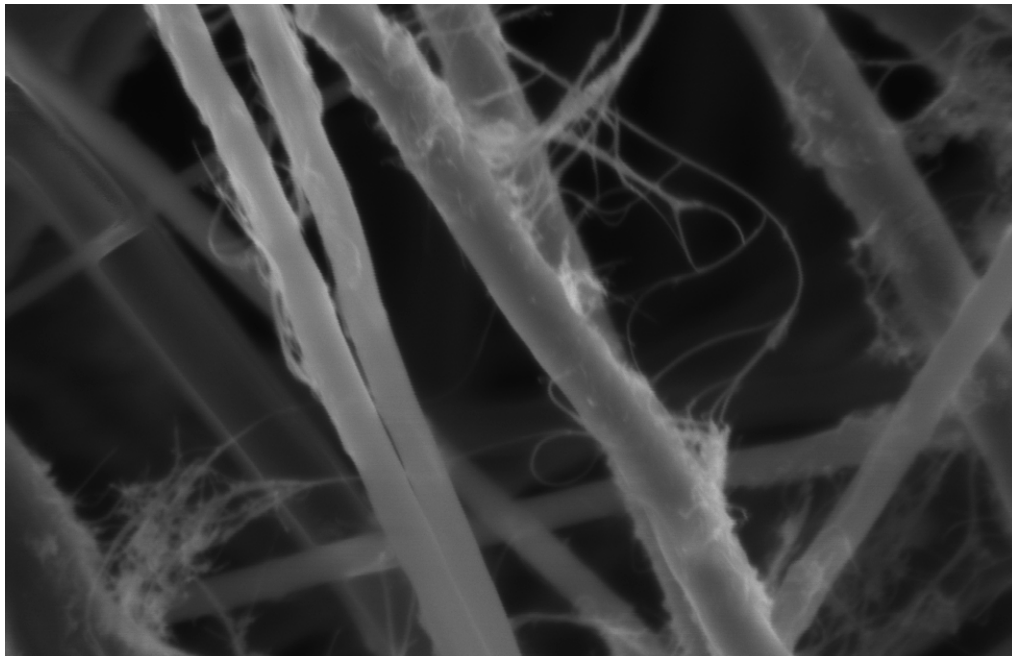


CHALMERS



Modification of nanocellulose by double-walled carbon nanotubes and graphite carbon nanopowder for sensor applications

Master of Science Thesis

FARSHAD TOOMADJ

Department of Microtechnology and Nanoscience
CHALMERS UNIVERSITY OF TECHNOLOGY
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Abstract

Electrically conductive nanocellulose films were prepared by immersion in dispersions of double walled carbon nanotubes or graphitized nanopowder. These solutions were prepared by using the surfactant cetyltrimethylammonium bromide (CTAB) under heating and stirring which were followed by short time sonications.

Electrospun cellulose and bacterial cellulose were used as a backbone of these films. Controllable modification of cellulose with conductive agents was performed by treatment with their dispersions for 24 – 72 hours.

In this project it has been showed that the conductivities of resulted films were changed depends on changing in type of modifying agent, type of cellulose which was used as a backbone, and immersion time.

The best electrical conductivity of the resulting films are 0.395 S cm^{-1} for bacterial cellulose modified by double-walled carbon nanotube, 0.0086 S cm^{-1} for electrospun cellulose modified by double-walled carbon nanotube and 0.334 for bacterial cellulose modified by graphitized nanopowder. These results are higher or comparable to previously reported results.

Some methods have been employed to study the electrical conductivity behavior of samples. The electrical conductance of the films displays a high sensitivity to strain when tensile stress is applied.

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1. Introduction

Sensors which are based on functionalized nanostructured material are a new class of electronic devices which have gained a significant interest due to their low power consumption, high sensitivity and selectivity, and prompt response[1-3]. During the last decade great advances have been made in the development of different classes of environmental sensors such as pressure and humidity sensors, but new requirements lead to looking for new generations of sensors with new properties. Conventional strain and pressure sensors are characterized by rigidity and fragility which significantly restrict their application area. Also biocompatibility problems limit their applications. Flexible large-area sensors can be produced by inserting nanoparticles with appropriate thermal and electrical properties into a suitable polymer matrix[4]. Currently there is much interest to use carbon nanotubes (CNTs) and carbon nanotube based materials as a building block for new generations of sensors [5, 6]. The CNT is a very strong material; it is super-elastic and can be highly bent without breakage [7]. Its Young's modulus is the highest among all materials [8, 9].

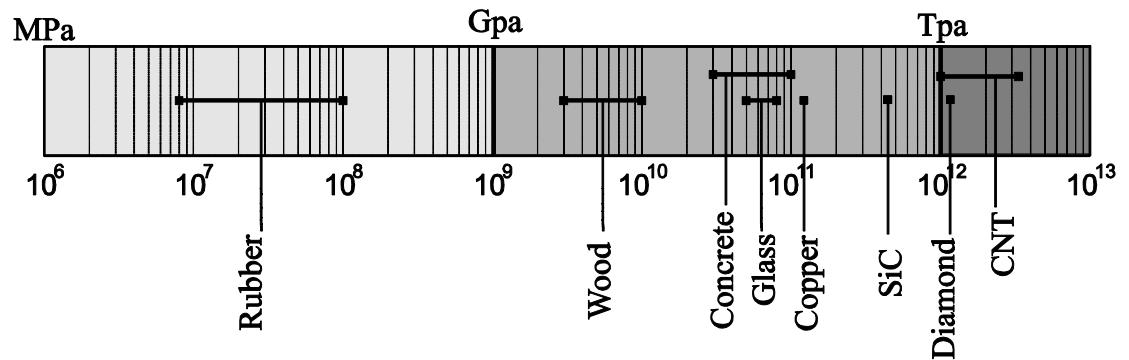


Figure 1. Young's modulus of carbon nanotube between few other material-taken with permission from reference [10]

Outstanding electrical and mechanical properties of CNTs such as high conductivity, low-weight, high aspect ratio, high electrical conductivity and very high sensitivity of this conductivity to even small environmental changes make it one of the best candidates to use as a building block of sensors. Some problems such as the complex and expensive fabrication process of pure carbon nanotubes, leads to the use of CNTs as a modifying agent for other materials.

Due to the strong van der Waals forces between CNTs, they are producing bundles which make them difficult to dissolve in water or other organic solvents [11, 12]. To process CNTs, a well dispersed and stable CNT solution should be approached. Different methods were studied which can be divided into covalent and non-covalent stabilization methods. Between these two methods, non-covalent methods have some specific advantages such as preservation of the structure and properties of the CNTs [13].

Different materials can be used as a backbone of sensors. Cellulose is one of the most widely used natural materials [14, 15]. Due to its biocompatibility, easy modification, and low price, nanocellulose is a good choice to combine with CNTs to make a backbone for sensors[16].

2. Purpose, Objectives and Scope

The following chapter states the overall purpose and the specific objectives of this research period which was done as a master thesis, as well as its scope.

2.1. Purpose

The overall purpose of the thesis project is to obtain cellulose based materials with controllable electrical conductivity to use in sensor applications.

2.2. Objective

The goal of this thesis can be expressed in three different, but coherent objectives:

1) Developing of methods

Developing of different methods which were used in different parts of the material preparation was one of the thesis goals. Dispersion process, treatment process and drying process are the most important methods the development of which was a goal of this thesis.

2) Studying the effects of developed methods on structural and electrical properties of final material

Using different types of cellulose, trying to change the cellulose structure in order to have better dispersion, changing the modifying agent material to obtain better

electrical properties, changing different experimental variables such as dispersion solution concentration and volume, and treatment time of cellulose in dispersed solution are some examples which were studied in this thesis. Studying and registering their effect was another goal of this thesis.

3) Sensing application

Finally, finding appropriate sensing applications which are matched with the obtained material properties and trying to prove it by using different experiments is the last but not least important goal of this thesis.

2.3. Scope

As mentioned above, the thesis has been defined to obtain cellulose based material for sensing applications. Biocompatibility and the cost of cellulose are two reasons to choose this material for this application. This means that we can use any types of cellulose, as long as they are cheap and biocompatible.

Suggesting sensing applications for the obtained material is an important goal for this thesis, but that does not mean that the application of this material is limited to the sensing area. For example capacitors and medical application are two tempting areas which can be suggested for future work.

3. Potential sensor applications

Sensors are devices that detect or measure physical and chemical quantities such as temperature, pressure, sound, bending, and concentration of different chemical compounds. Changes in these variables are detected and converted into an electrical signal.

CNT based materials are among the best candidates to use as sensors; the electrical properties of carbon nanotubes strongly depend on its atomic structure [17], and it has been shown that mechanical deformation of functionalized groups on the CNT surface like bending, twisting can induce changes in the electrical properties of the nanotubes [18].

3.1. Strain sensors

A strain sensor is the type of sensor in which strain deformation is converted into an electrical signal. The piezoresistivity of CNTs (change in the electrical properties of the material by strain) makes it a promising material to use as an active element in strain sensors. This sensor can be used in different areas such as structural monitoring systems [7].

In the bending process, if different sides of sample behave in a different way and respond differently to external stress, this sample can be used as a bending sensor. Directional bending sensitivity of the CNT and CNT based materials has been studied in different conditions. Wichmann *et al.* have developed directional sensitive bending sensors based on multi-wall carbon nanotubes embedded in an epoxy matrix [19]. It has been reported that this material shows nearly linear relation between resistance change and mechanical strain.

3.2. Humidity sensors

Due to the large surface to volume ratio, size [20], hollow geometry and large absorbance of foreign molecules on the surface, CNTs are attractive for demanding applications in the field of gas sensing [21, 22]. It has been reported that water vapor has a significant effect on the conductivity of different CNTs [21, 23] which shows that CNTs can be used for humidity sensors. Zahab *et al.* [21] reported that this conductivity variation is because the p-type carbon nanotubes would turn into n-type when the water molecules are added to the CNTs matrix.

Cellulose has been reported as a backbone for humidity sensors in different studies [24-26]. Its flexibility, low temperature coefficient and a good chemical resistance make it good choice to use in the humidity sensor structure [25].

It seems that cellulose papers which were modified by CNT can be a good candidate for this type of sensors which can be used widely in process controlling devices, environment monitoring, storage and other electrical devices.

4. Material and method

Bacterial cellulose (BC) and electrospun cellulose (EC) were used for obtaining conductive films. Owing to its high porosity, high crystallinity, water absorbance, mechanical properties, formability, and biocompatibility, bacterial cellulose has recently attracted a great deal of attention from both academic and industrial point of view [16, 27]. Electrospinning is a fast and simple process for forming submicron scale structures through the action of electrostatic forces in which polymers with well controlled properties such as diameter, orientation can be produced[28].

The EC was obtained by electrospinning of a cellulose acetate solution (17% wt) in acetone and dimethylacetamide (2:1 volume ratio). The cellulose regeneration process was carried out by deacetylation with NaOH in ethanol (0.05 mol/l) for 24 hours. Bacterial cellulose was produced from *Gluconacetobacter xylinum* bacteria in the static growing condition. In this case, a thick, leather-like whitish pellicle at the air-liquid interface of the culture was produced which were promising for our experiments. Celluloses which were obtained from different batches had some small differences in structural properties.

EC pellicles were not as thick and physically stable as BC samples, but its being easy to produce and also some structural advantages such as an open matrix make it promising to use as a backbone of electrical conductive cellulose.

In the experimental part of thesis, the electrical conductivity measurements were performed by using a four-point probe system (CMT-SR2000N, AIT, Korea). In order to calculate the resistivity, the thickness of samples should be determined with good accuracy which implied some difficulties. The problem and solutions that were employed will come in the next chapters.

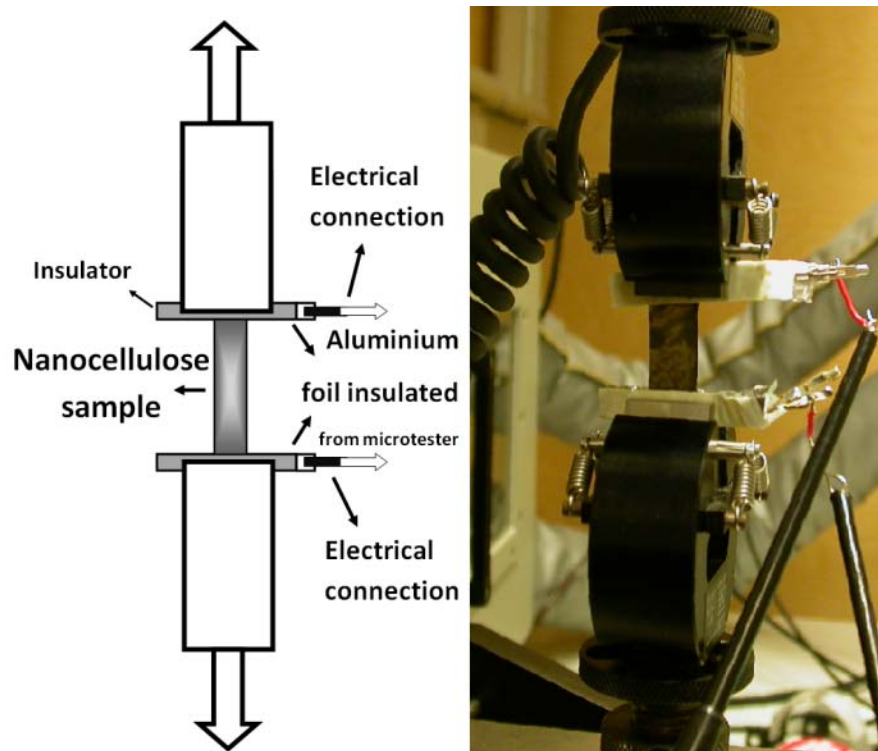


Figure 2. Experimental setup of tensile testing experiment. The angle between the applied force and the direction for measuring the electrical resistance is 0° in this setup.

Scanning electron microscopy (SEM) performed with Leo Ultra 55 FEG SEM was used to study the morphology of modified cellulose.

DWCNT modified with carboxyl groups (+90% purity, Nanocyl S A, Belgium) were used as a conductive agent for the impregnation of cellulose. Graphitized carbon nanopowder was purchased from Sigma-Aldrich (<500 nm particle size (DLS), >99.95% trace metal basis).

A microtester (Instron 5548) has been used for applying stress and a digital multimeter (Agilent 34401A) was used to register the variation in resistance. In order to measure the variation of resistance in the same direction as the applied force (orientation angle 0°), aluminum foil has been used which was insulated from the microtester clips (figure 2).

In this chapter, theoretical arguments which support practical processes and results of this work will be explained. Then processes which were developed will be explicated.

4.1. Four point probe; introduction and equations

In order to increase the accuracy of measurement, it has been decided to use four point probes method. This method makes more accurate measurement than conventional two point probe Ohm-meters by eliminating the resistance of wires and electrical connections. The four point probe, as depicted schematically in figure 3, contains four thin wires which are made to contact the sample under test. Current “ I ” is made to flow between the outer wires, and voltage “ V ” is measured between the two inner wires, ideally without drawing any current.

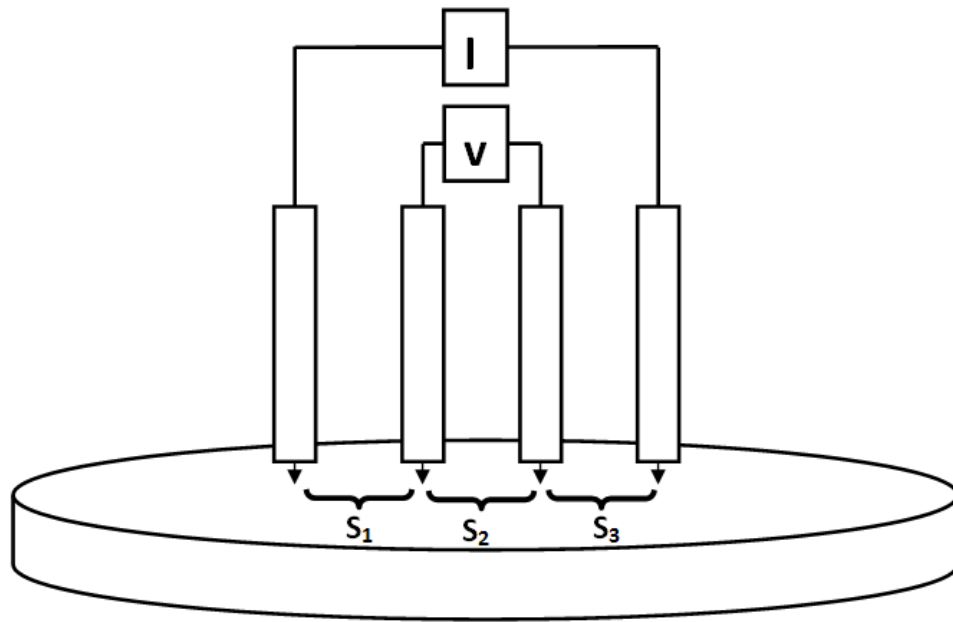


Figure 3. Schematic of the four point probe.

Sheet resistance is directly measured by a four-point probe measurement. The regular way to show how sheet resistance is calculated is by using the rectangular model. Knowing the resistance and geometry of the sample, the resistivity can be obtained using equation 1.

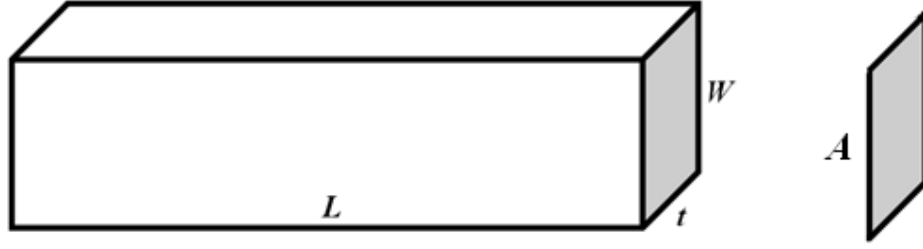


Figure 4. Schematic sheet which has been used to explain the calculation of sheet resistance and resistivity.

$$\text{Equation 1)} \quad R = \rho \frac{L}{A} = \rho \frac{L}{Wt}$$

Where ρ is the resistivity of sample, L is the length and A is the cross-sectional area which can be split into the width W and the sample thickness t .

By the grouping the resistivity and thickness the equation will be:

$$\text{Equation 2)} \quad R = \frac{\rho}{t} \frac{L}{W} = R_S \frac{L}{W}$$

Where R_S is sheet resistance of the sample. R_S can be defined as the resistance of a square sample, hence Ohms per square or Ω/sq conventionally assumed as unit for it.

Ideally “ R ” is independent of geometrical dimension and is therefore a function of the material which is measured. If the sample is of semi-infinite volume and if the spaces between the probes are $S_1 = S_2 = S_3 = S$, then the resistivity “ ρ ” which was used in equation 1, is given by equation 3:

$$\text{Equation 3)} \quad \rho_0 = 2\pi S \frac{V}{I}$$

The index 0 for the resistivity in equation 3 indicates that this resistivity is just for the condition in which the sample is of semi-infinite volume. Practical samples are of finite size which means that $\rho \neq \rho_0$. In 1954 Valdes [29] introduced a correction factor which is developed in next efforts [30]. It has been shown that if the “ D ”, the distance from probe to the nearest boundary is more than $5S$, then the correction factor is not

required. If the distance between probe and nearest boundary, in some cases thickness, is less or equal with 5S, then true resistivity can be calculated from equation 4.

$$\text{Equation 4)} \quad \rho_0 = 2a\pi S \frac{V}{I} = a\rho_0$$

The spacing between the probes of four point probe which was used in this project was 1 mm, and the thicknesses of different samples were between 15 μm to 55 μm which means that we cannot ignore correction factor.

Let's look at the plot 1 in the appendix. When the t/s is ≤ 0.5 , the line is straight. Since the plot is log-log the equation will be changed to the form of equation 5.

$$\text{Equation 5)} \quad a = K \left(\frac{t}{s} \right)^m$$

Where the “m” is the slope of the plot which in this case is 1. The “K” is the value of “a” at $t/s=1$, which is determined to be 0.72. The equation can be simplified to equation 6.

$$\text{Equation 6)} \quad a = 0.72 \left(\frac{t}{s} \right)$$

The result of combination equation 4 and equation 6 is new equation:

$$\text{Equation 7)} \quad \rho = 2a\pi S \frac{V}{I} = 4.53t \frac{V}{I}$$

So

$$\text{Equation 8)} \quad R_s = \frac{\rho}{t} = 4.53 \frac{V}{I}$$

Equation 7 and 8 apply for $t/s \leq 0.5$.

Up to now, in discussion we have assumed that the sample's size which is tested is big enough in comparison to the probe spacing to ignore the edge effects. The sizes of samples which were tested in our project were square with the 3 cm sides, and probe spacing of devices is 1 mm which means that it is better to include the edge effects in the correction factor (geometry effect). In 1957, Smits prepared a table which includes

different values of correction factors for samples with different d/s in which d is dimension of sample and s is probe spacing. Due to the previous work, it has been decided to use this table values instead of 4,53 values which is mentioned in equation 4. Based on this table, a value of 4.47 has been chosen for our samples (table 5, appendix).

4.2. Bacterial and electrospun cellulose; production processes and properties

Cellulose ((C₆H₁₀O₅)_n) is the most abundant organic compound in the world, and is present as a structural constituent in different plants. Figure 5 shows the molecular composition of cellulose in which units of monomers (D-glucose) linked from β(1→4) together form a linear chain of cellulose.

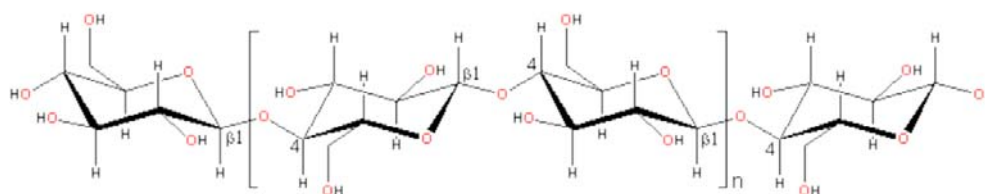


Figure 5. Schematic of molecular structure of cellulose [61].

Besides cellulose produced by plants, cellulose can be produced by bacteria and algae the structures of which is a little different from the plant cellulose: molecules in the cellulose polymer can connect together with two hydrogen bonds, and the location of this linkage can be different which leads to two different crystal structures.

Bacterial cellulose which is used for this thesis is produced by *Gluconacetobacter xylinum* bacteria and is characterized by high crystallinity, high water content and highly pure nano-fiber network structure. The reason for these outstanding properties should be searched in the micro and nano-scale structure of bacterial cellulose.

Bacterial cellulose has a highly porous structure which lets it absorb high amounts of liquid. Its high mechanical strength is due to the inter-fibril hydrogen bonds, which give stability to the structure [31, 32].

Bacterial cellulose is more ordered than standard cellulose, and as a result the level of hydrogen bonds is higher which leads to both superior reinforcement and thermal expansion properties when used with matrix materials [33]. When bacterial cellulose pellicles are dried, the nano-fibers are placed parallel to each other and more hydrogen bond will be formed which leads to increased strength and stability of dried pellicles [34, 35].

Cellulose made by plants, bacteria and algae form a natural family of cellulose, but there are other celluloses which are produced artificially. Electrospun cellulose is one of them.

Electrospinning is a simple, fast and straightforward process in which fibers with diameters of tens of nanometers are formed by applying an electrostatic voltage between a syringe which contains polymer solution and a collector on which a polymer mat will be formed. In this process, when the voltage exceeds a critical value, the electrostatic force overcomes the solution's surface tension which is responsible for keeping a liquid droplet together, and liquid will fly from the injector to the collector. If the environmental factors such as temperature and humidity are well controlled, solvents will be evaporated during this flight and fibers will form on the collectors (figure 6).

The type of cellulose solution, electrospinning flow rate, voltage, needle tip-target distance and as mentioned above, environmental factors, are just some parameters which can significantly affect the resulting polymers [36].

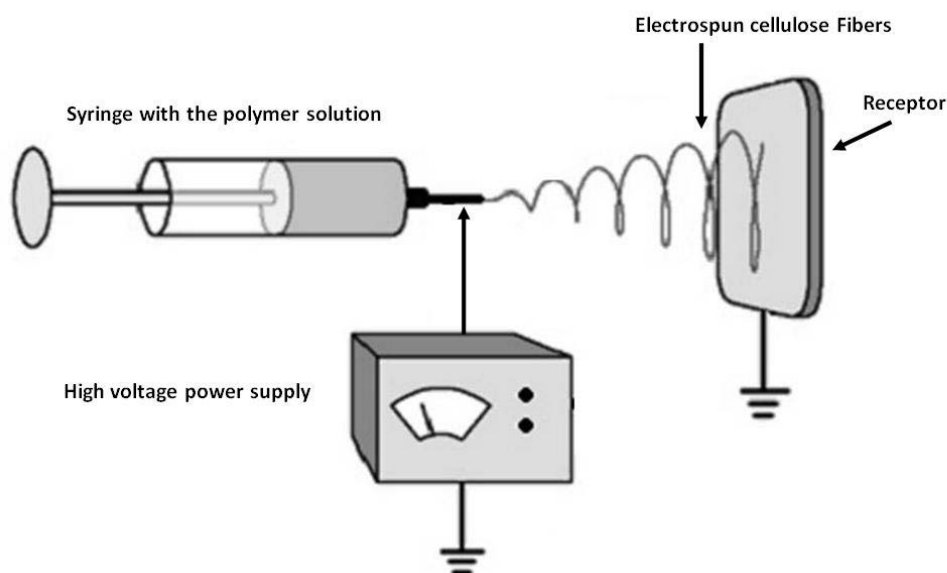


Figure 6. Schematic of electrospinning [37].

The properties of the obtained electrospun cellulose strongly depend on the solvent in which the cellulose is dissolved. Generally, mechanical properties of electrospun cellulose are different from bacterial cellulose.

Fink *et al.*[38] reported some mechanical properties of electrospun cellulose which are compared with the bacterial cellulose in table 1. The celluloses that have been compared in this table are not the same as we have used in this project, but the data can give an idea of how they are different.

Electrospun cellulose is still a young area although significant effort has been devoted to characterize films and membranes made from this type of cellulose. Still, the surface chemistry of the individual fibers of electrospun cellulose polymers is not clearly known.

	Young's modulus	Elasticity modulus	Tensile strength	Thermal properties

	(GPa)	(GPa)	(GPa)	(K ⁻¹)
Bacterial cellulose	138 (Nioshino <i>et al.</i> [39])	78±17 (Guhados <i>et al.</i> [40])	2 (Page and El-Hosseimy [41])	0.1×10^{-6} (Nioshino <i>et al.</i> [39])
Electrospun cellulose	Not available	11 (Fink and Ganster [38])	0.33 (Fink and Ganster [38])	Not available

Table 1. Comparison of bacterial cellulose and electrospun cellulose in mechanical properties.
The table content was taken from a review article [42].

4.3. Cellulose NaOH-treatment process

NaOH treatment is a process in which the residue of bacteria and unwanted non-cellulose organic materials are removed from the bacterial cellulose structure. This process is done after finishing cell culturing [43]. It has been reported that this process can change the cellulose structure and as a result the mechanical properties of the resulting cellulose will be different [44]. In 2009 Brigid *et al.* reported that bacterial cellulose which has been treated in NaOH has a lower density than native cellulose. It was mentioned in the report that this difference can be attributed to the removal of alkali-soluble bacterial material from the cellulose structure [45] .

We expected to obtain cellulose with higher porosity after NaOH treatment which might absorb CNTs better than native cellulose in all surfaces.

Cellulose swelling was performed by soaking cellulose pellicles in 0,5 mol/l NaOH solution for 1 hour at 70 °C. Before modifying with DWCNT or GNP, cellulose pellicles were washed until a pH of 7 was obtained. The washing process was conducted by rinsing and soaking in de-ionized water and checking the pH until it reached 7.

This process was done at room temperature and the cellulose pellicles were subjected to subsequent carbon nanoparticles exposure after the swelling process was finished.

4.4. DWCNT and GNP dispersion process

In the following sub-chapters different processes which have been developed in the dispersion step will be briefly described.

4.4.1. Type of dispersion

The dispersion is a critical step in the processing of CNTs and GNP. The as-produced CNTs are held together strongly due to van der Waals interaction between the tubes [46] which is problematic in the modification process. Many methods have been developed to disperse CNTs for polymer modification processes; they can be classified into three general branches: direct mixing of polymer and CNT, chemical surface modification and third component assisted dispersion of CNT [47].

In direct mixing, the dispersion is accomplished by applying ultrasounds in the presence of polymers and CNT [48]. This type of dispersion is simple but often the dispersity is not satisfactory. In order to reach a sufficient dispersity of CNTs, a long and intensive ultrasonic process should be applied which can damage the CNTs and fragment them to small tubes which is not desirable in our project.

The second process, chemical surface modification, includes creating some surface functionalized groups such as carboxylic groups (-COOH), ketenes (-C=O), and alcohols (-C-OH) via treating the CNTs with some strong acids such as nitric acid [49] or with some oxidizing agents such as $\text{KMnO}_4/\text{H}_2\text{SO}_4$ [50]; the effect is that the solubility of the CNT increases significantly in water and other organic solvents as well as enhancing the compatibility of the CNT and polymer. However, long treatment of CNTs in a strong and concentrated acid (or other oxidizing agents) leads to shortening of the tubes, and disturbs the conjugated electronic structure which can change the CNTs electrical and mechanical properties.

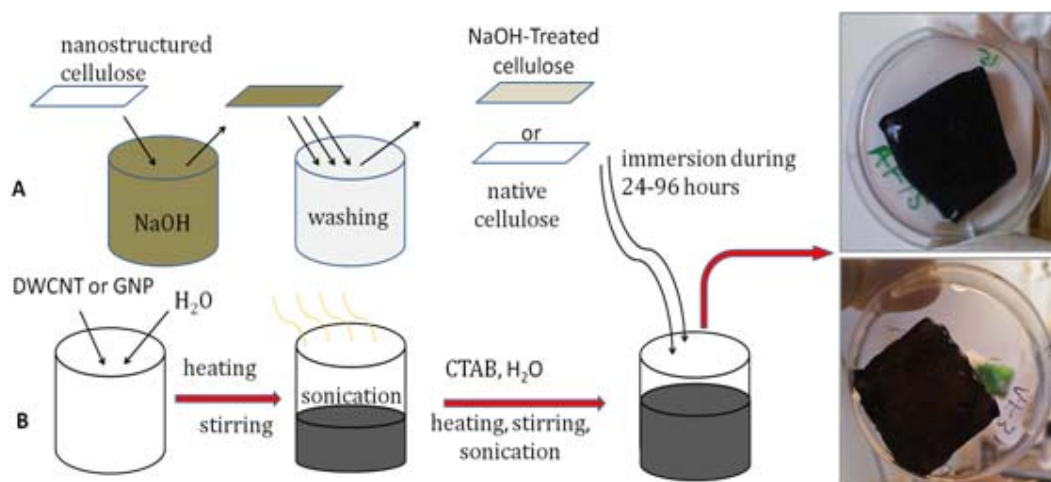


Figure 7. Preparation of the DWCNTs (or GNPs)/incorporated nanocellulose film: (A) NaOH-treatment process; (B) dispersion and modifying process. Resulting conductive films received from BC (top figure), and GNP (bottom figure).

In order to have better compatibility between filler and polymer, pre-treated DWCNTs have been used. The surface modification of purchased CNT is not in the level where the tubes break or are damaged.

The last type of modification uses a third component as a dispersing agent. In this process, the third chemical compound, which can be a surfactant [51], a polyelectrolyte [52] or an organic complex compounds such as a protein or DNA [53], is added to the mix of polymer and CNT. These compounds adsorb on the CNT walls during sonication and the dispersion is stabilized by repulsive electrostatic interaction between the CNTs and the surfactant. The result of this type of dispersion is effective and the resulting CNTs do not show significantly different electrical and mechanical properties.

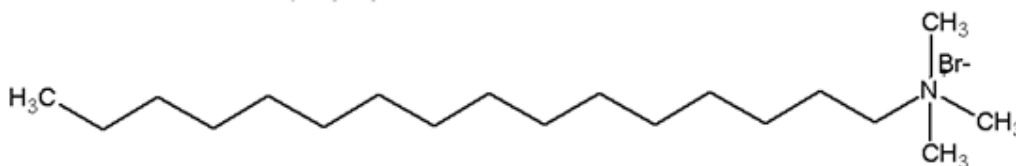


Figure 8. The chemical structure of cetyl trimethyl ammonium bromide (CTAB). This surfactant is cationic and can absorb on the negatively charged carbon nanotube surface properly.

The backbone of the dispersion process which was selected for our project is the third type. The third compound that has been used in our project was CTAB (cetyl trimethyl ammonium bromide) (figure 8). it is known that, the carboxyl functionalized CNT's surface are highly negatively charged when they are dispersed in water or similar solutions [54, 55].

CTAB is a cationic surfactant with the quaternary ammonium nitrogen core which can readily adsorb on the negatively CNT surface.

4.4.2. Sonication process

Sonication is the critical step in the dispersion process. Ultrasound like any other type of sound can be transmitted through any physical medium. During this passing, the molecular spacing of the medium is compressed and stretched and as a result the average distance between different molecules and atoms changes as they oscillate around their mean position.

When the negative pressure of ultrasonic sounds is strong enough, it can overcome the forces which link the constituent molecules of the liquid and then the liquid “breaks down” and voids are created [57]. These voids are so-called cavitation bubbles [57]. This process can happen also for atoms in the molecules; as a result of the ultrasound's negative pressure, the distance between atoms in the molecules exceeds the minimum and maximum distance required and as a result the chemical bonds between atoms break.

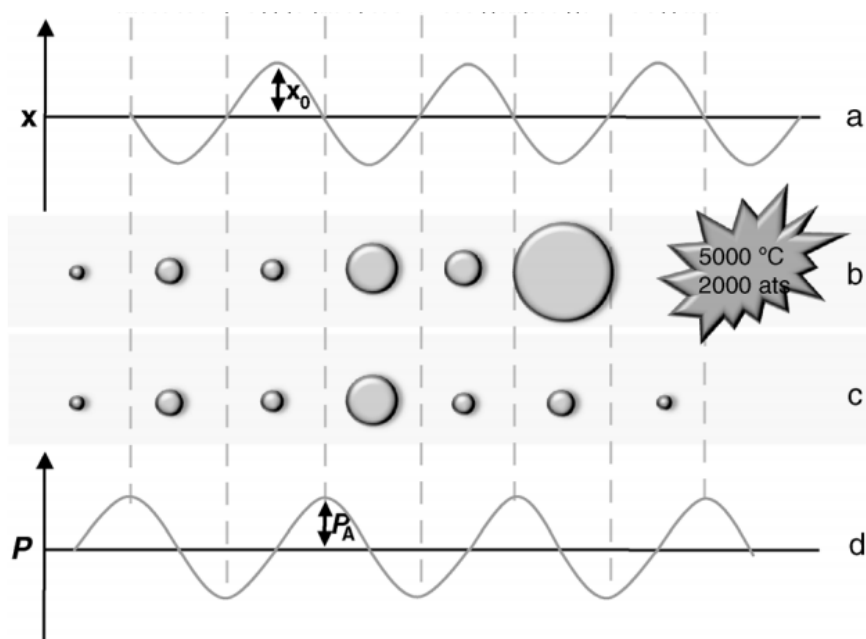


Figure 9. Creation of stable cavitations bubbles and transient cavitations. (a) Displacement, (x) displacement graph (b) transient cavitation, (c) stable cavitation, (d) pressure and (p) pressure graph. Adapted with permission from reference [56].

Cavitation bubbles can affect the medium in two ways: stable cavitations which are formed at low ultrasonic intensities and transient cavitations which are formed using sound intensities in excess of 10 Wcm^{-1} [57, 58] (figure 9). The second way, transient bubbles collapsing, play the main role in how ultrasound impacts on chemical compounds.

Carbon nanotubes can be damaged during the ultrasonic process. Ultrasonic time and energy are two important factors which determine the level of defects and damage of the CNTs. It has been reported that when the duration of sonication was increased during the dispersion process then CNTs showed more defects and serious damage [59]. Also more damage was observed on CNT and GNP surfaces when more energetic ultrasound was used [59].

Furthermore, in a sonication process, the structural deformation of CNTs is solvent dependent. Between different solvents, ethanol and water are two solvents which lead to less damage [59]. This may relate to the difference in efficiency of energy transfer in the cavitations in different solvents [58].

Temperature and pressure have been kept constant for all samples, and we expected to get the same level of dispersions for all prepared CNT and GNP

solutions. However, the conductivity results for BC modified in different dispersed solutions with the same concentration, immersion time and volume were significantly different (table 3).

In order to find the parameter which has led to this problem all steps of the dispersion process were scrutinized. Due to the importance of the ultrasonic step, this step was also taken into consideration. It was not possible to change the power in the ultrasonic bath which was used in our project, thus time and sample location are two factor which were suspected to change the results. In order to determine the main factor, different samples with the same properties were prepared and sonicated at the same time, but in different locations. The result showed that the ultrasonic intensity distribution inside the ultrasonic bath is not homogeneous which resulted in different levels of dispersion when the solutions were put in different locations.

However, a simple, cheap and fast method has been developed to find the best place with highest intensity inside the bath [60]. This “foil test” uses an aluminum sheet to find the most intensive location. The sheet is placed inside the bath; due to the ultrasonic waves the aluminum sheet will be perforated. The difference in perforation levels represents the differences in intensity (figure 10).

In order to investigate the sonication location effect on the obtained conductivities, two samples with the same experimental conditions were prepared and placed at different locations inside the ultrasonic bath; one of them in the middle and another one in the side of bath. As mentioned above, the foil test result reveals that the center of the bath is the most intensive place.



Figure 10. Foil test is a simple and fast method to find the most intensive location inside the ultrasonic bath. The aluminum sheet put in the bath (top image), due to the ultrasonic waves the aluminum foil is perforated (bottom image)

The electrical conductivity measurement results show that the BC is affected accordingly; samples modified in the solution which has been located in the middle of bath had twice the conductivity of the other one (table 3).

specification of sample	BC Modified in 30 ml of 2 mg/ml of DWCNT solution	BC Modified in 30 ml of 2 mg/ml of DWCNT solution
Location	Near to the center	Near to the side
Conductivity	$0.15 \pm 0.002 \text{ S}\cdot\text{cm}$	$0.08 \pm 0.002 \text{ S}\cdot\text{cm}$

Table 3, the conductivity results of BC pellicles which have been modified in the solutions. The location was the parameter which has been changed in this test.

But there are many factors and uncertainties which play major roles in this process, hence it has been preferred to assume the location effect is just one factor among different ones.

In our project, water was used as a solvent during the sonication process. The sonication time was 20 minutes for each step; enough for opening the CNT or GNP structure and not long enough to break or seriously damage the CNT structure.

4.4.3. Experimental setup of dispersion process

DWCNT and GNP water dispersion solutions were prepared in the presence of cetyltrimethylammonium bromide (CTAB). DWCNT or GNP were mixed with half of final volume and were heated and stirred (90 °C, 1 hour). The solutions were sonicated (20 minutes) and CTAB was added to solution (1:1 CTAB to NanoParticle weight ratio).

Water-DWCNT-CTAB (or GNP-CTAB) mixtures were heated (90 °C, 1 hour). This process was followed by sonication of solution for 20 minutes. Prepared dispersions were centrifuged for 20 minutes (3500 rpm, 21 °C) in order to remove undispersed carbon nanotubes.

In order to study concentration and volume effects on the dispersion process and on the conductivity of the obtained cellulose film, three different dispersed solutions with different volume and concentration were prepared which were 15 ml of 1 mg/ml dispersed solution, 15 ml of 2 mg/ml dispersed solution and 30 ml of 2 mg/ml dispersed solution. De-ionized water has been used in all steps and processes.

4.5. Modifying and drying process

At the beginning of the project, it was decided to treat BC in 15 ml of 1 mg/ml of CNT or GNP solutions for 24 h. But the solution became transparent after 4-5 h which represents all of dispersed nanoparticles having been adsorbed on the BC surface. In the next step higher concentrations of dispersed solution have been used which resulted in pellicles with higher conductivities. In this case, the solutions did not become transparent even after 24 h. Therefore it was decided to treat the BCs for a longer time. By increasing the treatment time and dispersed solution concentration, the conductivities of the pellicles varied in a regular manner which will be discussed later in the discussion part of the thesis.

The drying process is another step which can be problematic. In order to measure the pellicles' conductivities by a four point probe, flat pellicles were needed which should have a similar thickness in all regions. The drying of pellicles in a freeze drying process or leaving them in the fume hood led to severe shrinkage of the cellulose. In order to solve this problem, a special Teflon fixture was designed in which the pellicles can be dried without shrinking problems.

Cellulose pellicles ($3 \times 3 \text{ cm}^2$) were immersed in DWCNT dispersions under agitation for 24 to 72 h. BC pellicles subsequently were dried in a fume hood in a Teflon fixture. The thickness of the dried conductive films was $25 - 35 \text{ }\mu\text{m}$. The drying process was monitored by daily weighing of the pellicles.

5. Results and discussion

Due to the differences in the thickness of the fibers and the structure of their matrix, the same modification processes lead to different types of carbon nanoparticle incorporation in BC and EC.

The structure of BC is rather closed and it has smaller pores than electrospun cellulose, hence the modifying agents cannot penetrate into the cellulose structure. As a result, thin asymmetric layers of modifying agents were formed on both sides of the cellulose material (figure 11 and 12).

The thick fibers of electrospun cellulose form an open matrix with larger pore size. As a consequence the DWCNT can modify also the fibers which are not on the surface of EC films. This is clearly observed in the SEM picture and in the optical microscope image (figure 11 and 12).

It should be mentioned that all comparative data used in tables and graphs were obtained from the same BC resource and were from the same experiment series. These data are not necessarily best results.

The resistance of each pellicle was obtained as an average of 81 different discrete resistance measurements.

5.1. Variation of conductivity versus concentration and volume of DWCNT and GNP solutions

Different samples with different concentration and volume of DWCNT were prepared and their conductivities were tested. But before going deeper in this case, there are some uncertainties which we need to consider:

As was mentioned in the previous chapter, the sheet resistance is the parameter which is measured directly with a four point probe. In order to calculate the resistivity (and conductivity), the thickness of the samples should be known which is not possible for BC pellicles; the conductive layers on both sides are just a small part of the total thickness which was not possible to measure them.

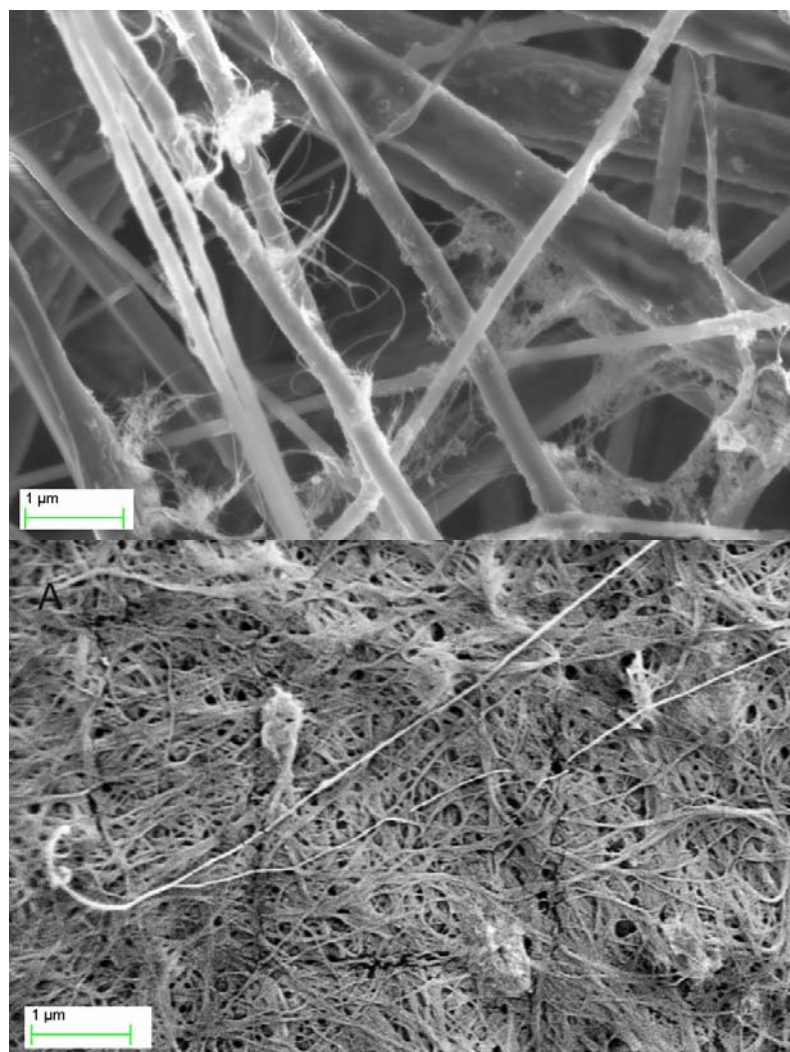


Figure 11. SEM images of electrospun cellulose modified with DWCNT (top image) and native bacterial cellulose without any modification. The electrospun cellulose displays a much more open fiber structure.

It was not possible to determine the thickness by microscope images with good accuracy, therefore it has been decided to use the total thickness (as measured by a micrometer) in the calculations.

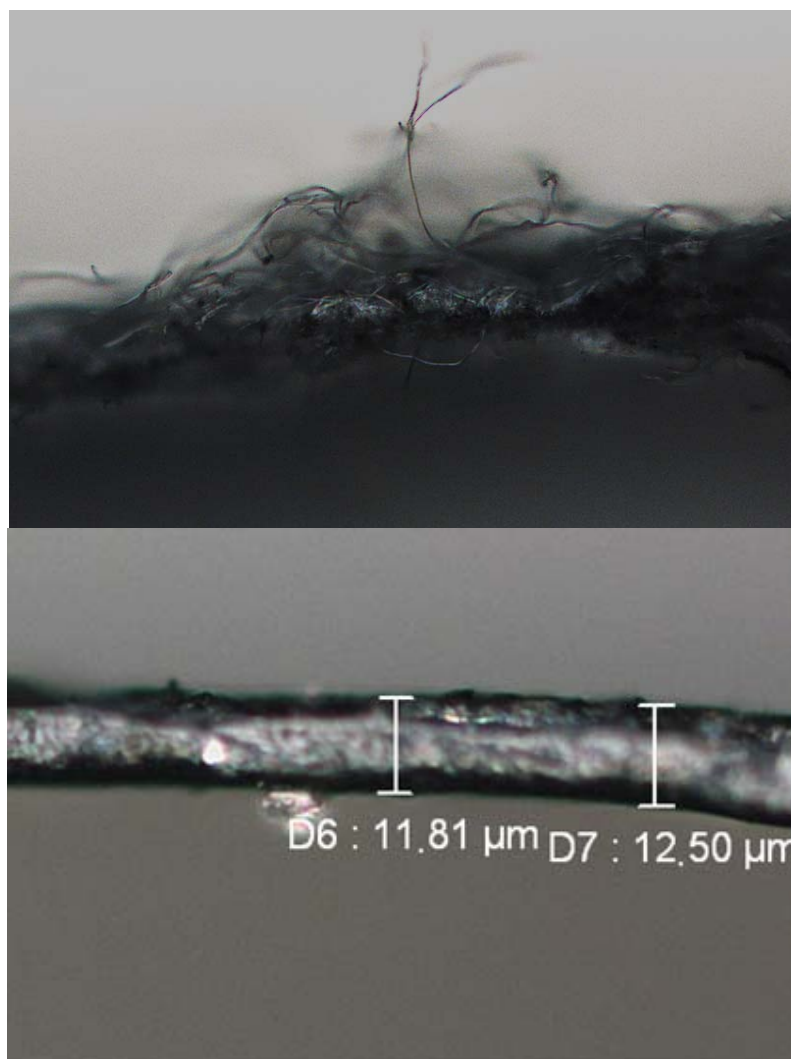


Figure 12. Optical microscope images of DWCNT modified electrospun cellulose (top image) and bacterial cellulose (bottom image). The labels D6 and D7 are names which are chosen by microscope automatically for length lines.

The second problem is even this unreliable measured thickness is not uniform in all locations of the sample and can vary up to 15% in different locations which means that the resulting conductivities have 15% errors (equation 1 and 2), therefore it has been decided to use thickness average for calculation which makes some errors in the final values. The errors have been shown as error bars in the plots.

Generally, the electrical conductivity of the modified celluloses and the distribution of DWCNTs in their volume appear to be affected by changing the volume and concentration of the solution (figure 13).

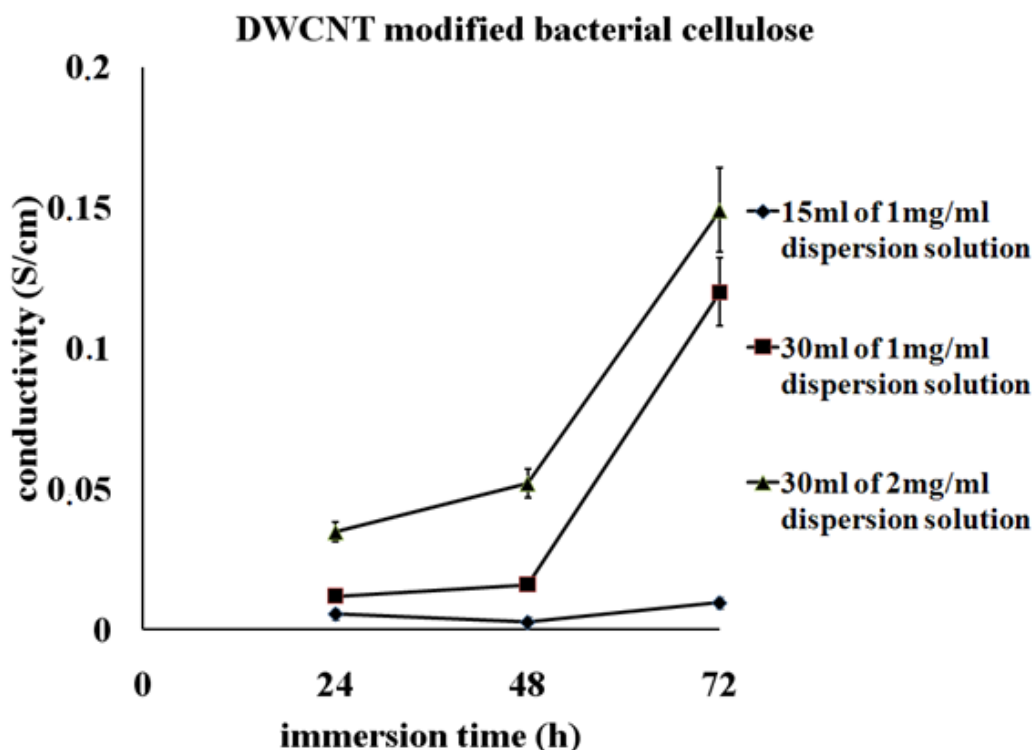


Figure 13. The conductivity of bacterial cellulose modified with DWCNT as a function of immersion time. Different samples which have been modified in different concentrations and volumes of DWCNT solutions have been tested.

Nanocellulose samples which were modified in 30 ml of 2 mg/ml DWCNTs solution have shown the best conductivities. Also, the distribution of DWCNT was better and more uniform CNT layer has been form on the surface. The same behavior was observed for GNP modified cellulose pellicles.

5.2. Conductivity versus treatment time for cellulose in DWCNT dispersed solution

After preparing the dispersed CNT solutions, cellulose pellicles were treated in them for 24, 48 and 96 hours. The results show that the treatment time has a significant

effect on the modification process giving different conductivities for the treated BC pellicles.



Figure 14. DWCNT dispersed solution after cellulose treatment. The CNT solution which has lowest amount of CNT (15 ml of 1 mg/ml) became transparent (right hand sample), but the solution with higher amount of CNT (30 ml of 1 mg/ml) was dark (left hand sample).

As figure 13 illustrates, the conductivities of the samples which were treated in 30 ml of 1 mg/ml and 2 mg/ml of DWCNT dispersed solutions increased with increasing treatment time. On the other hand, the BC pellicles which were immersed in 15 ml of 1 mg/ml did not show significant changes in conductivity when the immersion time was changed. The reason can be the amount of DWCNTs in the solution. As was mentioned before, after a couple of hours, all the CNTs in the solution were adsorbed on the BC surface. Figure 14 shows that the DWCNT solution with 15 ml of 1 mg/ml became transparent after 24 h, but the DWCNT solution with higher amount of CNTs (30 ml of 1 mg/ml) was still dark after the same immersion time.

5.3. Effect of alkali treatment on the modification level

A swelling process was conducted for bacterial cellulose to open its matrix during immersion. SEM images of BC treated by NaOH and native BC have been shown in figure 7. It seems that the porosity of BC pellicles has been increased after treatment. The reason might be dissolution of non-cellulosic organic compounds from the cellulose structure by the NaOH treatment (figure 15).

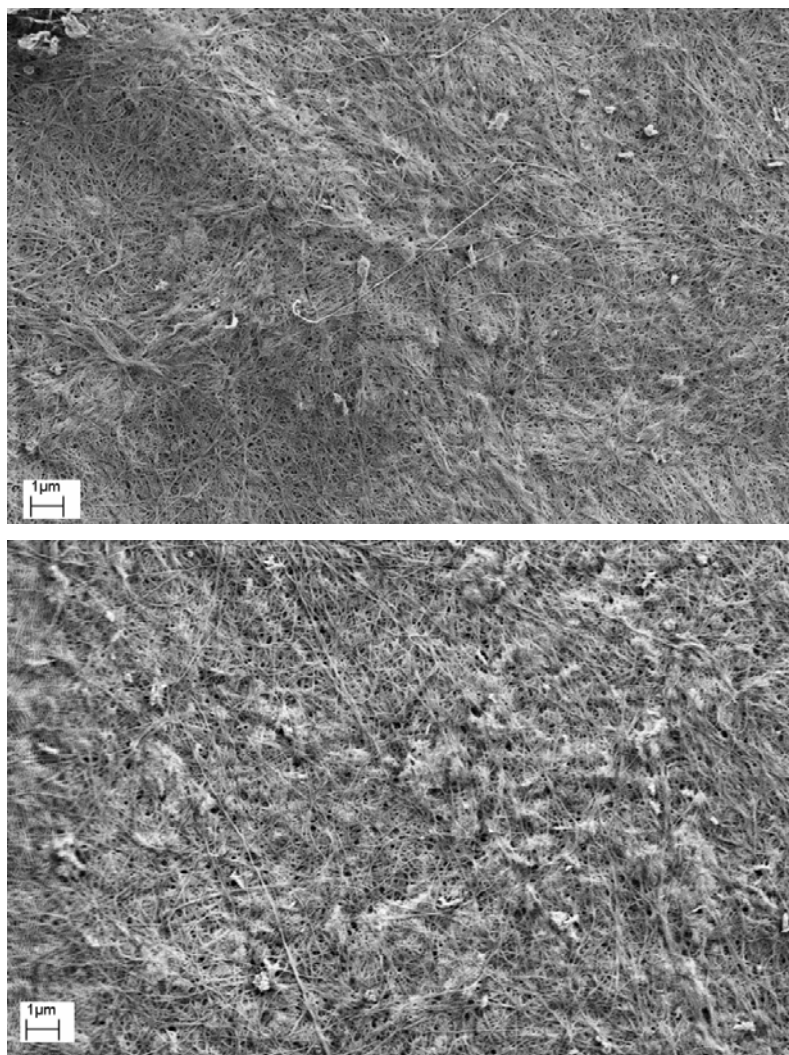


Figure 15. SEM image of native BC (top image) and after treatment with NaOH (bottom image).

The conductivities of NaOH treated and native BC which were modified in the same dispersion have been measured. The results show that the NaOH treatment had no measurable effect on the conductivities of the different pellicles (figure 16).

It seems that the increase in porosity was not at a level which could influence the outcome of the nanoparticle modification and resulting conductivities.

5.4. Effect of type of modifying agent on the final conductivities of BC pellicles

DWCNT and GNP were used to modify the bacterial cellulose surface. Generally, the BC pellicles which were modified with GNP are of a deeper black appearance and visually have a more homogenous surface color than CNT modified ones.

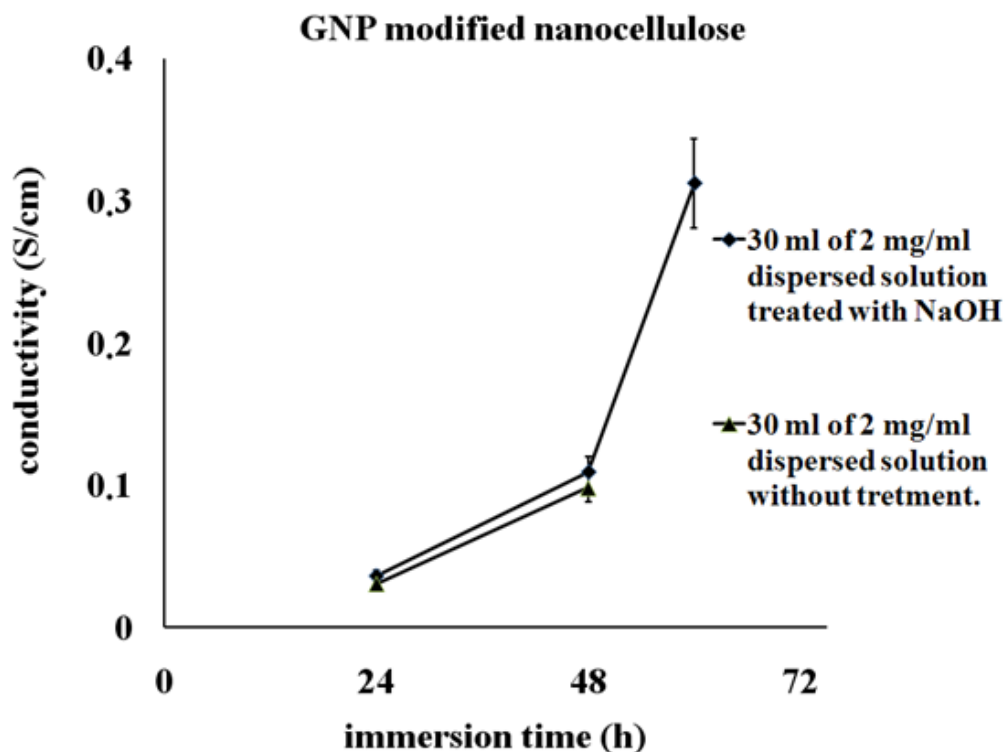


Figure 16. The conductivity of bacterial cellulose modified with GNP (native and treated with NaOH) as a function of immersion time. The resistivity results are almost the same.

What we observed visually should be translated to measurable quantities and robust evidence, hence 3D images of the resistivity of the sample surface and standard deviations have been employed to express differences in the surface homogeneity of samples.

Two samples with the same experimental modification scheme were chosen and their 3D image of resistivity versus positions was compared (figure 17). The only difference between them was the type of modifying agent which was DWCNT for one of them and GNP for the other one. The images illustrate that BC pellicles which are modified with GNP have a more homogeneous distribution than other pellicles.

Furthermore, the standard deviation (SD) for these two samples has been calculated. Generally, the SD of the CNT modified samples was higher than GNP samples. For

example, the SD of samples mentioned above was $23.2 \text{ S}\cdot\text{cm}^{-1}$ for DWCNT modified BC, whereas for the sample modified with GNP it was $6.6 \text{ S}\cdot\text{cm}^{-1}$.

The comparison of conductivities of pellicles shows that at the same condition and with the same bacterial cellulose resource, the conductivity of the BC modified with DWCNT is higher. The best results found were approximately $3.95\times 10^{-1} \text{ S}\cdot\text{cm}^{-1}$ for bacterial cellulose/DWCNT, $0.334\times 10^{-1} \text{ S}\cdot\text{cm}^{-1}$ for bacterial cellulose/GNP film. It should be noted that the data used in comparative tables taken from the tests which were done under the same conditions are different from the best values which are mentioned here.

5.5. Different level of modifications in different BC sides

The results for different bacterial celluloses have shown that the adsorption levels for CNTs and GNPs are different for different sides of the BC samples which lead to substantially different conductivities of these sides. After examining different parameters, the original difference in structural properties of the different sides has been found to be the most likely candidate to explain this result.

The bacterial cellulose which was used in this project has been grown by *Gluconacetobacter xylinum* bacteria in a static condition. The thick and whiteish BC pellicle is formed at the air-liquid interface of the culture [61, 62].

During cellulose growth, carbon dioxide which is produced by *G. xylinum* cells helps the bacteria to float and to reach the surface. But eventually some bacteria are trapped in the cellulose

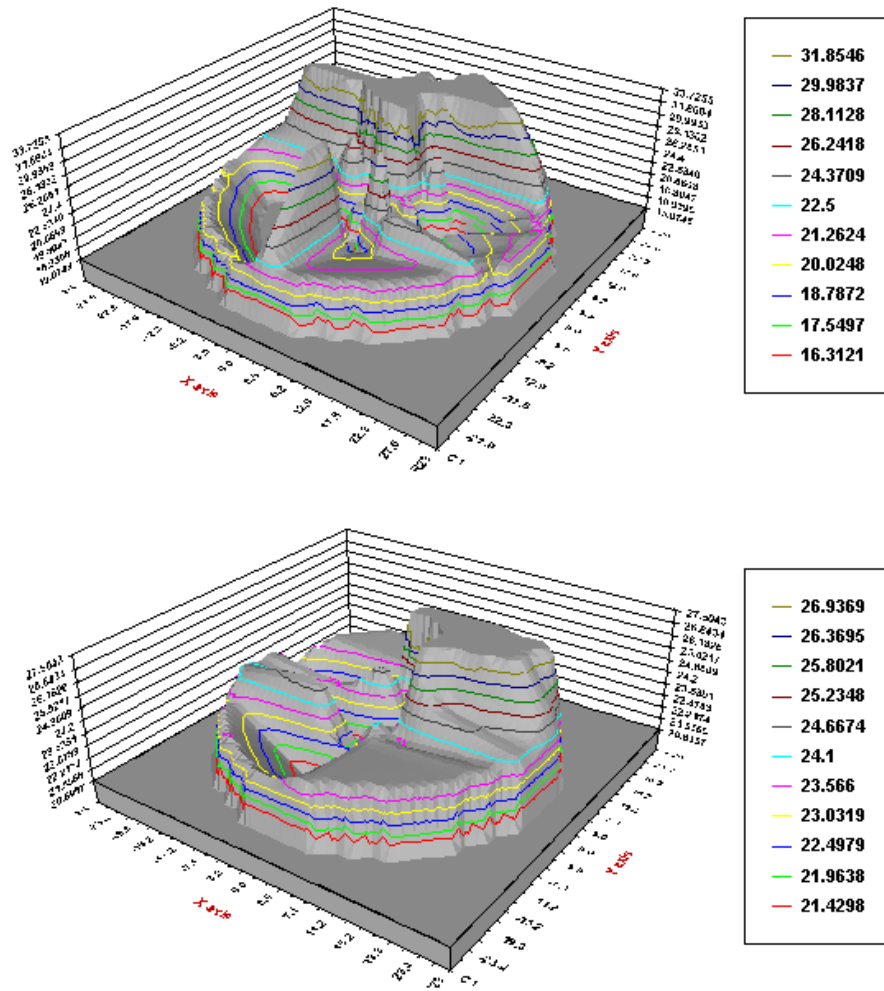


Figure 17. 3D image of modifying agent's resistivity distribution on the BC pellicles surface, BC modified with DWCNT (top image), BC modified with GNP (down image). Note: the images scale is not the same. The values in the right column is resistivity and their unit is ohm.cm.

. Also, the bacterial cellulose has a layered structure in the static culture; new layers are formed at the upper side of the film [63] which can be interpreted as a consequence of only the bacteria located at the air-liquid interface of the culture being able to produce cellulose [61, 62]. Resulting BC pellicles have two different layers with different morphology which can be observed by the naked eye; the upper side is smooth and clear and the bottom side is fuzzy with a faintly yellow tone which can be due to dormant bacteria.

5.6. Effect of type of cellulose on the final conductivities of pellicles

Structural differences between modified bacterial cellulose and modified electrospun cellulose have been taken into consideration in previous parts.

These differences lead to having better surface modification in the BC fibers which are located at the surface of pellicles than fibers which are enclosed inside the bacterial cellulose. For electrospun cellulose, due to the open structure, modifying agents can penetrate inside the cellulose and as a result all fibers in all levels were modified.

Table 4 shows resulted conductivities for two BC and EC pellicles modified in the same experimental setup. These pellicle were modified in 30 ml of 2 mg/ml DWCNT dispersed solution, and were immersed 72 h. the results shows that conductivity of BC pellicle was two times higher than modified EC pellicles.

Sample	Electrospun cellulose modified by DWCNT	Bacterial cellulose modified by DWCNT
conductivity	$8.6 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$	$7.8 \times 10^{-2} \text{ S} \cdot \text{cm}^{-1}$

Table 4, difference between EC and BC modified in the same conditions.

The conductivity result of two sides is different in bacterial cellulose. But in electrospun cellulose both sides have the same conductivities.

The best results were found approximately $3,95 \times 10^{-1} \text{ S} \cdot \text{cm}^{-1}$ for bacterial cellulose/DWCNT and $8.6 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$ for electrospun cellulose/DWCNT film.

5.7. Effect of strain on the conductivity of the bacterial cellulose

CNTs have been reported as a reinforcement agent for many polymers, therefore we expected to observe this effect on nanocellulose in a similar way. Moreover one of the main functions of CNTs or GNP in the cellulose structure is converting material

structural changes to electrical responses. These two reasons convinced us to test the sensitivity of pellicles conductivities to external forces.

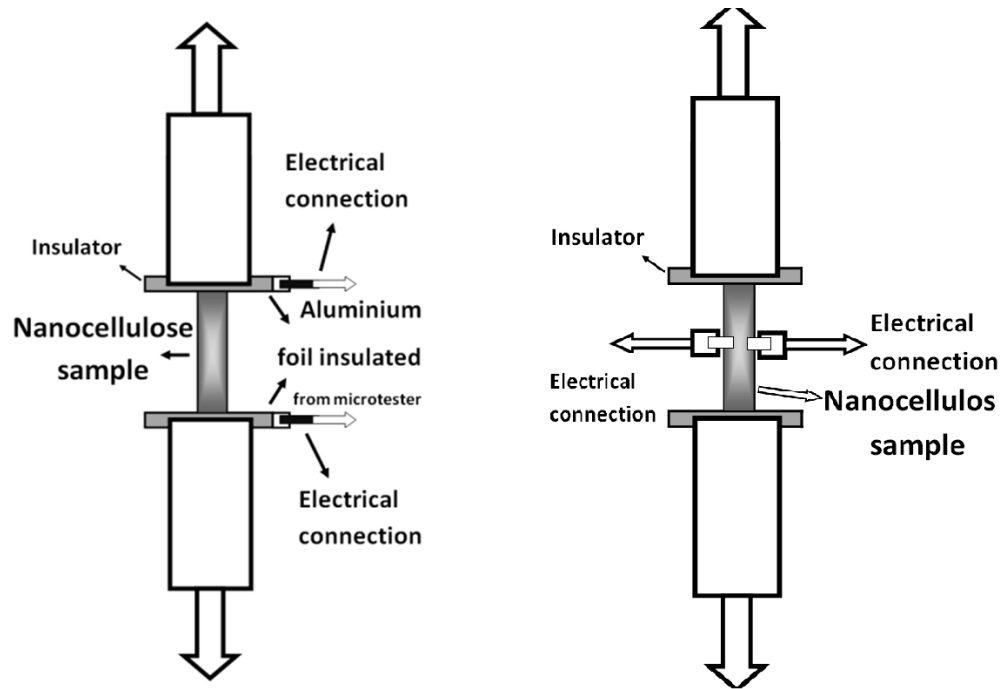


Figure 18, in the left picture electrical connections which are responsible to measure the conductivity is installed in the same direction with the microtester connection which apply the external force. In the right figure the angle between electrical connections and microtester connections is 90° .

Two different experimental set-ups have been used to study the variation of sample resistances as a function of tensile force. In one of them the angle between applied force made a 90° angle with the electrical connections which have measured the resistance changes and in the next step both external force and applied voltage were put in the same direction (figure 18).

Cellulose fibers in both electrospun cellulose and bacterial cellulose pellicles which have been used in this project are non-aligned. The pattern of carbon nanotubes which are impregnated in the cellulose is non-aligned too. This isotropy implies that the same mechanical or electrical changes should happen if we change the direction of applied forces. In both cases; native cellulose and modified cellulose this interpretation can be true.

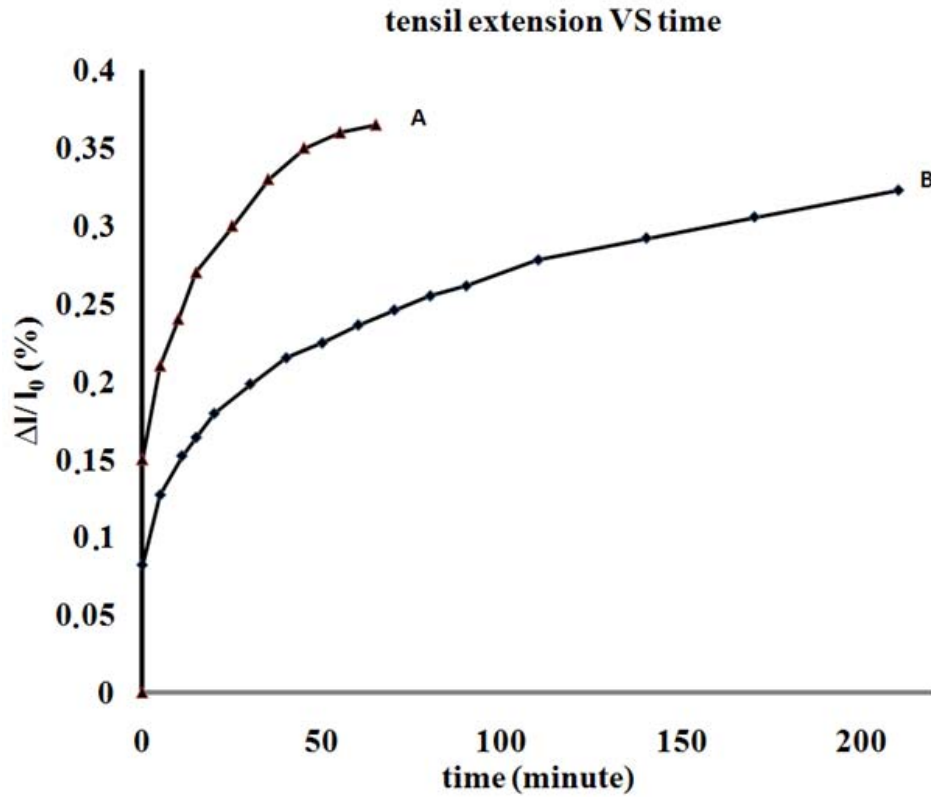


Figure 19. Creep test for BC modified with DWCNT. BC modified in 1 mg/ml of DWCNT solution (plot A) and BC modified in 2 mg/ml DWCNT solution.

Figure 19 shows the typical strain versus time plot which called creep test under 4 N force at room temperature. Creep is the prolonged deformation response to the constant external force. A transient response to constant deformation is called relaxation [64]. Both these parts can help to determine whether our material is linearly or non-linearly viscoelastic. All samples which have been modified with CNTs or GNP have shown the same behavior.

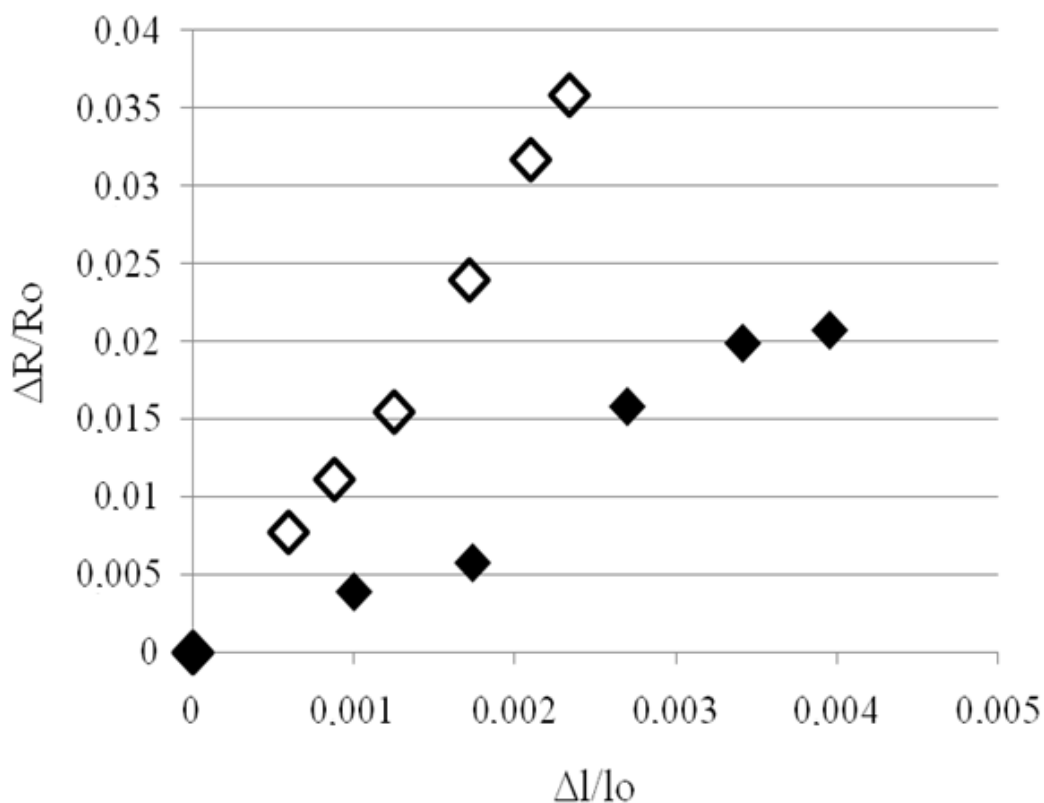


Figure 20. Fractional increase in resistance ($\Delta R/R_0$) as a function of the fractional extension ($\Delta l/l_0$) of a strain gauge for two different samples of bacterial cellulose. Bacterial cellulose which is modified in 30ml of DWCNT dispersion with 1 mg/ml concentration (filled markers) and bacterial cellulose which is modified in 30 ml of DWCNT dispersion solution with 2 mg/ml solution (open markers).

At the first moment of applying force, a big tensile extension was registered which might be the result of releasing the shrinkages which are formed during the drying process. This result was confirmed by DMA also. Comparing the two plots illustrates that the sample which was modified with a lower amount of CNT was more deformed under the same load.

Figure 20 illustrates the relatively large fractional increase in resistance with the fractional extension obtained by the application of tensile force for two samples of DWCNT modified nanocellulose. The nanocellulose pellicle which is modified with a higher concentration of DWCNT showed more sensitivity to an increase in the strain.

6. Conclusion

DWCNTs and GNP-incorporated bacterial and DWCNTs-incorporated electrospun celluloses were prepared by immersing cellulose films in DWCNT and graphitized carbon nanopowder water dispersed solutions.

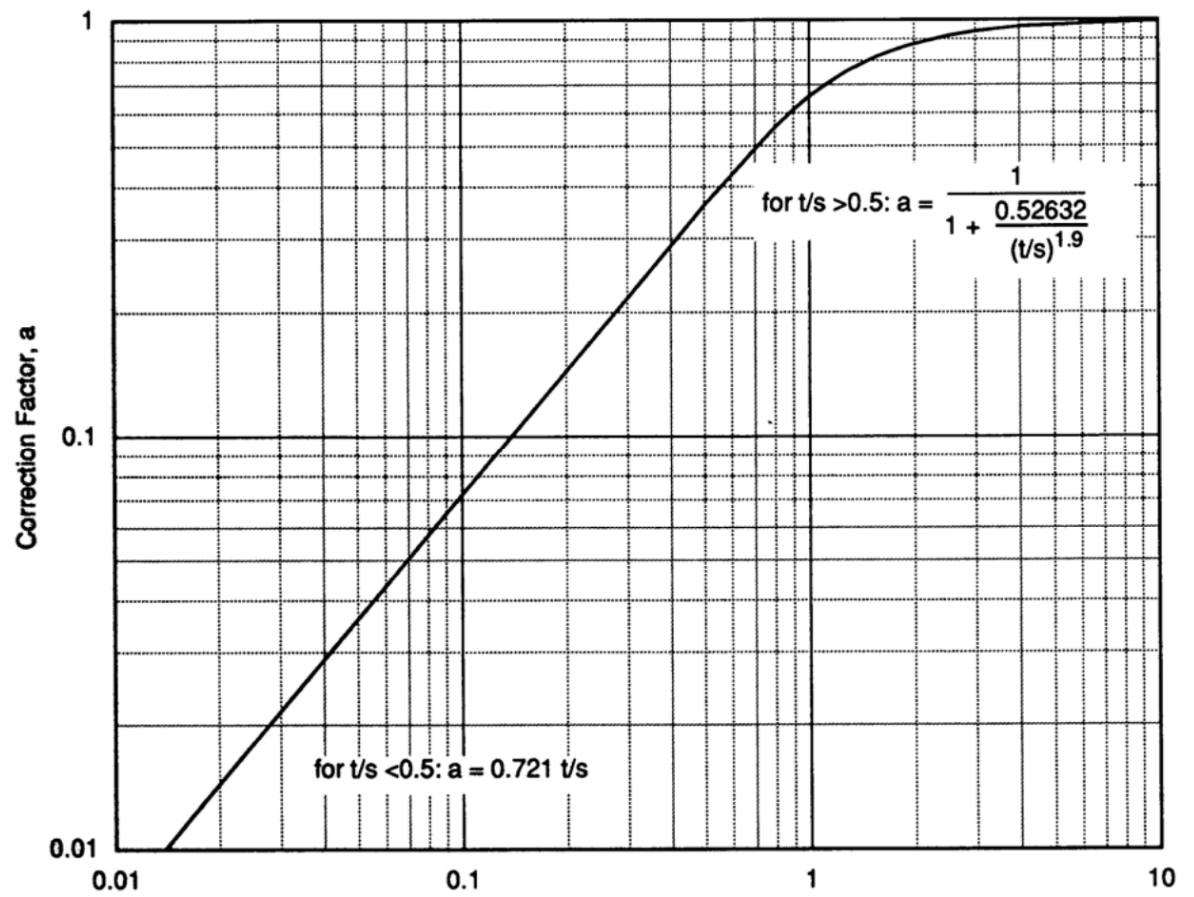
We have worked to improve the dispersion process. The morphology of the resulting electrical conductive cellulose material has been studied by optical microscope and SEM and the electrical properties were monitored by four-point probe measurements and resistance measurements under strain in a microtester.

It was found that the electrical conductivity of the obtained BC/DWCNT depends on fractional extension obtained from an applied force. Creep tests were done on the samples and it was found that the mechanical behavior depends on the modifying condition.

7. Outlook

We spend so much time in the chemistry laboratory part to improve the dispersion and modification processes. It is a time to improve the experimental setup to study the properties of our samples.

8. Appendix



Plot1, taken from University of Illinois Urbana-Champaign website [65]

points 1 and 2 is therefore

$$V = \Sigma \Delta \varphi_n = \rho_s I \frac{1}{C \left(\frac{a}{d}; \frac{d}{s} \right)}$$

where $C(a/d; d/s)$ is a constant defined by this equation. As shown in the Appendix, the summation can be done easily by expanding the logarithm and summing each term as a geometrical series. In almost all cases, the first term gives four-place accuracy. The sheet resistivity is thus given by

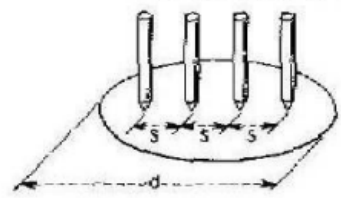
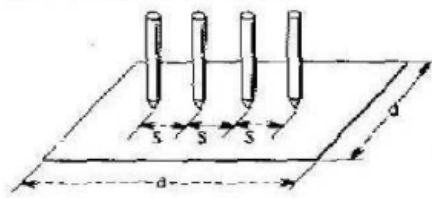
$$\rho_s = \frac{V}{I} C \left(\frac{a}{d}; \frac{d}{s} \right).$$

Table I gives this factor C for various geometries.

For small d/s the quantity $C' = (s/d)C$ is close to unity. In these cases the sheet resistivity can be expressed as:

$$\rho_s = \frac{V}{I} \frac{d}{s} C' \approx \frac{V}{I} \frac{d}{s}, \quad C = \frac{s}{d} C'$$

TABLE I — CORRECTION FACTOR C FOR THE MEASUREMENT OF SHEET RESISTIVITIES WITH THE FOUR-POINT PROBE

$\rho_s = \frac{V}{I} C$

d/s	circle diam d/s	$a/d = 1$	$a/d = 2$	$a/d = 3$	$a/d \geq 4$
1.0				0.9688	0.9994
1.25				1.2467	1.2248
1.5			1.4788	1.4893	1.4893
1.75			1.7196	1.7238	1.7238
2.0			1.9454	1.9476	1.9476
2.5			2.3532	2.3541	2.3541
3.0	2.9662	2.4575	2.7003	2.7005	2.7005
4.0	2.9289	3.1137	3.2248	3.2248	3.2248
5.0	3.3625	3.5098	3.5749	3.5750	3.5750
7.5	3.9273	4.0095	4.0361	4.0362	4.0362
10.0	4.1716	4.2209	4.2357	4.2357	4.2357
15.0	4.3648	4.3882	4.3947	4.3947	4.3947
20.0	4.4364	4.4516	4.4553	4.4553	4.4553
40.0	4.5076	4.5120	4.5120	4.5120	4.5120
∞	4.5324	4.5324	4.5324	4.5325	4.5324

Table 5, Correction factor. [66].

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Papers

1. F. Toomadj, S. F., A. Sanz-Velasco, O. Naboka, P. Lundgren, K. Rodriguez, G. Toriz, P. Gatenholm, and P. Enoksson (2011). Sensing application of nanocellulose modified with double-walled carbon nanotube and Graphite nanopowder. in MME2011. Toensberg, Norway
2. F. Toomadj, S. F., A. Sanz-Velasco, O. Naboka, P. Lundgren, K. Rodriguez, G. Toriz, P. Gatenholm, and P. Enoksson (2011). Strain Sensitivity of Carbon Nanotube Modified cellulose. Euroensors XXV, Athens, Greece.

SENSING APPLICATION OF NANOCELLULOSE MODIFIED WITH DOUBLEWALLED CARBON NANOTUBE AND GRAPHITIZED CARBON NANOPOWDER

F. Toomadj^{1,2}, S. Farjana^{1,2}, A. Sanz-Velasco², O. Naboka², P. Lundgren², K. Rodriguez³, G. Toriz¹, P. Gatenholm¹, and P. Enoksson²

¹Wallenberg Wood Science Center and Department of Chemical and Biological Engineering, Biopolymer Technology, Chalmers University of Technology, Göteborg, Sweden

²Wallenberg Wood Science Center and Department of Microtechnology and Nanoscience – MC2, BioNano Systems Laboratory, Chalmers University of Technology, Göteborg, Sweden

³Department of Materials Science and Engineering, Virginia Tech, Blacksburg, USA

Abstract — Electrically conductive nanocellulose films were prepared by immersion in well dispersed solutions of double walled carbon nanotubes or graphitized nanopowder. These solutions were prepared by using the surfactant cetyltrimethylammonium bromide (CTAB) under heating and stirring conditions which were followed by a short time sonication process. Electrospun cellulose and bacterial cellulose were used as a backbone of these films. Controllable modification of cellulose with conductive agents was performed by treatment with their dispersions for 24 – 72 hours.

Electrical conductivities of the resulting films are from 0,009 S cm⁻¹ to 0,395 S cm⁻¹ which is higher or comparable to previously reported results. Some methods have been employed to study the electrical conductivity behavior of samples. The electrical conductance of the films displays a high sensitivity to strain when tensile stress is applied.

Keywords : sensor, conductive cellulose, double walled carbon nanotube

I – Introduction

Strain sensors based on nanostructured materials represent a new class of microelectronic devices which have gained a great interest due to their low power consumption, high sensitivity, selectivity and prompt response [1]. Conventional strain and pressure sensors are characterized by rigidity and fragility which significantly restrict their application area. Flexible large-area sensors can be produced by inserting nanoparticles with appropriate thermal and electrical properties into a suitable polymer matrix [2]. The outstanding properties of carbon nanotubes e. g. with regards to electrical conductivity and piezoresistivity make them one of the best candidates to use as building blocks of sensors [3]. Due to the strong van der Waals forces between carbon nanotubes, they are forming bundles which are difficult to dissolve in water or other organic solvents [4,5]. To process CNTs, well dispersed and stable CNT solutions are required.

Cellulose is one of the most widely used natural materials (6). Owing to its biocompatibility, easy modification and low price, nanocellulose is a very appealing substrate for the development of carbon nanotube based sensors. Due to its high porosity, high crystallinity, water absorbance, mechanical properties, formability, and biocompatibility, bacterial cellulose has recently attracted a great deal of attention for academic and industrial point of view [7]. Electrospinning is the fast and simple process for forming submicron scale structures through the action of electrostatic forces in which polymers could be arranged in nonwoven fibrous materials with well controlled morphology such as fiber diameter, and surface area [8].

The goal of the present work is to prepare nanocellulose materials with controlled electrical conductivity by incorporation of double walled carbon nanotubes (DWCNT) or graphite nanoparticles (GNP) into the nanostructured cellulose and to investigate their strain sensing properties. Also the improvement of the dispersion process of CNT and GNP is a goal of this project too.

II - Experimental Details

Bacterial cellulose (BC) and electrospun cellulose (EC) were used to obtain conductive films. The EC was obtained by electrospinning of a cellulose acetate solution (17% wt) in acetone and dimethylacetamide (2:1 volume ratio). The cellulose regeneration process was carried out by deacetylation with NaOH in ethanol (0.05 mol/l) for 24 hours. Bacterial cellulose was produced from *Gluconacetobacter xylinum*. DWCNT modified with carboxyl groups (+90% purity, Nanocyl S A, Belgium) and graphitized carbon nanopowder purchased from Sigma-Aldrich (<500 nm particle size (DLS), >99.95% trace metal basis). were used as a conductive agent for impregnation of cellulose. Cellulose swelling was performed by treatment of cellulose pellicles in 0,5 mol/l NaOH solution for 1 hour at 70 °C in stirring condition. Before modifying with DWCNT or GNP, cellulose pellicles were washed until a pH of 7 was obtained.

The washing process was done with rinsing and soaking in de-ionized water and checking the pH until reaching a pH of 7. This process was done at room temperature. DWCNT and CNP water dispersions were prepared in the presence of cetyltrimethylammonium bromide (CTAB). DWCNT or CNP was mixed with half of final volume and was heated (90 °C, 1 hour). After, the solution was sonicated (20 minutes) and CTAB was added to the solution (1:1 CTAB to nano-particle weight ratio). Water-DWCNT-CTAB (or GNP-CTAB) mixtures were heated (90 °C, 1 hour) and sonicated for 20 minutes. Prepared dispersions were centrifuged for 20 minutes (3500 rpm, RT) in order to remove undispersed carbon. Three different dispersed solutions with different volumes and concentrations of DWCNT or GNP in water were prepared which were 15ml of 1mg/ml, 15ml of 2mg/ml and 30ml of 2mg/ml. Cellulose pellicles (3×3 cm) were immersed in DWCNT or GNP dispersions for 24 - 72 h. After treatment with conductive agent dispersion, the nanocellulose pellicles were washed carefully by de-ionized water to remove all free surfactants and they were subsequently dried in a fumehood in a Teflon fixture. The thicknesses of the dried conductive films were 25 – 65 µm. The drying process was continued until a constant weight of the samples was reached.

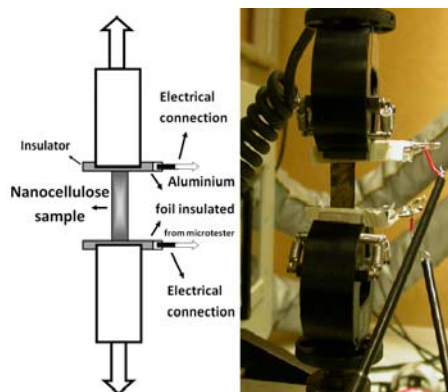


Figure 1. Experimental setup for tensile testing. The angle between the applied force and the direction for measuring the electrical resistance is 0° in this setup.

The surface morphology of all of the samples was observed by using scanning electron microscopy (SEM) performed with Leo Ultra 55 FEG SEM. The electrical conductivity measurements were performed by using a four-point probe system (CMT-SR2000N, AIT, Korea). To characterize the electromechanical properties of the modified cellulose an Instron Material Testing Instrument (Series 5500) was used. Constant tensile stress was applied to measure the resistivity of the modified cellulose. The sizes of the samples were 30 mm in length and 10 mm in width.

In order to measure the variation of resistance in the same direction as the applied force (orientation angle 0°), aluminum foil has been used which was insulated from the microtester clips (figure 1).

III - Results and Discussion

Due to the differences in the thickness of the fibers and the structure of their matrix, the same modification processes lead to different types of carbon nanoparticle incorporation in bacterial cellulose and in electrospun cellulose.

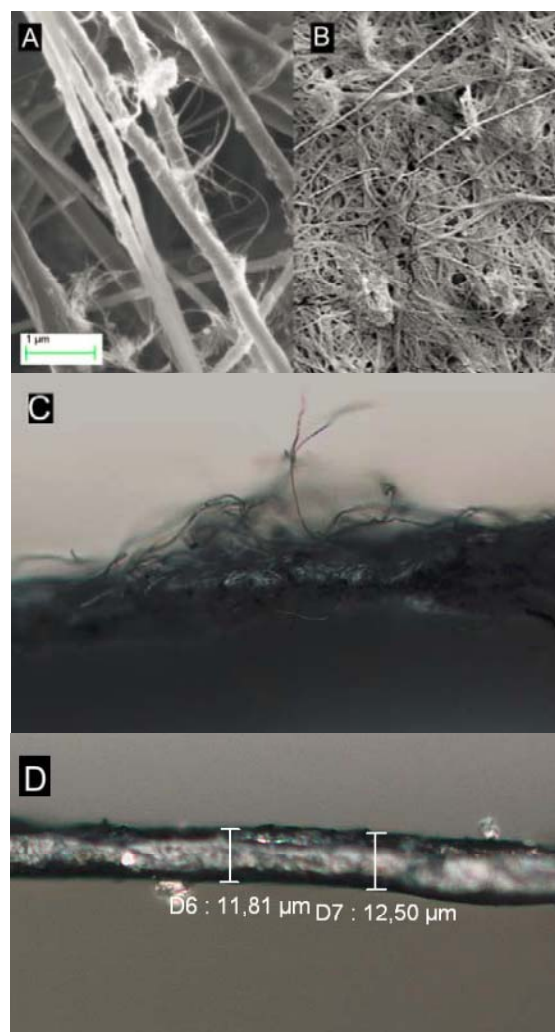


Figure 2. SEM images of electrospun cellulose (image A) and bacterial cellulose (image B) which have been modified with DWCNT. The difference in magnification of these two images is less than 6%. The electrospun cellulose displays a much more open fiber structure. Optical microscope images of DWCNT modified electrospun cellulose (image C) and bacterial cellulose (image D). Because of the rather closed porous structure and small pores in bacterial cellulose, the modifying

agents cannot penetrate the cellulose. As a result, thin asymmetric layers of modifying agent were formed on both sides of the cellulose material (figure 2 D). The thicker fibers of electrospun cellulose form an open matrix with larger pore size. As a consequence the DWCNT can modify also the internal surface of the electrospun cellulose. This is clearly observed in the SEM picture and in the optical microscope image (figure 2A, 2C).

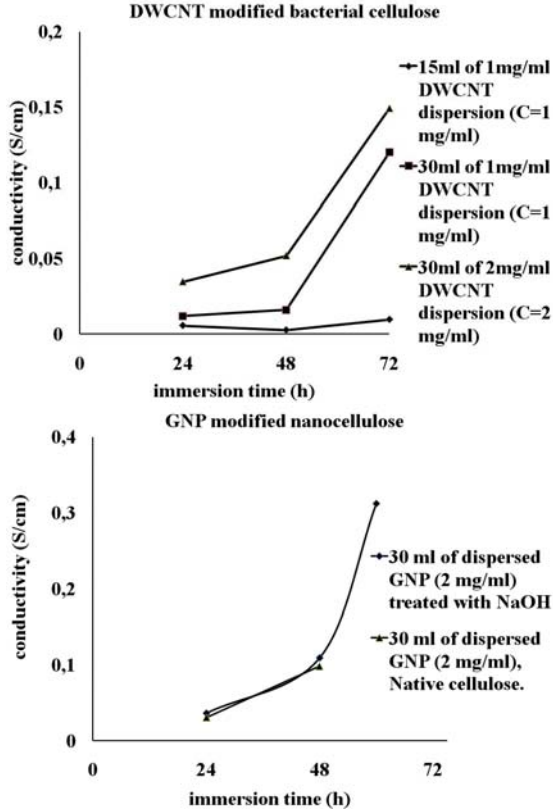


Figure 3. Conductivity of bacterial cellulose modified with DWCNT as a function of immersion time (top plot) and conductivity of bacterial cellulose modified with GNP (native and treated with NaOH) as a function of immersion time (bottom plot).

A. Conductivity as a function of immersion time and dispersed solution concentration

We measured the electrical conductivity of the modified nanocellulose when varying the immersion time, the concentration, and the volume of DWCNT dispersions. Fig. 2 shows typical SEM pictures of the morphology of the DWCNT modified EC- and BCnanocellulose respectively. Different conductivities were obtained from different cellulose pellicles which were modified under different conditions. The best results were found approximately $3,95 \times 10^{-1} \text{ S cm}^{-1}$ for bacterial cellulose/DWCNT, $0,334 \times 10^{-1} \text{ S cm}^{-1}$ for bacterial cellulose/ CNG film and $8,2 \times 10^{-3}$ for electrospun cellulose/DWCNT film.

Generally, the electrical conductivity of the modified cellulose and the distribution of DWCNT in its volume appear to be affected by changing the volume and concentration of dispersions and by increasing the immersion time. In the case of nanocellulose pellicles which were modified in the lowest concentration of DWCNT or GNP, increasing the immersion time did not show any significant effect on the conductivity of the resulting material. However, by increasing the concentration of the solutions, the immersion time starts to play a significant role (figure 3). The resulted conductivities which have been used in these two plots are from the same source of cellulose and were done on exactly the same experimental condition.

A swelling process was conducted for bacterial cellulose to open their matrix during immersion. Conductivity results shows that there is no significant difference between cellulose which has been treated by NaOH and cellulose which was not subjected to the swelling process (image 3, bottom plot).

The conductivities of the nanocellulose materials prepared in our work from electrospun and bacterial celluloses are higher than or comparable to previously reported results [9].

B. Variation of resistance as a function of strain

Figure 4 shows the relatively large fractional increase in resistance with the fractional extension obtained by the application of tensile force for two samples of DWCNT modified nanocellulose. The nanocellulose pellicle which is modified with a higher concentration of DWCNT showed more sensitivity to an increase in the strain.

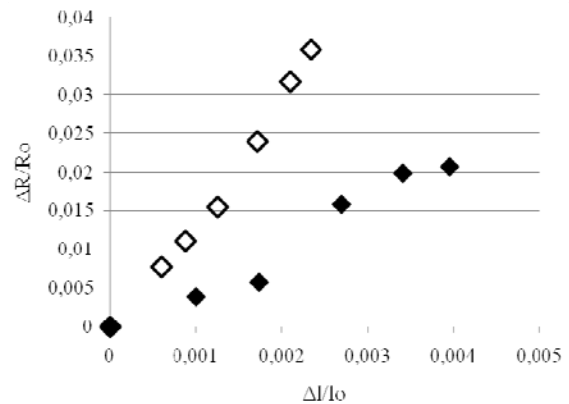


Figure 4, Fractional increase in resistance ($\Delta R/R_0$) as a function of the fractional extension ($\Delta l/l_0$) of a strain gauge for two different samples of bacterial cellulose. Bacterial cellulose which is modified in 30ml of DWCNT dispersion with 1 mg/ml concentration (filled markers) and bacterial cellulose which is modified in 30 ml of DWCNT dispersion solution with 2 mg/ml solution (open markers).

IV – conclusion

DWCNTs and CNGs-incorporated bacterial and DWCNTs-incorporated electrospun celluloses were prepared by immersing cellulose films in DWCNT and graphitized carbon nanopowder waterdispersed solutions. We have worked to improve the dispersion process. The morphology of the resulting electrical conductive cellulose material has been studied by optical microscope and SEM and the electrical properties were monitored by four-point probe measurements and resistance measurements under strain in a microtester. The electrical conductivity of the cellulose was found to be approximately $3,95 \times 10^{-1}$ S cm⁻¹ for bacterial cellulose/DWCNT, $0,334 \times 10^{-1}$ S cm⁻¹ for bacterial cellulose/CNG film and $8,2 \times 10^{-3}$ for electrospun cellulose/DWCNT film.

It was found that electrical conductivity of resulted BC/DWCNT depends on fractional extension obtained from applied force which make it good candidate for sensing application.

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Strain Sensitivity of Carbon Nanotube Modified Cellulose

F. Toomadj^{1,2}, S. Farjana^{1,2}, A. Sanz-Velasco², O. Naboka², P. Lundgren²,
K. Rodriguez¹, G. Toriz¹, P. Gatenholm¹, and P. Enoksson²

¹Wallenberg Wood Science Center and Department of Chemical and Biological Engineering, Biopolymer Technology, Chalmers University of Technology, Göteborg, Sweden

²Wallenberg Wood Science Center and Department of Microtechnology and Nanoscience – MC2, BioNano Systems Laboratory, Chalmers University of Technology, Göteborg, Sweden

Abstract

Nanostructured cellulose was modified by different concentration and volume of dispersed multi-walled carbon nanotube (MWCNT) and double-walled carbon nanotube (DWCNT) solutions and its electrical properties were studied. The resulting flexible cellulose films have an electrical conductivity sensitive to changes in CNT concentration and immersion time in solution. The conductivity increases with increasing immersion time and volume and concentration of dispersed solutions; the conductivity for bacterial cellulose (BC) pellicles modified with DWCNT was increased from $0.034 \text{ S}\cdot\text{cm}^{-1}$ to $0.15 \text{ S}\cdot\text{cm}^{-1}$ and for BC pellicles modified with MWCNT it was increased from $0.12 \text{ S}\cdot\text{cm}^{-1}$ to $1.6 \text{ S}\cdot\text{cm}^{-1}$ when the immersion time was increased from 24 h to 72 h. These results are significantly higher than in previously reported work [1].

The effect of strain on the resistance during application of tensile force is shown for a simple strain gauge employing cellulose with incorporated DWCNTs. The electrical resistance of the films displays a high sensitivity to strain. It seems that this sensitivity depends on the modifying conditions, where BC pellicles which are modified in a dispersed solution with a higher concentration of CNTs show larger changes in resistance with the changes in fractional extension.

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Keywords: sensor, conductive cellulose, carbon nanotube

1. Introduction

During the last decade, there has been a large interest in the development of different kinds of sensors based on nanostructured materials with high flexibility, high biocompatibility, low cost, and low weight; it has been reported that such materials can be obtained by inserting nanostructures with promising electrical and mechanical properties into an insulated appropriate insulating matrix polymer [2-4].

Among these nanostructures, different types of carbon nanotubes (CNTs) have attracted a special interest of researchers due to their remarkable mechanical and electrical properties. In addition, their electrical properties depend strongly on environmental changes so that for example a small mechanical deformation can significantly change the conductance of CNT-based resistors [5]. Farajian et al. [6] have tried to theoretically explain and calculate the change in CNT conductance under bending. They reported that the current decreases with increasing bending angle. All these properties make CNTs a promising material to use in smart sensors.

Owing to its biocompatibility, being easy to modify and having a low cost, cellulose is a promising material to use as a substrate for conductive nanoparticles in different applications [7,8]. Among different kinds of cellulose, bacterial cellulose (BC) can be an industrially viable material in the design of new electrical devices due to its mechanical and structural properties such as purity, high crystallinity, high mechanical stability, and low density [9].

Herein we report on a flexible electrical conductive nanocomposites based on BC cellulose and CNTs. Double-walled carbon nanotubes (DWCNT) and multi-walled carbon nanotubes (MWCNT) have been used to modify BC pellicles. Different dispersed CNT solutions with different volume and concentration have been used to modify the cellulose in order to find optimum conditions for making appropriate BC films. The conductivities of the resulting films have been compared and their behaviour has been studied as a function of induced strain.

2. Experimental

The BC used in this work was produced by *Gluconacetobacter xylinum* bacteria in a static medium. DWCNT (+90% purity, Nanocyl S A, Belgium) and MWCNT (+95% purity, Nanocyl S A, Belgium) modified with carboxyl groups have been used as a conductive agent for impregnation of BC.

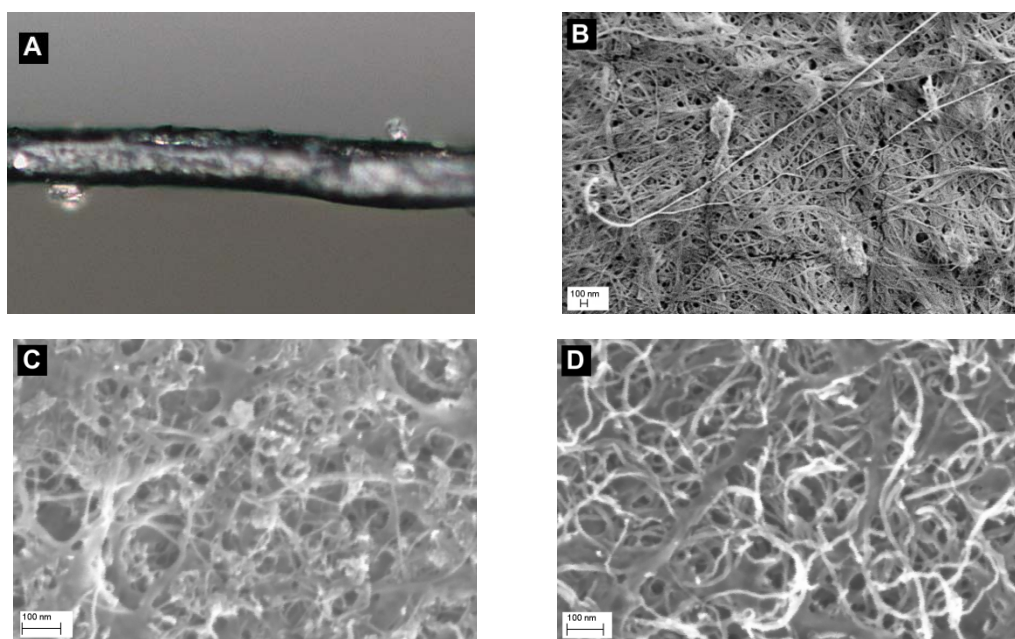


Figure 1. Cross sectional optical microscope image of bacterial cellulose pellicle modified with DWCNT which shows that there are two asymmetric conductive layers on the different sides of the pellicle (A). SEM images of BC (B). Samples which are modified with DWCNT (C) and MWCN (D).

The dispersion of CNTs was carried out using cetyltrimethylammonium bromide (CTAB) as a surfactant. The dispersion process consisted of a combination of heating, stirring and sonication followed by centrifuging to separate dispersed CNTs from undispersed particles. Three different dispersed solutions with different CNT concentrations and volumes were prepared: 15 ml of 1 mg/ml, 15 ml of 2 mg/ml and 30 ml of 2 mg/ml. $3 \times 3 \text{ cm}^2$ BC pellicles were immersed in the CNT solutions for 24 h to 72 h under shaking. After finishing the treatment step, all samples were washed with de-ionized water in order to remove free surfactant and CNT residue. The pellicles were dried in a fume hood.

The total thicknesses of the dried BC films were 25-65 μm as measured by a standard micrometer with $\pm 1 \mu\text{m}$ accuracy. A scanning electron microscope (SEM) has been used to observe the surface morphology of the samples (Zeiss Leo Ultra 55 FEG SEM and Zeiss Supra 60 VP SEM). The electrical conductivity measurements were performed by using a four-point probe system (CMT-SR2000N, AIT, Korea). In order to study the electromechanical properties of BC modified with DWCNT, constant tensile stress was applied using the Material

Testing Instrument (Series 5500) and the change in resistance was registered by a standard multimeter (Agilent 34401A).

3. Results and discussion

Due to the rather closed porous structure and small pores in the BC matrix, CNTs cannot penetrate into the cellulose. As a result, two asymmetric conductive layers were form on the different sides of the BC pellicles (figure 1A). Samples which were modified with MWCNT were uniformly black whereas the BC pellicles which are modified with DWCNT contain parts which are unmodified and transparent. The diameter of the BC fibers is 40-80 nm (Fig 1 B). According to SEM the CNT diameter is 6-8 nm for DWCNT and 14-16 nm for MWCNT (figure 1B-D). MWCNT are more homogeneously distributed on the BC surface comparing to DWCNT (figure 1D and 1C) which points to formation of better dispersion by MWCNT

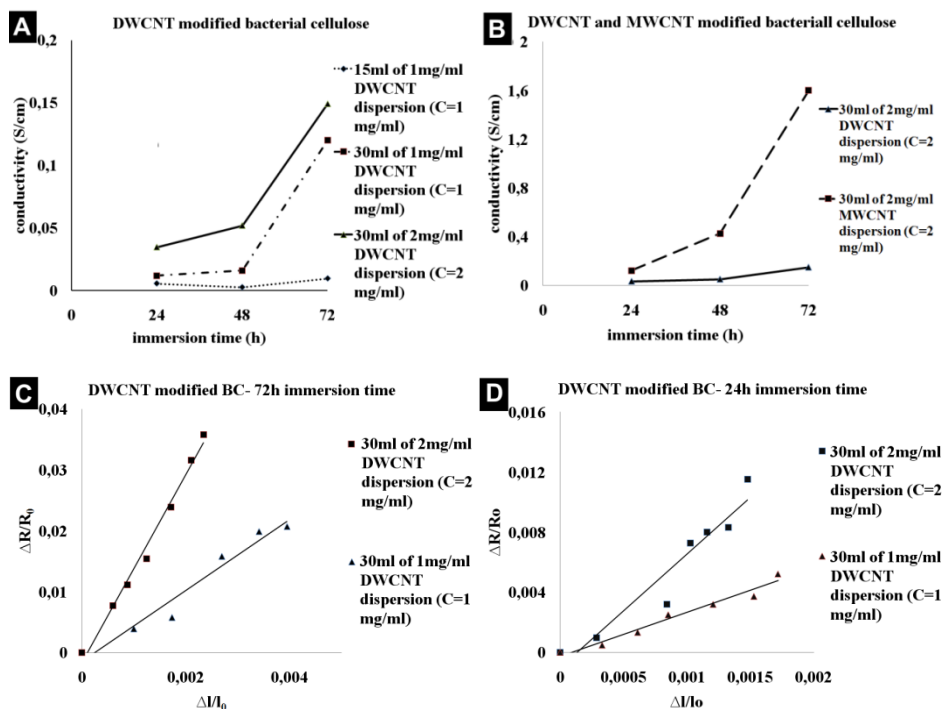


Figure2. Electrical conductivities of bacterial cellulose samples modified by DWCNT (A) and MWCNT (B) as a function of immersion time. Dependence of the fractional resistance on the fractional extension for BC sample modified with DWCNT during 72 h (C) and 24h (D).

3.1. Electrical conductivity measurement

The electrical conductivity of the cellulose modified with DWCNT and MWCNT appears to be affected by changing the volume and the concentration of the dispersions and by increasing the immersion time. In the case of the sample modified with lowest concentration and volume an increase the immersion time did not give any significant effect on the electrical conductivity of the modified BC pellicles. In this case, it seems that saturation capacity of cellulose for 1mg/ml DWCNT dispersions is not enough to form the conductive layer. However, by increasing the CNT concentration and volume, conductivity raise significantly with the immersion time (figure 2A) pointing to the substantial increase of the saturation capacity; the highest conductivities have been obtained for the pellicles modified in the 30 ml of 2 mg/ml solutions.

The conductivity of the BC pellicles has been increased by one order of magnitude when the modifying agent was changed from DWCNT to MWCNT (figure 2B). Results received could be explained with formation of more homogeneous dispersions by MWCNT which is probably caused by higher CTAB/CNT surface ratio for MWCNT (specific surface area 115 m²/g [10]) comparing to DWCNT (specific surface area >500 m²/g).

3.2. Electromechanical measurement

For strain sensor applications, we need to have a material which is able to transfer strain into an electrical signal with high sensitivity. Figure 2C shows the relatively large fractional increase in resistance with the fractional extension obtained by the application of tensile force for two samples of DWCNT modified nanocellulose. These two plots are related to the samples which are modified in different concentration of DWCNT dispersed solution. The nanocellulose pellicle which is modified with a higher concentration of DWCNT shows higher sensitivity to an increase in the strain.

In addition to the concentration of dispersed CNTs, the immersion time of the sample is another factor which appears to affect the sensitivity of the BC pellicles. Comparing figures 2C and 2D shows that by increasing the immersion time from 24 h to 72 h, the sensitivity of the resistance to the fractional extension is increased.

4. Conclusion

Flexible DWCNT and MWCNT-incorporated films have been prepared by treatment of bacterial cellulose in dispersed CNT solutions in the presence of CTAB. The effects of the dispersion procedures were observed by measuring the electrical conductivity of the resulting BC films. We show that the conductivity of the pellicles is related to the modification conditions such as the volume and concentration of the CNT solution, immersion time and also to the type of modifying agent, where the MWCNT modified BC shows significantly higher electrical conductivity than the DWCNT modified pellicle under the same processing conditions.

Electromechanical measurements show that there is a strong sensitivity of the sample resistance to strain, implying a piezoresistive response of the material. This sensitivity seems to be related to the modifying conditions; samples which have been modified in higher concentration CNT solutions show a higher strain sensitivity.

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