have shown that high pressure and low pressure condition, material mechanics state has a bigger difference, so the action mechanism of the friction shear stress surface sustained on the wear mechanism is also different.

Table 1 show the compression pressure of POB-PTFE composites for different whisker content when compression is 5%. It can be seen that with CSW and PTW whisker added, the compression stress of the composites significantly improve, when whisker content reaches 5%, the compression stress of the composites reach to the maximum, with the further increase of whisker content, compression pressure is slightly lower. Studies have shown that whisker adding can improve the compression strength of composites, at the same time, the ability to resist deformation will be mentioned. When PTW content is more than 5%, the compression strength did not have further improved. This suggests that when PTW content higher than 5%, whisker cannot continue to have the effect for load. Compared the effect of CSW filled POB-PTFE composites with PTW's, PTW has the better enhancement effect.



(a) Potassium titanate **(b) Calcium sulfate**

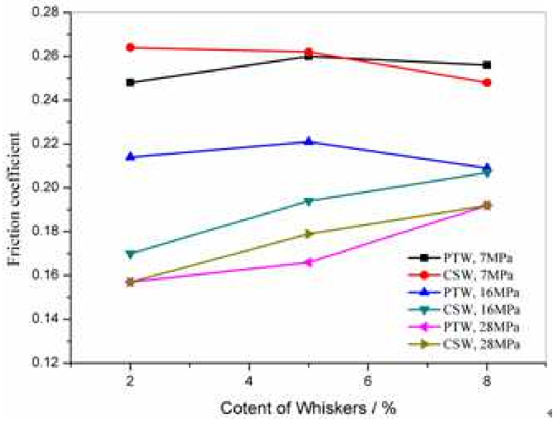
Fig. 4 Compressive stress-strain curves of POB-PTFE composites with different whiskers content

Effect of load on the friction and wear property of whisker filled POB-PTFE composites

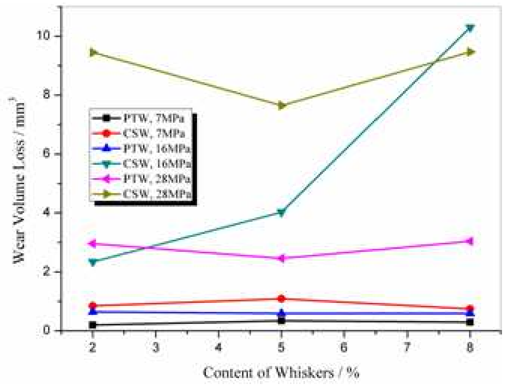
Dynamic seal friction coefficient of friction pair determines the power consumption of the Stirling engine, the wear resistance of sealing materials is to determine the key indicators of engine application life. The high performance of the Stirling engine dynamic seal material must have a low friction coefficient. Usually, when Stirling engine works, gas differential pressure changes with the piston reciprocating motion, thereby seal under load changes. For scientific simulation of sealing material in actual working environment, gas pressure differential effect on the tribological performance of sealing material, this research adopts the RFT-Ⅲ reciprocating friction and wear tester under different load to research the tribological behavior of whisker filled POB-PTFE composites, to analyze the differential effects of tribological performance on Stirling sealing material. Figure 5 shows when the linear velocity is 0.25m/s, the influence of friction and wear performance of PTW and CSW whisker filled POB-PTFE composites. It can be seen that with the increase of load, friction coefficient decreases gradually.

When the load is low (7MPa), with the increase of PTW content, friction coefficient keep relatively stable, stay in 0.25 to 0.26. That is to say, under the condition of low load, the friction coefficient of composites does not change with the increase of PTW. Also, 16MPa load show the same effect, the friction coefficient is 0.21 to 0.22. When the load is 28MPa, with the PTW content increasing, the friction coefficient of the composites increases slowly, from 0.16 to 0.19. From figure 5(b) can be found that with the increase of the content of PTW, wear volume remains relatively stable. Above studies show that PTW filled POB-PTFE composites under different pressure can maintain stable friction coefficient and wear resistance, and PTW can play a good resistance to shearing action.

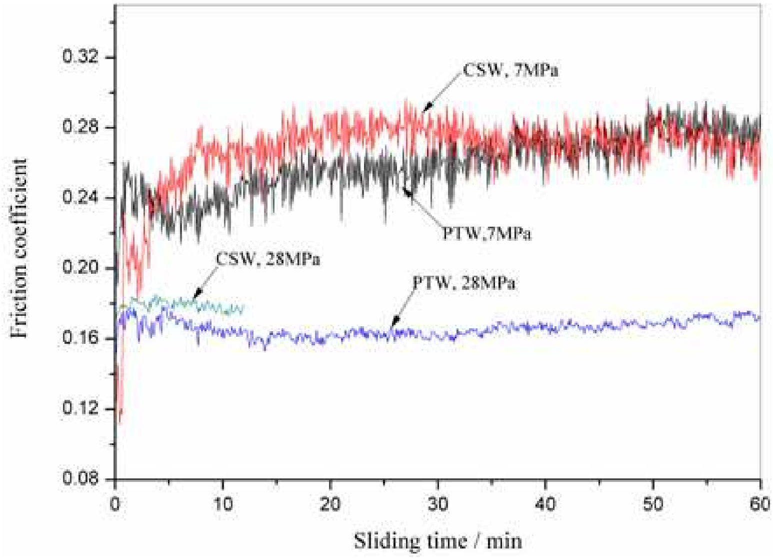
From figure 5(a) and (b), it can be seen that for CSW filled POB-PTFE composites, when the load is 7MPa, along with the increase of the content of CSW friction coefficient slowly lower and wear volume is relatively stable. When the load is 16MPa, along with the increase of the content of CSW increased, friction coefficient and wear volume also increased obviously. When load is 28MPa, along with the increase of the content of CSW also showed a rising trend, friction coefficient and wear volume to reduce, increase after. As can see from figure 5(c), under low load condition 7MPa, the friction coefficient of CSW filled composites is relatively stable, PTW filled composites need a certain period of time to reach equilibrium. Under the condition of high load 28MPa, CSW filled composites is causing wear failure only in 12min, but PTW filled composites run into the stationary state at the first operating period. The above phenomenon indicates that under low load condition, CSW whisker can effectively enhance effect on POB-PTFE composites, when the load increases, the CSW whisker lost creep resistance and shear resistance ability, this may related to its own intensity and structure. For POB-PTFE material system, therefore, CSW is not an ideal filling material, CSW whisker filled composites is not suitable for high load Stirling condition.



(a) Friction coefficient



(b) Wear volume loss



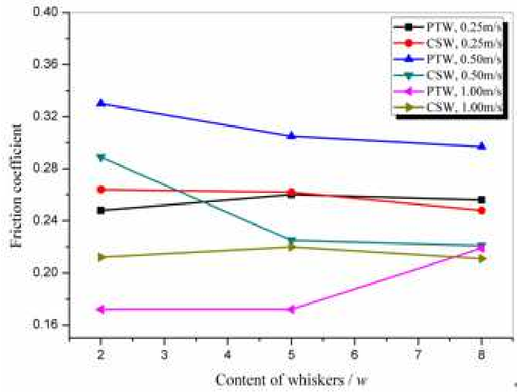
(c) The curves of friction coefficient with sliding time for the composites with 5% whisker

Fig.5 Effect of load on the friction and wear property of whisker filled POB-PTFE composites

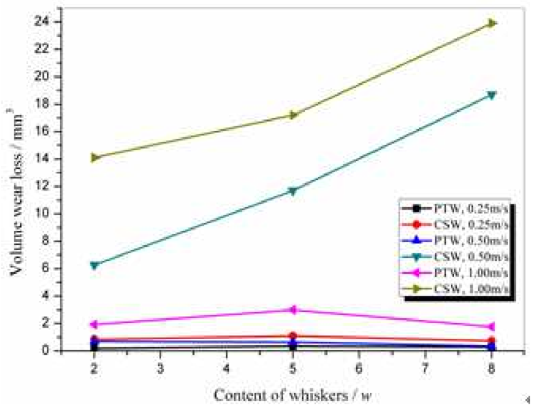
Effect of velocity on the friction and wear property of whisker filled POB-PTFE composites

Usually, the Stirling engine piston velocity is changing at work, so it is of great significance to study the effect of velocity on the friction and wear property of whisker filled POB-PTFE composites. Figure 6 shows the influence law curve of sliding velocity on the friction and wear performance of whisker filled POB- PTFE composites. It can be seen that when the linear velocity is 0.25m/s, with the increase of content of PTW, friction coefficient is stable; when the linear velocity is 0.50m/s, the friction coefficient increased significantly; but when the linear velocity is 1.0m/s, the friction coefficient lower. This is caused by the friction temperature plastic deformation of materials increase. When PTW filling quantity is 8%, the friction coefficient of the composites increase significantly, this could be due to the increase of PTW whisker content, because the material mentioned to improve the ability of the thermal deformation. In addition, the wear volume of PTW filled composites is small and no significant change with the increase of the content of PTW.

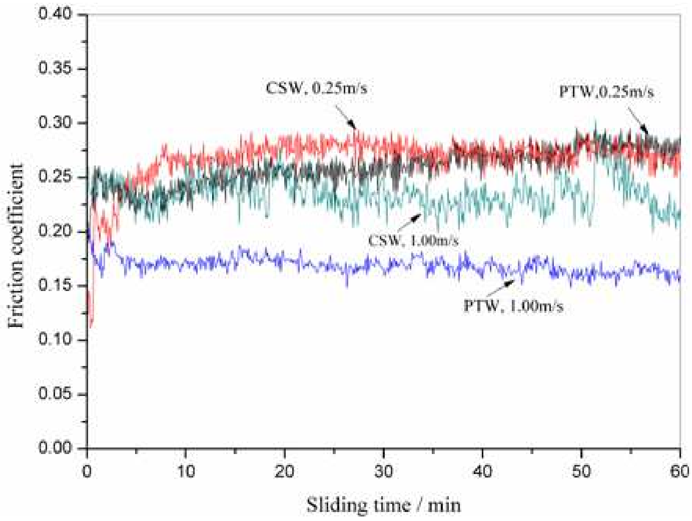
For CSW filled composites, when the linear velocity is 0.25m/s, the friction coefficient is comparable to PTW filled composites; When the linear velocity is 0.50m/s, with the increase of content of CSW, the friction coefficient gradually reduce; When the linear velocity is 1.0m/s, the friction coefficient does not change with the increase of the content of CSW, this is mainly due to the increase of friction heat, causing the size of CSW filled composites deformation increase. In addition, as can be seen from the figure 6(b), under the high speed, the wear volume of CSW filled composites increases rapidly.



（a）Friction coefficient



（b）Wear volume loss



c）The curves of friction coefficient with sliding time for the composites with 5% whisker

Fig. 6 Effect of sliding velocity on the friction and wear property of whisker filled POB-PTFE composites

As figure 6(c) shows, when the linear velocity is 0.25m/s, PTW filled composites gradually enter into the steady state after running-in period. When linear velocity is 1.0m/s, the friction coefficient of PTW filled composites in the process of sliding is stable, the main reason is because of friction heat in the process, at low speed the friction heat release rate slower, so to reach steady state needs a long time; And at high speed the friction heat is big, so the friction pair can reach thermal equilibrium in a relatively short period of time. The friction coefficient of CSW filled composites appear unstable fluctuation, this is because the material wear volume is larger, the high-speed sliding friction heat deformation is caused by material, the plastic deformation of the surface is severe, therefore the stability of friction coefficient is poorer. It can be seen from above research that PTW filled composites adapt to the technical requirements of dynamic seal under the conditions of different speed, and CSW filled composites are not suitable for high speed.

CONCLUSION

POB modified PTFE composites can be used as the substrate material for Stirling engine seal. In order to meet the requirements of Stirling engine on the properties of dynamic sealing material, further optimization is needed for the tribological performance of POB-PTFE composites.

Add a low content of whisker, whisker's own molecular structure and strength, stiffness will not affect the bearing capacity of the composites, and that only related with the filling quantity. When whisker content is higher, the chemical and physical properties of whisker itself will affect the composites' bearing capacity.

PTW filled POB-PTFE composites under the condition of different pressure difference can keep relatively stable friction coefficient and wear resistance, and it is an effective enhancer for Stirling sealing material. CSW filled composites is not suitable for high load of Stirling working environment.

PTW filled composites adapt to the technical requirements of dynamic seal under the conditions of different speed, and CSW filled composites is not suitable for high speed under the condition of dynamic seal technical requirements. Under the condition of high speed, the composites all show different degree of plastic deformation.

Acknowledgement
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