Technical paper

Evaluation of ionic fluids as lubricants in manufacturing

A. Libardi [a], S.R. Schmid [a,*], M. Sen [a], W. Schneider [b]

[a] Department of Aerospace and Mechancial Engineering, University of Notre Dame, Notre Dame, IN 46556, United States
[b] Department of Biomolecular and Chemical Engineering, University of Notre Dame, Notre Dame, IN 46556, United States

ARTICLE INFO

ABSTRACT

Ionic fluids are liquid salts that have been investigated for a number of applications, including catalysis, their use as solvents and electrically conducting fluids. Chemically, they consist of ionically bonded species, and depending on the cation and anion, can be extremely valuable in the chemical processing industry. Another characteristic that makes them useful is a high viscosity and good lubrication properties. This paper examines a number of ionic fluids, and determines their suitability as lubricants. This involves determining rheological properties, including viscosity and high-pressure viscosity, generally using a Barus law. In addition, their traction behavior is measured to evaluate their lubricating properties. Since metalworking fluids (and lubricants in general) are used in non-isothermal situations, the thermal conductivity of these fluids have also been measured.

© 2013 The Society of Manufacturing Engineers. Published by Elsevier Ltd. All rights reserved.

1. Introduction

Ionic liquids, which already have desirable characteristics including high thermal stability, nonvolatility, and low melting point, can be designed to have other characteristics, such as CO_2 solubility, advantageous extreme pressure properties, good electrolytic performance, high or low thermal conductivity, or they can be effective solvents. Their low vapor pressure makes them an attractive base oil for metal rolling because of reduced air emissions [1], and they have been recognized as a useful medium for environmentally safe or "green" chemistry. Many of these characteristics are essential for effective lubrication.

As discussed by Reich, et al. [1], most functional ionic fluids are based on the cation of alkylated methylimidazolium salts, as shown in Fig. 1. These cations can contain a hydrocarbon chain whose length can vary between 2 and 10 carbons. The chain length can vary physical and chemical properties such as melting point [2], viscosity [3], etc. Therefore, it should be recognized from this simple model that ionic fluids can be synthesized to achieve desired properties.

A number of candidate lubricant ionic fluids have been synthesized by collaborators at the University of Notre Dame for this research, and evaluated for their tribological performance. Their suitability as metal working or cutting fluids is the main focus of this paper. Indeed, it has been recognized that ionic fluids are ideal for this purpose [1], but are limited in their applicability because of unfavorable economics. Efforts are ongoing to reduce the cost

of ionic fluids, so this remains a potential future application. The same lubricants considered in this paper are also potential working fluids in CO_2-based refrigeration systems, where the ionic fluid will serve as the lubricant for a scroll compressor and associated components.

Among the ionic liquids considered to date are 1-butyl-3-methylimidazolium-trifluoromethanesulfonate (Bmim), tributyl(dodecyl)phosphonium 1,2,3-triazolide (P44412) and trihexyl(tetradecyl)phosphonium 1,2,3-triazolide (P66614). Many more have been synthesized, but these have the most promising lubrication characteristics. For comparison purposes, experiments were also performed on paraffin, hexadecane, and dodecane.

Ionic liquids were first considered as lubricants in 2001 because of their nonvolatility, thermal stability, nonflammability, and low melting point [4,5]. They have viscosities similar to oil and densities between 1 and $1.6 \, g/cm^3$ [6]. Studies have been conducted measuring film thickness of ionic liquids as lubricants. However, most studies conducted are difficult to compare because researchers use their own nonstandard methods, so there is a need for more standardized testing of ionic liquids as lubricants.

Additionally, the focus in many studies involving ionic liquids has been on chemistry and how to select the best anion to achieve certain characteristics [4]. The focus has also been on what will result in the best protective film on the surfaces in contact since the success of an ionic liquid as a lubricant often depends on this boundary layer. Because ionic liquids have only recently been investigated as lubricants, researchers have focused on developing stable ionic liquids, considering chemical properties and whether hydrophobic or hydrophilic anions should be used. These are valid concerns for boundary lubrication, and important for many manufacturing processes, especially sheet forming and machining applications.

* Corresponding author. Tel.: +1 574 631 9489.
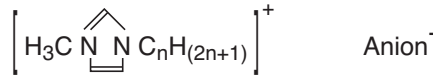E-mail address: schmid.2@nd.edu (S.R. Schmid).

$$\left[H_3C \; N \stackrel{\frown}{\underline{\quad}} N \; C_nH_{(2n+1)} \right]^{+} \qquad Anion^{-}$$

Fig. 1. Molecular structure of an ionic liquid formed from alkylated methylimidazolium salt. In the cation, n can generally range from 2 to 10.

However, for typical operating conditions where thick films can be generated, such as forging or rolling, the pressure-viscosity coefficient will need to be considered in chemical synthesis.

More theoretical than experimental work has been done to determine pressure-viscosity coefficients for ionic liquids, but these theoretical values are typically 2.9–4 times higher than the few published experimental values [7]. In general there is little experimental data regarding ionic liquids as lubricants under high pressure. Due to the variation in ionic liquids and the ability to control their properties, application-specific ionic liquids can be developed. Ionic liquids can be designed to have certain properties under different conditions, including high temperatures and pressures [1]. Based on the wide range of modifiable properties, developing an ionic liquid with high CO_2 solubility, desirable lubricating characteristics, and thermal properties comparable to existing refrigerants is a possibility. Ionic liquids successfully form films between contacting surfaces, making them viable lubricants. In the contact area, ionic liquids can form cationic and anionic supramolecular aggregates [8]. These supramolecular aggregates form when the packing density becomes high, resulting in an increase in viscosity because a larger force is required to move the liquid. In a study by Qu et al. [9], in a ball-on-flat sliding test, it was determined that boundary film formation is dependent on mechanical stresses and thermal effects of the testing. The mean film thicknesses measured were 60 nm, 200 nm, and 300 nm for steel, aluminum, and cast iron, respectively, where film thickness was measured with an SEM.

Experiments have shown that ionic liquids can be used as base oils, additives, and lubricants. Of the few studies, Liu et al. [10] studied benzotriazole-based lubricants to lubricate a variety of engineering materials, including steel/steel, ceramic/ceramic, and steel/aluminum contacts. For these surfaces, the coefficient of friction is lower with ionic liquids compared with synthetic lubricants. Additionally, the load carrying capacity of the ionic liquid, [C_2C_6im]BF_4, was much higher than that of the synthetic lubricants, PFPE and X-1P. While the synthetic oils could only carry 300 and 400 N before failing, the ionic liquid was able to support 600 N with a very low coefficient of friction. Liu et al. did not attempt to measure high-pressure rheology or film thicknesses that can be generated.

2. Lubrication theory and rheology

It is well-known that metal working fluids need to have a well-controlled range of viscosity at the desired temperature. In some applications, such as metal forging or rolling, a fairly inviscid fluid is desired to maintain some limited asperity-asperity contact between the workpiece and tooling to prevent gross surface roughening (orange peel). In other applications, such as sheet metal hydroforming or metal extrusion, the entrainment velocity is too low to result in hydrodynamic lubrication, and better film-generating properties are desired. The nature of the lubricant film is expressed in terms of the film parameter, given by

$$\Lambda = \frac{h_{avg}}{\sqrt{R_{qa}^2 + R_{qb}^2}} \tag{1}$$

where h_{avg} is the average film thickness, and R_{qa} and R_{qb} are the RMS surface roughnesses for the surfaces in contact. In boundary lubrication, the film thickness parameter is between 0 and 1. For mixed lubrication, it is between 1 and 3. In mixed lubrication, the lubricant and asperities each support part of the load, and film thicknesses are typically between 0.01 and 1 μm.

Full film lubrication, also referred to as hydrodynamic lubrication, occurs when the lubricant supports the entire load, with a minimum film thickness typically greater than 1 μm. The film thickness parameter is typically greater than 3. The load is fully supported by the lubricant and asperities rarely come into contact. In this regime, a layer of lubricant is pulled into the contact area where the pressure is sufficiently high to support the load. This is most common with highly viscous fluids or under high operating speeds. In this lubrication regime, asperities do not come into contact, decreasing wear.

In metal rolling, the well-known Wilson-Walowit [11] equation relates the lubricant film thickness to important process parameters according to

$$h = \frac{6\eta\gamma U}{\tan\theta(1 - e^{-\gamma\sigma})} \tag{2}$$

where h is the film thickness, U is the mean velocity, η is the lubricant viscosity, θ is the bite angle, and σ is the material flow strength. γ is used in the Barus law to compensate for the observation that many fluids have a much higher viscosity at elevated pressure than at normal atmospheric pressure. γ is called the pressure-viscosity coefficient, and is used in the Barus equation for lubricant rheology:

$$\eta = \eta_0 \exp(\gamma p) \tag{3}$$

Therefore, the lubrication effectiveness in terms of film thickness generation can be gaged from direct measurement of viscosity and pressure exponent. Viscosity measurement is straightforward, using a Saybolt universal viscosimeter and the approach described in Hamrock et al. [12]. Measurement of pressure-viscosity coefficient is much more difficult; there are approaches such as chambers that will pressurize while a viscosity measurement takes place, or jumping ball approaches. However, it is recognized that there is a potential for shear localization and molecule ordering in rolling or sliding that may not be simulated properly in the pressurized chamber approaches.

This paper uses the elastohydrodynamic lubrication (EHL) theory of Hamrock and Dowson [13] to determine the pressure viscosity coefficient in order to preserve rolling and sliding motion while conducting tests at pressures that are typically seen in manufacturing. Hamrock and Dowson developed film thickness equations suitable for bearing contact for both hard and soft EHL; hard EHL occurs with metal or ceramic contacts and piezoviscous fluids; soft EHL is restricted to soft materials (polymers, rubbers, biological tissue) or fluids that have a viscosity that is insensitive to pressure.

In hard EHL, the Hamrock Dowson equation for minimum film thickness is

$$\frac{h_{\min}}{R_x} = 3.63 U^{0.68} G^{0.49} W^{-0.073} (1 - e^{-0.68k_e}) \tag{4}$$

The dimensionless parameters used are the speed, material, load and ellipticity parameters, given by

$$U = \frac{\eta_0 \bar{u}}{E' R_x} \tag{5}$$

$$G = \gamma E' \tag{6}$$

$$W = \frac{P}{E' R_x^2} \tag{7}$$