A SIMULATION STUDY ON THE EFFECTS OF NANOTUBE ANISOTROPY AND NON-STRAIGHTNESS ON THE ELECTRICAL PROPERTIES OF CARBON NANOTUBE/POLYMER COMPOSITES

A. E. Eken [a,*], E. J. Tozzi [b], D. J. Klingenberg [c], W. Bauhofer [a]

[a]Institute of Optical and Microelectronic Materials, Technische Universität Hamburg-Harburg, Eißendorfer Straße 38, D-21073 Hamburg, Germany.
[b]Department of Chemical Engineering and Materials Science, University of California, Davis, CA 95616, USA.
[c]Department of Chemical and Biological Engineering, University of Wisconsin, Madison, 1415, Engineering Drive, WI 53706, USA.

* Corresponding Author:
Tel.: (+49) 40 42878 38 54 Fax: (+49) 40 42878-2229
e-mail: eken@tu-harburg.de

Introduction

CNTs can be used as filler materials to achieve high electrical conductivity in insulating polymer matrices. The use of CNT/polymer composites became the focus of industrial interest in the recent years. Applications such as electromagnetic shielding, electrostatic discharge and antistatic discharge do not require a high level of conductivity are suited for the use of these composites [1]. During the processing of CNT/polymer composites, significant shear and extensional deformation are exposed to the system that causes the movement of the nanotubes influencing the structure of the composite [2].

The purpose of this work is to understand the dependence of the electrical conductivity on the different microstructures of CNT/polymer composites. Composite structures composed of randomly oriented, aligned and sheared CNTs with different shapes were investigated in this study.

Model

Composite microstructures are generated using a fiber-level simulation method developed by Switzer and Klingenberg [3]. Fibers are modeled as connected rigid cylinders. The cylinders have hemispherical end caps and are connected to each other with ball-and-socket joints. Each segment can rotate and twist about the joints enabling simulation of flexible fibers. During flow, fiber motion is described by Newton's equations of motion. Hydrodynamic forces and torques, mechanical contact forces, constraint forces (inextensibility constraint that keeps fibers at constant length) and restoring torques (which resist bending and twisting the joints) are used in the simulations. Interparticle forces including short-range repulsion and van der Waals attraction are also considered. Periodic boundary conditions are employed to represent an infinitely periodic medium.

Randomly oriented suspension are generated by using a Monte Carlo method [4].

We use a resistor network algorithm to predict the electrical conductivities of the simulated composites [5]. The periodic composite box is modeled as an electric circuit composed of discrete resistive elements. Carbon nanotubes are represented as infinitely conducting nodes in the electrical circuit and each junction between adjacent CNTs is represented by a resistor. Tunneling conduction is also considered in our simulations. If the separation distance between the adjacent nanotubes is smaller than a tunneling length h, these two nanotubes are considered to be in electrical contact. When an external potential gradient is applied to the simulation box, nanotube potentials and induced currents are calculated by solving the linear systems of equations that represent circuits of resistors and potential constraints.

Results and Discussions

We show the dependence of the electrical properties on anisotropy and non-straightness of the nanotubes of sheared and non-sheared CNT/polymer composites. In a previous study [4] we have shown that using straight CNTs instead of using helical CNTs decreases the percolation threshold p_c in randomly oriented composites. In this study, we show that using aligned helical CNTs ($p_c = 0.025$) instead of using aligned straight CNTs ($p_c = 0.07$) decreases the percolation threshold in non-sheared CNT/polymer composites. Figure 1 shows the electrical conductivity as a function of volume fraction for aligned, randomly oriented and sheared CNT/polymer composites with helical or straight nanotubes. In agreement with previous research [6] we show that using aligned helical or aligned straight CNTs within polymer matrix enhance the electrical conductivity compared to the composites with randomly oriented CNTs. However, electrical percolation threshold increases using aligned CNTs ($p_c = 0.07$ for straight and $p_c = 0.025$ for helical) instead of using randomly oriented CNTs ($p_c = 0.008$ for straight and $p_c = 0.012$ for helical) (Figure 1). In sheared suspensions using helical nanotubes ($p_c = 0.0007$) instead of using straight ones ($p_c =$

0.0015)decreases percolation threshold [4]. The difference between the non-sheared and sheared suspensions is because of the dynamics of agglomeration in sheared suspensions. Increasing curvature of the nanotubes favors the conductive network formation in the sheared suspension.

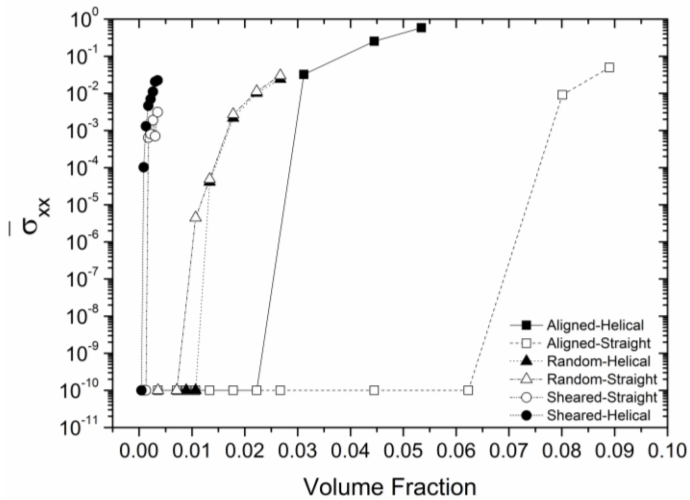

Fig.1. Electrical conductivity as a function of volume fraction for aligned, randomly oriented and sheared CNT/polymer composites with helical or straight nanotubes.

We performed simulations to show the behavior of the sheared suspensions with straight and helical nanotubes and with different starting configurations (aligned and random) on the electrical conductivity evolution during the shear flow. Figure 2 shows the conductivity, σ_{xx}, evolution as a function of shear strain $\dot{\gamma}t$ for different starting configurations of suspensions of straight and helical nanotubes. As previously reported [7], steady state conductivities and microstructures of the sheared CNT/polymer composites do not depend on the initial configuration. However, we show that suspensions with aligned helical nanotubes must be more strained to form a conductive network than the suspensions with randomly oriented helical nanotubes. Using randomly oriented straight nanotubes requires more strain to form percolating clusters than the aligned or randomly oriented helical nanotubes. Using aligned straight nanotubes can create a conductive network only when the total strain was increased.

Conclusions

Dependence of electrical properties on the anisotropy and non-straightness of the CNT/polymer composites were investigated using fiber-level simulations together with a Monte Carlo method and a resistor network algorithm. We showed that the formation of aggregates with sheared composites is a more efficient way in decreasing the electrical percolation threshold than using randomly oriented or aligned composites.

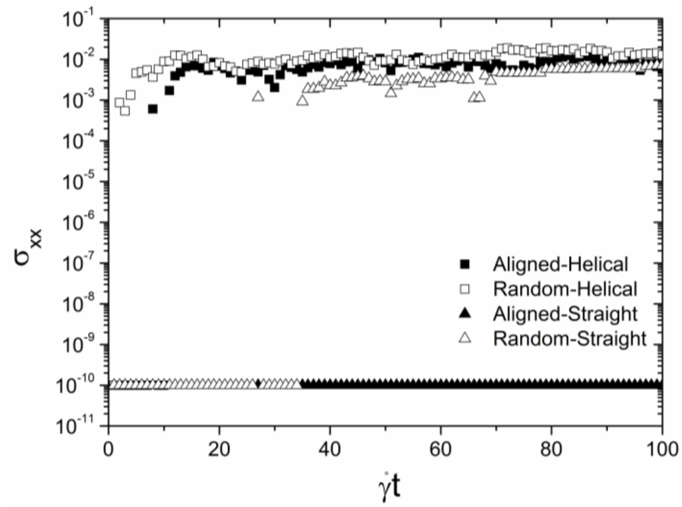

Fig. 2. The conductivity as a function of shear strain $\dot{\gamma}t$ for different starting configurations of suspensions of straight and helical nanotubes.

Using helical nanotubes increases the percolation threshold in randomly oriented composites whereas for sheared and aligned composites this effect is reversed. Starting configuration does not affect the final conductivity and the microstructure of the sheared suspension but the required strain to obtain percolating clusters changes.

References

1. Yang, Y., Gupta, M., Dudley, K. L., Lawrence, R.W. Novel carbon nanotube-polystyrene composites for electromagnetic interference shielding. *Nano Letters,* **5** (11) (2005) 2131.
2. Keshtkar, M., Heuzey, M. C. and Carreau, P. J. Rheological behavior of fiber-filled model suspensions: Effect of fiber flexibility. *Journal of Rheology* **53** (3) (2009) 631.
3. Switzer, L. H. Simulating systems of flexible fibers. University of Madison-Madison, 2002.
4. Eken, A. E., Tozzi, E. J., Klingenberg D. J. and Bauhofer, W. A simulation study on the combined effects of nanotube shape and shear flow on the electrical percolation thresholds of carbon nanotube/polymer composites. *Journal of Applied Physics* **109** (2011) 084342.
5. Tozzi, E. J. Hydrodynamics, rheology and conduction in suspensions of arbitrarily shaped fibers. University of Wisconsin-Madison, 2008.
6. Du, F., Fischer, J. E. and Winey, K. I. Effect of nanotube alignment on percolation conductivity in carbon nanotube/polymer composites *Rapid Communication Physical Review B* **72** (2005) 121204.
7. Bauhofer, W., Schulz, S. C., Eken, A. E., Skipa, T., Lellinger, D., Alig, I., Tozzi E. J. and Klingenberg, D. J. Shear-controlled electrical conductivity of carbon nanotubes networks suspended in low and high molecular weight liquids. *Polymer* **51** (22) (2010) 5024.