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Preparation of Composite Fluoropolymers with Enhanced Dewetting Using Fluorinated Silsesquioxanes as Drop-In Modifiers (Preprint)

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Composite fluoropolymers were prepared by solvent blending fluorinated POSS (F-POSS) with perfluorocyclobutyl (PFCB) aryl ether polymers. The semifluorinated PFCB aryl ether polymers were shown to be hydrophobic, but demonstrated complete wetting by hydrocarbon-based liquids. Upon the incorporation of F-POSS as a drop-in modifier at low weight percent loadings, the composite fluoropolymer spin cast films exhibited increased water in addition to hydrocarbon repellency as determined by contact angle analysis. Composite film surface characterization included SEM and AFM analysis which showed excellent F-POSS dispersion and increased surface roughness. Thermal properties of the blended films were performed using DSC and demonstrated the incorporation of F-POSS did not affect the bulk matrix properties inherent of PFCB aryl ether polymers. This work demonstrated that optimized F-POSS PFCB aryl ether polymer blend formulations have potential use as hydro- and oleophobic materials for seals, fibers, and coatings.

Introduction

Interest continues to seek a simple method for preparing artificial surfaces that exhibit both hydro- and oleophobic properties. There are numerous examples of materials that mimic naturally evolved biological systems, albeit they are mostly limited to exhibiting hydrophobicity.¹ Most notably, some species of the lotus leaf exhibit self-cleaning maintenance,^{2,3} repelling water entrained with debris by way of two-tier topographical roughness on both the micro- and nanometer scale.⁴ These features have been successfully mimicked employing surface treatments such as thermal,⁵ etching/exfoliation,⁶⁻⁸ patterning,⁹⁻¹¹ deposition,¹²⁻¹⁵ or self-assembly.^{16,17} From a practical, cost-effective, and scaleable standpoint, such elaborate post-treatments can compromise bulk material integrity, produce poorly adhered coatings, or require expensive patterning equipment. As such, there are still obvious challenges of fabricating materials from an operationally simple procedure that possess both water and hydrocarbon repellent properties. Such materials would be highly desired for commercial and military applications including anti-fouling coatings, separation membranes, cryogenic seals, or grease-resistant fabrics. Fluoropolymers are highly desired over their hydrogen-containing analogs because they possess the unique combination of thermal stability, chemical resistance, low refractive index, and high insulating ability.¹⁸ Due to the strong carbon-fluorine bond along the polymer backbone, they also inherently possess a high degree of hydrophobicity

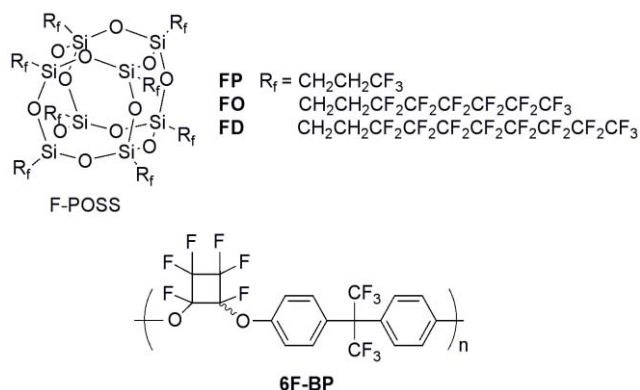


Figure 1 Fluorinated POSS (F-POSS) compounds **FP**, **FO**, and **FD** used to prepare blends using **6F-BP** PFCB aryl ether polymer.

and, to some extent, are inert to organic-based solvents. However, they suffer from the propensity to wet upon application of hydrocarbon-based liquids. Furthermore, many commercial fluoropolymers are inherently difficult to melt or solvent process due to their highly crystalline nature. Therefore, the concept of enhancing the oleophobic nature of fluoropolymers by way of incorporating fillers or surface modification still remains relatively unexplored. Perfluorocyclobutyl (PFCB) aryl ether polymers (see Figure 1 as an example), on the other hand, are an established class of semifluorinated polymers that exhibit the advantages of commercial fluoropolymers, yet are solution processable using common solvents.¹⁹ They are prepared from [2 + 2] thermal, step-growth polymerization of aryl trifluorovinyl ether (TFVE) monomers.^{20,21} PFCB aryl ether polymers can also be functionalized either as thermoplastics or thermosets tailored for a variety of applications. Some notable examples include, although not limited to, optics,²² space durable coatings,^{23,24} proton exchange membranes (PEMs) for fuel cells,²⁵ siloxane-based hybrid composites,^{26,27} electro-optics

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(EO) materials,²⁸ polymer light emitting diodes (PLEDs),²⁹ and liquid crystalline polymers.^{30, 31}

Polyhedral oligomeric silsesquioxanes (POSS) possess a discretely sized inorganic silicon–oxygen cubic core framework functionalized with organic groups at the apex of each silicon atom. Several consolidated accounts have been reported pertaining to POSS and POSS-functionalized polymers.^{32–35} The combination of this system creates an interesting paradox in terms of properties such that the ceramic core provides thermal stability whereas the peripheral hydrocarbon groups provide compatatality within an organic polymer host matrix. POSS has been used to enhance bulk properties in hydrocarbon-based polymers by influencing polymer chains at nanometer-scale domains. Low loadings of POSS covalently anchored into copolymers or blends has been well known to increase thermal stability and increased glass transition temperature and more recently light emission enhancement.^{36–38}

Few reports have incorporated POSS into primarily hydrocarbon polymers for improving hydrophobicity. One example, a diol-functionalized POSS was incorporated into poly(urethane) anionomers and showed modest increase in hydrophobicity due to the hydrophobic nature of *iso*-butyl POSS moieties and nanometer-sized surface roughness due to POSS aggregation.²³ Likewise, similar dewetting behavior, albeit modest, was observed utilizing partially fluorinated POSS in polycarbonates^{39, 40} and epoxy thermosets.⁴¹ Until recently, the use of fluorinated POSS (F-POSS, Figure 1) as a mechanical processing aid was shown to improve hydrophobicity of commerical fluoropolymers such as poly(chlorotrifluoroethylene) (PCTFE).⁴² Furthermore, low loadings of F-POSS has been used to successfully prepare ultrahydro- and ultraoleophobic non-woven mats from electrosinning blends with *hydrophilic* poly(methyl methacrylate) (PMMA).⁴³ Utility of F-POSS as a robust, dip coating for synthetic fibers,⁴⁴ complex natural surfaces,⁴⁴ and cotton fabrics⁴⁵ was demonstrated with good retention of native surface features. Expanding on utility, engineered surfaces employing F-POSS for tuning surface energy in addition to tailoring surface morpholgy produced omniphobic materials.⁴⁶

Various derivatives of POSS were shown to modestly improve hydrophobicity in PFCB aryl ether copolymers as chain terminated²⁶ or pendant architectures,²⁷ although no extent of oleophocicity was ever achieved. Since F-POSS has been shown to improve water and hydrocarbon dewetting in the aforementioned blended systems, it should serve as a suitable low surface energy drop-in modifier as a PFCB aryl ether polymer composite blend. This work entails the facile preparation of F-POSS PFCB aryl ether blends by solvent processing that possess enhanced hydrophobicity and, for the first time, a high degree of oleophocicity. The preparation of the resulting optically transparent, spin cast films of these blends were not previously known.

Results and discussion

Blend preparation

The components of the blends are shown in Figure 1. Fluorinated POSS (F-POSS) compounds (1H, 1H, 2H, 2H-trifluoropropyl)₈Si₈O₁₂ (**FP**), 1H,1H,2H,2H-tridecafluorooctyl)₈Si₈O₁₂ (**FO**), and (1H,1H,2H,2H-hepta-decafluorodecyl)₈Si₈O₁₂ (**FD**) POSS were solvent blended into PFCB aryl ether polymer (**6F-BP**, Figure 1). The **6F-BP** PFCB aryl ether polymer had a typical number-average molecular weight (*M_n*) of 30,000 with polydispersity typically of 2.2. Composite blends were prepared by dissolving a specified weight percentage of fluorinated POSS relative to PFCB aryl ether matrix in a minimal amount of hexafluorobenzene. Although the fluorinated POSS and PFCB aryl ether polymer readily dissolved in solution and produced a homogenous solution, the mixture was rigorously blended with a magnetic stirrer for five minutes. The blended solutions (typically 30 wt % (w/v)) up to 20 wt % POSS content were then spin cast onto glass substrate, producing optically transparent films (ca. 1–2 μm thick). **FP**, **FO**, or **FD** POSS loadings higher than 20 wt % produced phase separated, opaque films.

Surface wettability

It was previously shown **FD** POSS as a spin cast powder possessed the highest water contact angles (CA) of 154°. **FD** POSS has the highest fluorine content which also resulted in the highest hexadecane CA of 87° among the F-POSS series. The water and hexadecane CA comparison of **FD** POSS to **FP** and **FO** POSS is shown in Figure 2. There was a near linear progression of water contact angle in relation to the increasing fluorine content of the POSS compounds, whereby the calculated fluorine content (% F) of **FP**, **FO**, and **FD** is 38.2%, 61.9%, and 64.7%, respectively. A similar trend was observed for hexadecane contact angles, albeit the oleophocities of **FO** and **FD** POSS are the highest and nearly the same.

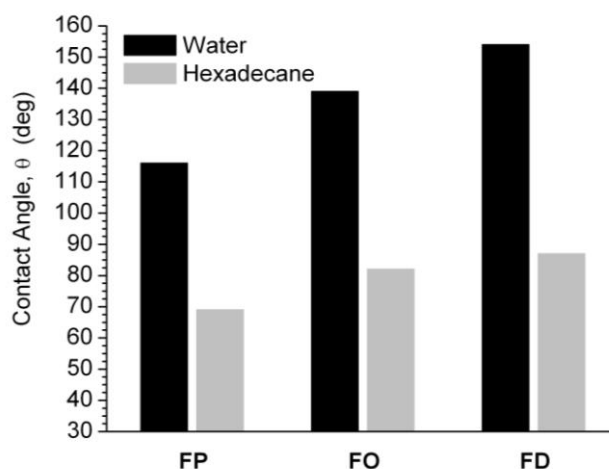


Figure 2 Water and hexadecane contact angles of spin cast powders of F-POSS compounds **FP**, **FO**, and **FD**.

Incorporation of **FD** POSS in **6F-BP** PFCB aryl ether polymer at increasing wt % loadings showed an increase in water and hexadecane contact angle (Figure 3). The **6F-BP** PFCB aryl ether polymer is to some extent hydrophobic and

produced water CA of 95°. On the other hand, hexadecane
 160 nearly wetted the surface and produced a measured CA of 31°. **FD** POSS loadings up to 15 wt % developed a plateau in water CA; the blend showed an overall 30% increase in water CA (124°). At the maximum of 10 wt % **FD** POSS incorporation, a maximum hexadecane CA of 80° was
 165 observed, increasing hexadecane repellency dramatically by 158%. The blends using **FP** POSS at 15 wt % loadings produced a negligible change in water CA and lowest

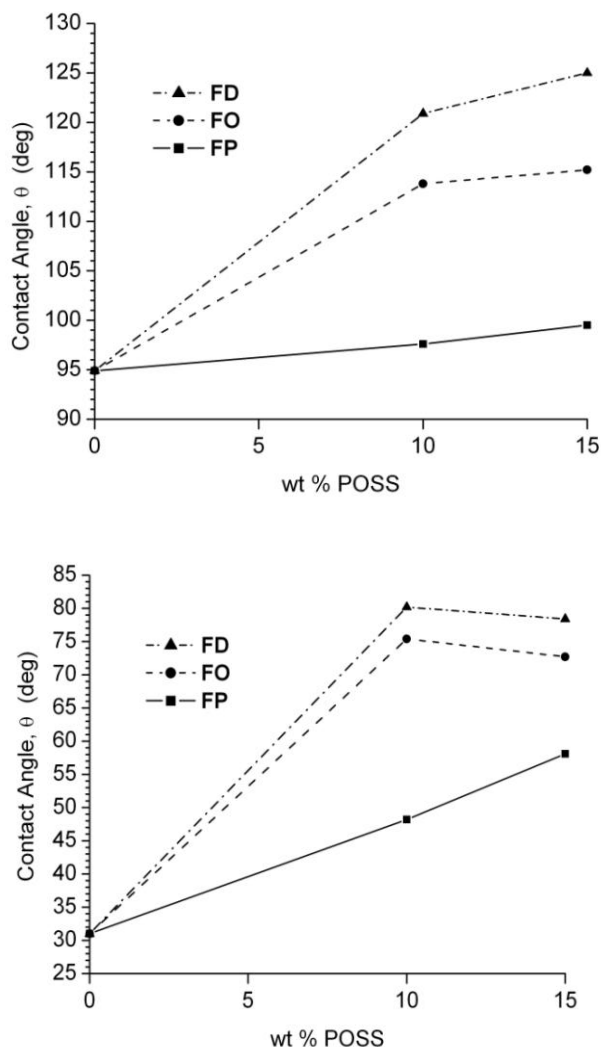


Figure 3 Static water (top) and hexadecane (bottom) contact angles of various wt % F-POSS compounds **FP**, **FO**, and **FD** blended with **6F-BP** PFCB aryl ether polymer.

hexadecane CA of 58°.

Dynamic water and hexadecane CAs were attempted to
 170 determine the degree of hysteresis of **FD** POSS blended into **6F-BP** PFCB aryl ether polymer. However, at all wt % of **FD** POSS blended into the polymer, the water and hexadecane drops remained pinned on the surface, even when the stage was tilted 90°. These results indicate a condition of high
 175 surface hysteresis whereby the surface energy (γ_{SV}) exceeds the surface tension (γ_{SL}) of the liquid drop.

While films prepared from 15 wt % **FD** POSS loading still appeared transparent and homogenous, 20 wt % **FD** POSS produced slight phase separation. At 30 wt % **FD** POSS,
 180 significant incompatibility was observed producing brittle, opaque films with visually apparent crystalline aggregates on the film surface. The remainder of this report will focus on the characterization of composite films of 15 wt% **FD** POSS and **6F-BP** PFCB aryl ether polymer based on optimized wetting
 185 properties.

Surface characterization

Atomic force microscopy (AFM) analysis of 15 wt % **FD** blend compared with unblended **6F-BP** PFCB aryl ether
 190 polymer showed an increase in surface roughness (Figure 4). From AFM analysis, unblended **6F-BP** polymer and 15 wt % **FD** POSS composite blend gave a measured surface roughness (RMS) of 0.527 nm and 1.478 nm, respectively. The incorporation of the fluorinated **FD** POSS structures produced
 195 a three-fold increase in surface roughness presumably due to blooming and/or aggregation of these structures on the surface during the spin casting process. The magnitude of the modest surface roughening observed for **FD** POSS was consistent with 15 wt % **FP** and **FO** POSS spin cast film compositions

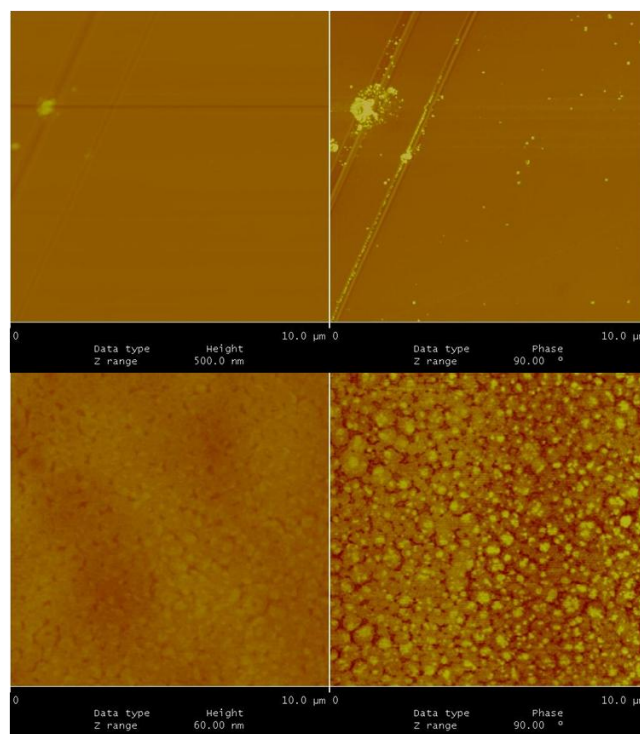


Figure 4 AFM height (left) and phase (right) images of **6F-BP** PFCB aryl ether polymer (top) and of 15 wt % **FD** POSS blend (bottom).

200 which is a minor contributing factor in of dewetting (*vide infra*).

The relationship of contact angle and surface energy is governed by Young's equation which relates interfacial tensions among the solid–vapor, liquid–vapor, and
 205 solid–liquid.⁴⁸ Furthermore, surface roughness influences liquid wetting as demonstrated by Cassie and Baxter⁴⁹ and

Wenzel.⁵⁰ From the aforementioned surface roughness obtained in the AFM analysis, such a slight increase in surface roughness (0.527 nm to 1.478 nm) is usually not enough to influence the overall macroscopic properties such as the contact angle.

It was shown that modeled nanometer-sized surfaces generated a modest increase in hydrophobicity due to changes in local water density gradients.⁵¹ Based on this report, the nanometer surfaces impressions disrupt the molecular water organization on the surface contributing an increase of ca. 7 mN/m to the surface–liquid tension. It is generally accepted average surface roughness (R_a) less than 100 nm has little effect on contact angles and hysteresis.^{52, 53} Indeed, many other examples have been reported that show nanometer surface roughness generated by POSS influence the hydrophobicity of the surfaces.^{12, 39, 40, 54-56} Therefore, it is presumed the low surface energy fluorine content contributed by F-POSS has the most influence on the surface contact angle, whereas the surface roughness is an important, but minor contributing parameter.

Analysis of 15 wt % **FD** POSS **6F-BP** PFCB aryl ether polymer composite film surface by scanning electron microscope (SEM) analysis using energy dispersive X-ray spectroscopy (EDS) elemental mapping showed excellent

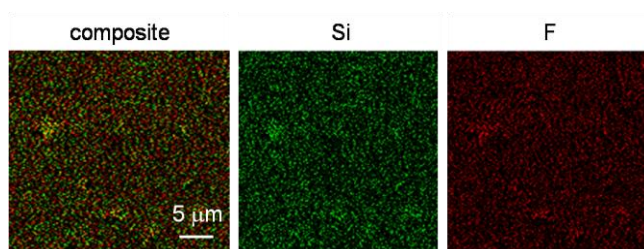


Figure 5 EDS elemental (composite, Si, and F, left to right) surface analysis of 15 wt % **FD** POSS **6F-BP** PFCB aryl ether polymer blend as a spin cast film.

dispersion of the POSS within the PFCB aryl ether polymer matrix (Figure 5).

Powder wide angle X-ray diffraction (WAXD) confirmed the presence of highly crystalline **FD** POSS aggregates from its spin cast film (Figure 6). The diffraction angles at 5.5°, 9.8°, and 11.0° produced the most intensity indicative of POSS (101), (210), and (012) planes, respectively.⁵⁷ The (113) and (300) planes are also present at around 17.1° and 18.3°, respectively, typical of overlapping reflections of different lattice spacings. The unblended **6F-BP** PFCB aryl ether polymer showed typical peak broadening at 10–40° indicative of the spin cast film's amorphous nature due to broad interlamellar regions of polymer chains. The spin cast film of 15 wt % **FD** POSS blended with **6F-BP** PFCB aryl ether polymers showed sharp diffraction of the (101) and (210) POSS planes at 5.6° and 9.7°, respectively.

The true utility of the F-POSS series is their compatibility in semifluorinated polymers over nonfluorinated POSS compounds. To demonstrate this, solutions of 40 wt % solids in hexafluorobenzene and accompanying spin cast films of *iso*-butyl POSS ($R = \text{CH}_2\text{CH}(\text{CH}_3)_2$) and **FD** POSS at 15 wt % loading in **6F-BP** PFCB aryl ether polymer were prepared.

While both formulations produced transparent solvent blended solutions, spin cast films of the nonfluorinated, *iso*-butyl POSS produced heterogeneous, opaque brittle films. This result indicates phase separation of the filler and polymer

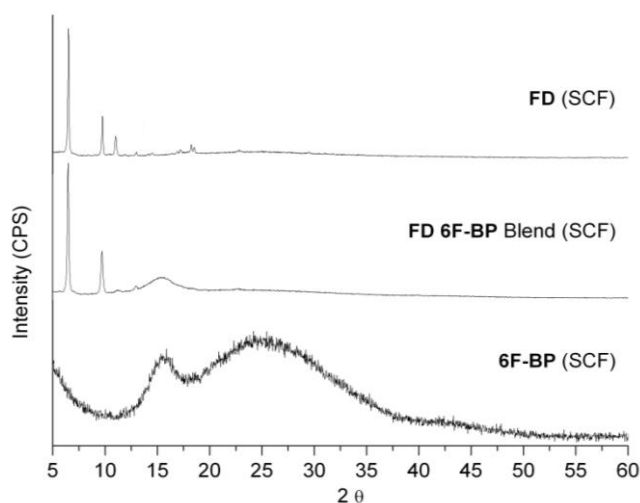


Figure 6 WAXD diffraction pattern of spin cast surfaces of **FD** POSS (top), **FD 6F-BP** PFCB aryl ether polymer blend (middle), and **6F-BP** PFCB aryl ether polymer with no POSS inclusion (bottom).

components due to their incompatibility.

Thermal properties

Differential scanning calorimetry (DSC) of 15 wt % **FD** POSS blended with **6F-BP** PFCB aryl ether polymer confirmed the presence of POSS inclusion. The DSC traces shown in Figure 7 represent the third reheating scan. **FD** POSS showed a melting endotherm at 142 °C which is present in the blended spin cast film. The unblended **6F-BP** PFCB aryl ether polymer produced a melting response at 186 °C consistent with a previous account.⁵⁸ An initial glass transition temperature (T_g) was observed for both the blended and unblended films at ca. 100 °C. The presence of **FD** POSS in this highly fluorinated PFCB aryl ether matrix showed no plasticizing effect by suppression of polymer melting temperature or change in T_g .

Experimental

Materials

Deionized water, hexadecane, and hexafluorobenzene were purchased through Aldrich and used without further purification. *iso*-butyl POSS was donated by the Air Force Research Laboratory (Edwards AFB, CA) and is also commercially available through Hybrid Plastics.

1H, 1H, 2H, 2H-trifluoropropyl₈-T₈-silsesquioxane (**FP**),⁵⁹ 1H, 1H, 2H, 2H-tridecafluorooctyl₈-T₈ (**FO**),⁴⁷ and 1H, 1H, 2H, 2H-heptafluorodecyl₈-T₈ (**FD**)⁴⁷ were prepared and fully characterized from previously published procedures.

6F-BP PFCB aryl ether polymer (M_n = of 22,000–25,000) was donated and is also commercially available from

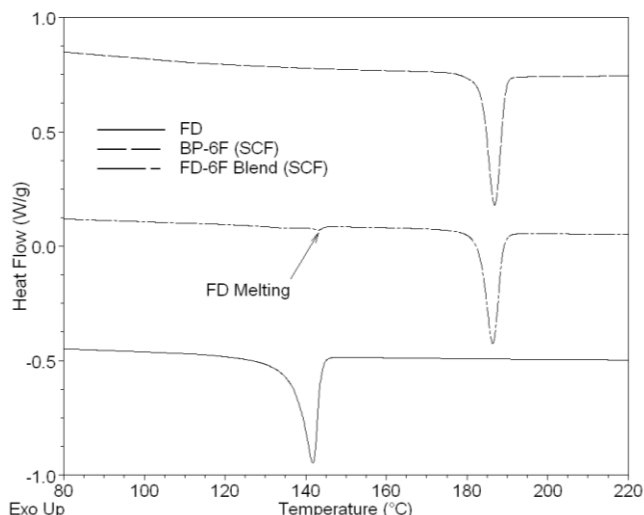


Figure 7 DSC of SCF of **6F-BP** PFCB aryl ether polymer (no POSS) (top), 15 wt % **FD POSS 6F-BP** PFCB aryl ether polymer blend (middle), and **FD POSS** (bottom).

Tetramer Technologies, L.L.C. and distributed through Oakwood Chemicals, Inc.

Instrumentation

Contact angle analysis performed on a FDS Dataphysics Contact Analyzer System was determined via the software suite using the captured image. Static contact angle values reported were an average of three values measured on various areas of the spin cast surface with an average standard deviation of ± 2 degrees ($^{\circ}$). The contact angle deviation was also consistent within $\pm 2^{\circ}$ when multiple spin cast films were prepared with the same solvent blended composition.

Atomic force microscopy (AFM) measurements were performed in tapping mode by a Digital Instruments Dimension 3100 Scanning Probe Microscope.

Scanning electron microscopy (SEM) were performed using an ISI CL6. Elemental mapping was performed using energy dissipation X-ray analysis with IXRF Systems analysis.

X-ray powder diffraction (XRD) were performed using a Scintag 2000 system with a voltage of 24 kV with a CuK_{α} source.

Differential scanning calorimetry (DSC) analysis were performed on a TA Q1000 instrument. Glass transitions temperatures (T_g) of polymers were obtained from the third heating cycle using DSC analysis at a temperature ramp of 10 $^{\circ}\text{C}/\text{min}$ in nitrogen.

Solvent blending

Fluorinated POSS PFCB aryl ether polymer blends were prepared by dissolving the appropriate weight percent of F-POSS relative to PFCB aryl ether polymer in the minimal amount of hexafluorobenzene (typically ca. 30–40 wt % solutions). Although the components in solvent produced a readily homogeneous solution, the mixture was rigorously blended with a magnetic stirrer for five minutes.

Spin cast film preparation

The solvent blended solutions were dispensed via a glass pipette on a glass substrate and then spin cast at 1800–2000 RPM using a Chemat KW-4A spin coater. The polymer coated substrate was dried in a vacuum oven at room temperature for 24 h. Spin and drop cast film thicknesses were approximately 1–2 μm thick and were measured on an Alpha-Step 200 profilometer.

For POSS powders, surfaces were prepared by dissolving the POSS in the minimal amount of hexafluorobenzene followed by mechanical agitation. The surfaces were spin cast using the prescribed conditions above producing a well-adhered, powder-like coating.

Conclusions

Formulations of fluorinated POSS compounds blended into a semifluorinated PFCB aryl ether polymer produced composites with enhanced repellency to water and hydrocarbon-based fluids. A high degree of hysteresis was observed for the optimized blended film composition. This indicates that nanometer surface roughening in combination with lowering the surface energy achieved by F-POSS dispersion was not enough to mimic the desired self-repellent behavior indicative of natural lotus leaves. These preliminary findings have prompted continued efforts in order to formulate composite systems in order to achieve higher omniphobicity with low surface hysteresis. Furthermore, the use of F-POSS did not compromise the processability, mechanical, and optical integrity desired for PFCB aryl ether polymers. Fluorinated POSS showed a clear advantage as a discretely-sized, low surface energy fillers for compatibility in primarily fluorinated polymer matrices. We anticipate the use of F-POSS as a drop-in modifier in commercial fluoropolymer systems for enhanced hydro- and oleophobicity.

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Notes and references

1. T. Sun, L. Feng, X. Gao and L. Jian, *Acc. Chem. Res.*, 2005, **38**, 644.
2. C. Neinhuis and W. Barthlott, *Ann. Bot.*, 1997, **79**, 677.
3. W. Barthlott and C. Neinhuis, *Planta*, 1997, **202**, 1.
4. B. Bhushan and Y. C. Jung, *Nanotechnology*, 2006, **17**, 2758.
5. Y. H. Erbil, L. A. Demirel, Y. Avci and O. Mert, *Science* 2003, **299**, 1377.
6. J.-J. Lin, C.-C. Chu, M.-L. Chiang and W.-C. Tsai, *Adv. Mater.*, 2006, **18**, 3248.
7. M. Morra, E. Occhiello and F. Garbassi, *Langmuir*, 1989, **5**, 872.
8. A. Ruiz, A. Valsesia, G. Ceccone, D. Gilliland, P. Colpo and F. Rossi, *Langmuir*, 2007, **23**, 12984.

9. W. Chen, A. Y. Fadeev, M. C. Hsieh, D. Öner, J. Youngblood and T. J. McCarthy, *Langmuir*, 1999, **15**, 3395.
10. D. M. Öner, T. J. , *Langmuir*, 2000, **16**, 7777.
- 375 11. E. Puukilainen, T. Rasilainen, M. Suvanto and T. A. Pakkanen, *Langmuir*, 2007, **23**, 7263.
12. L. Zhu, Y. Xiu, J. Xu, P. A. Tamirisa, D. W. Hess and C.-P. Wong, *Langmuir* 2005, **21**, 11208.
13. H. F. Hoefnagels, D. Wu, G. With and W. Ming, *Langmuir*, 2007, **23**,
380 13158.
14. K. K. S. Lau, J. Bico, K. B. K. Teo, M. Chhowalla, G. A. J. Amaratunga, W. I. Milne, G. H. McKinley and K. K. Gleason, *Nano Lett.*, 2003, **3**, 1701.
15. L. Zhai, F. C. Cebeci, R. E. Cohen and M. F. Rubner, *Nano Lett.*,
385 2004, **4**, 1349.
16. J. A. Howarter and J. P. Youngblood, *Adv. Mater.*, 2007, **19**, 3838.
17. G. Zhang, D. Wang, Z.-Z. Gu and H. Möhwald, *Langmuir*, 2005, **21**, 9143.
18. J. Scheirs, ed., *Modern Fluoropolymers: High Performance Polymers for Diverse Applications*, Wiley, Chichester, 1997.
- 390 19. S. T. Iacono, S. M. Budy, J. Jin and D. W. Smith, Jr., *J. Polym. Sci., Part A: Polym. Chem.*, 2007, **45**, 5705.
20. N. Mifsud, V. Mellon, J. Jin, C. M. Topping, L. Echegoyen and D. W. Smith, Jr., *Polym. Int.*, 2007, **56**, 1142.
- 395 21. B. K. Spraul, S. Suresh, J. Jin and D. W. Smith, Jr., *J. Am. Chem. Soc.*, 2006, **128**, 7055.
22. D. W. Smith, Jr., S. Chen, S. M. Kumar, J. Ballato, C. Topping, H. V. Shah and S. H. Foulger, *Adv. Mater.*, 2002, **14**, 1585.
23. J. Y. Jin, D. W. Smith, C. M. Topping, S. Suresh, S. R. Chen, S. H. Foulger, N. Rice, J. Nebo and B. H. Mojazza, *Macromolecules*, 2003,
400 **36**, 9000.
24. J. Y. Jin, C. M. Topping, S. Suresh, S. H. Foulger, N. Rice, B. H. Mojazza and D. W. Smith, *Polymer*, 2005, **46**, 6923.
25. L. A. Ford, D. D. Desmarteau and D. W. Smith, Jr., *J. Fluorine Chem.*, 2005, **126**, 653.
- 405 26. S. T. Iacono, S. M. Budy, J. M. Mabry and D. W. Smith, Jr., *Polymer*, 2007, **48**, 4637.
27. S. T. Iacono, S. M. Budy, J. M. Mabry and D. W. Smith, Jr., *Macromolecules*, 2007, **40**, 9517.
- 410 28. H. Ma, S. Liu, J. D. Luo, S. Suresh, L. Liu, S. H. Kang, M. Haller, T. Sassa, L. R. Dalton and A. K. Y. Jen, *Adv. Funct. Mater.*, 2002, **12**, 565.
29. A. R. Neilson, S. M. Budy, J. M. Ballato and J. Smith, D. W., *Macromolecules*, 2007, **40**, 9378.
- 415 30. J. Y. Jin, D. W. Smith, S. Glasser, D. Perahia, S. H. Foulger, J. Ballato, S. W. Kang and S. Kumar, *Macromolecules*, 2006, **39**, 4646.
31. D. W. Smith, Jr., H. W. Boone, R. Traiphol, H. Shah and D. Perahia, *Macromolecules*, 2000, **33**, 1126.
32. G. Li, L. Wang, N. Hanli and C. U. Pittman, Jr., *J. Inorg. Organomet. Polym.*, 2001, **11**, 123.
- 420 33. R. H. Baney, M. Itoh, A. Sakakibara and T. Suzuki, *Chem. Rev.*, 1995, **95**, 1409.
34. K. N. Pielichowski, J.; Janowski, B.; Pielichowski, J., *Adv. Polym. Sci.*, 2006, **201**, 225.
- 425 35. S. H. Phillips, T. S. Haddad and S. J. Tomczak, *Curr. Opin. Solid State Mater. Sci.*, 2004, **8**, 21.
36. S. Xiao, M. Nguyen, X. Gong, Y. Cao, H. Wu, D. Moses and A. J. Heeger, *Adv. Funct. Mater.*, 2003, **13**, 25.
37. A. Sellinger, R. Tamaki, R. M. Laine, K. Ueno, H. Tanabe, E. Williams and G. E. Jabbour, *Chem. Commun.*, 2005, **29**, 3700.
- 430 38. J. Lee, H.-J. Cho, B.-J. Jung, N. S. Cho and H.-K. Shim, *Macromolecules*, 2004, **37**, 8523.
39. S. Pal, H. Weiss, H. Keller and F. Müller-Plather, *Langmuir*, 2005, **21**, 3699.
- 435 40. P. F. Rios, H. Dodiuk, S. Kenig, S. McCarthy and A. Dotan, *J. Adhesion Sci. Technol.*, 2006, **20**, 563.
41. K. Zeng and S. Zheng, *J. Phys. Chem. B*, 2007, **111**, 13919.
42. J. M. Mabry, A. Vij, B. D. Viers, W. W. Grabow, D. Marchant, S. T. Iacono, P. N. Ruth and I. Vij, in *ACS Symposium Series 964*, eds. S. Clarson, J. J. Fitzgerald, M. J. Owen, S. S. Smith and M. E. Van Dyke, American Chemical Society, Washington, DC, 2007, p. 290.
- 440 43. A. Tuteja, W. S. Choi, M. H. Ma, J. M. Mabry, S. A. Mazzella, G. C. Rutledge, G. H. McKinley and R. E. Cohen, *Science*, 2007, **318**, 1618.
- 445 44. W. Choi, A. Tuteja, S. Chhatre, J. M. Mabry, G. H. McKinley and R. E. Cohen, *Adv. Mater.*, 2009, **21**, 1.
45. A. Vilcnik, I. Jerman, A. S. Vuk, M. Kozelj, B. Orel, B. Tomsic, B. Simoncic and J. Kovac, *Langmuir*, 2009, **25**, 5869.
46. A. Tuteja, W. Choi, J. M. Mabry, R. E. Cohen and G. H. McKinley, *Proc. Natl. Acad. Sci.*, 2008, **105**, 18200.
- 450 47. J. M. Mabry, A. Vij, S. T. Iacono and B. D. Viers, *Angew. Chem.*, 2008, **47**, 4137.
48. T. Young, *Phil. Trans. Roy. Soc.*, 1805, **95**, 65.
49. A. B. D. Cassie and S. Baxter, *Trans. Faraday Soc.*, 1944, **40**, 546.
- 455 50. R. N. Wenzel, *Ind. Eng. Chem.*, 1936, **28**, 988.
51. F. Müller-Plathe, S. Pal, H. Weiss and H. Keller, *Soft Mater.*, 2005, **3**, 21.
52. A. W. Neumann and R. J. Good, *J. Colloid Interface Sci.*, 1972, **38**, 341.
- 460 53. R. D. Schulze, W. Possart, H. Kamueswitz and C. Bischof, *J. Adhesion Sci. Technol.*, 1989, **3**, 39.
54. S. Turri and M. Levi, *Macromol. Rapid Commun.*, 2005, **26**, 1233.
55. H. Dodiuk, P. F. Rios, A. Dotan and S. Kenig, *Polym. Adv. Technol.*, 2007, **18**, 746.
- 465 56. K. Koh, S. Sugiyama, T. Morinaga, K. Ohno, Y. Tsujii, T. Fukuda, M. Yamahiro, T. Iijima, H. Oikawa, K. Wantanbe and T. Miyasitya, *Macromolecules* 2005, **38**, 1264.
57. A. J. Wadden and E. B. Coughlin, *Chem. Mater.*, 2003, **15**, 4555.
58. D. W. Smith, Jr., J. Jin, H. V. Shah, Y. Xie and D. D. DesMarteau, *Polymer*, 2004, **45**, 5755.
- 470 59. S. T. Iacono, A. Vij, W. W. Grabow, D. W. Smith, Jr. and J. M. Mabry, *Chem. Commun.*, 2007, **47**, 4992.

