Diamond & Related Materials 25 (2012) 13–18

Contents lists available at SciVerse ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Multi-walled carbon nanotubes/PMMA composites for THz applications☆☆

J. Macutkevic [a,]*, D. Seliuta [a], G. Valusis [a], R. Adomavicius [a], A. Krotkus [a], P. Kuzhir [b], A. Paddubskaya [b], S. Maksimenko [b], V. Kuznetsov [c], I. Mazov [c], I. Simonova [c]

[a] Center for Physical Sciences and Technology, Lithuania
[b] Institute for Nuclear Problems, Belarusian State University, Belarus
[c] Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia

ARTICLE INFO

Available online 12 February 2012

Keywords:
Carbon nanotube
Composite
Electromagnetics
Terahertz radiation

ABSTRACT

Dielectric properties of polymethyl methacrylate (PMMA) filled with small amounts (0.25–2 wt.%) of CVD made multi-walled carbon nanotubes (CNT) versus nanotubes diameter and oxidation degree have been investigated by terahertz time-domain spectroscopy. A high electromagnetic (EM) attenuation strongly increasing with frequency has been found for all types of CNT fillers. It has been demonstrated that the CNT oxidation treatment has a significant impact on electromagnetic response properties of CNT/PMMA composites in the THz frequency range for CNT content up to 1 wt.%, while the mean CNT diameter has not been found as an important factor influencing the EM behavior of composite films for particular nanotube geometry (CNT length is 10 μm; average outer diameter is 9 or 12–14 nm). At the same time, the THz transmission spectra of PMMA with 2 wt.% are proved to be very similar for all types of CNTs embedded. The resonance dielectric dispersion has been observed for all studied samples, which can be attributed to the phonon resonance in PMMA matrix.

1. Introduction

Since the discovery of carbon nanotubes, there has been great interest to their outstanding structural, electrical and mechanical properties [1,2] due to wide applications ranging from chemical and biological sensors and actuators to field emitters to mechanical fillers for composite materials. Among others, the study of CNTs as building blocks for nanoelectronics [3] and nanooptics [4] has continued to grow unabated owing to the great potentiality for the miniaturization and the increase of operational speed of optoelectronic nanocircuits, and for the use in near-field subwavelength optics. In that relation, the question of the EM response of CNTs arises. Many interesting physical effects have been revealed, such as excitation of surface plasmons [5], guiding of strongly slowed-down electromagnetic surface waves [6], antenna effect — controlled and enhanced radiation efficiency in infrared and terahertz ranges [7–9], enhanced spontaneous decay rate of an excited atom in the vicinity of CNT [10]. Recently, the nanoscale optical imaging of single-walled carbon nanotubes has been studied by means of high-resolution near-field Raman microscopy [11,12] and the nanoantenna operation of a CNT array has been demonstrated experimentally [13]. Ref. [14] reports multi-walled CNT as subwavelength coaxial waveguide for visible light. Carbon nanotubes have been studied extensively to develop useful functional materials based on their fascinating mechanical, optical, and electrical properties. In particular, CNT based composites are used as compact active and passive elements in the terahertz range of electromagnetic radiation [15,16].

Recent advances in terahertz generation, expanding THz market trends to bio-medicine and security applications have stimulated research of THz radiation interaction with new composites, especially those demonstrating high and/or frequency non-monotonous electromagnetic attenuation. In that sense CNT due to their unique electromagnetics [6] are very interesting for using in THz range.

However, the practical use of carbon nanotubes in composite materials is complicated because CNTs are highly aggregated structures, resulting in difficulty of the dispersion and distribution in a matrix. In addition, high chemical stability of the surface of carbon nanomaterials prevents a direct chemical interaction of CNTs with the host, which may adversely affect the properties of the final composites. One of the effective ways of increasing the degree of interaction between the tubes and the matrix is the chemical functionalization (the insertion of various functional groups on the surface of CNTs).

One of the most common methods of CNT functionalization is the treatment with various oxidizing agents (HCl, H_2SO_4, H_2O_2, $H_2O_2+H_2SO_4$, $1HNO_3+3H2SO_4$, HNO_3, $KMnO_4$, NaClO, $SOCl_2$, etc.). The result of oxidation is the formation on the CNT surface carboxyl (−COOH), alcohol (C–OH) and ketonic (−C=O) groups, with the number and type of oxygen-containing groups dependent on the method of oxidation. In addition, the oxidation rate of other carbon particles exceeds that of CNTs, which allows purifying CNTs from the amorphous carbon impurities. Moreover, the experimental evidences [17] indicate that multi-walled carbon nanotubes (MWNT) purified by acidic solution

☆☆ Presented at the Diamond 2011, 22st European Conference on Diamond, Diamond-Like Materials, Carbon Nanotubes, and Nitrides, Budapest.

* Corresponding author.
E-mail address: jan@pfi.lt (J. Macutkevic).

0925-9635/$ – see front matter. Crown Copyright © 2012 Published by Elsevier B.V. All rights reserved.
doi:10.1016/j.diamond.2012.02.002

increase the polymerization rate, and the composite films show better nanoscopic dispersion of MWNTs. Using MWNTs initially modified with carboxylic acid functional groups on their outside walls through the oxidation, the MWNT adsorption onto PMMA microspheres has been examined in [18] and the conductivity of CNT/PMMA has been found to be influenced by the oxidation treatment. At the same time, functionalization of nanotube surface reveals both higher nanotubes' dispersion and strong interfacial CNT–polymer interactions [19–22], which induces different effects on electrical and mechanical properties of CNT-based composites: hardness and Young's modulus are improved in composites filled with functionalized CNTs [19–22], while composite conductivity is reduced by the oxidation and the percolation threshold is shifted to higher concentrations [23].

The practical applications of CNT based composites in the high-frequency range are restricted though, because of deficit of deep understanding of dielectric properties of CNT composites in terahertz frequencies and their relations with the CNT microscopic parameters. The local maximum of the CNT composites conductivity is observed in the terahertz frequency range [24]. It can be explained in terms of the CNT finite length and (or) the finite radial curvature [25,26], or partially can be addressed to phonon resonance in polymer matrix [27]. That is why we concentrate here on the investigation of dielectric properties of CNT composites versus nanotube diameter and oxidation degree in the wide frequency range from 100 GHz to 4 THz, and propose some theoretical explanation of CNT-based PMMA THz behavior.

2. Experimental

CNT with different diameter distribution were produced via reaction of ethylene decomposition at 650–700 °C in standard CVD setup using Fe–Co catalysts [28]. Two types of MWNTs were investigated, named FCA and FCM series with average outer diameter ~ 9 nm and 12–14 nm respectively. As-produced CNT were purified by boiling in 15% HCl, washed until neutral pH and dried at 40 °C for 24 h. The structural changes and carbon nanotubes morphology were monitored by HR TEM (JEM-2010). The wall number has been estimated for thin nanotubes as 3–7, for the thick ones as 8–15 walls. For this, 400–500 tubes from 10 to 15 different images of different parts of Cu grid were analysed to calculate the average outer diameter of MWNTs.

Some of CNT samples (indicated as OXNA) were additionally oxidized using concentrated nitric acid in order to increase their interaction with polymethylmethacrylate matrix. After oxidation MWNTs were washed on filter with distilled water until neutral pH and dried in air and under vacuum. High resolution transmittance electron spectroscopy (HRTEM) images of prepared CNTs are presented in Fig. 1. According to the TEM investigation, the morphology of the tubes remains practically unchanged after oxidation, while the number of defects on the MWNT surface, such as individual particles of amorphous carbon and surface defects, is reduced significantly.

Polymethylmetacrylate with m.w. ~100,000 (Degussa, Germany) was used for preparation of composites via coagulation precipitation technique describes elsewhere [28]. Composites with CNT content 0.25, 0.5, 1.0 and 2.0 wt.% were prepared as follows. Dimethylformamide/DMF (Aldrich) was used as main solving agent due to its high possibility to dissolve organic compounds and to form dispersions of carbon nanotubes. PMMA was dissolved in DMF in content 0.05 g/ml, a necessary amount of CNT was placed in a water-cooled glass reactor, 60 ml of pure DMF and 40 ml of PMMA/DMF solution were added to CNT, and this mixture was sonicated with power up to 10 kW/cm^2 during 15 min. The temperature of dispersion was controlled during sonication and lower than 45–50 °C. Resulting black dispersion was poured into 1 l of distilled water with room temperature under continuous stirring. This results in coagulation of polymer due to dissolution of DMF in water and precipitation of the composite as black spongy powder. Additional samples of CNT/PMMA composites were prepared using CNT and N-methylpyrrolydone (NMP) as a dissolving agent for the preparation of CNT dispersion, which was later mixed with PMMA/DMF solution and treated in the described way. The powder was filtered, washed with 1.5 l of distilled water and dried at 60 °C for 10 h. Composite powders were used for preparation of polymer films via hot-pressing technique. The average sample thickness was 0.45 mm for CNT of d ~ 9 nm and 0.48 mm for CNT of d ~ 12–14 nm.

A home-made time-resolved coherent THz spectrometer, based on a Ti:sapphire laser with pulse of 120 fs duration at a wavelength of 800 nm with 80 MHz repetition rate, was used. In this setup the laser beam is split into two parts: the first one excites a low-temperature grown (LT) GaAs-based emitter, while the second, time-delayed pulse, gates the LT GaAs based detector. Free standing samples with large apertures and thickness from 0.3 mm to 0.6 mm were placed in the beam path, and the transmitted signal was recorded.

The electrical conductivity was measured by the capacitance bridge HP4284A for the frequency 129 Hz at room temperature. The sample was placed in the coaxial line between the inner conductor and short end, which were fresh polished for each measurement for better electrical contact.

3. Results and discussion

The results for electrical conductivity collected at 129 Hz and room temperature are presented in Table 1. One can see that the oxidation leads to some decrease of conductivity of CNT/PMMA films for all studied CNT concentrations. The same tendency was observed for densely packed MWNTs, both oxidized and as prepared [29]. Electrical measurements of powders of thin and thick MWNTs (FCA and FCM types) were

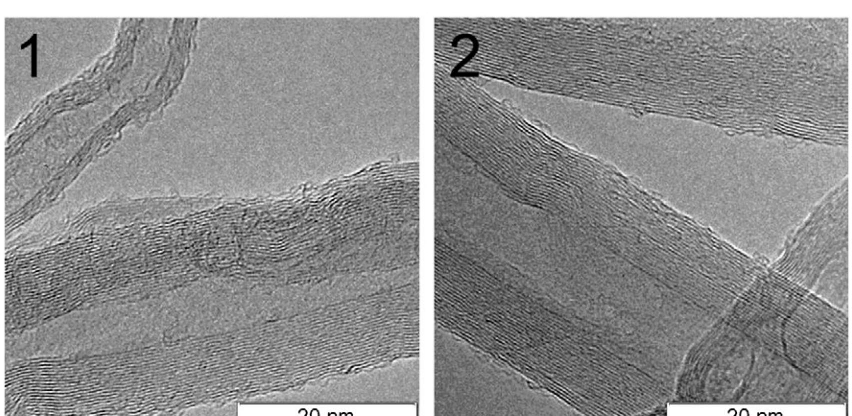

Fig. 1. HRTEM of CNT of FCA type as prepared (1) and oxidized (2).