

# Terahertz Time-Domain Spectroscopy of Graphene Nanoflakes Embedded in a Polymer Matrix

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Polymer nanocomposites are prepared by including a nanofiller (carbon, ceramic, metal/metal oxide, and/or others) in a polymer matrix to alter (or improve) its properties, such as mechanical, electrical, and optical properties, barrier properties, flame resistance, etc.<sup>1</sup> Recently, a great deal of interest has been focused on carbon nanofillers and, in particular, graphene. Graphene is a 2-D nanomaterial consisting of sheets of carbon atoms bonded by sp<sup>2</sup> bonds in a hexagonal configuration: its unique mechanical, electrical, thermal, and optical properties have been extensively studied.<sup>2</sup> These properties have been leveraged in the development of a wide range of different graphene–polymer nanocomposites,<sup>3</sup> using a variety of fabrication methods and polymer types, for numerous structural and functional applications,<sup>4</sup> including, e.g., biomedical devices,<sup>5</sup> biosensing,<sup>6</sup> and gas barrier membranes.<sup>7</sup>

Here we report the use of a THz time-domain spectroscopy (THz-TDS) to characterize graphene nanofiller dispersion within multiblock copolyester nanocomposite materials. Both the copolymer matrix and the nanocomposites were developed to serve as construction materials for extracorporeal heart-assist devices in the context of the Polish Artificial Heart Program.<sup>8</sup> The test samples used were processed using the same compression molding process as the prototype pneumatic membrane. To our knowledge, this is the first time that the dispersion of graphene nanoplatelets within a nanocomposite—prepared at an industrially relevant scale and using an economically viable process—has been studied by the THz-TDS method. Consequently, this work serves as an important proof of concept of THz-TDS of nanocomposites within the product development chain.

Two different neat copolymers were prepared, with different hard to soft segment ratios, resulting in a more elastic material with 40 wt% of hard segments (PET-DLA 4060) and a stiffer copolyester with 60 wt% of hard segments (PET-DLA 6040). Additionally, nanocomposites with the same hard to soft segment ratios but with 1 wt% of a commercial graphite nanoplatelet nanofiller (Graphene Supermarket, Grade A0-3) were prepared via *in-situ* polymerization.<sup>9,10</sup>

The THz-TDS system, used to measure the THz-range transmission spectra of both the neat copolymers and graphene nanocomposite samples, was based on a commercial, low-temperature-grown GaAs (LT-GaAs) photoconductive antenna emitter and detector from TeraVil Ltd, Vilnius, Lithuania.<sup>11</sup> The emitter and detector were excited and probed, respectively, by 100-fs-wide pulses, with an 800-nm wavelength and a 76-MHz repetition rate, generated by a femtosecond Ti:sapphire laser. The spectral range of the spectrometer was ~4 THz, with maximum amplitude at ~0.5 THz. The sample was placed directly between the emitter and detector, and measurements were taken at room temperature. To reduce the influence of water absorption, the THz emitter, detector, and sample holder were placed inside a Plexiglas<sup>®</sup> box that was purged with dry nitrogen, ensuring that the humidity during the measurement was below 5%.

For each sample, we first performed a reference run with no sample inside the spectrometer to confirm the performance of the system. Next, we took two measurements: one of a graphene nanocomposite and the other of a corresponding neat copolymer specimen. To get better results and reduce noise, each set of measurements consisted of at least ten averages. Our measurements were focused on two different sample types: nominally a 0.3-mm-thick, elastic PET-DLA 4060 copolymer (“thin sample”) and a 0.9-mm-thick, stiffer PET-DLA 6040 copolymer (“thick sample”). For both sample types, the nanofiller content was the same, i.e., 1 wt%. Since our further analysis crucially depends on the sample thickness, all measurements were repeated several times at different spots of the test sample.

Figure 1(a) presents time-domain signals transmitted through dry nitrogen (the reference measurement), the thin and thick neat copolymer, and the corresponding 1-wt% graphene–polymer nanocomposite samples, respectively, while Fig. 1(b) presents the corresponding power spectra of our time-domain signals obtained by means of fast Fourier transformation. We note that while both copolymers absorb THz radiation, as compared to the dry-nitrogen reference signal, adding graphene flakes to the polymer matrix substantially reduces the bandwidth of the power spectrum, obviously because of the extra absorption of THz radiation by nanoflakes. The cutoff frequencies for the thin copolymer sample and the corresponding 1-wt% graphene–polymer nanocomposite are  $\sim 3.1$  THz and 2.9 THz, respectively, while for the thick copolymer and the 1-wt% graphene–polymer nanocomposite, they are 2.25 THz and 1.75 THz, respectively.

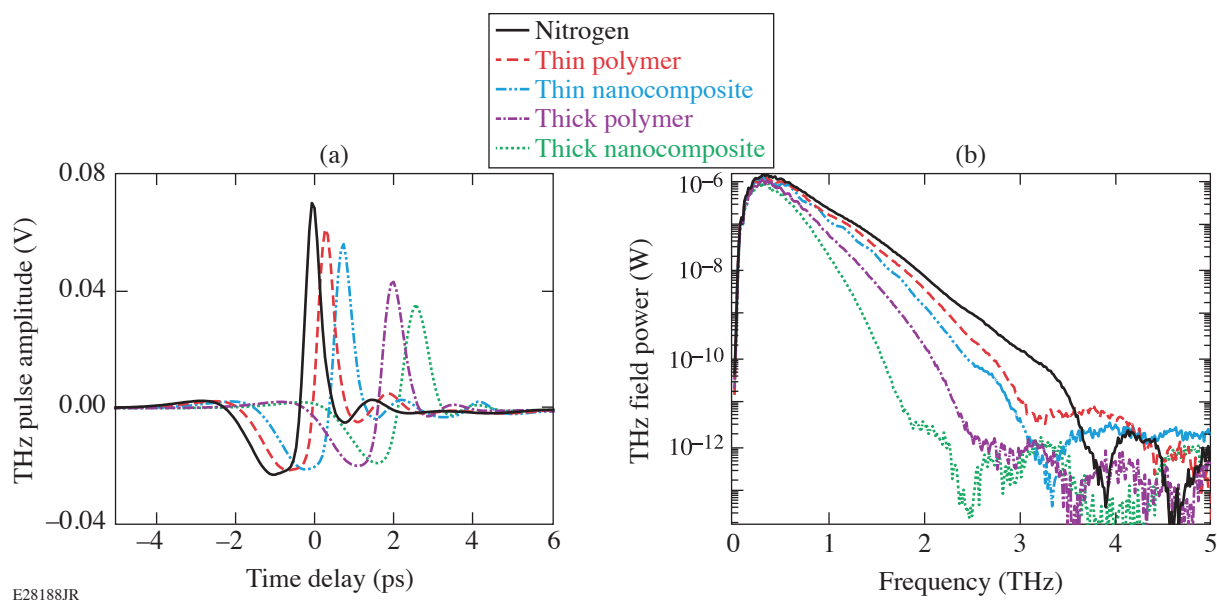


Figure 1

(a) Time-resolved transient signals for the tested thin and thick polymers and 1-wt% graphene nanocomposite samples and the empty spectrometer (nitrogen). (b) The corresponding power spectra showing absorption of the samples. Note: The thin samples consist of the PET-DLA 4060 copolymer, while the thick ones consist of PET-DLA 6040.

Using Fresnel equations, the THz-TDS approach allowed us to find the complex index of refraction  $\hat{n}(\omega) = n(\omega) + i\kappa(\omega)$  and the dielectric function  $\hat{\epsilon}(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ , as well as the complex  $\hat{\sigma}(\omega)$  of our graphene nanocomposite samples. The  $\hat{\sigma}(\omega)$  spectrum was, subsequently, fitted using the Drude–Smith model.<sup>12</sup> The excellent fit confirmed applicability of the Drude–Smith approach to modeling the carrier transport in our graphene–polymer nanocomposites, indicating that our nanofiller flakes were fully isolated in the polymer matrix. The high quality and uniformity of the dispersion were implied by the high value of the conductivity and moderate effective dielectric constant retained by the graphene nanoflakes.

In summary, the THz-TDS method probes the dielectric properties of the sample in an almost  $\text{cm}^2$  cross-section beam path, thereby providing “global” information regarding the dispersion of graphene and its *in-situ* electronic quality. Because it is a nondestructive testing method, it holds great potential for monitoring any nanofiller dispersion in a polymer matrix throughout the product-development chain: after polymer nanocomposite synthesis, following processing into a given prototype, and even after product testing.

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1. D. R. Paul and L. M. Robeson, *Polymer* **49**, 3187 (2008).
2. Y. Zhu *et al.*, *Adv. Mater.* **22**, 3906 (2010).
3. J. R. Potts *et al.*, *Polymer* **52**, 5 (2011).
4. K. Hu *et al.*, *Prog. Polym. Sci.* **39**, 1934 (2014).
5. M. Silva, N. M. Alves, and M. C. Paiva, *Polym. Adv. Technol.* **29**, 687 (2018).
6. P. Sobolewski, M. Piwowarczyk, and M. E. Fray, *Macromol. Biosci.* **16**, 944 (2016).
7. Y. Cui, S. I. Kundalwal, and S. Kumar, *Carbon* **98**, 313 (2016).
8. M. El Fray and M. Czugala, *WIREs Nanomed. Nanobi.* **4**, 322 (2012).
9. Z. Staniszewski and M. El Fray, *Polimery* **61**, 482 (2016).
10. Z. Staniszewski *et al.*, *Eur. Polym. J.* **107**, 189 (2018).
11. A. Geižutis *et al.*, *Opt. Mater.* **30**, 786 (2008).
12. N. V. Smith, *Phys. Rev. B* **64**, 155106 (2001).