3D Printing Hydrogel Artificial Muscles and Microrobotics

Final Report

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Abstract
The purpose of this lab was to investigate the printability of cellulose nanofiber/carbon nanotubes, their functions as actuators, and to compare these properties with MXene/nano cellulose gels. Data on MXene/nano cellulose gel was obtained from previous research made by Hamedi labs. Data on carbon nanotubes were collected through experiments evaluating different concentrations and sonication times to yield a gel with high conductivity and viscosity. While it was concluded that both gels could be printed into 2D or 3D shapes, the latter failed to maintain its structure over time due to issues with drying. However, it was found that only 2D MXene/CNF could be used as a reversible actuator.

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1. Introduction

The importance of sustainability in materials is increasing in society. Ideally, materials should be produced from renewable resources and have a small environmental impact. This has resulted in a greatly expanded market for tree-based materials. Paper, cartons and other cellulose materials substitute plastics at an ever-growing rate across several fields.¹ Cellulose can be combined with other materials to produce products with novel properties. Hydrogels can be used for intelligent, soft tissue, and life-like systems.² One example of a hydrogel is a conductive gel that allows mass transport of molecules and ions. This attribute can change its shape and cause the hydrogel to swell or deswell in an electrolyte when low voltage is applied. That is to say, it can be used as an actuator. Such a material can be fabricated as a nanocomposite made with cellulose nanofibrils, CNF, mixed with nano conductors such as 2D materials or carbon nanotubes. If the gel can be 3D printed in a way to sustain these actuator abilities, this can be used to develop future micro machines with dynamic capabilities. A promising hydrogel for this purpose can be made from carbon nanotubes, CNT, which are multi-walled nanotubes in cylindrical shapes, and CNF.

Mixing CNT and CNF could create a homogeneously dispersed hydrogel with conductive, as well as swelling, properties due to the structure of CNT. The aim of this research was therefore to test if such a hydrogel could be created and printed into a complex structure using 3D printing so that the structure could contract and expand when a low voltage was applied to it.

MXene is another material that has already been researched and proven to be able to create such a hydrogel. MXene is, therefore, a good reference that was used. This work investigates the question: Can an electronically actuating hydrogel be 3D printed?

1.1. Objectives

The objective of this study is to 3D print hydrogels made with CNF/CNT and CNF/MXene and compare their printability and actuator abilities. The structures should be able to be 3D printed, dried, and used as actuators when low amounts of electricity are applied.
1.2. Purpose
The purpose of this project is to investigate the printability of different hydrogels. A mixture of CNF and MXene will be compared with a mixture of CNF and CNT to see if the less expensive, and more available, CNT can be used instead of MXene. It will also be investigated if either one of the mixtures can be printed into 3D structures that can be used for actuators after drying.

This project will hopefully give important insight into the growing world of 3D printed materials and actuators.

1.3. Inks Composition
The following sections describe the materials used for creating the inks.

1.3.1. Cellulose
Cellulose comes from plant cell walls as it is its main component and can be extracted from wood, algae, bacteria, or fungi. Cellulose is made of fibrils that have a width in the nanoscale called nanocellulose. Nanocellulose can in turn be separated into three different categories depending on different structures: cellulose nanocrystals, CNC; cellulose nanofibrils, CNF, used for this project; and bacterial cellulose, BC. CNF is a material with a diameter of approximately 50-200 nanometers with both amorphous and crystalline properties. CNF can be produced through TEMPO-oxidation of cellulose, that allows the CNF to be completely dispersed in water by introducing electrostatic repulsion which reduces the hydrogen bonds between the fibrils.

1.3.2. Carbon Nanotube
Carbon can be made into a variety of different shapes and models, like multi-walled and single-walled carbon nanotubes. Single-walled nanotubes are carbon nanotubes with a wall thickness of one atom. Multiwalled carbon nanotubes, MWNT, which will be used in this experiment, are made up of multiple layers of nanotubes. Synthesis of CNTs occurs through e.g. physical processes or chemical processes. CNTs are commonly used in polymeric composites to improve properties such as electrical conductivity, hardness and thermal stability. In recent years, the usage of CNTs in combination with hydrogels has been
researched as it provides interesting qualities such as electrical conductivity and mechanical strength. These conductive properties are useful in applications such as conductive inks through mixing highly charged carboxymethylated CNF and CNTs, with potential application in printable electronics.\textsuperscript{10,11}

1.3.3. MXene

MXene is a 2D material produced from the bulk crystal $MAX$. The abbreviation is derived from the general formula of MXene, $M_{n+1}AX_n$, where M denotes which transition metal is incorporated and AX gives information of whether carbon or nitrogen is used.\textsuperscript{12} MXene is a family of materials and can be used in different combinations, as long as they are stable. MXene can be mixed with other materials in water to produce a composite material that is flexible, mechanically strong, highly stable, electrically conductive and has a hydrophilic surface.\textsuperscript{13} The conductive properties are due to its layer of two sheets that has the thickness of a few atoms. The space between the sheets can hold ions and molecules and its transition metal 2D sheets make the material conductive. The most common form of MXene is $Ti_3C_2Tx$, where T stands for O, OH or F groups. This form of MXene has high viscoelastic properties which makes it a good candidate for usage in 3D printing as a freestanding structure that is suitable as an electrochemical energy storage device.\textsuperscript{14} However, in order to obtain the rheological properties required for 3D printing, a large amount of MXene is necessary. This large MXene ratio is prone to self-restacking after drying. To prevent this, a smaller amount of MXene together with charged CNF can be used.\textsuperscript{14}

1.4. Methods Used

The following section describes the theoretical background used for methods, results, and 3D printing.

1.4.1. Rheology

Gels can flow with different behaviours depending on different factors such as shear flow and shear stress such as shear flow and shear stress.\textsuperscript{15} The shear flow can be described as where the maximum flow speed lies at the top layer and where the bottom layer is stationary, assuming that liquids flow in different layers. For the layers to flow a force needs to be applied over a certain area. This is called shear stress. If the force is applied to the top layer, the next layer will be stationary until the top layer gains enough momentum to overcome the
friction of the next layer. The second layer will move and the third will be stationary. This process continues over all the layers and creates a velocity gradient, called shear rate\(^{15}\).

Another way to examine a gel’s properties is by investigating oscillation stress. This is done by allowing a rheometer to oscillate, in other words allowing a round Peltier plate to spin around at the same time as pulsating up and down with an amplitude equal to the applied stress or strain. The complex modulus, \(G^*\), is the ratio between the applied stress and the measured strain, or the applied strain and the measured stress. From the complex modulus it is possible to calculate the elastic contribution, also called loss modulus \(G''\), and the viscous contribution, also called storage modulus \(G'\).\(^{15}\)

### 1.4.2. Crosslinking

Polymer crosslinking refers to covalent irreversible links between polymer chains formed by chemical reactions.\(^6\) Crosslinking is done to improve the properties of a polymer material. Previous experiments have reported an increased wet strength and transparency of TEMPO-CNF films that had been crosslinked using a crosslinking agent called polyamide epichlorohydrin resin. Other researchers have proved that double crosslinking of TEMPO-CNF can increase the mechanical properties as well as water resistance.\(^7\)

Heating with Rapid Köthen, a sheet forming machine, at certain pressure and temperature is also an effective way to make self stacking papers out of nanocellulose and carbon nanotube or MXene mixture.\(^8\) Another alternative which can be used as a chemical crosslinker to make the 3D printed structure self-standing is calcium chloride, \(\text{CaCl}_2\).\(^9\) However, these methods form non-covalent crosslinks such as hydrogen bonds.

### 1.4.3. Drying Methods after 3D Printing

One method for drying hydrogels is freeze drying. The hydrogel is usually crosslinked before it is freeze-dried to obtain a porous network-like structure. The crosslinking phase will determine these properties of the final product: pore size, shape, interconnectivity, the homogeneity, and mechanical properties. The more crosslinking there is in the gel, the stiffer it becomes until the maximum amount of crosslinks is reached. The stiffness of the sample can be expressed as the storage modulus, \(G'\).\(^{20}\)
A drying method which is common for MXene solutions is using a hot plate. It is important to use a temperature that dries the gel without flocculating the dispersed materials. MXene solutions start to flocculate as temperature rises over 100°C. The gel can be dried on a hotplate magnetic stirrer at 50°C for 1 hour and 700 rpm to obtain the desired viscosity. Although to completely dry the gel, it needs to be heated for a longer amount of time or at a higher temperature.21

Another common drying method for MXene is using a vacuum oven. A MXene solution can be kept at temperatures differing from 60°C to 80°C of varying durations to achieve products suitable for different applications.22

Another solution may be to use UV light treatment to cure the structure. MXene has been shown to absorb light at about 280 nm.21 However, in most cases, a photoinitiator is required for UV curing to work.23

1.5. Making Actuators
The following section is about the theory behind actuators and descriptions of key concepts in this area, as well as a short introduction to 3D printing.

1.5.1. Hyd rogels
Hydrogels are polymer networks that can swell by containing water inside the 3D structure due to their hydrophilic attributes. They are widely used in many applications because of this and their stability which comes from the bonds within the polymer.2 In this work specifically, hydrogels made using nanocellulose as their main constituents were used. These CNFs give the hydrogel a nanowire network structure which can absorb water and hold its structure through the non-covalent crosslinks and mechanical interlinking in the network.

1.5.2. 3D Printing
3D printing is an additive manufacturing process mainly applied in the production of engineering components due to its high versatility and complexity. The process is further defined by being three-dimensional and layer based. There are many promising aspects of 3D-printing technology such as sustainability, cost-effectiveness and complexity of the product. The latter is of great interest for engineering applications as 3D printing allows for
complex geometries in materials, giving them a fine strength-to-weight ratio and an overall reduction in weight. 3D printing is not just limited to manufacturing conventional materials such as polymers, mechanical parts and ceramics, but is also able to produce more advanced materials such as biopolymers, tissues and biocompatible scaffolds. 24

1.5.3. Soft Actuators

Actuators can produce motion, which can be either linear or rotary. This makes them essential in industrial applications. Historically, mainly mechanical and hydraulic actuators have been employed, although several alternatives exist today. Electrical actuation is likely the most used method of actuation today with great precision and power output. Actuators powered by pneumatics have the benefit of being used in soft robotics, making them applicable in many areas such as packaging and handling of food items and others which require more delicate handling. Hydrogel actuators have the potential to further increase the application of actuators, since they are even softer than pneumatic actuators and thus have many added advantages, such as being able to conform to their surroundings and also to function as membranes. Additionally, soft actuators like hydrogels have the potential to power artificial muscles in the future which require greater mobility than what non-dynamic actuation can offer. Some challenges exist for soft actuators; mainly being outperformed in power output by electrical and mechanical actuation. However, the field of soft actuation is sure to expand greatly due to the many potential benefits and applications. 25

1.6. Previous Research

L.A.E Müller et al published a report on 3D printed cellulose nanocomposites in April of 2022. They investigated if photoresponsive elastomers, LCEs, could be used as muscles in micro-robotics. It was concluded that 3D printing, using cellulose nanocrystals as reinforcement to the structure, “allows access to elaborated geometries”. The material produced is a photoresponsive material that allows for fast, reversible, shape recovery by increasing covalent bonding between the matrix and the particles, using methacrylate groups on the cellulose surface. They conclude that the material can be used in soft robotics with complex material geometry. 26

D. Cafiso et al also investigated light processing in 3D printed cellulose, but in their experiments, the material used was cellulose hydrogel. They use acrylated-carboxymethyl
cellulose as the base for the hydrogel and cellulose nanocrystals as reinforcement. This created a “hybrid polymeric network” that allows for pH sensitivity and controlled swelling that can be used for sensors, biomedical and soft robotics. It was concluded that 3D printing is an increasingly popular and practical way to produce materials in an eco-friendly way.\textsuperscript{27}

I. Must et al investigated how osmosis can be used on hydrogel to mimic plants’ movement and stiffness to use in soft robotics. They presented how low voltage can be used to drive reversible osmosis based on the electrosorption of ions. The hydrogel used is designed to have a morphology such that voltage in a humid environment promotes movement in the material. They describe how plant cells generate reversible movement using osmolyte gradients that provide local concentration differences, between the extra- and intracellular fluid, which generates an osmotic pressure. The difference between the osmotic pressure and the hydrostatic pressure drives a water flow that depends on the properties of the cell wall, “the osmotic barrier surface” and permeability. This promotes movement which is reversible due to the plant cells’ control over the concentration gradient. During an experiment, sodium chloride ions with 2 M initial concentration were used to produce movement in the structure. It was shown that the activation depended on the initial concentration, which is necessary to achieve reversibility. It is concluded that plant-based hydrogel can achieve movement and stiffness using osmosis at low voltage. It is proposed that future studies investigate the control feedback based on ion concentration and input charge.\textsuperscript{28}

Wenji Yang et al used Ti$_x$C$_2$Tx MXene to 3D print a gel with desired rheological properties, such as high storage modulus, $G'$. These properties were obtained by changing the MXene ratio until a gel with shear-thinning properties was obtained. The ink was printed layer-by-layer to obtain the desired design. Freeze drying the 3D printed structure at -103°C and 30 μbar, resulted in a freestanding structure that retains the printed shape.\textsuperscript{29} However, they did not report any actuators.
2. Method

Previous work made by Hamedi Lab, has shown that a ratio of 60% MXene and 40% CNF was the best in regard to homogenous mixing, printing abilities, and conductivity. This composite material also proved to have good actuator abilities with approximately 100% swelling and 100% deswelling when a low voltage of 1 V is applied. However, that experiment was made for 2D printing and not 3D printing as it will be in this case.

2.1. Resources

The following sections describe the equipment and materials used during the laboratory work.

2.1.1. Equipment

For all parts of experiments, beakers, spoons, scales, adjustable pipettes, glass plates, petri dishes, parafilm, aluminium foil, and falcon tubes were used. For mixing of CNF, IKA T 25 digital ultra-turrax and CNF probe, see 6.6.1 Ultra-turrax. For making the inks more viscous, a hot plate with a magnetic stirrer and water crystal soil was used. To make papers, a filtration system using a Buchner setup was used.

For mixing CNT with CNF to make conductive gels, a Sonics vibra cell VCX 750 with a probe, also called probe sonication in the report, was used, see 6.6.2 Probe sonicator. A ROTINA 420/420R centrifuge was then used to centrifuge the samples, see 6.6.3 Centrifuge. For mixing MXene with CNF, ultrasonication cleansing, USC-T, was used.

For analysing results, several machines were used. A Rapid-Köthen was used to dry papers made with inks. For actuation and swelling measurements, a Nova 2.1.4 was used for adjusting voltage and the program Dino Capture was used to visualise the swelling. A three electrode setup was arranged in 10 mM NaCl electrolyte wherein an Ag/AgCl electrode was used as a reference and our samples as a working electrode, see 6.6.4 Actuation and swelling. For measuring the conductivity of papers made by the inks, a Keithley 4200A-SCS Parameter analyzer was used, see 6.6.5 Conductivity Measurements. For rheometer measurements, a Discovery HR-2 Hybrid rheometer was used, see 6.6.6 Rheometer.

For hand printing, a syringe and nozzle were used. For 3D printing, an Inkredible by Cellink, see 6.6.7 3D printer, was used along with an air pressure machine, syringe, and nozzle.
2.1.2. Materials
Milli-Q, MQ, water and ethanol were used in all parts of the experiments. For making the stock solution of 0.2 wt% CNF, a 1.206 wt% CNF solution with charge 1000 µeq/g was used.

For making CNT/CNF inks, carbon nanotubes Multi-walled (L=10-35 µm, OD < 8 nm, ID = 2-6 nm) were used. For making MXene/CNF inks, a 7.5 mg/ml MXene solution was used. For actuation and swelling, an electrolyte with 10 mM NaCl was used.

2.2. Cellulose Nanofibrils Solution
For all experiments, a solution of 0.2 wt% CNF was used. This was prepared in batches of 1000 ml and was stored in the refrigerator between uses. When one bulk ran out, a new one was prepared in the same way, using the same bulk solution of 1.206 wt% of CNF.

A 166 g bulk solution of 1.206 wt% nanocellulose in water, CNF, was added to a 1000 ml glass container. 834 ml of MQ water was added to the glass container and a solution with 0.2 wt% CNF was acquired. The CNF solution was then stirred for 15 minutes using an Ultrasonic cleanser, USC-T. Afterwards, the solution was mixed using an IKA Turrax for 10 minutes at 10,000 rpm. The 0.2 wt% CNF solution was then used for making the inks.

2.3. Carbon Nanotubes and Nanocellulose Inks
To make conductive inks for 3D printing, multiwall carbon nanotubes were mixed with nanocellulose. A 3D printable gel needs to have the right rheological properties. Therefore the rheological parameter was first optimised by varying sonication times to explore optimum conditions for dispersing the two components thoroughly. Concentrations of CNT and CNF were then varied to find optimal conductivity and actuator properties.

2.3.1. Different Sonication Times of CNT/CNF inks
Four samples were made for testing how sonication time affected the conductivity and actuator properties of the CNT/CNF mixture. A compilation of the tests is shown in Table 1. The solutions were made with a 45:55 concentration of CNT and CNF respectively. The solutions were then mixed using probe sonication for 5, 10, 15 or 20 minutes.
Table 1: The composition of the samples and their respective sonication time.

<table>
<thead>
<tr>
<th>Test</th>
<th>Sonication time [min]</th>
<th>CNT * [wt%]</th>
<th>CNF ** [wt%]</th>
<th>CNT * [g]</th>
<th>CNF ** [ml]</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>5</td>
<td>0.164</td>
<td>0.164</td>
<td>45</td>
<td>55</td>
</tr>
<tr>
<td>9</td>
<td>10</td>
<td>0.164</td>
<td>0.164</td>
<td>45</td>
<td>55</td>
</tr>
<tr>
<td>10</td>
<td>15</td>
<td>0.164</td>
<td>0.164</td>
<td>45</td>
<td>55</td>
</tr>
<tr>
<td>11</td>
<td>20</td>
<td>0.164</td>
<td>0.164</td>
<td>45</td>
<td>55</td>
</tr>
</tbody>
</table>

*Carbon nanotubes Multi-walled (L=10-35µm, OD < 8 nm, ID = 2-6 nm)

** 0.2 wt%

After sonication, the samples were centrifuged for 15 minutes with the settings 4799 RCF and 4121 RPM, and stored in four glass beakers. The samples were then tested with FTIR analysis and plotted in Figures 7, 8, 9, and 10, see 3.1.4. FTIR Spectroscopy. Thereafter 10 ml of each sample was collected and filtered on filter paper and dried using Rapid-Köthen to create four papers. These were used to measure the resistivity using a parameter analyser. The diameter of the papers, the distance between the clamps and the thickness of the papers were measured to be able to calculate the conductivity.

The papers were then made into smaller strands using a sharp knife and a hammer to cut the paper into small strips, which creates a smoother edge compared to cutting it with a scissor. The round paper was cut into two larger crescents and two smaller rectangles. These were used to measure the actuator properties, using a Autolab Potentiostat. The crescents were used as working electrodes to the rectangles and an Ag/AgCl electrode was used as reference. The counter electrode was made from the same material as the working electrode but was larger in size. Everything was dipped into a 10 mM NaCl electrolyte. The cross-sectional view of the rectangles was recorded using the program DinoCapture. Amperometric measurements were employed using potentiostat with the program Nova 2.1.4 and parallely captured the swelling/deswelling behaviours. Initially, -1 V was applied for 5 minutes and thereafter +1 volt was applied for another 5 minutes.

During the measurements, 15 water absorbent beads were added to the original beakers and were left for 3 hours. Thereafter, the mixture was mixed and left for 3 more hours before the beads were taken out.
Thereafter, the weight percentage of the samples was tested since they had to be known for later comparisons. Two trials were made for samples 8, 9, 10 and 11 because of an attempt to make the weight percentage the same for them. Firstly, the four glass plates were weighed. Thereafter 0.1 ml of each sample was placed on each glass plate. The four glass plates with the samples on were placed in an oven at 120°C for 24 hours. The samples and glass plates were weighed again and the weight percentages were calculated.

2.3.2. Rheological Analysis for CNT/CNF inks

The rheological properties were explored to see if the inks had properties suitable for 3D printing. Flow sweep and oscillation frequency measurements were made for all the samples. The rheometer was set up using a Peltier plate and a parallel plate with a diameter of 25 mm. Thereafter, the machine was calibrated and the zero gap was decided. Thereafter a small amount of the sample was placed on the plate and tested using a 1000 μm gap and the setting for flow sweep and oscillator frequency shown in Table 2. The results were therefore plotted in four graphs. Test 8, 9, 10 and 11 can be seen in Figures 2, 3, 4 and 5 under 3.1.1. Rheometer Values for Different Sonication Time. Test 9, 12, 13 and 14 can be seen in Figures 12, 13, 14 and 15 under 3.2.1. Rheometer Values Different Concentrations.

Table 2: The settings for the flow sweep and oscillator frequency.

<table>
<thead>
<tr>
<th>Flow sweep</th>
<th>Oscillation frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>• 25°C</td>
<td>• 25°C</td>
</tr>
<tr>
<td>• Sheer rate 0.01-1000 s⁻¹</td>
<td>• Soak time 0.00</td>
</tr>
<tr>
<td>• Equilibrium time 5.0 s</td>
<td>• Strain 0.0125</td>
</tr>
<tr>
<td>• Average time 30 s</td>
<td>• Angular freq 1-100 rad/s</td>
</tr>
<tr>
<td></td>
<td>• 20 points per decade</td>
</tr>
</tbody>
</table>

2.3.3. Different Concentrations for CNT/CNF inks

The sonication times of 10 minutes and 15 minutes were the ones resulting in the highest conductivity and swelling properties. Although, during sonication, the mixtures increase in temperature as the sonicator heats up which can interfere with the desired properties of the solution which is why 10 minutes of sonication time was chosen as the best alternative. This was used in the next step where the concentration of CNT was investigated in order to
determine which concentration would have the highest conductivity and best rheological properties.

Four samples were made to test how the concentration affected the conductivity and actuator properties of the CNT/CNF mixture. A compilation of the tests is shown in Table 3. Observe that sample 9 is from the previous test, see Table 1.

**Table 3:** The concentration and composition of the samples used during the experiment. All samples were sonicated for 10 minutes.

<table>
<thead>
<tr>
<th>Test</th>
<th>CNT *</th>
<th>CNF **</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[wt%]</td>
<td>[g]</td>
</tr>
<tr>
<td>9</td>
<td>45</td>
<td>0.164</td>
</tr>
<tr>
<td>12</td>
<td>15</td>
<td>0.0353</td>
</tr>
<tr>
<td>13</td>
<td>30</td>
<td>0.0857</td>
</tr>
<tr>
<td>14</td>
<td>60</td>
<td>0.3</td>
</tr>
</tbody>
</table>

*Carbon nanotubes Multi-walled (L=10-35µm, OD < 8 nm, ID = 2-6 nm)

** 0.2 wt%

Three samples were prepared for this trial according to Table 3, notice that the forth one, test 9, is the one from the previous trial. The mixtures were mixed using probe sonication for 10 minutes. Thereafter the samples were centrifuged for 15 minutes with the settings 4799 RCF and 4121 RPM, and thereafter stored in four glass beakers. The samples were then tested with FTIR analysis and plotted in Figures 16, 17, 18 and 19 under 3.2.4 FTIR Spectroscopy.

Thereafter 10 ml of each sample was collected and made into paper. These were used to calculate the conductivity and measure the actuator properties, as described in 2.3.1 Different Sonication Times.

During the measurements, 15 beads were added to the original beakers and were left for 3 hours.

The weight percentage of samples 12, 13 and 14 were made using the same procedure as the one described in 2.3.1 Different Sonication Times. Note that only one trial of the weight
percentage was done. Thereafter rheological properties were measured using the same method as in 2.3.2 Rheological Analysis.

2.4. MXene and Cellulose Nanofibrils Inks

Lists over MXene trials are shown in Table 4.

Table 4: Reference tests with MXene

<table>
<thead>
<tr>
<th>Test</th>
<th>MXene* [wt%]</th>
<th>[ml]</th>
<th>CNF ** [wt%]</th>
<th>[ml]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>60</td>
<td>3</td>
<td>40</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>60</td>
<td>3</td>
<td>40</td>
<td>2</td>
</tr>
</tbody>
</table>

*7.5 mg/ml  
**0.2 wt%  

The MXene solution was then made where 6 ml MXene and 4 ml CNF solution were used. The mixed 10 ml solution was then put in the USC-T for 30 minutes and then separated into two separate bottles, 5 ml in each. This was done in order to test two different methods of drying the solution, to then see which of those methods led to the solution with the highest viscosity.

The two bottles containing the 5 ml MXene solution were labelled 1 and 2. Solution 1 was dried by stirring the solution using a magnet and adding heat. The bottle was then covered with a parafilm and two holes were made in the film to let steam out while heating. The solution was then stirred at 30 °C at 370 rpm.

Solution 2 was dried using water-absorbing beads from BaRaPo. Six beads were placed inside the bottle and were stirred every half hour. A parafilm was also used here to cover the bottle. After 2 hours neither of the solutions had dried and the viscosity was low.

2.5. Exploring 3D Printability of Gel Inks

2.5.1. Carbon Nanotubes and Cellulose Nanofibrils Inks

Tests 9 and 10 were 3D printed onto petri dishes that were left to dry at room temperature.
A CNF membrane was prepared by mixing 30 ml of CNF, CM-CNf charge 1071, and small fibrils 0.86 wt%, with 200 ml of MQ water. The solution was put in the USC-T for 10 minutes and then mixed using an Ultra-turrax for 5 minutes. The membrane was then made by using buchner filtration.

Test 9 was printed in a net structure on the film and was dried using Rapid-Köthen. The swelling properties of the structure were tested by dipping the gel in NaCl electrolyte and applying -1V for 20 minutes.

2.5.2. MXene and Cellulose Nanofibrils Inks Printing Manually

The samples were printed onto glass plates using a handheld syringe. Different structures were made: Two triangles, two 3D rectangles and a few smaller circles. These were dried using different methods: Freeze drying, drying on a hot plate, and drying in a vacuum oven. The freeze-dried one turned into an aerogel and was the only one that did not collapse into a 2D paper.

The actuation properties were tested on all of the structures. All of them swelled when they were dipped into water but none of them showed actuator properties using voltage.

After drying, the actuation properties were tested on all of the structures, testing both passive swelling and electroactive swelling. Passive swelling was tested by putting the hot plate dried structure into a petri dish containing distilled water for 10 minutes. The structures swelled by about 60%. Electroactive swelling was made on the freeze-dried material for 5 minutes at -1 V and another 5 minutes at +1 V, it did swell a little bit on one side but not uniformly due to it being an aerogel. The same thing was done to the oven-dried sample, during the 10 minutes it bent 90 degrees.

Since the structures showed good signs of electroactive expansion and contraction it was decided to try 3D printing using the MXene/CNF gel.

2.5.3. Cellink 3D Printing

The machine used for 3D printing complex models is called Cellink which was connected to an air pressure system and an electrical output available in the lab. Thereafter the machine
needed to be calibrated regarding the syringe and the required air pressure for the gel to flow evenly during printing.

During the first trials, a pre-existing design of a 3D cube was used. Some issues were discovered, such as clogging and the delay in gel flow that made the structure uneven. The printed structures were dried using air drying (~20°C), UV light exposure (280 nm for 20 minutes) and chemical crosslinking using CaCl₂ (20 minutes) respectively. All of the structures collapsed and became 2D papers.

Simultaneously, new designs were made, see 6.3.1 Blender Designs. These were more complex than a cube but were designed to be thinner to avoid collapsing.

It was also investigated if the machine could print using two syringes at the same time.

2.6. Drying
Different drying methods were tried for the printed 3D models. This was done by observing if the structures could retain their 3D model instead of flattening out into a 2D model. The four methods used were drying through: UV light, chemical drying, and freezing.

For drying through UV-light exposure, the printed model was placed under the light at 280 nm. The light with the printed model was then covered with a box. This method of drying was done over periods of 20 minutes.

Chemical crosslinking was done by lowering a 3D-printed model placed on a glass petri dish into a beaker of 5 mM CaCl₂ solution. After 20 minutes the 3D-printed model was then carefully retrieved from the beaker without disturbing its structure. Thereafter, it was placed on a petri dish and stored in a fume hood where it was left at room temperature until dried. After it had fully dried the structure of the model could be observed.

The final method that was tested was freeze-drying. A 3D printed model was placed on a petri dish and put in a freezer for four hours with subsequent drying in a freeze dryer for 24 hours.
3. Results

The results from optimising inks, including rheological, conductive and actuator properties, are shown in section 3.1. *Ink Optimisation: Different Sonication Times* and section 3.2. *Ink Optimisation: Different Concentrations*. The results from 3D printing, including drying, are shown in section 3.3. An overview of all the inks made is given in 6.2. *Compilation of Inks Made*.

3.1. Ink Optimisation: Different Sonication Time

The samples made for trying how sonication time affects the properties of the ink are concluded in *Table 5*.

<table>
<thead>
<tr>
<th>Test</th>
<th>Sonication time</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>5 min</td>
</tr>
<tr>
<td>9</td>
<td>10 min</td>
</tr>
<tr>
<td>10</td>
<td>15 min</td>
</tr>
<tr>
<td>11</td>
<td>20 min</td>
</tr>
</tbody>
</table>

*Table 5*: Compilation of samples and associated sonication time

The papers made using the CNT/CNF inks from tests 8, 9, 10 and 11 are shown in *Figure 1*. In the figure, the papers are labelled with their associated sonication time. It can be seen that the longer the gel is sonicated, the shinier it becomes.

*Figure 1*: Papers made of the CNT/CNF inks from tests 8, 9, 10 and 11. The papers are labelled with their associated sonication time.
The weight percentage for the inks was calculated two times. Table 6 shows the weight percentage from the first trial and Table 7 shows the weight percentage from the second trial.

**Table 6:** Weight percentage from the first trial for tests 8, 9, 10 and 11.

<table>
<thead>
<tr>
<th>Test</th>
<th>Test before oven [mg]</th>
<th>Test after oven [mg]</th>
<th>Weight percentage [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>21.5</td>
<td>1.49</td>
<td>6.93</td>
</tr>
<tr>
<td>9</td>
<td>17.4</td>
<td>1.32</td>
<td>7.59</td>
</tr>
<tr>
<td>10</td>
<td>18.8</td>
<td>0.96</td>
<td>5.11</td>
</tr>
<tr>
<td>11</td>
<td>21.2</td>
<td>1.96</td>
<td>9.25</td>
</tr>
</tbody>
</table>

**Table 7:** Weight percentage from the second trial for tests 8, 9, 10 and 11.

<table>
<thead>
<tr>
<th>Test</th>
<th>Test before oven [mg]</th>
<th>Test after oven [mg]</th>
<th>Weight percentage [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>57.5</td>
<td>1.97</td>
<td>3.42</td>
</tr>
<tr>
<td>9</td>
<td>44.3</td>
<td>1.76</td>
<td>3.97</td>
</tr>
<tr>
<td>10</td>
<td>51.1</td>
<td>0.36</td>
<td>0.704</td>
</tr>
<tr>
<td>11</td>
<td>66.7</td>
<td>2.32</td>
<td>3.48</td>
</tr>
</tbody>
</table>

**3.1.1 Rheometer Values for Different Sonication Time**

The results from the rheometer tests for tests 8, 9, 10 and 11 are plotted in the following graphs. *Figure 2* shows the shear rate vs viscosity for the tests. *Figure 3* shows the shear rate vs the shear stress for the tests. *Figure 4* shows the time vs viscosity for the tests. *Figure 5* shows the oscillation stress vs the storage modulus, G’, and the oscillation stress vs the loss modulus, G”, for the tests. It was shown that 10 and 15 minutes of sonication time gave the highest viscosity. Plots over each parameter for each sample are shown in *Appendix 6.4*. 
Figure 2: Shear rate vs viscosity for tests 8, 9, 10 and 11.

Figure 3: Shear rate vs viscosity for tests 8, 9, 10 and 11.

Figure 4: Time vs viscosity for tests 8, 9, 10 and 11.
3.1.2. Conductivity Using a Parameter Analyser for Different Sonication Time

The conductivity was calculated using 6.1.1. Electrical Conductivity Equation. The area of the papers was calculated with Equation 1. The diameter for all the samples was 3.5 cm. The values used for the calculations and the conductivity is shown in Table 8.

\[ \text{Area} = \text{Diameter} \cdot \text{Thickness} \quad (1) \]

Table 8: Conductivity for sample 8, 9, 10 and 11.

<table>
<thead>
<tr>
<th>Test</th>
<th>Sonication time [min]</th>
<th>Thickness ( \cdot 10^{-3} ) [cm]</th>
<th>Resistance [Ω]</th>
<th>Length [cm]</th>
<th>Area ( \cdot 10^{-3} ) [cm²]</th>
<th>Conductivity [(Ω • cm)⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>5</td>
<td>2.8</td>
<td>970</td>
<td>2.2</td>
<td>9.8</td>
<td>0.231</td>
</tr>
<tr>
<td>9</td>
<td>10</td>
<td>2.6</td>
<td>430</td>
<td>2.3</td>
<td>9.1</td>
<td>0.588</td>
</tr>
<tr>
<td>10</td>
<td>15</td>
<td>2.8</td>
<td>175</td>
<td>2.2</td>
<td>9.8</td>
<td>1.28</td>
</tr>
<tr>
<td>11</td>
<td>20</td>
<td>2.6</td>
<td>208</td>
<td>2.5</td>
<td>9.1</td>
<td>1.32</td>
</tr>
</tbody>
</table>

The results from the conductivity measurement are plotted in Figure 6.
3.1.3. Swelling for Different Sonication Time

The swelling tests for tests 8, 9, 10, and 11 are shown in Table 9. For each sample, two trials were made. Observe that the second trial for test 8 is missing from the table. This is because the machine did not work when the experiment was made. The swelling and the deswelling percentage were calculated using equations for swelling and deswelling, see Appendix 6.1.3. The measurements were recorded in Table 9, where $I$ stands for initial, the width before swelling; $F$ stands for final, the width after swelling for 5 minutes; and $D$ stands for deswelling, the width after deswelling for 5 minutes. Swelling indicated how much the width had swelled after 5 minutes compared to the initial width, deswelling indicated how much the width had deswelled after 5 minutes compared to the $F$ width and $T$ stands for total swelling indicating the change in width after the experiment was done compared to the initial width.

Table 9: Swelling for tests 8, 9, 10 and 11.

<table>
<thead>
<tr>
<th>Test</th>
<th>Sonication time [min]</th>
<th>Trial</th>
<th>Swelling</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$I$ [cm]</td>
</tr>
<tr>
<td>8</td>
<td>5</td>
<td>1</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>-</td>
</tr>
</tbody>
</table>
### 3.1.4. FTIR Spectroscopy for Different Sonication Time

FTIR spectrums for tests 8, 9, 10, and 11 are shown below. *Figure* 7 shows the spectra for test 8. *Figure* 8 shows the spectra for test 9. *Figure* 9 shows the spectra for test 10. *Figure* 10 shows the spectra for test 11.

<p>| | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>10</td>
<td>1</td>
<td>1.7</td>
<td>2.1</td>
<td>2</td>
<td>23.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>1.1</td>
<td>1.3</td>
<td>1.4</td>
<td>18.2</td>
</tr>
<tr>
<td>10</td>
<td>15</td>
<td>1</td>
<td>2.5</td>
<td>2.9</td>
<td>2.9</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>2.6</td>
<td>3.1</td>
<td>3.1</td>
<td>19.2</td>
</tr>
<tr>
<td>11</td>
<td>20</td>
<td>1</td>
<td>1.5</td>
<td>1.9</td>
<td>1.9</td>
<td>26.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>1.5</td>
<td>1.7</td>
<td>1.6</td>
<td>13.3</td>
</tr>
</tbody>
</table>

*Figure* 7: FTIR spectra for test 8.

*Figure* 8: FTIR spectra for test 9.

*Figure* 9: FTIR spectra for test 10.

*Figure* 10: FTIR spectra for test 11.
3.1.5. Summary of the Results for Different Sonication Times

It was shown that 10 and 15 minutes of sonication was the best taking viscosity, conductivity, and deswelling into consideration. Although, 10 minutes of sonication was the only one that showed any signs of deswelling, which is crucial for actuator purposes. Therefore, 10 minutes of sonication time was concluded to be the best alternative.

3.2. Ink Optimisation: Different Concentrations

The samples made for trying how different concentrations affect the properties of the ink are concluded in Table 10. Observe that test 9 is the same as the one from Table 9, see 3.1.3 Swelling.

Table 10: Compilation of the samples

<table>
<thead>
<tr>
<th>Test</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CNT * [wt%]</td>
</tr>
<tr>
<td>9</td>
<td>45</td>
</tr>
<tr>
<td>12</td>
<td>15</td>
</tr>
<tr>
<td>13</td>
<td>30</td>
</tr>
<tr>
<td>14</td>
<td>60</td>
</tr>
</tbody>
</table>

*Carbon nanotubes Multi-walled (L=10-35µm, OD < 8 nm, ID = 2-6 nm)
** 0.2 wt%

The papers made using the CNT/CNF inks from tests 12, 13 and 14 are shown in Figure 11. In the figure, the papers are labelled with the test number.

![Figure 11: Papers made of the CNT/CNF inks from tests 12, 13, and 14.](image)
The weight percentage for the inks is shown in Table 11.

**Table 11:** Weight percentage for tests 12, 13 and 14.

<table>
<thead>
<tr>
<th>Test</th>
<th>Test before oven [mg]</th>
<th>Test after oven [mg]</th>
<th>Weight percentage [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>65.6</td>
<td>0.21</td>
<td>0.320</td>
</tr>
<tr>
<td>13</td>
<td>53.5</td>
<td>0.44</td>
<td>0.822</td>
</tr>
<tr>
<td>14</td>
<td>85.3</td>
<td>0.23</td>
<td>0.270</td>
</tr>
</tbody>
</table>

### 3.2.1. Rheometer Values for Different Concentrations

The results from the rheometer tests for tests 9, 12, 13 and 14 are plotted in the following graphs. *Figure 12* shows the shear rate vs viscosity for the tests. *Figure 13* shows the shear rate vs the shear stress for the tests. *Figure 14* shows the time vs viscosity for the tests. *Figure 15* shows the oscillation stress vs the storage modulus, G’, and the oscillation stress vs the loss modulus, G’”, for the tests. Plots over each parameter for each sample are shown in Appendix 6.5.

![Shear rate vs Viscosity](image)

*Figure 12:* Shear rate vs viscosity for tests 9, 12, 13 and 14.
Figure 13: Shear rate vs shear stress for tests 9, 12, 13 and 14.

Figure 14: Time vs viscosity for tests 9, 12, 13 and 14.
3.2.2. Conductivity for Different Concentrations

The conductivity was calculated using 6.1.1 Electrical Conductivity Equation. The area of the papers was calculated with Equation 2. The diameter for all the samples was 3.5 cm. The values used for the calculations and the conductivity is shown in Table 12.

\[ \text{Area} = \text{Diameter} \cdot \text{Thickness} \]  \hspace{1cm} (2)

<table>
<thead>
<tr>
<th>Test</th>
<th>CNF/CNT [ratio]</th>
<th>Thickness ( \times 10^{-3} ) [cm]</th>
<th>Resistance [Ω]</th>
<th>Length [cm]</th>
<th>Area ( \times 10^3 ) [cm²]</th>
<th>Conductivity [(Ω \cdot cm)^{-1}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>85/15</td>
<td>1.8</td>
<td>8400</td>
<td>3.1</td>
<td>5.94</td>
<td>0.0621</td>
</tr>
<tr>
<td>13</td>
<td>70/30</td>
<td>2.3</td>
<td>1270</td>
<td>2.6</td>
<td>8.05</td>
<td>0.254</td>
</tr>
<tr>
<td>9</td>
<td>55/45</td>
<td>2.6</td>
<td>430</td>
<td>2.3</td>
<td>9.1</td>
<td>0.588</td>
</tr>
<tr>
<td>14</td>
<td>40/60</td>
<td>4.9</td>
<td>633</td>
<td>2.5</td>
<td>17.2</td>
<td>0.230</td>
</tr>
</tbody>
</table>

It was shown that 45% CNT gave the gel with the highest conductivity. This means that 45% CNT and 10 minutes of sonication time give the best gel regarding viscosity and conductivity.

3.2.3. Swelling for Different Concentrations

The swelling tests for tests 9, 12, 13, and 14 are shown in Table 13. For each sample, two trials were made. The swelling and the deswelling percentage were calculated using equations
for swelling and deswelling, see Appendix 6.1.3. The measurements were recorded in Table 13, where $I$ stands for initial, the width before swelling; $F$ stands for final, the width after swelling for 5 minutes; and $D$ stands for deswelling, the width after deswelling for 5 minutes. Swelling indicated how much the width had swelled after 5 minutes compared to the initial width, deswelling indicated how much the width had deswelled after 5 minutes compared to the $F$ width and $T$ stands for total swelling indicating the change in width after the experiment was done compared to the initial width. Observe that test 9 is numbered “9” as it has the same sample values as test 9 from Table 9, see 3.1.3 Swelling.

**Table 13:** Swelling for tests 9, 12, 13 och 14.

<table>
<thead>
<tr>
<th>Test</th>
<th>CNF/CNT ratio</th>
<th>Trial</th>
<th>Swelling</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$I$ [cm]</td>
</tr>
<tr>
<td>12</td>
<td>85/15</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>3.4</td>
</tr>
<tr>
<td>13</td>
<td>70/30</td>
<td>1</td>
<td>3.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>2.2</td>
</tr>
<tr>
<td>9</td>
<td>55/45</td>
<td>1</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>1.1</td>
</tr>
<tr>
<td>14</td>
<td>40/60</td>
<td>1</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>3.5</td>
</tr>
</tbody>
</table>

* Negative sign means that it is swelling and not deswelling.

**3.2.4. FTIR Spectroscopy for Different Concentrations**

FTIR spectrums for tests 9, 12, 13, and 14 are shown below. Figure 16 shows the spectra for test 12. Figure 17 shows the spectra for test 13. Figure 18 shows the spectra for test 9. Observe that the spectra are the same as in Figure 8 from different sonication times. Figure 19 shows the spectra for test 14.
3.2.5. Summary the Results for Different Concentrations

Although a gel with high viscosity and conductivity was produced using 45% CNT and 10 minutes of sonication, none of the CNT gels showed any reversible actuator properties. CNT gels made into nano papers showed a maximum swelling of 58% but none of the CNT/CNF 3D printed materials could deswell.

3.3. 3D Printing

Four different methods of drying were used to observe if any of the methods would work so that the printed models kept their 3D structure.

The printed model that was placed under UV light for 20 minutes did not change much in structure. However, it also did not dry during that time. Therefore, it was put under the UV light for an additional 20 minutes where the structure did not fully dry but started to flatten out at the edges, meaning that it was slowly losing its 3D structure as it was drying.
The second 3D printed model that was treated with 300°C air for drying started to flatten out and regress into something more akin to a 2D model as time progressed. After roughly 40 minutes, most of the 3D structure had flattened out onto the glass petri dish.

The chemically treated structure, that was dipped in CaCl₂ for 20 minutes, also flattened out after it had fully dried at room temperature.

Freeze drying was made by putting the structure into a freezer for four hours followed by drying it in a freeze dryer for 24 hours. Freeze drying successfully retained the structure of the printed gel. However, when actuation was tried for the structure it did not work despite its successfully maintained 3D structure, meaning that cross-linking of the structure was not successful.

*Figure 20* and *Figure 21* were printed using a handheld syringe. These were later used for the first trial of drying methods. Since none of the drying methods worked, no photos were taken of the dried structures.

*Figure 20*: MXene printed with handheld syringe.  
*Figure 21*: MXene printed with handheld syringe.

*Figure 22*, *Figure 23*, *Figure 24*, and *Figure 25* show pictures from the second trial on drying methods. *Figure 22* shows the UV-cured sample after CaCl₂ treatment and *Figure 23* the chemically treated sample after CaCl₂ treatment. *Figure 24* shows the air-dried sample before drying and *Figure 25* shows the air-dried sample after drying.
**Figure 22:** The UV-cured sample after CaCl$_2$ treatment.

**Figure 23:** The chemically treated sample after CaCl$_2$ treatment.

**Figure 24:** The air-dried sample before drying.

**Figure 25:** The air-dried sample after drying.

*Figure 26* shows test 9 when 3D printed and *Figure 27* shows test 9 when left to dry at room temperature. *Figure 28* shows test 10 when 3D printed and *Figure 29* shows test 10 when left to dry at room temperature. The figures show that the structures made with CNT gels collapsed and could not be used for 3D printing.

**Figure 26:** Test 9 when 3D printed.

**Figure 27:** Test 9 when left to dry at room temperature.
Figure 28: Test 10 when 3D printed.

Figure 29: Test 10 when left to dry at room temperature.

Figure 30 and Figure 31 both show test 9 printed on CNF paper, dried with Rapid Köthen. The figures show that CNT can be used to print 2D structures on a dried CNF film. Figure 32 and Figure 33 both show test 9 printed on CNF film after swelling in water for 20 minutes using a low voltage. Both the dried and swelled structure remains even and has complete contact with the surface. This shows that CNT can be used to create 2D gels that swell, but not 3D actuators.

Figure 30: Test 9 printed on CNF paper, dried with Rapid Köthen.

Figure 31: Test 9 printed on CNF paper, dried with Rapid Köthen.
It was also investigated if the machine could print in layers. The first try was made using two nozzles at the same time, this led to the machine printing two identical designs beside each other and overlapping in the middle.

*Figure 34* and *Figure 35* show the 3D-printed structure using two syringes before and after drying at room temperature. The middle part is overlapping and the outer parts are not completely filled in due to clogging. Additionally, since the ejection of material was continous, the gaps in the model were not produced correctly. It can also be seen that the dried structure becomes flaky and fragile. *Figure 36* shows the non-dried 3D printed structure using only one syringe and in a smaller size. *Figure 37* shows the associated Blender-model, see Appendix 6.3.
Figure 36: The non-dried 3D printed structure using only one syringe and in a smaller size.

4. Discussion

4.1. Comparing Inks and Printability

Previous research on MXene showed that a ratio of 60% MXene and 40% CNF would yield a product with good conductivity and high viscosity that can also swell up to 100% and deswell up to 100%. During this experiment, it was investigated if CNT could be used as a cheaper alternative.

To create a CNT gel homogeneously, an ultrasonicator needed to be used. It was investigated at what time would yield the best conductivity and viscosity. Tests 8, 9, 10 and 11 were made to compare 5, 10, 15 and 20 minutes of sonication time respectively. Figure 1 shows the gels when they had been filtered and dried into paper. The papers become increasingly shiny the longer it has been sonicated.

The papers were used to try to measure the conductivity which can be seen in Table 8. The table shows that the conductivity increases with increased sonication. Theoretically, this should not be the case since sonication breaks apart the CNTs, which makes them shorter and would decrease conductivity. However, the sonication was done without pauses, which increased the temperature of the gel, and in some cases melted the surrounding ice that was used to prevent heating. The heating could be the reason for the results, although this was not further investigated. Figure 2 shows that the viscosity generally is higher for higher sonication times. Figure 3 shows that the shear stress decreases for increased sonication time,
except for 5-minute sonication time which has a steeper slope than the rest. The gel with only 5 minutes of sonication is the gel whose temperature increased the least. Figure 5 shows that all the samples have very similar G’ and G” with increasing oscillation. This could indicate that they are equally crosslinked. Figures 7, 8, 9 and 10 show that there is no difference between the FTIR spectrums of the different sonication times. Table 9 shows the swelling behaviour of the gels. Test 9 is the only one that showed signs of deswelling behaviour, which is required for it to be an actuator. However, both test 9 and test 11 showed “negative” deswelling, which means that the strand kept swelling during the supposed deswelling period. When all of this was taken into consideration, both test 9 and test 10 were good candidates. However, since the gel was heated during the sonication and that test 9 was the only test that showed signs of deswelling, 10 minutes of sonication was considered the best.

After that, it was investigated what concentration would be the best for actuator purposes, using 10 minutes of sonication time. Figure 11 shows the papers made with tests 12, 13 and 14. It seems as though the paper becomes slightly more shiny with a decreased amount of CNT. Figure 12 the viscosity seems to increase with the amount of CNT until 45% CNT and that decreases after that point. A similar pattern is shown in Figure 13 where the shear stress increases with the shear rate for all of them but 45% CNT increases the most. Figure 14 shows that 45% of CNT has the highest viscosity over time. Figure 15 shows that 45% CNT generally has the highest G’ and G” with increased oscillation stress. Figures 16, 17, 18 and 19 show that there is no difference between the FTIR spectrums of the different concentrations. The figures can be compared with Figures 7, 8, 9 and 10, and there seems to be no difference between any of the figures. The same pattern repeats in Table 12 where the conductivity increases with an increased amount of CNT up to 45% and then it decreases again. Table 13 shows the swelling properties for the different concentrations, once again none of them shows clear signs of deswelling and all behaviours seem to be uneven and non-reliable. Tests 8 to 14 show that 45% of CNT and 10 minutes of sonication time yields the gel with the highest conductivity and viscosity. However, none of them show good actuator properties since all of them showed swelling behaviour but none of them showed clear deswelling properties.

Figure 26 and Figure 28 shows how test 9 and 10 were 3D printed but could not hold up the 3D structure. Figure 27 and Figure 29 show how the structures completely collapse after drying at room temperature. The figures can be compared to Figure 25 and Figure 35 where
MXene gels have been left to dry at room temperature. It can be seen that CNT gels dry more evenly and lie flat on the surface compared to MXene which becomes flaky and lifts from the surface.

*Figure 30* and *Figure 31* show test 9 printed in a 2D net structure on a CNF film. It can be seen that the structure once again is much more even than the MXene structures. *Figure 32* and *Figure 33* show how the structure swells and the CNF film swells. No deswelling was done since it had already been concluded that CNT does not have this property.

Before this experiment was performed, the supervisor of this project had done experiments with MXene and 0.2 wt% CNF. These experiments showed that 60% MXene would be the best ratio to create a gel with high viscosity and conductivity. This report aimed to further investigate that research using both CNT and MXene gels. Since the CNT gels proved to be poor actuators, the rest of the research was done with MXene gels.

*Figure 20* and *Figure 21* show the first printing trial, made using a handheld syringe, printing structures on glass plates. It was discovered that a too-viscous gel would clog the syringe nozzle and that the walls of the structure could not be too thin, since this made the structure collapse. A few thicker structures were made that could stand on their own. These were used to try different drying methods. Drying on a hot plate and in a vacuum oven made the structures collapse because the crosslinking was too weak, although the structures did show signs of actuator properties. Freeze drying preserved the structure but it made the gel turn into an aerogel which made it lose its actuator properties.

Thereafter the inks were printed using the 3D Cellink printer. The machine used air pressure to push out the gel. 40 kPa of air pressure made the gel print in a steady flow. However clogging still occurred after a while, even if a pressure of 90 kPa was applied.

Nevertheless, different structures were made and new drying methods were tried. Drying at room temperature over a long period of time made the structure collapse. UV light exposure was tested for 20 minutes, although this did not affect the gel at all. This may be because no photoinitiator was added, which is due to time limitations. Chemical treatment using CaCl$_2$ for 20 minutes also did nothing to the gel.
Different designs were made to try and improve the printing abilities. Since the structure collapsed in on itself, 2D structures were made. These were left to dry at room temperature and became very thin and fragile, see Figure 34 and Figure 35.

*Figure 34* shows a design made to try the effects of using two syringes at the same time. The machine printed the same structure twice and due to its size, there was some overlap in the middle. The figure also shows the effects of the clogging since the 3D printing machine made the outlines of the designs first and then aimed to fill them in. However, due to clogging, there were large parts missing and since the two syringe nozzles were clogged at different times the structures look different from each other.

MXene is a known 2D actuator and no other research could be found on 3D-printed MXene actuators. So compared to previous research, MXene behaved as expected. The experiments done on CNT were different from a lot of previous research done on the subject. Although, since no procedure of 3D printing a CNT actuator was found, CNT also behaved as expected compared with previous research.

### 4.2. Conclusions
The goal of this project was to create a 3D-printed actuator of CNT and to compare it with MXene. This goal was not completely reached since no actuator was made.

It was concluded that a gel with 45% CNT and 55% CNF that was sonicated for 10 minutes created a viscous and conductive gel. It was also concluded that this gel could be printed to swell in a 2D format, which becomes extra stable on a CNF film. Although 3D structures were possible to print, we found it challenging to make a self standing 3D structure after drying. Freeze drying is the best option as of now. However, it becomes an aerogel in the process which can passively absorb a lot of electrolyte. Therefore, it was challenging to control the swelling behaviour electroactively in this case.

A gel with 60% MXene and 40% CNF can be used as a reversible actuator and can be 3D printed into complex structures. However, no drying method was found that could dry the 3D-printed gel in a way that retained the structure. Although we printed 2D designs taking nanocellulose paper as a substrate and crosslinked them by heat-drying using Rapid-Köthen. We also observed their swelling behaviour in a three-electrode system.
For future research, more experiments would need to be done to determine the optimal viscosity needed for the gel, as a recurring problem was that the gel was either not viscous enough to retain a complex 3D structure or so viscous that it caused clogging while 3D printing. Future research also needs to focus on finding a suitable drying technique that can enable the creation of complex structures with preserved structure and functionality, expanding the potential applications of these gels.
5. References


(19) Iowa State University; Shi, X. Printability Of Hydrogel Composites Using Extrusion-Based 3D Printing And Post-Processing With Calcium Chloride. *Food Sci.*


6. Appendix

6.1. Equations

6.1.1. Electrical Conductivity Equation

\[ \sigma = \frac{L}{R \cdot A} \]

* Thickness • diameter

L = Length between probes [cm]
A = Area* [cm²]
R = Electrical Resistance of a uniform specimen of the material [Ω]
\( \sigma \) = Conductivity \( [1 / (Ω \cdot cm)] \)

6.1.2. Ohm's Law Equation

\[ I = \frac{V}{R} \]

I = Current [A]
V = Voltage [V]
R = Resistivity [Ω]

6.1.3. Swelling and Deswelling

Swelling = \( \frac{F-I}{I} \cdot 100 \)

Deswelling = \( \frac{D-I}{I} \cdot 100 \)

F = Final length [cm]
I = Initial length [cm]
D = Deswelling [cm]

6.2. Compilation of Inks Made

6.2.1. Carbon Nanotubes and Cellulose Nanofibrils

Compilation of all tests that were made using CNT/CNF, including different sonication times and ratios, are shown in Table 14. Wt% means the weight percentage of the substance in the final solution.
Table 14: Compilation of all tests made using CNT/CNF including different sonication times and ratios.

<table>
<thead>
<tr>
<th>Test</th>
<th>Sonication time [min]</th>
<th>CNT [wt%]</th>
<th>CNT [mg]</th>
<th>CNF [wt%]</th>
<th>CNF [ml]</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>45²</td>
<td>181</td>
<td>55</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>45²</td>
<td>360</td>
<td>55</td>
<td>220</td>
<td>After sonication, it was in the USC-T for 6 minutes.</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>45³</td>
<td>327</td>
<td>55</td>
<td>200</td>
<td>Centrifuged</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>45³</td>
<td>135</td>
<td>55⁴</td>
<td>82.5</td>
<td>118 ml of MQ was added. Centrifuged</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>45³</td>
<td>164</td>
<td>55</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>45²</td>
<td>180</td>
<td>50</td>
<td>100</td>
<td>5 wt% CMC⁵ was added (0.02 g)</td>
</tr>
<tr>
<td>7</td>
<td>-</td>
<td>45²</td>
<td>82</td>
<td>55⁶</td>
<td>20</td>
<td>Too thick to sonicate.</td>
</tr>
<tr>
<td>8</td>
<td>5</td>
<td>45³</td>
<td>164</td>
<td>55</td>
<td>100</td>
<td>Centrifuged</td>
</tr>
<tr>
<td>9</td>
<td>10</td>
<td>45³</td>
<td>164</td>
<td>55</td>
<td>100</td>
<td>Centrifuged</td>
</tr>
<tr>
<td>10</td>
<td>15</td>
<td>45³</td>
<td>164</td>
<td>55</td>
<td>100</td>
<td>Centrifuged</td>
</tr>
<tr>
<td>11</td>
<td>20</td>
<td>45³</td>
<td>164</td>
<td>55</td>
<td>100</td>
<td>Centrifuged</td>
</tr>
<tr>
<td>12</td>
<td>10</td>
<td>15³</td>
<td>35.3</td>
<td>85</td>
<td>100</td>
<td>Centrifuged</td>
</tr>
<tr>
<td>13</td>
<td>10</td>
<td>30³</td>
<td>85.7</td>
<td>70</td>
<td>100</td>
<td>Centrifuged</td>
</tr>
<tr>
<td>14</td>
<td>10</td>
<td>60³</td>
<td>300</td>
<td>40</td>
<td>100</td>
<td>Centrifuged</td>
</tr>
<tr>
<td>15</td>
<td>5</td>
<td>45³</td>
<td>164</td>
<td>55</td>
<td>100</td>
<td>Centrifuged</td>
</tr>
<tr>
<td>16</td>
<td>20</td>
<td>45³</td>
<td>164</td>
<td>55</td>
<td>100</td>
<td>Centrifuged</td>
</tr>
</tbody>
</table>

1: 0.2 wt%. 1000 charge kind of CNF if nothing else is said under the wt% column
2: Carbon nanotube Multi-walled, 60-100 nm (diam.), >5μm (length)
3: Carbon nanotubes Multi-walled (L=10-35µm, OD < 8 nm, ID = 2-6 nm)
4: 590 Charge
5: Carboxymethyl cellulose, sodium salt (Typical Mₘ 90,000, DS: 0.70)
6: 0.5 wt%.
6.2.2. MXene and Cellulose Nanofibrils

Compilation of the gels made using MXene/CNF, including ratio and mixing methods, are shown in Table 15.

Table 15: Compilation of gels made using MXene/CNF including ratio and mixing method.

<table>
<thead>
<tr>
<th>Test</th>
<th>MXene(^1)</th>
<th>CNF</th>
<th>Mixing method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[wt%]</td>
<td>[mg]</td>
<td>[ml]</td>
</tr>
<tr>
<td>1</td>
<td>60</td>
<td>45</td>
<td>6</td>
</tr>
</tbody>
</table>

\(^1\) 7.5 g/L
\(^2\) 0.2 wt\%, 1000 charge.

6.3. 3D Printing Designs

6.3.1. Blender Designs

*Figure 37* shows the design which was made through Blender. The dimensions of the object were as follows: X=17 mm, Y=14.6 mm and Z=0.531 mm. This model corresponds to the printed structure shown in *Figure 34, Figure 35* (dried) and *Figure 36*. The other Blender models shown in *Figure 38, Figure 39* and *Figure 40* were also used in order to test the 3D-printing potential of the different CNT/CNF tests.

*Figure 37*: Design made through Blender.  
*Figure 38*: Design made through Blender.
6.4. Rheometer Values for Different Sonication Times

6.4.1. Test 8

The following graphs illustrate the results from test 8 which was 5 minutes of sonication. *Figure 41* and *Figure 42* show how the viscosity and shear stress changes with the shear rate for test 8. It can be seen that viscosity decreases with shear rate and shear stress increases with shear rate. *Figure 43* shows viscosity decreases with time for test 8. *Figure 44* shows that both $G'$ and $G''$ increase with oscillation stress for test 8.

**Figure 41**: Shear rate vs viscosity for test 8.

**Figure 42**: Shear rate vs shear stress for test 8.
Figure 43: Time vs viscosity for test 8.

Figure 44: Oscillation stress vs G’ and G’’ for test 8.

6.4.2. Test 9

The following graphs illustrate the results from test 9 which was 10 minutes of sonication and a concentration of 45:55. Figure 45 and Figure 46 shows how the viscosity and shear stress changes with the shear rate for test 9. It can be seen that viscosity decreases with shear rate and shear stress increases with shear rate. Figure 47 shows viscosity decreases with time for test 9. Figure 48 shows that both G’ and G’’ increase with oscillation stress for test 9. Observe that test 9 is used to show the properties of 10 minutes of sonication time and 45% CNT.

Figure 45: Shear rate vs viscosity for test 9.

Figure 46: Shear rate vs shear stress for test 9.
Figure 47: Time vs viscosity for test 9.

Figure 48: Oscillation stress vs $G'$ and $G''$ for test 9.

6.4.3. Test 10

The following graphs illustrate the results from test 10 which was 15 minutes of sonication. Figure 49 and Figure 50 show how the viscosity and shear stress changes with the shear rate for test 10. It can be seen that viscosity decreases with shear rate and shear stress increases with shear rate. Figure 51 shows viscosity decreases with time for test 10. Figure 52 shows that both $G'$ and $G''$ increases with oscillation stress for test 10.

Figure 49: Shear rate vs viscosity for test 10.

Figure 50: Shear rate vs shear stress for test 10.
Figure 51: Time vs viscosity for test 10.

Figure 52: Oscillation stress vs G’ and G” for test 10.

6.4.4. Test 11

The following graphs illustrate the results from test 11 which was 20 minutes of sonication. Figure 53 and Figure 54 show how the viscosity and shear stress changes with the shear rate for test 11. It can be seen that viscosity decreases with shear rate and shear stress increases with shear rate. Figure 55 shows viscosity decreases with time for test 11. Figure 56 shows that both G’ and G” increase with oscillation stress for test 11.

Figure 53: Shear rate vs viscosity for test 11.

Figure 54: Shear rate vs shear stress for test 11.
6.5. Rheometer Values for Different Concentrations

Observe that test 9 was used for investigating both different sonication times and different concentrations.

6.5.1. Test 12

The following graphs illustrate the results from test 12 which was 15:85 concentration. Figure 57 and figure 58 shows how the viscosity and shear stress changes with shear rate for test 12. It can be seen that viscosity decreases with shear rate and shear stress increases with shear rate. Figure 59 shows viscosity decreases with time for test 12. Figure 60 shows that both $G'$ and $G''$ increases with oscillation stress for test 12.
Figure 59: Time vs viscosity for test 12.

Figure 60: Oscillation stress vs G’ and G” for test 12.

6.5.2. Test 13
The following graphs illustrate the results from test 13 which was 30:70 concentration. Figure 61 and Figure 62 show how the viscosity and shear stress changes with the shear rate for test 13. It can be seen that viscosity decreases with shear rate and shear stress increases with shear rate. Figure 63 shows viscosity decreases with time for test 13. Figure 64 shows that both G’ and G” increases with oscillation stress for test 13.

Figure 61: Shear rate vs viscosity for test 13.

Figure 62: Shear rate vs shear stress for test 13.
**Figure 63:** Time vs viscosity for test 13.  

**Figure 64:** Oscillation stress vs G’ and G” for test 13.

### 6.5.3. Test 14

The following graphs illustrate the results from test 14 which was 60:40 concentration. *Figure 65* and *Figure 66* show how the viscosity and shear stress changes with the shear rate for test 14. It can be seen that viscosity decreases with shear rate and shear stress increases with shear rate. *Figure 67* shows viscosity decreases with time for test 14. *Figure 68* shows that both G’ and G” increases with oscillation stress for test 14.

**Figure 65:** Shear rate vs viscosity for test 14.  

**Figure 66:** Shear rate vs shear stress for test 14.
Figure 67: Time vs viscosity for test 14.

Figure 68: Oscillation stress vs $G'$ and $G''$ for test 14.

6.6. Images of Equipment

6.6.1. Ultra-turrax

The model used was the IKA T 25 digital ultra-turrax, see Figure 69. In the picture to the right, the CNF probe can be seen.

Figure 69: IKA T 25 digital ultra-turrax. In the picture to the right, the CNF probe can be seen.
6.6.2. Probe Sonicator

The model used was Sonics vibra cell VCX 750, see Figure 70.

![Figure 70: Sonics vibra cell VCX 750.](image)

6.6.3. Centrifuge

The model used was the ROTINA 420/420R centrifuge by Hettich, see Figure 71.

![Figure 71: ROTINA 420/420R centrifuge](image)

6.6.4. Actuation and Swelling

The program used for voltage was Nova 2.1.4 and the camera program used to record the swelling was DinoCapture 2.0. Figure 72 shows the workstation and Figure 73 shows a close up of the set-up.
**Figure 72:** Workstation.

**Figure 73:** The set up for actuation.
6.6.5. Conductivity Measurements

The model used was the Keithley 4200A-SCS Parameter analyzer, see Figure 74, and the program used was Clarius.

![Figure 74: Keithley 4200A-SCS Parameter analyzer.]

6.6.6. Rheometer

The model used was the Discovery HR-2 Hybrid rheometer, see Figure 75, and the program used was TA instruments trios V4.

![Figure 75: Discovery HR-2 Hybrid rheometer.]

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6.6.7. 3D Printer

The model used was Inkredible by Cellink, see Figure 76. The program used for modelling was Blender STL and the 3D-printing program was PrusaSlicer.

Figure 76: Inkredible by Cellink.