Design, Development and Evaluation of Super Hydrophobic Coatings

Super hydrophobic surfaces have attracted the interest of scientists and engineers for both fundamental research and their practical applications, such as contamination prevention, self-cleaning, antifouling surface designs, anti-icing coatings, corrosion resistance of metals and their alloys, and biomedical and biological applications, among others. Coatings with hydrophobic surfaces can be fabricated by controlling their topographic features and surface energies. A surface's water repellency is an important phenomenon in natural and technological processes. A super hydrophobic surface is defined by a water contact angle (WCA) greater than 150° and a sliding angle (SA) lower than 5°.[1] There are plenty of super hydrophobic surfaces in nature, including lotus leaves, butterfly wings, duck feathers, etc.[2] Inspired by nature, super hydrophobic surfaces can be derived by employing two kinds of approaches. In the first approach, the solid surface is chemically modified with a low-surface-energy material. In the second approach, nano- and micro-scale structures are created on the substrate to prevent water from completely being in contact with the surface. In this approach, the water droplets sit mostly on the air. Water droplets on super hydrophobic surfaces can be nearly spherical and therefore have a tiny liquid-solid contact area, leading to easy roll off. Based on Cassie's law, which describes how simply roughing up a substrate increases the apparent contact angle of a surface, the formation of appropriate surface patterns on hydrophobic surfaces leads to a general change in their wettability, and the contact angle increases substantially.

Extensive research has been conducted to understand the formation of super hydrophobicity on various substrates.[3, 4] Organic/inorganic hybrid coatings using the sol-gel technique provide a simple and cost-effective approach to functionalize different surfaces. The presence of aliphatic hydrocarbon or perfluoro chains in the sol-gel precursors can substantially decrease the surface energy of the derived coatings. The mechanical properties of the films and adhesion strength to the substrate can be enhanced by crosslinking the silanol groups in the matrix and introducing chemical bonding between the coating and the substrate.[5, 6]

In the present study, we attempted to design a super hydrophobic coating by combining both the low surface energy and surface topographic features through the sol-gel technique. A sol-gel precursor containing a perfluorinated chain was used to obtain low surface energy, and hydrophobic nano/microsilica particles were incorporated to control surface roughness at the Micro/nano scales. The other sol-gel precursors such as tetraethoxy orthosilicate (TEOS) and methyltrimethoxy silane (TMOS) were also used to provide sufficient crosslink density and mechanical strength to the coatings. The sol-gel coatings were derived from an application bath consisting of the silane precursors, silica particles, water, alcohol and an acid catalyst. These coatings, deposited by dip-coating application on aluminum alloy test panels, were studied for their hydrophobicity as a function of surface energy alone, and the combination of surface energy and surface roughness. The effect of the fluorinated silane precursors and the type and amount of hydrophobic silica particles on the super hydrophobicity and mechanical properties were investigated. The descriptions for various samples studied and their corresponding bath compositions are shown in Table 1.

Aluminum test panels were degreased and chemically etched before the sol-gel coatings were applied. After application, the panels were placed vertically in a panel stacker for 15 min of air drying, followed by 30 min of thermal curing in an air-circulating oven at 120 °C. The typical dry-film thickness of the coatings was ~ 5-7 microns.

Design of Hydrophobic/Super Hydrophobic Coatings

Conventional sol-gel coatings were prepared using MTMOS and TEOS as silane precursors to form a smooth, clear and dense organic/inorganic network on an aluminum alloy substrate. Such coatings are known to have excellent adhesion due to their ability to form Al-O-Si linkages at the coating/substrate interface. Sample-II in this study represents such a conventional sol-gel coating. In order to reduce surface energy, and hence increase hydrophobicity, we incorporated an organo-silane containing a fluorooctyl chain, in addition to MTMOS and TEOS (sample A). Alkyl chains containing fluorine atoms are known to provide substantial hydrophobicity. Such chains, when attached to the polymer network via flexible siloxane linkages, would have a tendency to orient at the surface and hence reduce the surface energy of the coatings, as depicted in Figure 1. Since the hydrophobic property depends not only on the chemical composition of the surface, but is also influenced by the topography of the films, we attempted to produce coatings with varying degrees of surface roughness. In samples B and C, micro and nanosilica particles, respectively, were incorporated to create surface roughness that would enhance hydrophobicity. The use of microparticles (sample B) and micro + nanoparticles (sample C) were used to understand the effect of orientation of such particles at the surface, and hence, the resultant hydrophobicity. Figure 2

shows the schematic representation of hypothesized surface topographies of coatings with and without nano/microparticles, and their water contact angle on such surfaces.

Water-Contact Angles and Hydrophobicity of Coatings

Table 2 shows water contact angles and sliding angles of a bare substrate and different sol-gel-coated surfaces. The cleaned and deoxidized aluminum alloy surface (sample I) would have substantial Al-OH groups at the surface that are responsible for high surface energy. Therefore, sample I shows a very low contact angle of 29.4°, indicating good wetting by water droplet, as well as a high sliding angle of 90°, indicating the affinity of water for this surface. Coating a bare aluminum alloy surface with a hybrid organic/inorganic coating (sample-II) resulted in a substantial increase in the water contact angle. This was expected due to the fact that sol-gel coating of sample II had lower surface energies owing to the presence of alkyl chains on silane precursors. This also resulted in a reduced sliding angle.

The dramatic increase in the water contact angle for sample A can be attributed to the presence of perfluoro chains in the polymer matrix that are responsible for surface energy reduction by segregation at the surface. Thus, the fluorine-enriched surface of the coatings showed increased hydrophobicity. Sample A also showed significant decrease in the sliding angle as compared to sample II due to increased water repellency. In order to study the effect of surface energy lowering the perfluoro component on hydrophobicity, samples with increasing fluorine content were evaluated. These results (Table 3) showed that increasing fluorine content from 1% up to 5% only slightly increased the water content, and a super hydrophobic state could not be achieved. This can be due to the saturation of fluorinated segments at the surface at a certain level, beyond which a further increase in fluorine content would not reduce surface energy appreciably. Thus, it is not possible to attain super hydrophobicity merely through surface energy reduction strategy.

Samples B and C show very interesting results. These two samples contain, in addition to perfluoro alkyl chains, hydrophobically treated nano and microsilica particles. The increase in contact angle from 105º (sample A) to 123º (sample B) and the dramatic decrease in their sliding angles by about 90% is a clear indication of a change in surface topology that is responsible for water droplets sliding off the surface. The presence of microsilica particles seems to have uniformly protruded out at the surface, creating desirable-roughness to cause the sliding off of water droplets (see Figures 3 and 4). Figure 3 shows five different images that were taken from the DCA software for water contact angle measurements, and Figure 4 shows the photographic images of water droplets on the surface of the samples.

Water droplets on such surfaces would have a large water/air interface between the peaks on which droplets would rest. This would cause a significant increase in the water contact angle, and hence, their hydrophobicity.

As can be seen from Table 2, and Figures 3 and 4, sample C showed super hydrophobic behavior. Sample C showed a contact angle of 152º and a sliding angle of < 5º, putting this coating in the category of a super hydrophobic coating. In addition to the low surface energy contributing perfluoro alkyl chains on the polymer matrix and microsilica particles creating surface roughness, sample C contains nanosilica particles. The dramatic change in hydrophobicity of this sample,

therefore, can be attributed to the change in film morphology and topography brought about by incorporating nanosilica particles. We believe that the orientation of nanosilica particles may have created a surface topography that would increase the water/air interfacial area when a drop of water is placed on such a surface. Thus, the Cassie state can be attained to achieve super hydrophobic surfaces with both high contact angle and low hysteresis.

This would result in a situation, as per our hypothesis, shown in the far right hand side of Figure 2. The extremely lower sliding angle of sample C also supports our hypothesis.

Surface Mechanical Properties

The surface mechanical properties of the coatings were studied using a nano-indentation instrument. In the indentation test, the tip indents the surface to a predetermined load, i.e., to a predetermined depth, in 15 sec, held at the load for 30 sec to observe visco-creep, if any, and then unload in 15 sec. Based on the indentation curve, the hardness and elastic modulus can be calculated. Figure 5 shows the surface hardness, load on sample and modulus of the hybrid films. It can be clearly seen that the modulus of sample A (70 GPa) is significantly greater than those for samples B and C. This can be attributed to the highly crosslinked hybrid network for sample A. The presence of silica particles in samples B and C, (and corresponding reduction in sol-gel precursor) would cause reduced crosslink density of the film matrix, leading to the reduction in hardness and load. The presence of nano/microparticles would also have caused the formation of a certain degree of film porosity, resulting in drop in modulus of films in samples B and C.

Topography and Scanning Electron Microscopy

SEM was used to study the surface morphology of the films to relate that with their hydrophobicity. Figure 6 shows the SEM micrographs of samples A, B and C. It can be seen that sample A has an apparently smooth and uniform surface without any cracks. The introduction of micro and nanoparticles distorted the uniform structure of the surface, and a porous layered surface structure was formed. Furthermore, in Figure 6B it can be seen that the microparticles were uniformly dispersed throughout the polymer matrix. Thus, it can be said that a homogenous hybrid network was successfully formed. It can be seen from the SEM image of sample C that the surface becomes rough as the nanoparticles were incorporated into the polymer matrix. There are many nanoparticles irregularly dispersed on the microparticles of the film of sample C, and the branches could trap air in them. Micro cracks between the micro blocks could also be found, which can be attributed to poor film integrity and hence poor mechanical properties of samples B and C. Although film B has a relatively good micro structure, it is too disconnected to provide super hydrophobicity.

Conclusion

The aim of this study was to design hydrophobic or super hydrophobic coatings based on sol-gel chemistry by incorporating hydrophobic moieties and controlling surface morphology. The properties of sol-gel coatings containing perfluorinated structures as well as those with both perfluorinated structures and surface roughness created using micro and nanosilica particles were studied and compared. This study reveals that incorporating perfluorinated structures significantly improves hydrophobicity of coatings as well as their mechanical properties. However, perfluorinated structures alone could not provide super hydrophobicity. The super hydrophobicity could be achieved by using, in addition to the perfluorinated structures, nano and microsilica particles, thereby controlling the surface topography. This study provides very useful insight into the designing of sol-gel-derived hydrophobic/super hydrophobic coatings with tunable surface properties.

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