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Study of Surface Modification of Al_2O_3 Nanoparticles with KH-560

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The Al_2O_3 nanoparticles were prepared by *in situ*-modified method and modified with KH-560. The particle size analysis confirmed that the mean particle size of modified Al_2O_3 nanoparticles was 90 nm and its distribution was uniform. The dispersion of modified Al_2O_3 nanoparticles was analyzed by the absolute value of Al_2O_3 nanoparticles zeta potential. Through scanning electron micrograph, it was found that KH-560 improved the dispersibility of Al_2O_3 nanoparticles. The hydroxyl groups on the surface of Al_2O_3 nanoparticles can interact with the hydroxyl groups of KH-560 and an organic coating layer was formed. The formed covalent bands were testified by Fourier transform infrared spectra. Because of the introduction of grafted polymers on the surface of nanoparticles, the dispersion stabilization of modified Al_2O_3 nanoparticles in lubricating oil is significantly improved.

Key Words: Additive, Surface modification, Al_2O_3 nanoparticles, Lubricants.

INTRODUCTION

When the viscosity of a lubricant decreases, the frictional force in the hydrodynamic lubrication regime decreases. The decrease of the lubricant viscosity causes a lower extreme pressure of the lubricant, so the friction surface is damaged at high load due to the metal contact, which makes reliability worse[1]. With the development of nanostructured materials, numerous nanoparticles used as lubricating oil additives. Nanomaterials were added into lubricating oil can improve anti-wear and friction-reduction properties of lubricating oil and make the bearing more durable[2-7]. Nanomaterials are better than the traditional solid lubricant additives and become a promising new lubricating material. Ming *et al.*[8], reported that using $CaCO_3$ nanoparticles as PAO base oil additives can dramatically improve the load-carrying capacity, as well as the anti-wear and friction-reduction properties of PAO base oil. In addition, higher applied load, moderate frequency, longer duration time and lower temperatures were beneficial to the deposition of $CaCO_3$ nanoparticles accumulating on rubbing surfaces. Song *et al.*[9], revealed when TiO_2 nanoparticle added into the lubricating oil, the nano-lubricant which was a mixture of nanoparticles and lubricating oil increased the extreme pressure of the lubricant and reduced the friction coefficient.

But nanoparticles have a strong tendency to agglomerate due to its high surface energy and have weak combination with the polymer matrix because of badly consistent interface[10-13]. So the surface modification of nanoparticles is a difficult task. The crux lies in the fact how to well disperse inorganic nanoparticles in lubricating oil and how to improve their interfacial interaction. This has been the critical procedure to prepare high-performance nanocomposites.

In previous work, a series of molecular coupling agent, such as tercopolymer BA-MAA-AN[14], tercopolymer BA-MMAVTES[15] were synthesized to modify nanoparticles, which was applied to prepare nanoparticles composites. Due to the strong interface action, these nanocomposites exhibit unique hybrid properties including good heat-resistance, good wear-resistance and good dynamic mechanical properties.

In this paper, Al_2O_3 nanoparticles were prepared with *in situ*-modified method and surface was modified by KH-560. Such modified Al_2O_3 nanoparticles showed good dispersion stability in lubricating oil. The dispersion of modified Al_2O_3 nanoparticles as well as the mechanism of stable colloidal dispersion was discussed in lubricating oil, whose polar is quite low. The using efficiency of KH-560 as a modifier was also studied.

EXPERIMENTAL

Surface modification of Al_2O_3 nanoparticles: The experimental method involved the following steps: (1) Measured quantity of aluminum isopropanol, isopropyl alcohol and PEG-6000 was dissolved in distilled water (100 mL) at room temperature and then 1.5 wt %of KH-560 was weighed and added into the solution. (2) After ultrasonic irradiation for 10 min, the solution was magnetically stired for 15 min and named A. (3) 1 mL nitric acid was put into solution A to form sol, then the pH value of sol was set at 9 by ammonia dropping. (4) After the Al_2O_3 precursor was washed three times with alcohol, the Al_2O_3 precursor was put into the autoclave and the reaction conditions were set as follows: temperature 220 ºC, pressure 3.6 Mpa, time 2 h. (5) The product was obtained until the reactor cooled to room temperature. Then the modified Al_2O_3 nanoparticles were prepared. (6) The native Al_2O_3 composite nanoparticles were prepared by without KH-560.

Al_2O_3 nanoparticles were analyzed by laser particle size analyzer and zeta-potential analyzer. Through scanning electron micrograph, it was found that the dispensability of Al_2O_3 nanoparticles was improved. The formed covalent bands were testified by Fourier transform infrared spectra. By these instrumental analysis, the nanoparticles size, morphology and modification effect were observed.

RESULTS AND DISCUSSION

Particle size of Al_2O_3 nanoparticles: The Al_2O_3 composite nanoparticles suspension in alcohol was prepared by the ultrasonic vibrating method. On the basis of dynamic light scattering (DLS) principle, the number average diameter and size distribution of Al_2O_3 nanoparticle was analyzed by laser particle size analyzer (Fig. 1). Compared with the native particles, the particle size of Al_2O_3 nanoparticles modified with KH-560 is uniform. Because of the new chemical bond's form between KH-560 and Al_2O_3 nanoparticles, the interaction among nanoparticles is broken down and the agglomeration is controlled effectively. According to the result, the average diameter of native Al_2O_3 nanoparticles was 109 nm while that of modified Al_2O_3 nanoparticles is 90 nm.

Decentralized stability of Al_2O_3 nanoparticles: The reunions between nanoparticles were characterized by zeta potential absolute value. The value is greater; the reunion is slighter. Zeta potential absolute value of nanoparticles were measured six times and then averaged to ensure the data accuracy. The zeta potential absolute value of Al_2O_3 nanoparticles is shown in Table-1. As shown in Table-1, zeta potential absolute value of modified Al_2O_3 nanoparticles is greater than native Al_2O_3 nanoparticles. These indicate that static repellency of modified Al_2O_3 nanoparticles becomes bigger than native Al_2O_3 nanoparticles. The dispersibility of modified Al_2O_3 nanoparticles is better than native Al_2O_3 nanoparticles.

SEM morphology of Al_2O_3 nanoparticles: In order to represent detailed morphological information of the specimens, the SEM images of native Al_2O_3 nanoparticles and modified Al_2O_3 nanoparticles were obtained (Fig. 2). The obvious agglomeration can be seen in the image of native Al_2O_3 nanoparticles (Fig. 2(a)) and the homogeneous dispersion can be seen in the image of modified Al_2O_3 nanoparticles [Fig. 2(b)]. This suggests that chemical bonding or physical bonding occurs between the polarity bonds of KH-560 and hydroxide group. The macromolecular chains grafted on the surface of Al_2O_3 nanoparticles bring mutual exclusion and steric hindrance effect, thus the surface free energy has been reduced correspondingly and the agglomeration is controlled. All the

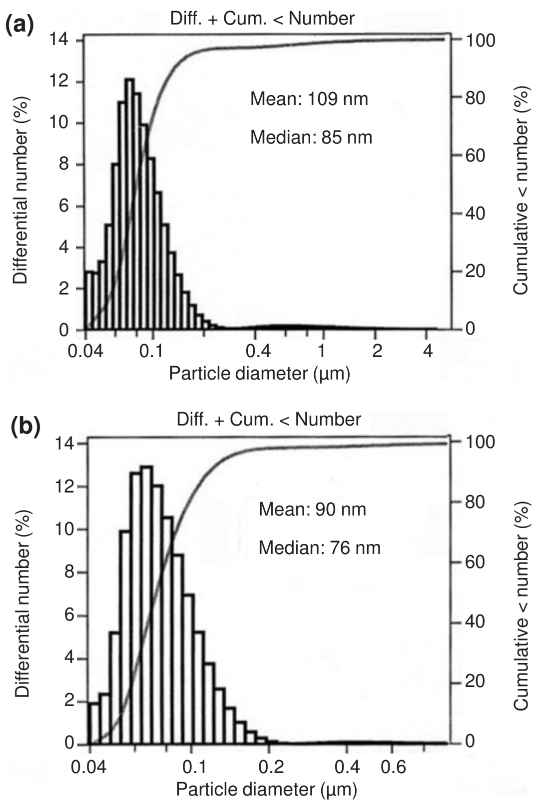

Fig. 1. Image of particle size distribution of Al_2O_3 nanoparticles (a) native Al_2O_3 nanoparticles (b) modified Al_2O_3 nanoparticles

TABLE-1
ZETA POTENTIAL ABSOLUTE VALUE OF Al_2O_3 NANOPARTICLES

Number	1	2	3	4	5	6	Mean
Native nanoparticle	4.9	4.7	5.2	5.1	5.4	5.2	5.1
Modified nanoparticle	8.1	8.4	8.0	8.4	8.2	8.5	8.3

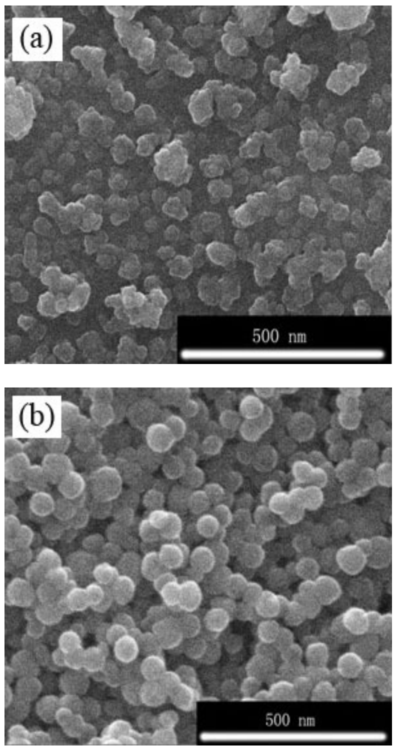

Fig. 2. SEM images of Al_2O_3 nanoparticles. (a) native Al_2O_3 nanoparticles (b) modified Al_2O_3 nanoparticles

results further illustrate that KH-560 had played an important role in the dispersion of Al_2O_3 nanoparticles.

FT-IR analysis: Fig. 3 shows typical FT-IR spectra of KH-560 and modified Al_2O_3 nanoparticles with KH-560, respectively. From the FT-IR spectra of modified Al_2O_3 nanoparticles, the peak at 3093 cm^{-1} is attributed to -C-H stretching mode. Correspondingly, the absorption peaks in the 1072 cm^{-1} correspond to the -CH_2-O-CH_2- of KH-560. And the bands near 759 cm^{-1} correspond to the -Si-O-Al. This is because that the chemical reaction happened between Al-OH groups and KH-560.

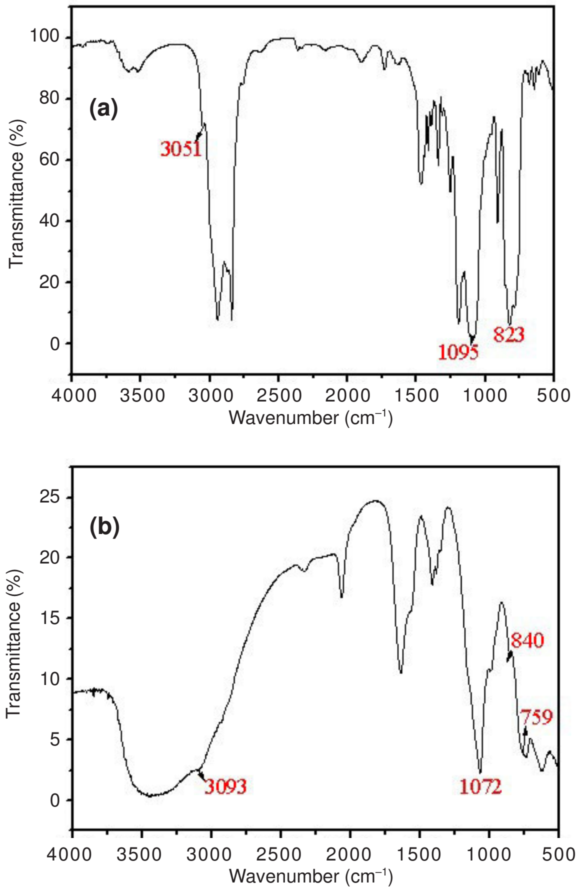

Fig. 3. Infrared spectra of sample (a) KH-560 (b) modified Al_2O_3 nanoparticles

Dispersion stability test in lubricating oil: The dispersion stability of modified Al_2O_3 nanoparticles in lubricating oil was compared with native Al_2O_3 nanoparticles (Fig. 4). The Al_2O_3 nanoparticles were added into the lubricating oil. The absorbency of lubricating oil with nanoparticles was measured by UV spectrophotometer (λ = 190 nm). In lubricating oil, the better dispersibility of nanoparticles was shown by the higher absorbency. After 56 h (Fig. 4), the absorbency of nano-oil with modified Al_2O_3 nanoparticles was stable. But the absorbency of nano-oil with native Al_2O_3 nanoparticles was still becoming little. This indicate that the modified Al_2O_3 nanoparticles can steadily exist in lubricating oil.

The nano-oil was put aside at room temperature with time and the results of sedimentation tests of Al_2O_3 nanoparticles suspended in lubricating oil were carefully watched. For sample native Al_2O_3 nanoparticles, the sedimentation mainly

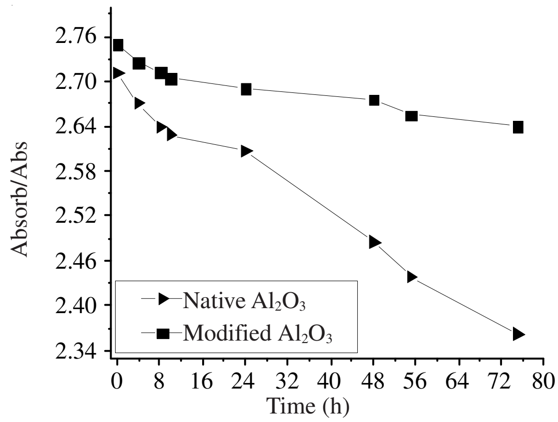

Fig. 4. Absorbency curve of nano-oil with time

occurred by flocculation mechanism. The suspensions separated very quickly into sediments and a clear supernatant on top of the sediment was observed. The separation interfaces between the sediment and the supernatant were sharp and moved downward with time. This sedimentation behaviour was typical of flocculated suspensions. For samples modified Al_2O_3 nanoparticles, solution exhibits the most turbidity. This behaviour is typical of well-dispersed suspensions and smaller particles have much slower settling rates, which might be counter balanced by Brownian which remained in the supernatant for long times. It indicates that KH-560 modification can lead to increase stability of nanoparticles in non-polar organic media.

Conclusion

The preparation and modification of Al_2O_3 nanoparticles were finished at the same time. The modified Al_2O_3 nanoparticles had an average diameter of 90 nm. The results showed that KH-560 had been anchored on the surface of Al_2O_3 nanoparticles. The modified Al_2O_3 nanoparticles presented a more stable colloidal dispersion in lubricating oil than that of native Al_2O_3 nanoparticles

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