Tuning the insulator to conductor transition in a multiwalled carbon nanotubes/epoxy composite at substatistical percolation threshold

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A fine tuning of the electrical conductivity from insulator to conductor behavior has been obtained for a multiwalled carbon nanotubes epoxy composite at a fixed substatistical percolation threshold content by varying the organization of the nanotubes network. A multiscale characterization has been carried out by transmission optical microscopy technique and small angle x-ray analysis that revealed a two level structure characterized by different topological arrangements for the micron sized clusters and nanosized isolated bundles, respectively. A picture of the multidimensional organization of the nanotubes network has been proposed to account for the observed transition modulation. © *2009 American Institute of Physics*. [doi:10.1063/1.3242017]

In the field of composite materials, a promising approach for the development of engineered materials is the use of carbon nanotubes (CNTs) as fillers in polymeric matrices, because of their high surface to volume ratio, that is a key parameter in reducing the critical concentration to obtain a percolative insulator to conductor transition.[1–3]

Experimental results showed that conductive materials can be produced from a wide range of matrix polymers at very lower CNTs content than the statistical percolation threshold

$$\left(\Phi_{st} = \frac{1}{2}\frac{D}{L}\right)$$

and that such percolative transition is modulated by the dispersion/reaggregation phenomena occurring during the specific manufacturing process.[4–8] Recently, Brown *et al.*[9] showed that CNTs may arrange within an epoxy matrix in networks with hierarchical morphology, showing the existence of a multiscale dispersion state, where nanotubes are aggregated into disordered ropes that are further agglomerated into micron sized fractal clusters. From a theoretical point of view, research mainly describes interactions between nanoparticles considering a percolative approach that suffers of the fact that mainly equilibrium structures can be predicted, while the real attained aggregation topologies are characterized by a kinetic nature, such as nonequilibrium features.[3,4]

In line with this argument, here we describe the manufacturing of multiwalled CNTs (MWNTs) epoxy based composites whose percolative insulator to conductor transition has been tuned by using different process parameters at a fixed nanotubes concentration. The main objective of this work is to produce a set of materials whose electrical connectedness varies according to the development of different nanotubes networks being their global concentration constant.

Catalytic carbon vapor deposition (CCVD) MWNT (Nanocyl 3150) with an average diameter of 9.5 nm, an average length less than 1 μm, and a purity exceeding 95% have been used. MWNTs dispersion step has been alternatively conducted using, as solvents, either the thermoset epoxy matrix, bisphenol-A/epichlorohydrin, EPON 828, (E samples), or its amine curing agent, triethylenetetramine (TETA) (*T* samples) under two different sonication times, t_s, (30 and 120 min). MWNTs concentration in the two initial solutions vaires, being TETA/MWNTS solutions more concentrated than EPON/MWNTs ones.

The curing steps have been performed isothermally at 25, 70, and 120 °C (T_c), for each sonication time and solvent, after the manual mixing of the complementary reactant. All composites have been fabricated at a fixed final concentration of 0.05 wt % MWNTs, that is well below the statistical percolation threshold, estimated to be 1 wt %.

Electrical conductivity has been evaluated by means of dc electrical resistance measurements. Figure 1 shows that, at a fixed MWNT content, the transition between insulator to conductor behavior can be tuned by varying the sonication parameters and the curing temperature. Dashed area indicates the uncertainty zone of the picoammeter used for the current measurements.

The notable result is related to the possibility to finely tune the electrical conductivity, induced by the curing temperature, in the samples prepared by sonicating nanotubes for 30 min in TETA, while all the *E* samples show high conductivity values being only slightly affected by the curing temperature. In *E* composites the relative invariance of the electrical conductivity highlights that the full percolative behavior has been obtained for MWNT content lower than 0.05 wt %.

Transmission optical microscopy images of thin nanocomposite films are shown in Figs. 2(a)–2(d). The micron scale morphology of the *T* composites is characterized by a coarse distribution of particles having dimensions ranging from few microns to some tens of microns. Upon an increase of curing temperature, the number of the observable particles increases (T_70 °C) as does the particle agglomeration (T_120 °C).

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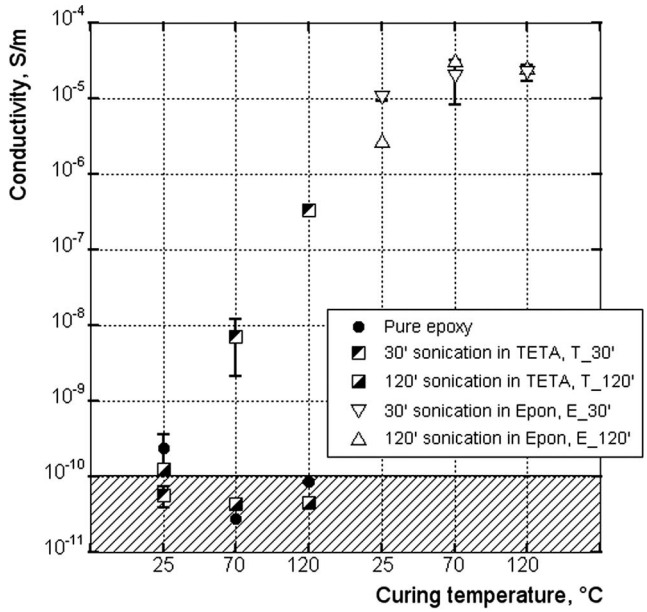

FIG. 1. Conductivity of the four sets of manufactured nanocomposites and of pure epoxy as a function of curing temperatures.

On the contrary, the composites prepared by sonication in EPON have all shown a finer and more homogeneous space filling topology than *T* samples. This morphological difference is mainly due to the structure induced during the initial sonication. For *T* samples, both the high numerical concentration of nanotubes within the initial sonicated mixture and their high affinity with amine hardener[9] promote the formation of a micron sized cluster structure. While for *E* composites, the preparation from a dilute solution of MWNTs in epoxy leads to a more homogenous dispersion state.

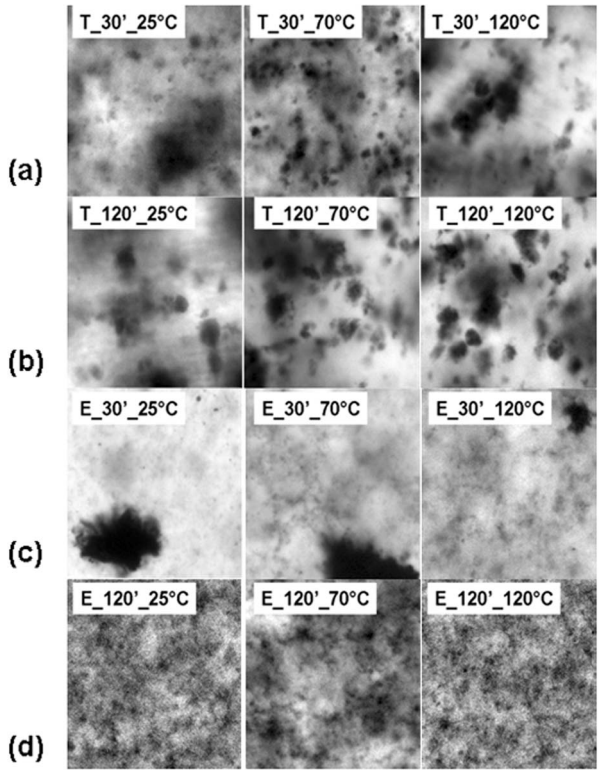

FIG. 2. Transmission light micrographs at 20× magnification (100 ×100 μm^2) of 0.05 wt % MWNT composites sonicated for (a) 30′ in TETA, (b) 30′ in EPON, (c) 120′ in TETA, and (d) 120′ in EPON and then cured at 25, 70, and 120 °C.

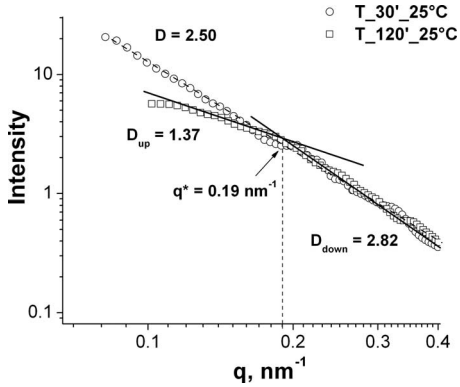

FIG. 3. Background subtracted scattering data for samples *T* and *E* sonicated for 30 and 120 min and both cured at 25 °C.

This different dispersion state strongly affects the electrical conduction mechanisms: in *E* samples, the electrons transport occurs through a fully percolated network of conductive rods or bundles; in *T* samples, the electrical percolative network is very "weak" (removal of few bonds can reduce it to a nonpercolative net) and it is dominated by the particle clusters that act as "blobs" for the electron transport.[4]

Small angle x-ray scattering (SAXS) investigations have been further used to assess the morphology of MWNTs within the composites at length scales ranging between 10 and about 90 nm, evaluated as $d=2\pi/q$, where q is the scattering vector. The Porod plot (log-log) of the scattering intensity, I versus q may show both linear regions, where the power law with D exponent is related to the fractal dimension of the nanotubes structure and Guinier regimes, where crossover features are reasonably associated with the size of scattering objects.[10]

Figure 3 shows, as a reference, the Porod plots of the background subtracted SAXS spectra related to *T*_25 °C samples. The spectra have been obtained by subtracting the scattering intensity due to the neat epoxy structure. For $q > 0.5$ nm^{-1}, data are affected by large error due to the comparable magnitude of the pure epoxy matrix and nanocomposites scattering intensity signals and they have been omitted for the sake of the graph quality. The *T*_30′_25 °C sample spectrum is linear within the investigated range and it is characterized by a single D exponent, while the *T*_120′_25 °C sample exhibits a knee-scattering feature with a crossover at a q^* that separates two linear regions associated with two different fractal like morphologies, i.e., D_{up} and D_{down} for $q<q^*$ and $q>q^*$, respectively (Table I).

TABLE I. SAXS structural data referring to *T* and *E* samples sonicated for 30 and 120 min and cured at 25 and 120 °C.

	TETA		EPON		
t_s	25 °C	120 °C	25 °C	120 °C	
30′	2.5	2.72	2.5	3.32	D
120′	31	30	32	48	d^* (nm)
	2.82, 1.37	3.45, 2.23	3.12, 1.43	2.95, 1.72	D_{down}, D_{up}

Although the background subtraction may introduce additional uncertainty in estimating the contribution of the MWNTs, the crossover is a reliable scattering feature which is related to a peculiar morphology of manufactured composite systems. Regardless of the dispersing medium, 120′ sonicated samples exhibit a knee-scattering feature with a crossover which reasonably leads to the estimation of the size of the smallest scattering object within the composites evaluated as $d^*=2\pi/q^*$.[11]

In this case, for $q>q^*$, the scattering objects exhibit a fractal dimension, D_{down}, related either to a mass or a surface fractal morphology. In particular, the fractal morphology is more compact than that of the 30′ sonicated samples cured at the correspondent temperature, and the scattering objects surface corresponds to a fractally rough surface.[10] Scaling exponent, D_{up}, for $q<q^*$ has been always found to be lower than D_{down}, approaching the value 1, indicating the existence of somehow linear or flexible linear objects.[12]

Regardless of the dispersing medium, 30′ sonicated samples do not show any scattering structure. The scaling exponents do reveal the existence of mass fractal objects whose compactness increased with the curing temperature.[13]

A notable result is the detection itself of such nanostructures by means of SAXS, not yet observed in literature for MWNT/epoxy composites systems. SAXS analysis indeed reveals that for both *T* or *E* samples, irrespective of the topological morphology of the microsized dimensional scale, nanosized structures are formed as t_s is increased. Such findings not only confirm the debundling action of the sonication technique,[7,14,15] but also suggest that the energy provided by the sonication enables and promotes nanotubes rearrangements within the bundles network. In *E* samples, because of the persistence of a percolative network of nanotubes, the variations of the nanoscale structural parameters do not induce significant electrical conductivity modulation on the macroscale.

On the other hand, for *T* samples, where the composite conductivity is associated to the "weakness"[4] of the percolative path, the variation of nanoscale structural parameters influences the conductivity modulation on the macroscale. In fact, the *T*_120′ samples are not conductive at all due to the presence of small matrix isolated nanotubes bundles which do not contribute to the formation of the percolation path and contemporary increase the number of electrical junctions between tubes.[14] Moreover, sonication could induce damaging and shortening of the nanotubes with the reduction of their aspect ratio and the consequent decreasing of the electrical conductivity.[16]

Based on the present experimental findings and partially according to Brown *et al.*,[9] a picture of the multiscale organization of CNTs has been proposed. Starting from the single MWNT, two higher length scales have been observed, such as the nanosized bundles and the micron sized clusters, whose intrinsic electrical conductivity and connectedness determine the conductivity at the macroscopic scale. Moreover, on the micron scale, two different topologies are proposed here for the structure of the clusters. Both the topologies have to be regarded as constituted by CNTs bundles (whose dimensions and connectedness depend on the sonication time) that are the building block of the resulting micronetworks. For *T* systems, a "tumbleweed" topology is proposed, in which bundles connect each other mainly forming closed micrometric loops. In the case of the *E* systems, microscopic observations suggest the presence of a "dendritic" morphology, in which bundles are connected mainly forming branched open structures (Fig. 4).

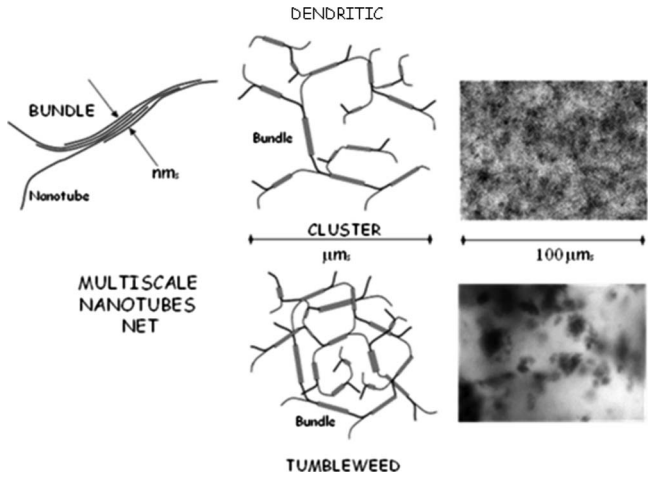

FIG. 4. Multiscale nanotubes net for *T* and *E* composites.

In summary, we report on the method to produce MWNTs/epoxy composites at a fixed tubes concentration below the statistical percolation threshold, whose electrical conductivity has been fully modulated between the insulator to the conductor behavior by varying the initial dispersion medium, the sonication time, and the curing temperature.

Two distinct cluster topologies within the final composite induced by means of sonication aided dispersion procedure have been found by SAXS analysis. Moreover, the extent of conductivity tuning is regulated by such nanoscale bundle structures. A multiscale organization of nanotubes in bundles then in micron sized clusters has been proposed accounting for the development of the conductive percolative path.

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