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α-Zirconium phosphate nanoplatelets as lubricant additives

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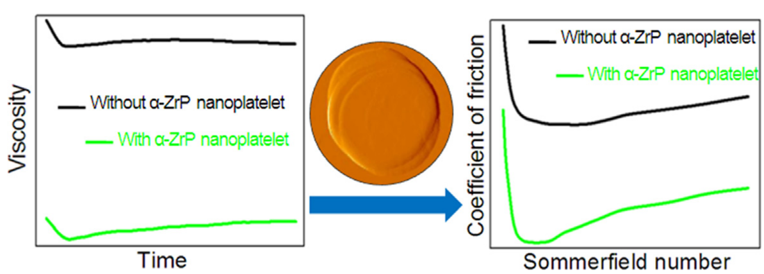
HIGHLIGHTS

- A novel approach to minimize friction.
- 2D nanostructured α-ZrP nanoplatelets additive.
- Viscosity modification & intermolecular interaction.

GRAPHICAL ABSTRACT



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ABSTRACT

Two dimensional (2D) nanostructured α-zirconium phosphate (ZrP) was studied for its effects on lubrication. Tribological characterization revealed that these nanoplatelets were effective as lubricant additives in both non-aqueous and aqueous media. Friction was reduced as much as by 65% and 91%, respectively in mineral oil and water when they were added. Two mechanisms of friction were proposed: viscosity modification and intermolecular interaction. This research has uncovered a novel approach for minimizing energy loss by friction reduction and should benefit many sectors such as manufacturing and consumer automobiles. Additionally, a clear understanding of properties-performance relationship of 2D nanoparticles would enable innovative design of novel materials for a variety of end uses.

1. Introduction

Recently developed nanomaterial additives are promising in improving lubricating performance [1–6]. In particular, the two dimensional (2D) nanomaterials that are van der Waals-bonded have been reported extensively as solid lubricants and film-forming additives for lubricants [7–13]. The existing tribological applications of 2D nanomaterials have been found in graphite and its derivatives, hexagonal boron nitride (h-BN), and transition metal dichalcogenides. The weak van der Waals force between adjacent atomic layers enables them to be exfoliated under a shearing force while in a lubricant [14–18]. As such those nano-additives are effective in boundary and mixed lubrications. However, low surface energy of the basal planes after exfoliation limits their applications in hydrodynamic lubrication. This is due to their poor intermolecular interactions with lubricants. In addition to as-mentioned nanomaterials, there are many alternative materials possessing 2D nanostructured features, e.g. oxides, hydroxides, nitrides, carbides, and phosphates [19–23]. These materials have relatively strong inter-atomic-layer bonding that makes them difficult to be exfoliated. The high surface energy enables the edges and the dangling bonds of the basal planes to be passivated by the environment, i.e. lubricant molecules in this study. This makes it highly desirable to use certain types of 2D nanostructured

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materials as lubricant additives. Montmorillonite-like zirconium phosphates (either α-ZrP or γ-ZrP) is such a 2D nanostructured compounds with high surface energy [24,25]. We explore the feasibility using α-ZrP nanoplatelets as lubricant additives. Here we report a novel application of α-ZrP [$Zr(HPO_4)_2{\cdot}H_2O$] nanoplatelets as viscosity modifier in non-aqueous and aqueous lubricants.

The viscosity of a fluid is used to describe the resistance of relative movement between flow-layers. The viscosity of a lubricant determines its performance in friction reduction. When solid additives are added into a lubricant, fluid drag that acts on a solid surface affects the fluid viscosity and the hydrodynamic pressure. It has been reported that the shape of an additive affects the amount of fluid drag [26,27]. The additives that align in the fluid direction could reduce the fluid drag [28,29]. We hypothesize that the 2D nanostructured materials can align in a fluid. As such viscosity and friction can be used as indication for effective lubrication. In this study, the 2D α-ZrP nanoplatelets are utilized as lubricant (mineral oil and water) additives. The enhancement in the lubrication is found via modification of lubricants' rheological performance. The novel application of 2D nanoplatelets as viscosity modifiers provides a new solution to reduce the friction-induced loss in liquid lubrication. In the presence of 2D nanostructured additives, more fundamental research in nano-fluid and nano-lubrication is highly anticipated on the basis of this current study.

2. Experimental

2.1. Materials

The heavy mineral oil [Sigma-Aldrich (USA)] was used without further purification. The 2D α-ZrP nanoplatelets used in this research were synthesized using a hydrothermal method. Detailed results about their synthesis and characterizations have been reported elsewhere [25]. Briefly, 10 mL of $ZrOCl_2$ aqueous solution (12.5 mmol of $ZrOCl_2{\cdot}8H_2O$) was added drop wise to a 30 mL solution of H_3PO_4 (12 M) into a Teflon®-lined pressure vessel under constant stirring (final $[H_3PO_4]$ = 9 M). Then the pressure vessel was sealed and heated at 200 °C for 24 h. The product was washed several times with deionized (DI) water and dried at 70 °C. The resulting powder was grounded with a mortar and pestle into fine particles. Sample lubricants consisted of a base liquid (mineral oil or DI water) and the additives (α-ZrP nanoplatelets). The additives with different concentrations were simply dispersed in the lubricant via ultrasonication for 15 min before the measurements. Glass slides and E52100 alloy steel ball (ø 6.35 mm) were purchased from VWR International and McMaster-Carr, respectively.

2.2. Characterizations of α-ZrP nanoplatelets

Powder X-ray diffraction (XRD) patterns were collected with a Bruker D8 diffractometer using Cu $K\alpha$ radiation (1.5418 Å) at 40 kV and 40 mA. The measurements were recorded from 5° to 40° (2θ range). An atomic force microscope (AFM, Nano-R2, Pacific Nanotechnology), a transmission electron microscope (TEM, JEOL 2010), and a field emission scanning electron microscope (FESEM, JEOL JSM-7500F), were used to image the 2D nanostructural features of the α-ZrP nanoplatelets. A FT-IR spectrometer (Thermo Scientific Nicolet 380) was used to record the infrared spectra at resolution of 4 cm^{-1} by averaging 250 scans. The α-ZrP powder was measured using the attenuated total reflection (ATR) technique. A small amount of the liquid samples was measured after putting it between two blocks of KBr. Using a He–Ne laser source (532 nm in wavelength), the Raman spectra were recorded by a JobinYvon iHR-550 spectrometer.

2.3. Lubricating and rheological experiments

The coefficients of friction were recorded using a pin-on-disk tribometer (CSM Instruments). The tribological measurements were carried out via a pin-on-disk configuration consisting of a rotating disk (glass slide) and a fixed pin (E52100 steel ball, ø 6.35 mm). 100 μL of liquid (mineral oil or DI water with or without the additives) was added on the disk, and the radius of the wear track was set at 3 mm. The reason to set this parameter is to avoid spill of the liquid during high speed rotating. The rotating speeds were from 10 rpm to 600 rpm under different load, 1 N, 0.5 N, 0.25 N, and 0.15 N. Coefficient of friction at specific speed and loaded was recorded. The duration of each test was 1 min. The information about various lubrication regimes in mineral oil is available in Fig. S1 in Supporting Information. To plot the Stribeck curve, the averaged friction coefficients were obtained from original data and the standard deviation was used to calculate corresponding error (see Fig. S2 in Supporting Information). The viscosity was measured using an AR-G2 rheometer (TA Instruments) with the shear rate ranging from 10 s^{-1} to 18,740 s^{-1}. During experiments, a stainless steel parallel spindle (ø 25 mm) rotated while the lower Peltier plate was stationary. A test liquid filled the gap of 200 μm between parallel plates. The temperature was maintained at 25 °C. The fluid shear was examined under a constant shear rate of 10,000 s^{-1} for 10 min. The change in viscosity was tracked in time.

3. Results and discussion

3.1. Nanoplatelets of the α-ZrP

The morphology of α-ZrP nanoplatelets was characterized using FESEM, TEM, and AFM. As shown in Fig. 1a, the circular α-ZrP nanoplatelets have sizes ranged from ∼600 nm to 1 μm. Those nanoplatelets aggregate together. The TEM image in Fig. 1b shows the 2D morphology and stacked layers (as indicated by arrows) of the α-ZrP nanoplatelets. In Fig. 1c, a representative thickness of ∼30 nm was obtained for the α-ZrP nanoplatelets using the AFM. The high aspect ratio was about ∼20–30 for the 2D α-ZrP nanoplatelets. The XRD pattern (see Fig. S3 in Supporting Information) confirms that crystal structure of the ZrP nanoplatelets is alpha phase. In α-ZrP, zirconium atoms connect to phosphate groups via oxygen atoms and form the layered structures atomically [30,31]. Uniformly distributed hydroxide groups, –POH, point into the space between the two layers and maintain the spacing 7.6 Å wide through hydrogen bonding, electrostatic, and van der Waals interactions. The inter-atomic-layer interaction between two adjacent layers of ZrP is stronger than that those in the 2D nanomaterials with van der Waals bondings, e.g. graphite and its derivatives, h-BN, and transition metal dichalcogenides. To prove this, dry friction experiments were carried out and results are shown in Fig. 2. In comparison to a known solid lubricant, graphite, it is seen that that α-ZrP nanoplatelets do not show reduced friction while the graphite shows otherwise. As noted that, the dry friction measurements were carried out by moving a steel ball on a stainless steel (Grade 316) plate. The α-ZrP cannot be deemed as a solid state lubricant. There is no report in using these nanoplatelets as additives in lubricants.

3.2. α-ZrP nanoplatelets as lubricant additive and viscosity modifier

In order to examine the lubricating ability, Stribeck curves (Fig. 3a and b) were obtained by plotting the coefficient of friction against the Sommerfield number containing the rotational speed and the applied force [32,33]. Details about the