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Aqueous lubrication of polymers: Influence of surface modification

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Abstract

We have investigated the influence of surface modification of an elastomer, poly(dimethylsiloxane) (PDMS), on its aqueous lubrication properties. A dramatic reduction in frictional forces has been observed upon hydrophilization by oxygen-plasma treatment or by surface coating with amphiphilic co-polymers, when PDMS was slid against PDMS in an aqueous environment. This effect is attributed to the removal of the strong hydrophobic interaction between PDMS surfaces in water, thereby enabling the isoviscous-elastic lubrication (or soft EHL) mechanism to predominate. This study demonstrates the significance of surface modification in allowing effective soft EHL of an elastomer.

Keywords: Aqueous lubrication; Poly(dimethylsiloxane) (PDMS); Oxygen-plasma-treatment; Hydrophilization; Soft EHL; PLL-*g*-PEG; PEO-*b*-PPO-*b*-PEO

1. Introduction

Many theoretical models have been developed to predict the film-thickness for fluid-film lubrication of non-conformal contacts [1–4]. In these models, the elasticity of the tribopairs and the viscosity of the lubricant are typically considered as the two main parameters that determine the fluid-film lubrication regime, such as isoviscous-rigid, piezoviscous-rigid, isoviscous-elastic, and piezoviscous-elastic lubrication. According to a model proposed by Hamrock and Dowson [1] (later revised by Esfahanian and Hamrock [2]), for instance, a specific fluid-film lubrication regime can be easily identified based upon the elasticity and viscosity parameters of a given tribosystem, and the fluid-film-thickness for a specific condition (such as load, mean speed) can be predicted. In reality, however, the theoretically predicted lubricating films are frequently not observed, and consequently the desired reduction of friction is not achieved. This is mainly because many other parameters than those used to model the fluid-film-thickness, such as the surface roughness of contacting bodies, also influence the interfacial friction forces. It is noted that most film-thickness models assume non-interacting and ideally smooth tribopair surfaces.

Among the aforementioned fluid-film lubrication regimes, isoviscous-elastic lubrication is often known as soft elastohydrodynamic lubrication (soft EHL) and typically occurs for lubricated contact involving an elastomer. In this lubrication regime, deformation of the tribopair plays a significant role in determining film-thickness due to the low elasticity moduli involved, whereas the increase of the lubricant viscosity with increasing pressure is negligible. Since an increase of lubricant viscosity is not a prerequisite for this lubrication mechanism, even liquids with extremely low pressure-coefficients of viscosity, such as water, can be used as lubricants when the tribopair is constructed from elastomeric materials. Some examples for this type of lubrication include human and animal synovial joints, tyres on wet roads, and various machines that are constructed from elastomeric materials [5–11]. While for rigid materials surface roughness is a common cause of premature breakdown of lubricating films, for elastomeric materials, surface interactions (e.g. hydrophobic) between the tribopairs often dominate, hindering the formation of stable lubricating films. For soft EHL of elastomers by water, for instance, the failure of the fluid film is often related to an increase in the adhesive component of friction, since most rubber-like materials tend to display surface hydrophobicity [11,12]. Thus, the control of the surface properties appears to be of prime importance to

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ensure effective aqueous lubrication of rubber-like materials.

In this work, we have employed a silicone elastomer, poly(dimethylsiloxane) (PDMS), to investigate the influence of surface modification on its aqueous lubrication properties. PDMS was chosen for these studies, since it not only possesses a low elasticity modulus, but also can be readily fabricated into (hemi)spherical and plane shapes with a smooth surface finish. Thus, the influence of surface roughness can be ruled out in achieving a lubricating fluid-film, leaving the surface interaction as the dominant factor. We thus demonstrate that surface modification of PDMS, either by oxygen-plasma-treatment or by surface coating with amphiphilic co-polymers, can significantly modify its frictional properties in an aqueous environment, by facilitating the formation of a lubricating film.

2. Materials and methods

2.1. Tribopairs

Poly(dimethylsiloxane) (PDMS) has been employed as an elastomer and was used for both slider (pin) and track (disk). A commercial silicone elastomer kit (SYLGARD® 184 silicone elastomer, base and curing agent, Dow Corning, Midland, MI, USA) was purchased to prepare both PDMS pin and disk. For the preparation of hemispherical pin and flat disk, corresponding molds were fabricated; a commercial polystyrene cell-culture plate with round-shaped wells (96 MicroWell Plate™, NUCLON™ Delta Surface, Roskilde, Denmark) was used as a pin master (radius 3 mm) and a home-machined aluminum plate with flat wells (diameter 30 mm and depth 5 mm) was used as a disk master. The PDMS pin and disk were prepared according to a conventional recipe [12]. Briefly, the base and the curing agent of SYLGARD® 184 silicone elastomer kit were mixed at 10:1 ratio by weight. After removing the foams generated during mixing by a gentle vacuum, the mixture was transferred into the masters and incubated in an oven ($\sim$70 °C) overnight. The water-contact angle for the PDMS prepared according to this method was 110° ($\pm$2°). The elasticity modulus and Poisson ratio of PDMS were ca. 2 and 0.5 MPa, respectively. The surface roughness (Ra) of the PDMS disk surface was 0.5 nm over $10\times10\ \mu m^2$ (for the side exposed to ambient during the curing process) as measured by atomic force microscopy (Dimension 3000, Digital Instruments, Santa Barbara, CA, USA). The surface roughness (Ra) of the PDMS pin was estimated as ca. 2 nm over $10\times10\ \mu m^2$ by measuring the morphology of the polystyrene master by AFM. Polypropylene (PP) and polyamide 6,6 (PA-6,6) have also been employed for tribopairs. Both pin and disk materials were purchased from Maagtechnic (Dübendorf, Switzerland). The PP and PA-6,6 sphere pins (3 mm in radius) were polished by the manufacturer and were used as received. Five millimetre thick disks of both polymers were machined from 30 mm-diameter rods. The surfaces of the disks were also polished with silica paper on a rotating polishing wheel (grade P600 followed by grade P1200). The surface roughness (Ra) of the polymer pins characterized by AFM was 80 ± 10 and 250 ± 20 nm over $10\times10\ \mu m^2$ for PP and PA-6,6, respectively. The surface roughness (Ra) of the polymer disks was characterized as 30 ± 10 nm over $10\times10\ \mu m^2$ by AFM. The surface and mechanical properties of the tribopairs are summarized in Table 1.

2.2. Pin-on-disk tribometry

The frictional properties of the tribopairs during aqueous-lubricated sliding have been characterized by means of conventional pin-on-disk tribometry (CSM, Neuchâtel, Switzerland). In this approach, the load was determined by dead weights (0.5–5 N) and the frictional forces measured by a strain gauge. After forming a contact between loaded pin and disk, the disk was rotated at a controlled speed by a motor, thus generating sliding friction forces. The raw data for the friction forces were recorded as a function of time (or the number of rotations) over a fixed track, using a Macintosh Power PC with a Labview program and an ADC card of the MIO family (both from National Instruments, Austin, TX, USA).

To characterize the lubricating properties of water for a variety of tribopairs, load- and speed-dependent frictional data have been measured. Frictional forces were measured as a function of load at a fixed sliding speed (at 0.005 m/s unless otherwise mentioned), and μ ($\mu = F/w$, where F is friction and w is load) was measured as a function of speed (from 0.00025 to 0.1 m/s) at a fixed load (1 N unless otherwise mentioned). For both types of measurement,

Table 1
Some mechanical and surface properties of the tribopairs employed in this work (viscosity of water, $\eta_0 = 9\times10^{-4}$ Pa s and pressure-coefficient of viscosity of water, $\xi = 3.6\times10^{-10}\ Pa^{-1}$)

	Elasticity modulus (MPa)[a]	Poisson ratio	Surface roughness ($nm/10\times10\ \mu m^2$)		Static water contact angle (°)	
			pin	disk	as is	O_2 plasma
PDMS	2	0.5	2 ± 0.5	0.5 ± 0.2	110 ± 2	<3
PP	1100-1300	0.3	80 ± 10	30 ± 10	107 ± 2	48 ± 2
PA-6,6	2000	0.3	250 ± 20	30 ± 10	82 ± 2	20 ± 2

[a] The elasticity moduli of PP and PA-6,6 are from the manufacturer, and the mid-values were used for the calculation shown in this table.