THE INFLUENCE OF SHEARING AND ELECTRIC FIELDS ON THE PERCOLATION THRESHOLD IN CARBON NANOTUBE EPOXY COMPOSITES

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The efficiencies of electric field alignment and shear induced flocculation were compared with respect to the resulting sample conductivity. This work demonstrates for the first time that two percolation thresholds (PTs) can coexist in an insulator-conductor-system. The higher PT is determined by the filler geometry [1] (static PT) and the lower can be manipulated through shear forces (kinetic PT). This result could explain the deviations often found in publications between the experimental PT and the one expected from statistical percolation theory.

Carbon nanotubes (CNT) are used as fillers in an epoxy polymer based on bisphenol-A resin with an amine hardener. Shearing was performed with a conventional stirrer, electric fields were provided by a bipolar power supply and conductivities were measured with an impedance spectrometer.

We show that shearing has a huge impact on the (kinetic) PT. This is reflected in the conductivity results (Fig. 1) as well as in the optical micrographs (Fig. 2). Slow stirring (50 rpm) turns out to give the lowest PT and to be most efficient in generating a superstructure of flocs spanning the whole sample.

Our results identify a second, static PT (Fig. 1): at 0.1 wt% a conductivity crossover from saturation to power law behavior is clearly visible in the slow and medium stirred samples.

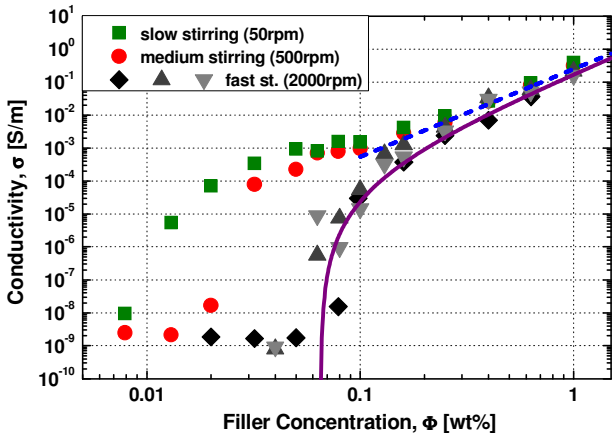

Fig. 1. Log–Log plot of conductivity vs. nanotube weight fraction for the three sample preparation methods. Both, the scaling law $\sigma \sim \Phi^t$ (solid line) and power law dependence $\sigma \sim (\Phi - \Phi_C)^t$ (dashed line) have t = 2.7

This is the region where the semi-diluted solution becomes concentrated [2], meaning that the CNT can no longer form a superstructure but touch each other directly. Fast stirring (2000 rpm) seems to generate no superstructure, since both PTs nearly coincide.

Our results could also explain why the scaling law exponent t used for describing a percolation behavior varies so much in literature. Evaluating the kinetic PT seems to yield a lower exponent (t = 1.7; dashed line in Fig. 3) than evaluating the static PT (t = 2.7; solid line). Other researchers [3] even find a lower kinetic PT (Φ_C

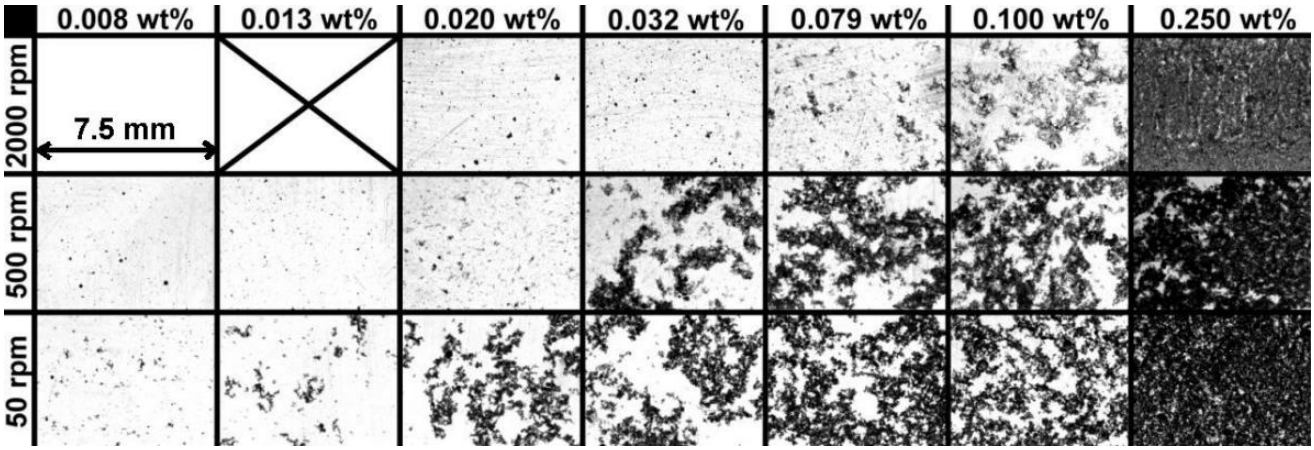

Fig. 2. Light micrographs of samples from each preparation method (rows) and varying CNT concentration (columns)

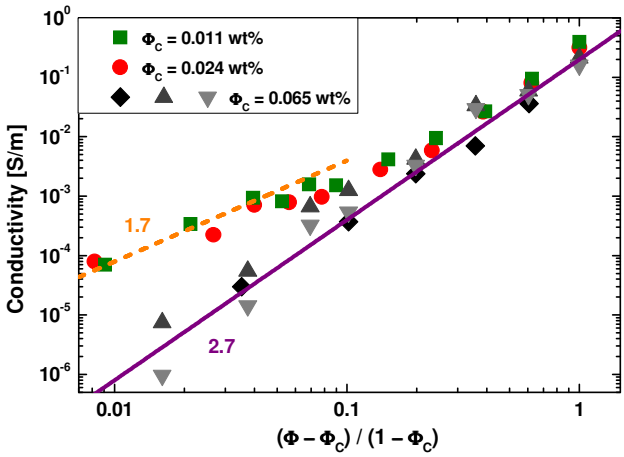

Fig. 3. Log–Log plot of conductivity vs. reduced CNT weight fraction for the three sample preparation methods

[1] Celzard A., McRae E., Deleuze C., Dufort M., Furdin G., Marêché J.F. "Critical concentration in percolating systems containing a high-aspect-ratio filler". *Physical Review B*, Vol. 53, No. 10, pp 6209-6214, 1996.

[2] Doi M., Edwards S.F. *"The Theory of Polymer Dynamics"*, 1st ed., New York: Oxford University, 1986.

[3] Sandler J.K.W., Kirk J.E., Kinloch I.A., Shaffer M.S.P., Windle A.H. "Ultra-low electrical percolation threshold in carbon-nanotube-epoxy composites". *Polymer*, Vol. 44, No. 19, pp 5893-5899, 2003.

[4] Kovacs J.Z., Velagala B.S., Schulte K., Bauhofer W. "Two percolation thresholds in carbon nanotube epoxy composites". *Composites Science and Technology*, doi:10.1016/j.compscitech.2006.02.037.

= 0.0025 wt%) and exponent (t = 1.2), meaning that such superstructures of flocs have a fractal dimension much lower than 3. We point out that t severely depends on the percolation threshold, since choosing Φ_C = 0.08 wt% – which fits better the samples denoted with rhombi – would give t = 2 [4].

The electric field alignment of filler particles leads to higher conductivities than the shear induced superstructures (compare the values of 0.04 wt% CNT in Fig. 4 and Fig. 1). At 0.08 wt% however – when reaching the static PT – the advantage of field alignment vanishes. It seems that even higher field strength cannot change this.

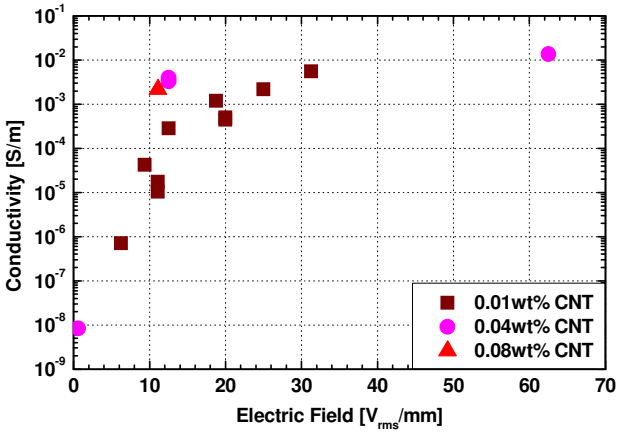

Fig. 4. Semi–logarithmical plot of the sample conductivity after applying an electric field while curing.