Rheological Effects of Montmorillonite and Ethyl Cellulose for *Xanthoceras sorbifolium* Bunge Oil-based Lubricants

Kai Zhang,[a,b,1] Zexin Li,[a,b,1] Rao Duan,[a,b,1] Mengyao Li,[a,b,1] Jingwen Wang,[a,b] Jian Sheng,[a,b] Hao Ren,[a,b] Shuo Wang,[c] Ximing Wang,[a,b] and Yinan Hao [a,b,*]

Xanthoceras sorbifolium Bunge oil exhibits favorable characteristics such as excellent low temperature fluidity, high flash point, and degradability. However, it also suffers from drawbacks including low kinematic viscosity at low temperatures and significant loss of kinematic viscosity at high temperatures. In view of these characteristics of *X. sorbifolium* oil, it was modified in this work with a combination of ethyl cellulose (EC), montmorillonite (MMT), and cetyltrimethylammonium chloride (CTAB). The effects of temperature, time, and additive content on the rheological properties of lubricating oil were studied. The kinematic viscosity of the prepared lubricating oil reached up to 433 mm^2/s at 40 °C and 51.1 mm^2/s at 100 °C. The coagulation point could be reduced to -25 °C, the friction coefficient was 0.026, and the average wear spot diameter was 0.81 mm, The anti-friction performance was enhanced, and the anti-wear performance decreased somewhat. The prepared lubricating oil had the characteristics of high kinematic viscosity at high temperature and excellent rheological properties at low temperature. It also met the energy and environmental application requirements of a green, environmentally friendly, and biodegradable sustainable development strategy. This study greatly broadens the application range of lubricating oil.

DOI: 10.15376/biores.19.1.1377-1393

Keywords: Natural oil; Lubrication; Xanthoceras sorbifolium Bunge; Kinematic viscosity; Viscosity index; Condensation point

Contact information: a: College of Material Science and Art Design, Inner Mongolia Agricultural University, Hohhot, 010018, China; b: National Forestry Grassland Engineering Technology Research Center for Efficient Development and Utilization of Sandy Shrubs, Inner Mongolia Agricultural University, Hohhot, 010018, China; c: Woqi Ecological Agriculture Limited of Jungar Banner, Ordos 017100, China; 1: These authors contributed equally to the manuscript;
** Corresponding author: nanyihao83@163.com*

INTRODUCTION

With the strengthening of global environmental awareness, the research and application of environmentally friendly lubricants have been strongly supported by countries around the world (de Souza *et al.* 2022). Lubricating oil plays an important role in mechanical operation and is an indispensable part of maintaining good mechanical performance and stable operation. In addition to reducing friction between mechanical parts and improving service life, lubricating oil can also play a role in cleaning, sealing, and cooling (Chen *et al.* 2020). Traditional lubricants are mineral-based, which means that they are generally composed of additives and base oils. Additives account for 1 to 30%, and base oils account for 70 to 90% (Zhang and Chen 2022). The chemical composition of

base oil mainly includes high molecular weight, high boiling point hydrocarbons and non-hydrocarbons. The specific classification is shown in Table 1 (Lu J. *et al.* 2018; Ding *et al.* 2020; Fan *et al.* 2021). Additives can be divided into antioxidants, friction modifiers, extreme pressure agents, condensation point depressants, viscosity modifiers, corrosion inhibitors, detergents, and defoaming agents (Wu *et al.* 2017). Lubricating oil based on mineral oil inevitably contains sulfur, phosphorus, and other elements that will cause harm to the environment. Commonly used lubricating oil additives are also mainly inorganic additives, which may be harmful to the environment. Liu *et al.* (2016) proposed a new method to effectively adjust the fluid properties and change the viscosity of lubricating oil by adding high concentration of inorganic nanoparticles. A stable, high concentration and viscosity controllable nano-SiO_2/PAG suspension was synthesized by *in-situ* Stober sol-gel method, and the suspension was used as a vegetable oil viscosity modifier. The smaller the nanoparticles of the suspension, the better the thickening effect of the lubricating oil, and the greater the viscosity. Kerni *et al*. (2019) prepared olive oil-based lubricants by epoxidation and modified them with Cu and hexagonal boron nitride (h-BN) nanoparticles. After adding Cu nanoparticles and h-BN nanoparticles, the shear stress and shear rate of the epoxidized olive oil showed a linear relationship. The mixture showed higher viscosity and better lubrication performance. Liu *et al.* (2020) synthesized two kinds of boron-nitrogen modified soybean oil additives BNS1 and BNS2 with different chain length structures. The addition of these two additives to rapeseed oil improved the anti-wear properties of rapeseed oil. Bhaumik *et al*. (2020) studied the application of different concentrations of nano-ZnO in castor oil, and prepared lubricants by dispersing nano-ZnO with different weight percentages. The experimental results showed that when the concentration of nano-ZnO was 0.1%, the anti-wear and compressive properties of castor oil were improved, but the wear rate was increased, and the friction coefficient was not significantly improved. Therefore, the search for environmentally friendly lubricants and additives has become the focus of attention.

Table 1. Classification of Lubricating Oil

Type	Component	Characteristics
Synthetic base oil	poly-α-olefin, synthetic ester, polyether, fluorosilicone oil, phosphate ester, *etc.*	Advantages: high viscosity index, low condensation point, high flash point, low volatility, oxidation stability, *etc.* Disadvantages: high production cost, complex preparation process
Mineral oil base oil	High boiling point high molecular weight hydrocarbons, non-hydrocarbon mixtures, *etc*.	Advantages: stable performance, wide application, low manufacturing cost, etc. Disadvantages: non-renewable, environmental hazards
Vegetable oil base oil	Natural vegetable oil, vegetable oil processing products	Advantages: renewable, easy degradation, small environmental hazards, high flash point, high lubricity, low evaporation loss Disadvantages: Narrow range of kinematic viscosity, Poor oxidation stability

The consumption of global lubricants has remained stable, the market concentration is getting higher and higher, the industry as a whole is developing in the direction of environmental protection and energy saving, and the product structure has undergone major changes. The domestic demand for high viscosity and high quality base oil is increasing. It is expected that by 2025, the global demand for lubricating oil will reach 57.31 Mt (Wang *et al.* 2014).

Before the discovery of oil resources, vegetable oil has been used as lubricants for machinery and means of transport. Compared with mineral-based lubricants, vegetable oils generally have the advantages of high flash point, high viscosity index, high lubricity, low evaporation loss, and good metal adhesion (Zeng *et al.* 2015). At the same time, vegetable oil also has disadvantages such as poor antioxidant capacity, poor low-temperature fluidity, and a narrow range of kinematic viscosity. Therefore, modification of vegetable oil is needed to make it suitable as a lubricant. People have successfully converted soybean oil, rapeseed oil, castor oil, and other vegetable oils into lubricating oil by various technical means and applied them to production (Wang *et al.* 2014; Dong *et al.* 2020; Liu *et al.* 2020; Liu *et al.* 2019). However, the research on *Xanthoceras sorbifolium* Bunge oil in the field of lubrication has not been reported.

EXPERIMENTAL

Materials

The oil used in this experiment was extracted from *Xanthoceras sorbifolium* Bunge (purchased from Chifeng, China) by ultrasonic-assisted extraction method in the laboratory.

Reagents and Instruments

Cetyltrimethylammonium bromide (W ⩾ 99 %), ethyl cellulose (Analytically pure), and montmorillonite (sodium-based, specific surface area 240 m^2/g) were all purchased from Shanghai Macklin Biochemical Technology (China) Co., Ltd. The experimental reagents were deionized water and anhydrous ethanol (W ≥ 98 %).

The four-ball friction and wear tester was obtained from Jinan Shunmao (MRS-1J, Jinan, China). The kinematic viscosity tester of petroleum products was obtained from Shanghai Changji Geological Instrument Co., Ltd. (SYD-265D-1, Shanghai, China). The petroleum product coagulation point tester was obtained from Shanghai Shenkai Petroleum Instrument Co., Ltd. (SYP1008-V, Shanghai, China).

Methods

Preparation of modified montmorillonite (OMMT)

A total of 5 g MMT was added to 100 mL deionized water, and the mixture was stirred at 60 °C for 30 min until MMT was fully dispersed. CTAB (10%, 15%, 20%, or 25%, based on the mass of dry MMT was added to modify MMT, and the mixing was continued for 3 h. After the reaction, deionized water, and absolute ethanol were used to centrifuge and wash in turn, until the supernatant was neutral, and the lower precipitate was a combination of CTAB and MMT. It was dried, ground, and then refrigerated for use.

Preparation of CTAB / MMT / EC combination

CTAB-MMT mixture and EC (in absolute dry mass) with a mass ratio of 1:1 were prepared into a suspension in anhydrous ethanol solution. After ultrasonic dispersion for 30 min, the mixture was stirred in a constant temperature water bath at 70 °C for 4 h. After the reaction was completed, anhydrous ethanol was used for centrifugal washing. The lower precipitate was designated as CTAB/MMT/EC. It was dried, ground, and then refrigerated at 4 °C for storage.

Preparation of CTAB/MMT/EC modified Xanthoceras sorbifolium oil

Amounts of 50 g of *Xanthoceras sorbifolium* oil were placed in three flasks. The constant temperature digital display oil bath was selected as the heating source, and the CTAB/MMT/EC combination at the mass ratios of 0.5%, 1%, 1.5%, 2%, 2.5 was accurately weighed. The oil was first heated to the target temperature (120, 150, 180, 210, and 240 °C). After reaching the target temperature, the CTAB/MMT/EC combination was added to control the reaction time (30, 60, 90, 120, and 150 min). The whole reaction process was carried out within the reaction container that was protected from the entering of more air; this was because oxidation will produce oxidation to produce insoluble glue and precipitate (Cheng and Wang 2016; Fazal *et al.* 2021; Sui *et al.* 2021a,b). After the reaction, the sample was cooled in a closed container, and the finished product was obtained by filtration.

Characterization of Structure and Properties of CTAB/MMT/EC

FTIR test

An appropriate amount of dried MMT, OMMT, EC, and CTAB/MMT/EC were mixed with potassium bromide after drying and tabletting. The samples were tested by ALPHA type Fourier transform infrared spectrometer. The test conditions were as follows: scanning speed 32 times/s, resolution 4 cm^{-1}, and wave number range 400 to 4000 cm^{-1}.

SEM analysis

A certain amount of completely dry samples to be tested were put on the double-sided conductive tape, fixed on the metal sample table and sprayed with gold. The morphology of the samples was observed by Regulus8220 scanning electron microscope.

Determination of kinematic viscosity of lubricating oil

The test was carried out according to the method of GB/T 265-1988. The kinematic viscosity of the sample was measured using the SYD-265D-1 kinematic viscosity tester for petroleum products. The first step was the choice of liquid in the bathtub. When the test temperature is between 20 and 50 °C, water was selected as the temperature control medium. When the test temperature was between 50 and 100 °C, glycerol was selected as the temperature medium.

When the flow time of the sample in the capillary is less than 200 s, a tube with a smaller diameter than this capillary should be selected for measurement. When the flow time of the sample in the capillary is higher than 500 s, a tube with a larger diameter than this capillary should be selected for measurement. When the flow time of the sample in the capillary is between 200s and 500s, it is the most suitable capillary for measurement. The third step, after determining the temperature control medium and capillary diameter, each group of measurements should be measured in parallel 4 times to take the average value to reduce the error.

Determination of viscosity index

According to the national standard GB/T1995-1998 method for testing and calculation, the viscosity index VI is calculated according to Eqs. 1 and 2,

$$VI = \frac{(antilog\ N) - 1}{0.00715} + 100 \quad (1)$$

$$N = \frac{LogH - LogU}{LogY} \quad (2)$$

where H is obtained from the kinematic viscosity reference table, U is the kinematic viscosity of the sample at 40 °C (mm^2/s), and Y is the kinematic viscosity of the sample at 100 °C (mm^2/s).

Determination of condensation point of lubricating oil

The SYP1008-V petroleum product coagulation point tester was used to test according to the method of NB/SH/T 0248-2019 (Zheng *et al.* 2022; Wang *et al.* 2021; Teng *et al.* 2020; Sui *et al.* 2019, 2021). First, the sample water bath was heated to 50 ± 1 ℃, and the test tube containing the sample and the thermometer was placed at room temperature and naturally cooled to 35 ± 5 °C. Then the test tube was placed in a cold bath. When the temperature of the cold bath reached the set temperature, the cold bath was tilted 45° and kept for 1 min, and then the sample test tube was taken out to observe whether the liquid surface moved. When the liquid level position did not move, the test temperature was raised by 4 °C, and the test was repeated. When the temperature caused the liquid level to stay still and an increase by 2 °C caused the liquid level to be movable, the temperature of the liquid was defined as the coagulation point of the sample.

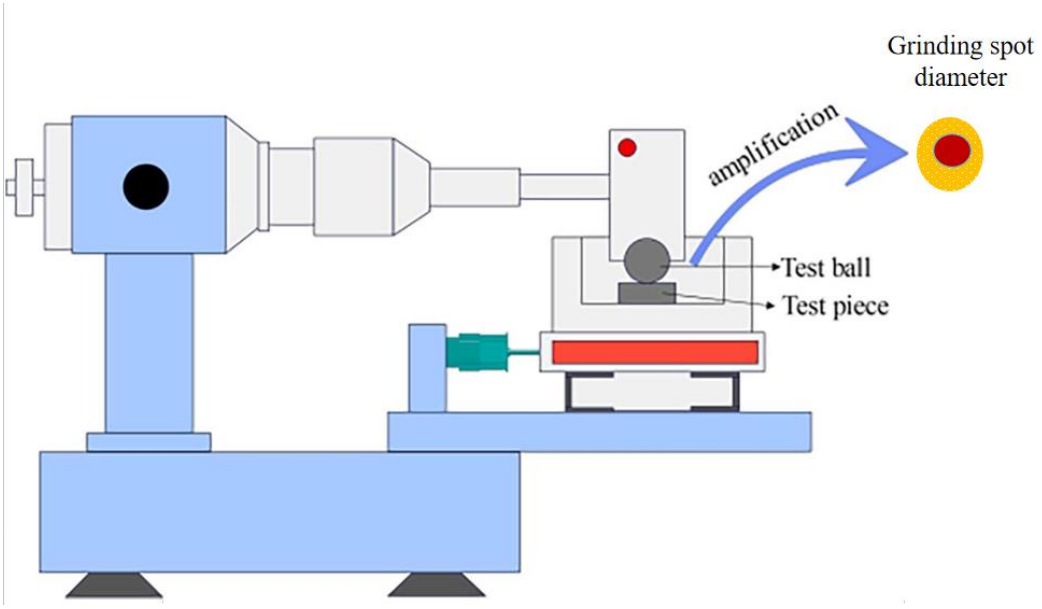

Fig. 1. high-frequency reciprocating friction and wear testing machine

Lubricity test

The friction and wear test of the sample was carried out using the MRS-1J high-frequency reciprocating friction and wear testing machine (shown in Fig. 1). A precision bearing steel ball with a diameter of 12.7 mm was selected as the friction ball, and the load was 392 N. Grinding for 30 min at a rate of 1200r/min, the lubrication performance of the lubricating oil was measured. First, 2 mL of the oil sample to be tested was injected into the tank to ensure that the contact surface of the steel ball and the gasket was completely immersed in the oil sample. A balance bar was mounted on the upper fixture and a load was applied by hanging a weight. After the test, the centralized computer control box was

used to monitor the friction coefficient, test temperature, test humidity, and other data in real time. At the end of the test, the test steel ball was removed and the grease on its surface was cleaned with methanol. Then, the diameter of the grinding point was measured in X and Y directions, and the average wear spot length (NWSD) was calculated by Eq. 3.

$$NWSD=\frac{X+Y}{2} \quad (3)$$

RESULTS AND DISCUSSION

Structural Characterization of CTAB/MMT/EC Combination

FTIR analysis

The FTIR spectra of CTAB/MMT/EC combination, MMT, and EC with different amounts of CTAB modifier are shown in Fig. 2. The vibration peaks of -CH_2 and -CH_3 appeared at 2926 cm^{-1} and 2855 cm^{-1}, indicating that CTAB was present on the MMT. The Si-O stretching vibration peak at 1036 cm^{-1} is weaker than that of MMT, which may be due to the addition of EC into the nanosheet structure of MMT and the Si-O group in MMT structure. When the amount of CTAB was increased to 20%, the peaks of CTAB/MMT/EC at 2926, 2855, and 1611 cm^{-1} were enhanced, which may be related to the symmetrical stretching vibration peak of CH at 2894 cm^{-1}, the bending vibration peak of-OH at 1611 cm^{-1}, and the stretching vibration peaks of C-C,C-OH and C-H at 1056 cm^{-1}, indicating that more EC entered into the interlayer of MMT under the intercalation of CTAB, forming CTAB/MMT/EC intercalated structures.

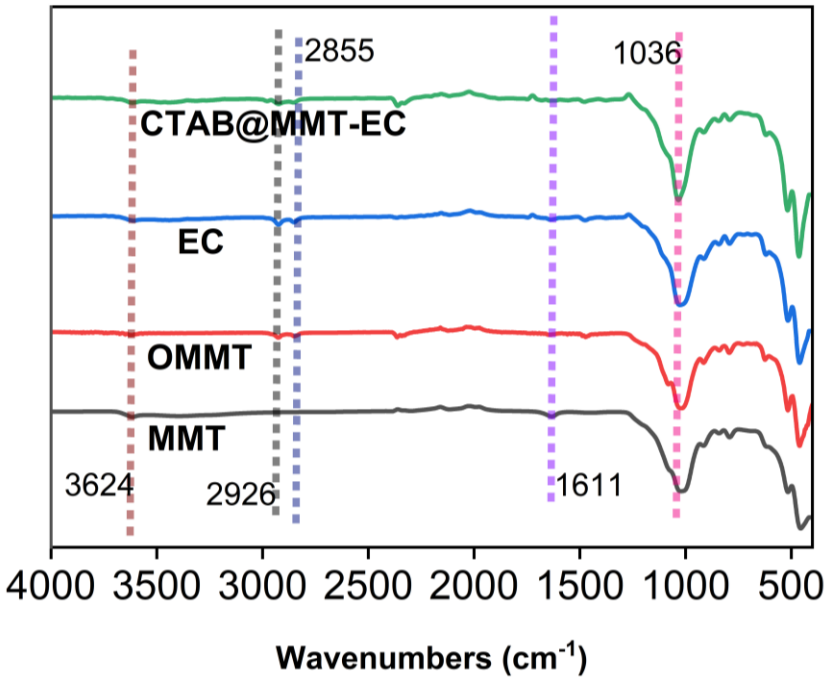

Fig. 2. FTIR spectra of raw materials, modified montmorillonite, and CTAB/MMT/EC

SEM analysis

The SEM images before and after the modification of MMT are shown in Fig. 3. The unmodified lamellar structure MMT was mostly present in coalescenced and stacked form. Under the modification of CTAB, there were layers of MMT dispersed in the image,

indicating that the modification and compounding of CTAB and EC caused the MMT to gradually become delaminated and peeled off. The edges of layered MMT particles showed obvious coalescence and edge overlap. This was attributed to the addition of EC, which appeared to make the modified particles bridge. A large amount of EC was evenly distributed on the surface and interlayer structure of MMT, and only a small amount of EC was aggregated, indicating that MMT had a good dispersion effect on EC.

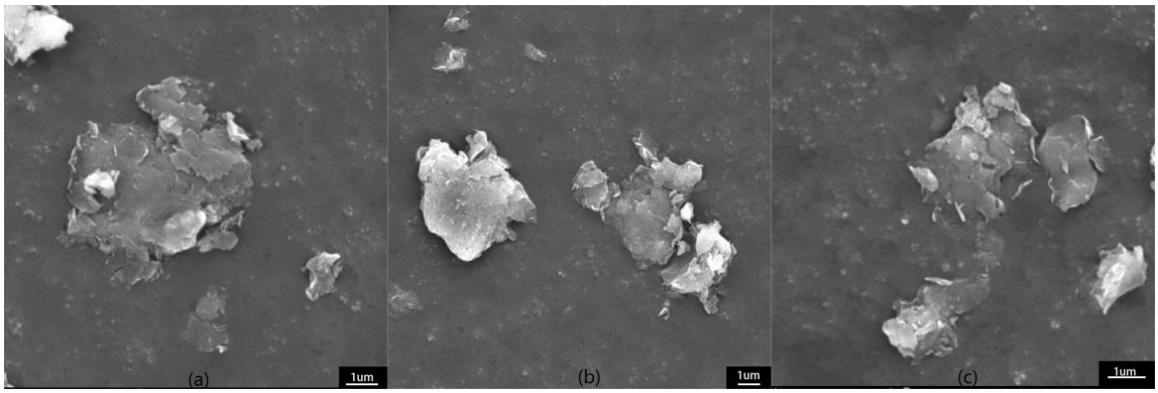

Fig. 3. Scanning electron microscopy of (a) MMT, (b) OMMT, and (c) CTAB/MMT/EC

TG analysis

The thermal stability of MMT modified by different amounts of CTAB was investigated, and the TG curve is shown in Fig. 4. MMT is an inorganic mineral particle. With the increase of temperature, only free water and interlayer adsorbed water in the particles are removed, and the residue percentage was 90.9% at 650 °C. EC showed a one-step pyrolysis reaction during the heating process. From room temperature to about 150 °C, the physical adsorption of water in EC was mainly removed, and the residue amount after weight loss was 95.8%. The pyrolysis of EC mainly occurred at 300 to 390 °C. The glycosidic bonds in the structural unit of EC were broken and rearranged to generate various macromolecular volatile components and small molecular gases. The residue amount after weight loss was 17.6%. After that, the degradation of EC was balanced and accompanied by the formation of coke and other residues, and the final residue percentage was 5.5%. CTAB/MMT/EC mainly underwent a two-step pyrolysis process during the heating. From room temperature to about 100 °C, physical desorption of water mainly occurred, and the residual after weight loss was 95.5 to 98.1%. The first step of pyrolysis mainly occurred at about 350 to 438 °C, which was attributed mainly to the thermal decomposition of EC, while the pyrolysis temperature of CTAB was 275 to 438 °C. The second step of pyrolysis mainly occurred at 340 to 450 °C, which mainly occurs the thermal degradation of CTAB and the bridging fracture between EC and MMT. With the increase of CTAB dosage, the initial temperature of the second step degradation of CTAB/MMT/EC increased. When the amount of CTAB increased to 20% and 25%, the minimum residue amount of CTAB/MMT/EC was 52%, indicating that more EC was inserted into the interlayer structure of MMT or complexed with MMT. MMT modified with 20% CTAB was used in subsequent experiments.

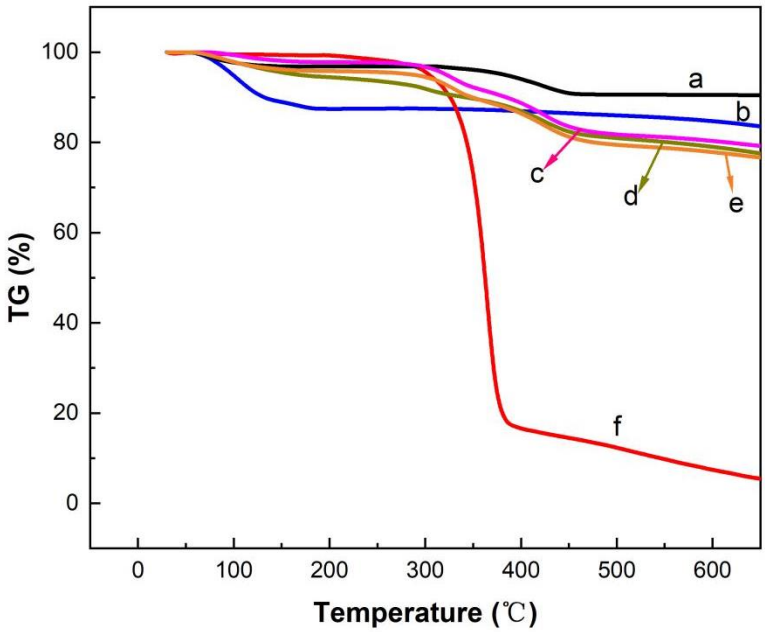

Fig. 4. TG curves of MMT and EC and CTAB/MMT/EC with different CTAB additions – (a) MMT, (b) 10% CTAB, (c) 15% CTAB, (d) 20% CTAB, (e) 25% CTAB, (f) EC

Kinematic Viscosity of Lubricating Oil

The kinematic viscosity of *Xanthoceras sorbifolium* oil at 40 and 100 °C are shown in Table 2. The results are shown in Fig. 5, (a), (c), and (e) indicate the changes of kinematic viscosity at 40 °C, whereas (b), (d), and (f) are the changes of kinematic viscosity at 100 °C. The kinematic viscosity of lubricating oil was found to change under different preparation conditions. Ethyl cellulose has a long chain structure. When the CTAB/MMT/EC combination is used as an additive, the long chain structure of the EC can be connected with the open double bond in *X. sorbifolium* oil to form a branched chain structure. The increase in the number of branched chains will increase the probability of entanglement with adjacent molecules, increase the flow resistance of the fluid, and increase the viscosity. When the preparation conditions were 300 °C, the reaction time was 2 h, and the content of CTAB/MMT/EC was 2%, the highest kinematic viscosity of the lubricating oil of 433 mm^2/s was reached at 40 °C, which was 396 mm^2/s higher than that of *X. sorbifolium* oil at 40 °C. At 100 °C, the maximum kinematic viscosity of the prepared lubricating oil was 51.1 mm^2/s, which was 42 mm^2/s higher than that of *X. sorbifolium* oil at 100 °C. With the increase of preparation temperature, the dispersibility of CTAB/MMT/EC in *X. sorbifolium* oil also increased. When the preparation temperature reached or exceeded the melting point of components in the CTAB/MMT/EC combination, the improvement of the kinematic viscosity of the oil by CTAB/MMT/EC in the heated state was more obvious. CTAB/MMT/EC reached the molten state and was blended with *X. sorbifolium* oil. When the temperature was cooled down, the sample did not precipitate and flocculate, indicating that the two formed a stable blending system, which made the kinematic viscosity have a more obvious improvement. With the increase of the percentage content of CTAB/MMT/EC, the kinematic viscosity began to decrease, which may be due to the great interaction of CTAB/MMT/EC in the reaction container, which made the kinematic viscosity decrease. Therefore, the optimum preparation conditions were 2 h, 300 °C, and 2% CTAB/MMT/EC.

Table 2. Kinematic Viscosity of *Xanthoceras sorbifolium* oil at 40 and 100 °C

Name	40 °C Kinematic Viscosity	100 °C Kinematic Viscosity
Xanthoceras sorbifolium oil	36.1 mm^2/s	9.1 mm^2/s

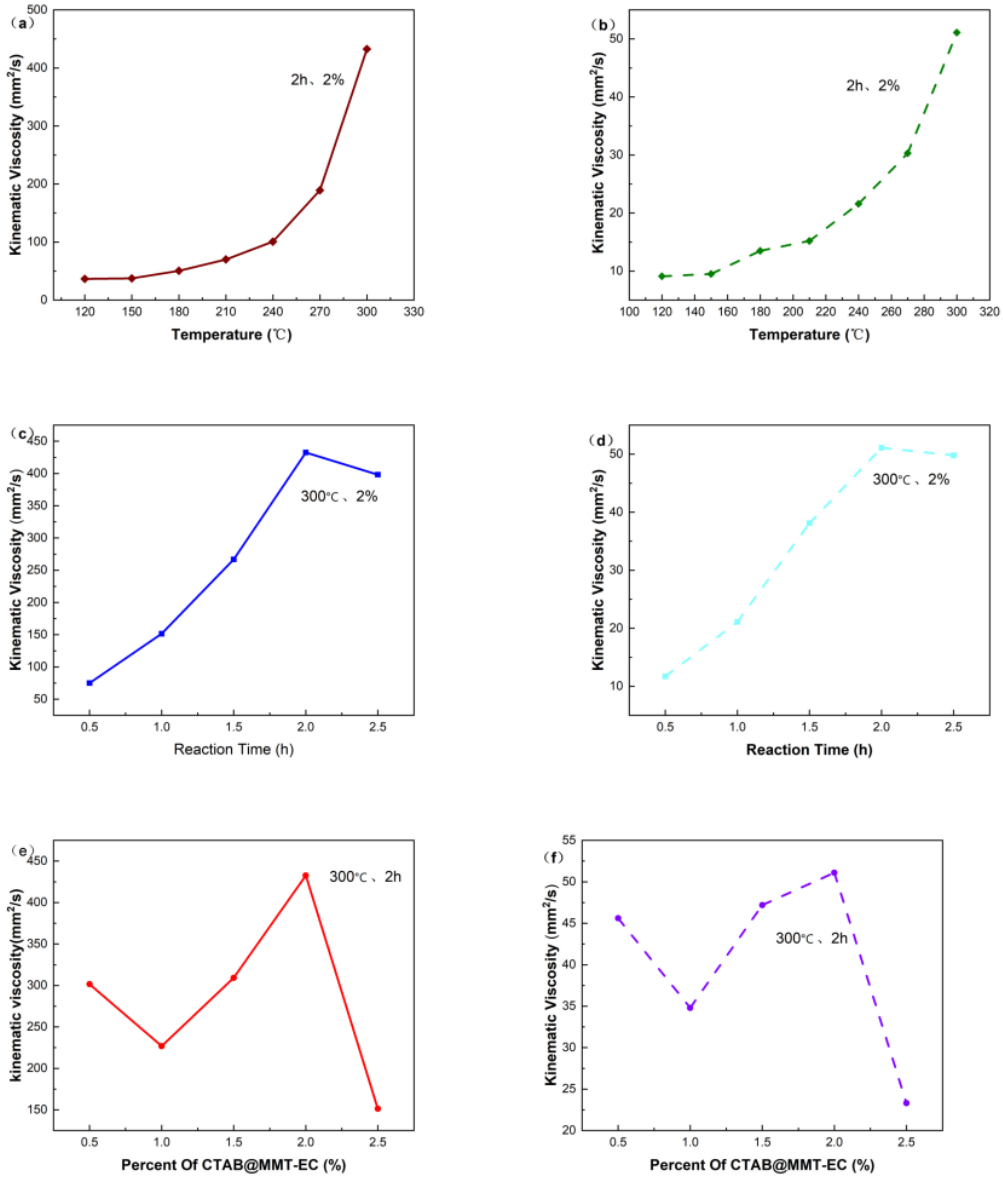

Fig. 5. Changes of kinematic viscosity of lubricating oil under different preparation conditions

Effect of Temperature on Kinematic Viscosity

The kinematic viscosity of *Xanthoceras sorbifolium* Bunge oil and the modified lubricating oil with CTAB/MMT/EC (content of 2%) from 40 to 100 °C are shown in Fig. 6.

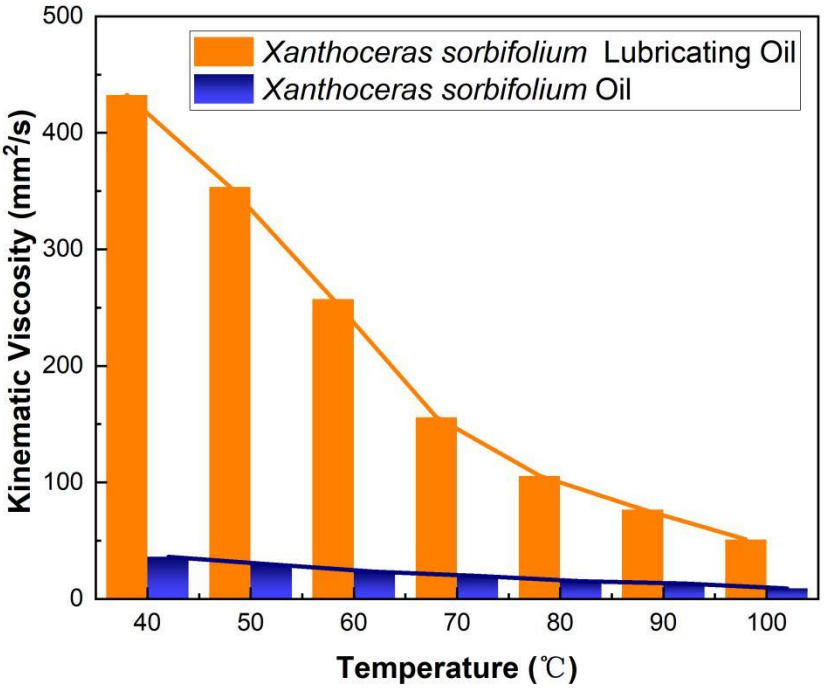

Fig. 6. Variation of kinematic viscosity of lubricating oil with CTAB/MMT/EC at different temperatures

The kinematic viscosity of both *X. sorbifolium* oil and modified lubricating oil with CTAB/MMT/EC decreased with the increase of temperature. From the change of the curve, it is not difficult to find that the modified lubricating oil exhibited a wider range of kinematic viscosity changes compared with the *X. sorbifolium* oil. The kinematic viscosity at the lowest measurement temperature and the highest measurement temperature was much higher than that of the *X. sorbifolium* oil. With the increase of temperature, the downward trend of kinematic viscosity slowed down. This trend of kinematic viscosity change shows that the modified lubricating oil can maintain a high and stable kinematic viscosity at high temperature (about 100 °C), while continuously and stably playing a lubricating role.

Determination of Viscosity Index

Figure 7 shows the change of viscosity index of lubricating oil with different CTAB/MMT/EC content under the condition of 300 °C and reaction time 2 h. Figure 8 shows the lubricating oil products with different CTAB/MMT/EC additions. The higher the viscosity index of lubricating oil, the smaller the influence of temperature on lubricating oil. When the CTAB/MMT/EC content was 1.5%, the viscosity index was the highest at 215, and the viscosity index was the lowest at 181 when the CTAB/MMT/EC content was 2%. When the viscosity index was the lowest (181), it was also far from the standard of super high viscosity index (above 110) lubricating oil.

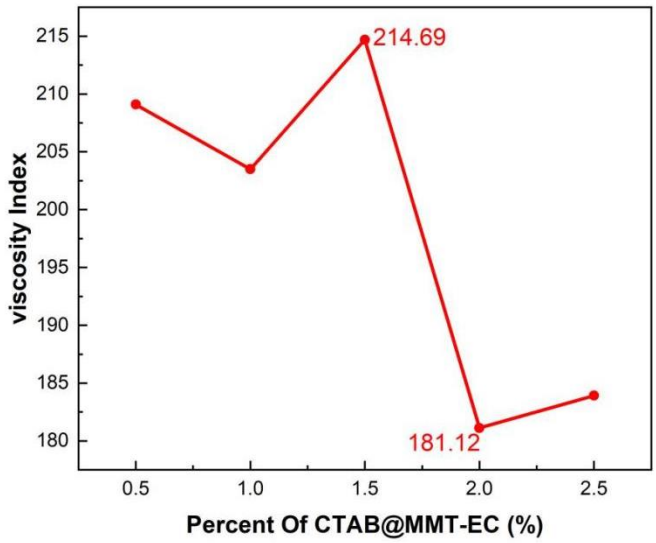

Fig. 7. Viscosity index of lubricating oil with different CTAB/MMT/EC content

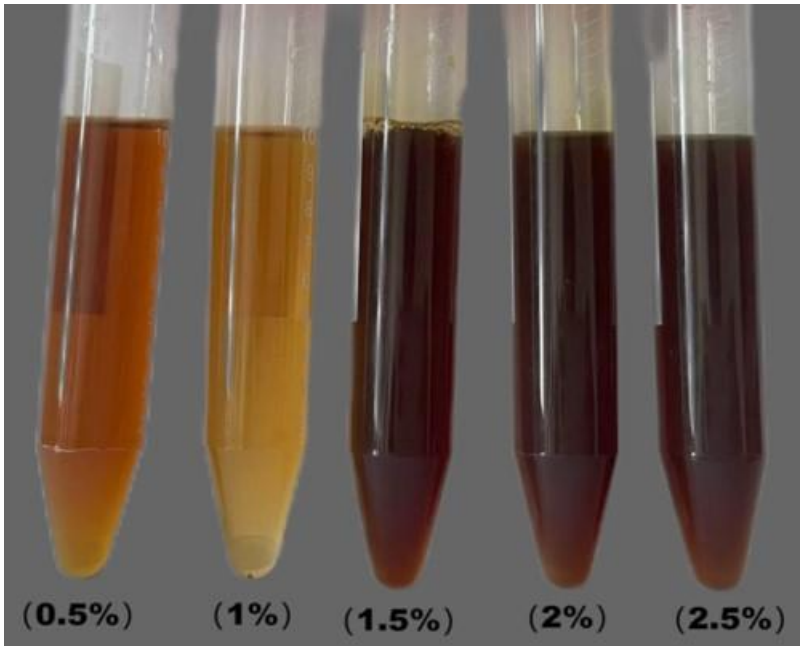

Fig. 8. Lubricating oil products modified by different CTAB/MMT/EC contents

FTIR analysis

FTIR analysis of *Xanthoceras sorbifolium* oil and lubricating oil modified with CTAB/MMT/EC (content 2 %) is shown in Fig. 9. The bending vibration of the trans-substituted group of unsaturated C=C appeared at 966 cm^{-1}, and the C-H bond was connected with the unsaturated C=C bond. Due to the influence of electronic effect, the thermal stability of the C-H bond will change, resulting in a change in the thermal stability of the compound. Therefore, the modified lubricating oil may have a downward trend in thermal stability. The C-H in plane bending vibration peak was at 1155 cm^{-1}, the C-H stretching vibration peak was at 2908 cm^{-1}, and the-OH stretching vibration peak was at 3500 cm^{-1}. From Fig. 9, the modified lubricating oil with CTAB/MMT/EC content of 2% retained the group properties of *X. sorbifolium* oil, and the peaks at 1155 cm^{-1} and 2908

cm^{-1} were weakened, indicating that due to the effect of temperature during the preparation process, the peak sizes can be shifted a lot due to various changes in the medium, this can cause errors in quantitation. The peak value of -OH group at 3500 cm^{-1} was enhanced. The enhancement of-OH polar group can promote the adsorption capacity of lubricating oil and metal friction surface, form a layer of physical adsorption or chemical adsorption lubricating film, and reduce friction and wear with metal surface. In the FTIR spectrum, the peak performance of the C-H bond connected with the unsaturated C=C or connected with other hetero atoms was not found, and the thermal stability of the modified lubricating oil may not be greatly affected.

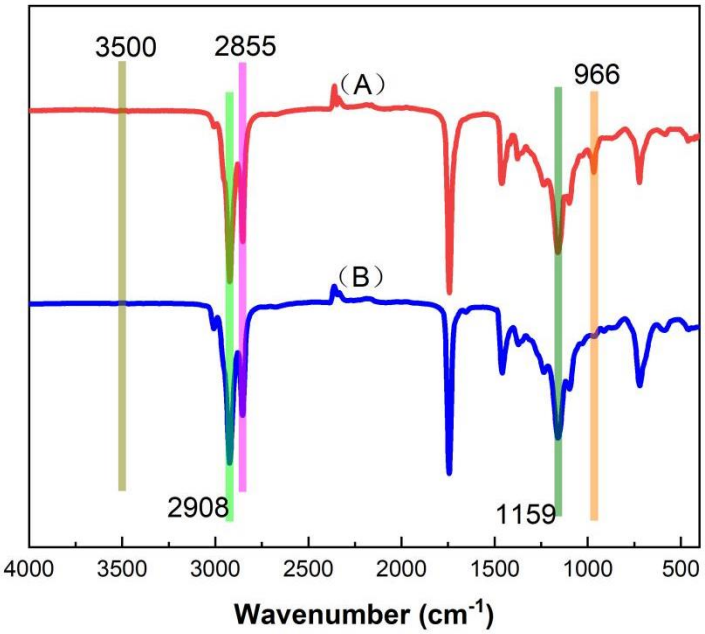

Fig. 9. FTIR diagram of (A) *Xanthoceras sorbifolium* Bunge oil and (B) lubricating oil containing 2% CTAB/MMT/EC

Thermal Stability Analysis

The TG-DSC curve of *Xanthoceras sorbifolium* oil is shown in Fig. 10(a), and the TG-DSC curve of CTAB/MMT/EC modified lubricating oil is shown in Fig. 10(b). As shown in Fig. 10a, the weight of *X. sorbifolium* oil remained constant from 0 to 300 °C, and there was no weight loss. Between 300 and 500 °C, the TG curve of *X. sorbifolium* oil changed greatly, and there was obvious weight loss. This may be because the increase of temperature accelerates the volatilization of *X. sorbifolium* oil, resulting in weight loss. The weight of the modified lubricating oil was constant between 0 and 200 °C, and the curve changed greatly between 200 and 500 °C, and there was obvious weight loss. Compared with *X. sorbifolium* oil, the prepared lubricating oil exhibited a decrease in the initial weight loss temperature, and the temperature at which the weight loss tended to be stable was the same, because the weight loss temperature of CTAB/MMT/EC was lower than that of *X. sorbifolium* oil. When the two formed a blend, the weight loss temperature decreased, which reduced the thermal stability. After 500 °C, the TG curves of both *X. sorbifolium* oil and lubricating oil tended to be stable, and the oil basically volatilized completely during the whole heating process. From 0 to 200 °C, the weight of the lubricating oil decreased more gently and the thermal stability was better, which also made it possible to meet the normal working conditions of the engine oil between 70 and 120 °C.

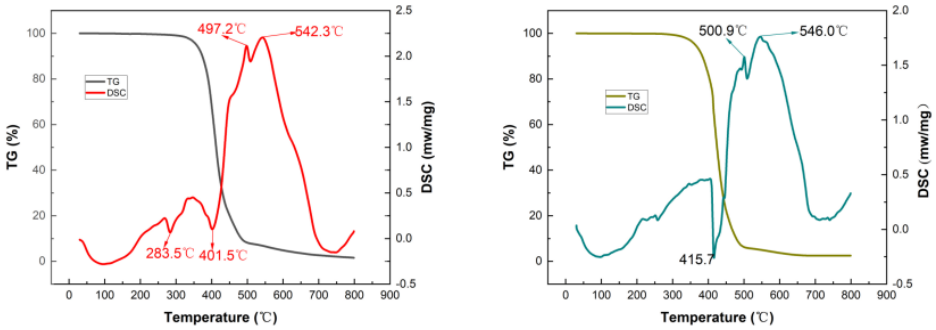

Fig. 10. TG-DSC curve of (a) *Xanthoceras sorbifolium* Bunge oil and (b) lubricating oil

According to the DSC curve of Fig. 10b, the *Xanthoceras sorbifolium* oil reached the decomposition vaporization temperature at about 402 °C, and there were obvious endothermic peaks at 497 °C and 542 °C, during which the enthalpy increased. This is consistent with the conclusion that *X. sorbifolium* oil has good thermal stability between 0 and 300 °C obtained by TG curve and can maintain good properties and state. From the DSC curve of the lubricating oil, it can be seen that there was an endothermic effect at 501 °C and 546 °C. During this period, the enthalpy increased and reached the decomposition vaporization temperature at about 416 °C. The results showed that the lubricating oil had good thermal stability between 0 and 200 °C, but the thermal stability was lower than that of *X. sorbifolium* oil, which is also consistent with the effect of group change in FTIR.

Determination of Condensation Point of Lubricating Oil

The solidifying point of lubricating oil changed under different preparation conditions. With the increase of preparation temperature, the coagulation point of lubricating oil also decreased. When the preparation conditions were 270 and 300 °C, the reaction time was 2 h, and the content of CTAB/MMT/EC was 2%, the lowest coagulation point of the lubricating oil was -26 °C and -25 °C, respectively, which was 8 °C and 7 °C lower than that of *Xanthoceras sorbifolium* oil. This may be because the preparation temperature reached or exceeded the effective melting point of CTAB/MMT/EC. The reduction of the coagulation point of *X. sorbifolium* oil by CTAB/MMT/EC in the molten state was more obvious. At the same time, the higher temperature also increased the solubility of CTAB/MMT/EC in *X. sorbifolium* oil, making the coagulation point have a more obvious reduction rate. The main reason for the decrease of condensation point is that the montmorillonite with good dispersion performance and layered structure made the wax crystal more regular, reducing the trend of mutual aggregation in crude oil, improving the stability and anti-aggregation ability. This achieved the purpose of reducing condensation point.

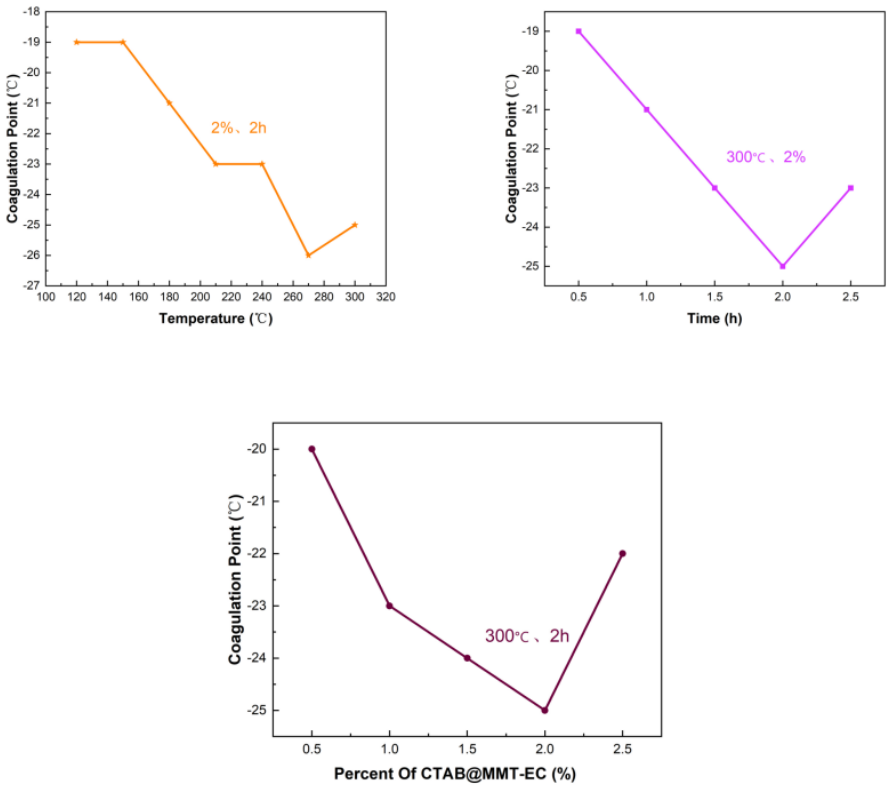

Fig. 11. Change of solidifying point of lubricating oil prepared with different CTAB/MMT/EC contents

Lubricity test

Antifriction performance

When the addition amount of CTAB/MMT/EC was 2 wt%, the friction coefficient of the prepared lubricating oil was much lower than that of *Xanthoceras sorbifolium* oil, and the friction coefficient was reduced to 0.026. From the relationship between friction coefficient and friction type in Table 4, the friction type was mixed friction. Compared with boundary friction, mixed friction can better reduce the friction resistance and wear, and it can better prolong the service life of mechanical parts under the same bearing capacity. This phenomenon occurs because the addition of CTAB/MMT/EC enhances the kinematic viscosity of *X. sorbifolium* oil and improves the adsorption capacity of the oil film and the metal surface, which can form a thicker protective oil film on the friction surface and improve the anti-friction performance.

Table 3. Friction Coefficient of Lubricating Oil with CTAB/MMT/EC Added

Name	Friction Coefficient
Xanthoceras sorbifolium Bunge oil	0.099
CTAB/MMT/EC 2wt%	0.026

Table 4. Relationship between Friction Coefficient and Friction Type

Type of Friction	Friction Coefficient
Dry friction	0.15 to 0.40
Boundary lubrication	0.08 to 0.10
Mixed lubrication	0.02 to 0.08
Fluid lubrication	0.001 to 0.005

Abrasion resistance

The transverse and longitudinal wear spot diameter (mm) of three small balls was used as the evaluation standard. The results are shown in Table 5. The average wear spot diameter of *Xanthoceras sorbifolium* oil was 0.69 mm, while the average wear spot diameter of the lubricating oil modified with 2%CTAB/MMT/EC was 0.81 mm. This difference was attributed to the fact that with the progress of high temperature reaction, some unsaturated carbon-carbon double bonds in *X. sorbifolium* oil are oxidized and broken. This conclusion can also be drawn from the FTIR of lubricating oil, and the double bonds can promote the formation of dense adsorption film on the metal surface of fatty acid esters and increase the strength of lubricating film, so the wear point diameter of lubricating oil is increased. The anti-wear performance of the lubricating oil modified with 2%CTAB/MMT/EC was decreased, However, the original anti-wear performance of *X. sorbifolium* oil was basically maintained.

Table 5. Wear Scar Diameter of *Xanthoceras sorbifolium* Oil and Lubricating Oil with CTAB/MMT/EC content of 2%

Name	Number one		Number two		Number three		Average spot diameter (mm)
	X1	Y1	X2	Y2	X3	Y3	
Xanthoceras sorbifolium oil	0.7	0.7	0.58	0.72	0.74	0.71	0.69
CTAB/MMT/EC 2wt%	0.81	0.83	0.80	0.83	0.78	0.84	0.81

CONCLUSIONS

1. Lubricating oil was prepared by modifying *Xanthoceras sorbifolium* Bunge oil, and the rheological properties of lubricating oil prepared under different modification conditions were very different.
2. The results indicated that the kinematic viscosity of the prepared *Xanthoceras sorbifolium* oil-based lubricant could reach 433 mm^2 / s at 40 °C, 51.1 mm^2 / s at 100 °C, and the coagulation point was − 25 °C. The viscosity index reached more than 181, which belongs to the category of super high viscosity index lubricating oil. The friction coefficient of lubricating oil was 0.026, and the average wear spot diameter was 0.81 mm. The anti-friction performance was enhanced, and the anti-wear performance decreased.
3. The results of this study can be directly explored in future work, such as the best process for preparing environmentally friendly plant-based lubricants.

ACKNOWLEDGMENTS

This work was supported by the Science and Technology Projects of Inner Mongolia Autonomous Region (No. 2022YFDZ0045); Science and technology projects of Jungar Banner (No. 2023YY-12). Transformation Fund for Science and Technology Achievements of Inner Mongolia Autonomous Region (No. 2019CG018).

REFERENCES CITED

An, J. X. (2021). "Analysis of the current situation and development trend of lubricating oil market at home and abroad," *Synthetic Lubricating Materials* 48(01), 42-47. DOI: 10.3969/j.issn.1672-4364.2021.01.012

Chen, H., Ding, M., Li, Y., Xu, H., Li, Y., and Wei, Z. (2020). "Feedstocks, environmental effects and development suggestions for biodiesel in China," *Journal of Traffic and Transportation Engineering(English Edition)* 7(6), 791-807. DOI: 10.1016/j.jtte.2020.10.001

Cheng, Q. L., and Wang, M. M. (2016). "Preparation of bio-lubricant from epoxidized soybean oil catalyzed by modified MMT," *Guangdong Chemical Industry* 43(02), 45-47

Ding, L. Q., Feng, H., and Nian, L. L. (2020). "Research progress in the synthesis of vegetable oil-based lubricating base oil and additives," *Synthetic Chemistry* 28(10), 924-931. DOI: 10.15952 /j. cnki.cjsc

Dong, Z. P., Kong, M. L., and Yu, H. (2020). "Analysis of the current situation of synthetic lubricating base oil," *Shandong Chemical Industry* 49(17), 70-74+76. DOI: 10.19319/j.cnki.issn.1008-021x.2020.17.026

de Souza, T. A. Z., Pinto G. M., Julio, A. A. V., Coronado, C. J. R., Perez-Herrera, R., Siqueira, B. O. P. S., da Costa, R. B. R., Roberts, J. J., and Palacio, J. C. E. (2022). "Biodiesel in South American countries: A review on policies, stages of development and imminent competition with hydrotreated vegetable oil," *Renew. Sustain. Energy Reviews*. 153, article 111755. DOI: 10.1016/j.rser.2021.111755

Fan, N. N., Luo, W., and Bai, Z. X.(2021). "Lubricating oil additives and their development trends," *Aging and Application of Synthetic Materials* 50(01), 140-143. DOI: 10.16584/j.cnki.issn1671-5381.2021.01.042

Fazal, M. A., Sundus, F., Masjuki, H. H., Rubaiee, S., and Quazi, M. M. (2021). "Tribological assessment of additive doped B30 biodiesel-diesel blend by using high frequency reciprocating rig test," *Sustainable Energy Technol. Assess*. 48, article 101577. DOI: 10.1016/j.seta.2021.101577

Kerni, L., Raina, A., and Ul Haq, M. I. (2019). "Friction and wear performance of olive oil containing nanoparticles in boundary and mixed lubrication regimes," *Wear* 426-427(01), 819-827. DOI: 10.1016/j.wear.2019.01.022

Liu, X. Y., Xu, N., Li, W. M., Zhang, M., Lou, W. J., and Wang, X. B. (2016). "Viscosity modification of lubricating oil based on high concentration silica nanoparticles colloidal system," *Journal of Dispersion Science and Technology* 12(20), 319-339. DOI: 10.1080/01932691.2016.1220319

Liu, P., Wang, X., Wu, J., Lin, W., Feng, Y. H ., Chen, B. S., Fang, J. H ., and Jiang, Z. Q. (2020). "Effect of boron-nitrogen modified soybean oil additive on biodegradability, anti-oxidation property and lubricity of rapeseed oil," *Journal of Engineering Tribology* 234(02), 282-291. DOI: 10.1080/01932691.2019.1667818

Liu, P., Wang, X., Wu, J., Fang, J. H., and Lin, W. (2019). "Effect of boron nitrided soybean oil on biodegradability and lubricity of rapeseed oil," *Petroleum Refining and Chemical Industry* 50(04), 88-93. DOI: 10.1177/1350650119861785

Lu, J., Zhang, Y., Duan, Q. H., Liu, Y. N., Yu, K., Wang, L. H., and Zeng, J. L. (2018). "Structural innovation and industrialization progress of bio-based lubricant base oil," *Petroleum Journal(Petroleum Processing* 34(02), 203-216. DOI: 10.3969/j.issn.2018.02.001

Panchal, T. M., Patel, A., Chauhan, D., Thomas, M., and Patel, J. V. (2017). "A methodological review on bio-lubricants from vegetable oil based resources," *Renewable & Sustainable Energy Reviews* 70, 65-70. DOI: 10.1016/j.rser.2016.11.105

Sui, M., Chen, Y., Li, F, and Wang, H. (2021a). "Study on transition metal ion Fe^{3+}catalyzed biodiesel oxidation and inhibition mechanism," *Fuel* 303, article 121288. DOI: 10.1016/j.fuel.2021.121288

Sui, M., Chen, Y., Li, F., Wang, W., and Shen, J. (2021b). "Study on the mechanism of auto-oxidation of Jatropha biodiesel and the oxidative cleavage of CC bond," *Fuel* 291, article 120052. DOI: 10.1016/j.fuel.2020.120052

Sui, M., Li, F.-S., Wu, X.-H., Wang, S., and Lim M. (2019). "Preparation of anionic functionalized biodiesel ionic liquid antioxidant[X][C_6H_5COO]," *Journal of Fuel Chemistry and Technology* 047(001), 66-73.

Teng, W., Chen, Y., Sui, M., and Li, F. (2020). "Effects of TEPA and [MI][$C_6H_2(OH)_3COO$] on antioxidant activity of biodiesel," *Chemical Industry and Engineering Progress* 39(11), 8. DOI: 10.16085/j.issn.1000-6613.2020-0104

Wan, Q. (2019). "Development and characterization of castor oil-based low-temperature lubricant base oil," *Huazhong University of Science and Technology* 03. DOI: 10.27157/d.cnki.ghzku.2019.004329

Wang, W., Li, F., and Wang, H. (2021). "The effect of tetrethylenepentamine (TEPA) on the oxidation stability and the lubrication performance of biodiesel," *Ind. Crops Prod.* 171, article 113910. DOI: 10.1016/j.indcrop.2021.113910

Wang, X. W., Chen, W. Y., and Zou, K. (2014). "Research progress on the relationship between structure composition and performance of lubricating base oil," *Application Chemical Engineering* 43(03), 539-542. DOI: 10.16581/j.cnki.issn1671-3206.2014.03.037

Wu, Z. H., Zhao, P., and He, D. L. (2017). "Review of research on vegetable oil-based bio-lubricant grease," *Lubricants* 32(05), 1-6. DOI: 10.19532/j.cnki.cn21-1265/tq.2017.05.001

Zheng, Z. Z., Li, F. S. , Zhang, H. C., Wang, S., Zhao, Z. J., Wang W. C., and Chen, R. Y. (2022). "Fishhook characteristics of biodiesel lubricity during autoxidation," *Fuel* 331, article 125897. DOI: 10.1016/j.fuel.2022.125897

Zeng, J., Liao, S. S., and Ren, X. N. (2015). "Study on the preparation of lubricating oil base oil from vegetable oil," *Food Industry* 36(05), 213-216.

Zhang, S., and Chen, W. (2022). "China's energy transition pathway in a carbon neutral vision," *Engineering* 14, 64-76. DOI: 10.1016/j.eng.2021.09.004

Article submitted: October 16, 2023; Peer review completed: December 2, 2023; Revised version received and accepted: December 14, 2023; Published: January 9, 2024.
DOI: 10.15376/biores.19.1.1377-1393