Transmission of Terahertz Waves through Graphene/Epoxy Samples – Correlation with Electrical Conductivity

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ABSTRACT

We report results from measuring the electrical conductivity and the terahertz (0.35 THz frequency) absorption coefficient of nanocomposite samples consisting of graphene powder dispersed in epoxy. Usage of a higher quality graphene, together with better dispersion of the graphene improves the conductivity compared to previous experiments [1]. However, the measured conductivity is not sufficiently high to explain the measured THz absorption.

1.0 INTRODUCTION

Graphene is a material consisting of one monolayer of carbon atoms tightly packed into a two-dimensional honeycomb lattice [2]. It conducts heat and electricity well, in addition to being a strong and lightweight material. One possible application of graphene is its use as an additive, where adding a low mass fraction of graphene powder into a polymer matrix, such as e.g. an epoxy, may enhance the properties of the polymer [3]. Examples of material properties that are enhanced by adding graphene to epoxy are fracture toughness, thermal conductivity and electrical conductivity [4-7]. Of these properties, the electrical conductivity is of special interest because of potential defense and security applications within electromagnetic shielding [8-10]. Potentially, graphene-based shielding materials could be light-weight, a great advantage in applications such as land and air vehicles, as well as wearable electronics. Generally, good electromagnetic shielding is associated with good electrical conductivity of the material. In this work, we investigate the electric conductivity and THz absorption coefficient of epoxy/graphene nanocomposites. This work is an extension of previous work, where a different type of graphene was employed [1]. Compared to the previous work, we find an increase in the electrical conductivity, most likely due to higher quality graphene and better dispersion of the graphene into the epoxy.

2.0 GRAPHENE/EPOXY NANOCOMPOSITE SAMPLES

Samples of graphene/epoxy nanocomposites were prepared. In addition, the neat epoxy polymer was included as reference. The graphene used in these experiments, with lateral size between 100 and 600 nm, was synthesized by plasma-enhanced chemical vapor deposition (PECVD). Figure 2-1 shows a transmission electron microscope image, as well as a Raman spectrum (inset), of the graphene used to prepare the samples.

The Raman spectrum of the graphene shows the FWHM of the 2D band to be 64.4 cm-1 and the ratio of the intensities of the G and 2D bands (IG/I2D) to be 1.1 indicating that the number of layers is less than 5 [13, 14].

To produce the graphene/epoxy nanocomposite samples, pristine graphene was first dispersed in Araldite LY 556 epoxy resin using a mechanical approach. Visual inspection and Raman mapping revealed that the graphene was homogeneously dispersed in the epoxy. After two months no sedimentation was observed, suggesting a stable dispersion of the graphene. As of yet, the interaction between the epoxy and the graphene has not been studied. This could be the subject of further investigations. Based on our good dispersion results we expect the epoxy resin to be compatible with the graphene, at least up to the concentrations we studied here.

After the graphene was homogeneously dispersed in epoxy resin the Aradur 917 anhydride hardener (0.9 weight ratio to Araldite LY 556) and accelerator DY 070 (0.01 weight ratio to Araldite LY 556) was mixed in. The concentration of graphene in the finished samples was 0 wt. %, 0.1 wt. %, 0.5 wt. %, 1.0 wt. %, 2.0 wt. %, 4.2 wt. %, 6.4 wt. %, 8.7 wt. %, 11.1 wt. % and 13.6 wt. %. The mixtures were heated to 60 °C and poured into disk-shaped molds with a diameter of 41 mm. Each mixture was used to make two samples with different thickness (1 mm and 2 mm), resulting in a total of 20 samples. The samples were cured in an oven before they were polished with fine sandpaper.

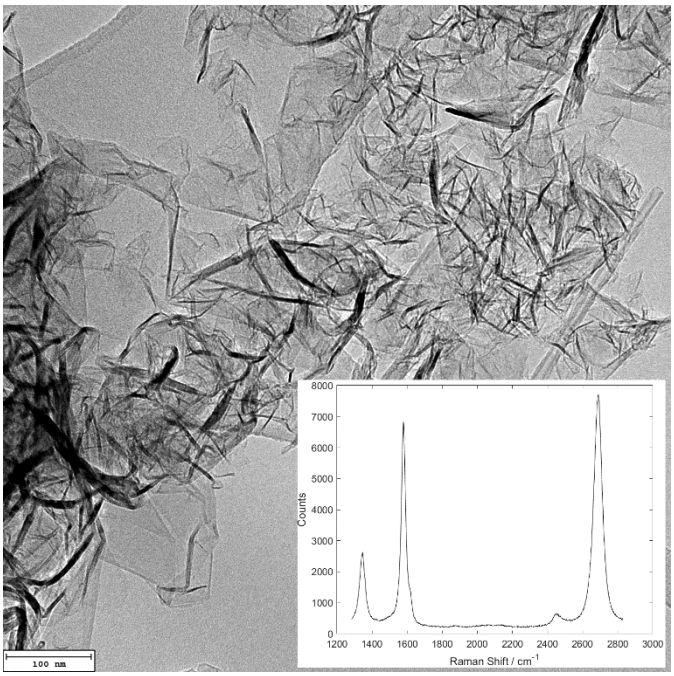

Figure 2-1: Transmission electron microscopy (TEM) image of the graphene used for making the graphene/epoxy nanocomposite samples. The inset shows measured Raman spectrum from the graphene used for making the samples.

Figure 2-2 shows an example of two samples. The density of the samples with graphene concentration up to 1.0 wt. % was 1.21 g/cm3. For the samples with the highest graphene concentration, the density increased to 1.24 g/cm3.

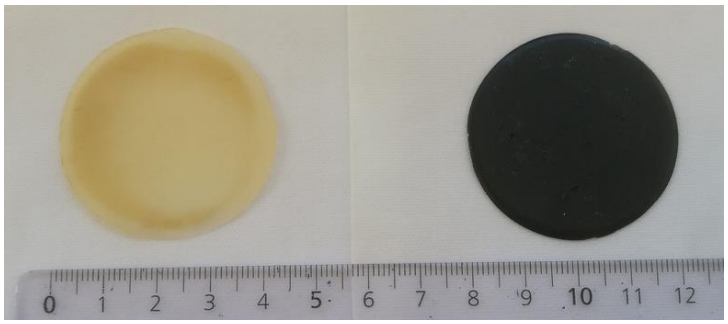

Figure 2-2: Example of a neat epoxy sample (left) and a graphene/epoxy nanocomposite sample (right).

3.0 ELECTRICAL CONDUCTIVITY MEASUREMENTS

We measured the DC conductance of the samples perpendicular to the flat surfaces. In order to ascertain good contact, the contact area was covered with indium foil between two large area electrodes placed in a vice. A Keithley 236 Source Measure Unit was used to generate a voltage of up to 110 V while measuring the corresponding current. The indium foil is pliable and assures good contact between the measuring electrode and the sample. A sketch of the setup is shown in Fig. 3-1.

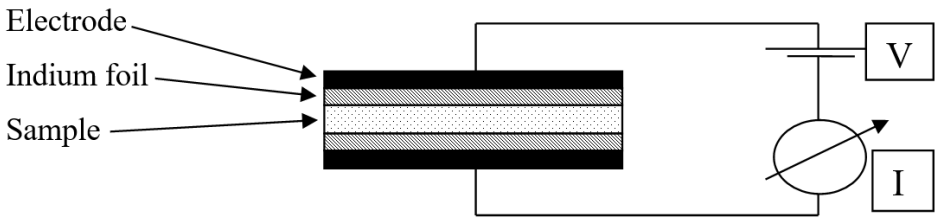

Figure 3-1: Setup for measurement of electrical dc conductivity. The sample to be tested is placed between two electrodes, which are pressed onto the sample using a vise. The current through the sample is measured as a function of applied voltage.

The current through the samples is measured for different applied voltages and the measured data is fitted to a straight line, giving the electrical conductivity as $\sigma \approx LI/(AV)$, where L is the sample thickness, A is the sample area in contact with an electrode, I is the measured current through the sample, and V is the applied voltage.

Figure 3-2 shows the measured electrical conductivity as a function of graphene concentration for all samples, except for the neat epoxy samples. The measured conductivity for the two samples without graphene was 10^{-13} S/m - 10^{-12} S/m, and was limited by the noise floor of the current measurement. The percolation threshold is the concentration at which the electrical conductivity of an insulating polymer matrix increases significantly. Above the percolation threshold, the graphene sheets come in contact and create a conducting path through the material [3]. It has previously been shown that graphene/epoxy composites exhibit a percolation threshold at a graphene concentration of 0.1-0.9 wt. % [7, 9]. We observe from Fig. 4 that adding 0.1 wt. % of graphene causes a jump in the conductivity by at least 7 orders of magnitude, which indicates that the percolation threshold has been reached at this concentration. This behavior was not observed in the previous experiments at such low graphene concentration [1], and might be due to a combination of better graphene dispersion in the epoxy and a higher quality of the graphene that was employed here, compared to the previous experiments. The conductivity approaches 1 S/m for the highest graphene concentrations, corresponding to a resistance of

a few Ohm through the sample. This conductivity is 4-5 orders of magnitude higher than what was observed in our previous experiments [1].

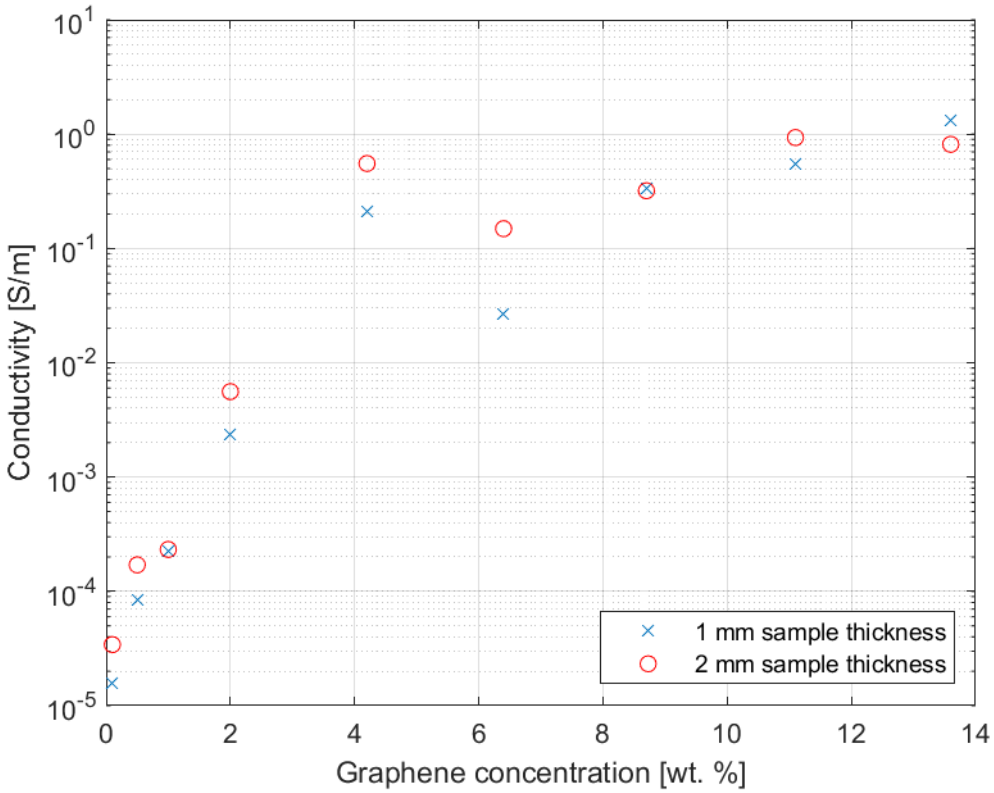

Figure 3-2: Measured electrical conductivity as a function of graphene concentration (0.1 – 13.6 wt.%) for the different samples. The neat epoxy samples (0 wt.%) had a conductivity of 10^{-13} – 10^{-12} S/m; this data is omitted from the graph for better clarity. The measurements were carried out for two different samples thicknesses for each graphene concentration.

4.0 TERAHERTZ MEASUREMENTS

Terahertz transmission measurements were used to characterize the electromagnetic transmission properties of the samples in the Terahertz (1012 Hz) frequency range.

4.1 Setup

The THz setup, schematically shown in Figure 4-1, is based on a fiber-coupled time-domain spectroscopy (TDS) system pumped by 100-fs pulses at 780 nm wavelength from a frequency-doubled erbium-doped fiber laser [12]. It is driven by a femtosecond laser that emits 120-fs-long pulses at a wavelength of about 1.55 μm. The wavelength of the pulses is halved (frequency doubling) using a nonlinear crystal, the power is split 50/50 and one-half of this power then illuminates the emitter. This is a piece of low-temperature grown GaAs where the incoming laser light pulses create electron-hole pairs that are accelerated in an applied electric field and in the process emit electromagnetic radiation that mainly covers the THz frequency domain. The frequency doubling of the laser light is necessary to excite electrons above the GaAs bandgap. The repetition rate of the

laser is 90 MHz. The THz radiation is pointed to a sample and a detector measures transmitted THz radiation. The detection principle is the inverse of the generation principle. The other half of the original laser light power is diverted through a variable delay line and directed onto the detector to create electron-hole pairs and prepare the detector for reception of the THz radiation. The E-field from the THz pulses produce a tiny current in the detector, which is detected by a lock-in amplifier by averaging over a large number of pulses to improve the signal-to-noise ratio. One then steps through the detected pulse by adjusting the delay line and in this way builds up the transmitted or reflected THz wave, measuring the THz E-field as a function of time. Fiber coupling of the laser light into the measurement heads allows for flexible placement of detector end emitter with respect to the sample [12].

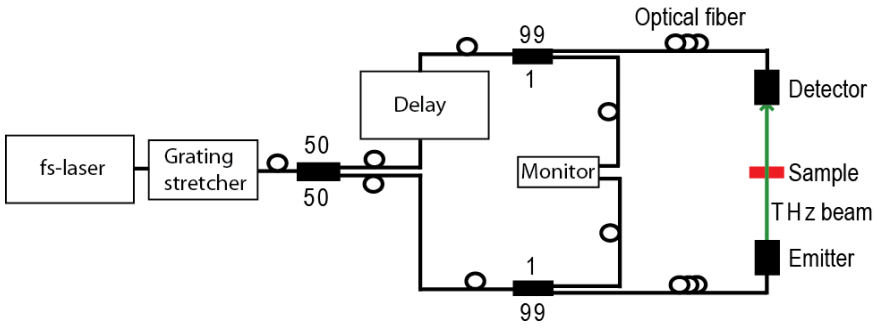

Figure 4-1: Schematic overview of the fiber-coupled THz-TDS system configured in transmission mode.

Figure 4-2 shows a typical reference measurement (transmission through air) and noise measurement (blocked beam). The THz spectra are determined from the time-domain signals by a Fourier transform.

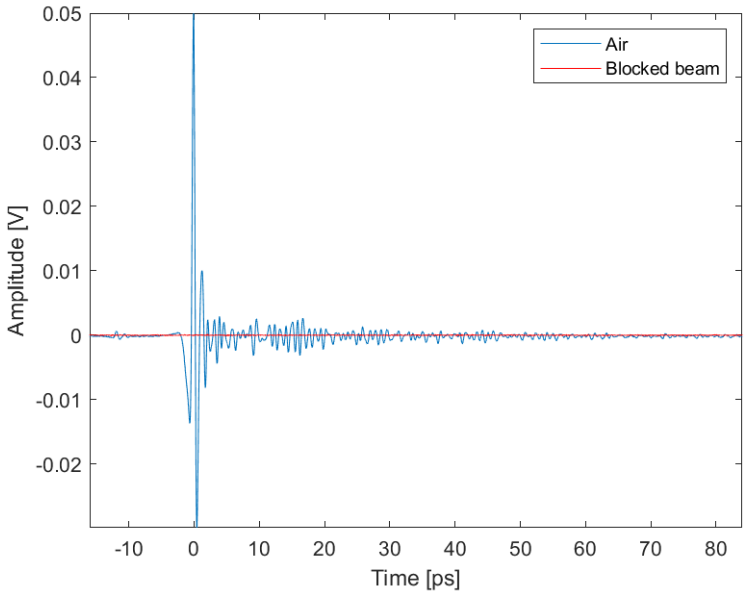

Figure 4-2: Typical reference (blue) and noise (red) signal for a THz transmission measurement in standard air. The reference measurement is taken with a blocked beam path.

4.2 Terahertz Absorption Coefficient

The transmission measurements are performed by measuring the THz amplitude with and without a sample present. By considering the transmission of plane electromagnetic waves through a homogeneous slab at normal incidence, assuming perfectly flat sample surfaces, and neglecting multiple reflections within the sample, one can derive an expression for the transmission coefficient [1], which takes into account the Fresnel reflection at the sample surfaces. The absorption coefficient is readily found from the expression for the transmission coefficient [1].

4.3 Measurement Results

Figure 4-3 shows measured transmission spectra for a reference measurement (air) and for epoxy samples with varying concentration of graphene. As observed previously [1], there were no characteristic absorption features for the samples. However, broadband absorption, which increased with increasing frequency and depended on the graphene concentration, was found to occur. For some of the thick (2 mm) samples with high graphene concentration, there was no measurable transmitted THz signal.

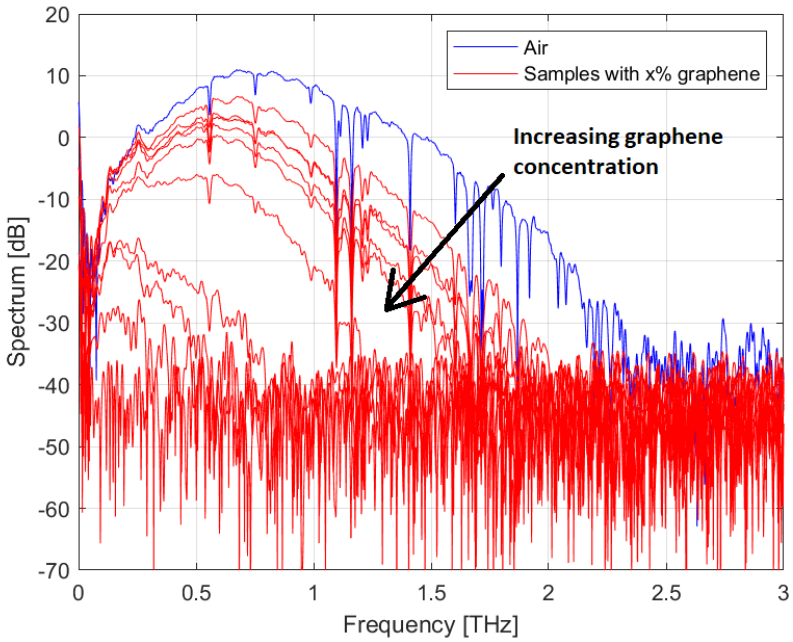

Figure 4-3: Examples of measured transmission spectra for a reference measurement in air and for transmission through samples with varying graphene concentration.

Figure 4-4 shows the absorption coefficient for the samples at a frequency of 0.35 THz. This frequency is chosen in the plot because the measurements had high signal-to-noise ratio at this frequency. We observe from the figure that the absorption coefficient increases linearly with increasing graphene concentration up to 2.0 wt. % graphene. For higher graphene concentration, there is higher variation in the absorption coefficient. We speculate that this variation may be due to difficulties in dispersing the graphene sufficiently in the epoxy resin at such high graphene concentrations. What is notable from Fig. 8 is that although there is a jump in the conductivity for 0.1 wt. % graphene concentration, there is no corresponding jump in the

THz absorption coefficient. The 2-mm samples with the highest graphene concentrations absorbed so much THz radiation that the transmitted signal drowned in the noise and are therefore missing in the plot.

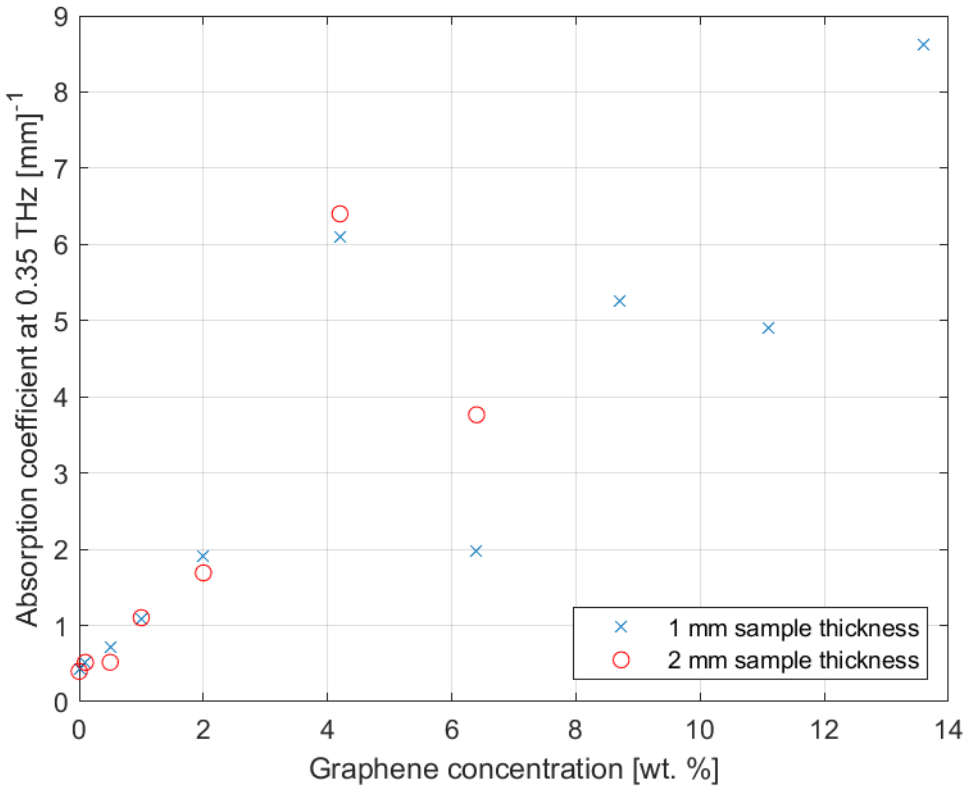

Figure 4-4: Measured absorption coefficient at a frequency of 0.35 THz as a function of graphene concentration for the different samples.

5.0 DISCUSSION OF RESULTS

We observed that both the absorption coefficient and the electrical conductivity increase with increasing concentration of dispersed graphene. For low concentrations of graphene, the conductivity is low (~10^{-12} S/m) and then rises abruptly when the percolation threshold is reached. This happens at a graphene concentration of less than 0.1 wt. %. The absorption coefficient increases with graphene concentration as well, but at a more moderate rate. The question arises naturally whether the observed absorption coefficient may be explained by the electrical conductivity. Using the same argument as before [1], we find that the THz absorption coefficient is more than an order of magnitude higher than what can be explained by the conductivity alone. For example, one can estimate that a conductivity of 1 S/m would lead to a THz absorption coefficient of about 0.2/mm, lower than we measured (see Figure 4-4.). Thus, other mechanisms than the electrical conductivity contribute to the THz absorption. Possibly, scattering of the THz radiation off the graphene flakes increases the absorption. This was not investigated further.

6.0 CONCLUSIONS

In conclusion, we have fabricated epoxy samples with various concentrations of dispersed graphene powder. The electrical conductivity of the samples was measured. In addition, THz transmission spectroscopy was used to retrieve the dielectric parameters of the samples, particularly the absorption coefficient. It was found that the electrical conductivity increased by several orders of magnitude with increasing graphene concentration and a percolation threshold of less than 0.1 wt. % of graphene was observed. The THz absorption, which increased with increasing graphene concentration, was higher than expected from the conductivity measurements. Other effects, as yet unidentified, must contribute to the absorption.

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