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A biocompatible ionic liquid as an antiwear additive for biodegradable lubricants ☆

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ABSTRACT

A biocompatible ionic liquid, tributyl(methyl)phosphonium diphenylphosphate, P_{1444}DPP (IL1) was investigated as an antiwear additive and compared against Amine Phosphate (AP), one of the commonly used conventional antiwear additives in biodegradable lubricants. IL1 showed excellent antiwear performance, using a pin-on-disc tribometer, when blended in biodegradable base stocks. The steel balls after the test were analyzed using SEM–EDS techniques which confirmed the presence of phosphorous. The tribological properties under reciprocating conditions were also carried out using Optimol SRV oscillating friction and wear tester and the steel discs were observed under Atomic Force Microscopy (AFM), to show the buildup of tribofilm formed by IL1. The thickness of the lubricant film was confirmed by Elastohydrodynamic (EHD) Ultra Thin Film Measurement System. It was observed that IL1 has a better film forming ability than AP.

1. Introduction

During the last decade, ionic liquids have become an area of interest for novel tribological studies because of their unique properties and their ability, in some cases, to reduce friction and wear significantly [1]. There is an increasing awareness of these ionic liquids in various engineering disciplines including electrolytes for many electrochemical devices, liquid crystals, plasticizers, dispersants, surfactants, anticorrosion coatings and as a lubricant in various applications [2]. Ionic liquids are salts formed by cations and anions and can be designed to be thermally stable and non-volatile, which makes them ideal candidates as lubricants for new generation equipment, where they can be used to protect the metal surface under severe friction and wear conditions [3–7]. The most common cations used in the field of lubricants are imidazolium [8], ammonium [9], pyridinium [10] and phosphonium [11], while some of the anions used are chlorides, bromides, tetrafluoroborates, hexafluorophoshates, etc. However, most of the studies have been concentrated on two readily available ionic liquids, imidazolium hexafluorophosphate and imidazolium tetrafluoroborate containing different alkyl groups. A number of these ionic liquids have also been categorized as biocompatible or green chemicals [12,13] and further investigation on toxicity features were carried out on pyridinium [14,15], imidazolium [16] and phosphonium [17] based ionic liquids. The term biocompatible ionic liquids refer to the ionic liquids which are non-toxic and do not produce any harmful effects on any biological systems [18].

Lubricant systems in general are required to be low cost and small amounts of functional additives are incorporated into cheaper base stocks. Ionic liquids have thus also been investigated as additives to improve tribological properties. A recent review explained the effectiveness of ionic liquid as an additive rather than as a neat lubricant [19]. It was concluded that even a low concentration of ionic liquid is enough to form a stable antiwear layer on the metal surface without causing extensive corrosion of the surface [20–22]. These ionic liquids were also studied as additives in liquid paraffin and it was concluded that ionic liquids as an additive are capable of extensive improvement in the antiwear ability and load carrying capacity [23]. However, in general, ionic liquid molecules have zero or very limited solubility in base oils and therefore, the majority of the previous research has been on unstable oil–ionic liquid emulsions. So far, little work has been carried out to fully understand the behavior of ionic liquid containing lubricant systems and considerable effort is still required to optimize ionic liquids into the base stock along with the antioxidant and corrosion inhibitor additives. Furthermore, because of the environmental considerations, there is an additional need to find ionic liquid additives that are bio-compatible. Recently a new class of phosphonium based ionic liquids was

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developed [24,25] and studies have been carried out on the tribological properties of these ionic liquids under variable load conditions by Somers et al. [26].

In this paper, tribological studies were conducted using a biocompatible phosphonium based ionic liquid, tributyl(methyl) phosphonium diphenylphosphate, P_{1444}DPP (IL1) for the development of biodegradable lubricants, and the results were compared with the conventional antiwear additive, Amine Phosphate (AP) by incorporating the ionic liquid in different biodegradable base stocks at very low concentrations. In general, such base stocks (plant oil and synthetic esters) are being used for preparing biodegradable industrial lubricants [27]. The results were also compared with another ionic liquid, trihexyl(tetradecyl)phosphonium diphenylphosphate, P_{66614}DPP (IL2), which has better performance as lubricant compared to IL1, but is less biocompatible. The oxidation stability of IL1 was also studied by Pressure Differential Scanning Calorimeter (PDSC) after incorporating optimized dosage of antioxidant additives in the base stock. After screening the tribological properties of ionic liquid in base stocks, the tribological properties under reciprocating conditions were also investigated using Optimol SRV oscillating friction and wear tester.

2. Experimental

The chemical structure of ionic liquids and Amine Phosphate (AP) investigated in this study are shown in Fig. 1. The synthesis and characterization of ionic liquids P_{1444}DPP (IL1) and P_{66614}DPP (IL2) are detailed elsewhere [24] and biocompatibility nature of these ionic liquids have been demonstrated by Zhang et al. [18].

For the current experimental study, two different classes of biodegradable base stocks were selected. The vegetable oil i.e. safflower oil (SO) with an Iodine value of 184 g I_2 per 100 g of oil and fatty acid contribution: 7% palmitic acid, 1.9% stearic acid, 13.2% oleic acid, 77.9% linoleic acid was purchased from local Indian market. The fatty acid distribution was analyzed by first hydrolyzing the oil and then transesterifying it with BF_3–methanol as per ASTM D 2800.

Two different types of neat Synthetic Esters (SEs) were selected for the study: one system comprised of a complex ester i.e. Polyol Ester (PE) which is based on the mixture of Trimethylolpropane (TMP) and pentaerythritol ester and commercially available as Hatcol 5033 (ISO VG 32) while the other synthetic ester is 100% Trimethylolpropane (TMP) ester which is blended with lower and higher viscosity grade base stocks available as Hatcol 2938 and

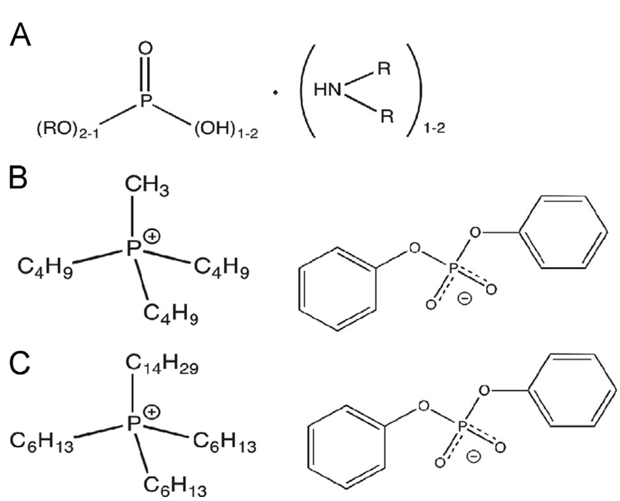

Fig. 1. Chemical structure of (a) Amine Phosphate (AP) (b) P_{1444}DPP (IL1) and (c) P_{66614}DPP (IL2).

Hatcol 3371 respectively to make ISO VG 32 grade base stock. Both the base stocks were sourced from Hatcol Corporation, a Chemtura Company, New Jersey, USA.

The base stocks along with the optimized antioxidant additives i.e. DBPC (dibutyl para cresol) and ODPA (octylated diphenylamine) and conventional antiwear additive AP used in the present study are described in our previous paper [27]. Two of the antioxidant additives were added in 2:1 ratio making a total of 0.6% (w/w) concentration in all the neat oils. For evaluation of the tribological properties, a commonly available antiwear additive AP was studied at 0.25% (w/w) concentration in both the base fluids i.e. vegetable oil and synthetic esters along with optimized antioxidant additives. In case of the ionic liquid containing blends, only AP was replaced by IL1 and IL2 and both the ionic liquids were optimized to 0.005 mol/kg. It was observed that these ionic liquids have 100% solubility in all the three biodegradable base stocks.

The tribological tests were conducted on a Nanovea pin-on-disc tester at ambient temperature according to ASTM G 99. Experiments were carried out at 40 N loads at contact pressure of 2.27 GPa and a speed of 0.1 m/s with a sliding distance of 1000 m where 100Cr6 steel ball surface (6 mm diameter) in contact with AISI E52100 steel disc (24 mm diameter) were used. 0.1 mL of lubricant was used in each test and results were obtained from the average of three tests. After the completion of the test the steel balls were sonicated in acetone for 1 min and then dried under nitrogen gas stream. The wear scar diameter (WSD) on the steel balls was measured using a Bruker GT-K1 Optical Profiler. The detailed analysis of the worn steel ball surfaces was carried out using Scanning Electron Microscopy (SEM)–Energy Dispersive X-ray Spectrometer (EDS). SEM was performed on Phillips XL 20 microscope attached with an EDS. All the SEM micrographs were obtained under 10 keV with 12 mm working distance and EDS results were analyzed using a Oxford Aztec software. XPS was performed on a Kratos AXIS Ultra DLD (Kratos Analytical Ltd., Manchester, UK), with a monochromated Al Kα X-ray as the exciting source. The XPS data at La Trobe was calibrated to C 1s at 285 eV.

After screening the ionic liquid in base stocks, the tribological properties under reciprocating conditions were carried out on Optimol SRV oscillating friction and wear tester. The upper ball (diameter 10 mm, SAE 52100) slides reciprocally at an amplitude of 1 mm against the stationary steel disc (diameter 24 mm, SAE 52100). All the tests were conducted at a frequency of 50 Hz at 50 °C. A load ramp test was carried out starting from 50 N loads. The test load was increased in 50 N increments until a seizure occurs. The test duration for each load was 5 min. This test method is used to quickly measure extreme pressure properties of the sample at selected temperature. Further to evaluate the WSD and average coefficient-of-friction (COF), the tests were carried out at constant load of 100 N at the frequency of 50 Hz at 50 °C for 1 h at contact pressure of 2.19 GPa. 0.1 mL of lubricant was used in each test and results were obtained from the average of three tests. After the completion of the test the steel discs were sonicated in acetone for 1 min and then dried under nitrogen gas stream. The surface topography of the steel discs was subsequently analyzed using Park Systems XE-70 Atomic Force Microscopy (AFM) in contact mode to observe the formation of tribofilm on the worn steel disc surface.

The thickness of the lubricant film was further confirmed by Elastohydrodynamic (EHD) Ultra Thin Film Measurement System using a ball on disc optical device. An EHD Ultra Thin Film Measurement System (PCS Instruments, UK) was used to measure the EHD film thickness in the Elasto hydrodynamic lubrication (EHL) regime [6]. The EHD system measures the film thickness in the EHL contact formed between a steel ball (diameter 19.05 mm, SAE 52100) and a rotating glass disc (coated with silica spacer layer). The ball is mechanically loaded against the underside of the disc and allowed to rotate freely. The load is controlled