lubricants

Article

Viscosity Variations and Tribological Performances of Oleylamine-Modified Fe_3O_4 Nanoparticles as Mineral Oil Additives

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Abstract: In order to improve the flowabilities and anti-friction and anti-wear properties of lubricants, the viscosity variations and tribological performances of oleylamine-modified Fe_3O_4 nanoparticles as mineral oil additives were systematically investigated via rotational parallel plate rheometer, ball–disc reciprocating tribometer, non-contact three-dimensional surface profiler, scanning electron microscope, energy dispersive X-ray spectrometer and X-ray photoelectron spectroscopy. Spherical monodisperse Fe_3O_4 nanoparticles were synthesized and dispersed into mineral oils to obtain lubricants with mass fractions of 1%, 3%, 5%, 8%, 10% and 20%, respectively. These lubricants have excellent stabilities within 12 months. Interestingly, the dynamic viscosity and kinematic viscosity of the lubricants first decrease and then increase with the increase in Fe_3O_4 content, and the lubricants' viscosity is at a minimum when the mass concentration is 5%. The tensile curves also show that with the mass fraction increase, the lubricants' tackiness and adhesion have the same change law, and both reach the lowest point when the mass concentration is 5%. Meanwhile, Fe_3O_4 nanoparticles can improve the tribological properties of the base oils. It is worth noting that the maximum reduction in the wear volume at 25 °C is up to 93.8% compared with base oils when the additive concentration of the Fe_3O_4 nanoparticles is 5 wt%.

Keywords: oleylamine-modified Fe_3O_4 nanoparticles; high dispersion stability; viscosity variations; excellent tribological performances

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1. Introduction

Friction is the main reason for unnecessary energy consumption during the use of equipment, resulting in additional failure caused by wear [1,2]. At present, the appropriate use of lubricants is an effective way to solve this problem. Lubricants are widely used in automobile manufacturing, machinery production, and other fields; they can enhance the durability and wear resistance of the equipment, prolong the service life and avoid unnecessary economic losses. With the rapid development of modern industry, the machinery's operating environment is becoming more severe, which puts forward higher requirements for lubricants. Using lubricating additives can improve the wear resistance of lubricants, showing the characteristics of low friction. Finding and preparing lubricating additives with good dispersion and obtaining high-performance lubricating systems have always been the focus of research, especially the rapid development of nanotechnology in recent years, which makes nanomaterials attract more and more attention. Nanomaterials refer to materials with characteristic dimensions ranging from 1 to 100 nm, including quantum dots, nanoparticles, nanowires and nanofilms, among which nanoparticles have become effective lubricating additives due to their small size and large specific surface area [3–6].

Compared with other nanoparticles, Fe_3O_4 nanoparticles as additives of lubricating oils can keep lubricants in the contact areas, which avoids environmental pollution caused by the leakage of lubricating oils [7]. Some scholars have studied the tribological properties of nano-Fe_3O_4 as lubricating oil additives [8–10]. Yang et al. [11] found that applying pulsed magnetic field can keep nano-Fe_3O_4 magnetic fluid in the friction area, thus improving its anti-friction and anti-wear effects. Gao et al. [12] studied the tribological properties of different morphologies (i.e., hexagonal, octahedral, and irregular morphologies) Fe_3O_4 NPs as lubricating additives. It is found that these nanoparticles have good antifriction properties. Compared with octahedral and irregular morphology of Fe_3O_4 nanoparticles, the friction surface of hexagonal nanosheets is smoother. Zhou et al. [13] modified Fe_3O_4 magnetic nanoparticles with oleic acid, dispersed them in the base oil, and then studied their tribological properties of steel-to-steel contact. The results showed that adding Fe_3O_4 nanoparticles could effectively reduce friction and wear. The average friction coefficient and wear volume decreased with the increase in Fe_3O_4 nanoparticle concentration, especially when the load was 10 N. Zuin et al. [14] found that as lubricating oil additives, stearic acid-modified Fe_3O_4 nanoparticles can reduce friction coefficient and wear volume under severe conditions. Related research reports showed that Fe_3O_4 nanoparticles had excellent anti-friction and anti-wear effects. However, due to its magnetism and high surface energy, Fe_3O_4 nanoparticles are easy to agglomerate, which is not conducive to its advantages as a lubricating additive [9].

Meanwhile, it is well known that the viscosity of liquid lubricating materials is the key index to determine the lubrication state of the system [15]. It greatly affects the oil film thickness and loading capacity on the friction surface [16]. However, in previous studies, researchers paid more attention to the friction and wear process of nano-additives and ignored the effects of additives on the viscosity changes of the system, especially the effects of different content additives on the viscosity changes and tribological properties. It is of great significance to understand the change rule of lubricant viscosity by nano-additives and explain the possible difference in tribological properties, which is important to realize the control of lubricant performance through nano-additives and obtain high-performance lubricant.

In the present work, 7 nm spherical Fe_3O_4 nanoparticles modified by oleylamine were synthesized by thermal decomposition and dispersed into mineral oils to obtain lubricants with mass fractions of 1%, 3%, 5%, 8%, 10% and 20%, respectively. The lubricants have good dispersibility even at the additive concentration of up to 20 wt% nanoparticles. The effects of nanoparticle concentration on the viscosity variations and tribological performances of the lubricants were discussed and the reason for their variable flowabilities and the tribological mechanism were analyzed.

2. Experiments

2.1. Materials

Iron (III) acetylacetonate (98%), oleylamine (80–90%) and ethanol were purchased from Macklin. All chemicals were used without further purification. Common mineral oil (150 N) was selected as the dispersion medium. Table 1 shows the properties of 150 N supplied by Qingdao Zhongke Runmei Lubrication Material Technology Company, Qingdao, China.

Table 1. Characteristics of the base oil 150 N.

Characteristic	Unit	Value
Kinematic viscosity at 40 °C	mm^2/s	29.73
Kinematic viscosity at 100 °C	mm^2/s	5.256
Viscosity index	-	116
Density at 25 °C	g/cm^3	8.314
Flash point	°C	232
Pour point	°C	−27

2.2. Preparation of Lubricants Containing of Fe_3O_4 Nanoparticles

In a classic procedure (Figure 1), oleylamine-modified Fe_3O_4 nanoparticles were synthesized by thermal decomposition of $Fe(acac)_3$ [17]. A 100 mL three-necked flask was used in which Iron (III) acetylacetonate (3 mmol, 1.058 g) was dissolved in oleylamine (30 mL). The mixture was stirred under a gentle flow of nitrogen at 110 °C for 1 h. Then, under a blanket of nitrogen, the solution was heated to 300 °C, and the reaction solution color gradually became black, which indicated that Fe_3O_4 nanoparticles were being formed. Then, the solution was refluxed at 300 °C for 1 h. After it cooled down to room temperature, 50 mL ethanol was added as a precipitating agent. The nanoparticles were precipitated by centrifugation at 7000 rpm and washed with ethanol. Finally, nanoparticles were dispersed into a 150 N Mineral oil, and six nano-Fe_3O_4 particles lubricating oil dispersion systems with mass concentrations of 1%, 3%, 5%, 8%, 10% and 20% were prepared, named NF-1, NF-3, NF-5, NF-8, NF-10 and NF-20, respectively.

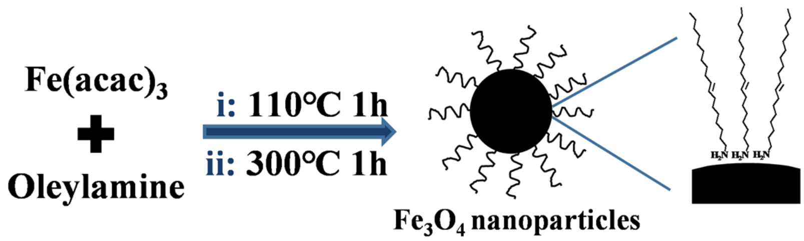

Figure 1. Schematic diagram of synthetic Fe_3O_4 nanoparticles.

2.3. Viscosity and Tribological Tests

In this work, the dynamic viscosities of lubricants with different mass fractions of the Fe_3O_4 nanoparticles were investigated by a rotational parallel plate rheometer (MCR302, Anton Paar, Ostfildern, Germany). The tensile curves were also conducted to explain the tackiness and adhesion of lubricants. The diameter of the parallel plate is 25 mm (PP25). The number of lubricants added between the plates was fixed in every test to reduce the experimental error. All the experimental tests are constant at a certain temperature, and the temperature error is less than 0.1 °C. The experimental results were supplemented by the lubricants' kinematic viscosity, which was tested by an automatic kinematic viscometer (S-Flow1200, Omnitek, The Netherlands).

The tribological properties of lubricants with different mass fractions were investigated on a ball-disc reciprocating tribometer (SRV-V, Optimol, Germany). The upper test steel ball in size of 10 mm in diameter and the lower test steel plate in size of 24 mm in diameter and 7.9 mm in thickness used in the test were made of AISI 52,100 steel with a hardness of HRC 60. The friction coefficients were automatically recorded by the computer.

2.4. Characterization

The crystal structure of the nano-Fe_3O_4 particles was analyzed by an X-ray diffraction (XRD, D/Max-2500/PC, Rigaku, Japan) device with Cu-Kα radiation at room temperature. Surface functional groups were characterized by a Fourier transform infrared spectrum (FT-IR, TENSOR 27, BRUKER, Karlsruhe, Germany). A transmission electron microscope (TEM, JEM-2100PLUS, JEOL, Tokyo, Japan) was used to observe the morphology and particle size of the Fe_3O_4 nanoparticles.

A non-contact three-dimensional surface profiler (MicroXAM-800, KLA-Tencor, San Jose, CA, USA) was used to measure the wear loss volume of the steel disc. A scanning electron microscope (SEM, EVO 10, ZEISS, Germany) was used to observe the surface morphology. An energy dispersive X-ray spectrometer (Xplore 15, Oxford Instruments, Oxford, UK) and an X-ray photoelectron spectroscopy (XPS, Axis Supra+, Kratos, Manchester, UK) were used to analyze elements of the wear tracks of steel discs.

3. Results and Discussion

3.1. Characterizations of Fe_3O_4 Nanoparticles

Figure 2a shows the XRD patterns of synthesized nanoparticles, which suggests that the positions and the relative intensities of diffraction peaks are in good agreement with those of the standard Fe_3O_4 peaks (JCPDS 19-629). The results of the FT-IR are shown in Figure 2b. The absorption peak located at 588 cm^{-1} can be ascribed to the Fe-O bond vibration of Fe_3O_4 [18]. The absorption peaks at 1330 -1650 cm^{-1} are observed due to the $–NH_2$ bending mode of oleylamine, and the absorption peaks around 2853 cm^{-1} and 2924 cm^{-1} are corresponding to ethyl ($-CH_2$) and methyl ($-CH_3$) stretching vibration [17,19]. The FT-IR spectra suggest that oleylamine is modified on the surface of Fe_3O_4 nanoparticles. The TEM image of Fe_3O_4 nanoparticles clearly exhibits that the Fe_3O_4 nanoparticles have a spherical morphology, narrow size distribution and are monodispersed (~7 nm), which can be seen in Figure 2c.

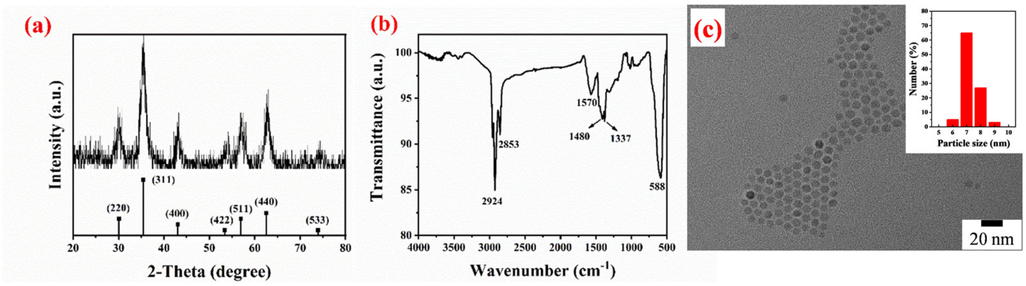

Figure 2. XRD patterns (**a**), FT-IR spectra (**b**) and TEM image (**c**) of the nano-Fe_3O_4 particles.

3.2. Settling Stabilities of Lubricants

The settling stability of the lubricants is judged by the static method. Figure 3a is the picture of NF-10 and NF-20 after 30 min ultrasonic. Figure 3b,c are the pictures of lubricants with different mass fractions after 12 months. It can be observed that these lubricants were no precipitation and stratification even at the additive concentration of up to 20 wt% after 12 months.

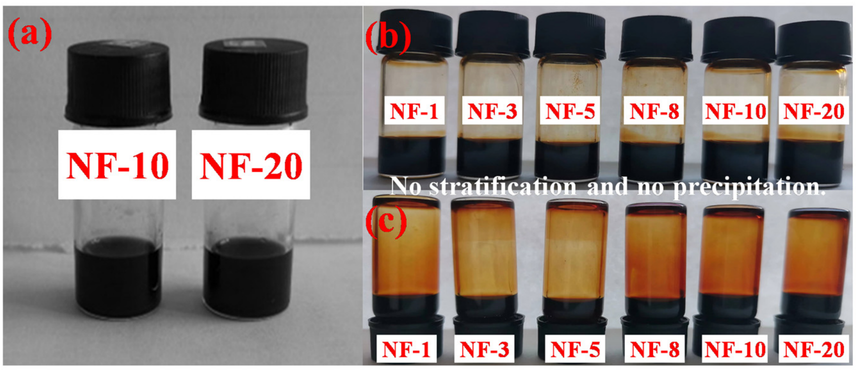

Figure 3. Stability of lubricants. After sonication (**a**) and after 12 months (**b**,**c**).

3.3. Flow Behaviors of Lubricants

Dynamic viscosity is an important parameter of lubricating oils. The viscosity change law between the viscosity of the lubricants and the mass concentration is obtained by studying the viscosity change of the dispersion system after adding Fe_3O_4 nanoparticles, which is of great significance to realize the viscosity control of the lubricants by adding lubricating additives and improve the lubricants' performance. The dynamic viscosities of lubricants were measured by linearly changing shear rates from 1 to 100 s^{-1} at 25 °C. The experimental data were fitted by Newton model in Equation (1).

$$\tau = \eta \dot{\gamma} \quad (1)$$

where τ and $\dot{\gamma}$ are shear stress and shear rate, respectively. A Newtonian rheological parameter is dynamic viscosity (η).

Figure 4 shows the dynamic viscosity of the lubricants with shear rate and the relationship between the fitting dynamic viscosity and the content of nano-Fe_3O_4 particles. According to Figure 4a, adding Fe_3O_4 nanoparticles will affect the dynamic viscosity of base oils. The viscosities of the lubricants used in the experiment obviously decrease at first and then increases with the increase in the mass concentration of Fe_3O_4 nanoparticles. When the mass fraction is 5%, the viscosity of the lubricants is the lowest, which is decreased by 8.57% compared to base oils. At 25 °C, only the dynamic viscosity of NF-20 is greater than that of the base oils. The fitting results of lubricants with different mass fractions at 25 °C are shown in Figure 4b according to the Newton fluid model. The coefficients of determination (R^2) of the fitting data were calculated to prove the accuracy of the results, as shown in Table 2. It should be noted that the coefficients of determination (R^2) of all the lubricants studied are greater than 0.999, which indicates that all the lubricants used in the experiment have good simulation results with the Newtonian model. The law presented is consistent with the above conclusion, as shown in Figure 4b.

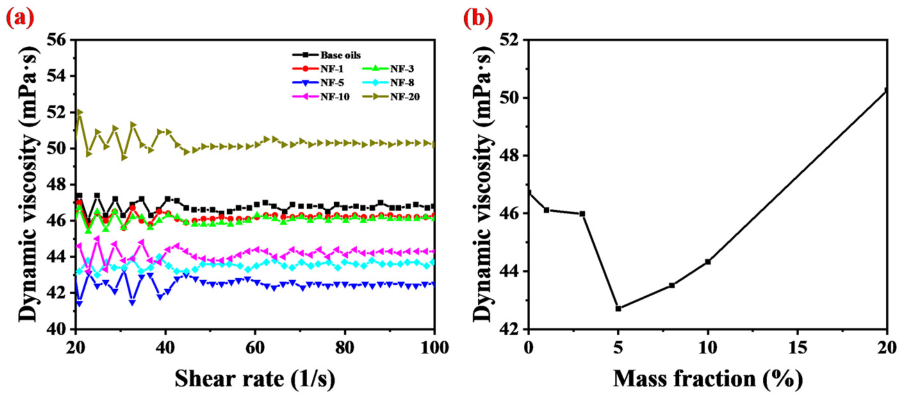

Figure 4. Viscosity versus shear rate (**a**) and the Newtonian rheological parameter versus mass fraction (**b**) of the lubricants tested at 25 °C, respectively.

Table 2. The fitting results of Newtonian model with respect to particles mass percentage.

Sample	Base Oils	NF-1	NF-3	NF-5	NF-8	NF-10	NF-20
η (mPa·s)	46.714	46.116	45.982	42.710	43.511	44.326	50.255
R^2	0.9999	0.9999	0.9999	0.9999	0.9999	0.9998	0.9998

In previous studies, most studies have shown that adding nanoparticles increased the viscosities of base oils and the viscosities of fluids increased with the increase of nanoparticles concentration [20–28]. The reason for this phenomenon is that the van der Waals force between particles increases with the increase of nanoparticles addition, resulting in the agglomeration of nanoparticles and the formation of larger nanoclusters, which inhibit the easy movement of the base oils and improve the viscosities of the fluids [27,29,30]. The lubricants studied are not consistent with the above discussion. In order to ensure the reliability of the viscosity law presented by the lubricants investigated, an automatic kinematic viscosimeter was adopted to test the kinematic viscosity of six dispersion systems. The test results are shown in Figure 5. It can be seen that the viscosity of the lubricants containing Fe_3O_4 nanoparticles does decrease first and then increase as the content of Fe_3O_4 nanoparticles increases.

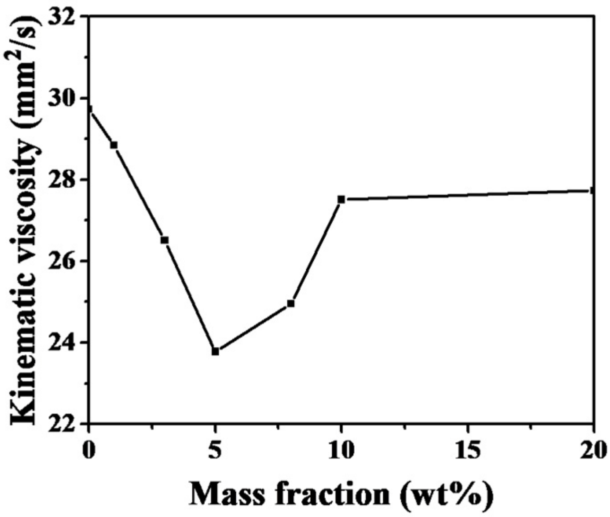

Figure 5. Kinematic viscosity versus mass fraction relations of the lubricants tested at 40 °C.

In order to further study the influence of nano-Fe_3O_4 particles on the viscosity variations of lubricating oil dispersion systems, the adhesion and tackiness of lubricants can be evaluated by tensile curves. Adhesion is caused by the intermolecular attraction between the lubricants and other materials in contact. Tackiness is caused by the intermolecular attraction within the lubricants [31]. To a certain extent, the tensile curve can reflect the viscosity changes of the lubricating oil containing nano-Fe_3O_4 particles. The tensile curves are tested by moving the rotor vertically. The specific test method is as follows. The initial gap between the upper and lower plates is 0.4 mm. Move the rotor downward until a normal load of 4 N is applied to the sample. Consequently, raise the rotor at a speed of 2 mm/s. During the test, the normal force on the rotor and the gap between the upper and lower plates are recorded, and the vertical upward normal force is defined as positive. Figure 6 exhibits four stages in the measurement of tensile curves. The tensile test is divided into four stages, denoted by I, II, III and IV in the figure. The first stage is when the rotor moves downward from the initial position until the rotor is subjected to the upward normal force of 4 N. The second stage is when the rotor begins to move up until the normal force on the rotor is 0 N. The third stage is that the rotor continues to move up until the rotor is subjected to the maximum downward normal force. The rotor continues to move until most of the lubricant is separated from the rotor surface, which is the fourth stage.

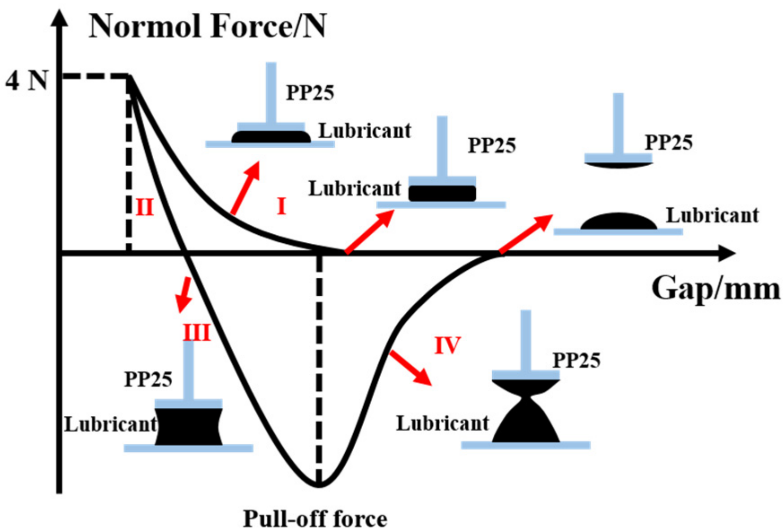

Figure 6. Schematic diagram of the measurement of tensile curves.

It is clear that the lubricant is stretched by the rotor from the third stage. Because of the lubricants the gravity, adhesion and tackiness, the rotor begins to receive a downward normal force, which is recorded as negative. At this stage, the normal force increases with an increase in the gap, and there is a maximum normal force called the pull-off force [32]. In the final stage, the lubricant tends to separate from the upper plate, and the normal force begins to decrease. When the rotor moves to a certain extent, most of the samples are separated from the upper plate, and only a small part of the samples is adsorbed on the rotor surface due to surface tension. This part of the samples is very few, and its mass is small, which can be ignored. Therefore, the normal force on the rotor caused by gravity is almost zero. The integration of the normal force and the gap in this stage is named after separation energy (E_s) [32]. The length of lubricant bonding (L) refers to the displacement from the maximum force (pull-off force) to the position where the lubricant is separated from the upper plate [32]. The ratio between separation energy and bonding length (E_s/L) refers to the energy required to separate per unit length. For lubricants, adhesive strength and tackiness can be evaluated by the value of pull-off force and the separation energy per unit length, respectively [31,32]. The larger the value of pull-off force, the stronger the adhesion. Similarly, the larger the value of the separation energy per unit length, the stronger the tackiness.

Figure 7 shows the tensile curves of the lubricants containing nano-Fe_3O_4 particles at 25 °C. The normal force versus gap curves in the third and fourth stages for the samples investigated at 25 °C can be seen in Figure 7a. It can be seen that the normal force and gap changed regularly with the increase in Fe_3O_4 content. The pull-off forces and separation energies per unit length of lubricants based on the mass fraction can be obtained by processing the data in Figure 7a, and the results are presented in Figure 7b,c, respectively. According to these pictures, it can be clearly seen that adding Fe_3O_4 nanoparticles have an obvious effect on the adhesion and tackiness of the lubricants tested. The pull-off forces and separation energies per unit length of the lubricants gradually decrease at first and then increase with the increase in the nanoparticles' content, and NF-5 has the smallest tackiness and adhesion. Figure 7 indicates that the interaction force between the lubricants and the rotor and the molecular force within the lubricants change with the contents of Fe_3O_4 nanoparticles. Adding Fe_3O_4 nanoparticles may weaken the interaction force between the molecules in the lubricants and reduce the tackiness and adhesion of the lubricants. The above conclusions are consistent with the results of the lubricants' dynamic viscosity and kinematic viscosity, and the minimum value is also obtained at NF-5.

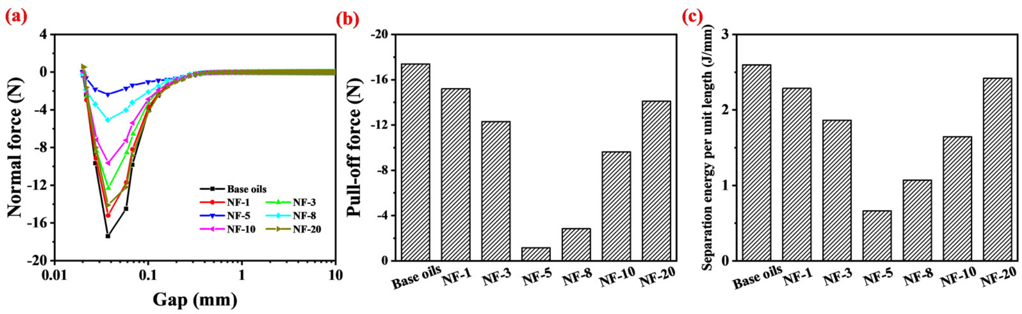

Figure 7. The normal force versus gap curves (**a**), the pull−off forces (**b**) and separation energies per unit length (**c**) for lubricants investigated at 25 °C.

3.4. Tribological Properties of Lubricants

The effect of nano-Fe_3O_4 particles' content on the anti-friction and anti-wear of the lubricants was studied via a ball–disc reciprocating tribometer. Figure 8 presents the tribological performances of lubricants tested at 25 °C, 100 N, 25 Hz and 1 mm. The friction coefficients (COFs) of lubricants containing Fe_3O_4 nanoparticles are lower than that of base oils during most friction test time, as depicted in Figure 8a. At the beginning of the friction test for 200 s, the COF of base oils is about 0.095, which is lower than those of lubricants containing Fe_3O_4 nanoparticles. However, when the friction time exceeds 200 s, the COF of the base oils suddenly increases to about 0.21 and then decreases slightly to about 0.18. Then, the COF curve does not fluctuate violently until the end of the experiment. The result shows that the stability of the base oil lubrication is poor, the bearing capacity of the formed oil film is weak, and it is easy to break during friction, which leads to the change of friction state. However, adding Fe_3O_4 nanoparticles can improve the bearing capacity of the lubricants and make them run smoothly with a low friction coefficient. The results show that Fe_3O_4 nanoparticles can improve the anti-friction performance of lubricating oil, but there is no obvious difference in the antifriction performance of lubricating oil systems with different mass concentrations.

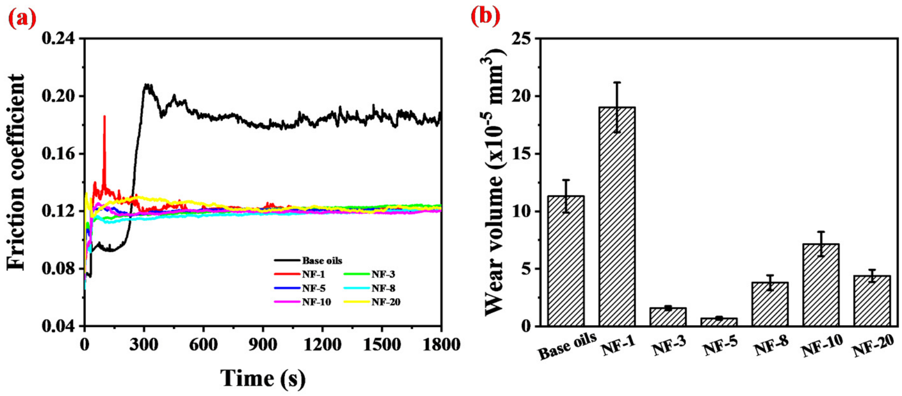

Figure 8. Tribological properties of lubricants studied at 25 °C. (**a**) Coefficient of friction versus time and (**b**) wear volume of lubricants tested based on mass fraction.

In order to further understand the anti-wear performance of the lubricants containing nano-Fe_3O_4 particles, the wear surface of the steel disc was characterized. As presented in Figure 8b, adding Fe_3O_4 nanoparticles reduces the wear volume of lubricants and improves the wear resistance of lubricants, as compared with base oils. Furthermore, the maximum reduction in the wear volume at 25 °C is up to 93.8% compared with base oils when the additive concentration of Fe_3O_4 nanoparticles is 5 wt%. The corresponding wear surface profiles are shown in Figure 9. It can be seen more intuitively that the width and depth of wear marks of NF-5 and NF-10 are obviously smaller than that of base oil, which is also consistent with the above conclusions. It is worth noting that the wear volume of NF-1 is larger than that of base oil, indicating that the addition of nano-Fe_3O_4 intensifies the wear at this time.

A scanning electron microscope was used to scan the worn surface of the lower plate to further analyze the role of Fe_3O_4 nanoparticles in the friction test process. Figure 10 exhibits SEM and EDS results of the wear scars of steel plate lubricated with base oils, NF-5 and NF-10 at 25 °C. As described in Figure 10a, it is obvious that a large number of noticeable furrows and pits exist on the frictional surface of the disc lubricated by base oils along the sliding direction. However, after adding Fe_3O_4 nanoparticles, the lubricants' anti-wear is improved, the wear marks on the worn surface of NF-10 are obviously shallow, and there are only a few furrows whose width is relatively small on the surface. The wear surface of NF-5 is relatively smooth, and there are no obvious wear marks. The results show that nano-Fe_3O_4 particles can improve the wear phenomenon on the surface of friction pairs and improve the wear resistance of lubricants. At the same time, according to the element content on wear marks, the content of C lubricated by the base oil is higher. After adding Fe_3O_4 nanoparticles, the content of C decreases, while the content of Fe increases slightly.

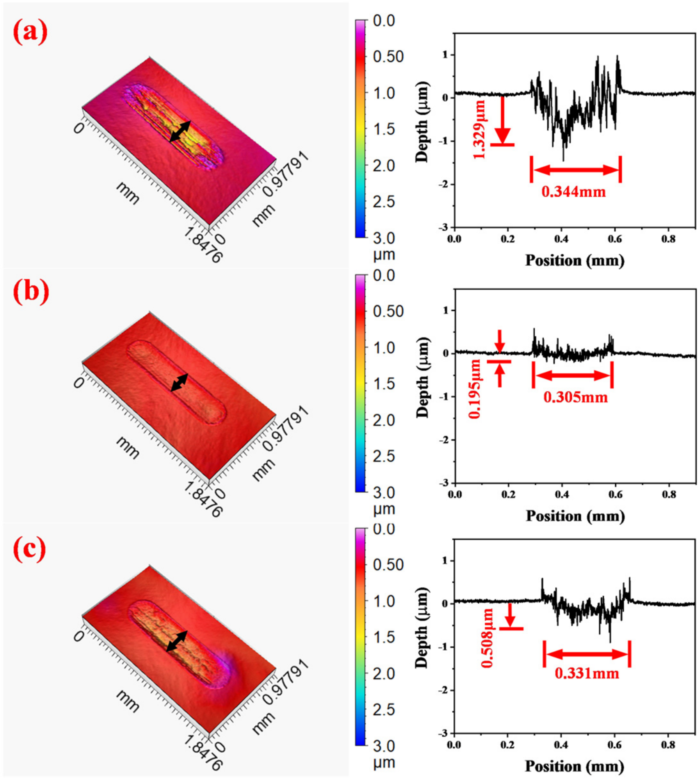

Figure 9. Surface profiles of wear tracks after friction test at 25 °C. (**a**) Base oils, (**b**) NF−5 and (**c**) NF−10.

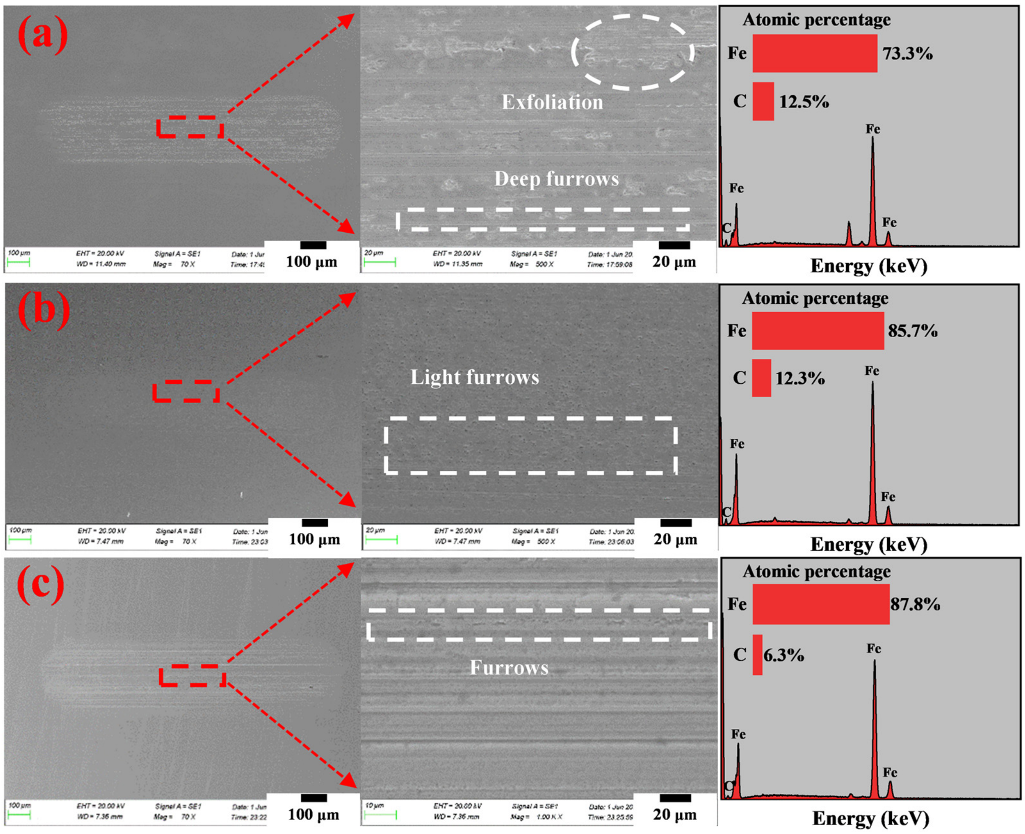

Figure 10. SEM images and EDS spectra of wear tracks after friction test at 25 °C. (**a**) Base oils, (**b**) NF-5, and (**c**) NF-10.

In order to further analyze the lubrication mechanism of Fe_3O_4 nanoparticles, XPS was used to analyze chemical elements on the worn surfaces lubricated by base oils and NF-5, as shown in Figure 11. The C 1s, O 1s and Fe 2p peaks appear in base oils and NF-1. The contents of elements C, O and Fe are listed in Figure 11a and Figure 11c, respectively. After adding Fe_3O_4 nanoparticles, the content of Fe element on the frictional surface increases from 7.05% to 8.26%, which is consistent with the EDS analysis results. In the XPS spectrum of Fe 2p, all spectra show two peaks corresponding to Fe $2p_{1/2}$ and Fe $2p_{3/2}$, respectively. Fe $2p_{3/2}$ is further divided into two peaks at 711.7 eV and 710.3 eV, corresponding to Fe^{3+} and Fe^{2+}, respectively [2,33]. The ratio of Fe^{3+} and Fe^{2+} can be represented by the ratio of the peak areas of the two peaks, i.e., A_1/A_2, which can indirectly explain the content of Fe_3O_4 nanoparticles in the rubbing surface. The area ratio lubricated with NF-1 is 1.88, which is obviously higher than that of base oils (1.30). The result shows that the proportion of Fe_3O_4 nanoparticles on the worn surface of NF-1 is obviously increased. The SEM, EDS and XPS results show that Fe_3O_4 nanoparticles may be deposited on the contact surface during the friction process to form a deposition film, and the surface can be repaired and filled so that the lubricants containing Fe_3O_4 nanoparticles have better lubricating performance.

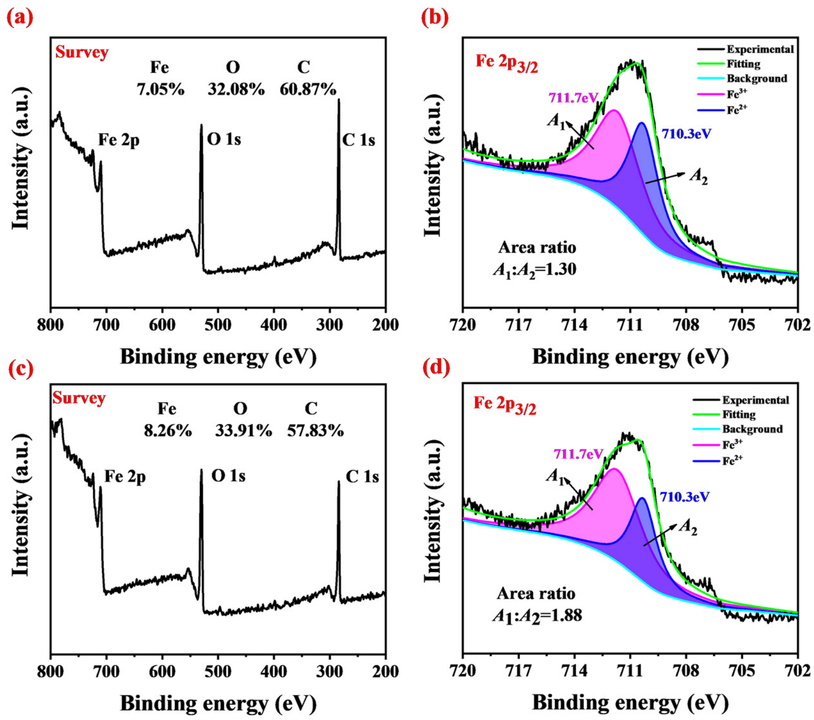

Figure 11. XPS analysis of the frictional surface lubricated by the base oils (**a**,**b**) and NF-5 (**c**,**d**).

Nanoparticles have a certain amount of research as lubricating additives. Various lubricating mechanisms have been put forward, including "micro-bearing" effects, film-forming mechanisms, repair effects and polishing effects [34–36]. As a lubricant additive, nano-Fe_3O_4 particles have great potential in regulating lubricant properties. Compared with other nanoparticles, the unique paramagnetism may make it more widely used to improve the friction-reducing and wear-resisting properties of lubricants. Compared with base oils, adding nano-Fe_3O_4 particles can improve the tribological properties of lubricants, and NF-5 has the best anti-friction and anti-wear properties among the lubricants containing Fe_3O_4 nanoparticles. This is because oleylamine-modified nano-Fe_3O_4 particles maintain good oil solubility and can be uniformly dispersed in base oils. Nano-Fe_3O_4 particles with spherical morphology have a size of about 7 nm, which makes it easier to enter the wear areas during the friction process, repair the surface of the friction pairs, and fill the pits and grooves caused by wear [13,37]. At the same time, spherical monodisperse Fe_3O_4 nanoparticles entering the relative sliding region act as "microbearings", changing the relative sliding friction into rolling friction [3,13,38]. It should be clear that adding Fe_3O_4 nanoparticles in a small amount or a large amount may adversely affect the tribological properties of the lubricant. For example, NF-1, because of its low content, cannot fully fill the wear interfaces and play a role in repairing. On the contrary, it may act as abrasive debris, causing abrasive wear and aggravating the wear phenomenon. For NF-10, due to the gradual increase in the content, nanoparticles are more likely to agglomerate and gather on the surface of the friction pair [27,39], which will also lead to poor tribological performance, and even with the continuous increase in the content, there may be more serious friction and wear than the base oil. Figure 12 is a schematic diagram of the lubrication mechanism of the lubricants containing Fe_3O_4 nanoparticles.

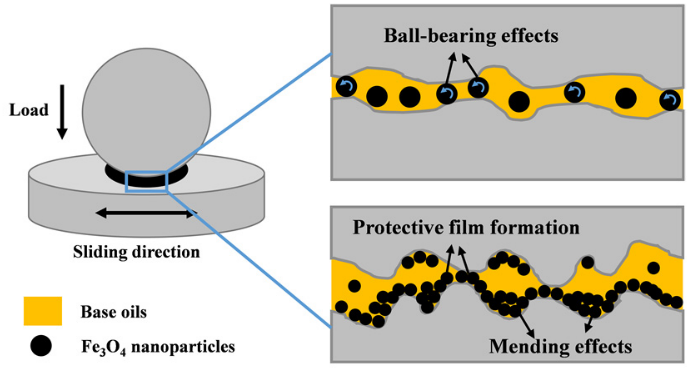

Figure 12. The lubrication mechanisms of lubricants containing Fe_3O_4 nanoparticles.

For the lubricants containing Fe_3O_4 nanoparticles, the good tribological performance and the emergence of the optimal dosage are satisfactory. More interestingly, we found that adding nano-Fe_3O_4 particles may also reduce the viscosity of the lubricants, which is inconsistent with general cognition. However, we also noticed that this has appeared in previous research reports [40]. Based on the fact that the viscosity changes of the lubricants containing Fe_3O_4 nanoparticles are consistent with its tribological properties, especially the viscosity and tribological properties of NF-5 are the smallest and the best, it may provide new ideas for us to study lubricating oil additives. In addition to its various lubrication mechanisms, whether the anti-friction and anti-wear effects of nano-additives in lubricating oil are related to the viscosity changes of the lubricants and whether there is a relationship between them may be our subsequent work.

4. Conclusions

In summary, we synthesized 7 nm spherical monodisperse oil-solubility Fe_3O_4 nanoparticles modified by oleylamine, and the lubricants with different mass concentrations were prepared. The viscosity changes and tribological properties of the lubricants were studied. Consequently, the relationship between viscosity and tribological properties of the lubricants with Fe_3O_4 nanoparticles content was discussed, and the lubrication mechanisms were also investigated. Based on the experimental outcomes, the following conclusions can be drawn.

(1) Nano-Fe_3O_4 was modified by oleylamine, and the lubricants with different mass concentrations were prepared. The results show that the oleylamine-modified Fe_3O_4 nanoparticles have good dispersibility in the lubricating oil even at the additive concentration of up to 20 wt% within 12 months.

(2) With the increase in nano-Fe_3O_4 content, the dynamic viscosity and kinematic viscosity of the lubricants first decrease and then increase. The tensile curve test also shows that the tackiness and adhesion of the lubricants have the same change law. Among them, NF-5 has the smallest viscosity and the lowest tackiness and adhesion.

(3) The obtained Fe_3O_4/mineral oil composite nanolubricants displayed excellent tribological properties. Remarkably, the maximum reduction in the wear volume is up to

93.8% compared with base oils when the additive concentration of Fe_3O_4 nanoparticles is 5 wt%.

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