Research Journal of Chemical Sciences ISSN 2231-606X
Vol. **9(2),** 16-23, April **(2019)** *Res. J. Chem. Sci.*

Dynamic behaviours of water droplet impacting antiwetting plant leaves

Anand Khistariya[1,2*], Rinat Nigmatullin[2,3] and Fengge Gao[2]
[1]School of Chemical and Physical sciences, Department of Industrial Chemistry, Atmiya University, Rajkot, 360005 India
[2]School of Science & Technology, Nottingham Trent University, Nottingham, NG11 8NS, United Kingdom
[3]Department of Engineering, University of Bristol, Bristol, BS8 1QU, United Kingdom
anand_khistariya@hotmail.co.in

Available online at: www.isca.in, www.isca.me
Received 26th December 2018, revised 15th March 2019, accepted 8th April 2019

Abstract

Natural minute structures have been analyzed on numerous kind of surfaces like rose leaves, which are helpful for the development of biomimetic materials for self cleaning, fluidic drag reduction, bio-surface, anti-biofouling and prevention of water corrosion. We examined the micro scale structure on the leaves of Leucophyllumfrutescens (Purple sage), Lactuca virosa (Wild lettuce), Montbretia (Crocosmia) and Corymbia (Eucalyptus). Water droplet impact velocity V of 2m/s and 4m/s from the fixed distance shows rebound, oscillations and fragmentation. These are due to uneven distribution of small micro dots, three dimension waxes and tiny horizontal lines on the surfaces. At comparatively low impact velocity, partial bounce back and oscillations, and fragmentation and splashing were observed as velocity was increased. For characterization of wettability of the surface, Contact angle experiments have been performed and Cassie-Baxter and Wenzel approaches are discussed. Highest static contact angle (118.02±7.46) was observed on Leucophyllumfrutescens (Purple sage) surface due to densely covered with three dimensional waxes. However, lowest static contact angle (98.38±4.91) was observed on Eucalyptus (Corymbia) surface with small dots on the surface.

Keywords: Droplet impact, hydrophobic natural surfaces, contact angle.

Introduction

The concept of hydrophobicity and superhydrophobicity of hard surfaces has been examined with significant notice over the earlier period of few decades and outstanding possibilities have been attained. It has been widely explored that water droplets on hydrophobic or alternatively ultraphobic surfaces can formed a contact angle between 90^o to 180^o. In short, $\Theta > 90^o$ defines a hydrophobic and $\Theta > 130–180^o$ defines superhydrophobic surface[1]. Due to such high contact angles, rain often bounces off surfaces. Some plants have the potential to resist against the water droplet, such phenomenon enables the water droplets to roll away carrying dust and dirt with them, that effect is referred as lotus effect[2]. Furthermore, based on various literature reviews, a few experimental replicas have been planned to exemplify water repellent properties, for instance, Wenzel[3] and Cassie-Baxter[4] models. Because of these models, researchers could understand the basic surface phenomenon like surface roughness and water repellence.

Since the hydrophobicity is a new concept in front of the modern era, research on the superhydrophobic coating methods, recently, more and more attraction has been attracted to manufacture various devices with the help of superhydrophobic fabrication. Moreover, superhydrophobic surfaces have important technical possibilities for a variety of uses because of their extreme anti-wetting properties. Dynamic effects for instance bouncing, splashing, rebound and fragmentation of a droplet on different types of polymer have been identified[5].

The bouncing action of droplet on superhydrophobic surfaces depends on the hydrophobicity of a surface. There are also numbers of natural superhydrophobic surfaces have been found in the nature, the basic concept of such types of surfaces tend to clean their leaves automatically. For example, according to Yan et al[6] *Colocasiaesculenta* (Taro) leaves and *Cannageneralis bailey* (India canna) have been stated to be superhydrophobic in nature due to their structures. To understand the superhydrophobicity of surfaces, 1.Wenzel and 2.Cassie–Baxter is well known, from the equations we can understand the relation between the surface roughness and wetting phenomenon.

The Wenzel model (Robert N. Wenzel 1936) explains the uniform wetting fact, as seen in Figure-1, and is distinct by the below equation for the contact angle on a rough surface[4].

$$\cos\Theta_w = r \cos\Theta_y$$

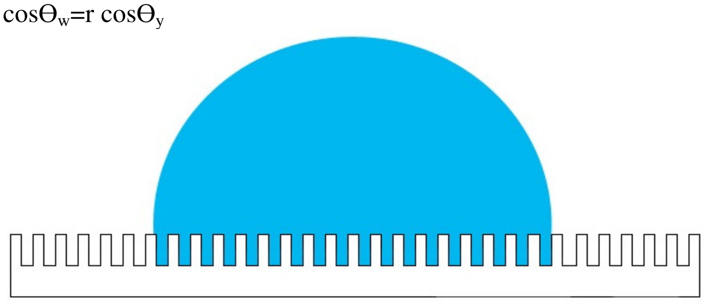

Figure-1: Wenzel model[4].

Where, Θ_w is the apparent contact angle that matches up to the steady equilibrium state. The roughness ratio, r, is a measure of how surface roughness affects a uniform surface. The roughness ratio is defined by the ratio of real area of the solid surface to the obvious area.

Wenzel model is constructive while the surface is homogeneous; however, it is not sufficient for the heterogeneous surface. Therefore, a Cassie-Baxter model is needed to measure the obvious contact angle on uneven surface, which is shown in Figure-2.

$$\cos\Theta_{CB} = r_f f \cos\Theta_Y + f - 1$$

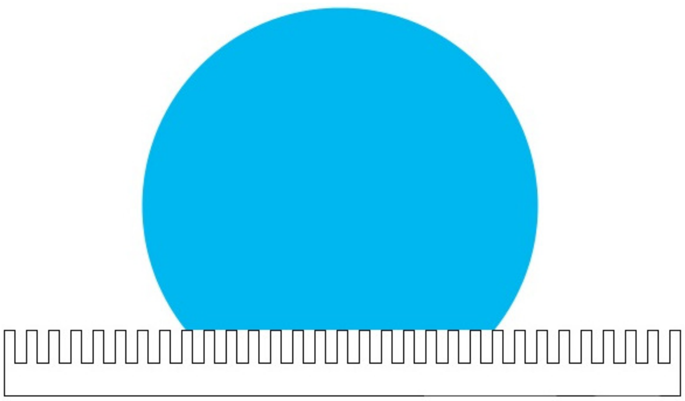

Figure-2: Cassie-Baxter model[4].

Where, Θ_{CB} is apparent contact angle, *r*f is the roughness ratio of the wet surface area and f is the part of solid surface area wet by the liquid. Both Wenzel and Cassie-Baxter models have been measured on the single mathematical basis.

Surface roughness and low surface energy of materials also play significant role to understand extreme water repellent properties of surfaces. There are plenty of natural superhydrophobic surfaces existing on the planet earth. Koch et al[7,8] suggested hierarchical sculptures in Salvinia leaves which foams hydrophobicity with the creation of air pockets. Some leaves protect itself from environment and organisms such as lotus leaf due to its hierarchical levels. In addition, advanced research has indicated that the plant cuticle and leaf hair are important features to make surface rough[8].

The Figure-3 represent the high contact angle (>150^o) of water droplet on the leaf of lotus. On such surfaces, the physical bond among the particle and the surface are very less therefore water droplets and other dust particles roll off the leaves. Hence, lotus leaves clean their surface according to above phenomenon with high static and hysteresis contact angle[8,9].

The capability of water to bounce on superhydrophobic surface gives an indication of surface roughness, high contact angle and extreme water repellent properties. A wide study has been carried out on the bouncing behaviour of water droplet. The diverse approaches (bounce, splash, fragmentation and so on) generally depends not only the volume of the drop but also the surface tension and velocity. In addition, the surface wettability associated mainly of the surface energy and geometrical structure of the solid surface.

Figure-3: Water droplet on lotus leaf structure[9].

Jung et al[1] reported that vibrant effects for example the bouncing and splashing of a drop could affect the solid-air-liquid interface of the surface. Due to the internal force and certain pressure of a liquid drop, the shift occurs between solid-air-liquid interfaces to a solid-liquid interface.

Materials and methods

All hydrophobic leaves have been used to measure drop impacts and contact angle measurement, *Leucophyllum frutescens* (Purple sage), *Lactuca virosa* (Wild lettuce), *Montbretia* (Crocosmia) and *Corymbia* (Eucalyptus) were collected from local region. Approximately 8µL water drop was positioned onto the middle of the sample surface. Then, the drop picture was taken and analysed by the IC capture 2.2 software and the contact angle was measured by the Image J launcher software. Experiment repeatability was achieved by running measurements with at least four cycles with every single sample. Surface morphology of the natural samples was characterised at microscopic level. Digital microscopy was used to analysed leaf roughness, hair and wax.

In order to test bouncing behaviour of water droplet, a manual built apparatus was used to regulate the flow of water with micro litre syringe which is shown in the Figure-4.

The water drop experiment was performed in the Nano-science and Catalysis Laboratory at The Nottingham Trent University. As shown in Figure-4, a syringe has been set steady at 35mm and 70mm distance above the targeted samples; distance has been raised to affect the impact velocity. The syringe-needle was controlled physically by pressing down to release 8µl drop of water. This required moderate patience as the syringe favours to expend a small stream. For recording the dataset, a movable high-speed camera, Casio Exilim EX-FH20 with recording speed up to 1000 fps and 20x optical zoom, Image J software, Virtual Dub Portable software and a high voltage lamp were used. The provided camera was placed at a fixed distance and height to the contact surface. Manual focus and zoom was used to adjust the suitable video capture quality. For the experiments, the camera was set to 420fps to record the water drop experiments. For these high frames per second recording, a large lamp was used to provide suitable light for each frame. A high-speed camera and an appropriate assembly were able to record the instants before and after the impacts of the water droplet on particular sample surface, which could later be possible to analyse each frame by Image J, Virtual Dub Portable software and a computer assembly.

The software programs Image J and Virtual Dub Portable were used for analysis of the data and understand the impacts frame by frame. Virtual Dub Portable software enables to analyse the video by each frame (in terms of droplet behaviour. For instance, splash, bounce, oscillation and fragmentation) and it was possible to extract particular images from the video.

Results and discussion

For the identification of leaf structure on micro level, leaf sample has placed under microscopy to identify its basic surface morphology as shown in Figure-5. The outline of wax, dots and hair on leaves are easily observable by microscopy.

Figure-4: The droplet measurement assembly with high-speed camera.

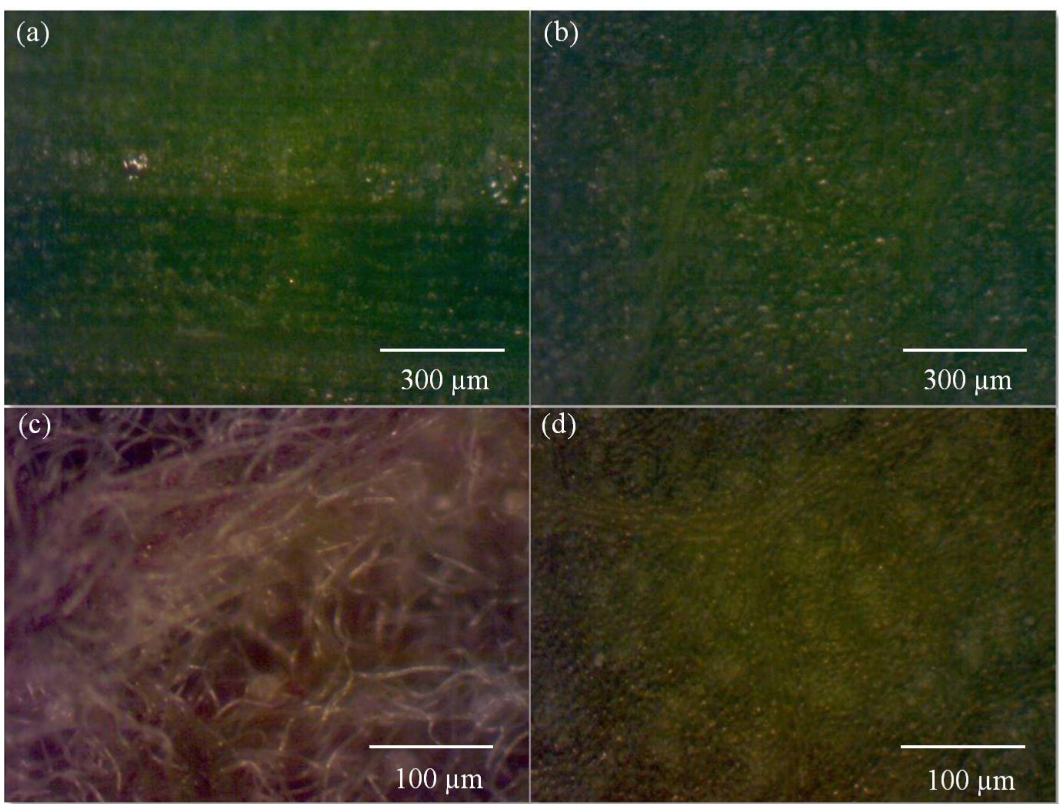

Figure-5: Microscopic images of the natural leaves. (a) Small horizontal lines were appeared on *Montbretia* (Crocosmia) leaf (b) On *Corymbia* (Eucalyptus) surface, small dots were observed (c) shows a brownish surface on (*Leucophyllumfrutescens)* (Purple sage), heavily covered with three dimensional hair (d) shows *Lactuca virosa* (Wild lettuce) surface with tiny dots.

Figure-6: Four water repellent natural species (a) *Montbretia* (Crocosmia) (b) *Corymbia* (Eucalyptus) (c) *Leucophyllumfrutescens* (Purple sage) (d) *Lactuca virosa* (Wild lettuce).

Contact angle measurement was carried out on four hydrophobic leaves using water. The contact angles on micro structure leaves such as *Montbretia* (Crocosmia), *Corymbia* (Eucalyptus), *Leucophyllumfrutescens* (Purple sage) and *Lactuca virosa* (Wild lettuce) are 107.50±1.96, 98.38±4.91, 118.02±7.46 and 107.31±0.88 respectively. As shown in figure-5 small horizontal lines are observed which are responsible for Cassie-Baxter regime and adequate contact angle on *Montbretia* (Crocosmia) leaf surface. Furthermore, a densely covered three-dimensional wax enables to produce highest static contact angle with Cassie-Baxter regime on Leucophyllumfrutescens (Purple sage). According to Koch et al[8] a water droplet on particular leaf shows Cassie-Baxter regime because of the three-dimensional epicuticle waxes which enables a droplet to sit gently on the surface. However, the lowest contact angle was identified on *Corymbia* (Eucalyptus) smooth surfaces. Small dots which allows to droplet to form Wenzel regime. Zhang et al[10] have proposed that the contact angle is not only just depending on the Cassie and Wenzel regime but also it be dependent on volume of the droplet. Lesser then 4µL volume of water droplet would not be able to set down on the hydrophobic surface because of the low adherence of the surface and this is the reason that we have chosen 8µL volume of water droplet. The micro and nano structures, small micro sized hair, wax on the upper part of the natural surfaces improve hydrophobicity. Thereby allowing droplet of water to roll off the leaf and eliminate dirt[11].

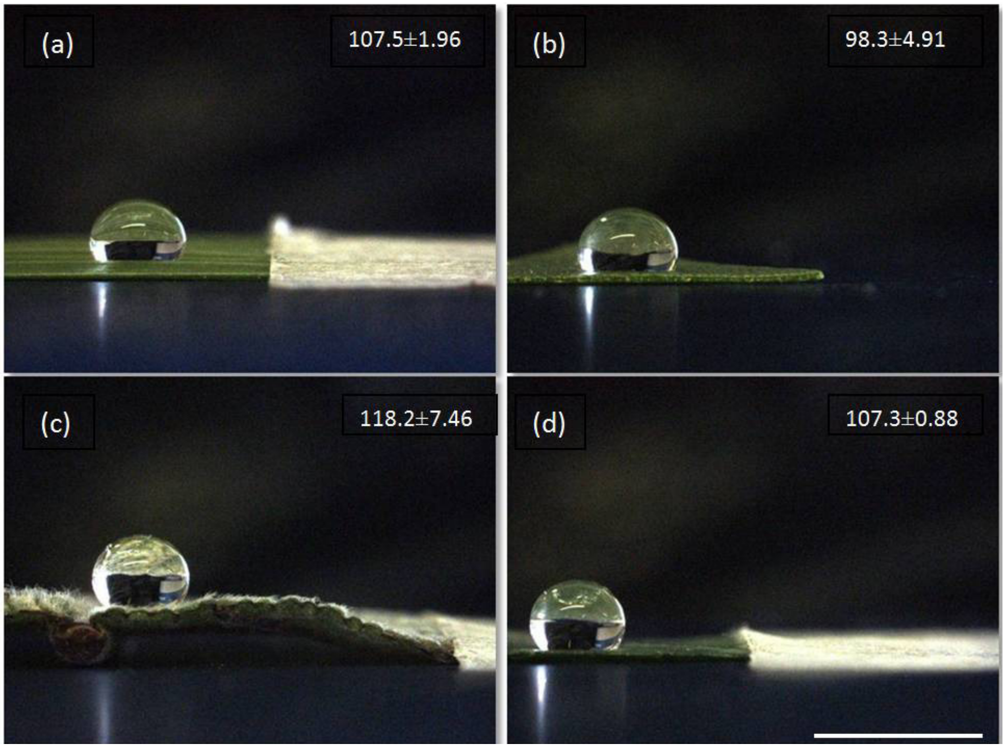

Figure-7: Water droplet resting on (a) *Montbretia* (Crocosmia) (b) *Corymbia* (Eucalyptus) (c) *Leucophyllumfrutescens* (Purple sage) and (d) *Lactucavirosa* (Wild lettuce) surface. (Scale bar 1cm).

Drop impact experiments were carried out with the distance 35mm and 70mm and impact velocities V of 2m/s and 4m/s respectively.

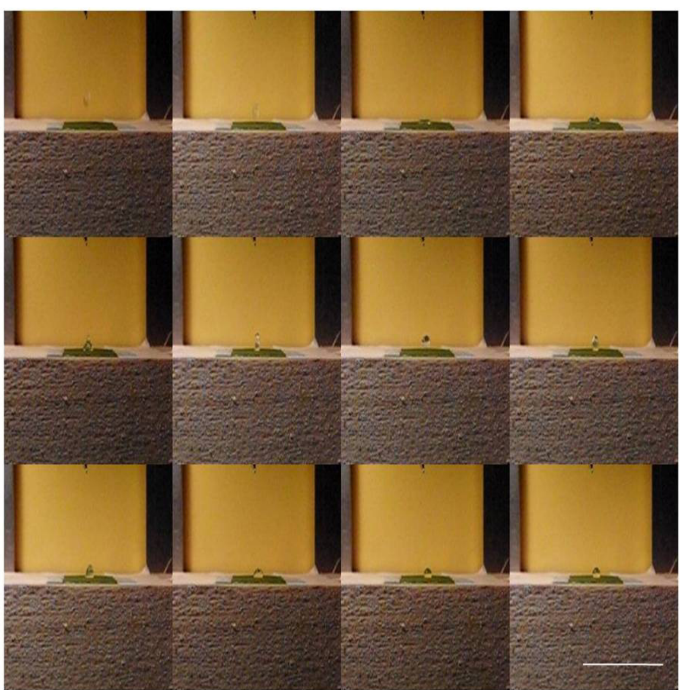

Figure-8: Drop impacts on *Montbretia* (Crocosmia) surface. (Needle to sample length 35mm, scale bar 1cm, V=2m/s).

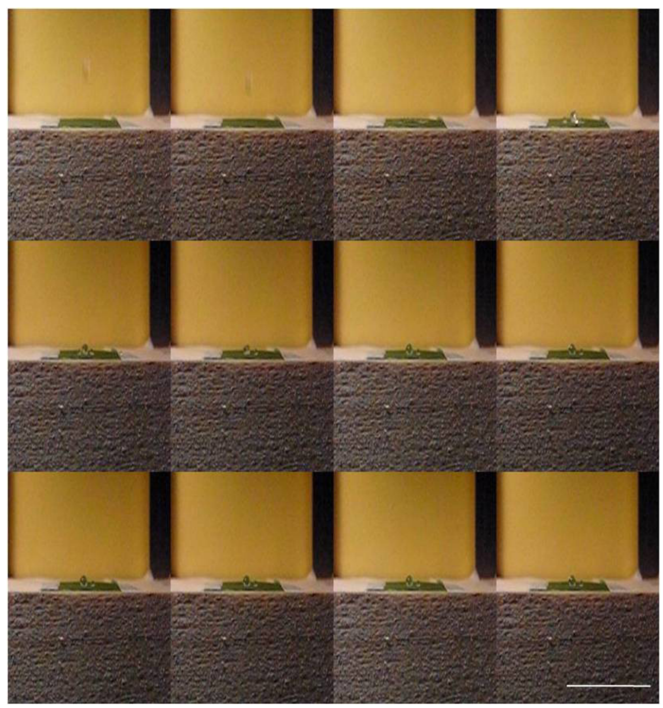

Figure-9: Drop impacts on *Montbretia* (Crocosmia) surface (Needle to sample length 70mm, scale bar 1cm, V=4m/s).

As shown in the Figure-8 and Figure-9, vibrating elastic rebound and fragmentation observed with low and high impact velocities respectively. Thus, when droplet comes into contact with tiny horizontal lines at low impact velocity, it will rebound with minimal contact with the surface. While at high impact velocity the water droplet convert into tiny fragments.

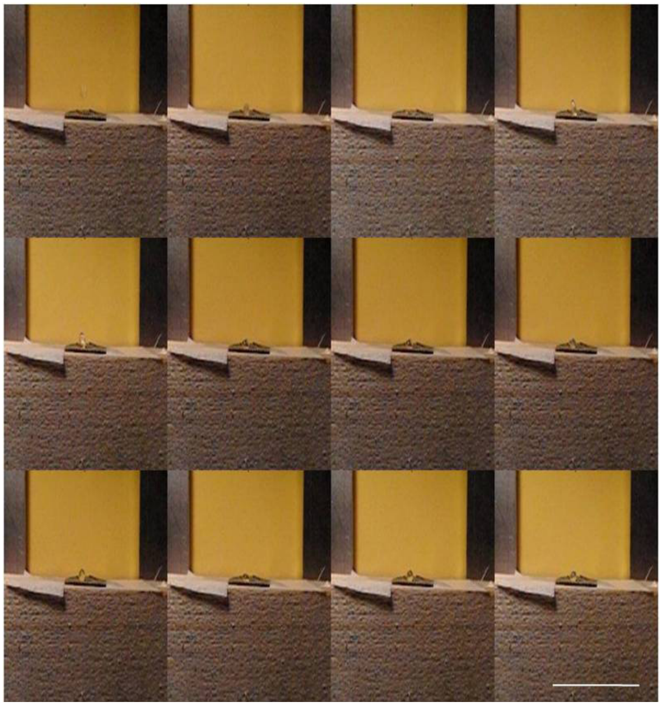

Figure-10: Drop impacts on *Corymbia* (Eucalyptus) surface. (Needle to sample length 35mm, scale bar 1cm, V=2m/s).

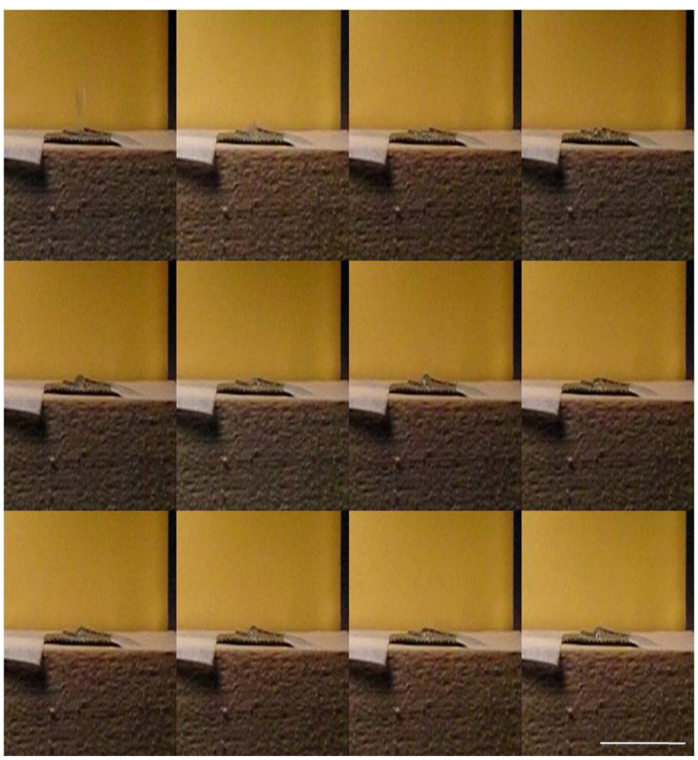

Figure-11: Drop impacts on *Corymbia* (Eucalyptus) surface. (Needle to sample length 70mm, scale bar 1cm, V=4m/s).

At low impact velocity (Figure-10) there was not any rebound observed. At beginning of the experiment, deposition occurs between the small dots and after touching the surface it was exhibited number of oscillations and it stayed on the surface. Conversely, Rebound and oscillations with intensive shaking and vibration were identified as velocity increased (Figure-11) due to uneven allocation of the micro dots.

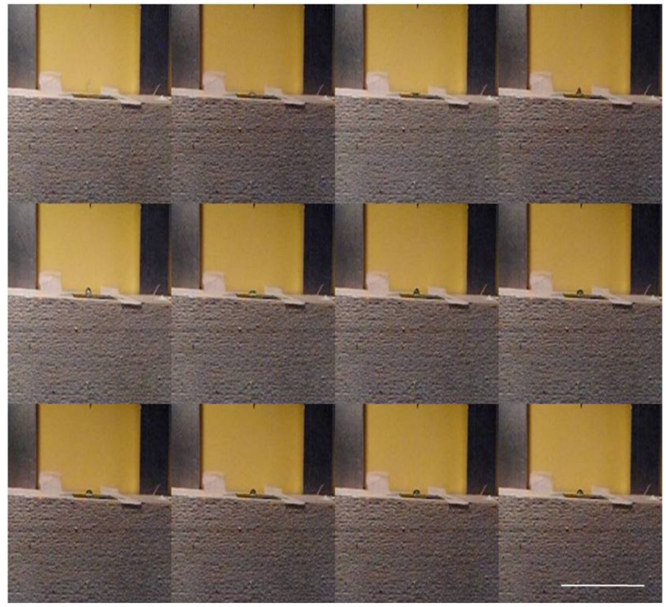

Figure-12: Drop impacts on *Leucophyllumfrutescens* (Purple Sage) surface. (Needle to sample length 35mm, scale bar 1cm, V=2m/s).

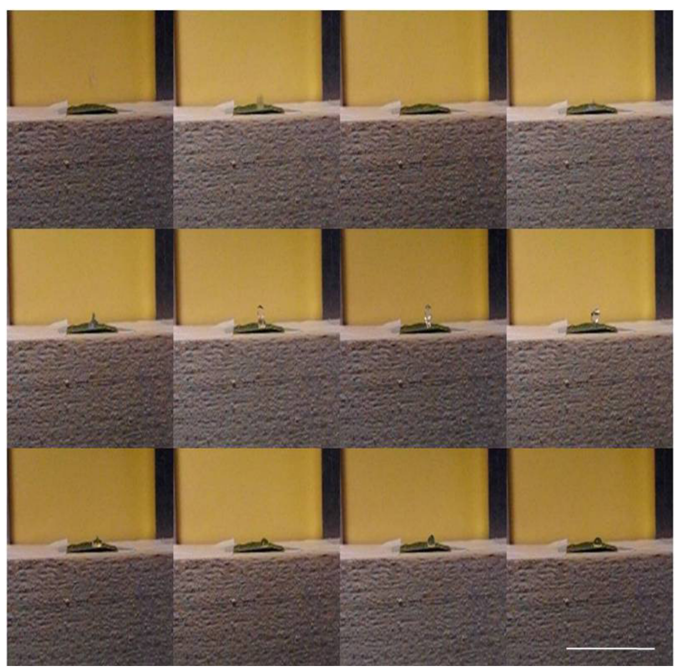

Figure-13: Drop impacts on *Leucophyllumfrutescens* (Purple Sage) surface. (Needle to sample length 70mm, scale bar 1cm, V=4m/s).

On the *Leucophyllumfrutescens* (Purple Sage) surface, partial rebound and vibrating oscillations were found. It was observed that the droplet was greatly stretched out before leaving the surface. Surprisingly, as the velocity increased, water did not bounce off the surface.

It was identified that the drop fragmented into many tiny drops during dispersal stage due to the higher impact velocity which is shown in the Figure-13. This process called splashing when water droplet turns into the tiny drops due to the higher impact velocity. According to Chen et al[12] splash occurs on dry and smooth surfaces because of the compressible stress from air, which tries to pull the liquid sheet up, and the stress of the surface tension.

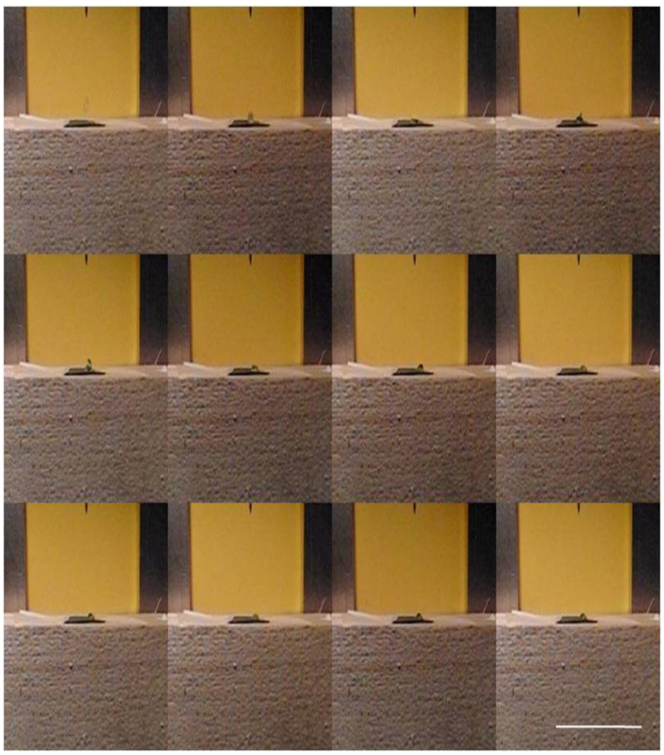

Figure-14: Drop impacts on *Lactuca virosa* (Wild lettuce) surface. (Needle to sample length 35mm, scale bar 1cm, V=2m/s).

As shown in Figure-14, when a droplet landed on a Wild lettuce (*Lactuca virosa)* surface, it deformed and tried to bounce off from the surface.

However, numbers of vibrational oscillations have been noticed after spreading stage. With further increase in velocity, rebound and intensive vibration was observed due to uneven allocation of the tiny dots. Chen et al[12] have studied and compared dynamic impacts on dual-scaled nano-grass surface with a lotus leaf with different impact velocities. They have identified regular rebound and air bubble trapping on both surfaces at relatively low impact velocities. In fact, on the lotus leaf, droplet bounced off and pinned on the surface because of the ununiformed micro dots on the surface.

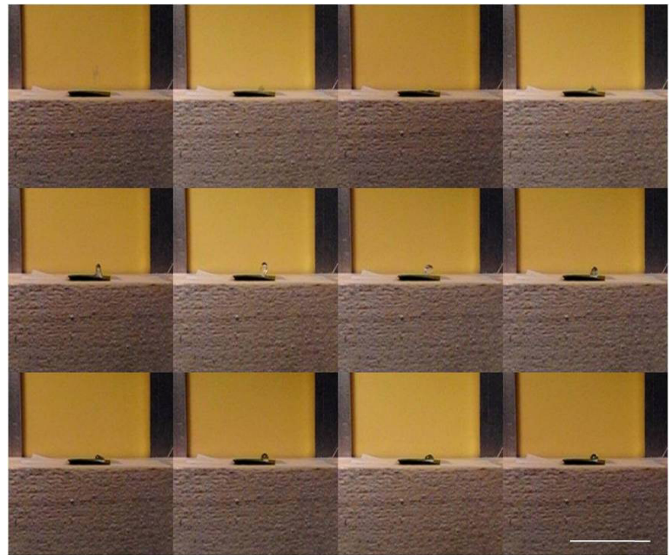

Figure-15: Drop impacts on *Lactuca virosa* (Wild lettuce) surface. (Needle to sample length 75mm, scale bar 1cm, V=4m/s).

Conclusion

Highest static contact angle (118.02±7.46) was observed on *Leucophyllumfrutescens* (Purple sage) surface due to three dimensional waxes on the surface. Lowest static contact angle (98.38±4.91) was observed on *Corymbia* (Eucalyptus) surface due to small dots. Droplet impact on natural hydrophobic surfaces such as *Montbretia* (Crocosmia), *Corymbia* (Eucalyptus), *Leucophyllum frutescens* (Purple sage) and *Lactuca virosa* (Wild lettuce) was studied with an approximately 8 μL water droplet.

Partially rebound and vibrational oscillations at low impact velocity were observed on *Montbretia* (Crocosmia) and *Leucophyllum frutescens* (Purple sage) surfaces due to uneven allocation of small micro dots and densely covered three-dimensional waxes on the surfaces. Furthermore, fragmentation was occurred on *Montbretia* (Crocosmia) and *Leucophyllumfrutescens* (Purple sage) surfaces under high impact velocity. No bounces were observed on both *Corymbia* (Eucalyptus) and *Lactucavirosa* (Wild lettuce) surfaces at low impact velocity due to low static contact angle. Under high impact velocity, however, splash and vibrational oscillations were identified on both *Corymbia* (Eucalyptus) and *Lactucavirosa* (Wild lettuce) surfaces. Further studies need to be made in order to increase the static angle and drop effects on such hydrophobic surfaces with the help of surface modification.

Acknowledgement

The authors are thankful to Nano-science and Catalysis Laboratory of Nottingham Trent University, United Kingdom for providing laboratory and instrumentation facility.

Table-1: Summary of contact angle and droplet behaviour of water

Plant name	Surface characteristics	Contact angle	Regime	Drop behaviour (V=2m/s)	Drop behaviour (V=4m/s)
Leucophyllum frutescens (Purple sage)	Densely covered with three dimensional waxes	118.2±7.46	Cassie-Baxter	Partial rebound and vibrating oscillations	Splashing
Montbretia (Crocosmia)	Small horizontal lines	107.5±1.96	Cassie-Baxter	Vibrating elastic rebound and fragmentation	Vibrating elastic rebound and fragmentation
Lactuca virosa (Wild lettuce)	Tiny dots	107.3±0.88	Cassie-Baxter	Deformed and tried to bounce off from the surface	Rebound
Corymbia (Eucalyptus)	Tiny heterogeneous dots	98.38±4.91	Wenzel	Intense oscillations	Rebound and oscillations with intensive shaking and vibration

References

1. Jung Y. and Bhushan B. (2009). Dynamic Effects Induced Transition of Droplets on Biomimetic Superhydrophobic Surfaces. *Langmuir,* 25(16), 9208-9218.
2. Crick C.R. and Parkin I.P. (2011). Water droplet bouncing-a definition for superhydrophobic surfaces. *Chem.. commun.*, 47(44), 12059-12061.
3. Whyman G., Bormashenko E. and Stein T. (2008). The rigorous derivation of Young, Cassie-Baxter and Wenzel equations and the analysis of the contact angle hysteresis phenomenon. *Chemical Physics Letters,* 450(4-6), 355-359.
4. Marmur A. (2003). Wetting on Hydrophobic Rough Surfaces: To Be Heterogeneous or Not To Be?. *Langmuir,* 19(20), 8343-8348.
5. Rioboo R., Voue M., Vaillant A. and Coninck J. (2008). Drop Impact on Porous Superhydrophobic Polymer Surfaces. *Langmuir,* 24, 14074-14077.
6. Yan Y.Y., Gao N. and Barthlott W. (2011). Mimicking natural superhydrophobic surfaces and grasping the wetting process: a review on recent process in preparing superhydrophobic surfaces. *Adv. Colloid Interface Sci.,* 169, 80-105.
7. Koch K., Bohn H. and Barthlott W. (2009). Hierarchically Sculptured Plant Surfaces and Superhydrophobicity. *Langmuir*, 25(24), 14116-14120.
8. Koch K., Bhushan B. and Barthlott W. (2009). Multifunctional surface structures of plants: an inspiration for biomimetics. *Progress in Materials science*, 54(2), 137-178.
9. Blossey R. (2003). Self Cleaning Surfaces-Virtual Realities. *Nature materials,* 2, 301-306.
10. Zhang X., Shi F., Niu J., Jiang Y. and Wang Z. (2008). Superhydrophobic Surfaces: From Structural Control to Functional Application. *J. Mater. Chem.,* 18(6), 621-633.
11. Byun D., Hong J., Saputra J., Hwan K., Jong Y., Park H., Byun B. and Lukes J. (2009). Wetting Characteristics of Insect Wing Surfaces. *Journal of Bionic Engineering,* 6, 63-70.
12. Chen L., Xiao Z., Chan P., Lee Y. and Li Z. (2011). A Comparative Study of Droplet Impact Dynamics on a Dual-Scaled Superhydrophobic Surface and Lotus Leaf. *Applied Surface Science,* 257, 8857-8863.