Superhydrophobic Structures on the Basis of Aspen Leaf Design

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ABSTRACT
This study is concerned with an analysis of the structural and mechanical design concepts in naturally occurring superhydrophobic structures. It is shown that the non-wetting behaviour of the leaves of two members of the aspen family can be primarily attributed to a dual-scale surface structure consisting of micro-papillae and nano-wax platelets. However, the non-wetting effect is further enhanced by the large leafstalk aspect ratio and associated low moment of inertia, offering little resistance to leaf bending. These leafstalk dimensions result in excessive shaking of the leaves even when there is no noticeable breeze, promoting efficient water droplet roll-off and dry leaf surfaces. It is tentatively concluded that this leaf design may contribute to the aspens' ability to quickly grow in a wide range of environmental conditions. Mimicking the combined effects of micro/nanostructure surface morphology and mechanical motion could be useful in developing a broader design concept range for superhydrophobic structures.

1. INTRODUCTION

Within the last several years there have been large research initiatives surrounding superhydrophobic surfaces mimicked after the well-known non-wetting lotus leaf. This anti-wetting property, known as the lotus-effect, has already been used to create a number of engineering materials with superhydrophobic and self-cleaning surfaces including Lotusan® house paint, Nano-tex™ spill/stain resistant fabrics and Bandai® aqua drop toys.

We have recently observed non-wetting properties on the leaves of two members of the aspen tree family. In addition to the lotus-effect, these species possess unique leafstalk dimensions which augment their ability to keep their leaves dry. Aspens are among one of the most widely distributed trees in North America [1]. They can be found from northwestern Alaska to Newfoundland and south to northern Mexico [2]. They dominate other species in over 100 habitats across the continent, and within Minnesota, Wisconsin and Utah occupy more land than any other forest type [3]. These trees are known for their ability to grow quickly in a wide variety of climates and be the first species to re-forest large areas recently destroyed by acute disturbances [1]. There are likely several reasons for this overwhelming capacity to thrive in such diverse conditions. One possible explanation involves the tough root systems of aspen trees and their proficiency in surviving massive wildfire outbreaks. Following a forest fire, new stems sprout from surviving aspen root systems and quickly grow to re-colonize the affected area [1, 4]. Perhaps there are other features related to different parts of these trees that allow for their great ability to thrive in a variety of environmental conditions. The objectives of this research are to focus on the relative importance of the leaf structure of aspen trees in this context and gain a better understanding of the advantages/limitations these types of functional surfaces may have with respect to fluid interactions.

This report characterizes for the first time the leaf surface structures, leafstalk dimensions and wetting properties of the adaxial side of the leaves of two types of aspen trees native to North America (*Populus tremuloides* and *Populus grandidentata*). The effects of temperature, droplet size and surfactant concentration on these leaves' wetting properties are investigated and tentatively linked to growth and survival of these trees. This study will increase the understanding of fluid nano/microstructure interactions under different environmental conditions which can aid in the design of synthetic superhydrophobic surfaces.

2. METHODS AND MATERIALS

Quaking (trembling) aspen leaves (*Populus tremuloides*) and Bigtooth aspen leaves (*Populus grandidentata*) were obtained from a forest outside Peterborough, Ontario. Their surfaces were characterized using scanning electron microscopy (SEM) and interferometric profilometry. Contact angle measurements were performed using different droplet sizes at varying temperatures and surfactant concentrations to illustrate the effect these conditions have on the observed wetting properties. The leaves were used for experimental work within 12 months after harvesting. Initially there were concerns with respect to differences in the wetting behaviour of fresh and dried leaves. However, wetting angle measurements showed insignificant changes in wetting angles ($< 5°$) even 12 months after harvesting. Furthermore, previous studies on other leaves also showed very small differences in the wetting characteristics of freshly collected and aged leaves [e.g. 5, 6].

Several 1 cm^2 sections of the adaxial side of the leaves were carbon coated (for electrical conductivity and optical reflectivity) and analyzed using an SEM (Hitachi S-4500 Field Emission Scanning Electron Microscope) and an optical profilometer (WYKO interferometric profilometer). After air-drying and freezing in liquid nitrogen, both quaking and bigtooth aspen leafstalks (and red maple (*Acer rubrum*) leafstalks for comparison) were fractured, at their mid-points, and their cross-sectional dimensions were measured using an SEM.

Larger 2×2 cm sections of the adaxial side of these leaves were used to quantitatively measure their wetting properties. Care was taken to ensure that the tested sections contained no major leaf veins and were not taken from areas close to the edges of the leaves. These sections were fixed to metallic substrates using double-sided adhesive tape to obtain a macroscopically flat surface. Several 5 μl droplets of pure de-ionized water or solutions containing different concentrations (up to 100 g/L) of a wetting agent (sodium dodecyl sulphate, SDS—Bioshop Canada Inc.) were carefully placed on each surface using a controlled dispensing micropipette (Clonex Corporation). Contact angle images were obtained using a horizontally positioned digital camera. The same solutions were placed on the surface of a maple leaf and coupons of smooth Teflon™ and Plexiglas™ to compare the effects of this surfactant on other representative hydrophobic and hydrophilic surfaces. Contact angle images were then analyzed using the contact angle function in ImageJ, giving static contact angles. A minimum of 10 measurements were taken for each sample.

A second set of identical samples was used to investigate the effect of temperature on the wetting properties of these leaves. Each sample from this set was heated to different temperatures on a hot plate and contact angle analysis using 5 μl drops was performed.

A third set of identical samples was used to investigate the effect of water drop size on the observed contact angles for these leaves. For these samples, drops of 5, 10, 15, 20 and 25 μl were used for contact angle measurements. Most contact angle studies use small droplet sizes of 5 μl [e.g. 7, 8]. However, larger droplets were included in this study to relate the wetting properties of the leaves to more realistic droplet sizes when they are exposed to rain.

Finally, the water roll-off angle for each leaf was measured using a controlled tilting stage. Each mounted leaf was attached to the tilting stage in its horizontal position and 25 μl drops were placed on each leaf. The stage was slowly tilted until the drop began to move and roll off at which point the tilt angle was measured.

3. RESULTS

3.1. Leaf characterization

Both aspen leaves exhibit a complex surface structure consisting of a dual-scale roughness comprised of micro-scale papillae and nano-scale wax platelets. SEM micrographs illustrating both roughness scales found on bigtooth and quaking aspen leaves are shown in figures 1 and 2, respectively. The nano-scale wax platelets on both aspens have similar lengths (0.5–1.5 μm) while their thicknesses differ: ranging from 50–100 nm for bigtooth aspen and 100–200 nm for quaking aspen.

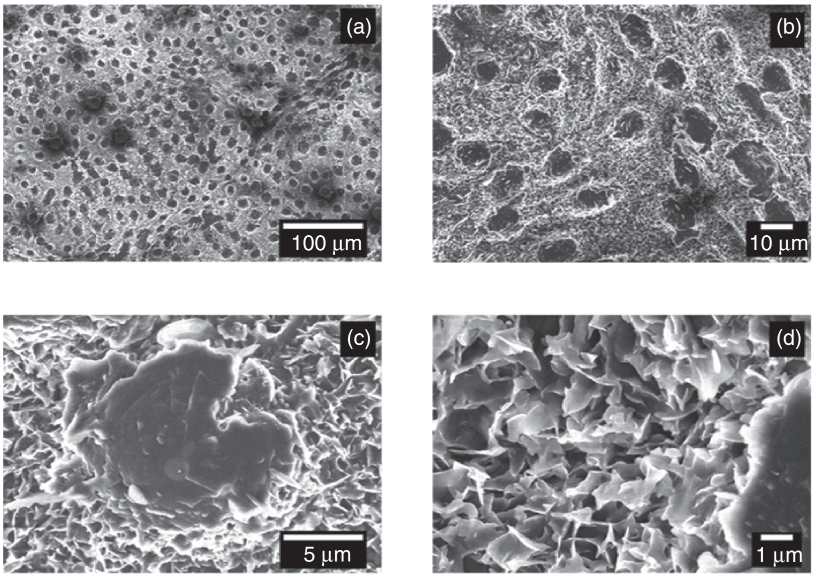


Figure 1. SEM micrographs of a bigtooth aspen leaf: a) low magnification overview, b) several micro-papillae, c) a single micro-papilla and d) nano-scale wax platelets.

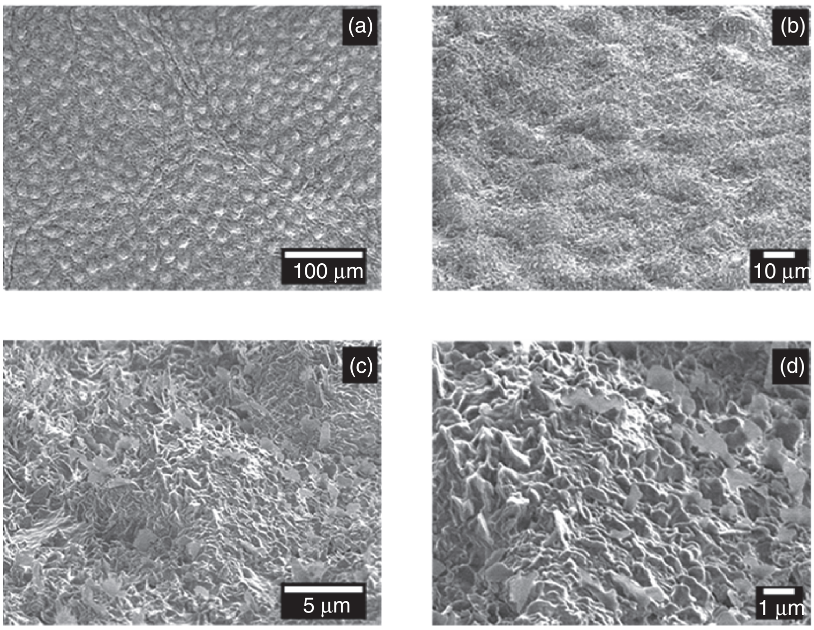


Figure 2. SEM micrographs of a quaking aspen leaf: a) low magnification overview, b) several short micro-papillae, c) a single micro-papilla and d) nano-scale wax platelets.

Optical profilometry images of both leaves (figures 3 and 4) were used to quantitatively measure the heights, diameters, density and spacing of the micro-sized papillae. Both leaves possess comparable micro-sized surface features. The quaking aspen's papillae are smaller/shorter and have larger inter-papillae spacing which results in a lower papillae density when compared to the bigtooth aspen. Results of this analysis are shown in Table 1.

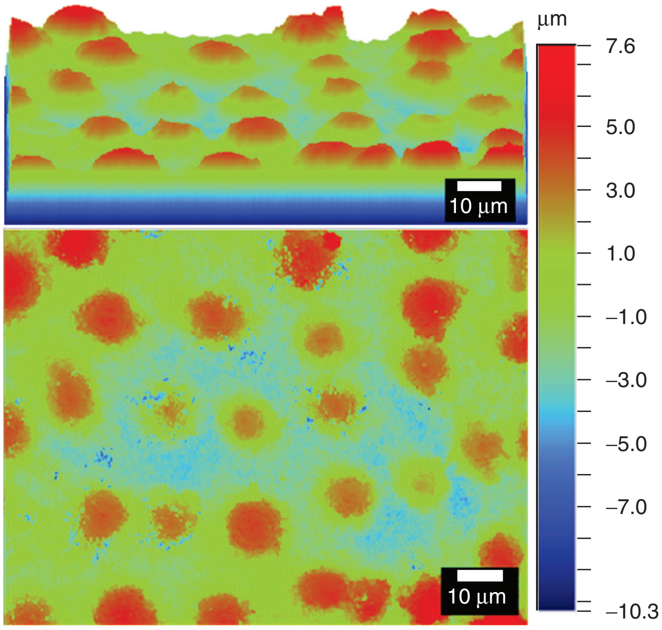


Figure 3. Optical profilometry images of a bigtooth aspen leaf: 3D (top) and surface (bottom) views.

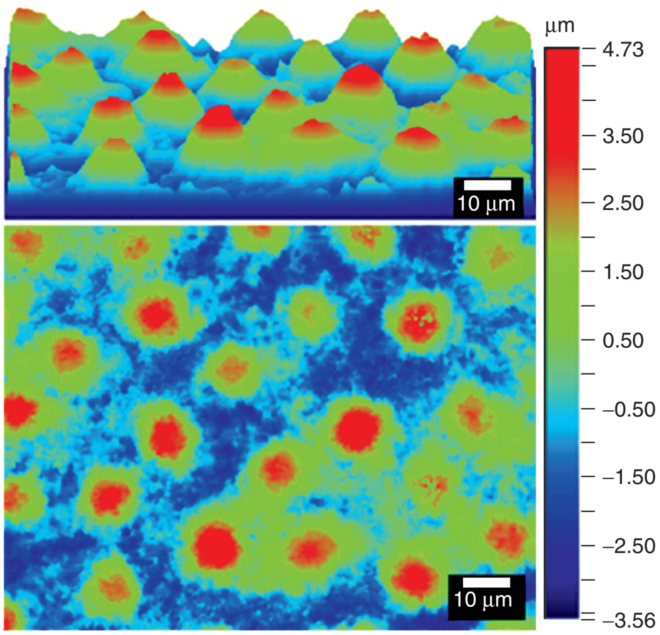


Figure 4. Optical profilometry images of a quaking aspen leaf: 3D (top) and surface (bottom) views.

Table 1. Surface Structure and Wetting Characteristics of Aspen Leaves.

	Average papilla size		Average papilla spacing/density		Average wax platelet size			
Leaf	**Height (μm)**	**Diameter (μm)**	**Interspacing (μm)**	**Density (μm^2)**	**Thickness (nm)**	**Length (μm)**	**Contact Angle (°)**	**Water roll-off angle (°)**
Bigtooth Aspen	6.5 ± 1.9	20 ± 4.5	7.8 ± 4.6	2656	75	1	157 ± 3	<5
Quaking Aspen	4.2 ± 1.4	12.5 ± 3.3	10.1 ± 5.8	2448	150	1	166 ± 3	<5

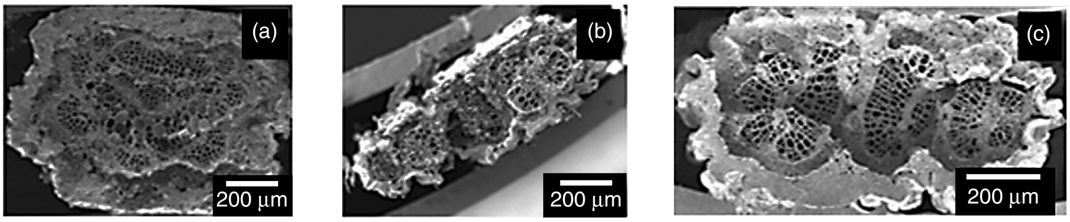
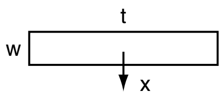


Figure 5. Cross-sectional SEM images of a red maple leaf leafstalk (a), a quaking aspen leaf leafstalk (b) and a bigtooth aspen leafstalk (c).

Table 2. Leafstalk Dimensions and Calculated Moments of Inertia.

Leafstalk	**Average width, w (mm)**	**Average thickness, t (mm)**	**Calculated area, A = wt (mm^2)**	**Calculated moment of inertia, I = $wt^3/12$ ($\times 10^{-3}$ mm^4)**
Maple	1.1	0.77	0.83	41
Quaking Aspen	0.84	0.33	0.28	2.5
Bigtooth Aspen	0.95	0.46	0.43	7.7



Cross-sectional images of quaking aspen, bigtooth aspen and maple leafstalks are shown in figure 5. The maple leaf was introduced for comparison with a species that does not exhibit extreme non-wetting properties. Leafstalks dimensions for cross-sectional areas and moment of inertia calculations are given in table 2. It should be noted that the leafstalks from both aspens are considerably more slender than the maple leafstalks, which results in significantly lower moments of inertia.

3.2. Contact angle measurements

The average water contact angle, using 5 μl drops of de-ionized water, from at least 10 measurements for bigtooth and quaking aspen leaves are 157° ± 3° and 166° ± 3°, respectively. Additionally, both surfaces have water roll-off angles below 5°, indicating that these leaves have superhydrophobic surfaces. In comparison the contact angle on the maple leaf was 124° ± 6°. The average contact angles on both aspen leaves, as well as on maple leaves, Teflon™ and Plexiglas™, as a function of SDS concentration are plotted in figure 6. As expected, the contact angles for all samples rapidly decrease with small additions of SDS and then begin to level out as the SDS concentration increases

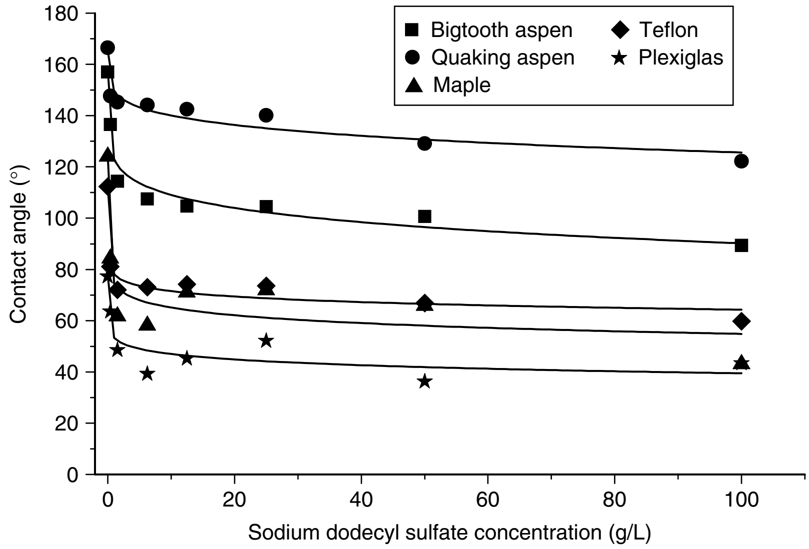


Figure 6. Effect of SDS surfactant concentration on water contact angles.

to higher values. Throughout the entire concentration range, both aspen leaves show significantly higher contact angles than all other tested surfaces. Figures 7 and 8 illustrate the change in aspen water contact angle as a function of temperature and drop size, respectively. Figure 7 shows a sharp drop in contact angles as the leaf temperatures begin to rise above 40°C, while figure 8 reveals the weak effect that water drop size has on contact angles. SEM images of both aspen leaf surfaces after being heated to 90°C for 30 minutes are shown in figure 9 to exhibit the changes in leaf surface morphology that are responsible for the drop in contact angles observed during exposure to elevated temperatures.

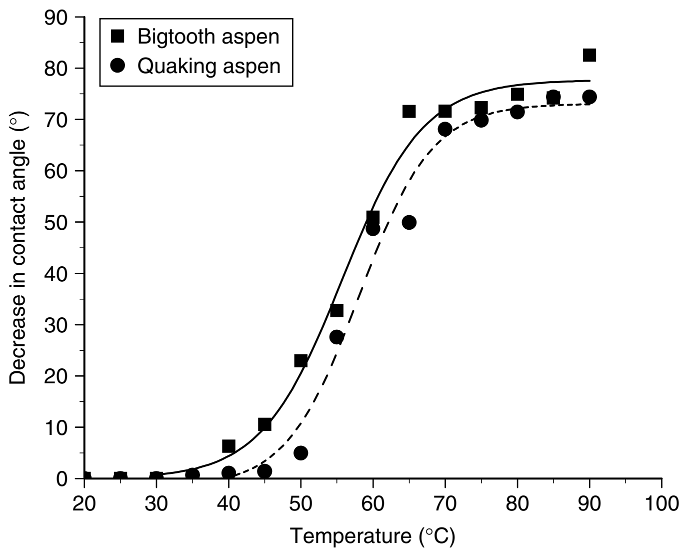


Figure 7. Effect of temperature on the water contact angle of aspen leaves.

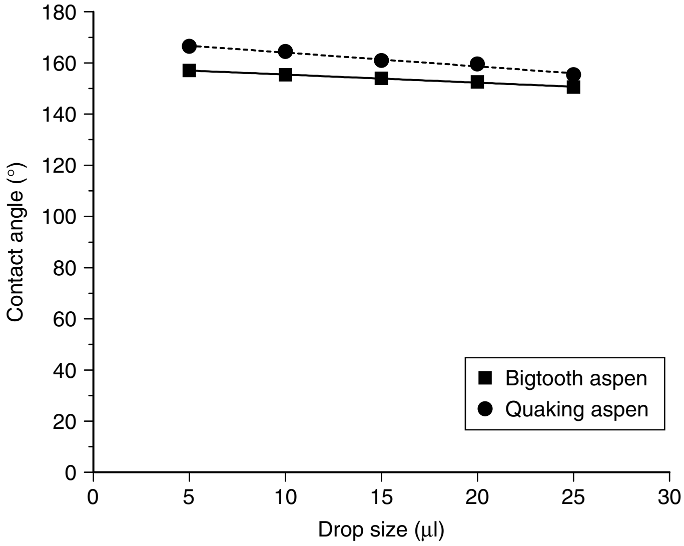


Figure 8. Effect of water drop size on the water contact angles of aspen leaves.

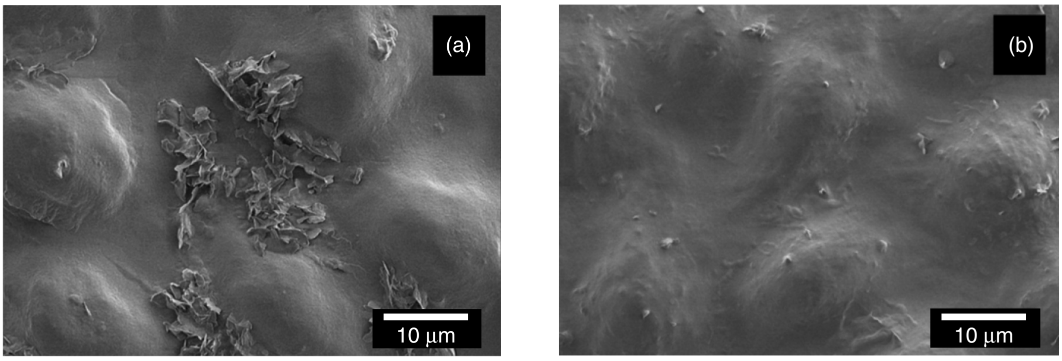


Figure 9. SEM images of a quaking aspen leaf (a) and a bigtooth aspen leaf (b) after being heated to 90°C.

4. DISCUSSION

4.1. Effect of surface roughness on wetting angle

Young's wetting equation, which relates the interfacial energies associated with each of the three phases (solid, liquid, vapour) present when a water drop is placed on a solid surface, dictates the equilibrium droplet contact angle (θ_0) [9]. This relationship is given in equation (1):

$$\gamma_{lv} \cos \theta_0 = \gamma_{sv} - \gamma_{sl} \tag{1}$$

where γ_{lv}, γ_{sv} and γ_{sl} refer to the interfacial energies of the liquid/vapour, solid/vapour and solid/liquid interfaces, respectively.

Wenzel modified Young's equation to incorporate the effect of surface roughness on the equilibrium contact angle [10]. It was shown that increasing the roughness (R_f) of an inherently hydrophobic surface ($\theta_0 > 90°$) enhances the hydrophobic nature of the surface and results in an increased contact angle as per equation (2):

$$\cos \theta = R_f \cos \theta_0 \tag{2}$$

where θ is the contact angle for a rough surface, θ_0 is the contact angle for a smooth surface and R_f is a roughness factor equal to the actual contact area of the solid-liquid interface (A_{sl}) divided by its foot print area (A_{fp}) (3):

$$R_f = A_{sl} / A_{fp} \tag{3}$$

By definition a rough surface will have an R_f value greater than one. Conversely, a perfectly flat surface will give an R_f value equal to one.

Cassie and Baxter further extended Young's equation to incorporate the effect of extreme surface topography, resulting in a heterogeneous interface where air pockets are trapped underneath the water drop [11]. This relationship is given in equation (4):

$$\cos \theta = R_f f_{sl} \cos \theta_0 - f_{la} \tag{4}$$

where f_{sl} and f_{la} are, respectively, fractional geometrical areas of the solid-liquid and liquid-air interfaces under the droplet. For certain surfaces with extreme surface topography a drop of water will rest on top of the 'peaks' of the surface rarely coming into direct contact with the solid material found in the 'valleys' of the surface. As the amount of air pockets trapped under the water drop increases, so does the observed contact angle [11]. In addition, an increase in trapped air results in a reduction in real contact area (since only the tops of the 'peaks' are in direct contact with the drop) which reduces the adhesion forces between the drop and the surface. With reduced adhesion forces between the drop and the surface, a lower surface tilt angle is needed to cause the drop to roll off the surface. When the drop rolls over the surface it collects dirt and contamination particles that are easily removed because their surface adhesion forces are reduced in the same manner as the drop's surface adhesion forces, as has been shown in many studies on the self-cleaning properties of rough surfaces [e.g. 6, 12].

Both quaking and bigtooth aspen leaves were found to have surface structures (figures 1–4, Table 1) very similar to the well-known extremely hydrophobic lotus leaves that have been the focus of a large number of studies [e.g. 13–16] over the past several years. These types of leaves possess surface topographies very similar to those described by Cassie and Baxter. When a drop of water is placed on one of these leaves, its shape remains almost completely spherical and it rests on top of the micro-papillae 'peaks'. When a small external force is applied to the drop (wind, gravity, etc.) it begins to roll from 'peak' to 'peak' collecting dirt and contamination particles along its way. The nano-scale roughness features present (figures 1d and 2d) on these surfaces further enhance this observed property. As Wenzel's equation links an increase in surface roughness with an increased contact angle, the localized contact angle at each micro-papilla is higher due to the presence of the finer roughness features (i.e. nano-sized wax platelets). This further reduces the adhesion forces between each micro-papilla and the drop, those forces that must be broken to allow the drop to roll freely over the surface from one papilla to another.

4.2. Importance of moment of inertia

Not only do aspen leaves have a complex lotus-type surface structure responsible for their non-wetting properties (figures 1–4), they also have very flat leafstalks (figure 5). As summarized in table 2, the rectangular aspen leafstalks have larger width to thickness aspect ratios, resulting in much smaller moments of inertia (I) given by equation (5):

$$I = w\, t^3 / 12 \tag{5}$$

when compared to maple leafstalks which show a more square shaped cross-section. Since moment of inertia is a measure of a specific geometry's ability to resist bending deformation [e.g. 17] it can be concluded that quaking and bigtooth aspen leafstalks have approximately one order of magnitude lower resistance to bending compared to maple leafstalks. This allows the leaves to freely shake in the presence of the slightest breeze: further facilitating water roll off.

4.3. Effects of temperature and surfactant concentration

It was previously shown that different environmental conditions (e.g. temperature and water content) can have a fairly drastic effect on the contact angles of superhydrophobic leaves [e.g. 6, 18]. Table 3 and figure 6 show that the water contact angles on bigtooth aspen leaves are more susceptible to changes in water surfactant concentrations than quaking aspen leaves. This signifies that bigtooth aspen leaves undergo the transition from Cassie/Baxter to Wenzel wetting regimes at lower surfactant concentrations compared to quaking aspen leaves, indicating their reduced ability to resisting wetting. This difference may be attributed to the variation in surface structures of both leaves. As shown in table 1, the papillae on the surface of a quaking aspen leaf are almost 40% shorter and smaller (diameter) than those found on the bigtooth aspen leaf. These smaller protrusions appear to be more effective in resisting wetting at all surfactant concentration investigated. Even at the highest surfactant concentration tested (100 g/L) quaking aspen leaves still exhibited a contact angle of 122°, while the bigtooth aspen at the same concentration had a contact angle of only 89°. However, both aspen leaves maintained a higher contact angle for all surfactant concentrations then maple leaf, Teflon™ and Plexiglas™ surfaces. Teflon™ and maple leaf surfaces, both slightly hydrophobic ($\theta_0 > 90°$), exhibited much more drastic decreases in contact angles with increasing surfactant concentration compared to the aspen leaves. This result indicates that the combination of dual-scale structure and hydrophobic surface chemistry of the aspen leaves is better suited to withstand the effect of surfactant wetting agents than hydrophobic surface chemistry alone. Plexiglas™, the only surface tested that was hydrophilic ($\theta_0 < 90°$), experienced a relatively smaller drop in contact angle with increasing surfactant concentration compared to the other samples. Surfactants, designed to be wetting agents, are used to allow liquids to more easily wet different types of surfaces. Since Plexiglas™ is already wetted without a wetting agent, the effect of the surfactant is significantly reduced on this surface. It should be noted that the possibility of leaves being exposed to high concentrations (> 5 g/L) of any type of surfactant in their natural environment is likely extremely rare. At lower, more expected surfactant concentrations (< 1 g/L) both aspen leaves retain relatively high contact angles and the ability to remain dry.

Figure 7 illustrates the decrease in water contact angle of both aspen leaves with increasing temperature. This graph can be broken down into three distinct regions. Region 1 ranges from 20°C–40°C and incorporates negligible or very small (< 6°) decreases in contact angles with increasing temperature. Region 2 ranges from 40°C–70°C and accounts for a rapid decrease in contact angle, while region 3, ranging from 70°C–90°C, shows an almost constant contact angle. Both quaking and bigtooth aspen leaves show very similar responses to increasing temperatures, however quaking aspen leaves appear to be slightly more resistant, requiring higher temperatures to achieve the same decrease in contact angle compared to bigtooth aspen. These changes can be explained by comparing figure 9 (SEM images of both aspen leaf surfaces after being heated to 90°C) with figures 1 and 2. After heating, each leaf still exhibits their micro-scale papillae, but most of the finer, nano-scale wax platelets have disappeared (figure 9). It has been suggested that it is the localized melting of these wax platelets that causes a drop of contact angles in other leaves [6]. In the absence of these small surface features the leaves are significantly smoother thereby reducing their roughness factor (R_f) and the observed water contact angle. However, even on hot summer days (e.g. +35°C) leaf temperatures are only ~ 5°C higher than their surroundings [19], which corresponds to less than a 10° decrease in contact angle for the two aspen leaves. Even at these high leaf temperatures both aspen surfaces remain superhydrophobic, and consequently dry.

4.4. Effect of water drop size

Figure 8 illustrates the effect of water drop size on the measured contact angle for both aspen leaves. This graph shows a general trend of slightly decreasing contact angles with increasing drop sizes. This response can be explained by considering the effect of gravity on the larger water drops. The increased weight of the larger water drops results in a stronger gravitational force that alters the curvature and shape of the droplet resulting in a decreased contact angle [20]. Although the contact angle decreases slightly with increasing droplet size, the leaves retain their extremely high contact angles throughout a considerable range of different rain droplet sizes they will be exposed to.

4.5. Design significance

In summary, decreases in contact angles were exhibited over the experimented ranges for temperature, surfactant concentration and droplet size. However, the ranges of temperatures and surfactant concentrations studied here far exceed the conditions present in the aspens' natural habitats. When considering the conditions their leaves are naturally exposed to, the reductions in contact angles are relatively small and the leaves retain their ability to remain dry for a fairly large range of drop sizes.

The aspen leaves' non-wetting properties are further augmented by their slender leafstalks which allow for significant shaking in the presence of the slightest breeze resulting in dry leaves—even when their surfaces are not displaying optimal non-wetting properties. The combination of non-wetting surfaces and low resistance to leafstalk bending facilitates rain water roll-off and results in dry leaves, in a variety of different environmental conditions. These non-wetting characteristics might increase the growth and survival rate of the aspen trees by allowing more rain to reach the forest floor and less to be evaporated off the leaf surfaces back into the atmosphere. This could result in a higher water potential in the soil surrounding aspen trees compared to other trees that do not possess non-wetting leaves. The increased soil water potential, coupled with low leaf water potential would drive more water (and nutrients) from the soil up through the trunk of the tree and into the leaves promoting higher rates of photosynthesis and respiration [21]. In addition, the leaves after a rain fall would be much cleaner than they were before thereby minimizing the chance of having a film of dirt or contamination that might interfere with subsequent photosynthetic reactions. This would be an interesting topic to be investigated through a plant physiological approach to gain a better understanding of the mechanisms behind these species' great ability to grow and survive.

The very effective combination of superhydrophobic surface structure and mechanical motion to create dry and clean surfaces, as demonstrated here for the aspen leaves, could be of considerable importance in the design of bio-inspired engineering applications such as complex-shaped self-cleaning highway signage, anti-icing surfaces for aircrafts and power lines, sporting goods or low-drag, water-immersed articles. Potentially a template based approach, to impart the desired surface features, coupled with the appropriate structural design, could be implemented to obtain this effect for different engineering applications.

5. CONCLUSIONS

Bigtooth and quaking aspen trees have extremely hydrophobic leaf surfaces. As for the case of the lotus leaf, this desirable property arises from the leaves' complex dual-scale surface structure containing micro-sized papillae and nano-sized wax platelets. This surface structure increases the observed water contact angle and decreases the water/surface adhesion forces resulting in a clean, dry leaf. However, in comparison to the relatively static, surface floating lotus leaf, the aspen leaves have one additional important design factor that allows them to maintain dry and clean surfaces. This is their large width to thickness aspect ratio of their leafstalks which reduces their resistance to bending and results in excessive leaf motion even when there is no noticeable breeze. While both leaves showed a decreasing contact angle with increasing temperature and surfactant concentration, they still retain their hydrophobic properties over a fairly wide range of environmental conditions, including the conditions they could be exposed to in their natural habitat. Leaves that remain dry and are cleaned by a rainfall are better suited for many important biological functions when compared to wet, contaminated leaves. Increased soil water potentials and the elimination of possible contamination films likely promote higher photosynthesis and respiration rates. These smart leaf structure design factors may help aspens to grow very rapidly and thrive in a wide variety of habitats. Similar design factors may be useful in the development of future superhydrophobic/self-cleaning surfaces for a variety of engineering applications.

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