

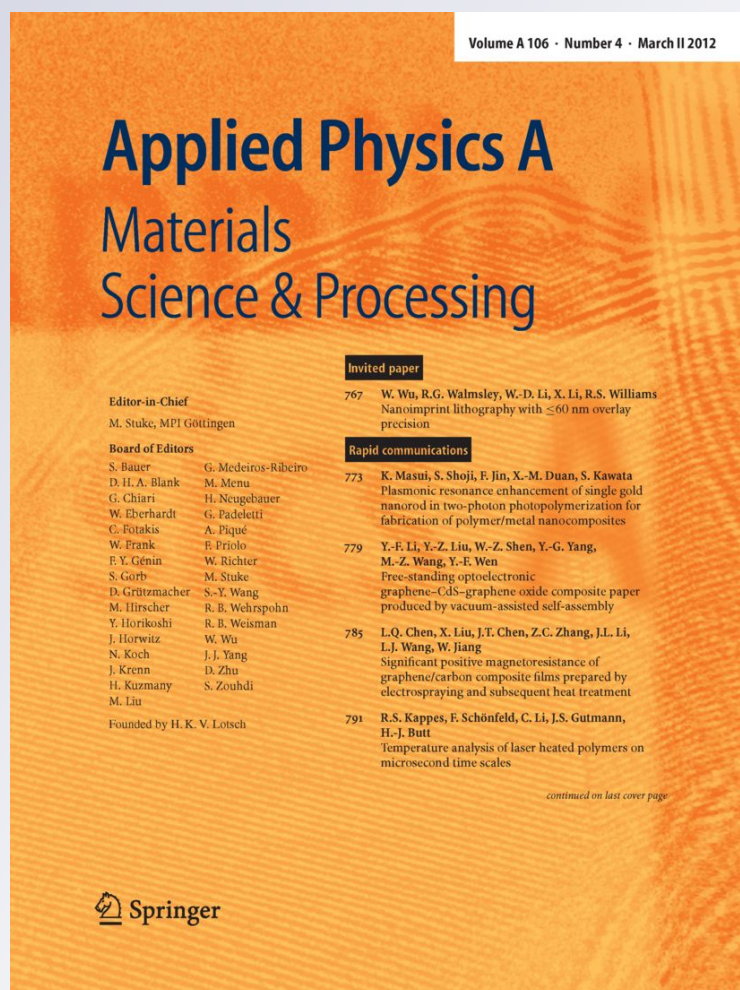
Microwave tunable dielectric properties of multilayer CNT membranes for smart applications

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Microwave tunable dielectric properties of multilayer CNT membranes for smart applications

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Abstract Multilayer multiwall carbon nanotube (MWCNT) silicone composite membranes with thickness greater than 10 μm were prepared with a spin-coating method. Dielectric permittivity and tunability of the circular membranes were measured from 0.1 to 7 GHz by using a single-port coaxial line method. The frequency and bias voltage dependent dielectric properties were interpreted based on percolation theory. The MWCNT membranes could be potentially used to develop smart components and structures working at radio wave or microwave frequencies.

1 Introduction

The outstanding properties of carbon nanotube (CNT) polymer composites have attracted considerable attention in the

last few years, and mainly include the remarkable electrical, mechanical and thermal properties [1]. For example, CNTs have shown better elastic modulus and strengths than strongest steels [2] and better electrical properties than copper wires [3]. Such properties make CNTs ideal fillers for composites with various applications, for example, electrostatic discharge and electromagnetic interference suppression, as well as absorption of undesired electromagnetic waves for indoor measurement or anti-reflection purposes [4, 5]. In fact, traditional types of carbon-based fillers, such as carbon black (CB) and carbon fiber (CF), were prepared for decades to improve electrical conductivity or to tailor the dielectric dispersion of composites at radio or microwave frequency [6]. Due to its spherical shape, large filling factor of CB is needed to fabricate composites with significantly improved properties, which may compromise their mechanical performance and increase fabrication cost. As compared with CB or CF, CNTs can be fillers of composites of high permittivity and distinct frequency dispersion at extremely low concentrations [7, 8]. CNTs are particles in nanoscale, whose diameter (between 1 to 100 nanometers) is two to four orders of magnitude smaller than that of CF. The small diameter and large aspect ratio of CNT fillers might result in high permittivity and low percolation ratio, as well as some distinct properties, like optical transparency [5] and adjustable permittivity under bias electrical field [9], which have not been discovered in their micron-sized counterparts, CF or CB composites.

Even the nonlinear voltage–current relation in CNTs was already discovered a decade before [10, 11], while the nonlinearity of the effective permittivity of bulk CNT-polymer composites has not been investigated until recent years. It was found that the composites with CNTs of above percolation ratio exhibited certain tunable dielectric permittivity at external bias voltages, with real part decreasing and imagi-

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nary part increasing with increasing voltage [9, 12, and 13]. However, the tunable permittivity was only investigated between 1 to 100 MHz due to the limit of the measurement facility [13]. Most wireless communication devices and radar systems have working frequencies from a few hundred MHz to a few GHz. Hence, it is of great interest to study the tunable dielectric properties at up to GHz frequency range.

Traditional approaches to prepare composites at industry or laboratory scales include spraying, molding, solution processing, melt processing and in situ polymerization. Recently, various new processing techniques were developed or employed to fabricate CNT composites with thin and uniform thickness, as well as controllable alignment. For example, buckypapers can be made by soaking thin sheets of SWCNT prepared with Buchner filtration in polymer solutions [14]. Thick composite films were formed by hot-pressing 3 to 5 stacked buckypapers incorporated with epoxy and hardener blend [15]. Layer by layer (LBL) assembly is an alternative method to fabricate thin CNT composites [16]. Layered composite films were built up by dipping a substrate alternatively in SWCNT and polyelectrolyte solutions. In this case, the structural integrity can be further enhanced through cross-linking. The advantages of LBL method include easy control of thickness and polymer–CNT ratio, as well as high CNT loadings. However, the yields of both buckypaper and LBL methods are rather low, so they are not suitable for fabrication of films with large size and thickness. Spin-coating method was employed to cover the top of CNT forests prepared with chemical vapor deposition (CVD) method [17]. The film can then be easily peeled from the substrate after curing. The advantage of this method is in that the pattern of CNT network can be predetermined by the growth condition. However, the CNT inclusions inside thin films were not uniform.

In this paper, we describe the preparation of multilayer composite membranes with MWCNT inclusions by using spin-coating processing. The reason to use the current method instead of molding method employed in our previous works [8, 9, 13] is the better alignment of CNT inclusion and better distribution, which may result in lower percolation and better performance. Compared with buckypaper method, a spin-coating method can prepare the multilayer structure with smaller and more uniform layer. It will take much less time and effort to prepare multilayer with spin-coating method than with LBL assembly. The limits of spin-coating method include the difficulty for composites with high concentration of nano-inclusions due to their high viscosity. Dielectric permittivity at microwave frequencies of the membranes is measured with a single port reflection method up to 7 GHz. To explore the fundamental dielectric mechanism of the membranes, we will discuss their permittivity spectra as function of concentration and bias voltage at microwave frequency.

2 Experimental

2.1 Characterization of MWCNT

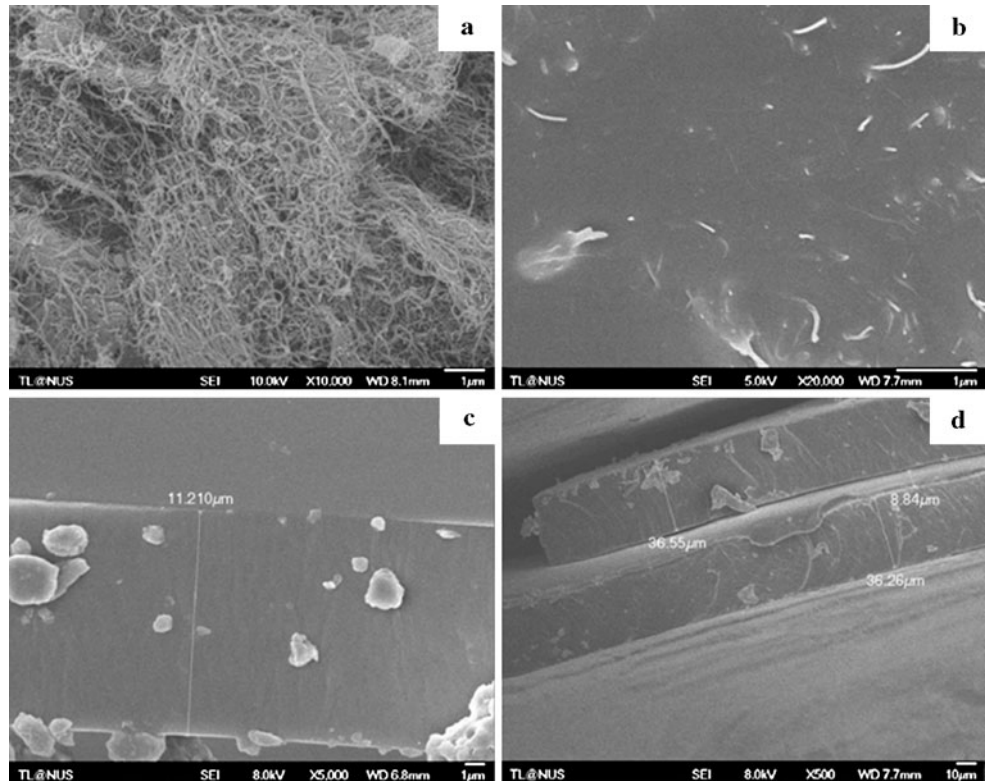
MWCNTs produced by CVD methods and purified with oxidation and acid washing, with average length of ~ 50 μm and diameter of 8–15 nm, were supplied by Timesnano, Chendu Organic Chemicals, China. The specifications are listed in Table 1. Figure 1(a) shows high resolution field emission scanning electron microscope (FE-SEM, JOEL JSM-6701F) image of the MWCNT powder. Purity of the MWCNT was confirmed with thermogravimetric analysis (TGA) in Fig. 2. The weight loss was about 100 % when temperature was above 700 °C. It suggested that metallic particles (impurities from catalysts) have been effectively removed by the acid washing. Differential thermal gravimetry (DTG) results also showed that most of the carbon contents can be oxidized in a narrow temperature range centered at the peak oxidation temperature. The narrow oxidation temperature range suggests that carbon species in the samples have similar structures (such as diameter and length).

2.2 Preparation of MWCNT membrane

The host polymer was two-component silicone elastomer or poly(dimethylsiloxane) (PDMS) supplied by Dow Corning Corporation. MWCNTs and silicone resin (component A) were dispersed in toluene (methylbenzene) with ultrasonication processor (Sonics VCX500) for 20 min. Dependence of resistance of the mixture on dispersion time showed that 20 min was long enough to disperse the mixture to a stable stage. The mixture of CNTs, silicone resin and toluene was heated at 90 °C for 8 h to remove the solvent. After that, ~ 11 % liquid hardener (component B) was added and mixed uniformly with mechanical stirring. Then the mixture was coated on a piece of glass substrate with spin-coater (LAURELL WS-400B-6NPP-LITE). Depending on concentration and spinning speed (from 2000 to 8000 rpm), the thickness of each layer varied from 10 μm to more than 70 μm . The thin layers on glass substrates were then cured on a hot plate at 120 °C for 10 min. Multilayer membranes were made by repeating the process. The thin layers were cut into disc samples by using a circular cutter with diameter of 13 mm before peeling from the glass substrates. Figure 1(b) shows SEM image of the membranes with MWCNTs embedded inside silicone matrix. It can be seen that the tubes are aligned along surface of the membrane due to the fact that lengths of the tubes (~ 50 μm) are comparable with thickness of each layer (10–70 μm). Figure 1(c) and (d) shows cross-sectional images of a single- and a three-layer MWCNT membranes. The single-layer membrane with uniform thickness and smooth surface on a glass substrate shown in Fig. 1(c) was spin-coated at 8000 rpm.

Table 1 Specification of MWCNT

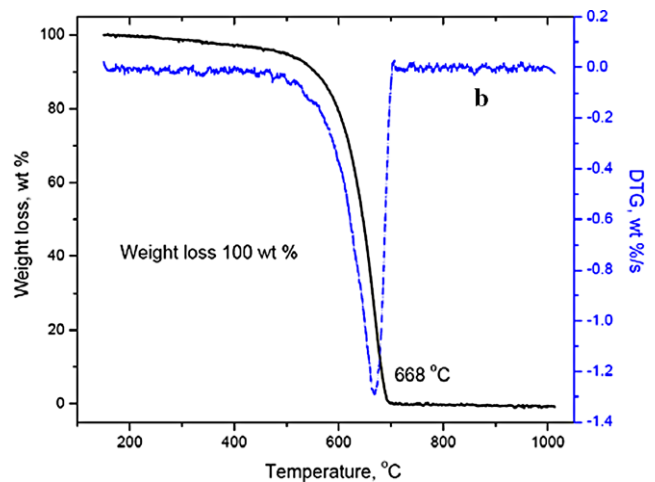
Purity	Purity method	Impurities	Length	Diameter
95 %	Oxidation & HCl wash	Ash, Metal	~50 μm	8 ~ 15 nm

Fig. 1 SEM images of the MWCNT powder (a), top view of a MWCNT membrane (b), side view of a single-layer MWCNT membrane (c) and side view of a multilayer MWCNT membrane (d)

The river-like patterns found in Fig. 1(c) and (d) are typical in fracture surface of the CNT-polymer composites [18]. In Fig. 1(d), the top and bottom layers are 1 wt% MWCNT silicone composites. The isolation layer is prepared with an 8 wt% polyvinyl alcohol (PVA) water solution to show the boundary of two layers of silicone. It is very easy to prepare multilayer membranes with thickness of up to a few millimeters. It is also possible to prepare membrane with thickness of less than 10 μm if a matrix polymer with viscosity lower than that of silicone is used. However, it could be quite difficult to peel off a very thin membrane from the substrates without breaking it. The spin-coated membranes have dense and uniform thickness, as well as smooth surfaces, which have better uniformity than these prepared by buckypaper infiltration processing [15]. However, only membranes with low MWCNT concentrations (up to 4 %) can be prepared because the viscosity of the mixtures at higher concentrations is too high for spin-coating.

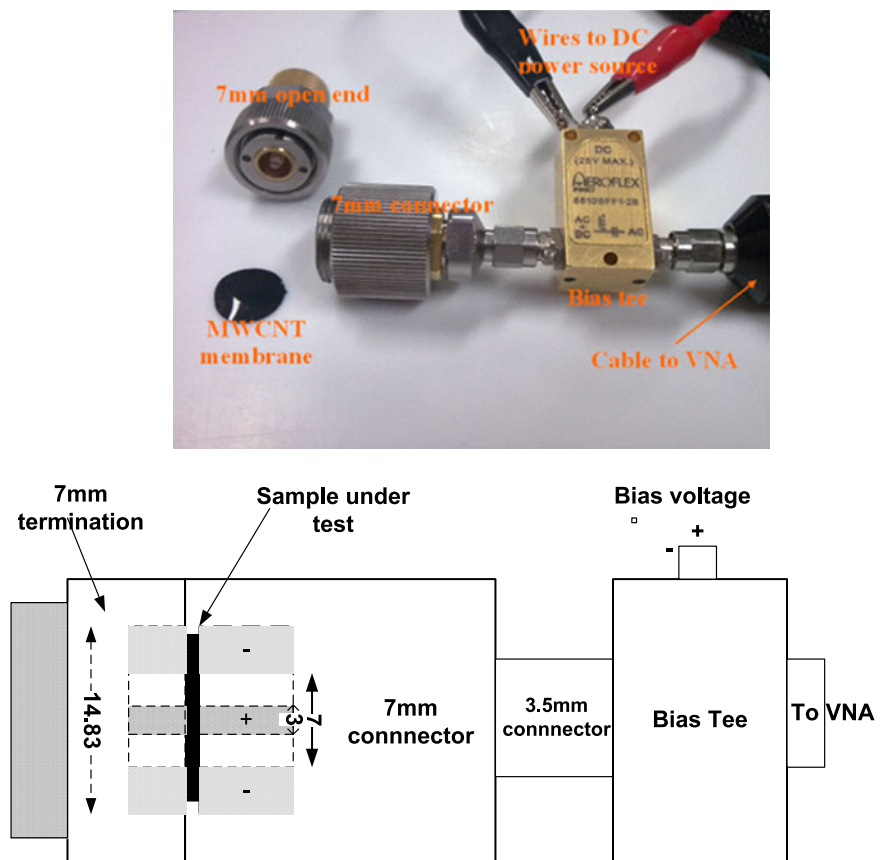
2.3 Measurement of permittivity with single-port methods

Impedance method can only be used to measure dielectric permittivity at low frequencies of below 1 GHz. Hence, a

**Fig. 2** TGA analysis of MWCNT powder

single-port reflection method was employed to measure permittivity of the membranes up to 7 GHz. The main consideration to use single-port instead of 7-mm airline method was the difficulty in cutting the thin MWCNT composite membranes into toroidal shape with precise inner and outer diameters (3 and 7 mm) and properly fitting the flexible

Fig. 3 Fixture for permittivity measurement and a circular membrane sample under test



sample under test into the coaxial line fixture. It is well known the air gap between sample and fixture would result in measurement errors and nonuniform bias field. These problems can be readily addressed by using the open-end coaxial probe method [19–21]. The key to obtain permittivity of the sample is the availability of an accurate model relating the reflection coefficient at the probe aperture. Approaches to modeling the probe include equivalent circuit models and full-wave moment methods [20].

Figure 3 shows the photograph of the test fixture, membrane samples and a schematic diagram of the measurement system. The bias tee (Aeroflex, 8810SFF1-26) has a working frequency range from 0.05 to 26.5 GHz and a maximum bias voltage of 25 V. The bias tee provides DC voltages to membrane samples and isolates the DC voltage from the AC signal transmitted to vector network analyzer (VNA). The whole setup was calibrated with short-open-load (SOL) method. The sample under test is not necessarily to have precise shape or certain level of hardness, as long as its diameter is larger than the outer conductor of the 7-mm coaxial line. Accuracy of the measurement depends on uniformity of thickness and dispersion of the CNT fillers in the samples. Permittivity measurement was conducted in two steps. Reflection of arbitrary termination (open termination used in this study) was measured first. After that, reflection of the disc membrane backed with open termination

was measured. Special care was taken to keep good electrical contact between the membrane and the test fixture by applying proper level of pressure. Permittivity was calculated from the two reflection coefficients with Agilent materials measurement software 85071E. The single-port reflection method can also be used to measure thin films with substrates provided another bare substrate with exactly same thickness and dielectric properties is employed to calibrate out the contribution from the substrate.

3 Results and discussion

3.1 Dispersive permittivity of MWCNT membrane

Figure 4 shows real and imaginary relative permittivity of the MWCNT membrane: ϵ'_N stands for real permittivity normalized by the permittivity of silicone matrix ($\epsilon' = 3$). Both real and imaginary parts increase with increasing concentration of CNTs, which can be understood in terms of effective medium theory. For the permittivity of 4 wt% sample, two resonances at 3 and 6 GHz were caused by the length of the calibration standard (airline) which is around 5 cm. When the length equals to half or one wavelength, the resonance peaks appear in S-parameter. It is quite common

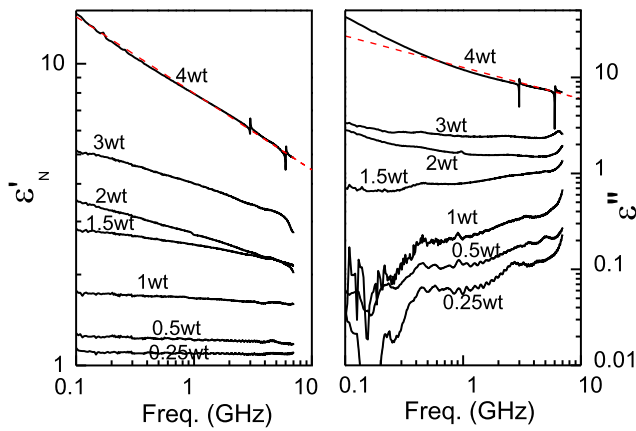


Fig. 4 Dielectric permittivity of the MWCNT membranes from 0.1 to 7 GHz

phenomena in measurement. The resonances cannot be attributed to the intrinsic properties of composite or sample size: it is a systemic error of the measurement.

Two different types of frequency dispersion can be observed from Fig. 4. When concentration is lower than 1.5 %, real permittivity is almost constant and dielectric loss is small, especially at MHz frequencies. For the concentration above 1.5 %, both real and imaginary parts decrease with increasing frequency. According to the percolation theory, both real and imaginary permittivity values decrease exponentially with increasing frequency when concentration is close to the percolation ratio [22]. It suggests that 1.5 % is the percolation limit of our prepared MWCNT membranes. The resistivity measured with high resistance meter also showed dramatic decrease as the concentration was increased from 1 to 2 %. It seems that permittivity still follows the power law dependence for the samples with concentrations above the percolation. Hence, the real and imaginary permittivity curves of sample with 4 % filler in Fig. 4 were fitted according to power law dependence. The exponents are -0.254 and -0.328 , respectively. However, the exponents are lower than those predicted by percolation theory, which are -0.5 for both real and imaginary permittivity [22].

The small deviation at high frequencies (above 6 GHz) can be attributed to resonance due to sample size. A circular disc sample with diameter of 13 mm, made of materials with both large dielectric permittivity and loss tangent, behaved like a cylindrical dielectric resonator. A resonance peak between 9 and 10 GHz could be observed from permittivity measured. The resonance distorted the dielectric permittivity curves of the composites even at lower frequency, which makes the dielectric responses deviating from linearity. This is the reason why the permittivity above 7 GHz is not shown in Fig. 4. The mechanisms that govern the dielectric phenomena of the samples with high and low concentrations of CNT are different. At low concentrations, the

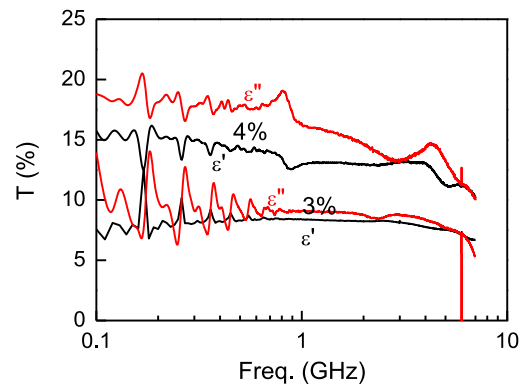


Fig. 5 Tunability of the MWCNT composite membrane with different concentration at a bias field of 10 V/mm

permittivity is determined by individual inclusions, namely, isolated tubes or tube clusters, which are not connected with each other. Therefore, the permittivity is less sensitive to frequency. However, at higher concentrations, most of the tubes or clusters are connected with one another to form a conducting network. The permittivity becomes more dispersive and is determined theoretically by the power law.

3.2 Tunability of membranes under bias voltage

Tunability of dielectric permittivity can be defined as the percentage of real or imaginary permittivity changed by the bias voltage applied:

$$T (\%) = \left| \frac{\varepsilon_0 - \varepsilon_e}{\varepsilon_0} \right| \times 100 \quad (1)$$

where ε_e and ε_0 are the measured permittivity with and without the applied bias voltage.

Practically, tunability at higher frequency, for example, from a few of hundreds MHz to a few of GHz, is more valuable for component and material applications, because most communication devices fall in this frequency band. Figure 5 shows tunability of real and imaginary permittivity of the membranes with 3 and 4 wt% of CNTs at a bias electrical field of 10 V/mm. The ripple at low frequency might be caused by the interference of bias DC voltage through the bias tee, which is supposed to fully isolate the DC from AC signal. Compared with our previous results measured with impedance analyzer at MHz frequencies, the tunability at GHz frequencies is relatively lower. With increasing frequency, the tunability decreases to less than 15 % at 1 GHz and less than 10 % at 7 GHz for sample with 4 % CNT. In our previous study, tunable permittivity could only be observable in composites with concentrations of more than 6 wt% [9]. However, with multilayer membrane prepared with spin-coating, tunable permittivity could be observed in the samples with lower concentrations and at much higher working frequencies. Also, the permittivity was measured

along in-plane instead of out-of-plane direction. These could be attributed to the better distribution of tubes inside silicon matrix and the alignment of the tubes as a result of the application of the spin-coating processing. Negligible tunability was found in the membrane with 2 wt% of MWCNT or lower concentrations. From the percolation threshold point of view it is understandable that most of the tubes are out of the conducting network. Therefore, no voltage can be applied to isolated tubes or tube clusters. It is expected that higher tunability may be achievable in composites with CNT concentrations of higher than 4 %. However, due to the high viscosity of the solutions with high concentrations of CNT, samples with higher CNT concentrations cannot be prepared by using the spin-coating method.

Compared with ferrite-based metamaterials or tunable photonic band gaps with magnetic rods [23, 24], CNT membrane has better tunability at GHz range. Also it is understandable that electrical field as small as 10 V/mm is much easier to obtain than magnetic field of up to a few thousand oersteds, especially at a large scale. Although giant dielectric tunability was found from bulk Y_2NiMnO_6 under a smaller bias field of 4 V/mm [25], the tunability was investigated in kHz frequency only. Therefore, it is not promising to use giant dielectric tunability for any radio or microwave applications.

4 Conclusions

Multilayer composite membranes of MWCNTs with thickness above 10 μm were prepared using spin-coating processing. The membranes have better quality and smaller thickness than those prepared with molding processing in our previous studies [13]. Their dielectric properties were measured using a single-port reflection method from 0.1 to 7 GHz. The membranes have an improved tunable permittivity at GHz frequencies when the MWCNT concentration is above the percolation threshold. These MWCNT membranes might be useful in fabrication of smart components and structures working at microwave frequencies.

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References

1. M. Byrne, Y. Gun'ko, *Adv. Mater.* **21**, 1 (2009)
2. M.F. Yu, O. Lourie, M.J. Dyer, K. Moloni, T.F. Kelly, R.S. Roff, *Science* **287**, 637 (2000)
3. P.G. Gollins, P. Avouris, *Sci. Am.* **283**, 62 (2000)
4. Q. Su, G. Zhong, J. Li, G. Du, B. Xu, *Appl. Phys. A* **106**, 59 (2012)
5. H. Xu, S.M. Anlage, L. Hu, G. Gruner, *Appl. Phys. Lett.* **90**, 183119 (2007)
6. J. Donnet, R. Bansal, M. Wang, *Carbon Black: Science and Technology*, 2nd edn. (Dekker, New York, 1993)
7. K. Kim, J. Lee, I. Yu, *J. Appl. Phys.* **94**, 6724 (2003)
8. L. Liu, S. Matitsine, Y. Gan, L. Chen, L.B. Kong, K. Rozanov, *J. Appl. Phys.* **101**, 094106 (2007)
9. L. Liu, L.B. Kong, S. Matitsine, *Appl. Phys. Lett.* **93**, 113106 (2008)
10. S. Tans, A. Verschueren, C. Dekker, *Nature* **393**, 49 (1998)
11. S. Heinze, J. Tersoff, R. Martel, V. Derycke, J. Appenzeller, P. Avouris, *Phys. Rev. Lett.* **89**, 106801 (2002)
12. L.B. Kong, S. Li, T.S. Zhang, J.W. Zhai, F.Y.C. Boey, J. Ma, *Prog. Mater. Sci.* **55**(8), 840 (2010)
13. L. Liu, L.B. Kong, W.Y. Yin, S. Matitsine, *IEEE Trans. Electromagn. Compat.* **53**(4), 943 (2011)
14. J.N. Coleman, W.J. Blau, A.B. Dalton, E. Munoz, S. Collins, B. Kim et al., *Appl. Phys. Lett.* **82**, 1682 (2003)
15. Z. Wang, Z. Liang, B. Wang, C. Zhang, L. Kramer, *Composites, Part A, Appl. Sci. Manuf.* **35A**, 1225 (2004)
16. M. Olek, J. Ostrander, S. Jurge, H. Mohwald, N. Kotov, K. Kempa et al., *Nano Lett.* **4**, 1889 (2004)
17. E. Lahiff, C.Y. Ryu, S. Curran, A.I. Minett, W.J. Blau, P.M. Ajayan, *Nano Lett.* **3**, 1333 (2003)
18. Q. Cheng, J. Wang, J. Wen, C. Liu, K. Jiang, Q. Li et al., *Carbon* **48**, 260 (2010)
19. E.C. Burdette, F.L. Cain, J. Seals, *IEEE Trans. Microw. Theory Tech.* **28**, 414 (1980)
20. D.V. Blackham, R.D. Pollard, *IEEE Trans. Instrum. Meas.* **46**, 1093 (1997)
21. D.L. Gershon, J.P. Caleme, Y. Carmel, T.M. Antonsen, R.M. Hutchen, *IEEE Trans. Microw. Theory Tech.* **47**, 1640 (1999)
22. Y. Gefen, A. Aharony, S. Alexander, *Phys. Rev. Lett.* **50**, 77 (1983)
23. Y.J. Huang, G.J. Wen, Y.J. Yang, K. Xie, *Appl. Phys. A* **106**, 79 (2012)
24. J. Shen, S. Liu, R. Cao, X. Fan, J. Du, H. Zhang, Z. Lin, S. Chui, J. Xiao, *Appl. Phys. A* **105**, 789 (2011)
25. M.H. Tang, Y.G. Xiao, B. Jiang, J.W. Hou, J.C. Li, J. He, *Appl. Phys. A* **105**, 679 (2011)