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RESEARCH ARTICLE

Investigation of the film formation mechanism of oil-in-water (O/W) emulsion

Liran MA[1], Chenhui ZHANG[1,*], Jianbin LUO[1], Jacob KLEIN[2], Hugh A SPIKES[3]

[1] State Key Laboratory of Tribology, Tsinghua University, Beijing 100084, China

[2] Department of Materials & Interfaces, Weizmann Institute of Science, Rehovot 76100, Israel

[3] Department of Mechanical Engineering, Imperial College London, London SW7 2AZ, UK

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Abstract: To reveal the film formation mechanism of oil-in-water (O/W) emulsion, nanofilms of aqueous paraffin oil emulsion stabilized with the nonionic Tween 80 and Span 80 surfactants were measured in confinement between two solid surfaces, by the use of relative optical interference intensity (ROII) approach. In contrast to single-phase oil lubricant, the film formation of oil-in-water emulsions normally possesses a hill appearance. The critical speeds of film formation of O/W emulsions with various emulsifier and oil concentrations were focused to study the film formation mechanism of oil-in-water emulsion. Droplets can be observed to concentrate and be broken before the contact under a low speed, which induces an oily pool. The oil pool was indicated to act as the provider to the lubrication of the contact during rolling process. A theoretical model was proposed to describe the reemulsification effect, which established a relationship between the critical speed and the concentrations of either oil or emulsifiers.

Keywords: emulsion; film thickness; reemulsification; critical speed

1 Introduction

Emulsion is a thermodynamically unstable system. The surfactants in the system can effectively decrease the interfacial tension by adsorbing on the oil-water interface [1, 2]. The surfactants on the oil-water interface prevent the oil droplets from coalescence, which results in a transitory equilibrium in the emulsion system. In view of wide applications of emulsion in pharmaceutics, food and other fields, the interface and stability behaviors have been paid great attention [3–5]. In both biologic and industrial applications, the emulsion responds to the solid surface has been of great interest and extensively investigated in the past several decades [6, 7]. O/W emulsion droplets have been found to spread and wet on hydrophobic surfaces as contact with the solid surface [8, 9]. Relatively thick hexadecane-rich layers persisting for about 150 Å have been reported by using high internal phase water/oil emulsions in contact with both hydrophobic and hydrophilic surfaces [10].

Numerous results have been reported on the film formation of emulsions at nanometer scale by using the optical interference approach [7, 11]. Dynamic concentration theory was also developed with the concept that oil droplets will concentrate before coming into the contact area to explain the existence of the continuous oil phase [12, 13]. The interaction between emulsion droplets and solid surface is seldom experimentally discussed in previous studies. As a consequence, the present work is aimed to illuminate the film formation mechanism by investigating the interfacial behaviors under confinement with the important role of surfactants.

*****Corresponding author : Chenhui ZHANG.
E-mail: chzhang@mail.tsinghua.edu.cn

2 Experimental details

Paraffin oil with a refractive index of 1.47 was used as the to-be-dispersed phase, while Span 80 and Tween 80 were used as the components of mixed emulsifiers. The confinement is formed between a highly polished glass disc and a high precision steel ball.

The measurement and observation of the film formation are realized by utilizing the relative optical interference intensity approach (ROII) [14, 15]. The confinement is formed between a highly polished steel ball and a glass disc covered with a layer of semi-reflective chromium. As shown in Fig. 1, the lower surface of the glass disc is submerged in the emulsion sample. The load applied to the contact is 30 N, which gives a maximum contact pressure of 0.54 GPa. The room temperature is around 25 °C.

3 Results

3.1 Effect of emulsifier concentration

The film formations were measured separately for emulsions with different emulsifier concentrations, while oil concentration *C* was kept as a constant of 2.5%. The highest film thicknesses and critical speeds of emulsions with various oil concentrations C (*m*=10% vol%) were listed in Table 1. It can be found that the critical speed has been decreased from 0.7 m/s to 0.2 m/s with increasing the emulsifier concentration *m*. In cleaning applications, surfactants have been well known to possess the ability of drawing the oil/grease contamination away from the solid surface into the aqueous bulk.

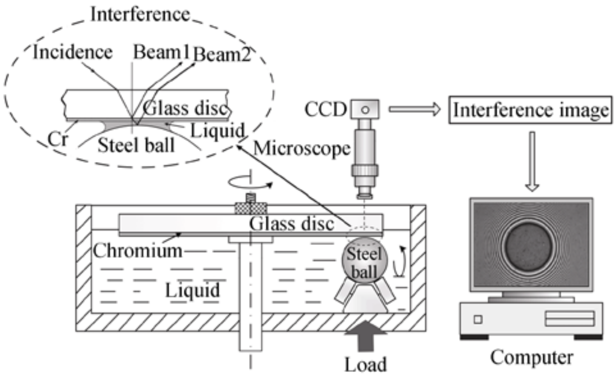

Fig. 1 Experimental set-up.

3.2 Effect of oil concentration

In earlier investigations, the collapse of film has been recognized as the typical profile of emulsion film formation. It should be noted that experimental results of emulsions with oil concentration lower than 0.5 vol% were seldom reported. In our present work as listed in Table 1, 0.005 vol% emulsion is utilized to investigate the film formation mechanism of oil-in-water emulsion. It can be confirmed that the critical speed will be decreased as increasing the oil concentration. This phenomenon is also inferred to be induced by the reemulsification effect mentioned above.

4 Discussion

4.1 Concentration effect

O/W emulsions have been confirmed to have growing film with rolling speed in a certain speed range between two confined surfaces under a low speed range despite of the type of oil, type of emulsifier and oil/emulsifier concentration [12]. To illuminate how the film comes into being, the droplets behavior was observed directly by using the present experimental set-up. To examine whether the droplet-concentration effect is kept to be effective at a high speed or not, the surface states were pictured after the film formation measurements (0–2.5 m/s) for different various oil concentrations separately were observed that the oil amounts remained on the glass disc surface are almost the same for 0.05 vol% and 2.5 vol% emulsions.

Table 1 The highest film thicknesses and the critical speeds of emulsions with various oil concentrations *C* (*m* = 10 vol%).

Oil concentration C (vol%)	Critical speed (m/s)	Max film thickness (nm)
0.005	0.70	54
0.050	0.60	57
0.500	0.25	56
2.500	0.21	58
5.000	0.20	65
10.00	0.20	68

4.2 Reemulsification effect

Figure 2 illustrates the reemulsification effect. Since it is very difficult to make the solid surface, especially metal surface, to be completely exposed in the water, the case presented in Fig. 2(a) can actually hardly to be obtained in practical situations. As a result, the situation presented in Fig. 2(b) will be more reasonable, which is named as the reemulsification effect in the present paper. In the present work, the mixed two kinds of emulsifiers can be taken as a whole surfactant on the oil-water interface, as the structure shown in Fig. 2(c).

The oil (paraffin)-water interfacial tension will be decreased by the adsorption of emulsifier, simplified to follow the relationship [16]:

$$\sigma = \sigma_0 - RT\Gamma_m \ln(1 + kmC) \tag{1}$$

where the σ_0 is the oil-water interfacial tension when the adsorption amount is 0 (σ_0 is 51.3 mN/m), R is the gas constant (8.314 J/k/mol), T is the absolute temperature (298 K), Γ_m is the ideal limited adsorption amount (usually is situated in 2–5 μmol/m^2 according to different systems [16]), and k is a constant which will be varied in different systems. Equation (1) will be used to quantificationally present the reemulsification effect coming from the existence of emulsifier to some extent.

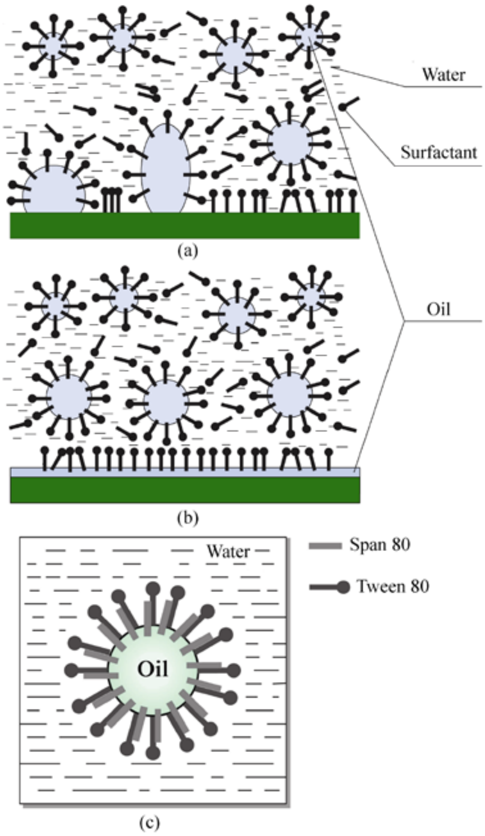

Fig. 2 Illustrations for the reemulsification effect when (a) oil is thoroughly removed, (b) oil is partly removed, and (c) emulsion droplet with mixed emulsifier.

In the present system, to work the mechanical shearing coefficient β out, the experimental results are first analyzed in the situation that $m = 0\%$. The critical speed has been measured to be around 0.7 m/s when $m = 0\%$. Thus the mechanical effect applied on unit area will be:

$$E_\tau = \beta u_c = W_{\mathrm{OW}} = 2\sigma_{\mathrm{OW}} = 102.6\ \mathrm{mN/m} \tag{2}$$

Substitute the $u_c = 0.7$ m/s into Eq. (2), it can be obtained that $\beta = 146.6\ \mathrm{mNm^{-2}} \cdot s$. Based on the Eqs. (1) and (2), the critical speed can be expressed by the following equation:

$$u_c = \frac{2}{\beta}[\sigma_0 - RT\Gamma_m \ln(1 + kmC)] \tag{3}$$

In the case of varying the emulsifier concentration while keeping C constant, the Eq. (3) can be described as:

$$u_c = \frac{2}{\beta}[\sigma_0 - a\ln(1 + bm)] \tag{4}$$

where a, b are required to be fitted with the experimental results. Thus the result can be fitted with Eq. (4) as shown in Fig. 3(a). The fitted parameters are $a = 0.009\ \mathrm{N/m}$, $b = 280$. In Fig. 3(b), the situation with varied oil concentration C while the m is kept as a constant is analyzed, when Eq. (3) can be expressed as:

$$u_c = \frac{2}{\beta}[\sigma_0 - a'\ln(1 + b'm)] \tag{5}$$

where a' and b' are the parameters required to be fitted. Using this expression, the film formation critical speeds of emulsions with various oil concentrations (0.005%, 0.05%, 0.5%, 2.5%, 5% and 10%) can be fitted as shown in Fig. 3(b).

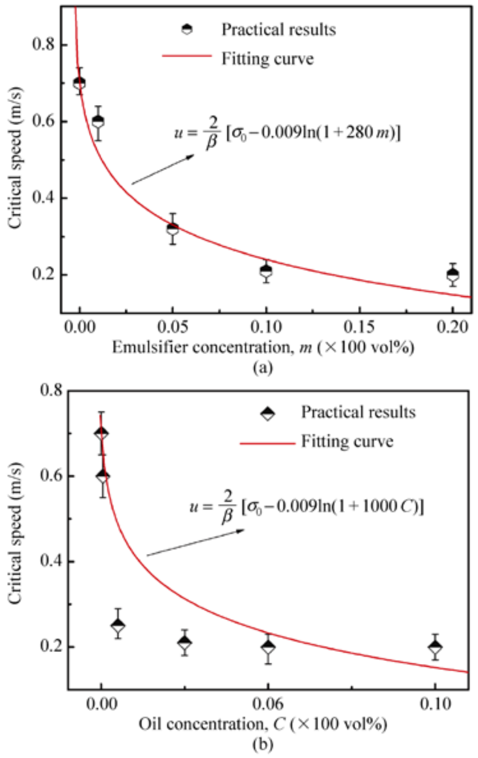

Fig. 3 The reemulsification model: (a) fitting result of emulsions with various emulsifier concentrations, (b) fitting result of emulsions with various oil concentrations.

5 Conclusions

In this study, the mechanism of film formation of oil-in-water emulsion under point contact was investigated utilizing optical interference approach. Emulsions were examined to undergo different critical speeds of the film formations under different experimental conditions. The reemulsification effect has been revealed to significantly remove the oil layer wetting on the solid surface off by emulsifying the continuous oil phase into droplets under both the mechanical shearing effect and emulsifier effect.

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Nomenclature

m	Volume ratio of emulsifier
C	Volume concentration of oil phase (paraffin oil and emulsifier)
σ_0	Oil-water interfacial tension when the surfactant adsorption amount is 0
R	The gas constant (8.314 J/k/mol)
T	The absolute temperature (298 K)
E_τ	Shearing energy
u	Rolling speed in the central contact area
β	Mechanical shearing coefficient

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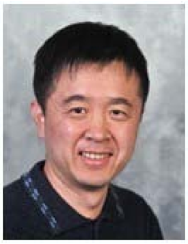
Liran MA. Assistant professor, obtained her Bachelor degree in 2005 from Tsinghua University and PhD degree in 2010 from Tsinghua University. She worked with Prof. Jacob Klein as a post doctor in Weizmann Institute of Science in Israel during 2010-2011. She worked as an assistant professor since 2012 at State Key Laboratory of Tribology at Tsinghua University. Her interested research areas include water-based lubrication, surface & interface behaviors and superlubricity. She has participated in many research projects and has published more than 10 papers on international journals during the past 5 years.



Chenhui ZHANG. Associate professor, obtained his Bachelor of Engineering degree and PhD degree in 1998 and 2004 from Tsinghua University. During this period, he was invited to visit the City University of Hong Kong as a Research Assistant. He was promoted to Assistant Professor in 2004 and then to Associate Professor in 2007 at Tsinghua University. From February 2011 to August, he was invited to Lulea University of Technology in Sweden as a Visiting Scholar. He is a member of The Youth Working Committee, Measuring Technology Committee and Wear and Surface Technology Committee of Tribology Institute of Chinese Mechanical Engineering Society. His interested research areas include application of superhard nanocomposite coatings, and anti-wear and self lubrication; the phenomena and mechanism of superlubricity. He successively presided and participated in many research projects like “The National Basic Research Program of China (973)”, “The National Natural Science Foundation of China”, and some international cooperation projects. He has published around 40 papers in leading engineering, applied physics and soft matter journals.