ELECTRIC FIELD ALIGNMENT OF MULTI-WALLED CARBON NANOTUBES THROUGH CURING OF AN EPOXY MATRIX

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Abstract
The electrical alignment of multi-walled carbon nanotubes (MWCNT) in an epoxy resin was studied through curing using electrical measurements and optical microscopy. The epoxy system was composed by diglycidyl ether of bisphenol-A and 4,4'-methylene bis-(3-chloro 2,6-diethylaniline). Long multi-walled carbon nanotubes were ultrasonically mixed with epoxy resin to form a 0.01 wt% MWCNT mixture. Samples were cured with alternating current electric fields applying different AC voltages. The electrical conductivity of the composite increased upon applied voltage as higher alignment of carbon nanotubes was achieved. The enhanced alignment was visualized by optical microscopy. Improvements in capacitance behaviour were also achieved with the highest value of current field.

Keywords: Carbon nanotubes; Epoxy resin; Electrical properties; Atomic force microscopy (AFM); Dielectrophoresis

1. Introduction

Many potential applications have been claimed for carbon nanotubes, including conductive and high-strength composites [1]. The unique atomic structure, very high aspect ratio and extraordinary mechanical properties, as strength and stiffness, make carbon nanotubes ideal reinforcing fillers [2,3]. On the other hand, epoxy resins have wide engineering applications due to their low cost, easy processability, good thermal, mechanical and electrical isolation properties, and so on. One of the most important disadvantages of epoxy resin is their brittleness. The combination of both materials can lead to enhanced composite materials with tunable electrical properties, from insulating to conductive composites [4] or mechanical properties, from brittle to high impact strength materials [5].

To take advantage of the attractive directional properties of carbon nanotubes, aligned composites are being fabricated by several ways [6]. Some researchers prepared aligned carbon nanotube composites by infiltrating monomers into chemical vapor decomposition-grown arrays of aligned multi-walled carbon nanotubes (MWCNT), followed by in situ polymerization [7]. Carbon nanotubes can also be aligned during or after the composite fabrication by mechanical stretching [8], solvent casting [9], reactive spinning [10] and other techniques. Dielectrophoresis can be one of the most attractive methods for manipulating carbon nanotubes to obtain anisotropic conductive composites [11-14]. This technique is also a useful method for the separation of metallic and semiconducting nanotubes [15-17] and for the fabrication of carbon nanotube field effect transistors [18,19]. Carbon nanotubes can be aligned well using only AC dielectrophoresis. Since the electric field strength increases by increasing applied voltage, i.e. the dielectrophoretic force, more CNT can be attracted to the electrodes. Similar effects are obtained by increasing the frequency of the alternating current [11,20].

The aim of the present work was to achieve sufficient alignment to enhance the electrical properties of a carbon nanotube/epoxy matrix composite by applying AC electrical field through curing. The matrix of the composite was formed by an epoxy/amine system, diglycidyl ether of bisphenol-A/4,4'-methylene bis-(3-chloro 2,6-diethylaniline), and a very low amount of multi-walled carbon nanotubes was used as filler. Electrical characterization was performed by I-V measurements. Optical microscopy (OM) was also used to characterize the aligned samples.

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2. Experimental

2.1 Materials.

The epoxy resin used was DER-332, a diglycidyl ether of bisphenol-A, kindly supplied by Dow Chemical, having an epoxy equivalent of around 175. The curing agent was an aromatic diamine 4,4'-methylene bis-(3-chloro 2,6-diethylaniline), MCDEA, with low reactivity, gifted by Lonza. Long multi-walled carbon nanotubes, having a mean diameter of 15 nm and average length of about 10 μm, were produced at 700 °C by chemical vapour deposition (CVD) over Fe-Co bimetallic catalyst by the Institutional Department of Chemical Engineering Science (Institute of Chemical and Process Engineering, University of Pannonia) using Fe-Co bimetallic catalysts on talc as catalyst carrier and ethylene as carbon source [21]. Degree of purity was MWCNT ~ 90 wt%, the remainder consisting of catalyst and support.

2.2 Sample preparation.

As-received MWCNT were added with the aid of a surfactant to the reactive sample formed by a stoichiometric mixture of epoxy-amine. The non-ionic surfactant poly(oxyethylene octyl phenyl ether) (Triton X-100, Sigma-Aldrich) was added at a concentration ten times the critical micelle concentration (CMC) [22]. The low reactive mixture was sonicated (Vibracell VCX 750, Fisher Bioblock Scientific, 750 W, 20 kHz) for 20 min at 60 % amplitude in a controlled bath at room temperature. A drop of this mixture was placed in the measurement cell consisting of a glass microscope slide with two parallel electrodes. The electrodes were segments of 50 μm-thick aluminium adhesive tape. The gap between the electrodes was 4 mm. A cover glass slide was placed on the top of the cell after the mixture was added. An AC power source was connected to the electrodes to apply the voltage desirable during the cure of epoxy resin. Curing cycle for all samples was 3 h at 150 ºC, controlling the temperature by a hot plate.

2.3 Morphological characterization.

Morphological characterization of nanotubes was carried out by atomic force microscopy (AFM) in tapping mode at room temperature using a Multimode microscope and Nanoscope IIIa controller, from Veeco, Digital Instruments. Phosphorus (n) doped Si probe RTESP, from Veeco, was used to perform the characterization, with nominal spring constant and resonant frequency of 40 N/m and 300 kHz, respectively. A Nikon Eclipse E600W microscope was used for optical characterization of MWCNT alignment in cured samples. The optical images were obtained under transmission conditions.

2.4 Electrical measurements.

An equipment Keithley, model 4200-SCS, was used to characterize electrical behaviour of samples using two-point electrical measurement technique. Manual micropositioners were used to connect sample electrodes with the analyzer and generate I-V curves. In order to determine the resistance, Ohm's law was used.

3. Results and Discussion

Atomic force microscopy images of the MWCNT were performed to evaluate their quality. Fig. 1 shows AFM images of MWCNT, where long nanotubes and poor purity are noticeable. Dark zones in nanotubes and small dots in phase image can indicate the presence of other type of material apart from carbon nanotubes belonging to the catalyst and support remainder. Besides the great length of nanotubes, a broad dispersion on size and large diameter can be observed.

Neat epoxy-amine system and the composite containing 0.01 wt% MWCNT were cured under different voltage conditions as follows: first sample

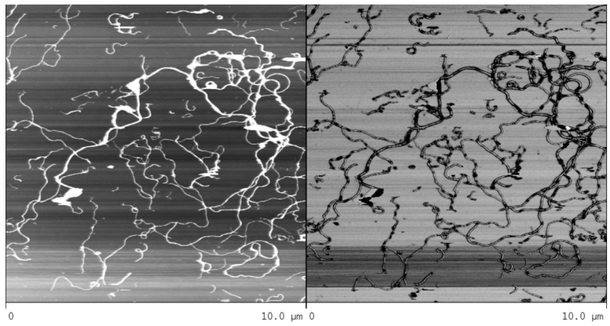

Fig. 1: AFM images of MWCNT. (Left) topography and (right) phase images of 10x10 μm.

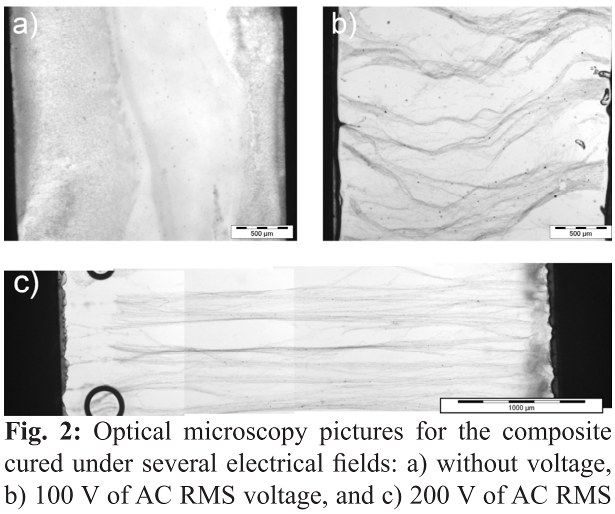

Fig. 2: Optical microscopy pictures for the composite cured under several electrical fields: a) without voltage, b) 100 V of AC RMS voltage, and c) 200 V of AC RMS voltage.

was epoxy-amine without nanotubes and AC voltage; second sample was composite without AC voltage; third sample was composite and AC RMS voltage of 100 V at a frequency of 50 Hz; and fourth sample was composite and AC RMS voltage of 200 V at a frequency of 50 Hz. Optical microscopy images of the composites after curing are shown in Fig. 2. There is no preferential orientation of nanotubes in the sample cured without voltage (Fig. 2a). However, in Fig. 2b a preferential orientation can be observed. In this case, when AC RMS voltage of 100 V was applied, carbon nanotubes were aligned mostly along the direction of the electrical field. Similar result can be observed in Fig. 2c, when AC RMS voltage of 200 V was applied. Indeed, higher alignment was obtained for increasing voltage in despite of distance between electrodes was higher (3.9 mm for 200 V and 2.3 mm for 0 and 100 V). Images also show the lateral agglomeration perpendicular to the field in the case of curing with voltage.

The formation and evolution of the aligned nanotubes-epoxy networks could be governed by two separated processes: the longitudinal alignment (parallel to the field), and the lateral agglomeration (perpendicular to the field) [14]. The formation of the longitudinal alignment of nanotubes can be explained using the theory of dielectrophoresis [23]. Carbon nanotubes, suspended in a dielectric medium, can be modeled as cylinder particles and will be polarized under the effect of a non-uniform external electric field. Thus, electric charge will locate at the two ends of the nanotubes. The interaction of induced electric dipole moments of nanotubes with the external electric field generates a torque that leads to the alignment of nanotubes along the direction of the electric field [14,20,24]. This polarization leads to an additional attractive interaction (dielectrophoresis) between dispersed individual nanotubes. The magnitude of the rotational force is strongly dependent on the magnitude and frequency of the electric field. Increasing the electric field, the particles form chains faster due to increased interactions. Nanotube alignment is expected to occur immediately after the electric field is exerted and favoured by the low viscosity of the system at high temperature before the gelation thereof. At the early stages of the epoxy-amine curing reactions the growing chains do not yet generate three-dimensional network and the viscosity remains at low values. Once gelation occurs no more nanotubes movements can take place due to the physical hindrance of the network. It should be pointed out that the increase in voltage would lead to an increase in sample temperature due to the Joule heating effect. This rise in temperature could vary gelation time, shortening the time available for nanotubes alignment. Therefore, a deeper study on the kinetics of both, curing reaction and nanotubes alignment should be carried out with the aim of optimizing the time-temperature-voltage parameters of curing.

On the other hand, the nanotube translation process to generate the lateral agglomeration takes relatively longer time periods. However, this theory does not explain the lateral agglomeration after the fast alignment, because the external electric field should not lead to perpendicular movement of nanotubes. A simplified explanation of the perpendicular movement and chain formation can be provided on the basis of the conductive nature of the particles, in this case, nanotubes and electrostatic interactions [14,23]. Since nanotubes are aligned along the electric field, dipole-dipole interactions can cause the movement of two nanotubes closer toward each other and gradually the formation of a larger dipole leading to the observed bundles. It is possible that the nanotubes in the bundles are held together by the mutual electrostatic force of attraction and van der Waals forces, instead of connecting with one another. The small lateral agglomeration in the system studied in this work is possibly related to the low reactivity of the used epoxy-amine system that leads to a long gelation time at the selected cure temperature and to the high aspect ratio of the nanotubes employed that can generate longer dipoles. Thus, the permanence of long dipoles in a low viscosity medium for long time periods at a high voltage seems to be the responsible for alignment and lateral agglomeration of the carbon nanotubes.

Electrical measurements were carried out to obtain I-V curves of the neat matrix and the composites cured under several electrical fields. Fig. 3a shows current versus voltage curve for all cured samples. Measurements were carried out between electrodes applying a voltage sweep from 0 to 19 V and recording the current intensity. The neat system showed the lowest intensity at all applied voltages. In the com-

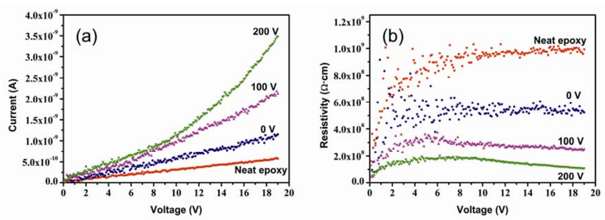

Fig. 3: I-V curves for neat epoxy matrix, and composites cured: without voltage; with 100 V AC RMS voltage, and with 200 V AC RMS voltage. (a) current vs. voltage and (b) resistivity vs. voltage curves

posites, for higher nanotube alignment, an increase in conductivity was observed as the measured current intensity was higher for the same applied voltage. This is still better seen in the resistivity-voltage plots (figure 3b), which are obtained from the normalization of the resistance for the section and the distance between electrodes. Thus, an increase in alignment of nanotubes leads to a decrease in composite resistivity. A decrease of 46 % was achieved for 0.01 wt% unaligned nanotubes, while for nanotubes aligned at 200 V a reduction of nearly one order of magnitude at 19 V from neat epoxy was obtained.

Fig. 4 shows complete I-V cycles. Measurements were carried out between electrodes applying a voltage sweep from -19 to 19 V and recording the current intensity. In addition to the increase in the conductivity by increasing alignment of nanotubes, wider hysteresis cycles can be also observed for composites. This fact can be due to the higher polarization achieved in the sample aligned with 200 V, indicating that the composite behaves as an improved capacitance when the alignment of nanotubes increased. Inset graph shows the hysteresis curve for the composite cured with 200 V AC RMS voltage for clarification. Arrows indicate the direction of cycle measurement. The direct current conductivity of a capacitor is theoretically zero. Thus, since the bias is changed the capacitor has to reach the new equilibrium amount of charge stored. Consequently, charge will flow in to or out of the device composed by the composite and the electrodes, generating the so-called displacement current. This displacement current versus the applied voltage generate the hysteresis cycle of I-V curves.

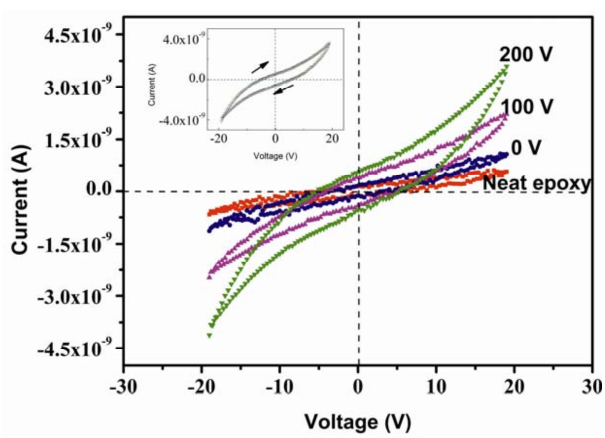

Fig. 4: Current vs. voltage cycles for neat epoxy matrix, and composites cured: without voltage; with 100 V AC RMS voltage, and with 200 V AC RMS voltage. Inset graph: current vs. voltage cycles for the composite cured with 200 V AC RMS voltage.

4. Conclusions

An alignment study of carbon nanotubes in an epoxy/MWCNT composite was performed as a function of the alternating current field level applied through curing. The increase in the applied alternating current field increased the alignment of nanotubes also increasing the conductivity of the composite. The increase of alignment was also characterized by optical microscopy where higher longitudinal and lateral agglomerations were observed for the composite cured at higher voltages. In addition, hysteresis results showed an improvement on capacitance behaviour of the composite aligned through curing with higher values of current field.

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References:

1. **Spitalsky, Z, Krontiras, CA, Georga, SN, Galiotis, C,** "Effect of oxidation treatment of multiwalled carbon nanotubes on the mechanical and electrical properties of their epoxy composites", *Compos Part A - Appl S,* **40**/6-7 (2009), 778-783.
2. **Shen, J, Huang, W, Wu, L, Hu, Y, Ye, M,** "Thermo-physical properties of epoxy nanocomposites reinforced with amino-functionalized multi-walled carbon nanotubes", *Compos Part A - Appl S,* **38**/5 (2007), 1331-1336.
3. **Chen, W, Auad, ML, Williams, RJJ, Nutt, SR,** "Improving the dispersion and flexural strength of multiwalled carbon nanotubes-stiff epoxy composites through β-hydroxyester surface functionalization coupled with the anionic homopolymerization of the epoxy matrix", *Eur Polym J,* **42**/10 (2006), 2765-2772.
4. **Li, C, Thostenson, ET, Chou, TW,** "Sensors and

actuators based on carbon nanotubes and their composites: A review", *Compos Sci Technol,* **68**/6 (2008), 1227-1249.

5. **Chen, ZK, Yang, JP, Ni, QQ, Fu, SY, Huang, YG,** "Reinforcement of epoxy resins with multi-walled carbon nanotubes for enhancing cryogenic mechanical properties", *Polymer,* **50**/19 (2009), 4753-4759.
6. **Moniruzzaman, M, Winey, KI,** "Polymer nanocomposites containing carbon nanotubes", *Macromolecules,* **39**/16 (2006), 5194-5205.
7. **Cheng, Q, Wang, J, Jiang, K, Li, Q, Fan, S,** "Fabrication and properties of aligned multiwalled carbon nanotube-reinforced epoxy composites", *J Mater Res,* **23**/11 (2008), 2975-2983.
8. **Ren, Y, Li, F, Cheng, HM, Liao, K,** "Tension-tension fatigue behavior of unidirectional single-walled carbon nanotube reinforced epoxy composite", *Carbon,* **41**/11 (2003), 2177-2179.
9. **Wang, Q, Dai, J, Li, W, Wei, Z, Jiang, J,** "The effects of CNT alignment on electrical conductivity and mechanical properties of SWNT/epoxy nanocomposites", *Compos Sci Technol,* **68**/7-8 (2008), 1644-1648.
10. **Che, J, Yuan, W, Jiang, G, Dai, J, Lim, SY, Chan-Park, MB,** "Epoxy composite fibers reinforced with aligned single-walled carbon nanotubes functionalized with generation 0-2 dendritic poly(amidoamine)", *Chem Mater,* **21**/8 (2009), 1471-1479.
11. **Shim, HC, Kwak, YK, Han, CS, Kim, S,** "Effect of a square wave on an assembly of multi-walled carbon nanotubes using AC dielectrophoresis", *Physica E,* **41**/7 (2009), 1137-1142.
12. **Park, C, Wilkinson, J, Banda, S, Ounaies, Z, Wise, KE, Sauti, G, Lillehei, PT, Harrison, JS,** "Aligned single-wall carbon nanotube polymer composites using an electric field", *J Polym Sci. Part B. Polym Phys,* **44**/12 (2006), 1751-1762.
13. **Prasse, T, Cavaille, JY, Bauhofer, W,** "Electric anisotropy of carbon nanofibre/epoxy resin composites due to electric field induced alignment", *Compos Sci Technol,* **63**/13 (2003), 1835-1841.
14. **Zhu, YF, Ma, C, Zhang, W, Zhang, RP, Koratkar, N, Liang, J,** "Alignment of multiwalled carbon nanotubes in bulk epoxy composites via electric field", *J Appl Phys,* **105**/5 (2009), 054319 (6pp).
15. **Lutz, T, Donovan, KJ,** "Macroscopic scale separation of metallic and semiconducting nanotubes by dielectrophoresis", *Carbon,* **43**/12 (2005), 2508-2513.
16. **Wei, C, Wei, TY, Liang, CH, Tai, FC,** "The separation of different conducting multi-walled carbon nanotubes by AC dielectrophoresis", *Diam Relat Mater,* **18**/2-3 (2009), 332-336.
17. **Liu, X, Spencer, JL, Kaiser, AB, Arnold, WM,** "Selective purification of multiwalled carbon nanotubes by dielectrophoresis within a large array", *Curr Appl Phys,* **6**/3 (2006), 427-431.
18. **Li, J, Zhang, Q, Yang, D, Tian, J,** "Fabrication of carbon nanotube field effect transistors by AC dielectrophoresis method", *Carbon,* **42**/11 (2004), 2263-2267.
19. **Kim, S, Xuan, Y, Ye, PD, Mohammadi, S, Lee, SW,** "Single-walled carbon nanotube transistors fabricated by advanced alignment techniques utilizing CVD growth and dielectrophoresis", *Solid State Electron,* **52**/8 (2008), 1260-1263.
20. **Wang, MW,** "Alignment of multiwall carbon nanotubes in polymer composites by dielectrophoresis", *Jpn J Appl Phys,* **48**/3 (2009), 035002 (5pp).
21. **Szentes, A, Horváth, G,** "Role of catalyst support in the growth of multi-walled carbon nanotubes", Hungar J Ind Chem, **36**/1-2 (2008), 113-117.
22. **Geng, Y, Liu, MY, Li, J, Shi, XM, Kim, JK,** "Effects of surfactant treatment on mechanical and electrical properties of CNT/epoxy nanocomposites", *Compos Part A - Appl S,* **39**/12 (2008), 1876-1883.
23. **Sharma, A, Bakis, CE, Wang, KW,** "A new method of chaining carbon nanofibers in epoxy", Nanotechnology, **19**/32 (2008), 325606 (5pp).
24. **Martin, CA, Sandler, JKW, Windle, AH, Schwarz, MK, Bauhofer, W, Schulte, K, Shaffer, MSP,** "Electric field-induced aligned multi-wall carbon nanotube networks in epoxy composites", *Polymer,* **46**/3 (2005), 877-886.