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Effect of TiO₂ nanoparticles on wettability and tribological performance of aqueous suspension



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ABSTRACT

Aqueous suspensions containing different concentration of nano-TiO $_2$ (50 nm) are prepared, in which sodium polyacrylate (PAAS) as the dispersant is used. Their wettability and tribological properties are discussed with Dataphysics OCA50 contact angle measurement device and the MRS-10A four-ball tester, respectively. The rubbed surfaces after friction tests are also analyzed by scanning electron microscope (SEM) equipped with Energy Dispersive Spectrometer (EDS). Wetting results show that the wettability of aqueous suspension is sharply deteriorated with the addition of PAAS, possibly caused by adsorption of PAAS on the substrate alters the characterization of the substrate, which promote the substrate change from homogeneity to heterogeneity, and eventually the wetting state transits from Wenzel to Cassie. And when the nano-TiO $_2$ is further added to the aqueous suspension, the wettability is slightly better, which is mostly due to adsorbed sodium polyacrylate desorb from substrate surface and return to the body phase. In another aspect, four-ball experimental results reveal that the nano-TiO $_2$ as the additive exhibits good anti-wear and friction reduction properties as well as load-carrying capacity. SEM analysis indicates that nano-TiO $_2$ is deposit on the rubbed surface and so prevents direct contact of tribo-pairs.

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1. Introduction

Water is a low cost lubricant with a high cool capacity, but its low viscosity and corrosive property makes it unacceptable for most tribological application. However with the development of nanotechnology, more and more scientists begin to attempt to add certain additives to the aqueous solution, so as to obtain double effects in both lubricating and cooling [1]. One of the most important applications is on the metalworking process, where the water acts a certain role on lubricating, cooling and washing [2].

In the 21st century, some researchers try to add the nanoparticles to the base oil, and satisfied results are gained on the lubricating aspects. Selected nanoparticles vary from metals such as Ag [3], Cu [4–6], Pd [7], Ni [8]; oxides such as CuO [9], Fe₃O₄ [10], ZnO [11], Al₂O₃ [12]; and to rare earth compounds such as LaF₃ [13,14], CeBO₃ [15] CeO [16]. Besides, the researches of nanoparticles in the aqueous solutions were also emphasized. Zhang [17] studied the tribological property of water-soluble copper/silica in the aqueous system and found that a tribofilm composed of FeS, FeSO₄ and SiO₂ was formed and so reduced the friction. Zheng [18] reported that Fe₃O₄/MoS₂ nanocomposites in the aqueous media showed excellent lubricating properties. Cho [19] investigated the hexagonal boron nitride nano-

sheets as a lubricant additive in water and found that repeated exfoliation and deposit of h-BN occurred on the sliding surfaces, forming tribo-films which can reduce friction and wear.

Currently, the dispersion of nanoparticles in lubricating oils is still a challenge for application of nano-additives. The main factor which affects the stability of nano suspension is the tendency of nanoparticles towards aggregation due to the presence of strong vander Waals attractive forces. To overcome this obstacle, a series of solutions are put into practice, the most popular way is the addition of dispersant. Low molecular weight sodium polyacrylate is the most commonly used dispersant [20,21], the dispersing mechanism is shown in Fig. 1. Since sodium polyacrylate contains hydrophobic carbon chain and the hydrophilic carboxyl, the carboxyl is adsorbed on the surface of the nanoparticles, and the carbon chain is free in water and acts as steric stabilized effect.

The nano-TiO₂ possess particularly physical chemical and electrical performance, its tribological behavior as the additive in lubricant oils is studied in several papers [22–24], and all results show that the tribological properties of lubricants are improved by the addition of nano-TiO₂. However, present works have been weighted heavily on the anti-wear and tribological properties of nanofluid, and seldom study the physicochemical properties such as viscosity and wettability. Therefore this paper chooses the nano-TiO₂ as the additive, add to the deionized water, where the sodium polyacrylate is used as the dispersant [25]. Wettability and tribological properties of these asprepared aqueous suspensions are analyzed.

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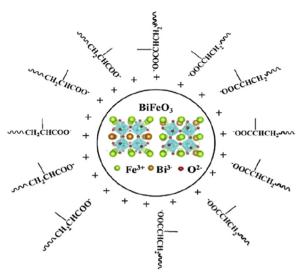


Fig. 1. Sketch of bismuth ferrite dispersed with sodium polyacrylate in aqueous media [20].

2. Experimental methods

2.1. Preparation of aqueous suspension

Nano-TiO₂ particles and sodium polyacrylate of this paper chosen are provided by Sinopharm Group Co. Ltd., China. Detailed parameters of TiO₂ nanoparticles are shown in Table 1. Molecular weight of sodium polyacrylate is 2100. The preparation process of aqueous suspension is as follows: 1 g is added to the 200 mL deionized water, which aims to prevent the aggregation of nano-TiO₂, and then stirs liquid until the hexametaphosphate is fully dissolved. pH value of the aqueous media is adjusted beyond 10, which is to increase the Zeta potential of aqueous media [25], so that better dispersing effect will be obtained. Subsequently, TiO₂ nanoparticles with different concentrations are added. Finally place the mixture in ultrasonic dispersion for 30 min. From this way, aqueous suspensions with various concentration of nano-TiO₂ (0%, 0.25%, 0.5%, 0.75%, 1.0%) that dispersed with 0.5% sodium polyacrylate are prepared. Likewise, aqueous suspensions with various concentration of nano-TiO₂ that dispersed with 1.0% sodium polyacrylate are also prepared by the above mentioned method.

2.2. Wetting tests

The contact angle measuring device is utilized to study the wettability of aqueous suspension, which is based on the sessile drop method. The droplet volume is precisely controlled at $4 \,\mu\text{L}$, it's so small that the influence of gravity can be negligible, So the sessile drop method assumes that the sessile drop is a part of an ideal sphere. As a result, the side view of the drop is an ideal circle. Thus, the contact angle is calculated with the height and the base diameter of the drop. Fig. 2 shows the schematic drawing of drop with an acute contact angle, in which, θ is the contact angle, h and d are the height and base diameter of the drop, respectively. Each

Table 1 Detailed parameters of nano-TiO₂.

_	Name	Crystal form	Size	Purity	Morphology	Specific sur- face Area	Density
	TiO ₂	Anatase	50 nm	99.8%	Spherical	120 m ² /g	0.05 g/cm ³

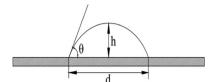


Fig. 2. Sketch of sessile drop method.

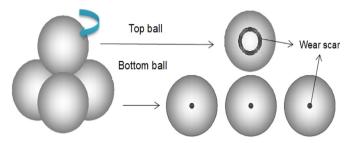


Fig. 3. Sketch of the tribo-paris and wear scar morphology.

example is measured 5 times, and then takes the average value.

2.3. Tribological tests

The tribological performances of as-prepared aqueous suspension are investigated using an MSR-10A four-ball apparatus, four bearing steel balls with a diameter 12.7 mm are made by GCr15 and their hardness is 64-66HRC. As shown in Fig. 3. In this technique, one steel ball under load is rotated against three stationary steel balls, these three stationary balls held in the form of a cradle. all balls are immersed in the lubricant. The P_B value tests are conducted at a rotary speed of 1450 rpm. And the wear tests are conducted at a rotary speed of 1200 rpm for 30 min while the load is 200 N. The wear scar diameter (WSD) on the three lower balls is measured using an optical microscope with an accuracy of 0.01 mm. The morphology of worn steel surfaces was observed with SEM.

3. Results and discussion

3.1. Effects of PAAS and nanoparticles on wettability

Wettability is the potential of a surface to interact with liquids with specified characteristics. The wettability of aqueous suspension directly affects the spreading process on the metal surface. And then affects its tribological properties acts on this metal. So it's imperative to study the wettability of the nano- TiO_2 aqueous suspension on the metal surface. Wettability as a very important physico-chemical property of materials is governed by both chemical composition and geometric structure of the substrate surface. The characteristics of substrate such as homogeneity, roughness and material have significant effects on wettability. So this paper chooses two stainless steels. And their roughness (R_a) are 0.30 μ m (rough metal surface) and 0.05 μ m (smooth metal surface) respectively. This experiment firstly investigates the wettability of aqueous suspension with different concentration of sodium polyacrylate (PAAS) and the results are shown in Fig. 4.

From Fig. 4 it's demonstrated that the contact angle of deionized water is 36.4° (on the rough metal surface) and 37.4° (on the smooth metal surface), when 0.25% sodium polyacrylate is added to the deionized water, the contact angle of this aqueous media raises dramatically, but with the further increase of dispersant concentration, the growth sharply slows down. Meanwhile, Fig. 4

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