Engineering Superhydrophobic and Superoleophobic Surfaces

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ABSTRACT

The combination of *surface chemistry* and *roughness* on multiple scales imbues enhanced repellency to the lotus leaf surface when in contact with a high surface tension liquid such as water. This understanding has led to the creation of a number of biomimetic superhydrophobic surfaces (i.e. apparent contact angles (θ^*) with water greater than 150° and low contact angle hysteresis). However, surfaces that display contact angles of $\theta^* > 150°$ with organic liquids having appreciably lower surface tensions (i.e. superoleophobic surfaces) are extremely rare. Calculations suggest that creating such a surface would require a surface energy lower than any known material. In our recent work (*Science,* 318, 1618, 2007) we demonstrated how a third factor, *re-entrant surface curvature,* in conjunction with chemical composition and roughened texture can be used to design surfaces that display extreme resistance to wetting from alkanes such as decane and octane. Here, we extend that work by designing a number of different nano-fiber surfaces (composed of a hydrophilic polymer (PMMA) and extremely low surface energy fluorinated molecules, fluoroPOSS) through electrospinning, which incorporate re-entrant curvature. By systematically changing the various design parameters we are able to assess the effects of surface geometry on both the apparent contact angle and hysteresis. Further, we perform a Zisman analysis on various PMMA - fluoroPOSS blends (using a series of alkanes) to estimate their surface energy. Rather surprisingly, it is observed that the Zisman analysis yields a negative value of surface energy for certain blends. These results are explained and reconciled with existing literature.

Keywords: superoleophobic, superhydrophobic, oil-repellent, self-cleaning, Zisman analysis.

1 INTRODUCTION

The most widely-known example of a natural superhydrophobic surface is the surface of the lotus leaf (*Nelumbo nucifera*). It is textured with small 10-20 μm protruding nubs which are further covered with nanometer size epicuticular wax crystalloids (see inset of Fig. 1a) [1]. Numerous studies have suggested that it is this combination of surface chemistry plus roughness on multiple scales [2-5] on the lotus leaf's surface that allows for the trapping of air underneath a water droplet (γ_{lv} = 72.1 mN/m), thereby imbuing the leaf with its characteristic superhydrophobicity (see Fig. 1a). However, a liquid with a markedly lower surface tension like hexadecane (γ_{lv} = 27.5 mN/m) rapidly wets the lotus surface leading to a contact angle of ~ 0° (see Fig. 1b), clearly demonstrating the leaf's oleophilicity. Indeed, in spite of the plethora of superhydrophobic surfaces now available, there are no naturally occurring superoleophobic surfaces [6-11] (i.e. surfaces that display contact angles greater than 150° with organic liquids such as alkanes having appreciably lower surface tensions than water).

2 RESULTS AND DISCUSSION

2.1 Electrospun superoleophobic fibers

Recent work in our laboratories [6] has led to the development of a new class of hydrophobic POSS molecules (radius 1-2 nm; see Fig. 2a) in which the rigid silsesquioxane cage is surrounded by fluoroalkyl groups. A number of different molecules with different organic groups (including 1H,1H,2H,2H-heptadecafluorodecyl (referred to as fluorodecyl POSS); 1H,1H,2H,2H-tridecafluorooctyl (fluorooctyl POSS) have now been synthesized, and this class of materials is denoted generically as fluoroPOSS. The fluoroPOSS molecules contain a very high surface concentration of fluorine containing groups, including $-CF_2$ and $-CF_3$ moieties. The high surface concentration and surface mobility of these groups, as well as the relatively high ratio of $-CF_3$ groups with respect to the $-CF_2$ groups results in one of the most hydrophobic and lowest surface energy materials available today [12]. By varying the mass fraction of fluoroPOSS dispersed in various polymers, we can systematically change the surface energy of the polymer-fluoroPOSS blend (see Fig. 3).

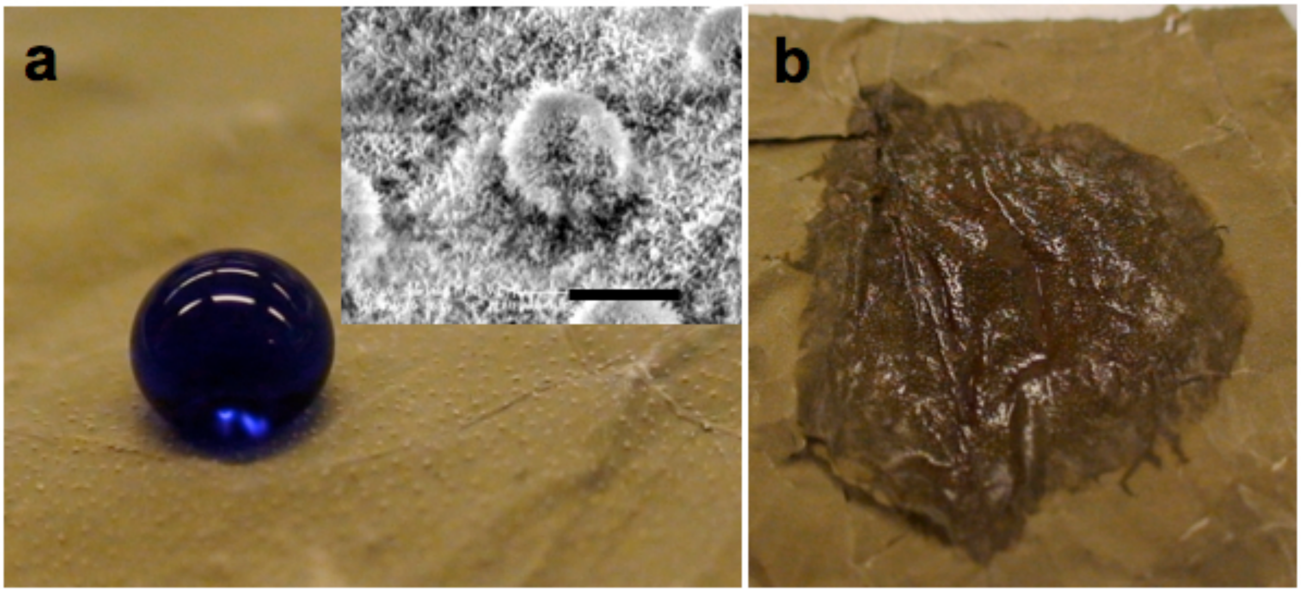

Figure 1. a. A droplet of water (colored with methylene blue) on a lotus leaf surface. The inset shows an SEM micrograph of the lotus leaf surface; the scale bar is 5 µm. **b.** The wetted surface of the lotus leaf after contact with a droplet of hexadecane. (Some images adapted from previous work [6].)

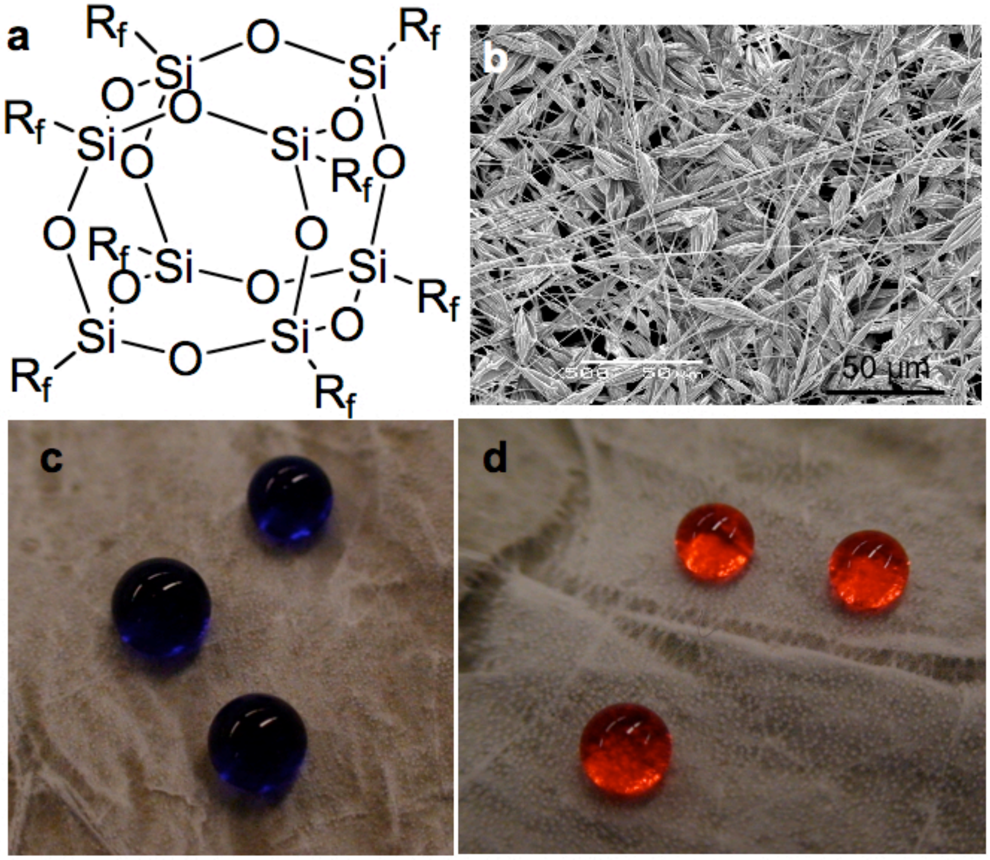

Figure 2. a. The general molecular structure of fluoroPOSS molecules. The alkyl chains (R_f) have the general molecular formula $–CH_2CH_2(CF_2)_nCF_3$, where n = 0, 3, 5 or 7. **b.** A scanning electron microscope (SEM) micrograph for an electrospun surface containing PMMA + 9.1 wt% fluorodecyl POSS. **c and d.** Droplets of water and hexadecane (colored with 'oil red O')

on a lotus leaf surface covered with electrospun fibers of PMMA + 44 wt% fluorodecyl POSS. A reflective surface is visible underneath the droplets in both pictures, indicating the presence of microscopic pockets of air. (Some images adapted from previous work [6].)

In the present work, we study blends of a moderately hydrophilic polymer, poly(methyl methacrylate) (PMMA, M_w = 540 kDa, PDI ~ 2.2) and fluorodecyl POSS as a model system. Fig. 2b shows the beads on a string morphology of these fluorodecyl POSS-PMMA blends created by electrospinning [13-16]. The complex re-entrant [4, 6, 11, 17, 18] topology allows us to support a composite (solid-liquid-air) interface with various liquids including water and alkanes such as hexadecane (see Fig. 2c and 2d), leading to extremely high apparent contact angles, even though the constituent nano-fibers themselves may be hydrophilic or oleophilic respectively. In contrast to many lithographic or vapor-deposition techniques, electrospinning is a benign single step process and the fluoroPOSS-PMMA blends can be deposited on a lotus leaf to confer it with oleophobicity, in addition to superhydrophobicity, as shown in Figs. 2c and 2d.

In our recent work [6] we also established the various design parameters that affect the robustness of the composite interface, allowing for the creation of extremely non-wetting rough surfaces, even though their corresponding smooth surfaces may be easily wetted by a given liquid. By systematically changing the various design parameters for the electrospun nano-fiber surfaces, we can evaluate the effects of surface geometry on both the apparent contact angle and hysteresis for various liquids. This enables us to develop surfaces that repel practically any liquid as evidenced by apparent contact angles greater than 150° with methanol (γ_{lv} = 22.7 mN/m), decane (γ_{lv} = 23.9 mN/m) and octane (γ_{lv} = 21.6 mN/m), on electrospun surfaces containing 56 wt% fluorodecyl POSS.

2.2 Estimation of solid surface energy ($\boldsymbol{\gamma_{sv}}$)

Previous work by Shibuichi et al. argued that for a chemically homogeneous, smooth surface to exhibit $\theta > 90°$ with any liquid, its solid surface energy (γ_{sv}) must be less than one-fourth the liquid surface tension, (γ_{lv})/4 [8, 9]. Careful studies of monolayer films by Zisman et al. [7] show that the contributions to the overall magnitude of surface energy of a flat surface decreased in the order $-CH_2 > -CH_3 > -CF_2 > -CF_2H > -CF_3$, and based on this analysis, the lowest solid surface energy is estimated to be ~ 6.7 mN/m (for a hexagonally closed packed monolayer of $-CF_3$ groups on a surface) [7, 19]. Taken in conjunction, these studies explain the absence of non-wetting surfaces displaying equilibrium contact angles > 90° with decane and octane [7-10, 20], as a solid surface would need to have a surface energy of ~ 5 mN/m to display $\theta > 90°$ with these liquids [6].

However, recently a few groups have reported extremely low γ_{sv} values; for example Coulson et al. [20, 21] report surface energy values as low as 1.5 mN/m for coatings created by pulsed plasma polymerization of 1H,1H,2H-perfluoro-1-dodecene.

Thus, the issue of the minimum surface energy seems to be a bit controversial and unresolved in the literature. The problem stems from the fact that measurement of equilibrium contact angles only provides an indirect estimate of the surface energy, and typically involves extrapolation or assuming an additive decomposition of γ_{sv} into dispersive and H-bonding / polar contributions. The most accurate determination of surface energies requires the measurement of the work of adhesion, and this is not often done [12].

There are several different methods of using contact angles to estimate the surface energy of a material (e.g. the Zisman analysis [7], the Owens-Wendt analysis [22], and Girifalco-Good-Fowkes-Young [23, 24] analysis), and each of these methods typically yields a different value for the computed surface energy, depending on the surface under study. Thus, previous studies have noted that these methods should only be used to obtain an estimate of the actual surface energy, which can be useful in comparing and ranking different surfaces (say with different degree of fluorination) as long as the same method is used for each surface [12].

Indeed, Coulson et al. also report two different measures of surface energy. They obtain values of γ_{sv} =1.5 mN/m (on a smooth glass substrate coated by pulsed plasma polymerization of 1H,1H,2H-perfluoro-1-dodecene [21]) and 4.3 mN/m (on a smooth glass substrate coated by pulsed plasma polymerization of 1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl acrylate [20]) using the Zisman analysis, or γ_{sv} =8.3 mN/m [21] and 10 mN/m [20] using the Owens-Wendt method for the same two surfaces. It is therefore unclear as to which method provides a more accurate value for γ_{sv}. An indication that the Zisman analysis might be providing a γ_{sv} value lower than the actual value for their surface comes from the values of octane contact angles obtained by Coulson et al. As mentioned above, if $\gamma_{sv} < \gamma_{lv}/4$, the equilibrium contact angle θ measured experimentally should be greater than 90°. In contrast, Coulson et al. report values of advancing contact angle, θ_{adv} = 74° and receding contact angle, θ_{rec} = 35° respectively on their coatings of 1H,1H,2H-perfluoro-1-dodecene when using octane (γ_{lv} = 21.7 mN/m).

We have also computed the surface energy of the various spincoated PMMA + fluoroPOSS surfaces (r.m.s

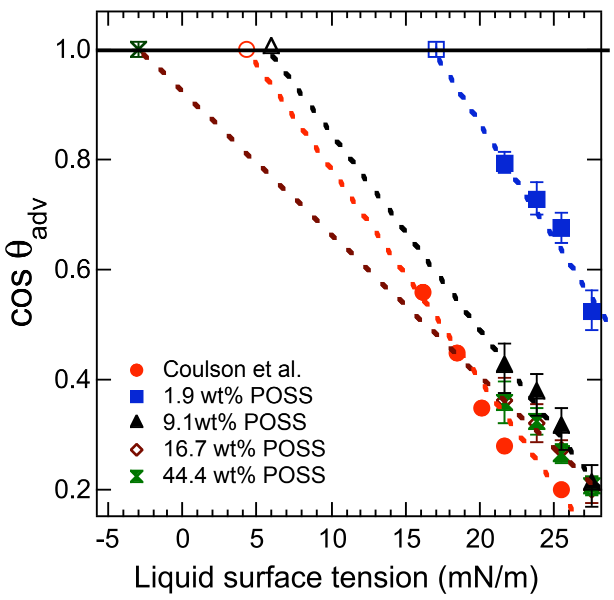

Figure 3. Zisman plot for various spincoated PMMA+fluoroPOSS films. The data from the Zisman analysis performed by Coulson et al. [20] for surfaces prepared by pulsed plasma polymerization of 1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl acrylate are also included for comparison. (Some data adapted from previous work [6].)

roughness for all spincoated surfaces was less than 4 nm) using the Zisman and the Owens-Wendt methods. For a spincoated surface containing 44.4 wt% POSS we obtain values of γ_{sv} = -3 mN/m and γ_{sv} = 7.8 mN/m (with the dispersive component of surface energy, γ_d = 6.6 mN/m and the polar component, γ_p = 1.2 mN/m) using the Zisman and the Owens-Wendt method respectively. Fig. 3 shows the Zisman analysis for four different spincoated PMMA + fluoroPOSS films, as well as, the data for the Zisman analysis done by Coulson et al. [20].

Clearly, the negative value of the surface energy obtained from the Zisman analysis of our surfaces are spurious (and arise solely form the extrapolation process employed), however, these calculations again point out the limitations of the various methods that use measurements of equilibrium contact angles to compute γ_{sv}. It is however clear from the data in Fig. 3 that, as would be expected, the surface energy of our PMMA + fluoroPOSS blends decreases with increasing POSS concentration and for high fluoroPOSS concentrations, the calculated interfacial energy seems to approach values consistent with those obtained by Coulson et al.

3 CONCLUSIONS

We have shown that in spite of the absence of any naturally oleophobic material, it is possible to engineer superoleophobic surfaces through the incorporation of re-entrant curvature within the surface texture. This enables us to create surfaces that repel practically any liquid as evidenced by apparent contact angles greater than 150° with methanol (γ_{lv} = 22.7 mN/m), decane (γ_{lv} = 23.9 mN/m) and octane (γ_{lv} = 21.6 mN/m), on certain electrospun surfaces. Further, we have also computed the surface energies of various PMMA-fluoroPOSS blends and found that the extrapolation involved is the Zisman analysis may lead to spurious values of the estimated solid surface energy.

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