Injection Molded Nanostructures Together with Hearing Instrument Materials

Frida Falkvall
Ulrika Orstadius

Master’s Thesis in Biomedical Engineering
Faculty of Engineering LTH
Department of Biomedical Engineering
Lund University, Sweden

LU Supervisor: Cecilia Eriksson Linsmeier
Oticon Supervisor: Morten Fuglsang-Philips

June 2016
Abstract

The purpose of this Master’s Thesis was to gain insight to how injection molded nanostructures could be used together with hearing instrument materials. The reason to investigate this new nanotechnology was to see if it is of interest for Oticon to invest in. To reach conclusions, literature was studied regarding surfaces wetting properties, capillary effects, adhesion and material properties. Surface properties of different polymers were determined by measuring contact angles and surface energies. Thereafter, two tools were designed in collaboration with Oticon and Transform in order to test how well Oticons hearing aid materials could replicate the nanostructures. The two test geometries were also created to test capillarity and glue adhesion.

From the contact angle and surface energy measurements, plus the two test geometries, some conclusions were made. All materials could replicate the nanostructured pattern, where the semi-crystalline polyamide gave the best results. From the glue adhesion test it could be seen that the nanostructured material with the highest surface energy, amorphous polyamide, gave best results. Further it was also possible to draw the conclusion that in capillaries a nanostructured surface, together with a chemical coating, is able to hinder water ingress to some extent.

From the results of this project it is possible to further investigate whether this is an interesting technology for Oticon. Future studies could consist of studying wear of the tools and how nanostructures are replicated on curved geometries.

Keywords: nanostructures, injection molding, superhydrophobic, superhydrophilic, capillarity, adhesion, polyamide, contact angle, surface energy, Oticon.
Acknowledgement

This Master’s Thesis project has been conducted as a part of a Master of Science in Biomedical Engineering at the Faculty of Engineering, Lund University. The project has been carried out at the company Oticon A/S located in Copenhagen, Denmark, and has been conducted in collaboration with Transform at Denmark’s Technical University (DTU). In this section of the report we would like to take the time to acknowledge the people that has been of extra importance for this work.

The main person we would like to thank is Morten Fuglsang-Philips who has been our supervisor at Oticon and the person that has made it possible for us to do this project. Morten has not only mentored us through the different steps throughout the process, but has also been available for questions and brainstorming sessions. Thank you again. Other than Morten and Oticon as a company, we would like to thank the people we have been in contact with at Oticon these past few months. Without the help and support from you this project would not have been as successful.

Another person that has been indispensable for this thesis is Cecilia Eriksson-Linsmeier. Thank you for all the pointers regarding our report and for helping us with finding a good structure for the project. Thank you for all the help and support.

We would also like to take the time to thank Carl Esben Poulsen and Nis Korsgaard Andersen, at DTU and Transform, for all the time and help with the nanotechnology they gave us from the beginning of the project until the end. Thank you for the collaboration.

Lastly we would like to individually thank our families for their support they provide throughout the years and also to the friends that inspired us to become better everyday. Thank you!
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Table 1: Showing the equations that will be used in this Master Thesis report.

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<td>4</td>
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<td>5</td>
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<tr>
<td>7</td>
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<td>$\cos(\theta) = R_f f_{SL}\cos(\theta_0) - 1 + f_{SL}$</td>
</tr>
<tr>
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<td>$\Delta p = \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$</td>
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1 Introduction

1.1 Background

This section will give a brief background to the project and the hearing instrument of today. The robustness of the hearing aid is very important for its users since they depend on their instruments. While many hearing aids of today are able to fulfill many functions that enables hearing (such as Oticon’s; BrainHearing, Speech Guard, Spatial Sound, Directionality, to mention some) a lot of the hearing aids provided still have room for improvement. This project is performed in cooperation with the hearing aid manufacturer Oticon A/S, with focus to understand if using injection molded nanostructures would improve robustness. Another collaborator in this project has been the company Transform, also based in Copenhagen, Denmark.

1.1.1 About Oticon

Oticon is a hearing aid company with the slogan “People first” - to empower people to communicate freely, interact naturally and participate actively. They are one of the three largest providers of hearing care solutions in the world and are known for, e.g. Opn™ which is Oticon’s most sophisticated hearing solution to date. Oticon designs and manufactures hearing solutions for adults as well as specialized paediatric instruments. In addition Oticon Medical, which is a part of the group, produces bone-anchored hearing solutions. Oticon and Oticon Medical employ more than 3000 people together around the world.

The company works by the principle “People first”. This means that Oticon continuously collect information about the users’ needs and everyday lives through test panels, end-user visits, in-depth interviews and focus groups. The test-user panel includes more than 1,000 users and a group of test-users are attached to each product development cycle and are involved from the analysis phase, right through to product testing.

According to Oticon, there is a prediction that the number of people in need of hearing support will increase by one third per generation over the coming century. Today around 500 million people around the world are suffering from hearing losses, predominantly by people with an age over 50. However, around 8 out of every 100 people with hearing loss are under the age of 18 (Oticon, 2015).

1.1.2 History of Hearing Aids

The history of devices for hearing impairment is long. Until the late 19th century, the devices were acoustic and called “ear trumpets”. They were used to modestly amplify the sound and worked by collecting sound waves and guiding them directly into the ear canal. The development of electricity should however provide for new technologies for better amplification. In 1876 Alexander Graham Bell patented the telephone, which was the first electrical device that could transmit speech. Some people with hearing impairment found the telephone helpful and easier to
use to listen to a conversation rather than listening to someone in person. This is because the receiver was held up to the ear. To continue the evolution some people tried to adapt the telephone to hearing aids in the beginning of the 20th century, but the results were obtrusive, heavy and only amplified speech by 15 decibel at most. Since a normal conversation has a volume that averages about 60 dB, and a person normally raises their voice by about 30 dB if a conversation partner has trouble hearing, the use of the early aids were limited.

The development of the vacuum tube in 1907, which is a device that controls electric current between electrodes in an evacuated container, was further used to produce the first technically superior hearing aids in 1920. These offered 70 dB of amplification and a more even frequency response. However, they were not portable and had a weight of 100 kilograms. Until 1924, the weight decreased to 4 kg but people refused to use them since the users needed to hold up the receiver to the ear and also because of the stigma attached to being visibly hearing impaired. In 1938 the first wearable hearing aid was developed. By using sub-miniature vacuum tubes it allowed for amplifiers to become smaller and also require less power.

In the late 1940s, two innovations from World War II were combined with these tubes to produce more compact and reliable models — the printed circuit boards and button batteries. This made it possible to produce one single unit that could fit in a person’s shirt pocket that combined batteries, amplifier and microphone. The unit was connected to an earpiece via a wire. However, the users wanted hearing aids that were invisible and worn as a one-piece unit at the ear. The solution came in 1948 with the invention of the transistor and in the late 1950s the first hearing aid worn entirely at the ear was introduced.

The evolution continued and in 1964 a behind-the-ear model using an integrated circuit amplifier and a button battery were sold which weighed just 7 grams. The microphone was placed inside the ear and connected by a wire to the amplifier and battery unit, which was then clipped to the ear. In the late 1980s several companies were applying digital signal-processing chips to hearing aids, initially in hybrid analog-digital models in which digital circuits controlled an analog compression amplifier. Fully digital models debuted in 1996 and programmable models, which allowed for greater flexibility and fine-tuning of the hearing aids according to the patients needs, became available in 2000. By 2005, digital hearing aids had captured more than 80 percent of the market (Hochheiser, 2013).

1.1.3 Robustness of Hearing Aids

There has been a major evolution of hearing aids during the last century but there is still room for improvement. Robustness of the hearing aid is very important for hearing aid users since they depend on their instruments. Therefore, the robustness is something many hearing aid companies use as a competitive advantage when marketing their products. There is no complete definition of robustness,
however, for this thesis robustness will be considered as the following:

- Protection against water ingress
- Protection against chemicals
- Mechanical strength
- Wear resistance

To ensure that the hearing instruments are robust and can withstand everyday situations they undergo tests where they are exposed to sun lotion, sunlight, high humidity in different temperatures, free falls et cetera. The company uses a classification system called the IP classification for definition of water- and dust proofness of the hearing aids. All hearing instruments are today classified with the IP58 classification. They use mechanical designs with barriers to prevent ingress of water and dust and many parts are nanocoated to repel water and moisture. The IP58 classification grade the level of protection where the digit “5” means that the device are protected against the amount of dust that could interfere with the normal functions. The digit “8” says that the device is protected against continuous water ingress if immersed in water with a depth of 1 meter. The classification does not include if the device gets in contact with salt water, chloride water, soap or other liquids that contains chemicals, meaning that it can not be used when swimming or showering (Fuglsang-Philips, 2016).

Some identified areas of improvements within robustness of hearing aids are water ingress, wax ingress and glue strength. The problem with water ingress lies in the fact that the hearing aids are composed of different parts that are joined together. This creates small gaps between the parts, where water ingress is a major problem when it gets in contact with the electronics inside the apparatus. In addition to water ingress, the hearing aids also suffer from ingress from ear wax. Ear wax is solid in room temperature, but if it is heated up it will become partially liquid, where the liquid can be transported into the hearing aid and clog up the sound outlet or the ventilation. Lastly, in some of the hearing devices, two or more parts are glued together. These parts need to be able to withstand for example free falls if the user drops the device. Also, if the adhesion of the glue is bad, the glue can move to unwanted parts of the hearing aid (Fuglsang-Philips, 2016).

1.1.4 Chemically Induced Water Resistance

There is a trend today to make waterproof plastics by decorating the surface with chemical coatings to obtain the desired properties. The advantage is that the coatings can be applied to a wide range of both flat and irregular surface. They can also modify surface topography and chemistry in one step (Søgaard, 2014). One way of producing water repellent, also called superhydrophobic, surfaces is by applying nanoparticles, namely nanocoatings. Nanocoatings are defined as the covering of materials with a layer in the nanometer scale, 10 - 100 nm in thickness.
If nanoparticles in different sizes are used, roughness can be created (Kylián, 2014). The most common materials employed for the fabrication of highly hydrophobic surfaces are fluorocarbons ($CF_x$), since $CF_x$ groups exhibit one of the lowest surface energies, which is provided for a hydrophobic surface. Concerning hearing instruments, hydrophobic coatings are mainly used to prevent water and other liquids from penetrating the device and thereby improve the corrosion resistance of the product (Søgaard, 2014).

Some disadvantages with chemical coatings are that it is hard to control where the coating is applied and if coatings are used it usually covers the whole instrument. Sometimes it can be a benefit not having the whole apparatus hydrophobic to be able to guide water or enhance the strength of glue. The production of coatings is also often expensive and time consuming (Søgaard, 2014).

1.1.5 Nanostructures and Injection Molding

Nanostructures can be used as a complement or substitute to chemical coatings where nanostructures can make surfaces superhydrophobic, superhydrophilic or even self-cleaning to minimize water and wax ingress. In addition to this, nanostructures could also improve adhesion of glue to plastic parts to improve strength and robustness. According to National Nanotechnology Initiative (NNI), nanotechnology is defined as the usage of structures with at least one nano dimension for the construction of systems with improved properties due to their nano size. In the same way, nanoparticles are defined as particles with an intermediate size between 0.1 and 100 nm (Deopura, 2008). Today most hearing aids use plastic shells and filters. The design of the surfaces of these plastic parts can have huge influence on water ingress and robustness of hearing aids. The most common production method for making nanostructures on surfaces of plastic products is based on injection molding. The principle of injection molding is that a melted polymer fills a predefined mold and the plastic part is removed once the polymer has solidified. The principle is simple, but in reality the process involves many complex steps. Injection molding of nanostructures is already used on a big scale and with very low cost by the industry on flat surfaces; such as everyday items like DVD and Blu Ray discs. Surfaces with self-cleaning effects that mimic for example the lotus flower are of huge relevance for the medical industries (Søgaard, 2014).

1.2 Purpose

The purpose of the project was firstly to understand the new injection molding technology of nanostructures developed by DTU. Secondly, we wanted to study if the molding technique was applicable on typical hearing instrument materials. By testing the technology with a focus point on hearing aids the hope was to reach conclusions regarding if this technique is interesting for Oticon to invest in.
1.3 Issues
To reach a conclusion regarding the purpose the following issues have been formulated:

- How does superhydrophobic surfaces behave?
- How can superhydrophobic surfaces be created?
- How does the nanostructures work on typical hearing aid materials?
- How shall parts be designed, to take advantage of superhydrophobic or hydrophilic surfaces?
- Can Oticon take advantage of nanostructured surfaces to improve robustness of hearing aids?

1.4 Deposition of the Report
This report is divided into five chapters. The first chapter gives a background to the project, to Oticon and hearing instruments in general. It also states the purpose of the study and the formulated issues that are to be answered. Chapter two gives the reader a thorough basis to the theory used in this project. Moreover, in chapter three, the methods used to conduct the studies and tests will be explained. This is followed by the results, which is presented in chapter four, and discussions and conclusions regarding the results can be found in chapter five.

1.5 Division of Work
During the project all parts of the project, as well as the report, were done in collaboration between the named authors. F. Falkvall was mainly responsible for the polymer knowledge, while U. Orstadius concentrated on the development of the CAD-design.
2 Theory

This section of the report will describe the theory behind how superhydrophobic surfaces behaves and can be created. Furthermore, the measurement methods concerning different materials hydrophobicity will be described.

![Image showing a droplet on a surface and the contact line where the three phases meet.](image)

In this image, Young’s angle, or the CA, is also present as \( \theta_0 \). \( \gamma_{SG} \), \( \gamma_{SL} \) and \( \gamma_{LG} \) are the surface tensions.

2.1 Wetting properties

Water does in some way affect all surfaces in everyday life. When a liquid droplet interacts with a surface the interaction can be described with terms such as wetting, spreading, adhesion and de-wetting. To be able to develop and manufacture surfaces with an enhanced quality, an understanding of these interactions are of importance in the surface science. Wettability describes the interaction when a liquid first meets a solid surface. Wettability is a degree of wetting that is determined by a force balance of adhesive and cohesive forces, where adhesive forces are the forces between the molecules in the droplet and the surface and the cohesive forces are between molecules in each material separately. The term wetting refers to the study of how a droplet is spread out, or not spread out, on a surface and its ability to maintain contact with the surface. The spreading and non-spreading phenomena can be described with the terms “hydrophilicity” and “hydrophobicity”. Hydrophilic and hydrophobic surfaces will be described in the next section of the report. The definition of wettability was first stated by Thomas Young in 1805, where he expresses that wetting of a surface by a liquid can be described by the shape of the droplet and the droplets contact angle (CA) (Law, 2016). The CA is also called Young’s angle or the static CA and is derived from the tangential angle at the solid-liquid-air interface, see Figure 1. How the surface is wetted by the liquid is also directly related to the surface energy, where surfaces with low energy will show large CAs (Li, 2006). It is know that surface energy is caused by the disruption of intermolecular bonds that occur when a surface is created, see Figure 2. For liquids this surface energy gives rise to a phenomena called surface tension. The surface tension occurs for a liquid-gas interface and is defined as the energy required to form the surface of a drop of liquid. The unit is \( J/m^2 \) or as force per length \( N/m \).
When a water droplet is placed on a surface, three surface energies \((\gamma_i)\) are represented. These are related to the surface \((S)\), gas \((G)\) and liquid \((L)\). The surface tension acting where these three phases meet is called the contact line. Together, these three surface energies forms the shape of the drop (Søgaard, 2014). The wettability of a surface expressed by the CA and the surface tensions can be described with Young’s equation (1):

\[
0 = \gamma_{SG} - \gamma_{SL} - \gamma_{LG}\cos(\theta_0)
\]  

(1)

where \(\gamma_{SG}\) is the projected surface tension at the interference between solid-gas, \(\gamma_{SL}\) is between solid-liquid and \(\gamma_{LG}\) between liquid-gas. \(\theta_0\) is the CA when the drop is at rest and the surface tensions has reached equilibrium, see Figure 1 (Søgaard, 2014, Li, 2006). However, Young’s equation describes the properties of a perfectly homogeneous and smooth surface, which is not the reality in most cases. Surfaces are often rough with natural or man-made structures covering it. Roughness affects the contact line of the liquid drop and can cause it to pin onto the surface. This leads to a fixation of the drop, leading to an influence of the CAs if the droplet moves on a surface. The advancing part of the drop causes an increase in CA, called advancing CA, \(\theta_{adv}\), and the receding part causes a decrease in CA, called receding CA, \(\theta_{rec}\) (Søgaard, 2014). The advancing and receding CAs can occur either when the volume of the drop increases or decreases, or when the drop is moved under influence of gravity when the surface is tilted, see Figure 3. The angle where the drop starts to move on a tilted surface is called the roll-off angle, \(\alpha\). The difference between the advancing and receding CA is called the CA hysteresis and is determined as (2):

\[
H = \theta_{adv} - \theta_{rec}
\]  

(2)

Many surfaces show higher hysteresis due to chemical heterogeneities and roughnesses (Li, 2006).

2.2 (Super)hydrophobic and (Super)hydrophilic Surfaces

The terms “hydrophilic surface” and “hydrophobic surface” are used to describe the behaviour of water on solid surfaces. A hydrophilic surface has strong affinity
2.2 (Super)hydrophobic and (Super)hydrophilic Surfaces

The CA is used to determine if a surface is hydrophobic or hydrophilic, where a hydrophobic surface has a CA larger than 90° and a hydrophilic surface a CA below 90° (Li, 2006). In addition, a superhydrophobic surface is defined when the CA is larger than 150° with a roll-off angle and hysteresis of 10° or smaller (Law, 2016). The superhydrophobic properties are often created on a surface with a proper two-level topography with micro- and nano-sized structures, which will be described further in the section 2.4. In the same way, surface roughness is of importance for superhydrophilicity, where a surface is said to be superhydrophilic if the CA is below 5°. The roughness of the surface enhances both the hydrophobic and hydrophilic properties. If a surface is hydrophobic, an increased roughness will make the surface even more hydrophobic. This also means that a hydrophilic surface will become even more hydrophilic if the roughness is increased, see Figure 4. As a matter of fact, a superhydrophilic or superhydrophobic surface can only be achieved with a manipulation of the surface roughness of hydrophilic or hydrophobic materials. There has been a lot of investigation of superhydrophobic surfaces but the superhydrophilic surfaces has only got attention during the past 15 years (Drellich, 2011).

How water wets surfaces can also be described by using the terms “polarity”
and “non-polarity”. A solid that has the same or similar molecular structure as water will dissolve in it. Since water is polar, with an electric dipole, surfaces that have polarity will be hydrophilic. This is based on the fact that “like spreads like” or “polar spreads polar”. Water will therefore spread out on polar surfaces. Most materials found in nature are hydrophilic, such as metal surfaces and the majority of polymers. Only saturated hydrocarbon-based materials such as wax, polypropylene and fluorine-based polymers are hydrophobic. When adding heteroatoms, such as oxygen, onto a hydrophobic surface it will add a polarity to the polymer reducing its hydrophobicity and introducing or enhancing hydrophilicity to the surface (Drelich, 2011).

Hydrophobic and hydrophilic surfaces also have different surface energies, where surfaces with low energies will show hydrophobic properties. Some well known surfaces with low surface energies are silicones and fluoropolymers, for example Teflon. For flat solid surfaces, $CF_x$-groups show the lowest surface energy and thereby the highest CA, about $120^\circ$. To obtain higher CAs the only way is to increase roughness (Søgaard, 2014).

Table 2: This table shows the requirements of hydrophobicity and hydrophilicity in terms of CA and surface energy.

<table>
<thead>
<tr>
<th>Type of Surface</th>
<th>CA</th>
<th>Surface Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Superhydrophilic</td>
<td>$&lt; 5^\circ$</td>
<td>Highest</td>
</tr>
<tr>
<td>Hydrophilic</td>
<td>$0 &lt; \theta &lt; 90^\circ$</td>
<td>High</td>
</tr>
<tr>
<td>Hydrophobic</td>
<td>$90^\circ \leq \theta &lt; 150^\circ$</td>
<td>Low</td>
</tr>
<tr>
<td>Superhydrophobic</td>
<td>$\theta \geq 150^\circ$</td>
<td>Lowest</td>
</tr>
</tbody>
</table>

2.3 Adhesion

Adhesion is defined as the attraction between two different substances that results from the intermolecular forces that are established between them (da Silva, 2011). These intermolecular forces occur between a droplet and a surface, but also when parts are glued together, where glue often are called adhesives. Adhesion should not be confused with cohesion, which concerns intermolecular forces that is inside one substance. There are two types of adhesion, the practical and the fundamental adhesion. The practical adhesion concerns the magnitude of mechanical force or energy that is required to break an adhesive bond, such as the load applied to a hearing aid when it is accidentally dropped. The fundamental adhesion thus concerns forces and mechanisms on the molecular scale, which holding together the different components of an adhesive bond. Hence, the practical adhesion is relying on the fundamental adhesion. The theories of adhesion are primary dependent on the extent of spreading and wetting of a liquid drop on a solid surface. When two materials come in contact, attraction forces will occur between them. These forces will depend on the chemical nature of the surfaces of the materials involved.

Micro- and nanostructures have an effect on adhesion properties on a surface, where studies have shown that a man-made pattern on a surface is enhancing the
adhesive strength (Majumder et al., 2007). This kind of pattern with different hierarchical differences on a nano- and microlevel can be viewed as a roughness of the surface and therefor this roughness has an effect on the adhesion of the material (Person & Scaraggi, 2014). The surface energy of a surface with a high roughness factor, which is made up by a hydrophilic material, will be higher than a surface that is smooth. A surface with a certain intrinsic hydrophilicity together with a roughness factor will determine the surface energy. With a high surface energy, which can be found at a surface with superhydrophilic properties, the adhesion forces will be strong (da Silva, 2011).

2.4 Lotus Flower Theory

Superhydrophobic surfaces are coveted in many areas such as the surface of the bottom of ships, in food packings or on medical devices and these superhydrophobic surfaces are often referred to as self-cleaning (Søgaard, 2014). In many cases, the developers tries to mimic the behaviour of natural surfaces of plants, when producing these surfaces. Most plants have water repelling effects on their leaves, where water droplets are formed on the surface and roll-off at small tilt-angles. The repelled water will adhere dirt and other particles, leaving the plant clean so it can absorb light needed for the photosynthesis (Søgaard, 2014). One example in the nature where these properties can be found is the Lotus flower. Based on the many experiments regarding this plant, it has been shown that water repellency causes a self-cleaning effect. This effect is called the Lotus effect which many man-made superhydrophobic surfaces are inspired by. From experiments it has also been shown that the interdependence between surface roughness, reduced particle adhesion and water repellency is a keystone in the self-cleaning mechanism of many plants (Barthlott, 1997). Roughness at two or more length scales, in this case micro and nano, has also been implicated to cause this effect (Gao, 2009, Law, 2016).

![Figure 5: An image showing a droplet on a Lotus leaf.](image)

10
The Lotus leaf has a CA of 162°, a roll-off angle of 4° and a contact hysteresis of 2° (Law, 2016, Li, 2006). The topography of the surface of lotus leaf shows two different scales to the outside environment. The rough structure is around 3–10 μm composed of hills and valleys, which are decorated with nanometer sized particles of a hydrophobic wax like material. The wax itself has a CA of 110° which is not highly hydrophobic. It is therefore assumed that the wax in combination with the roughness contributes to the superhydrophobic properties of the Lotus leaf (Li, 2006). The hills and valleys ensure that the surface area in contact with water is very low and and the hydrophobic nanoparticles prevent water from entering the valleys. SEM images from studies of the Lotus leaf’s have shown that air is trapped between the water droplet and the leaf surface, which suggests that the main contact areas between the water and the leaf surfaces are the tips of the papillae (Law, 2016). This means that the contact between droplets and the surface is minimal. The self-cleaning effect of the Lotus leaf and its underlying mechanisms has been thoroughly investigated in many studies. When a drop of water moves down a tilted superhydrophobic surface, an effective microscopic slip occurs due to the large CA, which minimizes the contact between the fluid and the surface. The drop of water behaves like an elastic ball rather than a fluid, see Figure 6 (Li, 2006). Because of this non-slip condition and the minimized solid-water interference of a water-repellent rough surface, the water drop will form a sphere, which collects particles from the surface, see right part in Figure 6. This phenomena can be compared to a normal hydrophobic surface, where the water drops falls across the surface and the particles will be displaced to the sides of the drop and re-deposited behind the drop, see left part in Figure 6 (Li, 2006).

![Figure 6: An image showing the self-cleaning effect on the right side, where dirt is collected by the droplet as it roll offs the surface. Image taken from Søgaard (Søgaard, 2014).](image)

In comparison to the Lotus leaf, another example from nature is the rose petals. These are also hydrophobic, but instead of the self-cleaning effects seen on the Lotus leaf the rose petals has the ability to retain small droplets on the surface that does not roll-off when the surface is tilted. The rose petal also has microstructures but with larger distances between them, assuming to cause this effect. When a water droplet is in contact with this kind of surface, the droplet will
penetrate into the structures resulting in a strong adhesion between the droplet and the rose petal surface (Lima, 2015). This is called the Wenzel state, which will be described in the next section.

2.5 Wetting States

2.5.1 Wenzel State

As mentioned earlier a surface often has a roughness, which can be either natural or man-made. This roughness will affect the surface energy and will in turn affect the CA and contact area between the liquid and surface. A more hydrophobic material will make the drop take a form that is spherical which is more energy efficient. This means that the drop will increase the CA, between itself and the surface, and decrease the contact area. To be able to describe the scenario, when the roughness of the surface is increasing, both the intrinsic CA of the surface and the roughness factor needs to be considered (Søgaard, 2014). This results in the Wenzel equation (3),

$$\cos(\theta) = R_f \cos(\theta_0)$$

where,

$$R_f = \frac{A_{SL}}{A_F}$$

$R_f$ is the roughness factor and is derived from the total liquid area that is in contact with the surface, $A_{SL}$, and the projected area, $A_F$, see Figure 7. $R_f \geq 1$ for a drop to be considered to be in Wenzel state, which means that the contact area between surface and liquid, $A_{SL}$, is always bigger than the projected area, $A_F$. When a liquid is in the Wenzel state it means that the surface, with its nano- and microstructured topography, is completely wetted (Ishino & Okumura, 2008). Even if a large CA is achieved by a surface and is considered hydrophobic, a liquid drop in a Wenzel state will stick to the surface and therefor not move. This means that the self-cleaning properties are yet not reached and the superhydrophobic requirements are not fulfilled (Søgaard, 2014, Ishino & Okumura, 2008).
2.5.2  Cassie State

Liquids in a Cassie state usually concerns surfaces that are made up by heterogeneous materials. The different materials in the surface of the solid part will have different CAs. Therefore, to calculate the CA for the surface, each intrinsic CA for the different materials needs to be considered. The Cassie equation (5) describes the CA by taking into account both the surface fraction of the materials, \( f_x \), that are in contact with the liquid as well as the intrinsic CAs, \( \theta_x \).

\[
\cos(\theta) = f_1 \cos(\theta_1) + f_2 \cos(\theta_2)
\]  

(5)

where, \( f_1 + f_2 = 1 \) if two materials are present. Looking at an interface between a liquid and a surface with a rough topography the droplet will be at the top of the structures with airpockets underneath. This means that there are some parts of the liquid that will be in contact with the surface, \( f_1 = f_{SL} \), and other parts that will be in contact with air trapped in the structures, \( f_2 = f_{LA} \geq 1 - f_{SL} \). It is known that the CA for air is 180°. Therefore the Cassie equation can be interpreted as

\[
\cos(\theta) = f_{SL} \cos(\theta_0) - 1 + f_{SL}
\]  

(6)

and this is called the Cassie-Baxter equation (6).

2.5.3  Cassie vs. Wenzel State

A drop is considered to be in Cassie state when it is keeping its drop shape and is not wetting the whole surface. A difference between the Cassie state and the Wenzel is that a drop in the Cassie state will be laying on top of structures with air pockets under itself while in a Wenzel state all parts of the structures will be completely wet. A drop in Wenzel state is penetrating into the surface material and has a high CA hysteresis. Because of this the drop will be sticking to the surface, while a drop in Cassie state will roll of easily (Ishino & Okumura, 2008). Looking at the different hierarchical structures when the drop is in a Cassie state,
2.5 Wetting States

**Figure 9:** An image showing droplets that are partly in the Cassie state and partly in the Wenzel state.

the smallest nanostructures will be in a Wenzel state, completely wet, while the bigger structures will not be wetted. This state is described by the Cassie-Baxter equation (6), but since there is a certain roughness of the surface of the material, the roughness factor also needs to be included.

\[
\cos(\theta) = R_f f_{SL} \cos(\theta_0) - 1 + f_{SL}
\]

From this equation one can see that, when in Cassie state, the CA of the solid surface is dependent of the roughness of the surface, the area of the surface in contact with the liquid and the equilibrium CA, \(\theta_0\). It is possible to say that the more hydrophobic the material is, the smaller the contact area will be between the solid surface and the liquid (Søgaard, 2014). However, even if the surface is made by a hydrophobic material, it is not certain that the droplet will stay in a Cassie state. It is possible that the Cassie state collapses because the air pockets are not stable enough. When a drop starts to transition from a Cassie state to a Wenzel it can end up in a state where some structures are in Cassie state and some in Wenzel state, see Figure 9. It is of importance that the liquid is in a stable Cassie state to be able to say that the surface is superhydrophobic (Søgaard, 2014).

To make sure that the drops stays in a Cassie state there are factors that needs to be considered when designing a surface, for example; the choice of material, the pressure from the liquid and the geometry of the structures. When choosing a material it is important to consider the intrinsic CA of the material. By controlling the choice of CA one also controls the contact area between the drop and the surface since these are in correlation with each other. A drop in Cassie state situated on top of a porous material will have parts of its liquid surface located on top of holes. The liquid on top of these holes will bulge into the cavities, creating a meniscus. This meniscus will slowly move downwards as long as the intrinsic CA between the meniscus and the surface of the sidewall is larger than the advancing CA. If the pressure increases it could lead to the liquid moving further into the air pockets (Søgaard, 2014).

If the air pockets are closed a counter pressure will be generated when the fluid is forcing its way into the pocket, see Figure 10. Therefore the geometry is also something needed to be considered when designing the surface. The Cassie state will be more stable when the structures are closely packed together. However, it
is of importance that the contact area between the surface and liquid, $A_{SL}$, does not become too large because that could result in that the CA will not be big enough to classify the surface as superhydrophobic. Also increasing the roughness of the walls of the structures will make it more difficult for the drop to penetrate the air pockets and therefore create a more stable Cassie state.

Design parameters affecting superhydrophobicity are summarized in the article from (Søgaard, 2014):

1. Advancing CA
   (a) CA of the material
   (b) Sidewall roughness

2. Liquid pressure
   (a) Open structures
   (b) Closed structures

3. Geometry of structure
   (a) Size
   (b) Height
   (c) Period

As mentioned earlier, when a liquid is lying on top of a porous surface and a pressure is applied, the meniscus will change shape and possibly start to move downwards. The shape of the meniscus can be derived from the Young Laplace equation (8) if the pressure is known,

$$\Delta p = \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right).$$  \hspace{1cm} (8)
Where $R_1$ and $R_2$ are the curve radii in two dimensions, $\Delta p$ is the pressure change over the liquid-gas interface and $\gamma$ is the surface tension of the liquid. From the Young-Laplace equation (8) one can see that if the $\Delta p$ is increased, the $R_j$ will decrease, changing the shape of the meniscus and resulting in the liquid moving further into the structures (Søgaard, 2014). This will be more closely examined in the next section about capillary effects.

In a situation where there are no external pressure, the penetration depth of the liquid can be derived by looking at the geometry, see Figure 10 (Søgaard, 2014). If the structure has a circular cross section, $R_1 = R_2 = R$, it is possible to use the following equation (9) to calculate the penetration depth, $h$.

$$h = R - \sqrt{R^2 - a^2}$$

(9)

Where $R$ is the radius of curvature and $a$ is the hole diameter. If the CA of the material is known $R$ can be derived through,

$$R = \frac{a}{\cos(\theta)}$$

(10)

As can be seen from the two equations (9) and (10), the smaller the diameter of the holes, the lesser the penetration depth will be. Another parameter that can affect the outcome whether the drop is in a Cassie or Wenzel state is the height of the structures. If the structures are very low, the water will reach the bottom faster making the droplet transition into a Wenzel state (Søgaard, 2014).

### 2.6 Capillary Effect

In microfluidics, different surface effects can occur because of the size difference between surface contact area and volume of the liquid. In this field one of the surface effects that can be studied is the capillary effect.

When talking about capillary effect one is referring to when liquid has the ability to spontaneously flow through a micro channel. This usually occurs when the cohesive force in the liquid is greater than the adhesive force between surface and liquid, which happens when the CA is less than $90^\circ$. When the CA between the capillary wall and the liquid is less than $90^\circ$ the liquid will start moving via the sides creating a inverted meniscus. This will result in a uncompensated Young-Laplace negative pressure, also called the capillary force or capillarity, which will pull the liquid further into the capillary (Bruus, 2007).

To understand this on a more detailed level, Gibbs free energy, $G$, needs to be studied. Gibbs free energy is defined by the function

$$G = H - TS$$

(11)

where $H$ is the enthalpy [J] of the system, $S$ - entropy [J/K], $T$ - temperature [K] and describes the thermodynamic potential of a system that is constricted to the requirements that $P$ - pressure, $T$ - temperature and $N$ - particle number, are constant. In a closed system where the temperature, pressure and volume of
2.6 Capillary Effect

Figure 11: Figure showing a curved surface with the area $A = \delta x \delta y$. By displacing a section by $\delta z$, the local radii, $R_i$, of curvature will change. The figure is taken from the book *Theoretical microfluidics* written by Bruus, H.

A substance is constant the function $G$ (11) can minimize and reach a minimum where the system is at an equilibrium (Perrot, 1998). To understand capillary effects it is interesting to look at the situations where a system is in equilibrium (Bruus, 2007).

$$\delta G = \partial G \delta \xi = \sum \left( \partial G_i \right) \partial \xi$$

Equation (12) is describing the minimum energy condition, where $\partial G$ is a small variation in free energy and $\xi$ is a variable describing the free surface of the system. $G$ is the total Gibbs energy, which is the combined free energies working in the system, i.e. the free energy of the surface and free energy from different subsystems. The subsystems could for example be a surface between the liquid and solid material and are described by the variable $\xi$. The variable is regarding a measurable quantity such as for example length, area or volume (Bruus, 2007). Equation (12) will be used to explain the equations regarding capillary effect.

Furthermore, it is necessary to regard the surface tension, $\gamma$, and Young-Laplace pressure to grasp the theory behind capillary effects. The surface tension between the interface of two materials where the pressure and temperature is fixed, can be derived from Gibbs free energy per area.

$$\gamma \equiv \left( \frac{\partial G}{\partial A} \right)_{p,T}$$

A molecule located within a liquid will bond to its neighbouring molecules, as seen in Figure 2. However, a molecule that is located at a surface will not form chemical bonds in the direction of the surface due to the lack of molecules in the air. Because of the lesser amounts of chemical bonds the energy will be higher for the molecules located at the surface and therefore surface tension can be described as the energy cost of forming a surface (Bruus, 2007).

Because of the surface tension cannot equal 0, there will be a Young-Laplace pressure drop, $\Delta p$, a so called negative Young-Laplace pressure, across the curved surface in thermodynamic equilibrium (Bruus, 2007). In order to derive the pressure drop equation (12) will be used. By changing the area, $A$, for a small part of the curved surface that is in equilibrium by expanding in the direction of a normal vector of the surface, it is possible to view the effects of a growing area, see Figure 11. When expanding the area, local radii of curvature will also change giving rise
2.7 Capillary Stop

A technique to hinder capillary effect and stop fluid flow in micro channels is to use a capillary stop valve. To generate this type of stop, the dimensions of the capillary must make a sudden change. If the cross section of the capillary is enlarged, see Figure 13, the liquid traveling in the micro channel will stop, when encountering the channel cross section dimensional change. When the pressure surpasses a threshold value, and reach the burst pressure, the fluid will flow into the container (Gliere, 2005). An example for when pressure exceed the threshold value could be when dropping a hearing instrument and the force generated from the impact creates a pressure driving the fluid into the reservoir.

In the following paragraph burst pressure for a symmetrical cylinder will be derived.

When the liquid encounters the enlargement of the cross sectional area, the meniscus of the liquid will stop at the edge of the micro channel. A capillary free

![Figure 12: Three tubes with different cross-sectional area, all immersed in a water tank. The height of the water column depend on the CA and the relationship between the area of the tube and the area of the tank.](image)
Contact Angle Measurements

2.8 Contact Angle Measurements

CA measurements are commonly used to characterize a surface and to study wetting and de-wetting properties (Law, 2016). As mentioned earlier, a surface is said to be hydrophilic if the CA is below 90° and hydrophobic if the CA is above 90°. In addition, a surface is characterized as superhydrophobic if the CA is larger than 150° and superhydrophilic if the angle is below 5°. The CA measurement can be either static or dynamic. The static method measures Young’s angle, whereas the dynamic method measures the receding and the advancing CAs. During the measurements the size of the liquid drops are normally in the milliliter range. The surface also has to be flat optically, since the capture of the CA are made with optics. The most common method for measuring static CAs is the optical-based

surface in this equilibrium state is defined by the Laplace and Young equations. The Laplace equation,

$$\Delta p = \gamma_{LG}(k_1 + k_2)$$

is concerning the pressure drop at liquid-gas interface, while Young equation

$$\gamma_{SL} + \gamma_{LG}\cos(\theta) = \gamma_{SG}$$

concerns the different tensions in the triple line together with the CA. The gravitational effect does not need to be considered to horizontal capillaries, which will be a condition in this project (Gliere, 2005).

The meniscus at the channel edge will, when an external pressure is present, change form until the CA between wall and meniscus reaches a critical advancing CA, see Figure 13. When reaching this critical value the meniscus will burst and the liquid will start climbing the chamber walls. The burst pressure can be derived from

$$\Delta p_b = -2\gamma_{LG}\frac{\cos(\theta_{adv} + \beta)}{r}$$

Where $\beta$ is channel expansion angle and $r$ is its radius (Gliere, 2005). The maximum $\Delta p$ is found when $\theta_{adv}$ and $\beta$ equals $\pi$ which gives the equation

$$\Delta p_b = -2\gamma_{LG}\frac{\cos(\min(\theta_{adv} + \beta), \pi)}{r}$$

2.8 Contact Angle Measurements
sessile drop method (Law, 2016). This is typically built up by a goniometer, which is an instrument used for precise measurements of angles, placed between a light source and a CCD camera. Thereafter, a certain amount of liquid is placed by a liquid dosing system onto the solid surface to form a sessile drop. Some of the goniometers of today also have functionalities such as it can withstand high temperatures, have nano dosing units, enables a tilting base and full automation for advancing and receding CA studies (Law, 2016).

2.9 Surface Energy Measurements

In this section the theory of how to measure surface energy will be described.

2.9.1 Owens Wendt Theory

In literature there are different approaches to reach a value for surface energy. For liquids the measurements are quite simple, since the surface energy for a liquid is equal to the surface tension and many techniques exists for measuring surface tensions. For a solid surface the surface energy can not be directly measured. One way to calculate a value for a solid surface is to look at the CAs of various liquids. To be able to do this it is necessary to know the surface tension for the liquids used in the calculations. It is advisable to use at least two different liquids where one of the liquids is polar and the other one is non-polar. However, the calculated surface energy will not be able to give an exact representation of the reality. This is because if you use a different liquid combination or another theory to make the calculations, the result will differ. Therefore, to be able to compare surface energies it is needed to use the same liquids and the same theories when calculating, for all the measurements. If using different liquids and different equations the values will not be comparable. In this project the methodology for measuring these energies is based on the Owen Wendt theory (Rulison, 1999).

When looking at surface energy through the Owen Wendt theory, the energy is regarded as consisting of two components, one polar and one dispersive component. These two components are representing different molecular interactions. By using these two parameters in combination with equations it is possible to reach a value (Rulison, 1999).

2.10 Fabrication

It exists several ways to create artificial superhydrophobic surfaces. The basic parameters of superhydrophobicity according to Wenzel and Cassie-Baxter are roughness and a hydrophobic surface coating. The injection molding technique for creating nanostructured surfaces can be divided into two major steps, i.e. the fabrication of the injection molding tool, followed by the injection molding process of the polymer parts. To understand the injection molding of nanostructures, it can basically be said that the structures are created on the injection molding tool
which are thereafter replicated on the surface of the polymers during the injection molding process.

### 2.10.1 Fabrication of Injection Molding Tools

A way to create an injection molding tool is to make a design of the desired tool in a CAD-program. After that the tool is milled in steel, based on the design in the CAD-drawing. To generate the nanostructure pattern on the surface of the tool, a laser technique used by the company *Transform* is applied.

### 2.10.2 The Injection Molding Process

The injection molding technique is quite complex in reality, but the principle of the process is simple - it converts thermoplastic granular into finished parts. It is based on the heating above the melting temperature of a thermoplastic polymer, which fills up a predefined mold tool for the production of parts. There is an importance of packing the polymer well into the mold to reduce shrinking of the parts and to be able to replicate the nanostructures onto the surface. This is controlled by adapting the settings for melt temperature, mold temperature and pressure. When the polymer has filled the mold it freezes and becomes solid and are thereafter de-molded. For the de-molding process to run as smoothly as possible, the design of the tool parts and how they close and open needs to be well thought out. For different polymers there are different recommended settings regarding melt and mold temperature, usually presented in a temperature interval. To create plastic parts when injection molding, temperatures within the recommended interval and different pressures are combined to find the preferred option. For Oticon it is of importance to not use temperatures outside this interval since it is a requirement from the Food and Drug Administration (FDA), which controls the regulation of medical devices in North America. Since hearing instruments are regarded as a medical device, it needs a FDA approval to be able to reach the North American market.

A schematically drawing of the injection molding machine can be seen in Figure 14. It is built up by a barrel with a screw, where the polymer is fed into it from a hopper. When the polymer transports through the barrel it will be compressed and melted before entering the screw. The screw increases the pressure and presses the polymer into the predefined mold cavity. After the mold tool has been filled the pressure increases further, a so called after pressure, to make sure that the finished parts gets the right dimensions and prevents the parts from shrinking too much. The polymer is thereafter cooled down to solidify and the mold opens and ejection pins presses the part out of the tool.

### 2.11 Plasma Treatment and Hydrophobic Coating Process

To make hydrophobic surfaces it is common to use hydrophobic coatings, often Teflon like coatings. The coating process depends on the material and the size
of the part, where different settings can be used. Before the coating is applied the samples are often plasma cleaned. The plasma treatment is done to clean the surfaces and to improve the adhesion of the coating onto the surface. Plasma is a gas fully or partially ionized, consisting of ions and electrons (Piel, 2010).

At Oticon, the hydrophobic coating is applied through a plasma polymerization process called Plasma Assisted Chemical Vapour Deposition (PA CVD). CVD is a process where a thin film of solid is produced from the gaseous phase by a chemical reaction. In the PA CVD process, the plasma is used for activation of precursor gas, which significantly decreases the deposition temperature (Xu, 2010).

At Oticon, the plasma treatment and hydrophobic coatings are applied at their production plant in Thisted, Denmark. The hydrophobic coatings can be created by two different methods at Thisted, which is with a rotary drum or with a shelf. With the shelf, the coating is mainly applied to one side of the sample. With the rotary drum, the sample is placed in a bulk that rotates so that all surfaces are exposed to the coating. In both cases, the coating is applied all over the exposed surfaces, meaning that if parts should not be coated they need to be masked before the process.

2.11.1 Nanostructures and Hydrophobic Coating in Combination

As mentioned earlier, an increased roughness of a surface will make it even more hydrophobic or hydrophilic depending on the materials properties. If a material is hydrophilic and nanostructures are applied on top of it, it will become even more hydrophilic. However, if this process is followed by applying a hydrophobic coating over the surface, it will become hydrophobic or even superhydrophobic. This is because it is the outermost layer, which is in contact with the liquid, that affects if the surface is hydrophobic or hydrophilic.

2.12 Polymers Used for Analysis

In this project, different polymers have been used for analysis of the surfaces. Polymers that are included are polypropylene (PP), which is the polymer used
for injection molding at DTU. It is a homopolymer with a good combination of mechanical properties suitable for injection molding. The recommended melt and mold temperatures for this material are 230°C – 260°C and respectively 10°C – 30°C. Further, three polymers that are used at Oticon are studied in this project. Polymers have different properties and therefore affects the various parameters required for the injection molding process. A polymer is chosen after its properties for the various parts of the hearing instrument where special mechanical or other properties are desired. The analyzed polymers at Oticon are based on Polyamide (PA), also called Nylon in popular speech. PAs are characterized by the amide linkages (-CONH-) on the main polymer chain. The structure of PA in the solid state can be either amorphous, semi-crystalline or crystalline (Chaichanawong, 2016).

In the case of crystallinity, the individual chains are folded and packed regularly in an orderly fashion with a long-range, three-dimensional ordered arrangement. When a polymer is melted, the polymer chains form entangled irregular bundles. In some cases the polymer retains this irregular order when solidified, and an amorphous polymer is formed (Søgaard, 2014). The amorphous structure is built up by chains that are incapable of ordered arrangement and compared to the long-range order of the crystalline they have a short-range order of repeating units. These are often glassy with randomly and entangled arranged molecular chains. However, since the molecular chains in the polymers are long, complete parallel alignment are never achieved since only a certain amount of chain clusters are aligned to form crystalline domains. This means that no polymer is 100% crystalline. A semi-crystalline polymer is thus build up by both crystals and amorphous parts, with a certain degree of crystallinity. For the amorphous and crystalline polymers the melting of the polymers marks the onset of disorder.

Polymers are sometimes reinforced to upgrade product performance and this can be done by adding glass fibres as a composite. Glass fibres can improve mechanical properties such as tensile and fatigue strength. Other advantages of glass fibers are high-temperature resistance, corrosion resistance, good dimensional stability, extremely lightweight, strong material and almost no moisture absorption (Chaichanawong, 2016). When choosing the polymer type for the hearing aids some different properties are desired. These are strength which increases the robustness, stiffness which can withstand vibrations, that the surface is able to be painted, the polymer should be assured for skin contact and finally it should be chemically resistant.

Materials tested and used for this project are;

- Amorphous PA with glass fibers
- Amorphous PA w/o glass fibers
- Semi-crystalline PA with glass fibers

The amorphous PA reinforced with glass fibres shows a very low tendency of distortion and is suitable for complex and thin walled designs. Some of it prop-
erties are high stiffness and strength, good impact resistance, high dimensional stability, low moisture absorption and easy processing with good melt flow. Recommended melt and mold temperatures are 280°C – 300°C and respectively 40°C – 80°C.

The second amorphous PA is without fibers and is a heat stabilized engineering thermoplastic designed for complex structural parts. It has properties such as very high stiffness and strength, excellent impact and notched impact strength, low water absorption, high dimensional stability, easy processing, good flow characteristics, high molding precision and low warpage. Recommended melt and mold temperatures are 245°C – 265°C and respectively 40°C – 60°C.

The last PA is a highly transparent semi-crystalline PA, reinforced with glass fiber, with high practical toughness and resistance to chemicals such as alcohol and cleaning agents. The semi-crystalline PA has properties such as improved flowability and de-molding, enhanced heat resistance and better UV-resistance suitable for outdoor use. This polymer contains no plasticizers, resists cosmetic chemicals and perspiration, does not irritate the skin and can enhance design and performance of personal care products. Recommended melt and mold temperatures are 270°C – 290°C and respectively 80°C – 100°C.

Since the polymers have some different properties, the replication of nanostructures onto the surface during the molding process will differ.

In comparison the PAs, an acrylonitrile butadiene styrene (ABS) is also included in the project during the glue strength measurements. This is an amorphous two-phase polymer blend that are classified as biocompatible, like all the PAs used at Oticon, and is used in medical devices. It is available in different colors and this project uses two of them, i.e one transparent and one beige.
3 Method

This section will describe the different steps in the project that were performed to reach a conclusion about the utility of nanostructures on hearing aids. Firstly, CA measurements were performed on different polymers. These polymers include the ones used at the company but also polypropylene (PP), which is the material used at DTU for creating nanostructures on surfaces. The CA measurements are performed on samples both with and without nanostructures and with and without the hydrophobic coating. In addition to the CA measurements, surface energies were also measured on nanostructured samples from some of the materials used at the company. After these measurements, two different test geometries were designed in AutoCAD, to be able to evaluate the nanostructures on a deeper level compared to only study surface properties. How and why these geometries were conducted will be described in detail. These two designs were thereafter used in two test scenarios; one capillary test and one glue strength test. The results from the different steps was thereafter compared and used to draw the conclusion.

![Figure 15: Test setup for CA measurements.](image)

3.1 Contact Angle Measurements

3.1.1 Contact Angle Measurements on Polyamide

To be able to investigate the effect of nanostructures on the surfaces of the PAs and also the combination of nanostructures and the chemical coating, there was a need of reference values for the polymers. Therefore CA measurements were performed on flat, non-coated samples to determine the intrinsic CAs. For the CA measurements, a drop shape analyzer was used (KRÜSS GmbH Germany FM41 EasyDrop) together with a computer software (DSA II). The drop shape analyzer consists of a CCD camera that can be used for live presentation of the setup and for taking images of the water droplets for the CA measurement. A light source is connected to the system to illuminate the measurement procedure and an additional lamp can be used if needed. The liquid used for investigations are demineralized water. The samples were placed on a stage that can be manually
3.1 Contact Angle Measurements

Figure 16: An image of the sessile drop with the baseline (green) and tangential CAs.

moved in both x-, y- and z-direction. For the placement of the water droplet onto the samples, a dosing system was used. The dosing system consists of a syringe that can be used with various types of needles and is hooked onto the drop shape analyzer. For measurements of CAs several methods exists. In this project a tangential method was applied, which enabled automatic calculations. The baseline, which can be seen in Figure 16, can be modified for better calculations.

After checking all the equipment and adjusting the line-up, the first material was tested. Materials included in this step were the semi-crystalline PA, the amorphous PA and the amorphous PA with glass fibers. Each sample was handled with a pincette to avoid leaving fingerprints. Fingerprints are making the surface greasy and oily and can therefore interact with the wettability and give incorrect results (Howarter & Youngblood, 2008). The sample was placed under the dosing system on the movable stage. Lights were set to maximum luminosity and an ion blower was turned on to neutralize static electricity. Thereafter a drop of water was placed on the sample. For each material three measurements were made, except for the amorphous PA with glass fibers where only one measurement was performed. The reason to only perform one measurement on the last PA is because the sample had a geometry that were difficult to place a droplet on. From the measurements on the different PAs, mean values were calculated.

After the CA measurements were performed on the flat, non-coated samples, some measurements were also made on flat samples with hydrophobic coatings. To investigate the hydrophobic effect of the Teflon like coating, four samples of semi-crystalline PA underwent plasma treatment followed by a hydrophobic coating process. For each of these samples, three CA measurements were performed. From these measurements a mean value were calculated.
3.1 Contact Angle Measurements

3.1.2 Contact Angle Measurements on Polypropylene

The Transform company from DTU mainly uses PP for the injection molding of nanostructures on surfaces. One reason to this is because PP has a high intrinsic CA, around 100° (Søgaard, 2014), meaning that it is hydrophobic. Since the company already had samples molded with nanostructures, they were used in this project for studying the surface properties using nanostructures in combination with a hydrophobic coating. Samples of PP molded at six different mold temperatures were available for analysis. The mold temperatures are 30°C, 40°C, 50°C, 60°C, 70°C and 80°C respectively. For each temperature, eight samples were studied, except for the temperature of 80°C where only seven samples were available. An image of the samples can be seen in Figure 17.

Before the coating was applied, half of the samples from each mold temperature underwent plasma treatment. This was to see if the plasma treatment had an affect of the surface properties compared to a non-treated sample. The three other samples from each molding temperature were only hydrophobic coated. The samples were sent to the production department in Thisted, Denmark, where both the plasma cleaning and the coating process were performed. The thickness of the coating is as thin as possible in the nanometer range, to prevent influence on the nano structures.

For each sample, three CA measurements were performed on each molding temperature which were used to calculate mean values.

In addition to the CA measurements on structured PP, some analyzes were also performed on flat samples of PP. Four of them underwent the coating process and four were both plasma treated and coated. For the coated samples, three CA measurements were performed on each sample which thereafter were used to
3.2 Design of Test Geometries

3.1.3 Contact Angle Measurements on Polyamide with Nanostructures

When performing measurements on PAs with a nanostructured surface the same method as was previously described were used. The measurements were performed on all three PAs, both coated and uncoated samples. Some polymers were molded at different temperatures, these temperatures are referred as *maximum* and *middle* which can be found in section 3.2.2. For the different PAs and mold setting, four samples were tested with three CA measurements conducted on each sample. From these values, mean CA values were calculated.

3.2 Design of Test Geometries

Since the injection molding tools are custom-made for this specific project, CAD sketches needed to be developed. This section will describe the process of how a decision was made about the most interesting tests to perform. It will also describe how the tool designs were conducted.

3.2.1 What We Want to Test

Firstly it was important to investigate how well the nanostructures were replicated on the PAs during the injection molding process. To be able to visualize this, SEM images were studied which can be viewed in the result section of the report.

From project start a search for different tests that can help answer the stated issues, has been carried through. From brainstorming and conversation with employees at Oticon, the main areas of interest for using nanostructures together with hearing instrument materials were broken down to six different fields of interest.

1. Molding angle of structures
2. Glue strength
3. Water and glue paths
4. Wear on the tool
5. Capillarity
6. Wax ingress.

To make sure that the project produced a qualitative analysis of the nanostructure technology it was decided to limit the number of tests. After comparing the recently stated test fields, it was decided that capillary effects and glue quality were the most relevant areas to study in relation to the stated issues of the project and in regards to the interests of the company.

The electronics within a hearing instrument or any other electrical device worn close to the human body, is in the danger of being exposed to liquids (Karamuk,
The hearing aids have openings, gaps and capillaries that can transport liquid into the hearing instruments. Liquids can either be sweat generated by perspiration, earwax wandering from the tube connected with the ear canal or water from an outer environment such as rain. This humidity can in turn affect the electronics and cause corrosion of components or batteries et cetera (Karamuk, 2008). To counteract this effect, capillary stops can be incorporated in the design of the devices. These capillary stops usually have the dimensions; capillary ø 0.01 mm and chamber ø 0.10 mm. It could be of interest to look at how well nanostructures work as a capillary stop to improve the resistance of water ingress.

As mentioned earlier in the report, the CA between the meniscus and the wall vs the advancing CA, controls the value for the burst pressure. Theoretically this means that if the nanostructures together with a chemical coating induces a higher CA the nanostructures could be more water hindering. It could be interesting to see if they could be more water hindering than a capillary stop that is created through a change in dimensions of the cross section.

To investigate the effect of nanostructures compared to a regular capillary stop, a tool was designed to test this statement along with theoretical calculations of the burst pressure. In the result section the theoretical value and the practical value will be presented. To calculate a theoretical value the equations derived in the section about capillary stops (equation (16)(17)), will be used. Also the fundamental expression to calculate pressure induced by a water pillar of an arbitrary height is an important equation for finding both the theoretical and the true value of the burst pressure, see Equation 19.

$$\Delta p_b = \rho gh$$

When applying micro- and nanostructures on a flat surface, the roughness of the surface will be affected. If the material from the beginning has intrinsic CA making the surface hydrophobic, an applied roughness will make it even more hydrophobic. This applies to hydrophilic materials as well. Having a superhydrophilic surface can be of interest when looking at glue quality. A more hydrophilic material generates higher adhesion forces, as mentioned in the section about adhesion, section 2.3. Some parts of hearing instruments are glued together. It is therefore interesting to test if a nanostructured surface has an effect on the glue quality. This will be tested through a pull test together with hearing aid parts that are commonly glued together. The pull test will also be done for parts without nanostructures to give a reference value. The reason to why choosing a pull test was because it is a test method that is widely used, both at the company but also in research over all.

3.2.2 Capillarity Tool Design

To be able to test the two chosen areas of interest, capillarity and glue strength, two different test geometries needed to be designed. These geometries defines the dimensions of the molding inserts and were created in the computer program AutoCAD.
3.2 Design of Test Geometries

For the test geometry designed for the capillary test, inspiration was taken from the samples molded at DTU, see Figure 17. The nanostructures are molded at the flat side of the samples and an idea took shape where two identical samples are placed with the nanostructures facing towards each other at a small distance and thereby simulating a capillary. Letting water or other liquid passing through the wells, it is possible to see at which pressure the liquid penetrates the capillary.

A new geometry were designed in CAD based on dimensions in a hearing aid, see Figure 18. The tool has a basis of a rectangle with a size of 2x4 cm and a thickness of 1 mm. This rectangle is divided into two test parts, each 2x2 cm in size. Both test parts have a well where the outer diameter of the wells is 4 mm. The wall of the well has a thickness of 0.5 mm, since the thickness needs to be smaller than 60% of the basis thickness. The reason for this is to avoid problems like sinkmarks or warpage. Sinkmarks and warpage are two types of molding defects that can occur when a faulty design is present (Maier, 2009).

Both test parts have an area around the wells used for simulating a capillary when holding two samples close to each other. This area has a diameter of 12 mm. Outside of this area, the two test parts are designed differently to simulating two different capillary stop. One test part has an enlargement of the dimension of the capillary, thereby creating a capillary stop used in the hearing aids today. This change in dimension is created by reducing the thickness of the basis with 0.2 mm, producing a larger gap when placing two samples together. The other test part has nanostructures instead of a change in dimension, increasing the hydrophobicity of the surface and thereby makes it more difficult for liquid to penetrate further in the capillary. The rectangle has four holes in each corner with a diameter of 2 mm, to be able to screw them together and keep them in place, see Figure 19.

Firstly, the test geometry was sent to the tool shop to 3D-print a prototype of the design. The prototype is without nanostructures and the reason for this is to be able to evaluate the design and the test setup created to measure capillarity. A description of the test setup can be found in the next section. When the test setup and the test geometry had been tested, the molding insert was ordered from the tool shop together with the molding tool designed for the glue test. The molding inserts are made of steel and consists of two parts that are held together during the molding process to produce the cavity for the melted polymer. After the inserts were created, they were brought to Transform at DTU who are responsible for
the production of nanostructures on the insert surface. The nanostructures were created with a laser in a machine named 3D MICROMAC. The structures on the molding inserts are made up by holes, which means that when the polymers are molded the structures will become pillars on the surfaces of the polymers. To make sure that the structures are perfectly created at the tools, different settings were tested on a dummy. The settings that were varied are for example the effect from the laser and the amount of repetitions with the laser over the surface. After studying the structures in the microscope, it was decided to use a power of 55 % with 25 iterations over each line. The spaces between the lines are 10 micrometers.

![Figure 19: An image showing the two samples facing each other during the capillary test. The tube connected from below is also visible.](image)

![Figure 20: This image shows the laser that was used for the production of nanostructures onto the molding tools.](image)

When the tools had been nanostructured, they were brought to the department in Thisted, Denmark, which are responsible for the injection molding of the polymers. The polymers used for the tests are amorphous PA, the semi-crystalline PA and the amorphous PA reinforced with glass fibers. The molding was started with
the amorphous PA without fibers, since the fibers can cause wear to the molding insert. For the injection molding process, different melt and mold temperatures were used to see at which temperatures the nanostructures were optimally replicated on the surface of the samples. For semi-crystalline PA and the amorphous PA with glass fibers, two different temperature combinations were used, whereas for the amorphous PA only one combination was applicable. The temperature combinations used are:

- Amorphous PA: mold temperature 60°C and melt temperature 265°C
- Semi-crystalline PA: mold temperature 90°C and melt temperature 280°C
- Semi-crystalline PA: mold temperature 100°C and melt temperature 290°C
- Amorphous PA with fibers: mold temperature 65°C and melt temperature 290°C
- Amorphous PA with fibers: mold temperature 80°C and melt temperature 300°C

After the injection molding of the polymers, some of them were plasma treated and hydrophobic coated.

3.2.3 Glue Test Tool Design

For the glue test a tool design were created using the same basis as for the capillarity test, meaning a rectangle with a size of 2x4 cm and a thickness of 1 mm. This rectangle is also divided into two test parts. One side of the test part has
3.3 Surface Energy Measurements

In this section the method to measure surface energy will be described. The surface energy measurements were performed on samples molded with nanostructures only. Two different materials are studied, the semi-crystalline PA and the amorphous PA without glass fibers. Both hydrophobic coated and non-coated samples are included, meaning that four surface energy measurements were performed in total. Measurements were done on samples based on the glue test geometry, since they are flat compared to the capillary test geometry.

3.3.1 Owens Wendt Theory

To find a value for surface energy, the same software for measuring CAs earlier in this project was used. On a specific surface type, measurements will be made with three different liquids. For each liquid three drops were placed on the surface and in turn ten measurements were made on each drop. In this project the liquids that

nanostructures whereas the other side is non-structured and flat. The reason for this is to be able to compare the difference between having nanostructures or not. For the injection molding of this part the semi-crystalline PA and the amorphous PA without fibers was used. The molding was started with the amorphous PA without fibers, since the fibers can cause wear to the molding insert. At this test, only the maximum temperature combination were applicable for the two polymers. The temperature combinations used are:

- Amorphous PA: mold temperature 60°C and melt temperature 265°C
- Semi-crystalline PA: mold temperature 100°C and melt temperature 290°C

Since the adhesion of glue is stronger at low surface energies, these parts was not coated with the hydrophobic coat. Together with the tool design, Ludo pieces were created, to be able to do the pull tests. These Ludo parts represents the design of the custom made apparatus, which has pieces that needs to be glued together. The Ludo parts are already commonly used at the company for this type of test and did not need to be designed specifically for this project. An image of the Ludo pieces together with the glue test designed parts can be seen in Figure 23.
were used to measure surface energy are; demineralized water, Diiodomethane and Ethylene Glycol, where the water is a polar liquid and Diiodomethane is a non-polar. The water has the surface tension of 72.80 \( mN/m \), Diiodomethane has 58.88 \( mN/m \) and Ethylene Glycol has a value of 47.70 \( mN/m \).

To begin the measurements a water drop is placed on the solid surface and ten measurements are carried out by the computer program. This is repeated on a new drop at a different location of the sample. After water droplets are measured, Diiodomethan is applied and after that, Ethylene Glycol. When finishing going through the different liquids, the program use the gathered data and generates a value for surface energy. In this project, the surface energy were measured for:

- Semi-crystalline PA with hydrophobic coating
- Semi-crystalline PA without hydrophobic coating
- Amorphous PA with hydrophobic coating
- Amorphous PA without hydrophobic coating
3.4 Tests of the Created Geometries

3.4.1 Test of Capillarity

The capillary tests were performed by placing two polymer parts, described in section 3.2.2, facing each other and thereafter screwed together. One separation plate was placed between the parts with a thickness of 0.01 mm. The gap between the parts now simulated a capillary of 0.01 mm. A tube was connected to the well from below and the other side of the well was plugged to prevent water from seep out and to ensure that the pressure could be increased. The two polymer parts with the tube were thereafter connected onto a stand, see Figure 24. The tube was filled with de-mineralised water and was held with the water surface at the same height as for the polymer parts. The tube was thereafter raised to increase the pressure in the well. Two heights were documented, firstly the height where the water entered the capillary and secondly the height where the water penetrated into the part with nanostructures. These two heights were thereafter used to calculate the corresponding pressure, by using equation 19.

All three PAs studied in this project were used for the measurements of capillarity. For each of the polymers three measurements were performed and from these, mean values were calculated.

3.4.2 Test of Glue Strength

To test glue strength for a surface with nanostructures, a pull test was performed. The glue used for this test was a Cyanoacrylate glue and the test was performed with two different Ludo parts. This type of parts are common to use at the company for pull tests, so if needed it would be possible to find reference values. The Ludo parts are made of ABS and are beige and transparent respectively. The Ludo parts were glued onto a faceplate, meaning the designed glue samples, and
3.4 Tests of the Created Geometries

Figure 25: An image showing the gluing process made by one of the employees at Oticon.

were allowed to dry for 24 hours. Eight different combinations of faceplates and Ludo parts were tested. These are:

1. Semi-crystalline PA w/o nanostructures, transparent Ludo
2. Semi-crystalline PA with nanostructures, transparent Ludo
3. Amorphous PA w/o nanostructures, transparent Ludo
4. Amorphous PA with nanostructures, transparent Ludo
5. Semi-crystalline PA w/o nanostructures, beige Ludo
6. Semi-crystalline PA with nanostructures, beige Ludo
7. Amorphous PA w/o nanostructures, beige Ludo
8. Amorphous PA with nanostructures, beige Ludo

An image of the samples during the gluing process can be seen in Figure 25 and an image of finished samples can be seen in Figure 26. To perform the pull test a Lloyd Instruments LRX Plus, from AMETEK, Inc. was used together with the program NEXYGEN Plus 3.0. An image of the test set-up can be seen in Figure 27 and Figure 28, where the Ludo part was separated from the designed faceplate by pulling it up with a force generated by the Lloyd Instruments LRX Plus. Before starting to pull the Ludo part, the machine had to stabilize and held a force of 1 N for 10 s and after that it pulled with a velocity of 10 mm/min. When a force...
gets high enough to separate the two parts, a force drop will occur and when this drop is more than 20% of the peak force the test will stop and maximum pressure can be noted. For each combination, five pull tests were performed.
3.4 Tests of the Created Geometries

Figure 27: The set up with the glue sample placed in the Lloyd instrument.

Figure 28: An image showing the Lloyd instrument that was used for the pull tests.
4 Results

4.1 Contact Angle Measurements

This section presents the results from the CA measurements performed on the different samples. All values of the CAs are mean values from the measurements.

4.1.1 Contact Angle Measurements on Polyamide

Table 3 shows the mean values of the CAs for the flat, non-coated PAs used at Oticon. All values are below 90° meaning that the polymers used at the company are hydrophillic in their natural state.

Table 3: Mean value of CAs for the flat, non-coated PAs used at Oticon.

<table>
<thead>
<tr>
<th>Material</th>
<th>CA (Mean value)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Semi-crystalline PA</td>
<td>76.31°</td>
</tr>
<tr>
<td>Amorphous PA</td>
<td>83.02°</td>
</tr>
<tr>
<td>Amorphous PA with glass fibers</td>
<td>81.61°</td>
</tr>
</tbody>
</table>

Table 4 shows the mean value of the CA measurements performed on the flat, plasma treated and coated semi-crystalline PA. This mean value also represents the CA of the hydrophobic coating used at the company. The CA is almost 115° which means that it is hydrophobic.

Table 4: Mean value of CAs for the flat, coated semi-crystalline PA.

<table>
<thead>
<tr>
<th>Material</th>
<th>CA (Mean value)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Semi-crystalline PA</td>
<td>114.65°</td>
</tr>
</tbody>
</table>

4.1.2 Contact Angle Measurements on Polypropylene

Table 5 shows the mean values of the CAs for the nanostructured, plasma treated and hydrophobic coated PP. As can be seen, all values are well above 90° meaning that they are hydrophobic. However, non of the values reaches the requirement for superhydrophobicity, meaning a CA value above 150°. What also can be seen is that the CA increases with molding temperature, where the highest CA is to be found in the mold temperature of 80°C.

In Figure 29 an image of droplets on one of the nanostructured, plasma treated and hydrophobic coated samples is presented. As can be seen, the droplets are highly spherical with a high CA.

Table 6 shows the mean values of the CA for the nanostructured polypropylene with hydrophobic coating, but without being plasma cleaned. As for the polypropylene with both plasma treatment and hydrophobic coating the mean values for this group also indicates hydrophobicity but not superhydrophobicity. For this group the CA also increases with molding temperature with the high-
Table 5: Mean value of CAs for the nanostructured, plasma treated and hydrophobic coated PP.

<table>
<thead>
<tr>
<th>Material</th>
<th>CA (Mean value)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polypropylene (mold temp. 30°C)</td>
<td>124.89°</td>
</tr>
<tr>
<td>Polypropylene (mold temp. 40°C)</td>
<td>136.31°</td>
</tr>
<tr>
<td>Polypropylene (mold temp. 50°C)</td>
<td>137.20°</td>
</tr>
<tr>
<td>Polypropylene (mold temp. 60°C)</td>
<td>140.47°</td>
</tr>
<tr>
<td>Polypropylene (mold temp. 70°C)</td>
<td>140.99°</td>
</tr>
<tr>
<td>Polypropylene (mold temp. 80°C)</td>
<td>142.34°</td>
</tr>
</tbody>
</table>

Table 6: Mean value of CAs for the nanostructured and hydrophobic coated PP.

<table>
<thead>
<tr>
<th>Material</th>
<th>CA (Mean value)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polypropylene (mold temp. 30°C)</td>
<td>127.93°</td>
</tr>
<tr>
<td>Polypropylene (mold temp. 40°C)</td>
<td>135.54°</td>
</tr>
<tr>
<td>Polypropylene (mold temp. 50°C)</td>
<td>138.28°</td>
</tr>
<tr>
<td>Polypropylene (mold temp. 60°C)</td>
<td>138.90°</td>
</tr>
<tr>
<td>Polypropylene (mold temp. 70°C)</td>
<td>139.63°</td>
</tr>
<tr>
<td>Polypropylene (mold temp. 80°C)</td>
<td>141.48°</td>
</tr>
</tbody>
</table>

Table 7 shows the mean value of the CAs for the flat PP with plasma treatment and hydrophobic coating, whereas Table 8 shows the mean value for the flat PP with hydrophobic coat but without plasma treatment. These values gives the CA for the hydrophobic coating and can be compared to the value in Table 4.
Table 7: Mean value of CAs for the flat samples of PP with plasma treatment and hydrophobic coating.

<table>
<thead>
<tr>
<th>Material</th>
<th>CA (Mean value)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polypropylene</td>
<td>115.26°</td>
</tr>
</tbody>
</table>

Table 8: Mean value of CAs for the flat samples of PP with hydrophobic coating but without plasma treatment.

<table>
<thead>
<tr>
<th>Material</th>
<th>CA (Mean value)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polypropylene</td>
<td>114.68°</td>
</tr>
</tbody>
</table>

4.1.3 Contact Angle Measurements on Polyamide with Nanostructures

Table 9 shows the CA for the nanostructured and coated samples molded in the three PAs at maximum temperatures. As can be seen, the maximum mean value is for the semi-crystalline PA, and is 143.91°. The maximum CA of all measurements is 148.33°, which also occurred for the semi-crystalline PA. This means that the surface is highly hydrophobic but has not reached the requirements for superhydrophobicity.

Table 9: Mean value of CAs for the nanostructured and coated PAs, molded at maximum temperature.

<table>
<thead>
<tr>
<th>Material</th>
<th>CA (Mean value)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous PA</td>
<td>121.67°</td>
</tr>
<tr>
<td>Semi-crystalline PA</td>
<td>143.91°</td>
</tr>
<tr>
<td>Amorphous PA with glass fibers</td>
<td>124.96°</td>
</tr>
</tbody>
</table>

Table 10 shows the CA mean values for the structured but non-coated samples molded in the three PAs at maximum temperature. All three polymers are hydrophobic when the surfaces are nanostructured.

Table 10: Mean value of CAs for the nanostructured but non-coated PAs, molded at maximum temperature.

<table>
<thead>
<tr>
<th>Material</th>
<th>CA (Mean value)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous PA</td>
<td>97.91°</td>
</tr>
<tr>
<td>Semi-crystalline PA</td>
<td>113.94°</td>
</tr>
<tr>
<td>Amorphous PA with glass fibers</td>
<td>98.06°</td>
</tr>
</tbody>
</table>

Some measurements were also performed on samples molded at a lower temperature, called middle temperature. These can be found in Table 11, where the first two are nanocoated and the second two is without coating.

Table 11: Mean value of CAs for the nanostructured but non-coated PAs, molded at middle temperature.

<table>
<thead>
<tr>
<th>Material</th>
<th>CA (Mean value)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous PA</td>
<td>97.91°</td>
</tr>
<tr>
<td>Semi-crystalline PA</td>
<td>113.94°</td>
</tr>
</tbody>
</table>

4.2 Design of Test Geometries

Figure 30 and 31 shows CAD-sketches of the capillary tool geometry and Figure 32 shows the CAD-sketch for the glue test geometry.
Table 11: Mean value of CAs for the nanostructured PAs molded at middle temperature. Both samples with and without coating are presented.

<table>
<thead>
<tr>
<th>Material</th>
<th>CA (Mean value)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Semi-crystalline PA with coating</td>
<td>139.62°</td>
</tr>
<tr>
<td>Amorphous PA with glass fibers and coating</td>
<td>121.90°</td>
</tr>
<tr>
<td>Semi-crystalline PA w/o coating</td>
<td>112.66°</td>
</tr>
<tr>
<td>Amorphous PA with glass fibers w/o coating</td>
<td>95.57°</td>
</tr>
</tbody>
</table>

4.2.1 SEM images

In the section below SEM images capturing the surface structures from the different PAs, will be presented.

Figure 33: Semi-crystalline PA w/o nanocoating. Image to the left shows the surface from a top view. Image to the right zooms in on the surface with a side-top view.
4.2 Design of Test Geometries

Figure 34: Amorphous PA with glass fibers and w/o nanocoating. Image to the left shows the surface from a top view. Image to the right zooms in on the surface with a side-top view.

Figure 35: Amorphous PA w/o glass fibers and w/o nanocoating. Image to the left shows the surface from a top view. Image to the right zooms in on the surface with a side-top view.

Figure 36: Semi-crystalline PA with nanocoating. Image to the left shows the surface from a top view. Image to the right zooms in on the surface with a side-top view.

Figure 37: Semi-crystalline PA with nanocoating, touched by a finger.
4.3 Surface Energy Measurements

The results from the surface energy measurements can be seen in Table 12. As can be seen, the surface energies are higher without a hydrophobic coating, where the maximum value of 37.64 mN/m is for the amorphous PA. For the non-coated samples, the lowest value is to be found for the semi-crystalline PA and is 5.09 mN/m.

Table 12: Surface energies for the nanostructured PAs, both with a hydrophobic coating and without.

<table>
<thead>
<tr>
<th>Material</th>
<th>Surface energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous PA w/o coating</td>
<td>37.64 mN/m</td>
</tr>
<tr>
<td>Semi-crystalline PA w/o coating</td>
<td>32.01 mN/m</td>
</tr>
<tr>
<td>Amorphous PA with coating</td>
<td>8.46 mN/m</td>
</tr>
<tr>
<td>Semi-crystalline PA with coating</td>
<td>5.09 mN/m</td>
</tr>
</tbody>
</table>

4.4 Test of the Created Geometries

4.4.1 Test of Capillarity

The height of the water column, where the water entered the first part of the capillary without nanostructures, were measured to 0.12 meters for all three materials. This corresponds to a pressure of 1178 Pa. Table 13 shows the measured mean value of the height for the water column that gave rise to the pressure needed to penetrate the capillary further, into the part with nanostructures. As can be seen, the values for the three different materials are approximately same. Semi-crystalline PA has the highest value, whereas the amorphous PA with glass fibers has the lowest.

Table 13: Measured height and calculated pressure for the capillary tests.

<table>
<thead>
<tr>
<th>Material</th>
<th>Height</th>
<th>Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorphous PA</td>
<td>0.49 m</td>
<td>4.8 kPa</td>
</tr>
<tr>
<td>Semi-crystalline PA</td>
<td>0.50 m</td>
<td>4.9 kPa</td>
</tr>
<tr>
<td>Amorphous PA with glass fibers</td>
<td>0.39 m</td>
<td>3.8 kPa</td>
</tr>
</tbody>
</table>

The calculated burst pressure for a capillary stop with a dimensional change in the cross-section is 29 kPa for a capillary gap of 0.001 mm.

4.4.2 Test of Glue Strength

Figure 38 shows the maximum pull force needed to break the glued samples. The breaking occurred either in the glue or in the Ludo piece. As can be seen, the pull forces varies slightly within each group, and therefor no mean values were calculated. The four highest values of the pull force are all found in combination 4, which is the nanostructured amorphous PA without glass fibers glued with the transparent Ludo piece.
4.4 Test of the Created Geometries

RESULTS

Figure 38: The pull force (N) needed to break the glued samples for eight different combinations. These combinations are described in section 3.4.2

Figure 39 shows a graph with information about two tests with different outcomes. The two curves correspond to test setups where the same material combinations were used, meaning the semi-crystalline PA without nanostructures together with the transparent Ludo.

Figure 39: A graph showing the load vs. time curve for two different samples, with two different breaks. One with a high break force and one with a lower.
5 Discussion

5.1 Contact Angle Measurements

Using the CA value to define if a surface is hydrophobic or hydrophilic have some limitations. The results is dependent on how the measurements are performed and under what conditions. In this project, the sessile-drop method was used where the droplet were placed on the surface. Factors that could have affected the results is that the amount of liquid was not the same for each measurement. This leads to different contact areas which could have an impact on the CA. Also, the time between the dispersion of the droplet and the measurement of the CA were not constant. If the measurements are performed too quick there is a risk that the droplet has not reached equilibrium and static state. However, water commonly only need less than one second to stabilize and all measurements were performed after that which means that the result probably not have been affected by a time parameter.

For the CA measurements it can be motivated to perform dynamic measurements as well to determine the advancing and receding CAs. These two angles can be used to define the hysteresis of the surface and shows if the droplet is in Wenzel state or Cassie state. Since the equipment at Oticon, used for the sessile drop method, did not allow tilting of the base, dynamic measurement were excluded. These kind of measurements could have quantified the determination of the surface properties since the definition of a superhydrophobic surface has requirements for the hysteresis and roll-off angle in addition to the static CA.

The results are also dependent on the settings of the computer program. Different methods can be chosen in for calculations of the angles. The chosen one is the automatic tangential method, which automatically measures the CA for each drop. The reason to this is because we wanted to be consistent during the measurements. If a manual method had been used instead, there would be a risk that the measurements would fluctuate between the different drops. However, a limitation with the automatic tangential method is that it sometimes seemed like it did not find the correct shape of the drop, which may affect the measurement of the CAs.

Despite the limitations, CA measurements is a simple method to define the behaviour of water on surfaces and are therefore commonly used.

5.1.1 Contact Angle Measurements on Polyamide

The CA measurements on the flat, non-coated samples made of the three PAs used at the company showed that the surface of all polymers are hydrophilic with an intrinsic CA below 90°, see Table 3. According to the theory, a hydrophilic surface will become even more hydrophilic if the roughness of the surface increases. Therefore an assumption was made that these polymers would become superhydrophilic when nanostructures are created on the surfaces. However, this turned out not to be true, which will be discussed in section 5.2.3.
5.1 Contact Angle Measurements

5.1.2 Contact Angle Measurements on Polypropylene

When looking at the results from the CA measurement it is possible to see that the CA is increasing with the rise of molding temperature, see Table 5. Of all the measurements on the different parts, the highest value of 145.91°, were found at a part that was molded at 80°C. This temperature is well above the recommended value but the CA did not exceed 150°. This could indicate that the PP is unsuccessful to replicate the nanostructures fully or that the chemical coating is not hydrophobic enough to reach the requirements for superhydrophobicity.

As mentioned in the method, during the measuring of CAs, four samples with the same molding and coating settings were studied. For each sample, three measurements were made at an arbitrary location of the part. When looking at the results it can be seen that the measured CAs differs a bit which could also be observed visually. Droplets with a higher CA tended to easier fall of the sample when it was tilted a bit after the measurements. This empirical observation enforces the statement that the higher the CA is, the more hydrophobic the surface will behave.

When looking at the samples that went through a plasma treatment before getting chemically coated, there is no significant difference in comparison to the non-plasma treated. This is probably because the parts were stored and packaged and never touched before treatment and coating. Therefore the plasma treatment did not make a specific difference when it comes to CA measurements. However it is still interesting to use this type of treatment since it theoretically should enhance the adhesion of the coating to the material.

Measurements were also made on PP samples without nanostructures on the surface, which can be compared to the measurements on the flat samples of semi-crystalline PA. Both type of materials were coated with the hydrophobic coating. What was observed were that the CA did not differ between the two different materials, with a mean value of 115°, proving that it is the top layer of the surface that gives its hydrophobic properties. This means that the coating together with nanostructures gives us a much more hydrophobic surface than without.

5.1.3 Contact Angle Measurements on Polyamide with Nanostructures

Like described in the methodology, CA measurements were made on PA parts, including different molding settings. Looking at the results it is possible to draw the conclusion that the semi-crystalline is the best material of the three PAs to replicate the nanostructured surface since it has the highest CA mean value. This can also be seen when comparing the SEM images. Why it is the better one could be because the material, when melted, more easily floats out in the cavity and therefore fills all the structures more successfully. This could implicate that without a chemical coating the semi-crystalline, that is a hydrophilic material from the beginning, would also be the most hydrophilic material of the different PA combinations. Based on the stated theory, the roughness increases hydrophobic-
ity/hydrophilicity depending on the material properties. This however, seems to not be true in our case. Looking at the CA for semi-crystalline with nanostructures, but without a chemical coating, it can be seen that the CA has increased and now has a hydrophobic value. A theory we have to this result is that the droplet is in Wenzel state. This is because the nanostructures creates air pockets and when a water drop is applied on the surface these air pockets traps air which prevents the liquid from penetrating the surface, giving it a higher CA than expected.

The results regarding the different molding temperatures indicates that the maximum temperatures gives higher values of the CAs. It is not perhaps a significant difference, but none the less maximum molding temperature does have a greater value and therefore our recommendation for the injection molding procedure would be to use a maximum molding temperature. Because of this discovery we decided to only perform capillary test on the samples with the maximum molding temperature.

When looking at all the different CA measurements it is possible to draw the conclusion that materials used when producing hearing instruments are able to replicate nanostructures with a good result. If we compare the measurements for the PAs to the measurements performed on PP, the PP also provides a high CA. However, the mold settings for PPs are well outside the recommended temperature interval, which was not relevant when analyzing the PAs. The reason to this is because the company would not use temperatures outside the recommended intervals during the production of the hearing aids.

5.2 Design of Test Geometries

5.2.1 What we want to test

As mentioned in the method section, many different tests were considered before deciding to test the capillarity and glue strength. Fields that were found interesting to investigate were; the molding angle of the structures, glue strength, water paths, glue paths, wear on the tool, capillarity, wax ingress. In the following text, reasons why some tests were more attractive will be discussed.

In the conversation concerning which tests to conduct in this project, the stated issue ‘Can Oticon take advantage of nanostructured surfaces to improve robustness of hearing aids?’ took a great part in the decision making process. Tests that could give the best feedback to the company in their decision if or if not to buy in the technique from DTU, was prioritized. While all of the mentioned tests above could give a good feedback to Oticon, some of the tests were prioritized before others. Also there was a time limit of the master thesis to consider and therefore the number of tests had to be narrowed down.

First of all what needed to be investigated was whether the nanostructures together with coating actually made a surface more superhydrophobic in comparison to just using a Teflon like coating and no nanostructures. When this was answered the next test could be carried out. The final tests needed to be able to show that
the nanotechnique either enhanced robustness or improved water resistance.

As mentioned in the theory, a nanostructured surface could either make the surface superhydrophobic or superhydrophilic depending on the top-coat covering the structures. Depending on if the structured surface is in contact with skin, the surface can become hydrophilic. The understanding of how the surface reacted to skin contact influenced the direction of what kind of tests that were prioritized. It was decided to look at how the nanotechnique could be used for improving the hearing instruments on the inside. Therefore there was no need to use the time to look at creating a test where nanostructures covering the outer shell to for example creating a water path. If water could be lead through a certain path, different areas such as the opening for microphone or the crease of the battery hatch, could be protected from water or wax ingress. However, this nanostructured path would be affected as soon as the surface were touching skin. Hence, this type of test was not prioritized.

When having a molding tool with micro- and nano-sized holes that will generate pillars on the surface of the plastic part, the angle of the hole will affect the quality of the structure on the surface. Since the part will be pulled out from the molding tool, a too severe angle of the holes might affect the quality of the pillars. If the holes are molded $90^\circ$ to the direction the part is going to be pulled out, chances are high that the pillars will break. Because of the different dimensions and angles of a hearing instrument surface, it is of interest to investigate for which angles of the pillars the hydrophobic and hydrophilic qualities are good or bad. However, because it was chosen to only look at surfaces within the hearing aid and not the outer surface, there are tests that are more interesting to conduct before looking at how different pillar angles of the molding tool affect the structures. With more time, this would be the next natural step to take to further investigate whether this technique is applicable to the company. What else that would have been interesting to investigate is how wear on tool affect the molding quality. This is to see how many parts the tool is able to produce before the structures are affected. This is something was not performed because of time constraints.

The two tests that we finally decided to conduct, the test of capillarity and the test of glue strength, were interesting because they gave results that helped answer the questions stated in the issues in section 1.3. Both tests also regarded parts located inside of the hearing aid and they gave an opportunity to quantify whether it will be interesting for Oticon to use this kind of molding technique.

5.3 Surface Energy Measurements

The surface energy measurements were performed as a complement to the CA measurements to quantify the determination of surface properties. As can be seen from Table 12 the surface energies are lowest for the hydrophobic coated samples, which correlates to the theory which says that the more hydrophobic surface the lower the surface energy. The values of the surface energies can be compared to the values of the CA. From Table 8, the highest mean value of the CAs is for
5.4 Fabrication

To find a good temperature combination regarding molding settings it is common to start with low mold and melt temperature values within the recommended span and then continuously increase these values until a satisfactory part is created. This was intended to be done, however, it was shown that the test geometry was faulty and the part could not be properly filled without using the maximum recommended values from the beginning. Therefore, only one mold setting was used when molding the glue samples. For the capillary sample, however, two mold temperatures were used for the amorphous PA with glass fibers and the semi-crystalline PA.

When started to mold the part had a defect called jetting which creates samples looking like Figure 40. There can be several factors that create this effect. Sometimes, the inlet hole is to small for the geometry where the melted polymer should fill. For this injection molding tool the size and geometry of the part should have the injection inlet placed on a more beneficial spot. Also, the part was too thin for the injection mold to spread properly and if the part had been thicker it would be easier to avoid this type of defect. To be able to produce acceptable samples from the glue molding tool it was needed to use maximum mold and melt temperature and a high pressure. This concerned both polymers.

An interesting observation that was made from the production of the parts was that when injection molding using the tools before they had undergone the laser treatment done by Transform, the molded parts were much easier to de-mold. When the molding tool had the nanostructured pattern engraved in the steel the de-molding process were significantly more difficult since the polymer seemed to get stuck in the structures. Therefore the tool had to be modified to make the de-molding easier.
5.5 Test of the Created Geometries

5.5.1 Test of Capillarity

The reason for choosing the capillary test is to see if nanostructures can be used as a capillary stop instead of an enlargement of the dimensions in the cross-section. Another reason is to get a deeper understanding of the surface properties compared to the CA measurements. This is because the CA measurements only gives one side of the coin but not the fully insight on the behaviour of wetting of the surfaces.

The test geometry was formed in a way that enabled both looking at a capillary stop made out of nanostructures and also a stop created by a change of dimension. Unfortunately the part of the sample where the dimension change were situated turned out to have a faulty design and could not be used in this project. However, it was possible to find a theoretical value for the burst pressure at a dimensional changed capillary stop. Since this is the only source of information present, this is the value that was used to compare the results from the capillarity tests with.

From the different tests it can be seen that the PA with the best stopping effect is semi-crystalline. For this polymer the burst pressure reach a mean value of 4,9 kPa. The pressure for entering the capillary was also measured, which were the same for all the PAs. This is not surprising since that part of the samples is flat and has a chemical coating top layer, which is the only thing affecting the hydrophobicity.

If a theoretical value of the burst pressure represents the reality of hearing instrument, then solemnly using nanostructures instead of dimension changes would not enhance the capillary stop. What could be observed is that the nanostructures did hinder the water ingress until a certain pressure was reached. This indicates that the enhancement of hydrophobicity the structures create does have a stopping effect. It would be interesting to apply this technique to the design of hearing aids to hinder water from entering a capillary from the beginning. Then to be on the safe side also use a dimensional change as a capillary stop for the water that do enter.

To be completely sure of which polymer is the best in this test is very hard to tell. The test concept is a good idea, but the actual set up needs to be revised. The test study an extreme case where the capillary gap had a radius of 0,005 mm. In calculations this gives a very high burst pressure for a dimensional capillary stop and therefore more gap heights should have been studied. Also a lot of different parameters in the set up were not constant throughout the tests. It was difficult to see the exact moment for when the liquid first entered the capillary and then to also see when it entered the second chamber after the capillary stop. The
measurement readings were also not as exact as we wished them to be. Therefore, if we could change our test set up it would be:

1. Create a better design for the dimensional capillary stop
2. Use equipment that generates a controlled pressure
3. A better way to control the distance between the parts

5.5.2 Test of Glue Strength

The results from the glue strength tests had some differentiation within the different sample groups, see graph in Figure 38. Due to this we deemed it irrelevant to calculate mean values. Looking at the graph it can be seen that amorphous PA together with the transparent Ludo part gave the highest pull forces. What is interesting is to look at the results from other tests regarding this polymer. Both the CA measurements and the surface energy measurements showed that this polymer has the most hydrophilic surface properties. Therefore these results could have been predicted by just looking at prior information about the material and the theory regarding adhesion and hydrophilicity.

![Image showing how the glue has been spread out over the sample.](Figure 41)

In comparison to values from similar pull tests conducted by Oticon, it can be seen that our results got lower values of the pull forces. This means that nanostructures did not enhance the glue strength quality. A reason to this could be that the PAs used at Oticon became hydrophobic when applying nanostructures to the surface. It would be interesting to gather more data regarding the glue quality by performing more pull tests because as it is now it is not possible to make statement whether nanostructures creates an improved hearing instrument in regard to glue quality. Another point we looked at besides the adhesion quality was if nanostructures could make the gluing process more efficient for the employee. However, from observing the process when applying glue, no remarkable improvements could either be reported as better nor worse except for the semi-crystalline part. For the semi-crystalline sample, which was the most hydrophobic polymer, the gluing experience were negative and time consuming since the glue got absorbed by the structures, see Figure 41.
5.6 Ethics

When encountering the term ethics, it can be hard to truly understand what it means. Many people may connect it to feelings or religion, laws or norms of society. While this is not completely untrue, because many laws do follow the ethical norms shared by many people, always following the norms of society or feelings one might have about a situation does not equal doing the ethically right thing. A lot question are both in religions and in some countries is answered unethically. Therefore, the way we have interpreted the meaning of ethics is by answering the question is this action right or wrong? The question needs to be answered from norms we have deep rooted within ourselves and not from temporary norms created by society and religions. Is the action we want to carry out defensible from a fundamental perspective. Fundamental norms can be considered as for example how we look at murder, theft, love, honesty, cheating et cetra.

Ethics has been something that has been present in many courses throughout the Biomedical Engineering program. Since engineers have a lot of responsibility in the development of society it is relevant to bring up ethics in the education. Something that has been a part of the education since day one is how to make society more available to everyone and this aspect is where our project were created from.

In the hearing instrument industry of today, there are almost no developer of waterproof hearing aid products. A result of this is that the hearing instrument user has to remove the hearing aid whenever he or she are walking in the rain, showering or going out for a swim. This not only reminds the person of the disability, it also limits the user to only being able to hear in certain situations. Of course if making the hearing aid 100 % water resistant other qualities will be affected such as sound quality or the size of the instrument. Therefore, ethics in this scenario might not be about creating a water proof hearing aid, but to find the perfect balance between properties to provide the best user experience.

In this project we have looked at solutions where we can enhance the robustness and water resistance. We might not have solved the problem with a completely waterproof hearing aid, but we hope to highlight the situation. Maybe with this project we have contributed to a step in the right direction - finding a water resisting technology that does not affect the other qualities. Because no one should have to be limited in everyday situations. To us it is not ethically defensible to accept that society is not available to everybody living in it.

5.6.1 Biocompatibility

Already in an early stage of the project thoughts arose concerning the biocompatibility of nanostructures on surfaces, more specific - will hydrophobic and hydrophilic surfaces affect human skin? Since the polymers used in the hearing aids already are biocompatible the nanostructures will not change this. However, since the nanofield still is relatively new, there lacks sufficiently of studies on nanostructures, nanoparticles and nanocoating and their effect on humans and
the environment.

5.7 Conclusion

The purpose of this project were to gain an insight whether using nanostructures when injection molding is a technology that could be appealing for Oticon. To reach a conclusion several aspects needed to be understood, mainly how the technique worked and also how did nanostructured surfaces behave on different hearing aid materials. In the work of evaluating surfaces the first step was to get an understanding of the basic theory, such as how superhydrophobic or superhydrophilic surfaces behave. This is thoroughly described in theory, however, the main conclusions reached are that to be able to define a surface as superhydrophobic the CA need to be above 150\(^\circ\), have a hysteresis below 10\(^\circ\) and a low surface energy.

In theory, if a roughness is applied on a hydrophobic material the intrinsic CA will increase. In the same way a hydrophilic material will become more hydrophilic when the roughness factor increases. This theory is what the project based its work on when trying to create a superhydrophobic surface. To increase roughness a laser technique was used to create a pattern with micro with superposed nanostructures on the molding tools.

Unfortunately a superhydrophobic surface status was not reached when using Oticon’s PAs. It was close though and the semi-crystalline PA replicated the nanostructures the best amongst the three different PAs. Semi-crystalline PA with nanostructures and together with the hydrophobic coating gave a mean value CA of 143,91\(^\circ\). Why this material works better than the others could be because it flows easier into the small cavities of the structures. An interesting observation that was made was that even if all the PAs were more or less hydrophilic from the beginning, when molded with nanostructures they all became hydrophobic. This goes against the theory this project is based on. The observation was made when looking at the CA and surface energy of nanostructured and uncoated samples and was confirmed when investigating if nanostructures could be included in the design of glue surfaces.

Since the theory said that hydrophilic material should become more hydrophilic with nanostructures it was hoped that the adhesion between surfaces and glue would both enhance and be more effective. Therefore, semi-crystalline that was the most hydrophilic material and replicated the structures the best should have become the most hydrophilic when it was uncoated. Surprisingly it became the most hydrophobic, having the same CA as the chemical coating on a flat surface. The samples with the best gluing qualities were amorphous PA. However, to be able to give a reliable statement regarding glue quality more tests needs to be conducted.

The second design that was investigated was to see if nanostructures together with hydrophobic coating could be used as capillary stops. Because the test looked at a very small capillary the theoretical burst pressure of a normal capillary stop is quiet high. The nanostructured surface was not able to hinder water to the same
extent, but what is possible to say is that it did stop the water until a certain pressure was reached. One conclusion that can be made is that the nanostructures are not as efficient in comparison to the theoretical burst pressure of a normal capillary stop. It would be interesting to see how this theoretical burst pressure correlates to a value obtained from a practical test of a normal capillary stop. Another conclusion from this test is that the structures do hinder water much more efficient than a flat surface. The idea of the capillary test is good, however, it needs some alterations.

It is of now not possible to give a clear answer whether Oticon can take advantage of nanostructures to improve robustness of the hearing aids and invest in this technology. It can be said that there is a significant increase of the CA when using nanostructures together with their chemical coating and this could be used together with capillary stops to hinder water ingress. It can also be stated that the PAs of Oticon are able to replicate the laser made pattern when injection molding. However, more tests would need to be done. It is of great interest to now look at how the structures behave during molding of geometries that are not flat. When the curvature of the molded sample reaches a certain angle, there is a risk that the structures will break during the de-molding process and it would be interesting to see for which values this becomes a risk. The design of tools also would need to be studied since the structures affects the de-molding process, making the molded part more attached to the tool. Further more, it would be important to study the wear of the structures on the tool, both tools that have gone through a hardening process and tools that have not, since the structures can be affected when mass-producing parts.

This being said, if Oticon are looking for a way to make their flat surfaces close to superhydrophobic, then yes, this nanostructured injection molding is a good way to reach that.
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