

SHIELDING EFFECTS IN THIN FILMS OF CARBON NANOTUBES WITHIN MICROWAVE RANGE

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The electromagnetic shielding properties of thin films comprising different types of carbon nanotubes (CNTs) were analyzed in the microwave frequency range (26–36 GHz). A comparative analysis of the shielding properties was achieved for films based on long and short single-, double- and multi-walled CNTs. The experimental results proved that long-length single-walled CNTs demonstrate the highest interaction with the electromagnetic (EM) field, thereby providing the best shielding efficiency. At the same time, double-walled CNTs demonstrate a higher level of absorption ability (50%) along with the overall high EM shielding efficiency (88%), which makes them attractive for using in nanoelectronics screens as they produce the smallest secondary EM pollution.

Keywords: microwave frequency range, electromagnetic response, carbon nanotubes

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1. Introduction

Progresses in nanoscience and nanotechnology continuously allow developing new applications, including communications and electronics. The development of new ultra-light and low-cost shielding nanomaterials for the microwave frequency range is a current task for improving the reliability of electronic equipment. This is the reason why intensive investigations of the shielding effect are carried out for new types of composite materials based on graphite, graphene [1], carbon nanotubes [2–4] and other fillers.

Due to a unique combination of high electrical conductivity, resistance to corrosion, flexibility, lightness and mass-production ability, composites based on polymer matrices containing conductive fillers are among the most attractive materials for shielding applications. As for various kinds of available conductive inclusions, carbon nanoparticles (amorphous carbon,

graphene, fullerenes, carbon nanotubes, etc.) are considered to be the most promising for developing efficient electromagnetic shielding materials. As already shown in our previous research works [5–8], carbon nanotubes (CNTs) are among the best candidates for designing EM shielding polymer materials, owing to their high aspect ratio (~1000) and unique electronic properties. Shielding effectiveness (SE) of CNT-based composites depends on the type of polymer matrix and on the characteristics of CNTs such as length [9], diameter [5, 10], and orientation [11]. However, composite production with a homogeneous distribution of CNTs in the matrix is still a non-trivial problem, due to the strong tendency of CNT to agglomerate. Such effect limits the CNT concentration in the composites and lowers the total EM effectiveness of the material.

In addition to composites prepared by means of traditional processes, e. g. by mixing polymers with CNT suspensions, other hybrid materials were recently

developed [12]. Thus, based on the idea that higher EM shielding might be obtained by using high concentration of separated CNTs (or their bundles), Wu et al. avoided the agglomeration problems and fabricated CNT microfilms on a polymer substrate (like sandwich structures) presenting high shielding effectiveness (SE up to 61–67 dB) in the X band [13, 14]. Wang et al. presented a screen printing technique for the commercial fabrication of low-cost thin CNT films on a polymer substrate with high shielding performances [15].

Unlike usual composites, for which EM properties mostly depend on those of CNT agglomerates and of small amounts of isolated CNTs, the shielding effectiveness of thin films is more sensitive to CNT geometrical parameters. In spite of numerous publications related to traditional CNT-based polymer composites, the proper choice of optimal parameters is still a problem to be solved and it motivated our investigations. In the present paper, we compared microwave properties of thin films comprising CNTs of different lengths and different natures (single-walled, double-walled and multi-walled CNTs).

2. Materials and methods

Single-walled CNTs (SWCNTs) produced by gas-phase catalysis (HiPco process) were purchased from *NanoIntegris Inc.* (<http://www.nanointegris.com>). The average diameter of individual SWCNTs was 0.8–1.2 nm and their length was $\sim 1 \mu\text{m}$. Double-walled CNTs (DWCNTs) were synthesized at CIRIMAT (Toulouse, France) by catalytic chemical vapour deposition (CCVD) through decomposition of CH_4 over a $\text{Mg}_{1-x}\text{Co}_x\text{O}$ solid solution containing small amounts of molybdenum [16, 17]. The DWCNT length was 1–10 μm (although bundles could measure up to 100 μm) with an outer diameter of 1–3 nm, and the sample contained 80% DWCNTs. Multi-walled CNTs (MWCNTs) were produced by the CVD method (Baytubes[®] C 150P, *Bayer MaterialScience AG*, Germany). As specified by the supplier, MWCNTs had inner and outer diameters of about 4 ± 2 and 11 ± 3 nm, respectively. The MWCNT length was more than 1 μm .

Short-length CNTs were produced by cutting long-length CNTs using the procedure detailed elsewhere [18]. Atomic force microscopy (AFM, Solver P47 PRO, *NT-MDT Inc*) showed that intensive ultra-sonication in an acid mixture (95% H_2SO_4 and 59% HNO_3 at volume fractions of 8:1, respectively) at low temperature ($< 8^\circ\text{C}$) allowed reducing the CNT length down to 100–300 nm for all kinds of tubes, without a significant change of their diameter distribution or modification of their electronic properties (Fig. 1).

CNTs films were fabricated by the vacuum filtration technique [19–22] as follows.

- 0.2 mg of each type of CNTs was dispersed into 1 wt.% of sodium dodecyl sulfate (*Sigma-Aldrich*) in water by ultra-sonication (44 kHz) for 1 h. Then,

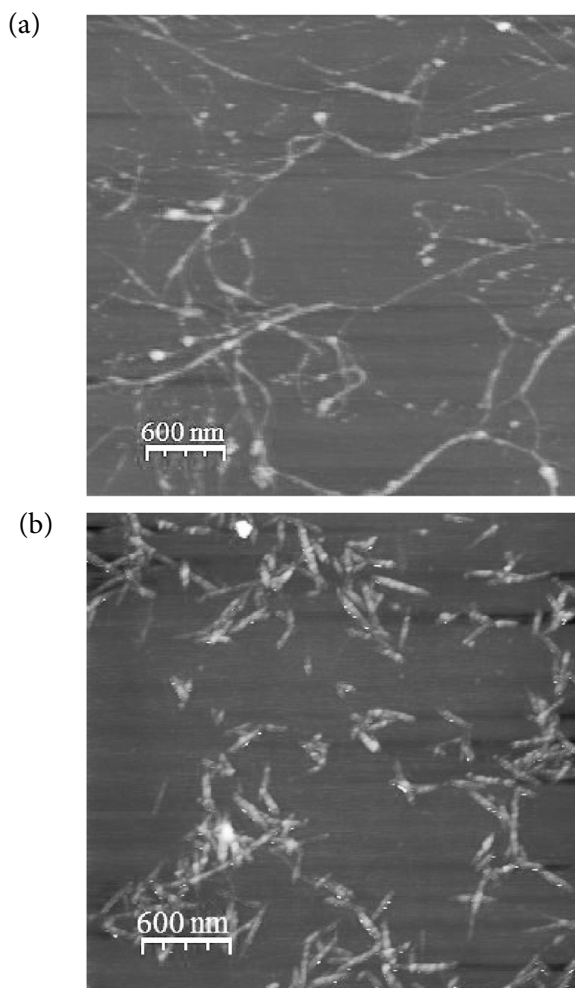


Fig. 1. AFM images of SWCNTs before (a) and after (b) cutting.

in order to separate them from undissolved CNTs bundles and from impurities (e. g. small amounts of amorphous carbon and catalytic particles), centrifugation was carried out for 10 min at 12000 g.

- After the centrifugation the supernatant was collected and then filtered with a cellulose acetate membrane (*Millipore*, 0.22 μm pore size). During the filtration process, the CNTs accumulated on the membrane surface, forming a homogeneous film.

- The surfactant was washed away with pure water. Finally, the filtration membrane was dissolved in acetone, the film was washed with water, and then transferred onto 10 μm -thick Teflon substrates. The substrate is almost transparent in the microwave frequency range and does not contribute to the total electromagnetic response of the investigated samples.

In order to measure the thickness of obtained films, a small part of each one was also transferred onto a silica substrate. The average thickness of each film was then determined with a digital profilometer Veeco Dektak 6M and is given in Table 1.

Table 1. Measured average thickness for each CNT film.

	SWCNT	DWCNT	MWCNT
	Long/short length	Long/short length	Long/short length
Thickness, nm	560/800	500/700	610/775

The microwave measurements of transmission/reflection coefficients in the Ka-band (26–36 GHz) were performed with a scalar network analyzer R2–408 (ELMIKA) after inserting the sample under study into a transmission line (waveguide of cross-section 7.2×3.4 mm) perpendicular to wave propagation [23]. The EM response of samples was measured as ratios of transmitted to input (S_{21}) and reflected to input (S_{11}) signals.

3. Results and discussion

The measured electromagnetic response (S_{11} and S_{21}) of thin films based on long-length and short-length SWCNTs is presented in Fig. 2. Frequency dependences of S-parameters for both types of SWCNT films were flat and did not show any special feature such as absorption peak or other trends. The same behaviour was observed for other composites based on DWCNTs and MWCNTs, and therefore the electromagnetic response was analyzed only at one frequency (30 GHz).

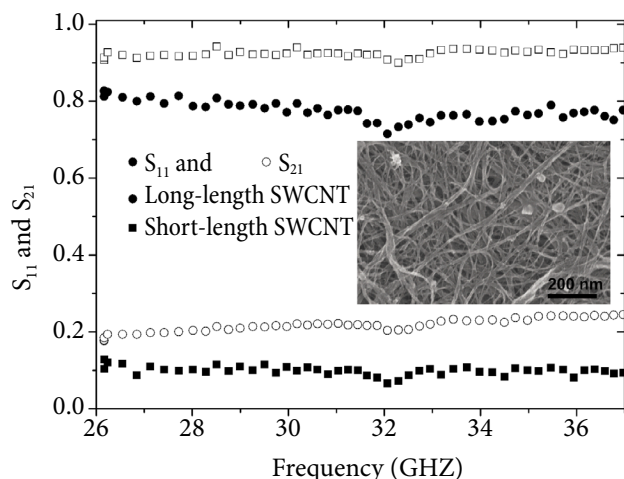


Fig. 2. Frequency dependence of S_{11} and S_{21} . Inset: scanning electron microscope image of a long-length SWCNT film. As can be seen, ultracentrifugation removed large particles and agglomerates, providing high-quality CNT films.

Reflectance ($R = S_{11}^2$), transmittance ($T = S_{21}^2$) and absorbance ($A = 1 - T - R$) of the electromagnetic radiation as well as the total shielding effectiveness ($SE = -20\log(S_{21})$) at 30 GHz for films comprising different natures of CNTs (SWCNTs, DWCNTs and MWCNTs) and lengths are presented in Fig. 3.

Our results reveal that thin films based on 200 nm-long CNTs are transparent to microwave radiation ($T \sim 84\text{--}92\%$) and give a negligible attenuation level ($SE \sim 0.35\text{--}0.75$ dB). It can be noticed that, in this case, such high transparency does not depend on the type of CNTs used for film fabrication.

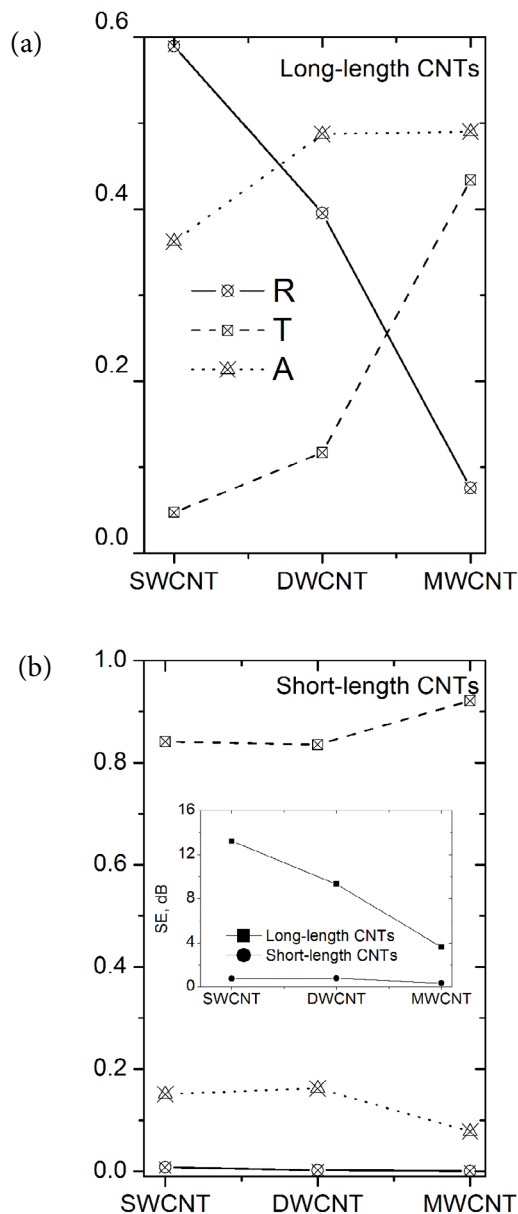


Fig. 3. Absorbance A , reflectance R and transmittance T at 30 GHz of films based on CNTs: (a) long-length CNTs, (b) short-length CNTs. The inset shows the corresponding SE.

Figure 3 shows that the SE of films based on SWCNTs is 13 dB, and decreased down to 3.62 dB as the number of walls increased. Such attenuation level was achieved due to high levels of both reflectance (58%) and absorbance (36%).

This result agrees with our previous theoretical predictions [7]. Indeed, as it has been shown earlier, the electromagnetic properties of composites are mostly determined by the polarizability α of the individual inclusions. The imaginary part of the polarizability α has a peak in the terahertz range (1.5–6 THz). The frequency position f_p of this peak depends on both length and diameter of CNTs. As demonstrated in [7], the frequency f_p splits the spectra into two different parts: quasi-static and dynamic regimes. In the quasi-static regime ($f \leq f_p$), the CNT polarizability is strongly influenced by the finite-length effect, leading to a strong screening as outermost shells screen the internal ones. Such a strong screening effect in the case of short-length tubes explains the transparency ($T > 80\%$) of the corresponding films as well as the absence of dependence on the type of CNTs. The increase in CNT length decreases the impact of such finite-length effect, resulting in the increase in the electromagnetic absorption from a moderate level of 15% up to 36–49%. As it was mentioned, the real part of the polarizability of long-length MWCNTs is larger than that of SWCNTs, but the substantial difference in reflection of thin films (58% against 1% for SWCNT- and MWCNT-based films, respectively) and high shielding effectiveness can be explained by a significant difference in their number density.

To conclude, the strong influence of the nanotube length and the number of walls on the electromagnetic response of thin CNT-based films was evidenced in the microwave frequency range. It has been shown that the thin films based on short-length nanotubes demonstrated the negligible attenuation level due to the strong depolarizing field and screening effect in CNT. The opposite was observed for the films based on long-length CNTs. The analysis of the obtained dependence for different types of nanotubes allowed us to conclude that the films based on long-length SWCNTs are more preferable in case we are looking for overall high attenuation ability (the transmission rate is less than 5% because of 60% reflection and 35% absorption for the film being approx. 500–600 nm thick). However, films made of double-walled CNTs are much more absorptive in comparison with SWCNT ones (50 vs 35%), which makes them in some sense more attractive as they do produce much smaller additional EM interference. Finally, MWCNTs demonstrate the smallest EMI shielding efficiency out of the three families of tubes investigated here, at the level of 55%, but still absorptive (50%), which also makes them suitable.

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EKRANAVIMO REIŠKINIAI PLONUOSIUOSE ANGLIES NANOVAMZDELIŲ SLUOKSNIUOSE MIKROBANGŲ RuoŽE

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Santrauka

Naujų ultralengvų ir mažų gamybos sąnaudų reikalaujančių nanomedžiagų paieška bei tyrimai yra vienas svarbiausių uždavinių gerinant mikrobangų ruožo elektroninių prietaisų darbo patikimumą. Šiame darbe tyrinėjami ekranavimo reiškiniai plonuosiuose sluoksniuose, sudarytuose iš įvairaus ilgio vienasienių, dvisienių ir daugiasienių anglies nanovamzdelių. Eksperimentiniai tyrimai 26–36 GHz dažnių ruože parodė, kad ekranavimo efektyvumas priklauso nuo anglies nanovamzdelių ilgio. Ilgi nanovamzdeliai intensyviai sąveikauja su mikrobangų elektromagnetiniu lauku ir užtikrina didžiausią ekranavimo efektyvumą. Sluoksniuose su trumpais

anglies nanovamzdeliais stebimas silpnas slopinimas dėl stipriai pasireiškiančio depolarizacijos efekto. Lyginant rezultatus prieita prie išvados, kad ilgi pavieniai anglies nanovamzdeliai labiau tinkami bendram efektyviam ekranavimui (88 % efektyvumas), dvisieniai nanovamzdeliai geriau absorbuoja mikrobangų spinduliuotę (50 % absorbcija), todėl tinkami naudoti kaip nanoelektriniai ekranai, padedantys išvengti papildomos elektromagnetinių bangų interferencijos, o daugiasieniai nanovamzdeliai ekranuoja mažiausia (55 % efektyvumas), bet išlieka tinkama absorbuojanti nanomedžiaga tirtajame dažnių ruože.