The Effect of Carbon Nanotubes Concentration on Complex Permittivity of Nanocomposites

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Abstract—There is growing interest in the use of nanocomposites based on carbon nanotubes (CNT) due to their excellent mechanical, thermal and electrical properties. The electromagnetic characteristics of nanocomposites with different types of multi-walled carbon nanotubes were investigated. CNTs with different geometries (length and diameter) were chosen in order to analyze the effect of the geometrical parameters on the electromagnetic properties. Nanocomposites with various percentages of CNT were made and the number of CNTs per cm^3 in the composite was computed. CNTs were characterized by Field Emission Scanning Electron Miscroscopy (FESEM) and Raman spectroscopy. The complex permittivity of the NCs was measured with two different techniques, and the variation of the permittivity with the number of CNT per cm^3 was investigated.

1. INTRODUCTION

Carbon nanotubes (CNT) are very attractive materials as they exhibit excellent electrical, thermal and mechanical properties. CNTs are capable of transferring their properties into the host polymer materials [1] when being used as fillers in polymer nanocomposites. Minimal number of CNTs is required in order to improve the mechanical and electrical properties of the host polymer materials [2, 3]. Multi Walled CNTs (MWCNTs) are less costly than Single Walled CNTs (SWCNTs). Their low cost makes MWCNTs suitable for the use in large scale and commercial applications in order to improve the electrical and mechanical properties of polymers in nanocomposites [3–6]. In many applications, it is important to know the complex permittivity in microwave frequency range of materials. For example, in electromagnetic compatibility applications (EMC/EMI), high values of permittivity are desired to obtain effective shields [6]. Moreover, it is important to understand the influence of the structural characteristics of CNTs on the complex permittivity of the host nanocomposites. A considerable amount of work has been done on the influence of the aspect ratio (length to diameter ratio) and the weight or volume percent of CNTs (see e.g., [7]). Not only the aspect ratio but also the number of CNTs per cm^3 seems to be an important parameter to consider in the characterization of the dielectric properties of nanocomposites based on CNTs. A preliminary result of the impact of the number of CNTs on the value of complex permittivity was presented in [8] for two types of CNTs. In this paper, the relation between the structural characteristics of CNT in nanocomposites and their electromagnetic properties has been investigated. A simple method of calculating the CNT density per cm^3 for structural characterization has been devised instead of the calculation of mere aspect ratio of individual CNT. In order to compare the electromagnetic performance of CNT based NCs, four different types of NCs are made, each involving CNT with different structural characteristics. Two methods, i.e., transmission/reflection (T/R) method [9, 10] and a commercial open-ended coaxial probe, are used for the measurements of permittivity of the NCs. The dependence of the permittivity on the two structural characteristics, i.e., the aspect ratio and the number of CNTs per cm^3 is discussed, and the suitability of each for structural characterization is analyzed.

2. CNTS CHARACTERISTICS

The average diameter and length values of the types of CNT used are shown in Table 1. The number of nanotubes per cm^3 in a nanocomposite can be estimated as explained in the following.

Table 1. Characteristic of the MWCNTs given by the manufacturer and average aspect ratio (AR).

Type	D (nm)	L (µm)	AR
1	6–10	> 10	2500
2	18–35	> 10	380
3	30–50	0.5–2	30
4	9.5	< 1	100

Considering a $1\,\text{cm}^3$ of epoxy resin (density $1.03\,\text{g/cm}^3$) and knowing the weight percentage of MWCNTs dispersed, the number of MWCNTs can be calculated by dividing the total mass of MWCNTs used per cm^3 in the nanocomposite preparation by the mass of a single MWCNT:

$$\text{CNT per cm}^3 = \frac{\text{grams of MWCNTs per cm}^3}{m_{MW}} \tag{1}$$

The mass of an individual MWCNT can be calculated assuming that a MWCNT is composed by a series of concentric hollow cylinders using the following formula:

$$m_{MW} = \sigma_m \pi L [N_w(D_{ext} + d_w) - d_w N_w^2)] \tag{2}$$

where σ_m is the mass density per unit area of a graphene sheet ($\sigma_m = 7,6 \cdot 10^{-4}\,\text{g/m}^2$, [11]), L the length of the single nanotube, N_w the number of concentric cylinders that can be obtained from the TEM images of datasheets (see Table 1), D_{ext} the diameter of the external cylinder, and d_w the distance between individual cylinders.

Results are reported in Fig. 1 for different kinds of MWCNTs and different filler percentages. The concentration of the NCs in terms of the number of MWCNTs per unit volume at a given wt.% depends on the diameter and length of MWCNTs. For example, a given wt.%, type 4 has a concentration about 2 orders of magnitude higher with respect to type 2. The concentration of type 1 is between those of type 4 and type 2, and the concentration of type 3 is slightly lower than that of type 1. In this work, a fixed weight percentage is considered (3wt.%), and the corresponding normalized numbers of CNTs are reported in Table 2.

Table 2. Analysis of the number of CNT for $3\,\text{wt.\%}$ concentration.

	Type 2	Type 3	Type 1	Type 4
average aspect ratio	380	30	2500	100
number of cnt $/10^{11}$	1	2	9	68

3. COMPOSITES CHARACTERIZATION

The NCs considered in this work are prepared as in [12–15]. Briefly, a micro dispersion tool was used to mix the epoxy resin with a pre-weighted quantity of MWCNTs. A homogeneous dispersion was subsequently obtained, which was mixed with a hardener followed by mechanical mixing of the composite mixture. The composite mixture was left to rest in appropriate molds until complete hardness was achieved. The MWCNTs have different grades of defect as confirmed by their Raman spectra (see Fig. 2).
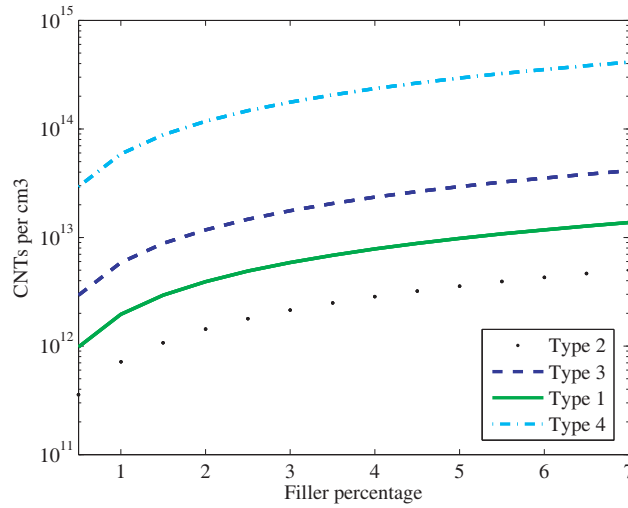
Figure 1. Analysis of CNT number.
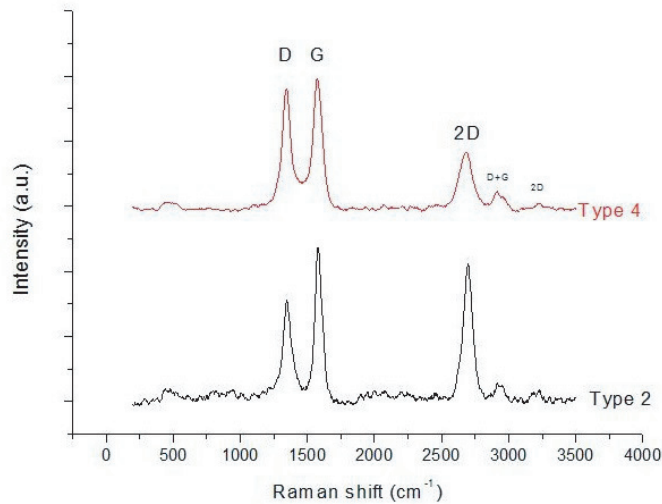
Figure 2. Raman analysis on MWCNTs of type 2 and type 4.

The characteristic bands for the MWCNTs are the D band, G band and 2D band [16]. The D band is present around $1350\,\mathrm{cm^{-1}}$ and is related to the presence of defects and impurities in the MWCNTs. The G band, present around $1580\,\mathrm{cm^{-1}}$, arises from the E2g mode of the carbon-carbon bonds in a graphite plane. 2D band, the second-order harmonic of the D band, sometimes labeled G band, is present between 2450 and $2650\,\mathrm{cm^{-1}}$. This band is associated with the degree of MWCNTs crystallinity. Other second-order peaks are D+G, around $2950\,\mathrm{cm^{-1}}$ and 2D around $3150\,\mathrm{cm^{-1}}$. A first-order characterization of MWCNTs can be made by looking at the relative intensity of D, G and 2D peaks. The ratio between D and G bands (ID/IG) for type 2 is lower than that of type 4. In addition, the ratio between the relative intensities of D and 2D bands (ID/I2D) is also lower for type 2 than that for type 4. Therefore, type 4 is more defective and less graphitized than type 2. These results are in agreement with the characteristics reported in the producer datasheets. FESEM (Zeiss Supra 40) images and Raman (Raman Renishaw, green laser 514 nm source) analysis of the two types of MWCNTs with the lowest and highest numbers of carbon nanotubes are reported in Fig. 2 and Fig. 3. As shown in Fig. 3(a) type 4 has diameters of around 10 nm while in Fig. 3(b) type 2 appears bigger than type 4. Lengths were not estimated by FESEM analysis, and their values were taken from the datasheets. Both MWCNTs types are entangled.
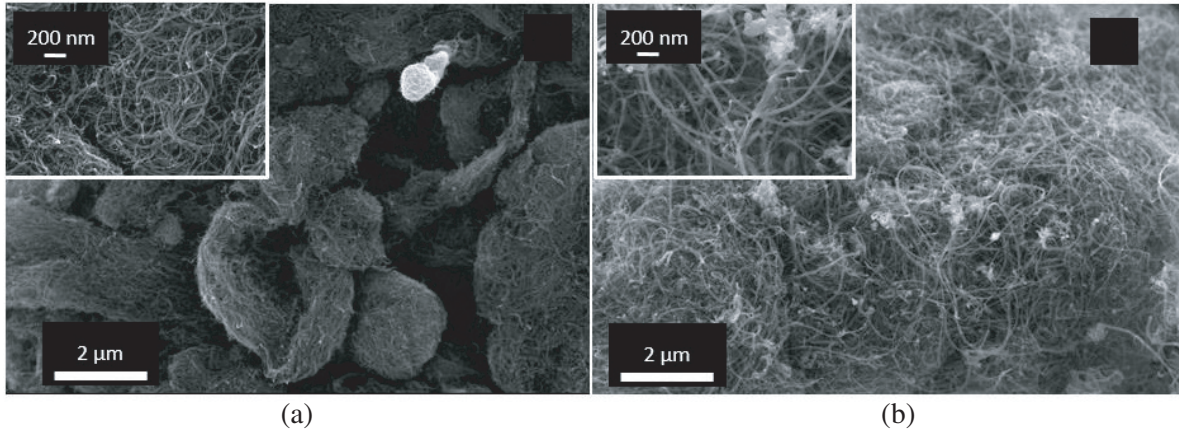
Figure 3. FESEM for MWCNTs (a) Type 4 and (b) Type 2 under analysis. Inset figure are related to details of material.

4. RESULTS

The interaction between an electric field and a material can be described in terms of the complex relative permittivity:

$$\epsilon_r = \acute{\epsilon_r} - j\acute{\epsilon_r''} = \acute{\epsilon_r} - j\left(\epsilon_d'' - \frac{\sigma}{\omega\epsilon_0}\right) \tag{3}$$

where ϵ_0 is the free-space permittivity, ω the angular frequency of the electromagnetic wave, σ the conductivity, and ϵ_d the dielectric losses. The real part of ϵ_r is related to the polarization of the material, and the imaginary part describes the power loss.

A commercial open-ended coaxial probe (Agilent 85070D) was coupled to a network analyzer and provided the complex permittivity values in the frequency band of 200 MHz to 20 GHz after a one-port calibration (short/air/water) (see Fig. 4(a)) [12]. Regarding the shapes of the samples to be measured, the open-ended coaxial probe is capable of measuring liquids and solids with a flat top surface and with a given minimum thickness depending on the values of permittivity. The results of the complex permittivity obtained with this setup were compared up to 4 GHz with a T/R method [9, 10]. The scattering parameters of two microstrip lines of different lengths placed on the nanocomposites as substrate were measured. The complex permittivity was then calculated by a de-embedding procedure from the measured scattering parameters. The scattering parameters were measured with an Anritsu microstrip test set connected to a network analyzer (see Fig. 4(b)). Both methods provide consistent values for both the relative permittivity and the conductivity as can be seen in Fig. 5 for type 2.
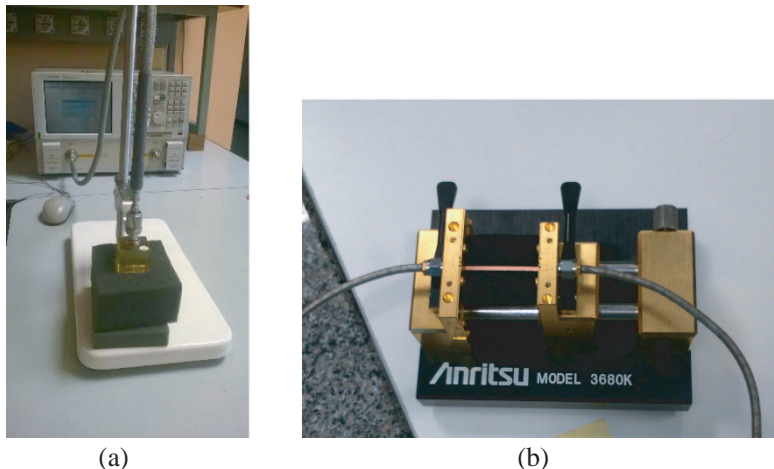

Figure 4. Setup (a) for the open-ended coaxial probe Agilent (85070D) and (b) for T/R method with the Anritsu test set.

Furthermore, the permittivity values increase with an increase in the filler wt.% in the composite matrix.

The four different types of NCs measured are based on MWCNTs which have different structural characteristics (aspect ratio, length and diameter). This gives such MWCNTs a very different number of CNT per cm^3 in the composite matrix as shown in Table 2. The influence of this can be seen on their real permittivity and conductivity values reported in Fig. 6. In order to acquire promising electromagnetic characteristic, all the samples analyzed consist of 3 wt.% of MWCNTs in the NC. As expected, the permittivity and conductivity values of type 4 are the highest in the group because they are the NC with the highest number of CNT per cm^3. Type 1 and type 3 have a medium number of CNTs per cm^3 and also moderate values of real permittivity and conductivity. Type 2 on the other hand has the lowest number of CNTs per cm^3 and the lowest values of real permittivity and conductivity. Among the group, type 3 and type 1 have a very similar number of CNTs per cm^3 and comparable values of permittivity and conductivity, even though their aspect ratios are very different.

When the aspect ratio is > 1000, the percolation threshold Φ_c can be evaluated approximately as $1/AR$ [17]. If the volume concentration of the filler is greater than the percolation threshold, the composite should have higher values of conductivity. For type 1, the average aspect ratio is 2500 and
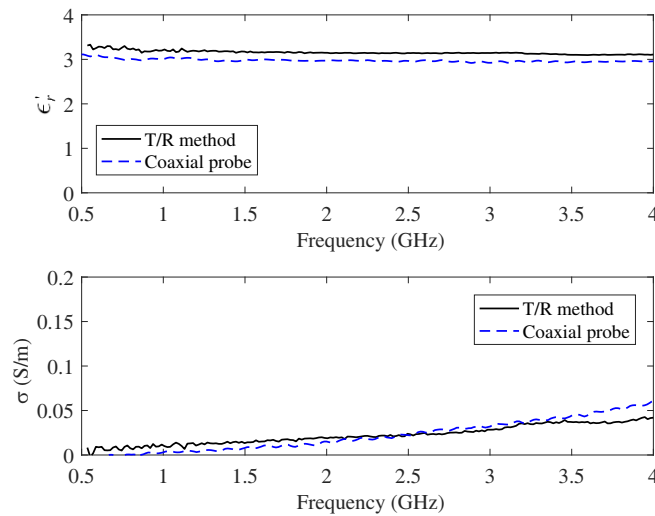
Figure 5. Real part of permittivity (above) and conductivity (below) for 1 wt.% of type 2. Comparison between T/R measurements (dotted line) and open-ended coaxial probe (dashed line).
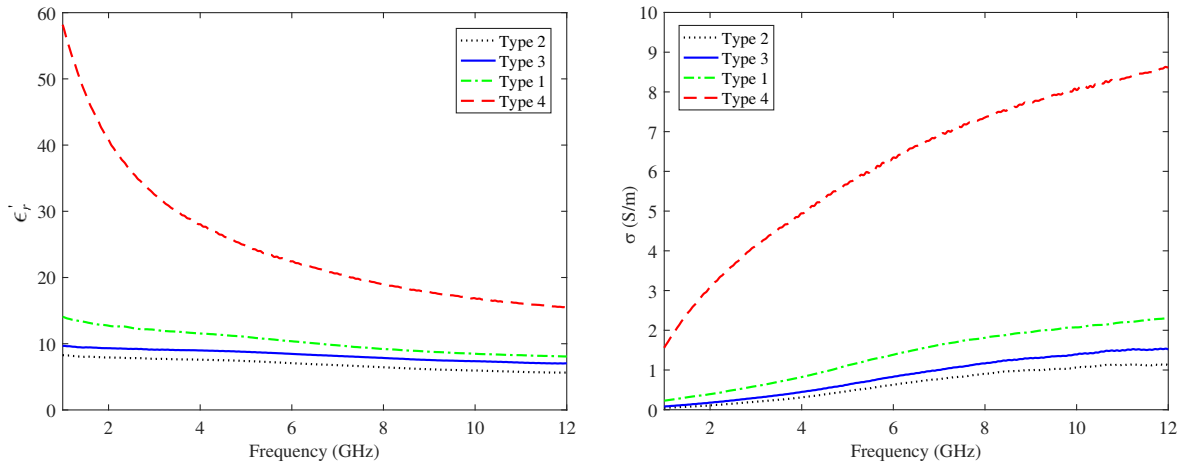
Figure 6. Permittivity values for NCs with different number of CNTs in the composite matrix.
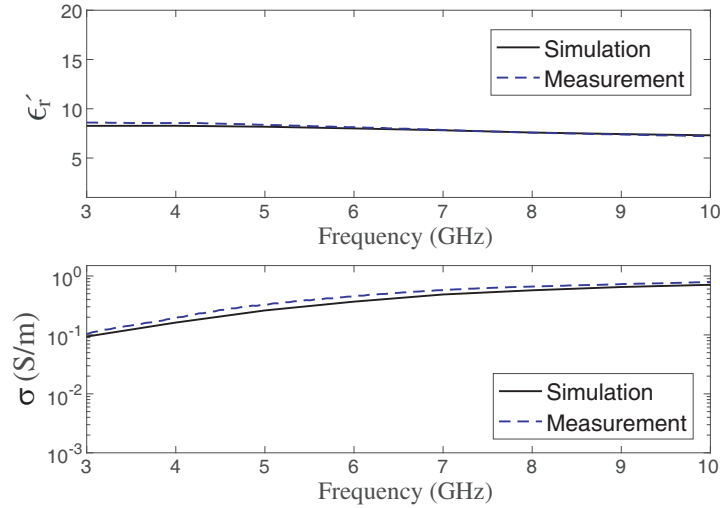
Figure 7. Comparison between the measurements and the Maxwell Garnett model for type 2.

$\Phi_c \sim 0.04\%$. A weight concentration of 3wt.% corresponds to a volume concentration of 2%. The composite should be above the percolation threshold, but if the CNTs are very long, the dispersion process is critical, and the presence of clumps can deteriorate the performances.

When the aspect ratio is small, the previous value of Φ_c cannot be used, and the percolation threshold can be determined from an experimental point of view by considering increasing values of weight (or volume) concentration of the filler. In this analysis, another parameter that can be used to understand the behaviour of the nanocomposites is the number of CNT. As shown in Table 2, types 2 and 3 have a low number of CNT and can be below the percolations threshold, while types 1 and 4 can be near it.

Below the percolation threshold, the nanocomposite can be modelled with a mixing theory as Maxwell Garnett [4]. As an example, in Fig. 7 the comparison between the measurements and simulation for type 2 is shown. A similar result can be obtained for type 3, while for types 1 and 4 that should be close to the percolation threshold this model cannot be applied.

In conclusion, from this analysis it seems that the higher the number of CNTs per cm^3 is, the higher the complex permittivity of the composite is. An high aspect ratio gives a low percolation threshold, but the dispersion of long CNT is critical. For a fixed value of concentration of the filler it could be better to consider CNTs with small aspect ratio in order to have a better dispersion and to increase the number of CNTs per cm^3.

5. CONCLUSION

Complex permittivities of composites filled with MWCNTs with different aspect ratios are analyzed. The results suggest that, especially for low aspect ratio, apart from the aspect ratio of individual CNT, there is a strong contribution of the CNT density towards the electromagnetic behavior of the NCs. In other words, denser NCs (NCs with higher number of MWCNTs per cm^3) deliver higher values of complex permittivity than NCs based on higher aspect ratio MWCNTs but with a lower number of MWCNTs per cm^3. Hence, it can be concluded that to guarantee good electromagnetic performances of nanocomposites based on CNTs, not only the aspect ratio of the individual CNT but also the CNT density should be taken into account.

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