Prediction of the Effective Dielectric Constant in SWNT Polyimide Nanocomposites Using the Bruggemann Model

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ABSTRACT: The Bruggemann model is used in this work to predict the effective dielectric constant of two kinds of single-wall carbon nanotube (SWNT) polyimide nanocomposites. Electrical conductivity and dielectric constant exhibit a dramatic enhancement at low content of SWNT fillers with a percolation threshold at 0.06 vol %. Results of the Bruggemann model are compared with the experimental values of the dielectric constant in CP2/SWNT and βCN/SWNT polyimide nanocomposites. A reasonable agreement for SWNT contents under the percolation threshold and a SWNT dielectric constant of 2000 was found between the Bruggeman model modified by Giordano and the experimental values. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 2264–2270, 2009

Key words: effective dielectric constant; polymer nanocomposites; SWNT; Bruggemann

INTRODUCTION

Electrical properties in carbon nanotubes (CNT) polymer nanocomposites are currently the focus of many investigations due to the search for multifunctionality that may be customized by judiciously choosing the polymer matrix and controlling CNT content.[1] Polyimides are a good choice as polymer matrix due to their excellent thermal, electrical, and mechanical properties.[1,2] Dielectric constant in polyimides is low compared with other polymers. Moreover, they are thermally stable in a wide range of temperatures.[2] These properties make polyimides an ideal material for a large number of applications in domains such as microelectronics, optics, and aerospace.[3–6]

Several investigations have quantified in the past years the enhancement of electrical properties such as electrical conductivity and dielectric constant in CNT polyimide nanocomposites. Park et al.[7] have reported percolation phenomena of single-wall carbon nanotubes (SWNT) in a CP2 matrix with electrical conductivity exhibiting a dramatic enhancement of 10 orders of magnitude. Ounaies et al.[8] have studied complementary aspects of this investigation such as the change of current and voltage of SWNTs. More recently, Zhu et al.[9] have investigated the processing and characterization of polyimide/multi-wall nanotubes observing a significant improvement in the mechanical and electrical properties. Other recent investigations such as those of Satyanarayana et al.[10] and So et al.[11] have confirmed the interest of polymide/MWNT nanocomposites. Although the dielectric constant does not exhibit an enhancement as dramatic as the one observed in the electrical conductivity, such increase may still reach several orders of magnitude as reported in the literature.[7–16] Another aspect provided by these investigations is the distinctive frequency dependence of the effective electrical conductivity and effective dielectric constant at different CNTs vol %.[7–11] These results evidence a change in the electric behavior of the CNT polymer composite that becomes conductive over the percolation threshold.

Some analytical/numerical modeling is necessary to understand and predict the dielectric properties of polyimide nanocomposites. Different approaches such as micromechanics, effective media approximation (EMA), finite element analysis (FEA) or molecular dynamics (MD) may be considered for this goal.[17] This work focuses on the validation of an EMA, such as the Bruggemann model, with experimental data of dielectric constant of two kinds of SWNT polyimide composites. The interest of using the Bruggeman approach is motivated by previous works, such as Chan et al.[18] on the thermal hysteresis of nano composites and Gehr et al.[19] on nonlinear optical response of composite materials, which demonstrate the interest of using the Bruggemann model to fit experimental data. Also Dang et al.[20] found a good agreement between the predicted values from

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the Bruggemann model and the experimental dielectric constant data for a three-phase composite. An advantage of the proposed modeling approach is the simplicity of the Bruggemann model compared with other numerical, MD, and FEA techniques, in which calculations are complex and demand more computational resources.

MODELING

Effective dielectric constant

Prediction of the dielectric constant in heterogeneous media has been a classical problem in physics and engineering. Many theoretical investigations referred to as effective media approximation (EMA) have focused on the computation of the dielectric constant for a generic composite material. The effective dielectric constant in EMA is a function of the dielectric constants of the particles, also called inclusions or fillers in the literature, the medium where they are dispersed, and the volume fraction of particles. A pioneering work in this field was carried out by Maxwell,[21,22] who investigated the effective electrical conductivity and optical properties of heterogeneous systems. The well-known Maxwell-Garnett equation proposed for very dilute concentrations of spherical particles in a given system have been largely used to calculate the effective dielectric constant of diluted binary mixtures. This equation is the result of the separate works of Maxwell[22] and Wagner[23,24] in which the effective dielectric constant of a system consisting in either spherical or cylindrical particles diluted in a milieu is calculated. Another important contribution to the calculation of the effective electrical properties of a mixture was proposed by Rayleigh, whose concern was the prediction of effective properties such as dielectric constant or electrical conductivity for binary mixtures.[23] The equation proposed by Rayleigh relating effective dielectric constant ε_{eff} to the dielectric constant of the medium ε_1, particles ε_2, and volume fraction c is given in eq. (1).

$$c\frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2} = \frac{\varepsilon_1 - \varepsilon_{eff}}{\varepsilon_1 + \varepsilon_{eff}} \tag{1}$$

The main assumption in the models above presented is the low concentration of particles in the medium. As a matter of fact, Maxwell and Wagner models may not be applicable for high concentrations of inclusions. To overcome this limitation, Bruggeman[25] proposed a differential approach that makes possible prediction of the effective dielectric constant at any volume fraction of inclusions. Bruggemann deduced in his known work a set of equations for the effective dielectric constant of a binary mixture composed of aggregates after the theory proposed by Rayleigh.[23] An additional contribution of Bruggemann in the formulation of the effective dielectric constant is that there is no distinction, as it is the case for previous models, between the inclusion and medium of the mixture. The resulting equation from this development is known as the generalized form of Bruggemann and is shown in eq. (2).

$$(1 - c) = \frac{\varepsilon_2 - \varepsilon_{eff}}{\varepsilon_2 + \varepsilon_1}\left(\frac{\varepsilon_1}{\varepsilon_{eff}}\right)^{1/2} \tag{2}$$

Equations corresponding to Maxwell, Wagner, Bruggeman, and other models, such as Lorentz and Clausius-Mossotti, may be derived from a general frame proposed by Aspnes[26] in eq. (3), where it is assumed that there is no interaction among particles. Percolation phenomena are not considered in this frame and need a different approach to be formulated.

$$\frac{\varepsilon - 1}{\varepsilon + 2} = c\frac{\varepsilon_1 - 1}{\varepsilon_1 + 2} + (1 - c)\frac{\varepsilon_2 - 1}{\varepsilon_2 + 2} \tag{3}$$

In an effort to extend the Bruggemann model to any inclusion shape, Giordano[27] reported recently a generalization of Bruggeman applicable to a generic ellipsoidal shape that may be aligned or randomly dispersed in a polymer matrix. From this frame, Giordano[27] proposes equations for different inclusion shapes such as penny shape or cylinders. The differential approach proposed by Bruggemann is used to determine the change of the effective permittivity $d\varepsilon$ when an infinitesimal volume fraction of inclusion dc is added to the medium. For randomly oriented inclusions in a medium, Giordano proposes eq. (4) for cylindrical shape or rod inclusions. According to the assumptions of Bruggemann model and Giordano's work, eq. (4) is supposed to be applicable in a wide range of concentrations c, with ε_1 as dielectric constant of the medium and ε_2 as the dielectric constant of the inclusion. The effective dielectric constant is calculated according to eq. (4) and will be referred in this work as Bruggemann model modified by Giordano hereafter.

$$1 - c = \frac{\varepsilon_2 - \varepsilon_{eff}}{\varepsilon_2 - \varepsilon_1}\left(\frac{\varepsilon_2 + 5\varepsilon_1}{\varepsilon_2 + 5\varepsilon_{eff}}\right)^{2/5} \tag{4}$$

In this work, we will focus on the specific case of a polymer matrix, a polyimide, containing cylindrical inclusions, SWNT, randomly dispersed as shown in Figure 1(a). We will also follow the notation ε_{SWNT} for the dielectric constant of the SWNT, $\varepsilon_{\beta CN}$, and ε_{CP2} for the dielectric constant of βCN-PI and CP2, respectively, and ε_{eff} for the effective dielectric constant. We do not consider any interface between

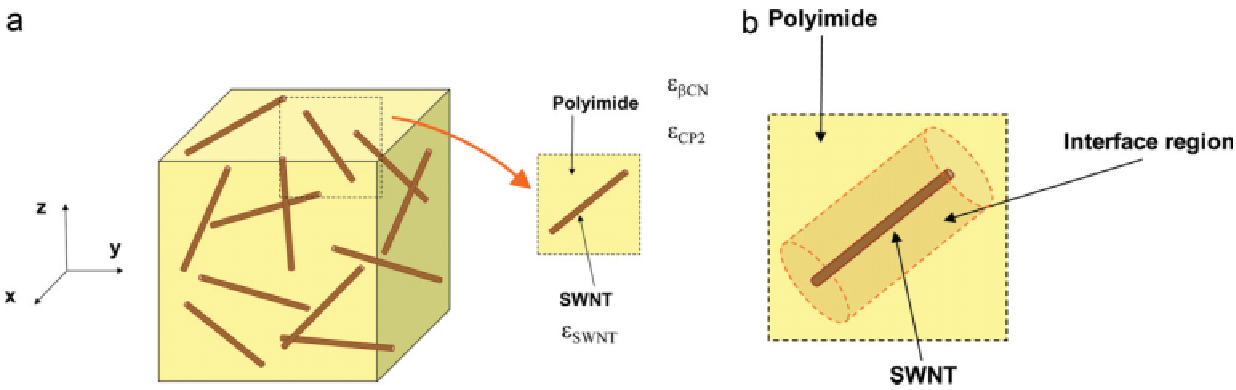

Figure 1 Cylindrical inclusions (SWNT) randomly dispersed in a polyimide matrix (βCN or CP2) considered in this work to validate the model proposed by Giordano. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the inclusion SWNT and the polyimide matrix as shown in Figure 1(b).

Table I shows the values for the dielectric constants considered in this work. Values corresponding to polyimides CP2 and βCN-PI were experimentally measured. Dielectric constant for SWNT was 2000 in agreement with assumptions in a recent work of Li et al.[28] This value was considered to study the manipulation of SWNTs by AC dielectrophoresis. The value proposed by Li et al. is much higher than the one obtained from theoretical calculations proposed by Kozinsky and Marzari.[29] Values in Table I have been taken into account to calculate the effective dielectric constant at different volume contents of SWNT. Figure 2(a) shows the predicted effective dielectric constant calculated for a SWNT/CP2 composite using the Maxwell, Bruggemann, and Braggeman model modified by Giordano models. It is observed from this comparison that the extension of the Bruggemann model proposed by Giordano predicts much higher values for the dielectric constant compared with those proposed by the other classical models. Figure 2(b) shows the variation of the dielectric constant as a function of the SWNT content and dielectric constant of SWNT. The increase of the dielectric constant of the nanocomposite increases exponentially with the volume content for a specific value of ε_{SWNT}. This value is parameterized in eq. (4) to calculate the effective value of the polyimide/SWNT nanocomposite.

TABLE I
Values of the Dielectric Constant ε′ of Materials Studied in This Work According to the Literature or Experimental Values

Sample	ε′
SWNT	2000[a]
βCN-PI	3.87
CP2	3.35

[a] According to Li et al.[28]

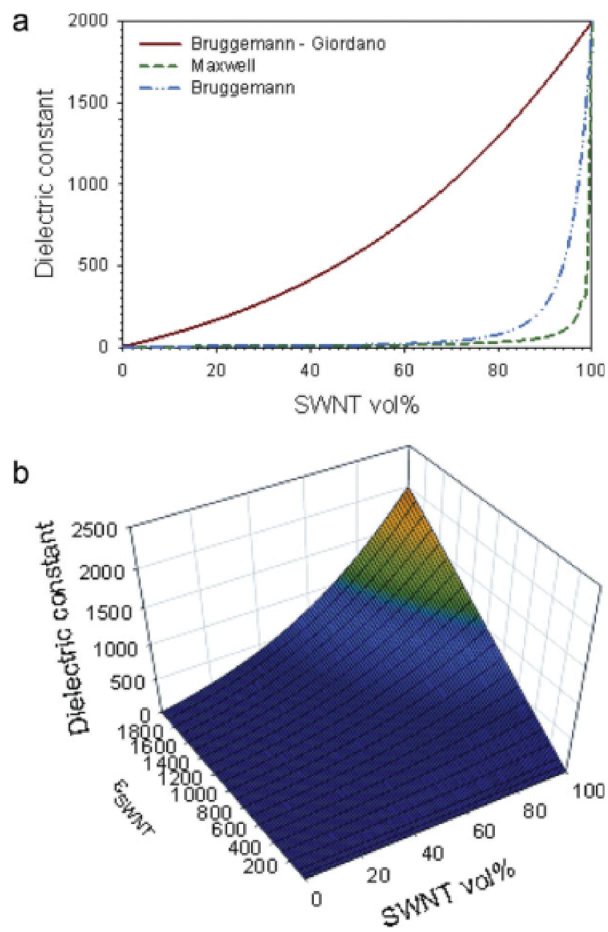

Figure 2 Comparison of Bruggemann model modified by Giordano with other effective media models such as Maxwell (a) and sensitivity of Bruggemann model modified by Giordano to concentration and dielectric constant of SWNT. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

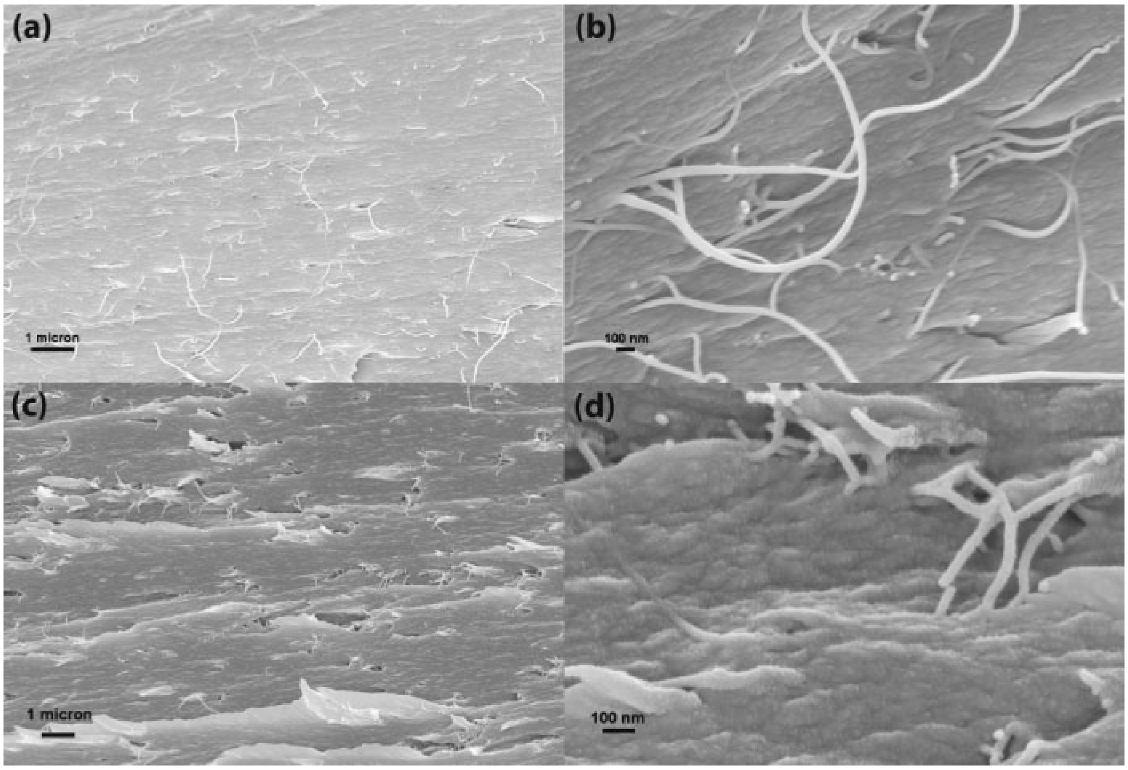

Figure 3 HRSEM characterization of specimens of CP2/0.5 vol % SWNT (a,b) and βCN/0.5 vol % SWNT (c,d) showing dispersion and morphology of SWNT bundles.

EXPERIMENTAL

Purified HIPCO SWNTs were purchased from CNI (Houston, TX). The diameter of SWNT is in the range of 0.85–1.22 nm based on Raman spectroscopy. Aromatic polyimides CP2-PI and βCN APB/ODPA, CP2 and βCN, respectively, were selected as polymer matrix to process the two-phase polymer nanocomposites investigated in this work. The SWNT-polyimide composites were prepared by in situ polymerization under sonication. Further details of the processing procedure may be found in[30] for CP2 and[8] for βCN. A series of SWNT-polyimide nanocomposite films were prepared with concentrations ranging from 0.0 to 2.0 vol %.

HRSEM was used to visualize dispersion and morphology of the SWNTs for specimens of CP2/0.5 vol % SWNT and βCN/0.5 vol % SWNT. Samples were prepared by fracture surface after immersion in liquid N_2, and the resulting crosssection coated with a 20-nm thick Pt–Pd layer. SWNT bundles in the HRSEM micrographs of Figure 3(a,c) exhibit a good dispersion in the polymer matrix either CP2 or βCN, respectively. Some network of SWNT bundles is also observed, indicating percolation. SWNT bundle diameter is in average 30 nm according to image analysis. Slight differences in the interaction polymer—SWNT bundle are also observed in Figure 3(b) for CP2-PI/SWNT and 3d for βCN-PI/SWNT.

According to Deshmukh et al.[30] percolation in SWNT/CP2 nanocomposites is observed at 0.04 vol %. Network in SWNT-CP2 samples is evidenced easily at different magnification values as shown in Figure 3(a-b). Morphology of network seems also to be slightly different compared with SWNT/βCN samples. This might be explained by the different interaction SWNT-polymer that takes place in SWNT/CP2 nanocomposites. For SWNT/βCN samples, percolation is reached at 0.06 vol % SWNT content.[8] This value for percolation threshold is higher to the one observed for SWNT/CP2 samples. This also could explain the different morphology observed in the HRSEM anylisis, where SWNT bundles seem to be wrapped by the polymer matrix in SWNT/βCN composites.

Measurements of dielectric constant and electrical conductivity for the composites studied in this work are shown in Figures 4(a,b) and 5(a,b). Values were measured by dielectric spectroscopy at frequencies ranging from 0.1 Hz to 10 MHz. Both dielectric constant and electrical conductivity exhibit a clear enhancement with the volume content of SWNT in CP2/SWNT and βCN/SWNT specimens. It is also observed that at high-SWNT loadings, the nanocomposite becomes a conductor showing constant electrical conductivity and decreasing dielectric constant with frequency. The transition from an insulator to a

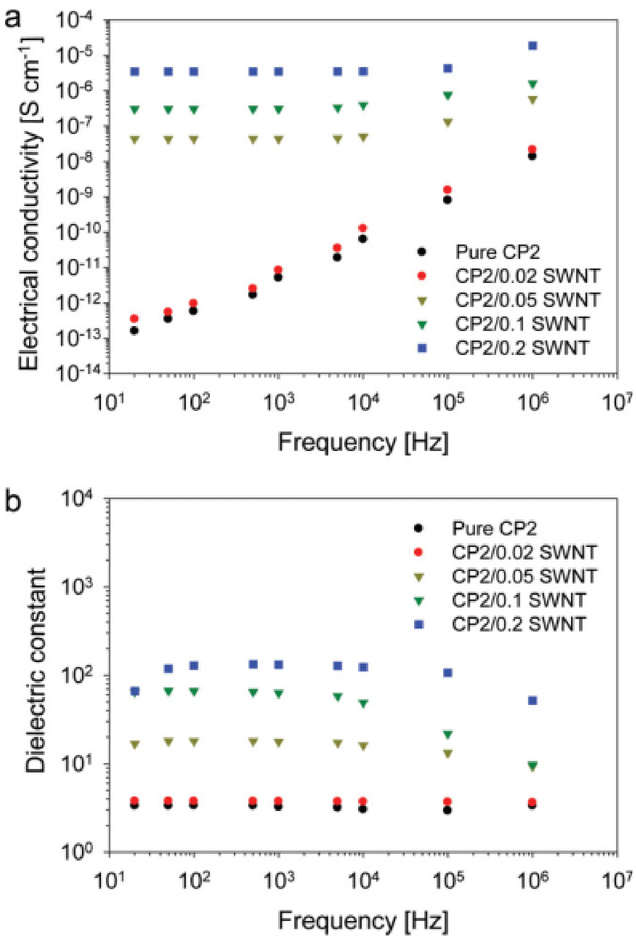

Figure 4 Measurements of electrical conductivity and dielectric constant for CP2/SWNT (a,b) nanocomposites studied in this work. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

conductor is due to percolation that takes place at 0.06 vol % SWNT. The dramatic enhancement observed in the conductivity may be explained by the network observed in the SWNT bundles in the HRSEM characterization in Figure 3.

Values of dielectric constant were next compared with the predictions of the Bruggemann model modified by Giordano. Also Maxwell and classical Bruggeman models presented in "Effective dielectric constant" section were compared with the experimental results. Figure 6(a,b) show the prediction values of the Bruggemann model modified by Giordanno in lines and the experimental measurements in closed circles for CP2/SWNT and βCN/SWNT nanocomposites, respectively. Experimental values of the dielectric constant correspond to measurements ranging from 10 to 20 Hz. Dielectric constant for SWNT is parameterized for values ranging from 2×10^3 to 6×10^4. Two observations may be outlined looking at Figures 6(a,b): (1) small volume contents under percolation do not increase the effective dielectric constant of the polyimide nanocomposites studied in this work and (2) percolation threshold is observed at a low volume content of 0.04 vol % for CP2/SWNT and 0.06 vol % for βCN/SWNT over which the dielectric constant is dramatically enhanced [see inset in Fig. 6(a)].

The inset figures show the comparison of Bruggemann model modified by Giordanno (referred as Bruggemann-Giordano in the legend), Maxwell and classical Bruggeman models with experimental results assuming a dielectric constant of 2000 for SWNTs in a range vol % from 0 to 0.06. Maxwell and classical Bruggemann predictions for the effective dielectric constant are not differentiated from each other. Only Bruggemann model modified by Giordanno gives slightly higher values for the effective dielectric constant that seem to be closer to the experimental values. We might conclude that the value of dielectric constant for SWNT proposed by Li et al.[28] from experimental observations seems to result in effective dielectric values that are

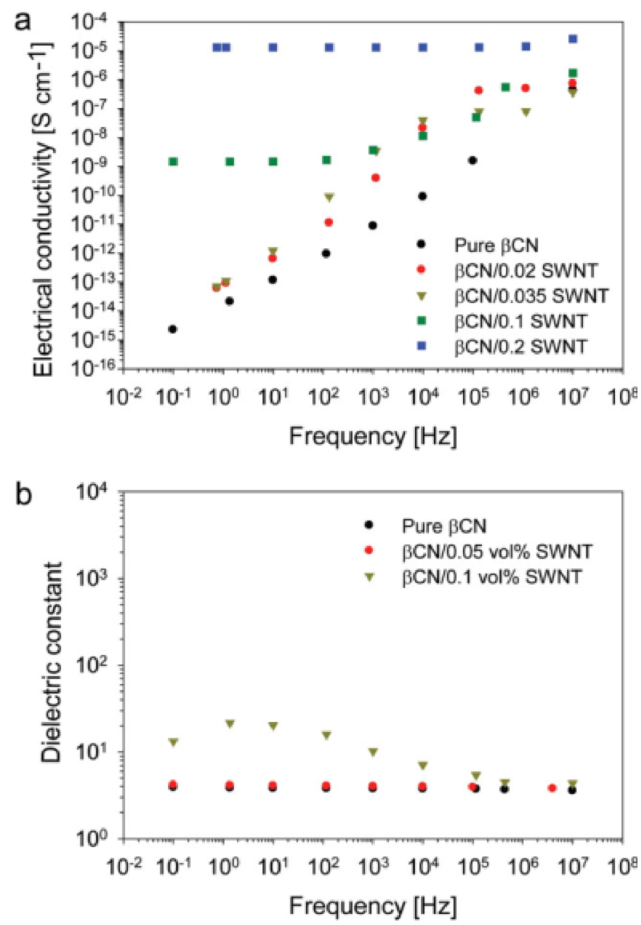

Figure 5 Measurements of electrical conductivity and dielectric constant for βCN/SWNT (a,b) nanocomposites studied in this work. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

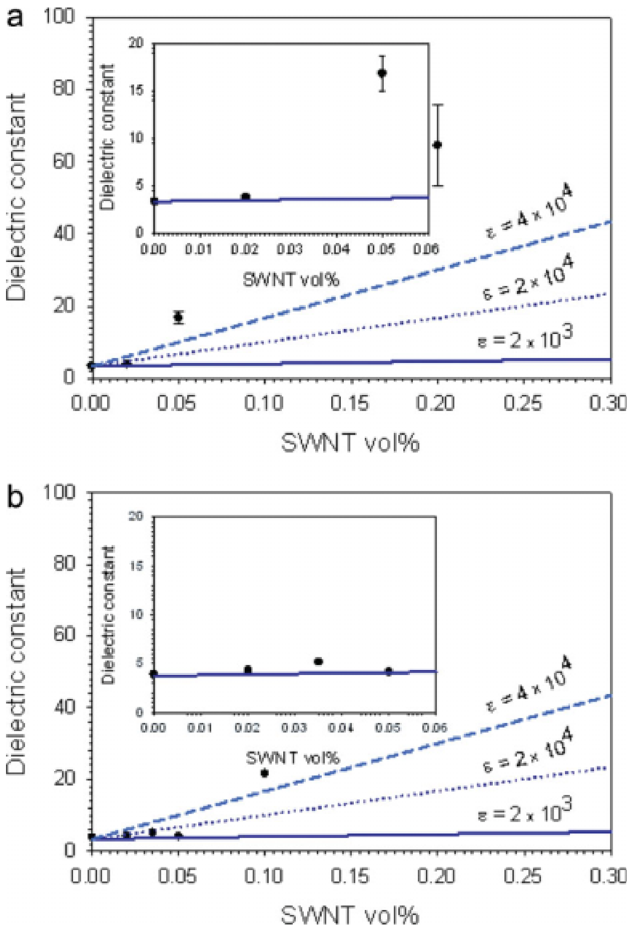

Figure 6 Comparison of the experimental data (dots) of the effective dielectric constant for CP2/SWNT (a) and βCN/SWNT (b) with the predicted values of the Bruggemann model proposed by Giordano (lines). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

comparable with measurements. The Bruggeman model modified by Giordano underestimates the effective values over the percolation threshold according to the inset figures. This is an indication of the non applicability of the proposed model for SWNT concentrations over the percolation threshold. Under this concentration, the Bruggemann model modified by Giordano seems to give a good estimation of the effective dielectric constant for the polyimide nanocomposites CP2/SWNT and βCN/SWNT studied in this work.

Over percolation threshold, none of the classical models considered in this work including the Bruggemann model modified by Giordano seems to reproduce the dramatic jumping and the plateau regime observed experimentally for the dielectric constant according to the literature.[8,30] This might be considered as a limitation of the proposed models for high concentration of inclusions. This limitation is, however, expected considering that these models are applicable at low content of inclusions well under percolation threshold. In addition, different values of dielectric constant considered for SWNT inclusions demonstrate the sensitivity of the Bruggemann model modified by Giordano to this parameter. For values $\varepsilon = 2 \times 10^4$ and $\varepsilon = 4 \times 10^4$, the model results in values that fit less well the experimental values under percolation threshold according to Figure 5(a,b). This might indicate that the proposed value for the dielectric constant of SWNT by Li et al.[28] is consistent with our experimental results.

CONCLUSIONS

In this work, we have studied the effective dielectric constant of two different polyimide nanocomposites: CP2/SWNT and βCN/SWNT. Experimental characterization shows a dramatic enhancement in the effective electrical conductivity and dielectric constant at very low contents of SWNT. These results are corroborated by the HRSEM, where the specimens studied exhibit a neat network of SWNT bundles at SWNT volume contents well over percolation that might explain the dramatic enhancement observed in the electrical conductivity. The Bruggemann model modified by Giordano and the Maxwell and classical Bruggemann models show that the assumed value of 2000 for a SWNT dielectric constant predict reasonable effective values for low volume contents of SWNT. The assumed value has been previously reported by Li et al. based on experimental characterization of polymer nanocomposites. The good fit found in this work might be an indication of the consistency of such value of dielectric constant for SWNTs in the studied samples.

Although the intrinsic complexity of some nanocomposites such as polymers with dispersed CNTs, the Bruggeman model modified by Giordano is able to determine effective values in a simple manner. The Bruggemann model modified by Giordano gives slightly higher values for the dielectric constants compared with Maxwell and Bruggemann models. At high-SWNT volume contents, it underestimates the effective dielectric constant and does not reproduce the plateau regime observed after percolation threshold. According to the literature, the plateau regime indicates that the material exhibits a different electrical behavior due to the interaction (connectivity) among the inclusions. Although the Bruggemann model modified by Giordano is applicable to a large range of concentrations, it does not take into account the interaction of the polymer with the inclusion for instance and the interaction among inclusions. This characteristic of the model might explain its limitation to model percolation phenomena and consequently to determine the dramatic enhancement exhibited by the dielectric constant over the percolation threshold.

Only polyimides CP2 and βCN with dispersed SWNTs were considered in this work. For generalization purposes and for a better understanding of the applicability of the Bruggemann model modified by Giordano, some other polymer media and other inclusions might be considered in future studies. The electrical nature of the inclusions and their size are some of the parameters to be analyzed. PZT powder, CNTs, carbon fibers, clay plates might be some of the inclusions to be focused on. Also two- and three-phase nanocomposites might be studied to investigate the applicability of the Bruggemann model modified by Giordano. These investigations might bring more understanding of the applicability of the Bruggemann model modified by Giordano as a function of concentration and inclusions/media nature.

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