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Rigorous Characterization of Carbon Nanotube Complex Permittivity over a Broadband of RF Frequencies

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Rigorous Characterization of Carbon Nanotube Complex Permittivity over a Broadband of RF Frequencies

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Abstract—This work presents a comprehensive characterization of the frequency dependence of the effective complex permittivity of bundled carbon nanotubes considering different densities over a broadband of frequencies from 10 MHz to 50 GHz using only one measurement setup. The extraction technique is based on rigorous modeling of coaxial and circular discontinuities using mode matching technique in conjunction with inverse optimization method to map the simulated scattering parameters to those measured by vector network analyzer. The dramatic values of complex permittivity obtained at low frequencies are physically explained by the percolation theory. The effective permittivity of a mixture of nano-particles of alumina and carbon nanotubes versus frequency and packing density is studied to verify the previously obtained phenomenon.

Index terms—Alumina, broadband, carbon nanotubes, coaxial discontinuities, complex permittivity measurements, mode matching technique, nano-particles, radio frequency.

I. INTRODUCTION

SINCE its discovery in 1991 by S. Iijima [1], carbon nanotubes (CNTs) have attracted strong interests. CNTs present a very high tensile strength, thermal conductivity, and high electrical conductivity due to the strong carbon-carbon covalent bonding. Many applications have been investigated such as radio frequency (RF) resonators, field-effect transistors, chemical and mechanical sensors [2]-[4]. Usually, CNTs are classified into two categories: single-walled CNTs (SWCNT) composed of a single graphitic cylinder where the diameter varies from 0.7 to 2 nm and multi-walled CNTs (MWCNTs) composed of several concentric graphitic layers where the diameter varies from 10 to 200 nm [4]. The knowledge of the electrical properties of CNTs over a broadband of frequencies is necessary to implement novel RF/microwave carbon nanotubes based devices. Different material characterization techniques used to extract complex permittivity are presented in [5]. Nevertheless, the electrical characterization of carbon nanotube networks can be challenging because it usually requires special preparation of either a thin film or embedding CNTs into a host medium which decreases the accuracy of extracted complex permittivity. The effects of a sample preparation are difficult to characterize which explains the variations of the extracted permittivity previously reported in [6]-[7]. EL Sabbagh et al. present a technique of extraction based on planar transmission line measurements where the metallic trace of the transmission line is replaced by CNT networks [8]. Nevertheless, in this technique, the maximum measurement frequency is limited to 400 MHz due to the restriction that only the fundamental mode propagates in the structure.

There are several advantages of the method used in this work: no special preparation is necessary; only a small fraction of material under test (MUT) is used; MUT can be solid, granular, or liquid; low cost; non-destructive; easily implemented; and only a single test structure is used to cover a broadband of frequencies from 10 MHz to 50 GHz [9]. The CNT networks as furnished by the supplier without any further processing is directly deposited in a hollow circular waveguide shorted at its end and connected at the other end to a vector network analyzer (VNA) via a coaxial precision adapter. A similar permittivity extraction procedure has been studied in [10] where coaxial discontinuities are characterized based on the computation of the input admittance of dominant mode including contributions from higher-order modes. In this work instead, the discontinuities encountered by an incident wave are characterized by computing their generalized scattering matrices (GSMs) based on the mode matching [11] technique (MMT) to obtain the generalized input reflection coefficient $S_{11}$ which is directly measurable by VNA. The accuracy of the discontinuity model is insured by considering all higher-order modes both propagating and evanescent in the different region of the setup shown in Fig. 1. The reflection coefficients obtained from MMT and measurements are compared. Knowing the complex permittivity of the MUT, the computation of the input reflection coefficient is straightforward. On the other hand, to extract complex permittivity from comparison between computed and measured reflection coefficients, an iterative first-order gradient optimization method is implemented. The analytical mode matching formulation used to extract the complex permittivity of any MUT over a broadband of radio frequencies (RF) was introduced in [12]. Detailed
convergence studies were presented to find the appropriate number of modes to rigorously characterize each discontinuity in the setup. Details about the inverse gradient approach used to find complex permittivity is included in Appendix at the end of paper. The validity of modeling was verified by comparison with other numerical technique such as Finite Element Method (FEM). The results presented in [12] show the superiority of MMT over FEM considering the structure shown in Fig. 1. Moreover, the procedure was applied to air as lossless material and to distilled water as lossy material where the results were compared with available data in the literature. Section II describes the actual test setup used in this work. Section III presents the extracted effective complex permittivity results for pure CNTs networks in its dry form as furnished by the supplier. The large values of the effective permittivity are physically explained based on the percolation theory and demonstrated by studying the complex effective permittivity variation with packing density and frequency. Moreover, the characterization of CNT networks mixed with nano-particles of alumina is studied and the results show the enhancement of effective permittivity versus packing density.

II. DESCRIPTION OF TEST SETUP

The test setup described in Fig. 1 consists of a hollow circular waveguide connected to a coaxial waveguide. The structure has been designed to be connected directly to the coaxial cable of a performance network analyzer (PNA): Agilent E8361A via a 1.85 mm to 2.4 mm precision adapter. The advantage of this test structure is that the calibration plane is in direct contact with the material under test avoiding any phase ambiguity in the measurements of the reflection coefficient [13].

For modeling purposes, the testing setup is divided into three main regions. Region I is the 2.4 mm male part of the adapter, modeled as a 50-Ω coaxial line. The other side of the adapter not presented here is a 1.85 mm female attached to a 1.85 mm male coaxial cable connected to the PNA on the other end. Region II represents the pin of the 2.4 mm male side of the adapter going inside the cell. These regions are modeled as coaxial transmission lines filled with different dielectric medium. Region III is the circular waveguide terminated by a short circuit. Regions II and III define the broadband circular waveguide holder where the MUT is inserted. The full-wave model based on the MMT depicted in Fig. 1 has been rigorously described in [12]. Fig. 2 shows the actual testing device which is made of soft copper material.

III. EXPERIMENTAL RESULTS AND DISCUSSION

For the purpose of accurate measurements over a broadband of frequencies, the calibration of the PNA is carried out over three different frequency ranges: first range from 10 MHz to 1 GHz, second range from 1 GHz to 20 GHz, and last range from 20 GHz to 50 GHz. In each frequency range, the short, open, load, and thru (SOLT) calibration is adopted. 201 frequency points are considered in each frequency range. The intermediate frequency (IF) bandwidth is set to 70 Hz which increases the dynamic range of analyzer; reduces noise; and minimizes calibration errors.

Fig. 1. (a) The schematic of test setup. (b) Generalized scattering matrices building blocks. Dimensions of design parameters are: $r_1^{(1)} = 1.2 \text{ mm}$, $r_2^{(1)} = 0.52 \text{ mm}$, $r_1^{(2)} = 1.26 \text{ mm}$, $r_2^{(2)} = 0.254 \text{ mm}$, $L_1 = 1.1 \text{ mm}$, $L_2 = 5.3 \text{ mm}$.

Fig. 2: Actual picture of the fabricated testing structures. Regions I, II, and III are the same as those shown in the schematic of Fig. 1.

The extraction technique proposed in this work has been successfully validated for the characterization of water as a lossy material and the characterization of air as a lossless material at room temperature [9] and [12].

A. Complex Permittivity of Carbon Nanotubes

In this part of study, bundled networks of single-walled CNTs are used as provided by manufacturer (Sigma-Aldrich):
the sample purity is 50 to 70 volume percentage as determined by Raman spectroscopy and scanning electron microscopy (SEM) which shows that the sample contains residual catalyst impurities of nickel and yttrium. The length of an individual CNT is approximately 20 μm. Several images are taken by SEM and they reveal the presence of multi-walled CNTs as well as single-walled CNTs within the sample which is in agreement with similar measurements reported in [14].

Fig. 3–Fig. 6 present the variation of the real and imaginary parts of the relative complex permittivity \( \varepsilon_r = \varepsilon_r - j\varepsilon_i \) over a broadband from 10 MHz to 50 GHz corresponding to different packing densities of CNTs. Packing density is computed using the relation:

\[
\rho = \frac{M}{V} \text{ (g/cm}^3\text{)}
\]

where \( M \) is the mass of MUT in grams weighed using an analytical balance and \( V \) is the volume of cavity in cm\(^3\) determined through optical measurements.

The plots are divided into two frequency bands to highlight the different trends of permittivity at the lower and the upper ends of measurement frequency range. The graphs given in Fig. 3 and Fig. 4 indicate that the highest value of the real part of the relative complex permittivity obtained at 10 MHz is \(1.6 \times 10^6\) and decreases continuously to finally reach 6.5 at 50 GHz. Similarly, the highest value of the imaginary part of the relative complex permittivity at 10 MHz is \(4.1 \times 10^3\) as shown in Fig. 5 and decreases to 7 at 50 GHz as shown in Fig. 6. The values of complex permittivity obtained at high frequencies are in agreement with those values reported in [15]. Moreover, the large values at low frequencies are consistent with those large values reported in [14] and [16].
The experimental results show an enhancement of complex permittivity with packing density. At low frequencies, the high values of relative effective permittivity can be attributed to the conductivity of carbon nanotubes as reported in [16]. These high values are consistent with the percolation behavior [17] of the mixture of metallic and semiconducting carbon nanotubes [18]. In other words, a percolation threshold frequency marks the onset of material changing behavior. Below this frequency, the material has dramatic values of effective complex permittivity. Above this frequency, the complex permittivity asymptotically saturates toward the expected value of permittivity for bulk material. It is noted that without any post processing after their manufacture, CNTs consist of a mixture of conducting and semiconducting nanotubes with a ratio of 1:2 depending on their chirality, i.e., 1/3 metallic tubes are mixed with 2/3 of semiconducting nanotubes. Fluctuations in the extracted values of dielectric properties especially at higher frequencies may be attributed to the random nature of CNT networks which includes randomness in number of semiconducting and conducting nanotubes, the randomness of orientation and alignment of nanotubes. To avoid this effect, statistical measurement variations are to be considered to get smooth results. Another reason is the assumption virtually considered in any modeling technique that surface roughness is neglected. This has quite a strong effect on the extracted dielectric constant as frequency goes up explaining why the fluctuations occur at the same frequencies independently of the packing density. A measurement scenario without CNTs which corresponds to air is included for reference purposes. This case was originally presented in [12] and added here to serve as a reference in Figs. 3, 4, and 6. We observe quite a constant value of dielectric constant as a function of frequency when the packing density of CNTs is little as it is dominated by air.

Above a packing density of 0.15 g/cm³, we observe a percolation behavior of permittivity versus density of CNTs as shown in Fig. 7 due to the dramatic increase of number of nanotubes and the reduction of air interstices. The data in Fig. 7 and Fig. 8 are obtained from results shown in Figs. 3, 4, 5 and 6 at 5, 10 and 30 GHz as well other measurements with different packing densities. The results in Fig. 7 indicate a percolation behavior which is quite significant for lower frequencies, e.g., 5 GHz. After the percolation threshold, the dielectric constant decreases as the packing density increases. The same behavior also occurs at higher test frequencies such as 10 and 30 GHz yet with slower variation of dielectric constant. These results are in agreement with those in Fig. 3 where it is shown that in the frequency range from 5 GHz to 15 GHz, the dielectric constant corresponding to the highest packing density is lower than the dielectric constant corresponding to intermediate densities. This effect is less prominent as the frequency goes higher. It is noted that while the dielectric constant is decreasing with packing density, the imaginary part is increasing as the packing density goes beyond the percolation threshold density ρ = 0.15 g/cm³ as shown in Fig. 8. Below this percolation threshold density, metallic CNTs are separated by semiconducting ones. As the packing density increases, the spacing between conducting CNTs becomes smaller creating nano-capacitors which significantly increases the real part of the effective permittivity until it reaches a peak value exactly at the percolation threshold density [19]. In other words, above the percolation threshold density, connected conductive paths are completely formed in the material which leads to the dramatic increase of losses (ε'' = σω where σ is the conductivity of the MUT and ω is the angular frequency) at a packing density of 0.4 g/cm³. Above the percolation threshold density, the effective real part of permittivity decreases since relative dielectric constant of a metallic material is unity.

B. Effective permittivity of carbon nanotubes mixed with nano particles of alumina

In this part of study, single-walled CNTs are mixed with nano-particles of pure alumina. The alumina used in this work is supplied by South Bay Technology, Inc. The nano particles of alumina have a diameter of 50 nm. The CNTs are used as provided by Bucky USA (product number BU-203) and they
have a purity > 90 wt%, ash < 1.5 wt%, diameter 1 nm to 2 nm, and length 5 μm to 30 μm. Fig. 9 is an image obtained by scanning electron microscopy (SEM) of the mixture of 1 g alumina and 0.2 g CNTs.

The real part of the effective permittivity of a mixture of 0.2 g CNTs and 1 g of nano particles of pure versus frequency is presented in Fig. 10 considering different packing densities of the mixture. For a low packing density, the effective permittivity of the mixture is low as it is dominated by air.

As the packing density increases, air interstices between particles are reduced and a sharp increase of the effective permittivity is observed due to the effective presence of CNTs mixed with alumina.

Fig. 11 shows a comparison between the real part of the effective permittivity of alumina mixed with CNTs and pure alumina to highlight the role of CNTs in the enhancement of the real part of the effective permittivity as the packing density increases. The results of alumina mixture with those CNT networks were measured at 60 MHz as we anticipate the most significant effect of CNTs on the mixture. The results in Fig. 11 verify the high values of permittivity of CNTs shown in Fig. 3. As frequency goes higher, we do not expect that CNTs have that comparable strong effect on permittivity as at low frequencies. Looking closely to Fig. 10, we observe that the variation of the dielectric constant at low frequencies is higher than at high frequencies for any packing density. The linear increase of permittivity of pure alumina versus packing density is due to addition of more material which replaces air and hence permittivity is increasing. It is noted that the value of dielectric constant for bulk alumina depends on the density of alumina. For example, CoorsTek reports a dielectric constant varying from 8.2 to 9.8 corresponding to Alumina density varying from 3.42 to 3.92, respectively. Ultimately, if we could reach an ultimate packing density of alumina close to 3.92 g/cm³, then we expect to have a dielectric constant equal to 9.8. The linear trend of permittivity is based on measurements and studies presented in [18] for the same material.

It is noted that the percolation behavior is enhanced due to the specific shape of nanotubes, the size of nano metallic particles. The cylindrical shapes of CNTs increase considerably the number of interconnection while the nanosize improves the dispersion in the medium.

IV. CONCLUSIONS

A non-destructive, low-cost, easily implemented technique where only a small fraction of material is needed is presented to characterize carbon nanotube based materials in powder form over a broadband of RF frequencies. Only a single measurement setup is required to achieve characterization over the broadband of frequencies from 10 MHz to 50 GHz.
Effective permittivity has been successfully obtained using an optimized gradient method by matching the simulated and measured reflection coefficients. Finally, the frequency dependence of effective complex permittivity and the effects of the packing density of CNTs networks are presented. The complex permittivity obtained for a mixture of carbon nanotubes with nano-particles of alumina suggest the possibility to dramatically increase the effective permittivity for the purpose of engineering novel composite materials.

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APPENDIX

Inverse gradient method

The complex permittivity is extracted by using an optimized first order gradient method. The scattering parameters are computed using the mode matching method and compared to the measured reflection coefficient. The complex permittivity \( \varepsilon_r = \varepsilon'_r - j\varepsilon''_r \) is converted in initial vector form:

\[
\hat{a}_0 = \begin{bmatrix} \varepsilon'_r \\ \varepsilon''_r \end{bmatrix}
\]

Then an error vector is defined to evaluate the difference between the measured and simulated S-parameters \( S_{11} \):

\[
\Delta \hat{S} = \begin{bmatrix} S_{11}^{(m)} - S_{11}^{(c)} \\ S_{11}^{(m)} - S_{11}^{(c)} \end{bmatrix}
\]

where \( m \) and \( c \) denote the measured and calculated S-parameters in rectangular coordinates. The error vector is associated to the complex permittivity vector via the derivative matrix:

\[
\Delta S = \begin{bmatrix} \frac{\partial S_{11}}{\partial \varepsilon'} \\ \frac{\partial S_{11}}{\partial \varepsilon''} \end{bmatrix} \begin{bmatrix} \Delta \varepsilon' \\ \Delta \varepsilon'' \end{bmatrix}
\]

The new values of the real and imaginary part of the permittivity are found by inverting the derivative matrix while the new search direction is given by:

\[
\hat{a}_n = \hat{a}_{n-1} + \begin{bmatrix} \alpha_1 \Delta \varepsilon' \\ \alpha_2 \Delta \varepsilon'' \end{bmatrix}
\]

where \( \alpha \) parameters defined the distance between the actual and next value of the permittivity. The convergence criteria are fixed when \( \| \Delta S \|^2 < 10^{-8} \) and \( \alpha < 10^{-6} \). In (27), the new value becomes the initial value for next iteration.

Then, a convergence study is carried out to optimize the computing time by limiting the number of modes in each regions. Previous study done in [12] shows that a minimum number of 10 modes is required to accurately model coaxial to coaxial discontinuity and 15 modes for coaxial to circular discontinuity considering the convergence of both the magnitude and phase of reflection and transmission parameters.

REFERENCES


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