Tribology International 95 (2016) 55–65

Contents lists available at ScienceDirect

Tribology International

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

In situ zwitterionic supramolecular gel lubricants for significantly improved tribological properties

Qiangliang Yu [a,b], Guowei Huang [a,b], Meirong Cai [a,*], Feng Zhou [a,*], Weimin Liu [a,*]

[a] State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China
[b] University of Chinese Academy of Sciences, Beijing 100049, China

ARTICLE INFO

Article history:
Received 15 June 2015
Received in revised form
25 October 2015
Accepted 26 October 2015
Available online 3 November 2015

Keywords:
Gel lubricants
Zwitterionic Gelator
Friction reduction and anti-wear
Boundary film

ABSTRACT

We report a new type of zwitterionic gelator, which cannot only gelate base lubricating oils by supramolecular self-assembly, but be used as additive in oils for significantly improved the tribological performances. The self-assembly mechanism is confirmed by NMR. The as-prepared zwitterionic gels have good thermoreversible and thixotropic characteristics, which make them as potential high performance semi-solid lubricants. The tribological results showed that the gel lubricants possessed excellent friction-reducing and anti-wear properties compared with blank 500SN and Li-base grease with 2 wt% MoS_2. The morphologies of the worn surfaces were analyzed by scanning electron microscope (SEM). The lubrication mechanism is proposed according to *in-situ* electrical contact resistance and the surface composition analysis at the worn surfaces.

1. Introduction

Friction and wear not only consume a large portion of energy, but cause serious damages to mechanical equipment [1–3]. The rational use of lubricant is one of the main technology to reduce friction and wear, to improve the mechanical efficiency, and to ensure long-term reliable mechanical work. The use of traditional lubricating oils are often accompanied by some problems, such as leakage, climb shift and volatilization, which not only result in the increased lubrication failure instances, also cause harm to human health and environment. To solve the problems, semi-solid greases are normally used as alternative lubricants. However, the use of semi-solid greases has also drawbacks, such as oil separation, poor lubrication caused by thickener, etc. Therefore, the development of a new type of intermediate lubricant between oil and grease to address these issues is especially urgent [4].

Gel is a class of soft solids, existing in our everyday life, such as shampoo, hair gel, jelly [5], and other cosmetics and food [6]. They can be obtained by the low-molecular-weight organic gelators (LMWGs) form entangled three-dimensional networks in which liquid is entrapped through weak intermolecular interactions, such as H-bonding, van der Waals force, etc. [7,8]. Nowadays, LMWGs supramolecular gels have attracted increasing interests because they have potential applications in sensor [9,10], catalysis [11,12], template synthesis [13,14], drug delivery [7,15], the gel electrolyte [16,17], and other fields [18]. Simalou et al gelated many organic solvents with fluorescent organic molecules with C3-symmetry structure, and used the organogels in sensors or optoelectronic devices etc [19]. Yang et al reported a new anti-cancer hydrogel formed by disulfide bond reduction and could sustainably release the original curcumin (Cur) through ester bond hydrolysis. This study provides new nano-materials to deliver the anti-cancer drug, curcumin [20]. Using a LMWGs -based gel electrolyte in conjunction with a high-absorptivity ruthenium sensitizer C105, Yu et al have demonstrated its application in solar cell with the advantage of good thermal and light-soaking stability during 1000-hour accelerated aging tests [21].

In the past few decades, LMWGs have gained huge attention not only ascribed to their many potential applications in different research field, but also they can immobilize variety of liquids by the formation of three-dimensional networks. Several researches related to the issues of gel lubricants have been reported. Takahashi et al reported a thermo-reversible gel lubricant (TR gel-lube), which obtained from by assembly of aliphatic-di-amide gelator in poly-a-olefin base fluid. The gel-lubes have low friction coefficient and low wear properties [22]. Recently, our group reports a novel anticorrosive LMWGs, which can supramolecular assemble in imidazolium-based ILs [23]. The prepared ionic gels have good conductivity, anticorrosion ability, and thixotropic character, which make them potential semi-solid electrolytes and high performance lubricant. And we reported a new gel lubricant obtained by supramolecular assembly of a nonionic surfactant gelator to form three dimension network and trap base oils. The gel lubricants not only have thermoreversible and thixotropic

* Corresponding authors. Tel./fax: +86 931 4968466.
E-mail addresses: caimr@licp.cas.cn (M. Cai), zhouf@licp.cas.cn (F. Zhou).

http://dx.doi.org/10.1016/j.triboint.2015.10.032
0301-679X/

characteristics, but also have excellent tribological properties. Thermo-reversible gel lubricants as new and unique lubricants were developed [24]. They were expected to replace common lubricants and used in peculiar machine components because that gels can effectively avoid base oil creeping and evaporating loss and extend the working life. However, in addition to above research works gel lubricant is still relatively small. Therefore, the design a new type of LMWGs is more urgent, which not only gelate the common used lubricating oils, but have excellent friction reduction and anti-wear performance. It is well known that the sulfonates are common used detergent and extreme pressure lubrication additives. Ammonium salts (such as thiophosphate amine, fatty acid amine salts and protic ammonium ILs) have been widely research duo to their excellent tribological properties. So combination of sulfonate anions and protic ammonium salts cation, gelator would have good tribological properties.

In this work we report a new type of low molecular weight zwitterionic gelator having sulfonate anions and protic ammonium cation, which can self-assemble in different base oils through the electrostatic interaction and hydrophobic interaction. The obtained gel lubricants have good thermoreversibility and the rapid creep recovery characteristics, which make them as potential quasi-fluid lubricants.

2. Experiment

2.1. Chemicals

Low molecular weight zwitterionic gelator (ZG) given in the Scheme 1 was synthesized according to a modified literature reported procedure [25,26], and the structure were characterized by proton nuclear magnetic resonance (^{1}H NMR, 400 MHz), carbon nuclear magnetic resonance (^{13}C NMR, 100 MHz) spectroscopy and mass spectrum (micrOTOF-Q II). The following reagents and materials were used as received: polyether (PEG 400), liquid paraffin (LP), and 150BS (Sinopharm chemical reagent Co., Ltd.), polyalphaolefin (PAO 10), 500SN and Esterex adipate ester A51 (Exxon Mobil Company). MACs oil (chemical formula: $C_{65}H_{130}$, exact mass: 911.02, kinematic viscosity (20 °C): 287.77 mm^2/s, density (20 °C): 858.30 kg/m^3) and Li-base grease (dropping point: 299 °C, Penetration (0.1 mm): 270) were synthesized by our laboratory. Other chemicals used in the synthesis were of AR grade.

2.2. Preparation of gel lubricants with ZG.

A known weight ZG was added in base oil in a sample tube, and the mixture was heated 70 °C and stirred until complete dissolution. The mixture was slowly cooled down to room temperature (RT) to form gels.

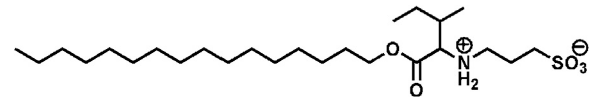
^{1}H NMR of ZG, ($CDCl_3$) δ: 8.88 (s, 3H), 4.25–4.12 (m, 2H), 4.00 (t, J=6.8 Hz, 1H), 2.06–1.89 (m, 2H), 1.84 (s, 1H), 1.68 (d, J=13.7 Hz, 2H), 1.28 (d, J=17.7 Hz, 26H), 0.99 (d, J=6.1 Hz, 6H), 0.88 (t, J=6.8 Hz, 3H).

^{13}C NMR ($CDCl_3$) δ: 168.45, 65.58, 50.70, 38.69, 30.91, 28.69, 28.65, 28.58, 28.51, 28.35, 28.18, 27.34, 24.75, 23.47, 21.67, 21.33, 21.01, 13.09.

HRMS (ESI+) m/z: calcd for $C_{25}H_{51}NO_5S$ [M+Na]+ 500.3380, found 500.3375.

2.3. Thermal analysis

STA 449C Jupiter simultaneous thermogravimetric (TG) and differential scanning calorimetry (DSC) Analysis (TG-DSC) was used to evaluate the thermal properties of all gels, which were heated from RT to approximately 800 °C at a rate of 10 °C min^{-1} in air. The gel-sol transition temperature was determined by DSC thermograms, which were performed on a Mettler Toledo DSC822 series. The gels were measured under a steady flow of liquid nitrogen (25 mL min^{-1}) and the rate of 2 °C min^{-1}.



Scheme 1. Chemical structure of ZG, showing zwitterionic structure (both positive ammonium and negative sulfonate group in a single molecule) with long alkyl chain.

Table 1
Conditions of the SRV test.

	Constant load	Variable temperature	Variable load	Variable frequency
frequency step	–	–	–	5 Hz
Load step	–	–	100 N	–
Temperature step	–	20 °C	–	–
Load (N)	300 N	300 N	100–400	300
Frequency (Hz)	25	25	25	15-40
Temperature (°C)	20	20–120	20	20
Amplitude (mm)	1	1	1	1
Duration (min)	30 or 120	30	45	30

2.4. Freeze-fracture transmission electron microscopy (FF-TEM) and Small angle X-ray scattering (SAXS) of ZG gel analysis

For FF-TEM characterization of specimens, about 4.0 μL of the viscous sample solutions were dropped into the specimen carrier and frozen quickly in liquid ethane at −175 °C. After, the sample was fractured and replicated by Leica EM BAF 060 equipment at −175 °C. For the replication, the Pt/C (45°) film was sprayed for 2 nm and the carbon (90°) film was sprayed for 20 nm. The replica was loaded on a copper grid and observed using a JEOL JEM-1400 electron microscope operating at 120 kV. SAXS measurements were performed on the SAXSess mc^2 X-ray scattering system (Anton paar) operated at 50 KV and 40 mA. The distance of the sample to the detector was 264.5 mm and the X-ray wavelength used in this study was 0.1542 nm (Cu Kα). The exposure time for samples was 900 s.

2.5. Rheological measurements

Rheological properties of gels were investigated by RS6000 Rheometer (Germany) with a cone-plate sensor system (Ti; radius, 17.5 mm; cone angle, 1 °C). Stress sweep: the shear stress and frequency was set as 0.01-500 Pa and 1 Hz, respectively. Frequency sweep: the shear stress and frequency was set as 10 Pa and 0.01–100 Hz, respectively. Step rate measurement of the ZG gel, step rate was a continuous measurement with the range of high shear rate $\gamma=300$ s^{-1} and low shear rate $\gamma=0.05$ s^{-1}.

2.6. Friction test

The tribological tests of all lubricants were performed on an Optimol SRV-IV oscillating reciprocating friction and wear tester. The corresponding friction curves and electrical contact resistance (ECR) were recorded automatically with a computer attached to the SRV test rig. Conditions of the friction and wear tests were shown in Table 1. The experimental details on SRV were consistent with our previously published articles [27,28]. Three repetitive measurements were carried out for each data point. A MicroXAM