

A new method of chaining carbon nanofibers in epoxy

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Received 20 March 2008, in final form 9 June 2008

Published 4 July 2008

Online at stacks.iop.org/Nano/19/325606

Abstract

In this paper, a new and innovative process for assembling chains of carbon nanofibers (CNFs) in epoxy, uniquely different from those generally used for chaining particles in a liquid medium, is presented. Chains of aligned CNFs are assembled in a region rich in CNFs and extended into regions where there are no CNFs. A physical explanation of the process is provided based on the conductive nature of the CNFs. By contacting the chains with the electrodes, the process of chain growth is expedited and well-ordered parallel chains with equal spacing are grown over distances of 2 cm.

1. Introduction

Carbon nanoparticles, such as carbon nanotubes (CNTs) and nanofibers (CNFs), show great promise as multifunctional nanofillers for thermoset epoxy composites due to their exceptional mechanical, electrical and thermal properties. As in conventional polymeric composites, it is desired to control the orientation of particles for enhancing direction-specific material properties. Under the influence of an electric field, particles suspended in a liquid medium arrange in an orderly fashion—such as chains parallel or perpendicular to the direction of the electric field [1–13]. The mechanism of particle assembly in the region between electrodes is attributed to dipole–dipole interaction [14], except in cases where the particles are assembled on rather than in between the electrodes due to the fluid movement [15, 16]. The attractive force between two polarized particles in the point dipole approximation varies inversely to the fourth power of the interparticle distance. Therefore, to facilitate assembly, the particles should be initially positioned close to each other by any of several possible approaches such as increasing the particle concentration or bringing the particles closer to each other using electrophoretic or dielectrophoretic (DEP) forces. To form chains, networks, or ordered structures of particles, the entire region between the electrodes is normally populated

with particles so that the particles can be easily and quickly added to tip of the growing chains [9, 17–20].

In this paper, an important new process of assembly and growth of chains of CNFs using electric fields is reported. In this case, the suspending medium of interest is epoxy because of its importance as a matrix material in structural composites applications. CNF chain development is studied in real time using a microscope. The new process requires that only a small region of epoxy between the electrodes contain CNFs, with the bulk of the region through which chains are developed being initially devoid of CNFs. It is proposed that the observed mechanism of chain assembly and growth depends on the conductive nature of CNFs and the self-repairing ability of these chains. A clear advantage of this new technique is that unidirectional conducting chains of CNFs can be assembled in regions where there are no CNFs, thus providing a means to fabricate CNF/epoxy composites with tailored anisotropy in nano-scale morphological texture leading to anisotropy in electrical, mechanical, thermal, and photonic properties. Using this technique, chains of aligned CNFs up to 2 cm long are grown in liquid epoxy, adding to the significance of the technique for the manufacture of multifunctional structural materials.

2. Experiments

The cell used for the visual observation of chain development consisted of a glass microscope slide with two parallel

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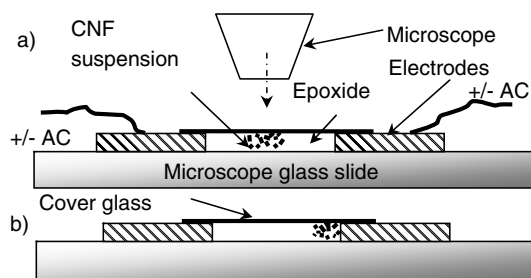


Figure 1. Schematic of the experimental setup: (a) CNFs in center of cell, away from the electrodes; (b) CNFs near one electrode.

electrodes (figure 1). The electrodes were segments of 100 μm -thick aluminum adhesive tape. The cell was 22 mm wide and was as thick as the electrodes. The gap between the electrodes was varied between 1 and 2 cm. After the gap was filled with plain epoxide, a 5 mg drop of CNF/epoxide solution was added into the cell in a localized position either midway between the electrodes or near one electrode. On account of the viscous nature of liquid epoxide (approximately 30 cP at the test temperature of 121 $^{\circ}\text{C}$), the CNFs did not diffuse far from the location of drop during the experiments. After all the materials were added to the cell, a cover glass was placed on top, as shown in figure 1. The cover glass was used in all experiments. As voltage was applied to the electrodes with an AC power supply, a microscope mounted on a positioning stage and equipped with a CCD camera was used to record the movement of CNFs in the cell.

The CNFs are a commercial chemical-vapor-grown product named Pyrograf[®]-III PR-24 HHT (Applied Sciences Inc., Cedarville, OH), with diameters in the range of 60–150 nm and lengths of 30–100 μm . Epikote 862 bisphenol-F epoxide (Hexion, Columbus, OH) was used as the suspending medium in the first two experiments discussed in this paper, while curing agent W (Hexion, Columbus, OH) was added at 26.4 pph epoxide in the third experiment where the suspending medium was cured. The suspension of CNF and liquid epoxide was prepared with the aid of a surfactant and ultrasonic agitation. The nonionic surfactant Triton X-100 (Bioworld, Dublin, OH) has a molecular formula ($\text{C}_{34}\text{H}_{62}\text{O}_{11}$) and was added at a weight ratio of 76 pph CNF. The concentration of CNFs in the epoxide drop was 0.1 wt%. The procedure detailed in [21] was followed for dispersing the CNFs in epoxide using an ultrasonic horn.

3. Results and discussion

The first two experiments used an electrode gap of 1 cm, no curative in the epoxide, and CNFs deposited in an oval region in the middle of the cell in one case and in a strip-like region along one electrode in the other case. On application of 200 $V_{\text{pk-pk}}$ at a frequency of 100 Hz, the CNFs were observed to assemble in chains. On continued application of the electric field, the chains extended into the regions of epoxide where there were initially no CNFs (figure 2), eventually spanning the distance between the electrodes. The chains that extended into plain epoxide had CNFs aligned in the direction of the applied

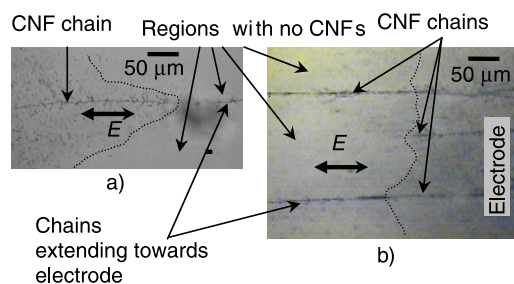


Figure 2. Chains of aligned CNFs extending into regions with no CNFs (border delineating regions initially with and without CNFs has been digitally enhanced by a dotted line): (a) CNFs in center of cell, away from the electrodes; (b) CNFs near one electrode.

electric field. The majority of the chains formed by this process are chains of individual CNFs as shown in figure 2.

Comparing the two experiments, the rate of growth of these chains is greater when the CNFs are suspended close to the electrode. It took 10–15 min for the chains to span the 1 cm distance between the electrodes when grown from one electrode. On the other hand, the chains that grew from the CNF drop midway between the electrodes took about 30–35 min to bridge the gap between both electrodes. The chains that grew from the electrodes were spaced equally and did not touch each other. However, when the CNFs were introduced in the center of the cell, the chains that extended into the region without CNFs were few in number and randomly spaced.

In a third experiment, curative was added to the epoxide to make rigid composites with parallel chains of aligned CNFs in a roughly 2 cm electrode gap. A voltage of 200 $V_{\text{pk-pk}}$ at 100 Hz was applied to grow the chains from the CNF/epoxy mixture placed in a strip-shaped region along one electrode. The chains were assembled at the 121 $^{\circ}\text{C}$ curing temperature of the epoxy. The chains had to be grown before the viscosity of the system markedly increased due to crosslinking. Chaining parameters were therefore selected to complete chain extension across the 2 cm gap in 30 min—the time required to double the viscosity of the Epon 862/curative W system at 121 $^{\circ}\text{C}$. Figure 3 shows multiple parallel chains grown over a distance of 2 cm in the fully cured epoxy. It was observed that the growth of some of the chains ceased or slowed down due to the depletion of CNFs close to the electrodes. This limitation can be easily overcome by using a higher concentration of CNFs in the solution.

The development of chains can be broken down into two fundamental processes: the addition of CNFs to chains and the stretching of chains. The addition of CNFs can be explained using the theory of dielectrophoresis [14]. In dielectrophoresis, the application of a nonuniform electric field polarizes the particles and develops particle–particle interaction forces. The particle interaction force is proportional to the square of the electric field strength. On increasing the electric field, the particles form chains faster due to increased interactions. On the other hand, the phenomenon of chain stretching is a localized phenomenon and requires knowledge of the electrostatic and van der Waals interactions. To provide understanding without too much detail and complexity, a

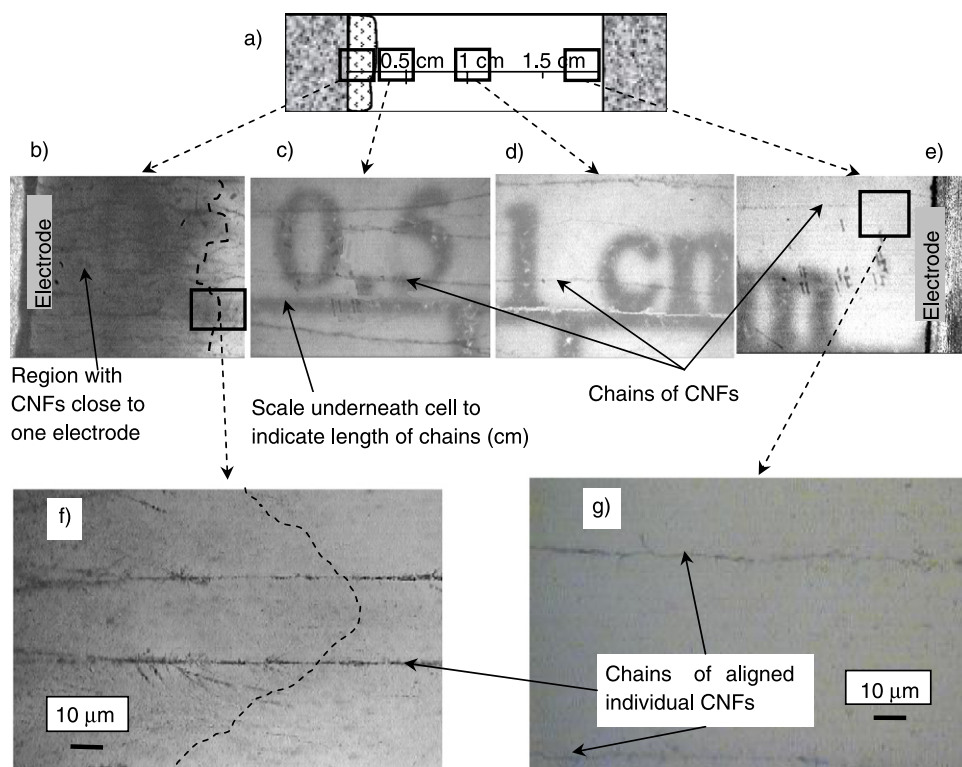


Figure 3. Chains of CNFs grown from the electrodes into a roughly 2 cm-long region that contained no CNFs initially: (a) schematic of the test cell (top view), (b) region with CNFs close to the left electrode, (c) region showing chains roughly 0.5 cm away from the left electrode, (d) region showing chains roughly 1 cm away from the left electrode, (e) region close to the right electrode, (f) magnified view of a small region close to the left electrode, (g) magnified view of the region close to the right electrode placed roughly 2 cm away from the left electrode.

simplified physical explanation of chain stretching is provided next, based on the conductive nature of the particles and electrostatic interactions.

Since the conductivity of CNFs is much higher than that of liquid epoxy, the composite material system can be approximated as a suspension of perfectly conducting particles in a dielectric fluid. The application of an electric field to the suspension polarizes the CNFs and causes alignment and chaining due to dipole–dipole interactions. Assuming physical contact between the CNFs in a chain, each chain can be treated as one large conductive particle. The polarization charges on the CNFs in the chain redistribute in a manner that maintains the two essential requirements for a conductor: (i) the surface of a conductor is equi-potential, and (ii) the net charge on the chain is zero if the chain is not in direct contact with an electrode [22]. The redistribution of the polarization charges results in an unequal net charge on individual particles in the chain [23]. The magnitude and polarity of the charge depends on the position of individual CNFs in the chain. If the chain is parallel to the direction of the electric field and unattached to an electrode, the CNFs at opposite ends of the chain are expected to have the highest polarization charge density, though of opposite polarity.

Chained CNFs are held together by the mutual electrostatic force of attraction (i.e., due to image charges) and van der Waals forces [14]. Forces pulling chained CNFs away from each other are exerted by the action of the electric

field on the polarization charges, the Brownian motion of the fluid molecules, and gravity. In the present investigation, it was experimentally observed that CNF chains could not be broken by Brownian motion and gravitational forces over the course of several days following removal of the electric field. However, CNF chains could readily be broken at a point where the forces holding the CNFs together were overcome by sufficiently strong field-induced forces. Once the electrical contact between chained CNFs breaks, the chain is transformed into a series of collinear sub-chains of smaller and possibly unequal lengths. Each sub-chain then behaves as an individual particle polarized by the electric field. The polarized sub-chains intensify the electric field strength and gradient around the region of separation. The intensified electric field not only produces a mutual force of attraction between the sub-chains, but also attracts nearby individual CNFs or short chains of CNFs towards the ends of the sub-chains.

The mobility of untethered individual and chained CNFs is primarily governed by the competition between the electrical force and the viscous drag. The viscous drag scales proportionally to the length of the CNF or chain, but the electrostatic force scales in proportion to the length and to the gradient of the electric field along the length. Therefore, for a given electric field, the excess of electrostatic force over the drag force is greater in individual CNFs than in short chains. Indeed, untethered individual CNFs, rather than short chains of CNFs, move most rapidly towards broken

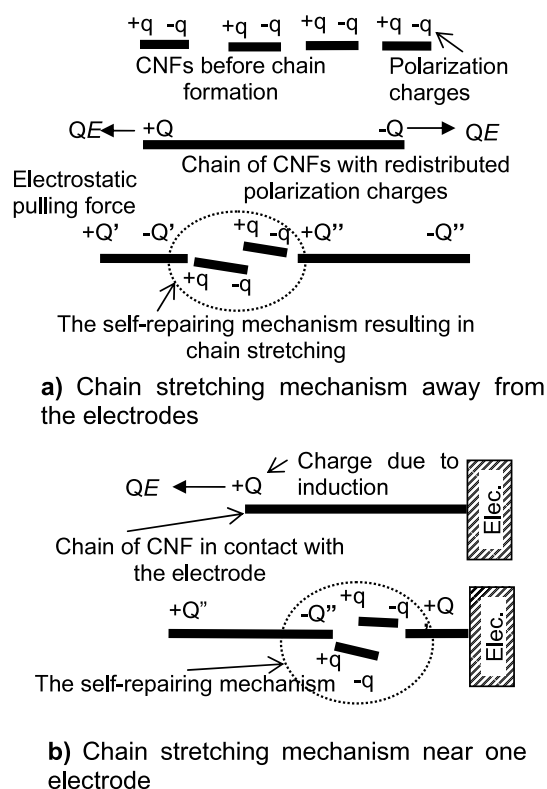


Figure 4. Schematics of the chain stretching processes.

connections in sub-chains and provide the most commonly observed means of restoring the broken connections. This self-repairing mechanism also allows the chain to stretch (figure 4(a)). Similarly, it has been observed that a chain can branch at the location of a break. If two or more individual CNFs approach the small gap in a broken chain, there is a possibility that only one of them bridges the gap while the other attaches to the original chain at an angle, like a branch in a tree. This branch provides a nucleus for the successive addition of more CNFs. The aforementioned explanation best explains the process of chain stretching and branching when the chains are formed away from the electrodes. The situation where the chains are in contact with the electrodes is discussed next.

It is well known that a conducting particle in contact with the electrode acquires a charge of the same polarity as that of the electrode [24, 25]. Similarly, when a chain of conducting CNFs is in contact with the electrode it acquires a charge due to induction [25]. The charged CNFs experience an electrostatic force away from the electrode that can break the chain if the interparticle attractive forces are overcome. The position where the chain breaks becomes a nucleus for the addition of fresh CNFs on account of dipole–dipole interactions (figure 4(b)). This self-repairing mechanism causes the chain to stretch. Because the charge acquired by conducting particles varies proportionally to the strength of the applied electric field [26], chains will stretch faster if the strength of the electric field is increased. It was observed in our experiments that the chains started to stretch rapidly as the voltage exceeded $100 V_{pk-pk}$ at 100 Hz. Below a voltage of

$100 V_{pk-pk}$, little to no stretching was observed. The addition of a CNF to the chain depends on its polarizability, which being a function of applied electric field frequency makes the process of chaining dependent on the electric field frequency. The effects of various electrical parameters on the assembly of CNFs will be the focus of future investigations. Other areas of potentially interesting investigation could interrogate the influence of the chemical/structural characteristics of the CNF on assembly.

4. Summary

A new process for chaining aligned conductive particles in a nonpolar liquid medium was identified. In this case, the particles were CNFs and the medium was epoxy. Real time movement of the CNFs was observed using a microscope to understand the mechanisms of chain development. The observed stretching of chains into regions of no CNFs revealed a new mechanism of chain growth that is different from the well-known assembly of polarized particles at the tip of the growing chain in a nonpolar medium. Chains of aligned CNFs were assembled and extended into regions where there were no CNFs. Possible explanations for these processes are associated with the conductive nature of the CNFs and their conducting chains in which the individual CNFs are physically connected to each other, making the entire chain at the same potential. By contacting the chains with the electrodes, the process of chain growth was expedited and well-ordered parallel chains were grown up to large distances (~ 2 cm). These chains of CNFs can be potentially used at μm to cm scales for applications in structures with electrical, thermal and photonic functions.

Acknowledgments

This research was performed under the partial sponsorship of the US Army Research Office, Contract W911NF-04-1-0111. Professor M Amanul Haque of Penn State is thanked for allowing the authors to use his microscope setup.

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