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# Natural Garlic Oil as a High-Performance, Environmentally Friendly, Extreme Pressure Additive in Lubricating Oils

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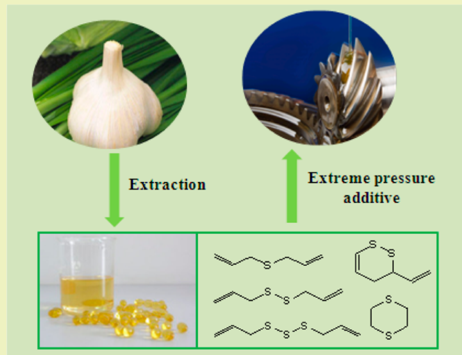
**ABSTRACT:** This paper describes natural garlic oil (NGO) as a high-performance, environmentally friendly, extreme pressure additive for lubricating oils. The chemical composition of NGO was analyzed by gas chromatography−mass spectrometry (GC-MS). The load-carrying capacities of NGO and sulfurized isobutylene (SIB) in different base fluids were comparatively evaluated by a four-ball tester and an optimol SRV-IV oscillating reciprocating friction and wear tester (SRV tester). The four-ball test results revealed that incorporation of 1 wt % NGO into the base fluids could significantly improve the weld point of the base fluids from approximately 126 to 800 kgf or higher. Moreover, the four-ball test and SRV test results demonstrated that NGO could provide superior load-carrying ability in the selected base fluids than the conventional extreme pressure additive SIB. In addition, X-ray photoelectron spectroscopy (XPS) results showed that NGO and SIB experienced a similar tribochemical process with the generation of tribofilms composed with iron oxides, iron sulfates, iron sulfide, etc. NGO showed great promise for use as an effective, eco-friendly, extreme pressure additive for application in environmentally sensitive areas.




**KEYWORDS:** *Natural garlic oil, Extreme pressure additive, Tribological properties, Sulfurized isobutylene, Environmentally friendly*

## INTRODUCTION

Presently, there is an increasing concern about the environmental impact of lubricants entering the environment either by spillage during use or improper disposal of the used oil. Several countries and organizations have enacted legislation to promote the usage of eco-friendly lubricating oils instead of mineral oil-based products, especially in environmentally sensitive areas.[1,2] Therefore, there is a trend toward better ecological and toxicological safe lubricants during the past decades.[3] Vegetable oils,[4] polyalkylene glycols (PAG), and synthetic esters,[5,6] which are characterized by high biodegradability, have been studied as eco-friendly lubricants. Because of the renewable, low cost, environmentally friendly, and nontoxic fluid properties, chemically or genetically modified vegetable oils are currently being considered as one of the most promising materials to formulate biodegradable lubricants.[7−15] However, it is necessary to point out that modern lubricants are formulated from a range of base fluids and chemical additive packages. Therefore, the biodegradable behavior of the lubricant is dependent upon both base fluids and additives. Most additives are chemically active and are more prone to cause water or soil pollution. Although biodegradable base fluids have been widely investigated, very few eco-friendly lubricant additives have been reported.[16−19] Thus, there exists a need to develop environmentally friendly additives that are compatible with environmental regulations.

Extreme pressure (EP) additives are vital ingredients for most industrial lubricant formulations that protect equipment from wear and seizure and enable it to operate smoothly under heavy loads, high temperature, and low speeds.[20] Commercially available additives that are utilized to provide extreme protection include alkyl and aryl disulfides and polysulfides, sulfurized hydrocarbons, fats, oils, fatty carboxylic acids, dithiocarbamates, chlorinated, etc.[21] Unfortunately, these extreme pressure additives are eco-toxic and not compatible with the environment.

Natural garlic oil (NGO), a mixture of a garlic-rich organosulfur compound (OSCs) complex, is extracted from cloves of garlic. Most garlic OCSs are derived from alliin via the action of alliinase and the following rearrangement. Even so, the species and quantity of OSCs in garlic products depend on several factors, such as the method of extraction, temperature, and pH. Steam distillation is widely used to extract and condense the volatile OSCs in garlic; the final oily product is called garlic oil.[22] The predominant OSCs in NGO are diallyl disulfides that are similar to SIB in terms of chemical structures.[23] Therefore, it is reasonable to expect that NGO could provide good load-carrying capacities for lubricants. Unfortunately, NGO has so far not been studied as extreme pressure additives in lubricating oils.

Herein, we report NGO as an environmentally friendly extreme pressure additive in high-performance lubricating oils.

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The load-carrying ability of NGO and sulfurized isobutylene (SIB) in different base fluids was comparatively investigated. The effect of additive concentration on the extreme pressure performance of the two additives was also studied on a four-ball tester and SRV tester. In addition, the load-carrying mechanisms of NGO and SIB are discussed based on the XPS results.

## ■ EXPERIMENTAL SECTION

**Materials.** Several kinds of base fluids distinct in their molecular structure or compositions were chosen as additive carriers to perform the following experiments. PAO10, a synthetic hydrocarbon base fluid with a viscosity of about 10 cSt at 100 °C, was supplied by Exxon Mobil Corporation; 3970 is a kind of synthetic polyol ester base fluid obtained from Croda International PLC. SDM-660, a water-soluble polyalkylene glycol oil, which is commonly applied in the formulation of metal working fluids, was purchased from Nanjing WELL Chemical Corp., Ltd. Refined rapeseed oil produced by Yihai Kerry Investment Co., Ltd. was obtained from a domestic market. The main physical properties of these bases fluids are collected in Table 1. All base fluids were used as supplied without any further purification.

**Table 1. Typical Physical Properties of Base Fluids**

| base fluids | kinematic viscosity (cSt) 40 °C | kinematic viscosity (cSt) 100 °C | VI[a] | flash point (°C) | TAN[b] |
|---|---|---|---|---|---|
| PAO10 | 66 | 10 | 137 | 266 | 0.01 |
| 3970 | 20 | 4.4 | 140 | 250 | 0.05 |
| SDM-660 | 146 | 26 | 210 | 220 | 0.05 |
| rapeseed oil | 37.1 | 8.41 | 213 | 321 | 1.03 |

[a]VI measured according to ASTM method D 2770. [b]Total Acid Value (TAN) measured according to ASTM method D 974, mgKOH/g.

Natural garlic oil was purchased from Xuchang Yuanhua Biotechnology Co., Ltd. Sulfurized isobutylene, a widely used extreme pressure lubricant additive, was purchased from a domestic market and used for tribological comparison in this work. Typical physical properties of NGO are listed in Table 2.

**Table 2. Typical Physical Properties of NGO**

| item | NGO |
|---|---|
| appearance | yellowish oily liquid |
| refractive index | 1.566 |
| specific gravity (20 °C) | 1.081 |
| acid value (mgKOH/g) | 1.6 |
| peroxide value (meq/kg) | 2.03 |

## ■ MEASUREMENTS

**GC-MS Analysis.** NGO constitutes were analyzed and identified with a GC-MS system (Agilent 7890/5975 C-GC/MSD). The chromatography column was an AT OV-1701(30 m × 0.25 mm × 0.25 $\mu$m) with a 280 °C injector temperature. The oven temperature was ramped from 80 to 250 °C at a rate of 10 °C/min and held at 250 °C for 10 min. Mass spectroscopy (MS) in electron impact (EI) mode was used. MS conditions were as follows: mass range, 50−500 amu; and electron multiplier, 200 V relative.

**Four-Ball Tester.** The load-carrying properties of the additive in different base fluids were assessed using MRS-1J four-ball testers. The weld loads of the lubricant were evaluated according to the Chinese national standard test method GB/T 3142−1982. Extreme pressure tests were conducted under the following conditions: speed, 1450 rpm; temperature, ambient; load, variable; and test duration, 10 s. In the extreme pressure test, a series of tests are conducted until welding is observed. New test balls and fresh lubricant are used in each test. The load at which welding occurs is the weld point, and it is a characteristic extreme pressure property of the lubricant. Balls for the four-ball extreme pressure test had the following specifications: chrome-steel alloy made from AISI E 52100 standard steel, 64−66 Rc hardness, 12.7 mm diameter, grade 25 extra polish. Prior to use in the four-ball EP experiments, the test balls were degreased by two consecutive 5 min sonications in hexane solvents in an ultrasonic bath.

**SRV Tester.** SRV tester was also employed to evaluate the extreme pressure properties of the natural garlic oil. The test was performed in a ball-on-disk configuration. The contact between the frictional pairs was achieved by pressuring the upper running ball (10 mm in diameter, AISI 52100 steel, hardness of approximately 59−61 HRC) against the lower stationary disk ($\varphi$ 24 mm × 7.9 mm, AISI 52100 steel) in the reciprocating mode under a normal load of 50−500 N at a frequency of 25 Hz and a sliding amplitude of 1 mm at ambient temperature.

**XPS Analysis.** The chemical state of the typical elements on the wear scars after the SRV test was determined using PHI 2702 multifunctional X-ray photoelectron spectroscope (XPS). A Mg K$\alpha$ X-ray source was used, and the binding energies of the target element were determined at a pass energy of 29.4 eV with a resolution of ±0.3 eV. The binding energy of contaminated carbon (C1s: 284.8 eV) was used as the reference.

## ■ RESULTS AND DISCUSSION

The GC chromatography of the natural garlic oil is shown in Figure 1. Each peak in the figure was labeled, and the corresponding retention time (RT) of each peak is listed in Table 3. It can be found that more than eight peaks appeared in the GC spectra indicating that the chemical composition of NGO is complex. The molecular structures of the sulfur-containing compounds in NGO were further identified by MS spectrum, and the results are given in Table 3. It can be found that organic sulfur compounds such as di-2-propenyl disulfide, 1-propene, 3,3′-thiobis, and diallyl trisulfide are the major components in natural garlic oil.

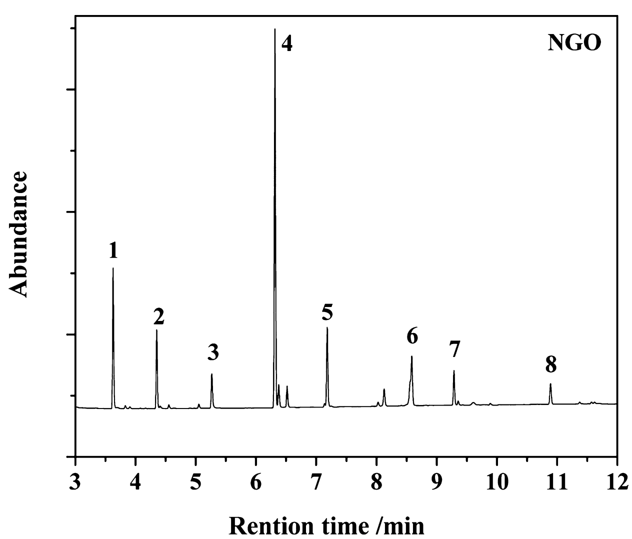
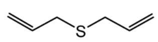
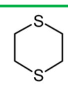
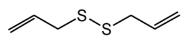
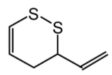
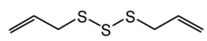



**Figure 1.** GC chromatography of natural garlic oil.

The four-ball tester is one of the most widely used laboratory setups designed for tribo-testing of lubricant. Its specific features are high uniformity of the test specimens (standard balls) and high reproducibility of experimental results. Many of the standard tribological tests of lubricating oils were developed based on the four-ball machine.[24] The weld point of the four-

**Table 3. GC-MS Test Results of Natural Garlic Oil**

| NO. | Retention Time (min) | Chemical Structure |
|---|---|---|
| 1 | 3.636 |  |
| 2 | 4.353 |  |
| 4 | 6.323 |  |
| 6 | 8.557 |  |
| 7 | 9.296 |  |
| 3,5,8 | 5.276, 7.187, 10.89 | Other oxygen and /or nitrogen containing compound |

ball tester is a commonly used parameter used to determination the load-carrying capacities of lubricating fluids. Weld point of the lubricant in the four-ball test can be defined as the lowest applied load in kilograms at which the rotating ball welds to the three stationary balls, indicating that the extreme pressure level of the lubricants force has been exceeded. The weld point can be used to characterize the extreme pressure properties of various lubricants, and in such investigations, a higher weld point means better extreme pressure properties of the lubricant.

Figure 2 compares the weld points for different neat base fluids and the base fluids with 1 wt % NGO or SIB. It is observed that without EP additives, all of the tested base fluids displayed very low weld points of less than 160 kgf, despite differences in terms of their chemical structures. Nevertheless, the mixtures comprised with base fluids and 1 wt % additives (NGO or SIB) exhibited a much higher weld point than their pure base fluid counterparts. The base fluids incorporated with 1 wt % SIB all gave a 315 kgf weld point, which suggests that an identical tribochemical reaction take place in the friction zones during the experiment. Unexpectedly, all of the mixtures comprised with different base fluids and 1 wt % NGO showed an extremely high weld point of 800 kgf, which is much higher than pure base fluids and their mixtures with SIB, demonstrating the outstanding loading carrying capacities of NGO. The outstanding extreme pressure performance of NGO can be explained by the following two reasons. First, the sulfides in NGO generally have lower molecular weight than SIB and thus are more active and readily decompose and react with metal surfaces. Second, the presence of an unsaturated double bond in the molecule makes it more polar and prone to adsorb onto the freshly exposed metal surface to participate in the tribochemical reactions.[20] On the basis of the weld point results, it can be concluded that the load-carrying capacity of NGO is overwhelmingly superior to SIB, which makes it a potential candidate utilized as a high-performance extreme pressure additive in various lubricating oils.

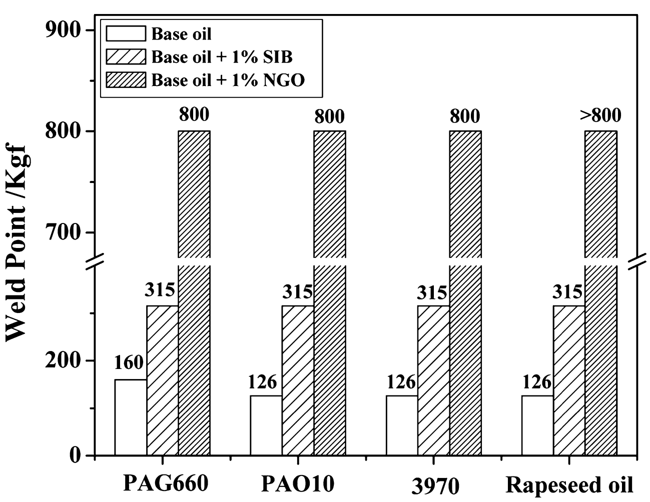



**Figure 2.** Weld points of different lubricant formulations.

Additive concentration is a crucial parameter in the formulation of lubricating oils. It is believed that an appropriate treatment level of the additive could significantly enhance the corresponding performance of the base fluids. We comparatively investigated the influence of additive concentration on the load-carrying capacities of NGO and SIB in rapeseed oil, a environmentally friendly lubricating base fluid, and the results are depicted in Figure 3. The results showed that all combinations have higher weld point values than the base fluid even at the relatively low concentration of 0.25 wt %. As for NGO, increasing the concentration of the additive caused the weld point values to increase, and in particular, the weld point value exceeds 800 kgf when the concentration reaches 1 wt %, implying that NGO is capable of effectively enhancing the load-carrying ability of the rapeseed oil in a wide range of concentrations. However, the mixtures of rapeseed oil and SIB displayed identical weld point values of 315 kgf in the range of 0.5−1.0 wt %, indicating that the load-carrying capacity of SIB in the tested concentration is limited.

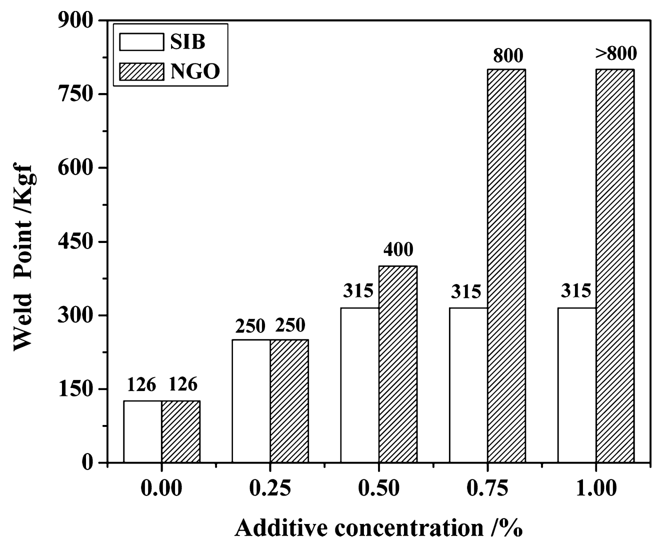



**Figure 3.** Variation of weld point with EP additive concentration in rapeseed oil.

Polyalphaolefin (PAO), which was produced by the polymerization of alpha olefin, is one of the most important and widely consumed synthetic base fluids of high-performance lubricants in various industrial applications. PAO10 with a kinematic viscosity of about 10 $mm^2/s$ at 100 °C was chosen as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the extreme pressure additive carrier. The load-carrying capacity of the mixtures was evaluated with a four-ball machine, and the results are given in Figure 4. It can be observed that the weld point of pure PAO10 is 126 kgf, and the extreme pressure performance of PAO10 showed considerable improvement with the addition of NGO and SIB. At the low additive concentration of 0.25 wt %, NGO and SIB give the same weld point of 250 kgf, while when the concentration is higher than 0.25 wt %, NGO resulted in higher weld points than SIB in PAO10, which is in good agreement with the results obtained in the rapeseed oil. Consequently, in order to formulate certain a lubricant with a specific weld point, much less NGO would be needed in PAO10 than SIB.

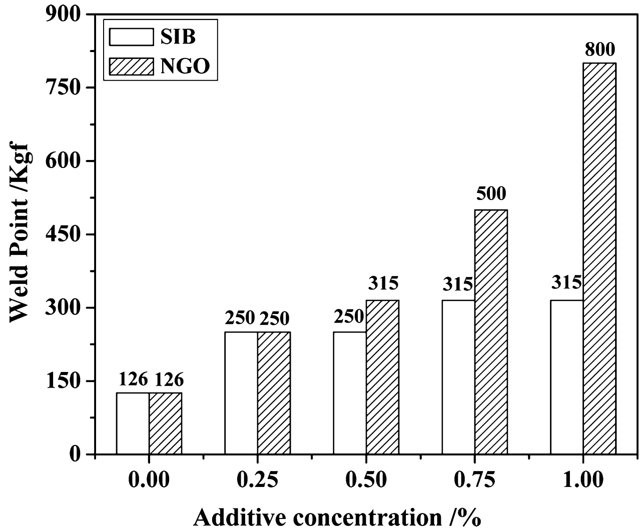


**Figure 4.** Variation of weld point with additive concentration in PAO10.

Four-ball tests have shown that NGO is an excellent extreme pressure additive in both rapeseed oil and PAO10. To gain a comprehensive study of the load-carrying ability of NGO, a SRV tester with a pin-on-block configuration is likewise employed to study the load-carrying ability of NGO. Figure 5 displays the load ramp test for pure PAO10 and PAO10 with 1 wt % NGO and SIB. It is shown that the friction coefficient of neat PAO showed a drastic increase when the applied load increases from 200 to 300 N, implying a seizure occurred between the friction pairs. It is evident that with the addition of SIB and NGO, the seizure loads increased to 400 N. It is worth noting that the friction coefficient of PAO10 with NGO is more stable than SIB. The highest seizure load (600 N) was achieved by rapeseed oil with 1% NGO, demonstrating the good load-carrying capacity of NGO. However, the load-carrying ability of both NGO and SIB on the SRV tester is less effective than in the four-ball testers, which can be explained by the difference in the configuration and the Hertz pressure between the friction pairs. It is recognized that EP additives function by thermal decomposition or hydrolysis and by forming products that react with a metal surface to generate a solid protective layer composed of iron sulfides, which could effectively reduce friction and prevent wear and weld of the friction pairs.[1] It is also acknowledged that sulfurs containing extreme pressure additives generally require a much higher load and temperature than their Cl- and P-containing counterparts to induce the tribochemical reactions in the friction zone; therefore, a higher contact pressure is essential and beneficial for sulfur carriers.[25,26]

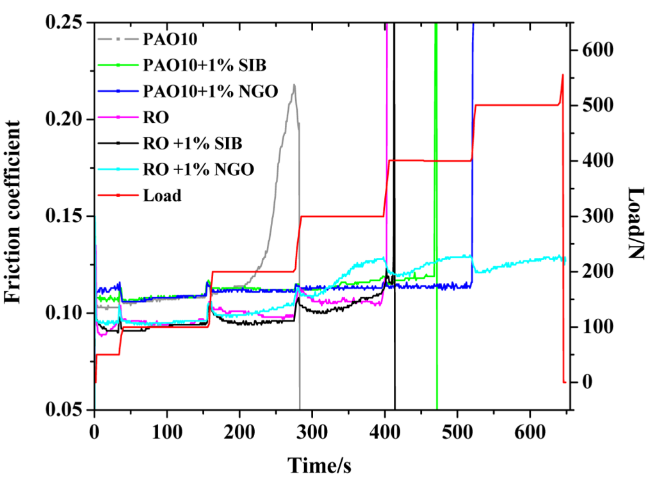


**Figure 5.** Evolution of the friction coefficient with time during a load ramp test for different lubricants at room temperature. RO = rapeseed oil. SRV test conditions: stroke = 1 mm; frequency = 25 Hz; and duration of 120 s.

In order to get further insight into the tribological mechanism of NGO and SIB, XPS was applied to characterize the chemical compositions of the rubbing surface after the test. Figure 6 presents the XPS spectra of the wear surface lubricated by PAO10 + 1 wt % NGO and SIB. It can be observed that the XPS spectra of NGO and SIB are almost identical, implying that similar tribochemical processes took place on the rubbing surfaces. The binding energies were calibrated with reference to C1s at 284.8 eV for adventitious hydrocarbon contamination. As shown in Figure 6, the O1s peak appearing around 532.3 eV is ascribed to $FeSO_4$.[27] The spectra of Fe2p appear at approximately 711 eV, which may correspond to $Fe_2O_3$, $Fe_3O_4$, and $FeSO_4$.[27] The absence of the pure iron peak at 706.8 eV suggests that the steel surface was covered with tribofilm. The XPS peak of S2p can be found at 161.57 and 168.7 eV, which corresponds to FeS and $FeSO_4$,[28] respectively. On the basis of the above analysis, an antiwear mechanism can be postulated that NGO and SIB experienced complex chemisorption and tribochemical reactions and generate a tribofilm with complex compositions containing iron oxides and iron sulfate and iron sulfide on the lubricating surface under the collective impact of high pressure, exelectron emission, and friction of heat, which explains the excellent load-carrying ability of the additives.

## ■ CONCLUSION

In this paper, the composition and tribological performance of NGO was studied. GC-MS analysis results reveal that the composition of natural garlic oil is complex, and the primary component of NGO is di-2-propenyl disulfide. Four-ball test results showed that the weld points of the base fluids were significantly improved with the addition of NGO and SIB. NGO could enhance the load-carrying capacity of different base fluids including PAO, synthetic esters, vegetable oils, and polyalkylene glycols. Additionally, the four-ball test and SRV test results proved that NGO exhibits superior extreme pressure properties than SIB under the same experimental conditions. Despite the distinct tribological performances between NGO and SIB, the XPS results verified that a similar

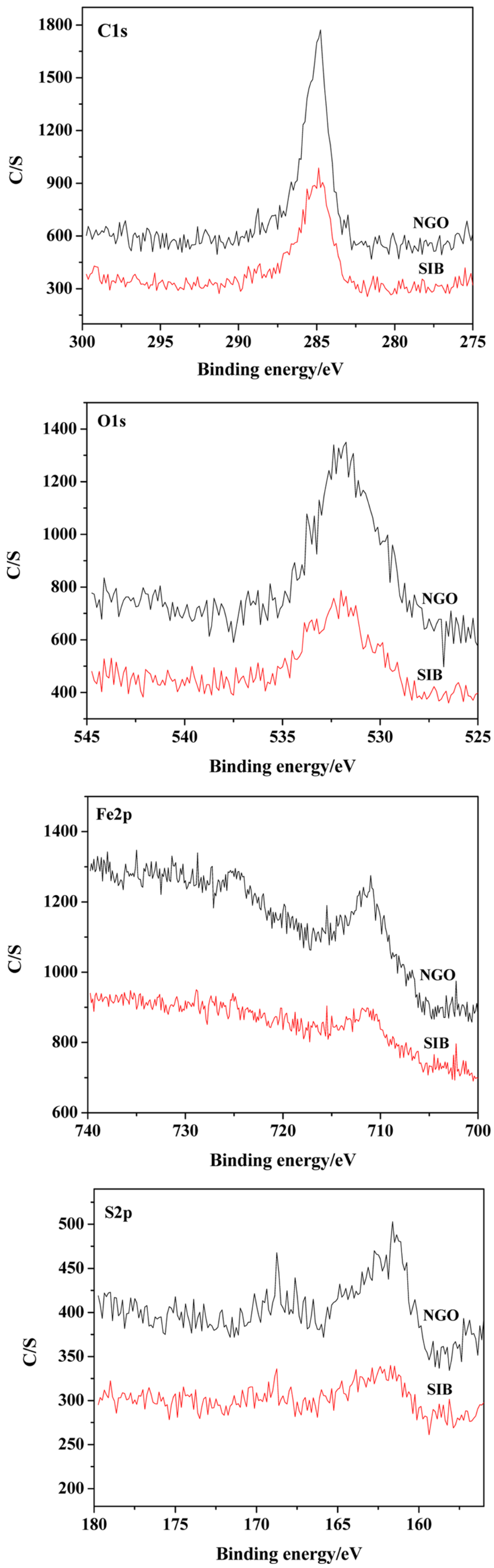


**Figure 6.** XPS spectra of C, O, Fe, and S of the worn surface lubricated by PAO10 with 1 wt % NGO and SIB in a four-ball test.

tribochemical process involves the formation of tribofilms composed of iron oxides and iron sulfates, with iron sulfide formed between the friction pairs. On the basis of the above results, it is reasonable to believe that NGO is a promising alternative to SIB to be used as an environmentally friendly extreme pressure additive in lubricating oils.

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### Notes

The authors declare no competing financial interest.

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