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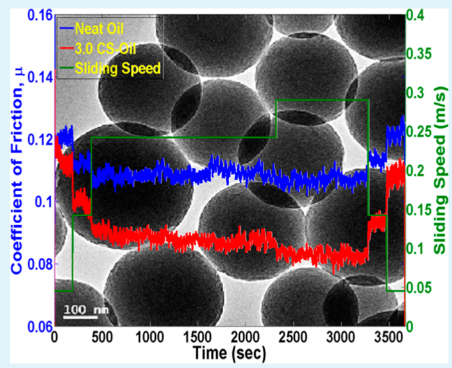
# Ultrasmooth Submicrometer Carbon Spheres as Lubricant Additives for Friction and Wear Reduction

Abdullah A. Alazemi,[†] Vinodkumar Etacheri,[‡] Arthur D. Dysart,[‡] Lars-Erik Stacke,[§] Vilas G. Pol,*[,‡] and Farshid Sadeghi*[,†]

[†]School of Mechanical Engineering, Purdue University, 585 Purdue Mall, West Lafayette, Indiana 47907-2088, United States
[‡]School of Chemical Engineering, Purdue University, 480 Stadium Mall Drive, West Lafayette, Indiana 47907-2100, United States
[§]SKF Engineering & Research Centre, Knowledge & Simulation Tools, SE-415 50 Göteborg, Sweden

Ⓢ *Supporting Information*

**ABSTRACT:** Ultrasmooth submicrometer carbon spheres are demonstrated as an efficient additive for improving the tribological performance of lubricating oils. Carbon spheres with ultrasmooth surfaces are fabricated by ultrasound assisted polymerization of resorcinol and formaldehyde followed by controlled heat treatment. The tribological behavior of the new lubricant mixture is investigated in the boundary and mixed lubrication regimes using a pin-on-disk apparatus and cylinder-on-disk tribometer, respectively. The new lubricant composition containing 3 wt % carbon spheres suspended in a reference SAE 5W30 engine oil exhibited a substantial reduction in friction and wear (10−25%) compared to the neat oil, without change in the viscosity. Microscopic and spectroscopic investigation of the carbon spheres after the tribological experiments illustrated their excellent mechanical and chemical stability. The significantly better tribological performance of the hybrid lubricant is attributed to the perfectly spherical shape and ultrasmooth surface of carbon sphere additive filling the gap between surfaces and acting as a nanoscale ball bearing.




**KEYWORDS:** *carbon spheres, lubricant additives, friction, wear reduction*

## 1. INTRODUCTION

Friction and wear are primary factors in energy loss and failure in all types of mechanical systems such as engines. The majority of friction and wear losses occur in the boundary and mixed lubrication regimes during engine startup/shutdown and low speed operation. In the boundary lubrication regime, lubricating surfaces generally are in contact with each other despite the fact that a fluid is present. While in the mixed lubrication regime, a thin lubricant film with an average thickness between 0.01 and 1 $\mu$m separates the lubricating surfaces.[1] The tribological performances of traditional fluid lubricants do not meet the demands of new generation mechanical devices. As a result, there is continuous research for improving the tribological performance of lubricants.

Previous reports suggested that performance of oil lubricants can be improved by adding solid particles.[2−10] These additives are beneficial in the boundary lubrication regime, where surface contact occurs even in the presence of fluid lubricant. Consequently, many high-performance lubricating oils contain solid additives in sizes ranging from 1 to 50 000 nm. Several types of carbonaceous nanoparticles including fullerene,[11,12] carbon nanotubes,[13−15] and carbon nano-onions[16−18] with particle sizes range from 1 to 30 nm have been tested as solid lubricant or additives. Furthermore, inorganic materials such as $MoS_2$,[19−21] $WS_2$,[22−24] Cu, Au, and Ag[25−27] with particle sizes ranging from 5 nm to 1 $\mu$m are widely used as oil additives or solid lubricants to improve tribological properties.

In spite of the good tribological behavior of current solid oil additives, there are several concerns about the complex synthetic methods used to create them and their toxicity and high cost.[28−31] Another serious issue is performance degradation on prolonged use due to the poor mechanical and chemical stability of the solid additives. For instance, inorganic fullerene nanoparticle additives were flattened or broken into individual sheets after tribometer tests under boundary lubrication and ultrahigh-vacuum conditions.[21,32] In order to mitigate these drawbacks, we have developed an ultrasonic assisted method for the rapid synthesis of ultrasmooth carbon submicrosphere oil additives possessing excellent mechanical and chemical stability. In this method, perfectly spherical carbon with ultrasmooth surfaces and diameters ranging from 100 to 500 nm are fabricated by ultrasound assisted polymerization of resorcinol and formaldehyde followed by controlled heat treatment. The tribological measurements proved a significant reduction in friction and wear (10−25%) in the boundary and mixed lubrication regimes by using a 3 wt % carbon sphere

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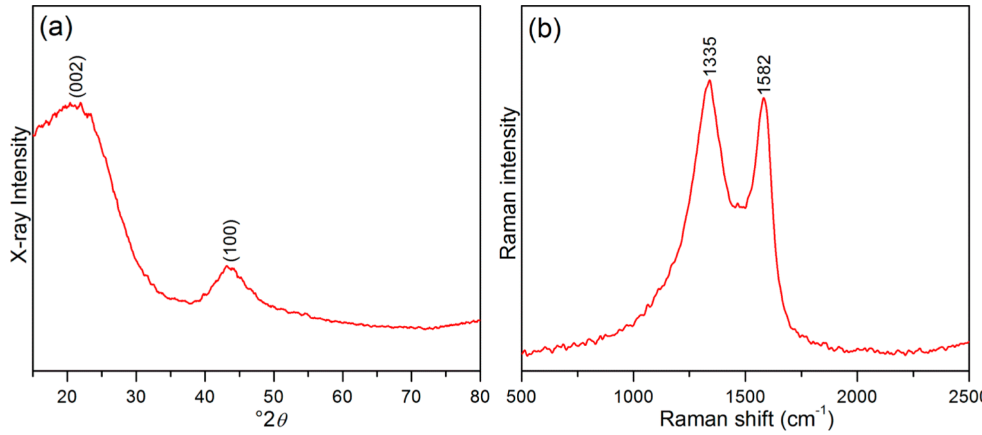


**Figure 1.** (a) X-ray diffraction pattern and (b) Raman spectrum of ultrasmooth carbon submicrometer spheres.

additive. Unlike conventional nanoparticle additives, the morphology and chemical composition of the carbon spheres were preserved during the tribological test conditions, suggesting rolling motion of carbon spheres as the lubricating mechanisms.

## 2. EXPERIMENTAL SECTION

**2.1. Material Synthesis.** Ultrasmooth submicrometer carbon spheres were synthesized by using our previously reported procedure.[33] Briefly, colloidal spherical polymer resins were synthesized in a short time via enhanced copolymerization of resorcinol with formaldehyde solution under ultrasonic irradiation. Submicrometer carbon spheres are then obtained from these polymer particles after a controlled heat treatment to a temperature of 900 °C for 4 h in an Ar atmosphere; heating and cooling rates were 1 °C/min.

**2.2. Characterization Techniques.** X-ray diffraction (XRD) patterns of carbon spheres ($2\theta$ = 15−80°) were recorded by Rigaku Smartlab X-ray diffractometer, operated at 40 kV and 40 mA using Cu−K$\alpha$ radiation ($\lambda$ = 0.154184 nm) at 25 °C with a $2\theta$ step size of 0.02 and a scanning speed of 2°/min. Thermo scientific DXR Raman spectrometer equipped with a 532 nm laser was used for recording the Raman spectra of carbon sphere samples. Laser power was limited to 8 mW to avoid sample burning. Scanning electron microscopy (SEM) images were recorded using Hitachi S-4800 microscope operating at an acceleration voltage of 25 kV. Transmission electron microscopy (TEM) measurements were carried out using an FEI-TITAN microscope operating at an accelerating voltage of 300 kV.

**2.3. Tribological Study.** Since the majority of friction and wear losses occur in the boundary and mixed lubrication regimes during engine transient operation, SAE 5W30 engine oil (Valvoline, USA) was used as a reference oil lubricant in the tribological investigation. The kinematic viscosity of the neat oil is 63 $mm^2$/s at 40 °C and 11 $mm^2$/s at 100 °C. Its density is 861 kg/$m^3$ at 15 °C. Ultrasmooth submicrometer carbon spheres (CS) were ultrasonically dispersed (10−20 s.) with a sonochemical tip irradiation under 20% power in the reference lubricant at different 0.5, 1, 3, and 5 wt % concentrations (identified as 0.5 CS-Oil, 1.0 CS-Oil, 3.0 CS-Oil, and 5.0 CS-Oil, respectively). The ultrasound mediated technique allows the carbon spheres to be suspended in the oil for a long period of time (2−3 weeks) without using any surfactant. Viscosity measurements of the neat oil and oils with 0.5−5 wt % carbon sphere were conducted using a tuning fork-type vibrating viscometer with accuracy of ±1% of the measured quantity. Each sample was heated above 75 °C, and the viscosity was measured as it cooled to ambient temperature. Tribology experiments were conducted at room temperature using three different test systems: (1) a pin-on-disk apparatus, which operates at high contact pressure and low rotational speed to investigate the tribology performance in the boundary lubrication regime; (2) a cylinder-on-disk tribometer that operates at low contact pressure and high rotational speed to examine the lubrication performance in the mixed lubrication regime; and (3) a glass disk test rig to observe the lubricant flow, friction force, and fluid film thickness during sliding motion. The arithmetic average (*Ra*) surface roughness of the specimens was measured using an optical surface profilometer. Friction and wear studies using the pin-on-disk apparatus were performed under the rotational motion of the disk with a stationary pin. A 12.7 mm diameter stainless steel ball with *Ra* surface roughness of 15 nm is used as the stationary pin specimen while TiCN coated steel disk with *Ra* surface roughness of 32 nm is rotating with a speed controlled by a DC servo motor. In the cylinder-on-disk tribometer (Bruker UMT-2), friction tests were conducted under the rotational motion of the disk with a stationary cylinder. The *Ra* surface roughness was 110 nm for the cylinder and 20 nm for the disk. A 10 mm diameter steel cylinder with 12.7 mm length and a 70 mm diameter stainless steel disk were used in the cylinder-on-disk tribometer. In the glass disk test rig, a stationary stainless steel specimen in contact with a rotating glass disk. The glass disk was driven by an AC motor while an infrared tachometer was used to measure the rotational speed of the glass disk. The *Ra* surface roughness was 120 nm for the stainless steel specimen. Additional experimental details are provided in the Supporting Information. Tribology experiments were repeated at least three times, and the measured friction and wear values were within a 5% error limit.

## 3. RESULTS AND DISCUSSION

**3.1. Formation of Ultrasmooth Submicrometer Carbon Spheres.** The XRD pattern of submicrometer carbon spheres heat treated at 900 °C exhibited broad peaks centered at 21 and 43.8° $2\theta$ (Figure 1a), which are characteristic of (002) and (100) graphitic planes of carbon.[34] Raman spectra of the carbon sphere sample is presented in Figure 1b, which displayed distinct D and G peaks at 1335 and 1582 $cm^{-1}$, respectively.[35,36] These bands correspond to the disordered carbon/structural defects and graphitic layers ($sp^2$ bonded carbon atoms) of the carbon spheres, respectively.[37] Increased D-band intensity compared to G-band ($I_D/I_G$ = 1.07) confirmed the disordered nature of submicrometer carbon spheres (Figure 1b). This implied the fact that 900 °C is not high enough to convert the resorcinol formaldehyde (RF) based resins to graphitic carbon in the absence of a transition metal catalyst. Area under the D and G peaks confirmed around 60% ($sp^3$) and around 40% ($sp^2$) type carbons present in these spheres.

Scanning electron microscopy (SEM) images of the carbon spheres at various magnifications are presented in Figure 2. It is clear that the carbon spheres possess an average diameter of 100−500 nm, and individual spheres are well separated from each other without any agglomeration. Moreover, high-


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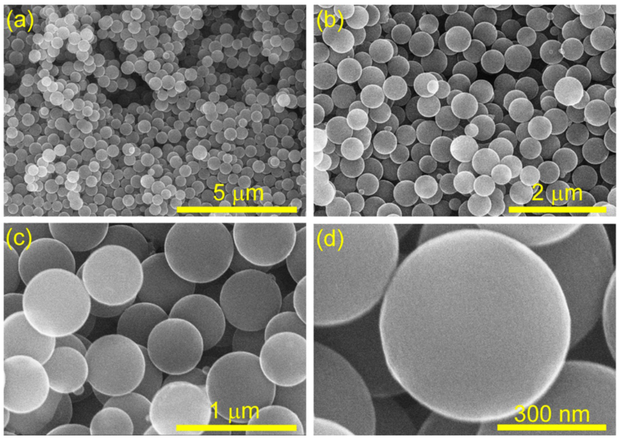


Figure 2. (a−d) SEM images of ultrasmooth carbon submicrometer spheres at various magnifications.

resolution images proved the perfectly spherical morphology and a high-degree of surface smoothness, which are highly beneficial for the tribological performance of lubricants. Morphology and microstructure of the carbon spheres were further investigated using high-resolution transmission electron microscopy (HR-TEM). Figure 3 clearly explained the perfectly

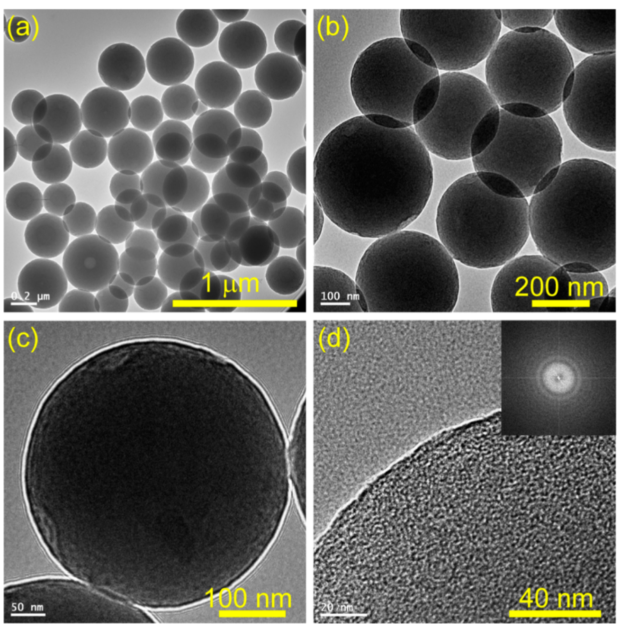


Figure 3. (a−d) TEM images of ultrasmooth carbon submicrometer spheres at various magnifications. (inset) Diffraction pattern.

spherical shape, and nanometer level surface smoothness of the 100−500 nm sized carbon spheres. Disordered graphitic planes and diffused selected area electron diffraction (SAED) patterns (Figure 3d inset) are in good agreement with the XRD and Raman results, confirming the disordered microstructure of carbon spheres. Figure 3d also demonstrated the nanometer scale (∼3 nm) surface irregularities that confirmed the ultrasmoothness of carbon spheres.

Formation of ultrasmooth submicrometer carbon spheres can be explained by the ultrasound induced polymerization of resorcinol and formaldehyde.[33] Sonochemical synthesis cause the continuous generation and collapse of bubbles, that can excite water molecules and dissociate into H● and OH● radicals.[38] These radicals are known for accelerating reaction rates, initiation of polymerization reactions, and shortening of gelation time.[39] Though RF resins have been previously synthesized (24 h reaction under similar experimental conditions) without ultrasonic irradiation, high degree of agglomeration and loss of spherical morphology was observed.[33] Therefore, we attributed the rapid polymerization and perfectly spherical morphology to the sonochemical effects. This method of ultrasmooth submicrometer carbon sphere synthesis is inexpensive and simple and can be easily scaled up for commercial applications.

**3.2. Tribological Performance of Ultrasmooth Submicrometer Carbon Spheres.** Viscosity measurements of the neat oil and oils with 0.5 to 5 wt % carbon sphere show that the change in the neat oil viscosity was less than 5% compared to the oil with carbon sphere additive. Figure 4 depicts viscosity as

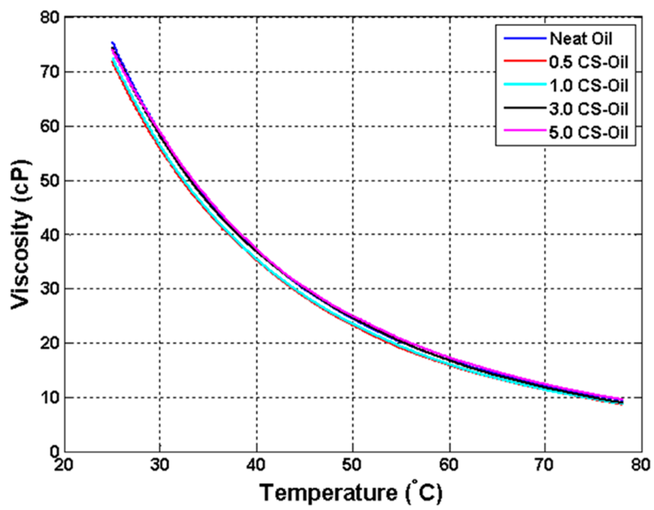


Figure 4. Viscosity/temperature relationship of the neat oil and oils with 0.5−5 wt % carbon sphere (error ±2%).

a function of temperature for the neat oil and oils with different carbon sphere concentration. Tribological performance of carbon spheres as oil additives in the boundary lubrication regime was investigated using pin-on-disk (POD) apparatus. The effect of carbon sphere concentrations in oil ranging from 0.5 to 5 wt % on the tribological performance was studied under 22.2 N of applied normal load (correspond to 1 GPa maximum Hertzian pressure) and variable sliding speed. The sliding speed was increased every 20 min by 0.1 m/s step from 0.1 to 0.3 m/s. On the basis of POD test conditions, material parameters, and surface roughness measurements, the lambda ratio ($\lambda$) was equal to 0.2, which confirm that the contact conditions were within the boundary lubrication regime.

As shown in Figure 5, carbon sphere additives reduced the coefficient of friction compared to the neat oil for all carbon sphere loading and sliding speeds. It can be seen that the oil containing 3 wt % carbon spheres (3.0 CS-Oil) exhibited the lowest coefficient of friction in contrast to the lower and higher carbon sphere concentrations and the pure reference oil. This can be explained by the fact that when two surfaces come into contact by an applied force, the real contact area is significantly less than the apparent area of contact because of surface roughness. The gap between surfaces in contact can be filled with carbon spheres. But after a certain point the contact area is saturated with carbon spheres and any more carbon spheres will


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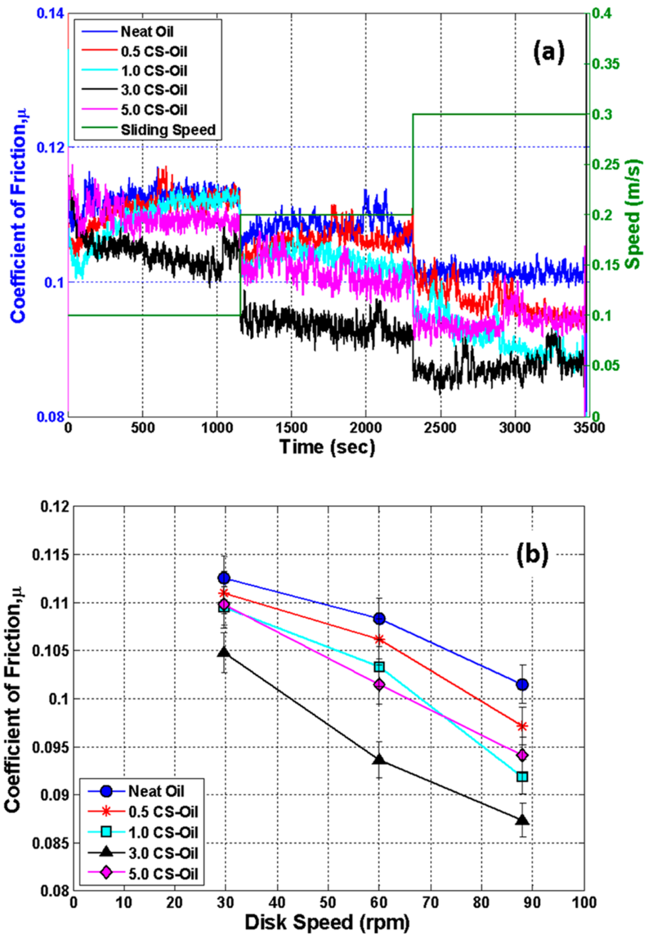


**Figure 5.** Coefficient of friction for different weight percent concentrations of carbon spheres in oil under 22.2 N normal load (1.0 GPa maximum Hertzian pressure) using POD apparatus versus (a) time and (b) disk speed (error ±5%).

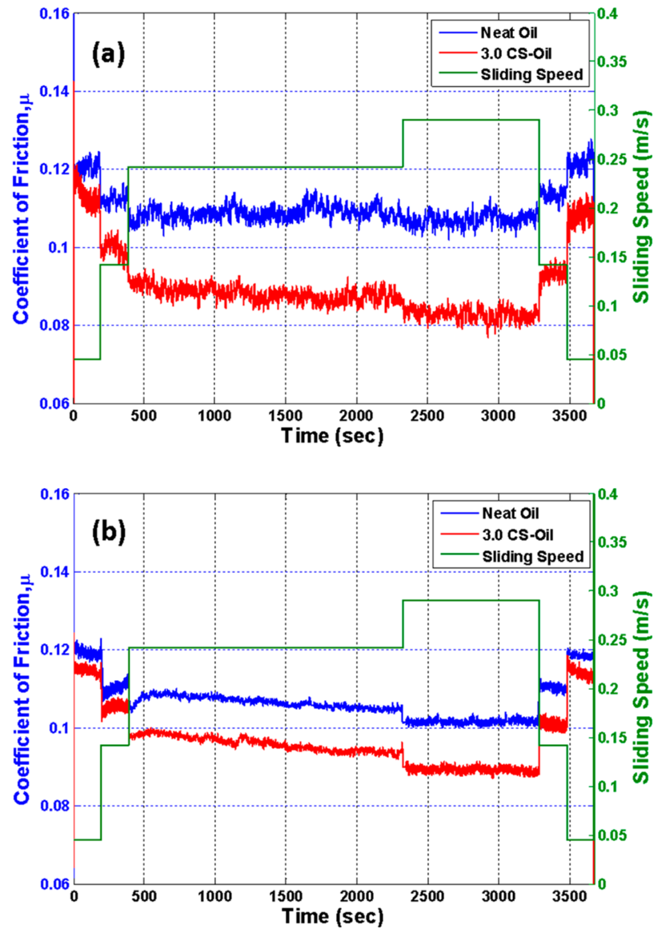


**Figure 6.** Coefficient of friction and sliding speed versus time for neat oil and 3.0 CS-Oil using POD apparatus under (a) 22.2 and (b) 93.7 N applied normal load (error ±5%).

not be beneficial. The optimum sample 3.0 CS-Oil represents the point where the oil is saturated with carbon spheres and the surface contact areas cannot contain more solid additives. The coefficient of friction (COF) was found to be 0.103 and 0.087 for the neat oil and 3.0 CS-Oil respectively at a sliding speed of 0.3 m/s. Figure 5b shows a decrease of the coefficient of friction with an increase of disk rotating speed. Furthermore, the friction reduction percentage increased with disk rotating speed. At sliding speeds of 0.045 and 0.3 m/s, the optimum composition 3.0 CS-Oil demonstrated a friction reduction of 7% and 16%, respectively compared to the pure reference oil.

The tribological behavior of the optimum lubricant composition 3.0 CS-Oil was further investigated at two different applied normal forces of 22.2 and 93.7 N (correspond to a maximum Hertzian contact pressures of 1.0 and 1.7 GPa respectively) as shown in Figure 6. The sliding speed varied from 0.045 to 0.290 m/s in a 1 h performance test of 3.0 CS-Oil. With an increase in sliding speed, lowering of COF was identified for both the pure reference oil and the 3.0 CS-Oil under two different Hertzian pressures. In the case of 1.0 GPa Hertzian pressure, an average friction reduction of 18% was obtained at various sliding speeds by adding 3 wt % of carbon spheres to the neat oil. On the other hand, 3.0 CS-Oil experienced a lower friction reduction of 10% at different sliding speed under a higher Hertzian pressure of 1.7 GPa. This reduced lubrication performance under high contact pressure can be explained by the gap diminution due to surface deformation in the area of contact that impede carbon sphere flow between contact surfaces. Table 1 summarizes the wear scar diameter and wear volume of the test specimen measured using an optical surface profilometer (using ASTM standards) after each test. It is clear that addition of 3 wt % carbon spheres reduced the wear scar diameter by 25% and wear volume loss by 66% under 1.0 GPa Hertzian contact pressure. Under high contact pressure of 1.7 GPa, 3.0 CS-Oil showed 10% wear scar diameter and 36% wear volume loss reduction. Optical micrographs of the tested ball specimen under 1.7 GPa Hertzian pressure with the neat oil and 3.0 CS-Oil are presented in Figure 7. Unlike the pure reference lubricant, the

**Table 1. Wear Scar Diameter and Wear Volume Loss Measurements for the Neat Oil and 3.0 CS-Oil under 1.0 and 1.7 GPa Maximum Hertzian Pressure on the Pin-on-Disk Apparatus (Error ±5%)**

| maximum Hertzian pressure, $P_{max}$ (GPa) | lubricant type | wear scar diameter ($\mu$m) | wear volume loss (mm$^3$) |
|---|---|---|---|
| 1.0 | neat oil | 490 | $0.45 \times 10^{-3}$ |
| 1.7 | neat oil | 610 | $1.07 \times 10^{-3}$ |
| 1.0 | 3.0 CS-Oil | 370 | $0.15 \times 10^{-3}$ |
| 1.7 | 3.0 CS-Oil | 545 | $0.68 \times 10^{-3}$ |


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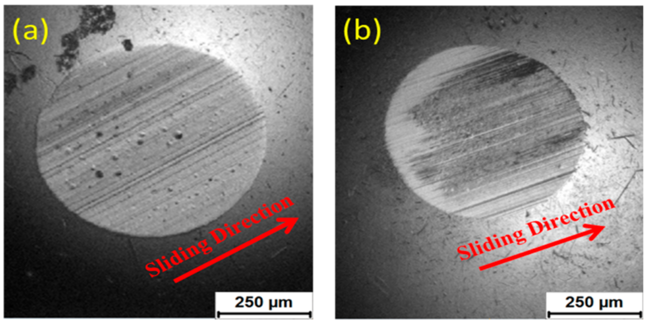


**Figure 7.** Wear scar optical micrographs on ball specimen under 93.7 N applied normal load using POD apparatus for (a) neat oil and (b) 3.0 CS-Oil lubrication.

hybrid composition 3.0 CS-Oil was able to react with the contact area on the ball to form a protective dark film that led to friction and wear reduction.

In order to further investigate the lubrication mechanism of the hybrid lubricant, glass disk test rig (GDTR) was used to visualize the lubricant flow, measure friction force, and fluid film thickness during sliding motion (Figure S1). Figure 8 depicts

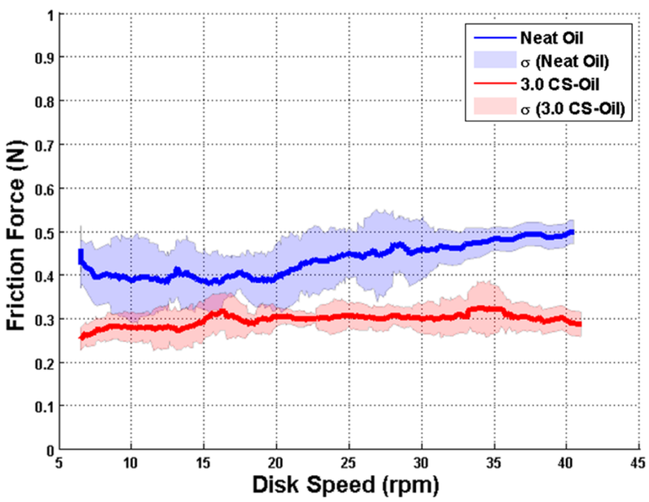


**Figure 8.** Friction force versus glass disk rotational speed under 1.5 N applied load in GDTR for a contact lubricated by the neat oil and 3.0 CS-Oil.

the results obtained under 1.5 N applied load and disk rotational speeds of 6 to 40 rpm. The shaded area represents the standard deviation ($\sigma$) of the experimental data while the solid line represents the average friction force. The hybrid lubricant composition 3.0 CS-Oil exhibited a friction reduction of 5−30% relative to the pure reference oil. This observation supported the results obtained from pin on disk apparatus. GDTR further confirmed the homogeneity of the lubricant mixture (3.0 CS-Oil) during surfaces sliding 1.5 N applied load (Figure 9). The vertical black line and the dark area to the left of the line represents the lubricant mixture as it flows on the specimen at three different stages as presented in Figure 9a−c. The film thickness measurements did not show any difference between the neat oil and the 3.0 CS-Oil during surfaces sliding. Since the specimen has a 120 nm *Ra* surface roughness, carbon spheres with diameter of 100 to 500 nm can act as third body particles filling the gap between surface asperities without significantly changing the lubricant film thickness. In addition,

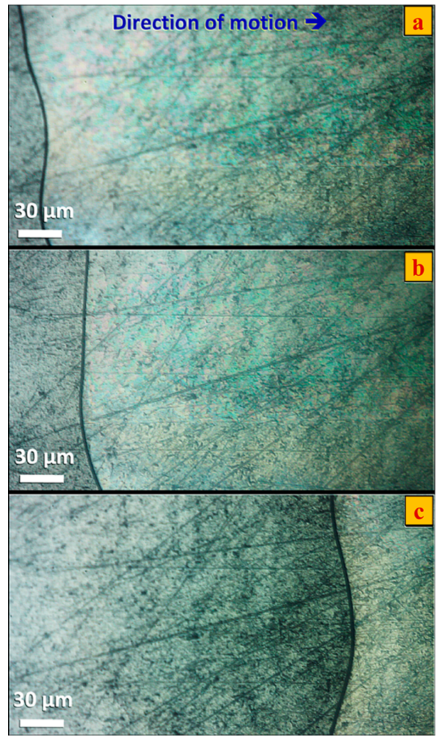


**Figure 9.** (a−c) Optical micrograph of the 3.0 CS-Oil flow in GDTR under 1.5 N applied load.

presence of carbon spheres between contacting surfaces in the boundary and mixed lubrication regimes can possibly result in rolling motion where the system may act as nanoscale ball bearing.

Tribological performance of the carbon sphere oil mixture in the mixed lubrication regime where lubricating surfaces are separated by a thin lubricant film (less than 1 $\mu$m and greater than 0.01 $\mu$m) was investigated using a cylinder-on-disk tribometer. Results obtained under 50 N normal load and various rotational speeds (15 to 400 rpm) is presented in Figure 10. The shaded area represents the standard deviation ($\sigma$) of the experimental data while the solid line represents the

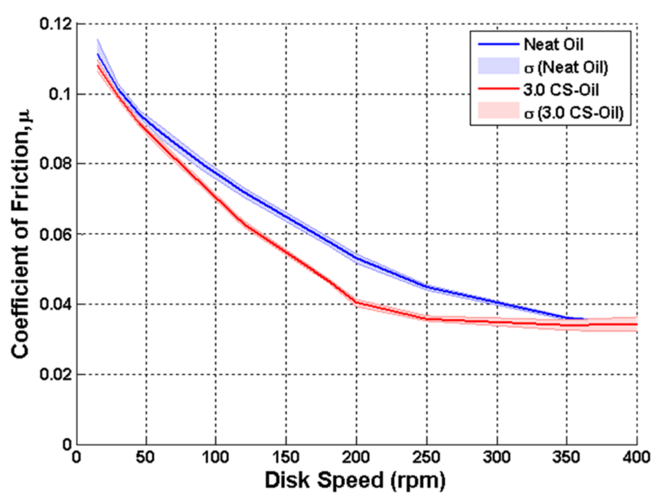


**Figure 10.** Coefficient of friction versus disk rotational speed under 50 N applied load in cylinder-on-disk tribometer for a contact lubricated by the neat oil and 3.0 CS-Oil.



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average coefficient of friction. A noticeable and rapid decrease in coefficient of friction values is observed with increasing disk rotational speed for both neat and hybrid lubricant. This rapid decrease with an increase in disk rotational speed confirms that the system is working in the mixed lubrication regime until the coefficient of friction reaches a lower plateau corresponding to the beginning of hydrodynamic lubrication.[1] For the cylinder-on-disk tribometer test conditions, material parameters, and surface roughness measurements, the lambda ratio ($\lambda$) was equal to 0.2 at disk rotational speed of 15 rpm while $\lambda$ was equal to 2.1 at disk rotational speed of 400 rpm. Which confirm that the contact conditions started within the boundary lubrication regime and then reached the mixed lubrication regime. The lubricant mixture of 3.0 CS-Oil displayed a friction reduction of 5−23% compared to the pure reference oil. A maximum friction reduction of 23% was achieved at disk speed of 200 rpm, which is about the middle of the mixed lubrication regime. The lubricant film thickness increased from 0.01−1 $\mu$m in the mixed lubrication regime with an increase of rotational speed of the disk. This clearly explained the superior friction reduction at increased disk speed for the hybrid lubricant compared to the neat oil. As the lubricant film thickness increases more carbon spheres are allowed to flow between the contacting surfaces. Once the film thickness reach greater than the carbon spheres diameter (~300 nm), then the role of carbon spheres diminishes and the lubricant mixture performs the same as the pure reference oil as seen at higher speeds (Figure 10).

In order to understand the mechanical and chemical stability of submicrometer carbon spheres, scanning electron microscopy and Raman spectroscopy analysis were performed for carbon spheres collected after 1 h test under 22.2 N applied load on the pin-on-disk apparatus. Interestingly, carbon spheres maintained their perfect spherical morphology (Figure 11a and b), the only difference being the appearance of a thin layer of oil on their surface. It is remarkable that carbon spheres maintain their spherical shape even after going under the extreme boundary lubrication conditions on the pin-on-disk (POD) apparatus. Isoenergetic D and G bands (at 1335 and 1582 $cm^{-1}$, respectively) of the carbon spheres before and after the POD test (Figure 11c and d) clearly explained their chemical stability. Morphology preservation of the carbon spheres under extreme boundary lubrication conditions also supports their rolling motion during tribological measurements. As mentioned earlier mechanical and chemical stability are very crucial for the lubricant additives. It is indeed the superior mechanical and chemical stability of ultrasmooth submicrometer carbon spheres make them an excellent lubricant additive.

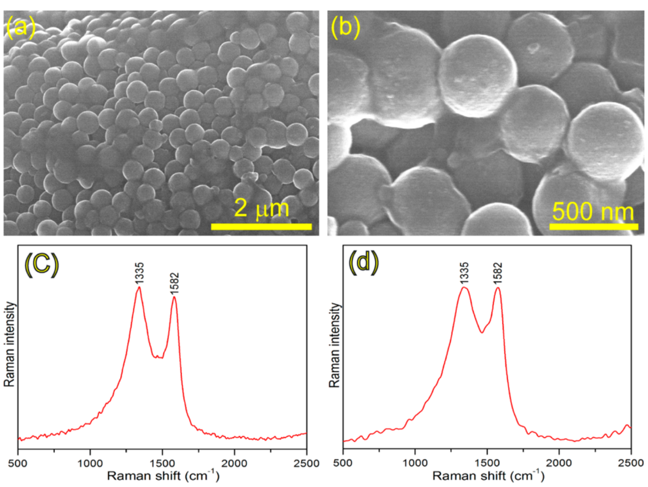


**Figure 11.** (a, b) SEM images of carbon spheres after 1 h tribometer test on the pin-on-disk apparatus. Raman spectra of carbon spheres (c) before and (d) after tribological measurements.

The significantly improved tribological performance of ultrasmooth submicrometer carbon sphere-oil hybrid lubricant can be explained by the fact that the carbon spheres act as a third body material filling the gap between surfaces asperities, increasing real contact area and reducing contact pressure.[40,41] In addition, the existence of carbon spheres between contact surfaces during boundary and mixed lubrication regimes may possibly result in rolling motion where the system act as ball bearing on the nanometer scale.[42] The ability of carbon spheres to maintain their spherical morphology even after going under extreme boundary lubrication conditions supports their rolling motion as the lubricating mechanism. Further mechanical and thermal properties investigation of these carbon spheres additives are in progress. This comprehensive study illustrated the potential of ultrasmooth carbon spheres to improve the tribological performance of current generation oil lubricants.

## 4. CONCLUSIONS

Ultrasmooth submicrometer carbon spheres are illustrated as effective additives in lubricating oils. An ultrasound assisted method was used for the rapid synthesis of these perfectly spherical and ultrasmooth carbon spheres with a diameter ranging from 100 to 500 nm. Tribological tests demonstrated a significant reduction in friction and wear (10−25%) by adding 3 wt % of carbon spheres to a reference oil. Friction reduction was dependent on the sliding speed and applied load, and maximum reduction was achieved at the highest sliding speed in the boundary lubrication regime. Excellent mechanical and chemical stability of the carbon spheres were evidenced by their microscopic and spectroscopic investigation before and after the tribological experiments. The notably improved tribological performance of the carbon sphere-oil hybrid lubricant was explained by the perfectly spherical shape and ultrasmooth nature of the carbon spheres. While operating in the boundary and mixed lubrication regimes, ultrasmooth carbon spheres can possibly cause rolling motion where the system may act as ball bearing on the nanometer scale. This investigation proved that carbon spheres have potential to improve the tribological performance of current generation oil lubricants.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental details and procedures, tests operating conditions, description of test rigs, and schematic of glass disk test rig setup. This material is available free of charge via the Internet at http://pubs.acs.org.

## ■ AUTHOR INFORMATION


### Corresponding Authors

*E-mail: vpol@purdue.edu (V.G.P.).
*E-mail: sadeghi@purdue.edu (F.S.).


### Notes

The authors declare no competing financial interest.


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## ■ REFERENCES

(1) Hamrock, B. J.; Schmid, S. R.; Jacobson, B. O. *Fundamentals of Fluid Film Lubrication*; CRC press, 2004; Vol. *169*.

(2) Chinas-Castillo, F.; Spikes, H. A. The Behavior of Colloidal Solid Particles in Elastohydrodynamic Contacts. *Tribol. Trans.* **2000**, *43*, 387−394.

(3) Golan, Y.; Drummond, C.; Homyonfer, M.; Feldman, Y.; Tenne, R.; Israelachvili, J. Microtribology and Direct Force Measurement of $WS_2$ Nested Fullerene-Like Nanostructures. *Adv. Mater.* **1999**, *11*, 934−937.

(4) Huang, H. D.; Tu, J. P.; Gan, L. P.; Li, C. Z. An Investigation on Tribological Properties of Graphite Nanosheets as Oil Additive. *Wear* **2006**, *261*, 140−144.

(5) Kalin, M.; Kogovšek, J.; Remškar, M. Mechanisms and Improvements in the Friction and Wear Behavior Using $MoS_2$ Nanotubes as Potential Oil Additives. *Wear* **2012**, *280*, 36−45.

(6) Tarasov, S.; Kolubaev, A.; Belyaev, S.; Lerner, M.; Tepper, F. Study of Friction Reduction by Nanocopper Additives to Motor Oil. *Wear* **2002**, *252*, 63−69.

(7) Akbulut, M.; Belman, N.; Golan, Y.; Israelachvili, J. Frictional Properties of Confined Nanorods. *Adv. Mater.* **2006**, *18*, 2589−2592.

(8) Winer, W. O. Molybdenum Disulfide as a Lubricant: a Review of the Fundamental Knowledge. *Wear* **1967**, *10*, 422−452.

(9) Rapoport, L.; Bilik, Y.; Feldman, Y.; Homyonfer, M.; Cohen, S. R.; Tenne, R. Hollow Nanoparticles of $WS_2$ as Potential Solid-State Lubricants. *Nature* **1997**, *387*, 791−793.

(10) Wu, Y. Y.; Tsui, W. C.; Liu, T. C. Experimental Analysis of Tribological Properties of Lubricating Oils with Nanoparticle Additives. *Wear* **2007**, *262*, 819−825.

(11) Bhushan, B.; Gupta, B. K.; Cleef, G. W. V.; Capp, C.; Coe, J. V. Fullerene (C60) Films for Solid Lubrication. *Tribol. Trans.* **1993**, *36*, 573−580.

(12) Yan, F. Y.; Xue, Q. J. The Antifriction Behaviours of C60/C70. *J. Phys. D: Appl. Phys.* **1997**, *30*, 781−786.

(13) Chen, W. X.; Tu, J. P.; Wang, L. Y.; Gan, H. Y.; Xu, Z. D.; Zhang, X. B. Tribological Application of Carbon Nanotubes in a Metal-Based Composite Coating and Composites. *Carbon* **2003**, *41*, 215−222.

(14) Miyoshi, K.; K, W. S., Jr; Wal, R. L. V.; Andrews, R.; Sayir, A. Solid Lubrication by Multiwalled Carbon Nanotubes in Air and in Vacuum. *Tribol. Lett.* **2005**, *19*, 191−201.

(15) Men, X. H.; Zhang, Z. Z.; Yang, J.; Zhu, X. T.; Wang, K.; Jiang, W. Effect of Different Functional Carbon Nanotubes on the Tribological Behaviors of Poly (Furfuryl Alcohol)−Derived Carbon Nanocomposites. *Tribol. Trans.* **2011**, *54*, 265−274.

(16) Matsumoto, N.; Mistry, K. K.; Kim, J. H.; Eryilmaz, O. L.; Erdemir, A.; Kinoshita, H.; Ohmae, N. Friction Reducing Properties of Onion-Like Carbon Based Lubricant Under High Contact Pressure. *Tribol.-Mater., Surf. Interfaces* **2012**, *6*, 116−120.

(17) Joly-Pottuz, L.; Matsumoto, N.; Kinoshita, H.; Vacher, B.; Belin, M.; Montagnac, G.; Martin, J. M.; Ohmae, N. Diamond-Derived Carbon Onions as Lubricant Additives. *Tribol. Int.* **2008**, *41*, 69−78.

(18) Street, K. W.; Marchetti, M.; Wal, R. L. V.; Tomasek, A. J. Evaluation of the Tribological Behavior of Nano-Onions in Krytox 143AB. *Tribol. Lett.* **2004**, *16*, 143−149.

(19) Sgroi, M.; Gili, F.; Mangherini, D.; Lahouij, I.; Dassenoy, F.; Garcia, I.; Odriozola, I.; Kraft, G. Friction Reduction Benefits in Valve-Train System Using IF-$MoS_2$ Added Engine Oil. *Tribol. Trans.* **2015**, *58*, 207−214.

(20) Rosentsveig, R.; Gorodnev, A.; Feuerstein, N.; Friedman, H.; Zak, A.; Fleischer, N.; Tannous, J.; Dassenoy, F.; Tenne, R. Fullerene-Like $MoS_2$ Nanoparticles and their Tribological Behavior. *Tribol. Lett.* **2009**, *36*, 175−182.

(21) Tannous, J.; Dassenoy, F.; Lahouij, I.; Mogne, T. L.; Vacher, B.; Bruhács, A.; Tremel, W. Understanding the Tribochemical Mechanisms of IF-$MoS_2$ Nanoparticles Under Boundary Lubrication. *Tribol. Lett.* **2011**, *41*, 55−64.

(22) Gullac, B.; Akalin, O. Frictional Characteristics of IF-$WS_2$ Nanoparticles in Simulated Engine Conditions. *Tribol. Trans.* **2010**, *53*, 939−947.

(23) Rapoport, L.; Fleischer, N.; Tenne, R. Fullerene-Like $WS_2$ Nanoparticles: Superior Lubricants for Harsh Conditions. *Adv. Mater.* **2003**, *15*, 651−655.

(24) Greenberg, R.; Halperin, G.; Etsion, I.; Tenne, R. The Effect of $WS_2$ Nanoparticles on Friction Reduction in Various Lubrication Regimes. *Tribol. Lett.* **2004**, *17*, 179−186.

(25) Zhou, J.; Wu, Z.; Zhang, Z.; Liu, W.; Xue, Q. Tribological Behavior and Lubricating Mechanism of Cu Nanoparticles in Oil. *Tribol. Lett.* **2000**, *8*, 213−218.

(26) Chinas-Castillo, F.; Spikes, H. A. Mechanism of Action of Colloidal Solid Dispersions. *J. Tribol.* **2003**, *125*, 552−557.

(27) Choi, Y.; Lee, C.; Hwang, Y.; Park, M.; Lee, J.; Choi, C.; Jung, M. Tribological Behavior of Copper Nanoparticles as Additives in Oil. *Curr. Appl. Phys.* **2009**, *9*, e124−e127.

(28) Tang, Z.; Li, S. A Review of Recent Developments of Friction Modifiers for Liquid Lubricants (2007−Present). *Curr. Opin. Solid State Mater. Sci.* **2014**, *18*, 119−139.

(29) Hakan, K. The Impact of Crankcase Oil Containing Phosphorus on Catalytic Converters and Engine Exhaust Emission. *Ind. Lubr. Tribol.* **2001**, *53*, 237−255.

(30) Deorsola, F. A.; Russo, N.; Blengini, G. A.; Fino, D. Synthesis, Characterization and Environmental Assessment of Nanosized $MoS_2$ Particles for Lubricants Applications. *Chem. Eng. J.* **2012**, *195*, 1−6.

(31) Njiwa, P.; Hadj-Aïssa, A.; Afanasiev, P.; Geantet, C.; Bosselet, F.; Vacher, B.; Belin, M.; Mogne, T. L.; Dassenoy, F. Tribological Properties of New $MoS_2$ Nanoparticles Prepared by Seed-Assisted Solution Technique. *Tribol. Lett.* **2014**, *55*, 473−481.

(32) Cizaire, L.; Vacher, B.; Mogne, T. L.; Martin, J. M.; Rapoport, L.; Margolin, A.; Tenne, R. Mechanisms of Ultra-Low Friction by Hollow Inorganic Fullerene-Like $MoS_2$ Nanoparticles. *Surf. Coat. Technol.* **2002**, *160*, 282−287.

(33) Pol, V. G.; Shrestha, L. K.; Ariga, K. Tunable, Functional Carbon Spheres Derived from Rapid Synthesis of Resorcinol-Formaldehyde Resins. *ACS Appl. Mater. Interfaces* **2014**, *6*, 10649−10655.

(34) Pol, V. G.; Thackeray, M. M. Spherical Carbon Particles and Carbon Nanotubes Prepared by Autogenic Reactions: Evaluation as Anodes in Lithium Electrochemical Cells. *Energy Environ. Sci.* **2011**, *4*, 1904−1912.

(35) Basavalingu, B.; M.Calderon-Moreno, J.; Byrappa, K.; Gogotsi, Y. G.; Yoshimura, M. Decomposition of Silicon Carbide in the Presence of Organic Compounds Under Hydrothermal Conditions. *Carbon* **2001**, *39*, 1763−1766.

(36) Dresselhaus, M. S.; Dresselhaus, G.; Pimenta, M. A.; Eklund, P. C.; Pelletier, M. J., Analytical Applications of Raman Spectroscopy. In *Analytical Applications of Raman Spectroscopy*; Blackwell: Oxford, UK, 1999; Chapter 9.

(37) Ferrari, A. C.; Robertson, J. Origin of the 1150 $cm^{-1}$ Raman Mode in Nanocrystalline Diamond. *Phys. Rev. B* **2001**, *63*, R121405−R121408.

(38) Gong, C.; Hart, D. P. Ultrasound Induced Cavitation and Sonochemical Yields. *J. Acoust. Soc. Am.* **1998**, *104*, 2675−2682.

(39) Suslick, K. S. *Ultrasound: Its Chemical, Physical, and Biological Effects*; VCH Publishers: New York, 1988.

(40) Reeves, C. J.; Menezes, P. L.; Lovell, M. R.; Jen, T. C. The Size Effect of Boron Nitride Particles on the Tribological Performance of Biolubricants for Energy Conservation and Sustainability. *Tribol. Lett.* **2013**, *51*, 437−452.

(41) Leonard, B. D.; Ghosh, A.; Sadeghi, F.; Shinde, S.; Mittelbach, M. Third Body Modeling in Fretting Using the Combined Finite-Discrete Element Method. *Int. J. Solids Struct.* **2014**, *51*, 1375−1389.
(42) Martin, J. M.; Ohmae, N. *Nanolubricants*; John Wiley & Sons: 2008; Vol. *13*.



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