

# Self-assembly of wires in acrylate monomer via nanoparticle dielectrophoresis

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## Abstract

This study investigates morphology and bulk growth rate of wires using dielectrophoresis in non-aqueous suspensions of carbon black nanoparticles dispersed in a diacrylate monomer. Growing anisotropic structures in adhesives to enhance thermal or electrical conductivity is highly desirable for many applications including semiconductor packing. As in aqueous suspensions, the wire growth threshold and growth rate depend on applied voltage and electrode separation. While assembly rate depends less on applied frequency than other field aspects, the morphology of assembled wires transitions from linear to fractal morphology with increasing frequency. Additionally, the wire growth rate in non-aqueous suspensions is temperature dependent and exhibits an upper threshold temperature for wire assembly.

## 1. Introduction

Embedding aligned nanowires into thin films and bulk materials creates materials having anisotropic optical, electrical, thermal and structural properties. Applications of these materials include conductive and non-conductive adhesives, films and underfills for semiconductor packaging and electro-mechanical connections in liquid crystal displays [1]. A significant limitation to the function of these materials is the ability to properly distribute nanoparticles within the epoxy. Often, a percolated network of nanoparticles is necessary to provide proper electrical and/or thermal conductivity at the cost of structural stability of highly particulate-loaded epoxies. High-density, high-precision interconnects are particularly difficult to fabricate. Flow-induced alignment of suspended nanowires achieves anisotropy, but requires high wire volume fractions to ensure a percolated network. Flow-induced alignment presents implementation challenges at the microscale because high volume fraction suspensions of difficult to predict rheology shear thin, thickening and even jam in confined geometries. In dilute systems it is difficult to ensure that fabricated wires actually contact electrodes.

One method to form highly anisotropic structures allowing percolation at low concentrations is through dielectrophoresis. Conductive particles forming dipoles as a result of a non-uniform ac electric field generate

dielectrophoresis. Fundamental studies of self-assembly in using dielectrophoresis nanoparticle suspensions have long been of interest [2, 3] and many fundamental studies focus on tuning rheological properties using electric fields [4, 5]. In addition, dielectrophoresis is commonly used to manipulate, transport, separate and sort particles in MEMS [6]. The dielectric force on each particle is given as [7]

$$F_{\text{DEP}} = 2\pi a^3 \varepsilon_l \text{Re}\{K(\omega)|\nabla(E^2)\}, \quad (1)$$

where  $a$  is particle radius,  $\varepsilon_l$  is the solution permittivity,  $K$  is the Clausius–Mossotti function that depends on the solution and particle permittivities and is a function of field frequency  $\omega$ , and proportional to the gradient of the square of electric field potential  $E$ . Dipole interactions that overcome electrostatic or steric interactions that stabilize the nanoparticles in solution lead to anisotropic particle–particle and particle–electrode aggregation. Positive dielectrophoresis denotes dipole induction within a conductive particle where negative dielectrophoresis is the formation of a dipole through charge transport in the ionic double layer surrounding a non-conductive particle primarily found in aqueous systems. Under certain conditions, when attractive dipole–dipole interactions overcome the forces stabilizing particles in solution, dielectrophoresis performed on a suspension of conductive nanoparticles results in the growth of these

aggregates into wires spanning the electrodes. Two types of wire growth have been previously observed as surface and/or bulk assembly [8,9]. Surface assembly occurs when particles aggregate along a substrate, while bulk assembly refers to 3D assembly in bulk solution. Dielectrophoresis is widely used in dilute suspensions for separations [10] and for depositing wires or carbon nanotubes to form precision interconnects between electrodes to study the wire or CNT physical and chemical properties as well as for assembling nanoscale circuitry for sensors [11]. Potential limitations in the use of aqueous suspensions for wire growth include hydrolysis at high voltages and the weakness and instability of assembled wires. Hydrolysis and agglomeration of particles are avoided in the study of dielectrophoresis with the use of non-aqueous nanoparticle suspensions.

Studies have investigated the growth of wires in epoxies and other polymer melts [12–17]; however, how growth rate scales with electrode spacing and electric field strength and frequency are largely unexplored for these systems. More often the conductivity of a composite film is studied eluding more to the structure and density of wires than the growth rate. This study investigates the growth of wires from a non-aqueous nanoparticle suspension of carbon black in a diacrylate monomer. The mode of wire growth was bulk assembly, as opposed to assembly of wires on a substrate, via positive dielectrophoresis. Scaling properties, which can be extrapolated to the microscale, were determined for growth rate and the threshold voltage of self-assembled wires over relatively large distances. The morphology of the wires is reported and was found to be strongly dependent on signal frequency. These phenomena agree well with previously reported studies in aqueous systems. In addition, growth rate reaches a maximum in temperature and demonstrates an elevated voltage threshold; this is one condition that may restrict the application of this technique with thermal-setting polymers.

## 2. Experimental details

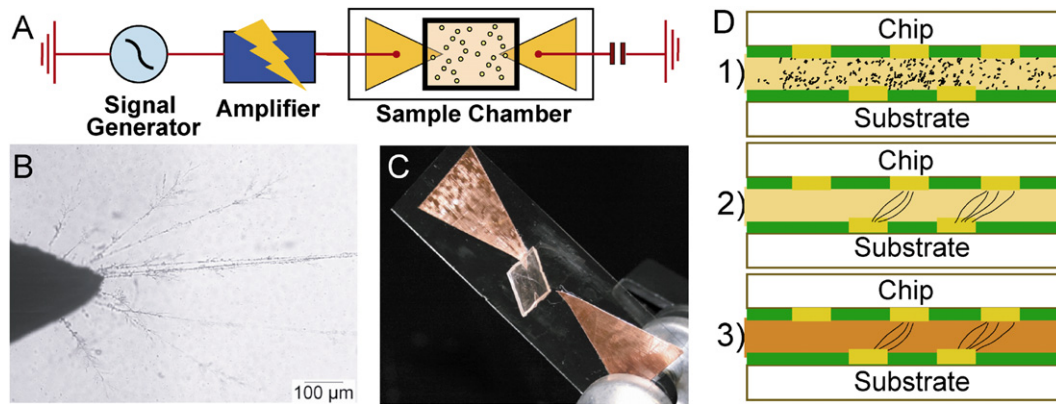
Suspensions of photosensitive monomer with carbon black nanoparticles were used to investigate microwires assembly using dielectrophoresis. The samples in this study consisted of acrylic monomer, photoinitiator and conductive carbon black nanoparticles. The carbon black nanoparticles have median particle diameter of 30 nm as determined by scanning electron microscopy. The volume fraction of carbon black nanoparticles in solution was held constant at  $1.1 \times 10^{-4}$  or  $\sim 10^{13}$  particles mL<sup>-1</sup>. The difunctional monomer ethylene glycol dimethacrylate (EGDA, SR206, Sartomer) was used as received and has molecular weight of 198 g mol<sup>-1</sup> and a viscosity of 6 cP at 25 °C. A general-purpose photoinitiator, 2,2-dimethoxy-1,2-diphenylethan-1-one (DMPA, Irgacure 651) was added to EGDA and used as received from Ciba Specialty Chemicals. Results presented are independent of initiator concentration for solutions that polymerize. The carbon black nanoparticles and a small amount of DMPA (less than 4.0 wt%) were added and dispersed via ultrasonication.

The dielectrophoretic sample chamber was fabricated from copper tape, number 1 glass cover slips, and Parafilm M. Triangular planar electrodes with a thickness of 88 μm were fashioned from copper tape. This geometry aided in characterizing the location of fastest wire growth. The electrodes were fixed to the cover glass using a conductive adhesive with the gap between the electrodes varying from 2 to 30 mm. The well holding the solution between the electrodes consisted of several layers of Parafilm M forming a square cavity that were bonded to the glass cover slip at 90 °C. Once the monomeric solution of nanoparticles was loaded into the sample chamber, electrodes were connected to the electrical circuit outlined in figure 1(a). An alternating electrical field of square waves was applied using an FG-8002 function generator (EZ Digital Co.). The frequency of the square waves was varied between 10 and 10 000 Hz. In order to reach the minimum threshold voltage for wire assembly, an EPA 007-012 piezo linear amplifier was used to enhance the signal from the function generator. The voltage output of the amplifier was measured using a Tektronix TDS 2004B 4 channel oscilloscope and reached a maximum of 225 V. A 1 μF capacitor was included in series to inhibit the surge of current upon electrode-spanning microwire formation. The amplified field was transferred to the electrodes via copper wire and electrical tape. Initial stages of growth were visualized via microscopy (figure 1(b)) and by eye for small and large electrode gaps, respectively. After assembly UV flood exposure of the sample photopolymerized the acrylate and the sample was released from the substrate by peeling the Parafilm from the substrate after heating. In studies modulating temperature, the experiment was conducted atop a temperature controlled hotplate (900W, Thomas Scientific).

## 3. Results and discussion

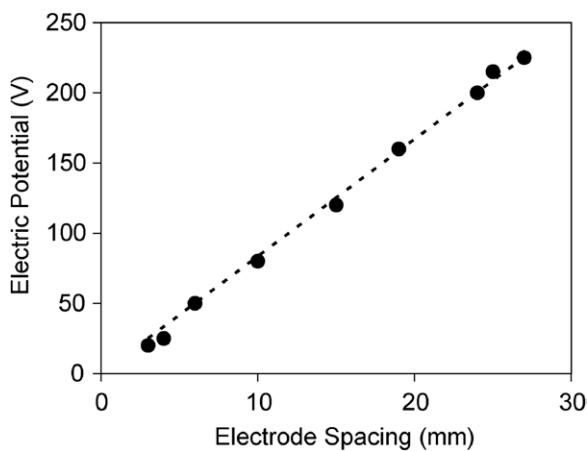
The process outlined in figures 1(a)–(c) mimics some semiconductor packaging conditions envisioned (figure 1(d)) while allowing direct visualization of the process (figure 1(b)). Under an ac electric field particles form dipoles and aggregate via dipole–dipole interactions. Shown in figure 1(b), initial wire assembly nucleates multiple wires at the electrode that can form linear or fractal structures. Nanoparticle wires nucleate in the bulk fluid as well, although they grow much more slowly than those connected to the electrode. Wires formed in the bulk eventually merge with those growing from the electrode. Particle pair interactions are much weaker than particle chain heteroaggregation and the heteroaggregation of single particles and other particle chains. Wires range from single particle chains to multiparticle thick wires having diameters of tens of particles.

A minimal threshold in the field strength is needed to initiate wire growth [18] and depends on electric potential, electrode spacing, fluid permittivity, particle radius, polarization and electrostatic stability. Below the threshold voltage wire growth cannot be achieved as interparticle dipole–dipole interactions do not overcome particle stability. The minimum electric potential required to grow an electrode-spanning wire with specified electrode spacing or conversely



**Figure 1.** (a) Schematic of experimental setup. (b) Initial wire growth from electrode. (c) Sample post-UV irradiation and removal from sample chamber. (d) Assembly process shown for use in anisotropic conductive adhesives where step (1) the solution is applied and particles are dispersed randomly, (2) the field is applied between electrode pairs in succession and wires assemble as designed, and (3) the adhesive is cured, encapsulating the assembled wires and bonding the chip to the substrate.

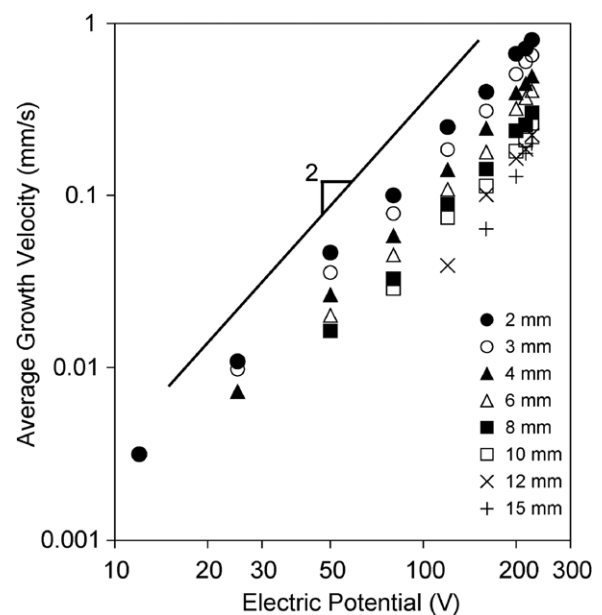
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**Figure 2.** The observed threshold voltage required to assemble wires bridging an electrode at a given spacing.

the maximum spacing a wire can bridge at a given electric potential is linear and shown in figure 2. This threshold voltage depends weakly on frequency and particle concentration [18], except at extreme values.

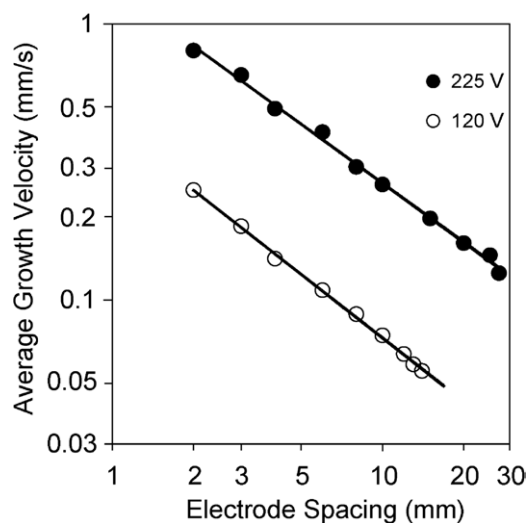
The effect of varying electric potential on wire growth rate was examined. Frequency and temperature were held constant at 100 Hz and 23 °C, respectively, while electric potential was varied from 12 to 225 V at spacings of 3 mm and 6 mm. Figure 3 shows the average bulk growth velocity as a function of electric potential and electrode spacing. Average growth velocity is defined as the electrode spacing divided by the time required for an assembled wire to span the electrodes. Accuracy of this measurement estimated at roughly 2% of the measured value. As expected, increased voltage increased the average growth velocity. The data follow a power law trend with a slope of 1.9—this is close to the theoretical slope of 2 related from  $F_{DEP} \propto \nabla(E^2)$ . Here, the dominate mode of wire formation is bulk growth, which ranges up to an order of magnitude larger than the surface growth of wires in aqueous suspensions [9]. To further examine the effects of field strength electrode spacing was varied from 2 to 27 mm while the voltage was held constant at 120 and 225 V. Increasing electrode



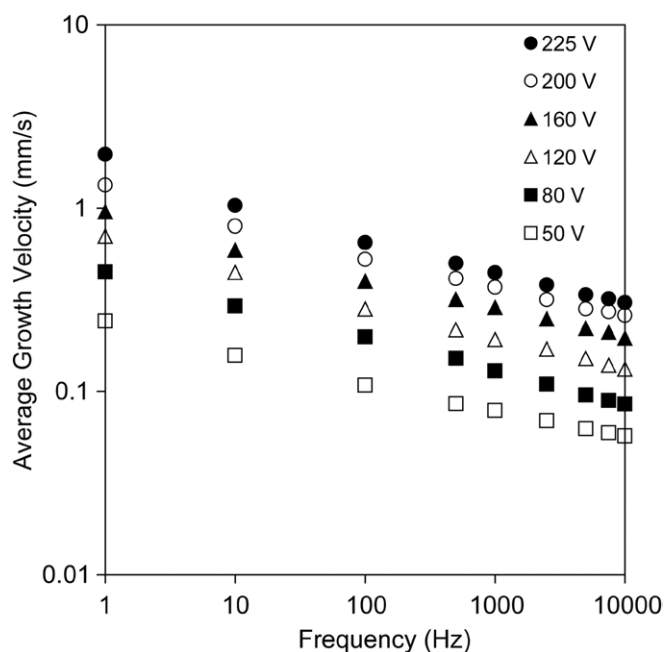
**Figure 3.** The average growth velocity ( $\text{mm s}^{-1}$ ) of carbon black microwires as a function of electric potential (V) and electrode spacing (mm) at 100 Hz and 23 °C.

spacing decreases the average growth velocity (figure 4). The growth exhibits power law decay with increasing distance with slope  $-0.75$ . This trend depends strongly on the geometry of the electric field. In practice, bulk dielectrophoretic growth of wires is faster near electrode edges where the field gradient is stronger. Also, gains in the reduction in wire assembly time by narrowing electrode spacing are significantly reduced.

The dependence of wire growth on electric field frequency was examined at various voltages, frequency ranging from 1 to 10 000 Hz, and constant temperature and spacing. As shown in figure 5, increasing frequency by four orders of magnitude decreases average growth velocity by roughly half. This frequency dependence arises from variation in particle polarizability, which is generally less significant than the effects of field strength and geometry. In contrast, assembled wires' morphology is strongly frequency dependent. As



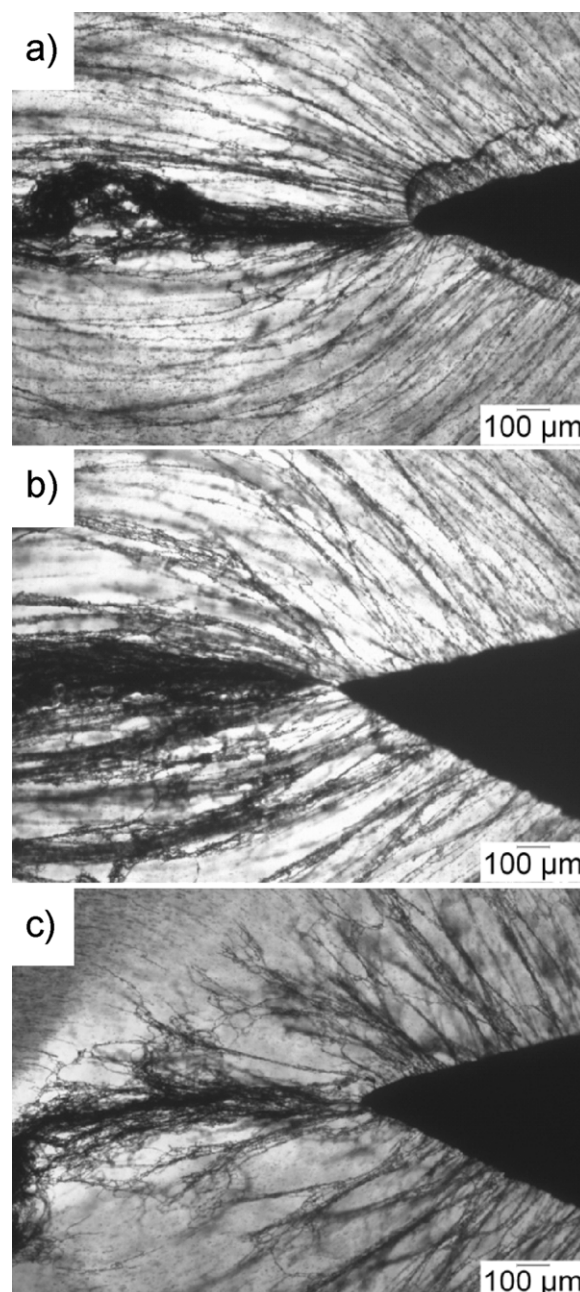
**Figure 4.** Wire growth velocity as a function of electrode spacing at 120 and 225 V.



**Figure 5.** The frequency dependence of average growth velocity ( $\text{mm s}^{-1}$ ) of carbon black microwires at varying electric potentials with 3 mm electrode spacing.

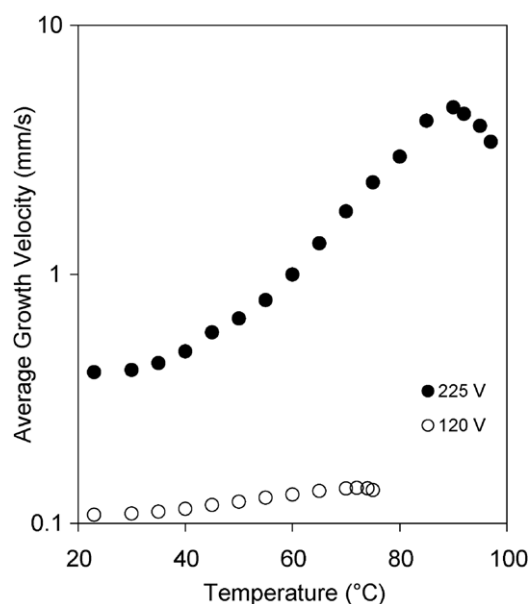
shown in figure 6, low frequency yields linear parallel wires while fractal branching occurs with increasing frequency. As current density depends on morphology, it can be controlled via tuning frequency [13, 17]. This observation is similar to that seen in aqueous suspensions [8]. When designing electrode interconnects, parallel wires are desirable as they create discrete connections between electrode pairs. Fractal wire morphology is useful in distributing current from a single source to multiple electrodes.

Finally, the effect of temperature on wire growth was examined at 100 Hz, 6 mm electrode spacing and 120 and 225 V. Temperatures examined ranged from 23 to 100 °C. Shown in figure 7, increasing temperature increased average wire growth rate. At 225 V, the average growth velocity increased by an order of magnitude under increasing



**Figure 6.** Images of carbon black wire growth at frequencies of (a) 1 Hz, (b) 100 Hz and (c) 10,000 Hz.

temperature. The velocity reached a maximum near 90 °C then decreased until 98 °C, above which wires ceased to form. At 120 V the velocity increase is slight, but once more the wire growth rate reaches a maximum before decreasing then falling sharply to zero. The monomer solution remains liquid throughout these experiments without any appearance of polymerization. This temperature dependence is complicated, increasing the temperature results in a small viscosity decrease, and moderate increases in Brownian motion and acrylate permittivity. At higher temperatures convection over the entire cell is evident, significantly altering transport in the cell. However, it is unclear why this sharp upper temperature limit exists for wire formation and why the limit decreases for lower voltage. Extrapolating these results to wire growth



**Figure 7.** Influence of temperature on wire growth at 100 Hz and 6 mm electrode spacing. A field-dependent temperature threshold exists for wire growth.

in thermosetting epoxies, this threshold may complicate deposition and curing.

#### 4. Summary

Dielectrophoretic wire growth is demonstrated in monomeric nanoparticle suspensions. This self-assembly of electronic interconnects embedded within polymers at relatively low particle concentrations avoids many pitfalls of conductive particle-laden systems. The properties of this wire growth in UV curable acrylate suspension of carbon black nanoparticles were investigated, with wire growth behaviour largely following that found in aqueous suspensions. These parallels include the influence of field strength on wire growth threshold and rate and of frequency on wire morphology. The study of temperature dependent wire growth in aqueous suspensions is limited and we report an increase in wire growth rate with increasing temperature up to an apparent temperature threshold. Further research regarding the fundamental influence of temperature and field geometry on wire growth is ongoing and studies of embedded wires' conductivity and the influence of embedded wires on adhesion and mechanical stability are necessary to demonstrate the viability of dielectrophoretic assembled wires in adhesives.

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