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Research Article

Conductivity-Dependent Strain Response of Carbon Nanotube Treated Bacterial Nanocellulose

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This paper reports the strain sensitivity of flexible, electrically conductive, and nanostructured cellulose which was prepared by modification of bacterial cellulose with double-walled carbon nanotubes (DWCNTs) and multiwalled carbon nanotubes (MWCNTs). 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 $0.034\,S{\cdot}cm^{-1}$ to $0.39\,S{\cdot}cm^{-1}$, and for BNC pellicles modified with MWCNTs it was from $0.12\,S{\cdot}cm^{-1}$ to $1.6\,S{\cdot}cm^{-1}$. The strain-induced electromechanical response, resistance versus strain, was monitored during the application of tensile force in order to study the sensitivity of the modified nanocellulose. A maximum gauge factor of 252 was found from the highest conductive sample treated by MWCNT. It has been observed that the sensitivity of the sample depends on the conductivity of the modified cellulose.

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 has received a great deal of attention [3]. Comparing with ceramic and semiconducting materials, sensors which are based on organic nanostructured material have gained in significance due to their attractive properties [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 (CNTs) 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 even with the incorporation of small amounts of CNT.

Cellulose, the most abundant natural polymer, is an inexhaustible raw material with fascinating structure and properties [6]. The properties of cellulose allow obtaining of environmentally friendly, biodegradable, and biocompatible 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 electroactive paper (EAPap) [7]. It has been discovered that the electric power consumption of EAPap is very low [8]. The actuation principle of cellulose-based EAPap has been analyzed in different research works [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 characterized.

Cellulose could be derived from various sources such as plants, bacteria, 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 a natural composite which consists of lignin, pectin, and hemicelluloses, the separation and purification of cellulose is difficult. BNC, on the contrary, belongs to the specific products of primary metabolism and could easily be purified [9]. Moreover, BNC consists of highly crystalline nanofibril which leads to higher mechanical strength compared to plant cellulose [10].

In this paper, we present a flexible electrically conductive nanocomposite based on BNC cellulose and CNT. Double-walled carbon nanotubes (DWCNTs) and multiwalled carbon nanotubes (MWCNTs) have been used to modify BNC pellicles. Different dispersed CNT solutions with different volumes and concentrations 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 ≥ 96%). The dispersion process consisted of a combination of heating, stirring, and sonication, followed by centrifugation to remove undispersed CNT. Dispersions of DWCNT and MWCNT with concentration of 1 mg/mL and 2 mg/mL were used. Also, $3 \times 3\,\text{cm}^2$ 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 deionized water in order to remove free surfactant and CNT residue. The pellicles were dried in a fume hood between polytetrafluoroethylene plates. Figure 1 shows the steps involved to prepare BNC samples.

The total thicknesses of the dried BNC films were 25–65 μm as measured by a standard micrometer with ±1 μm accuracy. A scanning electron microscope (SEM) has been used to study 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 Figure 2. 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.

It has been observed before that the mechanical properties of nanocellulose samples have been changed at different environmental conditions [7]. On the other hand, the electrical and mechanical properties of CNTs are sensitive to temperature. To ignore the environmental effect on treated nanocellulose sample, all samples have been kept in the lab at least 24 hours to get the samples adjusted with the humidity and temperature of the lab, and all tests were performed in the same room.

2.3. Experimental Procedure. To calculate the fractional increment in resistance ($\Delta R/R_0$), where ΔR is the difference between the momentary resistance (R) and the initial resistance (R_0), a constant force has been applied for at least 3 hrs. To calculate the fractional increment in resistance, the resistance change during the first 20 minutes was not considered, as this period was considered as the initial stability period for the sample after applying the load. The calculated initial resistance was the value of the resistance which was measured after 20 minutes once the load was applied. 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 the initial length of the sample (L_0), the initial length of the sample was considered to be 3 mm, less than the original length as some part of the sample was inside the clamp which was not affected by the load.

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 cross-section of the BNC pellicle shows no deep penetration of CNT (Figure 3(a)). Too small pores in the native BNC matrix (Figure 3(b)) prevent CNT from penetration into the cellulose. As a result, an asymmetric conductive layer was formed on the surface of the BNC pellicles.

According to investigations using SEM, MWCNTs are more homogeneously distributed on the BNC surface (Figures 3(d) and 4(a)) compared to DWCNT (Figures 3(c) and 4(b)), which is consistent with results of a visual check of samples (the surface of BNC films modified with MWCNT is uniformly black, whereas the surface of BNC pellicles modified with DWCNT contains colourless parts, Figure 1). This observation points to better dispersion of MWCNT in water which is probably caused by higher ratio of CTAB weight to CNT specific surface area for MWCNT (specific surface area $115\,\text{m}^2/\text{g}$ [11]) compared to DWCNT (specific surface area > $500\,\text{m}^2/\text{g}$).

To observe the effect of strain on the BNC samples, a tensile force of 4 N has been applied on both DWCNT treated

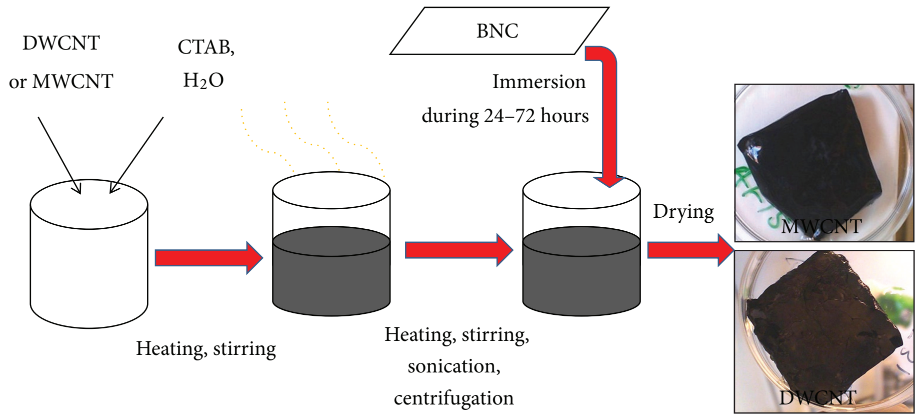


FIGURE 1: Steps involved in sample preparation.

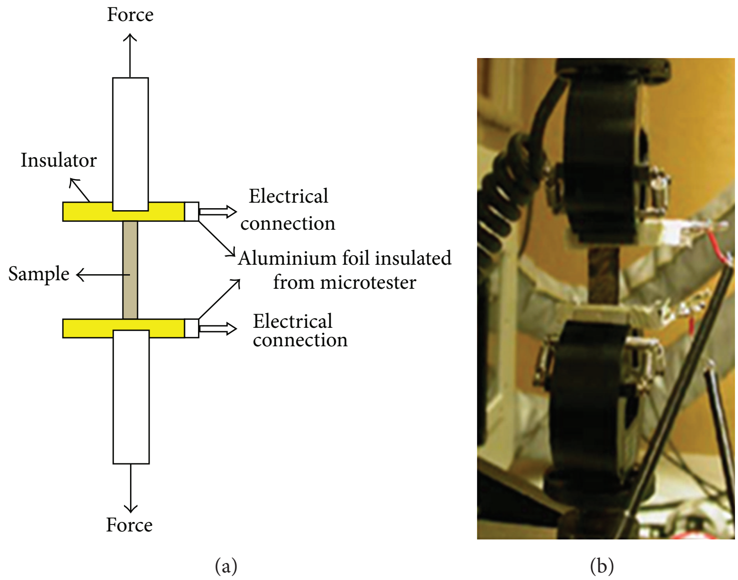


FIGURE 2: Experimental setup for tensile testing.

BNC sample and MWCNT treated BNC samples for three hours. According to SEM morphology of the conductive BNC samples, there were no change after the application of strain (Figure 4).

3.2. Electrical Conductivity Measurement. The electrical conductivity of the nanocellulose modified with DWCNT and MWCNT is 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 of the immersion time did not give any significant effect on the electrical conductivity of the modified BNC pellicles (Figure 5(a)). Therefore, one could conclude that saturation capacity of cellulose for DWCNT in 1 mg/mL dispersions is not enough to form the conductive layer using small volume of dispersion (15 mL). Indeed increasing the CNT concentration and volume, the conductivity rises significantly with the immersion time (Figure 5(a)), indicating 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 (Figure 5(b)). These results could be explained by the formation of more homogeneous layers on the surface of BNC by MWCNT than DWCNT. The highest conductivities have been obtained for the pellicles modified in the 30 mL of 2 mg/mL solutions: 0.39 $S\cdot cm^{-1}$ for DWCNT and 1.6 $S\cdot cm^{-1}$ for MWCNT, which is significantly higher than previously reported [12].

3.3. 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 10 minute intervals. It has been observed that the sample continuously extends under a fixed tensile force (Figure 6).

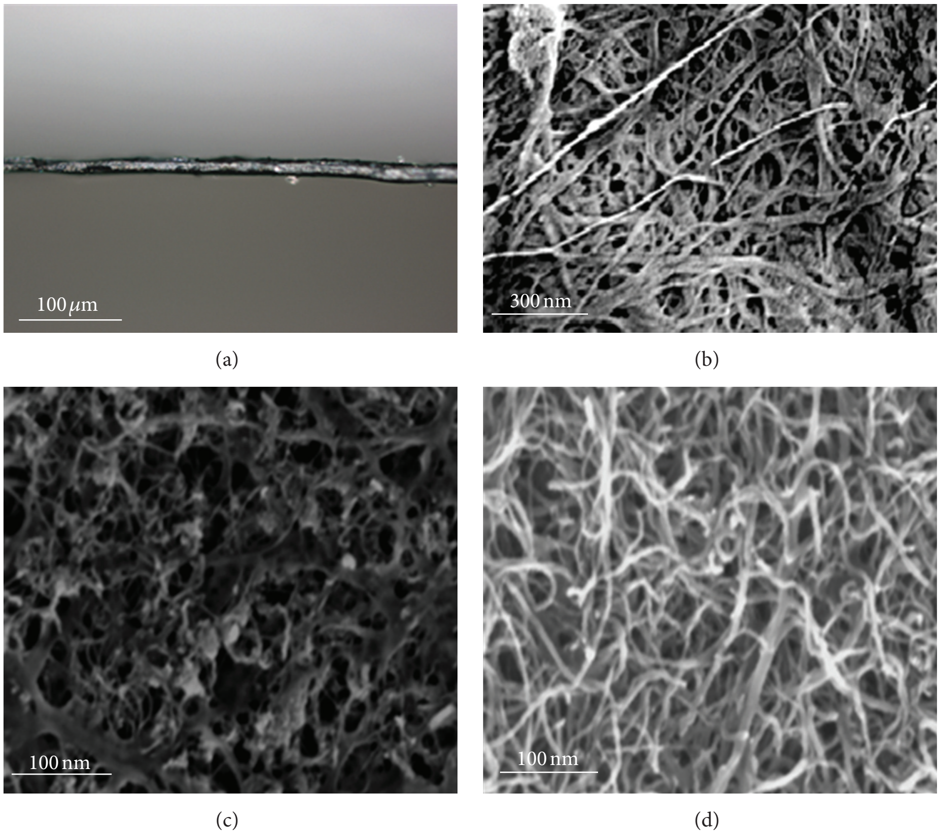


Figure 3: SEM images of BNC. (a) Cross-sectional optical microscope image of BNC pellicle modified with DWCNT. (b) SEM micrograph of native untreated BNC. (c) SEM micrograph of DWCNT treated nanocellulose. (d) SEM micrograph of MWCNT treated nanocellulose.

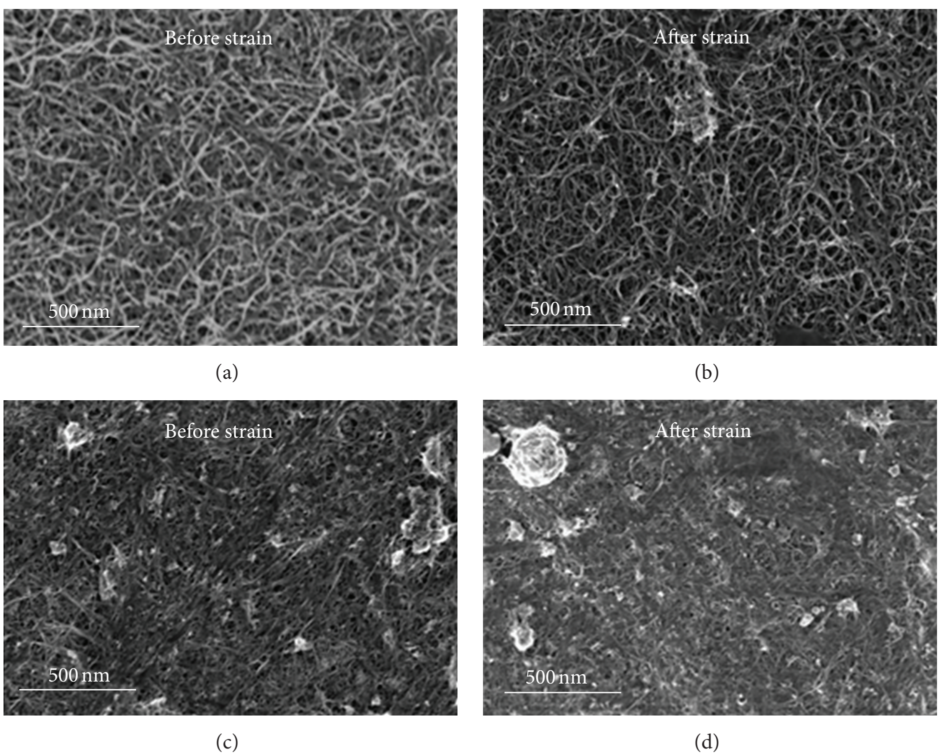
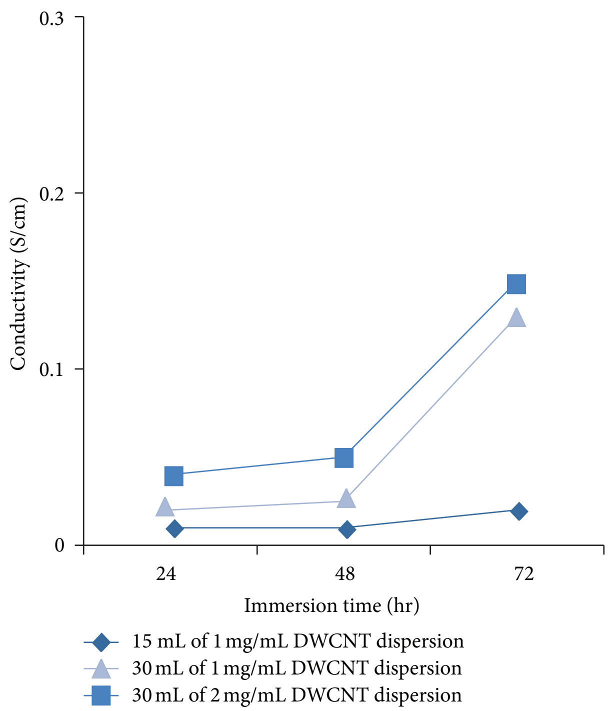
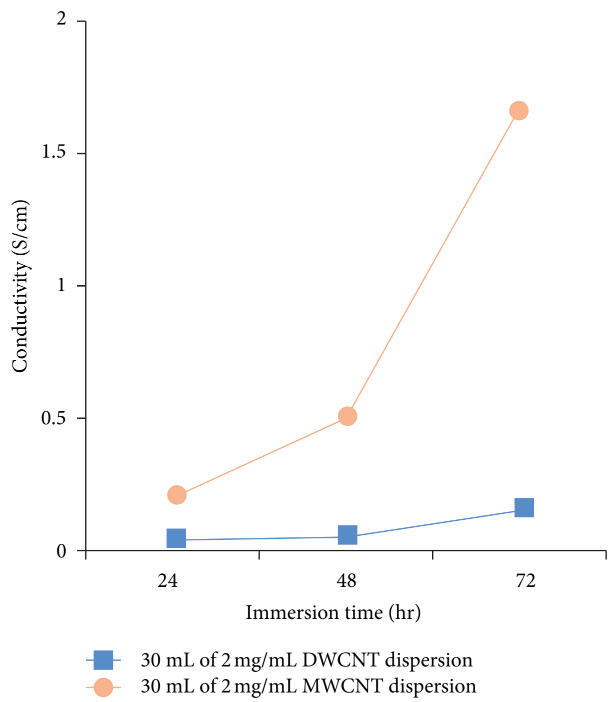


Figure 4: SEM images of BNC samples modified with MWCNT (a) and DWCNT (b) before and after application of strain.



(a)



(b)

FIGURE 5: Electrical conductivities of BNC samples modified with DWCNT (a) and MWCNT (b) as a function of immersion time.

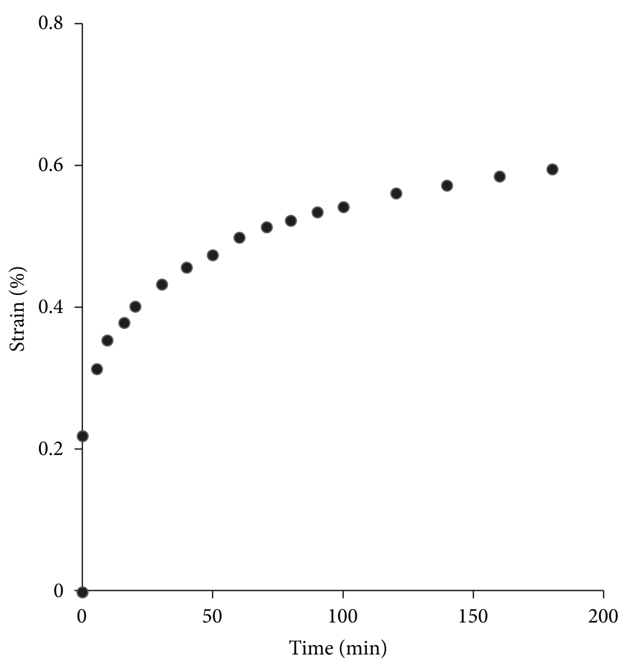


FIGURE 6: Strain versus time plot for DWCNT treated BNC sample. Sample shows continuous extension under a fixed tensile force.

We tested samples modified with different concentrations of modifying agent and yielding different conductivities between 0.05 S/cm and 0.395 S/cm. As discussed in Section 3.2, the conductivity of the treated samples depends on the treatment parameters such as concentration of the modifying agent and the dispersion time; the BNC samples used in this case are prepared under different conditions.

The gauge factor is the parameter which is used to define the sensitivity of a sensor. It measures the ratio of relative change in electrical resistance to the mechanical strain ε, which is the relative change in length, of the sensor [13].

In this case, the sensitivity factor (gauge factor) S can be defined as

$$S = \frac{\Delta R/R_0}{\Delta L/L_0} \times 100\%. \quad (1)$$

It has been observed that as the conductivity of treated BNC sample treated with DWCNT increases, the strain sensitivity of the sample also increases. Figure 7 shows that a treated BNC sample of conductivity 0.05 S/cm has a lower gauge factor than one with a conductivity of 0.395 S/cm. Some reports claim that the sensitivity of a strain gauge increases with the conductivity of the sample unless the conductivity of the sample reaches a certain level [14]. The correlation between conductivity and gauge factor may depend on the percolation threshold level of the CNT network. It can be presumed that after reaching percolation threshold, sensitivity will not change with conductivity. In this work, percolation threshold level was not reached since we could observe continuous change of sensitivity in the studied range of conductivity.

When MWCNT treated BNC samples have been tested, the same results have been obtained. Comparing Figures 7 and 8, it has been observed that the MWCNT treated cellulose shows the same type of response as that of DWCNT treated BNC. The highest gauge factor has been obtained

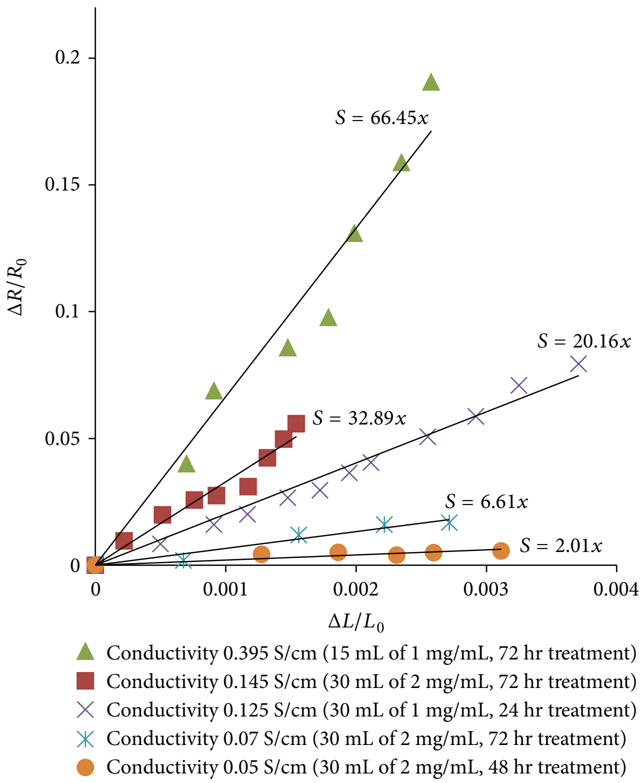


FIGURE 7: Fractional increase in resistance versus fractional increase in length plot for BNC samples subject to different DWCNT treatments resulting in different conductivities.

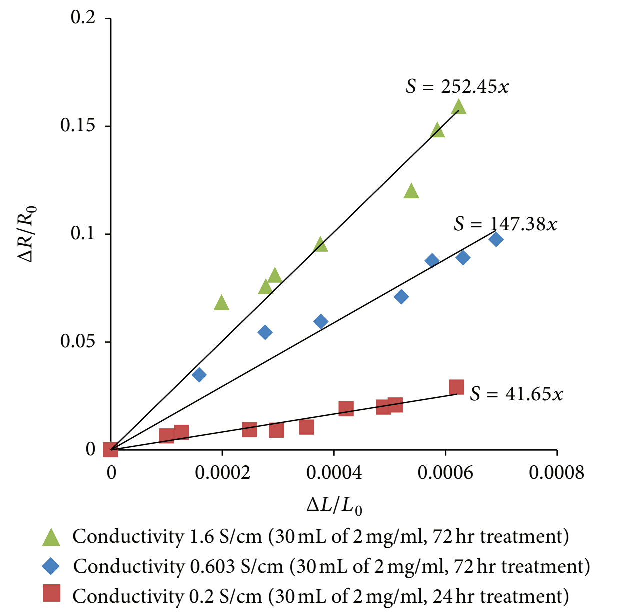


FIGURE 8: Fractional increase in resistance versus fractional increase in length plot for BNC samples subject to different MWCNT treatments resulting in different conductivities.

by MWCNT treated BNC sample since it has the highest conductivity.

Figure 9 shows the sensitivity of the modified BNC films as a function of conductivity. The plot contains sensitivity values for both MWCNT impregnated samples and DWCNT impregnated samples. From Figure 9, it is clear that the sensitivity of the sample depends on the conductivity of the sample. Since samples impregnated with MWCNT display the highest conductivity, they exhibit highest sensitivity.

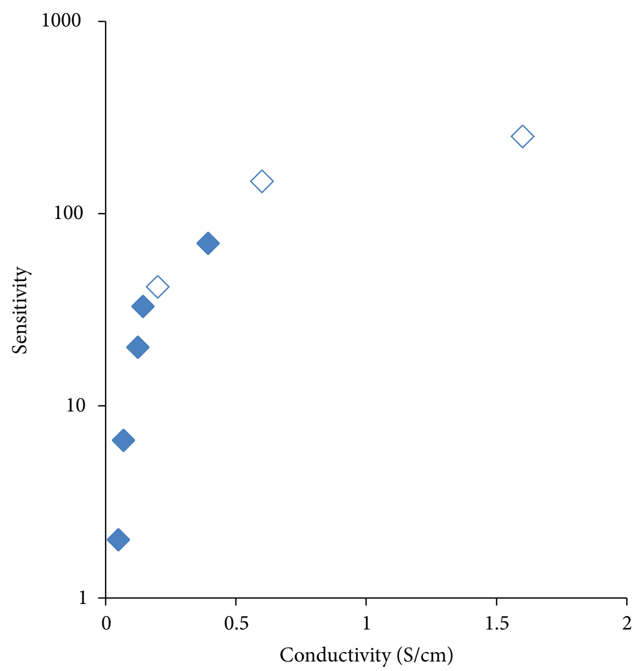


FIGURE 9: Conductivity versus sensitivity plot of DWCNT (filled mark) and MWCNT (open mark) treated BNC.

3.4. Repeatability Test. 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.

The repeatability of any sample depends on its 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 CNT treated BNC samples have been repeatedly subjected to a 4 N force, the response behaviour of the samples has not been changed during the first 20 minutes; however, some changes were observed starting from 30 minutes (up to 16%) (Figure 10). This makes the results repeatable only to limited extend. This type of materials could be used as disposable (single use) sensors or as multiuse sensors where very high sensitivity is not required.

4. Conclusion

Electrically conductive bacterial nanocellulose (BNC) films were prepared by treatment of BNC with dispersions of

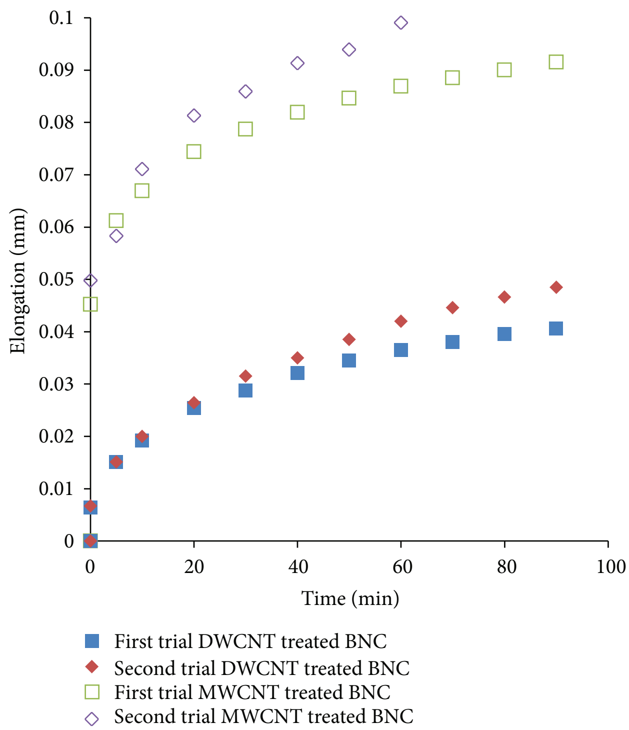


Figure 10: Repeatability test of DWCNT (filled mark) and MWCNT (open mark) treated BNC sample.

double-walled carbon nanotubes (DWCNTs) and multi-walled carbon nanotubes (MWCNTs) 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. The highest conductivity obtained by the treatment of BNC with DWCNT was 0.39 $S{\cdot}cm^{-1}$, and by the treatment of MWCNT, highest conductivity obtained was 1.6 $S{\cdot}cm^{-1}$.

The strain-induced electromechanical response of treated BNC films was investigated. MWCNT treated cellulose showed higher sensitivity than DWCNT treated cellulose. A gauge factor of 252 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.

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