Formulation of lyotropic liquid crystal emulsion based on natural sucrose ester and its tribological behavior as novel lubricant

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Abstract: The tribological behavior of oil-in-water emulsions formulated with natural lyotropic liquid crystal (LLC) emulsifiers based on natural sucrose ester was studied for the first time. Polarized optical microscopy, synchrotron radiation small-angle X-ray scattering, wide-angle X-ray scattering, and synchrotron radiation infrared microspectroscopy demonstrated that LLC emulsifiers were tightly ordered at the oil–water interface with a distinct nematic texture. The viscosity of emulsion was observed to change over time. Moreover, the zeta potential and laser particle size distribution verified the emulsion’s satisfactory stability. The frictional shearing test proved that the coefficient of friction of the emulsion versus pure oil decreased by 34.2%. The coefficient of friction of the emulsion with liquid crystal decreased 10.1% versus that without liquid crystal. Although liquid crystal emulsion did not exhibit outstanding anti-wear performance compared with pure oil, its wear volume was 29.4% less than the emulsion without liquid crystal. X-ray photoelectron spectroscopy and scanning electron microscope–energy dispersive X-ray spectroscopy (SEM–EDS) proved that the tribo-film of the emulsion with liquid crystal was formed synergistically by the liquid crystal phase with the base oil. The formulation affecting the lubricant quality was further studied by orthogonal experiments. The resulting Stribeck curve behavior suggested that proper composition with a slightly higher viscosity can better reduce friction in both boundary lubrication and mixed lubrication regimes. The lubrication mechanism indicated that the periodically ordered liquid crystal was transported to the sliding asperity in the form of emulsion droplets, which bored the pressure and released the oil to form a tribo-film. This LLC emulsion is environmentally friendly and potentially non-irritant to the skin. Thus, it has promising application prospects as novel water-based and biological lubricants.

Keywords: lyotropic liquid crystal (LLC); emulsion; aqueous lubrication; tribological behavior

1 Introduction

What extent the unique rheology of liquid crystals translates into their behavior as lubricants has been explored [1], for energy conservation. It is favored because of its mesophase, which enhances the load-carrying capacity of the crystalloid structure in the vertical direction. Moreover, because of its low viscosity, it timely fills the contact sliding surface in the sliding shear direction, thus reducing the coefficient of friction (COF). The liquid crystal can be classified as thermotropic liquid crystal (TLC) and lyotropic liquid crystal (LLC) according to formation conditions and composition [2]. The lubrication effect of TLC is
affected by temperature, and thus the relationship between the environment and the temperature range of liquid crystal phase must be considered for its practical application [3]. Furthermore, TLC exhibits a typical alkyl cyanobiphenyl feature [4], which is a latent contaminant of the environment. The LLC exists in an ordered chemical system of amphiphilic molecules within polar solvents, such as water. The main forces include the interaction among amphiphilic molecules, the electrostatic force among polar groups, and the van der Waals force among hydrophobic groups [5]. Typically, the behavior of LLC depends on the concentration of surfactants. Above the critical micelle concentration, the lyotropic phase, as a function of the concentration of amphiphilic molecules in water or other solvents, is regularly ordered by amphiphiles in a form similar to a sphere, disk, or rod, depending on the molecular shape [6].

Due to its orientation behavior and low cost, the LLC has broad applications, functioning as a versatile template for the synthesis of nanostructured materials [7–10] or drug delivery system [11]; however, its application to lubrication is limited. In the early 1990s, Friberg et al. [12] systematically studied the lubricating properties of LLC based on the glycerol–triethanolamine–oleic acid system. In 2000, Boschkova et al. [13] reported the lubrication performance of amphiphile cetyltrimethylammonium bromide. The study proved that the water-based system of lamellar liquid crystals provided better lubrication than pure liquid crystals due to the formation of fluid and lubricating friction film on the sliding surface. In the field of tribology, Avilés et al. [14] reviewed the research progress of ionic liquid crystals and found that the number of carbon atoms in the chain exceeding 12 was a necessary condition for mesogen. The study also clarified the synergistic interaction of these materials, emphasizing the advantages of fatty acid derivatives for their application to the lubrication field due to their reproducibility and environmentally protective characteristics. Sulek and Bać-Sowińska [15] prepared 60% aqueous solutions of maracuja oil ethoxylated with 60 mol of ethylene oxide with hexagonal liquid crystal. The COF was significantly reduced by approximately 81%, and the wear scar diameter decreased by approximately 60% with respect to water as base.

However, most of the developed lubricating liquid crystals use mineral oil or synthetic lubricants containing harmful or toxic components, such as polycyclic aromatic hydrocarbons [16], halides, or phosphorus [17]. In-depth research on new green lubricants and bio-lubricants focused on increasing the water content, reducing the ratio of oil phase to additives, or using green degradable mesogen remains necessary. Alkyl polyglycoside, a harmless solvent, was used by Sulek et al. [18] as a lubricant to form liquid crystals in water at a low concentration. The influence of alkyl chain length and polymerization degree was also investigated. All of them were found capable of reducing friction and wear relative to water; however, the influence of the alkyl chain length was not evident. Glycoside liquid crystal emulsifier is also a type of biodegradable surfactant, frequently used as an ingredient in cosmetics, medicines, and daily chemicals. Its aqueous solution has certain anti-friction and anti-wear properties [19].

The LLC is widely used in the cosmetic industry. In this study, we leveraged one of the widely used LLC emulsifiers in skincare (i.e., natural sucrose ester-based emulsifiers) to formulate the LLC emulsion for lubricants. The interfacial behavior and lubrication mechanism of the constructed LLC emulsion during frictional sliding were studied. It was compared with an emulsion without liquid crystals to determine the role of liquid crystal structures. The influence of oil phase ratio, ratio of main emulsifier to co-emulsifier, and total compound emulsifier ratio on the emulsion quality and lubricating effect was systematically investigated. Based on the results, the LLC emulsion formula was optimized, and its Stribeck curve behavior was revealed.

2 Experimental

2.1 Preparation

2.1.1 Materials

The main emulsifier, co-emulsifier, and oil phase were based on sucrose cocoate (SC; Croda, UK) emulsifier, stearyl alcohol (1-octadecanol, Sinopharm Chemical, China), and poly-α-olefin (PAO4, Ineos, Switzerland), respectively.
2.1.2 Formulation of LLC emulsion

A typical aqueous emulsion is composed of 90%–95% water. Its remaining components are oil, emulsifier, and additives (e.g., brighteners, bactericides, and detergents) [20]. The preparation of LLC emulsion with sucrose ester emulsifier was based on the improvement of the method developed by Wang et al. [21] for producing Fischer–Tropsch oil-in-water wax liquid crystal emulsions. The specific processes are as follows. Two beakers were prepared to weigh oil and water phases, separately. The beaker containing the oil phase is filled with the main emulsifier (liquid crystal emulsifier) and co-emulsifier (stearyl alcohol). It is heated up to 85 °C and stirred to obtain the oil phase mixture. This mixture is gradually added to the preheated water-phase mixture and continuously stirred for 0.5 h using a mechanical stirring paddle rotating at 900 r/min. Then, the emulsion is homogenized at 5,000 r/min for 1 min and cooled to room temperature while it is mechanically stirred at 200 r/min for approximately 0.5 h.

The formulation of LLC emulsion was designed such that the compound liquid crystal emulsifier content was 4% (main emulsifier:co-emulsifier = 1:3), and the percentage of PAO4 was 10%. To study the lubricating effect of the liquid crystal phase during sliding, a contrast emulsion was prepared with the same formulation but with the inclusion of broken liquid crystal. It was homogenized for 5 min using an ultrasonic breaker (300 W) that intermittently ran every 3 s for a total of 5 min. The emulsions with and without liquid crystal were coded as A-1 and A-0, respectively.

The formulation of the LLC emulsion was optimized by studying three factors: the ratio of main emulsifier to co-emulsifier, the concentration of compound emulsifiers, and the oil phase concentration. The investigation focused on emulsion quality, stability, and Stribeck curve behavior. The details of an experiment designed to examine these three factors are summarized in Table 1. Orthogonal experiments have also been conducted; the details are listed in Table 2.

### 2.2 Characterization

The phase textures of the liquid crystal emulsions were fully characterized by the polarized optical microscope (POM, XP-330C, Shanghai Caikon Optical Instrument Factory, China). A sample of 10 μL equilibrated between two glass slides with a full wavelength retardation plate was used to investigate birefringence. Synchrotron radiation small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) were performed at Beamline BL19U2 in Shanghai Synchrotron Radiation Facility (SSRF), China. The X-ray wavelength was 0.103 nm, and a Pilatus 1M detector (with a pixel size of 172 μm) gathered data 2,463 mm away from the sample irradiated for 20 s. Synchrotron radiation infrared microspectroscopy (SR micro-IR) was conducted at BL01B beamline in SSRF. An emulsion sample was prepared on a BaF2 substrate. Fourier transform infrared spectra were collected by a Nicolet 6700 spectrometer coupled with a Nicolet Continuum XL microscope. A narrow-band mercury cadmium telluride detector cooled with liquid N2 was used. The transmission mode resolution and aperture dimensions were set to 128 scans/4 cm and 10 μm × 10 μm before mapping, respectively. The zeta potential and droplet size distributions of the emulsion were measured by the dynamic light scatterer (DLS; Malvern Zetasizer Nano ZS90, UK) using the refractive indices of emulsion droplets and aqueous phase (1.52 and 1.33, respectively). All data were average values calculated from three runs. Rheological characterization was performed using a
rotational and oscillatory rheometer (MCR302, Anton Paar, Austria) to derive flow curves expressed as a function of shear rate of 0.01–1,000 s$^{-1}$. In addition, a viscometer (DV2T, Brookfield, USA) was used to investigate the stability of the emulsion regularly for a month with Rotor 91# at 200 r/min for 60 s at room temperature. The tribo-film that formed on the wear track through absorption and tribological reaction during the sliding interaction was scanned by the X-ray photoelectron spectroscopy (XPS; K-alpha, Thermo Scientific, USA). The morphology and element distribution of the scar were examined by the scanning electron microscope (SEM; ZEISS Gemini 300, Germany) and the energy-dispersive X-ray spectroscope (EDS; Oxford Xplore, UK) for line scan.

2.3 Tribological measurements

The interfacial interaction between the developed LLC emulsion and steel surface during sliding was studied by tribological measurements. A universal mechanical tester (UMT; Tribolab, Bruker, USA) with both reciprocating and rotation modes was employed for tribological testing. The UMT’s reciprocating mode was used to study the prominent role of liquid crystal in lubrication with the frictional pairs composed of the upper ball (6 mm in diameter, bearing steel) and stationary plate (20 mm × 20 mm, 304 stainless steel sheet). A three-dimensional (3D) optical surface profiler (Contour GT-K, Bruker, USA) was used to measure the stereoscopic topography and wear volume of the worn surface after the friction test. It was jointly operated with XPS and SEM–EDS to analyze the composition of the interfacial lubrication film. The UMT’s rotation mode was used to obtain the Striebeck curves of various emulsion formulas to examine the influence of composition on emulsion quality and Striebeck curve behavior.

3 Results

3.1 Role of liquid crystal structure in lubrication

3.1.1 Structure of liquid crystal emulsion

Figure 1 shows the SAXS and WAXS profiles of A-1 LLC emulsion, widely used in crystalline investigation and phase transformation [22, 23]. The LLC emulsion exhibits three single peaks at $q = 0.020, 0.037$, and 0.058 nm$^{-1}$, where the scattering vector $q = (4\pi/\lambda)\sin(\theta/2)$, in the SAXS profile with a ratio of approximately 1:2:3, which corresponds well with the (001), (002), and (003) planes, respectively. Further, this indicates that the liquid crystal structure in the LLC emulsion is an exact lamellar phase [24]. The calculated repeat distance (i.e., $d$ spacing) is 314.10 nm, using the equation: $d = 2\pi/q$, where $q = 0.02$ nm$^{-1}$. The peaks in WAXS at $q = 13.02, 14.14, 15.12, \text{and } 20.47$ nm$^{-1}$ also arise from the crystalline phase [25] at a spacing range of 0.31–0.48 nm.

Figure 2 shows the POM and optical images of A-1 and A-0 droplets as well as chemical group distribution in and around the droplet measured by SR micro-IR. Figure 2(a) exhibits the fluorescent liquid crystal texture of A-1 emulsion under polarized light with the exact classic Maltese cross [26], suggesting the presence of a lamellar liquid crystal structure. There is no fluorescent in the A-0 emulsion (Fig. 2(b)), indicating that the liquid crystal structure has been destroyed by a mechanical force as expected. Optical microscopy by SR micro-IR captured the images of A-1 (Fig. 2(c)) and A-0 (Fig. 2(d)). Typically, clear droplets can be observed for the A-1 emulsion with liquid crystal. In contrast, the droplet size of A-0 emulsion is considerably reduced because the high-energy input overcomes the Laplace pressure [27]. SR micro-IR mapping demonstrates the chemical group distribution inside and around one droplet. First, the Fourier
transform infrared spectroscopy spectrum of the SC emulsifier, the micro-IR spectra of A-0 and A-1 emulsions, and the A-1 emulsion droplet surrounding area were analyzed to determine the characteristic chemical group peaks. The results are shown in Fig. 2(e). The strong and broad peaks (i.e., 3,000–3,700 cm$^{-1}$) and sharp and broad peaks (i.e., 1,500–1,600 cm$^{-1}$) are mainly attributed to –OH from the polar groups of emulsifiers and the water phase. The stretching vibrations of CH$_3$ and CH$_2$ (2,916, 2,847, 1,466, and 1,378 cm$^{-1}$) mainly corresponded to the alkyl chain in the emulsifier and the oil phase [28]. To determine the distribution of emulsifiers at the oil–water interface, the peaks of –OH at approximately 3,030 cm$^{-1}$ and CH$_2$ at approximately 2,847 cm$^{-1}$ were selected. Their distributions in and around one droplet are displayed in Fig. 2(f). These are highly consistent with the optical profile shown in the inset of Fig. 2(c) because the LLC emulsifiers are tightly ordered at the oil–water (O/W) interface.

Figure 3 shows the bulk properties of A-1 and A-0 emulsions via zeta potential, kinetic particle size distribution, and rheological curve. The zeta potential was used to quantitate the surface charge of droplets [29]. Figure 3(a) shows that the average zeta potentials of A-0 and A-1 are –23.8 and –44.5 mV, respectively. The absolute zeta potential of A-1 is significantly greater than that of A-0, indicating that the LLC emulsion resists aggregation. It therefore provides better stability than the emulsion without liquid crystals due to the non-excessive energy input. The values of the volume-weighted mean (De Brouckere mean diameter), $D$ [3, 4], of the droplet obtained by DLS were 19.05 μm for A-0 and 23.68 μm for A-1, respectively. Simultaneously, size distribution in Fig. 3(b) shows that the polydispersity is both low before and after breaking liquid crystal phase. The rheological curve in Fig. 3(c) shows that the emulsion system of the SC emulsifier represents a typical shear-thinning effect for pseudoplastic materials because viscosity regularly decreases with the shear rate increase [30]. Figure 3(d) exhibits the regular viscosity pattern of emulsions with time. Based on this pattern, the viscosity of A-0 emulsion is found to be considerably larger than that of the A-1 emulsion. Because ultrasound or high-shear homogenization decreases the size of droplets [31], viscosity increases and the shear-thinning amplitude weakens. This is not conducive to the spread

![Fig. 2](image-url)
of emulsion but conducive to the physical adsorption on the interface. Moreover, the viscosity of both emulsions remains constant after attaining equilibrium for a certain time at room temperature, indicating the satisfactory stability of the developed emulsions.

3.1.2 Lubricating properties of liquid crystal emulsion

Lamellar liquid crystals exhibit excellent lubrication properties due to their bilayer structure and have many applications, such as the combination of drug molecules in joint lubrication and treatment [32] and the combination with ionic liquid for water and biological lubrication [33]. Using pure oil (i.e., PAO4) for comparison, tribological experiments were performed on the formulated liquid crystal emulsion and the corresponding liquid crystal-free emulsion using the reciprocating mode of UMT. Based on the frictional profile and average COF shown in Figs. 4(a) and 4(b), respectively, running-in during the friction test was observed to decrease considerably when emulsions were employed as lubricants compared with solely using PAO4. Moreover, the frictional profile exhibited less fluctuation when emulsions were applied than PAO4 used alone. The average COF is in the order: A-1 < A-0 < PAO4. The A-1 emulsion with the liquid crystal structure reduces the COF by 34.2% compared with that of PAO4, and 10.1% compared with that of the A-0 emulsion without liquid crystal structure. The foregoing suggests the excellent friction-reducing capability of emulsions with the liquid crystal structure.

Figures 4(c) and 4(d) show the anti-wear properties. The wear volume resulting from the use A-1 emulsion with the liquid crystal structure is similar to that of...
pure PAO4; however, the A-0 emulsion without the liquid crystal structure increases the wear. The emulsion with liquid crystal does not show outstanding anti-wear performance compared with pure oil. However, its resulting wear volume is 29.4% less than that of the emulsion without liquid crystal. The 3D wear scar image of the surface lubricated with the A-1 emulsion is more narrow and shallow than that of A-0, as shown in Fig. 4(e). This further suggests that the emulsion with liquid crystal has better anti-wear properties than that without liquid crystal.

3.1.3 Lubrication mechanism of liquid crystal emulsion

To determine the interfacial behavior of emulsion with liquid crystal, tribo-film characterization and lubrication mechanism analysis of the worn surface were conducted by element and chemical group distributions. The XPS fitting peak spectrogram of stainless plates lubricated with the emulsions is shown in Fig. 5. The results of A-0 emulsion without liquid crystal are shown in Figs. 5(a)–5(d). The results of A-1 emulsion with liquid crystal are shown in Figs. 5(e)–5(h). Because the two emulsions are made with the same formula, the XPS data summarized in Table 3 indicates similar types of chemical groups. The fitting peak of C1s is composed of three parts (i.e., 285.0 eV (C–C bond), 286.0 eV (C–O), and 288.0 eV (C=O)), indicating that an adsorption film is produced at the friction interface. The O1s spectrum has three characteristic peaks at 529.8 eV (FeO, Fe2O3, Fe3O4, FeOOH, and other iron oxides), 531.0 eV (C=O and O–H), and 532.0 eV (C–O, C–O–C, etc.) [34]. All these peaks confirm that frictional reaction occurred on the rough sliding surfaces, further explaining the formation of the tribo-chemical reaction film. Based on the two main peaks and two accompanying peaks of Fe2p, Fe3p3/2, and Fe3p1/2 fitting peaks (Figs. 5(d) and 5(h)), 706 and 720 eV are found to belong to Fe, and 710 and 720 eV belong to FeO, Fe2O3, Fe3O4, FeOOH, and other iron oxides. The analysis suggests the occurrence of tribo-chemical reactions and the formation of adsorption films during the frictional interaction. Their synergistic effects considerably contribute to friction reduction and anti-wear functions.
Although the peak positions are similar for both emulsions, the intensity of each peak differs. This indicates that the composition of the interfacial lubrication film generated by the emulsions is similar, whereas the content differs, as listed in Table 3. This shows that the interfacial film generated by the A-0 emulsion without liquid crystal contains more iron oxides (up to 74.84\%) than A-1 (up to 44.42\%). The interfacial film generated by the A-1 emulsion with liquid crystal was still dominated by more carbon oxides (up to 34.72 \%) than A-0 (up to 24.24\%). This indicates that more organic films are formed on the surface lubricated by the A-1 emulsion with liquid crystal than that without liquid crystal, resulting in better protection performance.

The wear scar morphology can be observed from the SEM–EDS analysis results shown in Fig. 6. The wear scar generated by the A-0 emulsion without liquid crystal is distinctly rougher (Fig. 6(a)) than that generated by A-1 (Fig. 6(c)). The tear morphology indicates that adhesive and abrasive wearing may occur simultaneously [35]. The insets show the magnified grooves and distinguish the extent of wear more intuitively. These suggest that the quantity and width of scars generated by the A-1 emulsion became lesser and narrower compared with those generated by the A-0 emulsion. Similar C, O, and Fe signals are detected by EDS, indicating that the tribo-film is generated with significant contributions from the A-0 and A-1 emulsions. The EDS results in Figs. 6(c) and 6(f) show no distinct difference in the chemical composition of the friction film. However, consistent

**Table 3** Chemical group composition in interfacial lubricating film generated by A-0 and A-1 emulsions.

| Corresponding chemical groups | \( C_{1s} \) | \( O_{1s} \) | \( Fe_{2p} \) |
|------------------------------|----------------|----------------|----------------|
| \( C=O \)                  | 288.40         | 532.78         | 723.73        |
| \( C-O \)                  | 286.46         | 531.52         | 719.83        |
| \( C=O \)                  | 284.79         | 529.93         | 710.50        |
| \( C-C \)                  |                |                | 706.97        |
| \( C-OH \)                 |                |                | 706.58        |
| \( C-O-C \)                |                |                | 706.58        |
| \( O-H \)                  |                |                | 706.58        |

**Binding energy (eV)**

**Bond content (%)**

A-0: 14.34 9.90 75.76 12.62 50.00 37.38 17.04 7.51 57.80 17.66

A-1: 9.61 25.11 65.28 54.78 15.60 29.61 1.28 2.78 43.14 52.80
with the XPS analysis results above, the interfacial lubricating film generated by the emulsion with liquid crystal is more uniform and stable than that without liquid crystal.

3.2 Factors affecting quality and interfacial behavior of liquid crystal emulsion

3.2.1 Influence of factors on stability

Viscosity and rheological behavior are both important characteristics from the perspective of water-based lubricant applications. Although the above emulsions with liquid crystal have satisfactory lubricating properties, their optimization remains necessary. Therefore, an orthogonal experiment, whose details are summarized in Table 2, is designed to optimize the formulation and interfacial properties of the sucrose ester-based LLC emulsion.

First, the stability of the emulsions was evaluated by monitoring the change in their appearance and viscosity with time. The appearance of nine groups of emulsions in the orthogonal experiment after 30 d is shown in Fig. 7(a). Figure 7(a) shows that emulsions 1, 4, and 7 are not stable, and a certain amount of water separates at the bottom of the bottle. These three emulsions all contain 2% compound emulsifiers, indicating that a 2% compound emulsifier is insufficient to formulate a stable sucrose ester-based LLC emulsion.

The viscosity of emulsions versus time is shown in Fig. 7(b). In general, viscosity slightly increases after 24 h of preparation; however, no significant change is subsequently observed, except for emulsions 3 and 9, which exhibits not only a higher viscosity but also a sharp increase in viscosity after two weeks. This may
be because both have high emulsifier and oil phase, considerably thickening the emulsions and rendering them unstable. This suggests that these two emulsions are also unsuitable as lubricants.

3.2.2 Influence of oil phase ratio on lubrication

The Stribeck curve can comprehensively reveal the interfacial lubricating behavior of emulsions from the boundary lubrication and mixed lubrication regimes to elastohydrodynamic lubrication (EHL) regimes [36]. In the boundary lubrication and most mixed lubrication regimes with dominant solid–solid asperity contacts, several effects, by extension, are extremely important. These include adhesion, plastic deformation, fracture, real contact area, roughness, and chemical changes. In the EHL regime where solid–solid surfaces barely come into contact, the friction force mainly depends on the viscosity and wettability of the lubricating oil [37].

Accordingly, the Stribeck curve test was conducted on emulsions stabilized by an 8% compound emulsifier (main emulsifier:co-emulsifier ratio = 1:3) with different oil phase contents. As shown in Fig. 8, the Stribeck curves of emulsions exhibit three distinctive lubrication regimes. In the boundary lubrication regime, although the oil phase content seemingly has inconsiderable effect on the COF, the emulsion with the lowest oil phase content (i.e., 3%) exhibits the best performance. In the mixed lubrication regime, the emulsions with more oil are more conducive to the formation of tribo-film and reduce the COF; however, the lubrication performance of emulsions with oil in the 5%-10% range is not distinctive. This suggests that the addition of more oil is beneficial to the reduction of friction in the mixed lubrication and EHL regimes. The foregoing composition is assumed to provide greater viscosity (the inset in Fig. 8) as a result of the formation of a complex liquid crystal cross-linked network. Nevertheless, the emulsion with an oil ratio of only 5% is extremely weak to reduce friction in the EHL regime, implying that this composition is ineffective under a wider range of working conditions than the emulsion with 10% oil.

3.2.3 Influence of ratio of main emulsifier to co-emulsifier on lubrication

The influence of the ratio of main emulsifier to co-emulsifier (1:1 and 1:3) was further studied under the condition of 8% emulsifier and 5% or 10% oil content. The liquid crystal content of the emulsion with the ratio of main emulsifier to co-emulsifier of 3:1 is lower than that of the emulsions with the other two ratios; thus it is not considered in this section. Interestingly, the data in Figs. 9(a) and 9(b) show that emulsions with 5% and 10% oil contents and 1:1 ratio (main emulsifier:co-emulsifier) exhibit better friction-reducing ability in the boundary lubrication regime than the emulsions with a 1:3 ratio. The assumption is that more SC emulsifiers can yield better liquid crystal phases (Figs. 9(c) and 9(d)) and improve the bearing capability. This is because the crystalline texture structure on the interface suffers from the direct contact of metal surfaces; with the formation of tribo-film, this synergistically results in reduced sliding friction. Nevertheless, with EHL, the emulsion with a compound emulsifier (1:3) and 10% oil sharply reduces the COF because of the liquid crystal phase. Under extreme working conditions of high speed and low load, its state of viscosity is favorable because excessive viscosity can damage the interaction on the interface and block the supplemental regeneration of the friction film (Fig. 9(b)). The foregoing shows that the optimized formulas of emulsions perform better under suitable lubrication regimes. Nevertheless, the load-bearing capacity, i.e., the ability to sustain force during the shearing process, requires further improvement.
4 Conclusions

Despite its relatively limited scope, this study offered valuable and novel insights into the formulation of LLC emulsion based on natural sucrose ester, examining its interfacial behavior as a promising lubricant. Emulsions with the same formula but different treatment processes (A-1 emulsion with liquid crystal and A-0 emulsion without liquid crystal) were prepared to study the role of LLC structure on the tribological behavior and lubrication performance.

The structures of nematic texture and droplets were characterized via POM, SAXS, and SR micro-IR. The O/W interface was orderly arranged by the liquid crystal with fluidity among emulsifier molecule layers. The emulsion with such a specific structure caused the formation of a tribo-film that reduced friction by 10.1%. In contrast, the emulsion without liquid crystal compared with pure oil reduced friction by 34.2%. Theoretically, the lubrication mechanism of emulsions is related to the buildup and removal of the tribo-film.

The XPS and SEM–EDS analyses revealed the chemical composition of the worn surface and the actual sequence of events. This is with the assumption that the tribo-film of the emulsion with liquid crystal was formed synergistically by the liquid crystal phase with the base oil on the interface. Moreover, the emulsifier and oil phase ratio were observed to be extremely important. The Stribeck behaviors, viscosity, and stability were discussed to examine the two aforementioned factors. The emulsion with 8% emulsifier (1:3, ratio of main emulsifier to co-emulsifier) and 10% oil content exhibited the best performance. Nevertheless, the EHL regimes are complicated to study here. Hence, further research must be performed to calculate and predict the lubrication model at the friction interface and analyze the parameters involved.

The research on aqueous lubrication additives has advanced; however, detailed and systematic studies on their interfacial behavior at the sliding interfaces remain limited. The research on environmentally
friendly lubricants must focus on those that are water-based and naturally derived to reduce the pollution from mineral oil and economic cost. Despite its limitations, this study also contributes to the research on water-based and biological lubricants by laying the groundwork for future research on lubrication using liquid crystals, particularly LLC.

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