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Individual Strings of Conducting Carbon Particles in Polymer Matrix: Electric Field Induced Preparation and Electromechanical Properties

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Abstract

We present a method to make strain sensors by aligning carbon nanocones (CNCs) and carbon black (CBs) particles in polymers into single strings using alternating electric field (dielectrophoresis). The strings were stabilized by curing the polymer matrix and characterized using diverse electromechanical methods. Two different polymers have been used, urethane methacrylate based thermoset polymer and silicone based elastomer with the glass transition points below and above room temperature, respectively. The CNCs have higher conductivity than the CBs but have a lesser probability of creating a conducting string. Bending single strings of CNCs and CB particles in polymers matrices gave a reversible effect in resistivity similar to what was reported earlier by Gammelgaard et al. (APL 2006 88 113508) for isotropic CBs in a SU8 polymer. Finally we demonstrate how strings aligned either in-plane or out-of-plane between two electrodes can be used as a touch sensor by observing a reversible change in resistance due to compression.

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1 Introduction

The sensor industry is an enormous industry and is growing rapidly [1]. Demand for sensors in the US will rise 6.1 % annually to 2014 [2]. Sensors can be found everywhere in our everyday lives in areas like automobiles, touchscreens, wireless communication, automotive, medical, industrial, and aerospace. An area that is becoming more and more important is sensors that help solve some of the world's toughest environmental problems known as "green sensors" [3]. Sensors can for instance be made to monitor reduce fuel consumption by boosting efficiency and reliability of diesel vehicles. The world market for chemical sensors alone is projected to reach $17.28 billion by the year 2015 [4]. Nanotechnology will no doubt play an important role in sensing [1]. In one instance multi-walled carbon nanotubes (CNTs) offer an ultra-high surface area and low energy consumption, as well as superior adsorption/desorption characteristics compared to other known materials. Potential problems using CNTs in sensor applications are that they are still fairly difficult to produce in large quantities, and therefore fairly expensive. A possible solution is to use aligned particles instead of CNTs.

Particles dispersed in polymers can be aligned in different directions by applying an electric [5, 6, 7] or magnetic field [8, 9, 10]. It is also possible to align particles by mechanical alignment [11]. The alignments in this project will be done by alternating electric field which occurs because of an effect called dielectrophoresis [12]. This is the effect that causes movement of charge-neutral particles in a medium due to an inhomogeneous electric field because of the differences in the dielectric constants of the particles and the matrices. A medium with a large dielectric constant subjected to an electric field will acquire a large polarization and will

consequently contain many dipoles [13]. The medium may be more polarizable than the particles and then you will get "dielectric holes", i.e., the particles may appear to be polarized opposite to the electric field. Because dielectric particles in this project are more polarizable than the medium they will be pulled towards the dielectric regions of increasing field strength, which occurs at the periphery of the electrode fingers [14]. Dielectrophoresis can make electrically conductive particles align into conductive strings in an initially insulating particle-polymer mixture [15, 16, 17]. This can be achieved while keeping the particle concentration well below the percolation limit. Particles can also be aligned in an electric field without the use of a polymer [18].

Carbon particles like carbon black (CBs) and carbon nanocones (CNCs) [19] have intriguing electrical properties which make them very interesting as fillers in polymer composites. CNCs are the fifth form of carbon when it comes to topological organization [20]. Carbon nanocones were accidentally discovered [21] in 1997 in the so-called Kvaerner Carbon Black & Hydrogen Process (CB&H) [22]. These nanocones are distinctly different from the naturally occurring helically wound graphitic cones [23] and from carbon nanohorns [24]. The nanocones can be found as 5 types with different apex angles. The apex angles ϕ are given by

$$sin(\frac{\phi}{2}) = \frac{2\pi - n\frac{\pi}{3}}{2\pi}, \tag{1}$$

were n is the number of pentagons. The strain at the cone tip will give rise to the formation of (6-n) pentagons near the tip and the cone angles of $\phi = 112.9^\circ, 83.6^\circ, 60.0^\circ, 38.9^\circ$ and 19.2° for 1, 2, 3, 4 and 5 pentagons, respectively. The CNC material in this project contains all these angles. The size of the particles range from 300-3000 nm.

By applying an alternating electric field it is possible to align particles like CNCs and CBs and make them form into conducting strings in polymers [25]. The alignment can be in-plane or out-of-plane depending on the positioning of the field. The polymer composites can be cured after the alignment to lock the particles into place. By using interdigidated electrodes, bulk samples have been made [26], as seen in Fig. 1. The conductivity of a aligned sample can be 5 orders of magnitude higher then a non-aligned sample. These types of samples cover relatively large spatial areas (centimeters times centimeters) and all data reported to date represent an average of thousands of strings. In order to understand these materials better single strings should be considered separately.

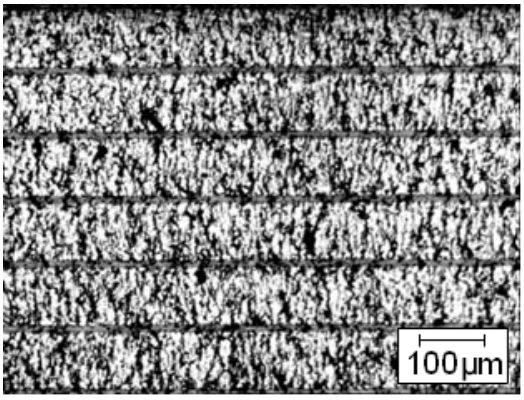

Figure 1: By using larger interdigidated electrodes multiple strings have been aligned. The matrix is in this case a UV-curable polymer.

Compressing or elongating composites containing conductive particles leads to large piezoresistive effects [27, 28]. By subjecting the polymer to external stresses the distances between the particles will increase which can lead to higher resistances. Bending nanowires like CNTs by a strain of 0.6 % results in a drop in conductance by a factor of up to 4 and gauge factors of $\sim$ 500 [29] (see theory section for definition). There are also

reports of the electromechanical properties of carbon-polymer mixtures such as report of Gammelgaard et al. [30] but all these reports concern isotropic carbon particle-polymer systems.

In this report, a novel method for making single strings of carbon particles in polymer matrices using alternating electric fields is presented. The polymer matrices containing these strings can thereafter be subjected to various types of external stresses in order to measure the electromechanical properties of the aligned strings. The polymer matrices were located on top of electrodes made specifically for this project. Two different particle types were used, CNCs and CB. Two different types of polymers were used, one UV-curable thermoset polymer and one humidity-curable elastomer. This gives a good selection of different composites that will be examined. The results are compared to those of Gammelgaard et al. who reported on the electromechanical properties of non-aligned CB particles in a SU8 polymer on top of a cantilever and will serve as a reference through this report. This paper shows the difference and potential benefit of aligning particles. This work is important for materials science point of view by illustrating first time properties of single strings. Strain and deformation sensors are areas where this alignment process might be utilized. Implications may also be found in an area of bio- and chemical sensors [31, 32] and gas micro sensors as shown elsewhere for aligned CNTs on silicon [33].

We find that the aligned single strings connect their ending points electrically, the strength of these connections vary with the substrate deformations the strings, the system thus acting as deformation sensors as the conductance and admittance change. The single string appears to be more sensitive to the deformations compared to the randomly oriented

mesh. Moreover, single strings were found to act as capacitive sensors. Generally speaking, if the substrate deformations vary as a response to an external input, the conductivity variation can be used to sense this input, and the whole system forms a sensor.

These results give us the following visions. In one future application the layer could be located on a force microscope cantilever, particularly on an atomic force microscope (AFM) cantilever whose tip is detecting a sample surface which acts as an external input for cantilever deformation. An application for these types of deformation and capacitive sensors could also be in touchscreens as shown in Fig. 2. Touchscreens are a rapidly increasing industry due to the extreme increase in popularity of smartphones and now tablets. Problems with the current technologies for producing touchscreen panels are that transparent conductors such as indium tin oxide are expensive and have limited durability, and that resistive screens must be produced with several layers. By aligning particles out-of-plane it should be possible to prepare a semitransparent array of particle strings and detect the change in resistance when the polymer composite is compressed.

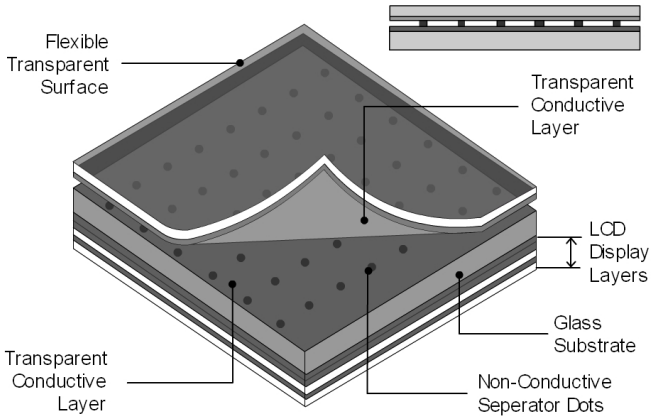

Figure 2: A schematic of a basic touchscreen showing its complexity, cross section seen in inset. Adapted from HowStuffWorks.com [34].

2 Theory

2.1 Dielectrophoresis

The effect which causes movement of charge-neutral particles in a medium due to an electric field is called dielectrophoresis. Having needle-like electrodes help to make the particles stick to the electrodes because the field gradient is largest near the tip. As mentioned earlier a medium with a large dielectric constant subjected to an electric field **E** will acquire a large polarization and will consequently contain many dipoles. The induced dipole moment **p** of the dielectric medium is given by

$$\mathbf{p} = \alpha \mathbf{E}, \tag{2}$$

where α is the polarizability. The dielectric force $\mathbf{F}_{dip}$ acting on a dipole moment **p** situated in an inhomogeneous electric field **E** is given by

$$\mathbf{F}_{dip} = (\mathbf{p}\nabla)\mathbf{E}. \tag{3}$$

We study a case where we have a dielectric sphere with the radius a, this is the starting point of calculating the force on an object of any shape. The dipole force in a inhomogeneous electric field on a dielectric sphere of radius a is a dielectricophoretic force $\mathbf{F}_{DEP}$

$$\mathbf{F}_{DEP}(\mathbf{r}_0) = 2\pi\epsilon_1 K(\epsilon_1, \epsilon_2) a^3 \nabla[\mathbf{E}_0(\mathbf{r}_0)^2], \tag{4}$$

where $K(\epsilon_1, \epsilon_2)$ is the Clausius-Mossotti factor and ϵ_1, ϵ_2 is the dielectric constants of the dielectric fluid and particle respectively [12]. This force is independent of the sign of $\mathbf{E}_0$ but is given by the sign of the Clausius-Mossotti factor. If $\epsilon_1 < \epsilon_2$ the dielectric force pulls the dielec-

tric particle towards the region of strong **E**-field, while for $\epsilon_1 > \epsilon_2$ the particle is pushed away from this region. The dielectric constant for the polyurethane is $\epsilon_1 =\sim 9$, while for the carbon particles the dielectric constants are in the region of $\epsilon_2 =\sim 2-3$ When dielectric particles are suspended in a dielectric fluid it is possible to trap them. The dielectric particles suspended in the liquid flowing through the microchannels will be attracted by the electrodes in a presence of a inhomogeneous field. The particles will get trapped by the electrodes if $\mathbf{F}_{DEP}$ is stronger than the viscous drag force $\mathbf{F}_{drag}$ thus fulfilling the condition

$$|\mathbf{F}_{DEP}| > |\mathbf{F}_{drag}|. \tag{5}$$

So far we have only looked at cases where a DC voltage has been driving the DEP trap. An AC field has many advantages compared to the DC field. One advantage is that the DEP trap will also work even if the liquid and the particles have non-zero conductivities. Another advantage is that Clausius-Mossotti factor depends on the frequency and can change sign. This means that we can control in situ whether the DEP force should be attractive or repulsive. Dielectrophoresis can make conducting particles align into conductive strings in an insulating polymer matrix.

2.2 Gauge Factor

The gauge factor is defined as the relative change in resistance divided by the relative change in length of a piezoresistor. A high gauge factor is desirable because that means the piezoreistor will have a big relative change in resistance even with a low strain. The relative change in resistance $\frac{\Delta R}{R}$ is given by

$$\frac{\Delta R}{R} = K \cdot \epsilon, \tag{6}$$

where ϵ is the strain and K is the gauge factor. K is then given by

$$K = \frac{1}{\epsilon} \cdot \frac{\Delta R}{R}. \tag{7}$$

2.3 Strain

Strain is in this thesis defined as the relative displacement of particles in a polymer due to deformation.

An expression of the strain can be obtained using $W(x)$ which is the vertical deflection of the beam as a function of distance x from one of the clamping points, and is given by

$$W(x) = C_4(L^2 \cdot x^2 - 2 \cdot L \cdot x^3 + x^4), \tag{8}$$

where L is the length of the beam between the clamping points, see Fig. 3, and C_4 is a constant that depends on material properties, dimensions and the applied force [35].

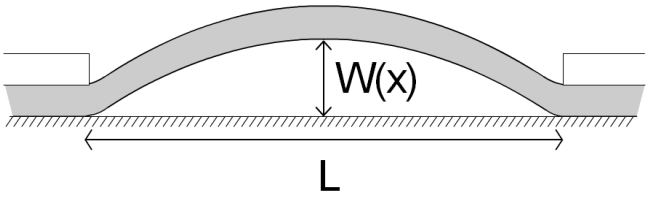

Figure 3: A schematic of the double clamped setup, showing the vertical deflection W(x) and the length L of the beam.

This gives $W(x = 0) = 0$ and $W(x = L) = 0$, since this two positions corresponds to the clamps. The maximum deflection occurs on the midpoint between the two clamps, i.e. at $x = L/2$.

The analytical calculation of the relation between the surface strain and the deflection is found using the variational method, where one first "guess" a suitable solution to the beam equation, in this case a fourth order polynomial, and then determine the parameters in the polynomial from the boundary conditions. This gives a mathematical function describing the shape of the beam and thereby also the beam curvature, which can be converted into surface strain.

The strain S as a function of the deflection D of a cantilever is given by

$$S_{cantilever}(D) = 1.5 \cdot \frac{H}{L^2} D, \tag{9}$$

where H is the thickness of the cantilever and the polymer composite on top of it. D is defined by $D = W(x = L/2)$.

The strain as a function of the deflection D of a doubly-clamped beam is given by

$$S_{doubleclamp}(D) = 8 \cdot \frac{H}{L^2} D, \tag{10}$$

here L is the distance between the clamps.

2.4 Glass transition of polymers

Polymers are molecules which consist of a long, repeating chain of smaller units called monomers. Polymers have the highest molecular weight among any molecules, and may consist of billions of atoms [36]. The translation freedoms of molecules vary in large limits. The glass transition is the transition of the polymers from a hard and relatively brittle state into a rubberlike state [37]. The transition temperature T_g is the temperature at which a polymer goes from a glassy state to a rubbery state. At temperatures below T_g the molecules in the polymer are immobile. When the temperatures are above T_g portions of the molecules can wiggle around [38]. Glass transition must not be confused with melting which is another effect. The polymers used in this project will not be subjected to noticeably high temperatures so if the $T_g < T$ the polymer will be in the glass state, and if the $T_g > T$ it will be in the rubbery state, where T is the room temperature.

3 Experimental

3.1 Preparation of the samples

Before the electromechanical properties could be measured the carbon particles had to be aligned into single strings. This meant that new type of electrodes had to be produced. The electrodes consisted of two thin fingers facing each other with a spacing d of 10, 20, 30, 50 or 100 μm as shown in Fig. 4. These electrodes were made in the cleanroom at NanoSYD [39] in Denmark. The mask for the photolithography was designed by us at IFE and manufactured by Delta Mask [40] in the Netherlands. These electrodes were made of a thin layer of gold deposited on a glass wafer.

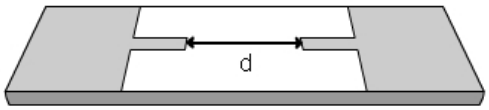

Figure 4: Schematic of the electrode with spacing d used for the alignment of single strings.

3.1.1 Materials

Carbon nanocones

CNC material represents the primary choice of conductive particles in this work. A a single nanocone can be seen in Fig. 5. It is important to note that the material used in this project does not just contain cones but flat carbon discs as well. The material contains about 70% discs and 20% nanocones. The material has been heat treated to 2700°C prior use and was supplied by n-Tec AS (Norway) [41].

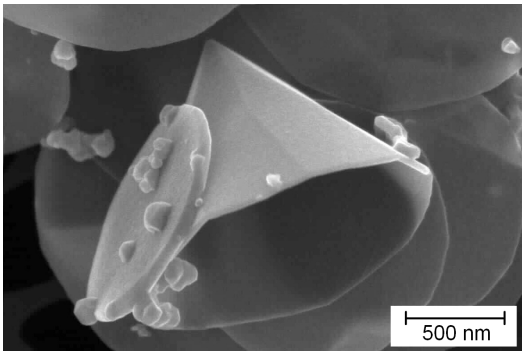

Figure 5: SEM image of a carbon nanocone.

Carbon Black

CB particles were used to provide a comparison to the CNCs. The CB particles consist of greater than 97% elemental carbon arranged as aciniform (grape-like cluster) particulate [42]. The employed CBs were supplied by Alfa Aesar [43]. A SEM image of the particles is depicted in Figure 6.

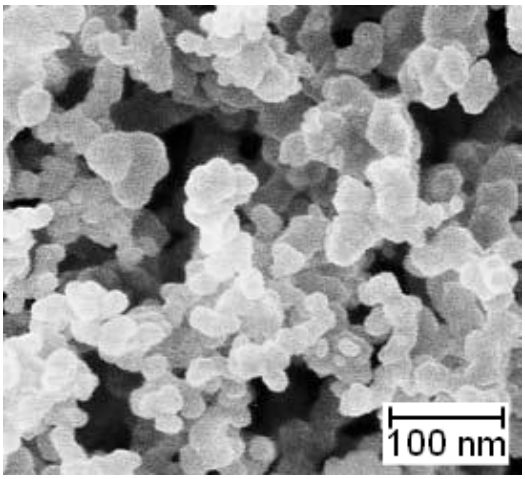

Figure 6: SEM image of carbon black particles.

Polymers

Two different polymers were selected for this project, one UV-curable and one humidity-curable. The UV-curable polymer was Dymax Ultra Light-Weld 3094 and the humidity-curable polymer was Dow Corning 734 Flowable Sealant. The former polymer is urethane methacrylate based thermoset polymer whereas the latter polymer is silicone based elastomer. The glass transition of Dymax 3094 is above and the one of Dow Corning 734 below room temperature and the cured materials appear as glassy and flexible, respectively. Both polymers were provided by Lindberg & Lund AS (Norway) [44].

3.1.2 Alignment of carbon particles

An AC-field can be applied over the electrodes to get a symmetrical alignment between them, forming long conductive strings parallel to the electric field. The AC field was produced by an in-house voltage source and measured by a Keithley 2000 multimeter.

In these experiments the anisotropic electric conductivity has an unidirectional conductivity. By changing the direction of the applied field one can form strings in different directions. The directions studied in this project are in-plane and out-of-plane as shown in Fig 7.

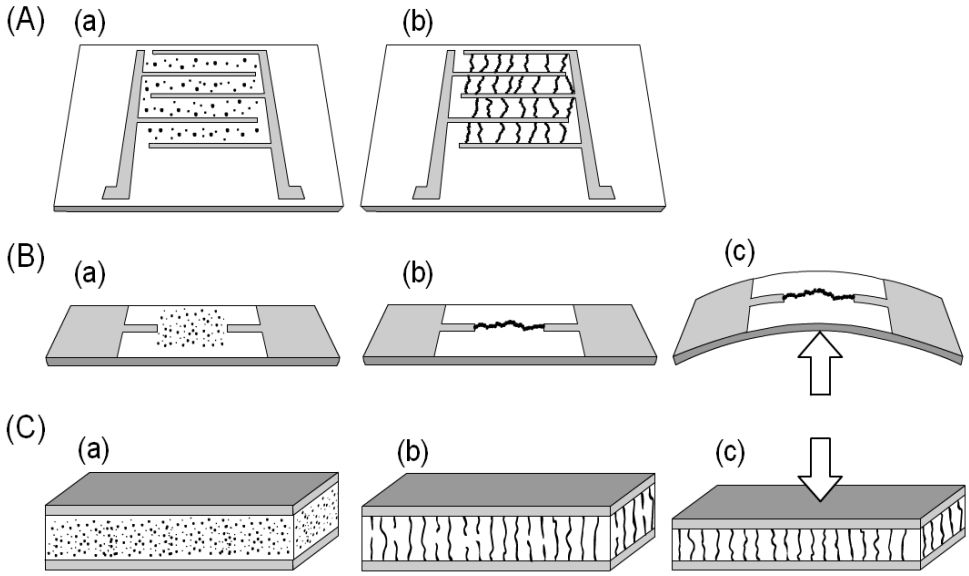

Figure 7: (A) Dispersed CB and CNC particles in polymers on interdigidated electrodes can be used to make several strings in-plane. (B) Particles will form into single strings if the electrodes are thin enough. This setup can then be bent and the resistivity of the strings is measured as a function of deflection. (C) Using conducting plates as electrodes strings can be formed out-of-plane and then compressed. The resistance can be measured as a function of compression. In this process a low particle fraction is spread over the electrodes (a) and aligned into strings (b) prior to deformation (c).

The AC-field can have a frequency ranging from 10 Hz to 10 MHz. The frequency used in this project will be 1 kHz. The electric field can also be a DC-field, this results in another type of effect. The strings will just be growing on one of the electrodes when a DC-field is applied. In this case it is not possible get conductive strings through the sample. This will also happen if the frequency of the AC-field is very low (< 10 Hz).

The electric field applied can be in the order of 0.05 to 10 kV/cm. With a typical alignment distance in the range of 10 μm to 1 mm, the voltage can be in the range of 0.1 to 100 V.

3.1.3 Single strings in polymers

CNCs and CBs were dispersed in polymers by a magnetic stirrer for about 30 minutes at 300 RPM. Single strings of these particles were aligned in the two different polymers by an alternating electric field. This meant that four different kinds of samples were produced. This gave a good distribution of the different polymers and particles used.

It is important that the concentration of conductive particles is below the percolation threshold of an isotropic dispersion. This is because concentrations above this threshold will make the particles form continuous strings on their own, without applied electric field.

UV-curable polymer

CBs and CNCs were dispersed in the polymer with a particle concentration of about 0.1 vol-%. The spacing of the electrodes varied but the applied electric field was in every case E = 4 kV/cm. The sample was then UV-cured under a mercury lamp for 20 minutes. The schematic of alignment of a single string is shown in Fig. 7(B).

Humidity-curable polymer

CBs and CNCs were also aligned in a humidity-curable polymer. This polymer was a clear silicone solvent. The polymer had a higher viscosity than the UV-curable polymer so 2-Butanone (Sigma Aldrich [45]) was used as a solvent. An equal amount of solvent and polymer was used.

The particle concentrations were about 0.1 vol-%. The CBs and CNCs were aligned on top of the electrodes by an electric field of E = 4 kV/cm. The composites were then cured at room temperature at 25 percentage measured air humidity for a couple of hours.

3.2 Electrical characterization of aligned strings

Experimental setup for measuring sample conductivity

For bending, the electrodes were symmetrically clamped from both ends that allowed deformation in the middle with simultaneous electrical connections via probe-station (Fig. 8a-b). The Two probes were connected to a Stanford Research Systems SR570 low noise current preamplifier which was connected to Stanford Research Systems SR830 lock-in amplifier. A GW Instek GDS-2102 oscilloscope was used to monitor the applied voltage. The whole setup is shown in Fig. 8. The applied AC voltage was a sine wave. The frequency and amplitude of the wave were varied and the corresponding currents and phase angels of the single string were measured. The frequency and amplitude ranging from 7.2 Hz to 7.2 kHz and 0.01 to 0.1 V respectively.

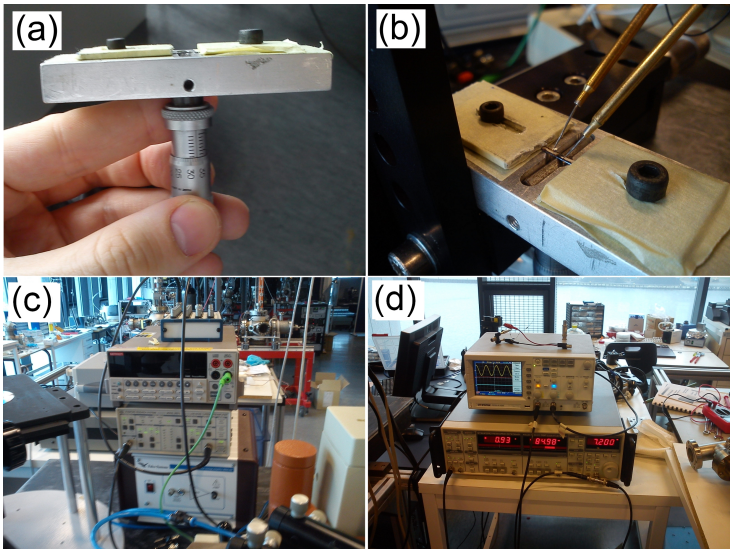

Figure 8: (a) The device used for bending the samples (b) measuring the current with two probes. The measuring setup consisted of (c) low noise current preamplifier and (d) lock-in amplifier and an oscilloscope, used for the measurements of the current and phase angle.

Distribution of conductivity

What effect the difference in the particle topology has on the conductivity of single strings was examined by making 20 similarly aligned samples. The CB particles were aligned on electrodes with spacing of 30 μm. The electrodes used for the CNCs had spacings of 20 μm. The conductivity was measured after each alignment. The UV-curable polymer was used in both cases, but the samples were not UV-cured.

IV characterization

The IV curve for the CBs and CNCs were measured by sweeping the voltage V from 0 to 100 mV and plotting the corresponding current I through the sample. This was done with the Labview software. Both aligned and isotropic samples were used for the measurements. By doing this we were able to see what effect the alignment had on the IV curve. In this series of measurements, the electrodes used for the isotropic and aligned samples with CNCs had a spacing of 50 μm and 100 μm respectively. For the isotropic and aligned samples with CBs electrode spacings of 50 μm and 30 μm were used respectively. The particles concentration of both of the aligned cases were about 0.1 vol-% while the concentrations of the isotropic cases were about 12 vol-%.

Impedance and phase angle vs. frequency

The impedance and phase angle were measured by the setup shown in Fig. 8 (c) and (d). The samples were connected to a low noise current preamplifier and then to a lock-in amplifier. The frequency of the sine wave was first set with the lock-in amplifier to 7.2 Hz then 72 Hz, 720 Hz and 7.2 kHz and the corresponding impedances and phase angles were measured.

3.3 Electromechanical properties of aligned strings

3.3.1 Bending single strings in polymers.

The schematic and experimental facility of the electromechanical measurements are shown in Fig. 7 and Fig. 8, respectively. The particles were dispersed in the polymers and were aligned in both in-plane and out-of-plane directions. The in-plane aligned samples were bent and the out-of-plane samples were compressed in order to measure their electromechanical properties.

Because it was not possible to make the glass wafers thin enough without breaking them another substrate than galss had to be used. The choice fell on silicon wafer with a thickness of 250 μm. These electrodes were also produced by thin film deposition at the cleanroom at NanoSYD. The mask used was the same as what was used previously on the glass wafer. The setup used for bending the samples can be seen in Fig. 8. The sample was clamped between two points and a micrometer screw was used to control a small blade at the center of the device. The blade would push up under the sample and eventually begin to bend it. The amount of deflection used could then be read from the micrometer screw. Two probes were used to measure the current passing though the strings. These probes were fastened to a metal plate by a vacuum pump to ensure that they did not move when the sample was bent.

The strain of the bent samples where calculated by using Eq. 10. Using a thickness of the cantilever and polymer of $H \approx 250\mu m$ and a length between the clamps of $L \approx 10mm$ the strain was calculated for deflections D from 0 to $100\mu m$.

Bending single strings in UV-curable polymer (Dymax 3094)
CBs and CNCs were aligned in the UV-curable polymer on top of the electrodes made on the silicon substrate. The CBs were aligned on an electrode with a spacing of 30 μm while the electrode spacing of the electrode used for the CNCs was 100 μm. The polymers were cured by a Nikon mercury lamp with wavelength λ=365 nm for about an hour.

Bending single strings in humidity-curable polymer (Dow Corning 734)
The same procedure as with the UV-curable polymer was repeated with the humidity-curable polymer. The CBs were aligned on an electrode with a spacing of 30 μm while the electrode spacing of the electrode used for the CNCs was 100 μm. The polymers were cured at room temperature at 25 percentage measured air humidity for a couple of hours.

3.3.2 Compression of aligned strings

In order to make a touchscreen the particles have to be aligned out-of-plane. To make this possible another setup had to be used. By coating two microslides with a conducting paint and connecting them to electric wires the slides could be used as electrodes, as seen in Fig. 7(C). CBs were dispersed in the humidity-curable polymer and the composite was smeared between the electrodes. The spacing between the electrodes was 100 μm. 30 V were applied over the electrodes for 5 minutes. The sample was set to cure in room temperature overnight. By using a micrometer screw for the compression and a Keithley 2000 multimeter for measuring the resistances, the resistance as a function of applied compression was found.

4 Results

4.1 Preparation of samples

4.1.1 Single strings in polymers

Mixing

Both CNC and CB particles form uniform isotropic mixture with Dymax 3094 or Dow Corning 734 when the particle concentration is low ($\ll$ 1 vol-%). This volume fraction is lower than the $\sim$2 vol-% percolation threshold of these materials [46]. These mixtures were used as starting materials in alignment experiments. Isotropic mixtures with very high particle particle fraction ($\sim$ 10 vol-%) were prepared for comparison. This particle fraction is above the percolation threshold and these conductive mixtures were compared to aligned strings in electrical measurements. Optical micrographs of both mixtures are shown in Fig. 9.

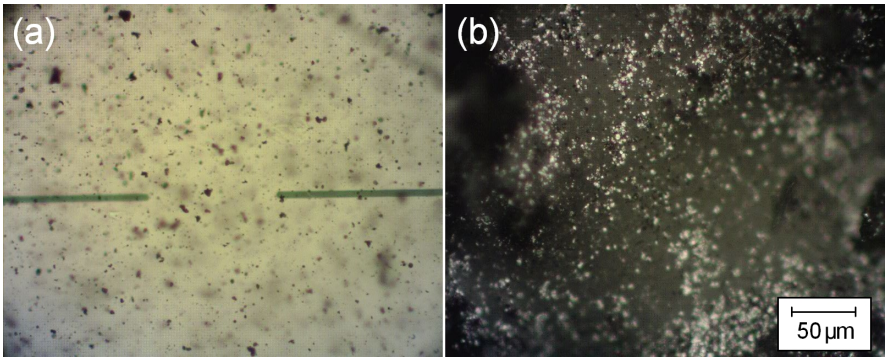

Figure 9: (a) A mixture with low particle concentration ($\sim$ 0.1 vol-%) and (b) a mixture of high particle concentration ($\sim$ 11.5 vol-%). The white spots is light penetrating the polymer.

UV-curable polymer

CNC and CB particles became aligned into single conducting strings in Dymax 3094 by electric field. An alignment of CNC particles over time is depicted in Fig. 10. By applying an electric field of E = 4 kV/cm over the electrode with a spacing of 100 μm a conducting string was produced in less than two and a half minutes. This aligned string had a resistivity of $\rho = 40 m\Omega \cdot m$.

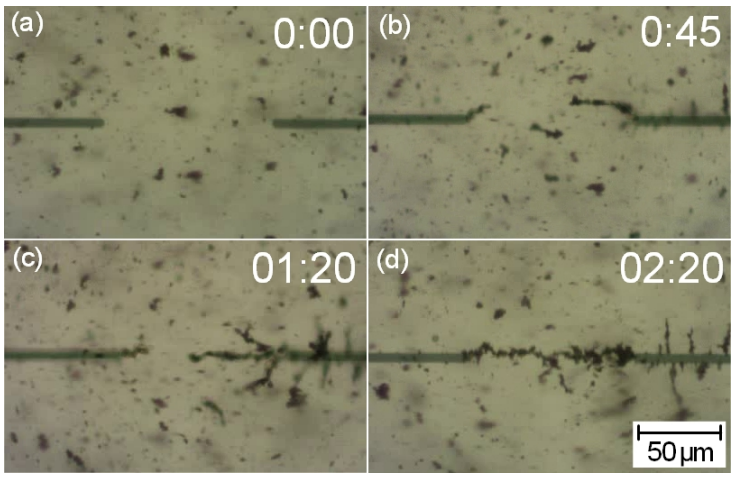

Figure 10: Alignment of CNC particles versus time. The applied field is E = 4 kV/cm over an electrode spacing of 100 μm. Originally isotropic mixture with the particle fraction of $\sim$ 0.1 vol-%. (a) Particles dispersed in the polymer before the electric field was applied. Snapshots of the alignment process after 45 seconds (b) and 1 minute 20 seconds (c). The single string was formed within 2 minutes 20 seconds (d).

Humidity-curable polymer

Both CNC and CB particles align well also in the humidity-curable Dow Corning 734. The single strings aligned in the humidity-curable polymer had a much higher resistivity than the strings the UV-curable polymer. The resistivity values fell in the region of 1-5 $\Omega \cdot m$ which was 100 times higher than with the UV-curable polymer. The strings became non-conducting to DC currents after the curing.

The UV-curable polymer had a $T_{g,UV} < T$, where T_g is the transition temperature and T is the room temperature. The humidity-curable polymer had a $T_{g,humidity} > T$. The two polymers are different from each other after curing. Therefore, while the aligned composite with the UV-curable polymer was fairly hard, the one with humidity-curable polymer had a softer rubberlike texture.

4.1.2 The difference between aligned CB and CNC

Distribution of conductivity

The conductivity of the Dymax 3094 polymer with no dispersed particles is ~ 0. The distribution of the conductivity of aligned single strings CB and CNC in Dymax 3094 polymer is shown in Fig. 11.

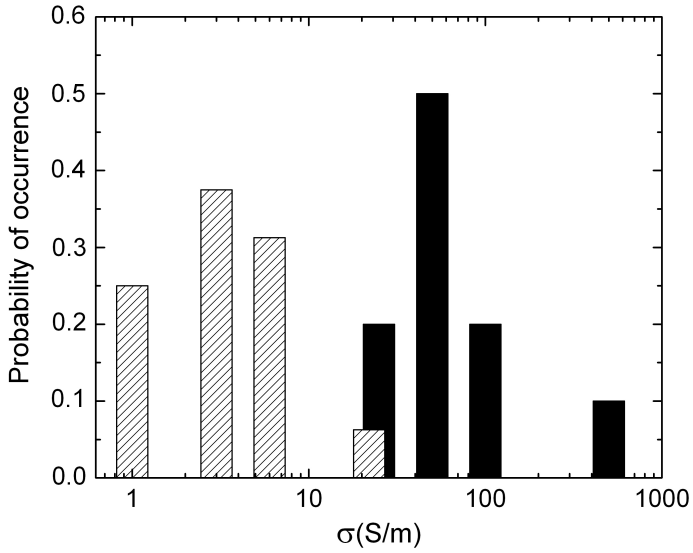

Figure 11: The resistivity of single strings of CB (striped) and CNC (black) in Dymax 3094 versus conductivity. The CNCs have higher conductivity but have a smaller probability to produce a conducting string. Only fifty percent of the aligned single strings of CNC were conducting.

The Fig. 11 shows that the CNCs have a higher conductivity than the CBs. The CB particles have conductivity ranging from 1 to 22 S/m with most falling in the region from 1 to 6 S/m. The CNC particles have a conductivity ranging from 25 to 500 S/m with most falling in the region from 25 to 100 S/m. It is important to note that the figure is normalized

so that the probability of getting an alignment is 1 in both cases. Though the CNC particles have a higher conductivity the probability of getting a conducting string is only about fifty percent, 10 out of 20. Fig. 12 shows an example of a non-conducting CNC string and a conducting CB string.

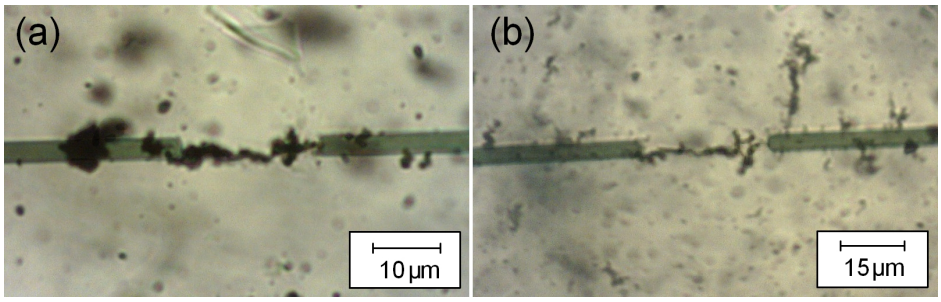

Figure 12: (a) A non-conducting string of CNC particles and (b) a conducting string of CB particles.

IV characterization

The current-voltage IV- curves of the CNCs and the CBs in Dymax 3094 and Dow Corning 734 are presented in Fig. 13 and Fig. 14 respectively. The solid lines represent aligned samples while the dashed lines represent isotropic (non-aligned) high particle fraction samples. The currents through the samples grow linearly with increasing voltages. The currents for the different samples range from 0 to 1200 nA. The isotropic samples have higher conductivity than the aligned ones. The aligned samples have very similar IV curve, the CBs have a slightly higher current. The difference for the isotropic is much bigger. This might be because the isotropic CNC sample has fewer conducting strings than the CB sample as seen earlier.

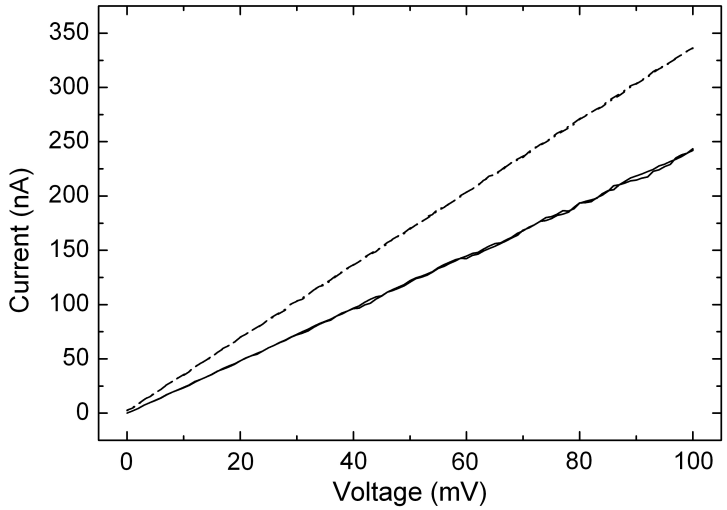

Figure 13: I-V curves of aligned (solid line) with a particle fraction of $\sim$ 0.1 vol-% and non-aligned (dashed line) CNCs with high particle fraction of $\sim$ 13 vol-% in Dymax 3094. The aligned sample had an electrode spacing of 100 μm while the spacing of the isotopic sample was 50 μm. The isotropic sample has larger currents than the aligned one.

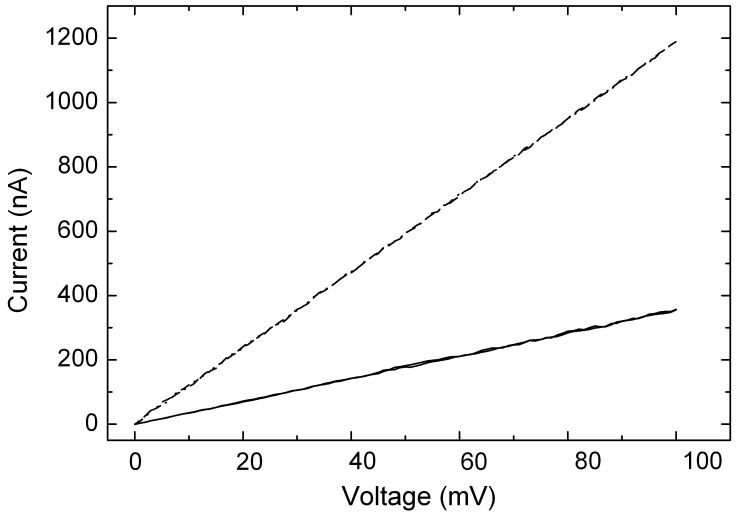

Figure 14: I-V curves of aligned (solid line) with a particle fraction of $\sim$ 0.1 vol-% and non-aligned (dashed line) CBs with high particle fraction $\sim$ 12 vol-% in Dymax 3094. The aligned sample had an electrode spacing of 30 μm while the spacing of the isotopic sample was 50 μm. The isotropic sample has larger currents than the aligned one.

Impedance and phase angle vs. frequency

The impedance and phase angle vs. frequency results of aligned samples and non-aligned high particle fraction samples are shown in Fig. 15 and Fig. 16. The aligned and isotropic samples behave very similarly when the frequency is increased. The difference in impedance of the aligned CBs is about twice that of the aligned CNCs. The phase angles are nearly identical for the different particles and concentrations.

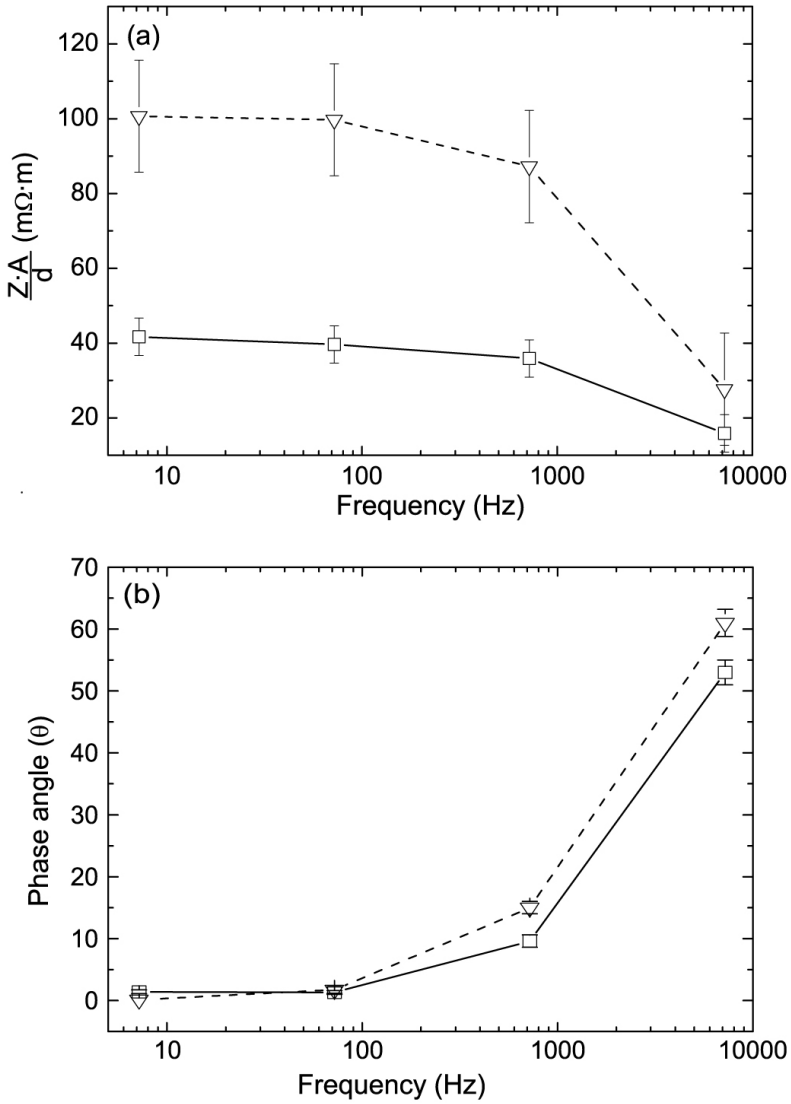

Figure 15: AC impedance data of aligned CNC strings (squares) and isotropic CNCs with high particle fraction in polyurethane based Dymax 3094 polymer (triangles). (a) Impeditivity as a function of frequency. (b) Phase angle as a function of frequency.

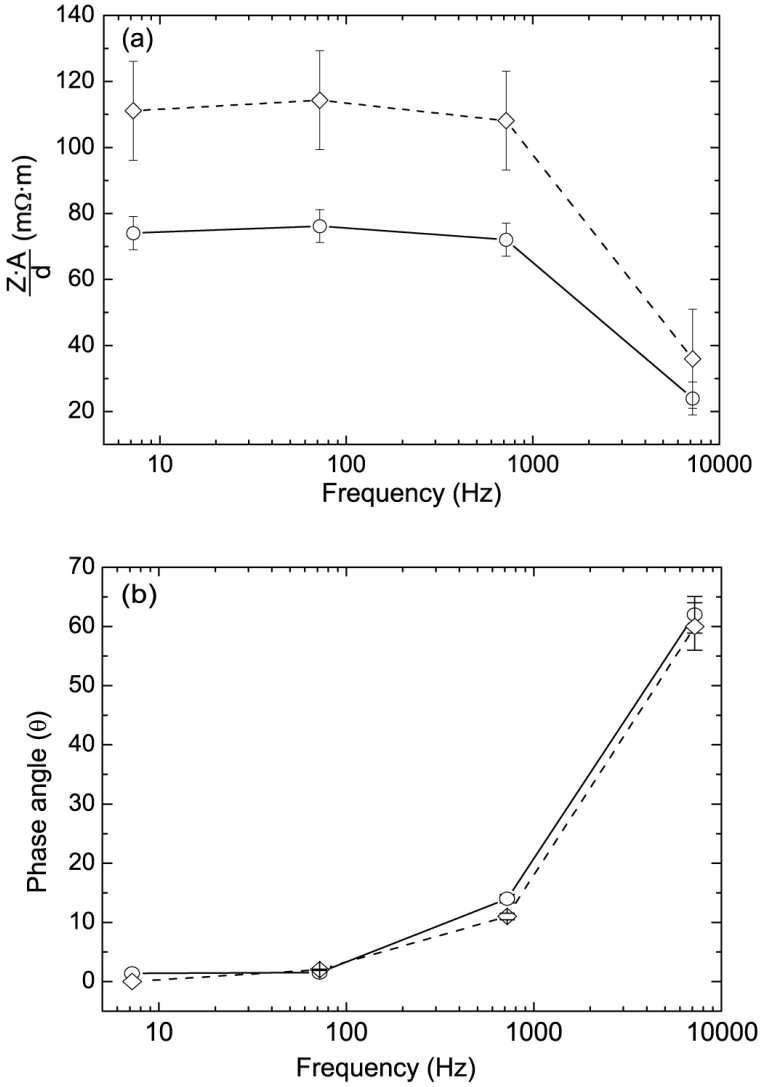

Figure 16: AC impedance data of aligned CB strings (circles) and isotropic CBs with high particle fraction in polyurethane based Dymax 3094 polymer (diamonds). (a) Impeditivity as a function of frequency. (b) Phase angle as a function of frequency.

4.2 Electromechanical properties of aligned strings

4.2.1 Bending single strings in polymers.

Bending of the single strings were studied next, see Fig. 7(B). A micrograph of a single string of CNCs in Dymax 3094 after UV-curing can be seen in Fig. 17. An electric field of E = 4 kV/cm was used and resulted in an aligned string with the resistivity of $\rho = 33\ m\Omega \cdot m$. The electrode spacing was 100 μm. Exactly this sample was used for the bending experiment corresponding to the data shown in Fig. 18. This single string contained about 30 particles with sizes ranging from 1-5 μm. The single string had a length of $\sim 125 \mu m$.

The strain of the bent strings were calculated. The expression strain = 20 $\cdot$ deflection was obtained and values of the strain for deflections from 0 to 100 μm were calculated. Similar calculations were made using a simulation package COMSOL. From these caculations the relation became strain = 17 $\cdot$ deflection. Since the calculations done in COMSOL were more deemed accurate, the latter relation for the strain was used. The same deflection of a cantilever and a doubly-clamped beam, with similar height and thickness, causes a 8 / 1,5 $\approx$ 5 times higher surface strain in the doubly-clamped beam than in the cantilever.

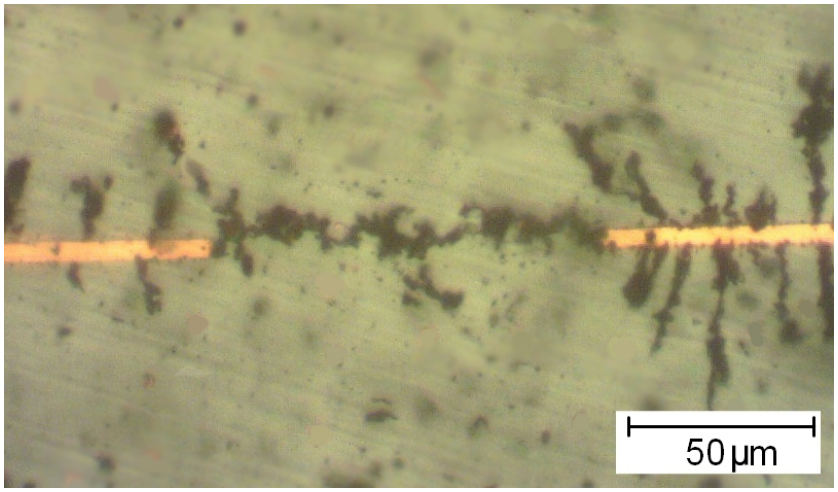

Figure 17: A single string of CNC particles after UV-curing in Dymax 3094.

Bending single strings in UV-curable polymer

By bending the same sample multiple times and measuring the resistivity for every deflection the reversible effect shown in Fig. 18 and Fig. 19 was obtained and represent CNCs and CBs in Dymax 3094. Each resistivity was calculated by fitting from separate IV curves. This method is justified by the omhic behavior of strings for DC and low measurement frequencies (Figs. 15 and 16). The top axis shows the strain of the strings and is of the order of 0.01 % to 0.1 %.

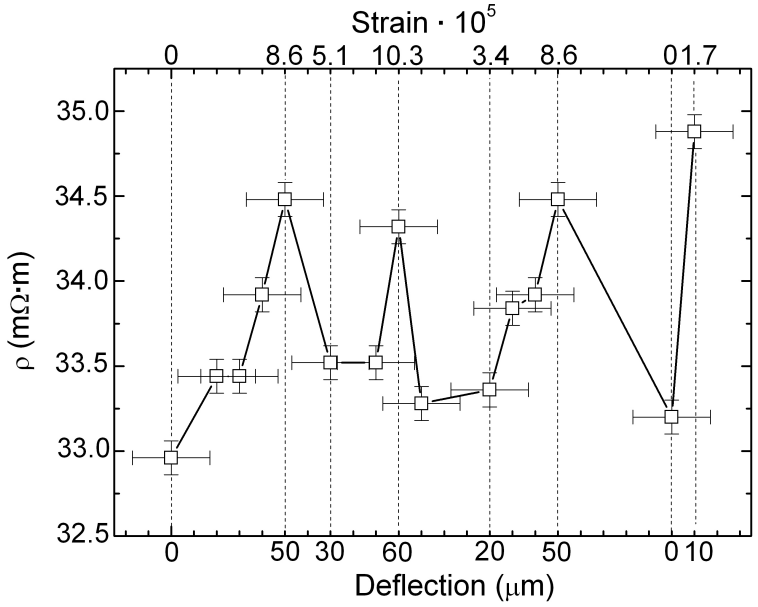

Figure 18: Resistivity of an aligned single string of CNC particles in Dymax 3094 as function of deflection. Bending was repeated 4 times and a reversible change in resistivity was observed. The dotted lines mark the change of deflection direction. The measurements were carried out in a continous fashion so that the measurement was continued with the same sample after each deflection - release cycle. These data were obtained from the sample shown in Fig. 17.

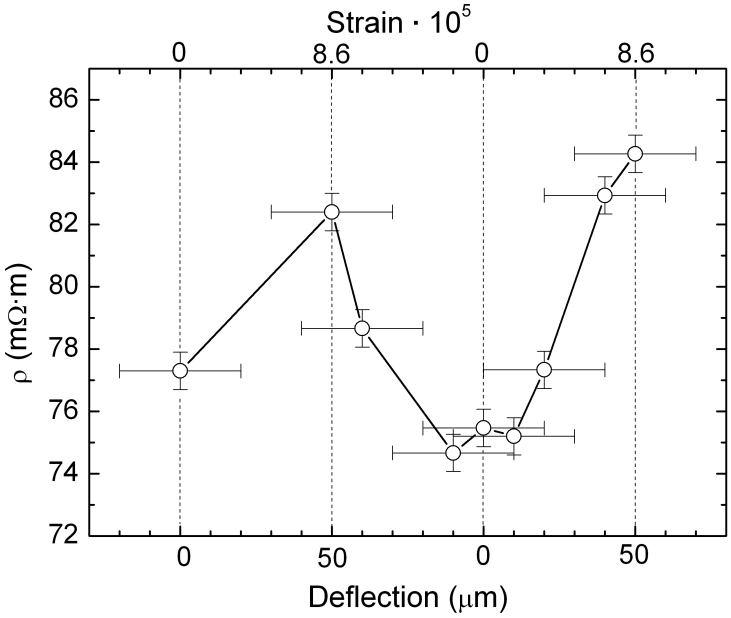

Figure 19: Resistivity of an aligned single string of CB particles in Dymax 3094 as function of deflection. Bending was repeated 2 times and a reversible change in resistivity was observed. The dotted lines mark the change of deflection direction. The measurements correspond to two subsequent deformation - release cycle of the sample.

The vertically dotted lines mark the change of deflection direction. When the deflection goes from 0 to 50 to 30 in Fig. 18, for example, it means that the sample was bent from a relaxed state at 0 deflection to a bent state at 50 μm and relaxed to a less bent state at 30 μm. These measurements were done continuous with the same samples.

The relative change in resistance of the CNCs and CBs in Dymax 3094 are depicted in Fig. 20 and Fig. 21 respectively. The data correspond to the first and second deflections as well as the first releases of the samples.

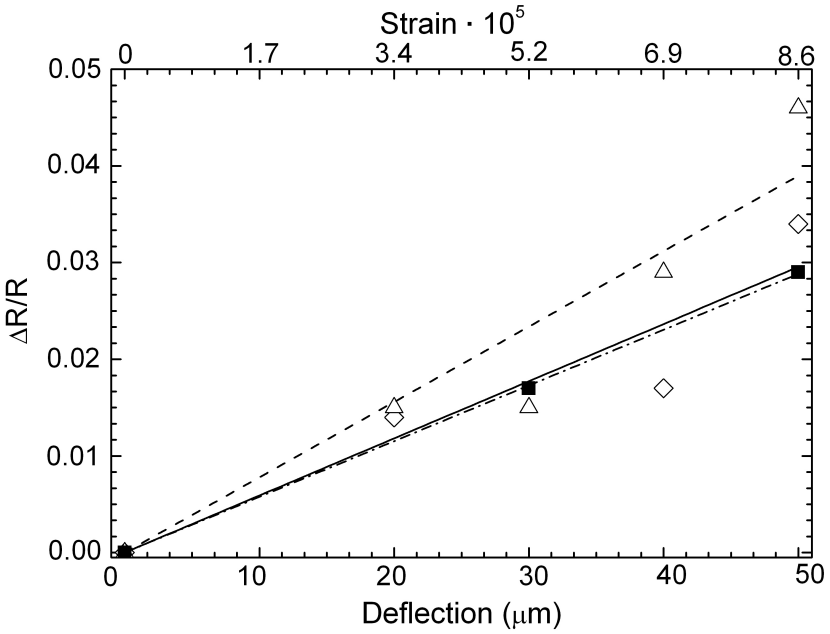

Figure 20: The relative change in resistance as a function of deflection for CNC particles in Dymax 3094. The open triangles show the first deflection while the open diamonds represent the third deflection. The data correspond to those shown in Fig. 18. The solid squares show the first release. Dashed, dash dotted and solid lines are corresponding linear fits.

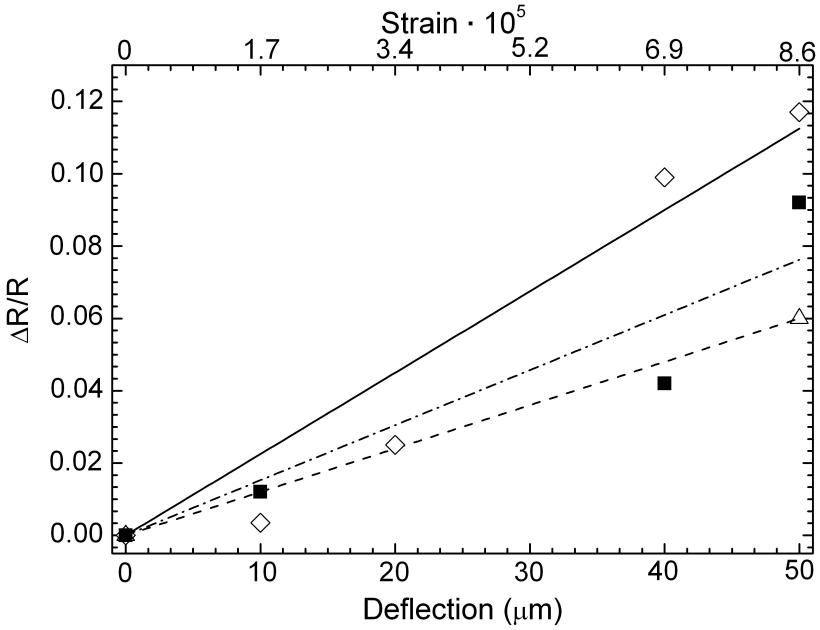

Figure 21: The relative change in resistance as a function of deflection for CB particles in Dymax 3094. The open triangles show the first deflection while the open diamonds represent the third deflection. The data correspond to those shown in Fig. 19. The solid squares show the first release. Dashed, dash dotted and solid lines are corresponding linear fits.

The deformed samples show little sign of getting fatigued after the two first deflections, especially the CNC strings. The CB sample have nearly three times as a high value of the relative change in resistance. The gauge factors were calculated using Eq. 7 and the following results were obtained.

Gauge factors:

The measured gauge factors for the CNC and CB strings in Dymax 3094:

$K_{CNC} = 50 \pm 9$

$K_{CB} = 151 \pm 18$

Bending single strings in humidity-curable polymer

The conductivity of the aligned strings in the humidity-curable polymer Dow Corning 734 could not be detected using our instrument. By instead using AC currents the strings proved to act like capacitors. The capacitance was measured as a function of deflection as shown in Fig. 22 and Fig. 23 for CNCs and CBs respectively. The measurements were also here continuous. The strain is shown at the top axis. The capacitance values are in the order of 0.1 nF.

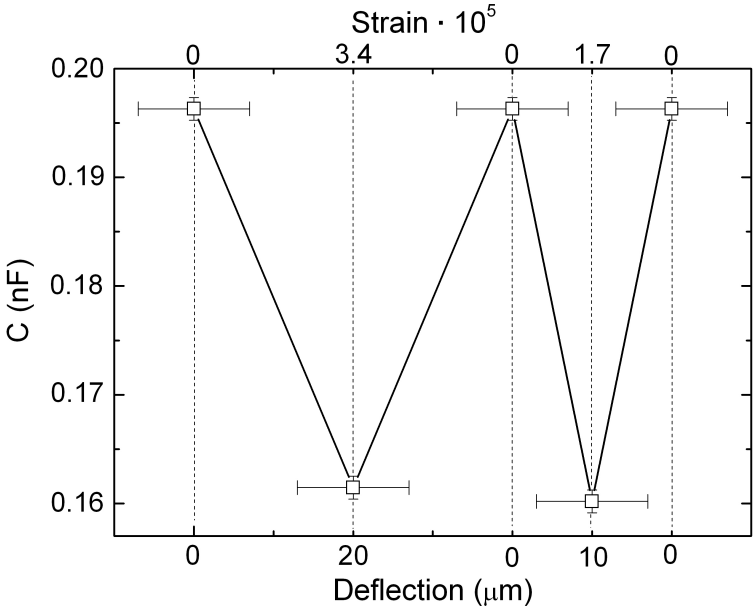

Figure 22: Capacitance as a function of deflection of aligned CNC particles in the humidity-curable polymer. The electrode had a spacing of 100 μm.

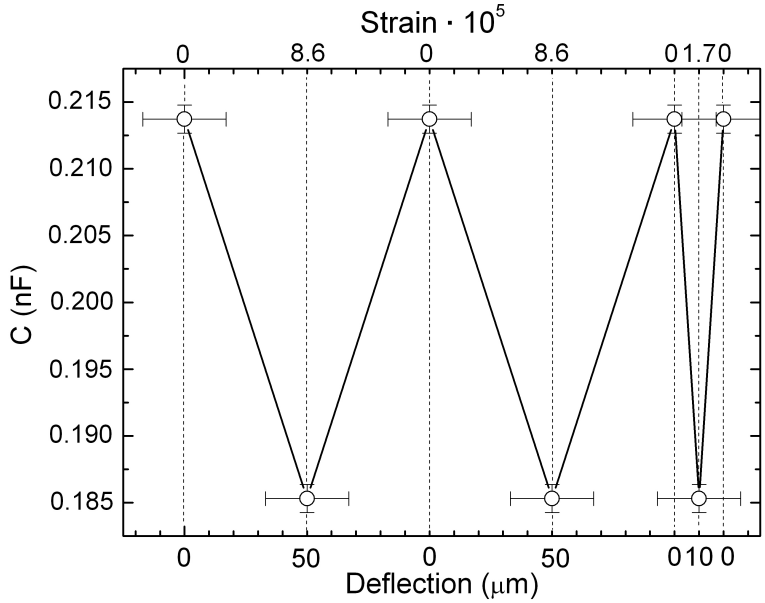

Figure 23: Capacitance as a function of deflection of aligned CB particles in the humidity-curable polymer. The electrode had a spacing of 30 μm.

A reversible decrease in capacitance was observed when the samples were bent. The maximum and minimum values where fairly stable. This makes these samples usable as switches where for instance the maximum values mean "on" and the minimum value mean "off". The CNCs had a max. value of 0.1963 nF and a min. value of 0.16145 nF. The CBs had a slightly higher max. value of 0.21372 nF and a min. value of 0.1853 nF.

4.2.2 Compression of aligned strings

By compressing the electrodes with an aligned polymer situated in between one gets a reversible decrease in resistance as seen in Fig. 24. This situation corresponds to the situation shown in Fig. 7(C).

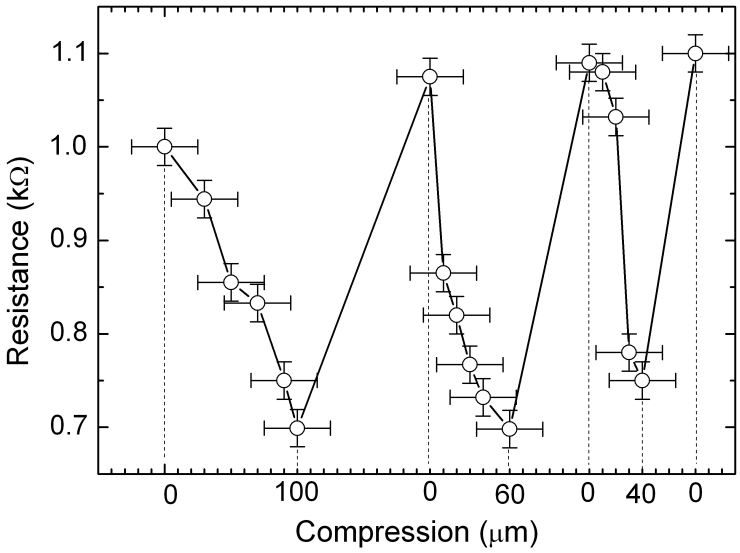

Figure 24: Resistance versus compression of out-of-plane aligned CB particles in Dow Corning 734. The electrode had a initial spacing of $\sim$150 μm. The data corresponf to the three subsequent compressions.

5 Discussion

Single strings of CBs and CNCs were produced by alignment in an electric field. The aligned CBs had a lower conductivity than the CNCs. The conductivity of the aligned CB particles fell in the range of from 1 to 6 S/m. Sánchez-González et al. [47] studied the conductivity of CB particles under compression and reported conductivities of 7-38 S/m at 25 kPa and 44-251 S/m at 742 kPa. The order of magnitude at 25 kPa is similar to the conductivity level obtained here, illustrating how alignment may lead to good particle contact akin effects induced by moderate compression.
Fig. 12 shows a non-conducting CNC string and a conducting CB string. The electrode spacing for the CNC and the CB strings was 20 μm and 30 μm, respectively. This difference in spacing is too small to explain the large difference on the conductivity of the particles. The CNC string in Fig. 12(a) appears visually complete and should therefore be conductive. A reason for this difference may stem from the particle topology. Another reason may be the polydisperse nature of the CNC particles as seen in Fig. 5. The cones and disks might have difficulties creating good connection between each other due to the shape of the cones.

The conductivity of an intact string provides an estimation for the uppermost conductivity of the earlier reported multi-string samples. As the former is higher (for CNCs 1-100 S/m, see Fig 11) than the conductivity of multi-string samples normalized to the volume fraction of particles (0.1-1 S/m) [48], this indicates that a large partition (at least tens of percentages) of seemingly intact strings in the multi-string samples are actually broken. This fact is also seen when considering individual strings whereby about 50 % of seemingly intact CNC strings are actually insulators. The conductivity gap between single strings and multi-string samples could

be potentially reduced by optimizing the preparation of larger samples for example using even and vibration free preparation setups.

Gammelgaard et al. [30] report of a very similar relative change in resistance for their SU-8 polymer composite with CB as what we got. Note that the relation between strain and given deflections are not the same between these two cases. Which is due to the difference in the experimental configuration used in our projects. They use a simple clamped setup, while we use a double clamped setup. In the setup used by Gammelgaard et al. a certain deflection of its end point would lead to a surface strain that it significantly lower than the surface strain induced in a doubly-clamped beam with similar dimensions deflected by the same distance. We therefore induce significantly more strain with the same deflection which is also why our gauge factor is much higher. The gauge factors obtained by Gammelgaard et al. were in the range of 15-20 while we obtained ~ 150 for CB in Dymax 3094, as calculated from Eq. 7.

In our work, the strain was calculated at the top surface of the substrate, and then we assumed that the strain experienced by the composite layer, string of particles, was the same. This is only correct if the composite layer thickness is well below the substrate thickness, but this condition was fulfilled in our experiments. So the gauge factor represents aligned composite and not the composite with the substrate. This difference cannot be explained by experimental error.

Generally speaking, a gauge factor of 150 is high compared to metal materials which have gauge factors in the order of 10. But not that high compared with single-walled CNTs which can have gauge factors in the range 500-1000 [49].

The strings in the humidity-curable polymer Dow Corning 734 stopped being conducting to DC currents after the curing. The reason for this was probably that the polymer released acetic acidic gases when it cured which may have caused small gaps in between aligned particles.

The current-voltage curves showed the same effect for both CBs and CNCs, the isotropic samples had higher current values than the aligned sample. This is expected since the isotropic samples consist of multiple conducting strings while the aligned sample only consist of a single one. Bending the samples show a reversible effect in both resistivity and capacitance. This reversible effect seen is a good indication that the aligned single strings can be used as strain sensor on for instance an AFM cantilever.

Compressing the out-of-plane aligned sample gave reversible change in resistance. This is most likely because a number of strings are not completely aligned through the whole sample. By compressing the sample some of the incomplete strings will be completed and therefore conducting and a decrease in resistance is observed. When the sample is relaxed some of the strings will be incomplete once more and one gets an increase in resistance. This reversible effect is observed and can be potentially utilized in touch screen applications.

The results were qualitatively similar to those obtained for piezoresistive isotropic CB SU8 polymer composite investigated by Gammelgaard et al. The alignment investigated here allows, however, the use of orders of magnitude lower particle fraction, which may be beneficial if exceedingly expensive particles are employed. The cheapest CB particles from Alfa Aeasar cost about €42 for 250 mg, while the cheapest CNTs cost €7570 for 250 mg. The materials combination demostrates also higher gauge factors and thus higher electrical sensitivity as a function of mechanical deformations. These facts may have implications in potential commercial applications of alignment methodology introduced in this thesis.

6 Conclusion and outlook

In conclusion, single strings of aligned carbon particles in polymers matrices have been shown to make good candidates as strain sensors. CNCs and CB particles were aligned in two different polymers, one with glass transition temperature above and one below room temperature. CNC string proved to have higher maximum conductivity than the CBs but the aligned CNC strings had a smaller probability of being conducting in the first place. By bending these single strings in-plane a reversible effect in resistivity and capacitance was observed, similar to what was reported by Gammelgaard et al [30] for non-aligned high particle fraction material. However, gauge factors of 50 and 150 were found for CNCs and CBs, respectively, these values exceeding the values (15-20) reported by Gammelgaard et al. This means that the sensitivity of single strings exceeds that of the system reported by Gammelgaard et al. Strings aligned out-of-plane showed a reversible effect in resistance when they were compressed. The alignment allows the use of low particle fraction which renders material fairly transparent. This may turn valuable if the strings were used in touchscreens.

The future studies should include investigating other materials with different properties and experiment with the particle concentrations. By having even lower particle concentrations it might be possible to make true single particle strings. Such strings might be more sensitive with bending and the ON/OFF ratio might be improved. They would also provide understanding of the particle-particle interactions and contact points. Using direct imaging by means of scanning or transmission electron microscopy for investigating deformed CNC strings would most likely give a further insight over their electromechanical properties.

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