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Sustainable Drag Reduction of Fatty Acid Amide-Based Oleogel Surface Under High-Speed Shear Flows

*Ali Zain Hameed and Sang Joon Lee**

***Nepenthes alata*-inspired micro/nano-textured lubricant-infused surface (LIS) has shown strong potential in the fields of drag reduction (DR), anti-biofouling, and self-cleaning. However, its surface-slippery property is largely degraded under turbulent shear flow conditions due to the loss of the impregnated oil. This condition inhibits its practical applications to marine vehicles. The mucus-impregnated tissue systems of marine creatures are primarily based on fatty acid amides (FAAs), such as erucamide or oleamide, which have been commercially utilized as solid-slip additives. A stable lubricant interface of erucamide-PDMS composite (EPC) oleogel is formed by cross-linking erucamide with PDMS gel network prior to infusion of silicon oil. In this study, the surface stability and lubricant retention of EPC are investigated in consideration of DR applications. The fabricated EPC-oleogel surface exhibits shear stable DR under harsh conditions, such as high pressure, temperature, and shear flow conditions. The surface shows a shear stable DR performance of about 14% even up to a high-speed flow of 12 ms^{-1}, corresponding to friction Reynolds number (Re_τ) of approximately 5000. The superior lubrication stability of FAA-oleogel at the flow conditions of cruising ships ensures its strong potential for sustainable fuel economy of marine vehicles.**

1. Introduction

LIS has a textured solid surface morphology, in which a viscous liquid lubricant is infused.[1] Either the capillary force or chemical affinity of the lubricant and the surface structures holds the lubricant inside the surface. Most immiscible liquids can slip on these LIS surfaces without sticking. Therefore, LIS has been applied to various fields including anti-biofouling, drag reduction (DR), anti-icing, and droplet manipulation.[2–7]

Energy consumption of marine vehicles is majorly dissipated to overcome skin friction, induced by prevailing shear flows around the hulls. Hence, sustainable DR capability of LIS under turbulent shear flow conditions is a challenging research topic. The capillary force of the rough surface structures of LIS is insufficiently strong to hold the lubricant layer on the surface from high-speed shear flows, thereby leading to the depletion of lubricant.[1,4,5,7–11] Marine creatures have evolved to develop specialized surface structures for holding the lubricating mucus inside their surface structures to avoid the deposition of fouling matters.[12,13] FAAs such as oleamide and erucamide, have been utilized as commercial slip additives. They are a major chemical component of the slippery surface of marine creatures, especially mussel shells.[14]

Eco-friendly erucamide or oleamide-PDMS composite surfaces were developed for sustainable anti-biofouling performance given that FAAs have excellent anti-biofouling properties.[15–17] The anti-biofouling potential of these composite surfaces can be enhanced by the impregnation of oil in these surfaces to obtain FAA-PDMS composite oleogel surfaces.[18] Lubricants are absorbed into the porous PDMS polymer networks, contributing to the formation of a continuous liquid lubricant film on the surface. The low sliding angle (SA) and contact angle hysteresis (CAH) of the FAA-oleogel surface indicate the DR potential of this surface in practical applications.

In this study, we focused on stabilizing the slippery property of the FAA-oleogel. Thus, the interaction of slip and anti-blocking agents (inorganic filler materials) in FAA-oleogel surface was utilized, and the effects on the stability of shear-induced DR performance were investigated. We also enhanced the retention of lubricant layer of the FAA-oleogel by adopting the capillary effect of rough surface structures. The fabricated FAA-oleogel samples were tested under harsh conditions of high pressure, turbulent shear flows, and large temperature variations in consideration of harsh environments encountered by the ship hull in the oceans. As a result, the proposed FAA-oleogel samples successfully maintained their slippery property with slight degradation under adverse temperature and high-pressure conditions. The lubricant film was strongly adhered to by the retention of slippery property under strong shear force and shear flow conditions. These results demonstrate strong

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potential of FAA-oleogel surfaces in practical application to marine vehicles.

2. Results and Discussion

2.1. Slippery Property of Fatty Acid Amide (FAA)-based Oleogel

Figure 1 illustrates a schematic of FAA-oleogel impregnated with solid and liquid lubricants. The liquid lubricant is confined in a molecular mesh of the PDMS polymeric network. It is replenished when the network experiences external stimuli, such as shear force.[18] The irregular deposition of erucamide with flakier surface structures leads to a formation of nanoscale surface roughness with the aid of hydrophobic carbon chains, which always face outward the coated surface.[19–21] The surface roughness exhibits slippery features under the action of external shear forces. It is also responsible for the solid slip behavior of the Erucamide-PDMS composite (EPC) surface (Figure 1c,d (iv)). The solid and liquid lubricants work in synergy, and they complement each other's slippery properties. The extension of the erucamide surface structures helps in the confinement of the infused silicon oil molecules, thereby increasing the thickness of the lubricant film (Figure 1a). The impregnated silicone oil provides free mobility to the erucamide layers in the pool of liquid lubricant (Figure 1a,c).

Erucamide molecules have two ends, a hydrophilic amide group and a hydrophobic carbon chain (Figure 1b). When FAAs are dispersed into the PDMS polymer in the liquid state, they are absorbed in the amorphous regions of the polymeric material. In the solidification phase, they start to migrate toward the surface, owing to the difference in the surface energies of the polymer and FAAs in the solid state. The ease of migration of FAAs depends upon their size. A monolayer is formed by the embedding of carbon chains of the FAA molecule into the polymer because of their similar chemical properties and the amide group faced outside. Subsequently, bilayer is formed by the interaction of the amide groups of the first and second layers by hydrogen bonding.[19–22] These bilayer structures are irregularly stacked on the polymer surfaces in a form of thin overlapping sheets. Thus, they can glide smoothly over each other under the influence of external forces (Figure 1a,c,d (iv)).[20,23] This condition is the basic principle of the sliding phenomena of the solid lubricant layer, contributing to the slip property of this material.

DR surfaces used for marine applications require a shear-stable slip agent without surface degradation due to the depletion of FAA. The surface structure of erucamide bilayer is thermodynamically stable among various structures.[19–21,23,25] The gliding of multilayer structures under the action of a shear force is attributed to the lack of affinity between the carbon chains of the two adjacent bilayer structures (Figure 1c). These loosely bound structures of erucamide surface are prone to depletion of the material in contact with it, thereby changing the wettability of the erucamide surface.[20,24–26]

Inorganic filler materials, such as silica or talc, have been used as anti-blocking agents (ABs). They are utilized to regulate the surface depletion of slip additives.[27–30] Hydroxyl groups on their surfaces preferably interact with organic slip additives by hydrogen bonding and slow down the migration of the slip additives.[31] They also enhance surface roughness, providing positive impact on the reduction of surface friction.[23,30,32] To check the feasibility, various ABs with different weight percentages (wt.%) were incorporated into 5 wt.% EPC gel. ABs affect the stability of the surface slip additives in terms of durability in the slippery property of the oleogel surface. The sliding time (ST) of a 10 μL water droplet was recorded on a 75 mm long glass substrate inclined at a SA of 15°. The slippery property of EPC gel was considerably decreased with the increase in washing time. However, the AB-modified EPC samples exhibited almost consistent properties irrespective of the washing time, consistent with the results of previous studies (Figure S1, Supporting Information).[23,30,32]

Silica microparticles were preferably used as ABs, owing to their low cost, compatibility with polymer network, and dispersion property in the EPC solution. The effect of silica concentration on the depletion of FAA and stabilization of slippery property of EPC-oleogel surface was examined through shear force experiments. The FAA-oleogel samples modified with different concentrations of silica particles were mounted on the platform of a spin coater to experience shear forces applied by the rotations of the spin coater (Figures S2a,b, Supporting Information). Two experiments were conducted using the spin coater. In the first experiment, the ST was compared with the rotation speed (RPM) of the spin coater while maintaining constant rotation time (RT) at 10 s. In the second experiment, the ST was compared with RT while maintaining the rotation speed at 1000 RPM. No intermediate impregnation of lubricant was observed in both experiments. The excess lubricant that appeared on the surface was removed prior to the shear force experiment by tilting the samples at approximately 70° for 15 min. After the exposure to a strong shear force, the ST value of a 50 μL droplet was recorded for an FAA-oleogel sample at 15° inclination.

As a general trend, the ST increases with the increase in RPM or RT. The EPC control sample (0 wt.% silica) shows a considerable degradation in the slippery performance for RPM and RT variations. The applied shear force induces variation in the wettability of the EPC gel surface, which contributes to the depletion of the impregnated lubricant. On the contrary, silica-modified EPC samples (0.25 wt.%, 0.5 wt.%, and 0.75 wt.%) exhibit consistent sliding performance. In addition, the stability tends to be enhanced with the increase in silica concentration. The performance of ABs is further enhanced after 48-h interval due to the delayed blooming time of the slip additives and enhancement of surface asperities.[30] However, as the concentration of silica increases further, the slippery property is substantially degraded. The concentration of filler affects the density and viscosity of the EPC solution, which in turn affects its flowability (Figure S2c, Supporting Information). The high density of the EPC solution reduces the absorption capacity of lubricant (silicon oil) in the oleogel surface. It also decreases its flowability, resulting in uneven surface coatings, which in turn increase the ST. The ST versus RT curves indicate an initial degradation of slippery performance for a certain time at constant RPM conditions, and the slippery property is regenerated subsequently (Figure S2c (iii, iv), Supporting Information). The exposure to a constant shear force for a long exposure time leads to the depletion of slippery property until the equilibrium

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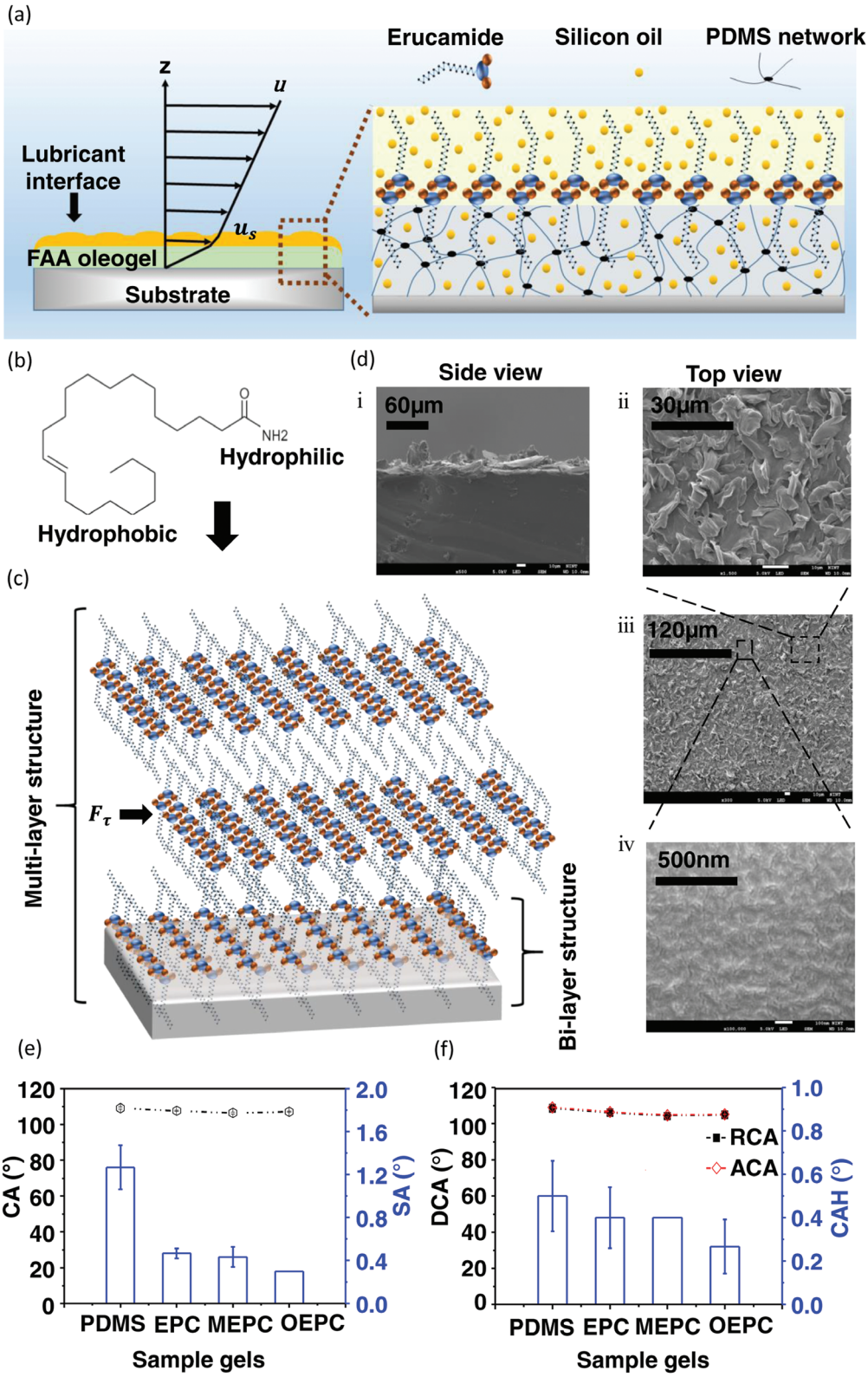


Figure 1. a) Schematic of surface slip over the FAA-oleogel surface (left) and conceptual illustration of the EPC-oleogel (right). b) Chemical structure of erucamide with dual wettability. c) Conceptual surface structure of erucamide on EPC surface and sliding of bilayer structure under the action of an applied shear force (F_τ). d) SEM images of silica NC coating over MEPC surface with side view (i) and top view (ii–iv). The top view of the NC-coated MEPC (iii) has randomly distributed NC μ-structures (ii), and flakier surface nanostructures are exposed to the middle of μ-structures (iv). e) CA of 5 μL droplet (left) and SA of 10 μL droplet (right) of PDMS and FAA-oleogel samples. f) DCA (right) and CAH (left) of a 10 μL droplet.

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lubricant concentration is maintained in the oleogel. Further exposure to the same constant shear force gives rise to replenishment of the lubricant film on the oleogel surface, which regenerates the slippery property of the surface. The ST versus RT curves also represent more pronounced effects of the applied shear force compared with the ST versus RPM curves in terms of the degradation of slippery property. These results indicate that the proposed FAA-oleogel is more stable to the applied shear force, compared with the exposure time. Subsequently, silica concentration was optimized for the modified EPC (MEPC) sample with 0.75 wt.% silica as AB material.

In general, the gel-based surfaces are facile, scalable, and cost-effective, compared with textured LIS surfaces. However, the smooth surface morphology of the gel-based surfaces induces a major problem in the depletion of lubricant film under the conditions of applied pressure or shear flows. The chemical affinity between the polymer matrix and the liquid lubricant is insufficiently strong to sustain the shear flow conditions encountered by actual marine vehicles. The capillary force induced by rough surface structures holds the surface lubricant film. The utilization of LIS under harsh conditions is essentially required for practical applications.[11,33] Hexamethyldisilazane glycidyloxypropyltrimethoxysilane (HMDS-GPTMS)-modified titania silica nanocomposite (NC), with a contact angle (CA) of 161.5°, was coated on the MEPC surface to enhance the capillary.[34] Silica NC coating has high stability, scalability, and affinity to silicon oils, considerably enhancing the sliding performance of optimized MEPC (OEPC) gel surface. On this basis, we establish a micro/nano-structured gel-based interface in which the NC-coated μ-structures are spaced apart by the nanostructures of erucamide layered surface (Figure 1d).

The CA of PDMS gel is slightly higher than that of the FAA-oleogel samples due to the surface presence of migrating contents in the EPC gel samples. PDMS gel exhibits a SA of approximately 1.3°, higher than the EPC and MEPC gels (≈0.5°). The OEPC gel shows an excellent slippery property with an SA of approximately 0.3°. This finding is attributed to the enhancement of lubricant film thickness, owing to the additional layer of surface roughness (Figure 1e). The CAH measured through the dynamic CA (DCA) analysis was evaluated from the difference between advancing and receding CAs (ACA and RCA). The CAH of PDMS gel is approximately 0.5°. The EPC and MEPC gels (CAH ≈ 0.4°) show enhanced slippery properties because the activation energy used by a droplet to move between different metastable states is required. Especially, the OEPC gel further reduces the CAH to approximately 0.3° because of the combined effect of the micro/nanoscale roughness of silica NC and the surface structures of erucamide (Figure 1f).

2.2. Stability of FAA-Oleogel

Practical applications, such as surface coating of marine vehicles, would face a series of sustainability challenges due to extreme marine environments. For sustainability in temperature variations, the fabricated FAA-oleogel samples were placed at a low-temperature condition by maintaining the temperature close to 0 °C for seven days in a refrigerator. The daily temperature variation is shown in Figure S3, Supporting Information. The excess surface lubricant was removed by tilting the samples, as explained earlier. The ST value of 50 μL droplet on the 75 mm glass substrate with 15° SA was recorded at an interval of 24 h. PDMS gel shows a droplet pinning phenomena after 48 h at low-temperature conditions. All the FAA-oleogel samples exhibit consistent sliding performance with almost no variation (**Figure 2**a). The smooth PDMS gel surface forms a thin lubricant film with inefficient replenishment of lubricant. Weak retention of lubricant film at low-temperature conditions was demonstrated by high ice adhesion strength of PDMS gel.[35] ST values of all FAA-oleogel surfaces are very low (< 1s). The proposed OEPC gel stands out from the rest, owing to its strong retention of thick lubricant film, caused by the capillary force of the NC coating (Figure 2b,c).

The high-temperature sustainability of the oleogel samples was tested at 100 °C for 24 h, by placing them into an oven. Marine vehicles do not experience such high temperatures; however, this type of harsh condition can prove the applicability of FAA-oleogel to other engineering fields. The ST of each sample was measured immediately after removing it from the oven every 1 h, under the same conditions as conducted in the low-temperature experiment. In this high-temperature case, PDMS gel loses its slippery property after 4-h exposure to high temperature.

This condition is attributed to the depletion of lubricant film due to the weakening of the Van der Waals force between silicon oil film and PDMS gel surface. FAA-oleogel samples, on the contrary, show initial weakening of the sliding property in the first 2 h and thereafter sustained (Figure 2d). Some oil contents deposited on the FAA-oleogel samples evaporated, leading to a slight initial degradation of ST. The surface structures of erucamide are also responsible for the entrapment of silicon oil in the oleogel surface, leading to the stabilization of sliding times for 24 h. The filler materials incorporated with surface roughness help the MEPC gel to obtain better performance than EPC gel. The fabricated FAA-oleogel samples show a slight loss of slippery property up to 6 h, and then become stabilized afterward. OEPC gel also loses the excessive lubricant in the first 2 h, and the micro/nano-roughness maintains a consistent slippery property until 24 h.

The fabricated FAA-oleogel samples were mounted in a custom-built high-pressure flow facility to check the high-pressure sustainability of the test samples under dynamic pressure conditions (**Figure 3**a) (Figure S4, Supporting Information). The applied pressure under shear flow conditions was considerably higher than the pressure encountered by marine ships under normal operation conditions. The pressure in the flow facility varied from 0.1 to 0.6 MPa, and each test sample was exposed to the given high-pressure flow conditions for 10 s. The sliding velocity (SV) of the test samples was measured for a 50 μL droplet on a glass substrate with 15° SA. Each sample was tested at instances immediately after the experiment, that is, after 1 h and after 8 h of the high-pressure flow exposure, to observe the lubricant retention and replenishment capability of the FAA-oleogel samples. Samples were lubricant impregnated for 12 h between two consecutive pressure channel experiments. Flow velocity through the test section was calculated by dividing the flow rate with cross-sectional area. The slippery property of PDMS gel

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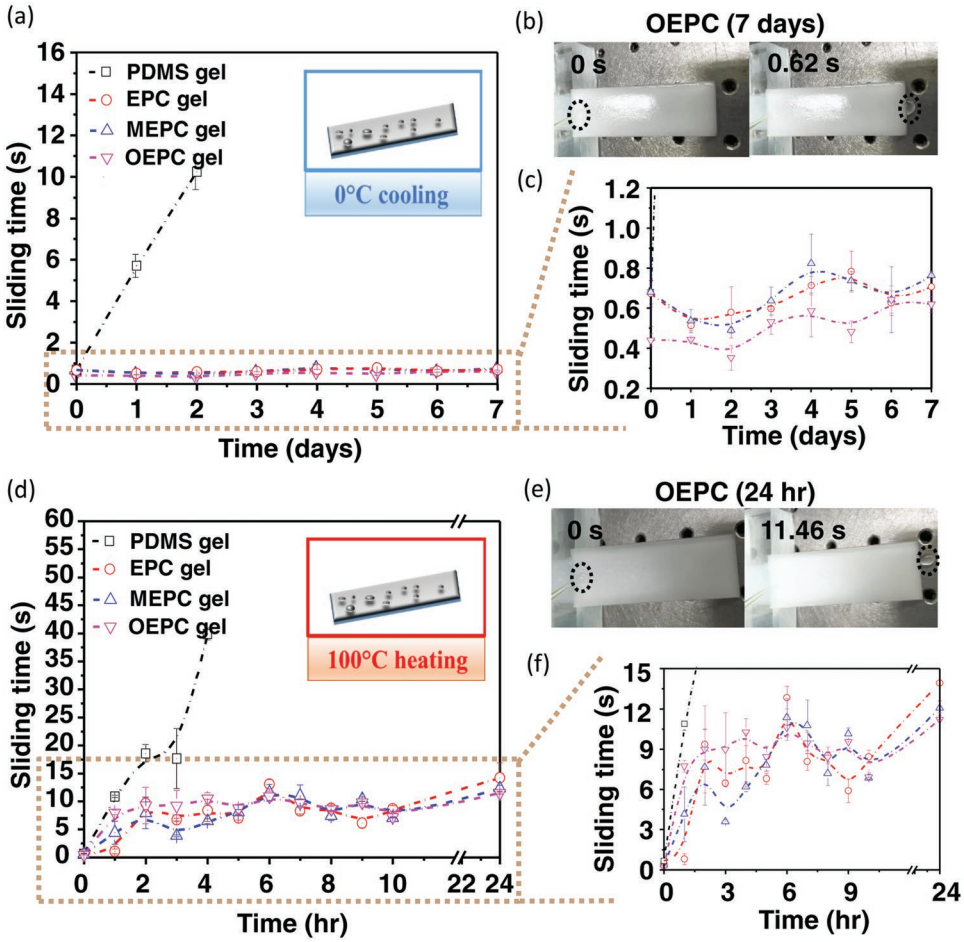


Figure 2. Temperature sustainability of the oleogel samples; slippery property of 50 µL droplet on a 75 mm length substrate with 15° SA was evaluated by exposing the PDMS gel and FAA-oleogel samples to extreme temperatures. a) Comparison of ST values of the test samples maintained at 0 °C for seven days and c) magnified version for better comparison. d) Comparison of ST values of the test samples maintained at 100 °C for 24 h, and f) their magnified view. ST of OEPC b) after seven days at 0 °C and e) after 24 h at 100 °C.

degrades linearly with the increase in pressure in the channel. Thus, SV continuously decreases and ultimately ends up with droplet pinning at 0.6 MPa, immediately after the experiment. The intrinsic weak slippery property and insufficient replenishment of lubricant result in insignificant regeneration of SV at t = 1 and 8 h after the experiment. However, all the FAA-oleogel samples show reliable slippery properties at t = 0 h even for the extremely high pressure of 0.6 MPa. The lubricant replenishment of FAA-oleogel samples is also reliable, compared with PDMS gel, at t = 1 and 8 h (Figure 3c). Especially, OEPC gel has a higher SV value than EPC and MEPC gels at lower pressure conditions of 0.1–0.2 MPa at t = 0 h (Figure 3c (i, ii)). The capillary force induced by the micro/nano-structures helps the lubricant film to sustain the slippery property under pressure-induced harsh environment in the channel.

At high-pressure values of 0.4–0.6 MPa, OEPC gel exhibits almost similar sliding performance to other FAA-oleogel samples at t = 0 h. In general, high-pressure environments limit the capability of the µ-structures of OEPC gel to effectively hold the lubricant film (Figure 3c (iii, iv)). As a general trend, all FAA-oleogel samples have higher SV values with the increase in flow velocities than PDMS gels at all times under high-pressure exposure, owing to their superior lubrication property. At a flow velocity of 17 ms^{-1}, which is higher than the cruising speed of large-scale marine vehicles, FAA-oleogels show sustainable lubrication retention behavior. MEPC gel improves slippery property and enhances lubricant replenishment compared with EPC gel, as demonstrated by its high SV values at high flow speeds.

Shear force sustainability experiment was conducted under the same conditions used for the sample optimization experiment (Figure S2, Supporting Information). This study is helpful for comparing the shear responses of the oleogel samples in more detail. PDMS gels show a shear-induced depletion of the lubricant film due to its weak adhesion (Van der Waals force). ST values are continuously increased in the curves for RPM and RT for PDMS gel. EPC-oleogel (0% silica sample) performs differently for RPM and RT conditions. MEPC gel exhibits a very stable slippery performance for RPM and RT conditions, compared with PDMS and EPC gel surfaces (**Figure 4**c,d). ABs restrict the depletion of lubricant from surface structures,

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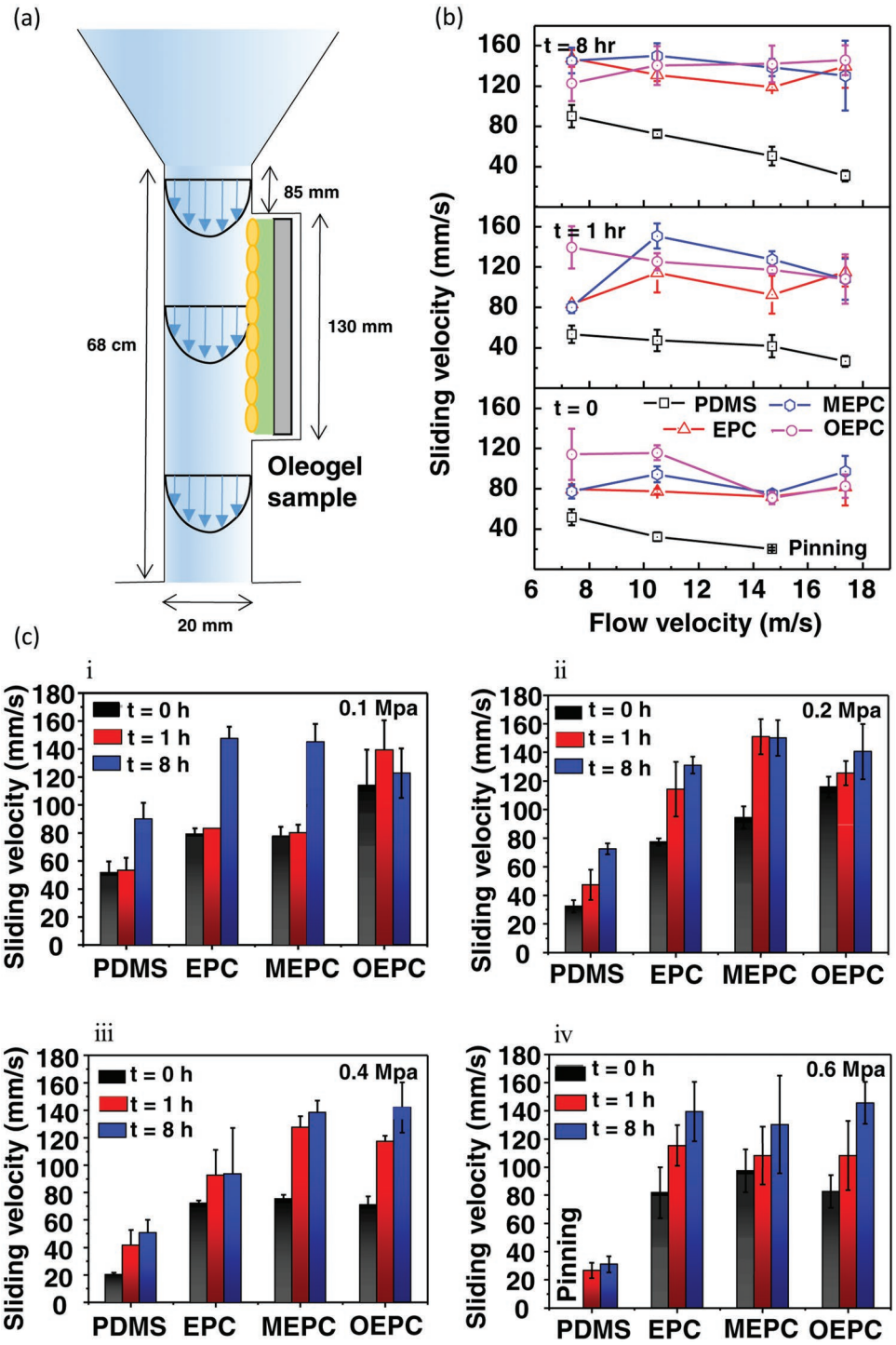


Figure 3. Sustainability of the oleogel samples under high-pressure flows; slippery property of 50 µL droplet on a 75 mm substrate with 15° SA was evaluated by exposing the PDMS gel and FAA-oleogel samples to high-pressure flow conditions. a) Schematic of the pressure channel with a test sample flush mounted along the side wall of the channel. b) Comparison of SV with FV immediately after exposing to high-pressure flow for 10 s (base), after 1 h (middle), and 8 h (top). c) Comparison of SV values of different oleogel samples under high-pressure flow conditions. The SV was evaluated at t = 0, 1, and 8 h after high-pressure exposure for 10 s, and the tests were conducted at different pressure conditions of 0.1 (i), 0.2 (ii), 0.4 (iii), and 0.6 MPa (iv).

thereby ultimately stabilizing the wettability of the surface under the applied shear force. In addition, the stability of the solid slip additive helps in regulating the depletion of liquid lubricant. As a result, MEPC has enhanced shear force stability. OEPC slightly enhances the slippery property of MEPC and reduces the sliding time from 1.42 s to 1.05 s at 3000 RPM and

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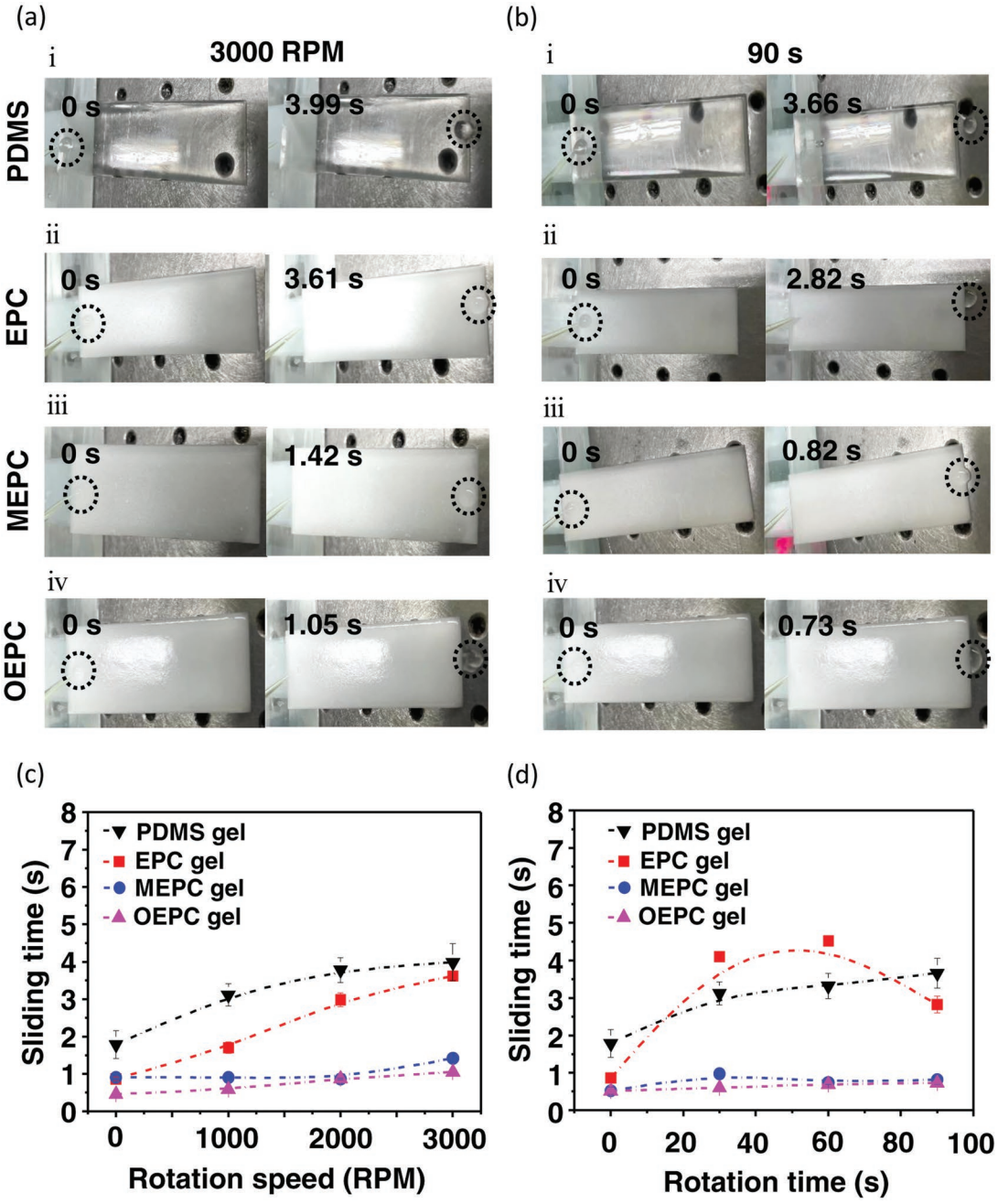


Figure 4. Shear force sustainability of the FAA-oleogel surfaces; slippery property of 50 µL droplet (75 mm substrate with 15° SA) was evaluated by maintaining the PDMS gel and FAA-oleogel samples under exposure of strong shear forces applied by the rotation of a spin coater. ST of test samples after rotating at a) 3000 RPM for 10 s and b) 1000 RPM for 90 s. c) Comparison of ST versus RPM at a constant RT of 10 s, d) ST versus RT at constant rotation speed of 1000 RPM.

from 0.82 to 0.73 s at 90 s RT ((Figure 4a,b)). This enhanced slippery property results in higher surface slip velocities on the surface. The thick lubricant film formed on the surface is sustained by the combined effects of capillary action and chemical affinity of silica NC coating. In addition, the stiff µ-structures of silica NC reduces the shear impact on the flakier EPC nanostructures, thereby avoiding their depletion. This approach is an essential prerequisite for long-term lubrication of the FAA-oleogel surface.

2.3. Shear-Stable DR of FAA-Oleogel

Shear flow sustainability experiment was also conducted at the high-speed cavitation tunnel (HCT) at the Korean Research Institute of Ship and Ocean Engineering (KRISO, Daejeon, South Korea) (Figure S5, Supporting Information). The DR capability of FAA-oleogel surfaces was evaluated at high-speed flows, and the corresponding Reynolds number ranged from 1.3×10^6 to 7.6×10^6. The frictional forces acting on the oleogel

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samples were recorded at flow speeds ranging from 2–12 ms^{-1} at intervals of 1 ms^{-1}. Each measurement required approximately 4 min at each flow condition. Friction forces were recorded two times for each flow speed, and each force value is a statistical average of approximately 1200 instantaneous force data. After mounting each sample in the test section, water was circulated in HCT for approximately 15 min at 6–7 ms^{-1} to remove air bubbles and excess lubricant deposited on the oleogel sample. This removal process is helpful for accurate measurement of the lubrication property. Water temperature was maintained in the range 16–17 °C through the experiments. OEPC sample was selected for the DR experiment because of its stable and sustainable excellent slippery property. DR measurement for OEPC was conducted two times for checking the experimental reliability, and the results of the two experiments were averaged. Consecutive experiments using the same oleogel sample show approximately 5% difference in DR performance. All the experimental conditions were maintained consistent; thus, the difference might result from the installation (alignment) error of the test sample on the test plate. (**Figure 5**). A period of 12 h lubricant (silicon oil) impregnation was observed between consecutive tests.

The output data include the friction coefficient (C_f) of the sample plate in terms of Reynolds number along the flow direction (Re_L). The length (L) used in the calculation of Re_L is the distance 690 mm from the leading edge of the platform to the endpoint of the second plate, as depicted in Figure 5a. Local friction coefficient for a turbulent boundary layer flow over a flat plate with a sharp leading edge under no-slip boundary conditions can be expressed by Equation S1, Supporting Information. The experimental results of C_f agree well with Equation S1, Supporting Information, unto Re_L of 4.5×10^6, and they diverge thereafter. This finding may be attributed to the limitation of the experimental facility for which high Re_L leads to the pressure build-up in the test section, thereby slightly increasing the friction coefficient. The reduction in C_f for the OEPC gel supports the presence of slip velocity on the oleogel surface, compared with a flat anodized aluminum plate. The C_f values show nearly consistent variation, irrespective of Re_L, demonstrating sustainable slippery performance. On the contrary, C_f values of PDMS gel are similar to those of the flat aluminum plate at the beginning of the experiment. It starts to diverge subsequently, and then exhibits slightly higher surface friction than the control sample (Figure 5b). This finding indicates that PDMS gel cannot sustain its lubricating ability on the surface. A bare PDMS gel surface with depleted lubricant film may have a high potential for droplet pinning. The drag coefficient was calculated by integrating the friction coefficients over the surface of the plate, which in turn obtains drag force (Equations S2 and S3, Supporting Information).

Re_τ is used to compare the DR capability of different surface technologies under various flow conditions (Equation S4, Supporting Information). The average frictional DR ($C_{f,\text{flat plate}} - C_{f,\text{oleogel}}/C_{f,\text{flat plate}}$) of the proposed OEPC has nearly stable and consistent values, irrespective of Re_τ (Figure 5c). The DR performance of OEPC is in the range of 12% to 16% with an average value of ≈14% up to $Re_\tau = 5000$. However, the PDMS gel begins with a slightly negative DR at the beginning of the experiment. This result indicates that the PDMS gel depletes most of its lubricant during the preparatory high-speed water circulation to remove air bubble inside the cavitation tunnel. The increase in Re_τ significantly increases the frictional drag. Especially after $Re_\tau = 2700$, the PDMS gel exhibits a large increase in drag of approximately 15% compared with the smooth aluminum plate. The high DR performance of the OEPC is compared with different drag-reducing surfaces introduced in the literature (Figure 5d).[6,36–50] Conventional micro/nano-textured surfaces focused on the stability enhancement of air layer as the source of their slippery properties. However, the inherent problem of these techniques is that the flowing fluid can easily diffuse into these rough textured structures under shear-flow conditions. As a result, most textured/superhydrophobic surfaces lose their slippery property at high-speed flow beyond $Re_\tau = 2000$. Xu et al. obtained a DR ability for a short period of time unto $Re_\tau = 6000$.[48] However, the DR performance was evaluated for a very short time duration and was unstable due to the stability issue of the air plastron on their superhydrophobic surface. In addition, DR starts to decrease after $Re_\tau = 4000$, indicating its technical limitation in practical applications to drag-reducing surfaces under high-speed shear flows. This type of surface also has scalability problems owing to scale-up difficulties of the patterned surface morphologies. On the contrary, the proposed FAA-oleogel provides a facile, scalable, and sustainable skin friction drag-reducing solution with a stable DR even performance under highly turbulent shear flow conditions.

3. Conclusion

The proposed FAA-oleogel surface is composed of an erucamide as a solid lubricant in a pool of silicon oil as a liquid lubricant. Surface depletion of slip lubricant (FAA) is a potential challenge to securing stable lubrication surface of FAA-oleogel. ABs were utilized to suppress the surface depletion of FAA for maintaining stable sustainability of the slippery property under the conditions of applied shear force. In addition silica NC coating was found to enhance the retention of the surface lubricant film with the aid of capillary force of the random structures in surface roughness. The DR and lubrication stability of the PDMS gel and FAA-oleogel samples were tested under harsh flow conditions that can be encountered by hulls of marine vehicles. The PDMS gel used as a control surface shows droplet pinning because of the weak adhesion of the lubricant film and inefficient replenishment of the infused lubricant. The FAA-oleogel samples, on the contrary, exhibit a sustainable slippery property even under severe pressure, temperature, and shear flow conditions. The nanoscale roughness on the surface structures of erucamide helps in the retention of liquid lubricant, and the sliding of the erucamide surface layer enhances the slippery property. The fabricated FAA-oleogel shows a shear-stable friction DR performance of approximately 14%, irrespective of Reynolds number. The developed oleogel surface maintains high DR sustainability up to $Re_\tau = 5000$, whereas most DR surface technologies fail in terms of DR performance prior to $Re_\tau = 2000$. The shear-stable slippery property of the FAA-oleogel surface under highly turbulent flow conditions can be utilized for achieving sustainable DR of marine vehicles.

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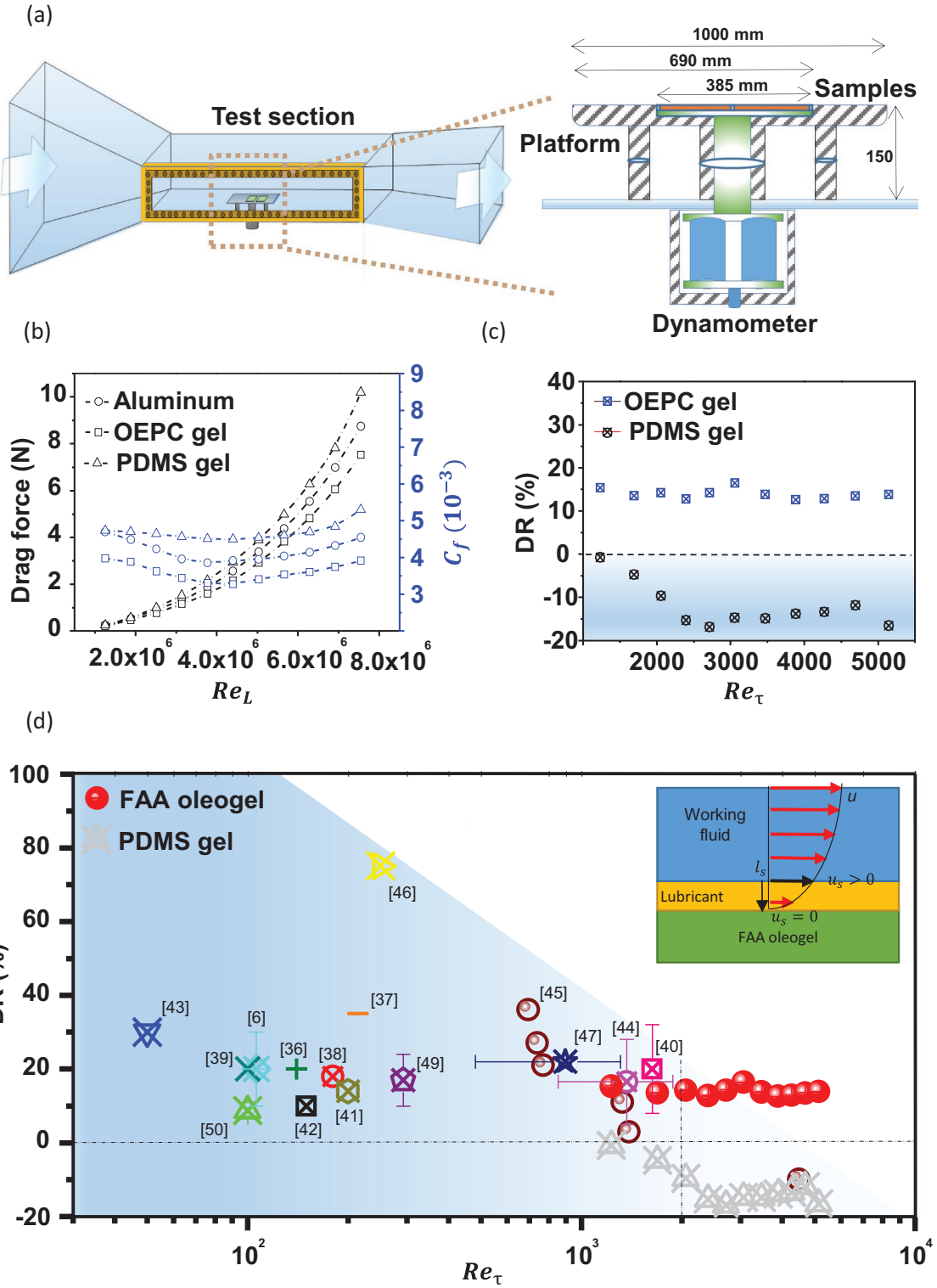


Figure 5. a) Schematics of the test section (left) and sample installation platform (right) of the KRISO cavitation tunnel. b) Comparison of drag forces (left) and C_f values (right) according to Re_L for aluminum plate (control), OEPC, and PDMS gel samples. c) Variation of DR according to Re_τ for OEPC and PDMS gel samples. d) Comparison of frictional drag-reducing (textured/ superhydrophobic) surface technologies from literature with the present FAA-oleogel and PDMS gel surfaces. The horizontal and vertical error bars of the data points represent the achieved range of DR for the given range of shear Reynolds number, respectively. The horizontal dotted line (c,d) indicates the reference line for a surface with 0% DR. Vertical dotted line (d) indicates $Re_\tau = 2000$, before which most surfaces in literature show DR feature. Illustration of surface slip of the FAA-oleogel with surface slip velocity (u_s) and slip length (l_s) (top right).

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4. Experimental Section

Materials: Erucamide ($C_{22}H_{43}NO$, MW = 337.59, purity >85.0%) was obtained from Tokyo Chemical Industry (Japan). Polydimethylsiloxane (PDMS, Sylgard184) was purchased from Dow Chemical (MI, USA), and toluene ($C_6H_5CH_3$, MW = 92.14, ACS reagent, purity ≥99.5%) was obtained from Sigma Aldrich (South Korea). Primer coating (1200 OS primer) was purchased from Dow Corning (USA). Silicon oil ($[\text{-}Si(CH_3)_2O\text{-}]_n$, ν = 5 cSt (25 °C)), titanium tetraethoxide ($Ti(OC_2H_5)4$, MW = 228.11, technical grade), tetraethylortho-silicate ($Si(OC_2H_5)_4$, MW = 208.33, 98%), glycidoxypropyltrimethoxysilane (GPTMS) ($C_9H_{20}O_5Si$, MW = 236.34, purity >98.0%), hexamethyldisilazane (HMDS) ($(CH_3)_3SiNHSi(CH_3)_3$, MW = 161.39, 98.0%), acetic acid (CH_3CO_2H, MW = 60.05, purity >99.7%), propanol ($(CH_3)_2CHOH$, MW = 60.10, anhydrous, 99.5%), silica gel (230–400 mesh ASTM, MW = 60.08), and ethanol (CH_3CH_2OH, MW = 46.07%, 94.5%) were purchased from Sigma Aldrich (South Korea). Ammonia solution (H_3N, MW = 17.03, 28%) was obtained from Junsei Chemical (Japan).

Synthesis of Silica Nano-Composite Coating: The HMDS-modified hybrid TiO_2–SiO_2 gels were obtained by following the reference without any modification.[34] A 0.6 g of the gel was dispersed into 40 mL of propanol by ultrasonication for 20 min in a water bath at room temperature. A 5 g of HMDS was added into the solution, and then again subjected to ultrasonication for 1 h. From this solution, 0.5 g of GPTMS was incorporated and stirred using a magnetic stirrer for 30 min.

Synthesis of the FAA-Oleogel Samples: EPC sample was fabricated with a 5 wt.% erucamide by following the recent reference without any modification.[18] Gel adhesion to a substrate material was ensured using a primer foundation. Primer was deposited on the substrate by dropping to cover the entire surface. Thereafter, a spin coater (spin-3000D, Midas System, South Korea) was obtained, at 900 RPM for 30 s to remove the excess amount of primer on the substrate. This primer-coated substrate was dried for 20 min at ambient conditions. EPC solution was then deposited on the substrate by spin coating for 10 s at 900 RPM. The sample was cured in a vacuum oven for 25 h at 61 °C, and then under a vacuum condition of −0.1 MPa to evaporate the toluene content in the sample. The dried and cured sample was dipped into a silicon oil bath for 12 h to obtain an EPC-oleogel sample.

FAA-free PDMS gel sample was prepared as the control sample by following the procedure used for fabricating the EPC-oleogel samples, except the replacement of EPC solution was replaced by PDMS solution. The ratio of the PDMS pre-polymer to the curing agent was 10:1.

The MEPC samples were fabricated by incorporating silica with different concentrations in the range of 0–1 wt.% of the PDMS solution, prior to the use of vortex generator. For example, 0.75 g of silica was incorporated into 5 wt.% EPC sample containing 10 g of PDMS solution to obtain a 0.75% silica-modified EPC sample. The remaining fabrication procedure was the same as the EPC-oleogel sample.

OEPC was fabricated by dropping the prepared silica NC solution on the MEPC sample mounted on a spin coater. Uniform silica NC coating was achieved after spin coating at 1500 RPMs for 30 s. Thereafter, the sample was dried at room temperature for 1 h and cured at 75 °C for 40 min. Finally, the OEPC gel was obtained by impregnating silicon oil in the same manner performed for EPC gel preparation.

Material Characterization: The wettability analysis was conducted using a CA analysis device. After the oil impregnation in the oleogel gels, the prepared samples were mounted on the CA measurement device (SmartDrop instrument, Femtofab, South Korea), and CA was analyzed using a 5 µL water droplet. However, in the DCA analysis, a 10 µL droplet was utilized, and the test platform was tilted with 0.1° tilting interval (resolution 0.001°). ACA, RCA, SA, and CAH was recorded at an instance when a droplet starts moving on the test sample.

Pressure Sustainability: The test section of the high-pressure flow facility was 68 cm long, and the cross-sectional area was 100 mm × 20 mm. The sample slot was positioned 85 mm downstream from the entrance part of the test section. The substrate was bolted firmly to the vertical wall of the test section with a rubber seal to avoid leakage and vibration of the pressure channel. An acrylic substrate was used in the high-pressure flow experiments with a sample slot of 130 mm × 60 mm × 5 mm. The oleogel-coated glass substrate with physical dimensions of 75 mm × 25 mm was attached to the sample slot using adhesive tape (Figure S4a, Supporting Information). The sample surface was perfectly flush mounted to the channel surface (Figure 3a). The pressure in the test channel was varied by controlling the bypass valve and recorded by a pressure gauge. High-pressure flow was supplied by a vertical multistage pump (Dooch pump, XRL90-30, South Korea), and the flow rate was recorded by a turbine flow meter (FTT-S-S 100A, Auto Flow, South Korea) (Figure S4, Supporting Information).

Drag Force Measurement: DR performance of the fabricated oleogel surfaces was evaluated for turbulent rectangular channel flows, in which the test section size was 3 m long, 0.3 m wide, and 0.3 m in height (Figure S5, Supporting Information). The maximum water speed was 20.4 ms^{-1}, water capacity was 58 tons, and the absolute pressure was between 0.01 and 0.2 MPa. Test samples were coated on an anodized aluminum flat plate of 150 mm × 155 mm × 15 mm in physical dimension. They were mounted on a flat plate platform with curves at the leading and trailing edges to avoid flow separation. A 1000 mm in length of the platform was positioned 2.6 m from the entrance point of the test section. Two test plates were arranged one after another, in such a way that the longer side of the plates was aligned with the flow stream. The test plates were fitted on top of the platform, which was connected to a dynamometer with a resolution = 1 µN. The test samples were located 690 mm downstream of the leading edge of the platform (Figure 5a). The output of the dynamometer was recorded in a computer with varying flow speeds in the channel.

Statistical Analysis: Except for Section 2.3, all the data presented in this manuscript was recorded with a sample size of 3. The mean and standard deviation of the presented data was evaluated with Microsoft Excel and data was plotted using Origin Pro. For Section 2.3, the sample size was 2, and data were presented as an average of both experiments.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

drag reduction, fatty acid amides, oleogel, shear-stable lubrication, turbulent flow

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