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Electrical Properties of Single Walled Carbon Nanotube Reinforced Polystyrene Composites

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Summary: Composites of carbon nanotubes (CNT) in polymeric matrices have attracted considerable attention in the research communities due to their good electrical conductivity, high stiffness and high strength at relatively low CNT contents. Effective utilization of CNT in composites depends primarily on the ability to disperse them homogeneously throughout the polymer matrix, avoiding the formation of bundles due to van der Waals interactions existing between the nanotubes. In this work composites of polystyrene at various percentages of SWNT were fabricated using Latex Technology technique, a polymer type-independent method based on using a surfactant as a dispersing agent. An electrical characterization of SWNT composites was performed both in DC and AC modes. From the analysis of DC data a percolative behavior was found for the conductivity as function of SWNT content. The innovative contribution of this work consists in the modeling of the composite material upon its electrical properties. AC measurements and the analysis of impedance as function of angular frequency lead to the formulation of an equivalent circuit able to model the composite material in correspondence of the percolative threshold.

Keywords: carbon nanotubes; dispersion technique; electrical properties; percolation behavior; polymer composites

Introduction

Since the documented discovery of carbon nanotubes (CNTs) in 1991 by Iijima, a considerable research focused on their unique physical properties, including mechanical, thermal and electrical and many attempts have been done in order to fabricate advanced CNT composite materials, with an improvement of one or more of these properties. For example, as conductive filler in polymers, CNTs are quite effective compared to traditional carbon black microparticles, primarily due to their high aspect ratios.[1,2] However, the current bottleneck to CNTs' application in composite materials field consists in the difficulty of dispersing them in a polymeric matrix. As a result of strong van der Waals interactions, as produced CNTs are tightly bundled in ropes of several tubes, rendering the carbon-powder insoluble in aqueous and organic liquids, and thus unprocessable.[3] To unlock the potential of carbon nanotubes for application in polymer nanocomposites much effort has been invested over the last years in achieving a good dispersion method for CNTs in polymer matrices and many are the techniques used for this purpose.[4]

In this study SWNT-polystyrene composites at various percentages of polystyrene were fabricated by using a polystyrene latex

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as polymer matrix and a surfactant as dispersing agent. Morphology, thermal and electrical properties of the as prepared nanocomposites films were investigated by an extensive experimental characterization. In particular, electrical characterization in both DC and AC modes was conducted on the composite samples in order to evaluate respectively their percolative and dielectric behavior.

The dielectric behavior of the threshold concentration sample was modeled by an equivalent circuit able to describe the conductive nature of the nanocomposite, at low frequencies, and the capacitive one, at high frequencies. A good agreement between experimental and analytical data was found, confirming the model capabilities.

Materials and Methods

Materials

Closed-ended SWNT made by Arc-method were purchased from Carbolex. The tubes average diameter was 1.4 nm with a length of 2–5 μm; the purity was about 70% and the residual catalysts consisting of Ni, Y particles. Samples include both semiconducting and metallic tubes.

Polystyrene latex at 20 PSwt% (Mw = 690 kg/mol) was prepared by emulsion polymerization using Sodium Dodecyl Sulfate (SDS) as a dispersing agent in a reactor at 75 °C for 24 hours.

Techniques

In this work, latex technology was used to fabricate single-walled carbon nanotube (SWNT) polystyrene composites. Latex technology technique is a polymer type-independent method based on using a surfactant as a dispersing agent in order to enhance nanotubes dispersion in high viscous polymer matrixes without any functionalization.[5]

SWNT (0.2 wt%) were dispersed in an aqueous solution of Sodium Dodecyl Sulfate (1 wt%). In order to enhance SWNTs dispersion, the solution was sonicated in an Ultrasonic Processor (Fisher mod GEX 500) so that the energy transferred to the sample was 120 J/g and then put in the thermal bath for one hour. As prepared solution was centrifuged for one hour phase-separating in into a solid precipitate and an ink-like supernatant, which was decanted and used further. Calculation of the amount of SWNT in weight percent was based on the assumption that all NTs were in solution. Actually, the real content of NTs in the solution after the centrifugation was not the same as the initial one. The solid precipitate consisted not only in catalyst particles, but also in heavy carbonaceous nano-particles and nanotubes, because generally catalysts are encapsulated in the head of the nanotube, so that an undefined amount of nanotubes was lost during the centrifugation. An attempt in evaluating the real amount of nanotubes present in the samples was done by collecting the solid precipitate, depriving of the water and SDS and then weighting it, so that the remaining material should be only nanotubes. This sediment study led to the conclusion that more than 70% of the raw material was lost during the centrifuge. However, it was not possible to identify the real concentration for each sample, so that the SWNT concentrations indicated in this study are nominal. Different amounts of the as treated aqueous solution were added to the same quantity of polystyrene latex in order to prepare composite samples at various SWNT wt% having the same weight (Table 1). As prepared composite solutions were freeze-dried over-night. The resulting powders were hot-pressed providing thin films having a thickness of about 0.1 mm.

Table 1.
SWNT composite samples.

	SWNT wt%
Film 1	0
Film 2	1
Film 3	1.5
Film 4	2
Film 5	2.9
Film 6	3
Film 7	5

Experimental Part

An extensive experimental analysis was conducted in order to evaluate composites morphology, thermal properties and electrical behavior.

Microscopic Analysis

Room-temperature TEM characterization of the composite films was conducted after embedding a 5 SWNT wt% sample in an epoxy resin and sectioning the cured composite by microtome. Direct microscopic observation of the SWNT dispersion in nanocomposites is difficult to apply due to their extreme high aspect ratio, i.e. the extreme difference in radial and axial dimensions.[6] Moreover, because of the similar nature, low contrast between nanotubes and the surrounding matrix can be obtained with conventional microscopic techniques. Figure 1 shows a SWNT having a diameter of about 2 nm and a few darker catalyst particles in its vicinity.

Thermal Properties

Thermal properties of CNT/polymer composites also attracted many attentions from scientists because CNTs have very high thermal stability. The addition of CNTs in polymer matrix can cause some composites to degrade at lower temperature[7] or to promote an increase in thermal stability.[8] The structure of the polymer matrix and the interaction between CNTs and the matrix may be the key factors for the thermal degradation behavior of CNTs filled polymer composites.

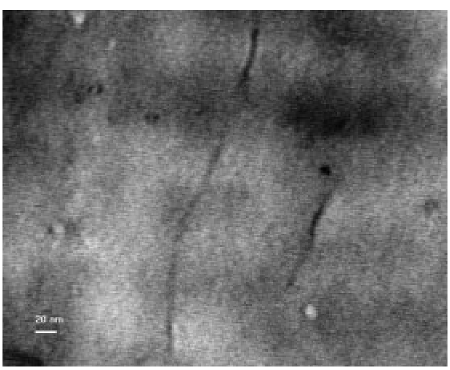

Figure 1.
TEM micrograph of a 5 SWNT wt% sample.

In this study, thermogravimetric analysis on five samples at different SWNT wt% (films 1, 2, 3, 7) was performed using a HiRes TGA 2950 Thermogravimetric Analyzer (TA Instruments). The thermal decomposition studies of the composites were performed over a temperature range of 30–1000 °C under air environment at the heating rate of 10 °C/min. TGA curves of pure polystyrene and SWNT-PS composites are shown in Figure 2. One step decomposition is found for the pure polymer and a two-step decomposition for the composite samples in the range 30–450 °C. The presence of CNTs induces the comparison of a plateau that is lower for higher SWNT wt%.

The oxidation of the composites starts with PS oxidation, because CNTs generally starts to degrade at about 500 °C. Many researchers have reported that CNTs can stabilize polymer.[9] Our observation is similar, as can be seen in Figure 3: degradation temperature of the composite increases upon an increase of SWNT content. The increased thermal stability of SWNT-PS composites over that of the pure PS is likely to be a result of absorption, by activated carbon nanotubes surface, of free radicals generated during the polymer decomposition.

Electrical Characterization

Generally, electrical properties of nanotube composites can be described using the percolation theory. This phenomenon is characterized by the presence of a conductive path through the matrix due to the formation of a three-dimensional network of conductive fillers which are the nanotubes. A sharp drop characterizes the percolation conductivity curve in correspondence of the percolation threshold, that is the frontier between insulator and conductive behavior of the composite. At the onset of the percolating network, electrical conductivity obeys the power law relation:

$$\sigma \propto (wt - wt_c)^n$$

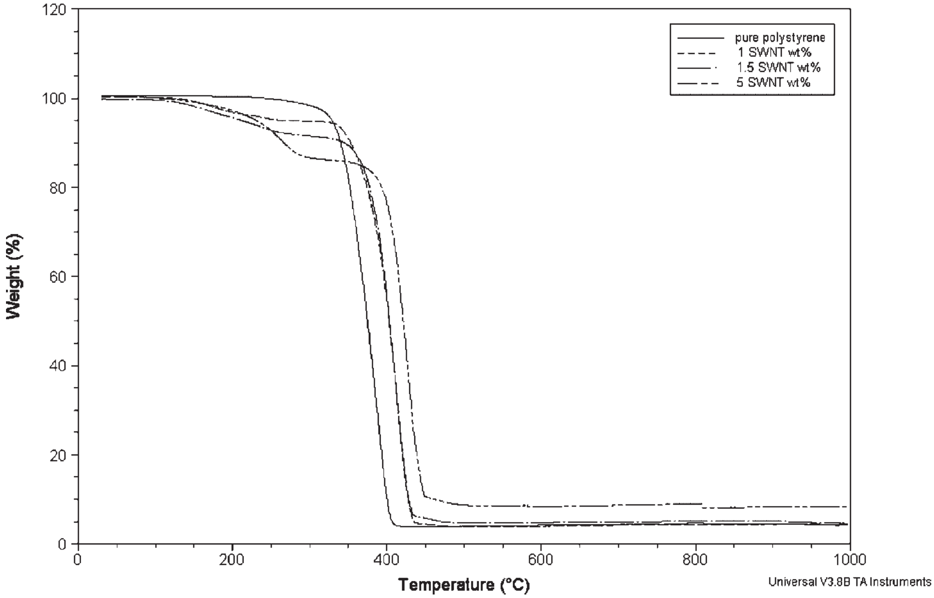

Figure 2.
TGA curves of SWNT-PS composites with different SWNT content under atmosphere.

where σ is the composite conductivity, *wt* is the nanotube concentration, wt_c is the percolation threshold and *n* is the critical exponent.[10]

In this study, all composite samples were electrically characterized both in DC and AC mode in order to evaluate percolative and dielectric behaviors.

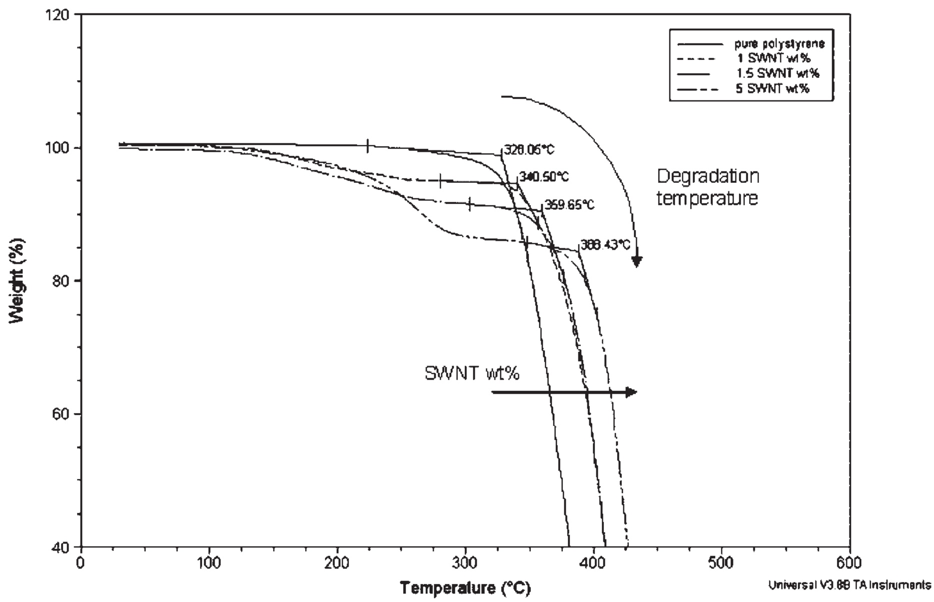

Figure 3.
TGA curves of SWNT-PS composites in the range 30–500 °C

DC Conductivity

Room-temperature DC conductivity was measured by using a Keithley Picoammeter and Voltage source 6487. Samples (all the films listed in Table 1) were shaped in a square form and placed on a plate between two copper electrodes. A tension between −50–50 V was applied between the electrodes and the current circulating in the samples was measured by the picoammeter and its values were acquired using Labview with a standard IEE-488. conductivity values for each sample was calculated from current and voltage data and plotted against SWNT wt% in order to evaluate the percolative threshold (Figure 4a).

The introduction of nanotubes increases the conductivity of the composite by up to six orders of magnitude, being the measured conductivity of the pure polystyrene 10^{-9} S/m. Between 1.5 and 2 SWNT wt% the composite conductivity displays a dramatic increase by two orders of magnitude, that's why 1.5 SWNT wt% was detected as the percolation threshold for the composite system. This indicates that for weight fractions of SWNTs below 1.5 wt%, the nanotubes are almost isolated and the electrical conductivity governed by the electrical characteristics of the polymer. As the fraction of SWNTs increases further, the average distance between the nanotubes becomes sufficiently small for electrons to tunnel through the polymer or by contact between nanotubes to be formed.

Thus, the electrical response of the composite was described by the power law:

$$\sigma = 2.59^{-6} \cdot (wt - 1.5)^{4,9}$$

found out by fitting the data above the percolation threshold (Figure 4b).

From DC electrical data it was possible to analyze also current-voltage curves of the composites at different SWNT concentrations. I–V characteristics for samples at low and high SWNT concentrations is nearly linear, on the contrary, for samples with an intermediate concentration, for example 3 SWNT wt% composite, the trend is not linear (Figure 5).

This phenomenon can be addressed to the simultaneous occurring in the composites of different electrical transport mechanisms. Because of the presence of polymer matrix, a series of different mechanisms could occur, such as tunneling and hopping effects. The concomitance of these different electrical conduction mechanisms, the possible lack in homogeneity of the composite, together with the mixed structures of the raw nanotubes, that have not only metallic but also semiconducting properties, could cause not linear I–V characteristics.

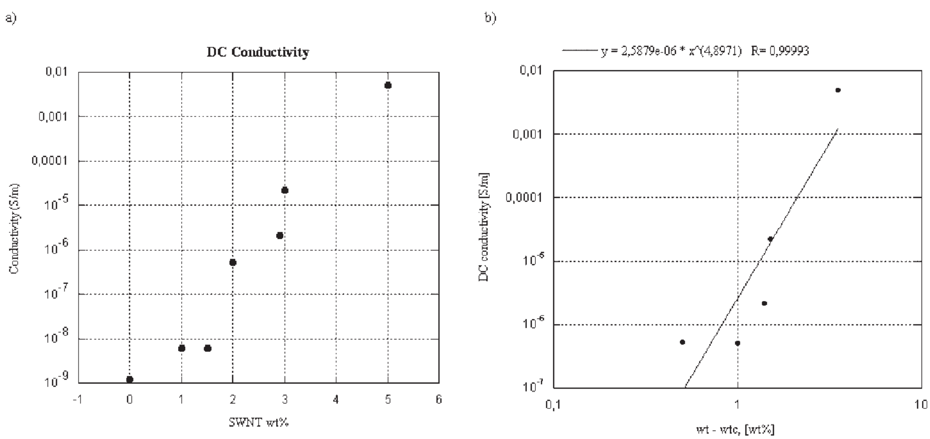

Figure 4.
a) DC conductivity of SWNT-PS composites; b) power law fit of data above percolation threshold.

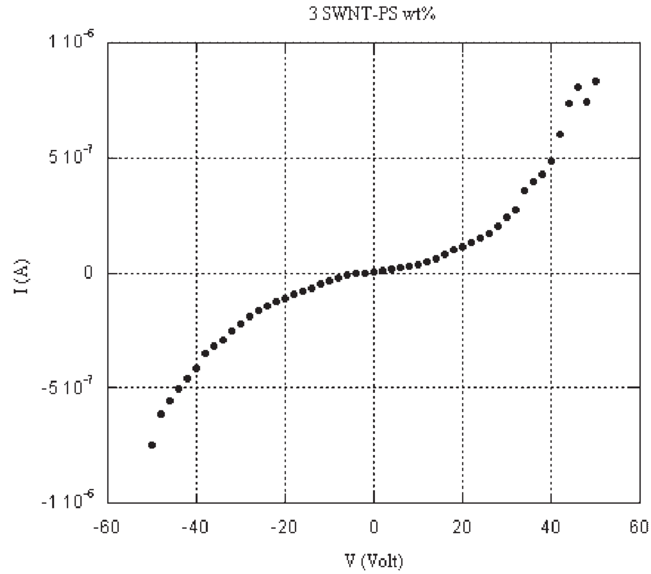

Figure 5.
Current-Voltage curve of 3 SWNT-PS wt% sample.

AC Measurements

The use of dielectric spectroscopy in CNT filled systems represents a novel and quite interesting research area. The knowledge of the frequency dependence of complex impedance, expressed as its modulus and phase, is a very useful technique to investigate AC behavior of composite materials.[11]

Impedance measurements in a frequency range 42Hz–5MHz were performed by using a Hioki 3532-50 LCR Tester. A thin Al coating was deposited on both sample surfaces in order to improve electrical contact with the tester leads. Experimental set-up consisted in a capacitor-like system where the sample was placed between two copper parallel surface at which alternating voltage was applied.

Hioki Tester data output were acquired using LabView with a standard IEE-488 and consisted modulus (Z), real part (R) and imaginary part (X) of impedance.

Figure 6 shows impedance modulus, Z as a function of the logarithm of angular frequency, ω (Bode plot) for some samples listed in Table 1. Impedance values decreases with increasing SWNT content because of the higher conductive filler content. Moreover, at 1.5 SWNT wt% impedance assumes a constant value in the range 700–4000 Hz. By the analysis of 1.5 SWNT wt% Bode plot the value of resistance can be obtained from the intersection of the frequency-independent line and log $|Z|$ axis and it is possible to observe that at higher frequency the dielectric response is purely capacitive and impedance is directly proportional to frequency with a slope of about -1. Upon increasing SWNT content this plateau disappears, up to 5 SWNT wt%, where the sample shows a different behavior, with a nearly constant value of impedance in the range 100 KHz-5 MHz.

In Figure 7 phase angle Φ, representing the out of phase between current and voltage, is plotted against the angular frequency, ω. Φ was evaluated from imaginary and real parts of impedance:

$$\Phi = arctg\frac{X}{R}$$

A frequency-constant capacitance is shown by the pure polystyrene, that behaves like a dielectric material with a phase angle of about -90°. Upon increasing SWNT con-

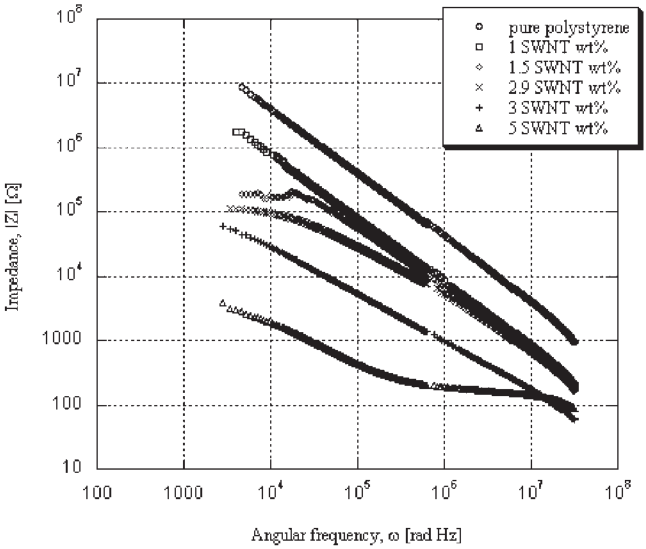

Figure 6.
Bode plot: absolute value of impedance as a function of angular frequency.

tent, phase angle shows a not linear trend as function of angular frequency. Because of the conductive nature of nanotubes, the material loses its dielectric nature, behaving more and more as a conductor. Moreover, this curve confirms that the conductive nature is predominant at low frequencies, while at higher frequencies the capacitive behavior provides a constant value for the phase curve. As mentioned above, the different behavior for 5 SWNT wt% sample can be observed also in the

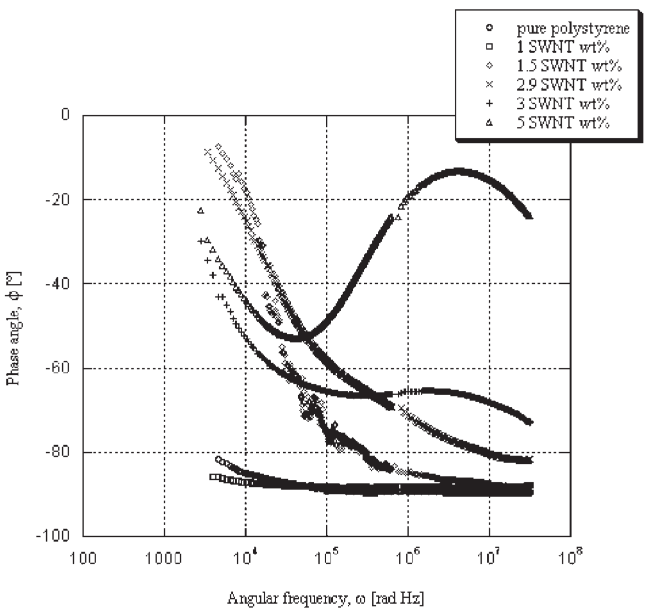

Figure 7.
Phase angle of SWNT-PS composites as a function of angular frequency.

phase curve. For this sample, the phase is not linear for the entire frequency range, as the other samples, but moreover, it doesn't show a constant value of the phase at high frequencies. This phenomenon can be due to the conductive nature of the composite, where SWNT content is predominant on the dielectric polymer.

Electrical Equivalent Circuit Model

In order to better understand the mechanism governing the composite AC behavior an attempt to electrically model the material was done.

The simplest modeling approach for a dielectric material is a R-C parallel circuit. However, in the case of a composite constituted by polymer matrix and nanotubes, the model should be more complex, in order to account the no ideal conductive behavior of nanotubes and the no ideal capacitive behavior of polymer. In this study, the nanocomposite was modeled as a circuit where a series of a resistance and a capacitance was in parallel with a parallel of a resistance and a capacitance. The first series represents the conductive nature of the composite, that is nanotubes, and the parallel represents the polymer matrix (Figure 8).

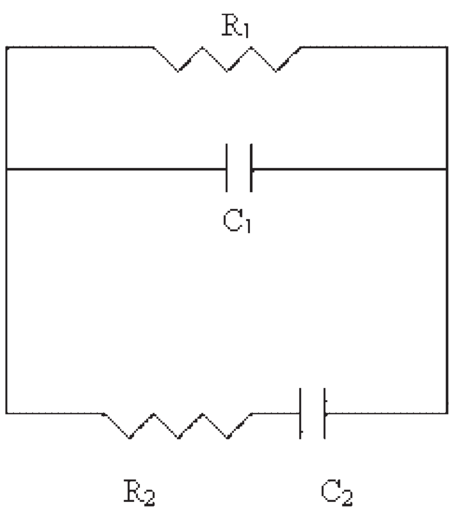

Figure 8.
Electrical equivalent circuit modeling 1.5 SWNT wt% composite.

In the model four parameters were identified, R_1, C_1, R_2, C_2, and used to best fit experimental data.

The best fitting was performed on Z modulus and phase angle for 1.5 SWNT wt%, that corresponds to the percolative threshold concentration.

Parameters values are indicated in Table 2. R_1 and C_1 represent polymer properties and R_2, C_2 the conductive nature of composite. The first two parameters affect Z modulus fitting curve in its high frequency region, while the other two parameters influence its low frequency region, coherently to the fact that the conductive nature of the composite can be detected at low frequencies and the capacitive one at higher frequencies (Figure 9).

The same parameters were used to best fit the phase curve as well (Figure 10).

A good agreement between experimental and fitted data was found, that confirms the good formulation of the equivalent circuit, that is able to describe the interaction between the percolative nanotubes network and the surrounding polymer matrix.

Conclusions

In this work nanocomposite materials with SWNTs in a polystyrene matrix were fabricated by using Latex Technology, with the aid of a surfactant as dispersing agent. Microscopic analysis using Transmission Electron Microscopy was performed on a sample, in order to evaluate its morphology. Thermogravimetric analysis was conducted on some of the prepared samples and an enhanced thermal stability was

Table 2.
Best fitting parameters.

Parameter	Value
R_1	$7.380e+08$ [Ω]
C_1	$1.085e-09$ [F]
R_2	$1.858e+05$ [Ω]
C_2	$1.350e-06$ [F]

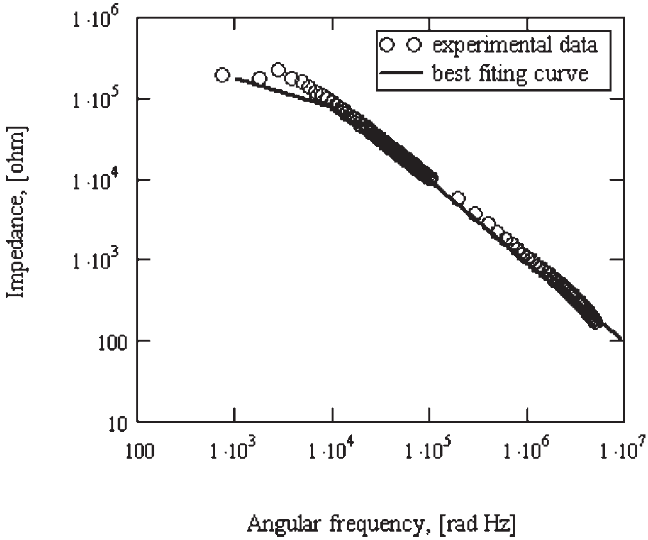

Figure 9.
Best fitting of impedance data: the solid line represent the fit curve and the dots represent experimental data.

evaluated upon an increase of SWNT content in the composites. Electrical characterization both in DC and AC modes was performed on the composite samples in order to evaluate respectively their percolative and dielectric behaviour. By the study of impedance and phase angle experimental data it was possible to formulate an electrical equivalent model with four parameters able to describe the electrical behaviour of the composite sample corresponding to the percolative

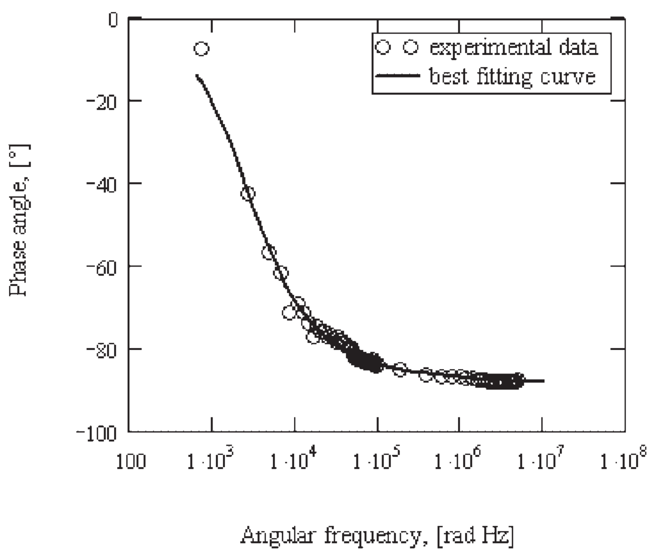

Figure 10.
Best fitting of phase angle data: the solid line represent the fit curve and the dots represent experimental data.

threshold. The good agreement found between experimental and fitted data lead to the conclusion that the formulated equivalent circuit was able to describe the composite nature of this material.

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