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# Microwave Dielectric Properties of Carbon Nanotube Composites

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## 1. Introduction

Carbon black (CB) (Donnet *et al.*, 1993) and carbon fiber (CF) (Burchell, 1999) have been used as fillers in radio wave and microwave composites for more than half century. Typical applications include electromagnetic compatibility (EMC) or electromagnetic interference (EMI), microwave absorbing coatings, and anti-electrostatic materials, *etc* due to their good electric/dielectric properties, stability and chemical resistance as compared to composites with metal powders of nano or micron meter in size. CB composites normally have frequency-dependent permittivity which is useful in the design of broadband absorbing or functional materials at microwave band. The frequency dispersion in CB composites is mainly caused by the effect of large agglomerate of CB spherical particles with diameter below 100 nanometers and usually appears in composites with large concentration of fillers. CF composites can have special microwave properties, such as high permittivity at relatively low concentrations of fibers (Lagarkov *et al.*, 1998). The dispersive property of CF composites at microwave band is determined by the frequency-dependent response of individual fibers or fiber clusters (Liu, *et al.*, 2007a). The dispersion can be observed even at very low concentration of fibers, for example, less than one percent in volume. This feature makes CF composites advantageous for many technical applications, such as lightweight absorbing materials (Neo & Varadan, 2004) and phantom materials for modeling the electromagnetic response of biological issue (Youngs, *et al.*, 2002). However, to obtain strong dielectric dispersion at microwave frequencies, CF must contain fibers which are at least millimeters in length to achieve large aspect ratio considering the diameter of commercial CF which is normally close to 10 microns. The large dimension of the fibrous inclusions restricts the practical application of CF composites. Also, the favorite processing methods, such as spray technique, are not applicable for CF composites. The planar CF composites are anisotropic with degraded dielectric response across the plane. Due to the heterogeneity of the composites, a surface layer of millimeters in thickness appears with properties different

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from those of the bulk composites (Simovski, *et al*, 2000 and Matitsine, *et al*, 2003). This gives rise to difficulty in modeling and designing composites with desired properties.

Carbon nanotubes (CNTs) have been fabricated since the early 1990s (Ijima, 1991). The primary research interests include the synthesis or growth of CNTs, because it was a challenging task to prepare enough amounts of CNTs with desired dimension and purity for measurement purpose during the early stage. With the development of processing method like arc discharge and laser ablation of graphite, as well as more productive chemical vapor deposition (CVD) and plasma enhanced CVD method, high purity CNTs with controllable wall-thickness/length and acceptable price are commercially available now (Meyyappan, 2005). Other research interests include the characterization and theoretical understanding of their basic properties of CNTs. The physical properties of carbon nanotubes were reviewed in literature (Saito, 1998), which have been considered as the classic monograph on CNTs. Due to the unique electronic structure depending on the diameter and chirality, CNTs could be the smallest semiconductor devices likely to be fabricated (Saito, 1998). And the extraordinary mechanical properties of CNTs make them suitable replacement of CF in continuous fiber reinforced composites for defence or aerospace applications. Other potential applications includes single- or multi-walled CNTs sensor for scanning probe microscopy, and biosensor or device applications such as CNT-based diodes, transistors and field emitter, *etc* (Meyyappan, 2005).

Due to their fibrous shape with extremely large in aspect ratio, CNTs may allow low resistivity and high permittivity and frequency dispersion to be obtained in composites with extremely low concentrations. As compared with CF, one significant difference is that CNTs are nanoscaled particles whose diameter is several orders of magnitude smaller than that of CF (typically about 10  $\mu\text{m}$ ). It is well known that the nanosized particles usually display distinct properties from microsized particles of the same composition, which is the primary reason for the great attention currently given to the radio and microwave frequency performance of CNTs composites. A number of novel features have been reported on CNTs in the literature, these results demonstrate the possibility to design CNTs composites with electric/dielectric properties which are more diverse than those obtainable with other carbon fillers. That is why in the last few years, main research interest in CNT was shifted from fabrication methods to the novel properties, such as the conductivity at low concentration and dielectric properties at low frequency (DC to 1MHz) and high frequency (above 1MHz, including radio wave, microwave, millimeter wave, Terahertz and Inferred wave frequency). Since the dielectric properties of CNT composites at microwave frequency are the main focus of this chapter, previous research works on the electric properties, dielectric permittivity at high frequency, as well as potential EMC/EMI and absorbing applications which are most relevant to our research objective, will be reviewed sequentially.

After the observation of a conductivity threshold in polymer/CNTs composites (Coleman, *et al*, 1998), around 200 publications have reported on the electrical percolation threshold of CNTs in different polymer systems by 2009 (W. Bauhofer & J. Z. Kovacs, 2009). Different CNTs, synthesis methods, dispersion treatment and polymer matrix have been employed in the previous research. Since it is established that the percolation theory or power law could

explain the electric conductivity of CNTs composite (Martin *et al*, 2004). Minimum percolation ratio and maximum conductivity at low frequency becomes the main research focus. Due to the dispersion method and difference in the holding matrix, percolation varies from less than 0.01 percent to a few percent. Theoretically, typical aspect ratio of 1000 produces percolation value about 0.1% (Balberg *et al*, 1984). Practically, a few order of difference could be found from composite with same CNTs and different polymer matrix (W. Bauhofer & J. Z. Kovacs, 2009). Maximum conductivity of MWCNTs composite could be realized when the weight concentration is larger than 10% (Skakalove *et al*, 2005). And the maximum conductivity seems insensitive to the types of CNTs and treatments. Nevertheless, it is a challenging task to disperse CNTs uniformly at such high concentration. The mechanism of charge transport in CNTs composites could be explained by hopping and tunneling effect among neighboring tubes (Kim, 2006). However, the morphology of CNTs in holding matrix seems difficult to be represented by the classical percolation theory.

Permittivity ( $\epsilon = \epsilon' - j \epsilon''$ ) instead of AC conductivity is normally used to describe the dielectric properties of CNTs composites as frequency is above 1MHz. Also, measurement methodologies and potential applications could be different from that at low frequency. Microwave properties are normally measured with impedance or network analyzer through coaxial line or waveguide fixture. A number of special features have been reported on CNT in the literature, such as excitation of localized electronic states resulting in high intrinsic permittivity (Watts *et al*, 2003). The microwave permittivity is found to exhibit smooth frequency-dependent (Browning, *et al*, 1998 & Sandler, *et al*, 2003). These results seem to demonstrate the possibility to obtain CNT composites with microwave properties which are more diverse than those obtainable with other types of carbon fillers, e. g., with various types of dispersive dielectrics, with high dielectric but having relative low dielectric loss (Yang, *et al*, 2009), and tunable dielectric under small bias voltage (Liu, *et al*, 2008). In addition, the nanoscaled size of CNT in composites may avoid the drawbacks of CF composites, which are limited by the macroscopic size of the fibers for thin structure and component applications.

Since the low resistivity of CNTs composite with low filling factor as compared with CB composite which are commonly employed as filler of rubber, conductivity polymer and shielding coating, the shielding effectiveness (SE) of CNTs composites are mostly investigated at microwave frequency (Huang *et al*, 2007). MWCNTs/Ceramic composites were measured at Ku-band with SE up to 25 to 30dB achieved (Shi & Liang, 2008). Some experimental results showed that absorption is the major shielding mechanism and reflection is the secondary mechanism (M. H. Al-saleh & U. Sundararaj, 2009). SWCNTs thin film demonstrated good shielding of EM wave at terahertz frequency while still maintaining good transparency for visible light (Seo, *et al*, 2008). Measurement results show that CNT sheets are more effective in providing EMI shielding compared with graphite and carbon black sheets over broad frequency range due to better electron transmission (Wang, *et al*, 2009). Radar absorbing structures with MWCNTs and polyurethane foam were designed with optimization method before measured with free space setup (Park, *et al*, 2006). 10 dB reflection loss at X-band could be achieved by MWCNTs layer of thickness about 3.3mm (Lee *et al*, 2006). Self-sensing and self-actuation response were found out from CNTs composites which could be explained by electrostriction effect (Lee & Shkel, 2007). The

tunability of both real and imaginary parts of the permittivity found from CNTs composites has potential applications for smart materials and structures (Liu, *et al*, 2008).

The shielding effectiveness and absorption of EM wave are functions of electric and dielectric properties; the objective of this chapter is to investigate the resistivity and dielectric permittivity of CNTs composites for different wall thicknesses. The organization of this chapter is as follow. Theoretical methods and models concerning dielectric properties of CNTs composites are reviewed briefly in Section 2. The materials, fabrication conditions and measurement method of dielectric properties are addressed in Section 3. The results in Section 4 include electric properties, frequency-dependent permittivity, tunable permittivity under bias voltage and potential applications. Last but not least, the conclusion of this research work are summarized in Section 5.

## 2. Theory

In CB composites, the microwave behavior is attributed mainly to the large agglomerates of carbon particles. In this case, the properties of the composite are consistent with the percolation theory that accounts for the statistical properties of clusters comprising many inclusions in electrical contact within the composite (Bergman & Imry, 1977). The percolation approach (Satuffer & Aharony, 1991) depends on the empirical percolation threshold  $p_c$  that cannot be derived from the percolation theory. The percolation threshold is defined as the least concentration at which a composite with conductive inclusions is capable of conducting direct current. For the permittivity ( $\epsilon = \epsilon' + i\epsilon''$ ) of a composite comprising conductive inclusions and a lossless dielectric host matrix of permittivity  $\epsilon_h$ , percolation theory predicts a power dependence on the frequency  $f$  (Gefen, *et al*, 1983):

$$\epsilon'' = A f^{-x}, \quad \epsilon' - \epsilon_h = B f^{-y}, \quad (1)$$

In (1),  $A$  and  $B$  are proportionality factors,  $x$  and  $y$  are critical exponents. In the classical percolation theory, the range of concentrations  $p$  where scaling law (1) is not expected to be observed in a wide frequency range, but typically very narrow, for example  $(p-p_c)/p_c \leq 0.1$  (Gefen, *et al*, 1983). However, in many measured data of CB composites, the scaling frequency dispersion is observed in a wide range of both concentrations and frequencies (Brosseau, 2002). If (1) is valid over the entire frequency range, it follows from the Kramers-Kronig relations that (Jonscher, 1999):

$$x = y \quad \tan \delta = \frac{A}{B} = \tan \frac{\pi y}{2} \quad (2)$$

where  $\tan \delta$  is the dielectric loss tangent, and the second of (2) is valid for  $\epsilon' \gg \epsilon_h$ . Therefore, the critical exponents for  $\epsilon'$  and  $\epsilon''$  are the same, while the dielectric loss tangent is frequency-independent. Equation (1) coincides with the "universal relaxation law" established for many types of dielectrics (Jonscher, 1999). In the percolation theory, the critical exponents are considered to be universal, *i.e.* the same for different composites,

independent of the type and properties of inclusions comprising the composite. The physical basis is that the behavior of the composite is determined by the statistical properties of the clusters, but not by the parameters of individual inclusions.

The universal values for critical exponents of frequency dependence are usually derived from the exponents for concentration dependence. For this, two different approaches are known, with exponent value of either 0.27 or 0.42 (Song, *et al*, 1986). Many numerical and experimental data are obtained within these limits. For example, numerical studies of random RC networks (Straley, 1977) produce 0.28 for 3-D bond problem, but 0.18 for 3-D site problem. For continuum percolation problem, the value of 0.38 is obtained from the studies of water-oil emulsions (Bordi, *et al*, 1996). Therefore, the critical exponent values are believed to be within the range of 0.2 to 0.4, with the uncertainty attributed to the difference in geometry between the bond, site, and continuum percolation problems that may result in different properties of the clusters. For CNT composites, the critical exponent of 0.34, consistent with percolation theory, is obtained (Kim, *et al*, 2003). In all cases,  $x$  is less than 1. Therefore, the AC conductivity of the composite must increase with frequency.

In actual composites, the percolation dispersion governed by (1) appears within a limited range of frequency. The high frequency limit is determined by the frequency at which the conductivity of the composite is equal to the conductivity of the inclusions, and therefore, no longer increases with frequency. The low frequency limit is as considered (Laibowitz & Gefen, 1984). Below this low frequency limit, the real permittivity or conductivity is independent of frequency at concentrations below  $p_c$  or above  $p_c$  correspondingly. Due to the finite frequency range for percolation dispersion, (2) is not exact for practical materials, with the discrepancy increases as the frequency approaches the limits of the percolation frequency range. If (1) is valid over restricted frequency range, then the dielectric loss tangent increases relatively with respect to the value given by (2), as the high frequency limit of this frequency range is approached. Near the low frequency limit, the loss tangent decreases for concentrations below  $p_c$  and increases for concentrations above  $p_c$ .

### 3. Experiment

#### 3.1 Characterization of CNTs

	SWCNT	DWCNT	MWCNT
<b>Purity</b>	95%	90%	95%
<b>Impurities</b>	MWCNT, Ash, Metal	MWCNT, Ash, Metal	Ash, Metal
<b>Length</b>	~30 $\mu\text{m}$	~50 $\mu\text{m}$	~50 $\mu\text{m}$
<b>Diameters</b>	1~2nm	2~4nm	8~15nm
<b>Aspect ratio</b>	~20k	~17k	~2k

Table 1. Specifications of three types of CNTs

Single-, double- and multi-walled carbon nanotubes (SWCNT, DWCNT, and MWCNT) produced by CVD method were obtained from the Timesnano, Chengdu Organic Chemicals Co. Ltd., the Chinese Academy of Sciences. As produced CNTs were purified by the supplier with Oxidation and HCL wash method. The specifications of these CNTs are given

in Table 1. Figure 1 shows the image of these CNTs with high resolution field emission SEM (JEOL JSM-6340F). The diameter of SWCNT and DWCNT seems larger than the values given by the supplier. Possible reasons can be the appearance of bundles or small amount of the CNTs may be multi-walled instead of single-walled. The aspect ratio is calculated based on the length over the average diameter of individual CNTs. It can also be observed from Figure 1 that length of CNTs are larger than the scope observed by SEM which is about a few micron meters.

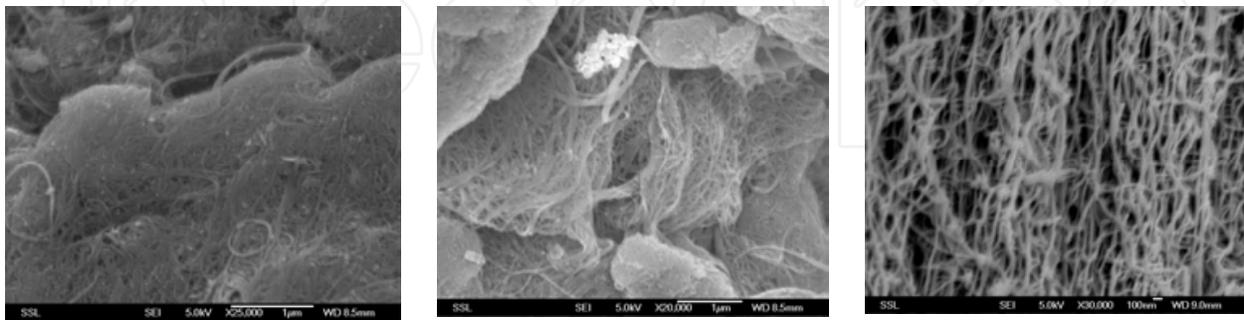


Fig. 1. High-resolution SEM of CNT (a) SWCNT (b) DWCNT (c) MWCNT

The results of thermal gravimetric analysis (TGA) shown in Figure 2 verify that the carbon content in samples is within the ranges provided by the supplier. The residual weights (which is usually contributed by metallic catalyst particles) of the SWCNT and MWCNT samples are almost zero. It suggests that metallic particles can be efficiently removed by the HCl wash. However, about 6 wt% of residues is still remained on the DWCNT sample, shown in Figure 2(b). This may be caused by the different purification method applied by the supplier. Differential Thermal Gravimetry (DTG) results in Figure 2 also demonstrate that most of the carbon materials can be oxidized in a narrow temperature range centered at the peak oxidation temperature ( $T_g$ ). The narrow oxidation temperature range suggests that carbon species in the samples have similar structures.  $T_g$  of the SWCNT sample is at 624 °C, which is higher than the oxidation temperature of purified SWCNTs with diameter of 0.7-1.0 nm (Wei, et al, 2008). The increase of  $T_g$  may be contributed by the large diameter tubes or certain amount of impurities, such as MWCNTs. The decrease of  $T_g$  for DWCNT samples is caused by the metallic residues remained on the sample which may catalyze the oxidation of carbon and result in the lower oxidation temperature at 604 °C. The DTG result of MWCNT shows a relative broader oxidation peak, as well as a higher  $T_g$ . The relative large range of wall thickness might contribute to the observed difference.

Raman spectroscopy was further applied to analyze the three CNT samples. Samples show three typical bands: radial breathing mode (RBM) between 150 and 350  $\text{cm}^{-1}$  characteristic for SWCNT or DWCNT, the D band at approximately 1300  $\text{cm}^{-1}$  assigned to defective and disordered carbon species, and the peak complex centered around 1600  $\text{cm}^{-1}$ , known as the G band, which is characteristic for ordered carbon species such as CNTs and graphite. The sharp RBM peaks from the SWCNT sample in Figure 3(a) and the DWCNT sample in Figure 3(b) verify the high content of SWCNTs and DWCNTs. The very low D band intensities also suggest that little amorphous carbon exists. Figure 3(c) shows the typical Raman spectrum of MWCNTs. However, it is difficult to quantify the purity of different CNT species. Instead, it is confirmed that there are significant amount of CNTs in the three samples.

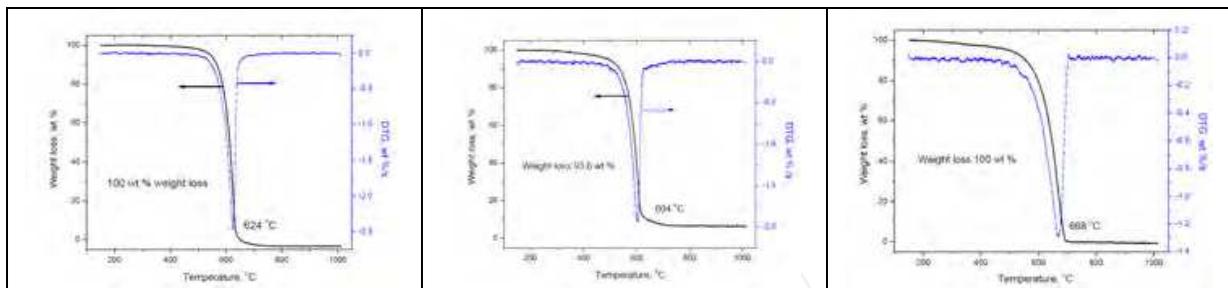


Fig. 2. Purity analysis of (a) SWCNT (b) DWCNT (c) MWCNT with TGA

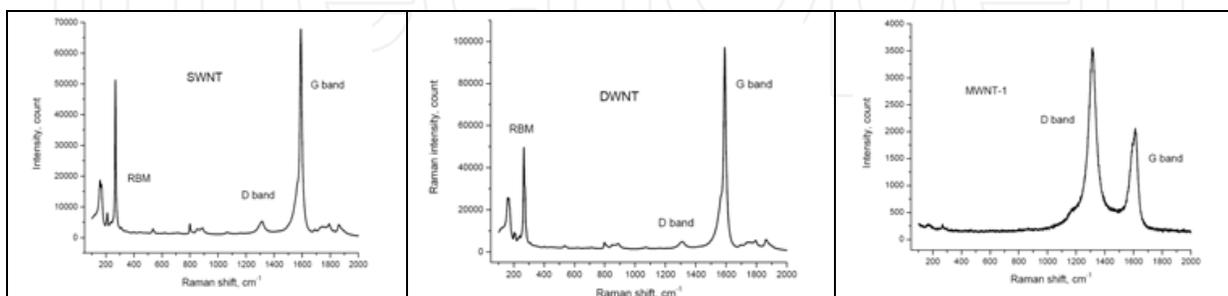


Fig. 3. Raman spectrum of (a) SWCNT (b) DWCNT (c) MWCNT

### 3.2 Fabrication of CNTs composites

The host polymer to prepare composites was commercial two-component silicone (KE1800T) from Shin Etsu. CNTs and silicone (Component A) were dispersed in Toluene (Methylbenzene) with Ultrasonication processor (Sonics VCX500) for 20 min. The resistance of liquid mixture with 0.01g of SWCNTs, 1g of silicone and 25ml of Toluene was monitored with a parallel-plate sensor connected with insulation multimeter (Megger BMM80). The dependence of resistance on the sonication time plotted in Figure 4 shows that 20 minutes sonication time is probably enough to disperse the mixture to stable stage. A SEM image (shown in Figure 5) of SWCNTs after sonication process shows that big agglomerates in Figure 1(a) were broken and no big bundles (larger than 1 $\mu$ m) could be found.

Mixture of CNTs, silicone and Toluene in a 25ml crucible was heated up with a hotplate at 90°C for 8 hours to remove the solvent. After that, the 10% of liquid hardener (Component B) was added and mixed manually before pouring into mould. The mould was put into convection oven to cure at 70°C for 24 hours. As a control, another group of SWCNT, DWCNT and MWCNT was mixed manually with silicone component A and component B for 15 min before cured under the same conditions. And the control group prepared by manual mixing will be used as the benchmark of the sonication process.

Two types of samples were fabricated with moulding method. Disk shape samples have diameter of 16mm and thickness of 2mm to measure the resistivity and permittivity from 0.001GHz to 1GHz. Toroidal shape samples for permittivity measurement at high frequency (from 0.05GHz to 5GHz) have outer diameter of 14mm, inner diameter of 7mm and thickness of about 2mm.

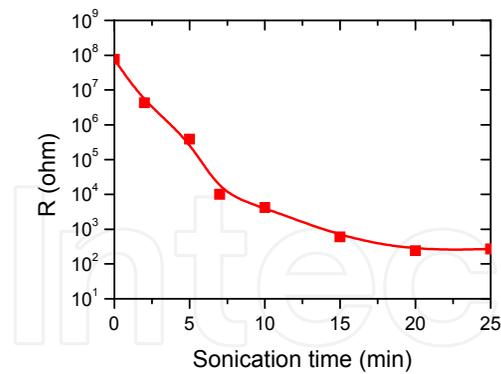


Fig. 4. Resistance vs. sonication time

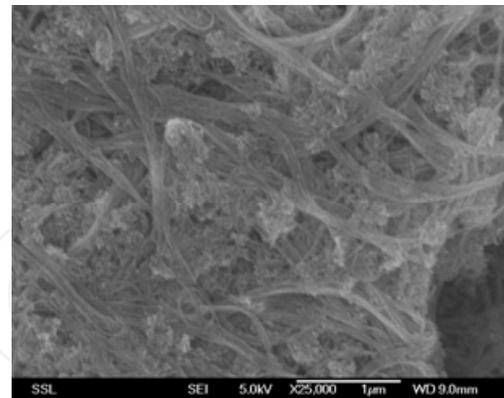


Fig. 5. SWCNT after sonication

### 3.3 Measurement methods

DC resistance of the samples was measured using a Megger™ BMM80™ insulation multimeter and a parallel plate fixture. Before measurement, the disk-shape samples were cleaned with ethanol to remove the release agent sprayed on the mould prior to casting. This is important since the agent contributed to the measured resistance. Resistivity was calculated from the measured resistance and dimension of the samples. Agilent 4991A RF impedance/materials analyzer was employed for permittivity measurement from 0.001GHz to 1 GHz. Figure 6 shows the test fixture (Agilent 16453A) for measurement of dielectric permittivity. During measurement, a bias voltage up to 40 volts was applied to the sample in between the upper and lower electrodes. The permittivity measured is in the direction of the bias voltage applied. Special care was taken to keep good electrical contact between the electrodes and the sample by applying certain pressure. Since there is no air gap effect, the impedance method can achieve good accuracy for measurement of conductive samples without correction [Liu, *et al*, 2007b, 2008].

To validate the measurement results by impedance analyzer, 14mm coaxial line fixture (as shown in Figure 7) and network analyzer (Agilent N5230A) was used to measure the permittivity of SWCNT composites samples from 0.05 to 5GHz. The permittivity was extracted from the measured S-parameters of the sample placed within the coaxial line. Since the outer diameter of the sample can be slightly smaller than the inner diameter of the test fixture due to the shrinkage of the sample after curing, the air gap in between is the largest contributor of uncertainty, especially when the concentration is high. Therefore, only 4wt% and below measured by the two different methods have been compared. The real and imaginary permittivity of SWCNTs composites of weight concentration from 0.5% to 4% are plotted in Figure 8. It shows rather good agreement between these two techniques over 0.05GHz to 1GHz for concentration up to 3%. Both real and imaginary permittivity measured by 14mm coaxial line fixture at 4% show lower values than these from impedance method, which could be properly explained through air gap effect (Liu *et al*, 2007b and reference therein). After correction of air gap effect, the real permittivity (dash line) shows better agreement with impedance measurement. It is proved that impedance measurement has better accuracy even at high concentration as compared with coaxial line method.



Fig. 6. Test fixture and sample for permittivity from 1MHz to 1GHz



Fig. 7. Test fixture and sample for permittivity from 50MHz to 5GHz

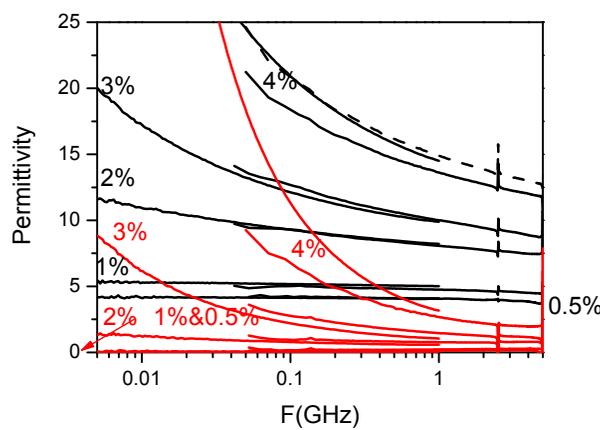


Fig. 8. Permittivity of SWCNT composites measured by Impedance and 14mm coaxial method

## 4. Results and Discussion

### 4.1 Electrical properties

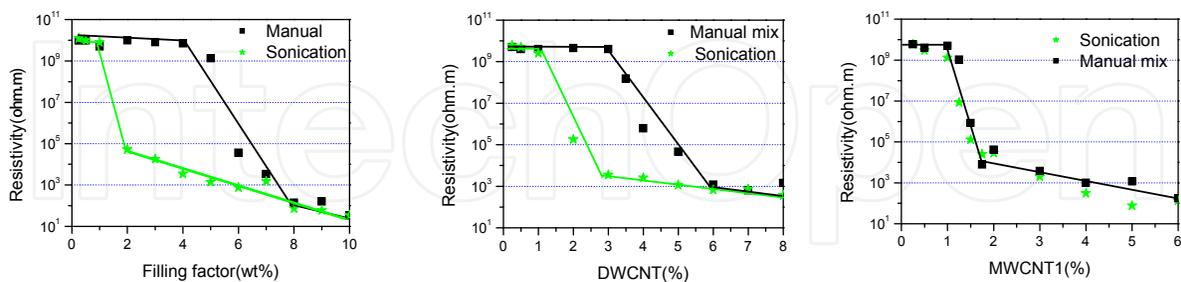


Fig. 9. Resistivity of (a) SWCNT (b)DWCNT (c)MWCNT

The measurement electrical properties of different types of CNTs are plotted in Figure 9. The marks are the measured resistivity of CNTs composites prepared by sonication process (stars) and manual mixing (squares). And the poly-lines are the guide of the dependence of resistivity on the concentration of CNTs instead of fitting curves. Due to the measurement range of the insulation multimeter is up to 200G  $\Omega$ , the resistibility measured at low concentration might be lower than the real value which could results in larger percolation threshold.

For SWCNT and DWCNT, the percolation threshold is around 1wt% if dispersed by sonication process. The percolation of manually mixed SWCNT and DWCNT composites could be up to 3~4wt%. For MWCNT composites, it seems the resistivity decreases before 1%. The percolation ratio could be between 0.5% and 1%. No obvious difference could be found from MWCNT composites dispersed by two different processing methods. Individual tubes instead of bundles could be observed from SEM image of MWCNT in Figure 1(c), as compared with SWCNT (Figure 1(a)) and DWCNT (Figure 1(b)). Therefore, manual mixing might be enough to disperse the tubes inside polymer matrix. However, sonication mixing could result in more steep percolation transition for SWCNT and DWCNT composites. And the bundle of SWCNT and DWCNT couldn't be broken by the manual mixing process.

#### 4.2 Frequency-dependent permittivity

Figure 10 to Figure 12 show the measured dielectric properties of SWCNT, DWCNT and MWCNT composites processed with sonication method respectively. The percolation for three types of CNTs is around 1%. It is sufficient to investigate concentration up to 5% from percolation phenomena point of view. In all of three figures, solid lines show the measured real (in black) and imaginary (in red) permittivity and dash lines show fitting curved using (1). The permittivity of silicone host ( $\epsilon_h$ ) is constant value, 3, according to impedance measurement. From the measured dependence of the permittivity, the dispersion curves for three types of CNTs appear to be similar and do not show any absorption peak that is typical of the Debye dispersion law and mixing rules. The frequency dispersion is smooth and resembles the dispersion of the percolation type. Therefore, the fitting of data made with scaling dispersion law instead of the Cole-Davidson law is validated (Liu *et al*, 2007b). The frequency dependence of the real and imaginary permittivity are fitted separately, to track deviations from the percolation law given by (2).

The parameters  $x$  and  $y$  obtained by curve fitting, which depend on the concentration, are shown in Table 2. Both  $A$  and  $B$  increase steadily with concentration which is understandable due to more conducting channels involved at higher concentrations. Therefore, they are not included in Table 2. Both  $x$  and  $y$  increase with filling factor. The critical exponent  $y$  is smaller than  $x$  for most of concentrations for all of three types of CNTs. Exponent  $x$  at percolation threshold fall in the the range (0.2 to 0.4) form theoretical calculation, but exponent  $y$  is relatively lower (0.1 to 0.2) for 2%. Deviation from the linear dependence (scaling law) can be found from 4% to 5% may explain the higher exponent value than the universal value.

Therefore, the scaling frequency dispersion is observed in the CNTs composites within wide frequency range and concentration around percolation. In the percolation theory, the scaling behavior depends on the geometric spread of the properties of clusters, which is a function of the number of inclusions comprising a cluster. In actual composites, certain reasons lead to an additional spread of the properties of the clusters, such as the dispersion in dimension and in the conductivity of the CNT. Another reason can be the imperfect electrical contacts among the inclusion in the clusters where the conductivity between adjacent inclusions is due to interparticle tunneling. An additional spread of the dispersion curve may be due to the elongated shape of CNT, because a net of tubes forms clusters of complex shape, which must be described by an assembly of RC circuits rather than by a single circuite. All these

phenomana change the distribution of properties of tube clusters and therefore, results different frequency-dispersion from and exponents.

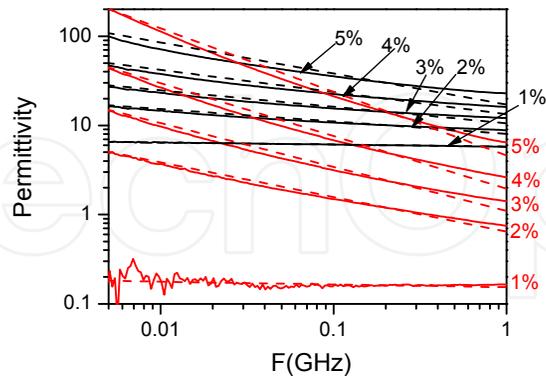


Fig. 10. Permittivity of SWCNT composite

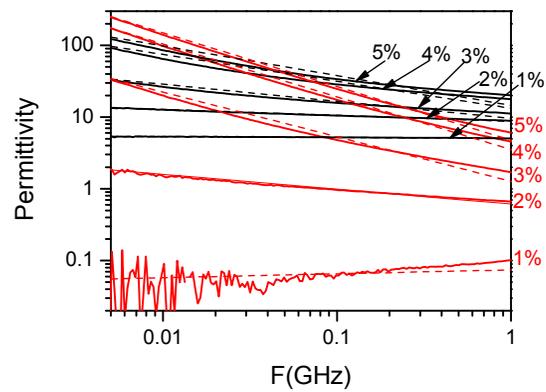


Fig. 11. Permittivity of DWCNT composite

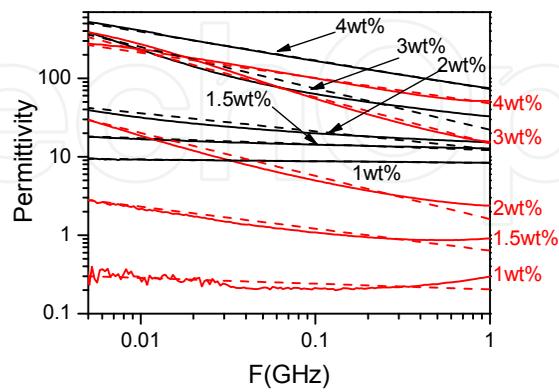


Fig. 12. Permittivity of MWCNT composite

SWCNT			DWCNT			MWCNT		
wt%	$y$	$x$	wt%	$y$	$x$	wt%	$y$	$x$
1	0.04	0.03	1	0.02	-0.05	1	0.03	0.07
2	0.18	0.39	2	0.11	0.21	1.5	0.09	0.28
3	0.217	0.491	3	0.276	0.62	2	0.26	0.55
4	0.275	0.591	4	0.402	0.736	3	0.54	0.59
5	0.368	0.713	5	0.438	0.747	4	0.37	0.32

Table 2. Critical exponents as function of concentration obtained by linear fitting of permittivity

### 4.3 Tunable permittivity under bias voltage

Figure 13 shows the dependence of normalized real and imaginary permittivity at 1 MHz, of the SWCNT composites at various concentrations, measured under a biasing voltage. The dependence of permittivity on bias voltage can be found at high frequency till a few hundred MHz. Figure 14 plots the tunability of permittivity of SWCNT composite from 1MHz to 100MHz. However, with increasing measurement frequency, the tunability becomes smaller. When the concentration is equal to or smaller than 2%, both real and imaginary permittivities do not change with voltage up to 15 V. It is understandable from the percolation threshold point of view because most of the tubes are out of the conducting network. Therefore, no voltage can be applied to isolate tubes or tube clusters. Once the concentration is higher than 3%, permittivity becomes sensitive to bias voltage. The tunability becomes more pronounced with increasing concentration. Samples with concentration of CNTs higher than 5% were not investigated due to extremely large imaginary permittivity. Obviously, bias voltage can decrease real permittivity but increase the imaginary part as shown in Figure 13. If the whole conducting network is treated as a circuit containing resistors and capacitors, replacing some capacitors with resistors will achieve the effect to reduce the real part and raise the imaginary part of permittivity. This is what was happening when bias voltage was applied to the samples in which junctions are formed by overlapping tubes. Electrons hop among tubes driven by bias voltages. The interaction among tubes becomes more resistive instead of capacitive under bias voltage. The tunability, defined as the change under bias over the original value, is more than 60% for the real permittivity and 80% for the imaginary permittivity for the sample with 5% of tubes. It is important to emphasize that the tunability of the CNT composites was reversible over a few thousand of cycles. Similar effect has also been found out from DWCNT and MWCNT composites when the concentration is large than percolation value within similar frequency range.

The novel tunable permittivity of the CNT composites may have potential applications in electromagnetic smart materials and structures. A smart materials or structures basically possess electrically or magnetically adjustable transmission or reflection coefficient to incident electromagnetic wave. The simplest solution is on-off switch, which was realized by pin diodes. One of the drawbacks of pin diodes is their relatively weak tolerance to high current, which is usually encountered in practical applications. A possible approach is to use a small piece of CNT composite to replace pin diode. Without the application of a bias voltage, the composite is insulating (off), while it becomes conducting under a certain bias voltage (on). Comparing with diodes, CNT composites can withstand higher current,

voltage and power. Although the tunability of the SWCNT composite is still not high enough to provide similar on-off effect as a pin diode, we are confident that it can be further improved through proper dispersion or alignment of CNTs within holding matrix.

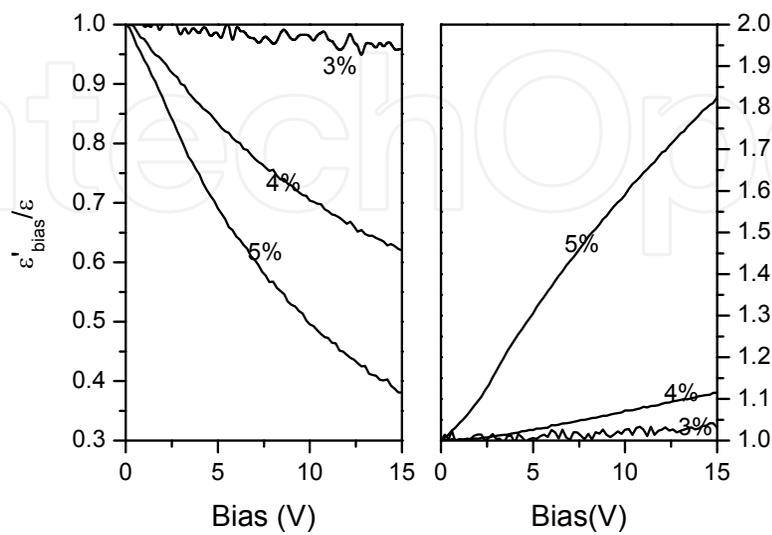


Fig. 13. Tunable permittivity of SWCNT composites (5MHz)

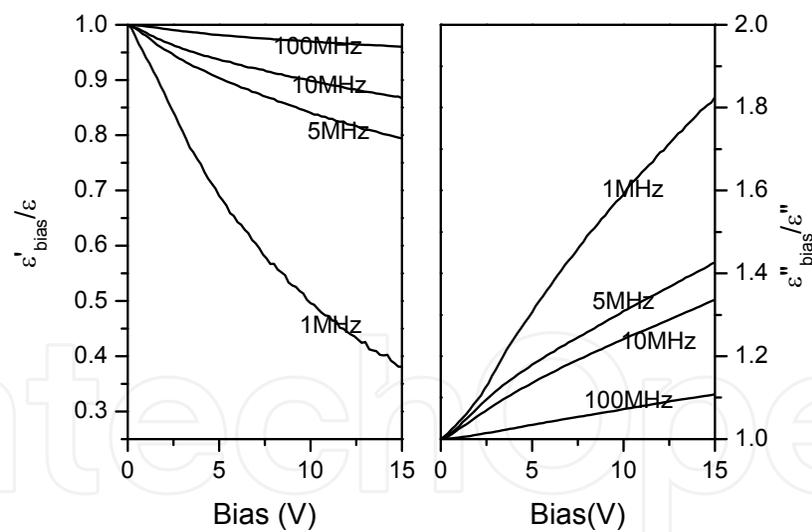


Fig. 14. Tunable permittivity of SWCNT composites (5%)

### 5. Conclusions

In this chapter, the complex permittivity of SWCNT, DWCNT and MWCNT composites at microwave band is obtained experimentally by the impedance method. The frequency dependence of the permittivity is well described by the scaling law based on the percolation theory. CNT composite is a system comprising clusters and conducting networks, the

microwave behavior of which depends on the cluster formation, instead of the properties of individual fibers. Strong frequency-dependent behavior may be observed in measurement due to size effects. The microwave properties of the composites are found to be very sensitive to the preparation method. However, certain deviations are observed in the scaling parameters derived from the percolation theory. Namely the critical exponents are different from conventionally accepted universal values. This may be attributed to the non-perfect electrical contacts within clusters, which typically are not considered in mixing laws.

The CNT composites have large real permittivity at microwaves, adjustable dielectric loss tangent, and noticeable frequency dispersion of permittivity, even at concentrations above the percolation threshold. For these reasons, CNT composites with  $p > p_c$  are probably useful as microwave dielectrics and frequency dispersive materials. CNT composites have been found to possess novel tunable effective permittivity under small bias voltages. The tunable properties can be attributed to flowing of electrons in the conducted network formed by tubes and tube clusters. Hence they are only obtainable at concentrations above percolation threshold. The tunability of both real and imaginary permittivity has potential applications in smart material and structure, which is the research subject that is currently on-going in our group.

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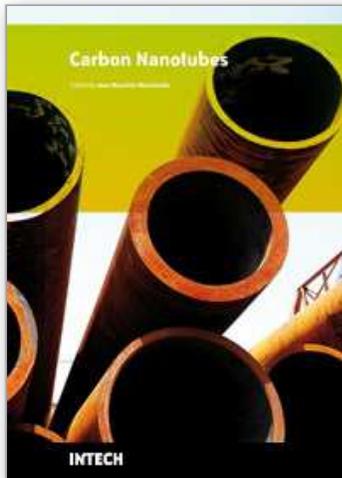
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This book has been outlined as follows: A review on the literature and increasing research interests in the field of carbon nanotubes. Fabrication techniques followed by an analysis on the physical properties of carbon nanotubes. The device physics of implemented carbon nanotubes applications along with proposed models in an effort to describe their behavior in circuits and interconnects. And ultimately, the book pursues a significant amount of work in applications of carbon nanotubes in sensors, nanoparticles and nanostructures, and biotechnology. Readers of this book should have a strong background on physical electronics and semiconductor device physics. Philanthropists and readers with strong background in quantum transport physics and semiconductors materials could definitely benefit from the results presented in the chapters of this book. Especially, those with research interests in the areas of nanoparticles and nanotechnology.

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