

# Commercial Applications of Oleophobic and Superoleophobic Membranes

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## ABSTRACT

Superoleophobic surfaces with contact angles over 150° and droplet sliding angles approaching zero have been developed (1). However, even superoleophobic surfaces are not adequate for separating oil from waste water. Conventional pressure-driven membranes experience little success for treating fracking wastewater because of either severe membrane fouling. The ideal membrane, especially for use in fracking wastewater applications needs to be both hydrophilic (or superhydrophilic) and oleophobic (or superoleophobic), both in air and when submerged under water (2). In this study performance of oleophobic and superoleophobic surfaces have been investigated for variety of membranes and filter applications. For these applications different fluorocarbon based oleophobic coatings were tested on glass and plastic and on PTFE and ceramic membranes. The wetting performance of these coated membranes were tested according to the AATCC test 118-1992. The effects of surface roughness and heat on the oleophobicity and film integrity was also investigated.

## INTRODUCTION

It is well known that oleophobic coatings create oil resistant and anti-fouling surfaces that are impervious to oils and other organics particulates resulting in surfaces that are easier to clean and maintain. Fluorocarbons are excellent oleophobic coatings, since their surface energies are extremely low, generally less than 20 dynes/cm. Oleophobic membranes are widely utilized as venting

membranes in the electronics, automotive and other industries.

The oleophobicity of a membrane is generally rated on a scale of 1 to 8 according to AATCC test 118-1992. This test evaluates the membrane's resistance to wetting by eight standard oils. The #1 oil is mineral oil (surface tension: 31.5 dynes/cm @25 degrees. C.) and the #8 oil is heptane (surface tension: 14.8 dynes/cm @25 degrees. C.) (1). Long chain perfluoroalkyl fluorocarbons with greater or equal to C8 have typically produced the highest oleophobic rating of 8. Due to environmental concerns that fluoroalkyl groups that contain C8 chains or longer can degrade to perfluorooctanoic acid, various approaches have been used to increase the oleophobicity of shorter chain C6 fluoroalkyl materials (3).

Both the chemical composition of the surface and the surface texture affect the contact angle of oil on a surface. Treating a surface with plasma can increase surface roughness. Sand paper can also be used to roughen smooth surfaces. On membranes fiber diameter and weave can be utilized to modulate surface texture and roughness.

In the first part of this study, we present data showing comparison of properties of membranes fabricated with different C8 and C6 materials. A comparison of filters coated with a perfluoropolyether and fluoroalkylsilane are also shown.

We are also conducting experiments with water and organics mixtures using perfluoropolyether coated ceramic filters, treated with plasma and nanoparticles to create superoleophobic and superhydrophilic surfaces (4). Fabrication

procedures, contact angle and flow profiles will be discussed in the meeting.

## EXPERIMENTAL

Material used for this study include PTFE membranes, metal dishes, microscope glass and plastic slides. Fluoroalkyl polymers and co-polymers and fluoro-silanes were synthesized at Cytonix. Oleophobicity grade was assessed using the AATCC Spec 118-1992 guidelines.

Films of fluoroalkyl polymers and co-polymers were made in metal boats and on glass slides and cured at 180°C for 60 minutes. After cool down microscopy was used to examine the films and compared to untreated control. Contact angles to water were measured by placing a 2 µl drop on the films and contact angles calculated using ImageJ and a plugin for drop analyses. Contact angles to mineral oil were also measured by placing a 2 µl drop on the films. This series was used to assess the robustness of fluoroalkyl polymers and co-polymers before and after exposures such as high heat.

Films were also made on PTFE-membranes and plastic slides. Films were made by dipping the substrates in a 2% solution of fluoroalkyl polymers and co-polymers. The dip-coated substrates were dried at 110 °C for 45 seconds and aged for over three weeks at room temperature to cure the films .

To further understand the performance of C6 fluoroalkyl membrane coatings on textured surface, plastic slides were selected as a substrate. To create the texture plastic slides, slides were roughened using 220 mesh size sandpaper (3M). In total 5 slides were prepared, first slide was created using 2 rubs of Sandpaper, second slide with 4 rubs, third with 6 rubs, fourth with 8 rubs and last with 10 rubs. All these textured slides dip coated with a 2% diluted polymer of C6 fluoroalkyl based membrane coating. After drying of coated surfaces, contact angles of mineral oil were measured on each slide at room temperature.

For high temperature stability of oleophobic coatings, three different coating formulations were prepared. The first coating prepared was C6 fluoroalkyl in a low temperature procedure, the second coating was prepared using C6 fluoroalkyl in a high temperature synthesis and the third was a C6 fluoroalkyl with 2% silane in a low temperature synthesis. The microscopic glass slides were dip coated with these coatings and heated up to 200°C for 24 hours on a hot plate to analyze the effect of heat on the coating properties. Film quality and uniformity of the coating film was assessed and each slide given a pass or fail grade.

## RESULTS AND DISCUSSION

To understand the effect of surface texture on oleophobicity, five textured surfaces (Figure 1a-f) were created using sand paper and compared with the smooth coated surface. As shown in Figure 1, the contact angle of the mineral oil on textured surfaces is increased as roughness of the surface is increased from 1a to 1f. Figure 1a being the smooth surface showed the lowest contact, hence higher wetting and Figure 1e being the highly roughened surface showing higher contact angle, hence lower wetting.

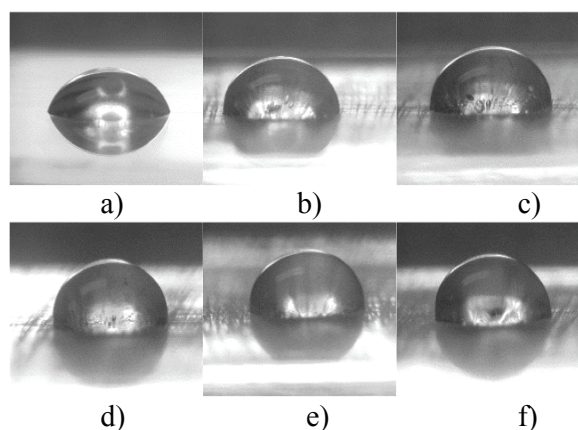


Fig 1. Effect of Roughness on the oleophobicity coated Plastic slides of the: a) Neat Plastic Slide, b) Plastic Slide with two rubs, c) Plastic Slide with four Rubs, d) Plastic slide with eight rubs, e) Plastic Slide with 10 rubs.

This surface phenomenon can be explained using Young's, Wenzel's and Cassie-Baxter's theory. In Young's model, the contact angle of a completely smooth surface is shown in Figure 2a. Wenzel's model behavior of liquid on a rough surface is shown in Figure 2b. Wenzel predicts that wetting is increased when contact angle is  $< 90^\circ$  and wetting is decreased when contact angle is  $> 90^\circ$ . The Cassie-Baxter's model (Figure 2c) where the grooves are filled with air and the liquid drop rests on the interface of air and rough solid, helps predict the roll of a droplet if the surface is superoleophobic. Contact angle increases with the increase of roughness because the effective surface area of the substrate increases, which helps reduce the surface energy of the substrate (5).

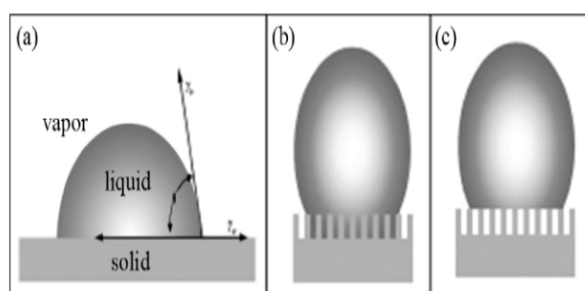


Figure 2. Theoretical background (5): a) Young's Model; b) Wenzel Model; c) Cassie-Baxter's Model.

**Table 1. Oleophobicity of PTFE membranes coated with fluoroalkyl polymers and fluorosilanes.**

	Oleo-Grade
Untreated	<1
C6 fluoroalkyl	7
C8 fluoroalkyl	8
C6 fluoroalkyl silane copolymer	6
C8 fluoroalkyl silane copolymer	7
Perfluoropolyether silane (MW~4000)	6
C6 fluoroalkyl silane	4
C8 fluoroalkyl silane	5

In Table 1 we show the relationship between C6 and C8 fluorocarbon polymers and oleophobicity grade. We also show that the oleophobicity grade

decreases for both the C6 and C8 polymers when a silane is copolymerized. In addition, we show that C6 fluoroalkyl silane has a lower oleophobicity grade of 4 compared to C8 fluoroalkyl silane. The 4000 molecular weight Perfluoropolyether silane (MW~4000) we tested showed an oleophobicity grade of 6.

For some commercial applications exposure to high temperatures is required. We have observed that some C6 fluoroalkyl acrylate membrane coatings performed well at ambient temperature, but exposure to 200°C for 24 hrs. caused the membrane to lose oleophobicity. We tested the heat stability of different fluoroalkyl materials after 24 hrs at 200°C. Various fluoroalkyl solutions (2% concentration) were used to dip coat glass slides. All coated slides were heated for 24 hours at 200°C. The results are shown in Table 2.

**Table 2: Results of heat tests on perfluoroalkyl and silane copolymers.**

Grade	Result
C6 fluoroalkyl polymer 1	Passed
C6 fluoroalkyl polymer 2	Failed
C6 fluoroalkyl polymer 2 fluorosilane copolymer	Passed

In Table 2, C6 fluoroalkyl Polymer 2 failed at 200°C due to a reduction in film uniformity resulting in uncoated regions. Polymer 1 on the other hand passed by retaining the film integrity. The reason for this result was the difference of monomers that appear to result in differential film hardness and integrity. Interestingly fluorosilane copolymerized polymer 2 passed the heat test and showed defect free films like the Polymer 1. Further testing of fluorosilane copolymers demonstrated reduced oleophobicity grade with increasing proportions of silanes to fluorocarbons. Work is continuing in understanding the different chemical and physical properties of polymer 1 and 2.

There is a need for oleophobic and superoleophobic filters for wastewater processing.

Since Dimethyl-Acetamide (DMA) is a common contaminant of fracking wastewater, we initially tested the static CA of fluoralkyl and fluorosilane coated filters to water, oil and DMA.

**Table 3: Fluoro coatings and contact angles.**

	FluoroSilanes on glass	FluoroAlkyls on glass
Water	110°	120°
Mineral Oil	75°	80°
Dimethyl-Acetamide	70°	65°

In Table 3 we show static contact angles for glass coated with the 4000 molecular weight Perfluoropolyether silane and the C8 fluoroalkyl polymer. Both polymers show good but different levels of repellency to water, mineral oil and dimethyl-acetamide that can be utilized to separate organics from water.

**Table 4. Dimethyl-Acetamide separation from water by fluoroalkyl polymers and fluorosilanes**

	Percent separation
Untreated	0 %
C6 fluoroalkyl	~70 %
C8 fluoroalkyl	~80 %
C8 fluoroalkyl silane copolymer	~70 %
Perfluoropolyether silane (MW~4000)	~60 %

In Table 4 we show draft results of dimethyl-acetamide separation from water achieved by using filters coated with various fluoropolymers. At the correct pressure, C8 fluoroalkyl provided the best levels of organics recovery. However, this membrane, like many types of conventional pressure-driven membranes used for treating fracking wastewater failed over-time because of membrane fouling. We are continuing to experiment with filters containing both oleophobic (or superoleophobic) surfaces and hydrophilic (or superhydrophilic) using perfluoropolyether coated ceramic filters, treated with plasma and

nanoparticles to create superoleophobic and superhydrophilic surfaces (5).

## REFERENCES

1. Tuteja, A., Choi, W., Ma, M., Mabry, J. et al. Designing Superoleophobic Surfaces. *Science* 318, 1618–1622 (2007).
2. Zhang, L., Zhong, Y., Cha, D., and Wang, P. A self-cleaning underwater superoleophobic mesh for oil-water separation. *Sci. Rep.* 3, 2326; DOI:10.1038/srep02326 (2013).
3. Honda, K., Morita, M., Otsuka, H., Takahara, A. Molecular Aggregation Structure and Surface Properties of Poly(fluoroalkyl acrylate) Thin Films. *Macromolecules* 2005, 38, 5699.
4. Brown, J. 6,767,587. Hydrophobic coating compositions, articles coated with said compositions, and processes for manufacturing same. July 27, 2004. Assignee Cytonix.
5. Latthe, S. S., Gurav, A. B., Maruti, C. S., & Vhatkar, R. S. (2012). Recent Progress in preparation of Superhydrophobic Surfaces: A review. *Journal of Surface Engineered Materials and Advanced technology*, 76-94.