Carbon nanotube networks dispersed in a polymer matrix: dielectric properties simulations and experiments

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The addition of carbon nanotubes (CNT) to a polymeric matrix is known to affect its mechanical and electrical properties. The changes can be significant even at small volume fractions of the reinforcement. The CNT concentration, aspect ratio, and dispersion are expected to affect the material response [1]. However, the precise mechanisms responsible for the described effects are not sufficiently understood. This is due to the complex nature of the behavior of polymers, which exhibit a complex structure and a variety of factors that influence the material behavior, such as the thermomechanical processing history, time-dependent behaviour, anisotropy, etc.

For CNT/polymeric composites it is assumed that the mechanism for the composite conduction is formation of conductive channels stretching across the entire length of the system [2]. The later assumption enables the use of the percolation theory were simple power laws can predict the composite conductivity and the effective dielectric constant. One of the fundamental concepts in the percolation theory is the percolation threshold (p_c). The percolation threshold is defined as the concentration (p) at which an infinite cluster appears in an infinite lattice. For a concentration $p > p_c$ a cluster spans the system and for $p < p_c$ the spanning cluster does not exist and the system is made of many small clusters. The value for the percolation threshold depends on the dimensionality of the domain and on the geometry of the filler. At the percolation threshold there are several physical properties that can diverge such as the conductivity and the dielectric constant. The relationship between the composite critical concentration in the conductivity and the dielectric constant was early studied by Bergman and Imry in 1977 [2] for heterogeneous mixtures of a conducting phase in an insulating matrix. Bergman and Stroud [3] used a scaling assumption in order to analyze the critical behavior of the composite dielectric constant, demonstrating that for metallic inclusions in an insulating matrix the real part of the dielectric constant has peak at ω = 0 Hz whose height is proportional to $\varepsilon_{matrix}\left|p - p_c\right|^{-s}$, diverging at p_c. The later yields the well known relation that holds for $p < p_c$ and $p > p_c$, $\varepsilon_{eff} \propto \varepsilon_{matrix}\left|p - p_c\right|^{-s}$. In the same article [3] Bergman and Stroud also demonstrates, using the same scaling relations, for the composite conductivity that for p > pc the composite conductivity is given with the following relation, $\sigma_{eff} \propto \sigma_{matrix}\left(p - p_c\right)^t$. On the later power laws **t** and **s** are called the conductivity – **t** – and superconductivity – **s** – critical exponents. The values for the conductivity exponent were determined by Kirkpatrick [4] using three different models. The value in 3D for **t** was 1.5 +/- 0.2. In more recent works the accepted value is ~1.8. For the superconductivity exponent using a bond percolation model, 3D, in conjugation transfer matrix algorithm, Herrmann and Derrida [5] found that the value is 0.75 +/- 0.04.

The critical values are assumed to be universal; depending only on the dimensionality of the system.

In recent experimental articles for multi wall carbon nanotubes (MWCNT)/polymeric composites were the superconductive exponent – **s** – and the percolation threshold are reported, a wide range of values have been reported (Table 1).

In this work, a numerical model based on the graph theory is presented which focuses on the effect on the dielectric constant and the dielectric strength of the inclusion of conductive fillers in a dielectric polymer matrix [6]. Experiments have been carried out in carbon nanotubes/poly(vinilidene fluoride) nanocomposites in order to compare to the simulation results Fig. 1. This work shows how the critical concentration is related to the formation of capacitor networks and that these networks give rise to the high variations in the electrical properties of the composites. Finally, based on numerical and experimental results, the origin of anomalous percolation behaviours has been identified.

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Figures:

Table 1, Experimental reported values for the percolation threshold in several MWCNT composites types.

Percolation Threshold	Aspect Ratio	s exponent	Composite	Reference
0.0077	62	0.268	MWCNT/PVDF	[7]
0.0114	116	1.007	MWCNT/PVDF	[7]
0.0191	437	1.795	MWCNT/PVDF	[7]
0.0161	833	0.31	MWCNT/PVDF	[7]
0.0079	-	0.35	Alumina/MWCNT	[8]
0.07	300	1.14	MWCNT/Polyimide	[9]
1.44	440	-	MWCNT/Polycarbonate	[10]

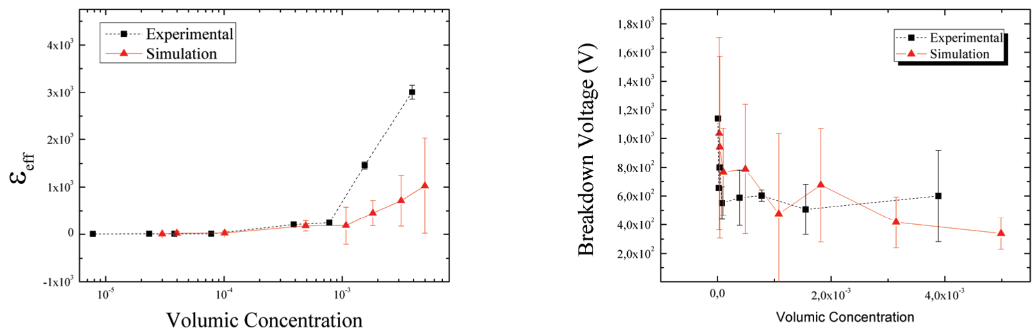

Figure 1, Comparison of the numerical results versus experimental ones.