Parallel integration of aligned carbon strings in polymer composite: Dielectrophoretic preparation, finite element simulation and electrical characterization

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We report on dielectrophoretic alignment of carbon black particles into radially arranged string-like assemblies in oligourethane mixtures followed by photopolymerization. Using finite element modelling and optical microscopy we find significant difference in field distributions depending on the substrate beneath aligned films. On glass, the field is concentrated between the electrode tips leading to string-like assemblies between the tips. On oxide covered silicon, the field is distributed along the electrode circumference leading to more distributed fractal assemblies. Using comprehensive dc resistance measurements and ac-impedance spectroscopy we show that the resistance of the strings varies from 120 kΩ to 5 MΩ with a mean of 1.03 MΩ. Strings on oxide covered silicon show significantly higher resistances than the strings on glass. We also demonstrate the effect of aging and an increase in resistance through elongating aligned strings.
INTRODUCTION

Particle manipulation [1] and composite anisotropy [2] are ubiquitous topics in composites fabrication [3]. Solid particles dispersed in a fluid can be manipulated by the dielectrophoretic effect if the dielectric properties of the particles differ from those of the surrounding fluid [4, 5]. This effect is caused by an alternating non-uniform electric field such that particles will be either attracted to or repelled from areas of higher field gradient. If the viscosity of fluid is sufficiently low, this gradient leads to the movement of the particles and diverse assemblies depending on the dielectric properties, particle density and field distribution, which is determined by electrode geometry but modified by growing particle assemblies.

Smith et al. [6] pioneered the dielectrophoretic alignment of metal particles while Lumsdon and Scott [7] introduced the same for colloidal particles. These authors performed alignment in solvent which was evaporated off thus setting particles in place on top of the substrate, while Prasse et al. [8, 9] and Schwarz et al. [10] were the first to align carbon black (CB) particles in an oligomer fluid followed by polymerization which locks the particles in place in a polymer matrix. In the following years the idea of aligned carbon was studied further [11] and extended to graphite sheets [12], carbon nanotubes (CNTs) [13-16] carbon fibres [17, 18] and carbon cones [19]. Common for all these reports is the use of an initial particle fraction much below the percolation threshold of the isotropic mixture, and thus initially electrically insulating mixture, and a conductivity jump due to the aligned strings forming conductive pathways through the polymerized matrix. Thus, one application of the dielectrophoretic effect is the formation of conductive strings in a polymer film forming an alternative to
electrospinning [20]. The applications of particle dielectrophoresis cover thermally
sensing polymer composites [21], among other things [22].

A piezoresistor exhibits a change in resistance when strained. This term refers originally
to microscopic changes in the bulk material property but the term has been extended for
use to conducting carbon polymer composites [23]. In this case the phenomenon stems
mostly from relative movements of particles while the bulk of the particle remains
primarily intact, as shown for CNT composites by Oliva-Aviles et al. [24].

In our previous paper [25] we investigated dielectrophoretic alignment of CB particles
and the possibility of using an aligned particle string as a piezoresistor, when aligned
between tip-like electrodes forming a bridge clamped on both ends and deflected in the
center. In another occasion, we shown that so prepared CB and carbon cone strings
show significant electrical differences, their inherent resistance varying between 0.1 and
100 MΩ [26]. These differences have not been quantitatively characterized,
representing an obstacle in their wider use.

Burg et al. [27] used single-walled nanotubes (SWNTs) to make a two-dimensional
piezoresistor. These authors employed an electrode configuration where SWNTs were
bridged between parallel, radially arranged electrode pairs, each set consisting of 19
pairs. This configuration was used not only as a sensor but also as an indirect research
tool to measure connection success in bridging. For example, they reported 20-30 %
successful bridging with SWNTs.

In this paper, we investigate CB strings, by combining these concepts --- the
dielectrophoretic alignment of CB particles and the parallel integration of carbon
bridges. The paper has two objectives. First, alignment of CB strings on a radial
electrode pattern is tested, and a quantitative analysis of their electrical properties is
presented, both on glass and oxide covered silicon substrate, and a tentative electromechanical characterization is shown. Simulations indicate clear differences in field distributions depending on the substrate type, leading to significant differences in the experimental observations. On glass, the field is concentrated in between electrode tips leading to the string-like assemblies between the tips. On oxide covered silicon, the field is distributed along the electrode circumference leading to more distributed fractal assemblies. Second, while the prior literature describes CB alignment as a function of diverse alignment parameters \[28\], we study CB strings using as identical alignment conditions as possible. A significant variation in resistance is observed even in the case where the alignment process is carried out using an experimental setting where macroscopic particle fraction, viscosity, field strength and alignment and curing times are exactly replicated from string to string. We suggest that this variation stems from the local variations in initial particle fractions and locally changing field strengths influenced by the growing strings.

**SIMULATION**

The electric field distributions in the two different device configurations were deduced from finite element calculations using the Electrostatics modelling that is a part of the AC/DC module in COMSOL MULTIPHYSICS 4.3. The employed configurations are illustrated in Fig. 1. The first configuration was simulated assuming a glass substrate with two gold electrodes of each 5 μm width and 0.07 μm height separated by 30 μm (Fig. 1(a)). The second configuration used a doped silicon substrate covered with a 0.1 μm thick layer of silicon dioxide and with two gold electrodes of the same dimensions as for the first device (Fig. 1(b)). The calculations were made with \(2 \times 10^7\) tetrahedral mesh elements for both configurations. The simulations were made by applying a
potential difference of 12 V between the two electrodes. The finest mesh was used in the vicinity of and in the gap between the electrodes with a maximum element size of 0.2 μm.

EXPERIMENT

Materials

The CB powder from acetylene (Alfa Aesar) had a room temperature density ca. 2.0 g/cm³ and consisted of spherical CB particles (diameter 100 nm) which formed further agglomerates (diameter of 400-500 nm). The polymer precursor was Dymax Ultra Light-Weld 3094 (Dymax Corp.) polyurethane oligomer mixture with the nominal room temperature viscosity of ~1,000 cP. Mixing of particles and oligomer mixture was carried out with a magnet stirrer at 160 rpm for at least 30 min, which led to an isotropic dispersion where the size of nearly all particles or particle clusters was below 1 μm. The particle concentration was 0.1 vol. %.

Electrical Alignment Procedure

Alignment electrodes used in the experimental work corresponded to the configurations used in the above-described simulations. The electrodes were 70 nm thick consisting of subsequent layers of titanium (10 nm) and gold (60 nm) and were made on glass and SiO₂ covered silicon substrates using photolithography. The glass was 510 μm thick.

The highly doped silicon substrate (Sb doping, resistivity ~ 0.005-0.020 Ω·cm) was 160 μm thick covered by 100 nm thick insulating SiO₂ layer.

The electrode geometry, Fig. 2(a), was adapted from Burg et al. [27]. Each electrode pattern consisted of a set of electrode pairs organized in a radial manner with 15 electrode pairs pointing towards the center of a circle. The diameter of the circular part of the inner electrode was 100 μm, and the distance between the electrode tips was 30
μm. The electrode width was 5 μm, thus exceeding the typical initial particle size. In this geometry, the inner electrode could be individually connected and could serve as a common electrode for the 15 gaps formed towards 15 opposing electrodes each connected to individual contact pads thereby making separate measurements of individual strings possible.

For the electric field alignment, an approximately 10 μm thick layer of isotropic 0.1 vol.% particle mixture was spread on the alignment electrodes, Fig. 2(b).

The alignment procedure was carried out by a Trek voltage source, with an alternating 1 kHz field with the field strength at around 4 kV/cm. This leads to the formation of chain-like carbon strings between electrode tips, Fig. 2(c). After alignment, the Dymax oligomer mixture was cured with UV light for 80-120 seconds. For comparison, similar cured films were prepared from 0.1 vol.% and 12 vol.% particle dispersions and from pure oligomer fluid without exposing them to electric field.

Electrical and Electromechanical Characterization

For comparison, electrical properties were characterized for aligned 0.1 vol.% CB samples and isotropic 0.1 vol.% and 12 vol.% samples, pure polymer and empty electrode chip, all with identical electrode configuration. Initial resistances were measured using Fluke 179 and Keithley 2000 multimeters and also determined from the current-voltage (IV) curves measured using an NI PCI6229 DAQ device by sweeping the voltage through the sample from zero to 0.5 V and back. The source current was measured with a SR570 current amplifier connected to the DAQ card. The AC impedance was characterized with a SR830 lock-in amplifier.

Impedance and phase angle were measured for each of the electrode pairs on both substrates which were connected to the lock-in amplifier via tungsten tips. An AC
voltage of 10 or 100 mV (RMS value) at different frequencies was applied and values for the current and phase angle measured. To minimize capacitive effects from the silicon, the backside of the SiO$_2$ covered silicon substrate was grounded through the metal sample holder. Conductance $\sigma$ was estimated from the measured resistances $R$ using the formula $\sigma = (d/A)(1/R)$. The cross-sectional area of strings, $A$, was assumed to be 30 $\mu$m as estimated from the width of the electrode (~3$\mu$m) and the thickness of the film (~10 $\mu$m). The distance between electrode tips $d$ was measured to be 30 $\mu$m.

A tentative electromechanical characterization of the strings was carried out by bending the substrate while monitoring the impedance through the strings. The silicon chip was held in place by clamps on both sides of the chip. The chip was bent using a sharp metal blade that was placed below the chip, perpendicular to the chip surface, having the sharp edge just below the middle point of a studied string as illustrated in Figs. 2(d) and (e). The movement of the strip was controlled by a micrometer screw. The electrodes connected to the studied string were connected to the micromanipulator tips that were further connected to the measurement instruments. The strip was then moved upwards 5 $\mu$m at a time, bending the silicon chip up to 30 - 45 $\mu$m and impedance and phase angle, as well as IV-curves, were measured for each displacement.
RESULTS AND DISCUSSION

Materials

Fig. 3 shows an optical micrograph of isotropic 0.1 vol.% mixture of CB particles in oligomer mixture. The mixture appears visually as a relatively uniform dispersion such that the particle cluster size is always well below 5 μm, which is the width of the alignment electrodes, and much below the electrode spacing. This was taken as a topological prerequisite for forming well-developed CB strings. The particles are not forming networks.

Electric Field Distribution

Fig. 4 shows the magnitude of electric field between one electrode pair for glass (Figs. 4(a) and (b)) and SiO₂ covered silicon substrates (Figs. 4(c) and (d)) corresponding to the setting shown in Fig. 1. Figs. 4(a) and (c) represent field distributions at 140 nm above the substrate surfaces. In the center between the two electrodes, the glass substrate exhibits a field strength of more than 10 kV/cm, while the field strength is below 1 kV/cm for the silicon substrate. When the substrate is insulating, the field is primarily located in between electrode tips, modulated by the electrode shape (Figs. 4(a)). In contrast, when the conducting substrate is covered by a thin insulating layer, the field is located along the electrodes and the peak values are not found in between the electrode tips (Figs. 4(c)). Figs. 4(b) and (d) indicate that the fields out-of-plane are approximately as strong as in-plane. They also imply that significant field exists out-of-plane across the experimentally studied 10 micron thick film.
**Electrical Alignment**

The alignment process was studied with electrodes prepared on two different substrates, glass and silicon covered by SiO$_2$. The process was optimized first on glass since this allowed easy optical inspection and the optimized parameters were subsequently applied to alignment on the silicon substrate. The silicon substrate was then employed for studying electromechanical properties, since this substrate, and thus the strings, could be bent slightly more before breaking than using the glass substrate.

Figs. 5(a)-(c) show micrographs of the alignment process on the glass substrate, from the beginning to 11 minutes alignment time. The dispersion contained 0.1 vol.% CB particles and the strength of the applied 1 kHz field was 4 kV/cm. Fig. 5(d) shows a magnified micrograph of an individual string. Fig. 6(a)-(c) shows micrographs of the alignment process on the silicon substrate covered by insulating SiO$_2$ layer. Fig. 6(d) shows a magnified micrograph of an individual string. The 11 minutes alignment time is of the same order of magnitude as reported before for CB in the oligomer mixture of similar viscosity and field strength in the 3-dimensional alignment configuration [10].

Strings on glass are predominantly linear corresponding to the earlier observations but the strings on silicon become branched and typically contain more than one bridge between electrode gaps [25]. Moreover, on glass most particles align in the gap between the electrodes, while on oxide covered silicon particles align between the electrodes but also in small fractal aggregates perpendicular to the electrodes.

The reason for this difference is attributed to the conducting silicon layer underneath the insulating layer of SiO$_2$ on which the electrodes are attached. As indicated by the simulated electric field (Fig. 4(b,d)), this configuration results in a modification of the
electric field between the electrodes compared to the glass substrates when an
alternating voltage is applied. The more complex field structure still results in particles
assembling between the electrodes.

*Electrical and Electromechanical Characterization*

Electrical characterization of the cured films was carried out for the visually intact
samples. Resistances through the samples were first measured using a multimeter.
Before the field was applied, the resistance across the electrode gaps was too high to
measure using our instruments (> 100 MΩ). This is plausible since the conducting
particles are not connecting electrodes or each other in the insulating polymer matrix.
However, after alignment the strings showed measurable resistances. In order to
simplify the classification of the prepared strings, we denote every string displaying
resistance below 5 MΩ as conducting and the others as insulating. The strings on glass
were predominantly conductive as expected for strings forming continuous bridges
between the electrodes. In contrast, only a few branched strings on silicon were
conductive, even though apparently forming several bridges between the electrodes.
They showed resistance around 20 MΩ or more.

The current-voltage (IV) curves and phase angles were subsequently measured for all
the samples. The impedance was found by dividing the voltage amplitude with the
absolute value of the current. Fig. 7(a) shows an example of a DC measurement of one
of the conducting strings on glass substrate. The current through the samples was
recorded when sweeping voltage from zero to 0.5 V and back to zero.

Fig. 7(b) shows the frequency dependence of the impedance. The IV-curves were both
linear and reversible upon cycling and the impedance was mainly resistive at the
frequencies below ~1 kHz. This means that the low frequency behavior is Ohmic and
the resistances could be calculated from linear fits of the IV-curves. Since strings on
glass were easier to observe visually, they were studied more closely. Seven samples
with 15 strings were studied, giving 105 strings in total. All the strings looked intact by
visual inspection.

Three of the samples contained only conductive strings with resistances between 0.12
and 5 MΩ, and a mean resistance of 1.03 MΩ. This corresponds to conductivity of
about 0.1 S/m. The other samples had some non-conducting strings. Altogether 65 % of
the strings on glass substrate had a resistance value lower than 5 MΩ. The distribution
of resistances of all the conducting CB strings is shown in Fig. 8.

We propose that the varying conductivity due to the different string patterns is likely
related to the three factors. First, the difference in local particle concentrations before
the field is turned on. Second, how and in what positions the incoming particles move
with respect to the emerging string. Third, how this emerging particle aggregate
influences the electric field by screening.

Since the initial CB polymer dispersion contains enough particles to completely fill the
electrode spacing, the complete filling with perfect particle-particle connection would
represent ideal string with conceptual maximum conductivity. Therefore, the
experimentally observed conductivity should be compared to the conductivity of
pressed bulk CB that ranges from 10-100 S/m depending on the particle quality and the
applied pressure enhancing particle-particle contacts [29]. The conductivities of intact
strings range from 0.1-10 S/m. This means that the conductivity of the best aligned
strings corresponds to the lower end of the reported CB bulk conductivities.

Fig. 9 shows the resistance distribution for all 15 strings on one cured sample,
calculated from the IV-curves like the one shown in Fig. 7(a). When 15 strings are
aligned at the same time on the same substrate, using the same applied voltage, the conditions are macroscopically equal for all 15 strings. Nevertheless, even under essentially identical conditions relatively large variations in resistance are observed. The aligned CB strings show a wide resistance distribution and a sample with 15 strings with a uniform resistance may not be possible to obtain.

If the particle concentration is even, we might expect that neighboring strings would be similar and have more or less the same resistance. However, the data shown in Fig. 9 imply that the string resistance on neighboring strings is not correlated. Since the global particle concentration is presumably constant on the millimeter scale, this implies that the morphological differences and thus resistance variation must stem from local variations on the microscopic, micrometer scale.

The resistance was also measured again three weeks after alignment, and a graph showing the relative change in resistance is shown in Fig. 10. Note that data in Fig. 8 is gathered from 68 strings, while data in Fig. 10 is gathered from 30 strings, all with resistance lower than 5 MΩ. The maximum change in string resistance was always less than 150 %. We interpret these changes as resulting from the curing not being complete immediately after sample preparation but evolves with time and influences microstrains, which may either squeeze or pull particles apart, leading to a decrease or increase, respectively, in the overall resistance. We expect that an individual string will remain Ohmic with time. This was indicated by AC impedance measurements showing purely resistive impedance up to 1 kHz (see Fig. 7(b)).

In order to demonstrate that the strings that were formed in these samples have similar piezoresistive properties to the individual CB strings described by us in Ref. [25], the strings were stretched by deflecting the silicon substrate. In this procedure the sample
was mounted such that the investigated string was oriented perpendicular to the triangular metal piece inducing the bending from below the substrate as indicated by an arrow in Fig. 2(d). A small test voltage was applied across this string and the values of current and phase angle were simultaneously recorded. For comparison, the same test was carried out with an isotropic CB polymer film with 12 vol.% particle fraction, which means safely above the percolation threshold of isotropic CB mixtures [30].

The applied AC voltage was 10 mV at 1.4 kHz for the well conducting, isotropic 12 vol.% CB, and 100 mV at 1.4 kHz for the other samples. The different test voltages were used since vastly different conductivities of tested samples did not allow similar measurement protocol. However, even this measurement illustrates the qualitative difference between isotropic and aligned samples.

Fig. 11 shows the current as a function of deflection for two CB strings on different silicon chips as well as for the isotropic 12 vol.% sample. The current through the aligned strings is significantly influenced by deflection, while isotropic samples show a smaller relative effect. These data do not allow calculation of gauge factor but demonstrate that the strings formed using radial electrode geometry are sensitive to stretching and thus qualitatively have similar properties to those reported before by us for a single-electrode setup [25].
CONCLUSIONS

This study shows the parallel integration of aligned CB strings in a two-dimensional geometry, consisting of 15 radially placed electrode pairs. Strings were aligned from isotropic CB - oligomer mixture with 0.1 vol. % particle fraction using a 1 kHz alternating 4 kV/cm electric field; and locked in place by subsequent photopolymerization of the oligomer matrix. Significant difference in field distributions was found for the two alignment substrates. On glass, the field is concentrated in between electrode tips leading to the string-like assemblies between the tips. On oxide covered silicon, the field is distributed along the electrodes leading to fractal assemblies. In one experiment seven identically prepared samples with 15 electrode pairs on each sample on glass substrates were compared. Three samples had 100 % electrical connectivity and Ohmic in nature with all strings having resistance below 5 MΩ. In the other four samples, a total of 38 % of the strings were connected, showing a resistance below 5 MΩ. The strings remain Ohmic but their conductivity is moderately altered when aged for three weeks' time. Electromechanical measurements of the strings on silicon substrate showed evidence for piezoresisitive changes on stretching. Local structure variations in the string growth stem presumably from differences in locale particle concentration before the field is turned on, from how the incoming particle move with respect to the aggregate, and from how the string or aggregate modifies the electric field. This may be explored in further studies. Furthermore, using additional anisotropic particles might bridge the gaps between aligned nearly spherical CB particles and improve connectivity as shown elsewhere for bulk composites [2].
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REFERENCES


FIGURES

FIG. 1. Schematics of alignment electrodes used in simulations. The electrode patterns on glass (a) or silicon substrate covered by insulating SiO$_2$ layer (b). Not drawn to scale.
FIG. 2. Schematics of alignment procedure.  (a) The electrode pattern deposited on substrate.  (b) CB - oligomer mixture spread on the electrodes.  (c) Aligned CB strings between electrodes after electric field treatment and polymerization of matrix.  (d) Bending of silicon substrate with aligned strings.  (e) Setting to measure strings individually.  Not drawn to scale.
FIG. 3. Isotropic mixture of CB particles in oligomer fluid.

FIG. 4. (a-b) Simulated magnitude of the electric field on glass substrate and (c,d) on conducting silicon substrate covered by insulating SiO$_2$ layer. The distributions (a,c) are along the surface normal, cut at 140 nm above the substrates and thus 70 nm above the electrodes. The distributions (b,d) are shown perpendicular to the electrode tips and the surface normal.
FIG. 5. Electric field alignment on glass substrate.
FIG. 6. Electric field alignment on conducting silicon substrate covered by SiO$_2$ layer.

FIG. 7. (a) IV-loop and (b) impedance for one aligned CB string on glass substrate.
FIG. 8. Resistance for 68 conducting CB strings on glass substrate.

FIG. 9. Resistance of aligned strings on one alignment substrate with 15 simultaneously used electrode pairs, counted clockwise around the electrode configuration.
FIG. 10. Relative change in resistance in 30 CB strings between measurements immediately after curing and after three weeks aging period.

FIG. 11. Relative changes of current as a function of deflection for two different aligned carbon strings on silicon substrate (black squares and red circles). Also shown are corresponding data for non-aligned film with 12 vol. % carbon loading (cyan diamonds).