Experimental Study on Tribological Properties of Polymer-based Composite Nano-additives Suitable for Armored Vehicle Engine Lubricating Oil

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Abstract. Lubricating oil is known as "the blood to maintain the normal operation of machinery", and additives are an indispensable and important part of lubricating oil. In this paper, the Polymer-based Composite Nano-additive (PCNA) suitable for armored vehicle engine lubricating oil was developed, the physical and chemical properties of lubricating oil containing additives were carried out. The results showed that adding an appropriate amount (3 vol.%) of additives could improve the low-temperature fluidity of lubricating oil and improve the kinematic viscosity of lubricating oil without affecting the viscosity-temperature characteristics of lubricating oil. The four-ball testing machine, high temperature end face testing machine and engine bench are used to measure the anti-friction lubrication effect and anti-wear ability improvement effect of the additive on lubricating oil. The experimental results show that the additive can effectively improve the antifriction, lubrication and anti-wear performance of lubricating oil. In addition, the addition of the additive can effectively improve the running state of the engine, and the engine noise is obviously reduced. Finally, the additives developed in this paper are compared with three common brand additives in the market by using the high temperature end face testing machine. The results show that the additive developed in this paper has certain advantages in improving the antifriction and lubrication effect of lubricating oil.

Key words: Polymer-based Composite Nano-additives; physical and chemical properties; Anti-friction lubrication; Anti-wear properties.

1. Introduction

Lubricating oil is known as "the blood to maintain the normal operation of machinery" [1], and the quality of lubricating oil has a huge impact on the service performance and life of mechanical equipment. Engine lubricating oil consists of base oil and additives [2,3]. The quality of base oil and the performance of additives determine the performance of lubricating oil. Due to the large amount of work and wide involvement in improving the quality of base oil, it is difficult to improve the quality of base oil. In contrast, the development of additives is much easier. Therefore, the research on improving the performance of lubricating oil mainly focuses on the research on additives [4].

Since 1930s, Exxon Company has carried out research on additives, and successively developed a series of lubricating oil additives with different functions, such as pour point depressant, antioxidant and anti-corrosion agent, detergent, ashless antioxidant, friction improver and ashless additive. By 1990s, the global pattern dominated by Lubrizol, Infineum, Chevron and Afton was basically formed, and the above four additive companies occupied 85% of the global market share of lubricating oil additives [5].

Pour point depressant, antioxidant and anti-corrosion agent, viscosity improver and ashless antioxidant in additives are closely related to the physical and chemical properties of base oil. Therefore, the research on the above additives is mainly led by lubricating oil companies and large additive companies. However, the academic circles focus on the research of friction modifiers, extreme pressure additives and other additives. In recent years, the research on additives such as friction modifiers and extrusion additives has mainly focused on carbon-based additives represented by graphite [6], graphene [7], carbon nanotubes [8], nano-diamonds, and layered inorganic additives represented by molybdenum disulfide,

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tungsten disulfide [9-10], and soft metal powders represented by nano-copper [11], nano-nickel [12], and inorganic represented by cesium trifluoride, cerium borate [13], as well as ionic liquids [6] (such as choline ionic liquids) and so on. Among them, nano-diamond has unique advantages because of its high hardness, good chemical stability and thermal stability. For example, Zhang Chuanan et al. [14] developed a lubricating oil anti-wear additive NGAW containing nano-diamond. When the addition amount of the additive is 5%, under the test condition of 392N test load, the friction and wear reduction rates of liquid paraffin wax, No.20 machine oil, CD30 oil and SF30 oil are 57%, 39%, 25% and 15% respectively. Moreover, the increase rates of unit load are 39.2%, 15.3%, 70% and 40%, respectively, which indicates that NGAW additive has good extreme pressure and anti-wear performance for different lubricating materials. At the same time, XPS analysis of the chemical composition of the friction surface shows that there are two substances on the friction surface: carbon in adsorbed organic compounds and carbon in diamond, which indicates that there is a surface film containing nano-diamond on the friction surface. Hu Xiaoli [15] used a four-ball friction and wear tester to study the friction and wear properties of two chemically modified nano-diamond particles in water-based solution. The results showed that when 0.1% nano-diamond sulfonic acid derivative was added to the water-based solution, its bearing capacity could be increased by about 10% and the diameter of wear spots could be reduced by 4.4%. In addition, metal additives such as nano-copper and nano-chromium and mineral additives such as molybdenum disulfide with layered structure are also widely used. Wang Xiaoli et al. [16] compared and studied the repair effect of copper additive with particle size of 20 nm on friction pairs under different friction test conditions, The results show that the nano-copper additive can form a protective soft film composed of clusters with a particle size of 0.1 m and low shear strength on the worn surface during the friction process, which can reduce the adhesion wear and abrasive wear, so that the nano-copper additive exhibits good anti-wear and antifriction performance. Zhao Jinzhen et al. [17] first obtained three kinds of nano-copper lubricants with 100SN, 150SN, 500SN, etc. as base oils through in-situ preparation method, and then carried out tribological and extreme pressure performance experiments on the above three kinds of lubricants. The results show that the nano-copper lubricating oil prepared in situ in 100SN base oil has higher bearing capacity and good antifriction and anti-wear properties, which can increase the maximum non-jamming load of the base oil by 27%, and at 392N and 1450r/min, the friction coefficient and wear spot diameter of the base oil can be reduced by 3.8% and 20%, respectively. However, nano-copper prepared in situ in 150SN and 500SN base oils has no obvious effect on the bearing capacity of lubricating oil. MoS_2 itself has a lamellar structure, and the binding force between layers is van der Waals force, which is easy to slide in the friction process, so it has excellent antifriction effect; For example, nanospherical MoS_2 prepared by Huo Yingjie et al. [18] as a lubricating oil additive significantly improves the extreme pressure performance of lubricating oil; Wohengzhou et al. [19] also found that compared with MoS_2 particles, nano-MoS_2 is more prone to chemical reactions and forms a surface film containing MoO_3 on the worn surface of steel balls. The extreme pressure, anti-wear and anti-friction properties of nano-MoS_2 additive are better than those of ordinary MoS_2. However, with the continuous progress of gasoline engine technology in recent years and the increasingly stringent environmental protection requirements, it is required to reduce the sulfur and phosphorus elements contained in lubricating oil as much as possible without reducing the anti-wear, anti-friction and high-temperature stability of engine oil [20]. At present, Molyvan855 (molybdenum content 10 wt.%) produced by R.T. Vanderbilt Company and Sakura-lube 700 (molybdenum content 4.4 wt.%) produced by Asahi Kasei Co., Ltd. In the market represent the advanced level of non-sulfur and phosphorus oil-soluble organic molybdenum additives [21,22]. Li Xiaolei and others have carried out research on the application of inactive oil-soluble organic molybdenum additives in low viscosity lubricating oils [22,23]. However, the above additives are mineral additives or oil-soluble additives, and the research on polymer-based composite Nano-additives (PCNA) is less and insufficient.

In this paper, the PCNA for engines of armored vehicle engine and automobiles was developed, and its physical and chemical properties were tested. The antifriction and lubricating effect of the additive on lubricating oil was investigated by tribological test and bench drag test. This study will provide reference for the subsequent research and development of such additives.

2. Experimental part

2.1 Preparation and Addition of PCNA

The polyisobutylene succinimide used to prepare composite Nano-additives in this study is of industrial grade and purchased from Shanghai McLean Biochemical Technology Co., Ltd.. Polyisobutylene (molecular weight 1300) was provided by Aladdin Reagent (Shanghai) Co., Ltd.. Nano boron nitride particles and nano aluminum nitride particles were purchased from Shanghai China Metallurgical New Materials Co., Ltd. With a particle size ≤ 30 nm. PA025 of Tiancheng Meijia Lubricating Oil (Beijing) Co., Ltd. is used as base oil without further treatment. A preparation method of the Polyisobutylene-based Composite Nano-additives (PCNA) is as follow:

(1) After grinding the polyisobutylene and polyisobutylene-based succinimide at high speed for 60-90 minutes, they were sprayed for homogenization, spraying pressure of 30-70MPa, and spraying duration of 60-120 minutes; Then dispersed by ultrasound for 120 minutes and extracted for later use;

(2) After mixing and shearing nano boron nitride, the nano aluminum nitride and the PA025 for 30-90 minute, mixed with mixed with polyisobutylene-based succinimide, they were sprayed for homogenization, spraying pressure of 90-130MPa, and spraying duration of 30-150 minutes;

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Then dispersed by ultrasound for 90 minutes and extracted for standby;
(3) After adding the materials obtained in the steps 1 and 2 into a reaction kettle, heating to 55 DEG C, fully stirring for 70 minutes, cooling and filtering, the PCNA was obtained and shown in Fig. 1.

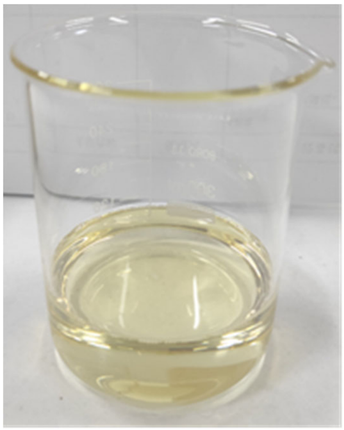


Fig. 1 PCNA

The experimental base oil are Kunlun brand general lubricating oil for heavy load power transmission (10W-40, CF-4 grade) and Great Wall Golden Star lubricating oil (10W-40), hereinafter referred to as K lubricating oil and C lubricating oil respectively. The 100ml lubricating oil and sufficient additives were added into a 500ml beaker in turn, then put the beaker under normal temperature and stir magnetically for 5min, and collect it for later use after stirring.

2.2 Physical and chemical performance test

The effects of additives on the physical and chemical properties of lubricating oil were evaluated by using kinematic viscosity and pour point as indexes. According to the standard GB/T265, the kinematic viscosity of samples at 40 ℃ and 100 ℃ was measured by Spike U-VISC 210 Automatic Viscometer (Fig. 2a). The Viscosity Tester is produced by Spitzer Technology (Beijing) and fully meets the requirements of ASTM D445 and D446 standards.

According to GB/T3535, a Multi-purpose Pour Point Tester (Fig. 2b) is used to measure the minimum temperature at which a sample can flow when cooled under specified conditions. The Pour Point Tester is produced by Hunan Jinshi Petrochemical Instrument Co. Ltd, which is suitable for measuring the freezing point and pour point of petroleum products. The equipment meets the standards of GB/T510 "Determination of Solidification Point of Petroleum Products" and GB/T3535 "Determination of Pour Point of Petroleum Products". The temperature control range is -70 ~ 0℃.

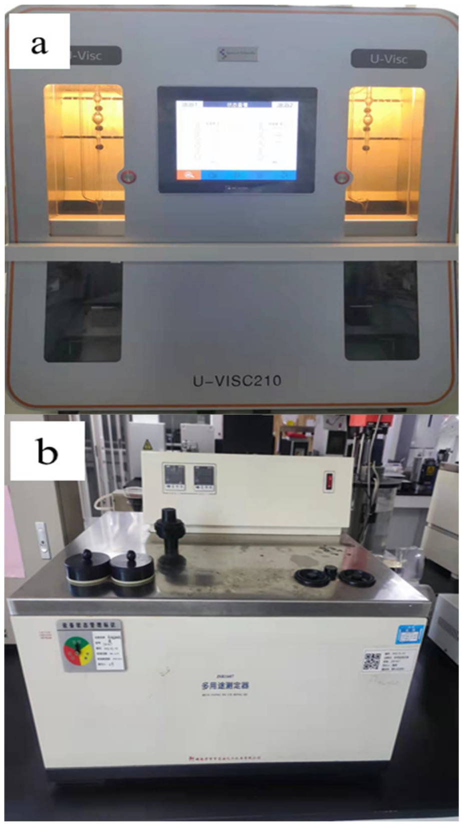


Fig. 2 Equipment for characterization of physical and chemical properties, a) Spike U-VISC 210 Automatic Viscometer and b) Multi-purpose Pour Point Tester.

2.3 Tribological performance test

According to the regulations of GB/T 3142-2019, the effects of different content additives on the anti-wear performance of lubricating oil were investigated by using a four-ball friction tester and taking the comprehensive wear value (ZMZ) as the evaluation index. The four-ball friction tester used is lever type, manufactured by Jinan Shunmao Test Instrument Co. Ltd., model MRS-10G, which meets the requirements of ASTM D2783 and SH/T 0189-92.

The MDW-5G screen-display high-temperature end-face friction and wear testing machine (Jinan Chenda Co., Ltd., China) was used to evaluate the effect of additives on the anti-friction performance of lubricating oil. The schematic diagram of the movement of the specimen is shown in Fig. 3. The material of the friction upper and lower samples refers to the piston ring and cylinder wall of a certain type of armored vehicle diesel engine. The material of the upper sample is 65Mn spring steel, and the material of the lower sample is RuT350 vermicular graphite cast iron. The upper sample is a ring with an inner diameter of 34 mm and an outer diameter of 40 mm, and the lower sample is a disk with a diameter of 43 mm. The setting parameters of the testing machine: the spindle speed is 1000r/min, the heating temperature is 80°C, and the applied load is 330N. The above test conditions were obtained by investigating an engine manufacturer located in Shijiazhuang, Hebei, China.

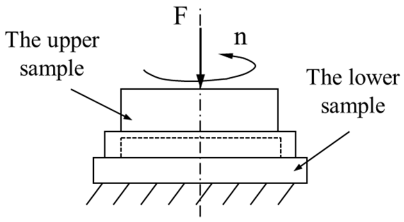


Fig. 3 Specimen motion diagram

2.4 Verification of bench reverse drag test

The 250kW Engine AC Power Dynamometer Test Bench (Fig. 4) was selected to carry out the evaluation experiment of the improvement effect of additives on the antifriction and lubrication effect of engine lubricating oil. The bench is produced by China Nantong Xindanuo Measurement and Control Technology Co., Ltd. And conforms to the provisions of GB/T 18297-2001 Performance Test Methods for Automobile Engines and GB/T 19055-2003 Reliability Test Methods for Automobile Engines. The engine used in the test is GW2.8TC diesel engine of Great Wall, which was purchased from Baoding Great Wall Scrap Car Recycling and Dismantling Co, Ltd. The bench reverse towing test is carried out according to GB/T 18297-2001 Automobile Engine Performance Test Method.

Fig. 4 250KW Engine AC Power Dynamometer Test Bench

3. Results and Discussion

3.1 Physical and chemical performance test

The kinematic viscosity and viscosity index of lubricating oil with additive content of 0%, 3% and 6% at 40℃ and 100℃ are shown in Fig. 5a and Fig. 5b, respectively, and the experimental base oil is K lubricating oil. The viscosity index is obtained by calculation [24]. It can be seen that with the increase of additive content, the kinematic viscosity of lubricating oil at 40℃ and 100℃ gradually decreases (Fig. 5a), while the viscosity index of lubricating oil remains unchanged first and then decreases (Fig. 5b). It is worth noting that the kinematic viscosity of lubricating oil decreased more obviously at low temperature (40℃) than at high temperature (100℃).

The standard of lubricating oil with good kinematic viscosity is that it has good fluidity at low temperature and can form a good oil film at high temperature [25]. The viscosity index refers to the degree of change of viscosity with temperature. The higher the viscosity index of lubricating oil is, the better its viscosity-temperature performance is, whereas the worse it is [26]. In addition, viscosity index is also related to equipment wear, and lubricating oil with higher viscosity index can greatly reduce the possibility of equipment wear [27]. To sum up, combined with the results of Fig. 5a and Fig. 5b, it can be seen that a proper amount (3%) of the additive can improve the kinematic viscosity of the lubricating oil without weakening the viscosity-temperature characteristics of the lubricating oil, thereby improving the starting performance of the engine and reducing the starting wear of the engine.

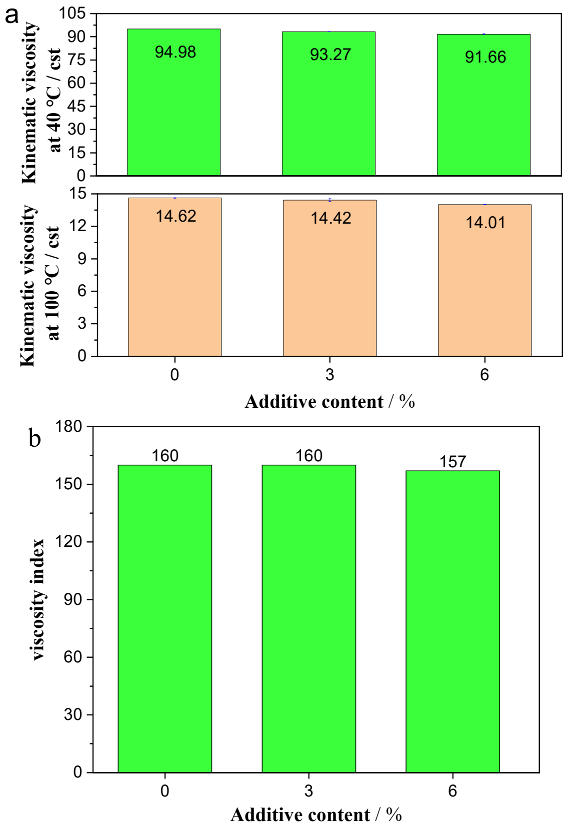


Fig. 5 Kinematic visibility a) and visibility index b) as function of additional content

Table 1 shows the pour point measurement results of lubricating oils with additive content of 0%, 3%, and 6%, and the base oil used in the experiment is K lubricating oil. It can be seen that with the increase of additive content, the pour point of lubricating oil decreases gradually. Pour point refers to the lowest temperature at which the oil sample to be tested keeps flowing under the corresponding specified conditions [28]. The lower the pour point, the better the low temperature fluidity of the lubricating oil [29]. The results shows that the additive can improve the low temperature fluidity of lubricating oil.

Table 1 Oil pour point measurement results

Additive content (%)	Oil pour point (℃)
0	-36
3	-39
6	-42

1.1 Tribological performance test

The combined wear value (ZMZ) test of lubricating oil with additive content of 0%, 3% and 6% was carried out by using a four-ball testing machine. The results are shown in Fig. 6, and the base oil used in the test is K lubricating oil. It can be seen that the combined wear value (ZMZ) of lubricating oil can be improved by adding different amounts of lubricating oil additives. The combined wear value is an index of the extreme pressure resistance of the lubricant. The greater the combined wear value, the higher the wear resistance of the lubricant [30]. It indicates that the additive can improve the wear resistance of lubricating oil, and when the additive content is 3%, the wear resistance improvement effect is the best.

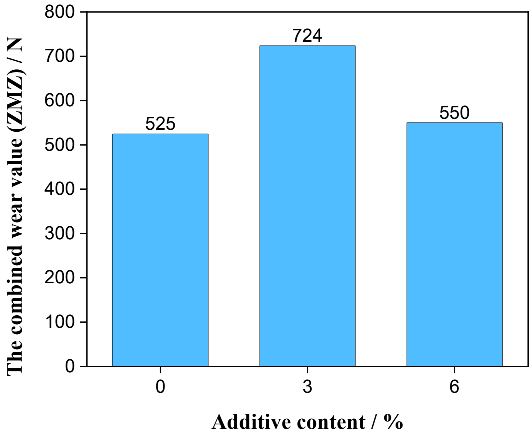
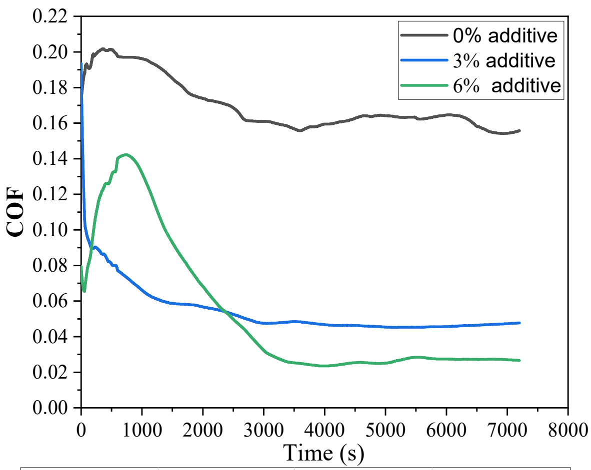


Fig. 6 The combined wear value of the oil

Fig. 7 shows the high-temperature end-face friction coefficient values of lubricating oils with additive content of 0%, 3%, and 6%. The base oil used in the experiment is K lubricating oil. It can be seen that after adding different contents of additives, the friction coefficient in the stable stage is much lower than that of pure lubricating oil, and the friction coefficient decreases from 0.15 to 0.03~0.05.



sample	Stable COF	sample	Stable COF
0% additive	0.153	6% additive	0.027
3% additive	0.046		

Fig. 7 The effect of additives on coefficient of friction

Based on the results of four-ball test and high temperature end face friction test, it can be seen that when the additive content is 3%, the lubricating oil can obtain good antifriction and lubrication effect and increase certain wear resistance.

3.2 Bench drag test

In order to further confirm the antifriction and lubricating effect of additives on lubricating oil, after completing the material-level test, this paper uses the engine bench to carry out the engine reverse drag experiment with the engine friction torque, friction work, noise and other evaluation indicators. The base oil used in the experiment is K lubricating oil. The experimental results are shown in Fig. 8. Adding different amounts of additives to the lubricating oil will reduce the friction torque value of the engine (Fig. 8a). Based on the friction torque results of 1500R and 2000R, adding 3% additive to lubricating oil has the best effect on reducing the friction torque of the engine using armored vehicle lubricating oil as lubricating medium, for example, at 1500R, the friction torque is reduced by 3.91%; At 2000R, the friction torque is reduced by 3.6%.

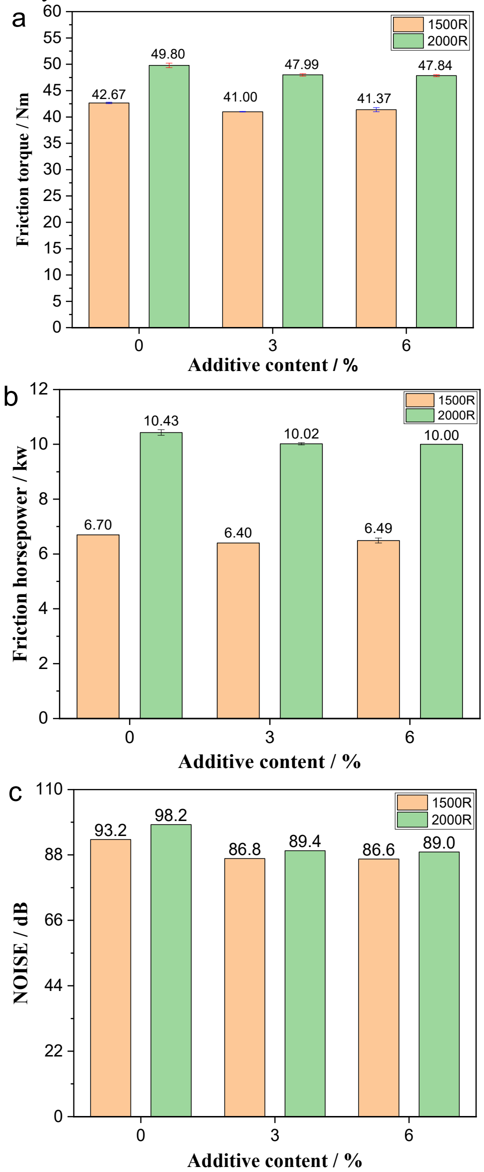


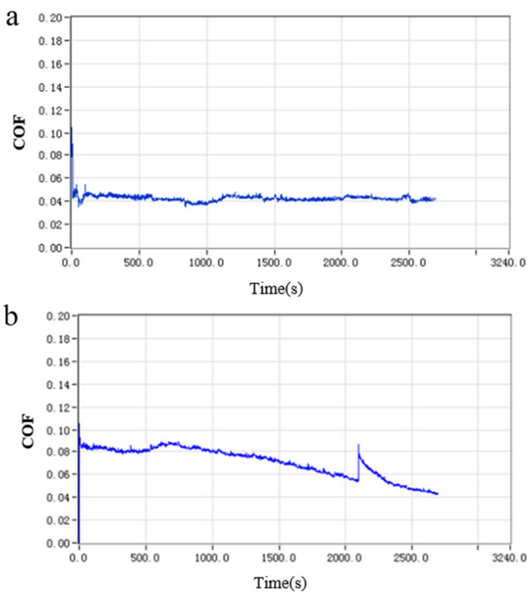
Fig. 8. Experimental results of engine reverse drag. a) Friction torque, b) Friction power, c) Noise.

The measurement results of engine friction power with lubricating oil containing different additive amounts as lubricating medium are shown in Fig. 8b. Friction power is the power consumed when the dynamometer drives the engine to rotate. It can be seen that the variation law of friction power with additive content is consistent with that of friction torque with additive content.

The experiment results of engine noise with pure lubricating oil and armored vehicle lubricating oil containing different amounts of additives as lubricating medium are shown in Fig. 8c. It can be seen that the addition of additives in different proportions reduces the engine noise. This shows that the addition of additives reduces the engine noise and improves the engine running state.

3.3 Comparative Experiment of Different Brand Additives

After completing the above experiment, in order to explore the difference between the additives developed in this paper and the common additives in the market in improving the antifriction and lubrication effect of lubricating oil, considering that most of the common additives in the market are lubricating oil additives for gasoline engines, three brand additives commonly found in the market that focus on improving the anti-friction lubrication effect of lubricating oil are selected in this paper. Taking Class C lubricating oil as the base oil, adding 3% of the above additives to the lubricating oil, the high temperature end face friction experiment was carried out. The obtained results were compared with the additives developed in this paper. Experimental conditions: spindle speed, 1000r/min, applied load, 330N, heating temperature, 80°C, experimental time, 45min. The experimental results are shown in Fig. 9. It can be seen that compared with the other three brands of additives, the additives developed in this paper have better antifriction and lubricating effects on lubricating oil, and the friction coefficient fluctuates less and the friction process is more stable.



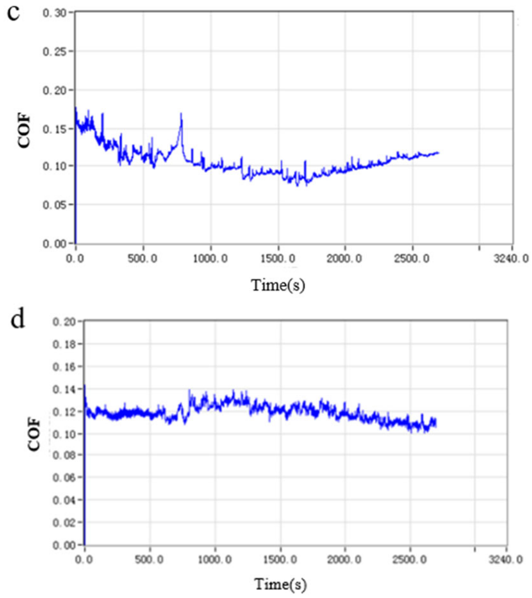


Fig. 9. Comparison experience of lustration performance of variable brand oil additives, a) PCNA, b) A brand, c) 3M brand, d) 1B brand.

The results obtained from frictional experiment of different brand additives indicate that the additives developed in this paper have certain advantages in improving the antifriction and lubrication effect of lubricating oil.

4. Conclusion

In this paper, the PCNA suitable for armored vehicle engine lubricating oil was developed. Firstly, the additive was added to lubricating oil, and its effects on the physical and chemical properties of lubricating oil were investigated. Secondly, using four-ball testing machine, high-temperature end testing machine and engine bench, the improvement effect of composite Nano-additives on anti-wear, anti-friction and lubrication performance of lubricating oil was explored. Finally, the additives developed in this paper are compared with three common brand additives in the market by using the high temperature end face testing machine. Through the above experiments, the following conclusions can be drawn:

(1) The additive developed in this paper can improve the low-temperature fluidity of lubricating oil, improve the kinematic viscosity of lubricating oil, improve the starting performance of engine and reduce the starting wear of engine without affecting the viscosity-temperature characteristics of lubricating oil.

(2) The additive can effectively improve the antifriction and lubricating effect of lubricating oil, and can also improve the wear resistance of lubricating oil when added in an appropriate amount (3%).

(3) The additive can effectively improve the running state of the engine and reduce the noise of the engine.

(4) Compared with the three common additives in the market, the additive has certain advantages in improving the antifriction and lubrication effect of lubricating oil.

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