University of Wollongong

Research Online

Faculty of Engineering and Information
Sciences - Papers: Part B

Faculty of Engineering and Information
Sciences

2019

Dual effects of TiSiO₄ composite nanoparticles on dispersion stability and lubrication performance of vegetable oil-in-water emulsions

Reza Taheri

University of Wollongong, rt795@uowmail.edu.au

Buyung Kosasih

University of Wollongong, buyung@uow.edu.au

Hongtao Zhu

University of Wollongong, hongtao@uow.edu.au

Anh Kiet Tieu

University of Wollongong, ktieu@uow.edu.au

Follow this and additional works at: <https://ro.uow.edu.au/eispapers1>

Part of the [Engineering Commons](#), and the [Science and Technology Studies Commons](#)

Research Online is the open access institutional repository for the University of Wollongong. For further information contact the UOW Library: research-pubs@uow.edu.au

Dual effects of TiSiO₄ composite nanoparticles on dispersion stability and lubrication performance of vegetable oil-in-water emulsions

Abstract

Vegetable oil-in-water emulsions are potential metal-working lubricants. These emulsions are susceptible to oil-water phase separation due to the oil droplets' coalescence. In this study, we enhance the dispersion stability and lubricity of such emulsions with TiSiO₄ nanoparticles (NPs). With 1 vol% soybean oil, stable emulsions are obtained with 0.25 to 0.75 wt% NPs, attributed to formation of shielding layers of NPs around the droplets. Lowest friction and wear are obtained without and with 0.25 wt% NPs, respectively. With increasing the NPs' mass fraction, NP-shielded droplets become less attracted to metal surfaces. Association of NPs within boundary film is also found when NPs' mass fraction is above 0.5 wt%, inducing third body abrasive behaviour. Further increasing the NPs' mass fraction results in the formation of agglomerates of NPs in emulsions which increases vibration, friction, and wear. Findings suggest that a mass fraction of NPs exists at which stable emulsions with improved lubrication performance are obtained.

Keywords

lubrication, dispersion stability, nanoparticles, emulsions, TiSiO₄ composite, oil-in-water, effects, dual, vegetable, performance

Disciplines

Engineering | Science and Technology Studies

Publication Details

Taheri, R., Kosasih, B., Zhu, H. & Tieu, A. Kiet. (2019). Dual effects of TiSiO₄ composite nanoparticles on dispersion stability and lubrication performance of vegetable oil-in-water emulsions. *Lubrication Science*, 31 (1-2), 21-39.

Dual effects of TiSiO₄ composite nanoparticles on dispersion stability and lubrication performance of vegetable oil-in-water emulsions

Reza Taheri, Buyung Kosasih *, Hongtao Zhu, Anh Kiet Tieu

School of Mechanical, Materials, Mechatronics, and Biomedical Engineering

University of Wollongong, NSW 2522, Australia

*Corresponding Author: buyung@uow.edu.au

Abstract

Vegetable oil-in-water emulsions are potential metal-forming lubricants. These emulsions are susceptible to oil-water phase separation due to the oil droplets' coalescence. In this study, we enhance the dispersion stability and lubricity of such emulsions with TiSiO₄ nanoparticles (NPs). With 1% *vol.* soybean oil, stable emulsions are obtained with 0.25 to 0.75% *wt.* NPs, attributed to formation of shielding layers of NPs around droplets. Lowest friction and wear are obtained without and with 0.25% *wt.* NPs respectively. With increasing NPs' mass fraction, NP-shielded droplets become less attracted to metal surfaces. Association of NPs within boundary film is also found when NPs' mass fraction is above 0.5% *wt.*, inducing 3rd body abrasive behaviour. Further increasing NPs' mass fraction results in formation of agglomerates of NPs in emulsions which increases vibration, friction and wear. Findings suggest that a mass fraction of NPs exists at which stable emulsions with improved lubrication performance are obtained.

Keywords: vegetable oil-in-water emulsion, TiSiO₄ nanoparticles, eco-friendly metal working lubricant

1. Introduction

Oil-in-water (O/W) emulsions are potential lubricants for metal working lubrication. In O/W emulsions, the dispersed oil droplets play the lubrication role and the continuous water phase carries heat away from the contact zone [1]. Considering the hazardous effects of non-biodegradable oils used in conventional metal working emulsions on health and environment, environmentally-friendly vegetable oils are adopted as potential alternatives [2-6]. With small oil concentration (*vol. %*), vegetable oil-in-water (VO/W) emulsions deliver good lubrication performance compared to neat oils when used in boundary regime lubrication [7]. This makes VO/W emulsions promising lubricants especially in total-loss lubrication applications.

Vegetable oils are mainly triglyceride molecules comprise of a polar glycerol attached to fatty acid triesters [5,6,8,9]. Lubrication properties of VO/W emulsions is owed to the polar nature of triglyceride molecules of the vegetable oil droplets with high deposition tendency on metal surfaces [3,5]. Deposition of vegetable oil droplets on surfaces occurs by ‘plating out’ of the droplets through anchorage of triglycerides’ carboxyl –COOH groups on the surface whilst the fatty acids’ alkyl –CH₃ groups form a closely-packed repelling layer near the surface [10]. Formation of these films is influenced by the deposition tendency of oil droplets on surfaces which in turn is related to dispersion stability of droplets [10,11]. For instance, highly stable droplets do not interact with surfaces, hence reduce the on-surface oil deposition. Despite that, strong inter-droplets attraction forces exist between hydrophobic oil droplets in bulk emulsions that result in oil/water phase separation and degradation of emulsions over time [12]. Therefore, moderately stable droplets are favourable in lubricating emulsions because of the adequate stability and good deposition tendency on metal surfaces.

Dispersion stability of droplets is a measure of the balance between the attractive and repulsive inter-droplets forces. To improve the droplets’ dispersion stability, various additives including conventional surfactants, surface-active polymers, and solid nanoparticles (NPs) have been studied [13]. NPs are more attractive additive for lubricating emulsions compared to others additives, owed to the combinative droplets-stability and lubricity properties [13-15]. Alternatively, ultrasonic emulsification of emulsions can increase the dispersion stability of the droplets in absence of additives [7]. This is caused by the adsorption of hydroxyl ions (OH⁻) from the aqueous medium on the droplets’ surface, providing electrostatic barriers against coalescence [16]. Further stability of the ultrasonically prepared droplets can be achieved with addition of ionisable NPs such as silica to the emulsions, through irreversible adsorption of

shielding layers of NPs on the surface of oil droplets which impede coalescence, similar to egg-shell structures [13,14]. The structural strength of these NP-shielding layers is influenced by factors including shape, size, and mass fraction (*wt. %*) of NPs, as well as adsorption tendency of NPs on the droplets' surface and inter-NPs interactions in the bulk emulsion [13].

With low temperature sensitivity and small chemical reactivity on metal surfaces [17], some NPs are effective antiwear and friction-reducing additives. For example, friction and wear reduction is reported when NPs such as Al_2O_3 , CuO , ZnO , and TiO_2 are used in either oil based or aqueous based lubricants [17-23]. Upon being entrained and squeezed into the contact zone, spherical NPs function as ball bearings and roll between the surfaces to reduce friction. This is augmented by mending and polishing actions of NPs that improve the surface quality for lower asperity contacts [23-26]. Lubricity of NPs mainly depends on shape, size, structure, and mass fraction of NPs [24]. Chemical properties of the base environment in which the NPs are used also affect the lubrication effectiveness of NPs. For instance, ZnO and CuO NPs enhance the lubrication performance of mineral and synthetic oils whereas adverse effects are seen when added to vegetable oil based lubricants [22,27]. In comparison, TiO_2 NPs reduce the friction and wear of vegetable oil based lubricants, providing a rolling-sliding mechanism as opposed to sliding-only contact in absence of NPs [24,28].

To benefit from the synergistic properties of different NPs, composite NPs have received widespread attention [28,29]. For example, antiwear capability of Al_2O_3 NPs and dispersion enhancing characteristic of SiO_2 NPs can be stacked in $\text{Al}_2\text{O}_3/\text{SiO}_2$ composite NPs [28]. $\text{Al}_2\text{O}_3/\text{TiO}_2$ and $\text{ZnO}/\text{Al}_2\text{O}_3$ composite NPs also show improved lubrication properties compared to Al_2O_3 , TiO_2 , and/or ZnO NPs [21,29,30]. However, as the performance of NPs depends on the base environment, composite NPs may show inferior behaviour compared to their constitutive NPs. Hence, further work is needed to understand the synergy of different types of NPs, especially when used in lubrication with VO/W emulsions.

Low concentration ($\sim 1\%$ *vol.*) of oil in VO/W emulsions shows promising lubrication properties [31]. However, unfavourable residue of oil is generally left on the surface after lubrication with VO/W emulsions [31]. In this study, the dispersion stability and lubrication properties of the soybean oil droplets of VO/W emulsions as well as the anchoring strength of oil residue on the lubricated surfaces are investigated in presence of varying mass fractions of TiSiO_4 (titanium silicate) composite NPs. Interactions between NPs and the oil droplets within the bulk emulsion and in the contact zone are also discussed.

2. Methodology

2.1. Materials' characterisation and emulsions' preparation

TiSiO₄ composite NPs and refined soybean oil were supplied from *Sigma Aldrich* and *Masterolfoods (Australia)* respectively. Molecular structuring of TiSiO₄ NPs and soybean oil was characterised using Fourier-transform infrared spectroscopy (FTIR) over wavelength range of 600cm⁻¹ to 4000cm⁻¹ on *Shimadzu IRAffinity-1* instrument. Structure and the average size of NPs were analysed by X-ray diffraction (XRD) using *GBC MMD* instrument with Cu K α radiation at 20kV over 2 θ range of 10° to 100°.

VO/W emulsions were prepared with 1% *vol.* oil and 0 (no NPs) to 1% *wt.* NPs by combined ultrasonication and mechanical stirring. First set of emulsions were prepared without NPs with varying input ultrasonication energies from 1.5 to 300kJ/m³ to determine the required amount of energy to produce monodispersed oil droplets. Size distributions of the oil droplets were measured immediately after emulsification using *Malvern Zetasizer Nano S* instrument. Second set of emulsions with varying mass fractions of NPs were then prepared. Initially NPs were dispersed in distilled water by mechanical stirring for 10 minutes at 1000rpm followed by 30 minutes ultrasonication in 3×10 minutes stages to prevent significant temperature changes. After the dispersion of NPs, 1% *vol.* oil was added and emulsions were prepared with 75kJ/m³ energy (see section 3.1 for details).

2.2. Oil droplets' size distribution and dispersion stability

Dispersion stability of the oil droplets without and with varying mass fractions of NPs was assessed by measuring the average size of oil droplets using *Malvern Zetasizer Nano S* instrument. Size distributions of droplets were obtained at different times after the preparation, namely immediately (day #1), 14 days (day #14) and 28 days (day #28) after the preparation.

2.3. Interactions between NPs and oil droplets

VO/W emulsions with and without NPs were characterised using *Shimadzu IRAffinity-1* FTIR. Interactions between NPs and the oil droplets were investigated using *Leica TCS SP8* confocal laser scanning microscope (CLSM). To increase their traceability, NPs were marked with *Rhodamine B* fluorescence dye (95%, excitation wavelength 552nm, supplied by *Sigma Aldrich*) [32,33]. The dye was initially dissolved in water and the dye solution was used to prepare the emulsions.

2.4. Mass deposition on surface model

Deposition of oily films on surface was estimated by measuring the oil mass deposition on 5MHz Cr/Au crystals as hydrophobic surface model [34], using *SRS QCM200* instrument. The deposited oil mass on surface (Δm , per unit area) was calculated using modified *Sauerbrey* equation (eq. 1) in terms of frequency shift Δf and resistance shift ΔR during the deposition, initial frequency f_0 , current frequency f , and the crystals' properties ($\rho_q=2.648\text{g.cm}^{-3}$, $\mu_q=2.947\times 10^{11}\text{g.cm}^{-1}\text{s}^{-2}$) [35,36].

$$\Delta f_T = \left(-\frac{2f_0^2}{\sqrt{\rho_q\mu_q}} \cdot \Delta m \right) + \left(-\frac{\Delta R}{4\pi L} \cdot \left(\frac{f_0}{f}\right)^{3/2} \right) \quad \text{eq. 1}$$

To determine if the NP shielding of oil droplets has any effect on the deposition of oily films, deposited mass measurements were carried out on day #1. Measurements were done at four consecutive stages. Crystals were first exposed to air for 10 minutes (stage I) to acquire stable initial frequency. In stage II, crystals were immersed in distilled water for 15 minutes to measure the viscous load from the aqueous medium on the crystals. This is followed by mass deposition stage (stage III) by immersing crystals in emulsions until steady-state measurements were obtained. Finally, crystals were again immersed in water for 15 minutes (stage IV, rinsing) to determine if the deposited oil mass can be flushed from the crystals' surface by water rinsing.

2.5. Friction and wear

Friction tests were conducted using Stainless steel *SS316* balls (4mm diameter) and discs (initial surface roughness $R_a \approx 10\text{nm}$) on *CETR UMT2* tribometer. The tests were run at 60rpm, 20mm radius, and under 6N load in the boundary lubrication regime [34]. Dynamic coefficients of friction (COFs) were obtained by simultaneous measurements of normal and tangential forces. Surface topography of the balls' wear scars and the discs' wear tracks were analysed using *Bruker contour elite* 3D microscope and *Jeol JSM6490LV* scanning electron microscope (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS).

3. Results and Discussions

3.1. Materials' characterisation

FTIR transmittance spectra of soybean oil sample and TiSiO_4 NPs in wavelength range of 600cm^{-1} to 4000cm^{-1} are shown in Figure 1. Vegetable oils are mainly made up of glycerol

molecules linked to three fatty acid chains by ester linkage, having various functional groups [5]. FTIR spectrum of soybean oil (spectrum ‘a’) shows distinct bands associated to vibration of these groups including two bands at 728cm⁻¹ and 916cm⁻¹ associated to out-of-plane bending of -CH=CH- (*cis*), a band at 962cm⁻¹ to out-of-plane bending of -CH=CH- (*trans*), three bands at 1096cm⁻¹, 1161cm⁻¹, and 1243cm⁻¹ to stretching of -C-O, a band at 1380cm⁻¹ to symmetric and a band at 1456cm⁻¹ to asymmetric bending of -C-H (CH₃), a band at 1651cm⁻¹ to stretching of -C=C- (*cis*), a band at 1743cm⁻¹ to stretching of -C=O, a band at 2853cm⁻¹ to symmetric and a band at 2921cm⁻¹ to asymmetric stretching of -C-H (-CH₂), and a band at 3011cm⁻¹ associated to stretching of =C-H (*cis*) groups [37-39].

FTIR spectrum of NPs (spectrum ‘b’) shows a band at 652cm⁻¹ associated to stretching of Ti-O-Ti in TiO₂ matrices and a band at 1097cm⁻¹ to stretching of Si-O-Si in SiO₂ matrices [40,41]. A band at 952cm⁻¹ is also obtained, associated to stretching of Si-O-Ti or presence of Si-O defect sites, formed by the inclusion of Ti⁴⁺ into SiO₄⁻⁴ structures [40-42]. The analysis indicates that TiO₂ species are embedded into SiO₂ matrices to form TiSiO₄ composite NPs [41,42], with chain-like SiO₂ acting as carriers of TiO₂ species [40,43]. Moreover, no bands associated to O-H bonds (1650cm⁻¹ or 3350cm⁻¹) are detected, postulating that no moisture is present within the TiSiO₄ sample [42].

Figure 2 shows the XRD pattern of NPs, indicating 2θ peaks at 25.3° (101), 37.75° (004), 47.95° (200), 53.95° (105), 55.03° (211), and 62.75° (204). All XRD peaks of TiSiO₄ NPs represent anatase TiO₂ phase [44], in accord with JCPDS card 21-1272. No diffraction peak is detected for SiO₂, indicating the amorphous shape of SiO₂ matrices. The crystalline size of NPs is calculated from the main diffraction peak angle at 25.3° (101 plane) using *Scherrer* equation (eq. 2) where *D* is the size of NPs, *k* is shape factor (0.9), *θ* is diffraction angle, *λ* is X-ray wavelength (1.5418Å), and *β* is full peak width at half maximum intensity (FWHM) after subtracting the instrumental line broadening, yielding an average size of 35nm for NPs. The small size of NPs is related to doping of SiO₂ NPs around TiO₂ NPs through the Si-O-Ti bonds (inferred by FTIR measurement) which further prevents the size growth and phase shift of TiO₂ species [41,42].

$$D = \frac{k\lambda}{\beta \cos \theta_T} \quad \text{eq. 2}$$

Figure 1 FTIR transmittance spectrum of (a) soybean oil, and (b) TiSiO₄ NPs.

Figure 2 XRD pattern of TiSiO₄ NPs (all peaks correspond anatase phase and parenthesis represent crystal planes).

3.2. Dispersion stability and size characterisation

The first set of emulsions were prepared without NPs and with varying input ultrasonic energies. Figure 3 shows that the average size of NP-free oil droplets reduces noticeably from

5700nm to 230nm as the input energy increases from 1.5 to 30kJ/m³, following an asymptotical decreasing trend. Hence, it is decided to maintain 75kJ/m³ input energy in the preparation of the emulsions with NPs.

Figure 3 Average size of oil droplets in absence of NPs in emulsions prepared with 1.5 to 300kJ/m³ ultrasonic energy.

The required mass fraction of NPs to produce stable emulsions depends on the bulk oil concentration. To determine the minimum required quantity of NPs, the average diameter of oil droplets in presence of 0 (no NPs), 0.1, 0.25, 0.5, 0.75, and 1% *wt.* NPs are obtained on day #1 and shown in Figure 4. Without NPs, two distinct size peaks are found. In presence of 0.1% *wt.* NPs, monodispersed oil droplets with average 600nm diameter are obtained. By increasing the NPs mass fraction to 0.25% *wt.*, the average diameter of droplets reduces to around 220nm. This suggests that presence of 0.1% *wt.* NPs is not enough to stabilise the emulsion, noted by large reduction in the average diameter with 0.25% *wt.* NPs compared to the latter. The average diameter of droplets increases slightly to 261nm when 0.5% *wt.* NPs are present in the emulsion whereas further increasing the mass fraction to 0.75 and 1% *wt.* does not alter the average diameter. Increasing the NPs mass fraction initially increases the surface coverage of droplets with NPs owed to the cumulative adsorption of NPs on the droplets' surface. This improves the droplets' stability up to a critical saturation mass fraction (0.5% *wt.*) at which the surface of droplets are fully covered with NPs. In above the saturation mass fraction, increasing the NPs' mass fraction is thought to merely results in the formation of agglomerates of NPs in the aqueous phase [45,46] due to the strong attractive van der Waals forces between the freely dispersed NPs [20].

Figure 4 Average size of oil droplets in emulsions with 0 (no NPs), 0.1, 0.25, 0.5, 0.75, and 1% *wt.* NPs on day #1.

Effect of varying mass fractions of NPs on dispersion stability is investigated over 28 days with emulsions without and with enough NPs (0.25, 0.5, 0.75, and 1% *wt.*). The droplets' size distributions are shown in Figure 5. Without NPs, droplets' size varies over a wide range of sizes in day #1 which apparently represents an overlap of two distributions with peaks at 170nm and 550nm. After 14 days, the two distributions diverge and form distinct distributions with more defined size peaks at 201nm and 2790nm. After 28 days, further coalescence of the droplets is observed, signified by the formation of larger droplets with a size peak between 2000nm to 3000nm. This is driven by the strong attraction forces between the polar oil droplets [12] which in absence of coalescence barriers results in the formation of larger droplets over time.

With 0.25% *wt.* NPs (Figure 5b), a stable size distribution with a peak at 220nm was achieved immediately after the preparation and remained stable up to 28 days. Considering the size of NP-free droplets, break-down of the large droplets and increased diameter of the small droplets from 170nm to 220nm with addition of 0.25% *wt.* NPs are thought attributed to the built-up of a NP layer on the droplets' surfaces. On the other hand, SiO₂ NPs adsorb on the droplets' surface in equilibrium with the freely dispersed NPs [14]. This results in association of free SiO₂ NPs to form agglomerates in the aqueous phase even when small quantity of NPs are present [45,46]. Similar behaviour is found for TiSiO₄ composite NPs, evidenced with the second size distribution in range of 5000nm to 6000nm during the test which is thought to represent the agglomerates of NPs [33].

Stable emulsions are also obtained in presence of 0.5 and 0.75% *wt.* NPs (Figures 5c and 5d). However, the emulsion with 1% *wt.* NPs was found to be stable for a limited time only where high dispersity index (≈ 0.89) was obtained after 7 days (not shown). This is due to

extensive formation of agglomerates of NP in the aqueous phase from excess NPs, disrupting the size measurements. On the other hand, stable monodispersed droplets are obtained with 0.25% *wt.* NPs in below the saturation mass fraction. This indicates that partial coverage of the surface of the droplets with enough TiSiO_4 NPs is sufficient to protect the droplets against coalescence. These results suggest that regardless of the mass fraction of NPs, NPs tend to (1) form a steric shielding layers on the surface of oil droplets, and (2) simultaneously, form large agglomerates of NPs within the aqueous phase of emulsions [33].

Figure 5 Oil droplets' size distribution in emulsions with (a) no NPs, (b) 0.25%, (c) 0.5%, and (d) 0.75% *wt.* NPs.

To investigate the NP-shielding layers on the surface of the oil droplets, CLSM images of the droplets in emulsions without and with 0.25 and 0.5% *wt.* NPs are obtained on day #1 and shown in Figure 6. Without NPs, droplets with varying sizes are dispersed in the dye solution. With addition of NPs, shielding layers of NPs on the surface of the oil droplets are noted, reflected by tracing the *Rhodamine B* dye to the droplets-water interfaces (TiSiO_4 NPs attract *Rhodamine B* dye due to electrostatic interactions). These layers provide steric repelling between the droplets and prevent the droplet-droplet interactions, more when higher mass of NPs is present [33]. This is evidenced by comparing the separations of oil droplets in presence of 0.25% *wt.* NPs (Figure 6b) and 0.5% *wt.* NPs (Figure 6c).

Figure 6 Bright-field and fluorescence images of emulsions with (a) no NPs, (b) 0.25%, and (c) 0.5% wt. NPs (scale bars 5 μm , NPs are marked and traced with *Rhodamine B* fluorescence dye).

To examine if the formation of NP-shields on the droplets' surface alters the emulsions' molecular structure, FTIR spectra of emulsions without NPs (spectrum 'a') and with 0.25% *wt.* NPs (spectrum 'b') are obtained on day #1 and shown in Figure 7. Similar spectra to spectrum 'b' are obtained for other emulsions with 0.5, 0.75, and 1% *wt.* NPs. In both spectra, two bands at 1641cm^{-1} and 3337cm^{-1} are seen, associated to water molecules' H-O-H scissoring bending and -O-H stretching respectively [47,48]. A band at 638cm^{-1} is also obtained, attributed to the frustrated rotation of water molecules, known as libration vibration [48]. In addition, several other bands are obtained in spectrum 'a' for the emulsion without NPs including a band at 1080cm^{-1} associated to stretching of -C-O, several bands between 1400cm^{-1} and 1600cm^{-1} to bending of -C-H, a band at 1751cm^{-1} to stretching of -C=O, and two bands at 2858cm^{-1} and 2914cm^{-1} to stretching of -C-H groups. These bands represent functional groups of soybean oil droplets and were observed in the FTIR spectrum of neat oil sample (Figure 1a).

Figure 7 FTIR spectra of emulsions with (a) no NPs, and (b) 0.25% *wt.* NPs.

FTIR spectrum of the emulsion with 0.25% *wt.* NPs (spectrum 'b') shows similarity to spectrum 'a', except with the addition of a peak at 1160cm^{-1} associated to the Si-O-Si bonds of

NPs. This indicates the existence of Si-O-Si chains, postulating the stabilisation mechanism of SiO₂ NPs in the emulsion.

3.3. *Mass deposition on surface model*

On-surface oil mass deposition from the emulsions with varying mass fractions of NPs is examined using Cr/Au crystals and the results are shown in Figure 8 (spikes represent phase changes). Initially, crystals are exposed to air to acquire stable initial frequencies (stage I). Immersion of crystals into water (stage II) results in a small increase in the deposited mass on the surface due to the viscous loads of the aqueous medium. By immersing the crystals into the emulsions (stage III), different results are obtained. Without NPs, a rapid increase in the deposited mass to around 95 µg/cm² is observed (Figure 8a), owed to the attraction of polar triglyceride molecules of oil droplets to the surface [8,9]. This is followed by slow spreading of the oily film on surface which increases the surface occupation until an equilibrium state is reached [49]. Hence, it is expected that NP-free VO/W emulsions possess good tribological performance prior to phase separation. Figure 8a also indicates that without NPs, rinsing the surface with water does not remove the deposited oil film from the surface, indicated by the approximately unchanged deposited mass in stage IV compared to III. This can be explained by strong attraction of polar deposited oil layers to the surface, preventing the layers to desorb easily.

Conversely, the deposited oil mass from the emulsion with 0.25% *wt.* NPs (Figure 8b) is around 3.8 µg/cm² in stage III. NP-shielded oil droplets have lower polarity compared to the NP-free droplets, hence show better anti-coalescence capability in bulk emulsions. However, lower polarity of the droplets reduces droplets-crystal interactions and consequently reduces the attraction of droplets to it. This is observed in Figure 8b where the deposited mass does not increase notably when the crystal is immersed in emulsion (stage II to III). Figure 8b also shows that with 0.25% *wt.* NPs, the deposited oil mass in stage III reduces by water rinsing (stage III to IV), indicating the ease of flushing the film from surface. This implies the reduced attraction between the film and the surface. Similar behaviour is observed when 0.5, 0.75, and 1% *wt.* NPs are present in the emulsion, indicating the reduced interactions between NP-shielded oil droplets and crystals' surface in presence of NPs.

Figure 8 QCM mass deposition traces from emulsions with (a) no NPs, (b) 0.25%, (c) 0.5%, (d) 0.75%, and (e) 1% wt. NPs during four stages (I. in air → II. in water → III. in emulsions → IV. in water).

Figure 9 QCM mass deposition on the surface from emulsions with 0 (no NPs) to 1% wt. NPs during stage III (mass deposition) and stage IV (rinsing).

The amount of deposited mass during ‘mass deposition’ and ‘rinsing’ stages (stages III and IV respectively) are summarised in Figure 9. It is thought that as the mass fraction of NPs

increases, not only higher number of NPs make up the deposited film on the surface and reduce droplets-surface interactions, more free agglomerates of NPs also form in bulk emulsion. This increases the interactions between the on-surface film and the bulk emulsion which results in the vibration of NP agglomerates near surface that further weakens the film deposition.

3.4. Dynamic friction analysis

In sections 3.2 and 3.3, emulsions with NPs are shown to have good stability albeit with lower film deposition on the surface. To determine if the deposited oil film on the surface can provide lubrication support, friction tests were conducted. Initially, discs were fully immersed in distilled water for 15 minutes and COFs were obtained. Water was then carefully replaced with emulsions having varying mass fractions of NPs and COFs were measured for another 30 minutes. The results are shown in Figure 10. COF reduces from 0.48 in water lubrication to 0.11 when the NP-free emulsion is introduced. This is attributed to the deposition of polar oil film on the surface and friction-reducing mechanism of this closely packed layer [8,9].

Figure 10 COF traces during lubrication with water and emulsions with 0 (no NPs) to 1% wt. NPs, and (inset) average COFs during emulsions' lubrication.

When emulsions with 0.25, 0.5, 0.75, and 1% wt. NPs are introduced, the steady-state COFs of 0.13, 0.15, 0.16, and 0.2 are obtained respectively. The increased COF with addition of 0.25% wt. NPs may be explained by lower oil mass deposition on the surface and NPs' 3rd body behaviour within the contact zone [22,27]. By increasing the mass fraction of NPs from 0.25 to 0.5% wt., higher number of NPs populate the film formed on the surface, resulting in the formation of amorphous flocs of NPs by association of several NPs within the deposited film. Further increasing the mass fraction of NPs significantly increases the formation rate of

NP agglomerates in the bulk emulsion. During sliding contact, NP flocs within the contact zone aggravate the severity of asperity contacts. In the meantime, NP agglomerates within the bulk emulsion do not enter the contact zone due to their large size, but instead flow around the sides of the contact zone and rub against each other, increasing the near-surface vibrations [50,51]. This results in inhomogeneous boundary regime lubrication with increased friction and wear, more as higher mass of NPs is added. This is reflected in the steady-state COFs of emulsions, increasing continuously from 0.11 without NPs to 0.2 with 1% *wt.* NPs.

To correlate the NPs' effects on film-forming and friction-reducing properties, dynamic friction tests are designed with different lubricants denoted as A, B, C, and D. Lubricants A, B and C are 1% *vol.* soybean oil emulsions having 0 (no NPs), 0.25 and 0.5% *wt.* NPs respectively and lubricant D is an aqueous dispersion of 0.5% *wt.* NPs. As reference, water is initially used as lubricant with average COF of 0.48 (stage I). After 10 minutes, water was carefully replaced with lubricants A, B, C, or D and COFs were obtained for 25 minutes (stage II). Lubricants were then replaced with water in stage III and COFs were obtained for 10 minutes. Figure 11 shows the COF traces of all samples. In stage II, COFs of 0.11, 0.13, and 0.15 are obtained for emulsions A, B, and C, following the previous findings (Figure 10). Employing the aqueous dispersion of 0.5% *wt.* NPs (lubricant D) yields a COF of 0.62, indicating the detrimental effect of NPs when added to water, due to their 3rd body abrasive behaviour. Interestingly in absence of the bulk lubricants in stage III, large differences in the COF values are observed showing COFs of 0.13 for lubricant A, around 0.42 for lubricants B and C, and 0.54 for lubricant D.

The slight increase in the COF of emulsion without NPs from stage II to III indicates that the film initially formed in stage II remains intact on the surface even after the bulk emulsion is replaced with water. On the contrary, the significant jump in COFs of emulsions with 0.25 and 0.5% *wt.* NPs to ~0.42 indicates the lack of an effective oil film on the surface in stage III. Hence, a different type of film is suspected to be formed in stage II and in presence of NPs compared to the NP-free emulsion. As pointed in section 3.3, strongly anchored fatty acids of NP-free oil droplets contribute to the formation of an effective film. With NPs, the film is weakly anchored and can easily be desorbed from the surface.

Figure 11 COF traces of lubrication with emulsions having (A) 0 (no NPs), (B) 0.25%, and (C) 0.5% wt. NPs, and (D) dispersion of 0.5% wt. NPs in water, in three stages (I. in water → II. in lubricants → III. in water).

3.5. Worn surface analysis

Wear scars and wear tracks on the balls and discs (corresponding to Figure 10) were analysed using *Joel JSM6490LV* SEM/EDS. Average roughness (R_a) of the worn area and the amount of removed material from the surface of the discs are also calculated over 100 μ m wear length from surface topographical images (see Figure 16) and results are summarised in Table 1. The amount of removed material is defined as the missing volume below the neutral plane and over full wear width, illustrated in Figure 16a. Figure 12 shows SEM images from the wear track on the disc lubricated with emulsion without NPs. In spite of having the lowest COF (see Figure 10), the SEM images show wide furrows, delamination, and signs of plastic deformation on the worn surface. With small amount of removed material from surface (see Table 1), this shows dominant two-body abrasive wear mechanism as a result of grooving asperity contacts [50]. Moreover, EDS spectrum from the worn area shows traces of Fe, Si, S, Ni, Cr, and Mn elements from the steel substrate and high amount of C (19.45%) and O (15.89%), from the triglyceride molecules of oil residue on the worn surface.

Figure 12 SEM images and EDS point analysis spectrum of worn area on the disc lubricated with emulsion without NPs (dashed arrow shows the EDS data acquisition point).

Figure 13 SEM images and EDS point analysis spectrum of worn area on the disc lubricated with emulsion with 0.25% wt. NPs (dashed arrow shows the EDS data acquisition point).

In comparison, Figure 13 shows lower (mild) wear on the worn area of disc lubricated with the emulsion with 0.25% *wt.* NPs. Presence of NPs within the deposited film promotes three-body abrasive wear with lower rate compared to the latter [50-52]. During the sliding contact and in presence of 0.25% *wt.* NPs, few NPs within the film get entrapped between the opposite surfaces and within void areas [53]. The entrapped NPs work as rigid 3rd bodies to distribute contact pressure and bridge the opposite surfaces' asperities to reduce wear [53,54]. EDS point spectrum from surface also shows signs of Si and Ti elements within the grooves. This indicates the mending action and possible tribo-sintering of NPs on the surface owed to the high temperature and high pressure of boundary regime lubrication [55].

Figure 14a shows the SEM images from the discs lubricated with 0.5% *wt.* NPs. Small plowing grooves and increased number of defect zones and removed material are evident with 0.5% *wt.* NPs compared to the latter (see Table 1). This is related to the presence of larger 3rd bodies (NP flocs) within the deposited film by association of several NPs, inducing abrasive wear [19,53]. To investigate the deposition propensity of NPs on worn surface, EDS mappings of the worn area on the discs lubricated with emulsions with 0.25 and 0.5% *wt.* NPs are shown in Figure 15, suggesting the deposition of NPs within surface asperities evidenced by tracing Si and Ti elements to the surface grooves whereas Fe element represents the steel substrate. Moreover, increasing the NPs mass fraction from 0.25 to 0.5% *wt.* appears to increase the deposition of NPs on the worn area surface [19], noticed by the increased presence of Si and Ti elements from 1% and 0.6% to 5.5% and 6.9% respectively.

By further increasing the mass fraction of NPs to 0.75 and 1% *wt.* (Figures 14b and 14c), larger and deeper grooves and higher removed material from surface are observed (see Table 1). In above the saturation mass fraction of NPs, more NP agglomerates are present in the bulk emulsion that interact with the deposited layer. Moreover, NP flocs within the deposited film and in the contact area are unable to penetrate between the surface asperities due to their large amorphous shapes, hence will remained entrapped between the asperities and aggravate the contact severity with higher wear and removed materials [28]. Therefore, it is suggested that while 0.25% *wt.* NPs reduces the dominant two-body abrasive wear of VO/W emulsion and results in a mild three-body abrasive mechanism, further increasing the mass fraction of NPs progressively increases the abrasive 3rd body contacts.

Figure 14 SEM images of worn area on the disc lubricated with emulsions with (a) 0.5%, (b) 0.75%, and (c) 1% wt. NPs.

	element weight (%)	
	0.25 wt% NPs	0.5 wt% NPs
Fe	57	41
Si	1	5.5
Ti	0.6	6.9

Figure 15 SEM images and EDS mapping of worn area on the discs lubricated with emulsions with (a) 0.25%, and (b) 0.5% *wt.* NPs.

Table 1 shows that average roughness (R_a) of the wear area on the disc does not change significantly when 0.25% *wt.* NPs are added to the emulsion, decreasing slightly from 0.447 μm with NP-free emulsion to 0.444 μm . The amount of removed material from the surface also increases insignificantly when 0.25% *wt.* NPs are added, from 15500 μm^3 to 17800 μm^3 . This shows the small induced abrasive role of NPs by providing 3rd body behaviour [55]. Increasing the NPs' mass fraction to 0.5% *wt.* has apparent negative effect on surface wear, increasing R_a to 0.593 μm and the removed material to 37700 μm^3 , thought related to formation of NP flocs within the deposited film with 0.5% *wt.* NPs. A second jump in R_a and the removed material is noted when 0.75% *wt.* NPs are present within the emulsion, increasing R_a to 0.825 μm and the removed material to 64000 μm^3 . This is thought related to extensive presence of agglomerates of NPs near the surface and around the contact area when the mass fraction of NPs is above the droplets' saturation mass fraction. This increases the near-surface vibrations and deteriorates the surface quality. Furthermore with 1% *wt.* NPs, R_a and the removed materials are 0.731 μm and 37200 μm^3 respectively. Wear track width also follows a same trend, increasing by addition of NPs with a peak of 1.147mm in presence of 0.75% *wt.* NPs.

Figure 16 3D surface topography and average 2D profiles of 100 μ m wear lengths on discs lubricated with emulsions with (a) no NPs, (b) 0.25%, (c) 0.5%, (d) 0.75%, and (e) 1% *wt.* NPs.

Table 1 Wear tracks' statistics on the discs lubricated with emulsions with 0 (no NPs) to 1% *wt.* NPs (wear length 100 μ m).

#	mass fraction of NPs within emulsion (<i>wt.</i> %)	average worn area roughness (μ m)	removed material from surface (μ m ³)	wear track width (mm)
1	no NPs	0.447	15500 $\pm$ 500	0.538
2	0.25	0.444	17800 $\pm$ 500	0.699
3	0.5	0.593	37700 $\pm$ 500	0.826
4	0.75	0.825	64000 $\pm$ 500	1.147
5	1.0	0.731	37200 $\pm$ 500	0.726

To find the correlation between NPs flocs' sizes and the worn surfaces topography, cross section profiles of the balls' wear scars were obtained over the full wear width and the scar profiles were characterised in terms of dominant wavelengths ($1/\lambda$) in space domain using Fast Fourier Transform (FFT) algorithm. The NPs flocs' sizes are estimated as half of the dominant wavelengths where NP flocs are assumed to remain entrapped within the surface asperities during contact [54]. As an example, Figure 17 illustrates sample surface profile 'a'. Using FFT algorithm, the constitutive sinusoidal waves of profile 'a' are found ('b' and 'c'), indicating dominant wavelengths of $1/5\mu\text{m}$ and $1/20\mu\text{m}$ ('d') and estimated particles' sizes of 100nm ('e') and 25nm ('f') respectively.

Figure 17 Schematic illustration of (a) sample surface profile, (b, c) constitutive sinusoidal waves, (d) FFT trace, and (e, f) size of abrasive particles corresponding to FFT peaks.

Figure 18 shows the SEM images, full width surface profiles, and associated FFT traces of the wear scars of the balls. Without NPs (Figure 18a), shallow grooves, homogenous surface profile, and signs of pits and scuffing are visible. FFT trace shows a peak near zero, indicating a dominant two-body abrasive wear. On the contrary Figure 18b shows that a more smooth wear surface is obtained with the emulsion with 0.25% *wt.* NPs. FFT trace shows two dominant frequency peaks near zero and 17 ($1/\lambda$). The near-zero FFT peak is attributed to two-body abrasive wear and the peak at 17 corresponds to a wavelength of 59nm , indicating the presence of 3rd bodies with average size of 29.5nm . This is in accord with the NPs' size measurement and supports the hypothesis of concurrent two-body and three-body abrasive wear in presence of 0.25% *wt.* NPs [50].

(A)

(B)

(C)

Figure 18 SEM images, 2D cross section profiles (black profile, $1\mu\text{m}$ units), and FFT traces (orange traces, arbitrary units, peaks are denoted by dashed arrows) of the wear scar on the balls lubricated with emulsions with (a) no NPs, (b) 0.25%, (c) 0.5%, (d) 0.75%, and (e) 1% *wt.* NPs.

In presence of 0.5% *wt.* NPs (Figure 18c), deeper and wider grooves compared to latter are noted. FFT trace shows a main peak at 8 $(1/\lambda)$, corresponding to the wavelengths of 125nm and the particle sizes of 62.5nm. This supports the hypothesis of the formation of NPs flocs by association of several NPs within the film by increasing the bulk NPs' mass fraction. Similar results are obtained for 0.75 and 1% *wt.* NPs with signs of pits and abrasive wear on the surface (Figures 18d and 18e respectively). FFT peaks of 8 and 7 $(1/\lambda)$ are measured in presence of 0.75 and 1% *wt.* NPs respectively, corresponding to particle sizes of 62.5nm and 71.4nm. This suggests that in above the saturation mass fraction, the size of NP flocs within the deposited film on the surface is relatively independent to the mass fraction of NPs. However, the rate of formation of agglomerates of NPs in the aqueous phase is thought to increase with increasing the mass fraction of NPs, aggravating the contact severity.

4. Conclusion

Effects of varying mass fractions of TiSiO_4 NPs on dispersion stability and lubricity of ultrasonically homogenised soybean VO/W emulsion are investigated. From the experimental results, following observations are noted.

- Dispersion stability of soybean oil droplets is low due to the hydrophobic attractions between the droplets. Dispersion stability can be enhanced by addition of TiSiO_4 NPs, through the steric shielding of oil droplets with NPs.
- 0.25% *wt.* NPs is adequate to stabilise the emulsions by partially covering the droplets surface. With 1% *vol.* oil, the surface of oil droplets becomes saturated with NPs in presence of 0.5% *wt.* NPs. Further increasing the mass fraction of NPs does not affect the droplets' size, but promotes the formation of NP agglomerates in the bulk emulsion.
- Polar soybean oil droplets have high adsorption tendency to metal surface, but shielding of droplets with NPs reduces the polarity and results in significantly less deposition of oil on the surface.
- Presence of NPs is detrimental to friction reducing property. The lowest friction on day #1 is obtained without NPs, attributed to the formation of an oil film on the surface rich in triglyceride molecules.
- With 0.25% *wt.* NPs, worn area roughness decreases and the mechanism of two-body abrasive wear with the NP-free emulsion moves towards a mild three-body mechanism. Increasing the mass fraction of NPs to 0.5% *wt.* results in the formation of NP flocs within the film which decreases the film's strength and results in a dominant 3rd body abrasive wear.
- Further increasing the mass fraction of NPs to 0.75 and 1% *wt.* does not affect the size of NP flocs within the film, but increases the rate of formation of NP agglomerates in the aqueous phase that increases near-surface vibration, friction and wear. However, further work is needed to determine the actual role of NP flocs and agglomerates in the bulk emulsion and in the contact area.
- Observations of the result suggest that for given oil concentration, there is a mass fraction of TiSiO_4 NPs to obtain good dispersion stability without compromising the lubricity properties.

5. Acknowledgements

Reza Taheri acknowledges the University of Wollongong APA/IPTA scholarships to carry out this research. Authors also acknowledge that some content of this paper was presented in the 6th World Tribology Congress (September 2017, Beijing, China).

6. References

- [1] Allende, D., Cambiella, A., Benito, J.M., Pazos, C., Coca, J., "Destabilization-enhanced centrifugation of metalworking oil-in-water emulsions: Effect of demulsifying agents", *Chemical Engineering and Technology*, 31, 2008, 1007-14.
- [2] Joseph, P.V., Saxena, D., Sharma, D.K., "Study of some non-edible vegetable oils of indian origin for lubricant application", *Journal of Synthetic Lubrication*, 24, 2007, 181-97.
- [3] Quinchia, L.A., Delgado, M.A., Reddyhoff, T., Gallegos, C., Spikes, H.A., "Tribological studies of potential vegetable oil-based lubricants containing environmentally friendly viscosity modifiers", *Tribology International*, 69, 2014, 110-17.
- [4] Norrby, T., "Environmentally adapted lubricants - where are the opportunities?", *Industrial Lubrication and Tribology*, 55, 2003, 268-74.
- [5] Adhvaryu, A., Biresaw, G., Sharma, B.K., Erhan, S.Z., "Friction behavior of some seed oils: Biobased lubricant applications", *Industrial and Engineering Chemistry Research*, 45, 2006, 3735-40.
- [6] Biresaw, G., Adhvaryu, A., Erhan, S.Z., "Friction properties of vegetable oils", *Journal of the American Oil Chemists' Society*, 80, 2003, 698-704.
- [7] Burton, G., Goo, C.-S., Zhang, Y., Jun, M.B.G., "Use of vegetable oil in water emulsion achieved through ultrasonic atomization as cutting fluids in micro-milling", *Journal of Manufacturing Processes*, 16, 2014, 405-13.
- [8] Adhvaryu, A., Erhan, S., Perez, J., "Tribological studies of thermally and chemically modified vegetable oils for use as environmentally friendly lubricants", *Wear*, 257, 2004, 359-67.
- [9] Fox, N., Stachowiak, G., "Vegetable oil-based lubricants - a review of oxidation", *Tribology International*, 40, 2007, 1035-46.
- [10] Chen, U.C., Liu, Y.S., Chang, C.-C., Lin, J.F., "The effect of the additive concentration in emulsions to the tribological behavior of a cold rolling tube under sliding contact", *Tribology International*, 35, 2002, 309-20.
- [11] Kimura, Y., Okada, K., "Lubricating properties of oil-in-water emulsions", *Tribology Transactions*, 32, 1989, 524-32.
- [12] Kamogawa, K., Akatsuka, H., Matsumoto, M., Yokoyama, S., Sakai, T., Sakai, H., Abe, M., "Surfactant-free o/w emulsion formation of oleic acid and its esters with ultrasonic dispersion", *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 180, 2001, 41-53.
- [13] Aveyard, R., Binks, B., Clint, J., "Emulsions stabilised solely by colloidal particles", *Advances in Colloid and Interface Science*, 100, 2003, 503-46.
- [14] Ridet, L., Bolzinger, A., Delepine, N.G., Dugas, P.Y., Chevalier, Y., "Pickering emulsions stabilized by charged nanoparticles", *Soft Matter*, 12, 2016, 7564-76.
- [15] Dai, W., Kheireddin, B., Gao, H., Liang, H., "Roles of nanoparticles in oil lubrication", *Tribology International*, 102, 2016, 88-98.
- [16] Marinova, K.G., Alargova, R.G., Denkov, N.D., Veleev, O.D., Petsev, D.N., Ivanov, I.B., Borwankar, R.P., "Charging of oil - water interfaces due to spontaneous adsorption of hydroxyl ions", *Langmuir*, 12, 1996, 2045-51.

- [17] Battez, A.H., J.L.Viesca, R.González, D.Blanco, E.Asedegbega, A.Osorio, "Friction reduction properties of a cuo nanolubricant used as lubricant for a nicrbsi coating", *Wear*, 268, 2010, 325-28.
- [18] Battez, A.H., Gonzalez, R., Felgueroso, D., Fernandez, J.E., Fernandez, M.d.R., Garcia, M.A., Penuelas, I., "Wear prevention behaviour of nanoparticle suspension under extreme pressure conditions", *Wear*, 263, 2007, 1568-74.
- [19] Battez, A.H., Gonzalez, R., Viesca, J.L., Fernandez, J.E., Fernandez, J.M.D., Machado, A., Chou, R., Riba, J., "Cuo, zro₂ and zno nanoparticles as antiwear additive in oil lubricants", *Wear*, 265, 2008, 422-28.
- [20] Kong, L., Sun, J., Bao, Y., Meng, Y., "Effect of tio₂ nanoparticles on wettability and tribological performance of aqueous suspension", *Wear*, 376-377, 2017, 786-91.
- [21] Luo, T., Wei, X., Zhao, H., Cai, G., Zheng, X., "Tribology properties of al₂O₃/tio₂ nanocomposites as lubricant additives", *Ceramics International*, 40, 2014, 10103-09.
- [22] Alves, S., Barros, B., Trajano, M., Ribeiro, K., Moura, E., "Tribological behavior of vegetable oil-based lubricants with nanoparticles of oxides in boundary lubrication conditions", *Tribology International*, 65, 2013, 28-36.
- [23] Kao, M.-J., Lin, C.-R., "Evaluating the role of spherical titanium oxide nanoparticles in reducing friction between two pieces of cast iron", *Journal of Alloys and Compounds*, 483, 2009, 456-59.
- [24] Arumugam, S., Sriram, G., "Preliminary study of nano- and microscale tio₂ additives on tribological behavior of chemically modified rapeseed oil", *Tribology Transactions*, 56, 2013, 797-805.
- [25] Liu, G., Li, X., Qin, B., Xing, D., Guo, Y., Fan, R., "Investigation of the mending effect and mechanism of copper nano-particles on a tribologically stressed surface", *Tribology Letters*, 17, 2004, 961-66.
- [26] Peng, D.X., Kang, Y., Hwang, R.M., Shyr, S.S., Chang, Y.P., "Tribological properties of diamond and sio₂ nanoparticles added in paraffin", *Tribology International*, 42, 2009, 911-17.
- [27] Trajano, M.F., Moura, E.I.F., Ribeiro, K.S.B., Alves, S.M., "Study of oxide nanoparticles as additives for vegetable lubricants", *Materials Research*, 17, 2014, 1124-28.
- [28] Jiao, D., Zheng, S., Wang, Y., Guan, R., Cao, B., "The tribology properties of alumina/silica composite nanoparticles as lubricant additives", *Applied Surface Science*, 257, 2011, 5720-25.
- [29] Song, X., Zheng, S., Zhang, J., Li, W., Chen, Q., Cao, B., "Synthesis of monodispersed znal₂O₄ nanoparticles and their tribology properties as lubricant additives", *Materials Research Bulletin*, 47, 2012, 4305-10.
- [30] Chen, Q., Zheng, S., Yang, S., Li, W., Song, X., Cao, B., "Enhanced tribology properties of zno/al₂O₃ composite nanoparticles as liquid lubricating additives", *Journal of Sol-Gel Science and Technology*, 61, 2012, 501-08.
- [31] Taheri, R., Kosasih, B., Zhu, H., Tieu, A., "Surface film adsorption and lubricity of soybean oil in water emulsion and triblock copolymer solution: A comparative study", *Lubricants*, 5, 2017, 1.
- [32] Vashisth, C., Whitby, C.P., Fornasiero, D., Ralston, J., "Interfacial displacement of nanoparticles by surfactant molecules in emulsions", *Journal of Colloid and Interface Science*, 349, 2010, 537-43.
- [33] Taheri, R., Kosasih, B., Zhu, H., Tieu, A.K., "Dispersion stability and lubrication performance correlation of vegetable oil-in-water emulsions with nanoparticle-shielded oil droplets", *Lubricants*, 6, 2018, 55.
- [34] Taheri, R., Kosasih, B., Zhu, H., Tieu, A.K., "Phase behaviour and lubricity of aqueous peo-ppo-peo and ppo-peo-ppo triblock copolymer solutions", *Tribology Transactions*, 60, 2017, 460-68.
- [35] Martin, S.J., Granstaff, V.E., Frye, G.C., "Characterization of a quartz crystal microbalance with simultaneous mass and liquid loading ", *Analytical Chemistry*, 63, 1991, 2272-81.
- [36] Kanazawa, K.K., Gordon, J.G.I., "The oscillation frequency of a quartz resonator in contact with a liquid", *Analytica Chimica Acta*, 175, 1985, 99-105.

- [37] Liang, P., Wang, H., Chen, C., Ge, F., Liu, D., Li, S., Han, B., Xiong, X., Zhao, S., "The use of fourier transform infrared spectroscopy for quantification of adulteration in virgin walnut oil", *Journal of Spectroscopy*, 2013, 2013, Article ID 305604.
- [38] Guillen, M.D., Cabo, N., "Relationships between the composition of edible oils and lard and the ratio of the absorbance of specific bands of their fourier transform infrared spectra. Role of some bands of the fingerprint region", *Journal of Agricultural and Food Chemistry*, 46, 1998, 1788-93.
- [39] Lerma-García, M.J., Ramis-Ramos, G., Herrero-Martínez, J.M., Simó-Alfonso, E.F., "Authentication of extra virgin olive oils by fourier-transform infrared spectroscopy", *Food Chemistry*, 118, 2010, 78-83.
- [40] Riazian, M., Montazeri, N., Biazar, E., "Nano structural properties of tio₂-sio₂", *Oriental Journal of Chemistry*, 27, 2011, 903-10.
- [41] Nilchi, A., Janitabar-Darzi, S., Rasouli-Garmarodi, S., "Sol-gel preparation of nanoscale tio₂/sio₂ composite for eliminating of con red azo dye ", *Materials Sciences and Applications*, 2, 2011, 476-80.
- [42] Zhang, S., Zhang, Z., Pei, J., Li, R., Zhang, J., Cai, J., Cui, J., "A novel tio₂-sio₂ aerogel nanocomposite absorbent: Preparation, characterization and photocatalytic degradation effects on automobile exhaust", *Materials Research Express*, 5, 2018, ID 025036.
- [43] Wei, D., Dave, R., Pfeffer, R., "Mixing and characterization of nanosized powders: An assessment of different techniques", *Journal of Nanoparticle Research*, 4, 2002, 21-41.
- [44] Machida, M., Norimoto, K., Watanabe, T., "He effect of sio₂ addition in super-hydrophilic property of tio₂ photocatalyst", *Journal of Materials Science*, 34, 1999, 2569-74.
- [45] Frelichowska, J., Bolzinger, M.-A., Chevalier, Y., "Effects of solid particle content on properties of o/w pickering emulsions", *Journal of Colloid and Interface Science*, 351, 2010, 348-56.
- [46] Chevalier, Y., Bolzinger, M.-A., "Emulsions stabilized with solid nanoparticles: Pickering emulsions", *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 439, 2013, 23-34.
- [47] Mojet, B.L., Ebbesen, S.D., Lefferts, L., "Light at the interface: The potential of attenuated total reflection infrared spectroscopy for understanding heterogeneous catalysis in water", *Chemical Society Reviews*, 39, 2010, 4643-55.
- [48] Bergonzi, I., Mercury, L., Brubach, J.-B., Roy, P., "Gibbs free energy of liquid water derived from infrared measurements", *Physical Chemistry Chemical Physics*, 16, 2014, 24830-40.
- [49] Stalgren, J., Claesson, P., Warnheim, T., "Adsorption of liposomes and emulsions studied with quartz crystal microbalance", *Advances in Colloid and Interface Science*, 89-90, 2001, 383-94.
- [50] Trezona, R.I., Allsopp, D.N., Hutchings, I.M., "Transitions between two-body and three-body abrasive wear: Influence of test conditions in the microscale abrasive wear test", *Wear*, 225-229, 1999, 205-14.
- [51] Allsopp, D.N., Trezona, R.I., Hutchings, I.M., "The effects of ball surface condition in the micro-scale abrasive wear test", *Tribology Letters*, 5, 1998, 259-64.
- [52] Kovaříková, I., Szewczyková, B., Blaškovitš, P., Hodúlová, E., Lechovič, E., "Study and characteristic of abrasive wear mechanisms", *Materials Science and Technology (online)*, 1, 2009, 1-9.
- [53] Ghaednia, H., Jackson, R.L., "The effect of nanoparticles on the real area of contact, friction, and wear", *Journal of Tribology*, 135, 2013, 041603/1-10.
- [54] Godet, M., "The third body approach. A mechanical veiw of wear", *Wear*, 100, 1984, 437-52.
- [55] Kato, H., Komai, K., "Tribofilm formation and mild wear by tribo-sintering of nanometer-sized oxide particles on rubbing steel surfaces", *Wear*, 262, 2007, 36-41.