Investigating the Interplay between Wetting and Droplet Friction

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Abstract

This research project studies the various factors which primarily affect the droplet motion on a tilted surface and explores different surface modification techniques which can be done to tune its wetting behavior. We explore various models used to characterize the extent of wetting and understand their applicability. We also determine the conditions within which the sample shows the best performance and its extent of durability by subjecting it to various tests simulating its practical applications and comparing our results.

Introduction

Droplet motion on a solid surface plays an important role in various phenomena including printing, self-cleaning, and heat transfer. An in-depth understanding of the wetting behaviour and other such properties proves critical to reduce the effort to remove particles and impurities from such surfaces, vis-a-vis a '*Self Cleaning Property*'. Our project also does explore different surface modification techniques which can be used to tune certain mechanical properties of the metallic substrate. The inspiration to study this type of droplet motion is actually derived from nature, where we try to mimic the 'Lotus Effect', a self-cleaning property exhibited in the leaves of the lotus flower which are a result of surface wetting and superhydrophobicity. We define wetting as the ability of a liquid to maintain contact with a solid surface, resulting from intermolecular interactions when the two are brought together. The degree of wetting (wettability) is determined by a force balance between adhesive and cohesive forces.

Due to the nanoscopic construction of the surface of the leaves which minimizes adhesion causing the droplet to roll off, dirt and dust particles are also collected within the water droplets, hence causing the self-cleaning property. The high surface tension of water (~72.4 mN/m) causes the droplets to assume a near spherical shape which happens to geometrically have the lowest surface area, resulting in a minimal surface energy between the droplet and the surface. The nano-architecture of the lotus surface has a hierarchical characteristic double structure, similar to nanopillars, along with wax which covers the entire surface, which directly results in the superhydrophobic property of the surface. The self cleaning property occurs as the adhesion between the dust particle and the water droplet as it rolls is much more than between the

particle and the surface. We try to replicate this phenomenon in the laboratory by creating nanopillars on our chosen substrate and then adding an organic coating to generate Self-Assembled Monolayers (SAM) which eventually impart hydrophobicity/superhydrophobicity to our sample and then perform various tests on the substrate. Superhydrophobicity and wettability of a surface can be quantified by measuring the contact angle. The contact angle is the angle, conventionally measured through the liquid, where a liquid–vapor interface meets a solid surface. The angle formed between the liquid–solid interface and the liquid–vapor interface is the contact angle. Surfaces with a contact angle less that 90° are termed as 'Hydrophilic Surfaces' while those with more than 90° are termed as 'Hydrophobic Surfaces'. Surfaces with a contact angle more than 150° are specially categorized as 'Superhydrophobic Surfaces'. A given system of solid, liquid, and vapor at a given temperature and pressure has a unique equilibrium contact angle. However, in practice a dynamic phenomenon of contact angle hysteresis is often observed, ranging from the advancing (maximal) contact angle to the receding (minimal) contact angle. The advancing contact angle can be described as a measure of the liquid-solid cohesion while the receding contact angle is a measure of liquid-solid adhesion.

The scope of our work has applications across domains and proves critical in for example designing nuclear power plants to self cleaning surfaces in clean-rooms. The main application that our work has is in the field of aeronautical and aerospace engineering, precisely the design of aircraft fuselage for various types of flight. An aircraft wing is essentially a type of fin which produces lift while traveling at very high velocity. Aircraft wings are subject to very extreme environments during operation, experiencing extreme stresses, especially thermal stresses generated due to the range of operation of almost +50°C to -50°C which affects the performance, durability and operating life of the wing. Aircrafts also operate in various environments, exposed to various contaminants such as residue from aircraft emissions, particulate matter, and other volatile and semi volatile organic compounds which may settle on the aircraft wing or fuselage. Not taking such factors into consideration can result in major safety hazards during operation which may ultimately result in failure during operation or loss of life. A specific aspect we look at in our work is condensation on the wing tip. Although this is a very common occurrence on aircrafts today, we try to minimize condensation as due to the extremely rapid change from 24°C (average ground temperature) to around -30°C before and after takeoff within a very short timespan, there exists a major ever present risk of the water

vapor subliming to form ice on the wing tip (termed as 'Ice Accretion' or 'Airframe Icing'). This ice may lead to the aircraft stalling which has resulted in numerous accidents in aviation history. Although flight under frigid conditions is possible, several methods exist to try and minimize icing such as using de-icing fluid, bleeding air through the engine in-flight etc. With the application of our work we try to tackle this problem in the design stage itself by tuning the material properties to ensure droplets rolloff the surface entirely clean.

Experimental Details

Materials Used

Our work initially started with an in depth study of various existing equations which model the behavior of droplets on inclined surfaces and the factors which govern them by observing various parameters. We then gather our experimental data to test the accuracy of these equations by initially preparing our substrates and then subjecting them to various tests. Our chosen sample material is AA5083, an Aluminium alloy (92%) with Magnesium (4%) and trace amounts of Manganese, Copper, Chromium, Iron and Silicon, chosen due to its potential applications in various industries especially the maritime industry. AA5083 exhibits superior performance at temperatures between 10 and 65 degrees celsius and is also highly resistant to attack by sea water and industrial Chemicals it also has its exceptional strength after welding and the has the highest strength amongst untreated alloys.

Synthesis

Our substrate preparation involved first machining commercially available Aluminium 5083 grade plates to dimensions of 10 x 10 x 5 mm sample, further polished using Abrasive Polishing sheets of different grades (80, 220, 400, 600, 800, 1000) (manufacturer: 3M). We then performed ultrasonication on our samples present in a Deionized (DI) water bath to get rid of any dust and debris for 10 mins at 35°C and followed that with Hot Water Treatment (HWT) of our sample mounted and submerged in DI water, for 10 mins at 450W and 800W for the preparation of two categories of samples to compare the microstructure. Following thermal drying for 60 mins on a hot plate set at 65°C, we coated the sample with a silanization agent triethoxy-1H,1H,2H,2H tridecafluoro-n-octylsilane (FOTES; 97%; T.C.I. Ltd, Japan), with a molecular weight of 510.37

g/mol, which was used to impart low surface energy to our samples.This was done through a vapor deposition process in an oven for 90 min set at 150°C, with a vacuum pressure of 400 mm Hg created prior to heating. All processes were carried out under highly sterile conditions and Acetone (99.9%) was used primarily as our cleaning agent during processing. As shown below in Fig 01, we see the difference in the static contact angles of the water droplet on the AA5083 substrate during various stages of processing. The as-cast sample displays hydrophobicity with a contact angle of 85°, however after processing and hot-water treatment at 800W, we note that the sample displays hydrophilicity with the contact angle drastically reducing to 5°. On further coating with the silanization agent, we see the sample displaying superhydrophobicity with the contact angle of around 160°. This indicates how with simple processing techniques, we are able to drastically tune the wetting properties of a substrate to match its desired application.

Fig 01: Comparison of the contact angle of the water droplet on the substrate as-cast (left), after HWT at 800W (centre) and after the FOTES coating (right)

Surface Characterization

The surface morphology of the processed and unprocessed samples were characterized and compared using a field emission scanning electron microscope (FESEM). The mapped surfaces are shown and compared in Fig 02. We used a scan size of at least 1.1 × 1.8 mm^2 for each scan having scanned a minimum of three random locations for each sample and average values were reported. We performed our wetting studies by measuring static and dynamic contact angles using a goniometer through the sessile droplet method. All measurements were performed using a 10ml DI water droplet under ambient conditions (24 ± 2°C and relative humidity of around 35%) unless mentioned otherwise. To understand the dynamic wetting behavior of the droplet on our prepared substrate, the liquid was pumped at a rate of 0.1 m/s with the tilting stage speed set to 8°/min. The energy dispersive X-ray analysis (EDAX) report has also been generated to understand the exact chemical composition of the sample (Fig 03). The

superhydrophobicity of the substrate was measured under varying conditions, controlling for various parameters and measuring both static and dynamic contact angles. We measured the variation of the tilt angle of the substrate at various temperatures (+60°C to -5°C), on exposure to liquids of different surface tensions (72 mN/m to 28 mN/m) and lastly under various contamination concentrations to observe the changes in tilt angles. The range of testing conditions we used matches the maximum applicable operating conditions and environment.

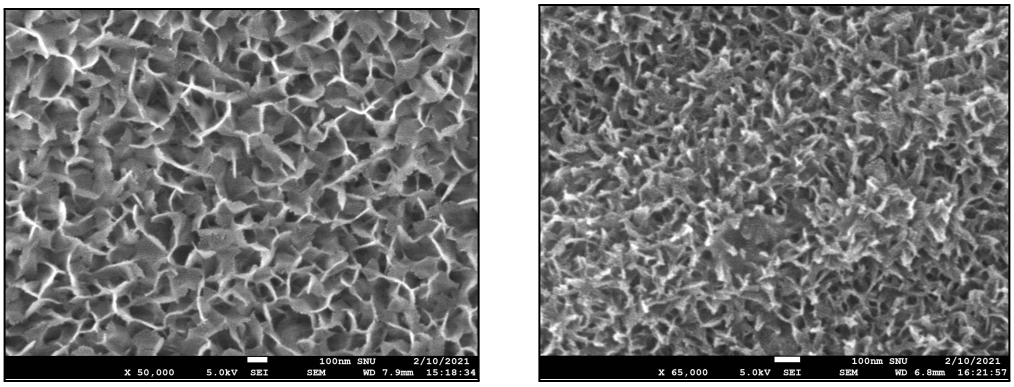
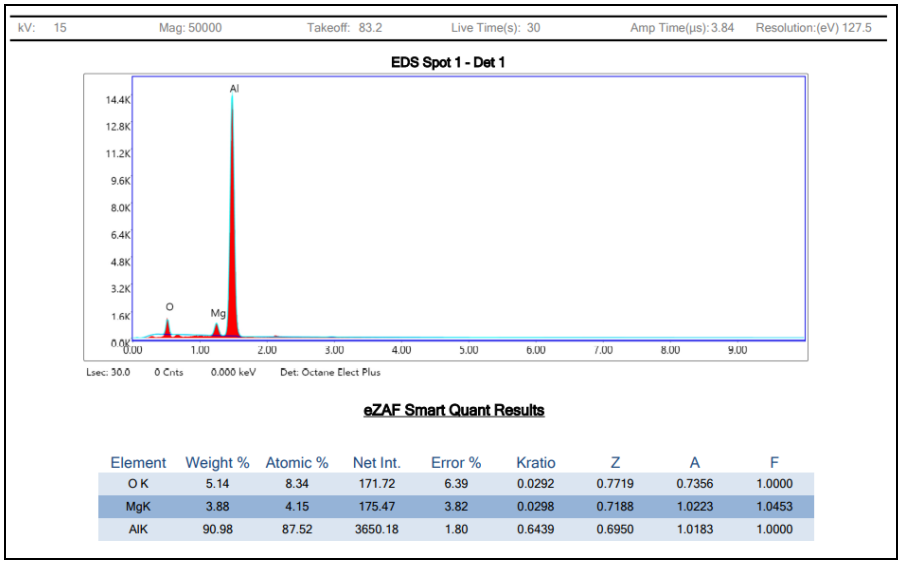


Fig 02: FESEM scan images of the 450W (left) and 800W (right) synthesized sample depicting the presence of nanostructures.



Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	A	F
O K	5.14	8.34	171.72	6.39	0.0292	0.7719	0.7356	1.0000
MgK	3.88	4.15	175.47	3.82	0.0298	0.7188	1.0223	1.0453
AlK	90.98	87.52	3650.18	1.80	0.6439	0.6950	1.0183	1.0000

Fig 03: eDAX results of the synthesized samples depicting it's composition

With this data, we are able to test and understand the durability of our substrate under different conditions and also compare the accuracy of the previously gathered equations under study by comparing the predicted values obtained with the data and experimentally determined values of

tilt angles and observing the differences. With our work, we were also able to comparatively study how differently processed samples perform under different sets of tests. The hot-water treatment stage was done at two different power settings for different sets of samples, 450W and 800W, and then subjected to the same sets of tests. We were also able to understand the difference in nanostructure generated and how they affect the wetting properties of the substrate.

Experimental Results and Discussions

Temperature Tests

The samples performance and wetting state durability at various substrate temperatures was measured using the tilt angle goniometer. The platform tilt rate was set to 8°/min and an electrical heating jacket and cooling plates were used to achieve platform temperatures above and below room temperature respectively. The temperature of the cooling plate was maintained using a continuously circulated mixture of Ethanol and DI water. The substrate surface temperature was measured using an Infrared Temperature sensor prior to each measurement and corresponding values of the static and dynamic tilt angles were noted as listed below.

Sample Specifications	Substrate Surface Temperature (°C)	Platform Tilt Rate (°/min)	Advancing Angle (°)	Receding Angle (°)	Tilt Angle (°)
800W	-2	8	-	-	**>90**
800W	0	8	-	-	**>90**
800W	10	8	-	-	**>90**
800W	15	8	152	150	**40**
800W	17	8	154	151	**35**
800W	20	8	154	152	**26**
800W	25	8	161	159	**5**
800W	40	8	160	158	**5**
800W	50	8	158	155	**12**
800W	60	25	156	153	**15**
450W	-2	8	-	-	**>90**
450W	0	8	-	-	**>90**
450W	10	8	-	-	**>90**

450W	15	8	150	147	**50**
450W	17	8	152	148	**47**
450W	20	8	154	150	**37**
450W	25	8	159	157	**6**
450W	40	8	158	155	**7**
450W	50	8	156	153	**11**
450W	60	25	154	151	**35**

One of the challenges that we also faced was that at elevated temperatures, due to the difference between the substrate surface temperature and the atmospheric temperature, condensation occurred on the surface of the substrate. However AA5083 is generally used where operating temperatures are between -10°C and 60°C and having tested the sample at these extreme temperatures we are confident with our results. At elevated temperatures, an increased evaporation rate is observed, hence the platform tilt rate was also increased from 8°/min to 25°/min to accurately calculate tilt angles. At lower temperatures, due to increase in adhesion between the droplet and the substrate surface again made it hard for us to understand performance of the substrate at sub zero temperatures.

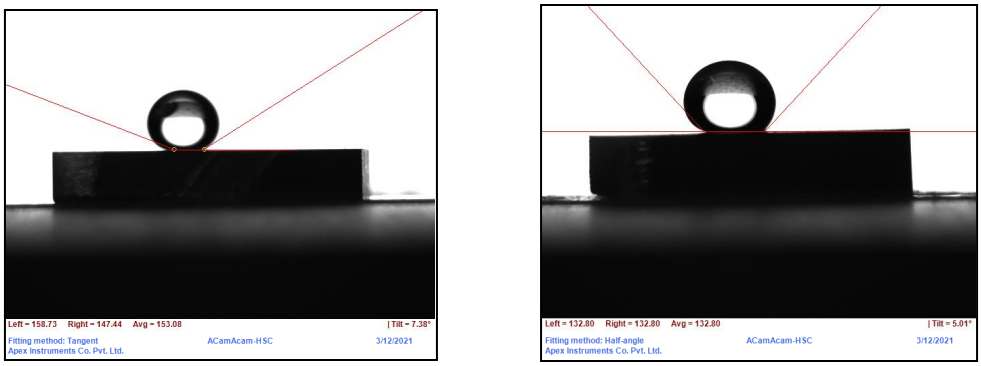


Fig 04: Tilt Angles observed during temperature test of the 450W (left) and 800W (right) samples at 40°C

Surface Tension Tests

The sample's performance and wetting state durability under exposure to liquids of various surface tensions was measured using the tilt angle goniometer. The platform tilt rate was set to 8°/min and all tests were performed under STP conditions. The liquids used in testing were prepared using varying molar proportions of Ethanol (C_2H_5OH) and distilled, deionized water.

The Ethanol used was of nominal purity (>99%) and the solutions were prepared by weight with deviations of less than 0.3% from the desired concentrations. The surface tension of the prepared liquids were also initially measured, using a Tensiometer which operated on the Wilhelmy Plate Principle, under STP conditions. The results of the various tests have been listed below.

Sample Specifications	Liquid	Liquid-Substrate Surface Tension (mN/m)	Static Contact Angle (°)	Tilt Angle (°)
800W	DI Water	72	158	5
800W	Ethanol and DI Water (5% w/w)	55	156	11
800W	Ethanol and DI Water (10% w/w)	47	145	>90
800W	Ethanol and DI Water (30% w/w)	33	137	>90
800W	Ethanol and DI Water (50% w/w)	28	130	>90
450W	DI Water	72	155	6
450W	Ethanol and DI Water (5% w/w)	55	151	30
450W	Ethanol and DI Water (10% w/w)	47	132	>90
450W	Ethanol and DI Water (30% w/w)	33	119	>90
450W	Ethanol and DI Water (50% w/w)	28	115	>90

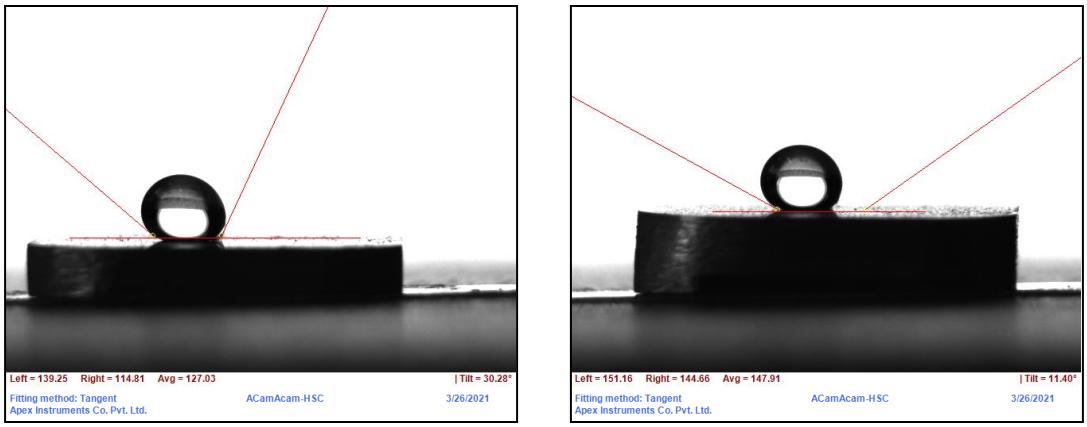


Fig 05: Tilt Angles observed during Surface Tension tests of the 450W (left) and 800W (right) samples with a liquid of surface tension 55 mN/m

Contamination Tests

We performed contamination tests to lastly test the durability of our samples under extreme operating conditions. Our setup consisted of an enclosed contamination chamber within which a pressurised nozzle inline with the lateral centre of the chamber, for compressed air along with a provision for sand to flow through from an external container. In the contamination chamber, our samples were secured together 4 inches away from the line of action of the pressurized air-sand gun and at an elevation of 2 inches from the base of the platform to prevent direct deposition of the sand on the surface of the substrate. Compressed air at a pressure of 0.5 bar was first allowed to flow and then fine sand (of particle diameter ~0.5 mm) was dispersed into the chamber. The samples were then left exposed within the setup untouched for a certain amount of time while the dispersed sand settled. The experiment was performed for various contamination concentrations and the subsequent tilt angles were measured using a goniometer, the results are listed as below.

Sample	Amount of Sand	Exposure Time	**Tilt Angle (°)**
800W	5 g	10 min	**3**
800W	15 g	10 min	**3**
800W	30 g	10 min	**3**
450W	5 g	10 min	**7**
450W	15 g	10 min	**12**
450W	30 g	10 min	**9**

The surfaces of the substrates were also photographed and compared before and after the contamination under an Optical Microscope under a 10x magnification. As shown, we were also able to note the contamination density of the contaminant on the surface substrate and can use these estimates in our further analysis.

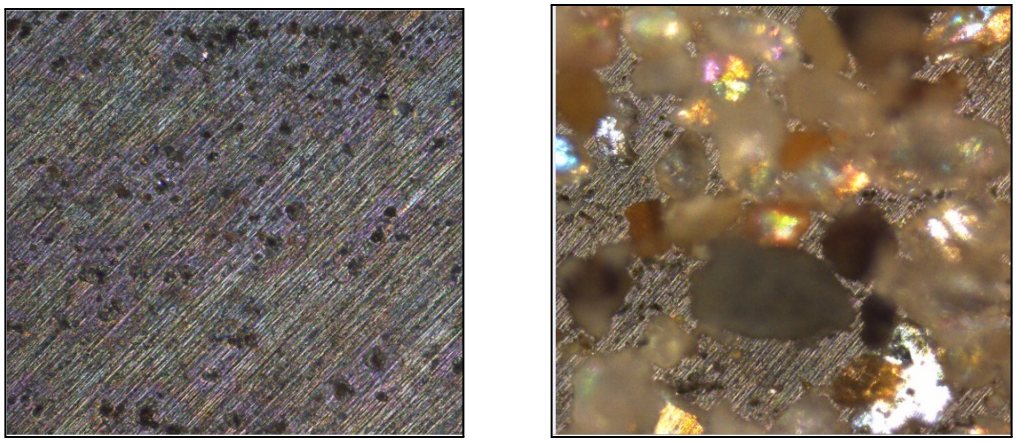


Fig 06: Comparative view of the synthesized 800 W sample before (left) and after (right) contamination as viewed under an optical microscope.

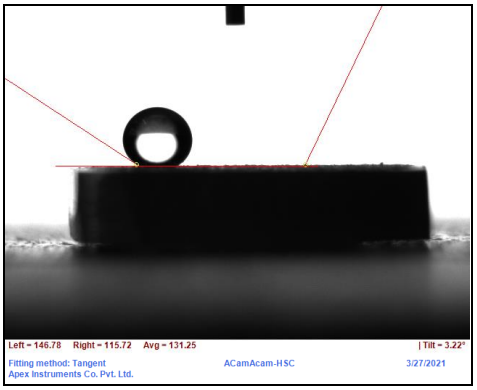


Fig 07: Tilt Angle observed after contamination testing of the 800W samples

Results & Discussion

We were able to understand the relationship and variation trends of the characteristic static and dynamic angles of our substrate with changes in temperature, contamination levels and liquid exposure with different surface tensions. With this, we are able to theoretically predict how variations in any of the above parameters will affect the contact angles of the substrate and can also determine the optimum operating conditions for the substrate.

For variations in temperature, we observe a linear increase in tilt angle as we go above and below room temperature, reaching a maximum at -5°C and +60°C before encountering experimental difficulties in accurately recording the angles due to increased adhesion below temperature and elevated evaporation rates and rapid coating wear above room temperature. Tilt angles are at a minimum (indicating superhydrophobicity) at temperatures between 20°C

and 35°C indicating this to be the optimal operating condition for best performance. This trend is valid for both 450W and 800W samples however to different extents as indicated below.

For the Surface Tension tests, we notice a non-linear decrease as we use liquids of increasing surface tension, implying that superhydrophobicity is maximally displayed with liquids of higher surface tension (above 72 mN/m).

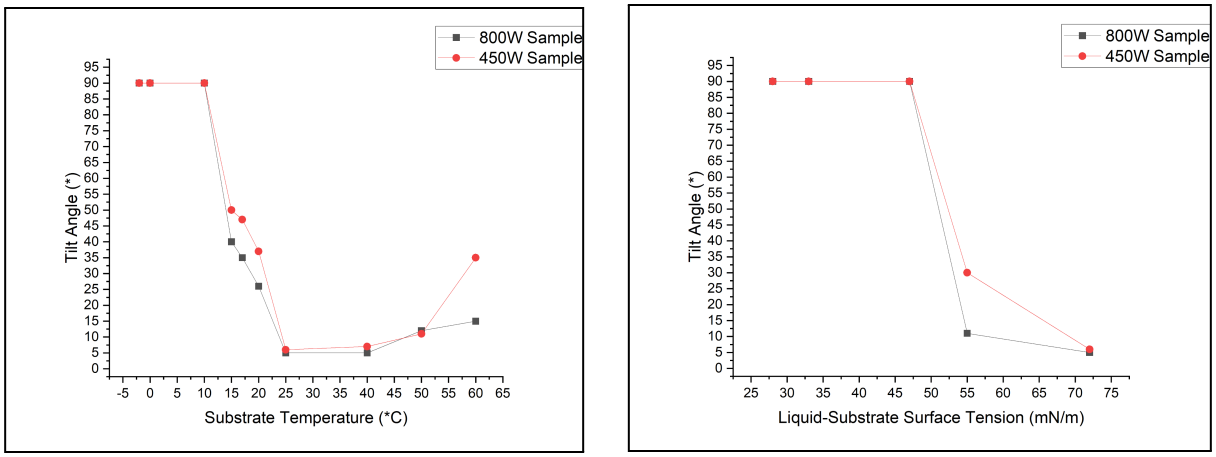


Fig 08: Graphical representation of the trends observed during Temperature Tests (left) and Surface Tension Tests (right).

Lastly, for the set of contamination tests performed, we were able to compare the surface contamination density levels of the samples and understand the variation in tilt angles. We see a relatively linear relationship between the tilt angles and contamination density, with a point to note that very less adhesion exists between the contaminant and the surface of the substrate. Hence during tilting, the contaminants do not offer much impedance to the motion of the droplet when the tilt angle is relatively high, but from our experimental data we see that with angles as low as 3° we see the roll off happening.

Theoretical Work

Apart from exploring the phenomenon of Wetting, one of the most difficult parts in this field was quantifying and characterizing the relationship between various factors and the extent of wetting which happens. Although using a mechanistic approach, one can theoretically determine the contact angle, we realised that practically the estimation of the interfacial tension and determining the geometry of the water droplet was the most difficult part in modelling the equation. Several different papers estimate the shape of the droplet as pendant shape, spherical or hemispherical leading to variations in the resulting values. Additionally, we couldn't find a model which directly accounts for additional factors which come into play during the sample preparation. We tried exploring different ways to tackle this problem.

After an extensive literature review, we found the following seven prominent, theoretically validated equations from various sources which model droplet wetting behaviour. These droplet-motion equations proposed by various researchers in the literature models the Tilt Angle as a function of various parameters such as droplet density, acceleration due to gravity, droplet volume, pinning parameter, texture parameter, advancing and receding contact angles, surface tension, and Bond number.

$$Eqn\ 1:\ \rho.g.V.\sin\alpha = \pi.\gamma_l.r.\left(\cos\theta_r - \cos\theta_a\right)$$

$$Eqn\ 2:\ \rho.g.V.\sin\alpha = \mu.\beta.2\pi r \ where\ \beta = \grave{}\ \frac{1}{1+\left(\frac{b}{a}\right)}$$

$$Eqn\ 3:\ \sin(\alpha) = \frac{2.\pi.\mu.\beta}{\rho.g}.\left(\frac{3}{\pi.V^2}\right).f(\theta)\ \ where\ f(\theta) = \frac{\sin\theta}{\left(2-3.\cos\theta+\cos^2\theta\right)^{\frac{1}{3}}}$$

$$Eqn\ 4:\ \rho.g.V.\sin\alpha = \frac{\pi.\gamma_l.r}{2}\left(\cos\theta_r - \cos\theta_a\right)$$

$$Eqn\ 5:\ \frac{\theta_r}{\theta_a} = 1 - 0.303\beta_o \ where\ \beta_o = \frac{\rho.g.D^2.\sin\beta}{\sigma}$$

$$Eqn\ 6:\ \rho.g.V.\sin\alpha = \gamma_l.r.\left(\cos\theta_r - \cos\theta_a\right)$$

$$Eqn\ 7:\ \rho.g.V.\sin\alpha = \sigma_a.2r \ where\ \sigma_a = \sigma_{lf} + \sigma_{fs} - \sigma_{ls}$$

Different Equations available in the literature for predicting tilt angle consideration for the present workt. (ρ: Density, α: Tilt Angle, θ: Advancing/Receding Angle, σ/γ: Surface Tension, β: Texture Parameter/Inclination Angle, r: Droplet Radius, V: Droplet Volume, D: Droplet Diameter, g: Acceleration due to Gravity, μ: Pinning Parameter, B: Bond Number)

These equations were firstly validated using theoretical data provided in the sources and the performances of these equations were compared using experimental data obtained from our work above. We used the Eotvos Rule to also understand the temperature dependency of the surface tension of a liquid. For a given molar volume of a liquid, we can use Eotvos' Rule to understand how any temperature variations will affect the surface tension of the liquid.

$$\gamma V^{2/3} = k(T_c - T)$$

γ: Surface Tension of the Liquid, V: Molar Volume of the Liquid, k: Eotvos Constant (2.1 x 10^{-7} J/$mol^{2/3}$ K), T_c: Critical Temperature of the liquid, T: Liquid Temperature.

For DI water, we used the following equation to determine this relationship (T_c: 647.14 K for water).

$$\gamma = 0.07275\ \mathrm{N/m} \cdot (1 - 0.002 \cdot (T - 291\ \mathrm{K}))$$

Contrary to our expectations, the tilt angle equations chosen for study were generating results noticeably different from our experimental results. Understandably there does always exist a disparity in results obtained theoretically and experimentally however we were getting results with too great a margin of difference to neglect. As a further extension of our work due to certain constraints, we look to develop an equation which models the wetting properties which not only meets the accuracy criteria but accounts for various additional experimental factors.

Conclusion

We started by identifying various parameters which affect the wetting properties of a substrate. With these parameters, we focused our work on firstly tuning the specific wetting properties of our chosen substrate using various advanced processing techniques and then testing the performance of our prepared sample under various experimental conditions. We were also able to compare the samples prepared under different processing conditions and studied how they would perform under different testing conditions. With our collected data, we now have a broad understanding of how we can further tune the wetting properties of our substrate to optimize its performance under extreme conditions, along with exploring how the sample reacts to further contaminant and immersion tests. We also chose to study the accuracy of existing equations which try to predict the dynamic contact angles of a substrate under certain conditions. We identified several equations and using data acquired from our experimental analysis, we saw that these equations could not, to the required degree of accuracy, predict the contact angles. As a further extension of our work, we look to identify the cause of this inaccuracy and also develop our own model to predict these values, the application of which would be in domains across engineering. We look forward to publishing our findings very soon in the international journal Wear, which focuses on the science and technology of friction, lubrication and wear.

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