Terahertz scattering by granular composite materials: An effective medium theory

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Terahertz (THz) spectroscopy and imaging have emerged as important tools for identification and classification of various substances, which exhibit absorption characteristics at distinct frequencies in the THz range. The spectral fingerprints can potentially be distorted or obscured by electromagnetic scattering caused by the granular nature of some substances. In this paper, we present THz time domain transmission measurements of granular polyethylene powders in order to investigate an effective medium theory that yields a parameterized model, which can be used to estimate the empirical measurements to good accuracy. [doi:10.1063/1.3674289]

In terahertz (THz) (or T-ray) time domain spectroscopy, the scattering of the broadband radiation within non-homogeneous media, such as polycrystalline materials, is a major problem in that it can obscure the THz signal of interest. When the sizes of scattering centers become comparable to THz wavelengths, the scattering process can no longer be described by a simple Rayleigh scattering model but has to be modeled by a more complex approach.

Various researchers have contributed to understanding the influence of scattering on the terahertz signal. Recently, in 2008, Franz *et al.*[1] discussed the applicability of Christiansen effect to explain the scattering observed in the THz time domain spectroscopy (THz-TDS) measurements of granular samples by fitting unknown theoretical parameters to the experimental observations using the theoretical description provided by Raman[2] on the propagation of electromagnetic radiation in an inhomogeneous media. On the other hand, in 2007, Zurk *et al.*[3] applied a quasi crystalline approximation (QCA) for a dense media model to study THz transmission through pressed pellets of granular polyethylene (PE) with varying grain sizes. The QCA model accounts for the multiple scattering between densely packed dielectric particles. The QCA solution not only requires knowledge of parameters such as particle size, bulk dielectric constant, and volume fraction of constituents but also relies on assumptions such as a spherical shape for particles, dense packing, and known positions within the sample, more precisely, a probabilistic Percus-Yevick (PY) pair distribution of particle locations.

In this letter, we apply the effective medium theory proposed by Chýlek *et al.*[4] to estimate the frequency dependent scattering loss from three different granularities of polyethylene and air samples and compare the theoretical analysis with the transmission THz-TDS measurements of these samples. Unlike previous approaches, our method does not rely on assumptions regarding position of particles within the sample or on experimental observations to fit unknown theoretical parameters.

Three different granularities of spectroscopic grade PE powder from two different manufacturers (Sigma-Aldrich and Inducos) were used for our experiments. Two of the PE powders, one from each manufacturer, had relatively small PE grain sizes, with approximately 60 μm (Inducos) and 72 μm (Sigma-Aldrich) diameters, while the third one, again from Inducos, had a larger grain size of approximately 360 μm in diameter. These dimensions were well within the range indicated by the manufacturer, but we used scanning electron microscope (SEM) images to confirm these dimensions. These images are shown in Fig. 1. In order to determine the volume fraction of PE particles and air voids for each sample, we carry out 3D x-ray tomography on each sample at every 0.68° rotation for a full 360° view. The images thus obtained are then used to construct a 3D model of the sample using software tool CTAN. From this 3D model of the samples, their respective porosity (volume fraction of air) and the average air void radius are obtained. The results are given in Table I.

The 3D model for each sample can be seen in Fig. 2. For a two-component composite material, where one of the components is PE (ϵ_1) and the other is air (ϵ_2), the mixing rule derived by Chýlek *et al.*,[4] based on the generalization of the dynamic effective medium theory of Stroud and Pan,[6] leads to an iteration scheme for calculation of an effective dielectric constant (ϵ_{eff}) of a two-component composite material

$$\epsilon_{\mathrm{eff}} = \epsilon_1 \frac{A(\epsilon_{\mathrm{eff}})(1-V) + B(\epsilon_{\mathrm{eff}})}{A(\epsilon_{\mathrm{eff}})(1-V) - 2B(\epsilon_{\mathrm{eff}})}, \tag{1}$$

where

$$A(\epsilon_{\mathrm{eff}}) = i\frac{12\pi^2}{\lambda^3}\epsilon_{\mathrm{eff}}^{3/2}, \tag{2}$$

$$B(\epsilon_{\mathrm{eff}}) = \int \sum_n (2n+1)\left[a_n\left(r,\frac{\epsilon_2}{\epsilon_{\mathrm{eff}}}\right) + b_n\left(r,\frac{\epsilon_2}{\epsilon_{\mathrm{eff}}}\right)\right]\rho(r)dr, \tag{3}$$

and V represents the volume fraction of air voids in the sample, λ represents the wavelength of the incident THz signal, ϵ_1 represents the bulk dielectric constant of PE particles, ϵ_2

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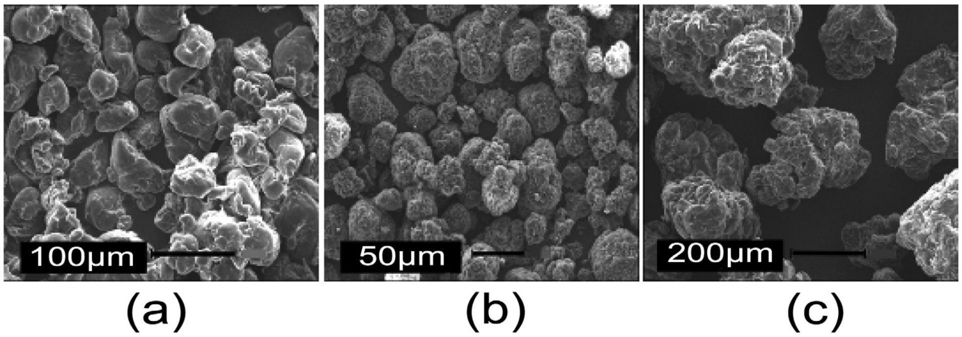

FIG. 1. Scanning electron microscope images of PE powder. Three granularities are shown, with particle diameters of (a) 60 μm, (b) 72 μm, and (c) 360 μm.

represents the dielectric constant of air voids, n represents the number of Mie partial waves, a_n and b_n are the corresponding Mie partial wave scattering amplitudes, r represents the vector of radius of air voids, and $\rho(r)$ represents the size distribution of air void in the composite sample. Following the calculation procedure suggested by Chýlek *et al.*,[4] the first approximation for $\epsilon_{\rm eff}$ is obtained by using the ordinary Bruggeman mixing rule,[7]

$$(1-V)\frac{\epsilon_1-\epsilon_{\rm eff}}{\epsilon_1+2\epsilon_{\rm eff}}+(V)\frac{\epsilon_2-\epsilon_{\rm eff}}{\epsilon_2+2\epsilon_{\rm eff}}=0. \tag{4}$$

In the case of our experiment, we carry out transmission spectroscopy of granular PE and air samples, the background is modeled as pure PE with a relative permittivity of 2.13 and air voids occupy 24%, 25%, and 44.5% by volume, and have a average radius of 24, 28, and 90 μm, for 60, 75, and 360 μm (PE particle diameter) samples, respectively. Note that in the terahertz region, these spherical scatterers are in the Mie regime, which means that low frequency Rayleigh scattering does not apply, which in turn leads to the requirement for multipole expansions, even in the case of spherical scatterers. As the software used only determines the average air void radius for each sample, we assume all air voids to be of the same dimensions and therefore the size distribution function $\rho(r)$ in Eq. (3) takes the form of a δ function

$$\rho(r)=N\delta(r), \tag{5}$$

where N is the number of air voids per unit volume. Hence, Eq. (3) becomes

$$B(\epsilon_{\rm eff})=N\sum_n(2n+1)\left[a_n\left(r,\frac{\epsilon_2}{\epsilon_{\rm eff}}\right)+b_n\left(r,\frac{\epsilon_2}{\epsilon_{\rm eff}}\right)\right], \tag{6}$$

where N is given by

$$N=\frac{3V}{4\pi r^3}. \tag{7}$$

Using the setup described by Fig. 3, we carry out transmission measurements of the three samples comprising PE particles and air voids, prepared by sandwiching the granular PE powder between the two plates of a sample holder made of Cyclic Olefin Copolymer (Topas, refractive index 1.6) of dimensions 5 mm inner thickness and 1 cm diameter. The effective dielectric constant, $\epsilon_{\rm eff}$, is computed using the effective medium theory as described above. We make use of the relation $k_{\rm eff}=\sqrt{\epsilon_{\rm eff}}\omega/c$ to obtain the effective wave number of the medium. Neglecting any intrinsic attenuation or absorption within the media, we can assume that the total attenuation here is entirely due to the scattering of the incident radiation and can be obtained from

$$\alpha_{\rm eff}=\Im(k_{\rm eff}), \tag{8}$$

where $\Im(\cdot)$ indicates the imaginary part. In this analysis, we assume a plane wavefront for the terahertz radiation in the far field. Fig. 4 illustrates the propagation of THz radiation propagates through a sample cell during measurements of the sample and reference data. By analyzing the propagation geometry, and assuming that the reflections are removed from the sample and reference data, the transfer function is given by

TABLE I. The porosity and average air void diameter obtained from the 3D model of the samples.

Sample	Porosity (%)	Average air void radius (μm)
PE (60 μm)	24	24
PE (72 μm)	25	28
PE (360 μm)	44.5	90

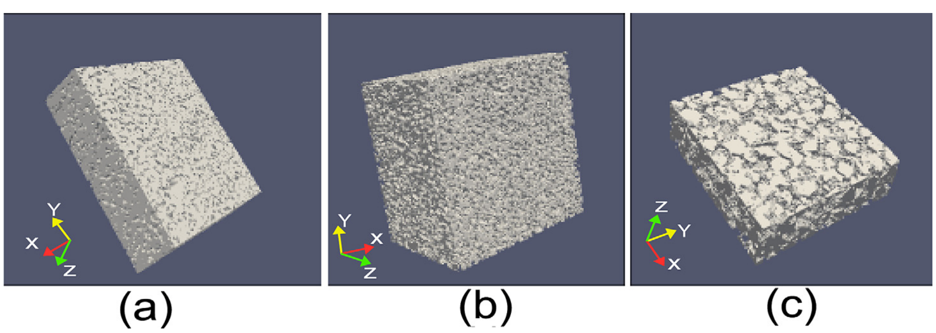

FIG. 2. (Color online) Three-dimensional model of the PE powder samples, constructed using software tool CTAN and PARAVIEW, from the sample scans obtained via x-ray tomography. From the 3D models, the sample porosity (volume fraction of air) and the average air void diameter are obtained. Three granularities are shown, with particle diameters of (a) 60 μm, (b) 72 μm, and (c) 360 μm.

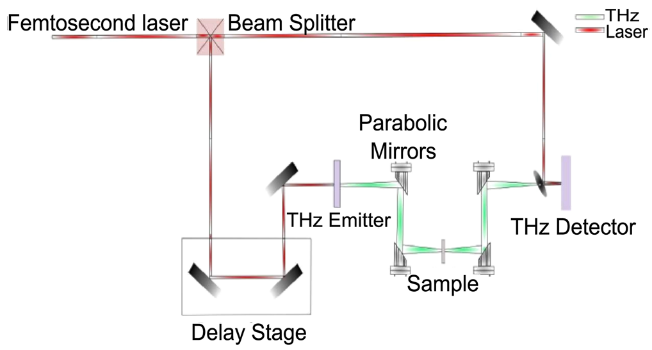

FIG. 3. (Color online) An illustration of the THz-TDS pump probe system: The system consists of an ultrafast optical laser, a THz emitter/receiver, an optical delay line, a set of parabolic mirrors, and the sample. The emitter and receiver shown are photoconductive antenna. The optical beam path is shown in red and the THz beam path in green.

$$H(\omega) = \frac{\tau_{\rm ws}\tau_{\rm sw}}{\tau_{\rm wa}\tau_{\rm aw}} \exp\left(-j(\hat{n}_s - n_0)\frac{\omega l}{c}\right), \tag{9}$$

where the subscripts a, s, and w are for air, sample, and window, respectively, l is the thickness of the sample, and τ represents the Fresnel transmission coefficients. Therefore, $\tau_{\rm aw}$ represents the propagation from air to window, $\tau_{\rm ws}$ represents the propagation from window to sample, etc. Here n_0 is the refractive index of free air and $\hat{n}_s$ is the complex refractive index of the sample given by the formula $\hat{n}_s = n_s + jk_s$ with n_s and k_s representing the measured real part of refractive index and the extinction coefficient of the sample, respectively. Thus, using the above equation and the relation $\alpha_s(\omega) = 2k_s(\omega)\frac{\omega}{c}$, the optical attenuation $\alpha_s(\omega)$ can be found from

$$\alpha_s(\omega) = \frac{2}{l}\left\{\ln\left[\frac{\tau_{\rm ws}\tau_{\rm sw}}{\tau_{\rm wa}\tau_{\rm aw}}\right] - \ln|H(\omega)|\right\}. \tag{10}$$

For each sample, we compare the measured attenuation loss, calculated using Eq. (10) with the attenuation loss given by Eq. (8), obtained by applying the model of Chýlek *et al.*, Eqs. (1), (2), (5), and (6). Fig. 5 shows this comparison.

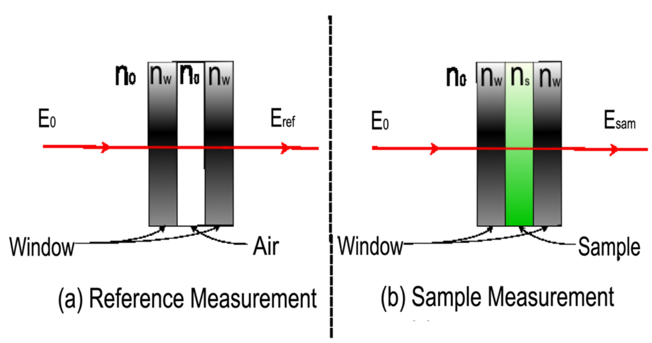

FIG. 4. (Color online) (a) THz radiation propagates through an empty cell as the reference. (b) THz radiation propagates through an identical cell filled with the powder sample, as the sample measurement.

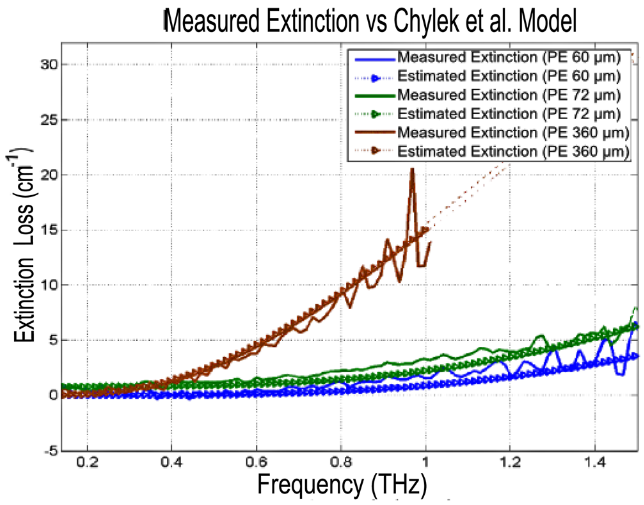

FIG. 5. (Color online) Comparison of measured (solid) and theory estimated (dotted) frequency dependent total attenuation (extinction) loss for the three different PE grain size samples, 60 μm, 72 μm, and 360 μm, with air void diameters 48 μm, 56 μm, and 180 μm, respectively.

From the visual analysis of Fig 5, it can be inferred that while small details of the transmitted field and attenuation are not captured by the simulation, the overall frequency dependent trends for the three media, as calculated by the model of Chýlek *et al.* were in good agreement with the experimental measurements.

In conclusion, we examine the use of the Chýlek *et al.*[4] effective medium model, for estimating frequency dependent scattering loss of terahertz by two-component composite granular materials. From the comparison of simulated and experimental results, it is found that the model of Chýlek *et al.*[4] is accurate in estimating optical properties of samples made of granular particles of dimensions comparable to the incident wavelength. For estimating the effective dielectric properties of a composite medium with more than two components, the general formula given by Eq. (12) of Chýlek and Srivastava[5] must be used.

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