Tribology International 121 (2018) 114–120

Contents lists available at ScienceDirect

Tribology International

journal homepage: www.elsevier.com/locate/triboint

Mesoporous silica nanoparticles-loaded methyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl) propanoate as a smart antioxidant of synthetic ester oil

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A R T I C L E I N F O

Keywords:
Mesoporous silica nanoparticles
Antioxidant
Synthetic ester lubricant

A B S T R A C T

Methyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl) propanoate (brand name T512) was loaded by mesoporous silica nanoparticles (MSNs) to afford the antioxidant for synthetic ester lubricant oil. Rotary oxygen bomb tests, pressure differential scanning calorimetry and oven oxidation tests were conducted to investigate the effect of the as-prepared antioxidant on the antioxidant stability of di-iso-octylsebacate (denoted as DIOS). When MSNs are combined with T512 at a properly selected mass ratio, the oxidation of the DIOS base oil is greatly slowed down while the oxidation induction time is significantly prolonged. This may be attributed to the gradual release of T512 from the MSNs and the adsorption of the oxidation products into the channels of MSNs.

1. Introduction

Lubricants, as the significant and indispensable compositions in the modern mechanical systems, play an important role in ensuring the safety and reliability during the service life of mechanical systems [1–3]. In order to restrain the oxidative degradation and prolong the lifetime of lubricants, many researchers have made great efforts to enhance the oxidation stability of lubricants by introducing antioxidants which can be classified into two categories according to structure and antioxidant mechanism: hydroperoxide decomposer and free radical scavenger [4–13]. Traditionally, lubricant additives are added only one time into the base stock before use, where the concentration of the additives decreases with the continuous use of the lubricating oil, due to the consumption of the additive. Therefore, it is necessary to develop a novel strategy towards the highly efficient application of additives, thereby allowing the addition of a high concentration of the additives and providing a substantial performance improvement of the lubricating oil.

In recent years, mesoporous nanoparticles have attracted attention as the excellent candidate carriers for disparate payloads (such as molecular drugs, proteins, and other nanoparticles) [14–20] and as promising components of the adsorbents for metal cations and organic compounds [21]. Their application in lubrication systems is also of significance. Ye et al. [22] reported that mesoporous silica nanoparticles (MSNs) as a reservoir for lubricating oil can reduce the friction coefficient, due to the effective release of liquid paraffin preserved inside the pores of MSNs. Gerardo et al. [23,24] revealed that molecular sieves could also act as the adsorbent for oxidation products. These researches remind us that MSNs could be used as the storage media to load antioxidant in the porous channels, thereby realizing the delayed release of the loaded antioxidant and prolonging the lifetime of the lubricant base oil. Namely, if the delayed release and the consumption of the antioxidant achieve a certain dynamic balance during the friction process, the concentration of the additive in the lubricating oil may maintain constant and existence time of antioxidant may be lengthened compared with adding them only one time. In the meantime, along with the continuous proceeding of the oxidation of lubricant base oil, MSNs could also act as the adsorbent for oxidation products, thereby prolonging the lifetime of lubrication oil. In such a way, novel smart additives for lubricant oils could be designed and developed.

Therefore, we select MSNs with a high surface area as well as good stability and biocompatibility to load methyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl) propanoate (denoted as T512), hoping to develop a smart antioxidant for di-iso-octylsebacate (denoted as DIOS). This article reports the preparation of the MSNs-loaded T512 and the effect of the composite antioxidant on the antioxidative performance of DIOS.

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https://doi.org/10.1016/j.triboint.2018.01.042
Received 6 November 2017; Received in revised form 12 January 2018; Accepted 17 January 2018

2. Materials and methods

2.1. Materials

Hexadecyl-trimethylammonium bromide (denoted as CTAB) as the surfactant and tetraethyl-orthosilicate (denoted as TEOS) as the silica source were purchased from Tianjin Chemical Reagent Company (Tianjin, China). Organic antioxidant additive T512 was purchased from Xinxiang Ruifeng Chemical Company (Xinxiang, China). Synthetic ester base oil DIOS with a chemical purity was provided by Lanzhou Institute of Chemical Physics of Chinese Academy of Sciences (Lanzhou, China). The GCr15 steel balls (diameter 4 mm, Poisson ratio 0.30, hardness HRC 61–64, elastic modulus 208 GPa) were bought from Shanghai Bearing Factory (Shanghai, China). 304 stainless steel disk with a size of $20\,mm \times 20\,mm$ (Poisson ratio 0.285, elastic modulus204 GPa) was provided by Xiamen Tenkey Automation Co., Ltd. All the other commercially obtained reagents are of analytical grade and used as-received.

2.2. Preparation of MSNs-loaded T512

Mesoporous silica nanospheres were synthesized with a soft-template method. Briefly, 30.4 g of CTAB and 5.25 g of triethanolamine were mixed in 2 L of deionized water and magnetically stirred at 80 °C for 1 h, and then 306.7 mL of TEOS was quickly added into the solution under vigorous stirring. The reaction system was kept at 80 °C for 2 h and then cooled to room temperature, followed by filtering and drying (electric oven; 110 °C, 4 h) to afford the MSNs crude product. The residual CTAB in the MSNs crude product was removed by refluxing with the mixture of methanol and HCl for 72 h. Then, T512 were supported in the channel of MSNs.

2.3. Characterizations

2.3.1. Analyses the morphology and microstructure of as-prepared MSNs

Nitrogen adsorption-desorption measurements were conducted with a Quadrasorb SI instrument to determine the specific surface area of MSNs. Before the adsorption measurement, the as-prepared silica powders were degassed under vacuum at 60 °C for 2 h. The pore size distribution of MSNs was analyzed by Barrett-Joyner-Halenda (BJH) method [25]. A Bruker VERTEX 70 spectrometer (BrukerOptics; USA) was performed to record the Fourier transform infrared (FTIR) spectrum of the as-prepared mesoporous silica. A JEOL JEM-2100 transmission electron microscope (TEM; Joel Corporation, Japan) was employed to observe the morphology and microstructure of the as-prepared MSNs.

2.3.2. Evaluation of antioxidant behavior and the tribological properties

The antioxidant behavior of MSNs added in DIOS was evaluated by rotary oxygen bomb test (denoted as ROBT). Briefly, a proper amount of the prepared sample was mixed with 5 mL of water and 55.6 ± 0.3 g of copper catalyst coil. The resultant mixture was then sealed in a rotary bomb and charged with oxygen at a pressure of 620 kPa under room temperature. Finally, the rotary bomb was heated in a dimethylsilane heating bath at a constant temperature of 150 °C. The oxidation stability of the additive is expressed as the time required for achieving a pressure drop of 175 kPa.

Pressure differential scanning calorimetry (denoted as PDSC) experiments were carried out with a NETZSCH DSC 204HP instrument (Bavarian, Germany) under an oxygen flow rate of 100 mL/min and a pressure of 3.5 MPa. Oxidation induction time (OIT) and oxidation onset temperature (OOT) were measured in isothermal and programmed temperature modes, respectively.

Moreover, the oxidation stability of the antioxidant was also estimated by oven oxidation test. Briefly, 100 g of the to-be-tested sample was placed into a 250-mL open glass beaker and heated with an electric oven at 150 °C up to a maximum duration of 240 h. During the heating process, a proper amount of the additive-oil dispersion was collected at a regular interval of 24 h, and its total acid number (TAN) and kinematic viscosity after heating at different durations were measured according to China National Standards GBT 4945–2002 and GB 265–88, respectively.

The tribological properties of sample were analyzed on UMT-2 using the mode of the reciprocating ball-on-disk at ambient temperature. The GCr15 steel ball with diameter of 4 mm was putted in the ball holder, which was used as the upper counterpart. 304 stainless steel disk with the oil containing the sample on the surface was mounted on the reciprocating table, which travel the distance of 5 mm. The tests were measured under the sliding frequency of 2 Hz and the duration of 30 min.

3. Results and discussion

3.1. Analyses the morphology and microstructure of as-prepared MSNs

TEM images of the as-prepared MSNs are shown in Fig. 1. It can be seen that the as-prepared MSNs particles have a uniform spherical shape with an ordered mesoporous microstructure, and their mean diameter is approximately 50 nm. Fig. 2 a shows the FTIR spectrum of the as-synthesized MSNs. The peak at 1100 cm^{-1} is assigned to the asymmetric stretching vibration of Si-O-Si. The symmetric stretching vibration of Si-O-Si appears in the wavenumber range of 792–800 cm^{-1} [26]. The absorption band at 960 cm^{-1} and 460 cm^{-1} are ascribed to silanol group (Si-OH) and tetrahedral silica, respectively. Besides, the broad band at 3442 cm^{-1} is ascribed to the O-H stretching vibration of silanol group [27,28] and the absorbed water [29,30], which can confirm by the peak at 1640 cm^{-1} due to the O-H bending vibration of the adsorbed water [31]. These FTIR data verify that the as-synthesized sample are silica which are reported elsewhere [32,33]. The FTIR spectrum of T512 and

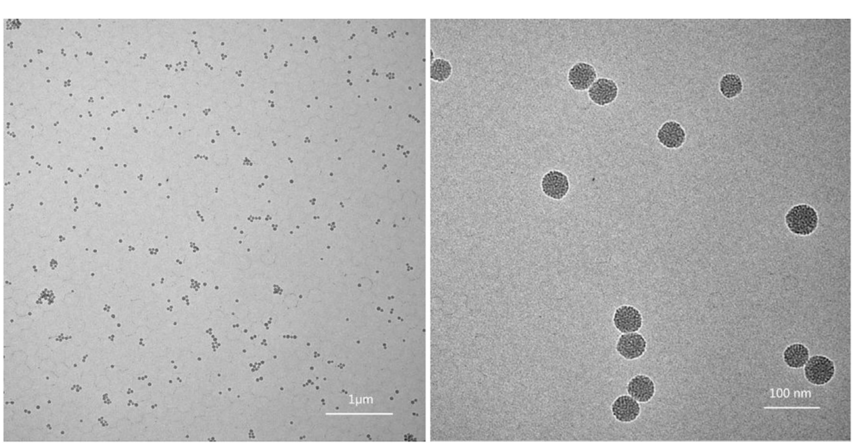

Fig. 1. TEM images of MSNs.