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Investigation of graphene and nanocellulose hybrid films as a
barrier material in packages

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Abstract

In this report, hybrid films of carboxymethylated cellulose nanofibrils (CNF) and graphene nanosheets (GNs) have been prepared to evaluate if the GNs can enhance the barrier properties of the CNF films. CNF already possess great barrier properties at low relative humidity (RH) but it is drastically lowered when the RH reaches above 50% due to its strong hydrophilicity of CNF. This report shows that the water vapour permeability (WVP) of the hybrid film can be lowered more than 25 times at 50% RH in comparison to the pure nanocellulose film due to the hydrophobic properties and good impermeability properties of GNs. The report also shows how different parameters such as sonication time, starting materials and ratios should be chosen when making films. A scale-up part of the project is also done in collaboration with the industry where an easier way of dispersion and a faster application of the film is evaluated.

Sammanfattning

I den här rapporten har hybridfilmer med cellulosa nanofiber (CNF) och nanoflak av grafén (GNs) tillverkats för att undersöka om GNs kan förbättra barriäregenskaperna hos rena CNF filmer. CNF filmer har redan en bra barriär vid låg luftfuktighet men den minskar drastiskt när den relativa luftfuktigheten går över 50% på grund av materialets starka hydrofilicitet. I den här rapporten visas att vattenångpermeabiliteten kan minskas 25 gånger genom att introducera grafénflak på grund av dess hydrofobiska natur. Rapporten visar även hur olika parametrar så som sonikeringstid, startmaterial samt mängdförhållande påverkar egenskaperna hos dispersionen samt den färdiga filmen. En del av rapporten består också av ett uppskalningsprojekt i samarbete med industrin där en förenkling av dispersionsmetoden samt en snabbare applicering av filmer är evaluerade.

Keywords: Nanocellulose, CNF, Graphene, Barrier, Dispersion, graphene nanosheets, coating, sonication, carboxymethylated

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in packages**

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Preface

This thesis was written in the autumn of 2018 as a final step at the engineering in nanotechnology program at Lunds tekniska högskola (LTH). The report was mostly conducted at RISE (Research institutes of Sweden) and partly in collaboration with BillerudKorsnäs, with the purpose to further extend the knowledge database regarding nanocellulose and graphene dispersions. The main author is Jens Bodelsson under supervision of Andreas Fall and Anna Carlmark from RISE and Baozhong Zhang from Lund university. A warm thanks to you all and also to the entire Bioeconomy group at RISE. A big thanks also to Thomas Gillgren and his team at Billerud Korsnäs in Frövi for letting me work together with you for one week.

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List of Abbreviations

CMF	Cellulose microfibrils
CNF	Cellulose nanofibrils
DS	Degree of substitution
GNs	Graphene nanosheets
MFC	Microfibrillated cellulose
OTR	Oxygen transmission rate
OX	A type of graphene used in this report
RISE	Research institute of Sweden
SEM	Scanning electron microscopy
WVP	Water vapour permeability
WVTR	Water vapour transmission rate
XL	A type of graphene used in this report

1 Introduction

1.1 Background

More and more concerned voices are today heard regarding the prevailing situation with the abundance of fossil based plastics in nature. The fact that many polymers take decades to degrade and can do harm in the ecosystem meanwhile makes the general opinion more and more demanding of a more nature friendly alternative. The problem is however that the society today is strongly built around the usage of fossil based polymers due to their good mechanical properties and low price. In recent years, researchers from all over the world have looked around for a more nature friendly solution and some have found an interest in cellulose based materials. This interest is also fuelled by the forest industry that has seen a decrease in the demand for some traditional pulp and paper products and therefore wants to find new exploration areas around the wood raw material.

Cellulose is the most abundant polymer on earth[6] and it consists of small fibres of polysaccharides that can be extracted from the cell walls in plants. When the fibrils are disintegrated from each other they form microfibrillated cellulose (MFC) or cellulose nanofibrils (CNF). This material has shown potential to become an environmentally friendly alternative to fossil based plastics due to its green nature, high stiffness and low gas permeability[29]. Many industries such as the packaging, electronic device and food industry are already looking for ways to improve their usage of cellulose into their processes to make them more environmentally friendly and at the same time enhance the properties of their products. In the packaging industry for example, nanocellulose can be of interest as a reinforcement of their cardboard or as a replacement for the current barrier materials used to keep the food fresh in the packages. The barriers today, often consists of a layer aluminium and plastic which holds a big percentage of the cost and corresponds to a large portion of the environmental impact of the package. One solution is instead to replace this barrier with a thin film of nanocellulose in order to replace the current materials with a more environmentally friendly one. The problem so far has been that its hydrophilic nature makes the water vapour permeability unsatisfactory at a higher air humidity.

One way that has been suggested as a solution to this problem is to integrate different 2D materials[1] in order to minimise the swelling of the film and therefore also keep the good gas barrier. One possible material could be graphene nanosheets which due to their hydrophobic nature and good impermeability could enhance the water vapour barrier of the nanocellulose films. CNF has also shown to be a good dispersing agent for graphene that otherwise is insoluble in water[37].

1.2 Interest from the industry

Many industries that desire to switch to a greener alternative are already today looking into the possibilities of using nanocellulose. The forestry industry is in particular interested and many companies such as Stora Enso and BillerudKorsnäs are looking into how fibrillated cellulose might be used as reinforcement in paper or as barrier coatings. RISE (research institute of Sweden) is a big part of this engagement since a lot of the research

is conducted in their regime. RISE and BillerudKorsnäs have a project ongoing together where the purpose is to evaluate how graphene disperse in nanocellulose which is a part of the national SIO-graphene project. This thesis work will be a part of this project with focus on evaluating the barrier properties of the composite films consisting of graphene and nanocellulose.

1.3 Purpose

In this report the change of properties of a cellulose nanofibril (CNF) film will be evaluated when different parameters regarding the integration of graphene nanosheets (GNs) into the nanocellulose matrix are changed. Since not much work has been done on this topic this study is very exploratory to try to find some tendencies of where the focus should be in the future. The property of highest interest is to see whether the graphene can limit the swelling of the CNF-films and therefore enhance the barrier properties of the nanocellulose. Also the parameters affecting the dispersion, the mechanical properties and the possibilities for scaled up processes will be evaluated.

2 Theory

2.1 Cellulose

Cellulose has played a major role in the evolution of humanity for thousands of years. First it functioned mainly as a building material and an energy source but it has also played a mayor role in the recording of human history as the main building block in paper. In the last decades, however, researchers have started to develop a new second generation of cellulose materials that are supposed to meet the demand of high performance material with minimal carbon foot print. This second generation utilises the cellulose's properties in a new way that enables better mechanical properties and a better customizability.

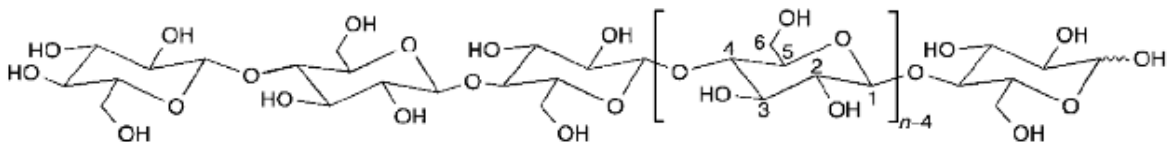


Figure 1: Image of the D-glucose unit that when repeated builds up the cellulose.[16]

Cellulose is a polysaccharide $C_6H_{10}O_5$ that together with hemicellulose, pectin and lignin are the main building blocks in most of our plant's cell walls[21]. It consists of a stiff, linear polymer chain of several $\beta(1 \rightarrow 4)$ linked D-glucose units with hydroxyl groups at the C2, C3 and C6 position as can be seen in Figure 1. Each glucose molecule is rotated 180° relative to its neighbours and when bundled together into fibrils at a nano- and microscale they give the plant an opportunity to create a strong and light structure

at a macroscale (see Figure 2). The cellulose is produced in the plasma membrane by proteins and almost immediately after, a crystallization process occurs and results in one dimensional particles comprising 20-50 chains each with a crystallinity of around 50-60%[13]. These particles are called microfibrils and they are the reinforcing structure in the cell walls in the plant. The fibrils then build up fibers that are arranged along the tree axis together with the other main components of the tree.

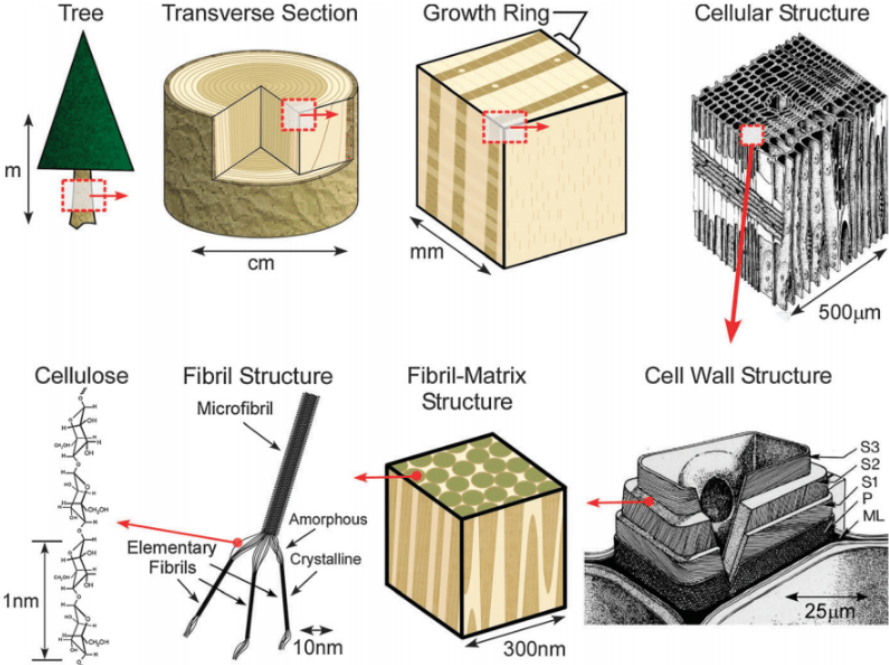


Figure 2: The hierarchical structure from a macro to a nanoscale.[21]

2.2 Nanocellulose

The strength in the plant is mainly owing to the cellulose fibrils which are the smallest crystalline components of the tree. Such one dimensional cellulose material is mainly referred to as cellulose microfibrils (CMF) or cellulose nanofibrils (CNF) depending on the degree of defibrillation. The fibrils are a couple of nanometers in diameter but could be several micrometers in length which gives them a very high aspect ratio which in turn gives the fibrils important properties such as high strength and interesting rheological properties[16]. The big gain with the extraction of the cellulose fibrils at a nanoscale is that the majority of the defects associated with the hierarchical structure are removed which leaves a bigger possibility to customize the material from the bottom. Nanocellulose can be classified in three different subcategories on the basis of their functions, dimensions and how they are prepared. The most common one is cellulose nanofibrils (CNF) which is when the entire fibril is used, both the crystalline and amorphous phase. If the less ordered amorphous phase is removed, a more crystalline material is obtained with lower aspect ratio. This is generally referred to as cellulose nanocrystals (CNC). Cellulose can also be produced bottom down with the use of bacteria. This cellulose is called bacterial nanocellulose (BNC) and is produced by acetobacter species cultivated in a

culture medium containing carbon and nitrogen sources[22].

2.2.1 Cellulose nanofibrils (CNF)

The cellulose nanofibrils (CNF) are disintegrated cellulose chains of a couple of nanometers in width and a length in the micrometer range. They consist of alternating crystalline and amorphous domains as in Figure 18 but with a high degree of crystallinity (around 50-60%). The CNF is generally produced by mechanical delamination of wood pulp before and/or after chemical or enzymatic treatment. The fibrils consist of stretched cellulose chain molecules that forms bundles of different sizes. The surface of the CNF is in its natural form covered with hydroxyl groups which create strong van der Waals and intermolecular hydrogen bonds between hydroxyl groups and oxygens of adjacent molecules which in turn results in a linear configuration[34]. These inter- and intra-chain hydrogen bonds makes cellulose a stable polymer and give its high stiffness but a low flexibility. They will also make the CNF surface easy to modify with a variety of different surface molecules. A common surface modification is carboxymethylation where a carboxymethyl group is added to some of the C6 carbons at the cellulose molecule, inducing a higher surface charge of the fibril[32].

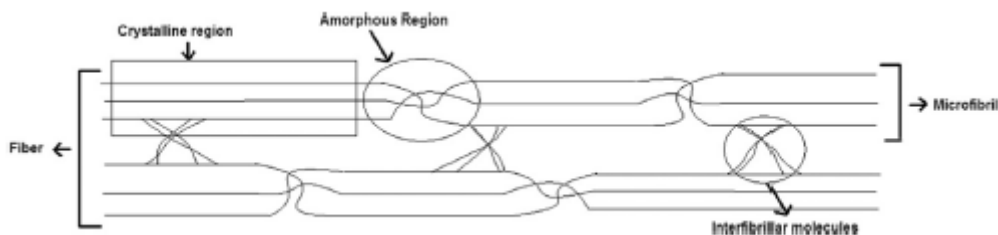


Figure 3: Schematic image of the crystalline and amorphous regions in cellulose.[14]

2.2.2 Cellulose nanocrystals (CNC)

Cellulose nanocrystals (CNC) are whisker or rod shaped particles that remains after an acid hydrolysis of cellulose fibers. The difference to CNF is that CNCs are shorter than the CNF (50-500 nm long)[15] and therefore have a lower aspect ratio. The theoretical tensile strength of CNCs was found to be in the range of 7.5–7.7 GPa[9] which is higher than of CNF. The CNCs will not be used in this work but are mentioned since high sonication forces can degrade CNF to behave more like CNC[4].

2.3 Fabrication

Before the woodfiber is defibrillated into smaller fibrils it is often purified from the other constituents. This process is similar to the pulping process used to make paper where the tree is chopped into pellets and then either mechanically or chemically treated to further separate the wood fibres. The next step is the liberation of the fibrils from the wood fibre cell walls which is not trivial due to the strong hydrogen bonds and VDW-interactions

that binds the fibrils together. Various mechanical methods such as disintegration by a high shear force in a microfluidizer or by high energy sonication have been used but with the drawback that it consumes a lot of energy (roughly 25000 kWh per ton[16]). Therefore the mechanical methods are often complemented by biological or chemical pretreatments such as enzymatic or carboxymethylation. In the enzymatic pretreatment, enzymes (often Endoglucanase or C-cellulase) are introduced that increases the fibre swelling which facilitates a further disintegration[17]. In this report a carboxymethylated cellulose is used. This is a common method often used to replace or introduce functional groups at the surface that blocks the collaborative bonding and introduces osmotic swelling of the fibre wall. This in turn lowers the energy consumption in the mechanical treatment with up to 96% [24]. It is the hydroxyl group at the C6 carbon that is grafted with carboxymethyl which leads to a negative surface charge when the pH is below 3. The number of substituted groups will affect the total surface charge and is described as the degree of substitution(DS) which is the ratio of substituted versus unsubstituted hydroxyl groups. The cellulose molecule after the carboxymethylation can be seen in Figure 4

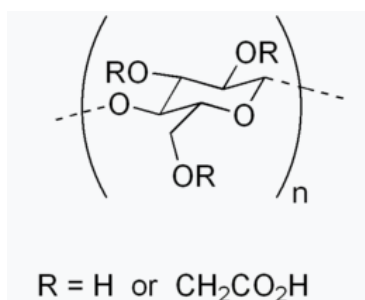


Figure 4: Image of the cellulose unit after carboxymethylation[33]

The first step in carboxymethylation process is to disperse the pulp (Domsjö dissolving plus) in deionized water at 10,000 revolutions in an laboratory reslusher. The fibres are then solvent exchanged to ethanol. The fibres are then impregnated for 30 min with a solution of 10 g of monochloroacetic acid in 500 mL of isopropanol. This carboxymethylation reaction is allowed to continue for 1 h. After the carboxymethylation step, the fibres are filtered and washed in three steps: first with deionized water, then with 0.1 M acetic acid, and finally with deionized water to clean the fibres from chemicals. The fibres are then impregnated with a NaHCO₃ solution (4 wt% solution) to change the counter ion to sodium. Finally, the fibres are washed with deionized water and drained on a funnel. After this treatment, the fibers are homogenized using a high-pressure fluidizer (Microfluidizer M-110EH, Mircofluidics Corp). Homogenization is made at a starting fibre consistency of 2 wt% and an operating pressure of 1,650 bar. Only 1 pass was through the homogenizator made. The 2% dispersion was then diluted to roughly 0.1 wt% which is optimal for film preparation[1]

2.4 Properties

Cellulose has very promising mechanical properties which can be tailored quite easily in the manufacturing process. The fact that cellulose is a biodegradable, abundant and renewable resource also increases its value as a material of the future.

2.4.1 Mechanical properties

The mechanical properties of cellulose fibrils such as the high stiffness[30], high strength and high aspect ratio[28] are really promising for a number of applications and especially when the low density of the fibres (around $1.5-1.6 \text{ g/mm}^3$) are taken into account. The weight normalised values such as the specific stiffness is comparable to that of Kevlar and specific tensile strength is comparable to that of steel[21].

Material	Density (g/cm^3)	Tensile Strength (GPa)	Stiffness (GPa)	References
Kevlar-49 fiber	1.4	3.5	124-130	[21]
Steel wire	7.8	4.1	210	[21]
Carbon nanotubes	-	11-63	270-950	[21]
Carbon fiber	1.8	1.5-5.5	150-500	[21]
Crystalline cellulose	1.6	7.5-7.7	110-220	[21]

Table 1: Properties of different reinforcement materials

Table 1 shows some properties of different reinforcements materials which shows that the cellulose fibril can compete with already commercial materials and especially when the low density is taken into account. The maximum stress values when made into a film are however lower than for the individual fibril and reaches up to around 300 MPa[26] and with a stiffness of up to around 15 GPa[29]. In this report, the mechanical data will be represented as the index values where the grammage of the films are taken into account since this gives a fairer comparison to similar low density materials.

2.4.2 Rheology

The rheology of the CNF is quite unique due to its high aspect ratio and hydrophilicity. Already between 0.5-2% the fluid turns into a gel (viscoelastic solid)[11] as seen in Figure 5. CNF also shows a shear thinning behaviour [23] and can be concluded as a pseudo plastic material. This behaviour is because at a critical shear rate, the nanocrystals align due to their rod like nature which make them flow easier[23]. The relaxation time is highly dependent on the aspect ratio. Higher aspect ratio means that the fibres stay aligned longer after shear.



Figure 5: Image of cellulose at 2%[36]

2.4.3 Optical properties

The optical properties are very important in several applications in the food- and packaging industry since it is desirable to use additives that are transparent. Since materials smaller than one tenth of the visible light are not expected to scatter light, and since the CNF are only a few nm in diameter, they appear almost transparent when in a film. The optical properties are highly dependant on the fabrication method since it strongly affect the sizes of the particles in the end.

2.4.4 Barrier properties

To qualify as a suitable barrier in packages a low permeability of both oxygen and water vapour is needed to protect the package content. Today, the most common barrier materials in packages are aluminium in combination with plastics such as PE and PET since they are relatively cheap and provides a very good oxygen and moisture barrier when combined. These materials are however, often associated with a large carbon footprint and can be difficult to recycle. An alternative for encapsulation and packaging materials is therefore CNF since the environmental impact is indeed lower than of synthetic polymers. The permeability of CNF to oxygen at 23°C and 0% relative humidity (RH) is equal to $0.0009 \text{ cm}^3\text{mm}/\text{m}^2/\text{day}/\text{bar}$ [1] which is more than 1000 times lower than Poly ethylene terephthalate (PET) and also below the desired gas transmission rates for modified atmosphere packaging which is of the order of a few $\text{cm}^3\text{mm}/\text{m}^2/\text{day}/\text{bar}$. It is believed that this low permeability is linked to the dense networks held together by hydrogen bonds/VdW-interactions in combination with the relatively high crystallinity. This means that a compact structure is formed with almost all of the cellulose fibres in one plane resulting in a physical barrier for permeating molecules. The permeability is however compromised in a humid environment which disrupts the ordered hydrogen bond network and swells the CNF network of the film which results in a less dense material with considerable higher permeability.[2]

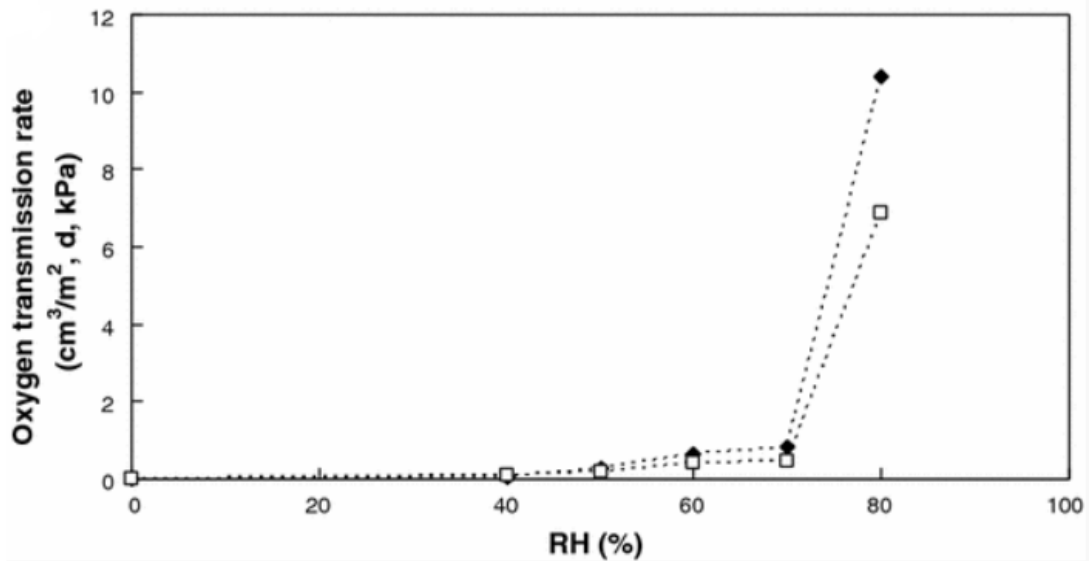


Figure 6: Effect of relative humidity (% RH) on oxygen transmission rate (OTR) of CNF films with grammages of 5 (filled diamond) and 8 (open square) g/m²[1]

As can be seen in Figure 6, the OTR is increasing rapidly at around 60% RH. This is due to the strict hydrophilic nature of the CNF films which causes the films to easily absorb water from the surroundings and thus resulting in weakened bonds between the fibrils. This creates a more flexible network but lowers the physical barrier for permeating molecules[20]. This is the big drawback of CNF as an oxygen barrier and therefore several studies have tried to decrease the OTR by the use of nanoclay[2], coatings[12] and thermal treatments[27]. This RH dependant behaviour does not occur for many polymers as can be seen in Figure 7

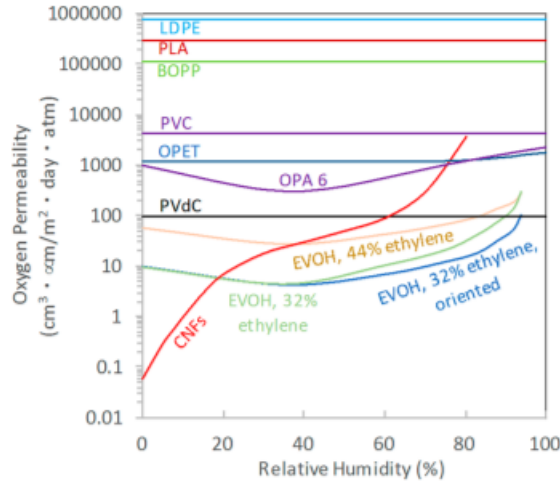


Figure 7: Graph of how the RH affects the oxygen permeability of different materials[12].

Due to the strong hydrophilicity of CNF - especially of the grades with a high DS - the same phenomenon as for the oxygen permeability occurs for the water vapor permeability as can be seen in Figure 8. When the material comes in contact with a higher RH, the -OH groups will attract the water molecules and cause a swelling that will weaken the water vapour barrier dramatically.

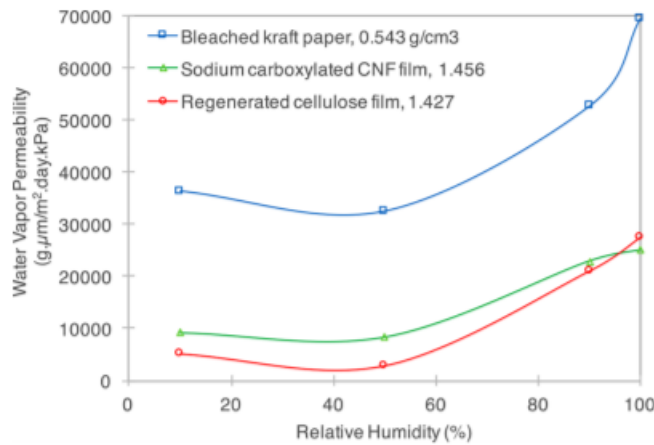


Figure 8: Effect of the relative humidity at the water vapor permeability of different cellulose films[12].

2.4.5 Thermal properties

Thermal degradation of cellulose materials and the reduction of mechanical properties at elevated temperatures is one limiting factor of using CNF in some applications. The thermal degradation onset is somewhere between 200-300 °C which limits some processing methods. However, the coefficient of thermal expansion (CTE) is of crystalline cellulose estimated as low as around 0.1 ppm/K [21] which make CNF well suited for usage in composite structures when a low CTE is desirable such as for flexible displays.

2.5 Applications

In the literature there are several applications for nanocellulose and here are some of the most commonly mentioned applications[16][21][6].

- Paper and paperboard applications, such as dry reinforcement and surface strength enhancer, due to good mechanical properties
- Absorbent products, due to the hydrophilic properties and swelling capacity
- Food and cosmetic applications, since CNF is nontoxic and have beneficial rheological properties
- Nanostructured foams. CNF can be freeze dried and create an entangled network as a foam.
- Coatings and membranes, due to its excellent gas barrier properties.

2.6 Graphene

Another material that have gained a lot of attention for its extraordinary properties such as its thermal, mechanical, and electrical properties is graphene. This two dimensional, honeycomb structured carbon material has shown great potential as sensors, carbon based electronics as well as an reinforcement material in composites. Graphene is also highly hydrophobic and impermeable which makes it a theoretical candidate to enhance the water vapour barrier in CNF films. Graphene in its purest form consists only of a single layer of carbon arranged in a hexagonal lattice with sp² hybridized σ -bonds in the plane and π -bonds out of the lattice plane. Many studies have explored the compatibility of CNF and graphene and found increased mechanical properties of the cellulose even at around 1% addition of graphene[5] and also at at RH up to 80% [19]. However, since graphene on the commercial market have different qualities and specifications it can be difficult to know how a specific products will behave. Since not much previous work have been done with the below mentioned graphene, exploratory tests are made to try to define how the different parameters affect the film properties and the CNF-GNs interaction. The GNs used in this study comes from Nanoinnova technologies and the main one is Graphenite-OX but the (Graphenite XL) is also used. Some of the graphene parameters of the graphene can be seen in Table 2 but the most significant differences is that OX has a higher oxygen content and has smaller flakes. Due to its size, graphene can be potentially dangerous to inhale so therefore strong precautions such as breathing mask, gloves and safety glasses are used in order to minimize contact with the graphene powder.

Material	O content	Bulk density	BET surface area	Sheet length	Layers
Graphenit-OX	2.28 wt%	0.2 g/ml	110 m ² /g	4 μ m	<5
Graphenit-XL	1.05 wt%	0.04 g/ml	N/A	40 μ m	5-10

Table 2: Properties of the GNs as reported by supplier

2.6.1 Dispersion of graphene

Graphene has a very low solubility in water whereas graphene oxide on the other hand is easier to dissolve. The reason for that is because, having oxygen atoms inserted somewhat reduces the repulsive Van der Waals forces by increasing the distance between the layers[31]. Getting a good dispersion is however of high importance to make sure that the resulting film is homogeneous and that the graphene is well exfoliated. The goal is to get as many CNF as possible to stick to the graphene surface so that the charges could electrostatically stabilise the GNs. The mechanisms behind what makes the CNF stabilise the graphene is not yet fully understood but it is believed that the CNF will attach to the GNs surface owe to the hydrophobic interaction occurring between the hydrophobic faces of the CNF and hydrophobic plane of GNs. There will also be an attractive interaction between the sp^2 carbon lattice and the fluctuation of counterions at the CNF[37]. If the CNF is above the critical concentration where it can form a network in the solution (around 0.1%)[7], this might also help to stabilize the graphene by trapping the GNs in the network.

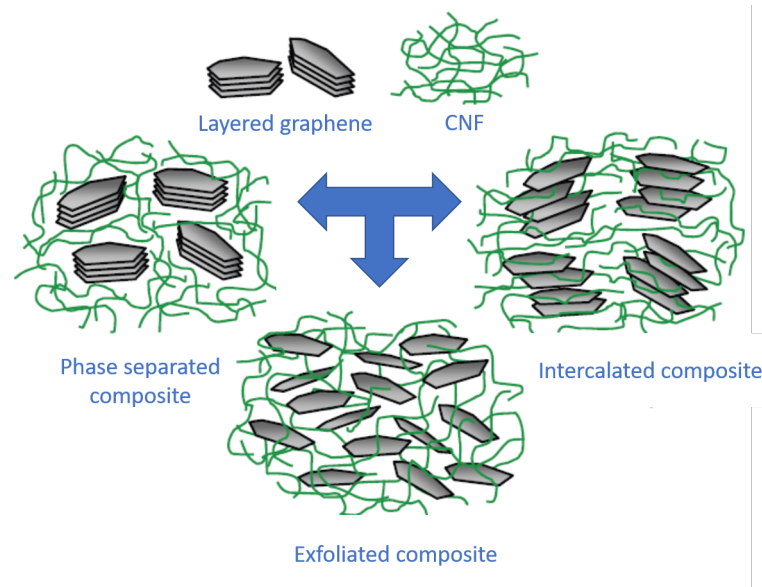


Figure 9: Image of different types of dispersions[8]

It is also important to get a well ordered structure (as in Figure 9 of the GNs to be able to increase the tortuosity in the produced films and therefore enhance the barrier properties. As can be seen in Figure 10 below, a GNs network with big and thin flakes that are ordered gives a better barrier than smaller, un-ordered and thicker flakes.

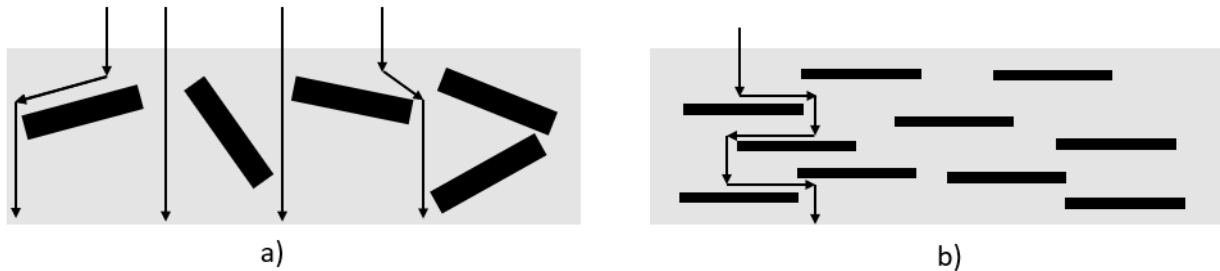


Figure 10: Image of how the tortuous path is changed dependent on the platelet size and orientation

3 Method

3.1 Choice of material

A study has shown that nanocellulose can stabilize carbon nanotubes (CNTs) by inducing dipoles in the sp^2 carbon lattice surface at the CNTs. This is hypothesised to be caused by a fluctuation of the counterions at the surface of the nanocellulose[10]. The charges on the nanocellulose will also induce an electrostatic stabilisation of the CNF-GNs complexes that will prevent aggregation. Based on this it was believed that a higher charged CNF would interact more with the graphene surface and therefore be able to stabilise more of it. This is why the highly charged nanocellulose DS03 was chosen. Since the nanocellulose reaches the concentration where it can form a network in the water at around 0.1% [7] this is the desired concentration for this project since a higher concentration will increase in viscosity quite fast and make the dispersion more difficult and with a lower concentration the network stabilization effect might be lost. The choices of the graphene were made simply by the desire to evaluate how different oxygen content and different sizes would affect the barrier properties. All experiments used ultrapure Milli-Q water with a resistivity of $0.055 \mu S/cm^1$ ($18.2 M\sigma$) and a total organic content of 3 ppb.

3.2 Experimental methods

3.2.1 Sonication

As mentioned above, some sorts of graphene can be difficult to disperse in water. To do this requires a strong force that manages to overcome the repellent force so the graphene and CNF come in contact. One powerful way to do this is to use an ultrasonication probe. Ultrasonication is a process that agitates particles in a sample by applying sound energy. In this case, the sound energy forces the GNs agglomerates that are formed when in contact with water to break up so that the individual GNs come in contact with the CNF. The machine used is a Sonics vibra-cell VCX-750 and two different sizes of sonication probes. The parameters that can be modulated except the probe size is the amplitude, the sonication time and if a pulse function shall be used. The amplitude affects the energy

that is used but a high amplitude will also damage the probe more. The longer sonication time in combination with a high amplitude will also increase the dispersion energy but a too long time with high amplitude will generate a lot of heat and also possibly damage the particles. To make the sonication a bit milder a pulse function can be used so that pulses of sonication is alternated with some time of rest.

3.2.2 Polytron & Magnetic stirring

A Polytron (seen in Figure 11) is a mechanical stirrer that rotates very fast in order to mechanically shear the particles apart. This method may also damage the particles and generate heat so therefore it is only used for a limited time. The RPM used in this report is 23500.

Magnetic stirring is a very gentle process where a magnet is rotated under the influence of a rotating magnetic field. This was always used at the CNF to keep it dissolved and it was also examined if it could be used to disperse GNs in CNF without destroying the particles.



Figure 11: Image of the Polytron used in this experiment

3.2.3 Vacuum filtration

To make the films, a vacuum filtration method was used. The set up is a filter funnel connected to a vacuum pump that sucks the water through a filter membrane so that a film with nanocellulose and graphene is left on the filterpaper. The filter paper used is a Durapore with a pore size of 650 nm but even if the particles used are smaller, they still form a network so only the water can penetrate through. After filtration the sample was dried in room temperature to pre-dry and then 8 hours in 50 °C. To limit the shrinking

and wrinkling of the film, it was fixated along the edges so the films were not allowed to shrink in planar direction but only in the vertical during the drying process.

3.2.4 Coating

Since the vacuum filtration process is fairly slow and not so easy to scale up and make industrially feasible, some short experiments were made to coat cardboard using a blade coater. Blade coating is one of many coating processes that aims to get a thin layer of a material to cover a substrate by using a blade to spread out the material. The advantages is that it is a simple and easily operated process to get a very smooth and plain surface but the drawback is that only very thin layers can be coated and especially for CNF due to its high viscosity already at low concentrations. The bar coater looks like in Figure 12 and the procedure is that a piece of cardboard that will be coated is fastened at the top and then a wire bar with $1000\mu\text{m}$ deep slits are attached with hooks over the cardboard. A small amount of fluid is then applied in front of the wire bar so that it spreads an evenly thick layer at the cardboard paper.

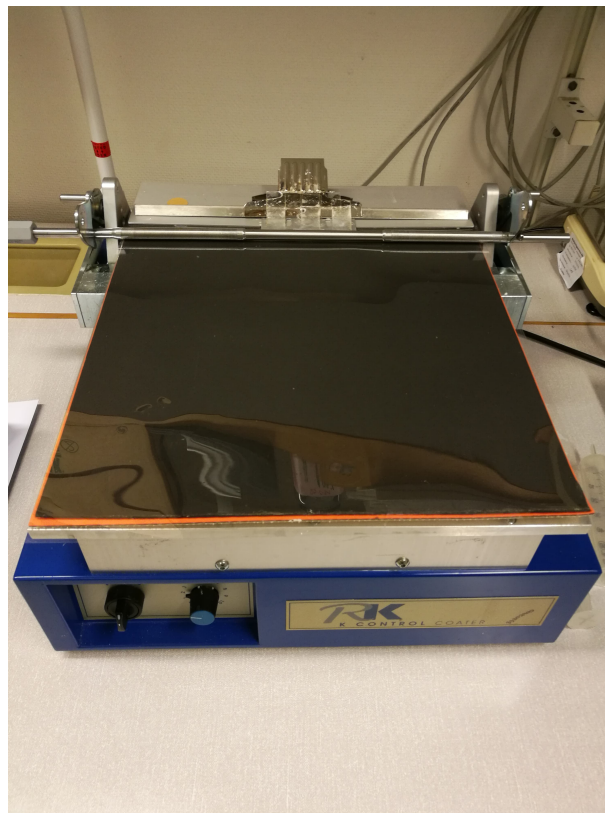


Figure 12: Image of the bar coater used in this experiment

3.3 Analysis methods

3.3.1 Mechanical testing

The interesting properties are the tensile strength, stiffness and strain which will give a good indication of how the CNF and GNs interact in the film. The tensile strength indicates how much load the material can withstand without breaking and is normally measured in Pa. Due to the porosity of the nanocellulose films (between $1 - 1.5g/cm^3$) a common unit is however kNm/kg which gives the strength per density. This is to make a fair comparison to heavier materials such as steel. The stiffness is to which extent the material can resist deformation when a force is applied[3] (“Stiffness” = “Load” divided by “Deformation”). Also this is sometimes mentioned as an index which takes the density in to consideration. The strain is how much the material can be tolerated to elongate before it breaks. In this report it is reported as a percent elongation of the original length. Since the nanocellulose particles consists of a very linear polymer in a crystalline arrangement the behaviour is normally fairly stiff with strain up to around 10 percent.

The tensile tester (MTS 400/M) was equipped with a 500 N load cell and the films were conditioned for at least 24 h prior to testing in 50% RH and the temperature 23 °C. The gap distance was 30 mm and the average width was 6 mm. The strain rate was 10%/min. Specimens from the films were made by punching strips with a length of 40 mm using a sharp puncher. At least 4 specimens were measured from each sample.

3.3.2 UV-vis

Ultraviolet-visible spectroscopy (UV-vis) refers to a spectroscopy method that uses visible light as well as light in adjacent wave length regions. The machine used in this report is a PerkinElmer PDA UV/vis Lambda 265. Molecules that contain π - or non-bonding electrons are able to absorb the energy from UV or visible light to excite these electrons to higher anti-bonding molecular orbitals. A lower energy gap between the two energy levels will result in longer absorbed wavelengths. The result will be that different materials absorb different wavelengths dependent on the composition. The formation of stable graphene dispersions from graphene oxide (GO) enables the process to be monitored using UV-vis spectroscopy[17]. As shown in Figure 13, the absorbance curve is red shifted from 231nm for GO to 270 for graphene which suggests that the electronic conjugation within the graphene sheets is restored.

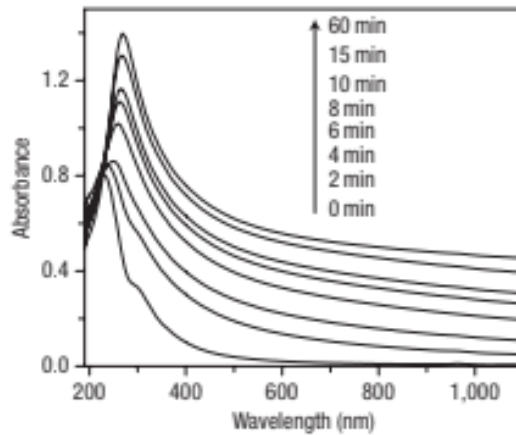


Figure 13: Figure showing the redshift of the absorbance curve when GO is reduced to graphene[17]

The intensity is also increasing over time which indicates that the sheets have been exfoliated, making the GNs thinner, increasing the number of sheets and hence the specific surface area. This means that these measurements can give an indication of both how the chemical composition is and also how well exfoliated the graphene is in the dispersion. The measurement can be useful to a variety of application such as giving data of the composition of a solution, measuring the transmittance T or as in the case of this report, make a comparison of the different GNs-CNF dispersion. The method is usually conducted on a liquid and simply measures the intensity I as a function of the wavelength of a transmitted, monochromatic beam through a sample as a comparison to the intensity of a reference sample I_0 . The transmittance T will decrease exponentially as a function of the added content of "contaminant" so to simplify the comparison of the samples, the absorbance spectrum will be used instead since it is $abs = -\log T$ and therefore scales linearly. In this report UV-vis is used as a measurement of the degree of dispersion of GNs in the CNF by comparing the different spectrum. Due to the very high absorbance of graphene, some of the samples with high GNs content needed to be diluted in order to get a high enough transmittance signal that could be measured. To confirm the linearity, different concentrations of GNs-CNF solution was diluted with different ratios milliq water and then recalculated to the actual value which turned out to be the same for the different measurements. In Figure 14, this linearity is shown when different dilutions show proportionally lower absorbance signal in comparison to the degree of dilution.

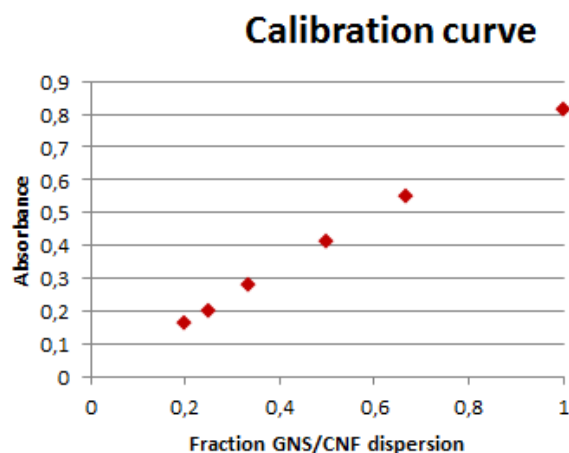


Figure 14: Absorbance as a function as different dilutions of the CNF/GNs solution.

3.3.3 Water vapour barrier

The water vapour transmission rate (WVTR) is a measurement of how much water vapour that can penetrate through a sample. This is very important to be able to limit in many industries such as packaging- and pharma industry where tight packages that maintains a controlled and stable environment for the content is needed. The machine used is a MOCON Aquatran and the set up consists of two chambers with the test sample dividing the two chambers and can be seen in Figure 15. On one side, water vapour flows at a predetermined temperature and relative humidity (RH). On the other side the RH is close to zero and it has a constant flow of nitrogen gas that transports the permeated water molecule away. The difference in water vapour content creates a humidity gradient that drives the water through the barrier sample. In the test with 23° and RH 50, the water vapour pressure was 0,01387 atm and at 23° RH 80 it was 0,02219 atm[18]. The amount of transmitted molecules through the sample was measured at the other side as $g/m^2/day$. A typical value of aluminium that are currently used as barrier in packages is as low as $0.001 g/m^2/day$ whereas for a fabric it can be several thousand $g/m^2/day$ [35].

Diagrammatic side view of WWTR test cell

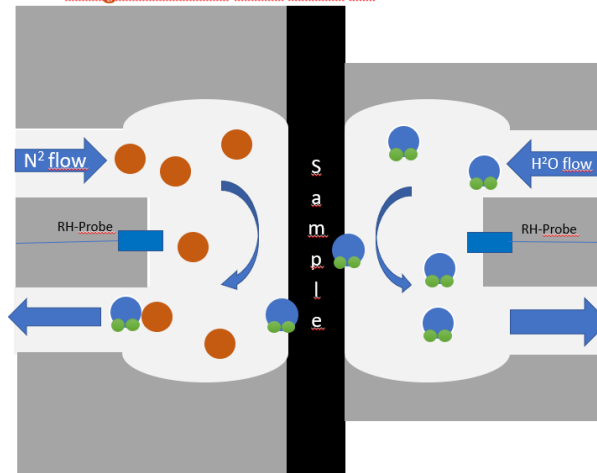


Figure 15: Schematic image of the WVTR measurement

3.3.4 SEM

Scanning electron microscope (SEM) is used to create images of the samples using the detection of electrons after they have interacted with the substrate. Before the samples are loaded into the SEM (Hitachi JU3500), they are coated with gold using a sputter machine to increase the conductivity and to avoid sample damage from the electron beam. The gold particles are roughly 5nm in size and can be seen at 30 000x magnification. The samples were glued on a conductive carbon tape are then viewed one by one and images are taken at different focus. Both the top and the bottom of the samples are examined to see the difference between them. The acceleration voltage used is 7kV to give a high resolution without risking sample damages. In SEM different types of electrons can be examined dependent on what information that is interesting. In this report only the secondary electrons (electrons emitted from atoms excited from the electron beam) are used since the topography of the sample is of interest.

3.3.5 Conductive tests

Since some of the films made in this project consists a relatively high fraction graphene, it is of interest to see if the high conductance from the graphene is kept when the CNF is introduced. The result can also give interesting results regarding how well the materials are mixed and also if any sedimentation occurs during the vacuum filtration. A simple four probe measurement consisting of a power supply with a high inimpedance and a simple measuring probe with two measuring channels for the current and voltage each. In a four probe measurement the current is applied between the two outer channels while the voltage is measured between the two inner ones to eliminate the contact resistance. To be able to compare the samples to each other they are punched out from the film so they have the same width (6mm).

4 Experiment & Results

4.1 Experimental structure

The purpose with this thesis is to obtain a better understanding of how different parameters affect the properties of films consisting of CNF and GNs. Since not much work has been done previously at Rise Innventia regarding dispersion of graphene and CNF before, the first parameter that was changed was the CNF-GNs ratio in order to establish a "preferred" ratio to continue to test with and also to see how the graphene affects the cellulose. After this first screening, the focus was guided towards evaluating the quality of the dispersions and what affects it so therefore the sonication time was changed as a second step. A step to make the films more homogeneous were also taken by fractionate the dispersions using a centrifuge after sonication to remove big agglomerates. The third parameter that was explored was what effects different GNs would have on the film properties. Some work was also done in collaboration with BillerudKorsnäs who were interested in possibilities to scale up the process. Therefore, some tries with different dispersion methods and coating were conducted at the end. The same experiments were not conducted with the different parameters due to a shortage of time and also due to the fact that previous experiments showed that some experiments were more promising than others. The following section is divided into parts in accordance to the different parameters that were changed rather than a chronological order to make it easier to discuss the variations later in the reflective part.

4.2 Nomenclature

To make the understanding of the results easier the report follows a strict nomenclature when presenting the different tests made. A test refers to a dispersion and a name could be written as 50XL30 as an example. The first number is the weight percent of GNs in the sample, the upcoming two letters is the type of graphene used (either OX or XL) and the last number is how long the dispersion was sonicated for. Exceptions to this nomenclature can be when a different dispersing method is used (magnetic stirring is shortened MAG and the polytron is shortened TOR as in TORAX) or when different nanocelluloses were used. DS01 represents 0.1 in degree of substitution and DS03 represents 0.3.

4.3 Prologue experiment

Before starting to use graphene which is very expensive and also difficult to handle, tests were made to make sure that the method worked and to build up an understanding of how the films behaved under the manufacturing process. The first films of pure CNF were made as a reference for later and also to try out the different testing techniques such as the tensile tester to find out possible sources of error and eliminate them. The technique of how the films should be handled to avoid wrinkling and breaking takes some tries to understand so the initial experiments were only to make sure that the process would be

sustainable and could produce films with a high accuracy. When these techniques were understood, the experiment with graphene could start.

4.4 Modify the graphene content

4.4.1 Experiment and overview

When the vacuum filtration technique was understood, the experiment continued with a screening of how different ratios of graphene added to the CNF affected the properties. The purpose was to first find out if it was possible to make films with GNs and if it was, then explore how the properties could be customised. It was decided to try the full spectrum of ratios from 0% to 100% GNs to make a survey that could function as a possible base to decide the next step. The process began with the weighing of the GNs. The amounts in the process look as in Table 3. Due to the low density and antistatic behaviour of graphene some measures were taken to make the weighing easier. An antistatic bracelet was used and the graphene was put in an aluminium beaker to avoid that static electricity affected the graphene. The graphene was then mixed together with the CNF in the ratios mentioned below in Table 3 and sonicated for five minutes with 5 second pulses. The resulting dispersions were then put in vacuum filtration but ca 40ml were used for analysis. To characterise the solutions, UV-vis measurements were made before and after centrifugation of the 40ml volume and the concentration was also measured before and after in order to get an indication of how much graphene that was stabilised. When the films had roughly 90% water content they were removed from the vacuum filtration and laid to air dry before they were fixated along the edges to avoid shrinkage and then finally put into the oven for 50°C over night. Before the films were tensile tested, they were conditioned in a room with constant temperature (23°C) and relative humidity (50%). The one with pure graphene did not create a film but left only graphene powder on the filter paper so that is why no tests were able to be conducted at the pure graphene. All of the other ratios turned out as nice and easy to handle films.

Sample name	100CNF5	4OX5	10OX5	50OX5	80OX5	100OX5
Dry weight GNS (mg)	0	12	29	142	250	300
CNF volume (ml)	300	288	271	158	50	0
Volume milliQ (ml)	0	22	29	142	250	300
Sonication time (min)	5	5	5	5	5	5
Vacuum filtration time	~8h	~8h	~8h	~12h	~12h	5s
Film thickness (μm)	35	29	29	25	24	N/A
Grammage (g/m^2)	35,4	29,6	32,1	27,56	22,11	N/A
Density (kg/m^3)	1009	1038	1095	1082	921	N/A

Table 3: Overview of the materials used and the film properties.

4.4.2 Optical analysis

Images were taken with an optical microscope (DINO-lite digital microscope) in order to see if there were any clear differences at the surface. As can be seen in Figure 16a, big fibrils of around 1-2 μm in length are clearly visible which indicates that some of the nanocellulose fibrils have not defibrillated completely in the homogenisation process. Figure 16b shows that the films are not homogeneous but that the GNs tend to gather at the bottom of the film during the slow filtration process. The graphene strongly limit the transparency of the films in comparison to the pure CNF film but in the case with the 4OX5 one, it is possible to see through it if it is held up towards a light source. The images from the other films can be seen in Appendix A.1.

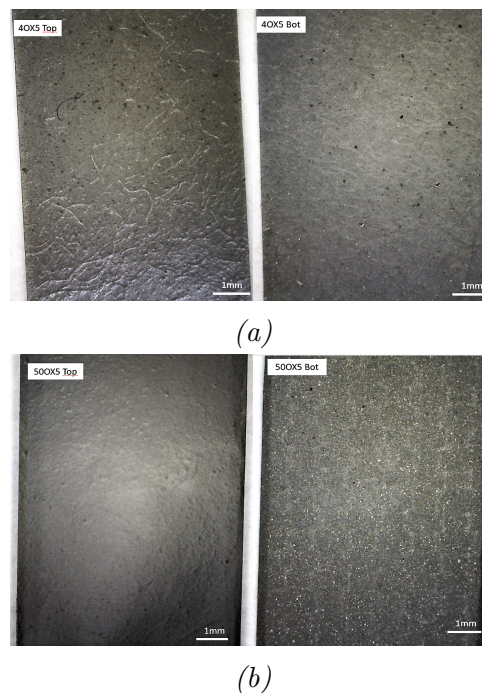


Figure 16: Microscope images of GNs/CNF composite with (a) 4% and (b) 50%

4.4.3 Mechanical testing

This first test shows that small amounts of added GNs doesn't affect the tensile strength or the tensile stiffness in any significant way. The strain at break is however lowered significantly which can be expected since the GNs are very stiff. A higher addition of GNs (50% and above) affects the tensile strength and stiffness in a more significant manner. This could be due to an inhomogeneous film that gets weaker because of the presence of big graphene agglomerates but also possibly because the CNF-GNs interactions are not as strong as the CNF-CNF ones. The reason why no tests are showed for the 100OX5 is because it did not form a film that could be measured. (Obs that only one film was tested per dispersion)

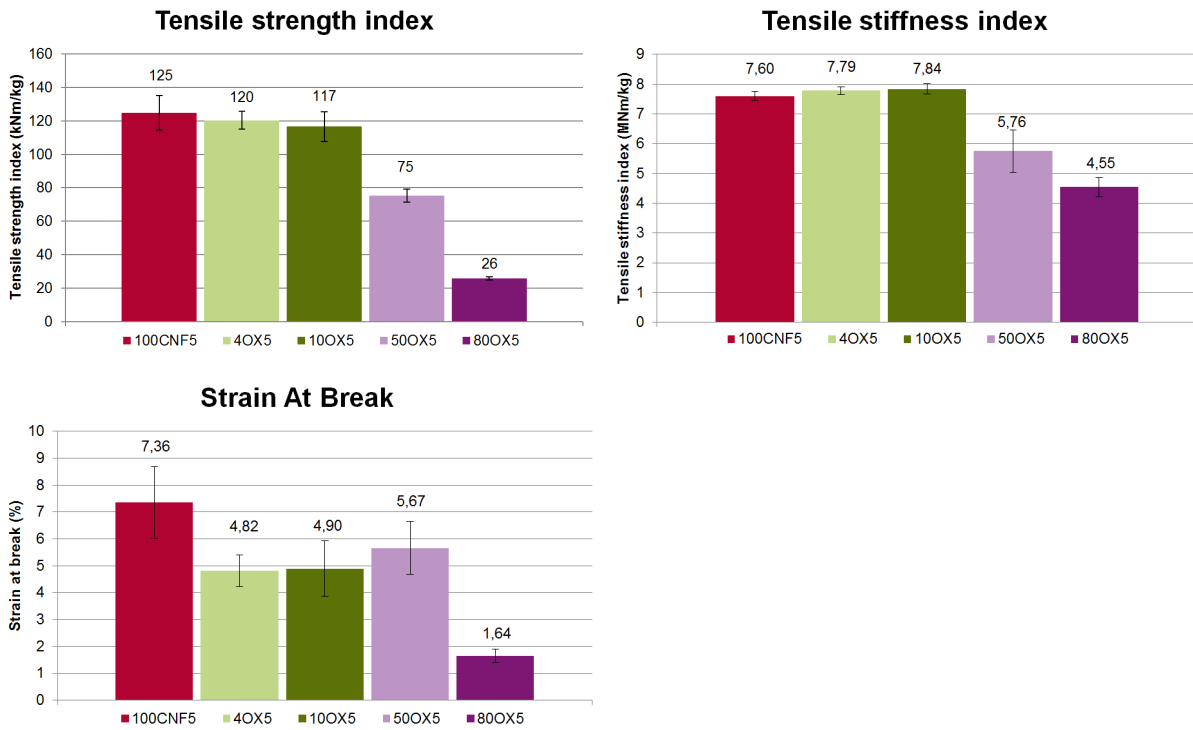


Figure 17: Mechanical properties of CNF/GNs composite films with different weight ratios

4.4.4 Swelling

To measure the absorbability of water, the samples were soaked in water for 15 minutes and weighed before and after an approximation of how much water they have absorbed. The results show very small differences in swelling as a function of the added GNs content until the 80OX5. This might be because the graphene itself is not as hydrophobe due to the higher oxygen content and therefore doesn't limit the absorption in any significant manner until it is added in a clear abundance. The fact that there isn't a clear decrease until 80% is however interesting since it indicates that there is some kind of percolation threshold that needs to be exceeded before the GNs starts to limit the absorbance. If the films would stay in water for a longer time they would dissolve completely.

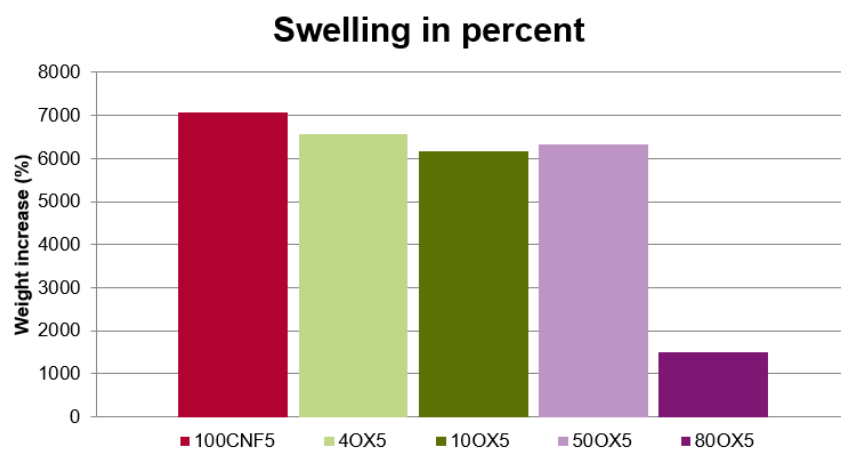


Figure 18: Diagram showing the swelling of CNF with different GNs ratios.

4.4.5 UV-vis

The evaluation of the dispersions were made using absorbance measurements with UV-vis since it scales according to how dark the sample is. The curves of 4OX5 and 10OX5 are shown in Figure 19 where the filled lines shows the dispersions before centrifugation whereas the dashed lines indicates after centrifugation. It is clear that a big portion of the graphene is lost in both cases. The curves does not show any peak at around 270nm which could mean that the structure is more graphite like or damaged during the sonication. The before centrifugation curve for 10% is around 3 times higher which seems reasonable since it is about 3 times more graphene in that dispersion.

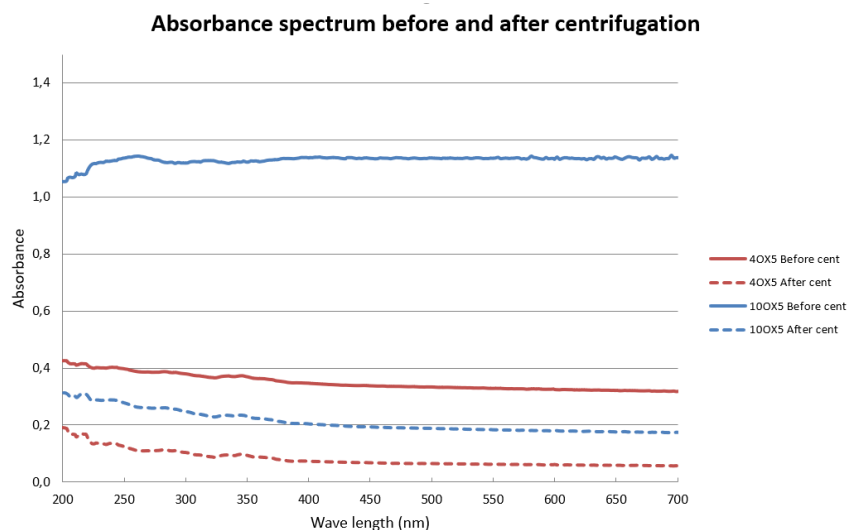


Figure 19: Absorbance curves of 4% and 10% addition of GNs.

In Figure 20 all of the samples absorbance values at 400nm are plotted. The dashed grey line is the absorbance value the dispersions would have had if they scaled proportionally to 4OX5. This is not the case of the dispersions with the highest graphene content which

could indicate that the GNs in those are more agglomerated still and should have been sonicated longer.

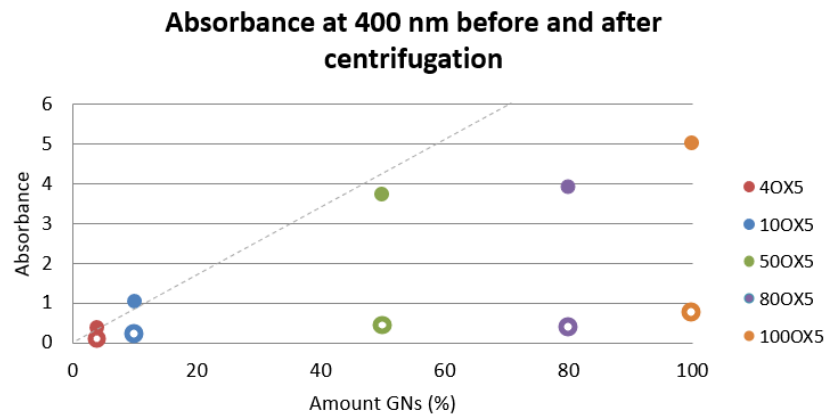


Figure 20: Absorbance at 400 nm all samples. Filled circles are before centrifugation and rings are after centrifugation.

By calculating the decrease in absorbance after centrifugation compared to before, an estimation of the quality of the dispersion can be made. As can be seen in Figure 21, a bigger fraction is lost when more graphene is added which further confirms that the sonication time should be increased if more material is added. The fact that the amount of graphene that is lost in pure water compared to in CNF is not significantly lower indicate that the CNF does not promote a better dispersion with this type of graphene.

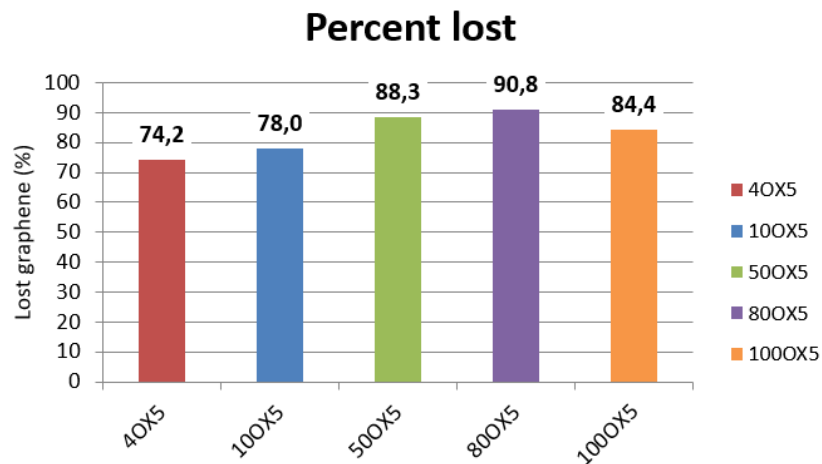


Figure 21: Amount of graphene lost according to the absorbance signal.

4.4.6 WVP

The water vapour permeability measurements only showed small changes with additions up to 50% but a big increase for the film with 80% graphene. Since the tests were only run at one sample, the margin of error could be fairly big but it is still clear that the

addition of this type of graphene did not enhance the barrier properties in any significant manner (Figure 22). The bad barrier of the 80OX5 might be due to inhomogenous zones that disturbs the order of the material and therefore result in a more permeable film.

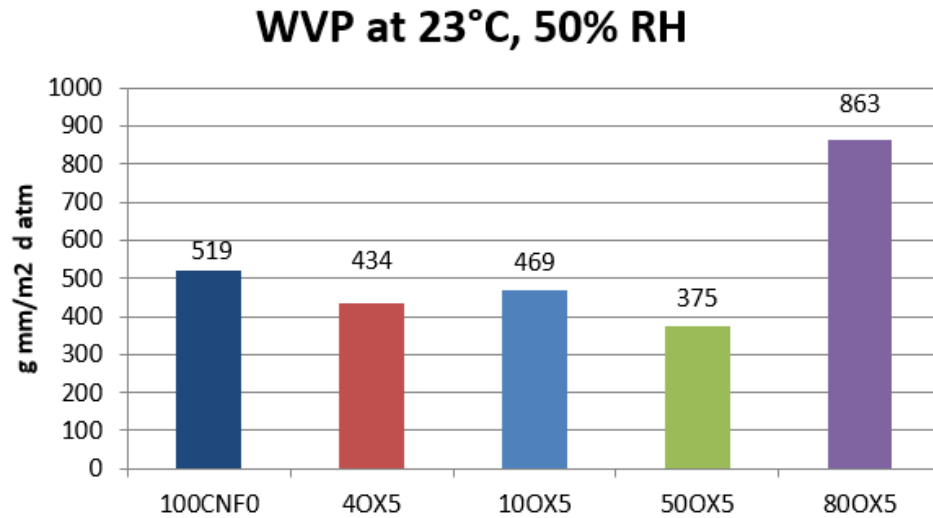


Figure 22: Diagram showing the water vapour permeability of CNF films with different ratio GNs.

Since the swelling tests indicated that the graphene did not prohibit swelling of the CNF, the relatively bad barrier properties is probably due to the fact that the fibres swell even at low RH and that the addition of GNs probably affects the arrangement of CNF.

4.4.7 SEM

The SEM images (shown in Figure 23) indicates a change in surface structure between the different films. The difference between the 100CNF0 and 4OX5 in terms of the number of bigger fibres which could show that the larger fibres defibrillate even at lower sonication times such as 5 minutes. In the samples with GNs, the increase in GNs can clearly be seen between the images and the nanocellulose can also be seen as a smoothing layer in the samples with CNF. In the 10OX5 one the GNs are seen independently and the sheets seem to be around 5 μm in size which corresponds to the data sheet provided by the supplier about the graphene. The increased amount of graphene can clearly be seen as a rougher surface which might be caused from bigger agglomerates that have not been separated in the sonication process.

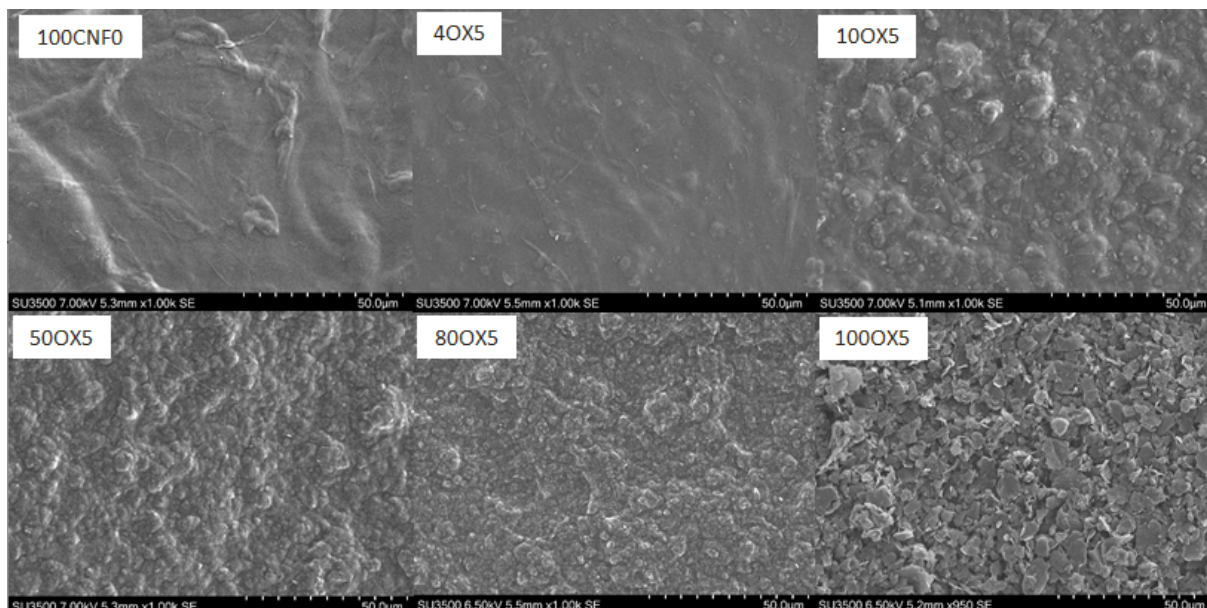


Figure 23: SEM images of the top side of CNF/GNs hybrid films. $\times 1000$ magnification

Also the SEM images shows a difference between the top and the bottom side of the films. Both the fact that it was easier to take high resolution images at the bottom side which indicates a higher conductivity hence a higher graphene content. Another difference was that the bottom of the films showed some damage in shape of a thin layer that looked cracked, shown clearly in 100CNF0 in Figure 24. This thin film is believed to be the thin layer of nanocellulose that is formed at the filter paper interface and that it is partly destroyed when the film is removed from the filter paper. The poor barrier properties of the 800X5 might be explained with the inhomogenous distribution of nanocellulose as can be seen in Figure 24

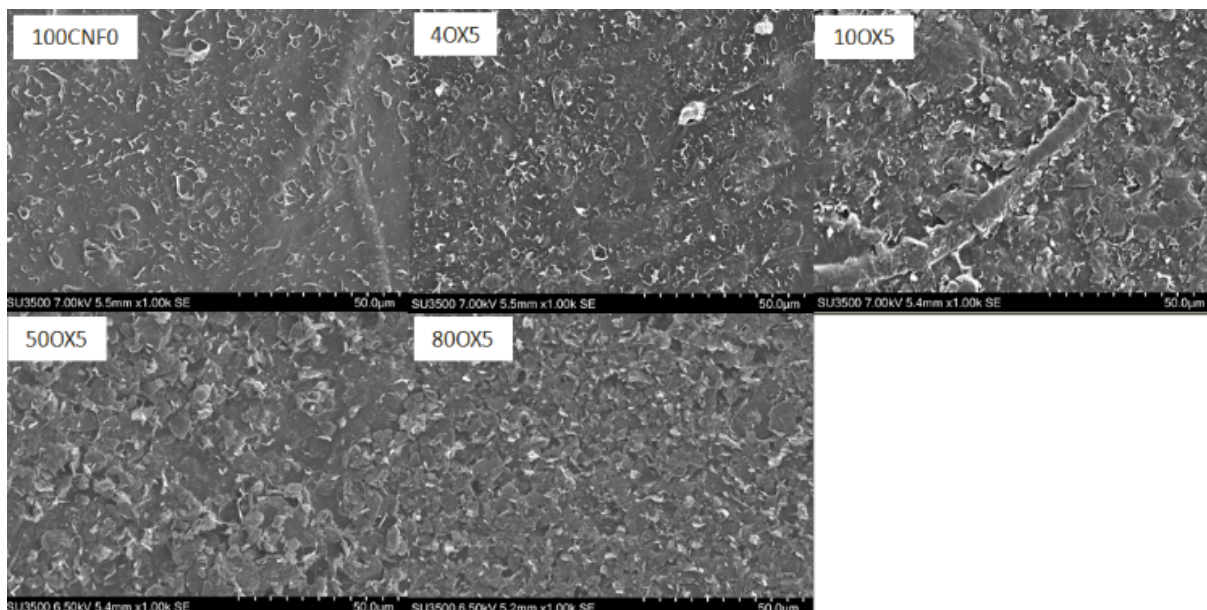


Figure 24: SEM images of the bottom side of CNF/GNs composite films. $\times 1000$ magnification

The reason why there is no 100OX5 bottom image is because it is only a powder at the surface of the filter paper. The top of the filter paper can instead be seen in Figure 25 where a scrape mark shows the powder structure. This clearly shows the benefit of using CNF as a film matrix material.

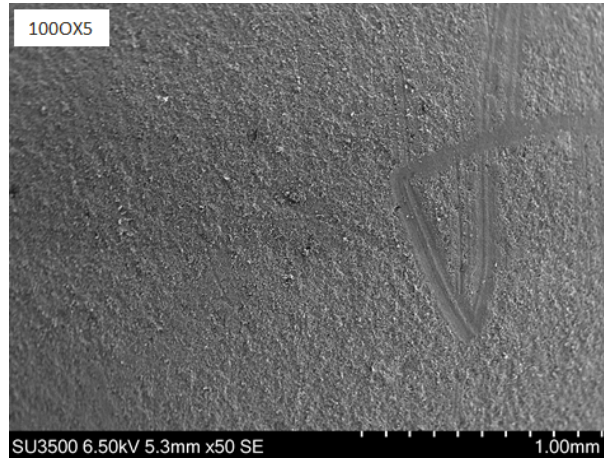


Figure 25: SEM images of the top side of the 100OX5 film. x50 magnification

4.4.8 Conductive tests

In an experiment to try to confirm the inhomogeneity of the films, resistance measurements were made. As can be seen in Figure 26, especially the films with the highest graphene content showed a strong tendency to conduct more at the bottom side due to the excess of graphene. This is a clear indication that the undispersed graphene sinks to the bottom during the vacuum filtration.

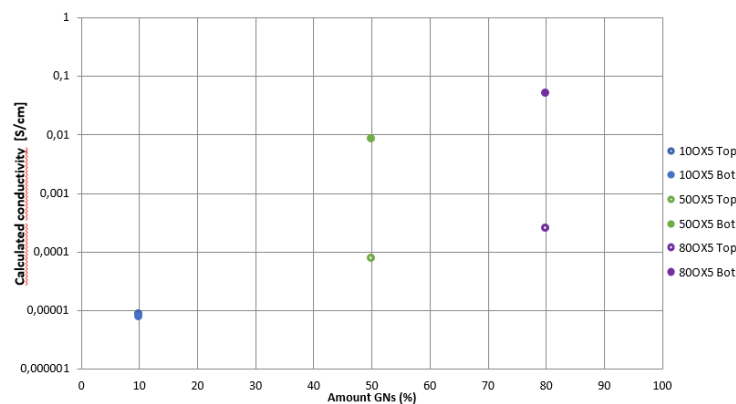


Figure 26: The calculated conductivity of the top and bottom side of the films with highest GNs content.

4.4.9 Conclusion different graphene ratios

The experiment with the different graphene contents could successfully show that it is possible to add up to 80% GNs to a nanocellulose film and still be able to handle it

as a film. The addition of graphene did not show any significant improvements of the mechanical properties but rather the contrary and the same for the barrier properties. This was believed to be due to the unstable dispersion that resulted in an inhomogenous film that was confirmed in the SEM and conductive tests. The different dispersions did not exfoliate properly according to the UV-vis experiment so the sonication time should probably be increased dependent on the amount of graphene in the sample. The next step in the project was to try to improve the dispersion quality by increasing the sonication time and also by centrifuge the dispersion before vacuum filtration.

4.5 Different sonication times

4.5.1 Experiment and overview

Since the experiment with the different ratios of graphene didn't affect the mechanical properties in the desired direction the hypothesis was that it might depend on the quality of the dispersion. Also the fact that after sonication the solution remained fairly turbid and unstable made us to further investigate if a better dispersed graphene could increase the properties of the films. In order to get a better dispersed film, a longer sonication time was investigated to increase the energy with which the GNs and the CNF where dispersed. The experiment was conducted at a 50% GNs sample to see how the stabilisation of the graphene was affected. In order to evaluate the effect the sonication had, the pure CNF was sonicated for 5, 10 and 30 minutes.

Sample name	Sonication time (min)	Graphene content (%)
100CNF0	0	0
100CNF5	5	0
100CNF30	30	0
50OX5	5	50
50OX30	30	50
50XL10	10	50
50XL30	30	50

Table 4: Overview of the experiment parameters

4.5.2 Mechanical tests

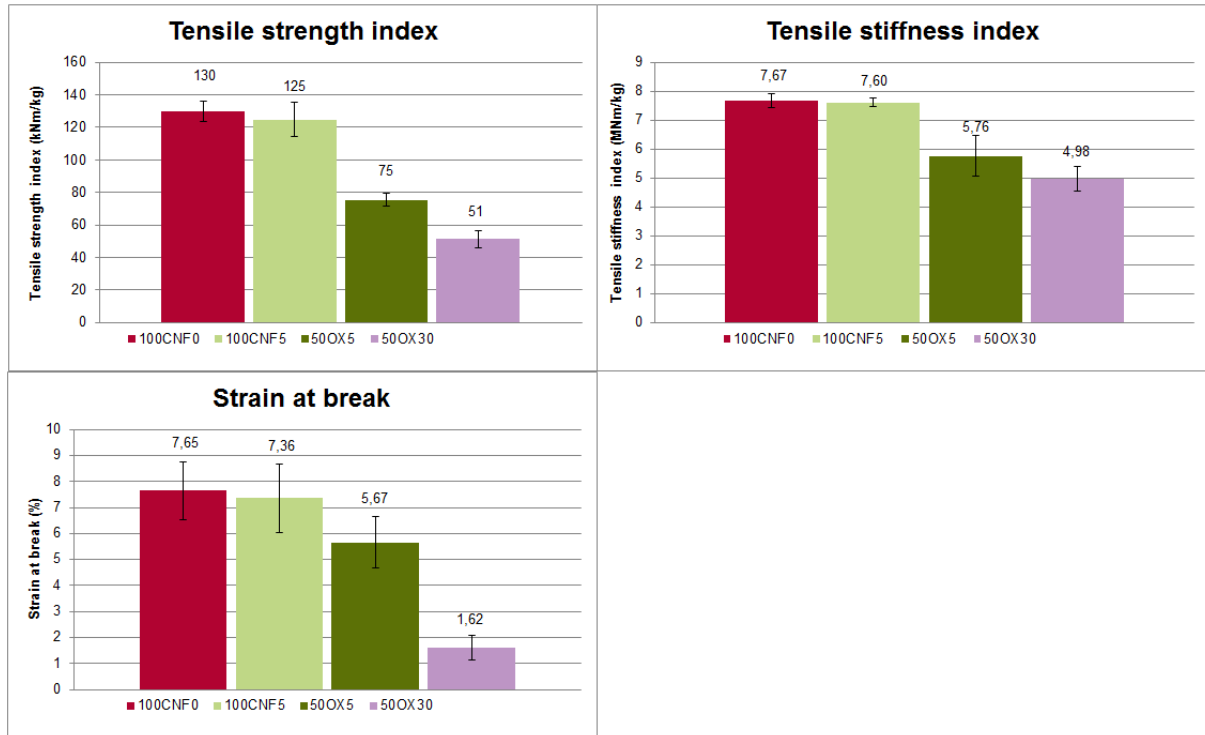


Figure 27: Mechanical properties of CNF/GNs composite films with different sonication times.

The difference between 0 and 5 minutes did not seem to affect the properties in any significant manner but for the 100CNF30 the CNF turned out damaged to that degree that everything went through the filter paper and only left gray fragments from the sonication probe which indicates that the fibrils have been damaged. When a new try was made with a $0.1\mu\text{m}$ filter paper, it resulted in a film but that one got stuck in the filter paper so no tests could be performed. For the 50OX samples, the mechanical tests shows a similar behaviour with a significant decrease in the strain at break value for the sample with the longest sonication time. This is believed to be because the sonication damages the amorphous phase of the fibrils and leaves a more crystalline material with lower elasticity. The fact that it was possible to create a film with the OX graphene after 30 minutes sonication could be due to that the CNF might be stuck absorbed to the GNs surface creating hybrid particles.

4.5.3 UV-vis

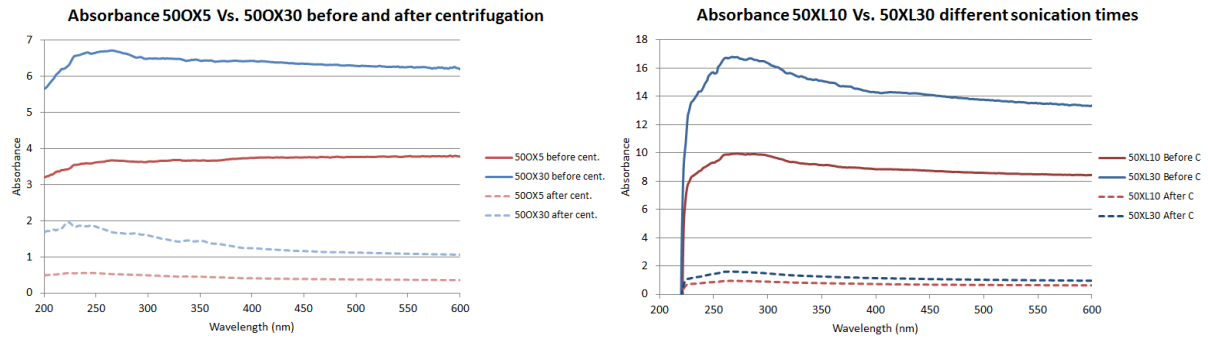


Figure 28: Absorbance spectrum of different GNs and sonication time.

As can be seen in Figure 28, the GNs did disperse better and also got a bigger portion stabilised after centrifugation after a longer sonication process. This is probably because more total energy is used in the sonication process and therefore can disperse the GNs mixtures better. It could also be because the sonication exfoliates the graphene further and that it therefore gives a higher absorbance signal. This theory could be confirmed by the more prominent graphene peaks that is present for the 50OX30 and 50XL30 since a higher peak could indicate thinner flakes.

4.5.4 SEM

The SEM images in Figure 29 shows a smoother and a more homogeneous surface for the 50OX30 than the 50OX5 which indicates that the materials have been dispersed better due to the longer sonication time.

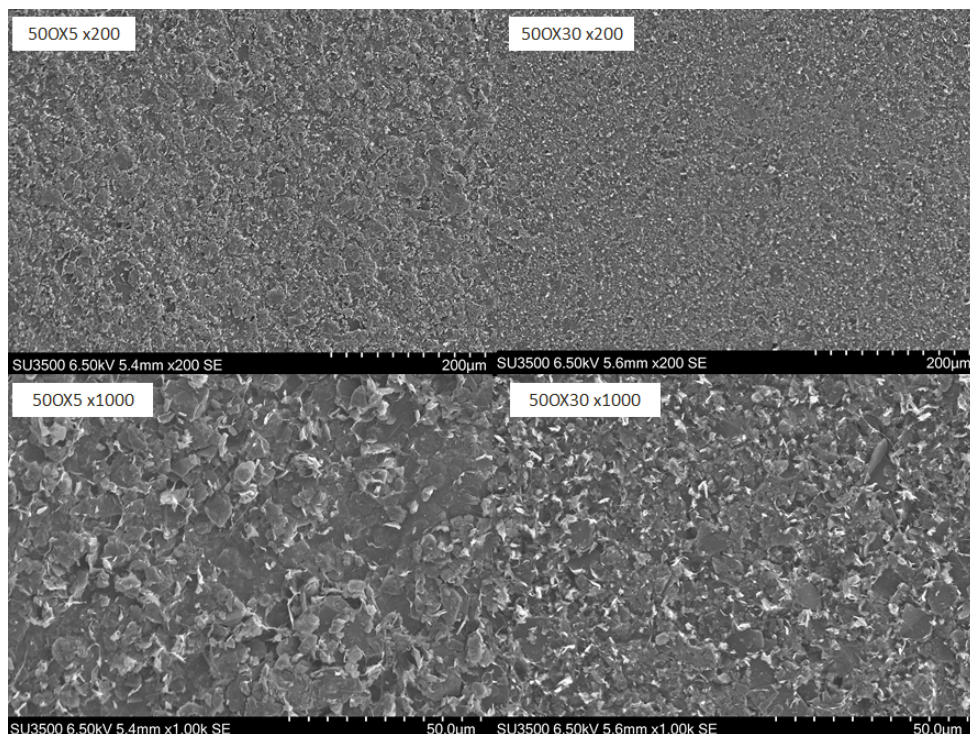


Figure 29: SEM images of the bottom side of CNF/GNs composite films. $x200$ and $x1000$ magnification

4.5.5 Conclusion different sonication times

It is clear that a longer sonication time will give smaller graphene particles and a more homogeneous film, but it will also damage the CNF particles to a big degree. The conclusion to draw after these results is that a balance between how homogeneous the film is needed to be and how much damage that can be inflicted to the CNF.

4.6 Different types of GNs

4.6.1 Experiment and overview

Since barrier properties have been linked to the tortuosity of the sample it is also interesting to evaluate how different sizes of GNs affect the different film properties. To do this the XL quality with a larger platelet size ($40\mu\text{m}$) is tested and compared with the previous tested OX GNs with ($4\mu\text{m}$). The XL is also slightly thicker with 5-10 layers in comparison to OX <5 layers according to the data sheets provided by the manufacturer. The process is the same as before mentioned experiments with the difference that a smaller 6 mm probe was used to disperse the small volumes. This will impact the sonication energy so they can only be compared to each other.

Method	Sonication time (min)	GNs content (%)	Volume (ml)
50OX30	30	50	300
50XL30	30	50	300
50OX10	10	50	40
50XL10	10	50	40
100OX10	10	100	40
100XL10	10	100	40
50OX5	5	50	300
50XL15	15	50	300

Table 5: Overview of the experiment parameters.

4.6.2 Mechanical tests

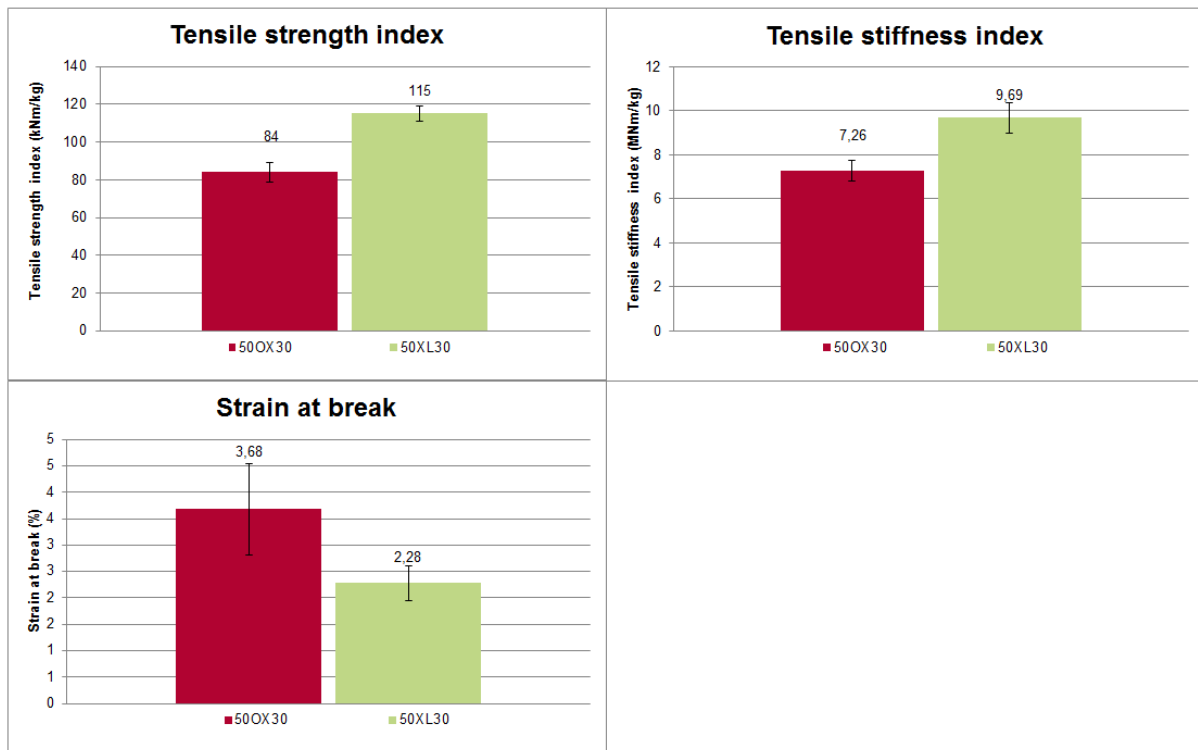


Figure 30: Mechanical properties of CNF films with different GNs types.

As can be seen in Figure 30, the tensile strength and tensile stiffness is increased but the strain at break is decreased. This might be due to the bigger aspect ratio of the XL since that gives a more overlapping network of the GNs. The decrease in strain is probably due to the less elastic behaviour of the XL GNs since they are both larger and thicker.

4.6.3 UV-vis

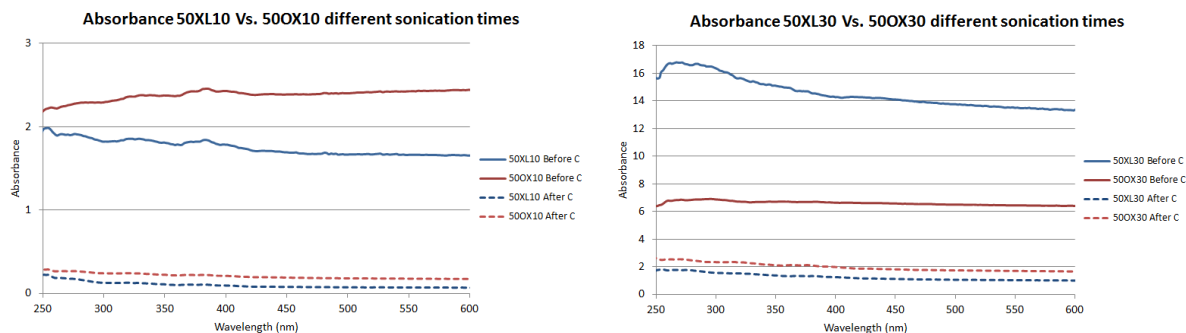


Figure 31: Absorbance spectrum of different GNs and sonication time.

The samples in Figure 31 indicates that the XL needs more energy to exfoliate since it gives a lower signal when sonicated a shorter time but a much higher signal with a longer sonication time. In both experiments, the OX GNs gives a higher signal after centrifugation which indicates that it is easier to disperse in CNF.

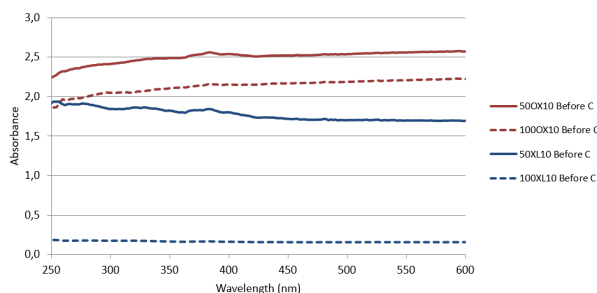


Figure 32: Absorbance of different GNs with different ratios.

The test to show if CNF really stabilize GNs better than in pure water showed a big difference between the different types of GNs as can be seen in Figure 32. The XL showed a much bigger difference in absorbance in CNF compared to when dispersed in water. The OX did not show a similar significant change which might be due to the higher oxygen content. It is worth noticing that since the dry content was kept constant through all experiments, the amount of graphene in the 100XX10 samples are 2 times higher than in the 50XX10 ones. This is compensated for by dividing the absorbance by two to get a fairer comparison. If the sonication time should be dependent on the graphene amount to show a fair comparison, the 100XX10 curves should have been sonicated longer.

4.6.4 Swelling

The swelling test showed a significant change in the water absorption for the different types of graphene. The OX increased in weight 60 times after 15 minutes when the XL

only increased 5 times. After 2h the 50OX30 was completely dissolved in water as can be seen in Figure 34. The XL had not increased so much more in weight even after 24 hours.

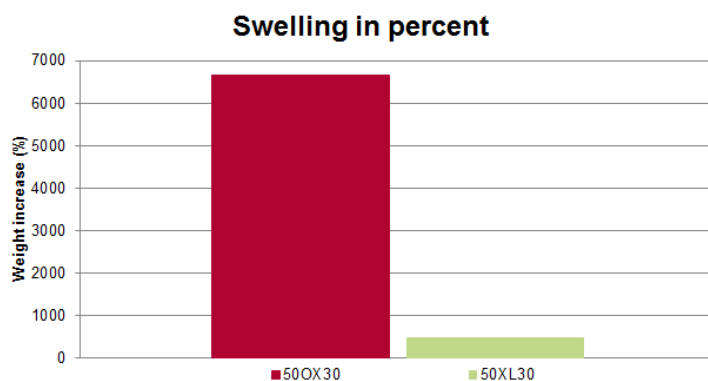


Figure 33: Weight increase in % of different GNs types when submerged in water.

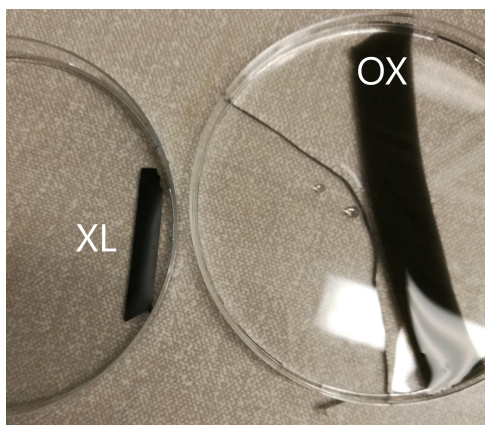


Figure 34: Image of films with different GNs submerged in water for 2h.

4.6.5 Barrier properties

The barrier properties were tested only once per sample and at 23°C, 50% RH. The 50XL15 film showed a significant drop in water permeability with over 25 times improvement compared to pure nanocellulose and 18 times better than 50OX5. This is believed to be due to the bigger aspect ratio of the XL which gives a better overlap of the sheets and therefore gives the diffusing molecules a more tortuous path. The comparison can however not exactly be compared since the 50XL15 dispersion was centrifuged so a lot of the graphene was removed.

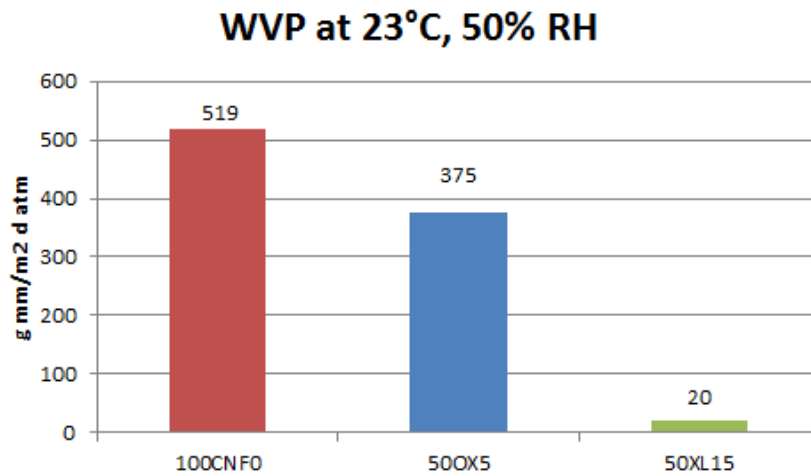


Figure 35: Water vapour permeability of films with different GNs

Since the 50XL15 showed such a significant increase in barrier property, this film was also tried at an elevated RH (80%) This shows an increase (seen in Figure 36) in the permeability but it is still significantly lower than of the pure nanocellulose.

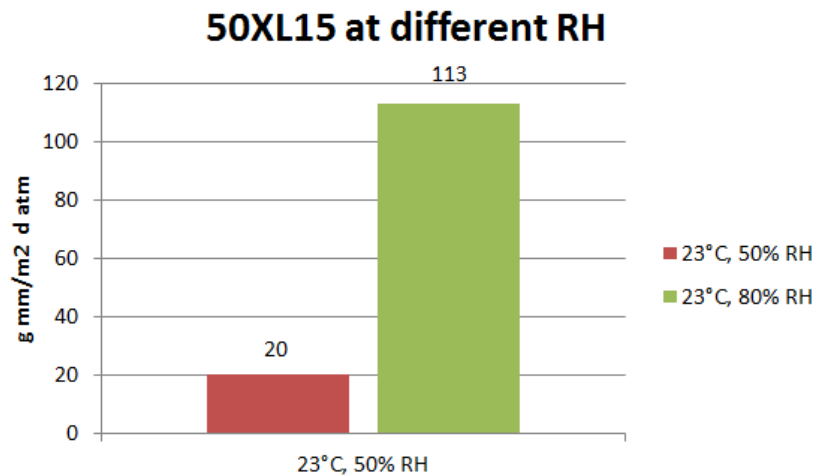


Figure 36: Water vapour permeability of 50XL15 at different RH

4.6.6 Conclusion different types of GNs

The change of GNs really showed a significant increase in both the mechanical and barrier properties. These improvements might be due to the more overlapping graphene sheets of the XL type that gives a stiffer structure and a more impermeable film. The WVP value did as expected increase when the RH increased but the final value was still better than of pure cellulose at a lower RH. Since the graphene content of the 50XL15 is unknown the comparison can however be a bit difficult to make. The higher oxygen content of the OX type is probably the reason why this is easier to disperse in the CNF than the XL.

4.7 Centrifuged Vs uncentrifuged cellulose

4.7.1 Experiment and overview

In the SEM images one could see bigger fragments of CNF that have not been fully exfoliated. This could affect the interactions between the cellulose and the GNs so therefore the cellulose were centrifuged at 3000g for 10 minutes in order to get rid of all the big fibrils. This did however not result in any big difference regarding properties and was therefore not further investigated. The centrifuged cellulose was however used in all of the upcoming experiments after the initial test with different ratios of GNs.

4.8 Mixing method

4.8.1 Experiment and overview

To try and minimise the damage done and also the metallic contamination by the probe tip, different experiments were done with alternative mixing methods. The first test was with a polytron that was used at a speed of 23500 rpm for 10 minutes. The second test was with a normal magnetic stirrer that stirred the dispersion over the weekend.

Sample name	Dispersion tool	GNs content (%)	Volume (ml)
50XLTOR	Polytron	50	40
50XLMAG	Magnetic stirring	50	40
50XL10	Sonication probe	50	40

Table 6: Overview of the test series

4.8.2 UV-vis

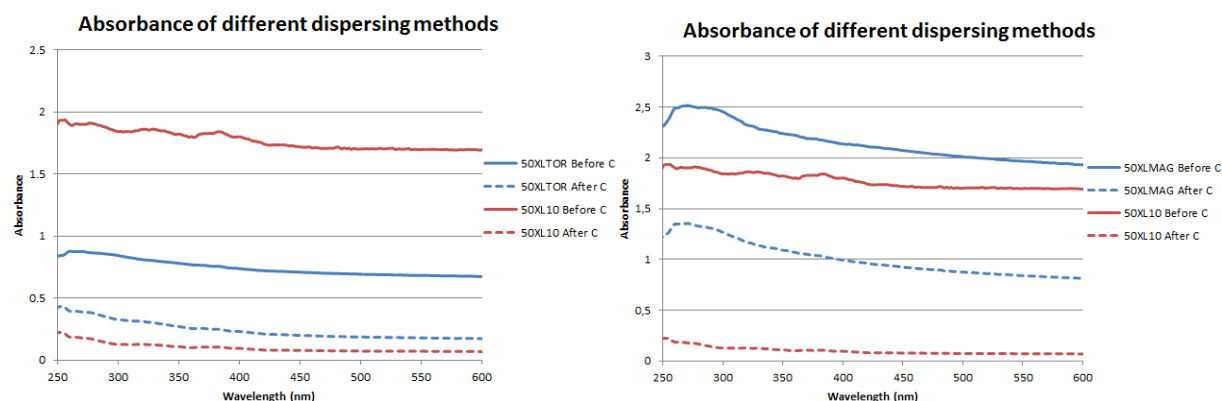


Figure 37: Absorbance spectrum of different dispersing methods. Image to the left shows polytron Vs. sonication probe and image to the right shows magnetic stirring Vs sonication probe.

Figure 37 shows the result of the polytron and magnetic stirring in comparison to sonication. One thing that can be seen is that sonication gives a lower absorbance signal after centrifugation than both polytron and magnetic stirring. This could indicate that a reevaluation of the preferred dispersing method should be done. It might however behave different if a different beaker is used since both the polytron and sonication was made in a 50 ml plastic tube. Another interesting observation is that magnetic stirring result in a higher absorbance signal than both the polytron and sonication probe and also shows a more prominent graphene peak. When this experiment is tried to be scaled-up however, the same high absorbance value was not obtained. Due to lack of time this phenomenon could not be further investigated but it could indicate that other parameters than the one in this report should be evaluated since they might have a stronger impact on the stabilisation of GNs.

4.8.3 Conclusion different mixing methods

This quick experiment shows that it is possible to get absorbance values higher than with a sonication probe using much simpler methods. If this is further confirmed and understood, these might be more efficient methods than sonication since they does not damage the cellulose as much and also do not leave any metallic residues. Since this experiment only was tried once due to lack of time, it is very difficult to extrapolate some significant conclusions from the data but it might, however show that there are more properties that should be closely examined when making CNF/GNs hybrids.

4.9 Type of nanocellulose

4.9.1 Experiment and overview

An experiment with a lower charged cellulose (carboxymethylated DS01) was made in order to evaluate if the barrier properties could be improved in a similar fashion as for the DS03. Both of the dispersions were sonicated with a 12mm sonication probe for 10 minutes 100% amplitude and later centrifuged for 10 min at 3000g. The 50XL10DS01 and 50XL10DS03 got roughly the same absorbance value before centrifugation but after centrifugation almost all of the graphene fell out from the 50XL10DS01 as can be seen in Figure 38. This might be due to the weaker electrostatic interactions between the CNF and the GNs. I also want to highlight that due to a lack of time, these results could not be properly evaluated to see if it really is the DS that is the cause of the weaker interactions or if other parameters could be interesting to evaluate such as the acidity or salinity.

Test serie

Sample name	DS	Volume (ml)	Sonication time (min)	Graphene content (%)
50XL10DS01	0.1	300	10	50
50XL10DS03	0.3	300	10	50

Table 7: Overview of the test series

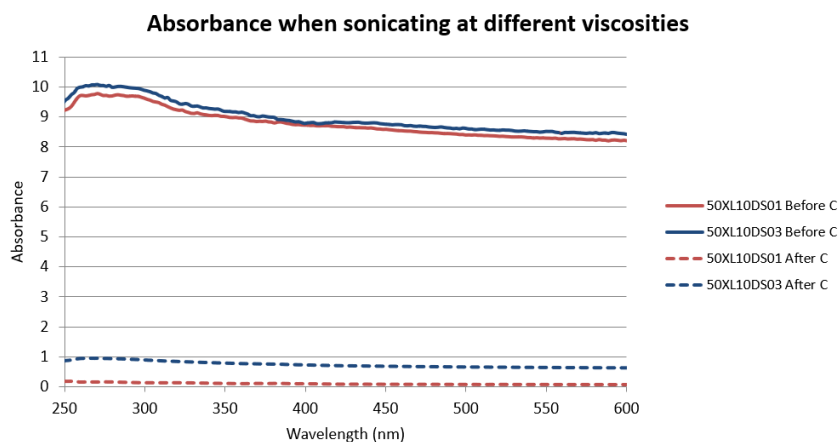


Figure 38: Absorbance of XL GNs together with CNF with different DS.

4.9.2 Conclusion different types of CNF

Almost all of the GNs fell out after centrifugation with the lower charged cellulose. This could indicate that the electrostatic interaction is too low but since no more tests were conducted it is difficult to eliminate other possible explanations.

4.10 Coating

4.10.1 Experiment and overview

From an industrial perspective, the vacuum filtration process or evaporating techniques is not especially relevant due to the limits to scale up the processes. Therefore experiments were made to try to coat a CNF/GNs film at a cardboard substrate using a bar coater. When coating a higher viscosity than the one in the previous experiments so therefore a suitable method for getting a dispersion with graphene at a high viscosity. Three approaches were evaluated

- Disperse at a low concentration and then evaporate at 50°C
- Disperse at low concentration and then use a ultra vacuum filtration method.
- Start with a higher concentrated CNF and then try to disperse GNs in the gel.

The simplest process would be to disperse the GNs into the CNF at a high concentration but it might be difficult to get it fully dispersed due to the gel like consistency of the CNF at concentrations 1%.

Test series

Method	Sonic. time	CNF content	Start conc.	GNs content
Evaporation (50%)	0	300 ml	0.1%	0
Ultra vacuum filtration	10 min	150 ml	0.1%	150 ml
Disperse in high conc.	10 min	30 ml	0.5%	50

4.10.2 Evaporation

The first explored method was to evaporate water from the CNF. To speed up the process, the temperature was set to 50 °C and then the 0.1% CNF were put in a glass beaker under magnetic stirring to avoid that a film is created at the top.

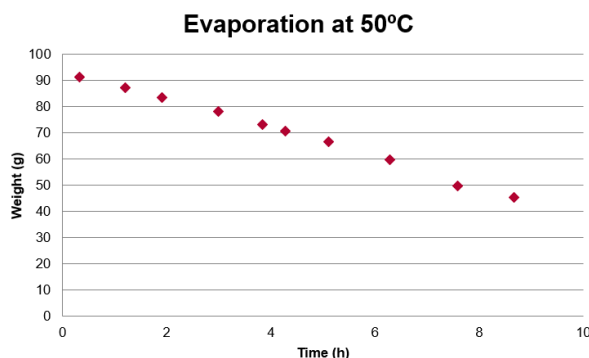


Figure 39: The evaporation rate at 50°C

The goal with the experiment was to evaporate 90% of the water so a concentration of 1% was reached. As can be seen in Figure 39, the process was relatively slow with only a pace of 5.6 grams per hour. Despite the stirring, a film was formed at the top and when reached lower concentrations, lumps of gel were formed. Due to the slow speed and the inhomogeneous result, this technique was quickly abandoned.

4.10.3 Ultra vacuum filtration

Another try was made with ultra vacuum filtration which is a method that utilises high pressure and magnetic stirring to force water through a membrane. The device can be seen in Figure 40 A first try with pure nanocellulose showed promising result since the method was fairly easy to set up and only took a couple of hours to filtrate 300 ml. Therefore a test with 0.1% CNF with 50% GNs was prepared and run through the ultra vacuum filtration cell. The starting volume was 300 ml and the desired volume was therefore 30 ml after filtration. The process took 4 hours and resulted in a homogeneous gel at around 1%.

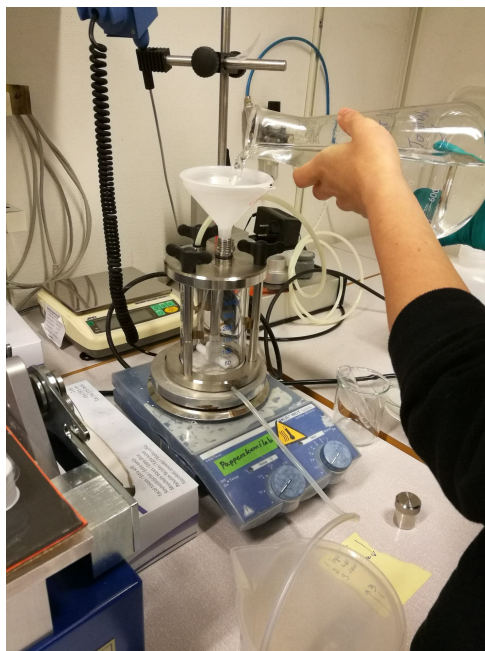


Figure 40: Image of the ultra vacuum filtration device used in this experiment

4.10.4 Disperse GNs in high concentration

To test if it was possible to disperse GNs directly into highly viscous CNF, 50mg GNs was sonicated into 30 ml of CNF with a concentration of 1%. During sonication it was clear that only the GNs closest to the probe was properly exfoliated and dispersed so therefore a continuous stirring was needed to get a uniform dispersion in all of the material. The final dispersion turned out quite well but the big flakes that were not fully dispersed were difficult to get rid of since the highly viscous material could not be centrifuged away. Because of that, the final film looked inhomogeneous and were not well suited for coating.

4.10.5 Bar coating

After the dewatering experiments, two dispersions were produced that could be tested for coating. One was made from dewatering after the sonication and one where the GNs was dispersed in the already concentrated CNF. The goal was to try to coat the material at cardboard

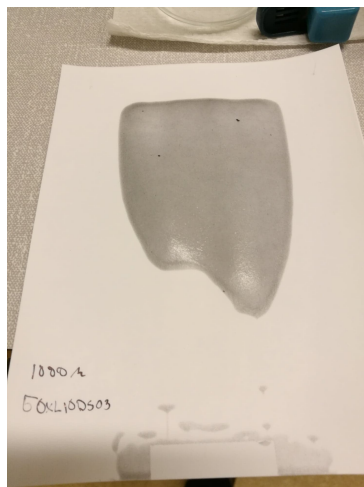


Figure 41: Result of bar coating with the ultra vacuum filtrated CNF/GNs dispersion. The bar used is a $1000\mu\text{m}$

4.10.6 Conclusion bar coating

After this experiments it is clear that a well dispersed and high viscous material is needed in order to get a homogeneous coating layer. The method in which the GNs was dispersed in a high concentrated CNF (1%) was difficult to sonicate and also the resulting dispersion did not turn out suitable for coating since the unstabilised particles could not be centrifuged away. The evaporation process was also not a suitable method since it took a long time and turned out inhomogenous in the end. The method with the ultra vacuum filtration device was way more efficient since it could reduce the water content with about 90% in a couple of hours. The result was also homogenous enough so a smooth layer could be applied using a bar coater.

5 Discussion

5.1 Modify the graphene content

By modifying the graphene content it was clear that CNF functions as a suitable matrix material with graphene. This since it has been shown possible to make films that are easy to handle even at as high graphene content as 80%. The mechanical properties such as stiffness and strength remained fairly unchanged at low concentrations but were reduced quite heavily for higher concentrations. This does not quite approve with the theory since graphene is much stronger and stiffer than CNF. Other studies such as [1] shows that the incorporation of a stronger 2D material should also increase the mechanical properties of the composite material. The reason might however be that the graphene is not fully dispersed but bigger aggregates are still present which result in a weaker film. The strain at break was reduced already at low concentrations which can be expected due to the low strain for graphene as a material. Since the experiment only was made with one of the

GNs sorts and also only one film was produced per dispersion, it is difficult to draw some significant conclusions but if I would recommend a preferred ratio, I would say somewhere between 5 and 50 percent since the mechanical properties were significantly lowered at a higher concentration and not many other properties were increased. A higher GNs amount will also need a longer sonication time which damages the CNF. The swelling was however significantly lowered and the conductance increased with the 80OX5 so one should probably not completely eliminate the idea of using a high GNs content. Other studies[37] has also showed that films with as much as 90wt% GNs can be manufactured with a high conductance as a result. To further increase the conductance, the film was compressed which might be a way forward if a high conductance is needed.

5.1.1 Sonication times

When the sonication time was increased it showed a clear increase in the homogeneity of the film and also in the absorbance signal of the dispersion. The CNF was severely damaged when sonicated for 30 minutes which make it important to be able to minimise the sonication time. Saito et al has previously shown that the fibrils might fragment under the influence of sonication[25]. It is however not only the time that is important since Yang et al sonicates for 30 minutes[37]. Measures that can be taken to avoid fibril damage might be to use a CNF with lower DS since it does not defibrillate as easily or lower the amplitude.

My results indicates that the sonication time should be modulated according to the GNs amount with a longer sonication time for a higher amount. This report does not give a full picture of how the sonication time should be determined in comparison to the GNs content but it shows that it might be worth to put into consideration. A more fair comparison would probably also be to use the effect or the sonication energy as a reference of the sonication process. That way it will be easier to compare different volumes, amplitudes and probe sizes.

5.1.2 Fractionation method

After the initial test with the different graphene ratios, it was clear that the films did not turn out homogeneous since more graphene was present at the bottom side towards the filter paper. This is a consequence of the unstable dispersion of GNs and CNF where the biggest aggregates will fall out over time. The homogeneity of the film seems to be of high importance which made us to try to fraction the dispersion so only the stable particles were left. This was made using a centrifuge in this report but other ways might also be of interest such as filtration since it will more selectively remove the biggest aggregates.

5.1.3 Different types of GNs

The change of GNs showed very different results in this report. The OX showed small differences in both mechanical- and barrier properties compared to the pure CNF but XL showed an increase in mechanical and a drastic increase in barrier properties in comparison

to the OX. This makes it very difficult to draw general conclusions for all types of graphene products on the market so my recommendation is to do some initial tests with the graphene to set specific parameters linked to the specific GNs type. Such experiments could be to evaluate how well it disperses in normal water so correct adjustments could be made in the sonication process or how long time that the specific GNs must be sonicated to achieve a satisfactory absorbance level. According to the case with

5.1.4 Barrier properties

It can clearly be seen that the GNs have lowered the WVP of the nanocellulose. It looks like the most important property in order to obtain a good moisture barrier is to have big structures that really increase the tortuosity of the sample. This is based on the good result that was obtained from the XL tests that showed a reduction in permeability by 25% at RH50 and a value of 113 at RH 80. However, the significantly lowered WvP value of the cellulose is roughly the same as for a lower charged cellulose (DS01) which have a value of 28 gmm/m^2datm [2]. If graphene could be used with a DS01 type of cellulose maybe the WVP-value could be lowered even more. In Aulin et al's report that uses nanoclay instead of graphene the lowest value at RH50 was 6.4 gmm/m^2datm which is 4 times lower than in this report but at RH80 the value is 185 gmm/m^2datm which is higher than 113 gmm/m^2datm as in this report. This might indicate a small favour to use GNs instead of nanoclay when reaching higher RH. If more time was at my disposal I would also do tests of the oxygen permeability but due to a heavily booked machine this was not possible to fulfil.

5.1.5 Other dispersion methods

This report touches the subject of different dispersion methods a bit after the CNF were destroyed when sonicated too long. The methods tested were polytron and magnetic stirring where both showed a higher absorbance signal of the dispersion than with sonication. Magnetic stirring also showed a more prominent graphene peak that could indicate a better exfoliation. Since the tests could not be repeated due to lack of time this should maybe be looked into more in the future since they do not damage the CNF as much as sonication.

5.1.6 Coating

The section about the coating was made in collaboration with BillerudKorsnäs and some different approaches were tried to disperse GNs in CNF and then reach a suitable viscosity for coating. The most efficient method found was to disperse the GNs before dewatering in a ultra vacuum filtration tube. It was possible to disperse GNs already at a higher viscosity but since it did not work to centrifuge the dispersion afterwards it was not a suitable process. However if it is possible to filter the big graphene aggregates through a filter paper, maybe that would be an even better solution.

5.2 Future work

5.2.1 Find a way to determine the exact amount of graphene in the films

During this work, ways to determine the exact graphene content of the centrifuged films have been tried without a complete success. TGA measurements were made, but it was not possible to say exactly what the graphene ratio was. This is of a high importance so if measurements can be made to find out a method to make the TGA curves more accurate it would be beneficial. One way that could be tried is to dip the films in an acid to make the CNF degrade at a lower temperature so a clearer difference between the CNF and GNs peak can be seen.

5.2.2 Try with more graphene types

Since the properties were significantly changed when the GNs types were changed, it would be interesting to further evaluate more types to see if a more suitable one could be found. It would for example be interesting to see if a thinner single layer GNs could further increase the barrier properties and at the same time also enhance the mechanical properties a bit.

5.2.3 Cross-section SEM images

To see if the GNs really lays completely in plane with the CNF, it would be interesting to see some SEM images of the film's cross-section. This was tried to be obtained but the graphene flakes were smeared out along the side as the knife could not cut through it. To make a better cross-section image, maybe breaking it in liquid nitrogen could be an option.

5.2.4 Modulate the environment

To make the dispersion a bit easier, experiments with the environment could be further investigated since small changes in acidity and salinity impacts the dispersion stability. A possible way could be to lower the pH below 3 to make the CNF uncharged before sonication. Then, maybe, more CNF can stick to the surface since they do not repel each other anymore and then when the pH is increased again after sonication more graphene will be stabilised.

6 Conclusion

In this report it has been shown that CNF is a suitable material to make hybrid films with GNs with maintained mechanical properties and a WVP that has been lowered 25 times at RH50 compared to pure CNF. One focus has been to try to optimise the dispersions so that a homogeneous film can be made. Parameters that have shown to

affect the dispersion quality are first of all the sonication time which when too short does not exfoliate the graphene aggregate properly but when set too long risks to damage the CNF. Two different types of GNs with different oxygen content and size have been evaluated and the results have indicated that the size of the GNs play an important roll in maintaining the mechanical- and barrier properties of the CNF. The difference in graphene ratio was also evaluated for one of the GNs types with the result that a high (80%) concentration of GNs limits the swelling of the CNF but in return results in weakened mechanical properties. It has also been shown how different parameters affects the dispersion and given a guideline of how they should be determined in future work. Due to an interest of a scaled-up process from the industry, some experiments were also made with the aim to simplify the dispersion method and speed up the film making.

References

- [1] Christian Aulin, Mikael Gällstedt, and Tom Lindström. “Oxygen and oil barrier properties of microfibrillated cellulose films and coatings”. In: *Cellulose* 17.3 (2010), pp. 559–574.
- [2] Christian Aulin, German Salazar-Alvarez, and Tom Lindström. “High strength, flexible and transparent nanofibrillated cellulose–nanoclay biohybrid films with tunable oxygen and water vapor permeability”. In: *Nanoscale* 4.20 (2012), pp. 6622–6628.
- [3] F Baumgart. “Stiffness-an unknown world of mechanical science?” In: *Injury-International Journal for the Care of the Injured* 31.2 (2000), pp. 14–23.
- [4] Qingzheng Cheng, Siqun Wang, and Qingyou Han. “Novel process for isolating fibrils from cellulose fibers by high-intensity ultrasonication. II. Fibril characterization”. In: *Journal of Applied Polymer Science* 115.5 (2010), pp. 2756–2762.
- [5] Luong Nguyen Dang and Jukka Seppälä. “Electrically conductive nanocellulose/graphene composites exhibiting improved mechanical properties in high-moisture condition”. In: *Cellulose* 22.3 (2015), pp. 1799–1812.
- [6] Alain Dufresne. “Nanocellulose: a new ageless bionanomaterial”. In: *Materials Today* 16.6 (2013), pp. 220–227.
- [7] Andreas Fall. “Colloidal interactions and orientation of nanocellulose particles”. PhD thesis. KTH Royal Institute of Technology, 2013.
- [8] Linda Fogelström. “Polymer nanocomposites in thin film applications”. PhD thesis. KTH, 2010.
- [9] Johnsy George and SN Sabapathi. “Cellulose nanocrystals: synthesis, functional properties, and applications”. In: *Nanotechnology, science and applications* 8 (2015), p. 45.
- [10] Alireza Hajian et al. “Understanding the dispersive action of nanocellulose for carbon nanomaterials”. In: *Nano letters* 17.3 (2017), pp. 1439–1447.
- [11] Tahani Kaldés et al. “Insights into the EDC-mediated PEGylation of cellulose nanofibrils and their colloidal stability”. In: *Carbohydrate polymers* 181 (2018), pp. 871–878.
- [12] Feyza Karasu et al. “Organic/Inorganic Hybrid Planarization and Moisture Barrier Coatings on Cellulose Nanofibrils Substrates”. In: *Frontiers in Chemistry* 6 (2018), p. 571.

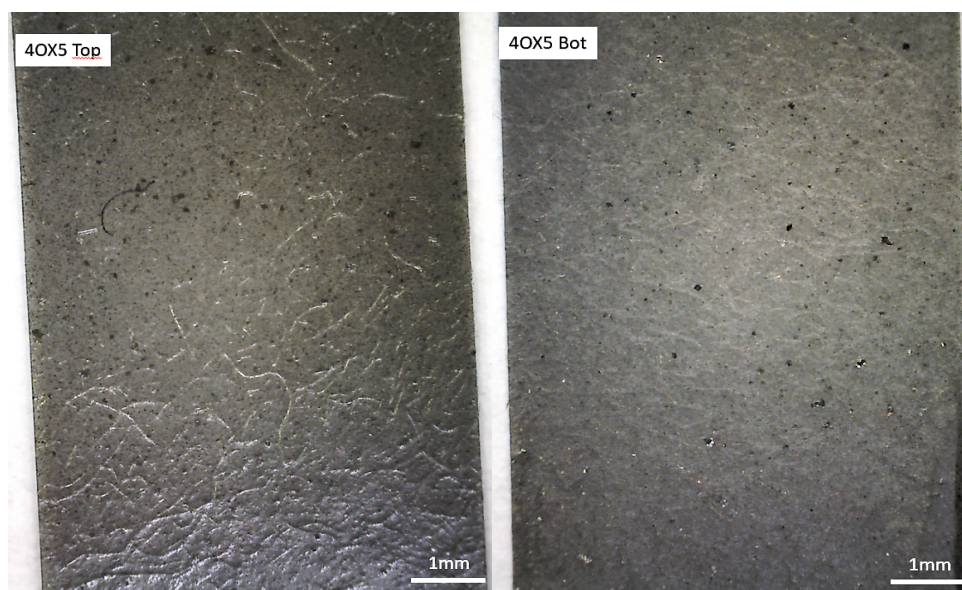
- [13] Kenneth Keegstra. “Plant cell walls”. In: *Plant physiology* 154.2 (2010), pp. 483–486.
- [14] HPS Abdul Khalil et al. “A review on nanocellulosic fibres as new material for sustainable packaging: Process and applications”. In: *Renewable and Sustainable Energy Reviews* 64 (2016), pp. 823–836.
- [15] HPS Abdul Khalil et al. “Production and modification of nanofibrillated cellulose using various mechanical processes: a review”. In: *Carbohydrate polymers* 99 (2014), pp. 649–665.
- [16] Dieter Klemm et al. “Nanocelluloses: a new family of nature-based materials”. In: *Angewandte Chemie International Edition* 50.24 (2011), pp. 5438–5466.
- [17] Jihua Li et al. “Homogeneous isolation of nanocellulose from sugarcane bagasse by high pressure homogenization”. In: *Carbohydrate polymers* 90.4 (2012), pp. 1609–1613.
- [18] D R Lide. In: *Handbook of chemistry and physics 75 th ed.* 1999, 6-15 and 15-25.
- [19] Jani-Markus Malho et al. “Facile method for stiff, tough, and strong nanocomposites by direct exfoliation of multilayered graphene into native nanocellulose matrix”. In: *Biomacromolecules* 13.4 (2012), pp. 1093–1099.
- [20] Matteo Minelli et al. “Investigation of mass transport properties of microfibrillated cellulose (MFC) films”. In: *Journal of Membrane Science* 358.1-2 (2010), pp. 67–75.
- [21] Robert J Moon et al. “Cellulose nanomaterials review: structure, properties and nanocomposites”. In: *Chemical Society Reviews* 40.7 (2011), pp. 3941–3994.
- [22] AN Nakagaito, S Iwamoto, and H Yano. “Bacterial cellulose: the ultimate nano-scalar cellulose morphology for the production of high-strength composites”. In: *Applied Physics A* 80.1 (2005), pp. 93–97.
- [23] M Pääkkö et al. “Enzymatic hydrolysis combined with mechanical shearing and high-pressure homogenization for nanoscale cellulose fibrils and strong gels”. In: *Biomacromolecules* 8.6 (2007), pp. 1934–1941.
- [24] Jong-Whan Rhim and Perry KW Ng. “Natural biopolymer-based nanocomposite films for packaging applications”. In: *Critical reviews in food science and nutrition* 47.4 (2007), pp. 411–433.
- [25] Tsuguyuki Saito et al. “An ultrastrong nanofibrillar biomaterial: the strength of single cellulose nanofibrils revealed via sonication-induced fragmentation”. In: *Biomacromolecules* 14.1 (2012), pp. 248–253.
- [26] Tsuguyuki Saito et al. “Individualization of nano-sized plant cellulose fibrils by direct surface carboxylation using TEMPO catalyst under neutral conditions”. In: *Biomacromolecules* 10.7 (2009), pp. 1992–1996.
- [27] Sudhir Sharma et al. “Thermally enhanced high performance cellulose nano fibril barrier membranes”. In: *RSC Advances* 4.85 (2014), pp. 45136–45142.
- [28] Ryuji Shinoda et al. “Relationship between length and degree of polymerization of TEMPO-oxidized cellulose nanofibrils”. In: *Biomacromolecules* 13.3 (2012), pp. 842–849.
- [29] Kristin Syverud and Per Stenius. “Strength and barrier properties of MFC films”. In: *Cellulose* 16.1 (2009), p. 75.
- [30] Supachok Tanpichai et al. “Effective Young’s modulus of bacterial and microfibrillated cellulose fibrils in fibrous networks”. In: *Biomacromolecules* 13.5 (2012), pp. 1340–1349.

- [31] S Uran, A Alhani, and C Silva. “Study of ultraviolet-visible light absorbance of exfoliated graphite forms”. In: *AIP Advances* 7.3 (2017), p. 035323.
- [32] Lars Wågberg et al. “On the charge stoichiometry upon adsorption of a cationic polyelectrolyte on cellulosic materials”. In: *Colloids and Surfaces* 27.4 (1987), pp. 163–173.
- [33] Wikipedia. *Carboxymethyl cellulose*. URL: https://en.wikipedia.org/wiki/Carboxymethyl_cellulose (visited on 01/03/2019).
- [34] Wikipedia. *Cellulose*. URL: <https://en.wikipedia.org/wiki/Cellulose> (visited on 01/03/2019).
- [35] Wikipedia. *Moisture vapor transmission rate*. URL: https://en.wikipedia.org/wiki/Moisture_vapor_transmission_rate (visited on 01/03/2019).
- [36] Wikipedia. *Nanocellulose*. URL: <https://en.wikipedia.org/wiki/Nanocellulose> (visited on 01/03/2019).
- [37] Weixing Yang et al. “Completely green approach for the preparation of strong and highly conductive graphene composite film by using nanocellulose as dispersing agent and mechanical compression”. In: *ACS Sustainable Chemistry & Engineering* 5.10 (2017), pp. 9102–9113.

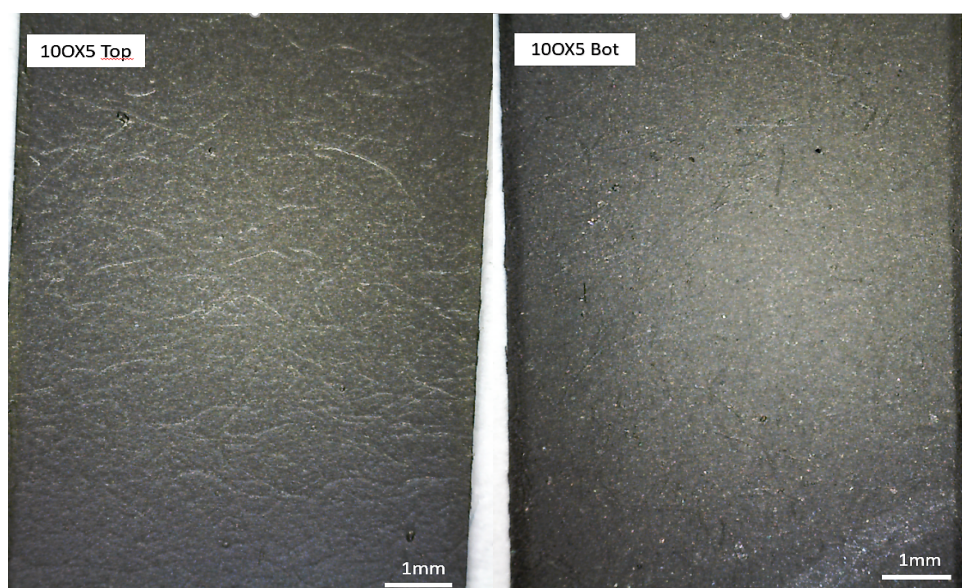
A Appendix

A.1 Optical microscopy images

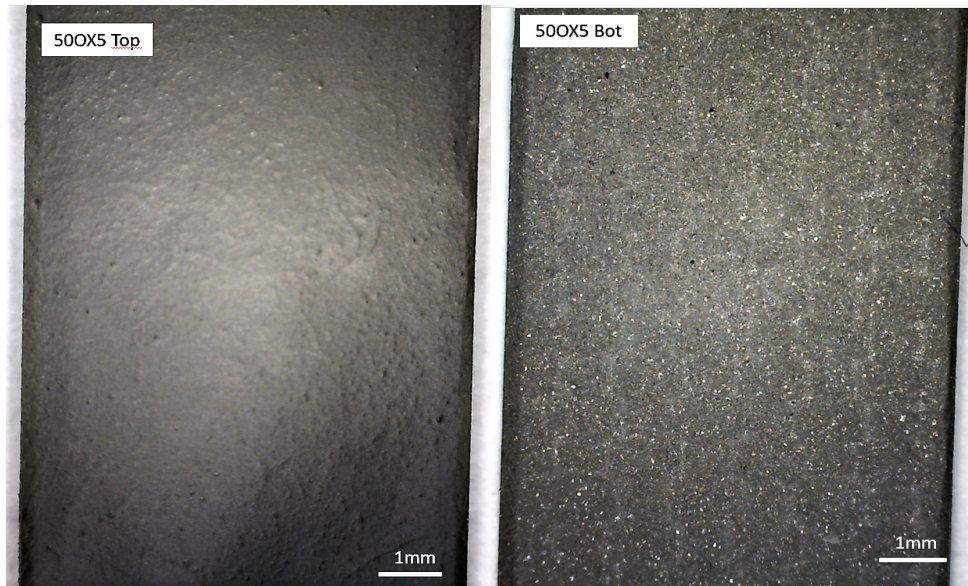
Top and bottom microscopy images of different GNs/CNF ratios.



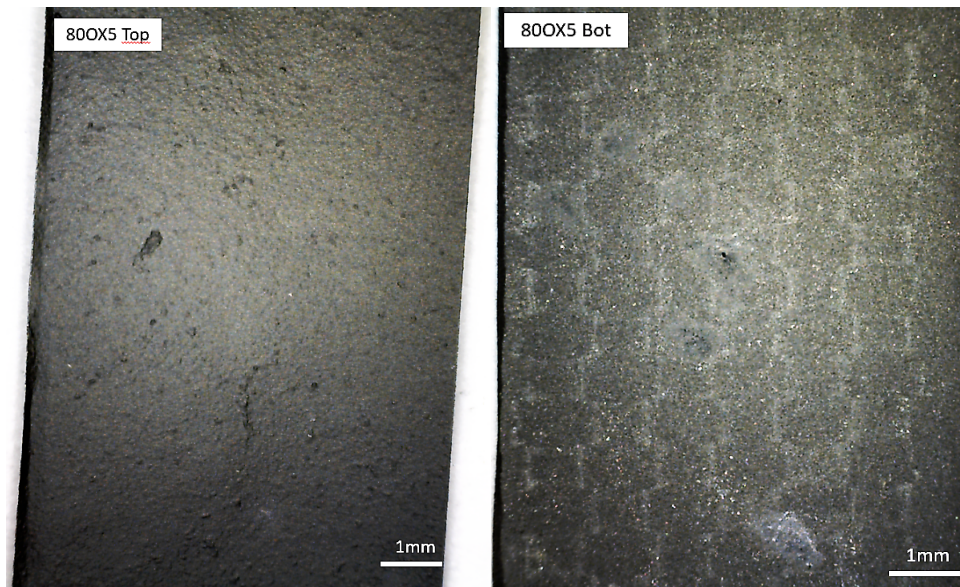
(a) Top and bottom images of 4OX5



(a) Top and bottom images of 10OX5



(a) Top and bottom images of 500X5



(a) Top and bottom images of 800X5



(a) Top image of 100OX5 (no bottom image because it is only powder on the filtration paper)