# TALLINN UNIVERSITY OF TECHNOLOGY

Faculty of Chemical and Materials Technology
Department of Polymer Materials
Chair of Woodworking

# MEASURING OF HYDROPHOBICITY IN AEROGELS

Bachelor's thesis

Maria Pogodajeva

Supervisor: Kärt Kärner, Engineer, Tallinn University of Technology
Instructor: Jaan Kers, Professor, Tallinn University of Technology

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PUIDUTÖÖTLEMISE ÕPPETOOL

# HÜDROFOOBSUSE MÄÄRAMINE AEROGEELIDES

Bakalaureusetöö

Maria Pogodajeva

Juhendaja: Kärt Kärner, Materjaliuuringute keskus, Insener

Kaasjuhendaja: Jaan Kers, Puidutöötlemise õppetool, Professor, Õppetooli juhataja

Puidu- ja Tekstiilitehnoloogia õppekava KAOB02/13

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I further declare that the material obtained from other sources has been duly acknowledged in the thesis.

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*(Name and signature)*

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# List of abbreviations

| | |
|---|---|
| AC | Algae Cellulose |
| BC | Bacterial Cellulose |
| CA | Contact angle |
| CNC | Cellulose Nanocrystals |
| CNF | Cellulose nanofibrils |
| MCC | Microcrystalline Cellulose |
| MFC | Microfibrillated Cellulose |
| NCC | Nanocrystalline Cellulose |
| NFC | Nanofibrillated Cellulose |
| NMMO | N-methyl-morpholine-N-oxide |
| PF | Plant fiber |
| SEM | Scanning Electron Microscopy |
| t-CNC | Tunicate cellulose nanocrystals |
| TEM | Transmission Electron Microscopy |
| WF | Wood fiber |

# Introduction

Aerogels are the world's lightest solid materials with unique structure that have been around for over 90 years. Being produced first in the late 1920s by Samuel Kistler, aerogels have paved the way towards the next generation materials. They are composed of up to 99% air by volume which makes them highly porous, thus, provides us with quite a few valuable properties.[1]

In the earliest stages of the development of aerogels, these materials were mainly used as thickening agents in paints, filters and even makeup. However, the production process was dangerous, toxic, expensive and time-consuming at that period, so much so that manufacturers had to discontinue their products in the 1970s.

Although the start of aerogel development was a bit shaky and uncertain, the researches haven't abandoned the material and have come up with a process that made production of aerogels less toxic and life-threatening. Being able to replace supercritical alcohol with supercritical carbon dioxide in the drying process has led to creating a safe environment and time-efficient processes. Aerogel became more commercially available and further developments are still being made, as scientists have grown interested in the possibilities of the material.

Nowadays aerogels are used in a variety of fields, such as homebuilding, sports equipment, spacecraft engineering and even nuclear weapons. Thanks to aerogel's high porosity it is mostly used as an insulator in construction.[2]

Measuring the hydrophobicity of aerogels, specifically the contact angle or a droplet, allows researchers to experiment with properties and potentially improve the functionality of the material as well as decrease its cost of production and, thus, make a leap forward in the technological world.

This next generation material promises big advancements in thermal insulation, electrochemistry and aircraft engineering as well as home renovation and development of 'green' technology.

This thesis is focused on reviewing the topical literature on aerogel technology, the nature of cellulose, the physical aspect of hydrophobicity and the experimental part which reviews the properties of aerogels.

# 1. Cellulose

## 1.1. History of discovery

Cellulose is considered to be one of the oldest natural occurring polymers with many years of industrial applications for making textiles, paper, plastics, etc. However, the science behind this polymer, its chemistry, structure, morphology, is relatively new. Most of the important discoveries have been made only in between 1920 and 1940.[3]

The discovery of flax excavation sites of the Swiss lake dwellers is a documented reference to one of the earliest uses of cellulose. It dates back to 7th and 6th centuries BC. Hemp was the main resource that was used for production of rope (4500 BC China). Cellulose was used in fabrics for garments in 4000 BC. Cotton and linen were produced in Egypt and India in 3000 BC, as well as papyrus sheets, which were widely used as writing material. Figure 1 shows parts of linen clothing of Ancient Egypt.[3]

Figure 1.Linen clothing of Ancient Egypt. (http://www.crystalinks.com/egyptclothing.html)

With time, more developments and improvements in harvesting of resources were made. The chemistry of cellulose didn't play a significant role until the 19th century. In 1833, Braconnot used nitric acid to dissolve a series of plant substances and produced a number of products he named 'xyloidine', which was the beginning of nitrocellulose chemistry. Through nitration, the first 'man-made' fiber from cellulose was developed. Thus, began the systematic study of cellulose chemistry. It was discovered that plant tissue yields a resistant fibrous substance when purified by acid-ammonia treatment followed by extraction with water, alcohol and ether. It was concluded that plant cells consist of a carbohydrate composed of glucose which in 1839 was name Cellulose by the French Academy.[3]

## 1.2. Structure

When considering macromolecules of any kind, three structural levels must be distinguished[4]:

1) *The molecular level*

Cellulose is reviewed as a single macromolecule.[4]

2) *The supramolecular level*

Cellulose molecules that interact with each other forming chains and/or macromolecules forming similar larger structures in a certain order.[4]

3) *The morphological level*

Entities that are formed by cellulose molecules. Includes review of complex structures.[4]

**1) Molecular level**

Cellulose is a natural substance that has a fibrous structure and is found in plant tissue. It cannot be classified as an absolutely pure chemical individual. It is not soluble in water. Through qualitative analyses purified cellulose has been found to consist of carbon, hydrogen and oxygen. Quantitative analyses revealed the proportion of 6 carbon atoms to 10 hydrogen atoms to 5 oxygen atoms. Further chemical investigation, confirmed by x-ray diffraction studies, have revealed that the 21 atoms are arranged as in β-glucose anhydride.[5]

These glucose anhydride rings are joined through the 1 and 4 positions by oxygen bridges to form a primary valence chain of unascertained length. This is the so-called molecular chain of cellulose. The chain may vary depending on the degree of polymerization. Cellulose a polysaccharide which is a carbohydrate - a natural organic compounds that has a formula $C_m(H_2O)_n$.[5]

### 2) Supramolecular structure of cellulose

Cellulose fibrils aggregate and form highly ordered chains and structural systems. This results in the molecules being stiff. Hydrogen bonds and the organization of the units contributes to this property.[4]

On the supramolecular level cellulose is seen as a structural chain with parallel alignments of crystallites and crystallite strands. Key factor in determining the orderly structure of the chains is hydrogen bonding between $C_6$-OH and $C_3$-OH. High spatial regularity and hydroxyl groups provide interchain interactions. The structure by itself isn't uniform throughout. It can be divided into two regions: low ordered (amorphous) and highly ordered (crystalline). Fibrils extracted from crystalline regions are called nanocrystals. This model is used to describe the hierarchy of cellulose derivatives.[4]

### 3) Morphological structure of cellulose

The morphological structure of cellulose includes a well-organized system of fibrillar elements. The smallest morphological unit - a fibril - has a size between 3-20 nm (cellulose nanofibrils or CNF). These fibrils form layers, thus, creating fibrillar textures. This is only applicable to natural cellulose sources. There is also regenerated cellulose fibers - fibrils form random structure depending on manufacturer's preference. These include viscose and cellophane. They are produced by dissolving the cellulose pulp in Schweizer's reagent. Morphology of cellulose can be studies by electron microscopy techniques such as scanning (SEM) or transmission (TEM) electron microscopy.[4]

## 1.3. Properties

Hydrolysis of cellulose is performed by raising the temperature of the compound in acid medium. Many different cellulose structures can be achieved through this reaction. Final product of hydrolysis is glucose.[6] Natural cellulose crystal phases are $I_\alpha$ and $I_\beta$. $I_\alpha$ is found in cell walls of algae and in bacterial cellulose (Fig. 2). Higher plants consists mainly of $I_{\beta.}$ Through processes of regeneration and mercerization structure of cellulose II can be achieved. Cellulose II has a monoclinic crystal system - a very stable structure.[7]

Processing cellulose I and cellulose II with ammonia produces cellulose $III_1$ which also has a monoclinic crystal system. The process of changing the structure of cellulose from cellulose I to cellulose II is irreversible.[7]

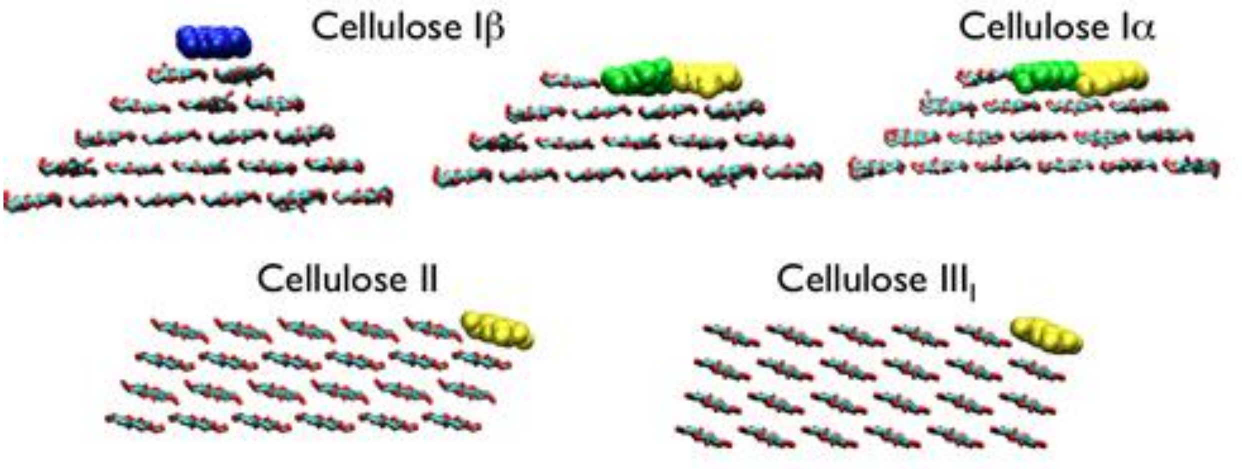

Figure 2. Cellulose crystal phases structures.
(http://www.nrel.gov/biomass/staff_pages/gregg_beckham.html)

The result of cellulose breakdown is the production of cellodextrins - molecules with small chain lengths that are soluble in water.[6]

Common key reactions for cellulose include the formation of esters. Each molecular fragment of cellulose contains 3 OH groups, which react with acetic acid and nitric acid[6]:

$(C_6H_7O_2(OH)_3)n + 3nHNO_3 = (C_6H_7O_2(ONO_2)_3)n + 3nH_2O$

$(C_6H_7O_2(OH)_3)n + 3nCH_3COOH = (C_6H_7O_2(OCOCH_3)_3)n + 3nH_2O$

Nitrocellulose (Fig. 3) is a combustive compound which is used to make fumeless gunpowder. Cellulose triacetate is used for creating polishes, films and acetate fiber.[6]

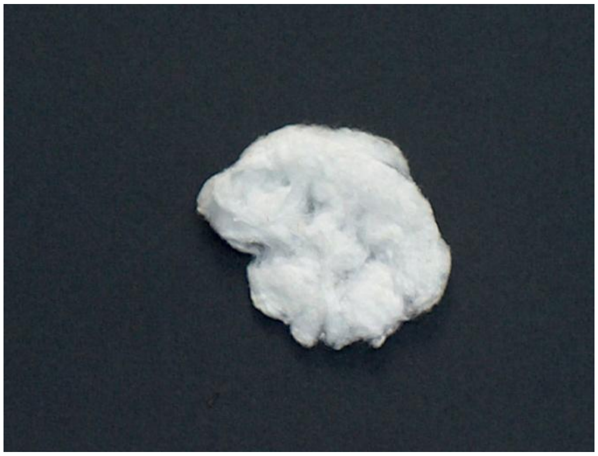

Figure 3. Nitrocellulose. (http://www.britannica.com/EBchecked/topic/249397/guncotton)

Cellulose is a semi-flexible polymer which has crystalline and amorphous phases with strong hydrogen bonds in its structure (Fig. 4). In addition, cellulose molecules have no branching. This causes stiffness of the molecule. Cellulose is able to crystallize easily and create fibrillar structures.[8]

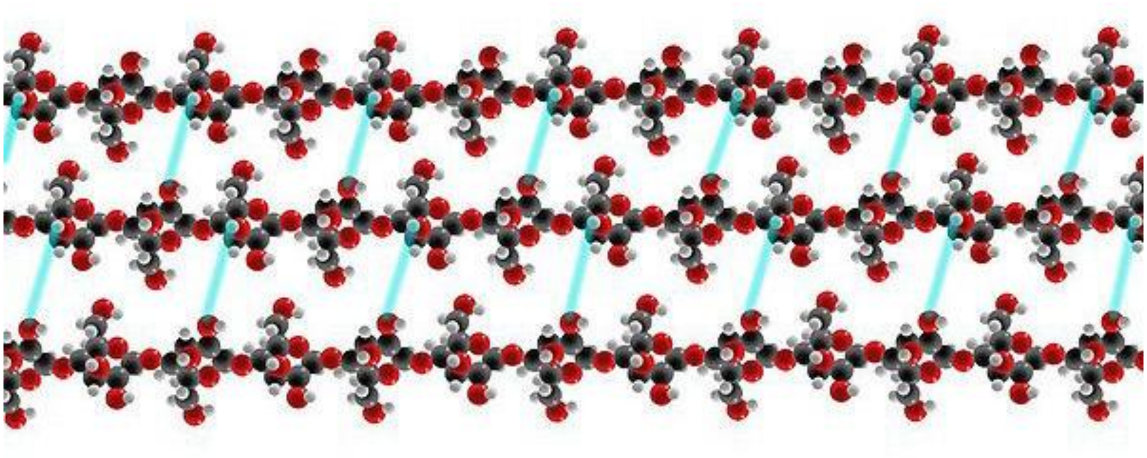

Figure 4. Cellulose structure. Blue lines represent the hydrogen bonds between glucose strands. (http://www.hhspolymers.com/polymer-of-the-month.html)

Cellulose does not have any specific taste nor odor. It is a natural polymer that is biodegradable and insoluble in water. Cellulose is hydrophilic and has a contact angle of 20-30$^{o}$. It has a transitional point of 320$^{o}$, which means that the required temperature is needed for it to become amorphous.[8]

Derived from wood pulp cellulose chain length varies between 300 and 1700 units, other fibers, such as cotton or bacteria have a chain length range from 800 to 10 000 units.[9]

## 1.4. Occurence

Cellulose is a natural occurring polymer. Its sources are primarily different types of plants along with other biopolymers in them. More specifically the most important source is wood as lignocellulosic material. Cellulose is the main part of cell walls in wood. The shapes of the cell and their position in relation to each other are the basis of plant morphology. Even structure that contain old cell walls are crucial functioning units of higher plants (xylem). However, cellulose is not the only building block of the cell wall. This also includes non-cellulosic components, such as pectins, hemicelluloses and proteins.[10]

Besides wood, highly pure sources, such as cotton (90% polysaccharide), have a higher water content and may be harvested for commercial use. [10]

When the primary cell wall is formed it creates a swollen jelly-like structure. Molecules in the primary cell wall have a high degree of polymerization which means the length of the molecular chains is very high. The chains are twisted and stabilized by hydrogen bonds. These chains contain elementary fibrils with a diameter of 5-30 nm. [10]

Secondary cell walls include microfibrils with diameters of 5-30 nm. These microfibrils form a crystallized structure which shows high levels of stability. Microfibrils are the main contributors to the mechanical strength of the plant cell wall. [10]

Naturally occurring cellulose is not 100% pure as it has organic byproducts. They may lead to problems during the chemical treatment. Nonetheless, certain processes of isolation and purification have been added to production to eliminate these byproducts.[10]

Tunicates are sea animals that have a mantle which consists of cellulose microfibrils embedded in a protein mix (Fig. 5). Thus, being the only animals that are known to produce cellulose microfribrils. The structure of microfibrils is similar, though not exact, to the plant source. The difference comes from the formation process in the mantle.[7]

Figure 5. Photo of tunicates. (http://ambergriscaye.com/pages/town/252.html)

Algae can be a source of cellulose microfibrils as well. The structural differences vary between the species because of the biosynthesis processes. Most of the research is based on the use of cellulose microfibrils of the green algae.[7]

Certain species of bacteria are known for producing cellulose. The most studies one is called Gluconacetobacter xylinus. Bacteria can produce cellulose microfibrils under certain culturing conditions. The product is a thick gel composed of cellulose microfibrils and 97% water, called pellicle. There are possibilities of altering the structure of microfibrils by changing the conditions in which the bacteria is grown.[7]

# 2. Nanocellulose

## 2.1. Nanotechnology definition

Materials that have nanometer-sized structure have been increasingly getting more popular among researchers and developers. Nanotechnology is a relatively new field of science, yet, undoubtedly, major progress has been made during the recent years.

Nano - from the Greek word for "dwarf" - means $10^{-9}$. It is one billionth of a meter on 1 nanometer (nm).[11]

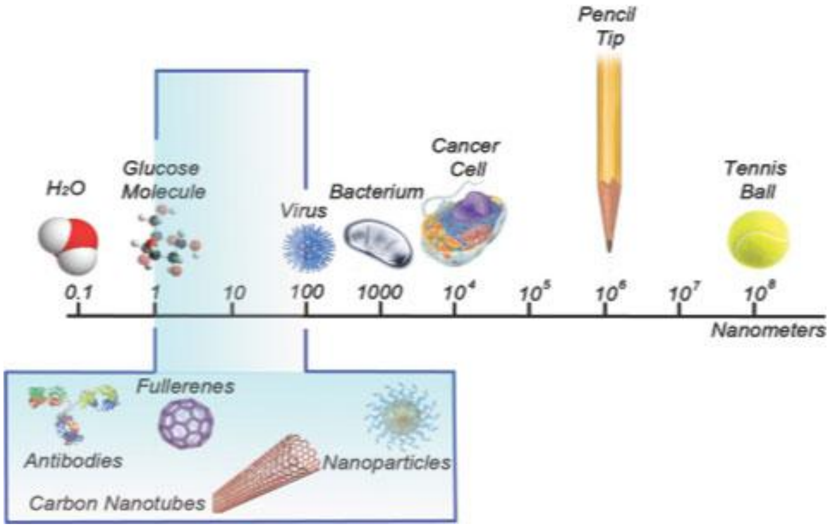

Figure 6. An example of a nanoscale. (http://inl.int/inl-outreach-3)

Nanotechnology is defined as study that revolves around matter of dimension between 1 and 100 nanometers which is called a nanoscale. (Fig. 6) Although the range is quite small, materials on this level can show outstanding properties and unique structure, not mention having a bigger surface to work with. Such materials include the use of cellulose and lignocellulose.[11]

Although, nanomaterials open up quite a few perspectives, it is not easy to work with them. The process of creating the system of nanoparticles should be heavily controlled, as they tend to aggregate due to interactions such as van der Waals forces or hydrogen bonding. Interparticle repulsion is needed in this case to slow down or prevent aggregation.[11]

Natural cellulose based materials play a big role in engineering thanks to their flexibility, high mechanical strength, low density and availability.[11]

Nanocellulose is a combined term for products or extracts from native cellulose that have a nanoscaled structure. These include cellulose nanocrystals (CNC) and its derivatives, such as nanocrystalline cellulose (NCC), cellulose whiskers; cellulose nanofibrils (CNF), with nano-fibrillated cellulose (NFC), microfibrillated cellulose (MFC), cellulose nanofibers; bacterial cellulose (BC), or microbial cellulose.[7]

## 2.2. Cellulose particle types

Individual cellulose molecules are brought together by biomass into larger units known as elementary fibrils or microfibrils, which are packed into larger units called microfibrillated cellulose. The latter are in turn assembled into familiar cellulose fibers. The microfibrils are formed during the biosynthesis of cellulose and are several micrometers in length. [12]

There are nine types of cellulose-based particle. They are differentiated based on the cellulose source and the methods of extraction. Each type has a distinct characteristic size, morphology, crystallinity, structure and properties.[7]

The nine particle types include[7]:

- Microfibrillated cellulose particles (MFC)
- Cellulose nanofibrils (CNF)
- Cellulose nanosrystals (CNC)
- Tunicate cellulose nanocrystals (t-CNC)
- Algae cellulose particles (AC)
- Bacterial cellulose particles (BC)
- Wood fiber (WF)
- Plant fiber (PF)
- Microcrystalline cellulose (MCC)

Nanoparticles have high tensile strength, low density and are very stable in terms of thermal effect. These properties open up new opportunities compared to traditional cellulose based particles. New composites with better mechanical properties and low defects can be created. In addition, nanocellulose is environmentally friendly, presents low health risks and is regarded as a sustainable resource.[7]

In this part of the thesis only the particles that have a structure within a nanoscale will be mentioned.[7]

### 2.2.1. Microfibrillated cellulose particles (MFC)

Microfibrillated cellulose (Fig. 7) is composed of expanded high-volume cellulose which is retracted by a homogenization process. The content of MFC is mostly aggregated cellulose microfibrils. The diameter range from 20 to 60 nm.[7]

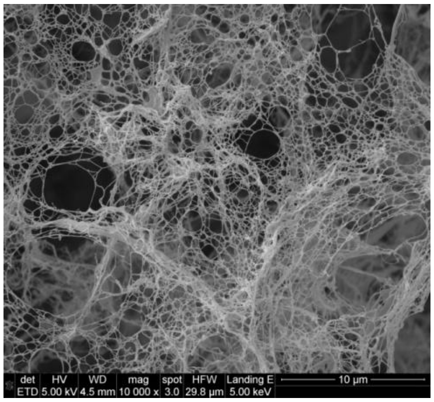

Figure 7. SEM of MFC. (http://goo.gl/6gDKD1)

### 2.2.2. Cellulose nanocrystals (CNC)

Cellulose chain consists of crystalline regions that have a uniform structure and amorphous regions fibrils of which create a more random system. Nanocrystalline cellulose (CNC) (Fig. 8) is produced from crystalline regions.[7]

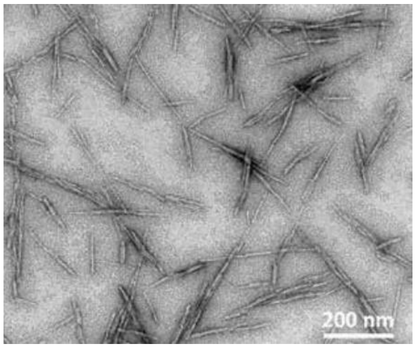

Figure 8. TEM of CNC.
(http://docs.lib.purdue.edu/cgi/viewcontent.cgi?article=1767&context=nanopub)

### 2.2.3. Cellulose nanofibrils (CNF)

CNF (Fig. 9) consists of a mixture of fibrils that are 3-5 nm in width and fibril aggregates 10-20 nm in width. It is widely used a replacement for glassfiber of inorganic fillers in composites.[11]

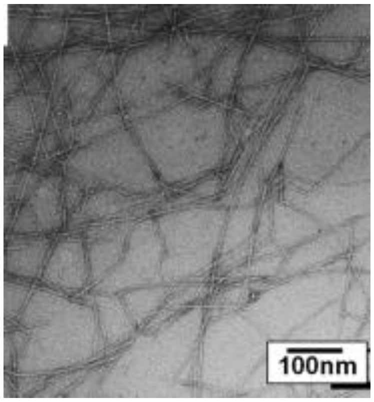

Figure 9. TEM of CNF.
(http://docs.lib.purdue.edu/cgi/viewcontent.cgi?article=1767&context=nanopub)

### 2.2.4. Tunicate cellulose nanocrystals (t-CNC)

Tunicate cellulose nanocrystals (Fig. 10) are nearly pure cellulose that have a high surface area (150-10 $m^2/g$), high crystallinity (95%) and good mechanical properties because of the presence of hydroxyl groups in the molecules. They are produced as a result of acid hydrolysis of tunicates.[13]

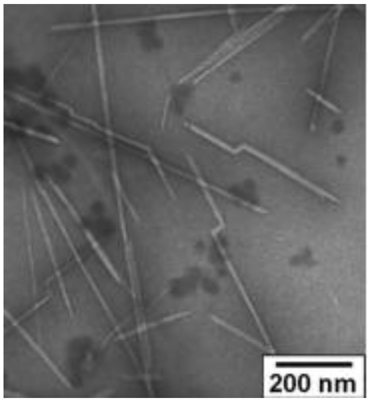

Figure 10. TEM of t-CNC.
(http://docs.lib.purdue.edu/cgi/viewcontent.cgi?article=1767&context=nanopub)

### 2.2.5. Algae cellulose particles (AC)

Certain algae secretes cellulose fibrils, which then can be extracted and used as raw material. Different species of bacteria produce different fibrils due to biosynthesis process. AC (Fig. 11) is removed from the cell wall by acid hydrolysis.[7]

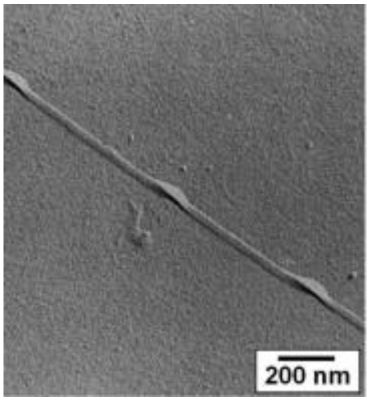

Figure 11. TEM of AC.
(http://docs.lib.purdue.edu/cgi/viewcontent.cgi?article=1767&context=nanopub)

### 2.2.6. Bacterial cellulose particles (BC)

Gluconacetobacter is typically used when extracting the cellulose particles as it has been widely studies. This bacteria secretes cellulose microfibrils (Fig. 12) in a form of a thick gel under appropriate conditions.[7]

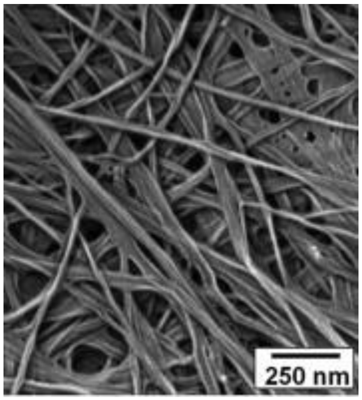

Figure 12. SEM of BC.
(http://docs.lib.purdue.edu/cgi/viewcontent.cgi?article=1767&context=nanopub)

## 2.3. Retraction of nanoparticles

The process of obtaining nanoparticle from cellulose is divided into two parts: purification and homogenization pretreatment of the source material and separation of the purified material into crystalline components.[14]

Pretreatment involves the removal of non-cellulose components in the biomass, such as hemicellulose, lignin, fats and waxes, proteins and inorganic contaminants, and the isolation of individual fibers.[14]

Second part is the isolation of purified cellulose. There can be several processes: mechanical, acid hydrolysis and enzymatic hydrolysis.[14]

Mechanical purification includes the use of high-pressure homogenizers, grinders, ultrasonic treatments, etc. Cellulose is run through mechanical treatment several times, each time the particles become smaller and have lower percentage of crystallinity. Unfibrillated or partially fibrilated fractions are removed with the help of the filtration system. Next step would often be chemical treatments to remove amorphous material of chemically functionalize the particle surface. After chemical treatment the fibrils are dried so that hydrogen bonds would form and create a stiff structure.[14]

Acid hydrolysis is accomplished by removing the amorphous regions of the cellulose microfibrils. The material is placed into water with a given concentration of acid. After a certain period of time, when the reaction has happened, the mixture is diluted with deionized water. Next step would be a series of separation processes, such as centrifugation of filtration, and washing or rinsing to completely remove the acid.[14]

The result is whisker-like particles that are 50-2000 nm long and have a structure of pure cellulose with high crystallinity.[14]

# 3. Aerogels

Aerogel is a type of material that has a porous structure and low density (0.0011 to 0.5 g $cm^{-3}$). They are usually 95-99% air (or other gaseous phase) in volume. Porous structure is open, meaning air is able to go through and the number of the pores can range from 1 to 100 nm in diameter. Aerogels are considered dry materials.[15]

Their unique properties give them an ability to effectively perform as thermal insulators, even better than standard polyurethane foams that are used widely today.[15]

## 3.1. History

The first time the term 'aerogel' was introduced in the world of chemistry was in 1927 when Samuel S. Kistler was working on developing gels where the liquid phase would be replaced by the gaseous phase. In 1931 Kisler officially published a paper in the journal *Nature*.[16]

First aerogel which was prepared by Kistler was made from silica gel from sodium silicate dispersed in water. It was made using supercritical drying technique, which is essentially getting rid of the liquid in the gel during its transformation to a supercritical fluid. Gel is placed in an autoclave where it reaches the critical temperature and pressure of the liquid phase (in which the water is removed by rinsing the gel with alcohol). Then the pressure is reduced while the temperature stays the same. This way the liquid does not evaporate and it transforms into a gas during the critical phase. In result, there is no surface tension and, thus, no pore shrinking. Air can replace the gaseous phase without ruining the structure.[16]

## 3.2. Methods of preparing cellulose aerogels

In this section cellulose aerogels preparation is described. Aerogels can use different materials, not only cellulose in order to achieve outstanding properties. However, for the purpose of experimentation with cellulose aerogels, other materials will not be discussed with great detail.[17]

The principal of creating cellulose aerogels essentially consists of dissolving the cellulose pulp in a specific solvent, replacing the liquid phase with specified alcohol, ketone or other organic compound and supercritical drying to achieve a certain surface area and volume.[17]

Cellulose on its own is insoluble in most liquids and is a chemically stable material. Therefore, it has to be broken down into elementary fibrils in preparation for making aerogels without derivatization. It is a part of a process to change the cellulose morphology and can be done so by using the specific solvent which can successfully break the hydrogen bonds in the cellulose structure without inducing derivative reactions on the polymer chains. Cellulose then breaks down into glucose units but high temperature is also needed.[17]

Important fact to consider is the hydrophilicity of cellulose. However, when cellulose is submerged into water, it does not fully dissolve but swells.[17]

Below are listed some of the well known methods of preparing cellulose aerogels. They are all based on the same principal. However, throughout the years scientists have been working on improving the method by using harmless substances and utilizing less raw material with more results.[17]

- Cellulose in a form of a swollen pulp has to be preserved in order to keep the future structure of aerogel intact. During the first experiments the pulp from paper and cotton was swollen by distilled water and ethylenediamine. Then the material was dried by replacing the water with alcohols and then the liquid phase was slowly evaporated out of the system. In result, the porous structure was shrunk. The surface area of the aerogels - 200 $m^2/g$.[17]
- Next samples of aerogels, which became quite popular later, used cellulose acetate. It was de-esterified and then cross-linked in an acetone solution with toluene-2,4-di-isocyanate. In result, after supercritical drying the surface areas of these aerogels was less than 400 $m^2/g$. An observation was made that if the cellulose ester concentrate was lower the cross-linker amount would be higher and, thus, produce more shrinkage. The surface area of the aerogels - <400 $m^2/g$.[17]
- Another method of producing cellulose aerogels was developed later and used lesser amounts of cellulose. The used material has the semicrystalline structure (amorphous and crystalline phases combined in one system). The solvent that was used to change the morphology of the material was salt-hydrate melt - mixture of water and Ca(SCN)2. The solvent has a low melting point and has the ability to dissolve the cellulose into a colloidal system. The solvent is mixed with cellulose to create a suspension. It is heated up next to create a clear solution. The schematic process is shown in Figure 13. The surface area of the aerogels - 105-200 $m^2/g$.[17]

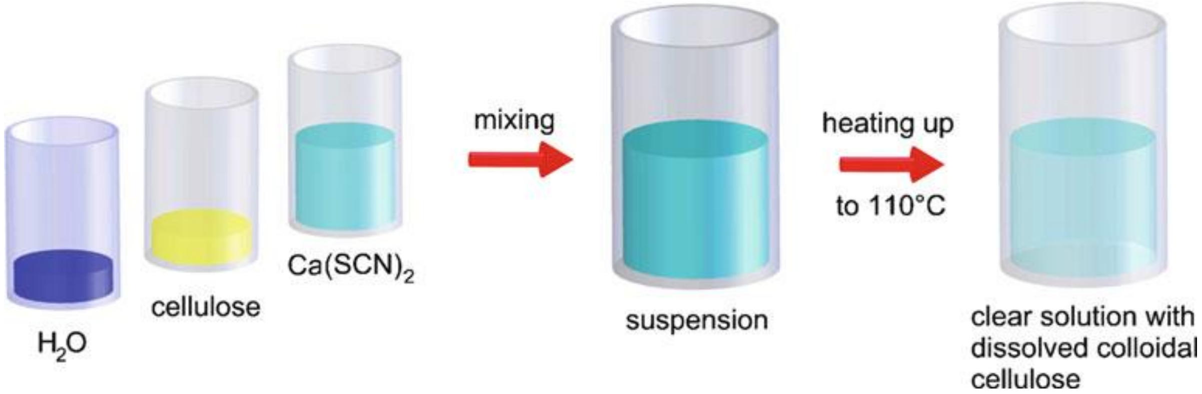

Figure 13. Schematic of the process developed by Jin and co-workers to produce cellulose aerogels. (Michael A. Aegerter, Nicholas Leventis, Matthias M. Koebel. Aerogels Handbook)

The solution then is spread along the surface to create 1 mm thick layers. After solidification the layer with the surface is submerged in a methanol bath. The aim of this step is to remove the salt and regenerate the cellulose as a complete gel. To neutralize the electrical conductivity of the resulted gel, it is washed with deionized water. Freeze drying was used to dry the samples. The aerogel was place in liquid nitrogen.[17]

The advantage of this method is low cellulose concentration and, thus, low density of the aerogels. Freeze drying, however, lead to low surface area and higher density.[17]

- Another solvent that may be used it sulphuric acid. The cellulose suspension is then spread onto a copper plate and solidified. This results in a powder material. The surface area of the aerogels - 32-178 $m^2/g$.[17]
- Popular solvent is N-methyl-morpholine-N-oxide (NMMO). It is an ionic liquid that dissolves in cellulose. The procedure goes on with washing the solution in alcohol and water, solvent exchange and supercritical drying with carbon dioxide. In result, there can be different shapes of aerogel: cylindrical monoliths, spherical beads and thin films. The surface area of the aerogels - 172-284 $m^2/g$.[17]

## 3.3. Other forms of aerogels

Not only cellulose can be used to prepare aerogels. Most used substances include[18]:

- Silica
- Metal oxides

- Organic polymers
- Biological polymers
- Carbon and carbon nanotubes
- Metals

Silica aerogels is the most common material. Is has a high surface area, high porosity and low density. Firstly, through sol-gel process the gel is created. Then the gel is aged in a solution to strengthen it and reduce shrinkage. Final step is drying the gel to remove the liquid from the pores.[18]

Metal oxide aerogels are prepared by hydrolyzing a metal alkoxide in a solvent to achieve hydroxyl groups which later on are combined into a metal-oxygen-metal bridge. After that the formed metal oxide sol cross-links into metal oxide gel. The next steps are purification and supercritical drying. The properties of these aerogels, however, are not effective enough.[15]

## 3.4. Properties

Aerogels consist of two main phases - solid backbone and the pore phase. Each phase is characterized by certain properties. It is important that the porous structure should be controlled during regeneration and drying. Key parameters of the system are connectivity between the two phases, molecular structure of the backbone phase, interface (area between the phases) characteristics.[19]

One of the most important factors to consider is the use of water during the making of aerogels. Water should be avoided to achieve the best results. It can cause breakage of the structure during the drying process, thus, it should be replaced by an organic solvent.[19]

Shrinkage is also an important factor to consider as it characterizes the ability of the aerogel to preserve its porous structure and create dimensional stability. Regeneration and drying processes influence shrinkage so it is best to use the most efficient combination of solvents and raw material.[19]

Shrinkage during regeneration mostly occurs when dealing with cross-linked cellulose acetates and other derivatives. It can be prevented by removing the mechanical stress during regeneration and effectively using the time of cellulose regeneration.[19]

Shrinkage during drying can be prevented by increasing the amount of cellulose in the solution. It creates more mechanical stability.[19]

In addition to having a porous, cellulose aerogel is also considered a biodegradable material and is included in the category of green technology.[19]

# 4. Hydrophobicity

## 4.1. Definition

The term "hydrophobicity" is derived from a wider concept of "lyophobicity" which characterizes the interraction between matter and liquid environment that it is in. If the liquid environment is water than the term "hydrophobicity" is used.[20]

The term was coined by J. Perrin in 1905. It came from Greek language, where "hydros" means water and "phobos" means fear. If water doesn't interact with the matter or its bond is really weak, then it can be called a hydrophobe. A hydrophobe and water usually have different chemical structures.[20]

The extent of intensity of intermolecular interaction is measured with the help of surface tension. The greater hydrophobe a matter is the lesser the surface tension between the phases.[20]

## 4.2. Contact angle

Hydrophobicity is determined by the angle at which two phases interact: liquid-vapor and liquid-solid. Geometrically it is found by applying a tangent line from the point of contact of the drop and the surface along the liquid-vapor phase.[20]

The phase where solid, liquid, and vapor co-exist is known as "three-phase contact line".[20]

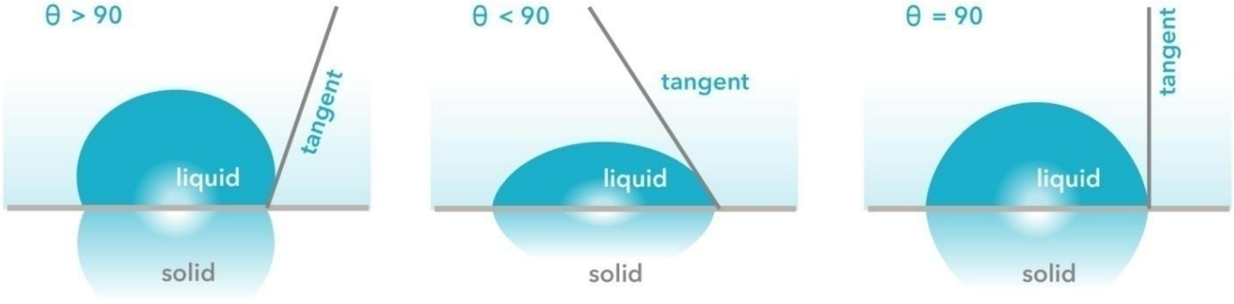

Figure 14. Schematic showing of contact angle.
(http://www.biolinscientific.com/attension/applications/?card=AA7)

This angle Θ is called a contact angle. (Fig. 14) If $\Theta > 90^o$ then the solid surface is hydrophobic and it gathers liquid droplets. If $\Theta < 90^o$ the surface is regarded as hydrophilic. Upon reaching the $0^o$ angle the liquid drop spreads on the surface and imitates a puddle. Hydrophobicity can be regarded as a lesser state of hydrophilicity because every material has a certain level of it. As the hydrophobicity increases, the contact angle of the droplets with the surface increases. The theoretical maximum contact angle for water on a smooth surface is 120°.[20]

Superhydrophobic surfaces are those surfaces that present apparent contact angles that exceed the theoretical limit for smooth surfaces, i.e. >120°. These surfaces do not show any contact between liquid drop and the surface which results in them having a "lotus effect".[20]

The lotus effect takes its name after the lotus leaves which, upon inspection, were discovered to have self-cleaning properties due to superhydrophobicity. Not only do the water droplets create a perfect spherical shape on the surface, they also remove dirt particles off of it. This results in having a highly repellant surface. This property is used to create superhydrophobic coatings.[21]

The shape of a liquid droplet can be described on a physicochemical level as a gathering of molecules as the bonds that connect them together create an internal pressure. Unlike the liquid form where molecules can freely create bonds with neighboring particles droplets try to find and maintain the point of lowest surface free energy. This point represents the spherical shape. The internal pressure on the molecules in the droplet is called the surface tension and it is this force that defines the shape and decreases the surface area of the drop. Reasoning behind the surface tension phenomenon is the appearance of intramolecular forces (Fig. 15), such as Van der Waals forces.[22]

External factors can also influence the shape of the droplet, such as gravity, and can deform it. Depending on the environment and the conditions the shapes can be characteristic to certain liquids.[21]

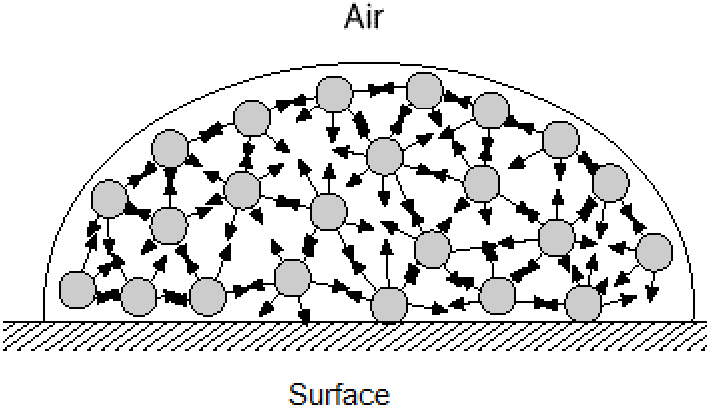

Figure 15. Intramolecular forces inside the droplet molecule.
(http://quest.nasa.gov/space/teachers/microgravity/6surf.html)

Mathematically, the contact angle can be defined by the following equation (Fig. 1.1)[21]:

$$\gamma lv \cos \theta Y = \gamma sv - \gamma sl, \qquad \text{(Fig. 1.1)}$$

(Fig. 1.1) Where $\gamma lv$ , $\gamma sv$, and $\gamma sl$ are the liquid-vapor, solid-vapor, and solid-liquid phase tensions, respectively, and $\theta Y$ is, as mentioned, the contact angle. The equation is named after Thomas Young, who, in 1805, defined the contact angle.[21]

Contact angle isn't always static. If there is movement in the three-phase contact line the angle is actually dynamic. Thus, contact angle is described as having both static and dynamic angles. These angles are formed when the liquid is either expanding or contracting and are called the advancing contact angle $\theta a$ and the receding contact angle $\theta r$ , respectively. The difference between the advancing contact angle and receding contact angle is referred to as contact angle hysteresis ($\theta a$ - $\theta r$).[21]

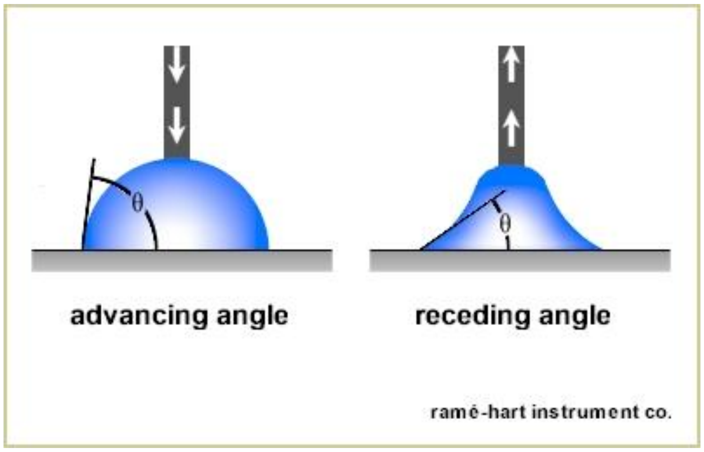

Figure 16. Dynamic angle
(http://burakeral.yolasite.com/resources/Contact_Angle_Hystresis_Review.pdf)

## 4.3. Methods of measuring the contact angle

The contact angle is an important criterion that characterizes the state of different surfaces as well as defines the shape of a specific liquid drop that is being rested on the surface.[23]

Measuring the contact angle is a necessary procedure in order to get a better understanding of surface energy, biological compatibility and testing out the surface ability to soak liquids.[23]

There are many methods of measuring the contact angle. However, only a few of them provide the most exact results. The main methods that will be described in this thesis are[24]:

- Sessile drop method
- Wilhelmy plate method
- Pendant drop method (used mainly to measure surface tension)

All three of these methods are widely used for research and all sorts of testing procedures. Sessile drop method provides the most accurate results and has several options for calculating the angle, which include[24]:

- Circle fitting  (most inaccurate)
- Tangent leaning; leans a tangent to the curve at the three phase point
- Ellipse fitting
- Young-Laplace fitting (most accurate)

Methods of measuring the surface tension will not be mentioned in great detail in this thesis as the experimental part did not require the determining of it. However, the property itself does influence the shape of the drop as it helps it to cover the least amount of surface area.[24]

### 4.3.1. Wilhelmy plate method

This method requires a vertical plate. The liquid placed near the plate when touching the surface of the plate generates the force due to wetting. It is measured using a tensiometer. It correlates with the surface tension and the contact angle. To calculate the contact angle the Wilhelmy equation is used (Fig. 1.2)[25]:

$$\theta = \cos^{-1}\left(\frac{F}{L*\sigma}\right), \qquad \text{(Fig. 1.2)}$$

(Fig. 1.2) Expresses the value of the contact angle where F is the force, conducted by liquid, L is the surface area, $\theta$ is the contact angle.

When trying to measure the contact angle the surface tension of a liquid is a known variable.[25]

The measurement of the dynamic contact angle is also possible with the Wilhelmy method. The advancing angle is measured during the wetting process and the receding angle during the de-wetting process. The scheme of this method is shown in Figure 17. [25]

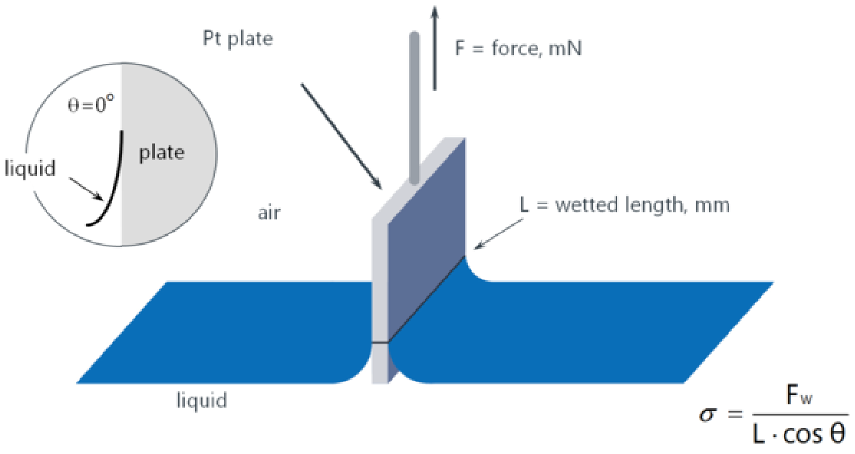

Figure 17. Scheme of Wilhelmy plate method.

(http://www.kruss.de/services/education-theory/glossary/wilhelmy-plate-method/)

### 4.3.2. Sessile drop method

Sessile drop method is a standardized procedure aimed at measuring the contact angle. It is this method that was used in the experimental part of the thesis. Scanned version of the instructions on how to prepare the sample, operate the machine that was used for the experimental purposes and other will be included in the appendix. The more specific information about the method will be described in the experimental section of the thesis. A brief description is given below.[24]

During the process a sessile drop is placed on a working surface of the machine, designed especially for this purpose. The surface is surrounded with a light on one side and a camera, through which the observer sees the drop, on another. The contact angle is determined with the help of 4 methods[24]:

- Circle fitting
- Tangent leaning
- Ellipse fitting
- Young-Laplace fitting

# 5. Experimental part

## 5.1. Brief introduction

The experimental part of the thesis includes measuring the contact angle of the aerogels of different consistency and analyzing the results of the experiment. The experiment was carried out in the Building of Woodworking with the assistance of Natalja Savest. There were 2 attempts total.

First attempt was unsuccessful due to the samples having uneven surface. The samples were put into Petri dishes. The contact angle machine was not able to detect the drop correctly because the borders of the glass covered the view field. In addition, it was difficult to retract the samples off of the Petri dishes using forceps as the layers were thin and broke off easily. Thus, new samples had to be made.

For the second attempt two samples of each aerogel were made in order to create more space for the liquid drops. Samples were put on cover glass in order to create the smoothest surface.

The total of 4 different liquids and 6 different aerogel samples were used.

## 5.2. Materials and methods

Aerogels were prepared by submerging the mixtures of cellulose pulp and agar of different ratios into sodium hydroxide (NaOH), potassium hydroxide (KOH) and urea ($CO(NH_2)_2$) in order to dissolve the material and begin the structural deformation and breakdown into glucose units. The next step was to replace the liquid phase with an appropriate compound. In this experiment acetone was used.

### 5.2.1. Samples:

- 0.25% cellulose + 1% agar
- 0.5% cellulose + 1% agar
- 1% cellulose + 1% agar
- 2% cellulose + 1% agar
- 4% cellulose + 1% agar
- 1% agar

### 5.2.2. Liquids:

- Distilled water ($H_2O$)
- Isopropyl alcohol ($C_3H_7OH$)
- Acetone ($C_3H_6O$)
- Ethanol ($C_2H_5OH$)

## 5.3. Equipment

- Dataphysics contact angle machine
- SCA 20 software
- Syringe and needle
- Cover glass

## 5.4. Agar

Agar was provided by Est Agar AS. Est Agar AS produces furcellaran from the red seaweed Furcellaria lumbricalis. This unique texturant is a polysaccharide that represents repeated disaccharide units of beta and kappa carrageenan. Figure 18 shows the (a) structure of furcellaran and (b) carrageenan disaccharide units.[30]

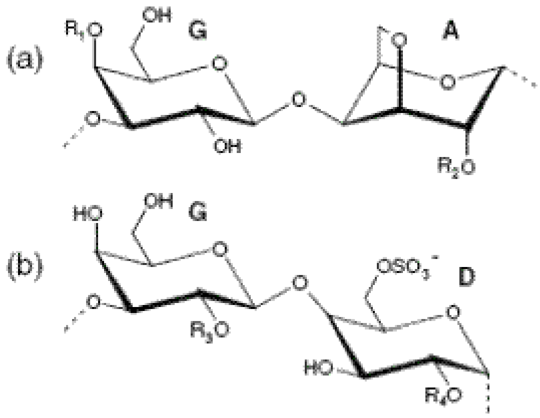

Figure 18. Furcellaran and carrageenan repeating disaccharide units. (http://www.estagar.ee/)

## 5.5. Woodpulp

Cellulose source was provided by EstonianCell. AS Estonian Cell is an aspen (tree species) pulp mill located in Kunda, Estonia. It handles coarse as well as really fine material and is able to utilize lower quality wood.[31]

## 5.6. Sessile drop method

In the following section the sessile drop method, with the help of which the experiment was conducted, will be described using the theoretical material.

The following steps in preparation for the measurements have to be made in order to produce the best results.

### 5.6.1. Surface preparation

The surface on which the droplet is going to be rested should be prepared. It is required for the surface to be smooth, clean and stable in order for the drop to keep its shape once placed upon it.[26]

- For the smoothness factor key element is the material. Generally metals and ceramics are used, depending on the nature of the liquid. The surface is usually polished to achieve the highest quality of smoothness.[26]
- Cleaning the surface includes the use of detergent, acidic of basic solutions, deionized water, alcohols, etc. UV light or ozone treatment may also be used to remove organic contaminants which may have precipitated after the use of chemical solutions.[26]
- Stability is provided by fixing the surface in place. Drop has to be balanced and not move or else inaccurate results may be produced.[26]

### 5.6.2. Experimental setup

The surrounding area in which the measurements are made is usually room temperature. It must not be heavily ventilated as certain liquids tend to be volatile. Better results may be achieved if the sample is isolated from the laboratory environment. This can be done by positioning the sample into a container which surface corresponds with the liquid. Isolating the sample may prevent the liquid from becoming contaminated by dust particles.[26]

The syringe and needle require a preparation as well. They need to be thoroughly cleaned and dried. Ideally, for each liquid it is advised to have an individual syringe. If this is not an option, as it was in case of the experiment, the probing liquid is filled in the cleaned syringe twice in order for the syringe and the needle to get completely covered with the liquid particles. After the use of the initial liquid the syringe and the needle are cleaned with distilled water.[26]

The material of the needle is also chosen depending on the liquid. Metal is commonly used, such as stainless steel.[26]

## 5.7. Measurement

The drop size is typically 2-3 mm in diameter. Once rested on the surface it is important to consider the possibility of the droplet distortion by the needle which can result in a lower contact angle value. Droplet sizes have to be exactly the same each time. The surface on which the droplet is dropped has to be as smooth as possible. Its heterogeneity may hinder the size and the shape of the drop. The needle must not move once releasing the drop at it can create vibrations within the drop which may change the contact angle.[26]

Once the drop has reached the surface it is being illuminated by the light to create the clearest picture of the sample. Further calculations are made, usually automatically using the specific software, such as SCA 20.

As it was mentioned four different methods of calculations are used[24]:

- Circle fitting
- Tangent leaning
- Ellipse fitting
- Young-Laplace fitting

### 5.7.1. Circle Fitting Method

In case of circle fitting method it is preferred to have a small contact angle. The shape of a drop is fitted to a circle segment equation as shown in Figure 19.[27]

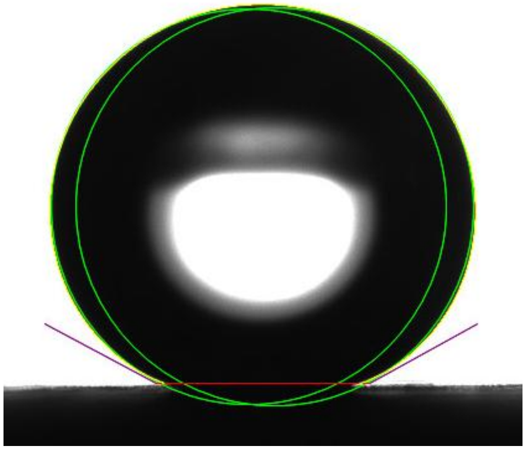

Figure 19. An example of circle fitting. (http://www.springer.com/cda/content/document/cda_downloaddocument/9783642342424-c1.pdf?SGWID=0-0-45-1368817-p174704744)

### 5.7.2. Tangent fitting

This method produces two results according to the two angles. Tangent lines are drawn using the software. They connect to the three phase point at each side. The contact angle is between the baseline of the drop and the tangent lines is measured as shown in Figure 20.[27]

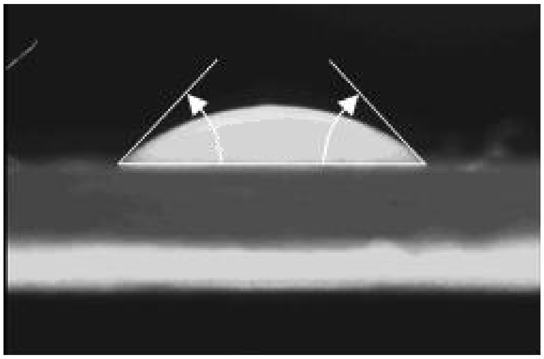

Figure 20. An example of tangent fitting. (http://www.springer.com/cda/content/document/cda_downloaddocument/9783642342424-c1.pdf?SGWID=0-0-45-1368817-p174704744)

### 5.7.3. Ellipse fitting

This method is more suitable for droplets that possess larger contact angles. The droplet shape is fitted to the ellipse equation. Through calculation according to the ellipse equation the lines from both sides of the drop are drawn which represent the contact angles as shown in Figure 21.[27]

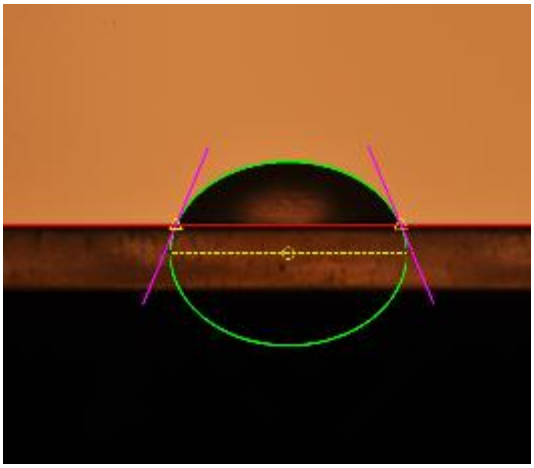

Figure 21. An example of ellipse fitting. (http://technology.sbkb.org/portal/page/249/)

### 5.7.4. Young-Laplace equation

The most accurate method that includes fitting the Young-Laplace equation around the droplet. The drop must not be asymmetrical nor must the surface be not level. Once these criteria are met the fitting is the extremely accurate with almost exact results of contact angles. The Young-Laplace fitting may also be used to calculate surface tension (Fig. 1.3).[25]

$$\Delta p = \sigma * \left(\frac{1}{r_1} + \frac{1}{r_2}\right); \qquad \text{(Fig. 1.3)}$$

(4) p - Laplace pressure; σ - surface tension; $r_1$,$r_2$ - radii of curvature.

## 5.8. Results and discussion

As it was mentioned in the introduction the experiment had to be carried out twice because of the unevenness of the sample surfaces. Aerogels that were prepared for the measurement had to be placed on cover glass in order for the drop to keep its shape for as long as possible. Two of each samples were created to make more space for the liquid drops. Each sample was divided into two parts. The total of four parts of the sample was used for four liquid droplets respectively.

Contact angle for each sample was measured three times and was calculated using four different methods which were described in section 5.9 with a total average contact angle calculated later. The following table shows the results of using water as liquid.

| Conent | Contact angle |
|---|---|
| 100% Agar | 55.4 |
| 0.25% cellulose + 1% agar | 37.4 |
| 0.5% cellulose + 1% agar | 34 |
| 1% cellulose + 1% agar | 29.1 |
| 2% cellulose + 1% agar | 26.2 |
| 4% cellulose + 1% agar | 25 |

Table 1. Contact angle of water on samples.

Tables that show the measured contact angles for each sample are included in the appendix as well as photographs of water droplets on different sample surfaces.

Based on the results the following graph shows the link between the contact angle and the sample content.

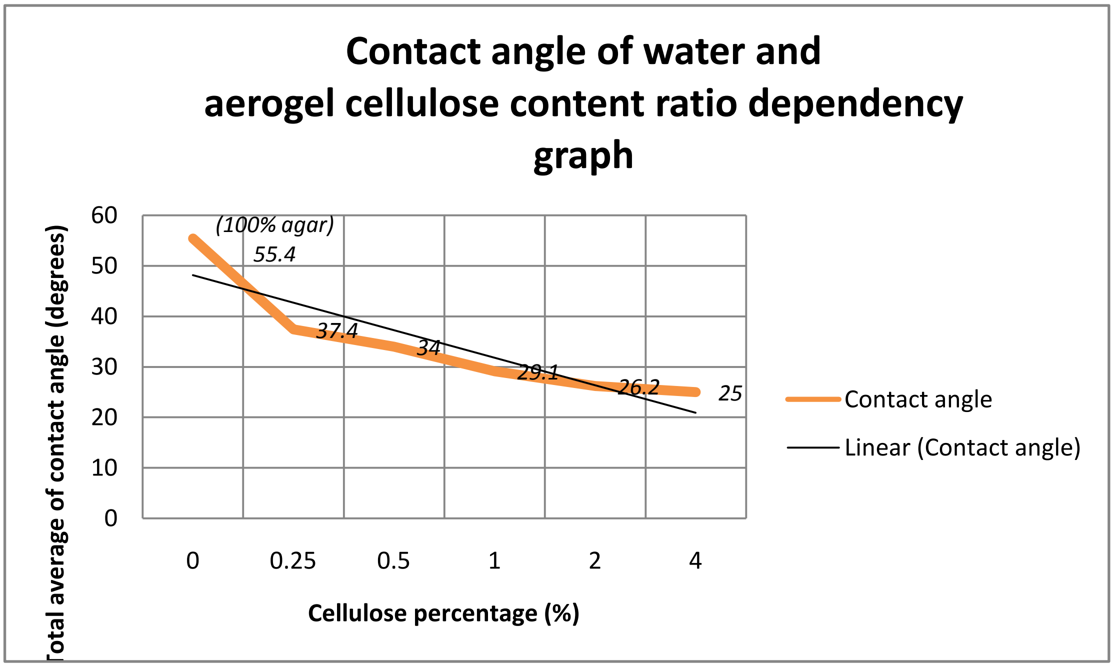

Figure 22. CA of water and aerogel cellulose content dependency.

According to Figure 22 it is clear that with the increase of cellulose content the contact angle decreases, thus, the surface of the material becomes more hydrophilic. 100% agar sample showed the highest value of contact angle of 55.7, yet it is still considered to be a hydrophilic material. 4% cellulose droplet was shown to have the lowest value of contact angle which means that the surface attracts water the strongest. This is happening due to the higher content of hydroxyl groups in cellulose molecules which form hydrogen bonds with water molecules and, thus, visually create a smaller droplet.

The only other experiment that was successful was carried out using ethanol and 100% agar. However, the resulted contact angle of 5.7 is extremely low. Table 2 shows the contact angle for ethanol. During the experimentation with liquids other than water, the drop instantly turns into a puddle or absorbs completely so it is not possible to capture the drop. The reason for that is that the ethanol, acetone and isopropyl alcohol are volatile liquids.

| Ratio | № of tries | Methods | Liquid: Ethanol | Average | Total average |
|---|---|---|---|---|---|
| 1% agar | 1 | 1. Ellipse Fitting | L: 7.1<br>R: 6.5 | 5.2 | 5.7 |
| | | 2. Circle fitting | L: 6.2<br>R: 6.2 | | |
| | | 3. Tangent leaning | L: 5.9<br>R: 2.1 | | |
| | | 4. Young- Laplace fitting | 2.2 | | |
| | 2 | 1. Ellipse Fitting | L: 4.2<br>R: 7.1 | 4.3 | |
| | | 2. Circle fitting | L: 4.5<br>R: 4.5 | | |
| | | 3. Tangent leaning | L: 3.8<br>R: 5.2 | | |
| | | 4. Young- Laplace fitting | 0.9 | | |
| | 3 | 1. Ellipse Fitting | L: 6.2<br>R: 6.2 | 7.5 | |
| | | 2. Circle fitting | L: 13.8<br>R: 10.7 | | |
| | | 3. Tangent leaning | L: 4.8<br>R: 4.8 | | |
| | | 4. Young- Laplace fitting | 5.7 | | |

Table 2. Contact angle of ethanol.

# 6. Conslusions

The results of the experiment show that cellulose aerogels are hydrophilic. However, upon reviewing the literature it was revealed that hydrophobic surfaces of aerogels are not only reachable but is being practiced quite frequently nowadays. Traditional pure cellulose aerogels definitely attract water. However, with the help of modern technology, hydrophobic, even superhydrophobic cellulose aerogels can be created.

It is possible to replace hydroxyl groups in the aerogel structure by having them react with a certain waterproofing agent. This results in non-polar groups that have a tendency to repel water. Waterproofing agents include hexamethyldisilazane which is compatible with silica aerogels.[15]

Cellulose aerogels are treated with fluorosilanes after the drying process to achieve hydrophobic surfaces. Contact angles of $160^{o}$ are achievable with this procedure.[27]

Another possibility is to coat the surface of prepared aerogel with a surface modifier. It creates a hydrophobic layer that block the water from reacting with hydroxyl groups. Such modifier is fluoroalkane, for example. The research that was done by Aalto University Foundation has revealed the hydrophobic properties of cellulose aerogel that was coated with (Tridecafluoro-1, 1,2,2- tetrahydrooctyl)-trichlorosilane.[28]

All these procedures open up new opportunities in the field of nanotechnology. Hydrophobic cellulose aerogels can be used to create water repellent surfaces for many purposes. The most important advantage it that cellulose aerogel is a biodegradable material that is considered a part of green technology. Thus, it is a very perspective material in terms of sustainable technology.

With advantages come disadvantages, however. There is still a lot of room for improvement. Improvements, such as creating a safe environment while producing the material, using organic, safe solvents, decreasing the cost of production as well as decreasing the number of raw materials, should be made in order to create a bright future for nanotechnology.

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# 8. Appendix

## 8.1. List of Tables

| Ratio | № of tries | Methods | Liquid: Water | Average | Total average |
|---|---|---|---|---|---|
| 1% Agar | 1 | 1. Ellipse Fitting | L: 57.8<br>R: 57.1 | 54.1 | 55.4 |
| | | 2. Circle fitting | L: 51.4<br>R: 51.4 | | |
| | | 3. Tangent leaning | L: 54.7<br>R: 52.7 | | |
| | | 4. Young-Laplace fitting | 53.5 | | |
| | 2 | 1. Ellipse Fitting | L: 54.8<br>R: 54.3 | 51.4 | |
| | | 2. Circle fitting | L: 49<br>R: 49 | | |
| | | 3. Tangent leaning | L: 52.6<br>R: 47.5 | | |
| | | 4. Young-Laplace fitting | 52.9 | | |
| | 3 | 1. Ellipse Fitting | L: 63.2<br>R: 65.3 | 60.6 | |
| | | 2. Circle fitting | L: 56.9<br>R: 56.9 | | |
| | | 3. Tangent leaning | L: 60.3<br>R: 57.5 | | |
| | | 4. Young-Laplace fitting | 64 | | |

Table 3. Contact angle of 1% agar aerogel.

| Ratio | № of tries | Methods | Liquid: Water | Average | Total average |
|---|---|---|---|---|---|
| 0.25% Cellulose + 1% agar | 1 | 1. Ellipse Fitting | L: 43<br>R: 40.9 | 32 | 37.4 |
| | | 2. Circle fitting | L: 37.8<br>R: 37.8 | | |
| | | 3. Tangent leaning | L: 30.8<br>R: 33.1 | | |
| | | 4. Young-Laplace fitting | 37.1 | | |
| | 2 | 1. Ellipse Fitting | L: 49<br>R: 48.2 | 40 | |
| | | 2. Circle fitting | L: 47.6<br>R: 47.6 | | |
| | | 3. Tangent leaning | L: 50.1<br>R: 35 | | |
| | | 4. Young-Laplace fitting | 51.6 | | |
| | 3 | 1. Ellipse Fitting | L: 40.2<br>R: 41.1 | 40.3 | |
| | | 2. Circle fitting | L: 41.3<br>R: 41.3 | | |
| | | 3. Tangent leaning | L: 38.4<br>R: 39.2 | | |
| | | 4. Young-Laplace fitting | 40.8 | | |

Table 4. Contact angle of 1% agar aerogel.

| Ratio | № of tries | Methods | Liquid: Water | Average | Total average |
|---|---|---|---|---|---|
| 0.5% Cellulose + 1% agar | 1 | 1. Ellipse Fitting | L: 36.4<br>R: 36.3 | 34.5 | 34.0 |
| | | 2. Circle fitting | L: 34.2<br>R: 34.2 | | |
| | | 3. Tangent leaning | L: 32.1<br>R: 33 | | |
| | | 4. Young-Laplace fitting | 35.4 | | |
| | 2 | 1. Ellipse Fitting | L: 35.9<br>R: 37.4 | 34.3 | |
| | | 2. Circle fitting | L: 34.8<br>R: 34.8 | | |
| | | 3. Tangent leaning | L: 27.4<br>R: 32.6 | | |
| | | 4. Young-Laplace fitting | 37.1 | | |
| | 3 | 1. Ellipse Fitting | L: 36.6<br>R: 33.4 | 33.1 | |
| | | 2. Circle fitting | L: 33<br>R: 33 | | |
| | | 3. Tangent leaning | L: 35.8<br>R: 29.8 | | |
| | | 4. Young-Laplace fitting | 30 | | |

Table 5. Contact angle of 1% agar aerogel.

| Ratio | № of tries | Methods | Liquid: Water | Average | Total average |
|---|---|---|---|---|---|
| 1% Cellulose + 1% agar | 1 | 1. Ellipse Fitting | L: 30.8<br>R: 30.3 | 29.9 | 29.1 |
| | | 2. Circle fitting | L: 29.9<br>R: 29.9 | | |
| | | 3. Tangent leaning | L: 26<br>R: 33 | | |
| | | 4. Young-Laplace fitting | 29.3 | | |
| | 2 | 1. Ellipse Fitting | L: 30.6<br>R: 30.6 | 29.2 | |
| | | 2. Circle fitting | L: 30.1<br>R: 30.1 | | |
| | | 3. Tangent leaning | L: 18<br>R: 34.5 | | |
| | | 4. Young-Laplace fitting | 30.6 | | |
| | 3 | 1. Ellipse Fitting | L: 30<br>R: 27.7 | 28.1 | |
| | | 2. Circle fitting | L: 29.8<br>R: 29.8 | | |
| | | 3. Tangent leaning | L: 24.9<br>R: 25.2 | | |
| | | 4. Young-Laplace fitting | 29.1 | | |

Table 6. Contact angle of 1% agar aerogel.

| Ratio | № of tries | Methods | Liquid: Water | Average | Total average |
|---|---|---|---|---|---|
| 2% Cellulose + 1% agar | 1 | 1. Ellipse Fitting | L: 31.2<br>R: 28.6 | 28.1 | 26.2 |
| | | 2. Circle fitting | L: 29<br>R: 29 | | |
| | | 3. Tangent leaning | L: 25.2<br>R: 24.2 | | |
| | | 4. Young-Laplace fitting | 29.4 | | |
| | 2 | 1. Ellipse Fitting | L: 28.8<br>R: 31.3 | 24.3 | |
| | | 2. Circle fitting | L: 25.7<br>R: 25.7 | | |
| | | 3. Tangent leaning | L: 13.1<br>R: 21 | | |
| | | 4. Young-Laplace fitting | 24.8 | | |
| | 3 | 1. Ellipse Fitting | L: 26.8<br>R: 26 | 26.2 | |
| | | 2. Circle fitting | L: 27.1<br>R: 27.1 | | |
| | | 3. Tangent leaning | L: 24.7<br>R: 23.2 | | |
| | | 4. Young-Laplace fitting | 28.5 | | |

Table 7. Contact angle of 1% agar aerogel.

| Ratio | № of tries | Methods | Liquid: Water | Average | Total average |
|---|---|---|---|---|---|
| 4% Cellulose + 1% agar | 1 | 1. Ellipse Fitting | L: 28.2<br>R: 28.7 | 25.8 | 25.0 |
| | | 2. Circle fitting | L: 28.2<br>R: 28.2 | | |
| | | 3. Tangent leaning | L: 15<br>R: 27.2 | | |
| | | 4. Young-Laplace fitting | 25.4 | | |
| | 2 | 1. Ellipse Fitting | L: 25.5<br>R: 25.3 | 23.9 | |
| | | 2. Circle fitting | L: 25.9<br>R: 25.9 | | |
| | | 3. Tangent leaning | L: 22.9<br>R: 15.8 | | |
| | | 4. Young-Laplace fitting | 26.1 | | |
| | 3 | 1. Ellipse Fitting | L: 27.3<br>R: 27.3 | 25.3 | |
| | | 2. Circle fitting | L: 26.8<br>R: 27.6 | | |
| | | 3. Tangent leaning | L: 14.3<br>R: 26.4 | | |
| | | 4. Young-Laplace fitting | 27.2 | | |

Table 8. Contact angle of 1% agar aerogel.

## 8.2. List of Figures

Figure 22. Ethanol drop on 100% agar.

Figure 23. Water drop on 4% cellulose + 1% agar.

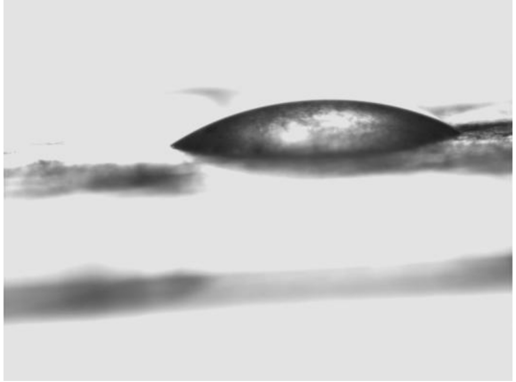

Figure 24. Water drop on 2% cellulose + 1% agar.

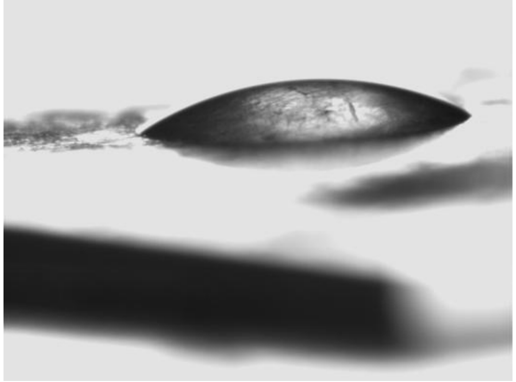

Figure 25. Water drop on 1% cellulose + 1% agar.

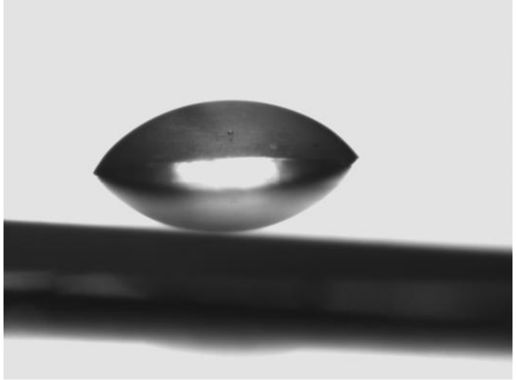

Figure 26. Water drop on 100% agar.

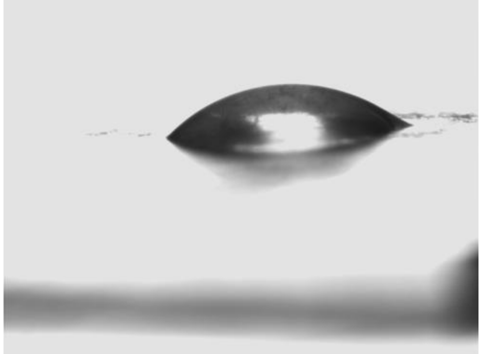

Figure 27. Water drop on 0.25% cellulose + 1% agar.

Figure 28. Water drop on 0.5% cellulose + 1% agar.

Tallinn 2015

# HÜDROFOOBSUSE MÄÄRAMINE AEROGEELIDES

## Maria Pogodajeva

## Referaat

Käesoleva töö eesmärgiks oli koostada kirjandusülevaade tselluloosi aerogeelidest ja tutvuda erinevate hüdrofoobsuse määramise võimalustega. Töö teoreetiline osa sisaldab ülevaadet tselluloosist ja tema erinevatest liikidest, esinemisest looduses, omadustest, keemilisest koostisest. Veel on esitatud ülevaade aerogeelide omadustest, valmistamismeetoditest ja ajaloost. Lisaks uuriti kontaktnurga määramise meetodeid. Töö katselises osas uuriti erineva koostisega aerogeelide pinnal mitmesuguseid vedelikke kontaktnurga meetodil.

Töö teoreetilisest osast selgus, et tselluloosi aerogeelid on küllaltki rabedad ja hüdrofiilsed, kuna nende struktuuris on hüdroksüülrühmad, mis tõmbavad ligi vee molekule.

Kirjandusest selgus, et kasutades teatud tehnoloogiat ja materjali, saab muuta tselluloosi aerogeeli hüdrofoobseks vedeliku tõrjujaks. Selleks saab kasutada erinevaid meetodeid, näiteks pinnamodifikaatoreid, pinna reaktsiooni veekindla ainega ja mittepolaarsete ainetega töötlust.

Töö eksperimentaalne osa koosnes kontaktnurga määramisest erinevate vedelike korral, mida oli tilgutatud erineva koostisega aerogeeli pinnale ja arvutustest.

Eksperimentaalsest osast järeldus, et kõige suurem kontaktnurk saavutati 55,4°, mis on iseloomulik hüdrofiilsetele materjalide pinnale. Kõige väiksem kontaktnurk 5,7° saavutati, kasutades etanooli 100%-se agari pinnal. Selgus, et teised veest erinevad vedelikud olid raskesti käsitsetavad, kuna osutusid lenduvateks või absorbeerusid liiga kiiresti materjali pinnale.

Peale eksperimentaalset osa uuriti töös hüdrofoobsete tselluloosi aerogeelide pindasid. Mitmed uurimustööd, kaasaarvatud patentide dokumendid[27,28] näitasid suuri kontaktnurga väärtusi ja seda, et on võimalik saavutada hüdrofoobseid pindu, kasutades õigeid töötlemisviise.

Tselluloosi aerogeele peetakse biolagunevateks materjalideks. Need on ka osa rohelisest tehnoloogiast ja tänu säästvale tootmisele paljulubav tootmisviis. Neil on omadusi, mida on juba tänasel päeval rakendatud tööstuslikult, näiteks isolatsioonmaterjal.

Kuid ikkagi on veel palju uurida ja arendada, et luua täiuslik materjal, mis vastaks kõikidele esitatud nõuetele.