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Identifying anisotropy in seemingly random CNT networks using terahertz techniques

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ABSTRACT

Characterizing and understanding carbon nanotube (CNT)-based polymer composites plays a crucial role for the ability to customize their properties. The (an)isotropy of CNT networks inside a composite can have significant effects on the final material's properties. However, characterizing the (an)isotropy of seemingly random CNT networks can be difficult using standard techniques. In this letter, we show that terahertz polarization sensitive measurements can provide a reliable, noninvasive and fast way of identifying anisotropy in seemingly homogenous CNT networks as based on criteria by standard techniques.

1. Introduction

Composite materials are of interest for both research and industry due to their well-known advantages of combining the properties of individual components in one material, in terms of mechanical [1–4], thermal [5–7] or electrical properties [8–10]. Carbon nanotubes (CNTs) are promising as filler particles because of their high aspect ratio combined with good mechanical, electrical and thermal properties [11–14]. However, the CNTs orientation, alignment or distribution in the composite material can have a significant effect on the material's properties [15–17]. Therefore, characterizing the (an)isotropy of the CNT networks inside composite materials plays a significant role in determining and understanding the behavior and properties of the final material. There are various common methods to characterize CNT networks (an) isotropy such as electron microscopy (EM) techniques [18], atomic force microscopy (AFM) [19] or X-ray scattering (XS) techniques [20]. However, these techniques have certain limitations and often require advanced and complex digital technologies to identify and characterize anisotropy in SWCNT networks that are intended or required to be randomly distributed.

Terahertz (THz) technologies are progressing at a rapid rate due to their diverse potential applications as they provide a noninvasive characterization option for various material properties. Terahertz polarizers have already been used to characterize electromagnetic properties [21] or electrical conductivity [22] of CNT-based polymer composites, but also to characterize anisotropy in aligned CNT ropes/stacks [23].

In this study we used terahertz polarization effects to identify anisotropy in single-wall CNT (SWCNT)-based polymer composites in a fast, noninvasive way, where all standard techniques failed to do so. The choice for SWCNTs may seem strange as multi-wall CNTs (MWCNTs) are more commonly used. However, the materials used were designed to study the conductivity of CNT composites and, in particular, the role of the network and the contacts between the CNTs (as discussed in detail in references [24,26]). As this is already a topic of some complexity, the range of structures and conductivities as exhibited by MWCNTs would obscure the matter and, hence, we opted for SWCNTs. Results showed that seemingly homogeneous and randomly distributed SWCNT networks/polymer composites (based on AFM, SEM, TEM and SAXS measurements) can still have a certain degree of anisotropy which affects the material's electrical performance.

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2. Materials and methods/Experimental details

2.1. SWCNT films preparation

All chemicals were used as received, without any further purification. Super High Purity SWCNTs manufactured by chemical vapor deposition (CVD) method were purchased from US Research Nanomaterials, Inc. SWCNT thin films were prepared from 0.1% SWCNT dispersions in water prepared with the aid of sodium carboxymethyl cellulose (CMC) $M = 90\ 000$ g/mol ($C_{28}H_{30}Na_8O_{27}$) from Sigma Aldrich, with a SWCNT/CMC ratio of 1/30, as described by Bârsan et al. [24] Using different gap sizes of the doctor blade coater (in the range of 15 μm–120 μm) to deposit the SWCNT/CMC dispersion on a glass substrate resulted in SWCNT films of different thicknesses in the final samples.

The SWCNT films prepared were further fixated on the glass substrate by impregnating them with an excess amount of epoxy/amine polymer as described in Bârsan et al. [24].

2.2. SWCNT films characterization

Sheet resistance measurements on the initial SWCNT films were performed using standard four-point probe measurements with 5 mm distance between the probes. An electrometer model 6517A and source-meter model 237 (Keithley Instruments, USA) were used to apply current and measure the resulting voltage drop. The results were converted to sheet resistance using correction factors for rectangular thin films from Smits et al. [25] Scanning electron microscopy (SEM) images were taken with a Quanta 3D FEG microscope (FEI Company, USA) and scanning transmission electron microscopy (STEM) images were acquired using a Titan electron microscope operated at 300 kV and High Angular Annual Dark Field (HAADF) detector (FEI Company, USA). Atomic force microscopy (AFM) was done using a SOLVER NEXT (NT-MDT, Russia) in tapping mode and a Veeco 150 Dektak profilometer (Bruker, USA) was used for thickness measurements. X-ray diffraction (XRD) measurements were performed on a Saxslab Ganesha vacuum system. This system contains a high brilliance Microfocus Source, a Genix3D motorized collimation system consisting of high precision 4-blade slits with single crystal low-scatter blades, a 3-axis detector motion of the detector, achieving sample-to-detector distances between 80 mm and 1450 mm and a Pilatus 300 K solid-state photon-counting 2D-detector. Cu radiation with a wavelength of 1.54184 Å was used. Measurements were done in transmission mode using a sample to detector distance of 80 mm and an exposure time of 600 s in the q-range of 0.069 $Å^{-1} < q <$ 2.97 $Å^{-1}$. A silver behenate standard was used to verify the sample to detector distance. The 002 signal was used to characterize anisotropy.

2.3. Polarization measurements

High frequency polarization measurements in a range of 50–60 GHz were done using a millimeter wave vector network analyzer (MVNA-AB millimeter 8–350) and a quasi-optical test bench for scattering parameters (AB Millimetre, Paris, France). An M-481-A metric rotation stage (Newport Corporation, USA) was used to rotate samples angularly and read rotating angles accurately. The sample is rotated in the field with an illuminated area less than the sample size, and hence the precise geometric position is relatively unimportant. The frequency range indicated has been chosen in accordance with the sample size and the accuracy of the measurement set-up. The used frequency range is the smallest frequency range whereby the THz wave beams can be fully focused on the sample under test and at the same time delivers the highest precision in the measurements. Data are reported for the central frequency 55 GHz as the principle applies over the whole frequency range and the results are largely independent of the frequency in this interval.

3. Results and discussion

A set of initial SWCNT films with a thickness range of 13–135 nm were prepared on glass substrates (details in Table 1). These films are composed of randomly dispersed individualized SWCNTs and bundles of aligned SWCNTs with a diameter in the range of 1–20 nm in the bulk network, as verified by SEM and TEM images (Fig. 1a and b). In addition, occasional ropes of aligned tubes as large as 100 nm form at the surface of the films during the preparation procedures (see AFM roughness profiles in Fig. 1c). These ropes are not considered when measuring the film thickness. In a previous study it was shown that after impregnating these initial films with an epoxy/amine polymer, the SWCNTs occupy ≈53% of the volume, excluding the excess polymer on top [26].

Based on different microscopy images the CNTs appear homogeneously distributed and randomly oriented on the glass substrate. X-ray scattering (XS) measurements are also typically used to identify structural ordering in various materials [20]. Therefore we performed small angle (SA) and wide angle (WA) XS measurements (Fig. 2a and b, respectively) on a 2 μm thick SWCNT film. Radial averaging of the intensity of the 002 signal was done as a function of q (0.015 $Å^{-1} < q <$ 0.03 $Å^{-1}$ for SAXS and 0.15 $Å^{-1} < q <$ 0.4 $Å^{-1}$ for WAXS, where $q = 4\pi \sin\theta/\lambda$) and the resulting intensities were plotted as a function of the azimuthal angle as shown in Fig. 2c. The constant intensity values at different azimuthal angles shows that there is no obvious structural ordering in the sample.

However, because the preparation procedure for the initial SWCNT films is based on doctor blade coating, a certain in-plane orientation, and implicitly a certain anisotropy, is expected. In fact, four point probe measurements have shown slight variations in the sheet resistance of each film, depending on the direction of the measurement.

In order to quantify these variations, square samples were prepared of each type of CNT film and the sheet resistance was measured in the center of the sample in both ox and oy directions (Fig. 3a). The same measurement was repeated after 3 h and the average of the two measurements was used further. Results showed that the average sheet resistance in the direction of the coating (defined as ox direction) is lower than the average sheet resistance measured in the oy direction for all CNT films, regardless of their thickness. This suggests that, despite their apparent homogeneity, the SWCNT films do have a certain orientation/anisotropy resuling from the coating process. In addition to that, the resistance increase from ox to oy direction is systematically more significant for the thicker films (Fig. 3b). For example, a SWCNT film 13 nm thin has a resistance increase of 2.3% from ox to oy direction while a 135 nm thick film has a resistance increase from ox to oy direction of almost 23%. Considering that all CNTs are prepared from the same dispersion using the same coating technique with the thickness being the only variable, the sample (an)isotropy is not likely to change. Therefore the resistance variation with the measurement direction is only related to the sample thickness and not to changes in the sample (an)isotropy. The consistent and systematic resistance variation with the direction of the measurement shows that resistance measurements are also a fast, cheap and easily accessible way of verifying network isotropy on their own. However, this method is not applicable for non-conductive composite materials.

In a next stage the anisotropy of seemingly random SWCNT networks was investigated by checking whether the transmission of an orthogonally incident linearly polarized THz wave is

Table 1
SWCNT films of different thicknesses and sheet resistances.

Sample name	S1	S2	S3	S4	S5	S6	S7	S8	S9
SWCNT film thickness (nm)	≈13	≈22	≈49	≈57	≈82	≈87	≈105	≈135	≈2000
SWCNT film sheet resistance (Ω/sq)	1489	988	402	359	118	136	110	111	67

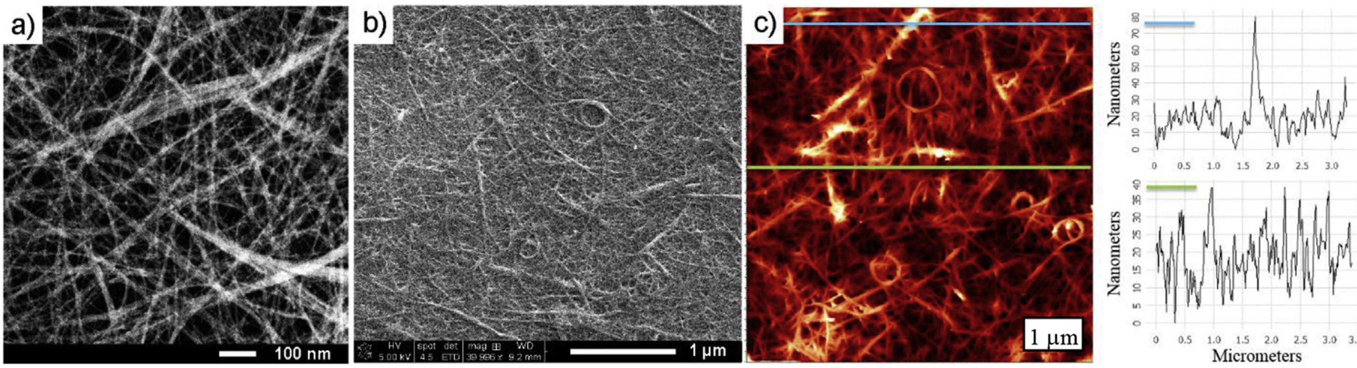

Fig. 1. SWCNT film with a thickness of ≈40 nm (before polymer impregnation) in a) STEM, b) SEM and c) AFM image with roughness profile.

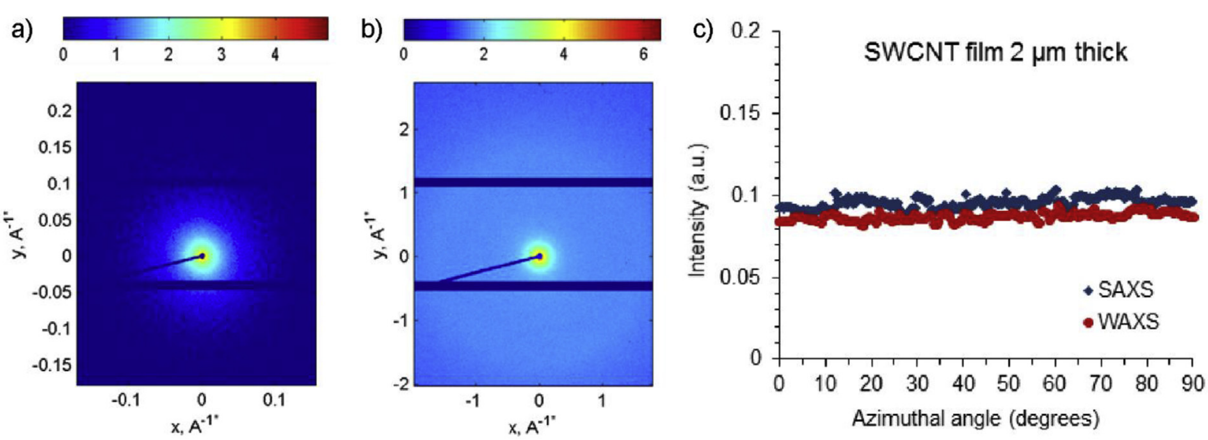

Fig. 2. a) 2D SAXS pattern and b) WAXS pattern of a 2 μm thick SWCNT film and c) intensity plotted as a function of azimuthal angle for the 2D patterns.

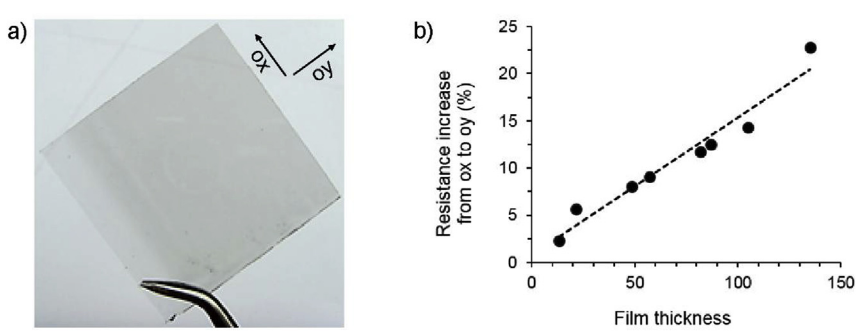

Fig. 3. a) Example of SWCNT film on glass substrate (tweezers visible at the bottom sample corner) and b) the increase in CNT film sheet resistance from measurements taken in the ox direction (coating direction) to measurements taken in the oy direction.

dependent on the relative orientation of the E-field with respect to the SWCNT samples. This polarization effects has been executed in the lower frequency (50–60 GHz) domain of the THz domain. Aligned SWCNTs act like a terahertz polarizer. When the alignment direction of SWCNTs is coincident with the terahertz wave E-field polarization orientation, electrons are accelerated by the incident terahertz waves, dissipate some of this energy and hence the energy transmission is at a minimum and the terahertz wave absorption of CNTs is at a maximum; when the alignment direction of CNTs is orthogonal to the terahertz wave polarization orientation, the terahertz wave excite electrons much less, the energy is maximally transmitted through the CNTs, and the terahertz wave

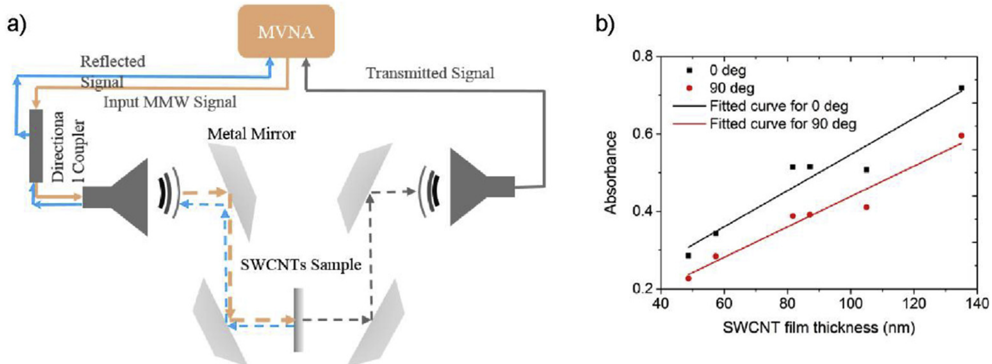

Fig. 4. a) Schematic diagram of polarization measurement, b) Absorbance at 0° and 90° direction versus CNTs thickness at 55 GHz.

absorption of CNTs reduces to a minimum. So, one can use the CNTs' anisotropic transmittance of the terahertz waves to analyze the CNTs' structural alignment. Indeed, previous studies have shown that SWCNT orientation and anisotropy can be detected via transmission measurements in the terahertz frequency range [23,27]. In addition, anisotropic electromagnetic properties were also observed in the terahertz regions for CNT-based polymer composites [21]. All of these studies have been done on materials comprised of and containing aligned CNTs, respectively. A schematic diagram of the polarization test system we used is shown in Fig. 4a. The SWCNT sample is placed on a holder, which one can use to rotate the sample angularly and accurately read out the rotated angle. The millimeter wave (MMW) signal is generated by a millimeter vector network analyzer (MVNA) radiated through a corn antenna and guided by metal mirrors to illuminate the WCNT sample. The wave reflected by the SWCNTs is decoupled by a directional coupler and detected by the MVNA, and the transmitted wave penetrating through the SWCNT sample is received by a horn antenna and detected by the MVNA. Using this test system, one can measure the reflection and transmission coefficients of the SWCNT network directly, and then calculate the absorption.

The absorption of SWCNTs almost linearly increases with SWCNTs thickness as shown in Fig. 4b for both the 0° and 90° rotating angle, because the thickness of samples increases and the related resistance in this frequency range increases as well. The absorption of SWCNTs for the 0° rotating angle is higher than for the rotating angle of 90° (Figs. 4b and 5b).

The correlation between the anisotropic THz absorption effect and the anisotropic electrical resistance measurement is as follows. The ox-axis is associated with the orientation of the SWCNTs on the substrate. The angle θ indicates the relative angular orientation of the ox-axis of substrate with respect to the E-field of the orthogonally incident THz wave beam. For an angle θ equal to zero degrees, the ox-axis of the substrate is oriented vertically and aligned

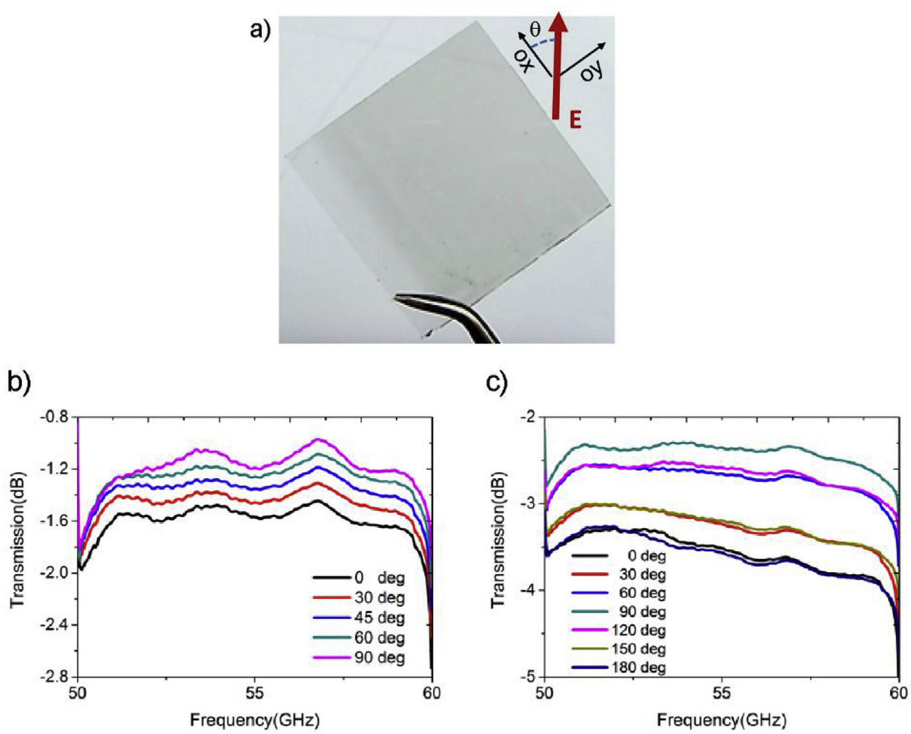

Fig. 5. a) Orientation of the linear polarized MMW field E with respect to the SWCNT film, b) and c) Transmission coefficients of SWCNT film in dB versus frequency for rotating angles from 0° to 90° for sample S3 and from 0° to 180° for sample S6, respectively. (The same measurements were done for samples S4, S5, S6, S7 and S8 with similar results shown in Fig. S3, Supporting Information).

with the E-field of the incident beam. For this orientation, the E-field can most efficiently excite the electrons in the SWCNTs and as a consequence the THz beam can be partially absorbed, leading to a minimum transmission coefficient. For an angle θ of 90°, the E-field is perpendicular to the SWCNT orientation and hence the excitation of electrons in the SWCNTs is minimal, leading to a maximum in the transmission coefficient. Hence the SWCNTs behave like a “wire grid” THz wave polarizer.

In principle, the electronic character of the SWCNTs (semi-conducting or metallic) might affect the transmission, but since the matrix is insulating the matter is of minor concern as the conductivity of both types is any way much higher than that of the matrix. Any remaining catalyst will be present in minute amounts and since the technique response is proportional to the volume probed, its effect on the transmission is negligible.

The expected orientation direction of SWCNTs is along the coating direction (ox direction as shown in Fig. 5a). The linear polarization MMW illuminates the SWCNT network with an angle θ to the original direction (Fig. 5a). The regular polarization behavior was studied for sample S3-S8 after polymer impregnation. Blank measurements showed that the thickness of the glass substrate or polymer layer on top of the SWCNT film has negligible contribution to the polarization effect (Figs. S1, S2 and S4, Supporting Information). Transmission coefficients in the whole frequency band for samples S3-S8 increase with rotating angle enlarging from 0° to 90° where they reach a maximum (example for S3 in Fig. 5b). When the rotating angle is increasing from 90° to 180°, the transmission coefficients decrease and fall almost on the same values as those of the rotating angles from 90° to 0° (example for sample S6 in Fig. 5c).

These contact-free THz measurements are fully coherent with the probe-based resistance measurements in the kHz-MHz region, whereby the smallest resistance is recorded when the electrical probes are aligned along the ox-axis of the substrate.

Finally, we note that in principle larger composite structures could be examined by moving and rotating the sample and simultaneously scanning and that the technique can be used also for films containing a CNT network with a volume fraction below the percolation threshold.

4. Conclusions

Our terahertz polarization sensitive results confirm that there is indeed a certain orientation/anisotropy in the SWCNT networks, even if not detectable via typical characterization techniques such as SEM, TEM, AFM and SAXS. Such degree of anisotropy, as small as it is, still has an effect on the CNT network's electrical behavior which emphasizes the importance and necessity of a reliable characterization technique that can provide information about the (an)isotropy of the conductive network. While resistance measurements on their own can provide an accessible way to verify a CNT network's isotropy, terahertz polarization studies provide a fast, noninvasive and reliable way to characterize the isotropy of SWCNT networks, alone and inside non-conductive polymer composites.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.compscitech.2017.08.004.

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