BIOLOGY INSPIRED NANO-MATERIALS:
SUPERHYDROPHOBIC SURFACES

by

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Department of Materials Science and Engineering
University of Toronto

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Abstract

In this research, a low-cost template-based process has been developed to structure the surfaces of polymeric materials rendering them superhydrophobic. This biology-inspired approach was developed using results from the first part of this thesis: the first known detailed study of superhydrophobic aspen leaf surfaces. Aspen leaves, similar to lotus leaves, possess a dual-scale hierarchical surface structure consisting of micro-scale papillae covered by nano-scale wax crystals, and this surface structure was used as a blueprint in the structuring of templates. These distinctive surface features coupled with a hydrophobic surface chemistry is responsible for these leaves’ extreme non-wetting property. Non-wetting is further augmented by the unique high aspect ratio aspen leafstalk geometry. The slender leafstalks offer very little resistance to twisting and bending, which results in significant leaf movement in the slightest breeze, facilitating water droplet roll-off.

The structured template surfaces, produced by sand blasting and chemical etching of electrodeposited nanocrystalline nickel sheets, resemble the negative of the superhydrophobic aspen leaf surfaces. Re-usable templates were subsequently employed in a hot embossing technique where they were pressed against softened polymers (polyethylene, polypropylene and
polytetrafluoroethylene) thereby transferring their surface structures. The resulting pressed polymer surfaces exhibited features very similar to aspen leaf surfaces. This process increased the water contact angle for all pressed polymers to values above 150 degrees. Additionally, after pressing the water roll-off angle for all polymer surfaces dropped below 5 degrees. The effects of water surfactant concentration, water drop size and temperature on the wetting characteristics of the structured polymers were studied to indicate in which applications these functional surfaces could be most beneficial. Coupling this attractive superhydrophobic surface property with mechanical motion (shaking, bending, or vibrating) could result in superhydrophobic surfaces with superior non-wetting properties suitable for a wide range of applications.
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List of Acronyms

CA  contact angle
CAH contact angle hysteresis
CE  chemical etching
CVD chemical vapour deposition
ESNi large grain nanocrystalline nickel (50-100nm)
nNi small grain nanocrystalline nickel (23.9nm)
Ni200 polycrystalline nickel
PDMS polydimethylsiloxane
PE  polyethylene
PMMA polymethyl methacrylate
PP  polypropylene
PTFE polytetrafluoroethylene
SB  sandblasting
SDS sodium dodecyl sulphate
SEM scanning electron microscope
TA  tilt angle
TEM transmission electron microscopy
XRD X-ray diffraction
### List of Variables

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>$A_{sl}$</td>
<td>actual contact area of the solid liquid interface</td>
</tr>
<tr>
<td>$A_f$</td>
<td>$A_{sl}$ projected onto a flat plane</td>
</tr>
<tr>
<td>$f_{la}$</td>
<td>fractional geometric area of the liquid air interface under a drop</td>
</tr>
<tr>
<td>$f_{sl}$</td>
<td>fractional geometric area of the solid liquid interface under a drop</td>
</tr>
<tr>
<td>$I$</td>
<td>second moment of area</td>
</tr>
<tr>
<td>$K$</td>
<td>torsional moment of area</td>
</tr>
<tr>
<td>$R_f$</td>
<td>roughness factor</td>
</tr>
<tr>
<td>$S$</td>
<td>spreading coefficient</td>
</tr>
<tr>
<td>$W_a$</td>
<td>work of adhesion</td>
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<tr>
<td>$W_c$</td>
<td>work of cohesion</td>
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</tr>
<tr>
<td>$\Theta_{ADV}$</td>
<td>advancing contact angle</td>
</tr>
<tr>
<td>$\Theta_{CB}$</td>
<td>Cassie and Baxter’s contact angle</td>
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<td>receding contact angle</td>
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<td>$\Theta_W$</td>
<td>Wenzel’s contact angle</td>
</tr>
<tr>
<td>$\varphi_B$</td>
<td>shape factor for elastic bending</td>
</tr>
<tr>
<td>$\varphi_T$</td>
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</table>
Chapter 1

1 - Introduction

For hundreds of years human beings have observed and been fascinated by the great diversity of biological species and the astonishing feats that they are able to accomplish. The development of airplanes, one of the first biology inspired devices, was motivated by the observation of birds in flight. In fact, the word aviation is derived from the Latin word *avis* which means bird. At this point in history very little was known about the different mechanisms of flight, but the observation of many different creatures soaring through the air sparked the interests of engineers and scientists to gain a better understanding of this amazing achievement.

Another great example of biological inspiration surrounds the origin of Velcro™. The creator of this simple yet effective fastening device, George de Mestral – a Swiss electrical engineer, was inspired by observing his dog’s legs after a walk through a local forest [McSweeny 1999]. He saw that many small burrs had securely attached themselves to the hair of his pet. After careful microscopic examination he found that the exterior of the burrs were covered by
hundreds of tiny stiff hooks. These tiny hooks were very effective at adhering to the soft tangled network of hair found on his pet. He envisioned the possibility of reversibly binding two materials if he could figure out how to artificially duplicate both the hooks on the burrs and the tangled network of hair on his dog. Today, this removable fastening device is extensively used for many different applications all over the world.

The idea of observing, understanding and learning new concepts from nature for the duplication of attractive biological properties is called ‘biomimetics’ and has recently been gaining a lot of interest with engineers at the forefront of advanced materials/device development [Bhushan 2007]. In one particular example these attractive biological properties are created through elegantly designed surfaces or interfaces containing structural features on the micro or nano-scale. With advancements in characterization techniques such as electron microscopy, observation of these tiny features is now possible allowing for a greater understanding of their mechanisms.

Since the 1990’s superhydrophobic and self-cleaning leaf surfaces have been studied in great detail; the most popular and first to be thoroughly examined being the lotus leaf [Barthlott and Neinhuis 1997; Bhushan and Jung 2006; Cheng et al. 2006; Koch et al. 2008; Neinhuis and Barthlott 1997]. From electron microscopy it has been shown that the extreme non-wetting properties of these leaves arise from a hierarchical dual-scale surface structure consisting of micro-scale papillae covered with nano-scale wax crystals [Cheng and Rodak 2005; Cheng et al. 2006; Koch et al. 2009]. Superhydrophobic leaf structures, possessing these non-wetting surface features, have been used as a biological blueprint in the structuring of a variety of materials, rendering their surfaces highly water-repellent [Burton and Bhushan 2005; Nosonovskiy and Bhushan 2007; Shirtcliffe et al. 2004; Thieme et al. 2001]. However, many of these structuring
processes are expensive and/or have size limitations that restrict their use for practical applications. Although there has been a considerable effort to characterize and mimic these leaf surfaces, less is known about the exact mechanism(s) for the formation of their surface features, and how they react to different external environmental stresses.

The aim of this research project is two-fold. First, to gain an understanding of the superhydrophobic wetting properties found on quaking and bigtooth aspen leaves: two species that have not been previously analyzed in this respect. To accomplish this, a detailed investigation into the structure/property relationship of these leaves’ surfaces and the effects of different environmental conditions on the formation of their surface features will be performed. Secondly, to use this new information to develop a low-cost, easily scalable structuring process to duplicate the surface features found on these aspen leaves onto engineering polymers using a template based approach.

This thesis is organized in the follow manner. Chapter 2 reviews the theory behind this attractive non-wetting property and presents many different naturally occurring superhydrophobic surfaces. Currently available synthesis techniques and their limitations are discussed with an emphasis on current and potential future applications. This chapter concludes with a detailed statement of research objectives.

Chapter 3 describes the steps taken for leaf sample preparation and the characterization techniques used to analyze the surface structures and wetting properties of the different surfaces investigated in this research project.

Chapter 4 introduces the two aspen trees investigated and gives a detailed description of their surface structures and wetting properties. In this chapter the effects of temperature, drop
size and surfactant concentration on these aspen leaves’ water contact angles are reported, and potential growth advantages resulting from their non-wetting leaf surfaces coupled with their high aspect ratio leafstalk geometries will be discussed. Their slender leafstalks further facilitate water droplet roll off through excessive shaking in the presence of small external forces such as wind. This chapter concludes with a section presenting the influences of different weather conditions on the wetting behaviour and surface structures of quaking aspen leaves harvested throughout the summer of 2011.

Chapter 5 describes the efforts taken to create a dual-scale hierarchical surface structure on metallic template surfaces that can be employed to structure softened polymers using a hot-embossing technique. An overview of the template synthesis techniques and results from specific experimental surface structuring methods are presented. Images of the surface structures and wetting property data of a variety of potential templates are given and used to determine the optimal template structuring process that results in the highest pressed polymer contact angles. This chapter concludes with a recommended metallic template that was subsequently used to press and structure softened polymer surfaces.

Chapter 6 presents an overview of the polymer pressing process and a detailed surface characterization of pressed polyethylene, polypropylene and polytetrafluoroethylene samples. Additionally, water contact angles and the effects of temperature, drop size and surfactant concentration on these values are examined. This chapter also discusses low-cost production scalability for the described pressing process that can result in the fabrication of large surface areas or complex shaped products possessing this attractive non-wetting property.
Respectively, chapters 7 and 8 give the conclusions and suggested future work for this research, and are followed by a list of references used throughout this study.
Chapter 2

2 – Superhydrophobic and Self-Cleaning Surfaces

This chapter introduces superhydrophobic/self-cleaning surfaces and the fundamentals in wetting properties that are necessary to understand this attractive non-wetting effect. Both naturally occurring and synthetic superhydrophobic surfaces are discussed and currently available synthesis techniques, their limitations and potential applications are examined. This chapter concludes with the motivation for this research based on two observations, and a detailed set of research objectives.

2.1 Basic Wetting Properties

The contact angle ($\theta_0$) is the quantitative measure of the wetting of a solid by a liquid. Thermodynamically it can be thought of as a balance between the interfacial energies for the
three phases present (solid, liquid, vapour). Young’s equation relating this balance is shown in equation 2.1:

\[ \gamma_{lv} \cos \theta_0 = \gamma_{sv} - \gamma_{sl} \]  

(2.1)

where \( \gamma_{lv} \), \( \gamma_{sv} \) and \( \gamma_{sl} \) refer to the interfacial energies of the liquid/vapour, solid/vapour and solid/liquid interfaces [Callister 2003]. A schematic diagram illustrating a water drop resting on a solid surface is given in figure 2.1. Equation 2.1 accounts for the difference in chemical nature of the three phases present and assumes that the solid surface is microscopically smooth.

![Figure 2.1: A water drop on a surface illustrating the contact angle (\( \theta_0 \)) and the relative interfacial energies. (\( \gamma_{lv} \): liquid/vapour interfacial energy, \( \gamma_{sv} \): solid/vapour interfacial energy and \( \gamma_{sl} \): solid/liquid interfacial energy).](image)

When a liquid droplet encounters a solid surface it may wet the surface to varying degrees. For a hydrophilic solid surface, water droplets will spread out and wet the surface resulting in a contact angle (CA) less than 90\(^\circ\); however, for hydrophobic surfaces a contact angle greater than 90\(^\circ\) will be created which is characteristic of dewetting surfaces. The difference in contact angles for these two types of surfaces arises from differences in the chemical nature of solid surfaces and liquid droplets. For hydrophobic surfaces, the energy
associated with the solid/vapour interface is lower than that for the solid/liquid interface. This results in a free energy driving force to create a small solid/liquid interfacial area, a large solid/vapour interfacial area and consequently, a contact angle above 90°. For hydrophilic surfaces the free energies of these interfaces are reversed resulting in a contact angle below 90°.

In general there are five types of wetting on solid surfaces which are shown schematically in Figure 2.2 with their contact angles indicated. Contact angles can range from 180° to 0° depending on the magnitude of the solid/vapour and solid/liquid interfaces. If a liquid creates a contact angle of 180° with a solid, a complete non-wetting condition is present and the droplet will only be in contact with the solid at one specific point (figure 2.2a). If the contact angle formed is above 150°, the surface is considered superhydrophobic (figure 2.2b). The majority of solid surfaces are classified as hydrophobic (150° > CA ≥ 90° - figure 2.2c) or hydrophilic (CA < 90° - figure 2.2d). In the case of complete wetting liquid drops easily spread out over the entire surface forming a thin liquid layer on top of the solid (figure 2.2e). A contact angle of 0° is characteristic of this type of wetting condition.

The spreading coefficient (S) is another useful way to describe the amount of wetting that will occur with a given solid surface and liquid drop. This coefficient is defined as the difference between the work of adhesion ($W_a = \gamma_{lv} + \gamma_{sv} - \gamma_{sl}$) for the solid/liquid interface and the work of cohesion ($W_c = 2\gamma_{lv}$) for the specific liquid [Jastrzebski 1987]. It is known that a liquid will spread over a solid surface if the spreading coefficient ($S = W_a - W_c$) is positive, and will not spread if this value is negative. Equation 2.2 [Jastrzebski 1987] gives the simplified version of the spreading coefficient in terms of the three interfacial energies present when a liquid comes in contact with a solid:
\[ S = \gamma_{sv} - (\gamma_{lv} + \gamma_{sl}) \]  

(2.2)

This equation indicates that spreading of a liquid on a solid surface will occur if \( \gamma_{sv} > (\gamma_{lv} + \gamma_{sl}) \). This is why solid surfaces with very low interfacial energies (\( \gamma_{sv} \)) such as many polymeric materials are much harder to wet by a given liquid than solids with larger \( \gamma_{sv} \) values.

Figure 2.2: Five types of wetting on solid surfaces: complete non-wetting (a), superhydrophobic (b), hydrophobic (c), hydrophilic (d) and complete wetting (e) [modified after Jastrzebski 1987].
2.2 Advanced Wetting Properties

When a liquid droplet encounters a rough solid surface, it may either form a homogeneous or a heterogeneous interface. A homogeneous interface is one where the liquid comes into complete contact with the solid and no air-pockets are formed between the two phases. On the other hand, a heterogeneous interface has trapped air-pockets between the liquid and solid making multiple areas where all three phases meet. In the case of a homogeneous interface, Wenzel [1936] modified Young’s contact angle equation to incorporate the effect of surface roughness, as shown in equation 2.3:

\[ \cos \theta_W = R_f \cos \theta_o \]  

(2.3)

where \( \theta_W \) is the contact angle for a rough surface, \( \theta_o \) is the contact angle for a smooth surface (Young’s contact angle) and \( R_f \) is a roughness factor equal to the actual contact area of the solid-liquid interface (\( A_{sl} \)) divided by its projection on a flat plane (\( A_f \)): \( R_f = \frac{A_{sl}}{A_f} \). This equation indicates that if roughness is introduced into an inherently hydrophobic (or hydrophilic) flat surface, the contact angle will increase (or decrease) making the surface more hydrophobic (or hydrophilic). Figure 2.3 and figure 2.4 illustrate the effect of roughness on an inherently hydrophobic surface.

Cassie and Baxter [1944] further extended Wenzel’s equation for a homogeneous interface to include the effect of a heterogeneous interface (formation of trapped air pockets) on contact angles. In certain cases with extreme roughness within the appropriate size range, a droplet of water will rest on top of the ‘peaks’ of the surface never coming into direct contact with the solid material found in the ‘valleys’ of the surface. Within these valleys, air pockets are trapped between the solid and liquid phases which consequently alter the wetting and surface
properties of the material. Figure 2.5 illustrates the formation of a 3-phase composite solid-liquid-air interface.

![Diagram of smooth surface and effect of roughness](image)

Figure 2.3: Effect of roughness on contact angle for an inherently hydrophobic surface [Jung and Bhushan 2006].

![Graph of contact angle vs. roughness](image)

Figure 2.4: Contact angle ($\theta$) as a function of roughness ($R_f$) for various contact angles of smooth surfaces ($\theta_0$) [Jung and Bhushan 2006].
Cassie and Baxter’s [1944] equation accounts for the liquid-air and the solid-air interfaces that are created underneath a water droplet when it is placed on such surfaces, as shown in equation 2.4:

$$
\cos \theta_{CB} = R_f \cdot f_{sl} \cdot \cos \theta_o - f_{la} 
$$

(2.4)

where $f_{sl}$ (shown in green in figure 2.5) and $f_{la}$ (red in figure 2.5) are fractional geometrical areas of the liquid-solid and liquid-air interfaces under the droplet, respectively. Figure 2.6 plots the effect of roughness on the contact angle with increasing $f_{la}$ values for three inherently hydrophobic ($\theta_o = 90^\circ$, $120^\circ$ and $150^\circ$) surfaces. From equation 2.4 and figure 2.6 it can be concluded that increasing the roughness factor ($R_f$) and the fractional area of the liquid-air interface ($f_{la}$) of an already hydrophobic surface can drastically increase the contact angle.
Figure 2.6: Contact angle for a rough surface (θ) as a function of roughness factor (Rf) for various fa values on a hydrophobic surface [Jung and Bhushan 2006].

For a surface to be classified as both super-hydrophobic and self-cleaning it must have a contact angle greater than 150° and a contact angle hysteresis (θH) less than 5°. Contact angle hysteresis is the difference between the advancing (θADV) and the receding (θREC) contact angles of a moving droplet over a solid surface [Jung and Bhushan 2006]. Schematic diagrams illustrating this and a surface’s tilt angle, another method the measure dynamic wetting properties, are shown in figure 2.7. Both of these values are a direct measure of a surface’s dynamic wetting characteristics and strongly correlate to self-cleaning properties. If the hysteresis is large water droplets would not roll off the surface carrying contaminants with them, but instead they would slide slowly off the surface smearing any dirt particles/contaminants along the way. Figure 2.8 illustrates the effect of surface roughness on wetting properties and self-cleaning behaviour, and this effect is shown on a real surface in figure 2.9.
Figure 2.7: Dynamic wetting measurements. Contact angle hysteresis is defined as the difference between advancing and receding contact angles (top). Alternatively, the tilt angle is defined as the angle a surface must be tilted to initiate droplet movement (bottom) [Jung and Bhushan 2006].

Figure 2.8: Illustration of the effect of surface roughness on wetting and self-cleaning properties. The left diagram shows a water droplet sliding off a smooth surface leaving dirt and contaminants behind. The right diagram shows a beaded water droplet rolling off a rough surface carrying any dirt and contaminants with it [Barthlott and Neinhuis 1997; Forbes 2005].
“To create a super-hydrophobic surface through structuring a hydrophobic surface, it is important for the surface to be able to form a stable composite interface with air pockets trapped between the liquid and solid phases. Capillary waves, nano-droplet condensation, hydrophilic spots due to chemical surface inhomogeneity and liquid pressure can destroy the composite interface” [Jung and Bhushan 2006]. Since these factors have different characteristic length scales, a combination of nano-structures and micro-structures is required to resist their effects, indicating that a dual-scale hierarchical roughness is best suited for the creation of superhydrophobic properties.

Up to this point, most of the discussion has been focused on contact angles and how they are affected by various surface features. As stated earlier, contact angle hystereses are equally important for self-cleaning surfaces; therefore, a logical question is: how do surface features affect the contact angle hysteresis of a surface? Unfortunately, there is no simple relationship for the contact angle hysteresis as a function of roughness or fractional geometric area of the liquid-
air interface. In 2006, Jung and Bhushan carried out an experiment to investigate the effect of roughness ($R_f$) and fractional geometric area of the liquid-air interface ($f_{la}$) on the hysteresis contact angle. They observed that for a homogeneous interface ($f_{la} = 0$) increasing roughness leads to an increase in the contact angle hysteresis, while for a heterogeneous interface ($f_{la} > 0$), increasing roughness provides both a high contact angle and a small contact angle hysteresis [Jung and Bhushan 2006]. This indicates that a combination of micro-features, that create a composite interface under droplets, and nano-features, which drastically increase the overall roughness of the surface, is optimum for obtaining a super-hydrophobic and self-cleaning surface. In lieu of these wetting property principles, it is apparent that surface topography is more crucial than surface chemistry for superhydrophobic surfaces: as long as the material’s inherent contact angle is above 90°.

2.3 Superhydrophobic Surfaces in Nature

There is a wide variety of superhydrophobic surfaces found in nature. Most of these are found on the surfaces of plants or insects. This section presents many different naturally occurring superhydrophobic plant surfaces, while superhydrophobic surfaces found on insects are discussed in appendix 1.

Many plant surfaces display a similar type of extreme non-wetting behaviour with the most well known being the extensively studied lotus leaf [Barthlott and Neinhuis 1997; Bhushan and Jung 2006; Cheng et al. 2006; Koch et al. 2006]. Similarly, the origin of this property for plants is a combination of a dual-scale hierarchical surface structure coupled with a low surface energy material: for plants, this material is their hydrophobic epicuticular waxes (waxes on top
of the cuticle). These waxes usually consist of a mixture of aliphatic hydrocarbons and/or their derivates, with the main components being primary and secondary alcohols, ketones, fatty acids and aldehydes [Koch and Ensikat 2008]. Long chain carbon molecules containing one or two hydroxyl groups (nonacosanol – \( \text{C}_{29}\text{H}_{60}\text{O} \) or nonacosanediols – \( \text{C}_{29}\text{H}_{60}\text{O}_2 \) (figure 2.10)) account for the majority of the wax crystal chemistry.

![Molecular structures of two alcohol molecules found in epicuticular waxes - nonacosanol and nonacosanediols: courtesy of NIST standard reference data.](image)

Figure 2.10: Molecular structures of two alcohol molecules found in epicuticular waxes - nonacosanol and nonacosanediols: courtesy of NIST standard reference data.

More often than not epicuticular waxes show great morphological variability, however they usually form three-dimensional structures having sizes within the nano-scale. Multiple different wax crystal configurations, such as 3D nano-platelets, rods, tubules and flakes have been observed on many different plant leaf surfaces [Koch et al. 2006; Koch et al. 2008]. In most cases, these hydrophobic 3D wax crystals are superimposed on top of an array of micro-scale protrusions (called papillae) usually created by convex upper epidermal cells (figure 2.11) [Neinhuis and Barthlott 1997]. The combination of these papillae and hydrophobic 3D nano-scale wax crystals imparts the non-wetting property that certain plant leaf surfaces display [Barthlott and Neinhuis 1997; Parkin and Palgrave 2004]. In 1997, Neinhuis and Barthlott conducted a detailed analysis on the surface morphology and related wetting properties of close to 200 plant species. Figure 2.12 shows SEM images for eight of the leaf samples they studied all of which show one important commonality. All eight surfaces are covered by a dual-scale
A hierarchical surface structure consisting of an array of micro-scale convex epidermal cells or papillae and nano-scale hydrophobic wax crystals that give these surfaces their superhydrophobicity.

Figure 2.11: Cross-sectional schematic diagram of a leaf [Davidson 2005].
Figure 2.12: Micromorphological characteristics of water-repellent leaf surfaces. Water repellent leaf surfaces of *Hypericum aegypticum* (A) and *Marsilea mutica* (B) are due to convex epidermal cells and a dense layer of epicuticular waxes. Bars=20 μm. C, *Nelumbo nucifera*; D, *Lupinus polyphyllus*. Every epidermal cell forms a papilla and is superimposed by a dense layer of epicuticular waxes. Bars=50 μm. E, *Gladiolus watsonioides*; F, *Sinarundinaria nitida*. The epidermal cells are subdivided into several papillae and covered by epicuticular waxes. Bars=20 μm. Increased roughness due to a differentiation within the wax layer: on the leaf surfaces of *Tropaeolum majus* (G) wax tubules aggregate to form larger clusters, while in *Melaleuca hypericifolia* (H) the wax layer is characterized by larger single platelets. Bars=20 μm [Neinhuis and Barthlott 1997].
A very interesting variation of this type of structure is found on the leaf surfaces of *Salvinia molesta*, a floating water fern. This species has tailored the wetting properties of certain parts of its surface to allow for significant air-retention when submerged (similar to the thorax of water treaders - Figure A1.5). These floating leaves are covered by a dense layer of complex multicellular hairs that are coated with nano-scale wax crystals. These hairs are split into four separate sub-hairs that join at their ends creating an eggbeater type structure (figure 2.13b and c). Nano-scale wax crystals (figure 2.13d) are present on every part of these structures except where the sub-hairs meet resulting is this local area being hydrophilic, while the rest of the surface is superhydrophobic. This causes only the eggbeater tips to adhere strongly to water drop surfaces and the rest of the surface is conducive to the formation of trapped air pockets [Barthlott et al. 2010]. The overall outcome of this elegant surface design is an extremely stable air-water interface created by the combination of hydrophobic repulsion (pushing the air-water interface away) and hydrophilic pinning at the eggbeater tips (attracting the air-water interface). This effect is enhanced by the elastic properties of the eggbeater hairs that allow them to experience relatively significant movement (caused by the air-water interface trying to penetrate closer or move away from the leaf) without breaking or being damaged. The end result is that these leaves are able to exhibit extremely high water contact angles while simultaneously having a very stable air-water interface.
2.4 Superhydrophobic Synthesis Techniques and their Limitations

To fabricate superhydrophobic surfaces using a template-based approach there are two main requirements: 1) the surface must be sufficiently rough to allow for the formation of trapped air pockets underneath water droplets and 2) the surface should be a low surface energy material that is inherently hydrophobic ($\theta_o > 90^{\circ}$). These conditions present two possible avenues for the production of superhydrophobic surfaces: roughening the surface of an inherently hydrophobic material or chemically modifying the rough surface of an inherently hydrophilic ($\theta_o < 90^{\circ}$) material. It is important to note here that roughness (surface topography) is considered to be the more critical property compared to low surface energy (surface chemistry).
[Bhushan and Jung 2011]. This conclusion has been made after recognizing that moderately and extremely hydrophobic smooth surfaces can display similar extreme non-wetting behavior when roughened to the same degree. Figure 2.14 gives a comprehensive list of the types of fabrication methods that have been used to create these types of functional surfaces.

![Fabrication techniques for creating micro/nanoroughness](image)

Figure 2.14: Typical methods to fabricate micro/nanoroughened surfaces [Bhushan and Jung 2011].

Over the past decade, there have been many successful attempts at artificially reproducing the surface structures found on natural superhydrophobic surfaces. However, many of these approaches are time consuming, expensive and/or have size restrictions that limit their use for practical applications. Common methods to create roughened dual-scale superhydrophobic surfaces are lithography [Bico et al. 1999; Oner and McCarthy 2000; Furstner et al. 2005; Martines et al. 2005; Cappella and Bonaccurso 2007], deposition [Erbil et al. 2003; Shirtcliffe et al. 2003; Hikita et al. 2005; Shang et al. 2005; Sarkar et al. 2010; Huang et al. 2011], chemical vapour deposition (CVD) [Lau et al. 2003; Huang et al. 2005; Sarkar et al. 2010], chemical etching [Qian and Shen 2005], plasma etching [Jansen et al. 1995; Teshima et al. 2005], self-assembly [Zhai et al. 2004] and nanocasting [Sun et al. 2005]. All of these
fabrication methods have one crucial commonality: they all create rough patterned or porous surfaces which have methyl or fluorine (chemically hydrophobic) terminal groups or to which a thin hydrophobic layer (low surface energy material) can be applied. Lithography and plasma enhanced CVD are expensive methods that use nanomasks and costly equipment to produced a highly structured surface. Etching procedures seem to be the most promising for a low-cost approach, but to date there have not been any publications indicating that large scale production or structuring of complex geometries can easily be achieved using this method.

Photolithography was employed by Bhushan and Jung [2007] to produce a patterned silicon surface that was subsequently rendered hydrophobic by means vapour phase deposition to apply a self-assembled monolayer of 1,1,-2,2,-tetrahydroperfluorodecytrichlorosilane (figure 2.15).

Figure 2.15: Surface height maps and 2D profile of the patterned Si surfaces using an optical profiler. The diameter and height of the pillar are D and H, respectively. The pitch of the pillars is P [Bhushan and Jung 2007].
Shirtcliffe et al. [2004] created a dual-scale copper surface by means of electrodeposition in a copper sulphate solution on to flat copper resulting an array of micro-scale features they call ‘chocolate chip cookies’ (figure 2.16). Afterwards they coated this surface with a fluorocarbon hydrophobic layer which drastically lowered the surface energy of their material and rendered their samples superhydrophobic.

![Figure 2.16: A) Scanning electron micrograph of electrodeposited copper. B) Drop of water on surface A, contact angle = 136°. C) Scanning electron micrograph of electrodeposited copper with copper ‘chocolate chip cookies’. D) Drop of water on surface C, contact angle = 160°. The electron micrographs were taken at an angle of 45° to emphasize roughness [Shirtcliffe et al. 2004].](image)

Chong et al. [2006] used a nanoporous anodic alumina template and a patterned porous gold film as a working electrode to selective electrodeposit a hierarchical nanowire array with periodic microscale voids that displayed a strong non-wetting property (figure 2.17).
Figure 2.17: SEM images of hierarchical nanowire arrays on substrate. (a) Top view of the nanowire arrays with hexagonally organized microvoids over large areas. (b) High magnification SEM image of (a). (c) Side view of the cleaved sample from (a), the concaves caused by voids are clearly apparent. (d) Side view of Au/Ni/Au/Ni segmented nanowire arrays. The side view shows clear contrast; brighter segment is gold portion. Scale bars in (c) and (d) is 500 nm [Chong et al. 2006].

Silica nanoparticles have been assembled on microsphere-patterned polymer precursors [poly(allylamine hydrochloride) – (PAH) and poly(acrylic acid) – (PAA)] by way of layer-by-layer assembly [Zhao et al. 2008]. These dual-scale surfaces were then treated with a fluoroalkylsilane to lower the solid surface energy, rendering these materials superhydrophobic (figure 2.18). The observed water contact angle on these types of surfaces increases as the number of assembly cycles increases. Although this process does create surfaces with high contact angles, the main drawback is that all surfaces fabricated this way possess relatively high contact angle hystereses (~20-40°).
Nanocasting using an actual lotus leaf surface as a template is perhaps the most practical approach, but the resulting non-wetting surface is limited in size by the dimensions of the lotus leaf used. This method (figure 2.19) involves creating a template by casting liquid PDMS (polydimethylsiloxane) onto a lotus leaf [Sun et al. 2005]. Once the PDMS solidifies, the template is removed from the lotus leaf and used as a mould to create the desired superhydrophobic surface. An anti-stick monolayer is evaporated onto the mould that acts a release agent in the next step. Another batch of liquid PDMS is then poured into the template, solidified, and is easily removed (due to the presence of the anti-stick monolayer), resulting in a
direct copy of the surface structure found on a lotus leaf. As mentioned earlier, this method only results in surfaces with dimension similar to those of a lotus leaf.

Figure 2.19: Illustration of the lotus leaf replication process (nanocasting) and creation of a superhydrophobic surface [Sun et al. 2005].

2.5 Current and Potential Future Applications

For many years researchers have attempted to reproduce the surface structures found on superhydrophobic leaves with the intention of creating superhydrophobic and self-cleaning surfaces suitable for many applications: self-cleaning windows, glasses, paints, textiles and fabrics; low-friction surfaces that could minimize flow resistance in micro-fluidic channels or macro-scale pipelines; anti-adhesive surfaces to reduce contamination and oxidation of important components, anti-icing surfaces [Sarkar and Farzaneh 2009; Saleema et al. 2011] to reduce or
eliminate ice build-up on important components and surfaces with controlled electrical properties for MEMS/NEMS (micro/nano electro mechanical systems) components. For all self-cleaning applications not only can these surfaces be considered as an important labour saving approach, they will also decrease the use of environmentally harmful cleaning agents, while for the other applications the introduction of this technology will result in more efficient and effective components. Specifically for MEMS/NEMS, which require both hydrophobic surfaces and interfaces with low adhesion and friction, these types of fabricated surfaces could be very attractive.

There are currently a handful of commercially available products that exhibit this type of non-wetting behavior, most of which are focused on keeping surfaces/textiles clean, stain-free and dry. For outdoor applications this results in surfaces degrading more slowly, therefore being replaced less often.

A German paint company (Sto Corporation) has developed a fairly cost-effective (similar in cost to traditional paints) method to fabricate a superhydrophobic paint suitable for most exterior applications. Being inspired by the naturally occurring lotus leaf, they have named this product the StoCoat Lotusan™ paint. Surfaces covered with this paint are kept clean through the self-cleaning mechanism described in section 2.2 (figure 2.8-figure 2.9). Rain water does not wet the painted surface but instead rolls over it collecting dirt and contamination particles (figure 2.20). For intellectual property reasons they do not disclose how they produce this paint, but it most likely a combination of surface roughness (perhaps created by micro-particles that rise to the surface as the paint dries) and a low surface energy material (likely a chemical addition to the paint). The one drawback to this product is associated with its initial application. The company gives a very detailed curing procedure outlining a specific amount of UV light and water that
must come into contact with freshly painted surfaces. This can create a difficult situation when there is a lack of environmental control (sun shine and precipitation) during the painting and curing of large exterior walls.

Figure 2.20: Illustration of the self-cleaning effect present on surfaces painted with Lotusan™ paint: courtesy of Sto Corporation.

Another effective superhydrophobic product has been developed by a company called Nano-Tex. Through the use of a proprietary polymer additive in the production of cotton threads, this company has developed cost effective non-wetting, stain resistant fabrics that have been used to produce many different types of functional clothing. Traditional polymeric additives used in similar processes result in a random cross-linked network of polymer molecules on each fiber (figure 2.21 top). Using their proprietary additive causes polymeric molecules to align (figure 2.21 bottom) which allows for the formation of trapped air pockets in between them and liquid droplets, rendering these fabrics non-wetting, and consequently stain resistant. The
drawback to this product is that the created composite interface is not very stable and breaks down after a few minutes resulting in a wet or stained article. It has also been found that the non-wetting/non-staining effect disappears after multiple washing (~10-15 washes) of the clothing [Erb 2009].

Figure 2.21: Conventional cotton fiber (top) and Nano-Tex cotton fiber illustrating the aligned polymer additive molecules that give these fabrics their stain resistant properties (bottom): courtesy of Nano-Tex.

It is interesting to note that the structure of Nano-Tex cotton fibers, shown at the bottom of figure 2.21 is quite similar to the superhydrophobic surface of water strider legs (Figure A1.1). Both surfaces show tiny aligned hair-like features that protrude out of micro-scale cylinders: actual legs in the case of water striders, and cotton fibers in the case of the Nano-Tex product.

A company called Lotus-Effect™ has created an anti-adhesive spoon, based on the non-wetting mechanism that repels and allows very viscous liquids like honey to freely roll off its surface. Unfortunately, this product is currently not being produced in large quantities, most likely due to high production costs coupled with low prices of traditional spoons.
Another product with less practical importance, but interesting nonetheless has been created by Bandai™, the largest toy manufacturer in Japan. They have developed a maze-type game (Aqua Drop - figure 2.23) that uses water droplets instead of metal ball bearings. The object is to get the droplets to gently rest in certain parts/depressions of the maze, or travel from one area to another. Bandai has devised a method for rendering the inside polymer surface of these toys extreme hydrophobic which causes the water droplets to free roll over the surface much like metal ball bearings. Again, because of intellectual property they do not disclose their fabrication process but, based on the aforementioned discussion it is likely through the structuring of an inherently hydrophobic material. They do indicate that the base material of these mazes is polyethylene which is known to be hydrophobic.
2.6 Research Objectives

The motivation behind this research stems from two different unrelated observations. First, after an autumn rain storm multiple aspen leaves found on a wet forest floor that were almost completely dry, except for a few areas that had near spherical water drops in contact with the leaves’ surfaces (figure 2.24) were observed. This increased interests surrounding this type of non-wetting property and led to a preliminary review of superhydrophobic leaves (namely the lotus leaf) followed by the first known study of aspen leaves in this context. This detailed study indicated that one of the main contributing factors for this effect is the presence of nano-scale roughness features on leaf surfaces.
Figure 2.24: Mainly dry quaking aspen leaf (showing only a few near spherical water drops) that was collected from a forest floor after an autumn rain storm.

The second observation came from a previous research project on the corrosion behaviour of nanocrystalline nickel electrodeposits produced in the Nanomaterials Research Group at the University of Toronto in collaboration with Integran Technologies Inc. (Toronto, Ontario). Results from this study showed that nanocrystalline nickel exhibits an extreme roughness surface on the nano-scale after nitric acid exposure (figure 2.25).

Figure 2.25: Nanocrystalline nickel that was exposed to nitric acid for 30 minutes [Tam 2004].
With these observations in mind, the objectives of this biology inspired research are to gain a sound understanding of the non-wetting effect found on aspen leaves and use this knowledge to develop an inexpensive and easily scalable procedure for fabricating superhydrophobic surfaces, similar to those found on aspen leaves, using Integran’s nanocrystalline nickel electrodeposits as a starting material. This material was selected for the study based on the above mentioned previous research that indicated nanocrystalline nickel exhibits an extremely rough surface on the nano-scale after being chemically etched in nitric acid [Tam 2004]. The main challenge for the current study is to produce micro-sized features on the surface of nanocrystalline nickel, knowing that nano-sized features can be created through a relatively easy chemical etching step. The overall approach is to drastically alter the surface of nanocrystalline nickel through a series of surface treatment steps (chemical etching in nitric acid included) and use this structured nickel surface as a template to press into softened polymers with the intention of creating a superhydrophobic surface on those polymers. These modified polymer surfaces were expected to have structures resembling the negative of the pitted nano-nickel, similar to the superhydrophobic features found on the aspen leaves used as the inspiration for this research.
Chapter 3

3 – Characterization Methods

This chapter gives the details about leaf sample collection and preparation. Different surface characterization techniques used in this research are introduced with their operating parameters listed. Additionally, the various types of wetting property measurements performed are described.

3.1 Leaf Sample Preparation

All leaf samples used in this research were collected from different areas in southern Ontario. Bigtooth (Populus grandidentata) and quaking aspens (Populus tremuloides) leaves were harvested from a natural forest near Fraserville, Ontario (44°11.43’N / 78°24.26’W and 214m altitude) and red maple leaves (Acer rubrum) were picked from a maple tree located in North York, Ontario (43°45.21’N / 79°26.88’W and 182m altitude). Lotus leaves (Nelumbo
*nucifera* were obtained from Humber Nurseries Botanical Garden in Brampton, Ontario (43°45.67’N / 79°38.70’W and 181m altitude). For most experiments, after harvesting all leaves were individually dried in books to ensure leaf edges did not curl up and macroscopically flat surfaces were available for surface characterization and wetting property measurements. Following this drying process, 1” X 1” leaf sections were cut and mounted on 1” X 1” poly(methyl methacrylate) (PMMA) coupons using double-sided scotch tape with their adaxial sides facing up. Special care was taken to ensure that no major leaf veins, wrinkles or curled edges were present on the mounted samples. This is necessary to ensure the most accurate surface structures and wetting property measurements. For conventional scanning electron microscopy (Hitachi S–4500 Field Emission Scanning Electron Microscope – SEM) and optical profilometry (WYKO Interferometric Profilometer) analysis leaf samples must be both electrically conductive and optically reflective. To achieve these surface properties all leaf samples were carbon coated (Edwards coating system – E306A) prior to electron microscopy and profilometry imaging. All wetting measurements and surface imaging were performed within 12 months of harvesting.

For a select set of leaf samples harvested during 2011 a newly available state-of-the-art environmental SEM (Hitachi SU6600 Analytical Variable Pressure Field Emission Scanning Electron Microscope) was employed for surface imaging. This advanced characterization device allows for high resolution imaging of non-conductive biological samples. Using this beneficial tool, leaf samples were able to be imaged very shortly after harvesting (within 48 hours) without carbon coating, to investigate the morphological differences between fresh and dried leaf surfaces. Additionally, this presented the opportunity to perform a detailed image analysis of the morphological changes that occur on live aspen leaves throughout a single growth season.
For the analysis of leafstalk resistance to bending and twisting, dimensional measurements were performed on fractured leafstalks. Leafstalks were cut from leaves, frozen in liquid nitrogen (to ensure a brittle failure mechanism that minimizes leafstalk deformation during fracture) and quickly fractured by bending at the leafstalks mid-point. The broken leafstalks were vertically mounted, so that their fractured cross-sections were facing up, and carbon coated. Subsequently, their cross-sectional dimensions were measured using an SEM.

3.2 Surface Characterization Techniques

Two types of surface characterization techniques were used to analyze all the surfaces in this research: scanning electron microscopy and optical profilometry. Scanning electron microscopy was employed to gain low magnification overviews and high magnification images of each surface. In some cases, samples were tilted during examination to obtain more three-dimensional images that emphasize the structural topography of the surfaces. Part way through this research an environmental SEM (Hitachi SU-6600) became available. This allowed some samples to be imaged without being coated by an electrically conductive surface layer, which has been hypothesized to potentially damage the surface features of softer, especially organic materials [Goldstein et al. 2003]. This environmental SEM allows non-conductive samples to be imaged by introducing a small amount of air into the SEM chamber. This low vacuum mode allows for the imaging of non-conductive samples at relatively low acceleration voltages without the occurrence of image degrading surface charging. Images from this SEM were taken using its environmental secondary electron detector at an acceleration voltage of 5 kV and an internal air pressure of 60 Pa. The induced variable pressure setting helps to eliminate electron charge build-
up on the surfaces of non-conductive samples. Micrographs obtained from carbon coated samples using the S-4500 were taken using a lower acceleration voltage of 1.5 kV and small working distances using the traditional non-environmental secondary electron detector.

Optical profilometry was utilized to record relatively low magnification color-coded topographical maps of all surfaces. Leaf and polymeric surfaces were carbon coated to increase optical reflectivity which is necessary for this characterization technique. Macroscopically flat sample surfaces were aligned orthogonally to the incident light beam during measurements to minimize deviations associated with sample tilt and/or curvature. Three main images resulted from this characterization technique: a surface view, a profile view and a 3D view. All of these images were used to determine the heights, widths, densities and spacings of all micro-scale surfaces features.

3.3 Wetting Measurements

Wetting measurements for all un-coated samples were performed in the same manner. For static contact angle (CA) measurements, 1” X 1” coupons with the surface to be tested facing up were placed at the front of a sample stage that had been carefully levelled beforehand. A horizontally positioned digital camera (Nikon D3000) equipped with a macro lens (Nikon – AF-S Micro Nikkor 40mm) was mounted on a tripod, levelled and adjusted so the plane of the surface being measured was centered and in line with the camera (figure 3.1). This ensured the best profile image of water droplets leading to accurate contact angle measurements. For static measurements, a controlled dispensing micro-pipette (Clonex Corporation) was used to gently place 5 µ1 droplets of de-ionized water on sample surfaces. For each droplet, at least two images
were taken and the contact angle on each side of the drop was analyzed using ImageJ’s angle measuring function. For each surface at least 5 water droplets were imaged, analyzed and the resulting contact angles were averaged to give the reported values.

Figure 3.1: Set up for contact angle measurements.

To measure a surface’s dynamic wetting properties tilt angle (TA) measurements were carried out using a home-made tilting stage. Using double-sided scotch tape, 1” X 1” samples were fastened to this stage which allowed for accurately tilting from its initial horizontal position to a vertical position. While still horizontal, a 25 µl de-ionized water droplet was gently placed on the testing surface, after which the stage was slowly tilted until this droplet began to roll/slide over the surface. At this point, the stage angle relative to horizontal was measured and recorded. This measurement was performed at least 5 times for each sample, and all reported tilt angles are averages of all measurements.
To investigate the effect of water surfactant concentration on these surfaces’ contact angles, several 5 µl droplets of solutions containing different concentrations (up to 100 g/L) of a commonly used wetting agent (sodium dodecyl sulphate, SDS – Bioshop Canada Inc.) were gently placed on each surface using the procedure described above. This experiment was performed to shed light on potential applications for these types of surfaces. In many real world cases, these surfaces would be exposed to solutions other than pure water (in many cases surfactant containing solutions) which could reduce/eliminate their non-wetting property due to the reduced surface tension of surfactant solutions. This specific anionic surfactant was employed because results of the effect of this molecule on the wetting properties of synthetic superhydrophobic surfaces has been previously reported [Mohammadi et al. 2004]. This allowed for the comparison between these previously published results and those obtained in the current study.

For the measurements of the effect of temperature on wetting properties, samples on a levelled stage in a small furnace (Thermolyne 1300) were heated to different temperatures. A small, supplementary K-type thermocouple (Omega Engineering) was kept in direct contact with the samples to ensure the most accurate temperature reading possible. At each desired temperature, the furnace door was opened, 5 µl water droplets were immediately placed on sample surfaces and a pre-aligned digital camera was used to quickly capture contact angle images. Special care was taken to minimize the duration the furnace door was kept open to guarantee reliable temperature data. This experiment was carried out to see how well these surfaces could withstand elevated water temperatures. These results will be extremely useful in determining potential applications involving the distribution of high temperature water.
To study the effect of water droplet size on the wetting properties of these surfaces, droplets with different volumes (5, 10, 15, 20, 25 µl) were placed on surfaces and analyzed in the same manner as described above. Again, in real world applications all droplets impinging on these surfaces will not be 5µl, so this experiment was employed to determine if the non-wetting property is strongly affected when exposed to larger droplet sizes.
4 - Quaking and Bigtooth Aspen Leaf Surfaces and Leafstalks

This chapter introduces and analyzes two tree species that were used as the inspiration for this biomimetic research. Their natural habitats and surface structures are discussed, and the effects of temperature, water droplet size and surfactant concentration on these leaves wetting properties are investigated. Additionally, growth and survival advantages brought forth by their superhydrophobic surface structures coupled with high aspect ratio leafstalks are considered. The last section of this chapter presents a study focusing on the effects that different weather conditions may have on the wetting properties and surface structures of these leaves.

The main results presented in this chapter have been summarized in the following publications: [Victor and Erb 2010; Victor and Erb 2012].
4.1 Description of Aspen Trees

The wetting characteristics of the leaves of quaking aspen (*Populus tremuloides*) (figure 4.1) and bigtooth aspen (*Populus grandidentata*) (figure 4.2) trees have previously not been studied. Both trees belong to the same genus and consequently possess many similarities. Quaking aspens are medium-sized trees which have almost completely round leaves with slightly pointed tips that have multiple (20-40) pairs of fine teeth on their edges. These relatively small (2-6 inches) leaves are attached to main branches with unusually flat leafstalks [Petrides and Wehr 1998]. The bark found on mature trees is mostly smooth and has a chalk white to yellow-green colouring. Quaking aspens usually reach heights of 40-70 feet and have diameters of 1-1.5 feet [Little 1980]. Bigtooth aspens are slightly smaller trees (30-60 feet tall with 1-1.5 foot diameters) with larger leaves containing fewer pairs (5-15) of bigger teeth compared to quaking aspens [Little 1980]. Similar to quaking aspens, bigtooth leafstalks are also unusually slender compared to most other tree species. One interesting aspect surrounding these species is the longevity that some aspen groves display. By combining radioactive carbon dating and aspen growth rates, it has been calculated that some aspen groves have lived more than 10 000 years: longer than many other tree species (pines, giant sequoias and California redwoods) that are commonly considered to be the leaders in prolonged life [Petrides and Wehr 1998].

Both aspen trees can be found in most areas across the North American continent and are usually situated close to each other in similar habitats. They grow from Alaska to Newfoundland and as far south as Arizona and New Mexico. They are able to grow in many soil types (esp. sandy and gravelly slopes) which allow them to thrive in a diversity of growth sites [Little 1980].
4.2 Surface Structures of Superhydrophobic Aspen Leaves

It is well known that many naturally occurring superhydrophobic surfaces exhibit a dual-scale hierarchical surface structure composed of micro-scale protrusions covered by finer nano-scale surface roughness coupled with a hydrophobic surface chemistry [e.g. Barthlott and
Neinhuis 1997; Bhushan and Jung 2011; Cheng et al. 2006; Cheng and Rodak 2005]. Lotus leaves, perhaps the most well-known naturally occurring superhydrophobic surface displays features of this type. SEM and optical profilometry images of the adaxial side of a lotus leaf are shown in figure 4.3 and figure 4.4, respectively [Victor et al. 2012]. It can clearly be seen that this surface is covered by an array of micro-scale protrusions (figure 4.3b), also known as papillae, with a finer layer of nano-scale surface roughness (3D wax crystalloids – figure 4.3d) superimposed on top.

Both aspen leaves investigated in this research display surface features very similar to the well-known lotus leaf. Respectively, figure 4.5 and figure 4.6 are SEM and optical profilometer images of the adaxial side of a quaking aspen leaf, while figure 4.7 and figure 4.8 are SEM and optical images of the adaxial side of a bigtooth aspen leaf. When comparing figure 4.3-figure 4.8, it is apparent that these three leaf surfaces exhibit very similar surfaces features. There are, however, subtle size and distribution differences of the micro-papillae between these three surfaces. The micro-scale papillae on the lotus leaf protrude further away from the surface compared to the two aspen leaves, but are much more slender. This causes the lotus leaf to have a larger density of micro-papillae but greater spacing between them. When comparing the two aspen leaves, it can be seen that the bigtooth aspen leaf has taller and wider papillae with slightly smaller inter-papillae spacing resulting in a slightly higher density. Table 4.1 contains the dimensional values obtained from optical images, for all micro-scale surfaces features found on these three leaves, and indicate that all three leaves have very similar surface structures. This table also contains average wax crystalloid sizes obtained from measuring these feature on multiple SEM images. This superhydrophobic leaf surface structure is summarized as a schematic cross-sectional diagram shown in figure 4.9.
Figure 4.3: SEM micrographs of the adaxial side of a lotus leaf: a) low magnification overview, b) and c) micro-scale papillae, d) nano-scale wax crystalloids [Victor et al. 2012].

Figure 4.4: Optical profilometry images of the adaxial side of a lotus leaf: 3D (top) and surface (bottom) views [Victor et al. 2012].
Figure 4.5: SEM micrographs of the adaxial side of a quaking aspen leaf: a) low magnification overview, b) and c) micro-scale papillae, d) nano-scale wax crystalloids [Victor and Erb 2010].

Figure 4.6: Optical profilometry images of the adaxial side of a quaking aspen: 3D (top) and surface (bottom) views [Victor and Erb 2010].
Figure 4.7: SEM micrographs of the adaxial side of a bigtooth aspen leaf: a) low magnification overview, b) and c) micro-scale papillae, d) nano-scale wax crystalloids [Victor and Erb 2010].

Figure 4.8: Optical profilometry images of the adaxial side of a bigtooth aspen: 3D (top) and surface (bottom) views [Victor and Erb 2010].
Table 4.1: Surface structure and wetting properties of superhydrophobic leaves [Victor and Erb 2010].

<table>
<thead>
<tr>
<th>Leaf</th>
<th>Average Papilla Size</th>
<th>Average Papilla Spacing/Density</th>
<th>Average Wax Crystalloid Size</th>
<th>Contact Angle (°)</th>
<th>Water roll-off angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Height (µm)</td>
<td>Diameter (µm)</td>
<td>Interspacing (µm)</td>
<td>Thickness (nm)</td>
<td>Length (µm)</td>
</tr>
<tr>
<td>Lotus</td>
<td>9.8 ±2.7</td>
<td>6.2 ±2.2</td>
<td>15.3 ±6.9</td>
<td>~100</td>
<td>~1</td>
</tr>
<tr>
<td>Quaking Aspen</td>
<td>4.2 ±1.4</td>
<td>12.5 ±3.3</td>
<td>10.1 ±5.8</td>
<td>~150</td>
<td>~1</td>
</tr>
<tr>
<td>Bigtooth Aspen</td>
<td>6.5 ±1.9</td>
<td>20 ±4.5</td>
<td>7.8 ±4.6</td>
<td>~75</td>
<td>~1</td>
</tr>
</tbody>
</table>

Figure 4.9: Schematic diagram of superhydrophobic leaf cross-section.

4.3 Wetting Properties of Superhydrophobic Aspen Leaves

Using 5µl droplets, the average static de-ionized water contact angle for lotus, quaking and bigtooth aspen leaves are given in Table 4.1 (see appendix 2 for examples of water drop
images). These values were obtained from multiple measurements on no less than 10 different samples for each leaf. Additionally, the water roll-off angle (or tilt angle – TA), using 25µl droplets are given in this table. These values indicate that all three leaf surfaces fall under the conventional criteria for superhydrophobic surfaces (both CA>150° and TA<5°) [Bhushan and Jung 2011; Mohammadi et al. 2004] as discussed in section 2.1. These extreme non-wetting properties are observed due to the combination of the unusual surface structure features on these leaves, consisting of micro-papillae and nano-scale wax crystalloids, and the associated low solid surface energy of the hydrophobic wax crystalloids [Koch et al. 2006]. The combination of these two factors causes water to bead up and easily roll-over, and ultimately off such surfaces. This property can be explained using Cassie and Baxter’s heterogeneous wetting equation (equation 2.4 – section 2.2) [Cassie and Baxter 1944]. This equation is used to describe the extent of wetting on a surface that creates a heterogeneous interface containing trapped air pockets underneath liquid droplets. Larger amounts of trapped air pockets (f_ab) and increased surfaces roughness (R_f) (nano-scale wax crystalloids) enhance this non-wetting effect. On these surfaces air pockets (visible in figure 4.10) are trapped between the micro-papillae of the leaves and the bottom surface of the droplet. This incomplete wetting of the surface results in a significantly reduced real area of contact, and consequently reduced adhesion between the droplet and the solid surface compared to a situation where complete wetting occurs. The trapped air pockets also act as a buoyancy force supporting the water droplet and inhibiting it from fully wetting between each papilla. The end result is that water droplets have very low adhesion to these types of surfaces and are easily removed with the application of a small external force (e.g. wind or gravity).
From previous research it has been shown that different environmental conditions, such as temperature and water content, can have a detrimental effect on the contact angles of superhydrophobic surfaces [Cheng et al. 2006; Mohammadi et al. 2004]. In the following three sections the effects of temperature, surfactant concentration and droplet size on the water contact angles of quaking and bigtooth aspen leaves are investigated.

4.4 Effect of Temperature on Water Contact Angles

Figure 4.11 plots the reduction in water contact angle for both aspen leaves as temperature increases. Both aspen leaf surfaces show very similar responses to increasing temperatures; however quaking aspen leaves require higher temperatures to achieve the same reduction in contact angle compared to bigtooth aspen leaves, indicating they appear to be
slightly more resistant to elevated temperatures. These responses can be broken down into three distinct regions, clearly visible in figure 4.11. Region 1 shows negligible (<6°) decreases in contact angles with increasing temperature from 20°C-40°C. Region 2, ranging from 40°C-70°C, accounts for the majority of the reduction in contact angles (~65°) while region 3, incorporating temperatures above 70°C, exhibits nearly constant contact angles.

**Figure 4.11:** Effect of temperature on the water contact angle of aspen leaves [Victor and Erb 2010].

Figure 4.12 displays SEM images of both aspen leaves after being heated to 90°C. These images can be used to explain the changes in wetting properties associated with leaf samples at increased temperatures. After comparing figure 4.5c and figure 4.7c with figure 4.12, it is clear that a rather drastic change in surface structure has occurred for both leaves during heating. The vast majority of nano-scale wax crystalloids found of both aspen leaves have disappeared due to heating. Similar results were observed by Cheng et al. in 2006 when they heated lotus leaves at
150°C for 1 hour. SEM images from their study showing both heated and un-heated lotus leaf surfaces are given in figure 4.13. In the current study and the work by Cheng et al., all leaves retained their micro-scale papillae, but most of the finer, nano-scale wax crystalloids have disappeared. It has been suggested that the localized melting of these finer wax crystals is responsible for the drop in contact angles associated with increased temperatures [Cheng et al. 2006]. In the absence of these fine crystals, leaf surfaces are significantly smoother which drastically reduces their roughness factor ($R_f$) in Cassie and Baxter’s heterogeneous wetting equation (equation 2.4, section 2.2). The result is that this equation gives notably lower water contact angles: a trend that was confirmed by current experimental results.

However, even on hot summer days (e.g. +35°C) leaf temperatures are only ~5°C higher than their surroundings [Darbah et al. 2010], which corresponds to a less than 10° decrease in contact angle for the two aspen leaves. Even at these high leaf temperatures both aspen surfaces remain superhydrophobic, and consequently dry [Victor and Erb 2010]. This is an important finding for both aspen species in regards to their ability to survive and grow in their natural habitats. In other words, the leaves of these trees do not lose their beneficial non-wetting properties in the range of temperatures they are naturally exposed to (section 4.7).

Figure 4.12: SEM images of a quaking aspen leaf (a) and a bigtooth aspen leaf (b) after being heated to 90°C [Victor and Erb 2010].
4.5 Effect of Drop Size on Water Contact Angles

Figure 4.14 illustrates the effect of water droplet size on the contact angles for both aspen leaf surfaces. Most researchers studying wetting properties of solid surfaces use relatively small droplet sizes of 5 µl [e.g. Smith et al. 1989; Wu et al. 2010]. For this study larger droplet sizes were included to relate the wetting characteristics of aspen leaves to more realistic droplets sizes they may naturally encounter during precipitation. Over the range of tested drop size (5-25µl), both leaves display similarly weak linear decreases in contact angle as water droplet size was increased. These contact angle decreases can be attributed to the larger gravitational force associated with larger drop sizes. The increased weight of larger droplets results in a stronger downward force that alters the shape and curvature of the water droplets resulting in lower contact angles [Fujii and Nakae 1995]. Although contact angles decrease 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 [Victor and Erb 2010].

![Graph showing the effect of drop size on the water contact angle of aspen leaves.](image)

Figure 4.14: Effect of drop size on the water contact angle of aspen leaves [Victor and Erb 2010].

### 4.6 Effect of Surfactant Concentration on Water Contact Angles

The average contact angles for both aspen leaf surfaces as a function of sodium dodecyl sulphate (SDS) surfactant concentration are plotted in figure 4.15. Additionally, the contact angles as a function of SDS concentration for maple leaf, Teflon™ and Plexglas™ surfaces are given in this graph. These surfaces have been included in this study to compare the effects of this surfactant on smooth, non-superhydrophobic surfaces: their contact angles were measured in the same manner as described in section 3.2. The adaxial side of maple leaves are relatively smooth, organic surfaces that exhibit hydrophobic wetting properties (CA=124°), while Teflon™
(CA=112°) and Plexiglas™ (CA=77°) are synthetic polymeric materials displaying hydrophobic and hydrophilic wetting properties, respectively. With small additions of SDS, contact angles of all tested surfaces quickly dropped. As the concentration of SDS increased, contact angles for all samples began to level out and remained relatively constant as the SDS concentration was further increased above 20g/L (figure 4.15). At all concentrations tested, both aspen surfaces remained hydrophobic (CA>90°) and displayed significantly higher contact angles than all other tested surfaces. On the other hand, all hydrophobic smooth surfaces (maple and Teflon™) lost their hydrophobicity after the addition of relatively small amounts of SDS (0.4g/L) and experienced large drops in contact angles over the tested concentration range (81° and 53° reduction respectively). As expected, the hydrophilic smooth Plexiglas™ surface consistently exhibited contact angles below all other surfaces at all concentrations tested.

Figure 4.15: Effect of SDS surfactant concentration on water contact angles [Victor and Erb 2010].
These results show that the wetting properties of both aspen leaves are less susceptible to changes in SDS concentration compared to the other tested surfaces. Quaking aspen leaves appear to be slightly less affected by SDS, compared to bigtooth aspen, as they only experience a $44^\circ$ reduction in CA (down to $122^\circ$ at 100g/L), and consistently have higher contact angles than bigtooth aspen leaves. Conversely, bigtooth aspen leaf surfaces experience a $67^\circ$ drop in contact angle, resulting in a contact angle of $90^\circ$ at the highest SDS concentration tested (100g/L). This difference may be a result of slight variations in surface structures of the two aspen leaves. The micro-papillae on quaking leaves are approximately 40% shorter and thinner than their bigtooth counterparts (Table 4.1). The results indicate that these smaller protrusions are better suited to resist SDS surfactant induced wetting. Additionally, figure 4.15 clearly shows that structured superhydrophobic surfaces (aspen leaves) appear to be much more resistant to surfactants than both smooth hydrophobic and smooth hydrophilic surfaces.

Similar results were reported by Mohammadi et al. in 2004 when they investigated the effects of different surfactants solutions (SDS included) and pure liquids with similar surface tensions on the contact angles of superhydrophobic alkylketene dimer (AKD) surfaces comprised of a prickly structure containing many small micrometer-sized pores. Their results (figure 4.16) show an expected general trend of decreasing contact angles with decreasing liquid surface tension. However, the effects of pure liquids compared to surfactant solutions of the same surface tension on contact angles are quite different. For their surface, pure liquids with surfaces tensions close to 40mJ/m$^2$ create contact angles below $20^\circ$, while surfactant solutions with similar surface tensions display significantly higher contact angles ($>100^\circ$) (figure 4.16) (Mohammadi et al. 2004). Using Mysels’ experimentally derived equation:

$$\sigma \text{ (mJ/m}^2\text{)} = 68.49 – 6.516 \ln c(\text{mM}) – 3.353 \ln^2 c(\text{mM})$$ (4.1)
which relates the amount of SDS (c in mM) in a solution to its surface tension (σ in mJ/m²), a concentration of 8.16 mM (2.3 g/L) of SDS is necessary to obtain a solution with a surface tension of 40 mJ/m² [Mysels 1986]. At this concentration of SDS quaking and bigtooth aspen leaves displayed contact angles of approximately 145° and 110°, respectively, which is quite similar to Mohammadi et al.’s results for SDS surfactant solutions on superhydrophobic AKD surfaces. They attributed the differences between contact angles for surfactant solutions and pure liquids to interactions of surfactant molecules with the AKD surface that can hinder the penetration of surfactant solutions into micro-scale surface pores [Mohammadi et al. 2004]. It is suggested that similar mechanisms may be present for structured aspen leaves exposed to SDS surfactant solutions.

![Figure 4.16: Surface tension versus contact angles on a structured superhydrophobic AKD surface for different surfactant systems and pure liquids. The dotted rectangle highlights the liquids (pure liquids shown with solid symbols and aqueous solutions of surfactants shown with open symbols) with close surface tensions having very different contact angles [Mohammadi et al. 2004].](image)

It is important to note that the possibility of aspen leaves being exposed to high concentrations (> 5 g/L) of SDS or any type of surfactant in their natural environment in likely
extremely rare. At lower, more expected surfactant concentrations (< 1g/L) both aspen leaves retain relatively high contact angles and the ability to remain dry [Victor and Erb 2010]. The potential for these leaves to encounter small concentrations of surfactants from pollutants in their natural environment is low, but still possible. Nevertheless aspen leaves have demonstrated that at these low surfactant concentrations they do not lose their non-wetting property and the beneficial aspects associated with this attractive property (section 4.7).

4.7 Advantages of Smart Aspen Leaf Design Coupled with High Aspect Ratio Leafstalks

Survival for any species, plant or animal, over a long period of time is dependent on their adaptability to changing environmental conditions. These could be changes in weather patterns, changes in concentrations of atmospheric constituents or changes in the types or numbers of neighbouring organisms. Not surprisingly, the most prosperous species in our planet’s history have the ability to survive in a wide variety of conditions and/or adjust to their changing surroundings. Such adaptations allow species to survive longer and/or spread to adjacent areas that would otherwise be uninhabitable to them.

For many organisms the most important components in terms of survival are the interfaces they create with their environment [Koch et al. 2009]. The dominant interface in plants, referred to as the cuticle (figure 2.15), is a continuous extracellular membrane that covers the organisms’ above-ground organs. Collectively it represents one of the largest biosphere/atmosphere interfaces on earth, totalling more than $10^9$ km$^2$ [Koch et al. 2008].
Leaves, bark and the root system are important components where the majority of chemical and physical interactions occur between trees and their surroundings [Koch et al. 2008]. Leaves, usually having their surfaces covered in a hydrophobic wax, are the most critical and account for all the energy production for the plant (photosynthesis), respiration, transpiration and the bulk of a tree’s ability to control its internal temperature [Pallas et al. 1967]. In addition to these functions, leaves (depending on their surface wetting properties) can indirectly affect the amount of precipitation that is absorbed by the soil and consequently the root system. When less water is absorbed by the soil, mass transport through the roots diminishes, reducing the amount of beneficial minerals and nutrients entering the tree.

Aspens, one of the most widely distributed trees in North America, can thrive on a diversity of sites [Stam et al. 2008]. They grow from north-western Alaska to Newfoundland and south to northern Mexico [Johnson et al. 1995]. They are the dominant tree species in over 100 habitats across the continent, and within Minnesota, Wisconsin and Utah occupy more land than any other forest type [Howard 1996]. These trees have been observed to grow quickly in a wide variety of climates and be the first species to re-forest large areas recently destroyed by acute disturbances [Stam et al. 2008]. There are likely several reasons for this overwhelming ability to thrive in such diverse conditions. One possible explanation involves the tough root system of aspen trees and their ability to survive massive wildfire outbreaks. Following a forest fire, new stems sprout from surviving aspen root systems and quickly grow to re-colonize the affected area [Binkley 2008; Stam et al. 2008]. Perhaps there are other features related to different parts of these trees that allow for their great ability to thrive in a wide variety of environmental conditions [Victor and Erb 2010]. In order to assess the importance of the entire leaf in this context the current study also looked at the leafstalk geometry of the two aspen leaves.
in comparison with the geometry of the red maple leaf which does not exhibit superhydrophobic properties (section 4.5).

Figure 4.17 displays cross-sectional SEM images of red maple, quaking aspen and bigtooth aspen leafstalks while leafstalk dimensions measured using these images are given in Table 4.2. Both aspen leafstalks show high geometric aspect ratios and have much more slender cross-sections than their square red maple counterparts. This geometric difference results in a reduced ability of aspen leafstalks to resist bending and twisting compared to maple leafstalks. Shape factors for bending and twisting of each leafstalk, and moments of area necessary for their calculations are displayed in Table 4.3. For these calculations, it is assumed that all leafstalks are solid rectangles comprised of the same material throughout each cross-section, and they do not undergo any plastic deformation. It is also important to note that for these calculations bending is assumed to occur along the leafstalks’ weakest axis (see diagram in Table 4.3).

From Table 4.3 it is clear that both aspen leafstalks display lower shape factor values for both bending and twisting compared to maple leafstalks. These shape factors are dimensionless numbers which characterizes a geometry’s resistance to a specific type of elastic deformation [Ashby 1992]. The values in Table 4.3 indicate that maple leafstalks are approximately 80% and 40% more resistant to bending and twisting, respectively than quaking leafstalks. Additionally, they are 45% more resistant to bending and 20% more resistant to twisting compared to bigtooth leafstalks. These considerably lower resistances to elastic deformation for aspen leafstalks result in significantly more leaf movement under the application of an applied external force (e.g. wind). This easily induced mechanical motion enhances the aspen leaves’ non-wetting properties by further facilitating water droplet roll-off.
Figure 4.17: Cross-sectional SEM images of a red maple leafstalk (a), a quaking aspen leafstalk (b) and a bigtooth aspen leafstalk (c) [Victor and Erb 2010].

Table 4.2: Maple and aspen leafstalk dimensions [Victor and Erb 2010].

<table>
<thead>
<tr>
<th>Leafstalk</th>
<th>Average Width, w (mm)</th>
<th>Average Thickness, t (mm)</th>
<th>Area, A=wt (mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red Maple</td>
<td>1.1</td>
<td>0.77</td>
<td>0.85</td>
</tr>
<tr>
<td>Quaking Aspen</td>
<td>0.84</td>
<td>0.33</td>
<td>0.28</td>
</tr>
<tr>
<td>Bigtooth Aspen</td>
<td>0.95</td>
<td>0.46</td>
<td>0.44</td>
</tr>
</tbody>
</table>

Table 4.3: Calculated moments and shape factors for elastic bending and twisting of leafstalks.

<table>
<thead>
<tr>
<th>Leafstalk</th>
<th>Second Moment of Area, $I = \frac{wt^3}{12}$ (mm⁴)</th>
<th>Torsional Moment of Area, $K = \frac{t^3w}{3} (1 - 0.58 \frac{t}{w})$ (mm⁴)</th>
<th>Shape Factor for Elastic Bending, $\varphi_B = \frac{4nl}{A^2}$</th>
<th>Shape Factor for Elastic Twisting, $\varphi_T = \frac{2\pi K}{A^2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maple</td>
<td>0.0418</td>
<td>0.0994</td>
<td>0.727</td>
<td>0.864</td>
</tr>
<tr>
<td>Quaking Aspen</td>
<td>0.0025</td>
<td>0.0078</td>
<td>0.401</td>
<td>0.625</td>
</tr>
<tr>
<td>Bigtooth Aspen</td>
<td>0.0077</td>
<td>0.0222</td>
<td>0.499</td>
<td>0.720</td>
</tr>
</tbody>
</table>

* [Ashby 1992]
Coincidentally, quaking aspens, also known as trembling aspens, have interesting folklore surrounding their extensive leaf movement. “The Utes have a legend about these deciduous groves. In older days they say, the aspens were the proudest trees. When the Great Spirit visited the Earth and all other things shivered with anticipation, the aspens remained stiff and unbending. The Spirit cursed them and ordered that henceforth they should tremble whenever an eye was turned upon them” [Blevins 2001]. Moreover, the Wordsworth Dictionary of Phrase and Fable writes “The aspen leaf is said to tremble, from shame and horror, because our Lord’s cross was made of this wood” [Brewer 2006]. Regardless of these entertaining anecdotes, aspen leaves have an immense ability to keep their surfaces dry through an exceptionally effective combination of non-wetting leaf surfaces and slender leafstalks which offer very little resistance to twisting and bending. Although these surfaces display reduced non-wetting characteristics when exposed to elevated temperatures, surfactant concentrations and larger droplet sizes, it is important to note here that they retain their extremely high contact angles and non-wetting properties throughout the realistic range of these external factors that they will be exposed to in nature.

To investigate the possibility that these unique non-wetting physical traits of their leaves could be the reason why aspen trees have been able to thrive in many different climates, the effects of wet and dry leaves on the growth and survival of all types of trees have been considered. Leaf surfaces account for the majority of the area where crucial interactions necessary for tree life and growth occur. Photosynthesis, respiration, transpiration and a large amount of the tree’s ability to control its internal temperature strongly depend on leaf surfaces [Cook et al. 1964; Gates 1964; Pallas et al. 1967]. Consider a situation where all the leaves of a tree are covered in a layer of water. In this situation, diffusion of important components for
survival is significantly reduced. Typically, diffusion of oxygen and carbon dioxide is ~10 000 times larger in air than water [Berg 1983]. This would result in drastically reduced photosynthesis and respiration rates, minimizing the amount of energy produced (photosynthesis) and consumed (respiration): both of which have strongly adverse effects on plant growth and survival [e.g. Koch et al. 2009].

Transpiration/evaporation of water through leaf stomata, acts as a control for the internal osmotic pressure of each leaf and for the internal temperature of the tree [Jones 1957; Pallas et al. 1967]. For maximum efficiency each leaf should have relatively low osmotic pressure in order to draw up water and nutrients from the soil through the roots and xylem. If the leaves are covered in a layer of water their stomata will remain closed to minimize the amount water that enters the leaves and ultimately causes an unwanted increase in leaf turgidity (excessive fluid content). Without water transpiring from the leaves the osmotic pressure inside the leaf will not drop enough to allow water to be drawn up through the xylem. This would remove the only mechanism trees have to obtain nutrients from the soil necessary for their growth and survival.

In the case of rainfall, if leaves are wetting, the forest foliage will intercept a significant amount of rain water, stopping it from reaching the forest floor [Waring and Running 1998]. The intercepted water will either evaporate back into the atmosphere and/or cause the stomata on the leaves to close. The closed stomata cause the internal osmotic pressure in each leaf to remain constant or increase which reduces the amount of water absorbed through the soil by the roots. In addition, the total amount of water reaching the forest floor is reduced by the amount intercepted via the leaves in particular for light rainfall events. This lowers the water potential in the soil and requires the leaves to obtain a lower than normal water pressure to recommence absorbing water and nutrients from the soil.
Another critical situation is when the leaves of a tree are covered by bacteria or fungi. In addition to the aforementioned ill-effects of water covered leaves, these tiny invaders will continuously degrade and deteriorate the surface until the leaf dies. Since bacteria and fungus growth is maximized in wet, stagnant environments, growth on superhydrophobic surfaces is less likely [Neinhuis and Barthlott 1997; Koch et al. 2008; Koch et al. 2009]. Much like dirt particles, fungal and bacterial spores would be carried off the aspen leaves by rolling water drops, removing them and their adverse effects.

4.8 Change in wetting behavior of quaking aspen leaves during one growth season

Near the end of this research, a state-of-the-art environmental SEM (Hitachi SU6600) became available that does not require samples to be electrically conductive (section 3.2). This allowed for close monitoring of the changes in surface morphology throughout an entire growth season which was done to shed light on the mechanisms for the natural formation and maintenance of surface features over a relatively long period of time. The overall goal of this section is to understand how these leaves are able to retain their non-wetting surface features throughout growth seasons in which they are exposed to different abrasive and erosive conditions (rain, wind etc.). For this part of the study, only the quaking aspen leaf was investigated.

Over the past five years, this study has been monitoring and analyzing the surface structures and wetting properties of quaking aspen leaves. Normally, shortly after leaf
emergence in the spring these leaves exhibit superhydrophobicity (water contact angle > 150°) that remains for the rest of their growth season, is maintained even after leaf abscission and is preserved in the dried state for many years thereafter [Victor and Erb 2010]. However, this trend was not observed during the 2011 growth season. At some point during this particular season (second half of August) the non-wetting properties of the aspen leaves were suddenly lost. It has been previously shown that the wetting characteristics of hydrophobic and superhydrophobic leaves are strongly influenced by the competition between i) the degradation of nano-scale wax crystals due to environmental factors and ii) the self-repair ability of the leaves through wax crystal regeneration [Baker and Hunt 1986; Koch et al. 2006; Neinhuis and Barthlott 1998; Neinhuis et al. 2001]. In an effort to understand this unusual loss of the superhydrophobic properties of quaking aspen leaves observed in 2011, the focus of this part of the current study was to establish a link between wax crystal loss/regeneration and environmental factors such as temperature, precipitation, wind and relative humidity (see appendix 3 for weather effects).

All quaking aspen leaf samples were collected throughout the 2011 growing season (May 14-October 9) from the same tree located in a forest near Fraserville, Ontario (44°11.43’N / 78°24.26’W and 214m altitude) and analyzed within 48 hours. To fully characterize a surface’s wetting behaviour both dynamic and static wetting measurements were again used. For the assessment of static wetting characteristics, the contact angles between water droplets and levelled leaf surfaces were measured, while for dynamic measurements the sample’s tilt angle (relative to horizontal) to initiate water droplet roll-off was recorded as described in section 3.3. The only difference between characterizations done in this section compared to the rest of the study is that only freshly harvested un-coated leaves were used in this part of the research and all SEM images were taken at a 45° tilt to emphasize structural differences.
Figure 4.18-figure 4.22 display multiple SEM images at different magnifications of quaking aspen leaves collected on five different days during the 2011 summer growth season (see appendix 4 for additional SEM images). SEM images of a quaking aspen leaf harvested on May 14, 2011 (just a few days after leaf emergence) are shown in figure 4.18. This young leaf surface does not exhibit the typical superhydrophobic leaf surface structure consisting of micro-scale papillae and nano-scale wax crystals that are responsible for non-wetting properties [Koch et al. 2009; Victor and Erb 2010]. Instead, the leaf shows multiple, randomly oriented folds in the cuticle and no nano-scale wax crystals are present on its surface (figure 4.18). Additionally, this surface contains many small contamination particles, indicating that it does not possess superhydrophobic/self-cleaning properties. In fact, the average water contact and tilt angles for these early leaves were 102° ±6° and 26°, respectively.
Figure 4.19 displays SEM images of a quaking aspen leaf harvested on May 22, 2011. It is clearly visible that multiple morphological changes have occurred during this relatively short growth period of only 8 days. The cuticular folds of the samples harvested on May 14, 2011 have acted as precursors for the random array of micro-scale papillae displayed on surfaces collected on May 22, 2011. Moreover, the entire leaf surface is now covered by a dense layer of nano-scale wax crystals, both on and in between surface papillae. Due to the development of these surface features, the non-wetting properties of these leaves have augmented to an average water contact angle of $148^\circ \pm 5^\circ$ and a tilt angle less than $5^\circ$. Effectively, the growth of this dual scale structure has rendered the quaking aspen leaves superhydrophobic and self-cleaning: a finding that is supported by the lack of surface contamination in figure 4.19.
It is important to note here the differences between figure 4.19 (fresh quaking aspen leaf) and figure 4.5 (dried quaking aspen leaf). Firstly, figure 4.5 is taken using a 0° sample tilt while figure 4.19 was taken with a 45° sample tilt which changes the observed aspect ratio of the micro-scale papillae. Additionally, there are differences in the shapes and densities of the nano-scale wax crystals present in both figures. On the dried sample (figure 4.5) there is a higher density of wax crystals (most likely attributed to this leaf being harvested much later in the growth season, *i.e.* more time for wax crystals to form) and the wax crystals are sharper, having more defined edges than those imaged in figure 4.19. This is likely due to air drying. Nevertheless, both leaf samples displayed similar non-wetting superhydrophobic properties.

Microscopy images from a quaking aspen leaf collected on June 5, 2011 are given in figure 4.20. Leaves harvested on this date showed micro-scale papillae and nano-scale wax crystals in between them, but most of the wax crystals that covered the papillae tops are no longer present. Nevertheless, leaves gathered on this date still displayed high contact (~160°) and low tilt angles (<5°), suggesting that for good non-wetting properties the presence of wax crystals in between papillae is more crucial than on top of them.

SEM images of a quaking aspen leaf harvested on August 7, 2011 are displayed in figure 4.21. Leaves obtained at this point in the summer exhibited similar surface features to those collected on May 22 and June 5, 2011. In fact, all leaves gathered between May 22 and August 21 showed similar micro and nano-scale surface features. The leaf imaged in figure 4.21 possesses slightly larger micro-papillae and a denser layer of wax crystals compared to figure 4.19. Moreover, this leaf appears to have regenerated the nano-scale wax crystals on top of each papilla that were present on leaves collected on May 22 (figure 4.19), but absent on leaves gathered on June 5 (figure 4.20). Surfaces of leaves harvested on August 7, 2011 still
demonstrated good non-wetting properties with an average water contact angle of 151° ±5° and a tilt angle less than 5°. In summary, all leaf samples harvested between May 22 and August 21, 2011 had similar superhydrophobic surface structures (essentially differing only in the amount of wax crystals on papillae tops) with the associated high contact angles (>150°) and low tilt angles (<5°).

Figure 4.20: SEM images of the adaxial side of a quaking aspen leaf harvested on June 5, 2011.

However, the surface structures of leaves which were collected on September 17, 2011 (figure 4.22) differ significantly from all other imaged samples. These coarsely degraded surfaces still exhibit micro-papillae (present on all leaf surfaces except those harvested on May 14, 2011), but the finer, nano-scale wax crystals are no longer visible; both in between and on
top of papillae. The lack of wax crystals on these surfaces reduced their non-wetting property, resulting in average contact angles of only $92^\circ \pm 5^\circ$. Furthermore, the tilt angles for these surfaces have significantly increased to the point where droplets still adhered to vertically positioned leaf surfaces (i.e. $TA>90^\circ$). In fact, all samples collected after August 21 did not display wax crystals on or in between papillae indicting that the regeneration process observed during June and July of the 2011 growth season was no longer occurring. For comparison, SEM images (taken at a sample tilt of $0^\circ$) of a quaking aspen leaf collected at the end of the 2009 growth season (late September) are given in figure 4.23. Leaves harvested at this time still displayed a significant amount of nano-scale wax crystals (figure 4.23d) and were able to retain their superhydrophobic properties throughout the growth season and even after two years of drying.

Figure 4.21: SEM images of the adaxial side of a quaking aspen leaf harvested on August 7, 2011.
Figure 4.22: SEM images of the adaxial side of a quaking aspen leaf harvested on September 17, 2011.

Figure 4.23: SEM images of the adaxial side of a quaking aspen leaf harvested late in September 2009.
The average contact and tilt angles for all quaking aspen leaves analyzed throughout the summer of 2011 are plotted in figure 4.24. This plot can be broken down into 3 distinct regions showing vastly different wetting properties. Leaves obtained the first week after emergence showed only a weak hydrophobic surface property with an average contact angle slightly above 90° and a relatively large tilt angle of 26°. Just eight days after the first sampling, significant changes in surface structure and wetting properties were observed. The surface structure of the second set of samples had substantially transformed (figure 4.19) resulting in much higher contact angles (148°) and much lower tilt angles (<5°). Following this initial change, for most of the summer season until August 21, 2011, aspen leaf contact angles remained high (140°-160°) and tilt angles remained low (<5°). During this time the contact and tilt angles fluctuated slightly but for the most part remained close to the superhydrophobic range (CA>150° and TA<5°).

Figure 4.24: Quaking aspen contact and tilt angles during the 2011 growth season.
Similar fluctuations in the contact angles throughout the growing season as observed here in region 2 were previously reported for ginkgo (*Ginkgo biloba*), oak (*Quercus robur*) and beech (*Fagus sylvatica*) leaves [Neinhuis and Barthlott 1998]. These fluctuations could be due to small surface structure differences on the different leaf samples. Another reason could be that leaves collected at different times throughout the year are at different stages in the wax crystal erosion/regeneration cycles. However, after August 21, 2011 (region 3 of figure 4.24) the non-wetting property of the quaking aspen leaves was permanently lost resulting in low contact and high tilt angles. Again, it is important to note that leaves harvested from the same tree in previous years (2007-2010) did not show a reduced non-wetting property at the end of past growth seasons [Victor and Erb 2010]. Moreover, leaves from previous years still exhibited non-wetting properties and associated superhydrophobic surface structures after leaf abscission, and even when re-measuring their wetting properties following several years of drying.

It has been previously shown that most leaves can be characterized into four groups based on their ability for wax crystal regeneration: (i) regeneration occurs at all stages of development, (ii) regeneration occurs only during leaf expansion, (iii) regeneration occurs only in fully developed leaves and (iv) plants are not able to regenerate wax crystals at all [Neinhuis et al. 2001]. This results in some leaves having good non-wetting properties throughout their entire life cycle while others only possess this property in certain stages of growth. It is also commonly accepted that wax crystals are constantly eroded by different environmental factors (wind, precipitation, temperature, etc.) resulting in substantial depletion of the outer most wax layer after prolonged exposure [Baker and Hunt 1986]. In all cases the depleted wax layer results in increased leaf wettability and reduced contact angles. Leaves exhibiting dual-scale surfaces structures (micro-papillae and nano-scale wax crystals) are known to be more resistant to natural
wax erosion due to their micro-papillae surface features [Neinhuis et al. 2001]. Leaves displaying this type of erosion resistant surface structure coupled with the ability to regenerate waxes at all stages of development typically show superhydrophobic properties throughout their entire life cycle. In all four years before 2011, quaking aspen leaves harvested from the same tree/forest fell into this group of leaves. Throughout each season, their wax crystals were constantly being naturally eroded, while simultaneously being regenerated.

A detailed study of the weather conditions present during the summer of 2011 and their affect on the wetting properties of quaking aspen leaves harvested during this year are given in appendix 3. It appears that the unusual hot and humid summer of 2011 resulted in reduced wax crystal regeneration rates which ultimately decreased the wax crystal density, consequently lowering these leaves contact angles.

4.9 Summary

This chapter contains a detailed analysis of the surfaces morphology and wetting properties of two types of superhydrophobic aspen leaf surfaces. Both surfaces display a similar dual-scale hierarchical surface structure consisting of nano-scale wax crystals superimposed on top of an array micro-scale papilla. The hydrophobic surface chemistry of wax crystals coupled with the unique surface topography (roughness) created through the dual-scale surface features imparts an extreme non-wetting behaviour to these surfaces.

The effects of temperature, water droplet size and water surfactant concentration on the wetting properties of these natural surfaces were investigated. At elevated temperatures, the
localized melting of surface wax crystals resulted in a drastic decrease in the wetting properties of these leaves removing their superhydrophobic property. A weak linear decrease in contact angles was associated with larger droplet sizes; however, even at the largest drop size tested (25µl) both aspen leaves retained their non-wetting properties. Initially, small increases in water surfactant concentration created drastic reductions in contact angles for all tested surfaces. Following this initial drop, further increases in surfactant concentration resulted in a levelling out effect whereby the addition of surfactant did not reduce contact angles any further. It is important to note that both aspen leaves were able to remain in the hydrophobic regime (CA > 90°), while other surfaces tested with the same solutions exhibited contact angles far below 90°. This finding indicates that structured surfaces of this type are better suited to resist surfactant-induced wetting.

The non-wetting properties created by the aspen leaves’ unique non-wetting surface structure is further augmented by their unusually slender leafstalks that offer very little resistance to twisting and bending. This results in excessive leaf movement in the presence of the slightest breeze which further facilitates water droplet movement, and ultimately removal. Potential evolutionary advantages brought forth from this unique combination of non-wetting factors were discussed and tentatively used to explain the remarkable widespread growth of these tree species.

The last section of this chapter studied an abnormal loss of superhydrophobicity observed on quaking aspen leaves during the end of the 2011 growth season. In previous years, quaking aspen leaves retained their extreme non-wetting property throughout the entire growth season, and even many months/years after harvesting. However, during August 2011, quaking aspen leaves lost their non-wetting property. A detailed investigation into the effects of different weather conditions (see appendix 3) occurring during this particular season on the wax crystal
erosion/regeneration processes was presented and used to explain this unexpected loss of the aspen’s non-wetting property. The unusually hot and humid summer of 2011 was found to drastically reduce the wax crystal regeneration process resulting in the gradual removal of the hydrophobic wax crystals and consequently the loss of superhydrophobicity.
5 – Template Synthesis and Characterization

This chapter describes the efforts taken to create a dual-scale hierarchical surface structure on nanocrystalline nickel surfaces. A previous research study [Tam 2004] indicates that chemically etching nanocrystalline nickel in nitric acid results in a heavily roughened surface on the nano-scale (figure 2.29). Therefore, the challenge for this part of the current study is to obtain micro-scale surface features in addition to the nano-scale surface features created during chemical etching. This chapter presents the steps taken to achieve the desired dual-scale surface structure on nanocrystalline nickel templates to be used in the structuring of polymer surfaces.
5.1 Overview of Template Synthesis Techniques

Chapter 4 provided a detailed analysis of the surface structure present on three different superhydrophobic self-cleaning leaves – *i.e.* the blueprint of the basic structure to be replicated onto polymer surfaces. Figure 5.1 summarizes this structure again, highlighting the important surface features responsible for the desirable non-wetting property. A series of schematic diagrams illustrating the processing steps to be developed to structure softened polymer surfaces using a template based approach are given in figure 5.2. The focus of this chapter is to describe the experimental efforts used to obtain a suitably structured nickel surface (step 2 in figure 5.2) possessing a dual-scale pitted structure, *i.e.* the negative of the aspen leaves’ surfaces. Pressing polymers with templates containing this structure (step 4 in figure 5.2) is expected to result in polymer surfaces displaying surfaces features similar to those present on the aspen and lotus leaves described in chapter 4.

![Figure 5.1: Cross-sectional schematic of a superhydrophobic leaf’s surface structure illustrating the presence of a dual-scale roughness.](image)
Two different sets of nanocrystalline nickel samples were electroplated onto titanium substrates at Integran Technologies Inc. (Toronto, Ontario) using their patented nanocrystalline bath chemistry and plating parameters. To fabricate these nickel deposits, pulsed current electrodeposition (figure 5.3) was used in a modified Watt’s type bath containing nickel sulphate, nickel chloride, boric acid and saccharin. The generalized cathodic and anodic reactions for this process are $\text{Ni}^{2+} + 2e^- \rightarrow \text{Ni}^0$ (as well as hydrogen evolution $2\text{H}^+ + 2e^- \rightarrow \text{H}_2$) and $\text{Ni}^0 \rightarrow \text{Ni}^{2+} + 2e^-$, respectively. Plating on a titanium substrate allowed for the easy separation of thick (1-2mm) nickel plates following the deposition procedure, resulting in a free-standing nickel deposit.
Multiple 6” X 6” plates of both large grain size (50-100nm – ESNi) (measured by Palumbo et al. [1997] using TEM) and small grain size (23.9 nm – nNi) (measured by XRD – see appendix 5) nanocrystalline nickel samples were fabricated. Each electrodeposited sample was cut into 25 (1” X 1”) square coupons which were ground flat, polished to a mirror finish and ultra-sonically cleaned in ethanol. Additionally, polycrystalline nickel (Ni200) was investigated with to determine what type of surface features would be created during structuring this material; however, this resulting surface structure was not suitable for the creation of dual-scale superhydrophobic surface features and was therefore omitted from the main part of this thesis (see appendix 6 for SEM images). Each nanocrystalline nickel coupon was subjected to different series of surface treatment steps involving plasma-etching, electro-etching, sand blasting and/or chemical etching. For most samples, the last step was chemical etching in 5% HNO₃, because from previous work [Tam 2004] this process is known to result in a heavily nano-scale roughened surface (figure 2.29 – section 2.6), which is crucial to the fabrication of superhydrophobic surfaces.
Different surface treatment steps were used to explore which treatment would produce a roughened surface on the micro-scale similar to the negative of the papillae found on superhydrophobic leaves. Samples were plasma-etched for various times (10-90 seconds) using an open air plasma etcher with a working distance of 10 mm, an air intake pressure of 40 psi and were electrically grounded to promote surface deformation [Jansen et al. 1995]. Some of the samples were electro-etched at temperatures between −20ºC and −40ºC using two different heavily agitated electro-etching solutions (33% HNO₃/67% ethanol and 10% HClO₄/90% methanol) with voltages between 20-40 volts for 5-30 seconds. Other samples were sandblasted (SB) using 180 grit Al₂O₃ particles at 87 psi during which the samples were positioned perpendicular to and ~10 cm from the outlet of the sand blasting barrel. Samples with suitable micro-scale surface deformation were then chemically etched (CE) in a heavily agitated 5% HNO₃ solution at room temperature (to obtain nano-sized features) for various times (1, 5, 10, 20, 30 and 60 minutes). After each surface modification step, all coupons were ultra-sonically cleaned in ethanol to ensure the complete removal of any remaining un-bonded material.

After all surface modification steps were finished, the surface of each nickel coupon was imaged using the same SEM and optical characterization techniques as described in chapter 3 for the characterization of leaf surfaces. The only difference in these characterization processes was the lack of carbon coating for nickel samples due to its electrically conductive and optically reflective properties. All optical images were inverted to allow for easy comparison with the leaf and pressed polymer surface images. Following the characterization process, nickel coupons with suitable dual-scale surface structures were selected to be used as pressing templates (step 4 in figure 5.2).
5.2 Results

5.2.1 Effect of Plasma Etching

Samples that were plasma-etched showed no significant surface deformation; even after relatively long etch times (90 seconds) surfaces showed no increase in surface roughness and sub-micron polishing marks were still visible. Figure 5.4 is a SEM micrograph of a small grain size nNi sample that was mechanically polished and plasma-etched for 90 seconds. Due to the lack of sufficient surface roughness this and others samples that were plasma-etched for shorter time periods were not characterized using an optical profilometer.

Figure 5.4: SEM micrograph of a nNi sample that was polished and plasma-etched for 90 seconds.
5.2.2 Effect of Electro-Etching

Two different electro-etching solutions were experimented with to determine which, if any, would result in an appropriately structured surface. Solution 1 (33% nitric/67% ethanol) produced a nice array of relatively small pits that are fairly evenly spaced (figure 5.5 and figure 5.6). Unfortunately, this type of surfaces structure is not well-suited for superhydrophobicity since the largest feature size is much smaller than the micro-scale papillae present on superhydrophobic leaves. Currently, nNi samples that were electro-etched using this solution are being experimented with to see if they can result in a suitable template that could be used for the production of anti-reflective surfaces. For these types of functional surfaces an ordered array of closely packed, similarly sized sub-micron scale protrusions is necessary. Perhaps changing process conditions such as etching time, voltage and temperature could result in appropriately structured nickel templates suitable for the pressing of polymers to create anti-reflective surfaces.

![Figure 5.5: SEM images of a nNi sample that was polished and electro-etched in a 33% nitric/67% ethanol solution for 30 seconds at 20 volts and -20°C.](image)
Figure 5.6: Inverted optical profilometry images of a nNi sample that was polished and electro-etched in a 33% nitric/67% ethanol solution for 30 seconds at 20 volts and -20°C: 3D (top) and surface (bottom) views.

Solution 2 (10% perchloric/90% methanol) produced a surface with many differently sized pits that are not evenly spaced (figure 5.7). This resulting surface structure does not resemble the negative of the hydrophobic leaves that were characterized, and for this reason, no optical imaging was performed on samples that were electro-etched in solution 2.
5.2.3 Effect of Sandblasting

Sandblasting proved to be the most effective way to heavily roughen the surface of nanocrystalline nickel samples on the micro-scale. Respectively, figure 5.8a and figure 5.9a are SEM images of small grain size (23.9nm) nNi and large grain size (50-100nm) ESNi samples that were sandblasted after mechanical polishing.

Following the sandblasting process, both ESNi and nNi samples were chemically etched in 5% HNO₃. Figure 5.9b-d shows the surface of an ESNi sample that was chemically etched for 30 minutes after sandblasting. This surface does not resemble the negative of the hydrophobic leaves (no micro-scale pits) and was not used further in this research. On the other hand, nNi samples that were chemically etched after sandblasting displayed a nano-scale surface roughness superimposed on an array of micro-scale pits (figure 5.8b-d). This is the type of surface that could produce structured superhydrophobic polymer surfaces using the proposed pressing procedure.

Figure 5.7: SEM image of a nNi sample that was polished and electro-etched in a 10% perchloric/90% methanol solution for 30 seconds at 40 volts and -40°C.
Figure 5.8: SEM micrographs of a nNi sample: a) sandblasted only, b), c) and d) sandblasted and chemically etched.

Figure 5.9: SEM micrographs of an ESNi sample: a) sandblasted only, b), c) and d) sandblasted and chemically etched.
5.2.4 Effect of Chemical Etching Time

From the previous section it appears the process that results in the best suited template surface structure will involve sandblasting followed by chemically etching in nitric acid. To evaluate the etching time necessary to obtain a fully and homogeneously etched surface, SEM images of nNi samples chemically etched for different times are given in figure 5.10. These images clearly show that longer etching times result in more significant surface roughening. The important finding from this study is that for all etching times less than 30 minutes nNi surfaces exhibit a non-uniformly etched surface structure figure 5.10a-c. Samples analyzed after 30 minutes of chemical etching displayed a homogeneously nano-scale rough surface similar to the surface shown in (figure 2.29 – section 2.6) [Tam 2004]. Since superhydrophobic leaf surfaces show a continuous network of nano-scale wax crystals, it is necessary for templates to undergo homogeneous etching to ensure all areas of each surface (both template and resulting pressed polymer) contain the required nano-scale surfaces features. In view of this, all subsequent samples used in this research have been chemically etched for 30 minutes to guarantee complete coverage of nano-scale surfaces features.

Figure 5.10: SEM images of nNi samples chemically etched in 5% nitric acid for 5 (a), 10 (b), 20 (c) and 30 (d) minutes.
5.2.5 Effect of Structuring on Template and Pressed Polypropylene Wetting Properties

In this section the results of wetting angle measurements for all nickel surface treatment procedures are summarized. While only the combination of sandblasting and chemical etching resulted in the desired surface morphology on the nickel template, the wetting characteristics for all other surface treatments are included in Table 5.1. Also shown in Table 5.1 are the wetting and tilt angles for a series of polypropylene (PP) coupons which were pressed against the nickel templates after the various surface treatments.

Table 5.1: Effect of different surface structuring techniques on the wetting properties of nNi templates and the resulting pressed PP samples.

<table>
<thead>
<tr>
<th>Structuring Process</th>
<th>nNi CA(°)</th>
<th>nNi TA(°)</th>
<th>Pressed PP CA(°)</th>
<th>Pressed PP TA(°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground Flat</td>
<td>86 ±5</td>
<td>&gt;90</td>
<td>93 ±5</td>
<td>38 ±9</td>
</tr>
<tr>
<td>Chemically Etched (CE)</td>
<td>121 ±8</td>
<td>&gt;90</td>
<td>99 ±6</td>
<td>25 ±6</td>
</tr>
<tr>
<td>Sandblasted</td>
<td>103 ±12</td>
<td>&gt;90</td>
<td>130 ±10</td>
<td>24 ±8</td>
</tr>
<tr>
<td>Plasma Etched</td>
<td>78 ±6</td>
<td>&gt;90</td>
<td>91 ±4</td>
<td>23 ±4</td>
</tr>
<tr>
<td>Sandblasted + CE</td>
<td>124 ±7</td>
<td>&gt;90</td>
<td><strong>153 ±5</strong></td>
<td>&lt;5</td>
</tr>
<tr>
<td>Sandblasted + Plasma Etched</td>
<td>67 ±8</td>
<td>&gt;90</td>
<td>128 ±9</td>
<td>37 ±5</td>
</tr>
<tr>
<td>CE + Plasma Etched</td>
<td>88 ±5</td>
<td>&gt;90</td>
<td>99 ±4</td>
<td>30 ±7</td>
</tr>
<tr>
<td>Sandblasted + CE + Plasma Etched</td>
<td>97 ±4</td>
<td>&gt;90</td>
<td>143 ±7</td>
<td>16 ±6</td>
</tr>
<tr>
<td>CE + Sandblasted</td>
<td>75 ±9</td>
<td>&gt;90</td>
<td>139 ±9</td>
<td>22 ±8</td>
</tr>
</tbody>
</table>
As indicated in Table 5.1, the only nNi surface structuring process that results in a pressed PP samples exhibiting both a high contact angle (>150°) and a low water roll-off angle (<5°) is sandblasting followed by chemically etching. The surface structure of this nNi template is shown in detail in figure 5.11 (SEM) and figure 5.12 (Optical) and will be used exclusively in all subsequent polymer pressing. It is important to note the array of micro-scale pits and nano-scale roughness that cover this entire surface. From optical images the depths and diameters of the created micro-scale pits are 17.5 ±8.5μm and 24.5 ±10.4μm, respectively with an average inter-pit spacing of ~25μm.

Figure 5.11: SEM micrographs of a structured nNi template: a) low magnification image illustrating the array of micro-scale pits, b) and c) a single micro-scale pit and d) high magnification image showing finer nano-scale roughness [Victor et al. 2012].
Figure 5.12: Inverted optical profilometry images of a structured nNi template: 3D (top) and surface (bottom) views [Victor et al. 2012].

### 5.3 Summary

This chapter introduced and discussed the effects of multiple surface treatment techniques on the resulting surface structure of two nanocrystalline nickel samples with different grain sizes. Open-air plasma etching, electro-etching using two different solutions, sand blasting, chemical etching, or combinations of these were explored to see which process(es) would give the best suited template resembling the negative of the surfaces of superhydrophobic leaves characterized in chapter 4. The main challenge associated with this part of the research
was the development of a process to create a dual-scale surface structure on nickel coupons where a fine nano-scale roughness is superimposed on top of an array of micro-scale pits.

Plasma etching did not significantly alter the surface of nickel samples and was not selected to be used as a pressing template. Electro-etching with a 33% nitric/67% ethanol solution produced a nice array of sub-micron sized pits that were, unfortunately, much smaller that the protrusions found on the surfaces’ of superhydrophobic leaves. However, these samples are currently being investigated to be used as pressing templates to create anti-reflective surfaces based on the ‘moth’s eye effect’ which requires much smaller surface protrusions compared to non-wetting surfaces. Electro-etching with a 10% perchloric/90% methanol solution produced slightly larger but shallow pits and their sizes and spacing were very inconsistent. Sandblasting produced a heavily roughened micro-scale surface and chemically etching this roughened surface resulted in the creation of micro-scale pits lined with the characteristic nano-scale roughness created during the chemical etching process. Etching for less than 30 minutes did not allow enough time for the entire surface of the nickel sample to be evenly etched, causing the etched surfaces to be non-homogeneous.

The structuring process that gives the highest contact and lowest tilt angles for both nickel templates and pressed PP samples was sandblasting a nNi sample followed by chemical etching in nitric acid. Templates structured in this way increased the contact angles for pressed PP from 93° to 153° and reduced their tilt angles below 5°. These values indicate that this process performed on nNi results in the best suited template surface for the production of superhydrophobic polymer surfaces. These templates were used for all subsequent sections of this research and all polymer pressing discussed in chapter 6.
6 – Polymer Pressing and Characterization

In chapter 5 a process was described to prepare nickel templates suitable for the production of superhydrophobic polymers using a pressing/imprinting procedure. This section presents and analyzes the surface structures and wetting properties of polymers pressed with these structured nickel templates.

The main results from this part of the study have been published in the following patents/papers: [Victor et al. 2011; Victor et al. 2011; Victor et al. 2012; Victor et al. 2012].
6.1 Polymer Pressing Procedure

Commercially available samples of polyethylene (PE) polypropylene (PP) and polytetrafluoroethylene (PTFE) (all from McMaster-Carr) were experimented with to obtain optimum pressing conditions that resulted in a complete surface structure transfer with minimal template-polymer adhesion. Once the appropriate pressing temperatures had been obtained for each polymer (150°C for PE, 160°C for PP and 280°C for PTFE), 1 inch x 1 inch samples (~4mm thick) were pressed into structured nano-nickel templates using the press and furnace shown in figure 6.1. The primary selection criteria for these polymers are that their Young’s contact angles ($\Theta_0$) are all above 90° and they are thermoplastics, allowing for their surfaces to be deformed at elevated temperatures. Additionally, these three polymers were selected because of their relative low costs and wide spread commercial use. Table 6.1 gives thermal properties, surface tensions, molecular structures and typical commercial applications for these polymers that were all considered during the selection process for this study.

![Figure 6.1: Press and furnace used in the structuring of polymer samples.](image_url)
Table 6.1: Polymer Properties and Applications [Fried 2003].

<table>
<thead>
<tr>
<th>Polymer Properties</th>
<th>UHMW-PE*</th>
<th>i-PP*</th>
<th>PTFE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting Temp. (°C)</td>
<td>144 - 152</td>
<td>165 - 171</td>
<td>327 - 342</td>
</tr>
<tr>
<td>Glass Transition</td>
<td>130 - 135</td>
<td>-10 - 0</td>
<td>160</td>
</tr>
<tr>
<td>Temp (°C)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermal Expansion Coefficient (*)</td>
<td>1.5 - 3.6</td>
<td>0.7 - 1.5</td>
<td>1 - 1.8</td>
</tr>
<tr>
<td>Surface Tension @ 20°C (mN/m)</td>
<td>35.7</td>
<td>30.1</td>
<td>20</td>
</tr>
<tr>
<td>% Crystallinity</td>
<td>80-95</td>
<td>82</td>
<td>90</td>
</tr>
<tr>
<td>Molecular Weight (g/mol)</td>
<td>2 - 6 million</td>
<td>110 000 - 350 000</td>
<td>14 000 – 1.2 million</td>
</tr>
<tr>
<td>Molecular Structure</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Commercial Applications</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-chemical resistant piping systems, fuel tanks and automotive parts, coating applications, plastic bottles, prescription bottles, coolers, etc.</td>
<td>-waterproofing roofing membranes, piping systems, medical equipment, moulded bottles, tops and fittings, clear plastic bags, retail packaging material, etc.</td>
<td>-gears, bearings, water-resistant clothing, cooking equipment, low friction/non-stick coatings, etc.</td>
<td></td>
</tr>
</tbody>
</table>

*UHMW-PE: ultra high molecular weight polyethylene
*i-PP: isostatic polypropylene
In the furnace, as received coupons of each polymer, a nickel template and a restraining device (to constrain all polymer deformation to the vertical direction) were heated inside the press (figure 6.1 and figure 6.2) to the desired pressing temperature. A K-type thermocouple was placed in direct contact with the metallic pressing apparatus during heating to ensure the most accurate temperature reading possible. Once the desired temperature was reached, the press (with a polymer coupon and nickel template in direct contact) was removed and immediately tightened using a set of pliers, transferring the roughened surface structure from the template to the polymer. This results in the negative of the metallic surface structure being transferred to the softened polymer. This process is also schematically summarized in figure 5.2. Once multiple polymer samples were pressed using a number of nickel templates, surface characterization of these polymer surfaces was performed using an SEM and an optical profilometer. As with superhydrophobic leaves, the polymer samples had to be carbon coated for electrical conductivity and optical reflectivity. Wetting properties were measured using the same technique described in the characterization section (chapter 3) of this paper. These results were
used to correlate different processing parameters and measured wetting properties, with the intention of finding the parameters that resulted in the largest static contact angle and the smallest tilt angle for pressed polymer surfaces.

### 6.2 Pressed Polymer Surface Structures

Examples of SEM and optical images of polymer surfaces pressed with suitable nickel templates are given in figure 6.3-figure 6.8. Dimensions of all micro-scale features (measured from optical images) present on these pressed polymers and the nNi template surfaces are given in Table 6.2. After comparing figure 6.3-figure 6.8 with SEM and optical images of the selected nickel template (figures 5.15 and 5.16) and the numerical results shown in Table 6.2, it is clear that the performed pressing procedure resulted in a good transfer of all surface features (both micro and nano) from the nickel templates to the polymer surfaces. In other words, the filling of the etched depressions on the template by the softened polymers is excellent.

All of the pressed polymers surfaces presented here (figure 6.3-figure 6.8) show similar surface structures as aspen leaves (figures 4.5-4.8). On these types of structured surfaces, micro-scale protrusions enable the formation of trapped air pockets between droplets and the solid surface, while the nano-scale features significantly increase the overall surface roughness. According to Cassie and Baxter’s [1944] heterogeneous wetting equation ($\cos \theta_{CB} = R_f f_{la} \cos \theta_o - f_{la}$), for an inherently hydrophobic material ($\theta_o>90^\circ$), increasing the surface roughness ($R_f$) and maximizing the amount of air trapped under a droplet ($f_{la}$) results in a superhydrophobic surface with a large contact angle ($\theta_{CB}$). See appendix 7 for estimations of $f_{la}$ values and calculated contact angles using the dimensions given in Table 6.2.
Figure 6.3: SEM micrographs of a pressed PE sample: a) and b) low magnification images illustrating the array of micro-scale protrusions, c) a single micro-scale protrusion and d) high magnification image showing finer nano-scale roughness [Victor et al. 2012].

Figure 6.4: Optical profilometry images of a pressed PE sample: 3D (top) and surface (bottom) views [Victor et al. 2012].
Figure 6.5: SEM micrographs of a pressed PP sample: a) and b) low magnification images illustrating the array of micro-scale protrusions, c) an individual micro-scale protrusion and d) high magnification image showing finer nano-scale roughness [Victor et al. 2012].

Figure 6.6: Optical profilometry images of a pressed PP sample: 3D (top) and surface (bottom) views.
Figure 6.7: SEM micrographs of a pressed PTFE sample: a) and b) low magnification images illustrating the array of micro-scale protrusions, c) an individual micro-scale protrusion and d) high magnification image showing finer nano-scale roughness.

Figure 6.8: Optical profilometry images of a pressed PTFE sample: 3D (top) and surface (bottom) views.
Table 6.2: Dimensions of micro-scale surface features on nNi templates and pressed polymers [Victor et al. 2012].

<table>
<thead>
<tr>
<th>Surface</th>
<th>Protrusion/Pit Size</th>
<th>Protrusion/Pit Spacing</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Height/Depth (µm)</td>
<td>Diameter (µm)</td>
</tr>
<tr>
<td>nNi Template</td>
<td>17.5 ±8.5</td>
<td>24.5 ±10.4</td>
</tr>
<tr>
<td>Pressed PE</td>
<td>15.4 ±7.4</td>
<td>24.0 ±11.3</td>
</tr>
<tr>
<td>Pressed PP</td>
<td>14.7 ±6.3</td>
<td>18.4 ±8.8</td>
</tr>
<tr>
<td>Pressed PTFE</td>
<td>16.7 ±8.1</td>
<td>26.5 ±9.6</td>
</tr>
</tbody>
</table>

6.3 Pressed Polymer Wetting Properties

Water contact angles using 5 µl droplets and roll-off tilt angles using 25 µl droplets for all pressed and un-pressed polymers are given in Table 6.3 (see appendix 2 for examples of water drop images). The data show that the pressing process increased the contact angles for PE, PP and PTFE from 96° to 151°, 104° to 153° and 108° to 159°, respectively. In addition, the tilt angles for all polymers dropped from over 30° to below 5°. Clearly the presented structuring process drastically increased water contact angles and decreased tilt angles for all polymer samples. In other words, all polymer surfaces have effectively been transformed from hydrophobic (CA>90°) to superhydrophobic (CA>150° and TA<5°) from this template-based surface modification process.

In order to assess a range of potential engineering applications these functional polymer surfaces may be suited for the effects of temperature, water droplet size and water surfactant
concentration on their wetting properties were also investigated. The following three sections report the results from these studies. It should be noted that only PP and PTFE which exhibited the highest wetting angles were used for these experiments.

<table>
<thead>
<tr>
<th>Surface</th>
<th>CA (°)</th>
<th>TA (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Un-pressed PE</td>
<td>96 ±5</td>
<td>38 ±7</td>
</tr>
<tr>
<td>Un-pressed PP</td>
<td>104 ±5</td>
<td>37 ±9</td>
</tr>
<tr>
<td>Un-pressed PTFE</td>
<td>108 ±3</td>
<td>36 ±4</td>
</tr>
<tr>
<td>Pressed PE</td>
<td>151 ±3</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Pressed PP</td>
<td>153 ±5</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Pressed PTFE</td>
<td>159 ±4</td>
<td>&lt;5</td>
</tr>
</tbody>
</table>

**6.4 Effect of Temperature on Water Contact Angles**

The effect of temperature on the water contact angles of pressed and un-pressed PP and PTFE are illustrated in figure 6.9. Not surprisingly, the influence of temperature on the wetting characteristics of both pressed and un-pressed PP and PTFE were quite similar. All samples showed a small linear decrease in contact angles (<10°) with increasing temperatures from 25°C up to 95°C. The observed reductions in contact angles are likely a direct result of the decreased liquid/vapour surface tension of water at higher temperatures [Adam 1941]. This reduced liquid/vapour surface tension allows water to better wet the polymer surfaces resulting in slightly
lower contact angles. However, even at the highest temperatures tested, both pressed polymer samples still exhibited relatively high contact angles indicating that these types of surfaces would be suitable for applications in which they are exposed to elevated temperatures up to 95°C.

It is interesting to compare the effect of temperature on the wetting properties of the structured polymer surfaces and their naturally occurring aspen counterparts. Recall figure 4.11 in section 4.4, which plots the effect of temperature on quaking and bigtooth aspen leaf surfaces. This plot shows a large drop in leaf contact angles occurring between 40°C and 70°C that was attributed to the localized melting (removal) of the leaves’ hydrophobic surface wax crystals. Since the melting points for PP and PTFE are much higher than for the aspens’ wax crystals this effect was not observed in this study. In this sense, these pressed polymer surfaces have enhanced superhydrophobic properties compared to aspen leaves at elevated temperatures.

![Figure 6.9: Effect of temperature on the water contact angle of pressed and un-pressed polymers [Victor et al. 2012].](image-url)
6.5 Effect of Drop Size on Water Contact Angles

Figure 6.10 illustrates the effect of drop size on the water contact angles of pressed and un-pressed PP and PTFE. All tested samples showed small, linear decreases in their respective contact angles with increasing drop size. Over the tested droplet size range (5-25 µl), the decrease in contact angle for the pressed PP samples (14°) was slightly higher than for the pressed PTFE samples (7°). While only the pressed PTFE samples retained contact angles above 150°, both materials still showed relatively high contact angles for the largest drop sizes, indicating their non-wetting, and potential self-cleaning properties are not lost for larger drop sizes. The small drop in contact angles 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 [Fujii and Nakae 1995]. This important result points out that these types of surfaces would be well suited for many exterior applications where they will be frequently exposed to rain of different drop sizes. A similar weak droplet size dependence on contact angles was previously observed for quaking aspen and bigtooth aspen leaves (figure 4.16 - chapter 4).

6.6 Effect of Surfactant Concentration on Water Contact Angles

All polymer samples tested exhibited a similar trend in their wetting behaviour to increasing SDS surfactant concentrations (figure 6.11). Initially, contact angles sharply dropped with small additions of surfactant (up to 10 g/L) and then levelled out as the concentration was
further increased to 100 g/L. Pressed PTFE was the only tested sample to retain its hydrophobic property at the highest SDS concentration tested of 100 g/L. Un-pressed PTFE and both pressed and un-pressed PP lost their hydrophobic/superhydrophobic properties at surfactant concentrations as low as 5 g/L. This response was expected since surfactants are compounds that promote wetting by collecting at the liquid interface where they act to reduce the liquid surface tension, and ultimately lower the contact angle on any solid surface [Rosen 2010]. However, even at the highest SDS concentration tested (100 g/L), at which all other samples had contact angles less than 90°, the pressed PTFE sample still demonstrated hydrophobic behaviour with a contact angle of ~128°. In comparison, at this concentration the contact angle on the un-pressed PTFE sample was only ~60°, indicating its loss of hydrophobicity. On the other hand, at this SDS concentration, the contact angle for pressed PP was ~72°, while the un-pressed PP surface only had a contact angle of ~45°.

Figure 6.10: Effect of drop size on the water contact angle of pressed and un-pressed polymers [Victor et al. 2012].
In general, structuring any surface will only result in an enhancement of the pre-existing wetting condition with a given liquid. Since both un-pressed PP and PTFE samples were wetted by the solution containing the highest surfactant concentration (CA<90°), it would be expected that the structuring process would enhance the pre-existing wetting condition for PP and PTFE resulting in lower contact angles; however, the opposite effect was observed. This implies that even though the intrinsic contact angles for these polymers are below 90° with this specific solution, a significant amount of air is still trapped between the liquid droplets and the pressed/structured solid surfaces. Theoretically, according to Cassie and Baxter’s [1944] heterogeneous wetting equation (equation 2.4, section 2.2) a surface with an intrinsic contact angle less than 90° can be structured to increase its contact angle, provided a sufficient amount of air is able to be trapped between the liquid and solid phases. This indicates that these types of structured surfaces are better suited to resist surfactant-induced wetting than their chemically equivalent smooth counterparts. It is interesting to note that the effect of SDS concentration observed in this current study for pressed PTFE is almost identical to what was earlier reported for quaking aspen leaves (figure 4.14 - chapter 4). In both cases the contact angle remained relatively high even at the highest SDS concentration of 100 g/L: 128° for pressed PTFE and 122° for quaking aspen leaves. This implies that both surfaces are indeed very similar not only with respect to overall surfaces structure characteristics but also in terms of their response to the wetting agent SDS.
6.7 Production Scalability

As discussed in section 2.4, one of the main barriers to having micro-nanostructured surfaces integrated into large scale production is their relative cost, and the difficulty associated with structuring more complex geometries. For the process described here the starting template material is an electrodeposited metal. It is relatively easy to plate the outside of a large roller and then structure this roller through a sandblasting and chemical etching process to be used as a template. This template roller could then be used in a continuous pressing process where large sheets of polymers are fed underneath the roller giving them the desired surface structure. Since...
template production is relatively inexpensive, this process could result in low-cost, large-scale production of superhydrophobic polymeric surfaces.

Additionally, this non-wetting property can be imparted onto the surfaces of complex shaped polymer articles by changing from a simple pressing process to an injection moulding process. It is possible to electroplate the inside surface of a complex shaped polymer mould by an electroforming method, again followed by sandblasting and acid etching. This would result in superhydrophobic surfaces on every part coming from this mould. This is one of the main advantages to this superhydrophobic production process compared to other currently available techniques.

6.8 Summary

A technologically viable and economically feasible template process for producing superhydrophobic polymeric surfaces has been developed. Polyethylene (PE), polypropylene (PP) and polytetrafluoroethylene (PTFE) samples were structured using this process which created a fine nano-scale surface roughness superimposed on larger micro-scale surface protrusions. This resulted in an increase in contact angle from 96° to 151° for PE, 104° to 153° for PP and 108° to 159° for PTFE and a reduction in tilt angles from above 30° to below 5° for all pressed polymer samples.

In addition, the effects of temperature, drop size and surfactant concentration on the wetting properties of PP and PTFE were investigated. An increase in droplet size, temperature and water surfactant concentration decreased the measured contact angles for all samples. The
effects of drop size and temperature were weak and resulted in all pressed polymer surfaces remaining hydrophobic for droplet sizes between 5 and 25 μl and temperatures up to 95°C. Initially, all samples except pressed PTFE showed drastic reductions in contact angles with increasing surfactant concentrations. At the highest surfactant concentrations of 100 g/L, all samples had completely lost their superhydrophobicity but pressed PTFE remained hydrophobic with a contact angle of 128°.

These results indicate that these structured polymer surfaces are well suited for a wide range of applications where they may be exposed to elevated temperatures or larger water droplet sizes. Pressed PTFE samples showed the strongest resistance to surfactant-induced wetting and would therefore be a good candidate for environments containing these types of chemicals. Additionally, the ease of production scalability for structuring large surfaces and complex shaped geometries was discussed.
Chapter 7

Conclusions

- The outstanding non-wetting properties found on quaking and bigtooth aspen leaves are a direct result of their hierarchical dual-scale surface structure coupled with the hydrophobic chemistry of their surface waxes. These aspen leaves display similar surface structural features and wetting properties as the well-known lotus leaf. The features on these types of superhydrophobic leaves are conducive to the formation of multiple tiny trapped air pockets underneath water droplets that minimize the real contact area and adhesion between the solid surface and liquid droplets. This results in very high water contact angles (>150°) and very small water roll off angles (<5°).

- At elevated temperatures (40°C-70°C) the nano-scale wax crystals present on quaking and bigtooth aspen leaves began to soften and melt, thereby smoothening the surfaces of these leaves. This response to increased temperature resulted in an approximate
reduction in contact angle of 65° for both aspen leaves, demonstrating the importance of nano-scale features for superhydrophobicity.

- In addition to their superhydrophobic leaf surfaces, quaking and bigtooth aspens also possess high aspect ratio leafstalk geometries which offer little resistance to twisting and bending, compared to their square counterparts found on other leaves (e.g. maple). This results in excess leaf movement even in the slightest breeze, further facilitating water droplet roll off and promoting dry leaf surfaces.

- Near the end of summer 2011, unlike previous years, quaking aspen leaves lost their superhydrophobic property. After a thorough analysis of the weather patterns and a detailed monitoring of the change in leaf surface structure over that summer, it was concluded that the loss of superhydrophobicity was due to a relatively hot and humid summer. These weather conditions drastically reduced the wax crystal regeneration rates resulting in the gradual removal of hydrophobic nano-scale wax crystals and consequently the loss of this extreme non-wetting property.

- Nanocrystalline nickel samples that were sandblasted before chemical etching in nitric acid displayed a dual-scale hierarchical pitted surface structure similar to the negative of the aspen leaves’ surfaces. These metallic surfaces contained arrays of micro-scale pits lined with finer nano-scale roughness features and were selected to be used as pressing templates in the structuring of polymer surfaces.

- Sandblasted and chemically etched nanocrystalline nickel samples were used as pressing templates to structure polyethylene, polypropylene and polytetrafluoroethylene samples. This pressing process resulted in a good transfer of all surfaces features and rendered all
three polymer surfaces superhydrophobic with water contact angles $>150^\circ$ and tilt angles $<5^\circ$.

- Production scalability can easily be achieved by adding a one-step pressing process to the end of pre-existing production lines. By placing an appropriately structured rolling template at the end of a polymer sheet manufacturing line, large scale polymer sheets with superhydrophobic properties could be obtained with minimal production line modifications. Additionally, superhydrophobic properties could be imparted onto complex shaped geometries by electroplating the inside of moulds used for injection moulding processes. After structuring the inside electroplated surface, all parts coming from these moulds are expected to have surfaces with superhydrophobic properties.
Future Work

- The study of the influence of weather conditions on the wetting behaviour of quaking aspen leaves described in section 4.8 did not specifically focus on the initial rapid increase of the wetting angle in the early stages of quaking aspen leaf growth (region I in figure 4.24) and the significant changes in leaf surface morphology over a very short period of time, as shown in figures 4.18 and 4.19. This issue should be addressed in a future study with the specific objective to shed more light on the initial growth of leaf wax crystals. Wetting property measurements and surface morphology images should be taken daily during this early stage of leaf growth.

- The above mentioned study only considered the growth of quaking aspen leaves. It could be equally insightful to analyze other aspen species (*i.e.* bigtooth aspen) in this same context. In early stages of growth, bigtooth aspen leaves possess a fine cotton-like fibrous (downy) material that covers the leaves’ top surface [Chao 2009]. Shortly after
leaf emergence this downy layer disappears and the leaf is superhydrophobic as described in this thesis. However, when the downy layer was mechanically removed, the leaf’s surface did not display, and did not regain its non-wetting effect [Chao 2009].

- It would be insightful to perform chemical analysis on these leaf surfaces, as well as the polymers used both prior to and after pressing to ensure their surface chemistries are not altered by the pressing procedure. Both Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) would be useful techniques for accurately determining the chemistry of these surfaces.

- In section 5 on template synthesis and characterization it was shown that nanocrystalline nickel samples which were electro-etched in a 33% nitric/67% ethanol solution (figures 5.5 and 5.6) showed an array of nano-scale pits (~100nm) that could be suitable for creating anti-reflective surfaces based on the moth eye effect. The eyes of these insects display an ordered array of tiny chitin protrusions (~100nm) that render the surfaces anti-reflective. It would be interesting to use the electro-etched nanocrystalline samples as a template in a similar manner as described in this thesis to press softened polymers to fabricate inexpensive anti-reflective surfaces.

- Although the structured nanocrystalline nickel templates used for pressing of polymer surfaces in this thesis were not superhydrophobic themselves, certain surface structuring processes (i.e. sandblasted followed by chemical etching) increased the measured contact angle (Table 5.1). This finding suggests the feasibility of creating superhydrophobic metallic surfaces, by depositing a low-surface energy layer directly onto structured nanocrystalline nickel templates. This should be further explored in future studies.
As discussed in section 6.7, the described method for producing superhydrophobic polymer surfaces has one major advantage over others: inexpensive process scalability. More work is required to determine the appropriate scale up parameters needed to structure the outside surface of a roller which could be used in a continuous polymer pressing process at the end of a pre-existing polymer sheet production line. Additionally, work needs to be done to achieve an evenly structured surface on the inside of individual polymer injection moulds that could be used to produce complex shaped components with superhydrophobic surfaces.

In sections dealing with the effect of sodium dodecyl sulphate (SDS) concentration on the water contact angles of superhydrophobic aspen leaves (figure 4.14) and pressed polymers (figure 6.11) fabricated during this research, all tested samples showed a relatively rapid reduction in contact angles with the introduction of small amounts of SDS. It would be interesting to test these samples using finer intervals in the low SDS concentration range from 0-10g/L. Furthermore, both aspen leaves and pressed PTFE samples did not show the same magnitude of contact angle reduction as the other samples tested (hydrophobic maple leaves, plexiglas™ and both pressed and un-pressed PP). A deeper investigation into the mechanisms present and the interaction between SDS molecules with aspen leaves and pressed PTFE samples is necessary.

A detailed investigation into the wear and abrasion resistance of the superhydrophobic surface features is necessary. Results from this type of study could be used to determine potential applications and the maximum operational lifetime for these non-wetting surfaces in service.
References


• Cullity BD (1978) *Elements of X-ray Diffraction, 2nd ed.* Addison-Wesley, MA, USA.


Appendix 1 – Superhydrophobic Insects

There are a variety of insects that possess superhydrophobic surfaces on one or more part(s) of their bodies. In all cases, this property is created due to a combination of micro/nano scale surfaces structures coupled with a low surface energy material. More often than not these functional surfaces are present for survival and/or growth advantages and are most likely the result of millions of years of species evolution. This section will introduce and discuss some of these interesting superhydrophobic surfaces.

The legs of water striders (Gerris remigis) have been shown to exhibit a hierarchical structure of a large number of oriented tiny hairs (microsetae) each containing fine nanogrooves [Gao and Jiang 2004; Ding et al. 2008]. It is this dual-scale superhydrophobic structure of their legs (Figure A1.1) that allows them to easily float on top of water surfaces. This anti-wetting property produces enough force to counteract gravity and keep the insect afloat, allowing it to move over the water’s surface with very little resistance. Since water striders spend most of their lives on water surfaces, this property allows them to capture food and avoid predators very effectively.

The wings of many insects also show non-wetting characteristics of this type. Both butterfly (Morpho peleides) and cicada (Terpnosia jinpingensis) wings display a unique surface structure that imparts a superhydrophobic property to this part of their body. The wings of these butterflies are composed of multiple micrometer sized scales, each possessing many tiny aligned rows of ridges. This structure in shown in Figure A1.2 and is thought to be the main contributing factor to superhydrophobicity for these surfaces [Ding et al. 2008].
Figure A1.1: SEM images of water strider legs. Low magnification image of a microseta (top) and high magnification image of multiple nanogrooves on a single microsetae (bottom) [Ding et al. 2008].

Figure A1.2: SEM images of a butterfly wing. Low magnification image of a wing scale (top) and high magnification image of multiple aligned ridges on a single scale (bottom) [Ding et al. 2008].
On the other hand, cicada wings gain their non-wetting property through an ordered array of nanostructured protrusions (Figure A1.3) [Hong et al. 2009; Sun et al. 2009; Watson and Watson 2004]. This surface only contains nano-sized features and although it does display high contact angles just below the superhydrophobic regime (~146°), it is not as well suited to resist wetting in as many different conditions (e.g., range of drop sizes and water content) as surfaces that contain both nano and micro-sized features [Sun et al. 2009]. Additionally, their study did not consider dynamic wetting properties such as contact angle hysteresis or surface tilt angles that are crucial for the ability of surfaces to self-cleaning. Nonetheless, both butterflies and cicadas wings are able to resist being wet by their special surface structure that allows for the formation of a composite interface (consisting of trapped air-pockets) under water droplets. These and other flying insects with superhydrophobic wings have most likely developed this type of self-cleaning surface structure to minimize the amount of water and particulate contamination that is able to adhere to their wings; both of which would drastically increase the weight of these crucial body parts, reducing the ability for these insects to fly [Wagner et al. 1995].

Figure A1.3: SEM image of the nanostructured protrusions found on a cicada wing (scale bar = 1 µm) [Sun et al. 2009].
A very interesting and extremely important mechanism for survival is found on the back of the Namib Desert beetle (*Stenocara gracilipes*). This beetle inhabits an extremely dry area and is able to capture water from morning fog-laden wind, through the elegantly designed surface structure of their wings. This surface structure consists of an array of tiny hydrophilic spots surrounded by superhydrophobic regions [Parker and Lawrence 2001; Zhai et al. 2006]. The hydrophilic regions are found on the wax free peaks of bumps located on the beetle’s wings (Figure A1.4a, b) while the troughs between these bumps are covered by an array of micro-scale mounds and a hydrophobic wax (Figure A1.4c) causing these areas to be superhydrophobic. Water molecules from morning fog condense on the hydrophilic spots and slowly grow in size, until a critical volume is reached. At this point, due to their increased weight the droplets break free from those hydrophilic spots and as the beetle tilts its wings, they roll through the superhydrophobic troughs into its mouth. This smart surface structure design allows these beetles to harvest water and survive in an extremely dry environment.

Another example of how superhydrophobic surfaces can be extremely beneficial for insect species can be found on the thorax (body cavity) of many water treading (*Mesovelia mulsanti*). Insects of this type are able to breathe for an extended period of time underwater through the formation of a respiratory bubble (thin layer of air) that completely surrounds their bodies while submerged. The two-tiered hierarchical hair structure found on these insects (Figure A1.5) imparts a superhydrophobic property to the surface which strongly resists wetting (even when completely submerged) and results in the formation of a respiratory bubble [Flynn and Bush 2008]. Since these insects breathe through small openings in their thorax (‘spiracles’ shown in Figure A1.5c and d) they are able to respire and survive for relatively long periods of time underwater through gas exchange with this respiratory bubble [Hilton and Jarman 1976].
Figure A1.4: The water-capturing wing surface of a *Stenocara* beetle. (a) Optical image of the beetle (scale bar = 10 mm). (b) Hydrophilic region (outlined) found on the peak of each ‘bump’ on the beetle’s back (scale bar = 200 µm). (c) Hydrophobic region found in the troughs between each ‘bump’ (scale bar = 10 µm) [Parker and Lawrence 2001].

Figure A1.5: SEM images of the thorax of a water treader. Two-tiered hierarchical hair structure (a, b and c) and a spiracle (c and d) through which this insect breathes [Flynn and Bush 2008].
Appendix 2 – Examples of Water Drop Images

Figure A2.1: Water drops (5µl) on the adaxial side of quaking (left) and bigtooth (right) aspen leaves.

Figure A2.2: Water drops (5µl) on the adaxial side of quaking at 65°C (left) and bigtooth at 50°C (right) aspen leaves.
Figure A2.3: Water drops (25µl) on the adaxial side of quaking (left) and bigtooth (right) aspen leaves.

Figure A2.4: Water drops (5µl) containing 100g/L of SDS on the adaxial side of quaking (left) and bigtooth (right) aspen leaves.

Figure A2.5: Water drops (5µl) on un-pressed (left) and pressed (right) polyethylene.
Figure A2.6: Water drops (5µl) on un-pressed (left) and pressed (right) polypropylene.

Figure A2.7: Water drops (5µl) on un-pressed (left) and pressed (right) polytetrafluoroethylene.

Figure A2.8: Water drops (5µl) on un-pressed polypropylene at 65°C (left) and pressed polypropylene at 65°C (right).
Figure A2.9: Water drops (5µl) on un-pressed polytetrafluoroethylene at 65°C (left) and pressed polytetrafluoroethylene at 65°C (right).

Figure A2.10: Water drops (25µl) on un-pressed (left) and pressed (right) polypropylene.

Figure A2.11: Water drops (25µl) on un-pressed (left) and pressed (right) polytetrafluoroethylene.
Figure A2.12: Water drops (5μl) containing 25g/L of SDS on un-pressed polypropylene (left) and pressed polypropylene (right).

Figure A2.13: Water drops (5μl) containing 25g/L of SDS on un-pressed polytetrafluoroethylene (left) and pressed polytetrafluoroethylene (right).
Appendix 3 – Influence of Weather on the Wetting Behavior of Quaking Aspen Leaves

Perhaps the differences in wax crystal density and wetting properties for leaves collected in 2011 compared to previous years (see section 4.8) can be explained by considering the environmental factors affecting both wax crystal erosion and regeneration rates. For this analysis all available weather data was taken from Environment Canada’s National Climate Data and Information Archive – Peterborough/Trent University weather station, which is within 20km of the quaking aspen tree examined in the current study. [http://www.climate.weatheroffice.gc.ca].

To study the factors affecting wax crystal erosion/regeneration of quaking aspen leaves during the 2011 growth season and a previous year (2009) where superhydrophobicity was observed throughout the entire season, a cumulative environmental effect approach has been employed. The most important environmental factors for wax crystal loss/regeneration are likely temperature, wind gusts and relative humidity (R.H.). In order to assess their relative effects the following analysis considers certain arbitrary thresholds for these factors: wind gusts >40km/hr, temperature >25°C and relative humidity >95%. Also considered was cumulative precipitation over the growth period. Using cumulative values for these environmental factors rather than day-by-day data has the advantage that the overall longer term impact on the critical wax crystal erosion/regeneration process is better captured. A single day event analysis was initially attempted, but no clear trends as with the cumulative analysis presented here were observed.

Figure A3.1 is a plot of the cumulative wind gust events greater than 40km/h for the 2009 and 2011 growth seasons, while Figure A3.2 and Figure A3.3, respectively, plot the cumulative precipitation and cumulative hours with temperatures above 25°C for the same two years. These
figures also contain the contact angles from figure 4.24 for quaking aspen leaves gathered on different dates during 2011. For 2009 and 2011 the wind gust and precipitation profiles are quite similar. On the other hand, the cumulative hours above 25°C for these two years differ substantially. In 2011, there was more than two and a half times the number of hours with temperatures above 25°C compared to 2009. Elevated temperatures have been shown to soften and in certain cases remove/melt leaf wax crystals, resulting in decreased water contact angles [Cheng et al. 2006; Victor and Erb 2010]. The elevated temperatures experienced during 2011 resulted in high wax erosion stresses on quaking aspen leaf surfaces. The warmer, softened wax crystals are more susceptible to wind and precipitation erosion.

![Graph showing cumulative wind gusts and quaking aspen contact angles](image)

Figure A3.1: Quaking aspen contact angles and cumulative wind gusts above 40km/h for the growth seasons of 2011 and 2009.
Figure A3.2: Quaking aspen contact angles and cumulative precipitation for the growth seasons of 2011 and 2009.

Figure A3.3: Quaking aspen contact angles and cumulative hours above 25°C for the growth seasons of 2011 and 2009.
The exact mechanisms for wax crystal regeneration are not fully understood, but a few possibilities have been proposed. It is widely accepted that for this process to proceed there must be a net movement of wax molecules through the leaf cuticle to the outermost layer. Initially it was thought that microchannels were present that allowed the transport of wax molecules through the cuticle; however a previous study found no such microchannels [Jeffree 1996]. In 2001, Neinhuis et al. proposed that wax molecules are co-transported across the cuticle with the continuous current of water molecules flowing through the leaf: a hypothesis that was well supported by their experimental data. This mechanism is further supported by the findings of Baker in 1982. They observed that wax production (regeneration) rates decreased with increasing relative humidity. If wax molecules do co-transport with water flowing through the cuticle, the amount of wax molecules getting to the leaf’s surface will decrease with reduced water flow through the plant. At higher relative humidity levels there will be a lower driving force pushing water through the leaves resulting in reduced transpiration rates, and consequently reduced amounts of wax molecules reaching the outermost layer of the leaves.

Figure A3.4 shows the cumulative hours above 95% R.H. for 2009 and 2011, again with the contact angles for quaking aspen leaves harvested during 2011. There is clearly a very large difference in the number of hours with R.H. above 95% between the two years. There were almost 300 hours where R.H. was above 95% in 2011 while this value was zero for 2009. It is also interesting to note that around the middle of August 2011, when the quaking aspen leaves’ contact angles drastically dropped, the cumulative R.H. increased significantly. Using Neinhuis et al.’s [2001] proposed mechanism for wax crystal transport, and Baker and Hunt’s [1986] inverse relationship for R.H. and wax crystal regeneration, it appears that the drastic drop in the contact angle for quaking aspen leaves during August of 2011 (which was not observed in 2009)
can be explained, at least in part, by this significant difference in R.H. for 2009 and 2011. Furthermore, a study performed by Koch et al. [2006] that monitored the morphology and leaf surface wettability of plants cultivated in different controlled humidity chambers, showed that plants grown at high R.H. exhibited significantly lower amounts of surface wax crystals and reduced contact angles compared to plants cultivated at lower R.H. All three plant species they studied (*brassicaceae*, *myrtaceae* and *tropaeolaceae*) showed notable decreases in both surface wax crystal density and contact angles when cultivated at very high relative humidity values of 98% or above. This observation was used to justify the selection of 95% R.H. as the threshold value in the current study.

Figure A3.4: Quaking aspen contact angles and cumulative hours above 95% R.H. for the growth seasons of 2011 and 2009.
It appears that in most years quaking aspen leaves are well suited to withstand the effects of wax crystal erosion through an effective mechanism for wax regeneration. Normally, this allows them to retain their superhydrophobic surface property throughout their entire life cycle. The effect of this continuous erosion and regeneration of wax crystals is illustrated by the fluctuating contact angles observed during the early and middle parts of the 2011 growth season. In unusual weather conditions, like those observed during 2011, wax erosion rates may increase and/or wax regeneration rates may decrease which can result in a less dense layer or complete loss of surface wax crystals and consequently reduced water contact angles. It should be noted that a considerable, but gradual, reduction of the wetting angle throughout the growth season due to the loss of wax crystals has previously also been reported for oak leaves [Neinhuis and Barthlott 1998]; however in their study the influences of weather conditions on the wax crystal loss/regeneration were not analyzed.

It is interesting to note that a similar reduction in quaking aspen contact angles was observed at elevated temperatures which caused the localized melting of the leaves finer nano-scale wax crystals (figure 4.11 - section 4.4). It appears that regardless of the mechanism(s) responsible for the removal of wax crystals the resulting contact angle ends up being ~90° indicating that the contact angle of quaking aspen leaves with only papillae (no nano-scale wax crystals) is ~90°.
Appendix 4 – Supplementary SEM Images

Figure A4.1: SEM images of the adaxial side of a quaking aspen leaf harvested on May 28, 2011.

Figure A4.2: SEM images of the adaxial side of a quaking aspen leaf harvested on June 19, 2011.
Figure A4.3: SEM images of the adaxial side of a quaking aspen leaf harvested on June 26, 2011.

Figure A4.4: SEM images of the adaxial side of a quaking aspen leaf harvested on July 30, 2011.
Appendix 5 – X-ray Diffraction Analysis for Grain Size Measurement of nNi

X-ray diffraction was used to measure the grain size of the nNi samples used in this research. A Rigaku miniflex diffractometer using Co-Kα (λ=0.179nm) radiation was employed and outputted the spectrum shown in Figure A5.1. A software program (MDI Jade 5.0) used the Scherrer formula (equations A5.1 and A5.2) [Cullity 1978] to calculate the grain size of 23.9nm for this material from peak broadening of the (111) peak measured as the Full Width at Half Maximum (FWHM) in radians.

\[
\begin{align*}
\text{Intensity (counts)} & \quad \text{Intensity (counts)} \\
(111) & \quad (200) \\
2\Theta(\degree) & \quad 2\Theta(\degree)
\end{align*}
\]

Figure A5.1: XRD spectrum of nNi using Co-Kα (λ=0.179nm) radiation.

The following two equations are used to obtain grains sizes within the range of 10-50nm:

\[
\begin{align*}
d &= \frac{0.9\lambda}{B\cos\Theta_B} \quad \text{(A5.1)} \\
B^2 &= B_M^2 - B_S^2 \quad \text{(A5.2)}
\end{align*}
\]

where \(d\) is the average grain size of the material (Å), \(\lambda\) is the wavelength of the radiation (Å), \(B\) is the true broadening due to grain size reduction (radians), \(\Theta_B\) is the Bragg angle for the specific peak considered (degrees), \(B_M\) is the measured broadening from the XRD spectrum (radians) and \(B_S\) is the standard broadening due to the equipment used.
Appendix 6 – SEM Images of Etched Polycrystalline Nickel

Figure A6.1 shows three SEM images of a polycrystalline nickel sample that was sandblasted prior to chemical etching in nitric acid for 30min. This surface exhibits no micro-scale pits necessary for the development of a dual-scale hierarchical surface unlike the nNi samples used in this research (figure 5.11). For this reason polycrystalline samples were not reported in the main part of this thesis. Moreover, polypropylene samples pressed with this polycrystalline surface exhibited contact angles of 122° and tilt angles of 30°, both of which are far from the accepted superhydrophobic values.

Figure A6.1: SEM images of polycrystalline nickel that was sandblasted and chemically etched for 30min in nitric acid.
Appendix 7 – Estimation of Real Contact Area and Calculated Contact Angles

In the past there have been efforts to calculate the real contact area between a liquid droplet and a rough or porous solid surface [e.g. Timsit 1982; Heichal and Chandra 2005; Xu et al. 2007]. These models are appropriate for an idealized surface where features all have the same dimensions and spacing. Unfortunately for the surfaces analyzed in this study, there is a rather wide range of feature sizes. In this research, average protrusion diameters and surface densities (Table 6.2) were used to calculate the real contact areas between liquid drops and solid surfaces (Table A7.1:) assuming that each protrusion is a vertical column and there is complete wetting on top of each one. In other words, the contact area for each protrusion was calculated and multiplied by the number of protrusions per square millimetre, giving values for \( f_{la} \), and consequently \( f_{sl} \).

<table>
<thead>
<tr>
<th>Real Contact Area</th>
<th>PE</th>
<th>PP</th>
<th>PTFE</th>
</tr>
</thead>
<tbody>
<tr>
<td>( f_{la} )</td>
<td>0.636</td>
<td>0.820</td>
<td>0.598</td>
</tr>
<tr>
<td>( f_{sl} )</td>
<td>0.364</td>
<td>0.180</td>
<td>0.402</td>
</tr>
</tbody>
</table>

Incorporating contact angles values for each un-pressed polymer (Table 6.3) and the values from Table A7.1: into Cassie and Baxter’s heterogeneous wetting equation (equation 2.4 - \( \cos \theta_{CB} = R_f \cdot f_{sl} \cdot \cos \theta_o - f_{la} \)) results in a range of calculated contact angles (\( \theta_{CB} \)), depending on
the roughness factor ($R_f$) for the pressed polymer surfaces. It is very difficult to obtain accurate data regarding the nano-scale roughness on these pressed polymer surfaces, which is why a range of roughness factors, and their corresponding calculated contact angles, have been used in Table A7.2. As displayed in Table A7.2, the contact angle of a heterogeneous surface is dependent on the roughness factor; however all calculated contact angles [especially those using roughness factors greater than 2 – which is expected based on SEM images of these pressed polymer surfaces (figure 6.3-figure 6.5 and figure 6.7)] are comparable to the measured contact angle values given in Table 6.3 and also shown in Table A7.2.

It is also important to note that these values are rather susceptible to changes in the diameters and densities of micro-scale protrusions. Due to the template sandblasting and etching process employed in this research, there is a wide range on protrusion sizes and spacing throughout each samples’ surface (as shown in plus/minus values of Table 6.2), which introduces a certain level of inaccuracy to these calculations.

Table A7.2: Calculation of contact angles on pressed polymers using values from Table 6.2 and Table A7.1: and equation 2.4.

<table>
<thead>
<tr>
<th>$R_f$</th>
<th>$\Theta_{CB}$ for pressed PE</th>
<th>$\Theta_{CB}$ for pressed PP</th>
<th>$\Theta_{CB}$ for pressed PTFE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>132°</td>
<td>150°</td>
<td>136°</td>
</tr>
<tr>
<td>1.5</td>
<td>134°</td>
<td>152°</td>
<td>142°</td>
</tr>
<tr>
<td>2</td>
<td>135°</td>
<td>155°</td>
<td>150°</td>
</tr>
<tr>
<td>2.5</td>
<td>137°</td>
<td>158°</td>
<td>155°</td>
</tr>
<tr>
<td>3</td>
<td>139°</td>
<td>162°</td>
<td>166°</td>
</tr>
<tr>
<td>$\Theta_{CB}$ measured</td>
<td>151°</td>
<td>153°</td>
<td>159°</td>
</tr>
</tbody>
</table>