

Cellulose-carbon nanotube composite aerogels as novel thermoelectric materials

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Abstract:

Thermoelectric materials based on cellulose/carbon nanotube (CNT) nanocomposites have been developed by a facile approach and the effects of amount (2-10 wt%) and types of CNTs (single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs)) on the morphology (films and aerogels) and the thermoelectric properties of the nanocomposites have been investigated. Composite films based on SWCNTs showed significantly higher electrical conductivity (5 S/cm at 10 wt%) and Seebeck coefficient (47.2 $\mu\text{V/K}$ at 10 wt%) compared to those based on MWCNTs (0.9 S/cm and 11 $\mu\text{V/K}$, respectively). Lyophilization, leading to development of aerogels with sub-micron sized pores, decreased the electrical conductivity for both types by one order of magnitude, but did not affect the Seebeck coefficient of MWCNT based nanocomposites. For SWCNT containing aerogels, higher Seebeck coefficients than for films were measured at 3 and 4 wt% but significantly lower values at higher loadings. CNT addition increased the thermal

conductivity from 0.06 to 0.12 W/(m·K) in the films, whereas the lyophilization significantly reduced it towards values between 0.01 and 0.09 W/(m·K) for the aerogels. The maximum Seebeck coefficient, power factor, and ZT observed in this study are 49 μ V/K for aerogels with 3 wt% SWCNTs, 1.1 μ W/(m·K²) for composite films with 10 wt% SWCNTs, and 7.4 x 10⁻⁴ for films with 8 wt% SWCNTs, respectively.

1. Introduction

Thermoelectric (TE) materials have gained scientific and technological attention over the past few years as a green source of energy by harvesting energy from waste heat. Thermoelectric energy is safe, environment friendly, and produced without mechanical moving parts. The efficiency of thermoelectric materials is designated by the figure of merit, $ZT = S^2 \sigma T / \kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, and κ is the thermal conductivity. The power factor (PF= $S^2 \sigma$) represents the conversion of heat into electricity and is the product of squared Seebeck coefficient (S) and electrical conductivity (σ). Typical inorganic materials (tellurium, bismuth telluride, antimony telluride, etc.) show ZT values as high as around 1 [1]. However, they are rare, toxic, and difficult to process. Hence, conductive polymeric materials are an attractive alternative owing to their good processability and flexibility, low intrinsic thermal conductivity, low cost, and upscaling possibility. Such polymeric materials can be intrinsically conductive polymers, like PEDOT:PSS, PANI, and P3HT, or conductively modified insulating polymers. Nevertheless, the ZT values for polymer based materials are comparatively low, with the maximum reported to be 0.5 for PEDOT:PSS doped with DMSO [2]. Among polymer based TE materials, conductive polymer nanocomposites are studied since their thermoelectric properties can be tuned by the selection of a variety of nano-inclusions [3-5]. Because of their high electrical conductivity and high aspect ratio [6, 7], carbon nanotubes (CNTs) are suitable fillers to impart conductivity to insulating polymer matrices at the low loadings [7] needed for thermoelectric

application. Using a thermoplastic polymer matrix and melt mixing as a dispersion method for multi-walled carbon nanotubes (MWCNTs), Liebscher et al. studied the influence of MWCNT surface functionalization on thermoelectric properties of polycarbonate based composites and could achieve Seebeck coefficients up to $11 \mu\text{V/K}$ and a maximum ZT of around 10^{-7} (at 2.5 wt% loading) [8]. Yu et al. fabricated poly(vinyl acetate) (PVAc)/CNT segregated-network composites by mixing CNT in a PVAc emulsion using ultrasound [9]. XD grade CNTs were used which consist of a mixture of metallic and semiconducting single-, double-, and triple-walled CNTs. They achieved a maximum Seebeck coefficient of $50 \mu\text{V/K}$ at the low CNT concentration of 0.5 wt% and a maximum ZT of 6×10^{-3} at 20 wt% CNT loading. Luo et al. prepared polypropylene/single-walled CNT (SWCNT) composites by melt mixing technique and attained a maximum Seebeck coefficient of $35.1 \mu\text{V/K}$ and a ZT value of 3.79×10^{-5} at 4 wt% loading [10]. When adding in addition 5 wt% copper oxide (CuO), a filler with an intrinsic high Seebeck coefficient, composites with 0.8 wt% SWCNTs reached S values of $45 \mu\text{V/K}$ [10]. Tzounis et al. fabricated SWCNT containing nanocomposite with amorphous and partially crystalline polyetherimides. They achieved a maximum Seebeck coefficient of $55 \mu\text{V/K}$ at a loading of 4.4 wt% and a maximum power factor of $0.037 \mu\text{W}/(\text{m}\cdot\text{K}^2)$ [11]. Nakano et al. prepared fluorinated rubber/SWCNT composites by the solution mixing method with the help of a probe sonicator and they reached a Seebeck coefficient of $\sim 80 \mu\text{V/K}$ at 2 wt% loading and a power factor of $15 \mu\text{W}/(\text{m}\cdot\text{K}^2)$ at 50 wt% loading [12]. The preparation of composites of SWCNT bundles in polystyrene (50 wt% CNTs) by ball milling resulted in a Seebeck coefficient of $55 \mu\text{V/K}$ and a very high power factor of $413 \mu\text{W}/(\text{m}\cdot\text{K}^2)$, as reported by Suemori et al. [13]. Wang et al. fabricated polylactic acid/ $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ (BST)/MWCNT composite by extrusion. In this study, effects of silane coupling agent and plasticizer on mechanical and thermoelectric properties were explored. They achieved a maximum Seebeck coefficient of $200 \mu\text{V/K}$ at a BST loading of 78.9 wt% without MWCNTs and a maximum ZT of 0.011 at a BST loading of 81.3 wt% and a

MWCNT loading of 4 wt% [14]. However, such thermoplastics have some disadvantages, such as the TE values vary with oxidative degradation, UV degradation, etc. [15].

Cellulose is the most abundant natural polymer on earth [16]. Besides being renewable and biodegradable, cellulose is insoluble in water and resistant to organic solvents. Cellulose can be converted into green aerogels with extremely low density (0.04 g/cm^3) and low thermal conductivity ($0.029\text{-}0.032 \text{ W/(m}\cdot\text{K)}$) [17] and very high surface area (up to $400 \text{ m}^2/\text{g}$) [17], which are described as promising candidates for thermal insulation applications. In addition, cellulose exhibits good thermal stability and is resistant to thermal degradation up to 280°C in air [18]. Thus, cellulose has great potential to be used as a matrix material for electrically conductive composites also applicable as thermoelectric materials. However, no reports about thermoelectric applications of cellulose-based composites could be found.

Cellulose based films, in which conductivity is reached by percolation of conductive fillers, are compact and the 3D filler network is more or less homogeneous. In contrast, aerogels made from such composites have segregated network structures as the pores containing air drive the filler in the walls around the pores. By this also different arrangement of the filler, especially concerning their oriented alignment, can be assumed which may change electrical properties slightly. However, the effect of both structure types on thermal conductivity is expected to be tremendous. Cellulose aerogels containing pores filled with insulating air were found to have very low thermal conductivity ($\sim 0.03 \text{ W/(m}\cdot\text{K)}$) at a density of 0.04 g/cm^3 [19]), whereas cellulose films are reported to have values of about $0.06 \text{ W/(m}\cdot\text{K)}$ [20]. Even if the addition of electrically conductive carbon based fillers was shown to increase the thermal conductivity slightly [8, 9], one can take advantage of this lower thermal conductivity of aerogels without degrading the electrical conductivity substantially. Thus, it is expected that higher ZT values can be realized using cellulose aerogels as compared to films.

Due to its large proportion of intra- and intermolecular hydrogen bonds, cellulose is difficult to process in solution or in the melt state. As reported, electrically conductive

cellulose/CNT nanocomposites can be prepared from mixed solutions of cellulose and CNTs in an appropriate solvent such as lithium chloride/*N,N*-dimethylacetamide (LiCl/DMAc) and *N*-methylmorpholine-*N*-oxide (NMMO) monohydrate [21-24].

Recently, a simple but efficient process was developed to prepare cellulose/MWCNT composites from aqueous NaOH/urea solution [25-27]. The obtained MWCNT/cellulose composite films and aerogels exhibit good electrical conductivity and mechanical properties. In this work, we fabricated both MWCNT and SWCNT-filled cellulose composites by using an alkaline aqueous system. The thermoelectric properties of cellulose/CNT composite films and aerogels (both from SWCNTs and MWCNTs) were investigated.

2. Experimental

2.1. Materials

Cellulose samples (cotton linters, DP 500) were supplied by Hubei Chemical Fiber Group Ltd. (Xiangfan, China). Commercially available multi-walled carbon nanotubes (MWCNTs, NC3150, Nanocyl S.A., Belgium) with an average diameter of 9.5 nm, a purity >95%, and an average length of 1.5 μm [28] and TUBALL™ singled walled carbon nanotubes (SWCNTs, OCSiAl Ltd., Russia) with an average diameter of 1.8 nm, length of 5 μm , and a CNT content >75% [29] were used. Polyvinyl alcohol (PVOH, $M_w=9,000-10,000$ g/mol, 80% hydrolyzed, Sigma-Aldrich) was applied as a surfactant. Other reagents were of analytical grade.

2.2. Preparation of cellulose/CNT composite films and aerogels

First, 100 ml of a 1 wt% CNT aqueous dispersion was prepared similar to our previous work [30]. Differently to this report, CNTs were added to a polyvinyl alcohol solution instead of a Brij76 solution to obtain 1 wt% CNT solution with a weight ratio PVOH/CNT of 1.5/1. Relatively harsh mixing conditions applying a horn sonicator for 30 min at a constant output

power of 140 W were needed in order to sufficiently homogenize the dispersions. At the concentration of 1 wt% CNTs the dispersion becomes already rather viscous but it is still possible to prepare homogeneous films with sufficient thickness. The PVOH/CNT = 1.5/1 weight ratio was proven before for MWCNTs to result in good dispersion [26] and for comparability the same ratio was used in case of SWCNT.

To prepare the cellulose based films with CNTs, an NaOH/urea/CNT aqueous system was prepared by mixing 7 g NaOH, 12 g urea, 77 g distilled water, and 4 g of the 1 wt% CNT aqueous dispersion. The resultant mixture was pre-cooled to $-12.0\text{ }^{\circ}\text{C}$ after stirring for 30 minutes. The desired amount of cellulose was added immediately into the mixture with vigorous stirring for 5 min to obtain the cellulose/CNT dispersion. After degasification, the resulting dispersion was cast on a glass plate to give a gel sheet with a thickness of $\sim 400\text{ }\mu\text{m}$, which was immersed into a coagulation bath of 5 wt% H_2SO_4 for 5 min at room temperature to coagulate and regenerate.

The resultant cellulose/CNT composite hydrogels were washed with excess deionized water to remove residual chemical reagents. Finally, hydrogels were frozen by applying the flash freezing method, in which the hydrogels were immersed in liquid nitrogen ($-196\text{ }^{\circ}\text{C}$) for about 1 min. Lyophilization of the frozen mixture was carried out at $-52\text{ }^{\circ}\text{C}$ under vacuum for 48 h to obtain the aerogel. In this way aerogels with 2, 3, 5, 8, and 10 wt% CNT loadings with thicknesses between 0.1 mm and 0.7 mm were fabricated. Corresponding films with the same composition were prepared by the same method but without the freeze drying step. Instead, after regeneration and washing, the wet films were air-dried at ambient temperature for 1 day. The film thicknesses varied between 40 and $100\text{ }\mu\text{m}$.

2.3. Characterization of morphology and microstructure

Cryofractures of films and aerogel samples were prepared in liquid nitrogen and the cross-sectioned samples were investigated using a NEON 40 (Carl Zeiss AG, Oberkochen,

Germany) scanning electron microscope (SEM) after coating with a ~3 nm thick platinum layer. A secondary electron detector (SE2) was used for imaging to characterize the surface morphology and an operating voltage of 3 kV with a working distance of 6 mm were used. The density of films and aerogels was determined by different ways. The bulk density of the films was calculated theoretically based on the densities of the components ($\rho_{F,theo}$, cellulose 1.50 g/cm³, MWCNT 1.75 g/cm³, SWCNT 2.10 g/cm³) and experimentally using the buoyancy method ($\rho_{F,buoyancy}$) in toluene. The density of aerogels was determined using the buoyancy method in toluene ($\rho_{A,buoyancy}$) or calculated according to geometrical conditions and weight ($\rho_{A,geo}$). The porosity was calculated from the measured geometrical density of the aerogels ($\rho_{A,geo}$) and the theoretical density of the films ($\rho_{F,theo}$) by the formula:

$$P_{r,A} = 100\% * (1 - (\rho_{A,geo} / \rho_{F,theo}))$$

The given values of the buoyancy method are the mean of 3 measurements. Pieces of the samples of app. 5-25 mg were weighted before and after immersion in toluene at 23°C with an accuracy of +/- 0.1 mg using the Sartorius kit YDK03 and Sartorius AC210S scales by applying the instrument's density software. Toluene was selected as it wets cellulose quite good and does not swell it significantly [25].

The specific surface area ($S_{A,BET}$) of the composites was determined by the nitrogen adsorption method as mentioned in our previous work [26] at 77 K using a Quantachrome Quadrasorb apparatus up to a pressure of 1 bar, and the surface area calculations according to the Brunauer–Emmett–Teller (BET) theory were performed with the Quantachrome software ASiQwin 2.01 in the relative pressure range of 0.08–0.25. Prior to the adsorption measurements samples were dried at 150 °C for 16 h under vacuum.

2.4. Characterization of physical properties

The electrical conductivity of the composite films and aerogels was measured at room temperature by a two-probe method. Conductive silver paste was painted on the two ends of the surface of the samples to ensure good contact with two electrodes of the instrument which is connected with a Keithley Model 2001 Multimeter (Keithley Instruments Inc., Cleveland, USA). Samples were of 4-5 mm in width, 15–20 mm in length and 0.05 to 0.3 mm in thickness. The mean values of at least five measurements for every film and aerogel sample were used.

The Seebeck coefficient was measured with a self-made set-up developed at the Leibniz Institute of Polymer Research Dresden (IPF). Samples of above mentioned size were mounted on two copper blocks and fastened with mounting clamps to ensure good contact. For all measurements, one block was kept at a constant temperature (T_C) ($\sim 40\text{ }^\circ\text{C}$), while the other one was heated up in a controlled manner in steps of 2 K from $35\text{ }^\circ\text{C}$ up to $45\text{ }^\circ\text{C}$ (T_H). The distance between the two blocks was set to 12 mm. The generated electric potential (or thermoelectric voltage (ΔV)) was measured by a Keithley Model 2001 Multimeter (Keithley Instruments Inc., Cleveland, USA). The temperature of the two blocks was continuously measured with K-type thermocouples to determine the temperature gradient, ΔT . The Seebeck coefficient was derived from the slope of ΔV vs. ΔT curves by linear fitting. Fig. 1a presents schematically the experimental set-up used for the Seebeck coefficient measurement, while Fig. 1b is a photograph of the apparatus.

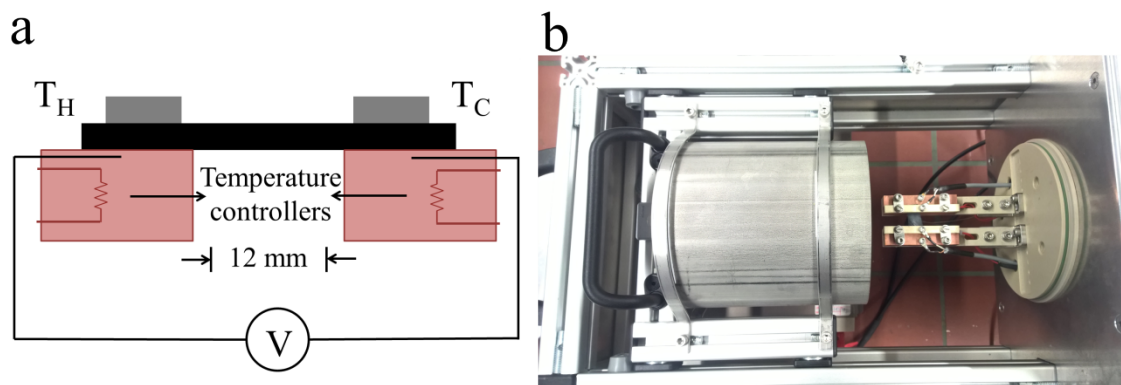


Figure 1. (a) The schematic and (b) photograph of the experimental set-up for thermoelectric measurements

The thermal conductivity of samples was measured using the Netzsch LFA 447 Nano Flash (Netzsch-Gerätebau GmbH, Selb, Germany) based on the laser flash principle. In this method, the density, specific heat, and thermal diffusivity are used to calculate the thermal conductivity of the samples in relation to the standard values of pyroceram. For the aerogels the density $\rho_{A,geo}$ was used for calculation, whereas for the cellulose films the density measured using the buoyancy method ($\rho_{F,buoyancy}$) was applied. The thermal diffusivity of each sample is measured and the specific heat is calculated by the instrument's software. The sample dimension was 13 mm x 13 mm with thickness between 0.04 and 0.1 mm for films and between 0.1 and 0.7 mm for aerogels.

3. Results and discussion

3.1. Structure and morphology of cellulose/CNT nanocomposite films and aerogels

By regeneration and drying, well dispersed CNT-cellulose composite films could be obtained. Freeze drying resulted in a homogeneous open-porous aerogel [25]. With the buoyancy method aerogel densities between 1.24 and 1.49 g/cm³ were measured which are only slightly lower than the theoretical densities and those of the films (Table 1). This proves that the

aerogels form open porous structures and nearly all pores can be filled with the solvent toluene. Furthermore, almost no isolated CNTs were found in the coagulation bath and washing water during the preparation process, indicating that the CNTs were almost completely incorporated in the cellulose matrix. This good dispersion can be attributed to the comparatively high energy employed during sonication. Fig. 2 shows photographs of cellulose/SWCNT nanocomposite films and aerogels. Fig. 2a illustrates that the film is soft and flexible and Fig. 2b that lyophilization does not hamper the flexibility of the composite. The solid film is very smooth while the aerogel surface appears to be rough due to the open cell structure of the aerogel, which scatters light on the surface.

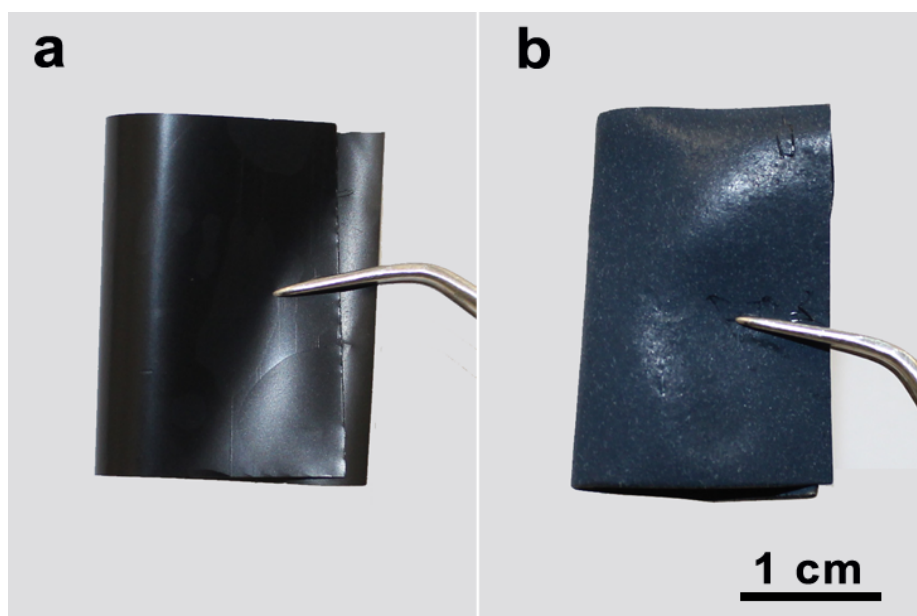


Figure 2. Photographs of flexible cellulose/SWCNT nanocomposites (5 wt% SWCNT): (a) solid film; (b) aerogel.

Fig. 3 shows the SEM images of fractured cross-sections of cellulose/CNT composite films and aerogels. Fig. 3a shows that the film has a layered morphology with the layers oriented in longitudinal direction which appears as a consequence of the shaping process during casting. The density determined by the buoyancy method is very near to the calculated one indicating that the films are dense containing only minor air inclusions (Table 1).

In the aerogels, the SWCNTs are well dispersed in the cellulose matrix, similar to the MWCNT dispersion in the cellulose aerogels in our previous work [26]. The aerogels exhibit a homogenous fine fibrillar and highly porous network morphology. The aerogels have a bulk density (determined from geometry and weight) of 0.16-0.17 g/cm³ (Table 1) which is about 40 times less than that of conventional thermoelectric material like tellurium (6.24 g/cm³) [31]. Using the theoretical density value of the bulk cellulose-CNT composites, the porosity of the aerogels is in the range of 88 – 90 %. The porous properties of the resulting cellulose-CNT composite aerogels are confirmed by nitrogen adsorption-desorption tests. Fig. 4 shows the typical nitrogen adsorption isotherm of cellulose/CNT nanocomposite aerogels with 5 wt% loading of CNTs. The specific surface areas of the resulting aerogels were determined from BET theory to vary from 176 to 202 m²/g (Table 1). As the CNT loading increases, porosity and surface area decrease slightly.

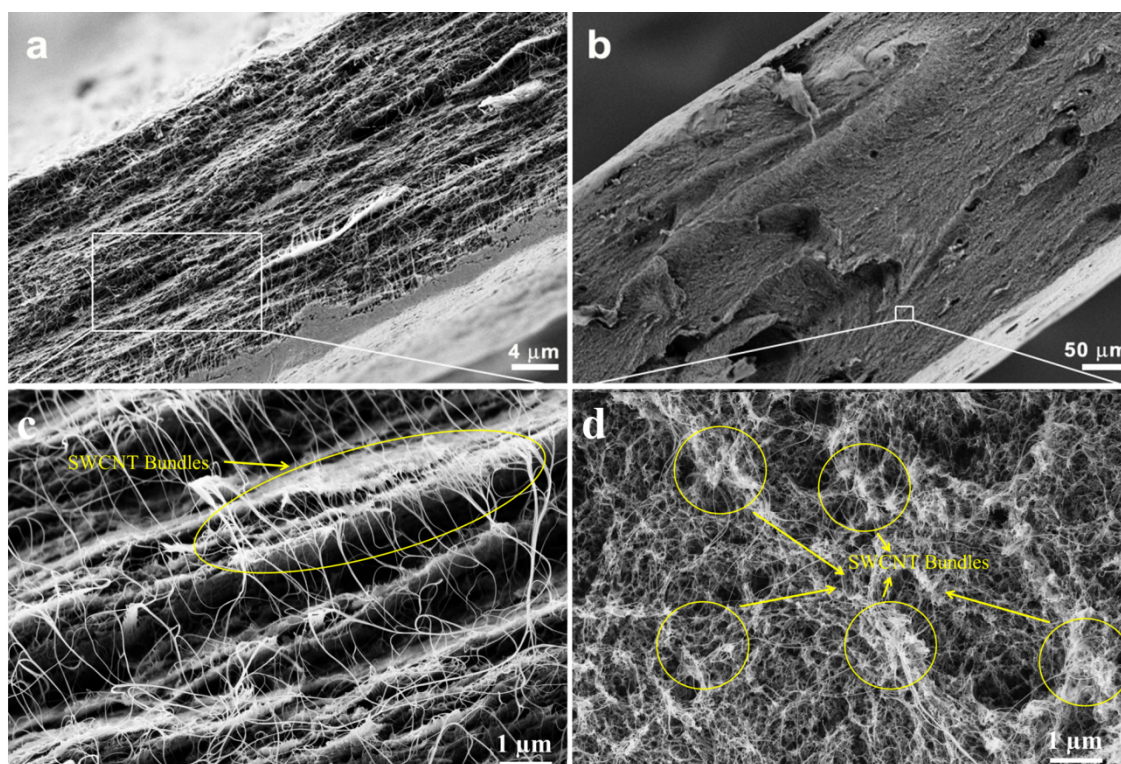


Figure 3. SEM images of fractured cross-sections of the cellulose/5 wt% SWCNT nanocomposite: (a) and (c) solid film; (b) and (d) aerogel.

As the hydrogel becomes frozen, the water in it expands as it transforms into ice. During this process the whole composite also enlarges and becomes frozen in this dimension. Slowly the ice sublimates at low pressure leaving a porous structure. In this process, the CNTs counteract against the expansion of ice. Therefore, at a higher CNT loading less expansion results in slightly lower porosity and surface area. The porous structure gives these cellulose/CNT materials low thermal conductivities, which will be discussed later.

Table 1. Density data of films and aerogels: Theoretical ($\rho_{F,theo}$) film density and density determined by buoyancy method ($\rho_{F, buoyancy}$); aerogel densities determined by buoyancy method ($\rho_{A,buoyancy}$) and calculated from geometry ($\rho_{A,geo}$); aerogel porosity ($P_{r, A}$), and surface area ($S_{A,BET}$)

Type of CNT	CNT (wt%)	$\rho_{F,theo}$ (g/cm ³)	$\rho_{F, buoyancy}$ (g/cm ³)	$\rho_{A,buoyancy}$ (g/cm ³)	$\rho_{A,geo}$ (g/cm ³)	$P_{r, A}$ (%)	$S_{A,BET}$ (m ² /g)
	0	1.500	1.51	1.49	0.15	90	n.d.
MWCNT	3	1.508	1.51	1.36	0.15	90	198.3
MWCNT	5	1.513	1.41	1.28	0.16	90	193.5
MWCNT	8	1.520	1.46	1.33	0.17	89	185.6
MWCNT	10	1.525	1.51	n.d.	0.18	88	176.9
SWCNT	3	1.518	1.50	1.42	0.15	90	201.5
SWCNT	5	1.530	1.49	1.24	0.15	90	193.7
SWCNT	8	1.548	1.43	n. d.	0.15	89	188.5
SWCNT	10	1.560	1.48	n. d.	0.18	89	180.4

n.d. = not determined

3.2. Thermoelectric properties of the cellulose/CNT nanocomposite films and aerogels.

Fig. 5a shows the electrical conductivity of the cellulose-CNT composites as function of the CNT content. As expected, the electrical volume conductivity increases with the CNT loading. Comparing SWCNT and MWCNT based composites, the former have higher electrical conductivity than the latter at all compositions. For both systems, the percolation threshold is below 2 wt% CNT and is already achieved at the lowest concentration investigated (2 wt% for films and 3 wt% for aerogels). At 10 wt% loading, the conductivity reached 5.0 S/cm for SWCNT based composite films and 0.9 S/cm for MWCNT based ones. These values are slightly higher than those observed for other polymer matrices using the same kind of SWCNT. For melt mixed polypropylene composites a conductivity of 0.5 S/cm was previously measured at 6 wt% loading [10], which compares to about 0.4 S/cm at 5 wt% SWCNT loading achieved in the cellulose/SWCNT composite films. Otherwise, for fluorinated rubber/50 wt% SWCNT composites 2 orders of magnitude higher conductivity values than in this paper were reported [12]. The conductivity values of the cellulose films with MWCNTs are in the same range like for melt mixed PC/MWCNT composites (Table 3) [8], when comparing the values of 2 and 4 wt% in cellulose with those at 2.5 wt% loading in PC.

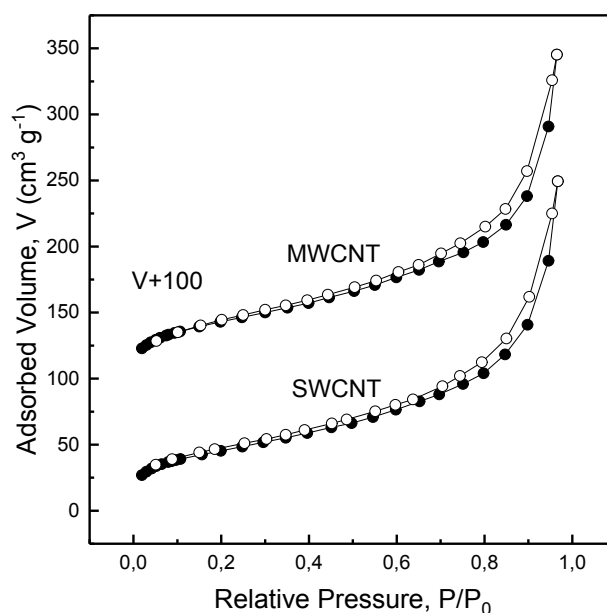


Figure 4. Typical nitrogen adsorption (●) and desorption (○) isotherms of cellulose/CNT composite aerogels (5 wt%, MWCNT and SWCNT). The data of MWCNTs are shifted by $100 \text{ cm}^3 \text{ g}^{-1}$ along the vertical axis to avoid overlapping.

Lyophilization resulted generally in a slight decrease in the electrical conductivity when comparing the composite films with the aerogels, as shown in Fig. 5b. Because the cellulose matrix is insulating, the CNTs are the only electrically conducting component of the composites. It was expected that the segregated CNT network structure in the cell walls of the aerogels could lead to higher electrical conductivity at the same wt% loading what was not found experimentally.

The Seebeck coefficients of all investigated cellulose/CNT composites are positive, that means they exhibit p-type behavior. In fact, SWCNTs are reported to be n-type when having no impurities and semiconducting tubes exhibit a larger magnitude of S than metallic ones [32]. In contact with air the physisorption of oxygen leads to doping with p-type carriers resulting in an alteration of their Fermi level so that buckypapers and SWCNTs stored under

ambient conditions as well as MWCNTs show typically p-type behavior. It is worth to mention that also some polymers, i.e. polyethylene imine, polyvinyl pyrrolidone, polyvinyl pyridine [33], and polyethylene glycol [34], have been found to push the Fermi level from the conduction band to the valence band making SWCNTs n-type. Other polymers like polystyrene, poly(methyl methacrylate), poly(vinylidene fluoride), poly(vinyl acetate), etc. only slightly affect the Fermi level, which is evident from the only slight variation in the Seebeck coefficient of those composites with SWCNTs [4].

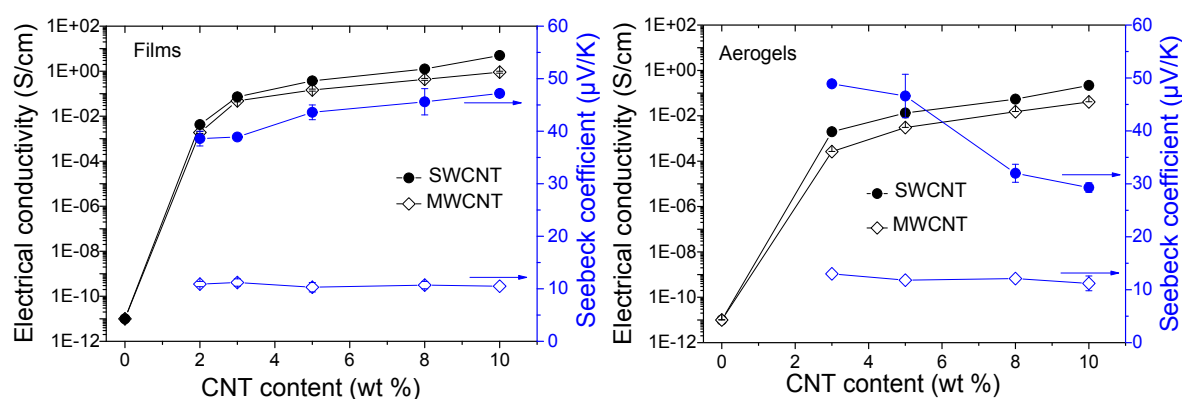


Figure 5. Electrical conductivity and Seebeck coefficient vs. wt% content of CNTs in the bulk of (a) cellulose/CNT films and (b) cellulose/CNT aerogels (The lines are to guide the eyes).

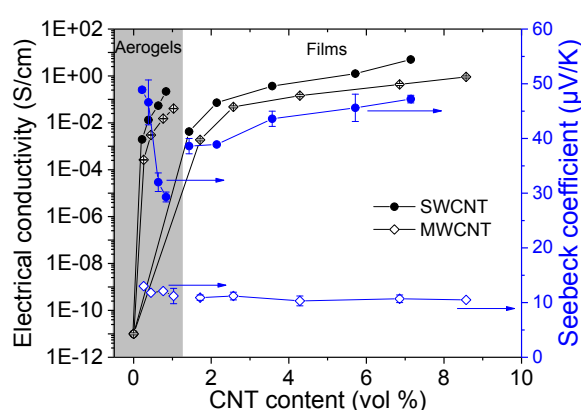


Figure 6. Electrical conductivity and Seebeck coefficient of films and aerogels vs. vol% content of CNTs (The lines are to guide the eyes).

As Fig. 5 illustrates, the SWCNT based composites have higher Seebeck coefficients than those with MWCNTs. The applied SWCNT material inherently shows a Seebeck coefficient of $60 \mu\text{V/K}$, while the MWCNT material has a Seebeck coefficient of $13 \mu\text{V/K}$. These values were measured after filtering the corresponding CNT dispersions in ethanol using a polyamide 6 membrane, by such forming a buckypaper. In MWCNT based composites the S values are with about $11 \mu\text{V/K}$ near the value of the buckypaper and rather independent of the nanotube loading. The values are also in the range reported for melt-mixed composites based on polycarbonate (Table 3) [8]. In the composite films with SWCNTs, S increases from $38.6 \mu\text{V/K}$ at 2 wt% loading to $47.2 \mu\text{V/K}$ at 10 wt% loading. SWCNTs contain both metallic and semiconducting CNTs. Semiconducting tubes are responsible for the high Seebeck coefficient of SWCNTs, whereas MWCNTs having shells of different chirality show predominantly metallic behavior. The as-received SWCNT material is in the form of aligned bundles of nanotubes which are closely packed in ribbon like structures [35]. This bundle-like structure of SWCNTs remains partially also in the composites as seen in Figs. 3c and 3d.

The lyophilization step resulting in the aerogels did not affect the Seebeck coefficient for MWCNT based composites. Also, the Seebeck coefficient is nearly independent of the CNT content with S values of $13 \mu\text{V/K}$ (at 3 wt% loading) and $11 \mu\text{V/K}$ (at 10 wt% loading). In contrast, in SWCNT based aerogels, the Seebeck coefficient decreases with CNT loading. At 3 wt% loading, the lowest concentration at which the Seebeck coefficient could be measured, the S value of the aerogel is with $49 \mu\text{V/K}$ about $10 \mu\text{V/K}$ higher than in the film. Even at 5 wt% loading the aerogel shows higher values than the composite film. At higher SWCNT loadings the values of the aerogels are significantly lower than those of the composite films. This unexpected behavior can be attributed to the long process of freeze-drying which involves holding the sample at vacuum (10^{-6} torr). This process of low pressure may remove oxygen impurities from the SWCNTs, thereby de-doping them and pushing them towards n-type behavior, as explained above [36]. In our case the Seebeck coefficient does not reach

negative values but it is shifted to lower positive values. There could be two reasons for this behavior: one is that after the process of vacuum treatment some of the oxygen impurities present in air would have again doped the SWCNTs, the other one is that the de-doping is incomplete: CNTs that were in contact with vacuum would have undergone de-doping and those completely covered by cellulose would have evaded de-doping, resulting in a mixture of doped and de-doped SWCNTs, which causes in summary a lower positive Seebeck coefficient. At 3 wt% and 5 wt% loading the SWCNTs are expected to be well encapsulated by cellulose molecules and at 8 wt% and 10 wt% loading some fraction of SWCNTs located at the interface between the cellulose and the pores may not be encapsulated so that they are directly exposed to the vacuum condition. Hence, at higher loading a higher amount of de-doped SWCNTs is expected leading to a lower positive Seebeck coefficient. The study of the influence of different treatments on the doping/de-doping and the resulting thermoelectric character of the SWCNTs in composites remains a topic of future research.

A striking difference between cellulose based films and aerogels is observed when plotting electrical conductivity and Seebeck coefficient as a function of CNT volume content (Fig. 6). Due to the porous aerogel structure, the CNTs are found to be percolated in the aerogel composites at significant lower volume concentration when compared with the corresponding film composites. The desired electrical conductivity or Seebeck coefficient is achieved at a much lower CNT volume fraction after the lyophilization.

The lyophilization generates a porous structure in the composites. With increasing CNT content, the effective surface area of the composites decreases slightly (see Table 1). The thermal conductivity of the pure cellulose film is 0.06 W/(m·K) which is in agreement with the value given in [20]. In case of films, as shown in Table 2, after the addition of CNTs a slight increase in thermal conductivity was observed; the values vary between 0.07 and 0.11 W/(m·K). At loading of 8 and 10 wt% CNTs, some of the samples were fragile and collapsed during the operating conditions of thermal conductivity measurements so that no values could

be obtained. Despite the high value of thermal conductivity reported for CNTs to be higher than 2000 W/(m·K) [37], the thermal conductivity of the cellulose composite films did only increase slightly as compared to pure cellulose. This behavior is likely a result of good filler dispersion, creating a huge amount of CNT/polymer interphase, which increases the phonon scattering and decreases phonon transport through the composites, resulting in low thermal conductivity. At the same time, the polymer interphase layers are thin enough to allow tunneling and hopping of electrons for high electrical conductivity. The observed thermal conductivity was lower than that of other nanocomposites, namely PP/2 wt% SWCNT/5 wt% CuO [10] and PC/2.5 wt% MWCNT [8] (Table 3).

As expected, the aerogels show lower thermal conductivity than the corresponding films. The values vary between 0.01 and 0.09 W/(m·K) and increase with the nanotube loading. Due to desired reduced thermal conductivity but at the same time unwanted reduced electrical conductivity, the power factor and ZT values are lower for the aerogels than for films.

Table 2. Thermal conductivity, Power factor (PF), and Figure of Merit (ZT) of cellulose/CNT nanocomposite films and aerogels.

	Type of CNTs in the cellulose composite	Mass content wt(%)	Thermal conductivity (W/(m·K))	Power factor PF ($\mu\text{W}/(\text{m}\cdot\text{K}^2)$)	ZT
Films	MWCNT	3	0.11	6.0×10^{-4}	1.57×10^{-6}
	MWCNT	5	0.08	1.5×10^{-3}	6.02×10^{-6}
	MWCNT	8	---	5.0×10^{-3}	---
	MWCNT	10	---	1.0×10^{-2}	---
	SWCNT	3	0.09	1.0×10^{-2}	3.82×10^{-5}
	SWCNT	5	0.07	7.0×10^{-2}	3.15×10^{-4}
	SWCNT	8	0.11	2.6×10^{-1}	7.40×10^{-4}

Aerogels	SWCNT	10	---	1.10	---
	MWCNT	3	0.02	4.4×10^{-6}	8.81×10^{-8}
	MWCNT	5	0.03	4.2×10^{-5}	4.66×10^{-7}
	MWCNT	8	---	2.2×10^{-4}	---
	MWCNT	10	---	5.0×10^{-4}	---
	SWCNT	3	0.01	4.7×10^{-4}	1.11×10^{-5}
	SWCNT	5	0.04	2.9×10^{-3}	2.10×10^{-5}
	SWCNT	8	---	5.5×10^{-3}	---
	SWCNT	10	0.09	1.9×10^{-2}	6.40×10^{-5}

Table 3. Overview of maximum values of electrical and thermoelectric properties of

Material	Electrical conductivity (S/cm)	Seebeck coefficient ($\mu\text{V/K}$)	Power factor ($\mu\text{W}/(\text{m}\cdot\text{K}^2)$)	ZT
PVAc/20 wt% SWCNT [9]	48.00	40.0	7.70*	6×10^{-2}
PP/2 wt% SWCNT/5 wt% CuO [10]	0.17	36.8	0.02	$1.5 \times 10^{-5*}$
PP/2 wt% SWCNT/5 wt% CuO/10 wt% PEG [10]	0.24	-56.6	0.06	$3.9 \times 10^{-5*}$
PP/4 wt% SWCNT [10]	0.53	35.1	0.06	$3.8 \times 10^{-5*}$
PC/2.5 wt% MWCNT [8]	0.07	7.5	3.90×10^{-4}	4.1×10^{-7}
PC/2.5 wt% MWCNT-OH [8]	0.07	8.5	5.30×10^{-4}	4.7×10^{-7}
PMMA/SWCNT [4]	12.50	40.0	0.02*	---
PVA/SWCNT [4]	7.50	45.0	0.015*	---
Cellulose/8 wt% SWCNT film (this work)	1.25	45.6	0.26	7.4×10^{-4}

composites consisting of insulating polymer and CNTs.

Cellulose/10 wt% SWCNT film (this work)	5.00	47.2	1.10	---
Cellulose/10 wt% SWCNT aerogel (this work)	0.22	29.3	0.019	6.4×10^{-5}

*calculated taking the values given in the reference

Table 3 summarizes thermoelectric properties of various nanocomposites based on insulating polymer matrices with different CNTs as reported in literature and compares them with data of this work. In some cases, within one measurement series the maximum Seebeck coefficient was found at a different CNT loading than the maximal power factor or the maximum ZT; here maximum power factors are referred. In this comparison, the values of thermoelectric properties for the here reported cellulose/SWCNT composite films and aerogels are higher than most of the composites. The highest power factor measured in this work was $1.1 \mu\text{W}/(\text{m}\cdot\text{K}^2)$ for the film with 10 wt% SWCNT, the highest ZT value 7.4×10^{-4} for the film with 8 wt% SWCNT. These values are only outperformed by poly(vinyl acetate) (PVAc) composites with a segregated structure containing 20 wt% SWCNTs [9]. As mentioned before, thermal conductivity could not be measured for all films and aerogels, so that not all ZT could be calculated.

4. Conclusion

Films and aerogels based on cellulose/SWCNT and cellulose/MWCNT (2-10 wt%) were successfully fabricated and their thermoelectric properties were measured. The cellulose/SWCNT nanocomposite (film or aerogel) showed higher power factor and ZT (about 2 orders of magnitude higher) than cellulose/MWCNT composites. The maximum power factor achieved was $1.1 \mu\text{W}/(\text{m}\cdot\text{K}^2)$ for films based on SWCNTs at a concentration of 10 wt%, which showed a Seebeck coefficient of $47.2 \mu\text{V}/\text{K}$. Lyophilization resulted in the formation of stable aerogels with pores in sub-micron size, however there was no

considerable change in thermal conductivity compared to that of the films. The electrical conductivity decreased slightly. For MWCNT based composites, Seebeck coefficients were nearly unaffected by the lyophilization. The highest Seebeck coefficient of this study (49 $\mu\text{V/K}$) was shown by an aerogel with 3 wt% SWCNT. With increasing SWCNT content Seebeck values reduced which is assigned to the assumption that the vacuum process involved in lyophilization induces de-doping of SWCNTs. In summary, cellulose/SWCNT composite films have relatively high power factors when compared with other composites of insulating polymers with CNTs. Thus, together with their flexibility and low price, they are promising materials for thermoelectrical applications.

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References

- [1] S. Hébert, D. Berthebaud, R. Daou, Y. Bréard, D. Pelloquin, E. Guilmeau, F. Gascoin, O. Lebedev, A. Maignan, Searching for new thermoelectric materials: some examples among oxides, sulfides and selenides, *J Phys-Condens Mat* 28(1) (2016) 1-23.
- [2] M. Culebras, C.M. Gomez, A. Cantarero, Review on Polymers for Thermoelectric Applications, *Materials* 7(9) (2014) 6701-6732.
- [3] C.A. Hewitt, A.B. Kaiser, M. Craps, R. Czerw, S. Roth, D.L. Carroll, Temperature dependent thermoelectric properties of freestanding few layer graphene/polyvinylidene fluoride composite thin films, *Synthetic Metals* 165 (2013) 56-59.
- [4] M. Piao, M.R. Alam, G. Kim, U. Dettlaff-Weglikowska, S. Roth, Effect of chemical treatment on the thermoelectric properties of single walled carbon nanotube networks, *physica status solidi (b)* 249(12) (2012) 2353-2356.
- [5] M. Piao, G. Kim, G.P. Kennedy, S. Roth, U. Dettlaff-Weglikowska, Thermoelectric properties of single walled carbon nanotube networks in polycarbonate matrix, *physica status solidi (b)* 250(8) (2013) 1468-1473.
- [6] M.H. Miao, Electrical conductivity of pure carbon nanotube yarns, *Carbon* 49(12) (2011) 3755-3761.
- [7] J.K.W. Sandler, J.E. Kirk, I.A. Kinloch, M.S.P. Shaffer, A.H. Windle, Ultra-low electrical percolation threshold in carbon-nanotube-epoxy composites, *Polymer* 44(19) (2003) 5893-5899.
- [8] M. Liebscher, T. Gärtner, L. Tzounis, M. Mičušík, P. Pötschke, M. Stamm, G. Heinrich, B. Voit, Influence of the MWCNT surface functionalization on the thermoelectric properties of

- melt-mixed polycarbonate composites, *Composites Science and Technology* 101 (2014) 133-138.
- [9] C. Yu, Y.S. Kim, D. Kim, J.C. Grunlan, Thermoelectric Behavior of Segregated-Network Polymer Nanocomposites, *Nano Lett* 8(12) (2008) 4428-4432.
- [10] J. Luo, B. Krause, P. Pötschke, Melt-mixed thermoplastic composites containing carbon nanotubes for thermoelectric applications, *AIMS Mater. Sci.* 3 (2016) 1107-1116.
- [11] L. Tzounis, M. Hegde, M. Liebscher, T. Dingemans, P. Pötschke, A.S. Paipetis, N.E. Zafeiropoulos, M. Stamm, All-aromatic SWCNT-Polyetherimide nanocomposites for thermal energy harvesting applications, *Composites Science and Technology* 156 (2018) 158-165.
- [12] M. Nakano, Y. Nonoguchi, T. Nakashima, T. Kawai, Flexible thermoelectric rubber polymer composites based on single-walled carbon nanotubes, *Jpn J Appl Phys* 54(4) (2015).
- [13] K. Suemori, Y. Watanabe, S. Hoshino, Carbon nanotube bundles/polystyrene composites as high-performance flexible thermoelectric materials, *Appl Phys Lett* 106(11) (2015).
- [14] J. Wang, H. Li, R. Liu, L. Li, Y.H. Lin, C.W. Nan, Thermoelectric and mechanical properties of PLA/Bi_{0.5}Sb_{1.5}Te₃ composite wires used for 3D printing, *Composites Science and Technology* 157 (2018) 1-9.
- [15] P. Gijsman, Review on the thermo-oxidative degradation of polymers during processing and in service, *E-Polymers* 8(1) (2008) 1-34
- [16] D. Klemm, B. Heublein, H.P. Fink, A. Bohn, Cellulose: fascinating biopolymer and sustainable raw material, *Angew Chem Int Ed Engl* 44(22) (2005) 3358-93.
- [17] J. Innerlohinger, H.K. Weber, G. Kraft, Aerocellulose: Aerogels and Aerogel-like Materials made from Cellulose, *Macromolecular Symposia* 244(1) (2006) 126-135.
- [18] M.K. Trivedi, G. Nayak, S. Patil, R.M. Tallapragada, R. Mishra, Impact of Biofield Treatment on Chemical and Thermal Properties of Cellulose and Cellulose Acetate, *Journal of Bioengineering & Biomedical Sciences* 5(3) (2015) 1-7.
- [19] S.T. Nguyen, J.D. Feng, S.K. Ng, J.P.W. Wong, V.B.C. Tan, H.M. Duong, Advanced thermal insulation and absorption properties of recycled cellulose aerogels, *Colloid Surface A* 445 (2014) 128-134.
- [20] M. Tian, L. Qu, X. Zhang, K. Zhang, S. Zhu, X. Guo, G. Han, X. Tang, Y. Sun, Enhanced mechanical and thermal properties of regenerated cellulose/graphene composite fibers, *Carbohydr Polym* 111 (2014) 456-62.
- [21] D.H. Kim, S.Y. Park, J. Kim, M. Park, Preparation and Properties of the Single-Walled Carbon Nanotube/Cellulose Nanocomposites Using N-methylmorpholine-N-oxide Monohydrate, *J Appl Polym Sci* 117(6) (2010) 3588-3594.
- [22] J. Lu, H.H. Zhang, Y.H. Jian, H.L. Shao, X.C. Hu, Properties and Structure of MWNTs/Cellulose Composite Fibers Prepared by Lyocell Process, *J Appl Polym Sci* 123(2) (2012) 956-961.
- [23] R.E. Anderson, J.W. Guan, M. Ricard, G. Dubey, J. Su, G. Lopinski, G. Dorris, O. Bourne, B. Simard, Multifunctional single-walled carbon nanotube-cellulose composite paper, *J Mater Chem* 20(12) (2010) 2400-2407.
- [24] R. Jung, H.S. Kim, Y. Kim, S.M. Kwon, H.S. Lee, H.J. In, Electrically conductive transparent papers using multiwalled carbon nanotubes, *J Polym Sci Pol Phys* 46(12) (2008) 1235-1242.
- [25] H.S. Qi, J.W. Liu, J. Pionteck, P. Pötschke, E. Mäder, Carbon nanotube-cellulose composite aerogels for vapour sensing, *Sensor Actuat B-Chem* 213 (2015) 20-26.
- [26] H.S. Qi, E. Mäder, J.W. Liu, Electrically conductive aerogels composed of cellulose and carbon nanotubes, *J Mater Chem A* 1(34) (2013) 9714-9720.
- [27] H.S. Qi, E. Mäder, J.W. Liu, Unique water sensors based on carbon nanotube-cellulose composites, *Sensor Actuat B-Chem* 185 (2013) 225-230.
- [28] Technical Data Sheet NC3150, V5, 25th January 2016, Nanocyl S.A. Sambreville, Belgium.

- [29] Technical Data Sheet TUBALL SWCNT, OCSiAl Ltd.
- [30] H. Qi, J. Liu, S. Gao, E. Mäder, Multifunctional films composed of carbon nanotubes and cellulose regenerated from alkaline–urea solution, *J Mater Chem A* 1(6) (2013) 2161-2168.
- [31] W. Martienssen, H. Warlimont, Springer handbook of condensed matter and materials data, Springer Science & Business Media, 2006.
- [32] Y. Nakai, K. Honda, K. Yanagi, H. Kataura, T. Kato, T. Yamamoto, Y. Maniwa, Giant Seebeck coefficient in semiconducting single-wall carbon nanotube film, *Applied Physics Express* 7(2) (2014) 025103.
- [33] Y. Nonoguchi, K. Ohashi, R. Kanazawa, K. Ashiba, K. Hata, T. Nakagawa, C. Adachi, T. Tanase, T. Kawai, Systematic Conversion of Single Walled Carbon Nanotubes into n-type Thermoelectric Materials by Molecular Dopants, *Sci Rep-Uk* 3 (2013).
- [34] J. Luo, G. Cerretti, B. Krause, L. Zhang, T. Otto, W. Jenschke, M. Ullrich, W. Tremel, B. Voit, P. Pötschke, Polypropylene-based melt mixed composites with singlewalled carbon nanotubes for thermoelectric applications: Switching from p-type to n-type by the addition of polyethylene glycol, *Polymer* 108 (2017) 513-520.
- [35] B. Krause, P. Pötschke, E. Ilin, M. Predtechenskiy, Melt mixed SWCNT-polypropylene composites with very low electrical percolation, *Polymer* 98 (2016) 45-50.
- [36] P.G. Collins, K. Bradley, M. Ishigami, A. Zettl, Extreme oxygen sensitivity of electronic properties of carbon nanotubes, *Science* 287(5459) (2000) 1801-1804.
- [37] Z.D. Han, A. Fina, Thermal conductivity of carbon nanotubes and their polymer nanocomposites: A review, *Prog Polym Sci* 36(7) (2011) 914-944.