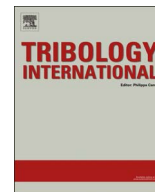




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# Low friction properties of associated carboxylic acids induced by molecular orientation

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## ABSTRACT

Molecular alignment is key to achieving an ultra-low friction coefficient. We prepared associated carboxylic acids using oleic acid and p-pentylbenzoic acid via hydrogen bonding, involving a benzene ring and an eight-membered cyclic carboxylic acid in the molecules. We investigated frictional properties when these were added into a base oil and found that the associated carboxylic acids decreased the traction coefficient in EHL and boundary lubrication, although the viscosity increased. An in situ micro Fourier transform infrared spectroscopy showed that both the eight-membered cyclic carboxylic acid and the benzene ring were oriented parallel to the shearing force, leading to the low friction coefficient.

## 1. Introduction

The tribological properties of lubricant oils are closely related to their molecular structures. For example, polymers that have been adsorbed or grafted to sliding surfaces offer low-friction systems when the friction forces correlate well with the conformations of the surface molecules [1–4]. With grafted so-called polymer brushes, a well-defined sliding plane combined with a stiff, load bearing layer, resulting from the parallel alignment of well-solvated polymers, leads to low friction. The interpenetration state between polymer brush pairs can be switched by simply adjusting the pH of the hydrating solution when one brush is a weak polyelectrolyte [5]. Such an effect may have significant implications in the design and operation of polymer brushes with controllable friction properties.

Based on their ability to form ordered molecular films near substrate surfaces during friction, liquid crystals (LCs) show low friction coefficient when used as lubricants [6–8]. Cyanobiphenyl liquid crystals (CB LCs) (nCB with n=5–12) with a flat structure of the cyanobiphenyl group show low friction coefficient, because of molecular alignment of the rigid structure in the direction of sliding under shearing conditions [9]. Smectic LC confined between surfaces will undergo surface-enhanced translation order, not just orientational rearrangement, which likely has a significant contribution to the lubricant effect [10]. Both external conditions such as shear velocity and internal molecular alkyl length dramatically affect the ordering process of nCB LC nano-lubrication films [11]. When a contact is lubricated by a nematic LC [4-pentyl-4'-cyanobiphenyl (5CB)] and a

carboxylic acid [hexadecanoic acid (HDA)], the boundary films formed by HDA induce surface anchoring that causes 5CB molecules to align perpendicular to the solid surfaces. This effect competes with the flow alignment and causes 5CB molecules to align themselves within the viscous region of the 5CB in the mixed lubrication regime and reduces the friction coefficient [12]. These observations provide evidence for the ordered liquid film model. Therefore, molecular alignment is critical to achieving a low friction coefficient.

Recently, much effort has been put into studying molecular behaviour in thin lubricant films [13–16]. Various molecular vibrational spectroscopy approaches have been reported as useful methods to detect the orientation between two sliding surfaces [17–19]. Polarized Raman spectrometry and infrared p-polarized multiple-angle incidence resolution spectrometry (p-MAIRS) can be used to calculate the orientation of molecules [20–22]. In situ Fourier transform-infrared spectroscopy (FTIR) can also detect the molecular orientation of lubricants [9,12].

In this study, we propose a new perspective to the application of carboxylic acids in lubricants to obtain low friction coefficient. In detail, we prepared associated carboxylic acids using oleic acid and p-pentylbenzoic acid via hydrogen bonding. The associated carboxylic acids feature two rings in their structures, an eight-membered ring and an aromatic ring, respectively. Noting that such associated carboxylic acids possess flat structures similar to the structure of LCs, we posed the question of whether they would show a low friction coefficient? We analysed the molecular orientation of the associated carboxylic acids during friction using an in situ micro FTIR spectroscopy and found that

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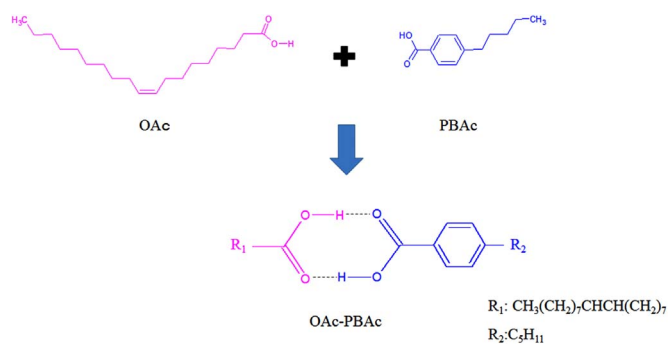
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**Fig. 1.** The preparation and chemical structure of associated carboxylic acids (OAc-PBAc).

the friction coefficient can be markedly decreased by orientation of the associated carboxylic acids.

## 2. Experimental details

### 2.1. Materials and sample preparation

In this paper, oleic acid (OAc) and p-pentylbenzoic acid (PBAc) were used to prepare the associated carboxylic acids. OAc (Wako 1st Grade) and PBAc (purity: 97%) were purchased from Wako Pure Chemical Industries, Ltd., Japan and used as supplied. OAc and PBAc were mixed in a 1:1 in molar ratio. Because both OAc and PBAc are dimers, they must be dissociated to form new bonds. We heated the mixtures for 30 min at 90 °C using a hot plate stirrer to break the hydrogen bonds in the original dimers. OAc and PBAc molecules could then be combined by hydrogen bonding. Such associated carboxylic molecules (OAc-PBAc) were characterized by an eight-membered ring connected with a benzene ring, as illustrated in Fig. 1.

We added the associated carboxylic acids at 50 wt% to a base oil, poly-alpha-olefin (PAO30), to evaluate the frictional properties. The mixed lubricant was named PAO-OAc-PBAc. Moreover, the friction coefficient of PAO and PAO-OAc were also investigated as references. Note that the same concentration of OAc in PAO-OAc was used as that in PAO-OAc-PBAc. We were unable to prepare PAO-PBAc because of the poor dispersibility of PBAc in PAO. The viscosities of the sample lubricants are given in Table 1.

### 2.2. Friction tests in EHL contact

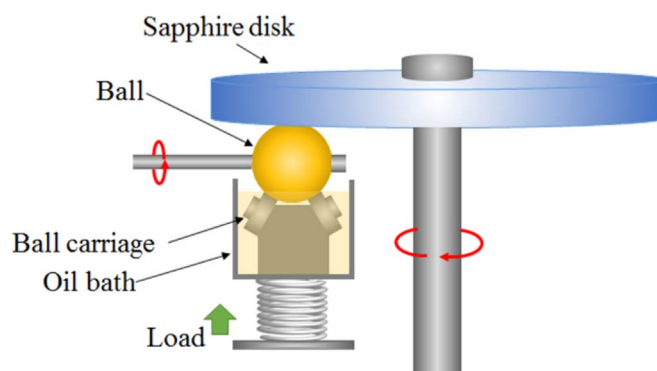
Traction properties were carried out using a custom-built ball-on-disk friction tester, illustrated in Fig. 2. The ball was made from AISI52100 steel, with a diameter of 19.5 mm. The disk was made of sapphire. The experimental conditions comprised a load of 20 N and an entrainment speed of 0.27 m/s. The slide/roll ratio or SRR ( $S$ ), defined using the following equation, was set from 0% to 100%.

$$S = 2(U_d - U_b)/(U_d + U_b) \times 100\%, \quad (1)$$

where  $U_b$  and  $U_d$  are the rotation speeds of the ball and disk, respectively. All tests were carried out at a room temperature of 25 °C. All friction tests were repeated at least three times for each test

**Table 1**  
Viscosity of sample lubricants.

Name (abbreviation)	Viscosity, mPa s (25 °C)	
	Mean	sd
Poly-alpha-olefin (PAO)	44.7	0.1
Oleic acid in poly-alpha-olefin (PAO-OAc)	32.9	0.1
Associated carboxylic acids in PAO (PAO-OAc-PBAc)	171.5	0.1



**Fig. 2.** Schematic of the friction tester used for EHL contact.

condition.

### 2.3. In Situ observation of lubricant films with a micro FTIR spectroscopy in EHL contact

Reflection FTIR spectra of oil films in EHL contact were obtained by in situ observation using a micro FTIR. The ball-on-disk friction tester was mounted to the micro FTIR spectroscopy, as shown in Fig. 3a. Contact was made between the steel ball and the flat surface of a transparent IR disk made of diamond. The entrainment speed was 0.27 m/s and the diamond disk was fixed, giving an SRR of 100%. The applied load was controlled at 1 N to protect the diamond disk from wear.

Fig. 3b shows the observed position where the IR spectra of the oil film were acquired. These spectra were obtained at the inlet, the edge, and the centre of the Hertzian contact region. The aperture size for IR sampling was 50×50 μm. The IR measurements were taken with a JASCO IRT-7100 instrument at a wavenumber resolution of 4 cm<sup>-1</sup>.

### 2.4. Friction tests in boundary lubrication

Friction tests in boundary lubrication were conducted on a ball-on-disk tribometer, as illustrated in Fig. 4. The ball and disk were made from AISI52100 steel. The diameter of the ball was 6.35 mm. The applied load was controlled at 10 N, and the rotating speed was 0.05 m/s. After the friction experiments, the wear scar width was measured using a laser microscope. All friction tests were repeated at least three times for each test condition.

### 2.5. In Situ observation with a micro FTIR in boundary lubrication

Reflection FTIR spectra of the oil film in boundary lubrication were obtained by in situ observation using a micro FTIR spectroscopy. A ball-on-disk reciprocating friction tester was mounted to the micro FTIR spectroscopy, as shown in Fig. 5. Contact was made between the AISI52100 steel ball and the IR transparent silicon disk. Lubricant oil was coated on the silicon disk. The observation position was fixed at the centre of the Hertzian contact region. The diameter of the steel ball was 13 mm. The test conditions were as follows: frequency, 0.25 Hz; stroke length, 8 mm; load, 2 N; IR instrument, Bruker LUMOS; aperture size for IR sampling, 30×30 μm; resolution wavenumber, 4 cm<sup>-1</sup>.

## 3. Experimental results and discussion

### 3.1. Characterization of the associated acids

Fig. 6 shows the FTIR spectra of OAc, PBAc, and the associated acids OAc-PBAc. The band at 1696–1710 cm<sup>-1</sup> was attributed to C=O stretching vibration. The peak position of the C=O stretching band in OAc was 1710 cm<sup>-1</sup>, while that in PBAc was 1696 cm<sup>-1</sup>. The shift in

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