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Electrical Characterization of Strain Effects on Bacterial Nanocellulose Treated with Carbon Nanoparticles

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Abstract

Nanocellulose, having attractive properties such as flexibility, biocompatibility, light weight, low cost and recycling possibilities, is a suitable material for sensors and actuators. Strain sensitive flexible, electrically conductive nanostructured bacterial nanocellulose (BNC) samples were obtained by modification with carbon nanoparticles. Different types of modifying agents such as double walled carbon nanotubes (DWCNT), multiwalled carbon nanotubes (MWCNT) and graphitized carbon nanoparticles (GNP) have been used to make the nanocellulose conductive. The electrical conductivity depends on the modifying agent and its dispersion process.

In this project the strain effects on the mechanical and electrical properties of treated BNC samples have been investigated. To observe the strain induced electromechanical response a constant tensile force has been applied to the sample. The samples have piezoresistive properties. There is a correlation between the conductivity and the sensitivity of the samples.

Keywords: strain sensor, nanocellulose, bacterial nanocellulose, carbon nanotubes, conductivity.

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1. Introduction

Nanocellulose, which is one of the most abundant of all natural polymers, consists of inexhaustible polymeric raw material with fascinating structure and properties [1]. The properties of nanocellulose are suitable for environmentally friendly, biodegradable and bio compatible products. Recently it was discovered that nanocellulose is a type of electro active polymer (EAP) [1, 2]. Materials which can sense environmental changes and create a useful response are called smart materials [2]. EAPs can be used as smart materials.

EAP materials offer a performance range and uniqueness that may not be achieved by other technologies [2]. Comparing with ceramic and semiconducting materials, EAPs provide the new extended material which is flexible and is simple to manufacture for various applications [3]. The most interesting application areas of EAPs are industrial, biomedical, entertainment, defense and even space applications, which show a promising future [2, 3]. Cellulose based materials can be used as electro active paper (EAPap). The main attractive properties of EAPap are: natural abundance, low material price, easy manufacturing process, relatively low cost, light weight, flexibility, transparency, large displacement, low actuation voltage, and low power consumption as well as available recycling [4, 5].

Before giving attention to nanocellulose other EAP materials, such as ionic polymer metal composites (IPMC), gel-polymers, conductive polymers, dielectric elastomer, grafted elastomer, electron-irradiated PVDF-TrFE co polymer of polyvinylidene fluoride, and electrorheological fluids, have been intensively studied and already commercialized to achieve the requirement of EAP applications [3].

Recently researchers have been working hard to use nanocellulose as sensors or actuators. But their working areas have been limited to the mechanical properties of the nanocellulose based material [4, 5]. In this present work nanocellulose samples treated with different modifying agents have been used to study their electromechanical properties.

The sources of nanocellulose can be different. It can be plant nanocellulose (PC) or bacterial nanocellulose (BC). Recently BC has gained attention due to some exclusive properties which

are not offered by PC. In this present work BC has been used as substrate and it has been treated by suitable modifying agents.

Nanocellulose consists of glucose chains arranged in linear chains which help nanocellulose based electroactive paper (EAPap) to be used for sensor and actuator applications [3]. To use nanocellulose as a sensor material it is important that it can give an electrical response. As pure nanocellulose has no conductive constituents, modifying agents are used to make it conductive. A previous study shows that nanocellulose can be treated by blending or mixing carbon nanotubes and other organic polymers such as chitosan, gelatin and poly (ethylene oxide)- poly (ethylene glycol) to satisfy the material requirement for micro electro mechanical system (MEMS) devices[6]. Carbon nanotubes (CNTs) have unique electronic, mechanical, and thermal properties which expanded the application field of CNTs to nanoelectronics and biomedical devices due to high mechanical strength, high aspect ratio, and large surface area [7]. Recently, the incorporation of CNTs into polymers has been investigated to reinforce the mechanical property of the polymers [7]. The elastic modulus and the strength of polymer composites increase with incorporation of a small amount of CNTs.

Recently sensors which are based on functionalized nanostructured material have gained in significance due to their low power consumption, high sensitivity and selectivity and prompt response [3]. Conventional sensors are restricted in their application area by rigidity and fragility. That is why sensor materials which are flexible and environmentally friendly have gained attention. Considering the properties of nanocellulose and CNTs, conductive nanocellulose has been prepared by modification of bacterial nanocellulose (BC) with double walled carbon nanotubes (DWCNT), multi walled carbon nanotubes (MWCNT) and carbon-graphitized nanopowder (GNP). It was found that the modification of nanocellulose with DWCNT and GNP played an important role to enhance the electrical conductivity of nanocellulose to a level suitable for sensor applications.

It has been observed that the modified samples display substantial electrical conductivity and that they can be used as sensors. But it is important to know the electrical and mechanical properties of a material before selecting possible application areas. The mechanical and electrical properties of CNTs and the mechanical properties of nanocellulose can be altered when they have been combined to a composite material. The mechanical response of treated nanocellulose

has been observed under a fixed tensile force and its electromechanical properties have been studied. The repeatability of measurements on the samples has also been analyzed.

1.1 Motivation of the work

Nanocellulose which offer various attractive properties such as flexibility, biocompatibility, light weight, low cost and recycle possibilities is a suitable material for sensors and actuators. But the main problem to use nanocellulose based material as a sensor material is its insulating property. To use nanocellulose based material in a sensor it should be electrically conductive and before selecting an application area it is important to characterize the samples in different ways. In this present work nanocellulose treated with DWCNT, MWCNT and GNP which is electrically conductive has been characterized.

Previous research done with nanocellulose proves that it shows an extended deformation response to constant loading for an extended period of time and this response is termed creep. Considering this creep behavior the electromechanical response of treated nanocellulose has been observed as the modifying agents used for the treatment of nanocellulose are sensitive to mechanical strain. While characterizing the electromechanical response of the treated samples another important property is its piezoresistive property. In this project the piezoresistivity of the samples has been tested. As it is also very important to know the effect of the modifying agent on the treated nanocellulose a comparison was done to check the similarities and differences among the samples.

2. Theory

2.1 Nanocellulose

Figure 1 shows the molecular structure of cellulose, which is a carbohydrate polymer generated from repeating β -D-glucopyranose molecules, covalently linked through acetal functions between the equatorial OH group of C4 and the C1 carbon atom (β -1,4-glucan). This results in an extensive, linear-chain polymer with a large number of hydroxy groups (three per anhydroglucose (AGU) unit [8]). Every other glucose residue is rotated in the opposite direction, approximately 180° . The number of constituent AGUs (degree of polymerization, DP) dictates the length of cellulose. The molecular structure imparts cellulose with its characteristic properties such as hydrophilicity, chirality, degradability, and broad chemical variability initiated by the high donor reactivity of the OH groups. It has ordered and disordered regions, in which the ordered domains are mostly crystalline and the disordered molecules maintain preferential direction parallel to the chains in a very fine fibril or fiber like strand which is called microfibril and they form surface disorder on the microfibrils. Extensive hydrogen bond networks give cellulose a multitude of partially crystalline fiber structures and morphologies.

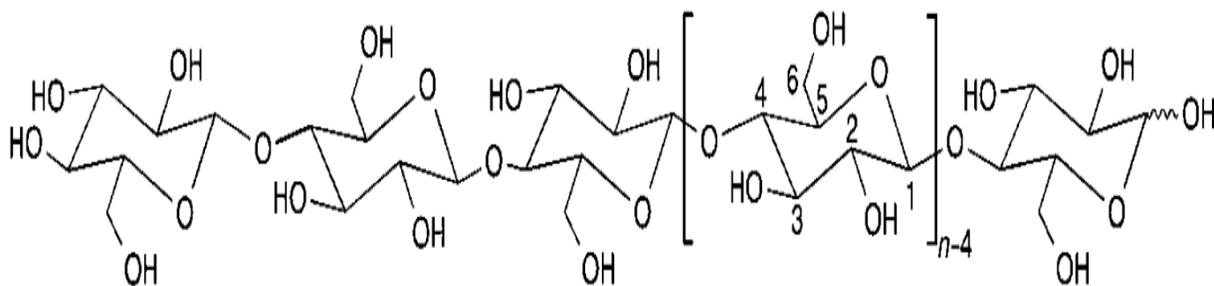


Figure 1: Molecular structure of cellulose ($n=DP$, degree of polymerization) [8].

In nanocellulose EAPap, the presence of disordered region gives rise to localized states associated with hydrogen bonding of nanocellulose chains. Since there are many localized states, the release or excitation of the carriers in these states may dominate the charge transfer process.

Thus, the disordered regions mainly contribute to the dipolar orientation, by stabilizing dipoles and leading to a permanent polarization, resulting in a piezoelectric behavior. By considering the piezoelectricity and ionic migration effect of nanocellulose, EAPap material can offer advantages over piezoelectric polymers and ionic polymers.

2.1.1 Background

Nanocellulose is found in nature as a constituent of wood, cotton, ramie and other resources [9]. Various research related to nanocellulose rediscovered its value for diverse applications including actuators and sensors and the researchers named this nanocellulose based material electro-active paper (EAPap) [2]. The application area of EAPap is very broad such as smart skins, micro-insect robots, flapping wings or flying objects and smart wall paper, MEMS, and so on. In different studies the actuation principle of nanocellulose base EAPap has been analyzed [4]. Research has been conducted to check the mechanical properties of nanocellulose and the effects of the environment on these properties [4].

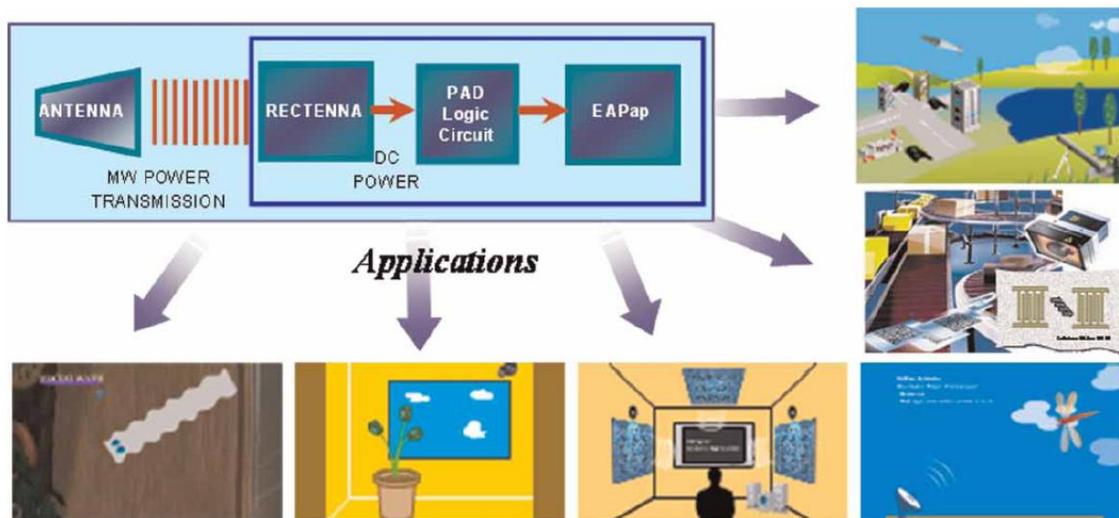


Figure 2: potential application of EAPap actuator [4]

2.1.2 Creep behavior of nanocellulose

A prolonged deformation response at a constant load for an extended period of time is called creep. It has been found that nanocellulose based material shows time dependent creep behavior. The creep behavior of a material helps to determine whether it is linearly or non-linearly viscoelastic. Different studies have investigated the creep deformation process by applying a stepwise dead-weight load to the EAPap. The creep strain of EAPap under ambient conditions increases steadily with an increase of the stepwise load [9]. Figure 3 shows the creep behavior of EAPap where the creep strain increases when the applied load increased.

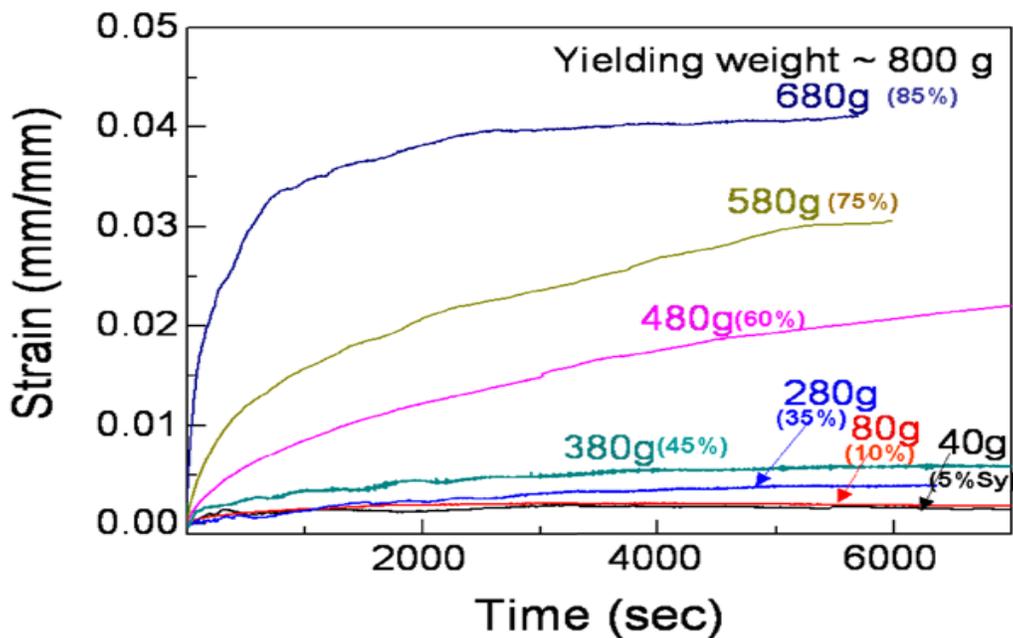


Figure 3: Strain–time curve of cellophane EAPap as a function of dead-weight load [9].

2.1.3 Structure of bacterial nanocellulose

In section 2.1 it was discussed that nanocellulose is an unbranched polymer of -1, 4- linked glucopyranose residues. Previous studies showed that BNC is chemically identical to PC, but its macromolecular structure and properties differ from the latter [8]. Chains of BNC are combined to form subfibrils, which belong to the thinnest naturally occurring fibers, comparable only to

sub elemental fibers of nanocellulose detected in the cambium of some plants and in quinee mucous. BNC subfibrils are crystallized into microfibrils, these microfibriles then turn into bundles, and the latter into ribbons. The ultrafine ribbons of microbial nanocellulose form a dense structure stabilized by extensive hydrogen bonding. The crystallinity of BNC is also very high in comparison to that of PC. Figure 4 below shows that structural difference between BNC and PC.

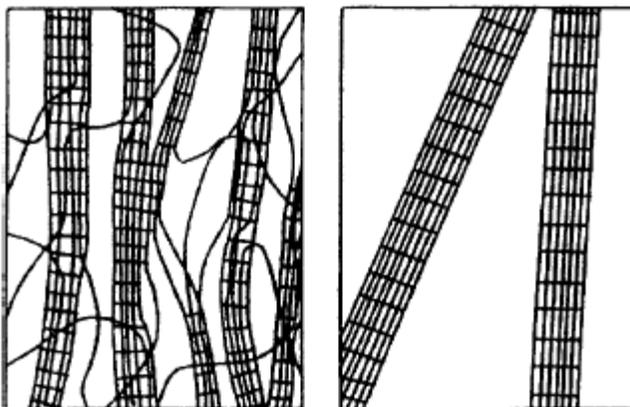


Figure 4: Schematic drawn model of nanocellulose fibers to compare the structure of PC (left image) and BNC (right image). [10].

Nanocellulose is recognized as the major component of plant biomass, but also a representative of microbial extracellular polymers. Plant cellulose (PC) contains impure compounds of lignin, pectin and hemicelluloses whereas bacterial nanocellulose (BNC) belongs to specific products of primary metabolism [9]. Compared to plant nanocellulose material BC displays some unique properties such as high mechanical strength, high water absorption capacity and high crystallinity [11]. Considering its unique properties BNC has been used in our present work.

2.2 Carbon nanotube (CNT)

Elemental carbon in the sp^2 hybridization can form a variety of amazing structures such as closed and open cages with honeycomb atomic arrangement. CNTs which have unique mechanical properties are the strongest and most flexible molecular material known due to the C–C covalent bonding and seamless hexagonal network. They can be either metallic or semiconducting, and display high thermal conductivity in the axial direction [12]. SWNT have a wall one atom thick and diameters of typically 1,4 nm. The nanotubes consisting of up to several tens of graphitic shells are called multi-walled carbon nanotubes (MWCNT)) with adjoining shell separation of $\sim 0,34$ nm, diameters of ~ 1 nm and high aspect ratio [13]. The morphology and properties of DWCNTs are similar to SWCNT. DWCNT consists of two coaxial single walled CNT, is a synergetic blend of both SWCNT and multi-walled characteristics, exhibiting the electrical and thermal stability of MWCNT and the flexibility of SWNTs. Electronically CNTs can be metallic or semiconducting depending on their chirality. When a graphene sheet is rolled up to form the cylinder, the ends of the chiral vector meet each other and connect two crystallographically equivalent sites and thus the length of the chiral vector is equal to the circumference of the nanotube and they define three different CNT structures; armchair, zigzag and chiral nanotube.

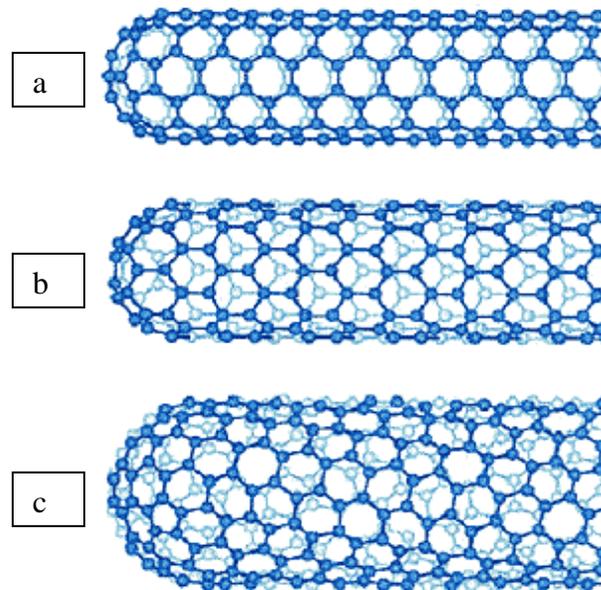


Figure 5: Three nanotube structures: (a) armchair, (b) zigzag, and (c) chiral [14].

Mechanical properties of CNT

Carbon-carbon sp^2 bonding makes CNTs stiff and increases their axial strength. By investigating its elastic response, the inelastic behavior and buckling, yield strength and fracture it was found that nanotubes are the stiffest known fiber with a measured Young's modulus of 1,4 TPa. They have an expected elongation to failure of 20-30% and a tensile strength well above 100 GPa [13].

Electrical properties of CNT

The unique electrical properties of carbon nanotubes are to a large extent derived from their 1-D character. They have extremely low electrical resistance. The electrons inside a carbon nanotube are not so easily scattered because of its very small diameter and a high length to diameter ratio. In 3-D conductor electrons have plenty of opportunity to scatter, since they can do so at any angle and this gives rise to a high electrical resistance. But in a 1-D conductor electrons can travel only forward or backward. The only reason of resistance in 1-D conductors is backscattering, which requires a very strong collision and thus the probability of backscattering is very low. This reduced scattering gives carbon nanotubes their very low resistance [12].

Piezoresistivity of CNT

CNTs are piezoresistive. It has been shown that the band structure of CNTs is altered by mechanical strain and that the conductance of CNTs changes depending on their chirality. When strain is applied on CNTs it affects the quantum states available to the electrons. In the case of semiconducting nanotubes there is a band gap and the electron should overcome this energy barrier to reach the conduction band. To overcome this band gap an extra energy is needed and this extra energy comes from heat or electric field or strain [12].

When strain is applied to CNTs it changes the band structure and thus the electrical properties of the nanotubes are varied, making them more or less conductive - the signature of piezoresistivity [12].

2.3 Application of conductive nanocellulose as strain sensor

When stress is applied to a strain sensor, any sensing property of the strain sensor changes and this results in a signal output, related to the stress value. Materials which can change their electrical response at a minimum of stress are suitable for strain sensors. CNTs offer attractive alternatives for developing new sensors. They have high strength besides other advantages like high thermal and electrical conductivities, and therefore can provide structural and functional capabilities simultaneously, including actuation and sensing [15]. Its composites show linear piezoresistivity useful for measuring strain of structures [15]. Several studies have proved that CNTs have mechanical deformations such as bending, twisting or flattening and these influence the electronic properties. On the other hand, nanocellulose offers a wide range of advantages including flexibility to use it as a nano sensor material. Due to its flexibility nanocellulose can change its shape significantly under an applied stress. So nanocellulose treated with CNT and GNP can be used as a strain sensor. Both nanocellulose and CNT are sensitive to the environment. To use these materials as strain sensors their sensitivity towards humidity and temperature should be considered.

2.3.1 Environmental issues of using conductive nanocellulose as a sensor

Recent attention to flexible sensors with good electrical performance showed that polymers of both resistive as well as capacitive type containing hydrophilic groups can be suitable for humidity sensors as they change their response as the humidity of the environment changes [16]. Moreover, the Young's modulus of the nanocellulose samples has been changed as the humidity of the environment changes. Figure 6 shows the effect of humidity on the elastic modulus of a nanocellulose sample. CNTs on the other hand, which have very large surface area to volume ratio, nanoscale structure and hollow center, can absorb large amounts of foreign molecules on their surface and with the presence of these molecules, many properties associated with CNTs would change [17]. It has been reported that water vapor has a significant effect on the electrical conductivity of a SWCNT mat as p-type carbon nanotubes would turn into n-type if water molecules are added [17].

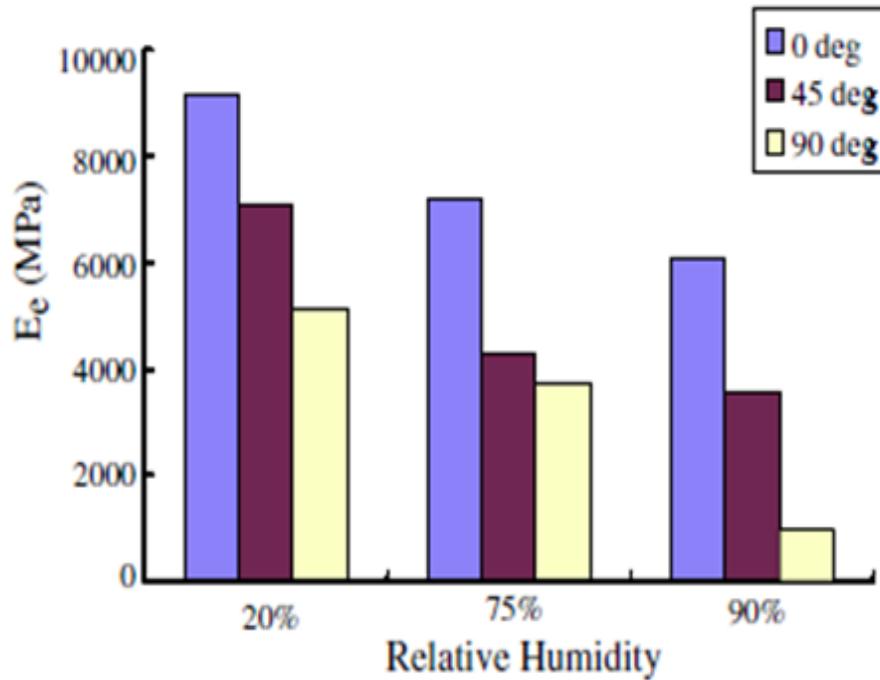


Figure 6: Effect of humidity on the elastic modulus of nanocellulose [3].

Nanocellulose is also sensitive to temperature. Different studies have shown that mechanical parameters of nanocellulose decrease as the temperature of the environment increases [3]. Also the electrical and mechanical properties of CNTs are sensitive to temperature. So to use CNT and GNP treated nanocellulose these issues should be taken into consideration. Figure 7 shows the temperature dependency of the mechanical properties of a nanocellulose sample.

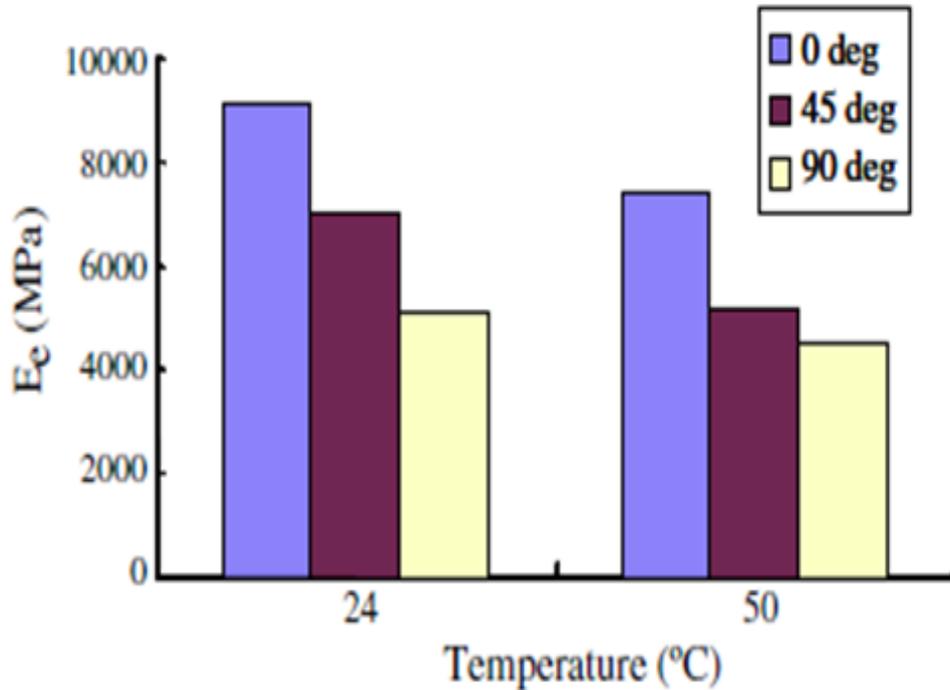


Figure 7: Effect of temperature on the elastic modulus of nanocellulose [3].

2.4 Working principle of strain sensor

The strain sensors can be the fundamental sensing element for many types of sensors, including pressure sensors, load cells, torque sensors, position sensors, etc. The sensing materials for strain sensors operate on the principle that as the sensing material is subjected to stress, one or more sensing properties changes in a well defined way. For most of the strain sensors this change in resistance is the sum of three effects. First, when the length of the sensing element or the conductor has been changed, it undergoes a resistance change approximately proportional to change in length.

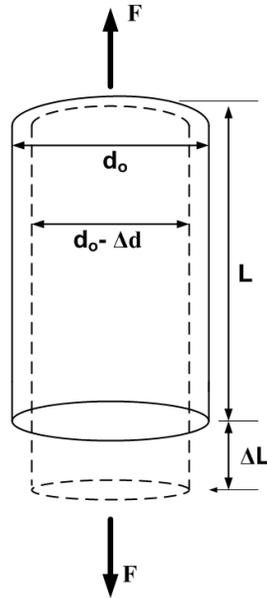


Figure 8: Effect of tensile force on a material.

Let us consider if the sensing element is elongated by ΔL , and thus it lengthens to L (original length) + ΔL (change in length). The ratio of this elongation ΔL , to the original length, L , is called strain. Strain in the same tensile direction as the external force is called longitudinal strain and it can be expressed as ϵ_1 .

$$\epsilon_1 = \Delta L \text{ (change in length)} / L \text{ (original length)} \quad (1)$$

Second, in accordance with the Poisson effect a change in the length of the sensing element or the conductor causes a change in its cross-sectional area and a resistance change that is approximately inversely proportional to change in area. Suppose that the original diameter, d_0 , is made thinner by Δd . Strain in the diametrical direction which is called lateral strain and is expressed by ϵ_2 .

$$\epsilon_2 = -\Delta d / d_0 \quad (2)$$

Each material has a certain ratio of lateral strain to longitudinal strain.

Third, the piezoresistive effect which is a characteristic of the material causes a change in the bulk resistivity of a material when it is strained. All strain gauge materials exhibit these three properties, but the piezoresistive effect varies extensively for different materials.

From the above discussion the working principle of a strain sensor can be expressed as follows

$$\Delta R / R = K \cdot \varepsilon \quad (4)$$

Where, ΔR : Elongation- or contraction-initiated resistance change, Ω (ohm)

R: Original resistance of strain sensing material, Ω (ohm)

K: Proportional constant (called gauge factor)

ε : Strain

The gauge factor, K, depends on material type.

2.4.1 Relation between dimension and resistance of a normal resistive material under a stretching force

Electrical conduction in solid materials is typically due to the flow of electrons. The electrons are distributed in energy bands. In a metal when an electric field is applied, these electrons can be lifted to higher energy levels but the deviations of the crystal lattice, determining the material's band structure, offer resistance. The reasons of deviations can be defects, impurities and thermal vibrations of the lattice. Moreover, the effect of the deviations can be thought of as the scattering of electrons from one band state into another. The result of the scattering is both a change in the direction of particles and a transfer of energy from the electrons to the lattice. So the result of the scattering is that the electrons that get accelerated by the electric field soon give up the energy to the lattice and thus go to a lower velocity parallel to the field. Finally it can be said that the electron moves with acceleration in between collisions with the lattice and after a collision the average electron's net velocity can be thought of as going to zero. From the above discussion it can be concluded that the rate at which charge flows from terminal to terminal is the result of the combined effect of electric potential and resistance of the material.

For any given circuit at steady state, $V = I \cdot R$ (5)

Where, V= Voltage

I = Current

The resistance of a homogeneous conductor of uniform cross-section is determined by its bulk resistivity and its geometry.

$$R = \rho l/A \quad (6)$$

Where, R= Resistance of the conductor

l= Length of the conductor

A= Cross sectional area of the conductor

ρ = Resistivity of the conductor.

When forces act on materials, the material tends to change its shape - deformation occurs under the influence of the forces that are applied. This change may be large or small, reversible or permanent, depending on the type of force and the material involved. If a strip of conductive metal undergoes a mechanical elongation it will become skinnier and longer and both changes resulting in an increase of the electrical resistance end-to-end.

Let us consider a resistive material of homogeneous conductivity which is subjected to a tensile force. The effect of this tensile force would be only on the geometry of the conductor if it is considered that the conductor is made of a normal material, the resistivity of which remains constant under tensile force. The change in geometry could occur in two different ways. Either the length and cross-sectional area of the conductor could be changed or only length of the conductor could be changed.

Assume that both length and cross sectional area of the conductor are affected by the tensile force. Then the resistance change of the conductor will be affected by both the increased length of the conductor and the decreased cross sectional area of the conductor. Then the gauge factor of the conductor can be derived by the following equation

$$\text{Gauge factor, } K = \Delta R/R_0 / \epsilon \quad (7)$$

Where, ΔR = Elongation initiated resistance change

R_o = Original resistance of the material

$$\epsilon = \Delta L / L / \Delta d / d_0$$

Theoretically the gauge factor should be 2 which is dependent on Poisson's ratio.

If the cross-sectional area will remain constant under the effect of this tensile force then it is the length of the material which can affect the total resistance. The resistance of the material will increase as the length of the material is increased and this relationship will be linear. So it can be said that the fractional change in resistance of the material will be proportional to the fractional change in length.

$$\Delta R/R_o = \Delta L/L_o \quad (8)$$

$$K = \Delta R/R_o / \epsilon \quad (9)$$

Where, ΔR = Elongation initiated resistance change

R_o = Original resistance of the material

ΔL = Change in length under tensile force

L_o = Initial length

$$\epsilon = \Delta L/L_o$$

The gauge factor for this type of material should be 1.

2.4.2 Relation between dimension and resistance of a piezo-resistive material under a stretching force

In case of normal resistive material the resistance change is measured along its longitudinal axis; along which the force is applied but a piezoresistive element behaves differently towards longitudinal and transverse strain components. If the stress is applied along the longitudinal direction and the change of resistance is measured along the same direction of the applied stress is called longitudinal piezoresistivity. On the other hand, the change of resistance along

transverse direction of the strain components is called transverse piezoresistivity. For any given piezoresistive material, the longitudinal and transverse gauge factors are different.

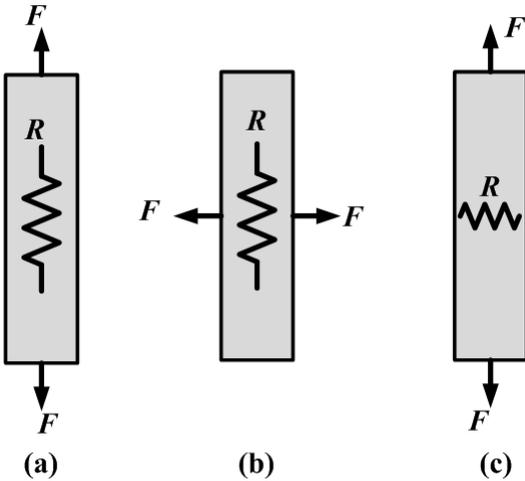


Figure 9: (a) Longitudinal piezoresistor, (b, c) transverse piezoresistor.

3. Experimental

3.1 Materials and method

The investigation of strain effects reported in this thesis employs materials prepared previously according to the following scheme. Bacterial nanocellulose (BC) produced from *Gluconacetobacter xylinum* has been used to obtain conductive films by incorporation of conductive agents. DWCNT and MWCNT treated with carboxyl groups (+90% purity, Nanocyl S A, Belgium) and GNP purchased from Sigma Aldrich (<500 nm particle size (DLS), >99.95% trace metal basis) have been used as conductive agents. Nanocellulose swelling has been achieved by treatment of nanocellulose pellicles. Before modifying with DWCNT, MWCNT or GNP, nanocellulose pellicles have been washed until a pH of 7 was obtained and this process was done at room temperature. DWCNT, MWCNT and GNP water dispersions have been prepared in the presence of cetyltrimethylammonium bromide (CTAB). Prepared dispersions have been centrifuged for 20 minutes (3500 rpm, RT) in order to remove undispersed carbon. Three different dispersed solutions with different volumes and concentrations of DWCNT and GNP in water were prepared which were 15 ml of 1 mg/ml, 30 ml of 1 mg/ml and 30 ml of 2 mg/ml. For MWCNT treated nanocellulose only 30 ml of 2 mg/ml concentration has been used. Nanocellulose pellicles (3×3 cm²) have been immersed in DWCNT, MWCNT or GNP dispersions for 24 - 72 h. After treatment with conductive agent dispersion, the nanocellulose pellicles have been washed carefully by de-ionized water to remove all free surfactants and they were subsequently dried in a fume hood 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. Table 1 shows data for all types of treated BNC samples.

Table 1

Sample type	Concentration of modifying agent	Conductivity, S/cm
DWCNT treated BNC	15 ml of 1 mg/ml, 30 ml of 1 mg/ml, 30 ml of 2 mg/ml	0,05- 0,4
MWCNT treated BNC	30 ml of 2 mg/ml	0,3- 1,6
GNP treated BNC	15 ml of 1 mg/ml, 30 ml of 1 mg/ml, 30 ml of 2 mg/ml	0,01-0,72

3.2 Experimental setup

Electromechanical characterization of treated nanocellulose has been done by using Instron material testing instrument (Series 5500). Constant tensile stress can be applied by this instrument. The Instron machine is programmed so that it will reach the desired load in a time period less than 10 per cent of the duration of the test so that it can minimize the effect of the rise time. However, in some of the tests performed, it is found that this rise time proved to be too high a load rate for the material and early failure occurred. Therefore, both the rise time and the test duration are adjusted to account for these occurrences. The position measurement accuracy of this setup is $\pm 0,02$ mm or 0,05% of displacement (whichever is greater), load measurement accuracy is $\pm 0,4\%$ of reading down to 1/100 of load cell capacity, $\pm 0,5\%$ of reading down to 1/250 of load cell capacity.

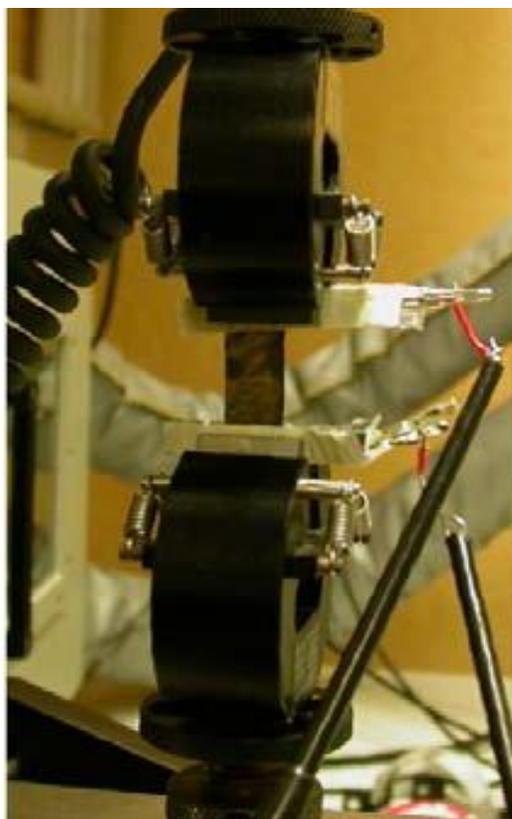


Figure 10: Instron material testing instrument for tensile testing.

The samples are placed in the Instron machine and the load is increased to the desired load and held there for a specified period of time at room temperature and humidity. Different loads have been applied to check the effect of constant load on treated samples. Creep behavior of the samples has been observed and the extension of the sample at different loads has been recorded, converted and displayed. A digital multimeter (Agilent 34401A) has been used to measure the resistance change with respect to the extension of the sample. Samples used in Instron material testing instrument were 3 cm in length and 1 cm in width. Aluminum foil has been selected as conductor as it has very high conductivity and then it has negligible effect on the measurement of the resistance of the treated nanocellulose. The aluminum foil has been insulated from the sample holder by an insulator in order to eliminate the effect of the sample holder. Crocodile clips have been connected to the aluminum foil to measure the resistance. All samples are kept in the lab at least 24 hours to get the samples adjusted with the humidity and temperature of the lab.

3.3 Experimental procedure

Forces of different magnitude have been applied on treated nanocellulose to check the extension rate and the effect of extension on resistance. Resistance change has been measured in two different directions; longitudinal and transverse.

To calculate the fractional increment in resistance ($\Delta R/R_0$) where ΔR is the difference between the current resistance (R) and initial resistance (R_0), a constant force has been applied for at least 3 hrs. But the resistance change of the first 20 mins was not considered for the calculation. So in the calculation the initial resistance is the value of resistance which was measured after 20 mins of applied stress. To calculate the fractional increment in length ($\Delta L/L_0$), where ΔL is the difference between the length of the sample after strain (L) and initial length of the sample (L_0), initial length of the sample was considered 3 mm less than the original length of the sample. As some part of the sample was inside the sample holder, the extension rate of that part of the sample was not considered for calculating the fractional increment in length of the sample. While calculating fractional increment in resistance the effect of contact point resistance was ignored since the resistance of treated BNC sample was high, between 4 k Ω to 32 k Ω . So the contact resistance should have negligible effect on the total resistance of the sample.

3.3.1 Resistance measured along longitudinal direction

The change of measured resistance under the longitudinal stress component is called longitudinal resistance of the material [16]. The relative change of measured resistance to the longitudinal strain is called the longitudinal gauge factor.

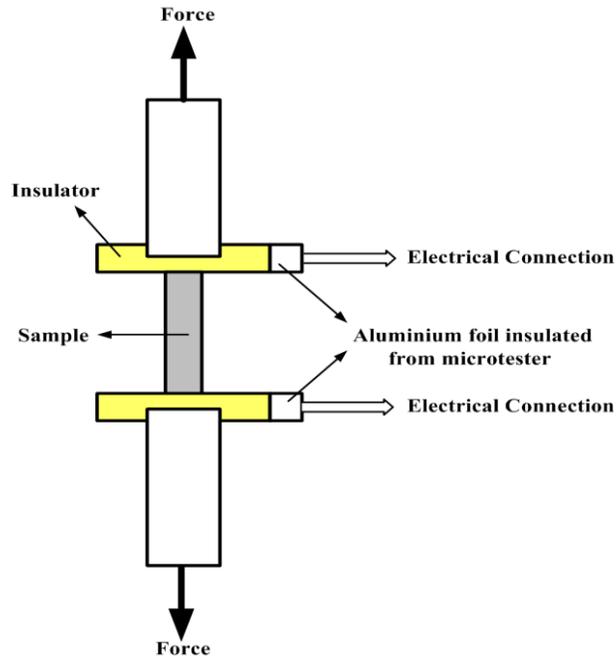


Figure 11: Experimental setup for tensile testing; resistance measured in longitudinal direction.

Figure 11 shows the experimental setup to measure resistance along the longitudinal direction of applied stress. The sample is mounted in to the holder and the samples holder should be insulated from the conductor by an insulator. The electrical connection was put on the upper and lower part of the sample as shown in figure 12. Aluminium foil has been used as conductor in this case. The resistance change is measured by the multimeter.

3.3.2 Resistance measured along transverse direction

The change of resistance under transverse strain components is called transverse resistance of the material [16]. The relative change of measured resistance to the transverse strain is called the transverse gauge factor.

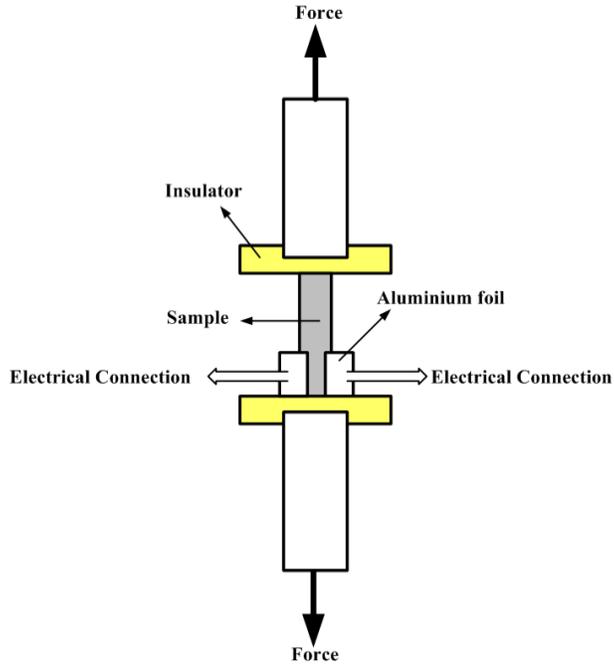


Figure 12: Experimental setup for tensile testing; resistance measured in transverse direction.

Figure 12 shows the experimental setup to measure resistance along the transverse direction of applied stress. To measure resistance change in the transverse direction the top and bottom part of the sample was insulated by using an insulator. The conductor was placed at the sides of the sample and it was made sure that the two conductors were separated from each other and there was no short-circuit between them. The electrical connection can be put directly to the sample but the conductors have been used to protect the sample from damage.

4. Results

4.1 Mechanical response of treated BNC

To check the mechanical response of DWCNT treated nanocellulose different tensile forces have been applied for at least one hour. The conductivity range of the treated sample varied from 0,099 $\Omega\cdot\text{m}$ to 0,378 $\Omega\cdot\text{m}$. It has been observed that a DWCNT treated BNC sample can respond to a very weak force.

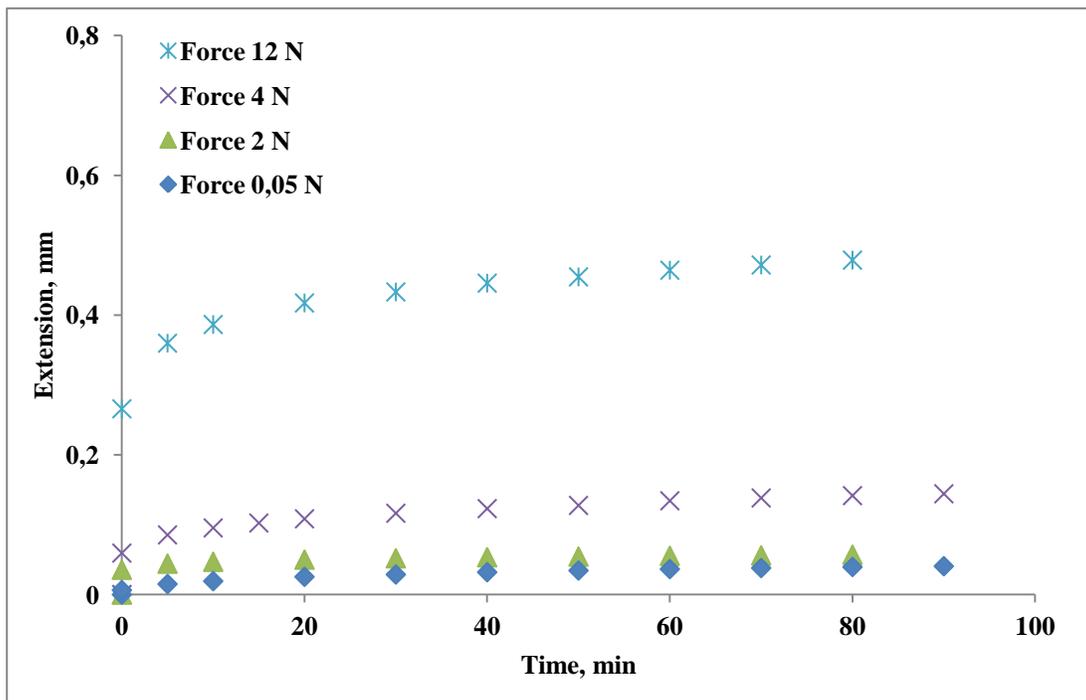


Figure 13: Extension of DWCNT treated nanocellulose at different forces.

To observe the response of nanocellulose samples treated with GNP, different tensile forces have been applied for at least one hour and the resistance along the longitudinal direction has been measured at every ten minutes. From figure 14 it appears that at 1 N and 2 N force the absolute extension of the GNP treated BNC sample was almost similar but as the tensile force is increased to 4 N then the extension of the sample increases.

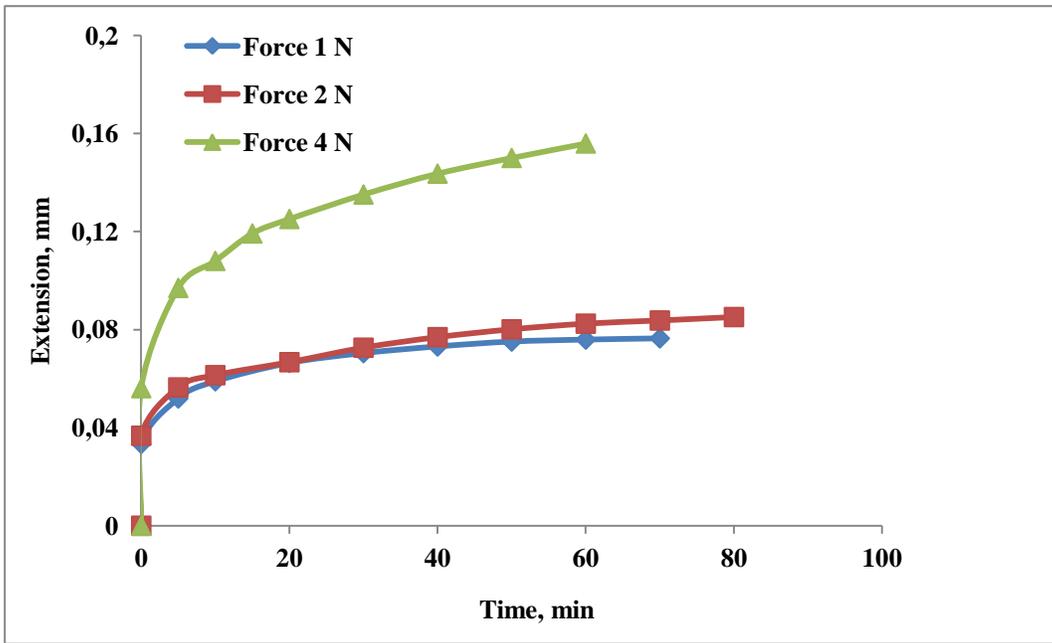


Figure 14: Extension vs time plot for GNP treated nanocellulose at different forces.

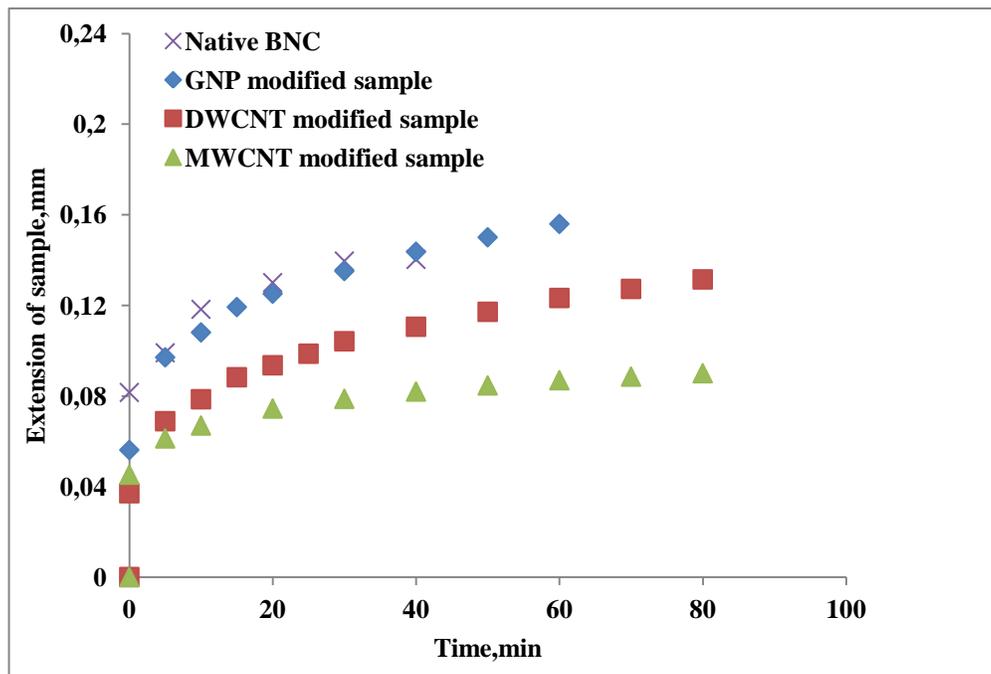


Figure 15: Extension of treated nanocellulose under a fixed load condition. The modifying agents are different in each case.

In order to compare the flexibility of the treated samples different types of samples have been tested under the same tensile force. Figure 15 shows the extension plot of different samples, when a 4 N load has been applied. It is clear from the graph that the rate of extension was not the same. The extension rate of GNP treated nanocellulose was higher than for the other samples under the same applied load condition. The graph shows that GNP treated nanocellulose is more flexible than the other samples. So the modifying agent may have an effect on the flexibility of the sample. From Figure 15 it is clear that MWCNT treated nanocellulose (which has the highest conductivity) is more rigid than the other samples.

4.2 Strain effect on electrical resistance

DWCNT treated nanocellulose, MWCNT treated nanocellulose and GNP treated nanocellulose have been tested under different tensile force and the effect of tensile force on electrical resistance has been observed.

4.2.1 Effect of conductivity of CNT treated nanocellulose

For the effect of the modifying agent on the strain induced electromechanical response of the samples, different treatment conditions such as the treatment time could have an impact. In this section we look at DWCNT treated BNC samples without limiting the scope to a particular treatment condition. Different conductive samples, prepared in different ways, have been tested to observe the correlation between resulting conductivity and the sensitivity of the sample.

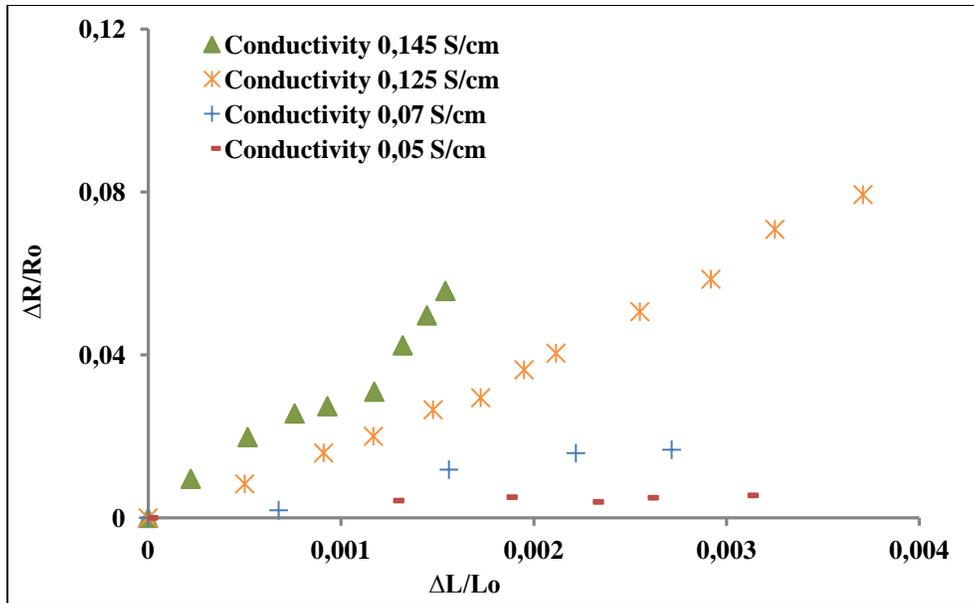


Figure 16: Fractional increase in resistance vs fractional increase in length plot for DWCNT treated nanocellulose samples of different conductivity.

When the conductivity of different samples treated with DWCNT has been measured and their electromechanical response has been tested it was observed that the electromechanical response directly relates to the conductivity of the samples. Figure 16 shows that the fractional increase in resistance is lower for samples with lower conductivity.

It was found that the conductivity of MWCNT treated nanocellulose was higher than that of DWCNT treated nanocellulose. It was observed that both MWCNT treated BNC and DWCNT treated BNC respond in the same way under strain and the sensitivity of the treated samples increases as the conductivity increases.

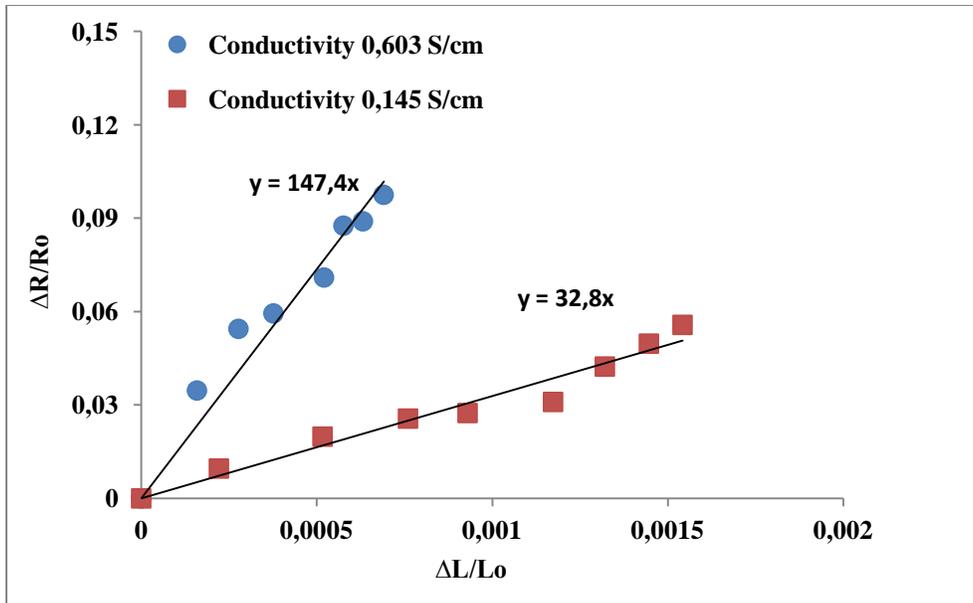


Figure 17: Sensitivity of MWCNT treated BNC sample and DWCNT treated BNC sample.

When the sensitivity of CNT treated BNC samples is plotted against the conductivity of the sample (Figure 18) a correlation can be observed between the conductivity and the sensitivity of the sample.

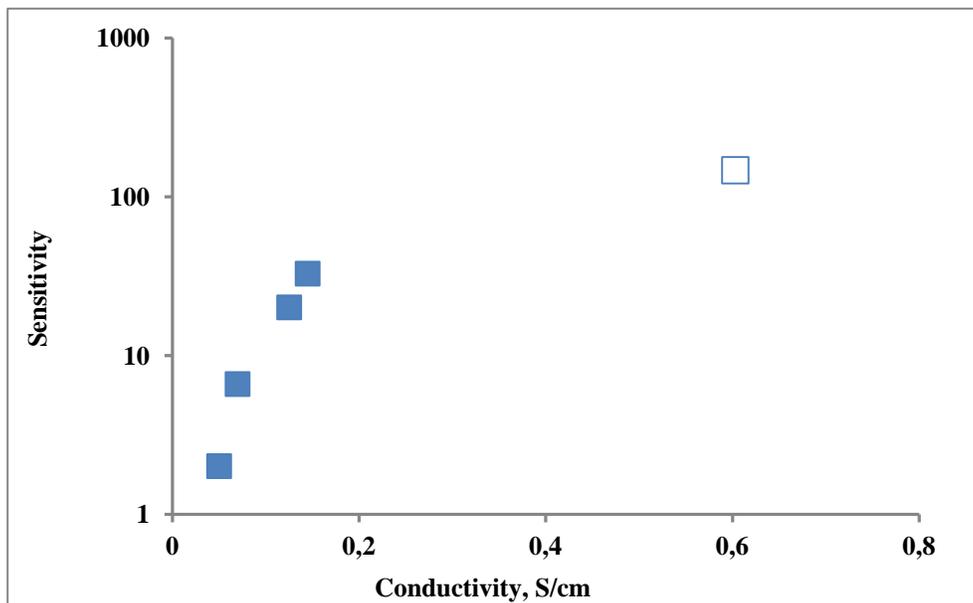


Figure 18: Conductivity vs sensitivity plot of DWCNT (filled mark) and MWCNT (open mark) treated nanonancellulose.

4.2.2 Strain effect on GNP treated nanocellulose

BNC samples treated with CNT have been tested at a tensile force of 4 N to measure their electrical response. When GNP treated BNC samples have been tested it was found that the samples can respond also at forces below 4 N. From Figure 19 it can be observed that the fractional change in resistance with respect to fractional change in length is almost similar for the cases of a force of 1 N or 2 N.

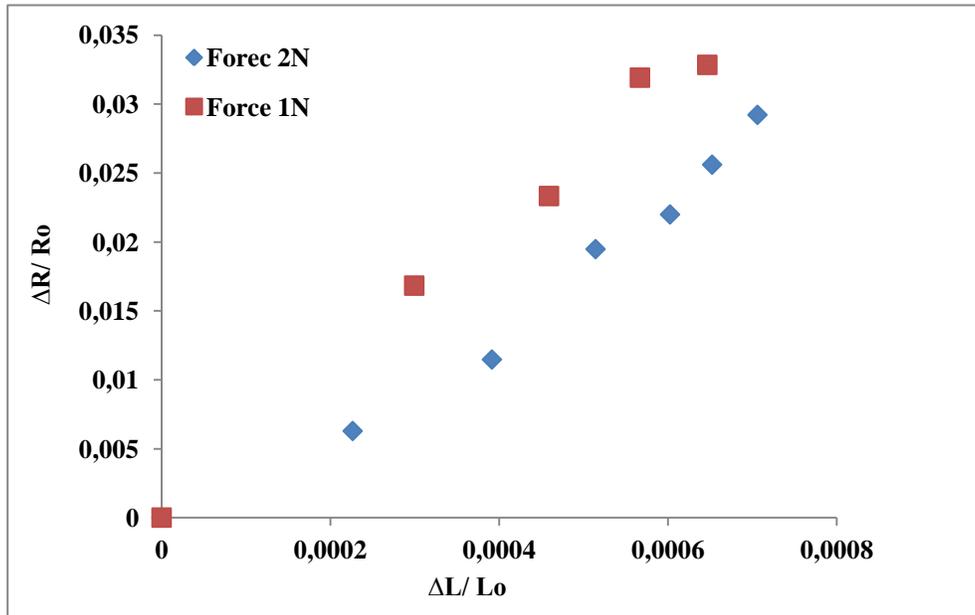


Figure 19: Fractional change in resistance with respect to fractional change in length of GNP treated nanocellulose samples at different forces.

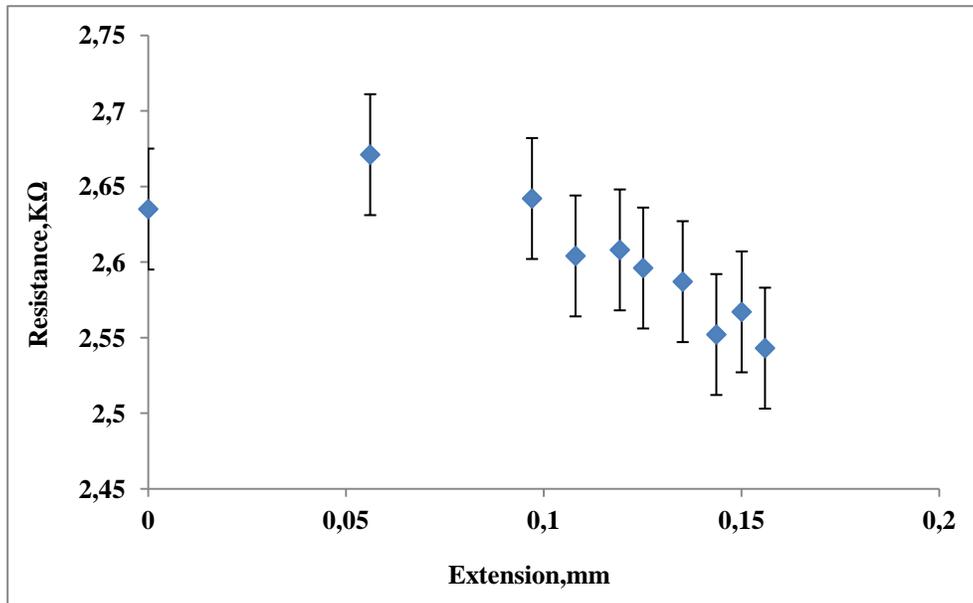


Figure 20: Resistance vs extension plot of GNP treated nanocellulose sample at 4 N tensile force.

Figure 20 shows the result when 4 N tensile force has been applied on a GNP treated nanocellulose sample. It is observed that the resistance decreases with the extension of the sample and the error bars in the graph reflect the instability of the resistance value at this load condition.

4.3 Transverse resistance

In the previous section the strain effect on both CNT and GNP treated BNC samples have been observed by measuring the resistance along the longitudinal direction of applied force. In this section the resistance value of treated BNC samples have been measured along the transverse direction of applied force.

In the case of DWCNT treated nanocellulose samples and MWCNT treated nanocellulose samples 4 N tensile force has been applied for at least one hour and the resistance has been measured every 10 minutes. In the case of GNP treated nanocellulose samples 2 N force has been applied as it has been shown in the previous section that at 4 N force the resistance of the sample decreased with the extension of the sample.

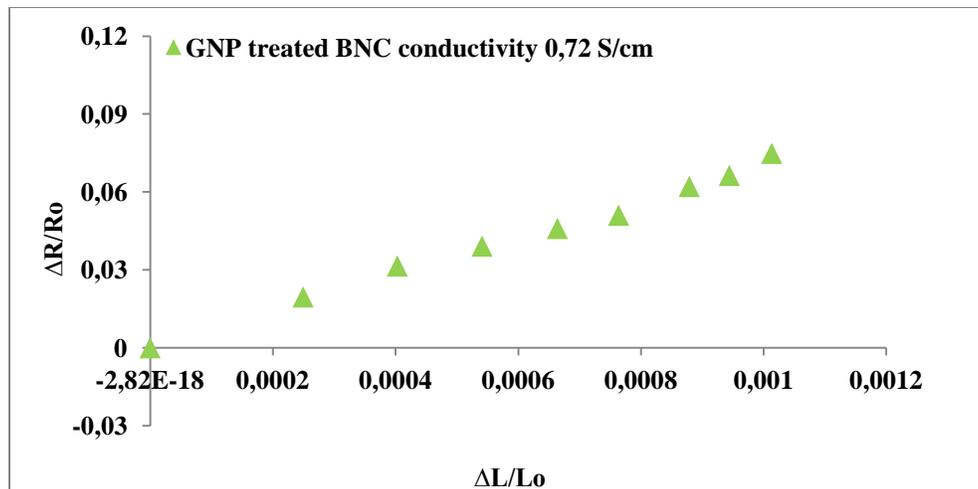
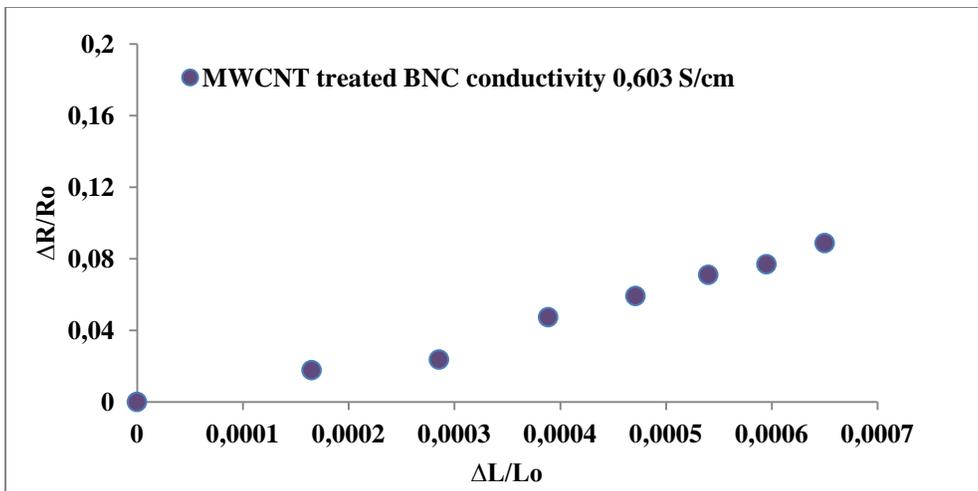
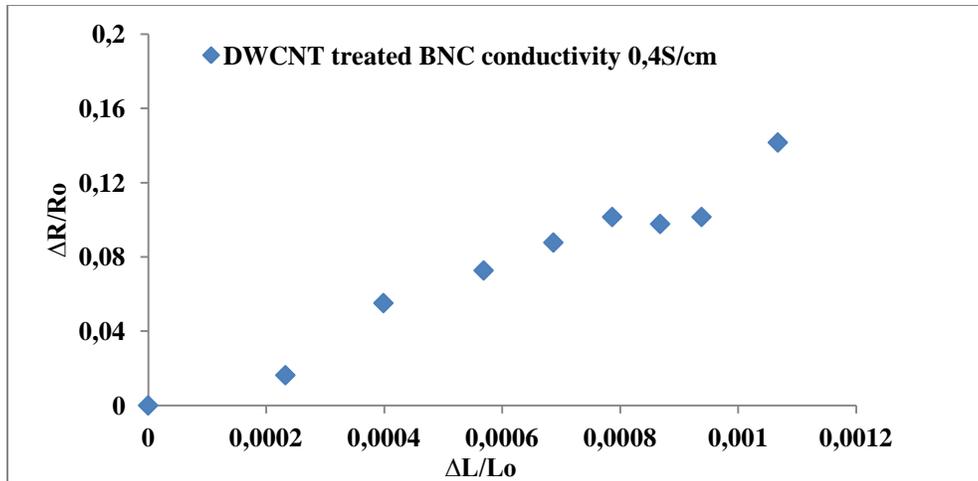


Figure 21: Fractional increment in resistance vs fractional increment in length plot for treated BNC sample. Resistance measured along transverse direction of applied load.

Figure 21 show that all types of BNC samples have a significant effect on their transverse resistance under tensile extension.

4.4 Comparison of transverse gauge factor and longitudinal gauge factor

To observe the relation between longitudinal gauge factor and transverse gauge factor of BNC samples a comparison has been done. It has been observed that for DWCNT and GNP treated BNC samples the transverse gauge factor is greater than the longitudinal gauge factor. For MWCNT treated BNC the longitudinal gauge factor is greater than its transverse gauge factor. But in every case the value of the transverse gauge factor is considerable.

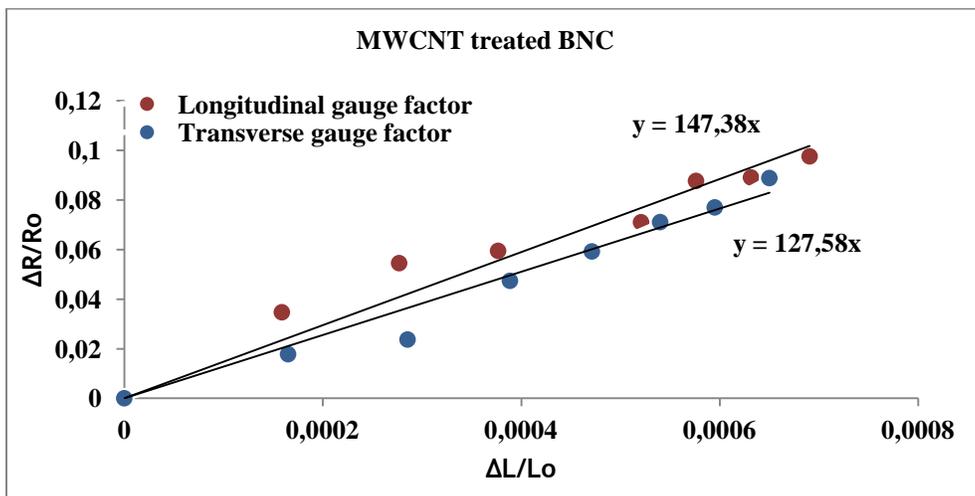
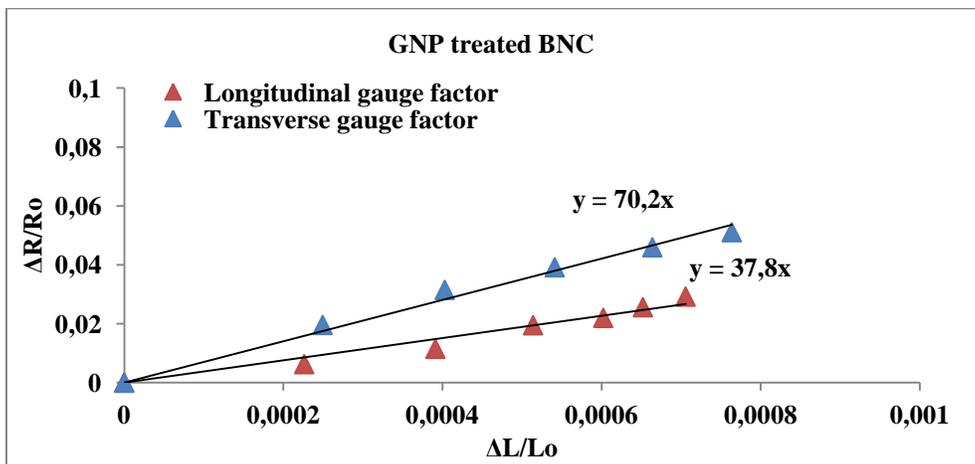
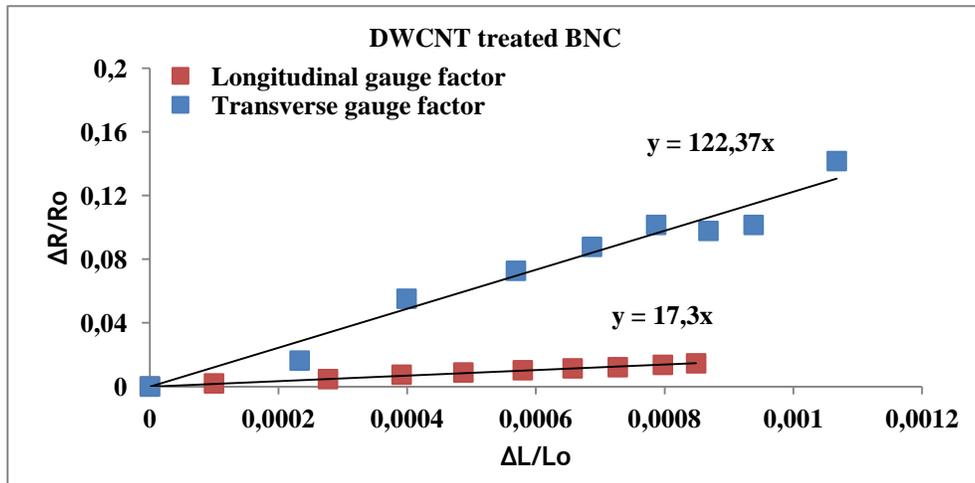


Figure 22: Fractional change in resistance vs fractional change in length plot of DWCNT, MWCNT and GNP treated nanocellulose samples along longitudinal direction and transverse direction.

4.5 Repeatability of treated BNC sample

If the input signal and other measurement conditions remain the same and the sensor provides the same response for every measurement then this ability of the sensor is called repeatability. This property is crucial to ensure the availability of the sensor for a long period of time and the reliability of the obtained measurement.

Repeatability of any sample depends on their elastic modulus and plastic modulus. If the applied stretching force is within the limit of elastic strength of the sample then it can be expected that when the force will be removed the sample will return to its previous shape and give the same response continuously. It has been found that when a DWCNT treated nanocellulose sample has been repeated under 4 N force, the response behavior of the sample has been changed significantly, so a very small force of 0,05 N has been applied on the treated sample to check the repeatability of the sample.

From Figure 23 it is clear that when 0,05 N force has been applied on DWCNT treated nanocellulose sample the elongation rate of the treated sample increased slightly when the sample has been tested under same tensile force for the second time. From the resistance vs time plot it can be clearly observed that the initial resistance was higher in the second trial.

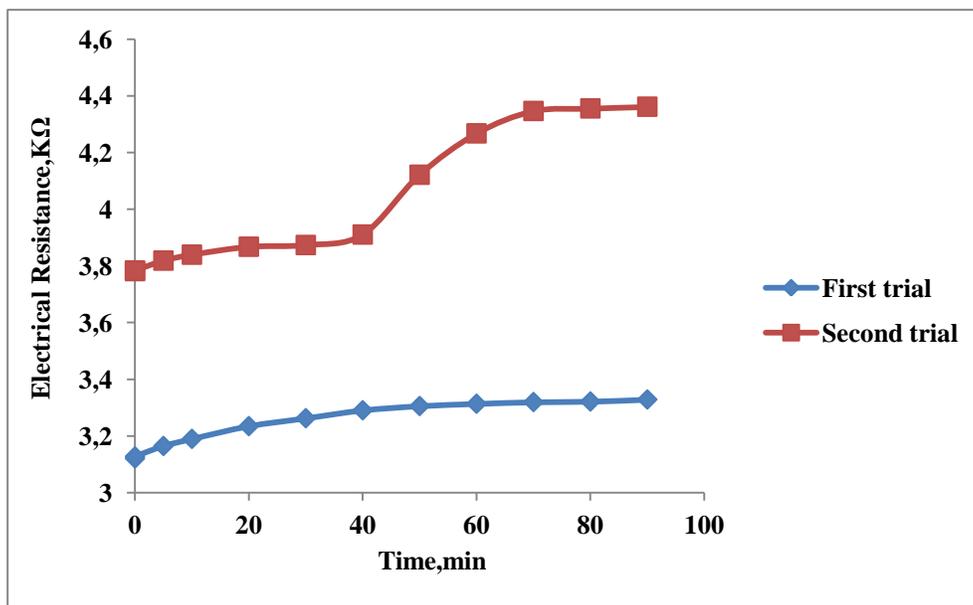
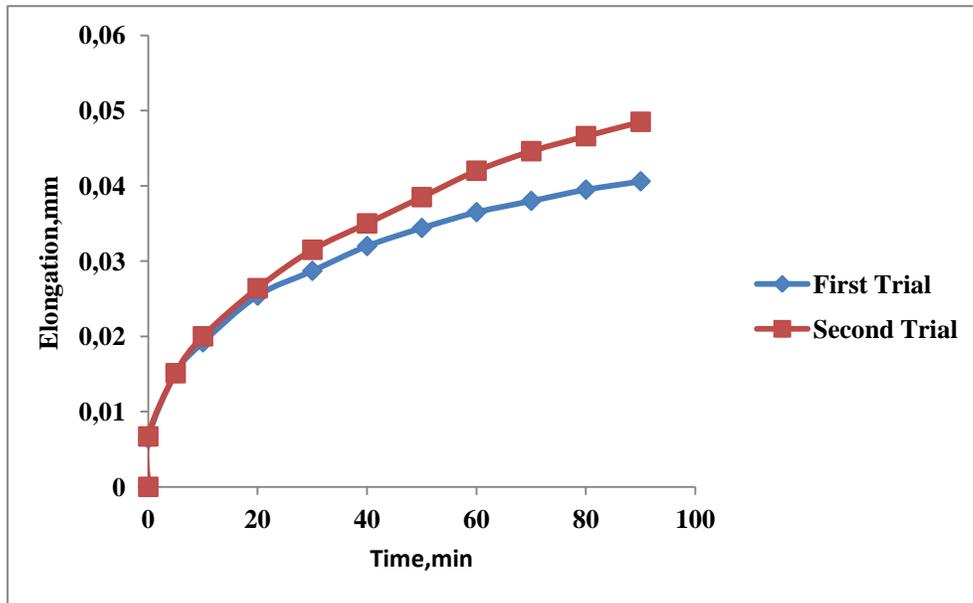


Figure 23: Elongation vs time plot and electrical resistance vs time plot of DWCNT treated nanocellulose sample for repeatability test.

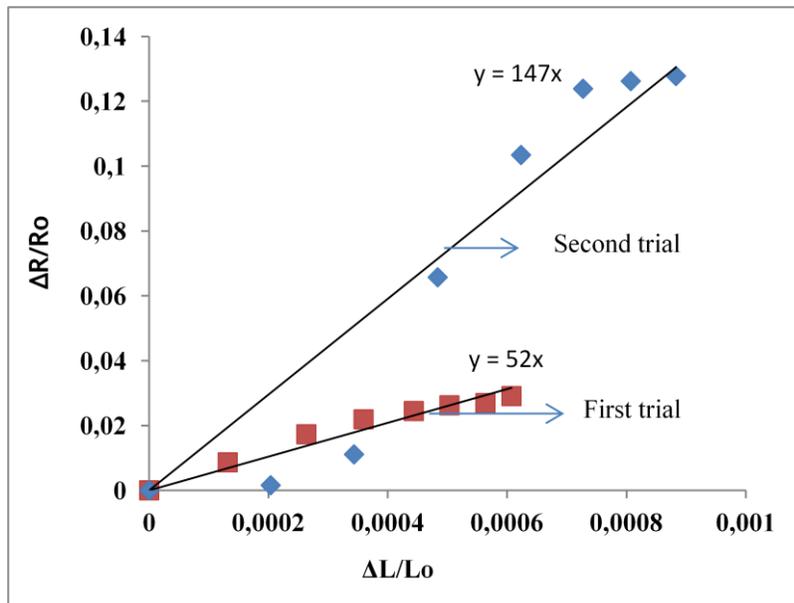


Figure 24: Fractional change in resistance vs fractional change in length plot of DWCNT treated nanocellulose for repeatability test.

5. Discussion

5.1 Electromechanical response of treated nanocellulose

When tensile force has been applied to treated BNC samples to observe the electromechanical response the electrical resistance increases with the extension of the samples. According to section 2.4, when a force has been applied on a homogeneous conductor there are three different factors which can affect the resistance of the sample: length, cross sectional area, and the resistivity of the sample material. But in the case of treated BNC samples when tensile force has been applied to them there is also the structure of the conductive layer to consider in order to explain the effect on the measured resistance.



Figure 25: Cross sectional image of treated BNC sample.

To check the electromechanical response the BNC samples have been cut into 3 cm in length and 1 cm in width. So the width of the sample is small and Figure 25 shows that the conductive layers were situated at the top and bottom of the sample and it is not possible to measure the thickness of the conductive layer reliably. Moreover the sample thickness was on the order of tens of μm and the thickness of the conductive layers would be very small.

Also it can be said that when force has been applied on treated BNC samples the change in length is equal for both the bulk cellulose and conducting surface layer but the effect of force on the thickness of these two different types of material will not be same. The thickness of top and bottom layer will not be affected in the same way as that of the middle layer, which is the bulk cellulose layer in case of treated BNC samples. When force has been applied on the samples and the samples goes through a geometrical change then the bulk cellulose layer will be compressed more than the conducting top and bottom layer. As the individual thicknesses of the conductive layers and the bulk cellulose were unknown and from the discussion above it can be assumed that mainly the thickness of the bulk cellulose layer was affected by the force so to calculate the resistance change of the samples it has been assumed that the cross-sectional area for the conducting part of the sample remains constant.

Then the main reason of resistance change under tensile extension could be the length of the sample or the structural change in the conductive layer. If only the length of the sample could affect the electrical resistance of the sample then the gauge factor should be 1, which was discussed in section 2.4.1. But in the results part it was clearly observed that the gauge factor of treated BNC samples was greater than 1. So it is not only the geometry of the sample which was affecting the electrical resistance changes.

Let us consider that the structure of the conductive layer has been affected by the tensile force. From Figure 26 it is clearly observed that when force has been applied to a CNT polymer composite then the fibers tried to be aligned. When the fibers started to align the proximity between the conductive layer and polymer matrix has been changed, which changes the resistivity of the sample. This fiber alignment increases the transverse resistivity of the sample. Increased transverse resistivity restricts the electric current from penetrating the entire cross section of the specimen and induces a longitudinal resistance increase [18].

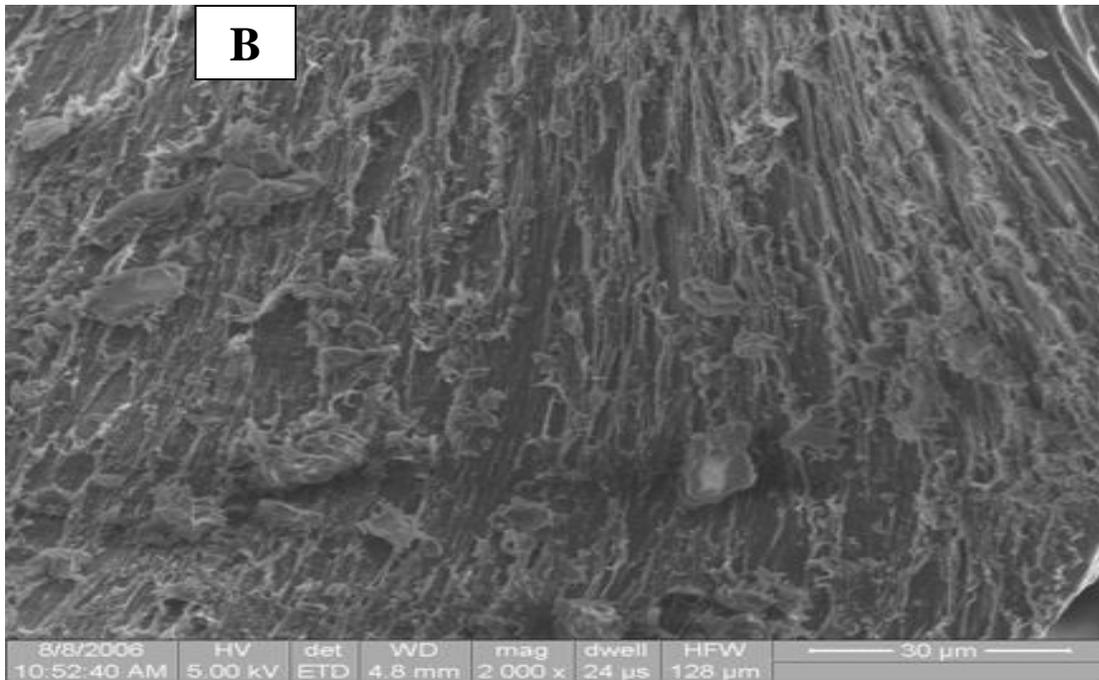
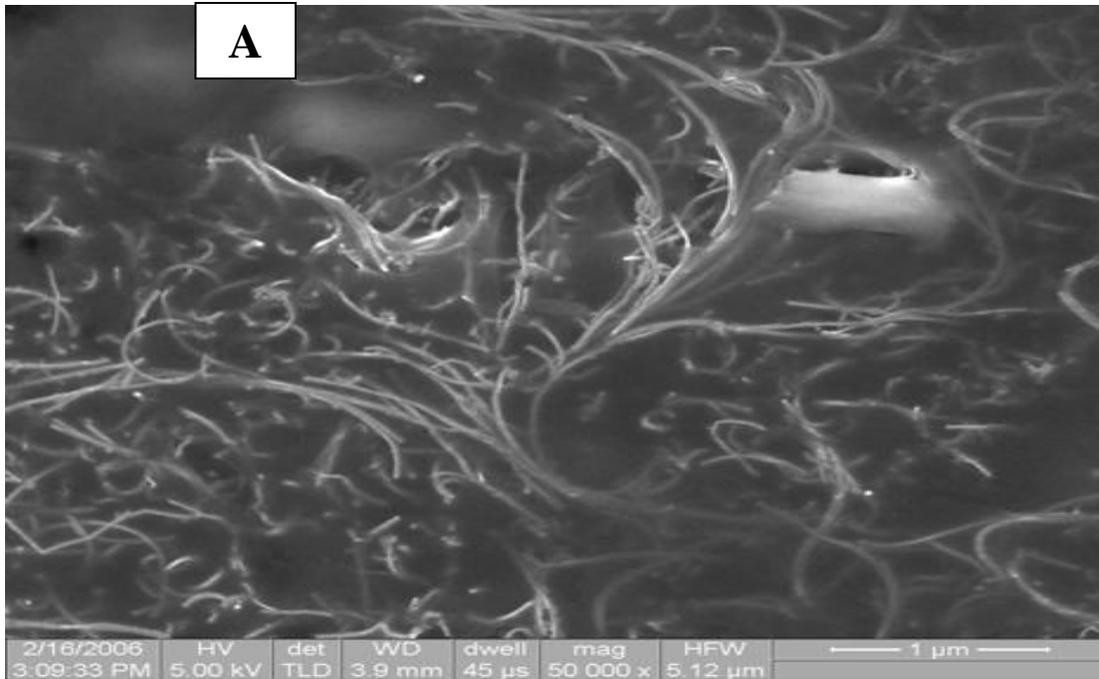


Figure 26: Microstructure of MWCNT /PEO composite before (A) and after (B) straining [18].

From the above discussion we can speculate that the structure of our conductive layers changes as for the composite material; the resistivity of the sample depends on the structure of conductive layer and polymer matrix. For the BNC samples the transverse resistance increases under tensile

force, so it can be said that this was the effect of increased transverse resistivity of the sample which also affected the longitudinal resistance. When all types of treated nanocellulose samples have been tested it was found that they have significant transverse gauge factor which can affect the total gauge factor of these samples. This case is similar to the behavior of a piezoresistive material. The total gauge factor of the piezoresistive material is the combination of longitudinal gauge factor and transverse gauge factor. Generally, the transverse gauge factor is smaller than the longitudinal gauge factor [19]. When the samples treated with DWCNT and GNP treated nanocellulose have been tested their transverse gauge factor was greater than longitudinal gauge factor but for MWCNT treated nanocellulose longitudinal gauge factor was greater than transverse.

5.2 Testing the repeatability of the treated sample

When DWCNT treated nanocellulose was tested to check its repeatability (Figure 23) the elongation rate was almost unaffected by re-measuring so the elasticity of the sample is not the crucial parameter. The electrical resistance vs time plot of Figure 23 shows that the initial resistance was not same and after the first test it increased. The reason could be the connectivity between the conductive particles of the sample, which has been decreased when the stretching force has been applied on the sample. When the force has been removed, the sample returns to its original shape as the force is below the ultimate strength level but the structure of the conductive layer has been changed and a rearrangement of the conductive layer is not possible.

6. Conclusion

Bacterial nanocellulose samples have been prepared by treatment of different modifying agents such as DWCNT, MWCNT and GNP by using different treatment conditions. To observe the strain induced electromechanical response of treated BNC samples both longitudinal resistance and transverse resistance of BNC treated cellulose have been measured. It was observed that the samples display piezoresistivity, as they give significant electrical response along both longitudinal direction and transverse direction of applied force with a gauge factor $\gg 1$. By observing the mechanical response of treated BNC samples it was found that it is dependent on the type of modifying agent. The strain sensitivity of the sample resistance depends on its initial conductivity. The resulting conductivity of the sample depends on the type of modifying agent and on the treatment conditions but its sensitivity correlates well with the conductivity of the sample alone. A higher initial conductivity of treated BNC samples gives a higher sensitivity to strain.

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Appendix

Paper A

Conductivity Dependent Strain Response of Carbon Nanotube Treated Bacterial Nanocellulose

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Conductivity Dependent Strain Response of Carbon Nanotube Treated Bacterial Nanocellulose

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Abstract

This paper reports the strain sensitivity of flexible, electrically conductive nanostructured cellulose which was prepared by modification of bacterial cellulose with double-walled carbon nanotubes (DWCNT) and multi-walled carbon nanotubes (MWCNT). The electrical conductivity depends on the modifying agent and its dispersion process. The conductivity of the samples obtained from bacterial cellulose (BNC) pellicles modified with DWCNT was in the range from 0.034 S·cm⁻¹ to 0.15 S·cm⁻¹ and for BNC pellicles modified with MWCNT it was from 0.12 S·cm⁻¹ to 1.6 S·cm⁻¹.

The strain induced electromechanical response, resistance vs strain, was monitored during the application of tensile force in order to study the sensitivity of the modified nanocellulose. A maximum gauge factor of 147 was found from highest conductive sample treated by MWCNT. It has been observed that the sensitivity of the sample depends on the conductivity of the modified cellulose.

Keywords: strain sensor, nanocellulose, bacterial nanocellulose, carbon nanotubes, conductivity.

1. Introduction

Recently sensors based on nanostructured material have attracted considerable attention due to their low power consumption, high sensitivity and selectivity, and prompt response [1, 2]. Conventional sensors are restricted in their application area by their rigidity and fragility. For this reason development of sensor materials which are flexible and environmentally friendly have received a great deal of attention [3]. It has been reported that such materials can be obtained by the introduction of nanoparticles with promising electrical and mechanical properties into a polymer matrix [4].

Among several nanostructures carbon nanotubes (CNT) have attracted a special interest because of their unique electronic, mechanical, and thermal properties which expanded the application field of CNT to nanoelectronics and biomedical devices [5]. Recently, the incorporation of CNT to polymers has been investigated to reinforce the mechanical properties of the polymers [4, 5]; it was shown that the elastic modulus and the ultimate strength of polymer composites increase with incorporation even of small amount of CNT.

Cellulose, the most abundant natural polymer has inexhaustible raw material with fascinating structures and properties [6]. The properties of cellulose allow obtaining environmentally friendly, biodegradable and bio compatible products. Recently, research related to cellulose demonstrated its value for diverse applications including actuators and sensors. The new class of flexible cellulose based electroactive materials was named electro-active paper (EAPap) [7]. It has been discovered that the electric power consumption of EAPap is very low [9]. The actuation principle of cellulose based EAPap has been analyzed in different research work [7, 8]. Also research has been conducted to investigate the mechanical properties of cellulose and the effect of ambient conditions on these properties. In the present work the strain induced electromechanical response of CNT modified cellulose has been synthesized and characterized.

Cellulose could be derived from various sources such as plant, bacterial or even animals [9]. Recently bacterial nanocellulose (BNC) has gained attention due to some exclusive properties which are not offered by plant cellulose. Since plant cellulose is part of natural composite which consists of lignin, pectin and hemicelluloses, the separation and purification of cellulose is

difficult. On the other hand BNC belongs to specific products of primary metabolism and could be easily purified [9]. Moreover, BNC is a gel composed of nanofibers which, when compared to plant cellulose, BNC displays some unique properties such as high mechanical strength, high water absorption capacity and high crystallinity [10].

In this report we present a flexible electrically conductive nanocomposite based on BNC cellulose and CNTs. Double-walled carbon nanotubes (DWCNT) and multi-walled carbon nanotubes (MWCNT) have been used to modify BNC 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 BNC films. The strain oriented electromechanical properties of DWCNT and MWCNT treated cellulose have been measured and characterized.

2. Experimental

2.1 Sample preparation

The BNC 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 agents for modification of BNC. The dispersion of CNT was carried out using cetyltrimethylammonium bromide (CTAB) as a surfactant (Fluka, assay $\geq 96\%$). The dispersion process consisted of a combination of heating, mild stirring and sonication followed by centrifugation to remove undispersed CNT. Dispersions of DWCNT and MWCNT with 1 mg/ml and 2 mg/ml were used. $3 \times 3 \text{ cm}^2$ BNC pellicles were immersed in the CNT dispersions (15 ml of 1 mg/ml, 15 ml of 2 mg/ml and 30 ml of 2 mg/ml) for 24 – 72 h under mild shaking. After finishing the treatment step, all samples were washed carefully with de-ionized water in order to remove free surfactant and CNT residue. The pellicles were dried in a fume hood between polytetrafluoroethylene plates.

The total thicknesses of the dried BNC 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 (Leo Ultra 55 FEG SEM). The electrical

conductivity measurements were performed by using a four-point probe system (CMT-SR2000N, AIT, Korea).

2.2 Experimental setup for electromechanical characterization

The strain induced electromechanical response of treated cellulose samples has been monitored by using an Instron Material Testing Instrument (Series 5500). Constant tensile force can be applied by this instrument. Samples used in the Instron instrument were 3 cm in length and 1 cm in width. Electrical contact was provided by an aluminum foil that was pressed to the sample by the Instron clamp. An insulating layer of plastic was put between the clamp and the aluminum foil. The resistance of the sample has been measured along the same direction as the applied force. The experimental setup for tensile test is shown in (fig. 1). The samples were placed in the Instron machine and the load was increased to the desired level and held there for at least two hours at room temperature and humidity. A digital multimeter (Agilent 34401A) was used to measure the resistance change with respect to the extension of the sample.

3. Results and discussion

3.1. Morphology of conductive BNC

Nanocellulose samples modified with CNT are characterized by the same flexibility as native cellulose. The surface of BNC films modified with MWCNT is uniformly black whereas the surface of BNC pellicles modified with DWCNT contains colorless parts. The cross section of BNC pellicle shows no deep penetration of CNT (Fig. 2A). A small pore in the native BNC matrix (Fig. 2B) prevents CNT penetration into the cellulose. As a result, asymmetric conductive layer was formed on the surface of the BNC pellicles

According to investigations using SEM MWCNT (diameter 10-16 nm, Fig. 2D) are more homogeneously distributed on the BNC surface compared to DWCNT (diameter 5-8 nm, Fig. 2C) which indicates better dispersion of MWCNT.

To observe the effect of strain on the BNC samples, 4 N tensile force has been applied on both DWCNT treated BNC sample and MWCNT treated BNC samples for three hours. According to SEM morphology of conductive BNC samples there was no change in the structure of treated BNC samples after application of strain (Fig. 3).

Electrical conductivity measurement

The electrical conductivity of the nanocellulose 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 which is modified with the lowest concentration and volume an increase the immersion time did not give any significant effect on the electrical conductivity of the modified BNC pellicles (Fig. 4A). Therefore one could conclude that saturation capacity of cellulose for 1 mg/ml DWCNT dispersions is not enough to form the conductive layer. However, by increasing the CNT concentration and volume, conductivity rise significantly with the immersion time (Fig. 4A) pointing to the substantial increase of the saturation capacity.

The conductivity of the BNC pellicles has been increased by one order of magnitude when the modifying agent was changed from DWCNT to MWCNT (Fig. 4B). These results could be explained by the formation of more homogeneous dispersions with MWCNT which is probably caused by higher CTAB/CNT surface ratio for MWCNT (specific surface area 115 m²/g [11]) comparing to DWCNT (specific surface area >500 m²/g).

The highest conductivities have been obtained for the pellicles modified in the 30 ml of 2 mg/ml solutions: 0,15 S·cm⁻¹ for DWCNT and 1,6 S·cm⁻¹ for MWCNT, which is significantly higher than previously reported [12].

Electromechanical response

Strain sensors can operate on the principle that as the sensing material is strained, the resistance of the material changes in a well defined way. To observe the strain sensitivity of treated BNC, different types of samples, treated with different concentrations of DWCNT or MWCNT were evaluated under a fixed stretching force (4 N). We measured the resistance value at ten minute intervals. It has been observed that the sample continuously extends under a fixed tensile force (Fig. 5).

We tested samples modified with different concentration of modifying agent and yielding different conductivities between 0,05 S/cm to 0,145 S/cm. As discussed in section 3.2, the conductivity of treated samples depends on treatment parameters such as concentration of modifying agent and dispersion time; the BNC samples used in this case are prepared under

different condition. Fig. 6 shows that as the conductivity of the samples increases, the fractional change in resistance increases with fractional increase in length.

A comparison of strain sensitivity of the samples modified with MWCNT and DWCNT treated nanocellulose has also been conducted. To compare between the two different types of modified samples we use the most conductive sample obtained from DWCNT treatment and the most conductive sample obtained from MWCNT treatment. Fig. 7 shows the fractional increase in resistance as a function of fractional increase in length plot for both DWCNT and MWCNT treated nanocellulose samples. The MWCNT treated nanocellulose shows the same type of response as for DWCNT treatment. Fig. 8 shows the sensitivity of the treated BC films as a function of conductivity. The highest sensitivity is obtained from the most conductive sample (treated with MWCNT).

4. Conclusion

Electrically conductive bacterial nanocellulose (BNC) films were prepared by treatment of BNC with dispersions of double walled carbon nanotubes (DWCNT) and multi walled carbon nanotubes (MWCNT) in the presence of cetyltrimethylammonium bromide (CTAB). It has been observed that the dispersion process for the modifying agent affects the electrical conductivity of the treated nanocellulose. The electrical conductivity increased when MWCNTs were used as modifying agent. $0,15 \text{ S}\cdot\text{cm}^{-1}$ was the highest conductivity that was obtained by treatment of BNC with DWCNT and by treatment with MWCNT the highest conductivity was $1,6 \text{ S}\cdot\text{cm}^{-1}$.

The strain induced electromechanical response of treated BNC films has been observed. MWCNT treated cellulose showed higher sensitivity than DWCNT treated cellulose. A gauge factor of 147 was obtained from the most conductive sample treated with MWCNT. Comparing the strain sensitivity of samples with different conductivity it has been observed that high strain sensitivity correlates with high conductivity.

Acknowledgement

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Figure Captions

Fig. 1: Experimental setup for tensile testing.

Fig. 2. SEM images of bacterial nanocellulose; (A) Cross sectional optical microscope image of BNC pellicle modified with DWCNT (B) SEM micrograph of native untreated BNC. (C) SEM micrograph of DWCNT treated nanocellulose. (D) SEM micrograph of MWCNT treated nanocellulose.

Fig. 3. SEM images of BNC samples modified with MWCNT (A) and DWCNT (B) before and after application of strain.

Fig. 4. Electrical conductivities of bacterial nanocellulose samples modified with DWCNT (A) and MWCNT (B) as a function of immersion time.

Fig. 5. Strain vs time plot for DWCNT treated BNC-sample. Sample shows continuous extension under a fixed tensile force.

Fig. 6. Fractional increase in resistance vs fractional increase in length plot for nanocellulose samples subject to different DWCNT treatments resulting in different conductivities.

Fig. 7. Fractional increase in resistance ($\Delta R/R_0$) as a function of the fractional extension ($\Delta L/L_0$) of the strain gauge for two different samples of bacterial nanocellulose. Open symbols MWCNT treated nanocellulose; filled symbols DWCNT treated nanocellulose.

Fig. 8. Conductivity vs slope plot of DWCNT (filled mark) and MWCNT (open mark) treated nanocellulose.

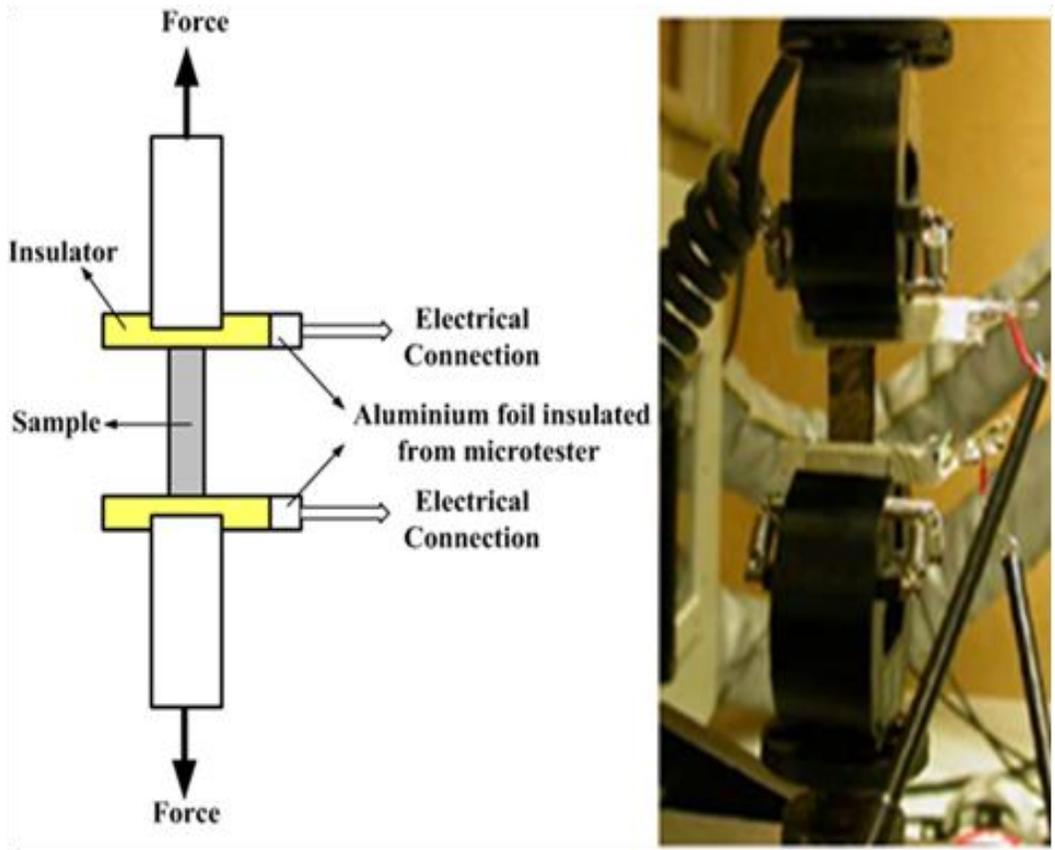


Fig. 1

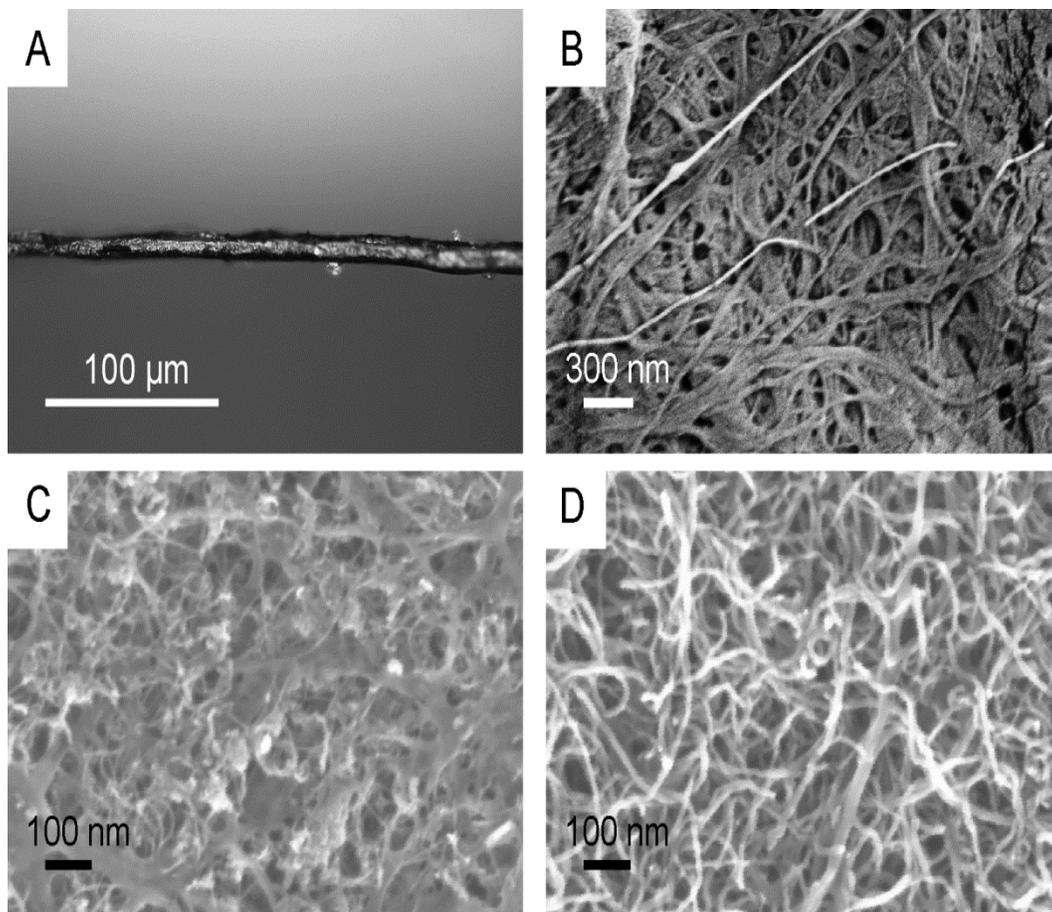


Fig. 2

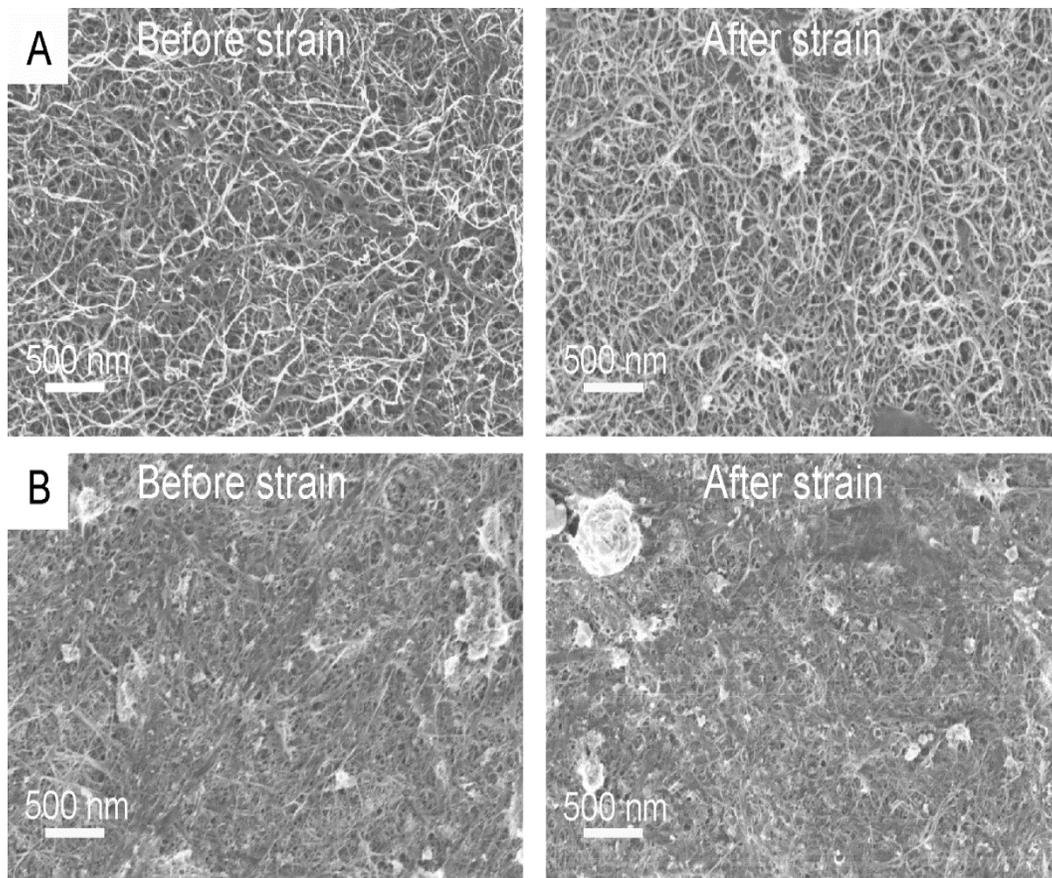


Fig. 3

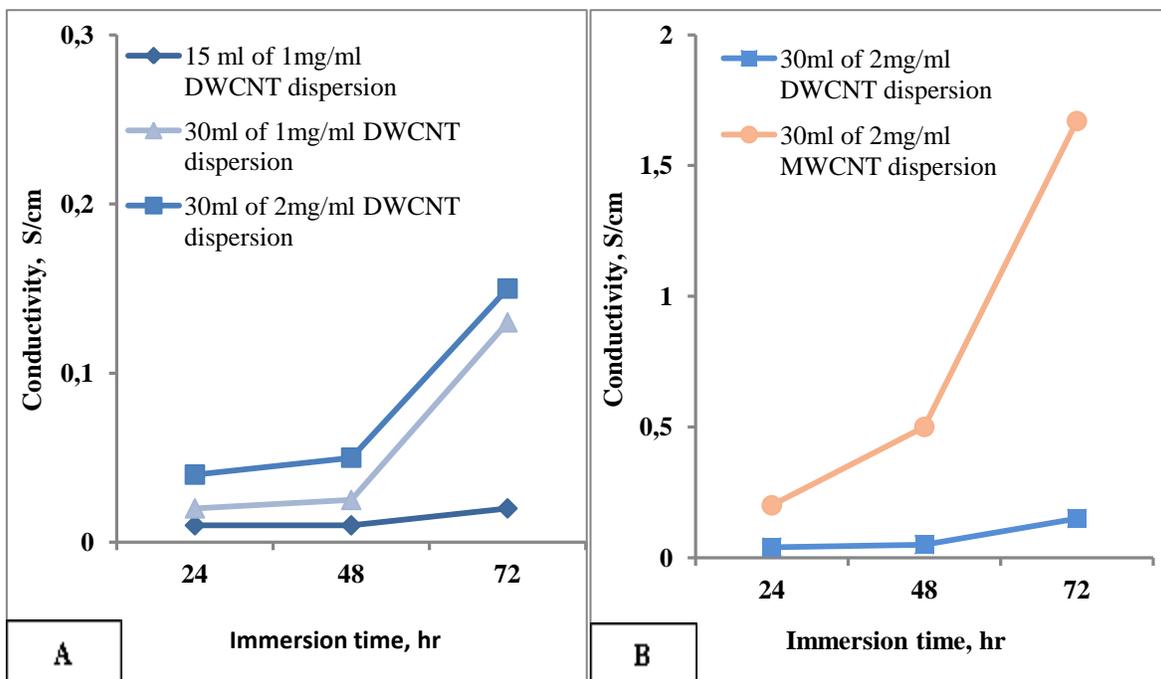


Fig. 4

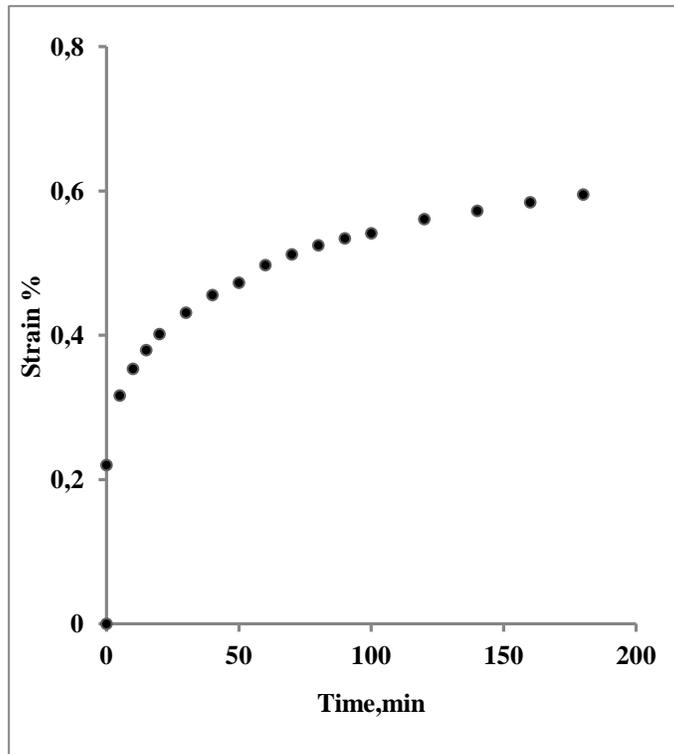


Fig. 5

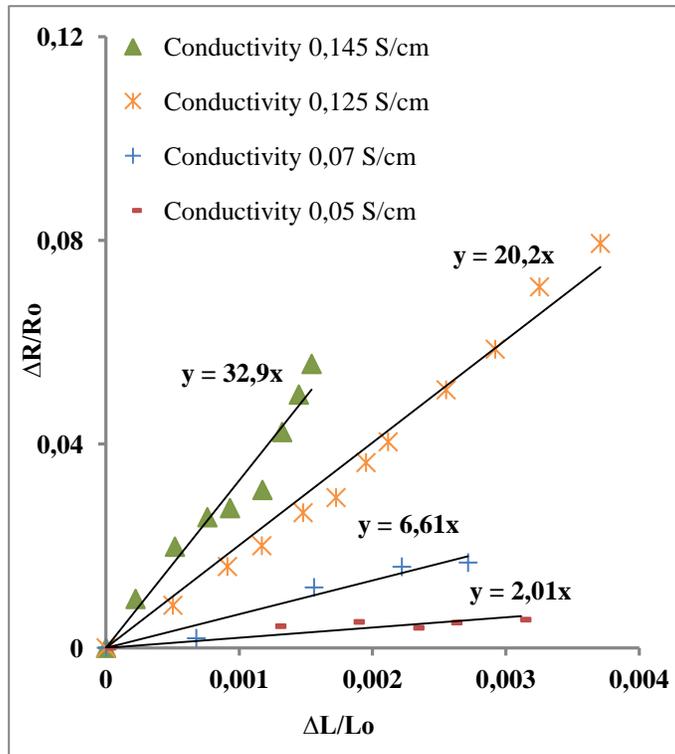


Fig. 6

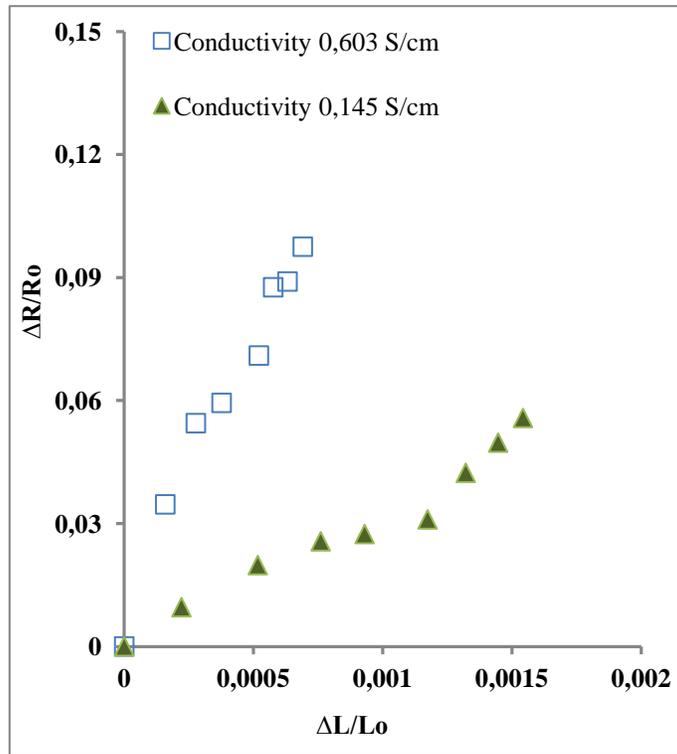


Fig. 7

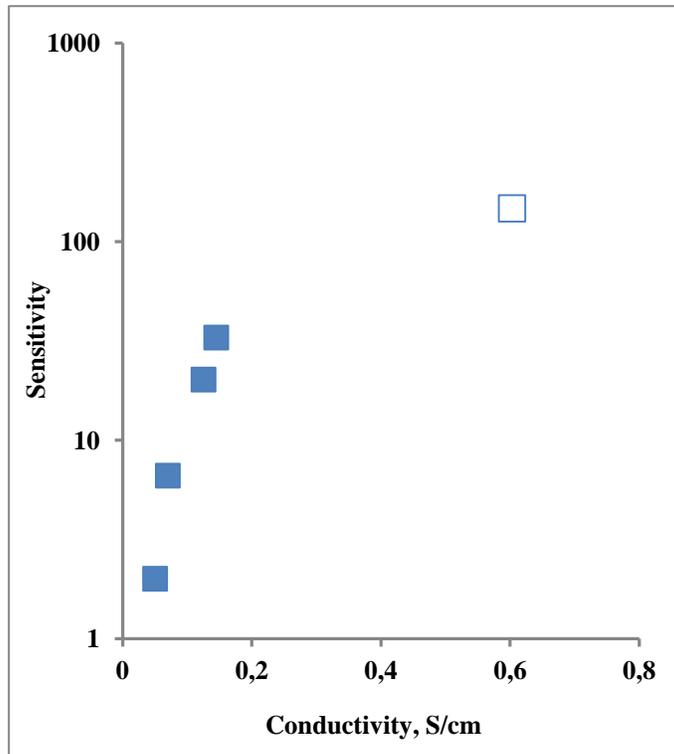


Fig. 8

Paper B

Strain Sensitivity of Carbon Nanotubes Modified Cellulose

F. Toomadj, S. Farjana, A. Sanz-Velasco, O. Naboka, P. Lundgren, K. Rodriguez, G. Toriz, P. Gatenholm, and P. Enoksson.

Strain Sensitivity of Carbon Nanotubes Modified Cellulose

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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 S·cm⁻¹ to 0.15 S·cm⁻¹ and for BC pellicles modified with MWCNT it was increased from 0.12 S·cm⁻¹ to 1.6 S·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.

Keywords: sensor, conductive cellulose, carbon nanotubes

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 [2-4]. Different types of carbon nanotubes (CNTs) have attracted a special interest of researchers due to their remarkable mechanical and electrical properties. It was shown that 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 [5,6]. All these properties make CNTs a promising material to use in smart sensor systems.

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 nanostructures in different applications [7,8]. Among various 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 electrically conductive nanocomposites based on BC modified with double-walled carbon nanotubes (DWCNT) and multi-walled carbon nanotubes (MWCNT). The conductivities of the resulting films have been compared and their behaviour has been studied as a function of induced strain.

Experimental

The BC was produced by *Gluconacetobacter xylinum*. DWCNT (+90% purity, Nanocyl) and MWCNT (+95% purity, Nanocyl) modified with carboxyl groups have been used as a conductive agents for impregnation of BC.

Dispersions with 1 mg/ml and 2 mg/ml CNT concentrations were prepared using surfactant cetyltrimethylammonium bromide (CTAB). $3 \times 3 \text{ cm}^2$ BC pellicles were immersed in the CNT solutions for 24 h to 72 h. After treatment all samples were washed with deionized water. The pellicles were dried in a fume hood.

The total thickness of the dried BC films was 25-65 μm . A scanning electron microscope (SEM) has been used to observe the surface morphology of the samples (Zeiss Leo Ultra 55 FEG SEM). The electrical conductivity measurements were performed using a four-point probe system

(CMT-SR2000N, AIT). In order to study the electromechanical properties of BC modified with DWCNT, constant tensile stress was applied using the Instron 5500 Material Testing System and the change in resistance was registered by a standard multimeter (Agilent 34401A).

Results and discussion

Cellulose samples modified with CNT characterized by the same flexibility as native cellulose. Films modified with MWCNT were uniformly black whereas the BC pellicles modified with DWCNT contain colorless parts. According to SEM MWCNT (diameter 10-16 nm, fig. 1a) are more homogeneously distributed on the BC surface comparing to DWCNT (diameter 5-8 nm, fig. 1b) which points to better dispersion of MWCNT.

In the case of the samples modified with the lowest concentration and volume an increase the immersion time did not give any significant effect on the electrical conductivity of the modified BC pellicles (fig. 2a). Therefore one could conclude 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 (fig. 2a) pointing to the substantial increase of the saturation capacity.

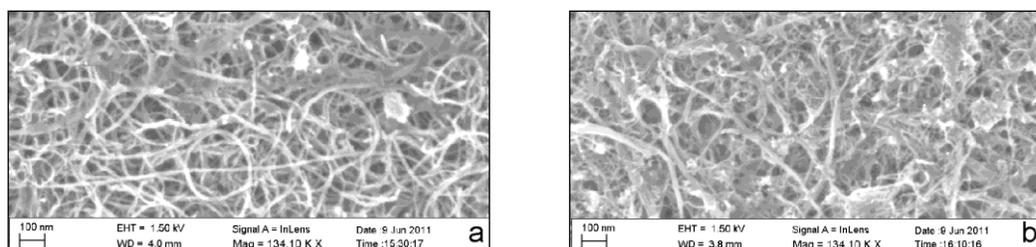


Fig. 1. SEM image of BC modified with MWCNT (a) and DWCNT (b).

The highest conductivities have been obtained for the pellicles modified in the 30 ml of 2 mg/ml solutions – $0,15 \text{ S}\cdot\text{cm}^{-1}$ for DWCNT and $1,6 \text{ S}\cdot\text{cm}^{-1}$ for MWCNT which is significantly higher than previously reported [1].

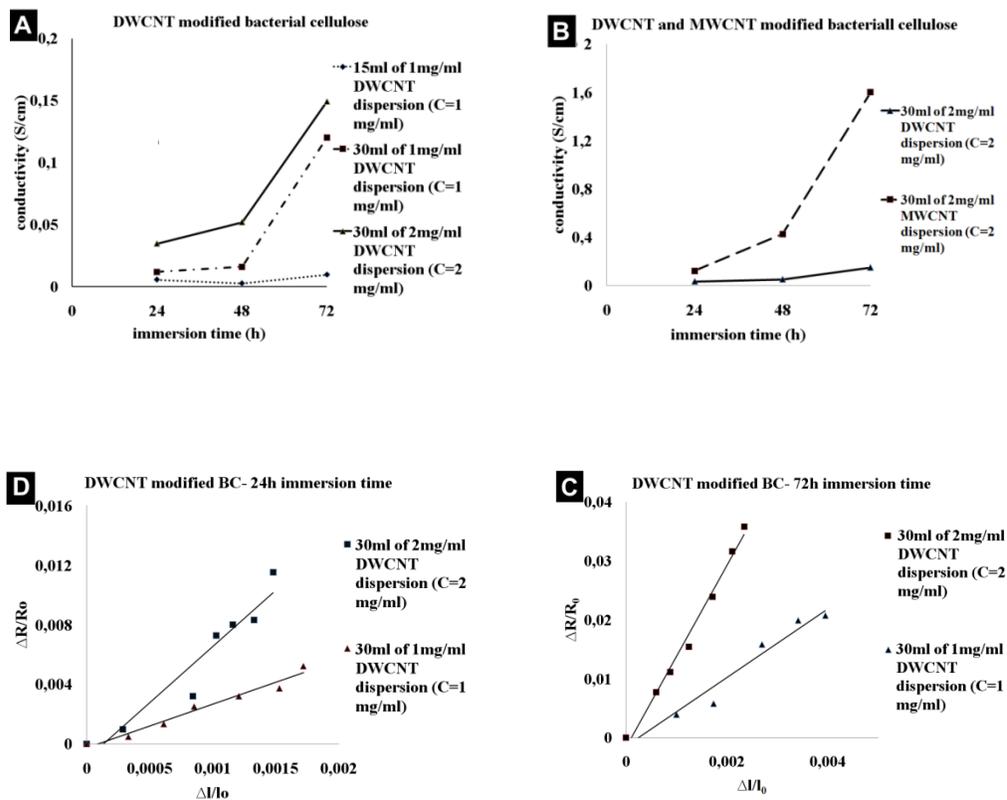


Fig. 1. Conductivities of BC samples modified by DWCNT (a) and MWCNT (b) as a function of immersion time. Dependence of the fractional resistance on the fractional extension for BC sample modified with DWCNT during 72 h (c) and 24h (d).

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 $115 \text{ m}^2/\text{g}$ [10]) comparing to DWCNT (specific surface area $>500 \text{ m}^2/\text{g}$).

For strain sensor applications, we need to have a material which is able to transfer strain into an electrical signal with high sensitivity. Fig. 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 fig. 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.

Conclusion

Flexible DWCNT and MWCNT-incorporated films have been prepared by treatment of bacterial cellulose in CNT dispersions in the presence of CTAB. We show that the conductivity of the pellicles is related to the modification conditions such as the volume and concentration, 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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