Development of cellulose nanocrystal sheet embedded with carbon nanotubes for sensor application

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Abstract. Cellulose is an important natural material, which is biocompatible and hydrophobic, and can form strong and stable stiff-chain monomolecular structures with film and hydrogel-forming properties. The focus of this investigation was to develop a mixed nano-materials sheet, which can be used as a gas sensor system. The Micro-cellulose sheet was treated with TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) oxidation to prepare TEMPO-Oxidised Nanocellulose (TONC). However, nanocellulose is not electrically conductive which is necessary for energy device applications. Therefore, the TONC was blended with various concentration of Multi-Walled Carbon nanotubes (MWCNTs) to get conductive nanocomposites, which are oven dried at various temperatures to determine the effect on the conductivity. The optimum drying temperature was determined to be 60℃, with conductivity increasing with MWCNTS loading. The extent of the oxidised cellulose (TONC) was characterised by field emission scanning electron microscopy (FE-SEM) to determine the morphology and the Fourier-transform infrared spectroscopy (FT-IR) to identify the functional groups in the neat TONC paper. The SEM showed an increasing porosity with increasing oxidation time. The carboxyl groups also increase with increasing oxidation time.

Keywords: Nanocellulose, conductivity, carbon nanotubes, TEMPO Oxidised Nanocellulose

1 Introduction

Products based on petrochemicals, such as plastics and inorganic semiconductors, are still essential for meeting the demand for energy. To reduce these materials' negative environmental effects, "green" compounds based on carbon must be found that are inexpensive, sustainable, and energy-efficient in order to replace conventional materials used in the production of energy devices. Cellulose is a naturally occurring carbon-based substance [1]. Cellulose is the amplest polymer on earth and is, a part of the biomass, renewed constantly through photosynthesis in quantities in the same order as the world reserves of minerals and fossils fuel [2]. Because cellulose is so diverse, it may be readily extracted from a large range of materials, including bacteria, paper, wood, and cotton [3]. Paper has recently been investigated for use in energy storage and electronics applications [4]. But since paper is composed of cellulose fibres of diameters of ~20μm (made of millions of cellulose nanofibrils with a cross-sectional diameter of ~4nm and a length of ~2mm) there are inherent disadvantages regarding emerging applications. Paper contains peak-to-peak roughness of up to hundreds of micrometres. Furthermore, the fiber diameter is typically not transparent since it is far greater than the visible light wavelength. Additionally, the fibers' total mechanical qualities are limited by their packing density [4]. Paper's use in several energy storage applications is restricted by these drawbacks. Using mechanical treatment is an additional method of creating a sheet of paper, acid hydrolysis, and enzymatic hydrolysis to isolate the individual

cellulose nanofibrils present in the micro cellulose paper. These are the three typical approaches to isolate the nanofibrils [1].

Mechanical treatment is the widely adopted treatment for nanocellulose fibrillation. The treatment procedure mainly consists of high-pressure homogenization, high intensity cryo-crushing, ultrasonic treatment, grinding and/ or micro-fluidisation [5]. However, the process usually leads to fibre shredding rather than the elementary separation of the cellulose fibrils. This results in micro-fibrillated cellulose with low levels of aspect ratio, polymerization, and crystallinity, which has comparatively poor mechanical qualities [3]. This approach is associated with excess energy consumption because the cellulose fibres are bound together by interfibrillar hydrogen bonds, this is among the main disadvantages that restrict the cellulose's usefulness. Therefore, different pre-treatment methods have been proposed to decrease the overall energy consumption such as using 2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO)-mediated oxidation [6]. The most popular chemical pre-treatment technique for chemically altering native cellulose by adding negatively charged groups to enhance the delamination of the nanofibrils is TEMPO-mediated oxidation [7]. A mechanical treatment often follows TEMPO-oxidation treatment, which can lower energy usage to less than 7MJ/kg total as compared to nanofibrils that were isolated using mechanical treatment which only consumes energy up to 700-1400 MJ/kg [8]. The resulting oxidised cellulosed, usually called TEMPO-oxidised Nanocellulose, (TONC) which gives rise to a porous structure gives the TONC paper its excellent flexibility. This allows the nanocellulose paper to bend in various angles without deforming, this is highly important especially in electronic devices or future wearable electronics which will have to be able to withstand various forms of bending. It also has a high tensile strength of about 200MPa, high Young's modulus of about 20GPa due to the fibre-to-fibre hydrogen bonds and tightly packed nanofibrillar network. Because of all these mechanical characteristics, it is ten times more flexible, lighter, and stronger than ordinary paper [9]. Another interesting property of nanocellulose paper is its ultrahigh transparency because the nanocellulose diameter and the interstices in the nanocellulose paper are much smaller than the wavelength of visible light, thus less scattering occurs when light illuminates nanocellulose paper. The minimal thermal expansion of the nanocellulose paper is seen as advantageous in heat-generating electronic components. Various thermal expansion coefficients have been reported for different kinds of nanocellulose with a thermal coefficient of as low as 0.1ppm/K [10]. However, nanocellulose is not electrically conductive which is necessary for energy device applications. Therefore, a conductive material needs to be added as an additive in order to render the nanocomposite conductive. Strong electrical and thermal conductivity as well as strong tensile strength are among the exceptional qualities of CNTs.

The objective of this study is to use the TEMPO reagent to oxidise the hydroxyl group on the surface of the micro cellulose fibre to the carboxyl group and homogenously blend with MWCNTs. The goal is to form homogenous TONC/MWCNTs paper that is conductive. The structure and morphology of the nanocomposite paper will also be examined using field emission scanning electron microscopy (FE-SEM), and the effectiveness of the TEMPO oxidation in changing the hydroxyl group into a carboxyl group will be assessed using Fourier-transform infrared spectroscopy (FT-IR). The relationship between composition and drying temperature and electrical conductivity will be investigated. Recently, [11] published a study on blending the additive (MWCNTs) with the substrate (TONC) using surfactants to uniformly distribute MWCNTs in the TONC fibre network. [12] Also published a

study based on blending TONC with Single-Walled Carbon nanotubes (SWCNTs). This study looks at blending unmodified MWCNTs on the TONC fibre network and observing its behaviour.

2 Experimental Methods

2.1 Materials

The source of cellulose fiber was micro-cellulose paper, which was supplied by SAPPI Saiccor Ltd., RSA. TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl, free radical, 98% Sigma-Aldrich), Sodium bromide (Pure, Riedel-De Haen), Sodium Hypochlorite (NaOCl, 13-15%, Rochelle Chemicals), Sodium Hydroxide (NaOH, 98 %, Merck), Methanol (HPLC, 99.9%, Sigma-Aldrich),Hydrochloric Acid (HCl, 32%, ACE), Multi-Walled Carbon Nanotubes (MWCNTs, 95% Sigma Aldrich) and Distilled water were used without further purification.

2.2 Preparation of TEMPO-oxidized Nanocellulose fibres (TONCs)

The TONC was prepared using a modified version of the procedure reported by [6] and [13]. Briefly, the 25g of Micro cellulose paper was shredded and left overnight in distilled water for pre-swelling (at a consistency of 0.5%). The cellulose solution was supplemented with 4.125g of sodium bromide and 0.4125g of TEMPO. The solution was stirred until the TEMPO was completely dissolved. The TEMPO-mediated oxidation was initiated by adding 250Ml of Sodium Hypochlorite and stirred with a magnetic stirrer at 745rpm. The addition of sodium hydroxide (0.5M) kept the pH at 10. The reaction was then terminated at a required time by adding 125ml of Methanol to salvage the remaining Sodium Hypochlorite and adjusted the pH to 7 by adding Hydrochloric acid (0.5M). The TONC was filtered and carefully cleaned with distilled water. After filtering, the cellulose was dissolved to a 2.8% consistency in distilled water. Ultra-sonication (Heilscher ultrasonic technique, UP200s, 1 cycle, 50% amplitude) was used for 20 minutes in an ice bath to further break it up. After that, the mixture was centrifuged for ten minutes at 10,000 rpm. The resulting insoluble fraction was stored at 4℃ before further use.

2.3 Preparation of the Conductive paper

TONC was diluted in distilled water at a consistency of 1% and dispersed using a magnetic stirrer for 5 minutes at 750rpm. The TONC solution was supplemented with MWCNTs at the appropriate concentrations (0.2–1% w/w). In an ice bath, the mixture was sonicated for half an hour. The solution was then centrifuged and dried in an oven drier at the appropriate temperatures (22–80°C). The dried TONC/MWCNTs that were produced were then sliced into sheets of paper.

3 Characterization

The Characterization techniques used were field emission scanning electron microscopy (FE-SEM) and the Fourier-transform infrared spectroscopy (FT-IR). The FE-SEM was used to observe the Morphology of the nanocomposite paper and the neat TONC paper. A single coating of gold-palladium was applied to the samples, and colloidal graphite was used to bind them to a metalized linter. The samples were scanned using 10kV accelerated electrons in a ZEISS SIGMA (SEM). The functional groups in the clean TONC paper were identified using the PerkinElmer Spectrum and FT-IR.

3.1 Morphology of TONC paper

Figure 1 shows the SEM of TONC paper at different oxidation times. An increase in porosity was observed with an increasing oxidation time. This is due to the carboxyl groups inducing repulsive forces which causes the fibres

to disperse more uniformly, hence the high porosity with increasing oxidation time. As seen in Figure 1 below, an increase in the carboxylate concentration would thus result in an increase in the porosity. The highest degree of fiber individualization was obtained at a maximum oxidation time of 96 hours.

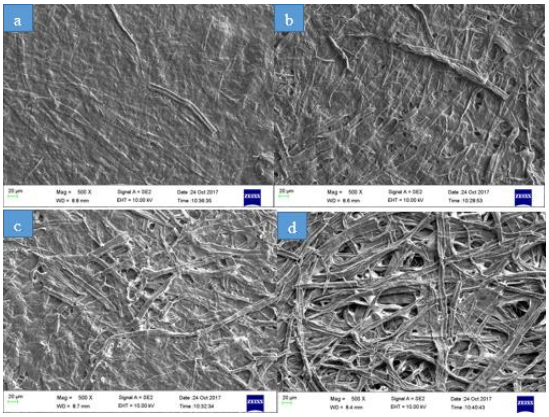

Figure 1: FE- SEM of TONC paper at different oxidation times. (a) 6 hours (b) 48 hours (c) 72 hours (d) 96 hours

The FE-SEM images of the TONC/MWCNTs composite paper containing different amounts of MWCNTs (0,2- 1 wt%) are compared in Figure 2. Figures 2a and 2b show the dispersed MWCNTs in the TONC fibre network with a bulk, especially in Figure 2b situated in the pores of the TONC fibres. The MWCNTs in Figure 2a are individually dispersed with little to contact between each other in the nanocomposite fibre network. Hence, at very low concentrations the number of contacts in the nanocomposite network increases. Although, most of the contact is situated in the pore structure of the composite as shown Figure 2b. The MWCNTs at 1 wt% can be easily spotted at the surface of the composite structure. However, agglomerates of the MWCNTs are observed (Figure 2c).
Figure 2c shows an inhomogeneous distribution of MWCNTs in the nanocomposite paper. Therefore, functionalisation of the MWCNTs is needed to increase the dispersion in the nanocomposite.

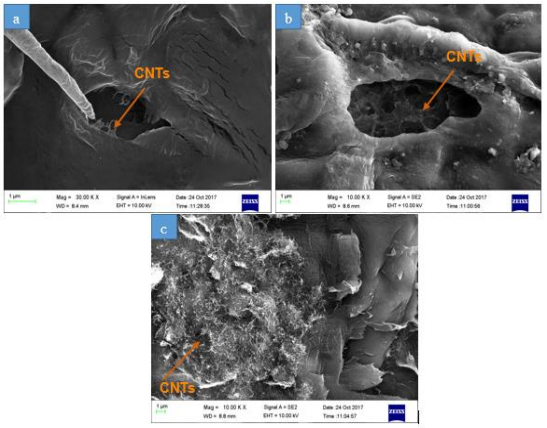

Figure 2: FE-SEM images of the TONC/MWCNTs composite paper containing different amounts of MWCNTs (a) 0.2 wt% (b) 0.6wt% (c) 1 wt%

*3.2 **FTIR***

The identification of distinct functional groups in cellulose that arise from the chemical changes that take place during different chemical treatments has made extensive use of FTIR Spectroscopy [14]. FTIR spectra of original micro-cellulose and treated TONC at 6, 48 and 72 hours are shown in Figure 3. The dominant increase in peaks is noted at 3300 cm-1 and 2900cm-1 which corresponds to the absorbance of O-H stretch and C-H stretch, respectively. The peaks are associated with carboxyl groups in the TONC. Other peaks at 1500 cm-1 are assigned to the C=O stretch vibration of carboxylate in its sodium form [15]. It is evident that increasing the oxidation time increases the abovementioned peaks and therefore means that the carboxyl group concentration increases with increasing oxidation time.

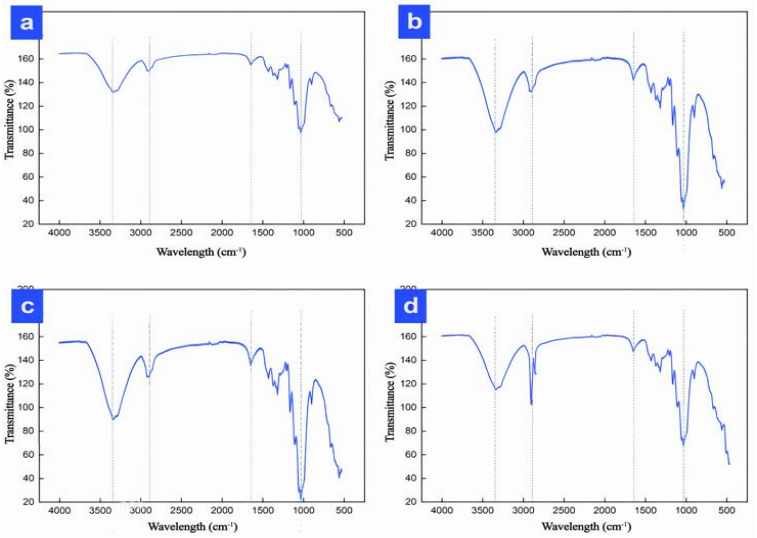

Figure 3: FTIR of microcellulose paper and oxidised nanocellulose. (a) microcellulose (b) 6 hours (d) 24 hours (c) 48 hours and (d) 72 hours

*3.3 **Conductivity***

Figure 4a shows the conductivity of the nanocomposite paper having varying concentrations of MWCNTs (0,2 – 1wt%). The conductivity is calculated by using equation 1 below.

$$\sigma = \frac{L}{A \times R} \ldots\ldots\ldots (1)$$

Where: $\sigma = conductivity(\text{k}\Omega.\text{cm})^{-1}$

$R = Resistance(Ohm)$

$L = Electorode\ legth(cm)$

$A = cross - sectional\ area\ (cm^2)$

The resistance of the nanocomposite is measured by placing the electrodes of the resistance meter at 0,5cm apart in each sample and then using equation 1 to calculate the conductivity of each sample. At concentrations below 0,4 wt%, the conductivity remains close to the conductivity of the TONC paper and therefore not observable on the resistance meter. In other words, the composites are very resistant to electrical flow. At concentrations from 0,4 wt%, the conductivity increases significantly with increasing MWCNTs concentration. The highest attainable conductivity is $0.16(\text{k}\Omega.\text{cm})^{-1}$.

The effect of temperature on the conductivity is also examined by drying the nanocomposite at different temperatures (22, 40, 60 and 80℃). This is shown by Figure 4b. The conductivity of the resulting nanocomposite paper increases with increasing temperature until a peak at 60℃ is reached. Temperatures above 60℃ resulted in a decrease in conductivity, which may be associated with the degradation of the nanocomposite structure. Elevated temperatures also drive the molecular contact between the nanofibrils and cause agglomeration. This causes the nanocomposite paper to not be uniform [16].

From Figure 4, it can be deduced that the optimum drying temperature is 60 degrees Celsius, which resulted in the highest obtained conductivity of $0.16(\mathrm{k\Omega}.\mathrm{cm})^{-1}$.

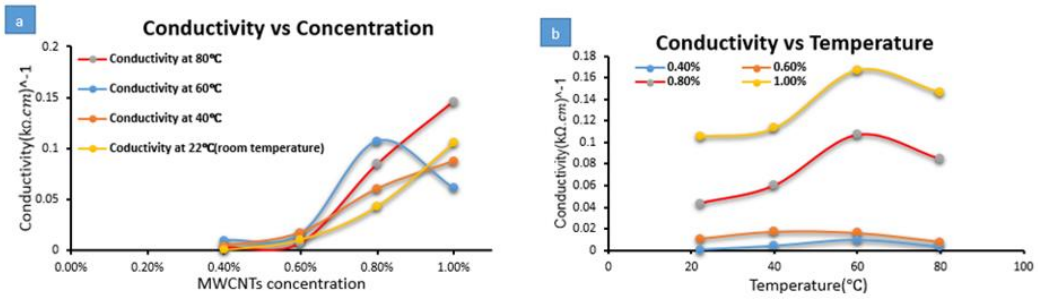

Figure 4: Conductivity of the TONC/MWCNTs nanocomposite paper at various concentration and dying temperature. (a) Effect of concentration on conductivity, and (b) effect of temperature on conductivity

3.4 TONC Paper

Figure 5 shows the TONC paper after drying. It can be seen that the transparency increases with increasing oxidation time, with 96 being the most transparent in comparison to the others. The transparency is due to the mechanical treatment provided by the mechanical stirrer and the ultrasound, which has an overall thinning effect on the oxidized nanofibrils. Optical transparency occurs when the width of the TONC decreases to a point where it is smaller than the wavelength of visible light. Therefore, minimal light diffraction occurs [17].

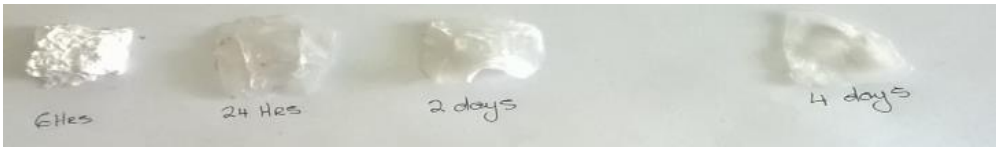

Figure 5: TONC paper at 6, 24, 48 and 96 hours of oxidation time

4 Conclusion

The MWCNT/TONC composite paper was fabricated via TEMPO oxidation of micro cellulose and mixing with MWCNTS at different concentrations. A variety of characterization and conductivity analyses were conducted in order to determine their properties. FE-SEM images show increasing porosity with increasing oxidation time. In addition, the images show individually dispersed MWCNTs in low concentrations with contact between the MWCNTs increasing with increasing concentration However, agglomerates appear with higher MWCNTs loading. FTIR confirmed the successful conversion of the hydroxyl groups to carboxyl groups which was shown

by an increase in peaks for C-H stretch, O-H stretch and C=O stretch, which are all associated with the presence of carboxyl groups in the nanocellulose.

Carbon nanotubes are hydrophobic in nature and tend to agglomerate in aqueous solutions due to their van der Waal forces. To overcome the forces, it is necessary to functionalize the carbon nanotube and introduce COO^- charged groups to insure inform dispersal in the TONC/MWCNTs nanocomposite paper. Comparison between other nanocomposites containing other conductive materials such as graphene and/or graphene oxide. The use of other drying techniques that minimize the damage in the structure of the nanocomposite during drying.

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