Tribology International 69 (2014) 39–45

Contents lists available at ScienceDirect

Tribology International

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

Boundary and elastohydrodynamic lubrication studies of glycerol aqueous solutions as green lubricants

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ARTICLE INFO

Article history:
Received 4 June 2013
Received in revised form
25 August 2013
Accepted 28 August 2013
Available online 4 September 2013

Keywords:
Glycerol
Boundary lubrication
Elastohydrodynamic lubrication
Green lubricants

ABSTRACT

In this paper, the boundary and elastohydrodynamic lubricating behaviour of glycerol and its aqueous solutions are discussed in both rolling and sliding contacts with a view on assessing the use of glycerol as a green lubricant. To understand the lubricating mechanism, the film thickness of glycerol and its aqueous solutions were studied at different velocities. The results show that the viscosity of glycerol can be controlled for a wide range by adding different amounts of water. The lubricating behaviour of glycerol in all lubricating regimes can be improved by adding water. The results suggest that glycerol aqueous solutions have great potential to replace rapeseed oils as environmentally friendly base oils in several applications.

1. Introduction

It is estimated that every year more than 10 million tons of mineral oil-based lubricants and hydraulic fluids leak into the ground or waterways, or are disposed of in the environment [1]. This is problematic from an environmental point of view since mineral-based oils may inhibit the growth of plants, are toxic to aquatic life, and can contaminate groundwater for up to 100 years [2]. One liter of oil released into the environment can cover an area the size of a football pitch and contaminate as much as one million liters of water [3].

There is growing interest in the use of green lubricants. Vegetable oils are potential replacements for mineral oils as base oils to solve the pollution problem [4,5]. However, the low thermal and oxidation stabilities, narrow viscosity range and poor flow properties at low temperatures are major problems for vegetable oils when used as lubricants [6,7]. On the other hand, glycerol aqueous solutions have good biocompatibility, low cost, and better low temperature properties than vegetable oils [8]. Glycerol may thus be a better green lubricant than vegetable oils in some applications.

During the past decades there has been a tremendous increase in the production of bio-diesel as a substitute for the traditional mineral oil-based diesel. Conventional production of bio-diesel, of the fatty acid methyl ester (FAME) type, is a chemical process based on transesterification of triglycerides such as vegetable oils or animal tallow with methanol, which results in glycerol being formed as an inevitable by-product [9]. The bio-diesel production process generates approximately 1 kg of glycerol for every 10 kg of bio-diesel produced [10]. The rapid growing production of bio-diesel has generated an oversupply of glycerol in the market, and novel applications of glycerol are therefore sought for.

Today, the main areas of glycerol usage are the production of food additives, pharmaceuticals, cosmetics, personal care products, and industrial applications [11,12]. Nevertheless, there is still a drive to find new application areas for glycerol to make use of the surplus glycerol produced and thus increases the profitability of bio-diesel production.

Recently, Martin et al. found that glycerol can generate a very low friction coefficient for boundary and elastohydrodynamic lubrication [13–15]. The friction coefficient could hardly be measured when glycerol was used to lubricate the contacts involving two surfaces coated with a hydrogen-free Diamond-Like Carbon coating [16]. X-ray Photoelectron Spectroscopy (XPS), Time of Flight Secondary Ion Mass Spectrometry (ToFSIMS), Karl Fischer titrations, NMR spectroscopy and computer simulations were employed to show that the sp^2-carbon atoms on the uppermost surfaces of the coating react with glycerol and that a tribo-degradation of glycerol occurs. This leads to the formation of water. Martin et al. believe that the water film is easily sheared and that is the reason for the super low friction.

Martin et al. were focusing on the investigation of the friction behaviour of pure glycerol. However, the freezing point of pure glycerol is about 18 °C [8], which means that pure glycerol cannot be used as a lubricant at low temperatures. The viscosity of pure glycerol

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http://dx.doi.org/10.1016/j.triboint.2013.08.013

at room temperature is about 890 Pa s [17], which is about 20 times higher than that of the most of mineral base oil. The high viscosity at low temperatures is unwanted in most applications since too high viscosity means that energy is wasted in shearing the thick lubricant. The excess energy is converted into heat which increases both the local temperature and the bulk lubricant temperature. This accelerates lubricant decomposition reactions and mechanical failure of the surfaces, leading to reduction in the lifetime of the lubricant and equipment. Our tests showed that the viscosity of glycerol can be controlled by blending different amounts of water with a quantity of glycerol. The freezing point of glycerol can thus be lowered to about −50 °C [8]. Interestingly, Martin et al. also reported a simulation of the tribological properties of glycerol using a thermal elastohydrodynamic model, which showed that film thickness and friction coefficient of glycerol decreased with increasing water content in the elastohydrodynamic lubrication regime [15].

Lubrication may be divided into three regimes: (1) full film or elastohydrodynamic lubrication, (2) mixed lubrication and (3) boundary lubrication [18]. The lubricating behaviour of these three lubrication regimes differs greatly. In full film lubrication, there is enough hydrodynamic lift from the lubricant to keep the surfaces separated, thus avoiding metal to metal contact. In this regime, the load is carried by the lubricant, and friction and wear is low. In boundary lubrication there is not enough hydrodynamic lift to keep the surfaces separated: this may for instance occur when the load is high or when the speed of the surfaces is low. The load is consequently carried by the asperities (small summits) on the contact surfaces. These contacts lead to high friction coefficients (typically around 0.1) and high wear rates. In mixed lubrication the load is carried both by the fluid and the asperities. Most lubricants are required to cover all lubrication regimes.

The boundary and elastohydrodynamic lubricating behaviour of pure glycerol and glycerol aqueous solutions were studied to investigate the effect of water on the lubricating properties of glycerol. The film thickness of the glycerol aqueous solutions in the contact region was measured in-situ to study the lubricating mechanism of glycerol aqueous solutions. The performance of glycerol and its aqueous solutions was also benchmarked against a representative for environmentally friendly base oils of today such as rapeseed oil.

2. Experiment

2.1. Material

Glycerol (purity ≥99%) used in this study was reagent grade purchased from Sigma-Aldrich. The glycerol aqueous solutions were prepared by mixing the glycerol with de-ionised water. The water content in glycerol was in the range 5–50 wt%. The commercially available rapeseed oil was supplied by Zeta Fernando di Luca, Sweden, and was used as received.

2.2. Rheology study

The viscosities of glycerol and its aqueous solutions at different shear rate were investigated using a Bohlin CVO 100 rheometer. A concentric cylinder geometry was used with a 25 mm diameter inner cylinder and a 27 mm diameter outer cylinder. During the experiments, the temperature of the lubricant was maintained at 25 °C throughout the measurement. In each measurement, the shear rate was increased logarithmically from 0.1 to 300 s^{-1}.

2.3. Elastohydrodynamic lubrication study

A WAM (model 11) ball-on-disc test rig (Wedeven Associates, Inc., Edgmont, PA, USA) was used for evaluating the elastohydrodynamic lubrication behaviour of glycerol and its aqueous solutions at room temperature (*ca* 25 °C), at a load of 100 N (1.35 GPa maxium Hertzian pressure), a speed of 1 m/s and a Slide-Roll Ratio (SRR) between 0 and 30%. A schematic figure of this tribometer is shown in Fig. 1. At slide-roll ratios larger than zero, the ball rotates faster than the disc. Before each test, the device and specimens were thoroughly cleaned with acetone and ethanol. Thereafter the specimens, the ball and the disc, were assembled, and the entrainment speed was set to 1 m/s. Then relative position of the ball and disc was corrected to pure rolling and the desired slide-roll ratio was set. The disc was constantly lubricated using a recirculation pumping system attached to the test rig. A full description of this equipment can be found in paper [19].

All specimens used in the tests, both balls and discs were made from AISI 52100 bearing steel. The balls are taken directly from the factory and the discs are processed in the same way as bearing raceway material. The balls are grade 20 with a surface roughness (Ra) of 30 nm, 20.637 mm as outer diameter, and a hardness of about 60 HRC. The discs have a surface roughness (Ra) of 90 nm, 101.6 mm as outer diameter, a circumferential grind and are through hardened to about 60 HRC.

2.4. Boundary lubrication study

An Optimol SRV-III oscillating friction and wear tester was used to evaluate friction-reducing and anti-wear properties of the lubricants under boundary lubrication conditions, in accordance with the ASTM D 6425 protocol. During the test, the upper steel

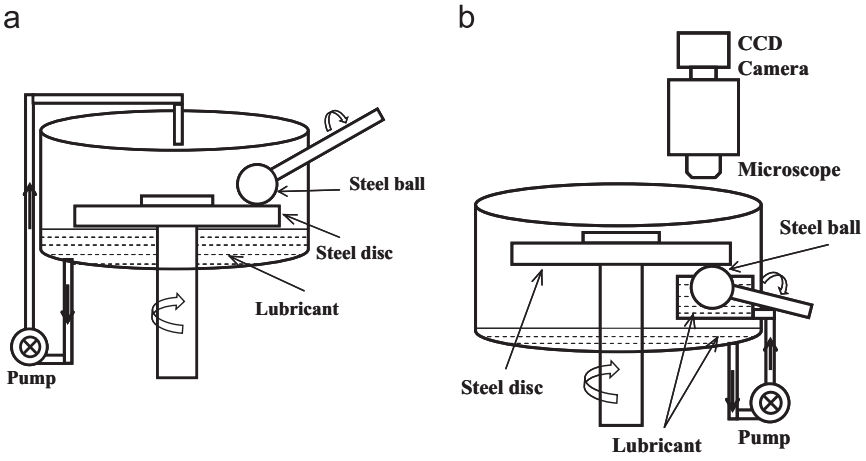

Fig. 1. Diagram of the ball on disc tribometer (WAM) for: (a) friction test; and (b) film thickness test.