Development of mechanically robust self-cleaning coatings for large structure protection

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**DEVELOPMENT OF MECHANICALLY ROBUST SELF-
CLEANING COATINGS FOR LARGE STRUCTURE
PROTECTION**

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DEVELOPMENT OF MECHANICALLY ROBUST SELF-CLEANING COATINGS FOR LARGE STRUCTURE PROTECTION

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To my late grandmother, who is fondly remembered.

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Abstract:

With increasing focus on sustainable and environment friendly solutions for day-to-day applications, several new technologies are being developed or existing ones are being improved upon. Self-cleaning coatings and surfaces is one such area which is getting constant attention from today's scientific and industrial community. These coatings can effectively reduce cleaning and maintenance requirements and also prevent unwarranted damage and failure of machines or structures due to surface contamination. There are several ways to introduce self-cleaning functionality to a surface viz. photocatalytic, superhydrophilic or superhydrophobic methods. This project mainly concentrates on the development of different superhydrophobic coatings that can be applied on a surface to make it self-cleaning. A surface that is superhydrophobic possesses a water contact angle (CA) $> 150^\circ$ and low sliding angles (SA). The main principle behind superhydrophobicity is that the surfaces with this functionality have high resistance to wetting. Typically the formulation of these coatings contains use of soft polymer blocks and various organic surface modifiers. This in turn compromises the mechanical durability of the coatings when exposed to harsh environments. The main objective of this project is to develop self-cleaning coatings for large outdoor structures like wind turbine blades and aircraft wings with enhanced mechanical properties. The project aims to achieve this through understanding the main factors affecting the key functionalities of abrasion and erosion resistant self-cleaning coatings. Further, there are no standardized test methods to evaluate the effectiveness of such coatings. This project also aims at developing basic tests to evaluate the performance of various self-cleaning systems.

This work includes formulation, synthesis, characterization and mechanical testing of three different coating systems. The first system was based on a sol-gel formulation for producing an organic-inorganic matrix using a silane, tetraethylorthosilicate (TEOS) and an epoxy silane, glycidoxypolytriethoxysilane (Glymo). The hydrophobic functionality was introduced by addition of low energy molecules like fluoroalkylsilanes and particulate silica fillers. Though this system yielded coatings that exhibited a combination of contact angle $> 150^\circ$ and sliding angle $< 5^\circ$, the mechanical durability, erosion and abrasion resistance were not extremely high. In order to further improve the mechanical properties of this system, amine cured Glymo was used. This modification produced coatings that showed improved mechanical resistance compared to the previous composition. The second system also involves TEOS as a precursor along with the viscoelastic polymer polydimethylsiloxane (PDMS) acting as the hydrophobic agent. The PDMS due to its Si-O-Si network also contributed to the formation of the matrix along with TEOS. At a particular composition, these coatings exhibited dynamic hydrophobicity (i.e.) sliding of water droplets at angles $< 10^\circ$ even though the contact angle of these coatings were not $> 150^\circ$. These coatings also proved to possess satisfactory mechanical properties and resistance to abrasion and erosion which is attributed mainly to the presence of the viscoelastic polymer PDMS. On adding particulate silica fillers (10-20 nm) to the coating, they moved from being dynamically hydrophobic to superhydrophobic. The final coating system studied was based on the thermoplastic fluoropolymer polyvinylidene fluoride (PVDF). PVDF is hydrophobic by itself but modification with particulate fillers produced coatings that were extremely superhydrophobic. Previous literature indicates that most PVDF based coatings do not

have good adhesion with the substrates. This was addressed by pre-treating the substrates with (3-Aminopropyl)triethoxysilane (APTES) which functionalizes the surface, improving coating adhesion significantly. Increasing filler concentration improves the hardness of the coatings though the Young's modulus decreases. The resistance to abrasive wear and erosion is seen to decrease with increase in filler concentration. Superhydrophobic functionalities of the coatings are retained after abrasion and erosion.

A test was developed to measure the self-cleaning performance of the coatings. The principle of spectrophotometry was used to establish the extent of self-cleaning performance shown by various coatings. An artificial dirt mixture prepared in the lab was used to test the self-cleaning performance. In order to establish which factors influence the self-cleaning performance of the coatings, the effect of various physical properties including CA, SA, roughness, interfacial surface energy, the work of adhesion and retention force were studied.

In conclusion, three different coating compositions with hydrophobic/superhydrophobic properties were developed. The various coating compositions were studied in detail for their mechanical properties and the effect of abrasive and erosive wear. Correlation between the physical parameters and self-cleaning performance of the coatings were established. A new method to systematically measure the self-cleaning performance of coatings is described and tested. From the various systems studied, it is seen that a balance between mechanical performance and hydrophobicity can be achieved by effective optimization of surface and chemical modification. This study opens a new avenue which shows that superhydrophobicity is not always necessary to achieve effective self-cleaning properties.

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List of equations

$$\text{Young's equation: } \cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad (2.1)$$

$$\text{Wenzel's model: } \cos \theta^* = r \cos \theta \quad (2.3)$$

$$\text{Cassie-Baxter model: } \cos \theta^* = f_1 \cos \theta - f_2 \quad (2.4)$$

$$\gamma(\cos \theta_R - \cos \theta_A) = gm \sin \alpha \quad (2.5)$$

$$\Delta\gamma = gm \sin \alpha^* \quad (2.6)$$

$$\Delta\gamma = \gamma(\cos \theta_R - \cos \theta_A) \quad (2.7)$$

$$U \sim (R^5 \rho g \sin \alpha) / \mu l^3 = (\sigma^{3/2} \sin \alpha) / \mu R (\rho g)^{1/2} \sim (\sigma \text{Bo}^{-1/2} \sin \alpha) / \mu \quad (2.8)$$

List of abbreviations

CA	Contact angle
SA	Sliding angle
TEOS	Tetraethylorthosilicate
Glymo	(3-Glycidyloxypropyl)trimethoxysilane
PDMS	Polydimethylsiloxane
PVDF	Polyvinylidenefluoride
APTES	(3-Aminopropyl)triethoxysilane
CVD	Chemical Vapor Deposition
FAS	Fluoroalkylsilane
PTFE	Polytetrafluoroethylene
PEG	Polyethyleneglycol
PS	Polystyrene
CBD	Chemical Bath Deposition
LbL	Layer by layer assembly
HI	Itaconic acid
EtOH	Ethanol
EDA	Ethylenediamine
THF	Tetrahydrofuran
DMF	<i>N,N</i> -Dimethylformamide
FTIR	Fourier Transform Infrared Spectroscopy

AFM

Atomic Force Microscope

FESEM

Field Emission Scanning Electron
Microscope

Chapter 1: Introduction

1.1 Background

A self-cleaning surface is one that has the ability to keep itself free of dust, dirt and other contaminants. There are three ways by which self-cleaning functionality can be introduced on to a surface. They are:

- Photocatalytic effect
- Superhydrophobic surfaces
- Superhydrophilic surfaces

It must be noted that the presence of sunlight or flowing water is required for the surfaces to exhibit their self-cleaning action. Photocatalytic materials like TiO_2 respond to the UV component in the sunlight and create electron-hole pairs. The photo-generated charges facilitate reduction and oxidation of adsorbed species on TiO_2 surfaces. The photocatalytic processes are capable of oxidizing complex organic molecules into water, carbon dioxide and mineral acids [1-5]. It should be noted that photocatalytic materials can only decompose organic materials and not inorganic ones.

Some surfaces use their affinity to water or the lack of it to keep away dirt and contaminants. The surfaces that have extremely high affinity to water, with a water contact angle (CA) close to 0° are called ‘superhydrophilic’ and those which exhibit extreme repellence to water with $\text{CA} > 150^\circ$ are called ‘superhydrophobic’. On superhydrophilic surfaces, water tends to spread rapidly and completely wet the surface. There are several plants in nature whose leaves are superhydrophilic (eg. *Ruellia devosiana*) [6]. As a result of complete wetting by water, the dust and dirt accumulated on

these surfaces get easily removed, thus giving them the ability to ‘self-clean’. There are also several other instances in nature where the leaves repel water completely. Some of the most common examples are that of the lotus leaf, cabbage and Taro leaf to name a few [6]. In these cases, the water droplets have the ability to roll or slide easily off the surfaces, carrying away contaminants keeping the surface perpetually clean. This phenomenon is commonly known as the ‘Lotus-effect’. Fig. 1.1 shows examples of common hydrophilic and hydrophobic surfaces occurring in nature.

Fig. 1.1 Leaves with varying wettability as seen in nature [6].

There has been considerable interest in replicating such self-cleaning surfaces for day-to-day applications from both the scientific and industrial communities. In this work, we focus on the formulation, synthesis, characterization and performance of self-cleaning coatings based on hydrophobic or superhydrophobic functionality for large scale applications.

1.2 Motivation

Though the lotus effect and the phenomenon of superhydrophobicity in nature was observed and studied extensively for a long time, the efforts to replicate this effect on artificial surfaces did not gain significant interest until the 1990's [7-11]. It was only with the advent of scanning electron microscopy and other technological advances that the factors leading to this phenomenon were better understood [12-14]. These studies showed that a combination of rough surface and low surface energy were required for a surface to exhibit good superhydrophobic functionality. The roughness of the surfaces is attributed to the presence of hierarchical structures found on the lotus leaves. There are two levels of roughness present, one on the microscopic level and other on the nanoscale level. Due to the two different scales of surface features, the lotus leaves are said to possess hierarchical roughness. Fig. 1.2 shows the surface morphology of the lotus leaf where the presence of hierarchical structures can be clearly observed. The leaves also secrete an epicuticular wax mainly made up of long chain alcohols like nonacosanol and fatty acids [15]. These waxy secretions help in lowering the surface energy of the leaf. This combination of surface (chemical) and structural (morphology) modifications in the lotus leaves make it extremely superhydrophobic with a water contact angle of around $161 \pm 2.7^\circ$ and a very low sliding angle. Due to this, any dirt that gets accumulated on the surface of the leaves rolls off along with the water droplets [6, 13, 14]. Though extensive work has been done in fabricating superhydrophobic coatings and surfaces from a variety of raw materials, there is a lack of clear understanding on the correlation between surface roughness, hydrophobicity and the self-cleaning performance of the surfaces [13, 16].

Fig. 1.2 Morphology of a lotus leaf as seen under a scanning electron microscope [13]

Aside from this, there are technological challenges associated with the materials perspective that limit the application of superhydrophobic coatings for large scale applications. One is the development of coatings that have good mechanical strength and resistance to various kinds of wear including abrasion and erosion when subjected to harsh environmental conditions. The second challenge lies with the lack of a standardized testing process to measure the actual self-cleaning performance of these coatings.

The methods used to produce superhydrophobic surfaces can be broadly classified as (i) top-down approach that uses techniques like etching or lithography and (ii) bottom-up approach which uses sol-gel method, CVD etc. The bottom-up techniques cannot be easily scaled up and are therefore not feasible for large scale applications. Though there have been several reports of superhydrophobic coatings produced using sol-gel approach or CVD, there are no clear reports on the mechanical properties and performance of these coatings. To be successfully scaled up and applied on external features like wind turbine blades, automobiles, buildings etc. mechanically robust self-cleaning coatings are needed [17].

In order to achieve coatings that have good superhydrophobic properties in addition to long service life, this thesis focuses on three key challenges mentioned above: (1)

development of coatings that possess good hydrophobic as well mechanical properties for effective application (2) understanding the correlation between surface roughness, hydrophobicity and the self-cleaning performance and (3) development of a systematic method to quantify the self-cleaning performance of said coatings and surfaces.

1.3 Research objectives and scope

Coatings with superhydrophobic functionality have been formulated and studied for more than two decades now. The sol-gel method is one of the preferred ways to synthesize coatings with desired functional properties. The main advantage of using the sol-gel method is that it can be used to impart different functionalities by modifying the precursors and additives. With respect to the formulation of coatings with superhydrophobic functionality, both surface chemistry and morphology need to be controlled. Silane based precursors remain the most preferred materials to form the sol-gel matrix [18-20]. Surface morphology is controlled by the addition of particulate fillers of varying size ranges and low surface energy is achieved by the addition of long chain fluorinated alkyl silanes [21-24]. Though coatings with good superhydrophobic properties have been achieved using this method, there is a marked lack of mechanical durability in these coatings as they have proven to be brittle and have poor hardness and elastic modulus [17, 25]. In order to achieve a good balance between mechanical and hydrophobic functionalities, a compromise has to be made on the functional additives that are used in the sol-gel formulation. Besides the sol-gel method, there are several different ways to incorporate self-cleaning functionality to coatings. This thesis work gives a comprehensive analysis of three different coating systems and a comparative study on

their performance. Further, with increasing concerns on the use of fluorinated chemicals, non-fluorinated or shorter chain fluorinated molecules also need to be considered as viable alternatives to lower the surface energy of coatings and surfaces as they are more environmentally benign [26].

Despite the number of superhydrophobic systems that have been developed in the last several years, there is still a gap regarding the various physical parameters that can affect the self-cleaning functionality of these systems. We hypothesize that by controlling the physical parameters that affect the coating performance, superhydrophobicity may not be a prerequisite to achieve mechanically robust self-cleaning coatings. Based on the above hypothesis and literature review, the key objectives of this project are as follows:

1. Develop coatings which are hydrophobic or superhydrophobic and mechanically robust
 - optimize coating composition such that both long term functionality and service life can be achieved
 - test different kinds of functional additives to achieve hydrophobic/superhydrophobic functionality
2. Understand the interaction between the matrix and fillers and the effect of these interactions on the coating properties
 - characterize the coating properties
 - understand structure-properties correlations and their effect on hydrophobic/superhydrophobic properties.
3. Study how various physical parameters affect self-cleaning functionality

- determine the how contact angle and sliding angle vary with the effect of interfacial surface energy, work of adhesion and roughness
 - determine which of the above parameters has a direct correlation with the self-cleaning performance of the coatings.
4. Develop a standard method to evaluate the self-cleaning ability of the coatings
- formulate artificial dirt and application procedure
 - design a test which can be adapted to any surface to measure self-cleaning performance.

1.4 Organization of thesis

This thesis is divided into nine chapters. The first chapter covers the background and introduction on the topic under study. Chapter 2 gives an overview on surface wetting followed by a review of different kinds of self-cleaning coatings that have been developed and studied in the last several years. Chapter 3 explains the synthesis and characterization techniques used to study the three different coating systems, including the detailed description of a novel method proposed to test self-cleaning performance of the coatings. Chapter 4 covers the result and discussions on the TEOS-Glymo-FAS system. Chapter 5 presents results and discussion of the amine modified TEOS-Glymo-FAS system. Chapter 6 and 7 report findings from the TEOS-PDMS and PVDF based coating systems. Chapter 8 makes a comparison of all three types of coatings in terms of the functionality, mechanical durability and self-cleaning performance. Chapter 9 concludes with the important findings from this study and recommendations for future work.

Chapter 2: Literature Review

This chapter presents an overview on the basics of surface wetting focusing the various wetting states and models. The factors affecting the synthesis and development of new superhydrophobic coating systems are discussed. A critical review of the different materials systems studied so far is presented with emphasis on those that have potential for further development.

2.1 Surface wetting

Wetting can be simply defined as the phenomenon in which a liquid is able to maintain contact with a solid due to intermolecular interactions. The adhesive forces acting between solid and liquid phases lead to spreading of the liquid on the solid surface. The cohesive forces acting within the liquid try to decrease the area of contact between solid and liquid. Wetting brings about a change in the interface, which in turn contributes to the net increase or decrease of the surface energy. The interaction of the adhesive and cohesive forces at an interface determines whether or not wetting takes place in a system. When a liquid does not completely wet a surface, it results in an incomplete spherical droplet resting on the surface with a characteristic contact angle (CA). Fig. 2.1 shows a schematic representation of a water droplet that does not completely wet the surface. The CA is a function of the surface energies of the system [27]. The relationship was given by Young in the following equation:

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad (2.1)$$

where, γ_{SV} , γ_{SL} and γ_{LV} are the interfacial surface tensions with S, L and V referring to the solid, liquid and gas phases respectively. θ is the water contact angle as shown in Fig. 2.1.

Fig. 2.1 Schematic representation of a droplet on a flat surface with the various forces acting on it at equilibrium conditions [28].

Depending on the contact angle θ , the surface can be classified as hydrophilic ($\theta < 90^\circ$) or hydrophobic ($\theta > 90^\circ$). Surfaces like the lotus leaf, where $CA > 150^\circ$, are classified as superhydrophobic or ultrahydrophobic. For practical purposes, two kinds of CAs are used: static and dynamic. Generally, the static CA is measured at equilibrium and is almost close to the Young's angle for flat surfaces [27]. The dynamic CAs on the other hand refer to the advancing contact angle θ_A and receding contact angle θ_R of the droplet under non equilibrium conditions like when the droplet is in motion. Fig. 2.2 represents θ_A and θ_R on a droplet sliding down a surface. The difference between θ_A and θ_R is called the contact angle hysteresis ($\Delta\theta$). The dynamic hydrophobicity of a surface can be inferred from the magnitude of the sliding angle (SA). The SA is the smallest angle at which the droplet starts moving down the surface [29, 30]

Fig. 2.2 Schematic representation of a droplet sliding down a flat surface [31].

An ideal surface which is smooth, flat and chemically homogeneous will have $\Delta\theta$ value of 0° implying that there is no difference between the advancing and receding CAs. On such a surface there is only one thermodynamically stable contact angle. Non-ideal surfaces are those which are not completely flat, smooth or chemically homogeneous. These surfaces have a difference between θ_A and θ_R leading to contact angle hysteresis. The state of non-ideality is generally attributed to the roughness of the surface [32, 33]. It was also suggested that the contact angle hysteresis arises due to adsorption of either the liquid or foreign molecules on the solid [34]. Wetting on a rough surface can be of homogeneous and heterogeneous types. The Wenzel and Cassie-Baxter models explain how wetting takes place in the two regimes respectively.

2.1.1 Homogeneous wetting – Wenzel’s model

The first study on the effect of roughness on wetting was carried out by Wenzel [35]. When a drop of liquid rests on a surface, the specific energy of the wet area under the drop is lower than the surrounding dry region causing the liquid to spread spontaneously. When a liquid spreads, the wetted area under the drop and the free liquid surface over it will increase. For the same increase of the free liquid area at the upper surface of the drop,

a greater amount of actual surface area is wetted under it if the surface is rough. Therefore, on a rough surface there is a greater net energy decrease to induce spreading [35]. So, a rough surface tends to be wetted more rapidly. Using the same principle, on a water repellant surface the dry area around the droplet has the lower specific energy making the droplet assume a more spherical form. As the process here is the opposite of wetting, the net energy decrease is greater for the rougher surface making it more difficult to wet [35]. In short, roughness tends to magnify the wetting or non-wetting property of the surface. On real solids, the actual surface area will be greater than its geometric area due to its roughness. Wenzel termed the surface ratio as the ‘roughness factor’, denoted by r , where:

$$r = \frac{\text{actual surface area}}{\text{geometric surface area}} \quad (2.2)$$

In homogenous wetting, the liquid penetrates the grooves on the rough surface, completely wetting it. Fig. 2.3 shows a representation of homogenous wetting on a rough surface.

Fig. 2.3 Schematic representation of homogenous wetting where the water droplet penetrates into the grooves on the surface completely wetting it [36].

According to Wenzel, for a rough surface that undergoes homogenous wetting,

$$\cos \theta^* = r \cos \theta \quad (2.3)$$

where, θ^* is the apparent contact angle for a surface that has a roughness factor r and θ is the equilibrium contact angle.

2.1.2 Heterogeneous wetting – Cassie-Baxter model

Though Wenzel's model accounts for the effect of surface roughness on its wettability, it does not consider the effect of porosity on rough surfaces and consequently its effect on the wettability of the surface. Cassie and Baxter proposed certain modifications to the system. In a unit area, if f_1 is the total area of solid-liquid interface and f_2 the total area of liquid-air interface when the liquid spreads; solid-air interface area f_1 is destroyed with an energy gain of $f_1\gamma_{sv}$. An energy $f_1\gamma_{sl}$ is used to form the solid-liquid interface over the same area. Also an energy $f_2\gamma_{sv}$ is expended to form the liquid-air interface. γ_{sv} , γ_{sl} and γ_{lv} are the interfacial energies between the solid-air, solid-liquid and liquid-air interfaces [37].

In heterogeneous wetting, the liquid does not completely penetrate into the surface features to ensure uniform wetting. As a result, a film of air is present between the solid surface and the wetting liquid forming a heterogeneous interface. Fig. 2.4 represents the heterogeneous wetting phenomenon that takes place in porous materials.

Fig. 2.4 Schematic representation of heterogeneous wetting with a film of air between the solid surface and the liquid [36].

Based on these energy considerations, Cassie and Baxter proposed the following equation for heterogeneous wetting regimes:

$$\cos \theta^* = f_1 \cos \theta_1 + f_2 \cos \theta_2 \quad (2.4)$$

where, f_1 is the fraction of the component 1 contact area, f_2 is the fraction of component 2 in the composite area, θ^* is the apparent contact angle for a surface θ_1 is the equilibrium contact angle of component 1 and θ_2 is the equilibrium contact angle of component 2.

When component 2 is air, $\theta_2 = 180^\circ$ and $f_2 = 0$, the above equation will reduce to Wenzel's equation.

2.1.3 Transition of wetting states

Most wetting phenomena follow the Wenzel or Cassie-Baxter models. But at times there is a gradual transition from the Cassie-Baxter to the Wenzel regime. This happens mainly because the air pockets that are formed in the heterogeneous interface are no longer thermodynamically stable. Consequently, the liquid slowly starts filling in the air pockets transitioning from heterogeneous to homogenous wetting [38]. Fig. 2.5 shows a droplet transitioning from the Cassie-Baxter to the Wenzel state.

Fig. 2.5 A droplet in transition from Cassie to Wenzel state [39].

Such transitions may affect the dynamic CA's and SA of the surface though not much change in the static CA is observed.

2.2 Lotus effect and Petal effect

As described previously, lotus effect refers to the phenomenon in which the water droplets roll easily off the surface of the lotus leaf. The hierarchical roughness and the waxy nature of the lotus leaf are the main contributors to this effect. But not all surfaces that have a high CA exhibit this phenomenon. For example, on rose petals the water droplets are almost spherical. But they do not detach from the surface even after being tilted by 180° . This is because the adhesive force between the petal surface and the water droplet is very high [13, 38, 39]. Further, the surface morphology of the rose petals also plays a role. Though they also possess hierarchical structures, the surface features are larger in scale when compared to the lotus leaf. The larger scale features on the rose petals are more easily penetrable, leading to a sticky effect rather than the sliding effect seen on lotus leaves. This is called the ‘petal effect’ [40]. In this state as the liquid penetrates the surface features, though not completely as seen in Wenzel’s state [41]. This is also called the Cassie impregnating wetting state [40]. Fig. 2.6 shows a droplet with high CA sticking to the surface exhibiting petal effect. But for droplets of larger volumes ($> 10 \mu\text{l}$), this sticky effect is not seen as the weight of the droplet is large enough to make it slide due to gravity.

Fig. 2.6 (a) A droplet on a rose petal with CA 152.64° and (b) shape of the droplet when the petal is tilted by 180° [40].

2.3 Validity of the wetting models

This section provides a critical review of the theoretical models governing the phenomenon of superhydrophobicity and their limitations.

2.3.1 Effect of roughness

As discussed previously in section 2.1.1, Wenzel put forth a theory stating that the roughness of a surface magnifies its wetting behavior, be it hydrophobic or hydrophilic. In the Cassie-Baxter model conversely, effect of roughness is not considered and the solid liquid and air fractions at the interface are identified as the factor controlling CA. To have a more elaborate understanding on the models suggested by Wenzel and Cassie-Baxter, superhydrophobic surfaces were carefully modeled with regularly distributed textures and features. Studies carried out by Bico and Patankar showed conflicting results with respect to the effects of roughness and surface fractions [36, 42]. Bico, Marzolin and Quere found that irrespective of the roughness factor, the CA followed the predictions of Cassie and Baxter. Patankar, however, found with square pillar textured surface that the height of the pillars and their spacing (altering roughness factors) would result in the interface fractions being inconsequential. Extrand proposed a model to help predict how specially designed surfaces will behave [43]. But these calculations can be made only if the exact dimensions of the surface features and asperities are known and cannot be applied on surfaces that are not designed to meet these specific requirements.

2.3.2 Transition of wetting states

It has been described earlier in section 2.2 how a water droplet on a superhydrophobic surface can transition from having a heterogeneous contact interface to completely

wetting the surface. Nosonovsky and Bhushan use surface energy to determine the validity of the Wenzel and Cassie equations [44]. For both homogenous and heterogeneous systems, there is a local energy minimum that is associated with a stable state. Small changes in the systems lead to a transition. There are several models describing the transition states. But each model is based on certain assumptions, thus imposing limitations on their validity and applicability on random rough surfaces.

2.4 Superhydrophobic surfaces – Rolling vs. Sliding

For a surface to exhibit good self-cleaning properties it is believed that a combination of high CA and low SA is required. In 1961, R.R.Davies described that rain water on hydrophobic leaf surfaces did not form a continuous film, but instead beaded away in beads [16]. In the earlier stages, the CA was the only measure of hydrophobicity of a surface. The sliding angle was not measured or tested until much later. The significance of the sliding angle and the droplet motion on the surfaces is still not clearly explained. Water droplets are said to roll down surfaces that are extremely superhydrophobic [16]. The factors which contribute to the rolling versus sliding motion of droplets on the hydrophobic surfaces is not clearly explained, though several scientists have been studying this phenomenon since the 1930's [45-47]. The critical angle of inclination at which the droplet starts running down the surface is called the sliding angle [45]. This definition was first provided by Frenkel in 1948. If the surface has poor wetting properties i.e., the surface is hydrophobic or superhydrophobic, the droplet does not leave a trail behind it as opposed to cases where the surface has good wetting properties. Frenkel went on to study the problem of capillarity in droplet shape on horizontal and inclined surfaces

[45]. He showed that the equilibrium condition between the lengthwise force components of surface tension and gravity of a droplet is given by:

$$\gamma(\cos \theta_R - \cos \theta_A) = mg \sin \alpha \quad (2.5)$$

where, θ_R and θ_A are the receding and advancing CA's respectively, g is the acceleration due to gravity, m is the mass of the droplet and α is the sliding angle.

From hydrodynamics, it is known that a fluid cannot 'slip' with respect to a solid surface. Therefore, the only mechanism with which a drop can run down is when the fluid is poured from the rear edge of the droplet to the front edge. Fig. 2.7 shows a schematic of the phenomenon described by Frenkel.

Fig. 2.7 Representation of a droplet moving on a surface [45].

Such a movement of the droplet can only begin when the work of the gravitational force is greater than or equal to the work of the adhesion forces on the drop's rear edge. Therefore, for a droplet to move a distance $A_1A_1' = dx_l$, as shown in Fig. 2.7, work of magnitude $\Delta\gamma * dx_l$ is required, where $\Delta\gamma = (\gamma_{LV} + \gamma_{SV} - \gamma_{SL})$, is the adhesion energy of the

fluid per unit area of the solid. Similarly, the front edge of the droplet is also shifted by the same profile, $dx_1 = dx_2$. Work done by the gravitational force is given as $gm.\sin \alpha. dx_1$.

So, for an angle $\alpha = \alpha^*$ at which the droplet first begins to slide can be determined by using the expression:

$$\Delta\gamma = mg.\sin \alpha^* \quad (2.6)$$

Substituting for $gm.\sin\alpha^*$ in equation 2.6,

$$\Delta\gamma = \gamma(\cos \theta_R - \cos \theta_A) \quad (2.7)$$

From equation 2.7, it can be seen that a droplet cannot roll down the surface when $m < 2\gamma/g$, (i.e. when $\sin \alpha^* \leq 1$). In this case, the droplet stays in place even when the surface is vertical or overturned. Fig. 2.8 shows Frenkel's interpretation of how a droplet rolls down the surface.

Fig.2.8 Depiction of a droplet rolling down a surface [46].

In 1950, J.J.Bikerman conducted a series of experiments to determine the effect of surface roughness on the sliding of droplets [46]. In this experiment, steel plates of varying roughness were used to test the contour and motion of water droplets as the plates

were slowly tilted. It should be noted that the static CAs of these plates were $< 90^\circ$, indicating that the surfaces were not hydrophobic. Water droplets of 0.05, 0.1, 0.2 and 0.4 cm^3 volume were used to perform this test. These volumes are much larger than those used in the modern contact angle instruments used in experiments today. Bikerman also measured the length (l), width (w) and diameter (Δ) of the droplets as the plate is tilted. The change in these values as the plate is tilted shows that the droplet undergoes a change in its shape and contour before it begins to slide down the surface [46]. Fig. 2.9 shows the different shapes of the droplet as the plate is tilted.

Fig. 2.9 Top view of the droplets (a) before tilting, (b) when the droplet first starts sliding and (c) during sliding without acceleration [46].

From this study it was shown that the sliding angle increases with the roughness of the surface. Most of the samples Bikerman used had CA's that were equal or almost equal. So it can be inferred that the effect of roughness was what influenced the sliding of droplets on the surface [46]. In this study, Bikerman also explained that instead of using the sliding angle α , which is independent of droplet volume ($W \sin \alpha$)/ w , where W is the weight of

the droplet should increase with increase in roughness. If $(W \sin \alpha)/w$ remains in the same range up to $\sin \alpha = 1$, the volume of the smallest drop that can slide along the surface can be calculated [46]. The resistance of a droplet sliding on a surface is the apparent friction between the liquid and the capillary action on the rough features of the surface which is manifested in the form of contact angle hysteresis.

A more recent study on lines similar to that carried out by Bikerman was done in 2005 by Le Grand, Daerr and Limat. From this study, it was established that when the Bond number (Bo) component based on gravity, parallel to the plane exceeds a threshold [48] the droplet starts moving at a steady velocity, which increases linearly with Bo_α . The Bond number is a dimensionless value measuring the importance of surface tension forces in comparison to body forces. Bo_α here refers to the change in Bond number with the sliding angle. As the inclination α of the surface increases, the velocity of the droplets also increases. There are three forces acting on the droplet while sliding down an inclined plane, the weight of the droplet, a viscous drag with the surface and the interfacial forces acting on them. On resolving these forces, a balance gives rise to the scaling law where a linear relationship between the Capillary number and Bond number [48]. Le Grand, Daerr and Limat go on to compare their data to the four different models of wetting dynamics proposed by de Gennes, Cox-Voinov, Blake and Ruschak and Dussan [49-52]. But the main limitations of these models are that they are all designed for cases where CA is very small so that $\sin \theta$ can be approximated to θ to simplify calculations. Consequently these models on dynamic wetting cannot be directly applied in cases where θ is very high.

In 1998, Mahadevan and Pomeau discussed the rolling of droplets on an inclined plane [53]. The primary factor to be considered here is that if the droplet partially wets the surface, it will slide along it; and if it is completely non-wetting, the droplet will roll down the surface. They provide a scaling law for the velocity of a viscous droplet moving on a plane with a small slope at a low velocity. The scaling law proposed by Mahadevan and Pomeau is given below:

$$U \sim (R^5 \rho g \sin \alpha) / \mu l^3 = (\sigma^{3/2} \sin \alpha) / \mu R (\rho g)^{1/2} \sim (\sigma \text{Bo}^{-1/2} \sin \alpha) / \mu \quad (2.8)$$

where U is the velocity of the droplet, R is its radius, ρ is the density of the liquid, g is the acceleration due to gravity, μ is the viscosity of the liquid, σ is the surface tension of the liquid and Bo is the Bond number.

As the size of the droplet increases, the contact area with the surface does not change much for a case where the liquid is completely non-wetting. Consequently, the velocities of the droplets become size-independent.

Several conclusions can be drawn from the various studies that have been carried out on the dynamics of wetting and droplet motion under different conditions. One is that two distinct kinds of droplet motion, sliding and rolling have been observed on inclined surfaces. The wetting behavior of the liquid is what determines whether a droplet rolls or slides down a surface. Two, contact angle hysteresis is observed when there is an apparent friction between the surface and the droplet. And finally, there is no study yet on how to establish the cases in which rolling of the droplets will occur predominantly over sliding and vice versa.

2.5 Preparation of superhydrophobic surfaces

This section gives an overview of the different methods used to prepare hydrophobic and superhydrophobic coatings and surfaces. As mentioned previously in section 1.2, hydrophobic properties can be introduced to a surface by two different ways, the top-down approach and the bottom-up approach. There are techniques which also use both approaches in combination to produce superhydrophobic coatings and surfaces. Techniques under these categories are discussed in detail in the following sections.

2.5.1 The top-down approach

The top-down approach in general, refers to using techniques like cutting, etching, carving, molding and machining bulk materials using various tools and equipment [54]. More specifically, as applied to hydrophobic and superhydrophobic surfaces, it involves using plasma treatment, etching, micromachining and template or lithographic techniques [11, 55-57]. Some of the earliest efforts to produce superhydrophobic surfaces was by using the fractal growth of alkyl ketene dimers on a substrate with a CA of 174° [9]. Mohammadi, Wassink and Amirfazli further tried to cast alkyl ketene dimers into molds and were successful in creating surfaces with a CA of 164° . The hydrophobicity is due to the formation of pin and needle like structures that occur over a period of time [58]. Templatation methods have been used to replicate features from the original surfaces of the lotus leaf, rose petals etc [59, 60]. Several materials can be used as the template for creating such surfaces. Different polymer materials like polystyrene (PS), polydimethylsiloxane (PDMS), polyethyleneglycol (PEG) and polytetrafluoroethylene (PTFE) have been used to produce surfaces with intricate micro and nano scale features

and patterns. Fig. 2.10 shows the steps involved in the templation process using PDMS as the substrate.

Fig. 2.10 Schematic representation of the templation process to produce a positive replica of the original material used [60].

Photolithography involves irradiating light through a mask with desired features on substrates (ex: silicon wafers) covered with a photoresist [54]. In the case of preparing superhydrophobic surfaces, an extra step of surface treatment using low energy materials is required. Plasma treatment and etching involves using reactive atoms or ions generated from a gas discharge. Considerable changes in surface structure can be achieved because of the anisotropic etching of the surface layers [54]. The photolithographic approach is shown in the schematic representation in Fig. 2.11.

Fig. 2.11 Photolithography technique [60].

Most of the top-down techniques cannot be easily scaled up for large scale applications. This project was specifically aimed at developing effective self-cleaning solutions for large structure protection. Therefore, we focus more on the bottom-up approaches which are more suitable to our application in the remainder of the literature review.

2.5.2 The bottom-up approach

The bottom-up approach involves combining small building blocks and components and integrating them together to form the final product. Self-assembly and self-organization are key techniques involved in nanofabrication methods such as those used to prepare hydrophobic and superhydrophobic surfaces [54]. The common bottom-up methods that have been used to fabricate superhydrophobic surfaces include chemical bath deposition (CBD), chemical vapor deposition (CVD), electrochemical deposition, layer-by-layer assembly (LbL), colloidal assembly and sol-gel method [21, 61-66].

2.5.2.1 Chemical deposition methods

These techniques involve chemical reactions that deposit the products via self-assembly on to the desired substrate. Depending on the deposition conditions the terminology used varies as CBD or CVD. This method was used by Hosono, Fujihara, Honma and Zhou to produce CoCl_2 and urea based nanopin structures. The resulting surface was treated by lauric acid which was the hydrophobic modifier. The CA recorded was as high as 178° [67]. This is the highest CA reported so far. Such high values can be attributed to the nanopin structures on the surface with diameters of only 6.5 nm. ZnO nanorods were fabricated on a surface by Wu, Zheng and Wu using $\text{Zn}(\text{NO}_3)_2$, NH_4Cl , urea, and ammonia as the chemical precursors. The nanorods were reported to have diameters of 400-600 nm forming a dense and uniform film. Various long chain alkanolic acids were used as the surface modifiers to ensure high CA [68]. Though very high static CA's have been achieved by using a combination of various chemicals to produce nanoscale structures on the surface, self-assembled monolayers (SAM) are required to render these surfaces hydrophobic or superhydrophobic. There are also no records of the SA or the contact angle hysteresis measured in these cases. As discussed previously in section 2.3, these values can give an idea about the apparent friction that exists between the surface and the water droplet in instances where such high CA is reported, which is not previously known.

2.5.2.2 Colloidal assemblies

The van der Waals interactions results in monodispersed particles forming close packed assemblies on surfaces. The particle assemblies provide roughness to the underlying

substrates. The roughness of the substrates can be further improved by using techniques like plasma treatment or etching [69]. The main advantage of colloidal assemblies is that it does not require any expensive lithographic techniques and is cost effective. Binary colloidal assemblies for superhydrophobic surfaces were studied by Zhang, Wang, Gu and Mohwald on silicon substrates. CaCO_3 hydrogel spheres were dip-coated to form a self-assembly. The monolayer was used as a template for the assembly of silica or PS beads. The difference in hydrophilicity between the silicon substrate and the CaCO_3 monolayer lead to irregular structures with hierarchical roughness. Treatment with SAM was required to achieve CA of 156° and 160° on the PS and silica based assembly respectively [70]. The schematic representation of the binary colloidal assembly by Zhang et al. is shown in Fig. 2.12. One limitation of such colloidal assemblies is the formation of irregular surface features as seen in the instance discussed here. It should also be noted that there is yet again a lack of SA and CA hysteresis data recorded in these studies.

Fig. 2.12 Formation of binary assembly on Si wafer [70].

2.5.2.3 Layer-by-layer deposition

Layer-by-layer deposition exploits the electrostatic charge interactions between the various polycation and polyanion layers. It allows for precise control of the thickness of the layers down to the molecular level [54, 71-73]. Hydrophobization of the system is a necessity as the polyelectrolytes are hydrophilic in nature. Roughness can be introduced by the addition of nanoparticles and other surface treatments. Jisr, Rmaile and Schlenoff have used fluorinated polyelectrolytes like Nafion and polyvinylpyridine thereby eliminating the need for further hydrophobic treatment of the system [74]. The static CA after 10 double layers was reported to be 114° . Naturally occurring clay mineral nanorods were incorporated to bring the CA up to 168° . The SA for this system was reported be around 1° [74]. Some others LbL systems developed show extremely high contact angle hysteresis and very often, high temperature thermal treatments is required to make the films stable [54]. These factors, in addition to the steps required to hydrophobically treat the surface and introduce roughness makes LbL a more time consuming process compared to other techniques.

2.5.2.4 Sol-gel method

The sol-gel technique is one of the best known methods to produce highly homogeneous networks of organic-inorganic composite materials. The earliest known reports of this technique goes back to Kistler in 1930 when he used it to produce aerogels [75]. This method was also used to study phase equilibrium in the earlier part of the 20th century [76, 77]. The process has since been evolving constantly and has become one of the most commonly used techniques to produce ceramics, gels, protective coatings, thin films,

fibres and refractory materials [23, 78]. The sol-gel process mainly involves hydrolysis followed by condensation of oxides, silicates etc. A large amount of solvent gets impregnated into the network during its formation, thus resulting in gels. The most important advantage of the sol-gel method is that it can be used to prepare homogenous multi-component systems, whose properties can be tuned and controlled by the addition of fillers in the sol. Further, the microstructure of the final product can also be altered by modifying the process parameters during the hydrolysis and condensation stages. These factors contribute to the versatility of the technique, making it one of the easiest and most cost-effective ways of producing a wide range of materials.

The sol-gel method offers a wide range of options to incorporate different functionalities and properties into a system. Tadanaga, Katata and Minami used the sol-gel method to produce Al_2O_3 films [79]. Surface features were introduced by immersing the coated substrates in boiling water for 10 min [80]. Heptadecafluorodecyltrimethoxysilane was used as the hydrophobic agent. It was reported that the roughness of the films increases with the immersion time in hot water. CA of 163° was observed on the alumina films produced using this method. The roughness of the surface was small enough not to scatter visible light, resulting in transparent coatings. Though the concept used in this study to produce transparent superhydrophobic coatings is simple and elegant, this technique is not suitable for producing coatings on an industrial scale. Nakajima, Fujishima, Hashimoto and Watanabe used sublimable aluminium acetylacetonate to introduce roughness into boehmite and silica films prepared by sol-gel method [81]. During calcination, the aluminium acetylacetonate was removed from the film due to its sublimable nature,

leaving behind surface features leading to roughness. Fluoroalkylsilanes were used to make the films hydrophobic [81]. In the absence of surface treatment with fluorinated silanes, the surface is hydrophilic. Aside from the techniques discussed above, the most common method of introducing surface roughness is by the addition of particulate fillers in the sol. Pilotek and Schmidt carried out a systematic study of the addition of silica fillers in a system with 1H,1H,2H,2H-perfluorooctyltriethoxysilane and TEOS [20]. The filler concentration ranged from 0 to 50 wt%, though the surface roughness remained constant after a critical value in the 30-70 nm range was reached. They also reported an observation that the contact angle hysteresis is more sensitive to morphological variations than roughness parameters and can therefore be seen as an analytical parameter by itself [20]. Shang, Wang, Limmer, Chou, Takahashi and Cao reported a sol-gel system using a combination of siloxane precursors like tetraethylorthosilicate, methytriethoxysilane and methacryloxypropyltrimethoxysilane [82]. Plasma etching was used to treat the surface before using the fluorinated silane to improve the self-assembly of the FAS on the surface. A static CA of 160° was reported using this method [82]. As there were no fillers particles added to the sol, the resulting coatings were optically transparent, which widened their possible areas of application. Other fluorinated silanes which have been commonly used to modify the functionality of sol-gel coatings include trifluoropropyltrimethoxysilane and hexamethyldisilazane (HMDS) [66, 83]. There are also several studies on using particles other than nanosilica as additives to increase the roughness of the coatings. CaCO₃, TiO₂, carbon nanotubes are some of the more commonly used alternatives to SiO₂ [23, 25, 84]. Besides other silanes and siloxanes, epoxy silanes are also seen to be suitable additives to the sol-gel network. 3-Glycidoxypropyltrimethoxysilane (Glymo) is the most common

epoxy silane used as a co-precursor in most sol-gel systems [63, 64, 85-87]. The main advantages of having an epoxy silane in the matrix is that it improves the durability of the coating as shown by Daoud, Xin and Tao [64]. Wu, Chua, Chen and Zeng also show in their work that addition of Glymo improves the scratch resistance and adhesion of the coatings to the substrate [87]. The studies by Macan and Ivankovic show that by controlling the hydrolysis and curing conditions of an epoxy silane specific properties can be incorporated into the sol-gel matrix [88]. Acid hydrolysis, more specifically, improves the mechanical properties in systems fully cured around 120 °C because of the more uniformly structured inorganic network and additional linkages to the organic epoxy groups by hydrogen bonding. From most of the sol-gel systems discussed here it can be seen that TEOS is one of the most preferred precursors to form silicate based coatings. The coatings systems summarized above are the traditionally used precursors and functional additives in the sol-gel synthesis of hydrophobic and superhydrophobic surfaces.

Silane based polymer PDMS is also seen to be used as the matrix for some sol-gel systems [89-92]. PDMS has a Si-O-Si backbone because of which the polymer can easily blend into the silane or siloxane based sol-gel network. Due to its elastomeric nature and inherent hydrophobicity because of the methyl groups present, PDMS is a viable alternative to incorporate in to the sol-gel system. Fig. 2.13 gives the schematic representation of how PDMS incorporates itself into a TEOS based sol-gel network.

Fig. 2.13 Schematics of co-condensation between PDMS and TEOS [93].

Being an elastomer, the PDMS can be more flexible and therefore less brittle compared to pure TEOS based networks [90]. Addition of PDMS as co-precursor in these cases can help improve the mechanical properties of the coatings [25]. Another advantage of using PDMS is that though insoluble in water, in soil it can hydrolyze into siloxanols with the ultimate product being the monomer dimethylsilanediol [94]. This ensures that, unlike the fluorinated polymers which are environmentally still a concern, PDMS can be disposed using safe methods.

2.5.3 Combination of top-down and bottom-up approaches

The combination of top-down and bottom up approaches can exploit the apparent advantages of both techniques. Such methods are useful in creating special architectures on the microscopic and nanoscale level to prepare surfaces with morphology similar to naturally occurring superhydrophobic surfaces.

2.5.3.1 Membrane casting based methods

This method is mostly used for preparation of polymer membranes with porous structures. Using the right combination of solvents and non-solvents helps form polymer rich and polymer poor phases. Macromolecules nucleate at the polymer rich phases leading to network formation, whereas the pores are formed in the polymer poor phase after the non-solvents are removed. Isotactic polypropylene was used to prepare superhydrophobic surfaces with xylene and methyl ethyl ketone as the solvent and non-solvent respectively [95]. The resulting surface was found to have a CA of 160° . Similar techniques have been tried using other polymers like low density polyethylene (LDPE) and combination of acrylates and urethanes [96]. Polyvinylidene fluoride (PVDF) which is a thermoplastic, hydrophobic fluoropolymer with excellent mechanical and properties and resistance to harsh environments has been used in several blended composites [97-100]. Schutzius, Bayer, Tiwari and Megaridis used PVDF in combination with acrylates and perfluoromethacrylate copolymers to fabricate superhydrophobic surfaces with CA as high as 170° [62, 97-100]. But one main disadvantage of using PVDF is that it has poor adhesion to the substrate because of its inherent hydrophobic nature.

2.5.3.2 Micelles

Surfactants in colloids form aggregates in the form of micelles. This occurs due to microscale separation. Block copolymers form micelles when dispersed in a suitable solvent due to selective solubility of one polymer block over another. Similar to the membrane casting techniques discussed above, selection of solvents for the block copolymers, temperature, humidity and other environmental factors control the

morphology of the surfaces. PDMS based block copolymers are commonly used and the superhydrophobicity of the resulting surfaces is attributed to the rearranging of the PDMS block during the phase separation [101]. Static CA around 160° has been reported. It is also possible to incorporate filler particles into the micelle solution. This addition results in coatings with CA of 170° and SA of 2° [102]. The main advantage of using this technique is that the diversity of polymeric materials available, a variety of morphological changes can be introduced on the superhydrophobic surfaces.

2.5.3.3 Electrospinning

Electrospinning is a technique usually used for preparing polymer based fibres. This method produces a continuous web of fibres that are non-woven. Along the trajectory of the extruded fibres, most solvents evaporate resulting in thin films. The surface roughness and features can be controlled using the viscosity of the polymer solution. Chemical modifications can also be introduced to make the films hydrophobic. Other techniques like CVD can be coupled with electrospinning. A combination of hierarchical roughness and low surface energy of the films produced using poly(caprolactone) and polymerized perfluoroalkyl ethyl methacrylate resulted in good hydrophobicity (CA = 175°) and oleophobicity [103].

2.6 Performance of hydrophobic and superhydrophobic surfaces

Though there are several ways to produce water-repellant surfaces, their application in large scale industrial and day-to-day applications has been hampered due to lack of reports on their mechanical durability and long term performance [17]. There are several

studies which test the durability of the hydrophobic/superhydrophobic surfaces by rubbing them with cloth, sandpaper, leather etc. with or without a specific load [25, 83, 104-108].

But these results cannot be objectively compared because:

- i. The tests used to study the effect of abrasion are not standardized.
- ii. The parameters that are used to measure the effect of said abrasion are not the same in all cases. For instance, CA, SA, roughness and co-efficient of friction are some of the physical parameters used as criteria to measure the impact of these tests.
- iii. Specific tests based on the applications of the surfaces (self-cleaning, anti-icing, anti-fingerprint etc.) have not been designed.
- iv. The mechanical properties of the coatings and surfaces, like hardness, modulus etc., are not reported in all studies. These values might have an effect on the other performance and durability tests conducted on the samples.

Any or all of the factors listed above serve to be a severe limitation on gaining better understanding of how these systems function when exposed to a working environment. Standardizing some of these test methods will ensure better analysis of the relationship between the chemical, physical, mechanical and functional performance of the hydrophobic and superhydrophobic coatings and surfaces.

2.7 Summary

From the literature summarized above, the following conclusions can be drawn:

1. Though there are several methods which are successful in producing coatings with high static CA, there is a dearth of information with regard to the contact angle hysteresis and SA. These parameters are vital for better understanding of performance of random rough surfaces as far as water repellency is concerned.
2. There are no reports on the durability of the superhydrophobic coatings and surfaces prepared. The mechanical properties, adhesion of coating to substrate and resistance to environmental weathering and erosion are not widely tested. A comprehensive study testing the effect of these parameters on such surfaces will be useful towards designing a robust superhydrophobic surface for outdoor applications.
3. Superhydrophobic coatings can be used for a wide range of applications like self-cleaning, anti-icing, anti-microbial and anti-slip surfaces to name a few. But there are no standard tests performed to determine which of these applications a particular coating will be most suitable for. Added to that, for most of these applications there are no standard testing methods outlined.
4. The field of superhydrophobic and water repellant surfaces have been studied for several decades now. But it is still not clear whether a high static CA alone is sufficient for a coating/surface to exhibit good self-cleaning performance. A clear understanding on which physical factors influence the self-cleaning performance is still lacking.

By preparing and testing different hydrophobic and superhydrophobic coating systems, the effect of various physical, chemical and environmental factors on the coating systems can be determined. Further, a self-cleaning test designed to quantitatively and qualitatively measure the self-cleaning performance of the coatings is proposed and described for the first time. The results from these studies can help improve the understanding of the performance of water repellant surfaces.

To summarize, there are a wide range of techniques available to fabricate superhydrophobic coatings and surfaces. As mentioned previously, the top-down approaches are difficult to scale up and are hence not considered to be suitable for the purposes of this project.

Out of the several bottom-up approaches available there are still limitations associated with methods like CVD, CBD and LbL as they cannot be used for large outdoor structures like wind turbine blades, automobiles, buildings etc. Consequently, sol-gel method is chosen, mainly because of the cost effectiveness, versatility and easy scalability of the technique. Out of the several sol-gel precursors available, TEOS is chosen because of its ease of processing and mixing with other common silicate and non-silicate precursors.

An epoxy silane is chosen in order to improve the mechanical performance of the sol-gel matrix. Silica fillers are used mainly because they can easily bond with the Si-O-Si network of the sol-gel systems.

PDMS, due to its inherent hydrophobic nature and elastomeric properties is chosen as the co-precursor for the second system. Its ability to form a sol-gel network with TEOS is an added advantage.

For the third system, a fluorinated polymer, PVDF is chosen as the base matrix. This material is chosen mainly due to its structural similarities to PTFE, the best known chemically water repellent material. The advantage of using PVDF is that it is easier to handle and process compared to PTFE.

Each of the three coating systems mentioned above will be characterized in detail for various properties and the results will be discussed in Chapters 4-7. The comparison between the systems in terms of their structure property relations, mechanical durability and self-cleaning performance will be made in Chapter 8. The conclusions and related findings from the experimental work and recommendations for future studies will be discussed in Chapter 9.

Chapter 3: Materials and methods

This chapter describes the coating formulation for the three materials systems shortlisted from the literature review in Chapter 2. The experimental methods for synthesis, characterization and testing of the systems are described in detail. A novel method for testing self-cleaning performance based on spectrophotometry is proposed.

3.1 System I: Sol-gel formulation based on TEOS-Glymo

The sol-gel system for the coating consists of the following materials:

- TEOS (99.999% trace metals basis, Aldrich) and Glymo ($\geq 98\%$ purity, Aldrich) as precursors to form the sol-gel matrix.
- Perfluorodecyltriethoxysilane (FAS-17, 97%, Aldrich) as the hydrophobic modifier.
- Itaconic acid ($\geq 99\%$ Aldrich) as catalyst for the sol-gel system.
- Ethanol (EtOH, 99%) and DI water as solvents
- Ethylenediamine (EDA, absolute, $\geq 99.5\%$, Aldrich) as curing agent
- Silica particles with average size of 10-20 nm (nanopowder, 10-20 nm particle size (BET), 99.5% trace metals basis), 200 nm (nanoparticles, mesoporous, 200 nm particle size, pore size 4 nm) and 1-5 μm ($\sim 99\%$, 0.5-10 μm , approx. 80% between 1-5 μm) as fillers.

All the chemicals were used as purchased without further modification.

3.1.1 Coating preparation

Stock solutions of TEOS and Glymo were first hydrolyzed separately with EtOH and DI water. Itaconic acid was used to maintain the pH of both stock solutions at 2-3. The separately prepared stock solutions were mixed together after stirring for 2 hours. The resulting mixture was left stirring for 24 hours. The final mixture had the various components in the following molar ratio; TEOS : Glymo : EtOH : Itaconic acid : H₂O = 1 : 0.6 : 1.34 : 0.16: 3.07.

The FAS-17 was hydrolyzed by mixing it in EtOH and DI water. The EtOH was the solvent for the FAS and the molar ratio of DI water to FAS-17 was 3:1. The hydrolyzed FAS-17 was also allowed to stir for a period of 24 hours.

The coating solutions were prepared by mixing the TEOS-Glymo sol with the hydrolyzed FAS-17 at a ratio of 1:1 by volume. This was further modified by addition of silica particles of different size ranges (10-20 nm, 200 nm and 1-5 μ m) at 5, 10 and 15 wt% with respect to the final weight of the coating.

Glass slides were used as the substrates for applying the coatings. The slides were cleaned by ultrasonication with EtOH and DI water. The coatings were applied on the glass slides using a spray gun at a pressure of 3 bar from a distance of 10-15 cm. The coated slides were allowed to dry for a while before curing at 80 °C for two hours.

3.1.2 Amine cured TEOS-Glymo sol

A modification was carried out in the TEOS-Glymo hydrolyzed sol by curing it with EDA (Glymo:EDA = 10:0.1 by volume). The amine cured the glymo molecules present in the network due to the presence of the epoxy group. The EDA was added after the TEOS,

Glymo, FAS and silica particles were all mixed together. The remaining coating process remained the same.

3.2 System II: Sol-gel formulation based on TEOS-PDMS

The coating system based on the TEOS-PDMS sol consists of the following materials:

- Tetrahydrofuran (THF, anhydrous, $\geq 99.9\%$, Sigma Aldrich), Isopropyl alcohol (IPA, $\geq 99.7\%$) and DI water as solvents.
- TEOS (99.999% trace metals basis, Aldrich) and PDMS, hydroxyl terminated (average $M_n \sim 550$, viscosity ~ 25 cSt, Aldrich) as precursors for the sol-gel matrix.
- Hydrochloric acid (0.01M), as a catalyst for the sol-gel system
- Silica particles with average size of 10-20 nm (nanopowder, 10-20 nm particle size (BET), 99.5% trace metals basis) as fillers.

3.2.1 Coating preparation

The three solvents, THF, DI water and IPA were first mixed at a volumetric ratio of 1:3:4 at a temperature of 80 °C with constant stirring. The hydrochloric acid was added to bring the pH to 2. This was allowed to stir for an hour. Following this, the TEOS and PDMS were added to the stirring mixture simultaneously. The molar ratio of TEOS:PDMS was maintained at 1:1. The TEOS:PDMS ratio (by weight) was varied as 70:30, 80:20 and 90:10 to produce coatings with different PDMS concentrations. The final sol was left stirring for 12 hours. 10-20 nm silica particles were added at 5 and 10 wt% (with respect to the original sols) and stirred for 3 hours.

The final TEOS-PDMS sols with 0, 5 and 10 wt% silica fillers were coated on glass slides cleaned by ultrasonication with EtOH and DI water. The coatings were applied using a spray gun at a pressure of 3 bar from a distance of 10-15 cm. The coated slides were dried at room temperature for an hour followed by curing at 120 °C for 90 minutes.

3.3 System III: PVDF based composite coating

The coating system is composed of the following materials:

- PVDF (average M_w ~534,000 by GPC, powder, Aldrich)
- N,N-dimethylformamide (DMF, anhydrous, 99.8%), Ethanol (EtOH, 99%) and DI water as solvents.
- 3-Aminopropyltriethoxysilane (APTES, $\geq 98\%$ Sigma Aldrich) as the functionalizing agent
- Perfluorodecyltriethoxysilane (FAS-17, 97%, Aldrich) as the hydrophobic modifier.
- Silica particles with average size of 10-20 nm (nanopowder, 10-20 nm particle size (BET), 99.5% trace metals basis) as fillers.

3.3.1 Coating preparation

5 and 10 % PVDF solutions were prepared by dissolving it in DMF and heating the mixture at about 50 °C. The FAS-17 was hydrolyzed as described in section 3.1.1. 10-20 nm silica particles were dispersed in the trimolar solution of hydrolyzed FAS-17. This was added to the PVDF solution at PVDF: SiO₂ = 1:0.5 and 1:1 by weight and stirred for 24 hours. A 5 mM solution of APTES in EtOH was prepared. The glass slides were first

cleaned by ultrasonication with EtOH and DI water and then immersed in the 5 mM APTES solution for 24 hours. After 24 hours, the glass slides were again washed with DI water and EtOH to remove excess APTES. The various PVDF coatings were applied by using a spray gun at a pressure of 3 bar from a distance of 10-15 cm. Glass slides not treated with APTES were also coated with the PVDF solutions for comparison. The coated slides were allowed to dry at room temperature for 1 hour and then cured at 80 °C for 3 hours.

3.4 Characterization techniques

The CAs and SAs of the coated samples were measured using a Dataphysics OCA 20 contact angle instrument. A water droplet of volume 1 μL was used for static contact angle measurements. The sliding angle was measured using the tilting base method with a droplet volume of 5 μL . The contact angle hysteresis was also measured using this method. The apparent surface energy of the coated surfaces were also measured using the same instrument. Three different liquids; DI water, toluene and glycerol were used for these measurements. All reported values are an average of 5 readings measured on each sample.

Fourier Transform Infrared Spectroscopy (FTIR) was used to analyze the surface chemical bonds. The ATR method was used to confirm the formation of the matrix and presence of functional groups that impart the hydrophobic functionality to the coatings.

The surface profiler (KLA Tencor ASIQ) was used to measure the average surface roughness (R_a , arithmetic mean) and the thickness of the coatings. A scan rate of 50 $\mu\text{m/s}$

was used to scan a length of 1000 μm over the surface. The reported values are the average of 5 scans performed on each sample.

Atomic force microscopy (AFM DI 3100) and confocal interferometry (Veeco instruments) were used to analyze the surface topography. Morphologies of the coatings were studied using secondary electron micrographs obtained from field emission scanning electron microscopes (FESEM JOEL 7600F).

3.5 Tests for mechanical properties and durability

The cross-cut tape adhesion test based on ASTM D3359-09 was used to measure the extent of coating adhesion to the substrate. This test was also used to evaluate the coatings based on its brittleness by observing the cross-hatch patterns made on the coating surface. A cross-cut pattern was made on the coating surface using the cross-hatch equipment from the TQC Cross-cut adhesion test kit. Following this a piece of scotch tape was applied firmly over the cross-hatch pattern. After 90 seconds, the tape was removed smoothly without any jerks. The extent of coating adhesion was evaluated based on the parameters mentioned in Fig. 3.1.

Surface	Description	ISO/JIS	ASTM
The edges of the cuts are completely smooth; none of the squares of the lattice is detached.	0	5B
Detachment of flakes of the coating at the intersections of the cuts. A cross cut area not significantly greater than 5% is affected.	1	4B
The coating has flaked along the edges and/or at the intersections of the cuts. A cross cut area significantly greater than 5%, but not significantly greater than 15% is affected.	2	3B
The coating has flaked along the edges of the cuts partly or wholly in large ribbons, and/or it has flaked partly or wholly on different parts of the squares. A cross cut area significantly greater than 15%, but not significantly greater than 35%, is affected.	3	2B
The coating has flaked along the edges of the cuts in large ribbons and/or some squares have detached partly or wholly. A cross cut area significantly greater than 35%, but not significantly greater than 65%, is affected.	4	1B
Any degree of flaking that cannot be classified even by classification 4 (1B).	5	0B

Fig. 3.1 Guidelines for evaluating adhesion of coatings based on ASTM standards.

The hardness and Young's modulus of the coatings were measured with a nanoindenter (Micromaterials Nanotest Vantage) up to a maximum depth of 2000 nm.

The coatings were tested for resistance to abrasive wear based on ASTM G65. Change in CA, SA, R_a , coating weight and thickness were used to characterize the effect of abrasive wear on the coatings. The abrasion was carried out on a rotating wheel apparatus with #220 sand paper (mean particles size $\sim 63 \mu\text{m}$). The abrasive wheel was set to rotate at a speed of 300 rpm for a period of 30 seconds for each cycle. The applied pressure was 15.6 kPa. Each sample was subjected to up to 20 cycles of abrasion (the abrasion distance for each cycle was around 75.4 m). The reported results are an average value of 9 tests for each coating condition.

To test for erosion resistance, micro-sand blast tester was used. Particles of a size of $63 \mu\text{m}$ (220 mesh) were blasted on to the coated surfaces from a distance of 10 cm under a pressure of 200 kPa for 30 seconds. The exposed area for the sand erosion was 2.43 cm^2 .

The loss in weight and change in CA and SA of the coatings were measured after the erosion test.

UV weathering tests were performed by placing the sample in a weathering chamber (ATLAS instruments) following the test standard by ASTM G154-12a. The procedure involves 4 hours of UV exposure, followed by 4 hours of water spray and condensation. The UV/water cycle was repeated over a period of 72 hours. Eight UV lamps (295-400 nm), each having the power intensity of 1.2 W/m^2 , were used. The CA and SA of the coatings were measured after the weathering cycle to evaluate any changes in coating functionality.

3.6 Test for self-cleaning performance

To evaluate the effectiveness of the coatings for self-cleaning applications, a spectrophotometer was used to monitor the change in lightness values. This method was chosen mainly because a spectrophotometer measures the energy response of an object with precise lighting and capture conditions. In this case, the $L^*a^*b^*$ color space was used. Here, L^* denotes the lightness which is the tone or the brightness of a sample in a color space. a^* denotes the extent of redness and b^* , the yellowness of a sample. The $L^*a^*b^*$ system was chosen in this case because it was designed to be a uniform color space. The coatings were sprayed with artificial dirt and then subjected to cleaning using a controlled water spray. The lightness (L) value was measured by the spectrophotometer at three stages of the self-cleaning test: before the spray of the artificial dirt solution, after the dirt was dried, and after dirt was cleaned using spray of clean water. The self-cleaning effectiveness was calculated based on the lightness values and compared among different

coatings. $L^* = 0$ indicates a completely black sample and $L^* = 100$ indicates diffuse white.

Artificial dirt was first prepared, consisting of 85 wt% nano-clay, 10 wt% silica particles (1-5 μm), 1 wt% carbon black, 2 wt% oil, and 2 wt% salts. The different components were thoroughly mixed using a mechanical mixer before use. The dirt mixture was then dispersed in water at a concentration of 15 g/L. After the artificial dirt solution was sprayed on the coatings, it was allowed to dry overnight and then heated at 60 °C for an hour. The contaminated samples were then mounted on a stand at a slanted angle of 45 °C before being cleaned with water spray using a fixed volume of 15 mL at a pressure of 3 bar from a distance of 25-30 cm away from the surface.

The change of the lightness value, which represents the luminance or the tone perceived by the spectrophotometer on the samples, was used as the measure of the extent of contamination and cleaning effectiveness. The lightness (L) of the pristine samples was measured at five points spread uniformly over the coating surface. The average reading was taken as L_1 . After the dirt solution was sprayed and dried, the lightness values were again measured and the average taken as L_2 . After the water cleaning, the lightness was recorded as L_3 .

The values of lightness (L_2) decreased after the samples had been sprayed with the dirt solution. The percentage dirt accumulated on the samples were calculated as $(L_1 - L_2)/L_1 * 100$. After cleaning, the dirt had been removed as indicated by the increase in L_3 as compared to L_2 . The difference between L_1 and L_3 , denoted as ΔL_3 was used to measure the extent of dirt removed after the water spray. We define $[100 - (L_1 - L_3)/L_1 * 100]$ as the self-cleaning efficiency (or index) of the coatings.

All the spectrophotometric measurements were carried out by placing the samples on a white background.

Chapter 4 Results and discussion - System I: TEOS-Glymo sol-gel formulation

4.1 Introduction

This chapter presents the results and discussions on the physical, chemical and mechanical properties of the TEOS-Glymo based coating system. The coating formulation and procedure are described in sections 3.1 and 3.1.1 respectively. The self-cleaning performance of the coatings was tested using the method described in section 3.6.

4.2 Contact angle and Sliding angle

The CA and SA were measured on the coatings with and without particulate filler loading. Fig. 4.1 shows the plot of change in CA with increase in filler concentration for different particle sizes.

Fig. 4.1 Change in CA with increasing silica content for different particle sizes.

All the coatings are seen to have a static CA $> 90^\circ$, making them hydrophobic. From the values listed in Table 4.1 it can be seen that the CA increases with increase in filler content but decreases with increase in filler size. The pristine coating with TEOS-Glymo and hydrolyzed FAS-17 without any filler loading has a CA of $105.57 \pm 1.78^\circ$. On introducing 5 wt% of filler particles (1-5 μm , 200 nm and 10-20 nm avg. particle size), the CA increases to $108 \pm 2.9^\circ$, $110 \pm 2.8^\circ$ and $127 \pm 5.1^\circ$ respectively. The addition of silica into the sol introduces roughness to the coating, which in turn influences the CA [20, 35, 109]. The different sizes of the silica particles leads to surface features that are formed due to the aggregation of the silica particles in the sol-gel network leading to different values of roughness. The correlation between the CA, SA, surface roughness and CA hysteresis values can be seen listed in Table 4.1.

Table 4.1 CA, SA, surface roughness and CA hysteresis for coatings with different filler size and loading.

Filler Size	Silica content (wt%)	Contact angle ($^\circ$)	Sliding angle ($^\circ$)	Roughness R_a (μm)	Contact angle hysteresis ($^\circ$)
10-20 nm	5 %	127 ± 5.1	15 ± 2.5	1.04 ± 0.18	10.2
	10 %	142 ± 1.7	7 ± 2.0	2.81 ± 0.31	7.8
	15%	164 ± 3.9	2 ± 1.5	3.44 ± 0.26	3.7
200nm	5 %	110 ± 2.8	30 ± 5.0	0.27 ± 0.03	16.4
	10 %	126 ± 3.8	18 ± 3.5	0.84 ± 0.07	12.6
	15%	130 ± 4.1	12 ± 3.5	1.62 ± 0.41	11.3
1-5 μm	5 %	108 ± 2.9	70 ± 10	0.19 ± 0.02	37.4
	10 %	113 ± 1.2	55 ± 10	0.28 ± 0.07	29.8
	15%	118 ± 3.6	45 ± 10	0.46 ± 0.06	26.5

From the values in Table 4.1, it can be seen that the average roughness values increase with decreasing particle size. The highest CA of 164° is achieved in the coatings with 15 wt% loading of 10-20 nm silica particles. Here, the fine silica particles aggregate together forming a hierarchical rough surface with the maximum R_a of $3.44\ \mu\text{m}$.

The sliding angle, as shown in Fig. 4.2, decreases with increasing surface roughness for each filler size. The coating with 15 wt% loading of 10-20 nm silica has a SA $< 2^\circ$, giving it the best superhydrophobic properties.

Fig. 4.2 Change in SA with increasing silica content for different particle sizes.

Surfaces with higher roughness tend to follow heterogeneous wetting as the water droplets roll off easily from the surface. In contrast, on surfaces with a comparatively lower

roughness, the water droplets do not slide or roll away very easily suggesting that homogeneous wetting starts to occur [35, 37]. Significance of the wetting conditions for the different coatings will be analyzed in later parts of the chapter.

From the CA hysteresis data reported in Table 4.1, it is clear that there is clear link between the SA and the CA hysteresis. This supports the theory that the difference between the advancing and receding CA is a measure of apparent friction of the droplets on the surface.

4.3 Chemical analysis

Fig. 4.3 shows the FTIR spectra of the sol prepared by mixing hydrolyzed TEOS, Glymo and FAS. The most prominent dip (peak) at around 1020 cm^{-1} is associated with the Si-O-Si bond. The appearance of this peak confirms that the expected network of Si-O-Si bonds has been formed. The peaks around 3000 and 3300 cm^{-1} correspond to -OH groups. Some of the OH groups formed during hydrolysis may not undergo condensation and were thus reflected in FTIR. These groups could also be present due to adsorption of water (moisture). The peaks at around 1000 and 1400 cm^{-1} belongs to C-F bond, confirming the presence of FAS in the coating [22]. In addition, the appearance of peaks at 900 and 1000 cm^{-1} shows the presence of the epoxy ring which is part of the Glymo molecule [23]. From the FTIR results, it can be concluded that the Si-O-Si network has been formed, contributing to the basic matrix of the system. Though TEOS is the main precursor leading to the formation of the matrix, the hydrolysis and condensation of Glymo also contributes to formation of the network. Further, the epoxy ring which is a part of the Glymo molecule serves as the organic component of the matrix. The Glymo molecule binds to the TEOS network through the three ethoxy groups following the hydrolysis.

Having TEOS and Glymo as the precursors promotes the formation of a blended organic and inorganic network.

Fig. 4.3 FTIR spectra of the coating with TEOS-Glymo and FAS mixture.

4.4 Surface morphology

The secondary electron micrographs of the TEOS-Glymo coating system is shown in Fig. 4.4. The pristine coating without particulate fillers is quite smooth, without any noticeable surface features as seen in Fig. 4.4a. Therefore the high CA is due to the presence of the long chain fluorinated alkyl silane, which is a part of the sol-gel system [19]. Fig. 4.4c corresponds to the coating with 15 wt% loading of 1-5 μm silica particles. There is no discernible morphological structure observed on this surface. This can mainly be

attributed to the size of the filler particles which are generally large and do not form clustered regions.

Fig. 4.4 SEM images of TEOS-Glymo-FAS coating with a) no fillers, b) cross-section of coating with 15 wt% nanosilica, c) 15 wt% 1-5 μm silica, d) 15 wt% 200 nm silica, e) 15

wt% 10-20 nm silica at low magnification and f) 15 wt% 10-20 nm silica at high magnification.

Due to the smoothness of the surface, the droplet behaves as would be expected on a chemically modified flat surface by showing only marginally hydrophobic properties.

Fig. 4.4d shows the morphology of the coating with 200 nm silica particles. The silica particles are spherical in shape, and the surface is uniform without observable clustering of the particles. Further, the pores between these larger particles are clearly visible; the size of the pores can be as large as ~100 nm and above. When water droplets come in contact with this surface, there is a high possibility that they will be trapped within the larger pore spaces between the particles [35]. Fig. 4.4e and f shows the morphology of the coating loaded with 15 % of silica particles of 10-20 nm diameters at low and high. The surface has dense clustering of nanoparticles leading to increased surface roughness and coating porosity. A hierarchical nature to the roughness can also be seen from the micrographs. The thickness of the coatings is measured from a cross-sectional image as shown in Fig. 4.4b. The thickness of the coatings both with and without filler loading ranges between 100-120 μm .

Based on the morphological features of the coatings from the FESEM images, the wetting behavior of the coatings is analyzed. By fitting the CA data into the Cassie-Baxter and Wenzel models, the following details can be summarized.

For the coating with 15 wt% loading of 10-20 nm silica, based on the CA and SA data, the Wenzel and Cassie-Baxter models were applied:

Case (i) $\cos \theta^* = r \cos \theta$, substituting for θ as 105.57° and θ^* as 164° , we get $r = 3.58$.

This implies that the actual surface area of the coating is 3.5 times the geometric area.

Case (ii) $\cos\theta^* = f_1\cos\theta - f_2$

Here, $f_2 = 1 - f_1$, substituting for θ as 105.57° and θ^* as 164° , $f_1 = 0.05$.

(i.e) the fraction of solid-liquid contact area is only 0.05 making the liquid-air contact area 0.95. This implies that the surface is highly porous with large amounts of air being trapped within the surface features. Therefore, in this case, the Cassie-Baxter model is more in agreement with the experimental data obtained in terms of the high CA and low SA.

On similarly testing the coatings with 200 nm and 1-5 μm sized filler particles for the Wenzel and Cassie models, the following results were obtained:

Table 4.2: Fitting Wenzel and Cassie-Baxter models to different coating samples.

Sample	$\theta (^\circ)$	$\theta^* (^\circ)$	r	f_1 and f_2
1-5 μm , 15 wt%	105.5	118	1.75	0.72, 0.28
200 nm, 15 wt%	105.5	130	2.42	0.48, 0.52
10-20 nm, 15 wt%	105.5	164	3.58	0.05, 0.95

Based on the values in Table 4.2, it can be seen that for the coatings with 200 nm and 10-20 nm filler particles, the solid-liquid interface area is lower than the liquid-air contact area. Therefore, the porosity of these coatings results in the wetting regime being more heterogeneous, leading to low SA. Conversely, for the coatings with 1-5 μm fillers, the large filler size does not increase the roughness by a significant margin. In this case, as evidenced by the higher value of SA ($\sim 45^\circ$), it can be concluded that the wetting regime is in a mixed state between homogenous and heterogeneous wetting [40].

The images of the water droplets interacting with these surfaces are shown in Fig. 4.5. Fig. 4.5a, b and c show the images of the water droplet on coatings with 15 wt% loading of 1-5 μm , 200 nm and 10-20 nm silica fillers. Fig. 4.5d shows the water droplet rolling off the surface of the coating with 15 wt% 10-20 nm silica at $< 2^\circ$ tilt of the base.

Fig. 4.5 Images of water droplet on TEOS-Glymo-FAS coating with a) 15 wt% 1-5 μm silica particles, b) 15 wt% 200 nm silica particles, c) 15 wt% 10-20 nm silica particles and d) droplet rolling away on 15 wt% 10-20 nm silica particles.

4.5 Cross-cut tape adhesion test

In order to measure the extent of coating adhesion to the surface, the cross-cut tape adhesion test was performed. It was observed that the coatings without any filler content showed better adhesion to the substrate when compared to coatings with silica fillers. The

standard ASTM D3359 explains a standard method used to quantify the extent of adhesion of a protective coating over the substrate using the grades 5B, 4B, 3B, 2B, 1B and 0B, where coatings rated 5B exhibit the highest adhesion to a substrate and 0B the poorest adhesion. The guidelines used for evaluating the extent of adhesion are included under section 3.5. Fig. 4.6 shows the images of the cross-cut test performed on the coatings with 10-20 nm fillers at 0, 5 and 15 wt% loading.

Fig. 4.6 Cross-hatch tape adhesion test for coatings with 10-20nm silica fillers. a) no fillers; b) 5 wt%; c) 10 wt%; d) 15 wt%.

From Fig. 4.6a, it can be seen that the cross hatch squares on the coating with no fillers shows no cracking or chipping, and the coating is rated as 5B according to the ASTM D 3359 standard. The coatings with increasing filler content progressively show higher removal of coating from the cross hatch squares and chipping around the cut lines, indicating increased brittleness of the coating. This could be attributed to the increased hardness and rigidity by the introduction of particulate fillers. The increased surface roughness and coating porosity would translate to increased severity of surface / coating flaws that lead to the observed brittleness of the coatings. From Figs. 4.6c and 4.6d, the cross-cut damage of the coatings with 10 and 15 wt. % silica nanoparticles were rated as 2B and 1B respectively according to ASTM D 3359.

The coating adhesion for all the compositions is listed in Table 4.3 below.

Table 4.3: Adhesion rating of coatings according to ASTM D3359.

Sample	Adhesion rating
No fillers	5B
1-5 μm , 5 wt%	4B
1-5 μm , 10 wt%	3B
1-5 μm , 15 wt%	3B
200 nm, 5 wt%	3B
200 nm, 10 wt%	2B
200 nm, 15 wt%	2B
10-20 nm, 5 wt%	3B
10-20 nm, 10 wt%	2B
10-20 nm, 15 wt%	1B

4.6 Nanoindentation studies

The coatings were tested for their hardness and Young's modulus values using nanoindentation. Table 4.4 lists the value of the hardness and Young modulus of these coatings measured over a depth range of 500-2000 nm.

Table 4.4: Hardness and Young's modulus measured by nanoindentation for various coating compositions.

Filler	Filler Concentration (wt. %)	Hardness (GPa)	Young's Modulus (GPa)
No Filler	-	0.57 ± 0.032	0.5 ± 0.122
10-20 nm	5	0.65 ± 0.091	0.97 ± 0.321
	10	0.62 ± 0.055	0.63 ± 0.163
	15	0.68 ± 0.051	0.7 ± 0.217
200 nm	15	0.33 ± 0.042	0.61 ± 0.202
1-5 μm	15	0.27 ± 0.035	0.54 ± 0.053

The pristine coating without any filler has a hardness reading at 0.57 GPa. Upon addition of 10-20 nm silica particles into the matrix, the hardness gradually increases to 0.68 GPa at 15 wt. % loading. But the addition of larger filler particles (200 nm, 1-5 μm) shows a reduction in the hardness. This could be due to the effect of particle size on the coating hardness. The polymer network formed in the sol-gel matrix is at nanoscale dimensions. Thus, addition of particles in similar size ranges brings about a better interaction with the

matrix resulting in better hardness compared to micro sized particles [110]. The trend in the variation of the Young's Modulus is similar to that observed in the hardness. The curves indicate that the addition of organics like Glymo leads to a decrease in Young's modulus and a greater tendency for energy absorbing behavior particularly in Glymo to minimize damage under contact loading when compared to pure TEOS coatings which are brittle [111].

4.7 Effect of abrasive wear

The effect of abrasion was characterized by measuring the weight, roughness, thickness and CA after the abrasion process. The results reported in Table 4.5 show that the average thickness and weight loss for coatings with different sized filler particles at 5, 10 and 15 wt. % loading are comparable despite the difference in the coating hardness and roughness.

This can be attributed to the interaction of the sol-gel matrix with the filler particles. In the case of 1-5 μm sized fillers, the difference in surface roughness for coatings with 5, 10 and 15 wt% loading is not very high. The agglomeration on the surface is not very high for these particles, leading to a surface without noticeable topographical or morphological features. In the coatings with 200 nm silica fillers, the surface features are highly uniform without increased presence of particulate aggregation, as seen from the FESEM images (Fig. 4.4d) previously. Therefore, even as the roughness increases on increasing filler loading, when the samples are subjected to abrasive wear, the significant absence of large agglomerates on the surface could result in weight loss similar to the coatings with 1-5 μm fillers. On the coatings with 10-20 nm silica fillers, the finer size of the particles results in extensive agglomeration of the fillers. This leads to the formation of prominent

morphological features on the surface with increased roughness (Fig. 4.4f). But due to the smaller size of the fillers, the particles have better interaction with the sol-gel network embedding them well into the coating matrix [110]. As a result, when the abrasion wear test is performed, the surface features which are very prominent get worn away, leading to a drop in the roughness values, but the hierarchical nature of the surface prevents all the surface features from being destroyed. Though the weight and thickness loss of coatings with 10-20 nm loading is slightly higher than that of the other coatings, the overall trend in weight and thickness loss is similar for all coatings.

Table 4.5: Thickness and weight loss after 20 abrasion cycles (total abrasion distance is 1508 m).

Filler	Filler Concentration (wt%)	Avg. thickness loss (μm)	Avg. weight loss (mg)
10-20 nm	5	13.3 ± 4.3	12.7 ± 0.7
	10	18.8 ± 7.4	15.5 ± 3.3
	15	24.6 ± 3.4	22.1 ± 3.7
200 nm	5	12.8 ± 2.4	12.2 ± 0.5
	10	17.1 ± 5.7	15.5 ± 1.3
	15	21.1 ± 4.2	23.7 ± 2.7
	5	12.0 ± 1.6	12.1 ± 0.3
	10	16.7 ± 5.4	16.6 ± 2.5

1-5 μm	15	20.6 ± 4.7	21.5 ± 4.3
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Fig. 4.7 shows the change in CA for the coatings containing 5, 10 and 15 wt. % loading of 10-20 nm silica particles at different stages of the abrasion process. The overall trend is similar to all three coatings in that the CA decreases with the number of abrasion cycles.

Fig. 4.7 Change in contact angle with different degree of abrasion. Filler size is 10-20 nm for all three coatings. The abrasion distances are 377, 754, 1131, and 1508 m, corresponding to 5, 10, 15, and 20 cycles of abrasion.

Coatings with 5 wt% loading of fillers lose their hydrophobicity and became slightly hydrophilic (CA 89°). Samples with 10 wt% fillers show a better performance in retaining the non-wetting behavior. The coating containing 15 wt% silica loading has the best retention of the non-wetting performance.

Table 4.6 shows CA, SA, and roughness values of coatings with 10-20 nm silica fillers before and after 20 cycles of abrasion. It is quite clear that the average roughness values of the surface decreases considerably for the coating with only 5 wt. % filler loading. This can be due to the fact that the quantity of fillers in this coating is much less compared to the others. As a result, on being subjected to continuous abrasion, the hydrophobically functionalized silica particles are removed from the surface making the coating hydrophilic. Though the coatings with 10 and 15 wt. % loading also show a decrease in the surface roughness, they still retain considerably higher R_a values. This could be one of the key reasons behind these coatings not losing their hydrophobicity completely.

Table 4.6: CA, SA, and roughness values of coatings (10-20 nm fillers) before and after abrasion (20 cycles, 1508 m abrasion distance).

Filler content (wt%)	CA (°)		SA (°)		R _a (μm)	
	Before abrasion	After abrasion	Before abrasion	After abrasion	Before abrasion	After abrasion
5	127 ± 5.1	89 ± 5.0	15 ± 2.5	35 ± 5	1.04 ± 0.18	0.02 ± 0.05
10	142 ± 1.7	120 ± 3.5	7 ± 2.0	30 ± 3.8	2.81 ± 0.31	0.1 ± 0.24
15	164 ± 3.9	133 ± 2.7	2 ± 1.5	22 ± 2.5	3.44 ± 0.26	0.6 ± 0.35

The confocal interferometry images and FESEM images of the coating with 15 wt% loading of 10-20 nm silica are shown in Fig. 4.8. It is clearly seen that the roughness was reduced due to the abrasive removal of the silica particles (comparing Figs. 4.8a and 4.8b; 4.8c and 4.8d). Though the CA of the coating did not change drastically for the 15 wt. % coating, the SA increased from around 2° before the abrasion to 22° after abrasion (Table 6). The scanning electron micrograph in Figs. 4.8d indicates the removal of coating with

silica fillers from the surface after the abrasion. The change in sliding angle was recorded at around 30° and 35° for coatings with 10 and 5 wt. % loading of 10-20 nm silica particles respectively. This indicates a possible transition of the surfaces from the Cassie-Baxter state to Wenzel or a mixed state.

Fig. 4.8 Confocal interferometry images of coating with 15 wt% loading of 10-20 nm silica a) before abrasion and b) after 20 abrasion cycles. FESEM images of coating with 15 wt% loading of 10-20 nm silica c) before abrasion and d) after 20 abrasion cycles.

The CA and SA of the coatings with 200 nm and 1-5 μm fillers are also seen to decrease and increase respectively after the abrasion cycles. But the magnitude of difference for

these coatings is much larger resulting in the loss of hydrophobic properties in some cases.

4.8 Effect of erosion

The coated samples were subjected to the accelerated micro-sand erosion test to study if the coatings could retain the required properties in an erosive environment. Loss in weight of the coatings was used to measure their resistance to erosion. The changes in the CA and SA of the coatings were measured after the erosion test to study how much of the original functionality was retained.

The coating parameters measured after the accelerated erosion are tabulated in Table 4.7.

Table 4.7: Surface roughness and average weight loss of the coatings after erosion.

Filler	Filler Concentration (wt%)	R _a after erosion (μm)	Avg. weight loss (mg)
10-20 nm	5	0.78 ± 0.22	9.3 ± 0.2
	10	1.24 ± 0.37	13.7 ± 1.6
	15	1.85 ± 0.12	18.1 ± 2.4
200 nm	5	0.16 ± 0.10	8.9 ± 0.5
	10	0.49 ± 0.11	12.4 ± 1.2
	15	1.07 ± 0.27	16.7 ± 1.9
	5	0.03 ± 0.01	5.6 ± 1.1
	10	0.12 ± 0.03	9.2 ± 1.7

1-5 μm	15	0.27 ± 0.11	15.0 ± 2.1
No filler	-	0.83 ± 0.24	5.1 ± 1.2

From the values in the table above, it can be seen that the change in surface roughness and weight loss increases with increasing filler content for all filler sizes. It should be noted that the coatings with 1-5 μm filler particles show the least weight loss and change in R_a . This is again due to the relatively smooth surface of the coating when compared to those with 200 nm or 10-20 nm fillers. The coatings without any filler addition show an increase in roughness from around 0.15 μm to 0.83 μm . This is because the impingement of particles at a high pressure creates new surface features, increasing the R_a . The pristine coating also shows the least weight loss of 5.1 mg. The CA and SA values for the coatings after accelerated erosion are listed in Table 4.8.

Table 4.8: Values of CA and SA for coatings before and after accelerated erosion.

Sample	CA ($^\circ$)		SA ($^\circ$)	
	before	after	Before	after
Pristine coating	105 ± 1.4	120 ± 4.2	-	-
1-5 μm , 5 wt%	108 ± 2.9	97 ± 5.7	70 ± 10	-
1-5 μm , 10 wt%	113 ± 1.2	101 ± 3.5	55 ± 10	-
1-5 μm , 15 wt%	118 ± 3.6	105 ± 3.1	45 ± 10	-
200 nm, 5 wt%	110 ± 2.8	103 ± 4.1	30 ± 5.0	60 ± 7
200 nm, 10 wt%	126 ± 3.8	117 ± 2.7	18 ± 3.5	54 ± 5
200 nm, 15 wt%	130 ± 4.1	126 ± 4.5	12 ± 3.5	24 ± 4
10-20 nm, 5 wt%	127 ± 5.1	92 ± 3.8	15 ± 2.5	29 ± 4
10-20 nm, 10 wt%	142 ± 1.7	122 ± 2.5	7 ± 2.0	24 ± 5
10-20 nm, 15 wt%	164 ± 3.9	139 ± 2.2	2 ± 1.5	18 ± 2.5

The values of CA on the pristine coating show that the CA increases due to increased roughness reported in Table 4.7. Meanwhile, the coatings with filler loading all show a decrease in the CA. The sliding effect is not observed on the coatings with 1-5 μm fillers.

This can be caused by the increased smoothness of the coatings after the erosion, leading to the droplets getting pinned more easily to the surface.

The coatings with 10-20 nm fillers at 15 wt% loading still retains its hydrophobic nature with a CA and SA of 139° and 18° respectively. It should be noted that the overall trend on the R_a , CA and SA are similar to that seen after the abrasion process indicating that the coatings with particulate fillers experience an overall decrease in their hydrophobic properties after abrasive and erosive wear.

4.9 Effect of UV weathering

Polymers and polymer-based composites tend to show deterioration in various physical properties upon exposure to UV radiation [112]. In order to test the effect of UV radiation on the organic-inorganic sol-gel coatings, the samples were subjected to UV exposure in a weathering chamber for 72 hours according to ASTM G154. Contact angle and sliding angles were measured after the weathering test. The results in Table 4.9 show that the changes in CA and SA of the coatings after the weathering test are insignificant.

Table 4.9: CA and SA before and after UV weathering.

Filler size	Filler content (wt. %)	Contact angle (°)		Sliding angle (°)	
		before	after	before	after
10-20nm	5	127 ± 5.1	115 ± 2.7	15 ± 2.5	15-25
	10	142 ± 1.7	130 ± 2.3	7 ± 2.0	12-14
	15	164 ± 3.9	154 ± 1.8	2 ± 1.5	5-10
200nm	15	130 ± 4.1	118 ± 1.4	12 ± 3.5	20-25
1-5 µm	15	118 ± 3.6	100 ± 0.8	45 ± 10	> 90

It is known in most polymeric epoxies, the bond dissociation energy of the covalent epoxy bond is similar to that of the UV photons [25]. However in the current case the epoxy is not present as a part of a polymer molecule, therefore extensive degradation of material properties was not observed. The slight changes in the measured CA and SA values may be due to additional curing of the material under UV [112]. In addition, the main silica network is comprised of Si–O bonds, which have higher bond strength and thus better UV stability than organic polymer materials. Further, the attachment of fluoroalkyl groups on the surface improved its thermal and UV stability due to the presence of a linear fluorocarbon chain on the silica surface [113].

4.10 Self-cleaning test

The self-cleaning test was performed on the as coated samples and coatings after 20 abrasion cycles. The lightness values, measured using the spectrophotometer, at different stages of the test are recorded in Table 4.10 for selected samples. Fig. 4.9 shows the percentage dirt accumulation before and after the abrasion of coatings containing different amount of 10-20 nm fillers. As mentioned under section 3.6, higher values of L indicate tones that are closer to white. The dirt accumulation index has increased to some extent for all samples after the abrasion as the surface tones get darker. The self-cleaning efficiency is plotted for the same samples before and after abrasion in Fig. 4.10. There is a significant decrease in the self-cleaning index for the pristine coating, coating with 5 wt. % nano silica and bare glass. Despite the small decrease, the 15 wt. % silica coating retains the highest self-cleaning efficiency after abrasion.

Table 4.10: Lightness values from spectrophotometric measurements before and after the cleaning test for different coatings.

Coating	L ₁ pristine coating	L ₂ dirt coated sample	L ₃ cleaned sample	Dirt accumulation (%)	Self cleaning efficiency (%)
Bare glass	85.98	27.77	54.43	67.70	63.3
Bare glass after abrasion	85.98	18.13	47.54	78.91	55.29
Pristine coating	51.81	19.41	34.81	62.53	67.20
Pristine coating after abrasion	51.81	11.81	32.17	77.21	62.10
5 wt% 10-20 nm	84.82	39.11	62.43	53.89	73.66
5 wt% 10-20 nm after abrasion	84.82	31.04	55.39	63.40	65.30
10 wt% 10-20 nm	87.17	68.83	77.69	21.03	89.12
10 wt% 10-20 nm after abrasion	87.17	65.64	72.00	24.70	82.60
15 wt% 10-20 nm	95.35	84.07	91.41	11.83	95.90
15 wt% 10-20 nm after abrasion	95.35	81.71	87.15	14.31	91.40
15 wt% 200 nm	94.23	82.19	89.76	12.78	95.25
15 wt% 200 nm after abrasion	94.23	73.41	85.81	22.09	91.06
15 wt% 1-5 μm	89.57	75.24	82.73	15.99	92.37
15 wt% 1-5 μm after abrasion	89.57	69.42	74.97	22.49	83.69

Fig. 4.9 Percent accumulation of dirt on various samples after subjected to dirt spray followed by drying.

Fig. 4.10 Self-cleaning efficiency of various samples after subjected to water spray.

Fig. 4.11 shows the images of the coatings before and after the dirt spray and cleaning actions. The images correlate well with the reported lightness values. The coating with 15 wt. % nano silica particles, which has the best superhydrophobic properties, shows the lowest extent of dirt accumulation and highest self-cleaning efficiency. The presence of high filler concentration induces heterogeneous wetting on the coatings with 15 wt. % nanosilica fillers. Consequently, the combination of high CA and low SA creates surfaces that not only retain less amount of dirt, but also remove dirt easily. With decreasing filler concentration, the wetting regime slowly transitions, becoming more homogenous and the tendency of the droplets to easily roll off the surface decreases. Thus, the extent of cleanliness decreases too. Overall, the developed coatings are able to retain the self-

cleaning functionality even after removal of up to 20-25 μm of the thickness, indicating reasonably good homogeneity in the coating composition.

Fig. 4.11 Optical images of coatings a) after dirt accumulation of as-coated samples; b) after cleaning; c) after dirt accumulation for samples after abrasion; d) after cleaning for samples after abrasion. The samples are arranged as (i) bare glass, (ii) coating without fillers (iii) coating with 5 wt% of 10-20 nm silica, (iv) coating with 10 wt% of 10-20 nm silica and (v) coating with 15 wt% of 10-20 nm silica.

4.11 Summary

Superhydrophobic coatings were prepared through the sol-gel method, using TEOS and Glymo as the precursors. FAS-17 was the hydrophobic modifier and silica particles of 1-5 μm , 200nm and 10-20 nm were used as particulate fillers.

It is seen that the particle size and concentration of the fillers had a direct effect on the hydrophobicity of the coatings. Based on the results from this study, only 10-20 nm silica particles were used as fillers in the other two coating systems.

The coating with 15 wt% loading of 10-20 nm silica particles is seen to have the highest CA at 164° with low SA and CA hysteresis. Though these coatings have the desired hydrophobic functionality, the mechanical performance in terms of brittleness, hardness and Young's modulus is not comparable to coatings without hydrophobic functionality. When subjected to abrasion and erosion at accelerated rates, the coatings were recorded to have a weight loss of $\sim 20\text{-}25$ mg. This corresponded to a drop in CA to the hydrophobic range. The SA also increased by more than 10° .

The self-cleaning test is performed to quantitatively and qualitatively measure the self-cleaning efficiency of the coatings. Both dirt accumulation and self-cleaning efficiency of the coatings with 15 wt% 10-20 nm silica were high. Even after accelerated abrasion wear, the coatings showed $\sim 90\%$ self-cleaning efficiency.

By improving the mechanical properties of the coating, the durability and performance of the coating system might be further improved.

Chapter 5: Results and discussion – Amine modified TEOS-Glymo system

5.1 Introduction

As seen in the previous chapter, the TEOS-Glymo based sol-gel system with 10-20 nm silica fillers has extremely good superhydrophobic properties, but the mechanical performance of the system requires further improvements to make the coating more robust. As a way to address this concern, crosslinking the epoxy group in Glymo was considered. The main reasons behind choosing this method are as follows:

- i. Amine curing of epoxy based hybrid sol-gel networks has been shown to significantly improve the thermal and mechanical properties of the system [114].
- ii. The coating can be made into a two component system where the amine can be added just before applying the coating on to substrates.
- iii. Depending on the properties desired in the final coating, different amines can be used to cure the system.
- iv. Properties ranging from improved adhesion to substrates, resistance to chemical attack, flexibility etc. can be introduced by using appropriate curing agents.

This chapter focuses on the properties of the amine cured TEOS-Glymo system as described under section 3.1.2. A detailed analysis of the results from physical, chemical and mechanical performed on the samples will be discussed.

5.2 Contact angle and sliding angle

From previous results obtained in section 4.2, it was seen that addition 10-20 nm silica particles provided better hydrophobic properties to the coating. Therefore, only these

fillers were used in the amine cured TEOS-Glymo system. The plot of CA and SA with increasing silica concentration is shown in Fig. 5.1.

Fig. 5.1 Plot of CA and SA with for coatings with and without EDA curing and increasing silica content.

Fig. 5.1 it can be seen that the CA of the amine cured system also increases with increase in silica loading. Introducing 15 wt% silica makes the coating superhydrophobic. The trend in the SA is also similar to that observed in the initial TEOS-Glymo system. The superhydrophobic coating composition exhibits a SA of $5 \pm 2.1^\circ$. From these results it can be concluded that the hydrophobic functionality of the coating is not affected on curing the epoxy silane with EDA. The values of CA, SA and average surface roughness are listed in Table 5.1.

Table 5.1: CA, SA and average surface roughness for coatings with and without amine curing and 10-20 nm silica fillers.

Silica content (wt %)	Contact angle (°)		Sliding angle (°)		R _a (μm)	
	w/o EDA	With EDA	w/o EDA	With EDA	w/o EDA	With EDA
0	105 ± 1.8	98 ± 2.3	25 ± 5	30 ± 4	0.31 ± 0.15	0.48 ± 0.12
5	127 ± 5.1	117 ± 2.8	15 ± 2.5	24 ± 5	1.04 ± 0.18	1.27 ± 0.31
10	142 ± 1.7	134 ± 4.5	7 ± 2.0	13 ± 5	2.81 ± 0.31	1.93 ± 0.65
15	164 ± 3.9	152 ± 3.1	2 ± 1.5	5 ± 2	3.44 ± 0.26	2.86 ± 0.84

The values of R_a from Table 5.1 support the trend seen in the CA and SA values. The effect of surface roughness on amine cured coatings is very similar to its effect on the initial sol-gel system.

5.3 Chemical analysis

The FTIR spectrum of the EDA cured TEOS-Glymo system shows that the epoxy ring in Glymo is no longer present. The mild peak at 1600-1700 cm⁻¹ indicates the presence of the N-H bond in amines. The mild intensity of the peak may be due to the low concentration of EDA in the sol. The rest of the spectrum is similar to that of the TEOS-Glymo sol seen in section 4.3.

Fig. 5.2 FTIR spectrum of TEOS-Glymo sol before and after EDA curing

5.4 Surface morphology

The scanning electron micrographs of the EDA cured sol-gel system are shown below in Fig. 5.3.

Fig. 5.3 Amine cured sol-gel coating with a) no silica fillers, b) no silica fillers at high magnification, c) 15 wt% nanosilica and d) 15 wt % nanosilica at high magnification.

Fig. 5.3a indicates that a homogeneous crosslinked system has been formed. Similar morphologies have been observed by González, Barcia and Soares in their studies on epoxy modified composite materials [115]. The micrographs of coatings with 15 wt% nanosilica fillers show them to have an extremely rough surface with particles aggregated uniformly over the surface, thus resulting in a high CA and low SA. The images of the water droplets on the surfaces of the coatings with no fillers and 15 wt% silica fillers is shown below in Fig. 5.4.

Fig. 5.4 Water droplet resting on amine cured coating a) without silica fillers, $CA = 98^\circ$ and b) with 15 wt% silica fillers, $CA = 152^\circ$.

5.5 Cross-cut tape adhesion test

The modified TEOS-Glymo sol-gel coatings were tested for adhesion to the substrate using the cross-hatch test based on ASTM D3359. Contrary to results seen on coatings without amine curing (Fig. 4.6), here the sample without 10-20 nm silica fillers show higher brittleness and is rated as 3B. The corresponding image is shown in Fig. 5.5a. On increasing filler content the adhesion to the substrate does not change though the brittleness coatings were seen to decrease significantly. The coatings with 5, 10 and 15 wt% loading of nanosilica are rated as 4B, 4B and 5B respectively. The cross-hatch images of the coated samples are shown in Fig. 5.5b, c and d.

Fig. 5.5 Optical images of EDA cured sol-gel coatings after cross-cut tape adhesion test. a) coating without silica filler, b) coating with 5 wt% nanosilica, c) coating with 10 wt% nanosilica and d) coating with 15 wt% nanosilica loading.

The crosslinking formed in the matrix as a result of amine curing leads to a difference in the interaction between the organic and inorganic matrices. This also causes a difference in the network structure of the coating, thus leading to different properties than those observed previously in the coatings. This could be the reason why the coatings without silica loading show slightly higher removal of coatings along the cross-hatch lines compared to coatings with silica fillers [114].

5.6 Nanoindentation studies

The coating samples were tested for hardness and Young's modulus using the nanoindenter. The test was performed over a depth of 500-2000 nm. The results obtained from the test are recorded in Table 5.2.

Table 5.2: Hardness and Young's modulus of TEOS-Glymo coating cured with EDA with 10-20 nm silica fillers.

Filler loading (wt %)	Hardness (GPa)	Young's modulus (GPa)
-	1.8 ± 0.8	3 ± 0.6
5	2.5 ± 0.6	3.5 ± 0.4
10	2.6 ± 0.5	3.7 ± 0.2
15	3.1 ± 0.5	4.2 ± 0.7

From the values in Table 5.2 it can be seen that the hardness and Young's modulus both increase with increasing filler content. This effect is similar to that observed in the mechanical properties of the TEOS-Glymo sol. But the values of hardness and Young's modulus in the cured coatings are significantly higher than those reported in section 4.6. The improved mechanical properties can be attributed to the effect of crosslinking in the organic component of the matrix. These results are in agreement with the previously reported studies on the increase in overall mechanical performance of the amine cured hybrid composites by Ochi and Takahashi [114]. The results of the cross-cut tape adhesion test also show that the brittleness of all the coatings has reduced by a significant extent reinforcing the improvement in mechanical properties of the TEOS-Glymo sol-gel system.

5.7 Effect of abrasive wear

The amine cured samples were tested for their performance under an accelerated abrasive environment. The test was performed as described in section 3.5. The weight and thickness loss of the coatings were as follows:

Table 5.3: Average thickness and weight loss in coatings after 20 abrasion cycles.

Filler loading (wt %)	Avg. thickness loss (μm)	Avg. weight loss (mg)
0	7.4 ± 1.2	8.2 ± 1.4
5	10.1 ± 1.7	10.8 ± 1.6
10	14.6 ± 2.8	15.9 ± 2.5
15	17.9 ± 3.1	19.0 ± 2.7

The values in Table 5.3 show that both thickness and weight loss is higher for coatings with higher filler content. This trend is similar to previous reports in section 4.7. The coatings with higher silica content have higher surface roughness due to the agglomeration and aggregation of filler particles. These surface features are susceptible to removal under the constant abrasive forces acting on the surface, leading to higher thickness and weight loss in the coatings. It should be noted that both thickness and weight loss in the amine cured coatings are lower than those reported in the previous composition. The effect of abrasive wear on the hydrophobic functionality of the coatings is reported in Table 5.4:

Table 5.4: CA, SA and average surface roughness after 20 abrasion cycles for amine cured TEOS-Glymo coatings with 10-20 nm silica particles.

Filler content (wt %)	CA (°)		SA (°)		Ra (μm)	
	Before	After	Before	After	Before	After
0	98 ± 2.3	93 ± 3.2	30 ± 4	33 ± 7	0.48 ± 0.12	0.29 ± 0.10
5	117 ± 2.8	112 ± 2.6	24 ± 5	23 ± 7	1.27 ± 0.31	0.84 ± 0.26
10	134 ± 4.5	130 ± 3.8	13 ± 5	13 ± 8	1.93 ± 0.65	1.37 ± 0.51
15	152 ± 3.1	147 ± 3.1	5 ± 2	7 ± 3	2.86 ± 0.84	2.25 ± 0.50

The superhydrophobic coating with 15 wt% loading of nanosilica still has good sliding properties, though the CA < 150°. The other coatings also show a drop in CA, but they still retain the hydrophobic functionality, which is a good indication that the FAS-17 is uniformly present throughout the thickness of the coating.

5.8 Effect of erosion

The effect of micro-sand erosion on the EDA cured TEOS-Glymo coatings is tested by measuring the CA, SA, Ra and weight loss after the erosion process as described under section 3.5. The average weight loss and surface roughness after the erosion are shown in Table 5.5.

Table 5.5: Average surface roughness and weight loss in amine cured sol-gel coatings with 10-20 nm silica fillers after erosion.

Filler loading (wt %)	Ra (μm)	Avg. weight loss (mg)
0	0.34 ± 0.17	6.7 ± 2.4
5	0.96 ± 0.33	9.2 ± 3.7
10	1.52 ± 0.79	12.8 ± 3.4

15	2.40 ± 0.65	16.5 ± 4.0
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From the values in Table 5.5 it can be seen that the average weight loss and roughness of the coating after erosion is similar to the trend seen after abrasion. The coatings with silica fillers show higher weight loss, but the values are slightly lower than that seen after abrasion.

The CA and SA values of the coatings before and after erosion are listed in Table 5.6. The CA and SA decrease and increase after the erosion. It is interesting to note that the drop in CA after erosion is higher than the drop in CA after abrasion. This can be possibly due to the fact that the sand blaster is focused on a specific area leading to increased removal of the coating in some parts.

Table 5.6: Change in CA and SA after micro-sand erosion.

Filler content (wt %)	CA (°)		SA (°)	
	Before	After	Before	After
0	98 ± 2.3	93 ± 4.1	30 ± 4	38 ± 5
5	117 ± 2.8	110 ± 3.7	24 ± 5	28 ± 7
10	134 ± 4.5	126 ± 4.2	13 ± 5	19 ± 6
15	152 ± 3.1	145 ± 4.5	5 ± 2	10 ± 5

5.9 Effect of UV weathering

A lot of studies have focused on the effect of UV degradation on amine cured epoxy composites to estimate the life of the coatings. But there are no specified parameters that are highlighted as the key factors affecting the performance of these materials [116]. The functionality of the coatings tested after UV exposures are given below in Table 5.7. Details of the UV weathering test were given in section 3.5

Table 5.7: CA and SA of coatings after UV exposure.

Filler content (wt. %)	Contact angle (°)		Sliding angle (°)	
	before	after	before	after
0	98 ± 2.3	97 ± 2.8	30 ± 4	30 ± 4
5	117 ± 2.8	117 ± 3.1	24 ± 5	24 ± 5
10	134 ± 4.5	132 ± 4.2	13 ± 5	13 ± 5
15	152 ± 3.1	151 ± 2.5	5 ± 2	5 ± 2

After UV exposure it was observed that the SA of the coatings did not change much and remained within the standard deviation for all the samples. Slight variations in the CA were recorded, but the overall functionality of the coatings did not change. Reports from literature indicate that the effect of UV weathering on amine cured epoxy is much more significant in predominantly organic polymers and aromatic amine cured systems [116].

5.10 Self-cleaning test

The self-cleaning test was performed on the amine cured coating system as described in section 3.6. The lightness values obtained at different stages of the test are given below in Table 5.8. The dirt accumulation and self-cleaning efficiency plots for the as coated samples and samples after abrasion are shown in Fig. 5.6 and 5.7.

Table 5.8: Lightness values measured at different stages of the self-cleaning test on amine cured coatings.

Coating	L₁ pristine coating	L₂ dirt coated sample	L₃ cleaned sample	Dirt accumulation (%)	Self cleaning efficiency (%)
Bare glass	85.98	27.77	54.43	67.70	63.3
Bare glass after abrasion	85.98	18.13	47.54	78.91	55.29
Pristine coating	63.70	24.67	40.82	61.27	64.08
Pristine coating after abrasion	63.70	15.67	38.10	75.40	59.81
5 wt%	71.86	33.13	52.93	53.89	73.66
5 wt% after abrasion	71.86	26.30	46.92	63.40	65.30
10 wt%	85.42	67.80	73.86	20.64	86.47
10 wt% after abrasion	85.42	63.74	70.21	25.38	82.19
15 wt%	89.63	79.92	85.26	10.83	95.12
15 wt% after abrasion	89.63	77.15	81.86	13.92	91.33

The self-cleaning test data shows that there is not much difference between the self-cleaning efficiencies of the coatings before and after amine curing. This goes on to indicate that amine curing improves the mechanical properties of the coatings, while at the same time retaining its hydrophobic functionality. The coatings with 15 wt% nanosilica

loading show the lowest dirt accumulation and highest self-cleaning efficiency ($> 90\%$) even after accelerated abrasion wear.

Fig. 5.6 Percentage dirt accumulation on amine cured samples before and after abrasion

Fig. 5.7 Self-cleaning efficiency of amine cured samples before and after abrasion

5.11 Summary

The results reported in this chapter confirm that amine curing of the silane-epoxysilane hybrid sol-gel system yields coatings that are mechanically robust with the same hydrophobic functionality. The main limitation of this system is that the coatings should be used as a two component system, where component A is the TEOS-Glymo-FAS sol and component B is EDA (curing agent). It should be noted that the pot-life of the amine cured sol is ~ 4 hours, which is an advantage over several other amine cured epoxy systems.

Chapter 6 Results and discussion - System II: TEOS-PDMS sol-gel formulation

6.1 Introduction

This chapter discusses the results from the studies and tests performed on the TEOS-PDMS based coating system. Coatings with different PDMS and filler concentrations were synthesized and tested. The coating formulation is described in detail under section 3.2. Only 10-20 nm sized silica particles have been used in this system as the results from the previous study on the TEOS-Glymo coatings indicate that increasing filler size did not have a significant impact on the coating properties and performance.

6.2 Contact angle and Sliding angle

To study the wetting behavior of the coatings, CA and SA measurements were carried out. Fig. 6.1 shows the plot of CA with respect to the PDMS content in the sol. CA of coatings without any silica fillers increases slightly with increasing amount of PDMS. Coatings with TEOS: PDMS = 70:30 have the highest CA at 112°. The reason for this can be attributed to the hydrophobic nature of PDMS. The higher the PDMS content in the coating, the larger the CA. Addition of nanosilica fillers increases the CA for all three groups, and in case of TEOS:PDMS = 70:30 coatings with 10 wt % fillers, CA of 154° was observed, making it superhydrophobic. This is because the addition of the particulate fillers increases the surface roughness [20, 91]. This can lead to a heterogeneous wetting regime due to increased air gaps in the solid-liquid contact line [117].

Fig.6.1 Change in CA with increasing nanosilica loading for various coating compositions

The roughness values of the coatings as measured using the surface profiler are listed in Table 6.1. The arithmetic mean roughness, R_a , increases from 0.16 μm for the coating without filler to 1.8 μm with 10 wt% fillers (TEOS:PDMS = 70:30). As a result the CA increased from 112 ° to 154°.

The SAs of the coatings were measured using the tilting base method using 5 μL water droplet. The plot of SA versus silica content of the coatings is shown in Fig. 6.2. Coatings with higher filler content have lower sliding angles. This is similar to the trend observed in the TEOS-Glymo system, showing the effect of roughness imparted by the fillers to the coating [20]. The length and continuity of the three phase (air-solid-liquid) contact line strongly affects the sliding angle of the water droplet. A shorter three phase contact line is

shown to be more likely to support a lower sliding angle [56]. It should be noted that the TEOS:PDMS = 70:30 coating without fillers has a sliding angle of less than 8° . This is of special interest because these coatings do not have CA greater than 150° (i.e. not superhydrophobic). Due to their good sliding properties, we classify these coatings as possessing good dynamic hydrophobicity (i.e. having low sliding angles despite not having CA $>150^\circ$).

Table 6.1: Contact angles, sliding angles and roughness values measured on various coating surfaces.

TEOS:PDMS	Filler (wt%)	CA ($^\circ$)	SA ($^\circ$)	Roughness, as coated (R_a , μm)	CA hysteresis ($^\circ$)
70:30	0	112 ± 1.6	7-8	0.16 ± 0.026	2
80:20	0	106 ± 2.3	14-15	0.27 ± 0.021	6.1
90:10	0	98 ± 1.2	19-20	0.34 ± 0.035	10.9
70:30	5	139 ± 2.6	<4	0.935 ± 0.038	7.4
80:20	5	131 ± 1.8	7-8	0.974 ± 0.057	9.6
90:10	5	119 ± 1.2	12-13	1.04 ± 0.041	12.1
70:30	10	154 ± 2.6	<1	1.82 ± 0.034	3.3
80:20	10	148 ± 2.1	<4	1.9 ± 1.04	5.8
90:10	10	131 ± 1.2	5-6	1.67 ± 1.06	11.2

Fig. 6.2 Change in SA with increasing nanosilica for various coating compositions.

6.3 Chemical Analysis

Fig. 6.3 shows the Fourier Transform Infrared spectrum of the TEOS:PDMS = 70:30 mixture. The most prominent dips at around 1000 cm^{-1} can be assigned to the Si-O-Si bond due to its bending and stretching actions [118]. The appearance of this peak confirms that expected network of Si-O-Si bond, mainly contributed to by TEOS and PDMS has been formed. Further, the presence of -OH group is also noted which is primarily due to the hydroxyl termination of the PDMS used. The broad peaks around 3000 and 3400 cm^{-1} were weaker for coatings with silica particles but do not completely disappear. The results can be attributed to the coexistence of hydroxyl groups, silica particles and free PDMS [118]. From the FTIR results, it can be concluded that the Si-O-Si network has been formed, contributing to the basic matrix of the system.

Fig. 6.3 FTIR spectrum for TEOS:PDMS = 70:30.

6.4 Surface morphology

The FESEM images of the coatings with TEOS:PDMS = 70:30 are shown in Fig. 6.4. It can be seen that the coating without any particulate fillers, Fig. 6.4a, is quite smooth without prominent surface features. Fig. 6.4b shows the same surface at a higher magnification.

Fig. 6.4 FESEM images of TEOS:PDMS = 70:30 coatings with a) no filler loading, b) no filler at high magnification, c) 5 wt% nanosilica fillers and d) 10 wt% nanosilica fillers.

Upon introducing 5 wt % silica nanoparticles, (Fig. 6.4c), slight agglomeration of the particles can be observed on the surface. For the coating with 10 wt% loading of silica particles, Fig. 6.4d, the surface is composed of a large number of particulate agglomerations. This leads to an increase in the air pockets, thus resulting in higher CA. On fitting the CA data to the Wenzel and Cassie-Baxter models, we get the following values for the roughness factor and surface fractions respectively.

Table 6.2: Fitting Wenzel and Cassie-Baxter models to TEOS:PDMS = 70:30 samples.

Sample	$\theta (^{\circ})$	$\theta^{*} (^{\circ})$	r	f_1 and f_2
No fillers	110.4	112	1.07	0.96, 0.04
5 wt%	110.4	139	2.17	0.38, 0.62
10 wt%	110.4	154	2.58	0.16, 0.84

The coatings with 80:20 and 90:10 TEOS:PDMS ratios are shown in Fig. 6.5. There are no discernible morphological differences on changing the PDMS concentration. The functional variation in the hydrophobicity of these coatings could be attributed to the distribution of $-\text{CH}_3$ groups on the surface due to PDMS.

Fig. 6.5 FESEM images of a) TEOS:PDMS = 80:20 with no filler loading, b) TEOS:PDMS = 80:20 with 5 wt% nanosilica fillers, c) TEOS:PDMS = 80:20 with 10 wt% nanosilica fillers d) TEOS:PDMS = 90:10 with no filler loading, e) TEOS:PDMS = 90:10 with 5 wt% nanosilica fillers and f) TEOS:PDMS = 90:10 with 10 wt% nanosilica fillers.

6.5 Cross-cut tape adhesion test

The coated samples were tested using the cross-cut tape adhesion test to determine the extent of adhesion of the coating to the substrate and also the brittleness of the coating. The optical microscope images of the cross-cut patterns on TEOS: PDMS = 70:30 coatings are shown in Fig. 6.6. It can be seen that the sample with no filler addition (Fig. 6.6a) shows the best adhesion to the substrate. Further, there were no noticeable cracks or chipping along the cross hatch boundaries, thus this coating is rated as 5B according to ASTM D 3359. The samples with 5 and 10 wt% loading of silica nanoparticles show increased level of brittleness and coating removal after the cross-cut test (Figs. 6.6b, c). The rating of these coatings is given as 3B and 1B respectively. Increased filler content has clearly increased the brittleness of the coatings.

Fig.6.6 Cross-cut tape adhesion test for coatings with TEOS:PDMS = 70:30. a)no fillers; b)5 wt%, and c)10 wt% of 10-20nm silica fillers.

The ASTM rating for the other TEOS:PDMS concentrations are listed in Table 6.3. From the adhesion rates presented in the table, it can be seen that similar to the previous results reported in section 4.5, coatings with no filler content in each of the series show better adhesion to the substrates and lower brittleness. The reason for the TEOS: PDMS = 80:20 and 90:10 coatings without fillers having a 4B rating is that there were slightly higher rates of chipping along the cross-cut intersection lines. This can be due to higher TEOS

content in these coatings, resulting in comparatively higher brittleness when compared those with a lower ratio of inorganic component in the matrix [119, 120].

Table 6.3: Adhesion rating of TEOS-PDMS coatings.

Sample	Adhesion rating
70:30, no fillers	5B
70:30, 5 wt%	3B
70:30, 10 wt%	2B
80:20, no fillers	4B
80:20, 5 wt%	3B
80:20, 10 wt%	1B
90:10, no fillers	4B
90:10, 5 wt%	2B
90:10, 10 wt%	1B

6.6 Nanoindentation studies

All the coatings were tested for their hardness and Young's modulus using nanoindentation. Table 6.4 shows the values of both hardness and Young's modulus against filler concentration. The TEOS:PDMS = 70:30 coating without fillers shows the highest hardness and Young's modulus at 0.9 and 5.8 GPa respectively. This is counter-intuitive as silica fillers usually are used to enhance the hardness and modulus. In the current work, however, we believe the agglomeration of the silica nanoparticles could introduce porosity into the coatings, leading to lower values in both hardness and Young's modulus. Further, reports on sol-gel coatings show that addition of fillers increases the hardness only in cases where high temperature curing ($> 400\text{ }^{\circ}\text{C}$) is used [120]. This phenomenon is similar to that reported by Tzetzis et al. in their work studying the mechanical properties of epoxy and fumed silica reinforced coatings [110]. Further, the overall trend shows that both hardness and Young's modulus decrease with decrease in

PDMS content. This can be attributed to the predominantly inorganic nature of the matrix due to higher TEOS content, making the coating more brittle [119-121]. Studies by Mackenzie in 1994 indicate that when the PDMS content was less than 20 wt%, the sample became brittle [122]. Mackenzie proposed that small concentrations of PDMS react in solution to form gels with a porous three dimensional network still dominated by the Si-O-Si linkages. However, as the PDMS content increases, the structure is characterized more by silicon clusters linked with flexible chains of PDMS making them less brittle [122].

Table 6.4: Hardness and Young's modulus values for various coating compositions.

TEOS:PDMS	Filler Concentration (wt. %)	Hardness (GPa)	Young's Modulus (GPa)
70:30	-	0.9 ± 0.05	5.83 ± 1.45
70:30	5	0.65 ± 0.09	4.91 ± 1.11
70:30	10	0.32 ± 0.06	4.51 ± 1.31
80:20	-	0.35 ± 0.07	3.81 ± 0.4
80:20	5	0.26 ± 0.02	3.66 ± 0.69
80:20	10	0.195 ± 0.03	3.28 ± 0.15
90:10	-	0.29 ± 0.02	2.74 ± 1.21
90:10	5	0.18 ± 0.01	2.43 ± 0.72
90:10	10	0.13 ± 0.01	2.09 ± 0.41

6.7 Effect of abrasive wear

The effect of abrasion on the TEOS-PDMS coatings was tested by recording the weight, roughness, thickness and CA after the 20 abrasion cycles. The results reported in Table 6.5 show that the average thickness and weight loss for coatings with filler loading at 5 and 10 wt. % loading are significantly higher than those on the coatings without fillers. It can also be seen from the values reported that the coatings with lower PDMS content also show a similar trend.

Table 6.5: Thickness and weight loss after 20 abrasion cycles (total abrasion distance is 1508 m).

TEOS:PDMS	Filler Concentration (wt. %)	Avg. thickness loss (μm)	Avg. weight loss (mg)
70:30	-	5.75 ± 1.64	17.87 ± 2.11
	5	7.65 ± 2.58	23.42 ± 2.58
	10	7.91 ± 2.63	24.19 ± 1.90
80:20	-	8.13 ± 2.30	26.24 ± 1.25
	5	8.64 ± 1.74	34.63 ± 2.97
	10	9.52 ± 2.10	37.81 ± 1.34
90:10	-	10.98 ± 1.24	28.20 ± 1.14
	5	11.46 ± 1.36	35.11 ± 2.40
	10	12.96 ± 1.20	42.68 ± 2.16

The combination of TEOS and PDMS serves to give an organic-inorganic hybrid matrix. In this instance, as the TEOS content increases in the coatings with 80:20 and 90:10 TEOS:PDMS. Therefore, the composition is not optimum to have hardness combined with elasticity, making it easier to abrade these surfaces [119]. The values of CA, SA and R_a are listed for the coatings with TEOS:PDMS = 70:30 in Table 6.6 below.

Table 6.6: CA, SA, and roughness values of coatings (TEOS:PDMS = 70:30) before and after abrasion (20 cycles, 1508 m abrasion distance).

Filler content (wt%)	CA (°)		SA (°)		Ra (μm)	
	Before abrasion	After abrasion	Before abrasion	After abrasion	Before abrasion	After abrasion
0	112 ± 1.6	104.7±2.6	7-8	20-23	0.16 ± 0.026	0.23 ± 0.10
5	139 ± 2.6	113.5±2.8	<4	25-27	0.935 ± 0.038	0.37 ± 0.19
10	154 ± 2.6	132.7±2.5	<1	25-27	1.82 ± 0.034	0.82 ± 0.27

The CA decreases after the abrasion cycle. This is similar to the trend seen in the TEOS-Glymo system. For coatings with 5 and 10 wt% silica loading, the abrasion process removes some of the surface features, thus decreasing the surface roughness. This also serves to increase the SA as the wetting regime undergoes transition. But for coatings without filler loading, the R_a increases from 0.16 to 0.23 μm. Though the increase is not very significant, it goes on to show that the abrasion process creates some surface features that change its topography. The confocal interferometry images before and after the abrasion process for the coatings without filler loading is shown in Fig. 6.7.

Fig. 6.7 Topographical image of TEOS:PDMS = 70:30 without fillers a) before abrasion and b) after abrasion.

6.8 Effect of erosion

The coated samples were subjected to the accelerated micro-sand erosion test to study if the coatings could retain the required properties in an erosive environment. Loss in weight of the coatings was used to measure the erosion resistance of the coatings. The changes in the coatings CA and SA were measured after the erosion test to study how much of the original functionality was retained.

From the values tabulated in Table 6.7, it can be seen that the coatings without any particulate fillers show the least weight loss of about 20 mg. The change in the CA from 112 to 108.7° for coatings with TEOS:PDMS = 70:30 after the erosion test is insignificant. The SA on the other hand increased by around 12°. The change in SA is due to the change in the wetting state which is the result of surface roughness change. The coating with $R_a = 0.16 \mu\text{m}$ before the erosion has increased to $R_a = 0.65 \mu\text{m}$ after the sand particle impingement (Table 6.1). The AFM images of the surfaces before and after sand blasting are shown in Fig. 6.8 for coatings with TEOS:PDMS = 70:30.

Table 6.7: Contact angle, sliding angle and weight loss measured on coatings after the micro-sand erosion test. The CA and SA before the erosion test are also listed for easy comparison.

TEOS:PDM S	Filler (wt%)	Weight loss (mg)	CA (°)		SA (°)	
			before	after	before	after
70:30	0	18 ± 1.58	112 ± 1.6	108.7±1.6	7-8	20-22
80:20	0	22 ± 1.12	106 ± 2.3	101.5±1.7	14-15	27-28
90:10	0	22 ± 1.79	98 ± 1.2	95.1±2.0	19-20	31-33
70:30	5	29 ± 1.84	139 ± 2.6	110.0±1.3	<4	17-18
80:20	5	32 ± 1.97	131 ± 1.8	106.2±1.1	7-8	10-12
90:10	5	35 ± 1.93	119 ± 1.2	103.4±1.9	12-13	13-14
70:30	10	26 ± 2.14	154 ± 2.6	127.7±2.1	<1	9-10
80:20	10	45 ± 2.43	148 ± 2.1	123.5±2.2	<4	14-16
90:10	10	66 ± 3.34	131 ± 1.2	120±2.5	5-6	16.5-19

Fig.6.8 AFM images of various coating surfaces. a), b) and c) show images of coatings with 0, 5 and 10 wt% filler loading. d), e) and f) show images of coatings with 0, 5 and 10 wt% filler loading after the micro-sand erosion test. All samples are for the composition with TEOS:PDMS = 70:30.

For coatings with 5 and 10 wt % filler loading, the weight loss was higher in the range of 30-65 mg. The CA decreased from 154 ° to 127 ° for TEOS:PDMS = 70:30. These changes are due to the loss of roughness on the surface after erosion. For example, the

surface roughness of the 10 wt% sample (TEOS:PDMS = 70:30) decreased from 1.82 μm to 0.72 μm . The higher removal rate of the coatings with fillers is likely due to the increase in surface roughness and coating porosity, which leads to increased brittleness of the coating. Early results on the cross-cut test in section 5.5 have confirmed the brittleness of the filler-containing coatings.

6.9 UV weathering

On being subjected to the weathering test, with parameters as described in section 3.5, the following results were obtained for the TEOS-PDMS coating system:

Table 6.8: CA and SA before and after UV weathering.

TEOS:PDMS	Filler content (wt. %)	Contact angle ($^{\circ}$)		Sliding angle ($^{\circ}$)	
		before	after	before	after
70:30	-	112 ± 1.6	109 ± 2.1	7-8	20-25
	5	139 ± 2.6	132 ± 3.7	< 4	20-25
	10	154 ± 2.6	146 ± 3.2	< 1	18-20
80:20	10	148 ± 2.1	136 ± 2.8	< 4	12-15
90:10	10	131 ± 1.2	122 ± 3.5	5-6	15-18

From the values listed in Table 6.8, it can be seen that there is a drop in both CA and SA for all the coatings. The decrease in CA is not very high, though SA values increase by a significant value. This is because organic polymers with low energy structures (like hydrocarbon groups) are vulnerable to UV irradiation. When impurities and UV absorbing groups are present, the polymer can undergo a photo-oxidation process to form carbonyl

or hydroxyl groups on the surface and thus degrade into smaller chains [113, 123]. The main Si-O-Si network is more stable under UV radiation as discussed in section 4.9 [113]. Therefore, it is the presence of the polymeric chain that affects the SA due to degradation.

6.10 Self-cleaning test

As described previously in section 3.6, the self-cleaning test was performed on the as coated samples and samples after 20 abrasion cycles.

The results of the self-cleaning test performed on all TEOS-PDMS coatings at various concentrations of PDMS and particulate fillers are tabulated in Table 6.9. The trend for dirt accumulation and cleaning is also plotted in Fig. 6.9 and 6.10. Fig. 6.11 shows the photographs of the corresponding samples at various stages of the self-cleaning test.

Table 6.9: L values from spectrophotometric measurements before and after the cleaning test.

Coating	L ₁ pristine coating	L ₂ dirt coated sample	L ₃ cleaned sample	Dirt accumulation (%)	Self cleaning efficiency (%)
Bare glass	85.98	27.77	54.43	67.7	63.31
Bare glass after abrasion	85.98	18.13	47.54	78.91	55.29
70:30, no filler	76.18	50.48	72.54	33.73	95.22
70:30, no filler, after abrasion	76.18	46.82		38.54	93.58
70:30, 5 wt%	83.64	52.46	79.21	37.27	94.70
70:30, 5 wt%, after abrasion	83.64	48.19	77.09	42.38	92.17
70:30, 10 wt%	94.58	61.48	90.68	34.99	95.87
70:30, 10 wt%, after abrasion	94.58	55.20	88.19	41.63	93.24

It is evident that the coatings with a high PDMS content (TEOS:PDMS = 70:30), which are dynamically hydrophobic, demonstrate a very high self-cleaning efficiency similar to the ones achievable by superhydrophobic coatings. All three coatings (0, 5, 10wt% silica fillers) performed equally well in self-cleaning. However if considering the mechanical performance, the one with no silica filler possesses the overall optimum properties and thus is recommended as the best choice.

Fig. 6.9 Dirt accumulation before and after abrasion.

Fig. 6.10 Self-cleaning efficiency before and after abrasion.

Fig. 6.11 Photographs of a) pristine coatings, b) coatings after dirt spray, and c) coatings after water spray for cleaning. From left to right the samples arrange are: bare glass, TEOS:PDMS-70:30, TEOS:PDMS-70:30 with 5 wt% nanosilica and TEOS:PDMS-70:30 with 10 wt% nanosilica.

6.11 Summary

TEOS-PDMS coatings were prepared using the sol-gel method. 5 and 10 wt% 10-20 nm silica particles were used to modify the surface features of the coating. PDMS served as the hydrophobic modifier.

TEOS:PDMS ratios were varied as 70:30, 80:20 and 90:10 to produce coatings of varying hydrophobicity. Higher the PDMS content, better the hydrophobicity of the coating. At 10 wt% silica loading, the coatings have $CA > 150^\circ$ and $SA < 1^\circ$. But, coatings with 70:30 TEOS:PDMS without silica fillers, exhibit good sliding properties even at $CA \sim 112^\circ$.

It is seen that the coatings without silica fillers possess the best mechanical properties. These coatings also show reduced weight and thickness loss when compared to the coatings which are superhydrophobic. These coatings also exhibited ~95% self-cleaning index, which is similar to the rates achieved by their superhydrophobic counterparts.

Chapter 7 Results and discussion - System III: PVDF based composite coatings

7.1 Introduction

This chapter examines the results from the studies and tests performed on the PVDF composite coatings. Effect of surface functionalizing agent APTES on improving coating adhesion is seen. The coating composition and synthesis are described in Chapter 3 under section 3.3. Similar to the TEOS-PDMS coatings studied, the filler size is limited to 10-20 nm, though effect of different PVDF:SiO₂ ratios on the coatings are studied.

7.2 Contact angle and Sliding Angle

Fig. 7.1 shows a plot of the change in CA of the coatings at different concentrations of PVDF and nanosilica loading. The CA increases with increase in filler loading for both 5 and 10 % PVDF in DMF. The trend seen in the increase of CA is very similar for both concentrations of PVDF. The highest CA of $159.16 \pm 1.38^\circ$ was achieved in the coating with 10 % PVDF and 1:1 PVDF:SiO₂ loading. The high CA can be attributed to the dense clustering of the silica particles on the coating surface leading to hierarchical roughness.

Table 7.1: CA, SA, surface roughness and CA hysteresis for PVDF composite coatings.

Sample	PVDF:SiO ₂	Contact Angle (°)	Sliding Angle (°)	R _a (μm)	CA hysteresis (°)
5 % PVDF	-	98 ± 4.62	35 ± 4	0.27 ± 0.02	23
	1:0.5	126 ± 3.42	19 ± 5	1.14 ± 0.15	12
	1:1	155 ± 4.03	< 5	1.68 ± 0.17	7
10 % PVDF	-	98 ± 1.78	27 ± 3	0.24 ± 0.05	22
	1:0.5	134 ± 2.67	13 ± 2	1.42 ± 0.23	10
	1:1	159 ± 1.38	< 1	1.90 ± 0.19	4

Fig.7.1 Plot of CA change with coating composition.

Fig.7.2 Plot of SA change with coating composition.

The CA, SA and average surface roughness values are listed in Table 7.1. From the values in Table 7.1 and Fig. 7.2 it can be seen that the SA decreases with increasing R_a on increasing the filler concentration. 10 % PVDF coating with 1:1 silica loading has a $SA < 1^\circ$ indicating a case of heterogeneous wetting [37]. On coatings that have no silica fillers or lower concentration of fillers, the wetting regime is more homogenous resulting in higher SA [35].

7.3 Chemical analysis

The FTIR spectrum of the coatings with 10 % PVDF with different concentrations of filler loading is shown in Fig. 7.3. The prominent dips (peaks) observed around 1680-1620 cm^{-1} corresponds to C=C from the PVDF. The C-F stretch bonds from FAS contribute to the peaks found at 1000-1400 cm^{-1} [22]. The presence of APTES is confirmed by the peak at 1600 cm^{-1} resulting from the bending of the N-H bonds and also the mild peaks around 1080-1360 cm^{-1} resulting from the bonds between the APTES and the PVDF. This confirms that the surface was successfully functionalized by the APTES which improves the binding of the PVDF to the substrate. The peaks around 1020 cm^{-1} are due to the Si-O-Si bonds from the hydrolyzed APTES. There is not much difference observed between the FTIR spectrum of the coatings with and without silica fillers except for the peak around 700-750 cm^{-1} which is due to the presence of the silica nanoparticles which is not observed in the pure PVDF coating.

Fig. 7.3: FTIR spectra of the coating with 10 % PVDF and 1:1 silica loading.

7.4 Surface morphology

Fig. 7.4a shows the image of pure PVDF coating (10%). A filament like structure with pores of microscopic dimensions is seen. But the roughness of this coating as recorded in Table 7.1 is not very high. There is a high possibility of the water droplets getting trapped within the pores on the surface thus making it hard for the droplets to slide on the surface [35]. On introducing nanosilica in the ratio 1:0.5 by weight with PVDF, a clustering of the nanoparticles in the form of microbumps is seen, resulting in hierarchical structures as shown in Fig. 7.4b. Addition of silica particles increases the R_a from 0.24 to 1.42 μm . In

Fig. 7.4c a more dense aggregation of silica particles is observed leading to increased surface roughness and coating porosity. The presence of hierarchical structures in coatings with 1:0.5 and 1:1 loading of nanosilica aids in heterogeneous wetting of the surface making it easier for the droplets to roll away [37, 98].

Fig. 7.4: FESEM images of coatings with a) 10 % PVDF, b) 10 % PVDF , 1:0.5 PVDF: SiO₂, c) 10 % PVDF , 1:1 PVDF: SiO₂.

Applying the Wenzel and Cassie-Baxter models to the above coatings, the roughness factor and surface fractions calculated are as follows:

Table 7.2: Fitting Wenzel and Cassie-Baxter models to 10% PVDF samples.

Sample	$\theta (^{\circ})$	$\theta^{*} (^{\circ})$	r	f_1 and f_2
No fillers	98	98.55	1.07	0.99, 0.01
PVDF:SiO ₂ = 1:0.5	98	134	4.99	0.35, 0.65
PVDF:SiO ₂ = 1:0.5	98	159	6.71	0.08, 0.92

7.5 Cross-cut adhesion test

On visual inspection it was observed that the coatings that were applied without pre-treating the surface with APTES did not adhere well to the substrate. The coated layers start delaminating from the substrates that were not functionalized. The samples that were pre-treated with APTES for 24 hours were found to have significantly better adhesion to the substrate. The use of amines and diamines to cross link fluoride and vinylidene fluoride polymers has been in use since the late 1950's. The mechanism is quite simple and only requires the presence of H atoms in the polymer backbone. As a result of using amine pretreatments, the adhesion of such polymers has been found to increase significantly [124]. The basic steps involved in crosslinking PVDF with amines is shown in Fig. 7.5.

Fig. 7.5 Mechanism of reaction between amines and PVDF [124, 125].

In order to measure the extent of coating adhesion to the substrate the cross-cut tape adhesion test was performed. Fig. 7.6 shows the images of 10 % PVDF coatings after the cross-cut test on samples with and without APTES functionalization. Fig. 7.6a shows the sample without APTES pre-treatment where the coating completely peels away from the substrate on using the cross-cut tester. Though the coating does not show signs of brittleness, it is graded at 0B due to its poor adhesion.

Fig. 7.6: Cross-hatch tape adhesion test for 10 % PVDF coatings with 10-20nm silica fillers. a) no fillers without APTES ; b) 1:1 without APTES ; c) no fillers with APTES and d) 1:1 with APTES

In Fig. 7.6b the sample with 1:1 PVDF:SiO₂ without APTES pre-treatment (graded 1B) is seen to have poor adhesion and highly brittle as the cross-hatch squares show increased removal of the coating. Fig. 7.6c and d are samples that were pre-treated with APTES. It

can be seen that the coating adhesion significantly improves. Fig. 7.6c is 10 % PVDF coating without silica loading. The cross-hatch squares remain intact with slight flaking at the edges. Therefore, this coating is rated at 3B. In Fig. 7.6d the coating with 1:1 PVDF:SiO₂ is rated at 4B as it shows very little flaking at the edges and the cross-hatch squares remain completely attached. This shows that the addition of APTES greatly improves the adhesion of the coating to the substrate. The ASTM rating for all the PVDF composite coatings are shown in Table 7.3.

Table 7.3: Adhesion rating of PVDF coatings with APTES treatment.

Sample	Adhesion rating
5% PVDF, no fillers	4B
5% PVDF, 1:0.5	3B
5% PVDF, 1:1	3B
10% PVDF, no fillers	4B
10% PVDF, 1:0.5	4B
10% PVDF, 1:1	4B

7.6 Nanoindentation studies

Nanoindentation was used to measure the hardness and Young's modulus of the coatings. Table 7.4 lists out these values measured over a depth of 500-2000 nm. The pure PVDF coating (10 and 5%) have a measured hardness of 2.6 and 2.4 GPa respectively. This agrees with the values previously reported in literature [126]. On addition of 10-20 nm silica particles the hardness increases up to 5.2 GPa for 1:1 loading of PVDF:SiO₂ for 10% PVDF. The presence of hydrolyzed APTES due to the functionalization provides a Si-O-Si network for the particles to bond with thus integrating well with the coatings. The Young's modulus conversely is seen to decrease from 5.13 GPa to 3.83 GPa on

introducing filler particles. This can be attributed to inhomogeneity of silica distribution in the composite and has been previously observed in similar composites prepared using TiO_2 and PVDF [127]. Unlike the previous coating systems where the base matrix was Si-O-Si, here the silica particles cannot bond very easily with the PVDF network. The trend in hardness and modulus for 5% PVDF coatings is similar to that seen in 10% PVDF coating.

Table 7.4: Hardness and Young's Modulus values for various coating compositions by nanoindentation.

Sample	Hardness (GPa)	Young's Modulus (GPa)
10 % PVDF	2.60 ± 0.09	5.13 ± 0.08
10 % PVDF, 1:0.5 PVDF:SiO ₂	3.85 ± 0.18	4.6 ± 0.27
10 % PVDF, 1:1 PVDF:SiO ₂	5.20 ± 0.28	3.83 ± 0.30
5 % PVDF	2.43 ± 0.05	4.57 ± 0.18
5 % PVDF, 1:0.5 PVDF:SiO ₂	3.29 ± 0.24	4.10 ± 0.20
5 % PVDF, 1:1 PVDF:SiO ₂	4.66 ± 0.31	3.27 ± 0.24

7.7 Effect of abrasive wear

The effect of abrasion on the PVDF composite coatings was tested. The CA, SA, R_a , thickness and weight are recorded after the abrasion cycles. The results reported in Table 7.5 show that the average thickness and weight loss for both 5 and 10 % PVDF coatings show a similar trend. The weight and thickness loss decrease with increase in filler content.

Table 7.5: Average thickness and weight loss of PVDF coatings after 20 abrasion cycles.

Sample	Filler Concentration (wt. %)	Avg. thickness loss (μm)	Avg. weight loss (mg)
5% PVDF	-	8.23 ± 1.44	7.5 ± 0.8
	1:0.5	10.06 ± 2.37	15.2 ± 1.5
	1:1	12.78 ± 2.91	23.7 ± 1.8
10% PVDF	-	8.54 ± 2.05	6.9 ± 1.4
	1:0.5	10.87 ± 2.19	16.3 ± 1.7
	1:1	13.02 ± 2.55	24.7 ± 2.1

The effect of accelerated abrasion on the hydrophobicity of the coatings is shown in Table 7.6.

Table 7.6: Change in CA, SA and average surface roughness after abrasion.

% PVDF and filler ratio	CA (°)		SA (°)		R _a (μm)	
	Before abrasion	After abrasion	Before abrasion	After abrasion	Before abrasion	After abrasion
5%, no fillers	98 ± 4.62	102 ± 2.84	35 ± 4	-	0.27 ± 0.02	0.58 ± 0.18
5%, 1:0.5	126 ± 3.42	118 ± 3.81	19 ± 5	22-27	1.14 ± 0.15	0.96 ± 0.34
5%, 1:1	155 ± 4.03	146 ± 3.06	< 5	10-13	1.68 ± 0.17	1.27 ± 0.23
10%, no fillers	98 ± 1.78	103 ± 2.10	27 ± 3	-	0.24 ± 0.05	0.49 ± 0.16
10%, 1:0.5	134 ± 2.67	128 ± 2.51	13 ± 2	20-25	1.42 ± 0.23	1.16 ± 0.41
10%, 1:1	159 ± 1.38	152 ± 2.63	< 1	8-13	1.90 ± 0.19	1.36 ± 0.52

The values of CA and SA for the pristine PVDF coatings increase after the abrasion. This is due to the change in R_a from around 0.25 μm to 0.5 μm. but correspondingly, the droplet does not show any rolling or sliding from the surface. This can be the result of the roughness changing the wetting state, as seen in the TEOS-Glymo and TEOS-PDMS systems previously. The topography of the 10% PVDF coating without fillers is shown before and after abrasion in Fig. 7.7 a and b respectively.

The coatings with fillers all show a decrease in CA and increase in SA. This change is reflected from the drop in R_a values during the abrasion process. But the changes are not very significant. This is mainly because bulk of the coating is composed of hydrophobic

PVDF. So, even if some of the surface features formed by the agglomeration of silica are worn away, the hydrophobic property of the PVDF matrix still remains.

Fig. 7.7 Confocal interferometry images of a) 10% PVDF coatings before abrasion, b) 10% PVDF coatings after abrasion, c) 10% PVDF coating with 1:1 PVDF:SiO₂ and d) 10% PVDF coating with 1:1 PVDF:SiO₂.

7.8 Effect of erosion

The coatings were tested for the resistance to erosive wear by using accelerated micro-sand blasting. Only samples pre-treated with APTES were tested as those without surface functionalization tended to delaminate very easily from the substrate. The changes in the coatings CA and SA were measured after the erosion test to study how much of the original functionality was retained.

From the values in Table 7.7 it can be seen that the coatings without any fillers show the lowest weight loss at 5-6 mg. There is also a slight increase in the R_a values of these

coatings which can be attributed to the formation of new surface features during the erosion process. The values of CA, SA and R_a after the erosion process are given in Table 7.8. Fig. 7.8 a and b show the surface topography of the coating without silica fillers before and after the erosion. The coatings with 5 and 10 % PVDF at different loading of SiO_2 show similar performance with the 1:1 coating having the highest weight loss at 22-27 mg. The change in CA and SA corresponding to this is mainly due to the loss in roughness during the erosion which smooths out some of the micro features on the surface. The drop in CA is not very high and the coatings remain highly hydrophobic. Fig. 7.8 c and d show the three dimensional surface topography of the 10 % PVDF coating with 1:1 PVDF: SiO_2 before and after the erosion.

Table 7.7: Average weight loss and change in R_a after sand erosion.

Sample	PVDF: SiO_2	Avg. weight loss (mg)	R_a (μm)	
5 % PVDF	-	5.2 ± 0.7	0.27 ± 0.02	0.42 ± 0.17
	1:0.5	18.1 ± 1.3	1.14 ± 0.15	1.08 ± 0.24
	1:1	23.4 ± 2.8	1.68 ± 0.17	1.52 ± 0.39
10 % PVDF	-	5.9 ± 0.5	0.24 ± 0.05	0.40 ± 0.13
	1:0.5	22.3 ± 1.8	1.42 ± 0.23	1.16 ± 0.11
	1:1	26.7 ± 3.1	1.90 ± 0.19	1.62 ± 0.28

Table 7.8: CA and SA values before and after sand erosion.

Sample	PVDF:SiO ₂	CA (°)		SA (°)	
		before	after	before	after
5 % PVDF	-	98.11 ± 4.62	101.72 ± 2.54	35 ± 4	45-52
	1:0.5	126.79 ± 3.42	118.37 ± 3.19	19 ± 5	15-19
	1:1	155.19 ± 4.03	142.05 ± 4.23	< 5	5-7
10 % PVDF	-	98.55 ± 1.78	101.86 ± 1.97	27 ± 3	33-37
	1:0.5	134.62 ± 2.67	125.70 ± 3.82	13 ± 2	15-17
	1:1	159.16 ± 1.38	150.85 ± 4.13	< 1	3-7

Fig. 7.8: AFM images of coating with 10 % PVDF with a) no silica before erosion; b) after erosion; c) 1:1 PVDF: SiO₂ before erosion and d) 1:1 PVDF: SiO₂ after erosion.

7.9 UV weathering

The PVDF composite coatings were exposed to UV weathering as described previously in section 3.5. The results are tabulated below in Table 7.9. From the values of CA and SA measured after UV exposure, it can be seen that there is not much change in both CA and SA values for the coatings. Reports in literature also show that there is not much degradation observed in PVDF even after extended periods of time [128, 129]. This indicates that the PVDF based coatings are suitable for applications involving prolonged periods of UV exposure.

Table 7.9: CA and SA before and after UV weathering.

%PVDF	Filler content (wt. %)	Contact angle (°)		Sliding angle (°)	
		before	after	before	after
5%	-	98 ± 4.62	98 ± 3.71	35 ± 4	35 ± 4
	1:0.5	126 ± 3.42	124 ± 2.13	19 ± 5	19 ± 5
	1:1	155 ± 4.03	154 ± 3.22	< 5	< 5
10%	-	98 ± 1.78	97 ± 2.10	27 ± 3	27 ± 3
	1:0.5	134 ± 2.67	134 ± 1.54	13 ± 2	13 ± 2
	1:1	159 ± 1.38	158 ± 2.19	< 1	< 1

7.10 Self-cleaning test

The self-cleaning test is performed using artificial dirt composition mentioned in section 3.6. The self-cleaning performance is measured using dirt accumulation and its subsequent cleaning on as coated samples and samples after abrasion. The various values of L, percentage dirt accumulated and extent of cleanliness are tabulated in Table 7.10. The extent of dirt accumulation and self-cleaning performance are plotted in Fig. 7.9 and

7.10. Using this method, we can see that it is the superhydrophobic coating, with 1:1 silica loading; which has the lowest dirt accumulation and highest self-cleaning efficiency at 97.5 %. This is due to the rough surface of the coating and heterogeneous wetting regime resulting in high CA and low SA. The pristine PVDF shows slightly higher accumulation of dirt, but still has very low retention of dirt after being sprayed clean with water. This may be due to the smooth surface of the coating leading to more homogenous wetting. The hydrophobic nature of the PVDF aids in dirt mixture easily running off the surface with the accumulated dirt thus resulting in low dirt accumulation. But there is no significant difference between L_2 and L_3 values of the coating. This indicates that the 3-5% of dirt accumulated on the sample still remains and is not removed on using the water spray. Fig. 7.11 shows images of the 10 % PVDF coatings before and after the dirt spray.

Table 7.10: Lightness values and self-cleaning performance of coatings.

Sample	PVDF:SiO ₂	L ₁	L ₂	L ₃	Dirt accumulated (%)	%cleanliness
Bare glass	-	85.98	43.53	53.45	49.37	62.17
Bare glass after abrasion	-	85.98	18.13	47.54	78.91	55.29
10% PVDF	-	79.91	42.72	71.99	46.53	90.08
10% PVDF after abrasion	-	79.91	39.85	64.91	50.12	81.23
10% PVDF	1:0.5	87.46	81.92	84.32	6.33	96.41
10% PVDF after abrasion	1:0.5	87.46	80.22	82.03	8.27	93.79
10% PVDF	1:1	91.28	88.54	89.07	3.00	97.57

10% PVDF after abrasion	1:1	91.28	86.73	86.82	4.98	95.12
5% PVDF	-	76.52	39.08	68.54	48.92	89.57
5% PVDF after abrasion	-	76.52	37.31	65.96	51.24	86.20
5% PVDF	1:0.5	86.11	80.10	81.03	6.98	94.10
5% PVDF after abrasion	1:0.5	86.11	77.92	78.91	9.51	91.64
5% PVDF	1:1	91.06	86.40	86.81	5.12	95.33
5% PVDF after abrasion	1:1	91.06	85.39	85.46	6.23	93.84

Fig. 7.9: Percent dirt accumulation on 10% PVDF composites before and after abrasion.

Fig. 7.10: Self-cleaning efficiency of 10% PVDF composites before and after abrasion.

Fig. 7.11: Optical images of coatings a) before dirt accumulation of as-coated samples; b) after dirt accumulation. The samples are arranged as (i) bare glass, (ii) 10 % PVDF coating without fillers (iii) 10 % PVDF coating with 1:0.5 PVDF:SiO₂ and (iv) 10 % PVDF coating with 1:1 PVDF:SiO₂.

7.11 Summary

PVDF based composite coatings with FAS-17 and silica particles were prepared. The hydrophobicity of the coatings does not change much on increasing the concentration of PVDF in the coatings. The composites with 10 % PVDF and 1:1 PVDF:SiO₂ by weight show the best hydrophobic functionality. These coatings also have the highest hardness and elastic modulus. The samples also show minimum weight and thickness loss on being subjected to accelerate wear tests. The self-cleaning performance of the coatings is ~95%. The main limitation with respect to these coatings is that they require surface pretreatment with APTES to have good adhesion with the substrates.

Chapter 8 Comparison of various coatings systems

So far, three coating systems have been developed and characterized in detail. One of the main gaps identified in the literature review was that there are no clear insights on which coating properties determine their effectiveness under various specific applications. This chapter will examine such correlation, as well as the field performance of the various coating formulations after being exposed to ambient weather conditions for a period of six months.

8.1 Correlations of physical parameters to self-cleaning performance

In order to determine which physical parameters correlate well with the self-cleaning capacity of the coatings, the values of sliding angle, contact angle hysteresis, apparent surface energy (γ_{sv}), interfacial energy (γ_{sl}), work of adhesion (W_{adh}), and retention force (R) were calculated. The values for each coating system are tabulated in Table 8.1. The solid-liquid interfacial energy is calculated using the Young's equation (2.1), and the work of adhesion (W_{adh}) is the difference between the sum of solid and liquid surface energies and the interfacial energy (i.e., $W_{adh} = \gamma_{LV} + \gamma_{SV} - \gamma_{SL}$) as described in section 2.4. Retention force of the water droplet against the direction of motion on the surface was calculated using the equation proposed by Carre et al. [130]:

$$R = \frac{1}{2}\pi r\gamma_{LV}(\cos\theta_R - \cos\theta_A) \quad (8.1)$$

where r and γ_{LV} represent the radius of the water droplet and the surface tension of water (72.8 mJ/m²), respectively. θ_R and θ_A correspond to the receding and advancing contact angles of the coating measured using the tilting base method.

Table 8.1: Apparent surface energy, interfacial energy, work of adhesion, retention force, CA hysteresis and sliding angle of various coatings and their self-cleaning efficiencies.

Sample	γ_{sv} (mJ/m ²)	γ_{sl} (mJ/m ²)	W_{adh} (mJ/m ²)	Retention force (mN)	ΔCA (°)	SA (°)	% self- cleanliness
Bare glass	250	194.7	128.1	0.45	26	90	63.3
TEOS- Glymo, 15 wt% nanosilica	1.41	71.37	2.83	0.005	3.7	2	95.9
Amine cured, TEOS- Glymo, 15 wt% nanosilica	3.47	67.75	8.57	0.006	4	5	95.12
TEOS:PD MS-70:30,	24.7	42.9	54.6	0.007	2	8	95.2
TEOS:PD MS-70:30, 10 wt% nanosilica	5.41	70.84	2.83	0.006	3.5	2	95.8
10 % PVDF, 1:1 PVDF:SiO ₂	3.52	71.48	4.84	0.005	4	1	97.57

Only the coatings which exhibit high self-cleaning efficiency are listed in Table 8.1. From the measured values of the apparent surface energy for the various coating surfaces (γ_{sv}), it can be seen that the superhydrophobic coatings all have very low values. Only the TEOS:PDMS = 70:30 coating has a value of 24.7 mJ/m², which is expected for a surface with CA ~ 112°.

The interfacial surface energy (γ_{sl}) and work of adhesion (W_{adh}) values do not reconcile to a trend which is reflective of the self-cleaning performance of the coatings.

The retention force, as calculated from eqn. 8.1, is a function of the advancing and receding contact angles of the coatings. When calculated for a droplet of volume 5 μL (volume at which SA and θ_A and θ_R were measured) for all the coatings, the values were within a standard deviation of 0.001mN/m. The values of ΔCA and the retention force correlate well with observed self-cleaning efficiencies of the coatings. It should be noted that the difference between the advancing and receding CAs (CA hysteresis, which represents the dynamic nature of the droplet) has a direct impact on the value of retention force as described in equation 8.1. Therefore, it can be concluded that the retention force is the parameter that gives the best correlation between the physical properties and the self-cleaning performance of the coatings.

8.2 Motion of droplets on hydrophobic and superhydrophobic surfaces

As discussed in chapter 2, the water droplets can either roll or slide down a surface. Several independent studies have established that the type of droplet motion depends on the wettability of the surface [45, 46, 53, 130]. All droplets have a rolling action taking place in the bulk of the liquid even if the droplet as a whole slides. Thampi, Adhikari and Govindarajan were successful in proposing a two-dimensional simulation of the representative motion of droplets on an inclined surface [131]. It is proved that the deviation of a droplet from a completely spherical shape plays an important role in determining the dynamics of the system. In two dimensions, an isoperimetric parameter ‘q’ is used to define how close a particular shape is being circular ($q=1$).

$$q = 4\pi \times \text{Area} / (\text{perimeter})^2 \quad (8.2)$$

$q < 1$ for all cases, except a circle as a circle always has the least perimeter for a given area. Based on this it is possible to determine what fraction of movement in the droplet is caused by rolling and sliding.

Here, the shape factor q can be redefined as approximately equal to $A/(h+w)^2$, where A is the area of contact of the droplet and h and w are the height and length of the droplet. Based on this the percentage of rolling motion in a droplet can be estimated as $(q)^{1/2}$. Therefore, as applied to the three coating systems in this case, the fraction of rolling motion in the droplets is as follows:

Table 8.2: Fraction of rolling action in motion of water droplets at SA.

Sample	A (mm ²)	h (mm)	w (mm)	q	%R
TEOS-Glymo, 15 wt% nanosilica	0.50	2.01	0.27	0.92	95.9
Amine cured, TEOS-Glymo, 15 wt% nanosilica	0.67	1.76	0.46	0.82	90.55
TEOS:PDMS-70:30,	2.77	1.31	3.35	0.63	79.37
TEOS:PDMS-70:30, 10 wt% nanosilica	0.79	1.79	0.43	0.89	94.34
10 % PVDF, 1:1 PVDF:SiO ₂	0.95	1.82	0.58	0.90	94.86

From the values mentioned in Table 8.2, it is clear that droplets that have a more spherical shape have a higher percentage of rolling action, which is why it is easier to observe.

Therefore, it can be clearly established that the shape of a droplet determined by its apparent CA is what determines whether a droplet rolls or slides down a surface.

8.3 Self-cleaning performance of the coatings

The coatings with the best self-cleaning performance in the laboratory tests were left exposed to ambient outdoor weather conditions for a period of six months from January to June 2015. The average temperature, rainfall and number of rain days for the duration of the test are shown in Fig. 8.1a, b and c respectively.

Fig. 8.1 a) Average temperatures, b) average precipitation and c) average number of rainy days in Singapore from January – June 2015.

The samples were evaluated on a regular basis to test for extent of dirt accumulation. Fig. 8.2 shows the images of the samples just before the six month exposure period.

Day 1

Fig. 8.2 Samples before outdoor exposure. From left to right: bare glass, TEOS-Glymo-FAS with 15 wt% 10-20 nm silica, EDA cured TEOS-Glymo-FAS with 15 wt% 10-20 nm silica, TEOS:PDMS = 70:30 w/o silica filler and 10 % PVDF with 1:1 PVDF:SiO₂.

The samples were photographed after one month intervals to evaluate their performance. The sequence of photographs with time is shown in Fig. 8.3. The values of CA and SA on each of the exposed samples were also measured periodically. These values are tabulated in Table 8.3.

Fig. 8.3 Samples left exposed to outdoor environment for different periods of time. From left to right: bare glass, TEOS-Glymo-FAS with 15 wt% 10-20 nm silica, EDA cured TEOS-Glymo-FAS with 15 wt% 10-20 nm silica, TEOS:PDMS = 70:30 w/o silica filler and 10 % PVDF with 1:1 PVDF:SiO₂.

From the values in Table 8.3 we can see that all the coated samples show a decrease in CA and increase in SA. The CA of the bare glass ($45 \pm 1.2^\circ$) does not change significantly. Superhydrophobic samples with high CA initially start showing a gradual decrease from the time second week (average drop in CA for superhydrophobic coatings after 6 months = 15.7°) of exposure whereas the hydrophobic TEOS-PDMS sample shows a much slower decline (average drop in CA for hydrophobic coating after 6 months = 4°).

Similarly, the SA increases for all the samples but the change is much narrower than those seen in the CA. Physical inspection of the samples reveals that the superhydrophobic TEOS-Glymo-FAS sample with 15 wt% nanosilica (initial CA 164°) shows removal of coatings around the lower right edge. The previous study on the mechanical properties of this coating in Chapter 4 agrees with this observation. The amine cured coating with the same composition appears intact showing improvement in the mechanical properties.

The TEOS:PDMS = 70:30 and 10% PVDF coating also appear to show no physical damage to the coatings.

Fig. 8.4 shows the exposed samples after 6 months on a white background for easier visual evaluation.

Fig. 8.4 Exposed samples on a white background after 6 months. From left to right: bare glass, TEOS-Glymo-FAS with 15 wt% 10-20 nm silica, EDA cured TEOS-Glymo-FAS with 15 wt% 10-20 nm silica, TEOS:PDMS = 70:30 w/o silica filler and 10 % PVDF with 1:1 PVDF:SiO₂.

Table 8.3: Change in CA and SA of the exposed samples over a six month period.

Period of exposure	TEOS-Glymo-FAS, 15 wt% nanosilica		TEOS-Glymo-FAS, 15 wt% nanosilica with EDA		TEOS:PDMS = 70:30, w/o fillers		10% PVDF with 1:1 PVDF:Silica	
	CA (°)	SA (°)	CA (°)	SA (°)	CA (°)	SA (°)	CA (°)	SA (°)
Nil	164 ± 3.9	< 2	152 ± 3.1	< 5	112 ± 1.6	7-8	159 ± 1.4	< 1
Day 1	164 ± 3.0	< 2	152 ± 4.0	< 5	112 ± 1.2	7-8	159 ± 1.7	< 1
Week 2	163 ± 1.4	< 2	152 ± 1.2	< 5	112 ± 1.4	7-8	158 ± 1.2	< 1
Week 4	160 ± 3.6	2-3	152 ± 1.2	< 5	112 ± 2.1	7-8	158 ± 2.6	< 1
Week 6	159 ± 2.4	2-3	151 ± 3.6	< 5	111 ± 1.7	7-8	157 ± 1.9	< 3
Week 8	157 ± 0.9	2-3	150 ± 2.9	< 7	111 ± 1.1	7-8	157 ± 1.5	< 3
Week 10	156 ± 2.7	2-4	149 ± 1.1	< 7	111 ± 1.6	8	155 ± 2.0	< 3
Week 12	152 ± 5.1	2-4	148 ± 1.6	< 7	110 ± 0.9	8	152 ± 3.1	< 4
Week 14	150 ± 2.2	3-5	148 ± 1.7	< 7	110 ± 1.5	8-9	150 ± 1.6	< 4
Week 16	149 ± 3.8	< 5	148 ± 2.2	< 7	110 ± 1.3	8-9	149 ± 2.4	5-6
Week 18	145 ± 2.0	< 5	147 ± 1.8	< 8	109 ± 3.1	< 10	148 ± 2.7	5-6
Week 20	144 ± 1.8	< 5	147 ± 3.1	< 8	109 ± 2.4	< 10	145 ± 3.4	5-6
Week 22	142 ± 3.6	< 5	146 ± 2.3	< 8	109 ± 2.2	< 10	144 ± 4.3	5-7
Week 24	140 ± 5.7	< 5	146 ± 1.5	< 8	108 ± 3.2	< 10	142 ± 5.8	5-7

The L values of the coatings before and after the outdoor field test are reported in Table 8.4. The extent of dirt accumulation is calculated based on these values.

Table 8.4: Extent of dirt accumulation after 6 month field test.

Sample	L ₁ (before field test)	L ₂ (after 6 months)	% dirt accumulation
Bare glass	85.98	58.17	32.34
TEOS-Glymo, 15 wt% nanosilica	95.35	85.10	10.75
Amine cured, TEOS-Glymo, 15 wt% nanosilica	89.63	82.06	8.45
TEOS:PDMS- 70:30,	76.18	74.92	1.65
10 % PVDF, 1:1 PVDF:SiO ₂	91.28	89.31	2.16

From Table 8.4 it can be seen that the bare glass and all the superhydrophobic samples show dirt accumulation similar to those seen in the laboratory tests (sections 4.10, 5.10 and 7.10). The exception is the TEOS:PDMS = 70:30 sample showing much lower dirt retention than that observed previously under section 6.10. The reason for the lower dirt accumulation on these samples can be attributed to the comparatively low R_a ($0.16 \mu\text{m}$) of these coatings when compared to the superhydrophobic samples (avg. R_a for superhydrophobic samples = $2.73 \mu\text{m}$). The high roughness on the samples with CA > 150° leads to accumulation of foreign particles in the grooves and surface features making it difficult to be removed with the action of water.

From this, it can be concluded that superhydrophobicity may not necessarily lead to the most effective self-cleaning performance in real-time applications. Hydrophobic coatings

with a combination of low CA hysteresis and moderately low surface energy may prove to function more effectively in the long run.

8.4 Summary

The effect of various physical parameters such as apparent surface energy, work of adhesion, CA hysteresis, SA and retention force were studied on all the coated samples. It was concluded that the CA hysteresis and therefore the retention force had the best correlation with the observed self-cleaning performances. Further, the apparent shape of the droplet determined by the CA controls the rolling vs. sliding motion of the droplets.

Outdoor field tests carried out on the samples indicate that though the superhydrophobic coatings show dirt retention similar to the observed experimental values, the TEOS-PDMS coating with dynamic hydrophobicity shows the least CA degradation after the prolonged test period. This indicates that hydrophobic surfaces with low CA hysteresis and moderately low surface energy could also display good self-cleaning performance under outdoor conditions making them very suitable for large scale applications.

Chapter 9 Conclusions and recommendations

This thesis focused on the study of three different coating systems for self-cleaning applications on large scale structures. Sol-gel based hybrid composite systems were studied. TEOS-Glymo based sol-gel systems were prepared with and without amine curing by EDA. It was found that addition of particulate fillers decreases the mechanical properties like hardness and Young's modulus. It further leads to increased weight and thickness loss in coatings under accelerated erosive and abrasive wear. Amine curing of the sol helps improve the hardness and modulus of the coatings significantly. Further, the damage experienced by coatings under accelerated wear conditions is much lower. The self-cleaning performance of the superhydrophobic coatings produced using this system is close to 95 %.

Another TEOS based system was studied. The co-precursor in this case was PDMS. The coatings with TEOS:PDMS = 70:30 by weight produced coatings with low SA despite having CA $\sim 112^\circ$. This coating further shows better mechanical performance when compared to the TEOS-Glymo system (without amine curing). The self-cleaning performance of the coating is also high, indicating that self-cleaning performance does not depend on the extent of superhydrophobicity in a system.

The third system studied was a PVDF composite with silica fillers. These coatings have the best mechanical properties of all the systems studied and exhibit a self-cleaning efficiency of 97%. The effect of abrasive, erosive and UV weathering on the coatings is also not very significant.

This study also showed that it is the retention factor of the droplet on the surface which has a direct correlation with the self-cleaning performance. Further, it is shown that it is the advancing and receding CA's which determine whether a surface can be effectively self-cleaning as illustrated in the TEOS-PDMS system studied.

9.1 Novel contributions from this thesis

Based on the studies carried out, the technological and scientific contributions from this work are summarized below:

9.1.1 Technological contributions

- Mechanically robust self-cleaning coatings have been produced using three different component systems. They can be coated by spraying, which is convenient for large scale structures with complex shapes.
- Optimization of particle size of the fillers to produce hierarchical structures to improve coating functionality.
- Investigating the effect of abrasion, erosion and UV weathering and using their effect on the physical properties of the coatings to study coating performance.
- Improved the adhesion of PVDF based composite coatings by using pretreatment with APTES.
- Evaluation of self-cleaning efficiency of coatings using simple spectrophotometric studies.

9.1.2 Scientific contributions

- Demonstrated that superhydrophobicity is not a prerequisite to achieve good self-cleaning functionality in coatings. Hydrophobic coatings can be equally effective.

- Demonstrated that advancing and receding contact angles, along with the retention force, which is a function of the dynamic contact angles, determine how effective a hydrophobic/superhydrophobic coating can be in self-cleaning applications.

9.2 Recommendations for future work

9.2.1 Studies on combining other functionalities with superhydrophobicity

Self-cleaning coatings and surfaces are only a small area in which superhydrophobic surfaces can be applied. Combining transparency with superhydrophobic functionality has a wide range of potential applications. Using particulate fillers decreases the extent of transparency that can be achieved. By controlling the surface features and the particle size of the fillers used, it is possible to combine transparency with superhydrophobicity [17, 54].

Superhydrophobic sprays suitable for cloth and fabric are being studied with great interest. Fluorinated materials like PVDF and FAS are not suitable for these applications. Further, the aesthetic appeal of the fabric is lost on being treated with existing superhydrophobic coatings. This can be achieved by using elastomers like PDMS long chain acids like myristic acid that are more suitable for application on cloth to make them stain resistant and easy to clean [63].

9.2.2 Hydrodynamic studies on droplet motion on superhydrophobic surfaces

In this thesis, an empirical correlation between the physical parameters and self-cleaning performance is given. By studying the droplet motion on a wide range of surfaces, it is possible to determine how the droplet interaction changes on each representative surface.

This can give insight into how the droplet behavior on a surface can be manipulated to achieve the best functionalities required [130, 131].

10. References

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List of Conference Presentations and Publications

- Divya Kumar, Jeffrey Ho, Pencheng Ye, Zhong Chen, Effect of Functional Additives on Hybrid Hydrophobic Coatings, 7th International Conference on Materials for Advanced Technologies, 2013, Singapore.
- Divya Kumar, Zhong Chen, Dynamically Hydrophobic Coatings for self-cleaning applications, 10th Coatings Science International 2014, Noordwijk, The Netherlands.
- Divya Kumar, Lin Li, Zhong Chen, Development of durable, water-resistant and self-cleaning coatings based on polyvinylidene fluoride composites for sports applications, 1st International Conference in Sports Science and Technology, 2014, Singapore.
- Divya Kumar, Xinghua Wu, Qitao Fu, Jeffrey Weng Chye Ho, Pushkar D. Kanhere, Lin Li, Zhong Chen, Development of sol-gel coatings for self-cleaning applications, *Applied Surface Science*, 2015, Vol. 344, pp. 205-212
- Divya Kumar, Xinghua Wu, Qitao Fu, Jeffrey Weng Chye Ho, Pushkar D. Kanhere, Lin Li, Zhong Chen, Hydrophobic sol-gel coatings based on polydimethylsiloxane for self-cleaning applications, Under review (*Materials and Design*).
- Divya Kumar, Lin Li, Zhong Chen, Mechanically robust PVdF based superhydrophobic coatings for self-cleaning applications, Under review (*Journal of Materials Chemistry A*).