Terahertz Scattering and Spectroscopic Characteristics of Polymethacrylimide Microstructures

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Abstract
We carried out systematic measurements of Polymethacrylimide (PMI)’s terahertz (THz) spectroscopic and scattering parameters with various thicknesses and models. The THz time domain spectroscopy (THz-TDS) which was employed in this study would be useful as a nondestructive testing (NDT) tool for PMI. While the index of refraction PMI is very close to that of air, with flat frequency dependency, the attenuation constant exhibits a remarkably strong frequency variation, suggesting a scattering dominated attenuation process. Based on the Mie scattering model, we gave a reasonable explanation: the THz wave propagating through the PMI suffers scattering from the micro-sized particles that make up the material, and the sizes of the particles (shown to obey a normal distribution) determine the frequency characteristics of the interaction.

Keywords: PMI, Mie scattering, Microstructure, Terahertz time-domain spectroscopy, Attenuation constant.

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1. Introduction

Industrial production of polymer foam materials is increasing globally due to their light weight, excellent thermal and acoustic insulation properties and high energy absorption capacity [1]. PMI is a heat-resistant foam material, with the highest strength and stiffness to weight ratio in its class. It is widely used in aerospace and aeronautics.

Structural analysis of PMI enables manufacturers and research facilities to optimize their products and production processes for applications such as building construction [2]. At the same time, the research results are of theoretical and practical significance for the realization of the quality control of foam production process as well as in NDT applications [3]. Therefore, the investigation of the PMI microstructure is important in order to characterize their physical and mechanical properties [3]. Compared with electromagnetic wave in other frequency bands, THz wave, in the detection of the foam composite material, has many unique characteristics. For example, in such materials THz wave is not strongly absorbed, and scattering is relatively weak at long wavelengths, spatial resolution is higher than microwave; and for such nonpolar and non-conducting materials THz radiation is only refracted, with little to moderate attenuation; last but not least, THz photons are less energetic than those of the infrared, and are much safer than X-ray. [4]. However, in the process of non destructive testing using the THz-TDS method, the scattering effect of the foams does consume energy, which makes the detection result not ideal. The scattering is mainly due to the granular nature of the material, which is composed of particles whose sizes range from a few tens of micrometers to submillimeter, largely coincident with the wavelengths of the THz radiation involved. Thus, the scattering events are largely governed by the Mie theory, where the size the scatters are comparable to the wavelength of the radiation. By measuring the difference between the terahertz waveforms and by
calculating the spectroscopic characteristics, we analyzed four models of PMI foam samples, obtaining such characteristics as stop frequency, refractive index, and extinction coefficient. Using Mie theory, we analyze these results to obtain the scattering relationships of microstructure diameters, density, and distribution.

The rest of this paper is organized as follows. Section 2 describes the related backgrounds based on Mie scattering theory. In Section 3, the THz TDS system and the samples used in our experiments are briefly introduced. We then compare the experimental data and our numerical simulation results. The effectiveness of the Mie theory applied in the PMI microstructure scattering analysis is demonstrated and discussed in Section 4. Finally, conclusions are presented in Section 5.

2 Theoretical backgrounds

Previous work showed that the THz extinction of granular Ammonium Nitrate of different grain sizes rises more slowly with frequency than expected of Rayleigh scattering where a dependence of the fourth power of frequency is predicted [5]. On the other hand, the Mie scattering theory, which is more comprehensive in dealing with spherical grains of arbitrary size in comparison with the wavelength of the radiation, is considered more appropriate for explaining this trend in the extinction spectra [6].

![Fig.1 Decomposition of electric vectors of the incident and scattered waves.]
As shown in Fig.1, the incident light intensity of complete polarized light $I_0$ and the wavelength of $\lambda$ impinge on the isotropic spherical particle along the Z axis. The angle $\theta$ is the scattering angle; $\phi$ is the angle between the planes of polarization of incident and scattered waves. We can find the scattered light intensity $I_s$ corresponding to polarization perpendicular to the scattering plane and the scattered light intensity $I_t$ with polarization parallel to the scattering plane, and the total scattered light intensity $I_s$, respectively [6]:

$$I_r = \frac{\lambda^2}{4\pi r^2} |s_1(\theta)|^2 I_0 \sin^2 \phi = \frac{\lambda^2}{4\pi r^2} i_1(\theta) I_0 \sin^2 \phi$$  (1)

$$I_t = \frac{\lambda^2}{4\pi r^2} |s_2(\theta)|^2 I_0 \cos^2 \phi = \frac{\lambda^2}{4\pi r^2} i_2(\theta) I_0 \cos^2 \phi$$  (2)

$$I_s = \frac{\lambda^2 I_0}{4\pi r^2} [i_1(\theta) \sin^2 \phi + i_2(\theta) \cos^2 \phi]$$  (3)

where $I_s = I_r + I_t$, $i_1(\theta) = |s_1(\theta)|^2$, $i_2(\theta) = |s_2(\theta)|^2$

$i_1(\theta)$, $i_2(\theta)$ are scattering intensity functions, $s_1(\theta)$, $s_2(\theta)$ are scattering amplitude functions, with

$$s_1(\theta) = \sum_{n=1}^{\infty} \frac{2m+1}{m(m+1)} \left\{ a_m \pi_m(\cos \theta) + b_m \tau_m(\cos \theta) \right\}$$  (4)

$$s_2(\theta) = \sum_{n=1}^{\infty} \frac{2m+1}{m(m+1)} \left\{ a_m \tau_m(\cos \theta) + b_m \pi_m(\cos \theta) \right\}$$  (5)

where $a_m, b_m$ are Mie scattering coefficients. In order to obtain the Mie scattering light intensity functions $i_1(\theta)$ and $i_2(\theta)$, the key is to solve for the scattering coefficients $a_m, b_m$.

Consider a layer of space containing a great number of small particles. A beam of electromagnetic radiation illuminates this layer and propagates through it. The transmitted intensity can be written as [7]:
\[ I_i = I_0 \exp\left[-\int_0^L \beta(\lambda) dx\right] \]  

where \( I_0 \) is the incident intensity, \( L \) is the thickness of the layer, \( \lambda \) is the wavelength and \( \beta(\lambda) \) is called the extinction coefficient of the material making up the layer. It is a parameter which describes the ability of the material to attenuate the incident energy at a given wavelength. It is a function of \( N \) and \( S \), which are respectively the number density of the particulates, and the extinction cross section of each particle. If all the particles are of the same material and the same size, and coupling among these particles is neglected, one has

\[ \beta(\lambda) = NS(\lambda) \]  

(7)

For a group of particles of different size, the above expression can be generalized to

\[ \beta(\lambda) = \int_0^\infty NS(\lambda, D)f(D)dD \]  

(8)

where \( f(D) \) is the distribution function of the sphere diameter \( D \).

In order to calculate \( \beta(\lambda) \), one has to know the expressions of \( S(\lambda, D) \) and \( f(D) \). For the spherical particle, \( S(\lambda, D) \) is given by Mie theory as

\[ S(\lambda, D) = \frac{\lambda^2}{2\pi} \sum_{m=1}^{\infty} (2m+1) \Re(a_m + b_m) \]  

(9)

In the present experimental set-up, the incident THz field is p-polarized. Hence, the theoretical extinction coefficient is calculated from the amplitude functions for \( \theta = 0 \) (\( s_1(\theta) \) and \( s_2(\theta) \) are equal for \( \theta = 0 \)) and is given by (\( c \) is the wave speed in vacuum, \( f \) the frequency),

\[ \beta(\lambda) = N \frac{c^2}{\pi f^2} \Re[s(0)] \]

\[ = N \frac{c^2}{2\pi f^2} \sum_{m=1}^{\infty} (2m+1) \Re(a_m + b_m) \]  

(10)

where
Here \( n \) is the complex refractive index of the particle material, \( u = nx, x = \pi D / \lambda \) and the prime denotes the derivative with respect to the argument. The functions \( \psi_m(z) \) and \( \zeta_m(z) \) are given respectively as

\[
\psi_m(z) = zj_m(z)
\]

and

\[
\zeta_m(z) = z[j_m(z) + iy_m(z)]
\]

where \( j_m \) and \( y_m \) are respectively spherical Bessel functions of the first and second kind, both satisfying the following two recurrence formulae

\[
\kappa_{m+1}(z) = \frac{2m+1}{z} \kappa_m(z) - \kappa_{m-1}(z)
\]

and

\[
\kappa_{m+1}'(z) = \frac{1}{2m+1} [m \kappa_{m-1}(z) - (m+1) \kappa_{m+1}(z)]
\]

Hence we get

\[
\psi_m'(z) = zj_{m-1}(z) - nj_m(z)
\]

\[
\zeta_m'(z) = z[j_{m-1}(z) + iy_{m-1}(z)] - n[j_m(z) + iy_m(z)]
\]

Using the first two spherical Bessel functions whose analytical forms are known:

\[
j_0(z) = y_{-1}(z) = \frac{\sin z}{z}
\]

\[
j_1(z) = -y_0(z) = \frac{\cos z}{z}
\]

One can obtain the rest of the functions in the sequence. Thus the scattering coefficient can be obtained, which in turn leads to \( S(\lambda, D) \).
It seems reasonable to assume that the granular material is composed of particles whose sizes (diameter D) follow a normal distribution around some mean value. The following lognormal function has been adopted for artificial powders [8].

\[
f(D) = \frac{1}{\sqrt{2\pi \sigma D}} \exp\left[ -\frac{(\ln D - \eta)^2}{2\sigma^2} \right]
\]  

(19)

where \( \eta \) and \( \sigma \) are the mean value of the logarithmic diameter, and the standard deviation from it, respectively.

The extinction coefficient of a material is defined as the total absorption which is the sum of intrinsic material absorption and the extrinsic losses associated with scattering, that is, extinction = material absorption + scattering loss. In this study, the experimentally obtained extinction coefficient is defined as [7-8]

\[
\varepsilon(\omega) = -\ln \left( \frac{|E_{\text{sample}}(\omega)|}{|E_{\text{reference}}(\omega)|} \right)
\]

(20)

where \( E_{\text{reference}}(\omega) \) is the reference frequency-domain signal without any sample, \( E_{\text{sample}}(\omega) \) is the reference time domain signal with the sample.

The absorption coefficient \( A(\omega) \) is given as the extinction coefficient divided by the thickness of the sample, L [9]:

\[
A(\omega) = -\frac{1}{D} \ln \left( \frac{|E_{\text{sample}}(\omega)|}{|E_{\text{reference}}(\omega)|} \right)
\]

Absorption coefficient,  

(21)

In the transmission mode the frequency-dependent refractive index [9] can be shown as:

\[
n(\omega) = \frac{\varphi(\omega)c}{\omega D} + 1
\]

(22)

where \( \varphi(\omega) \) is the phase difference between the reference and the sample signals, \( \omega \) is the angular frequency, L is the sample thickness.

3 Experimental setup and materials

The samples were investigated by THz spectroscopy in the transmission geometry, using a
T-Ray 5000 THz-TDS system manufactured by Advanced Photonix, Inc. USA. A schematic drawing of the THz system for spectroscopy in the transmission geometry is shown in Fig.2. The THz pulse is generated by an InAs wafer pumped by a Ti: sapphire laser and the center wavelength of the femtosecond laser pulse is 1064 nm. First, the original femtosecond laser beam is separated at beam disintegration into two parts: a pump and a probe beam. The pump beam is delayed for a few picoseconds (ps) and focused onto the THz generator. The THz generator generates THz radiation which is focused through the sample onto the THz detector using the parabolic mirrors. The pulsed laser-based technique uses photoconductive antennas to allow THz radiation to both be generated and detected at high signal-to-noise (SNR) ratio. By a photodiode detector, the signal is detected and the data are transferred to the computer for further signal processing [10].

Fig.2 Schematic diagram of the THz-TDS system in the transmission mode (M1~M5: mirrors; HDPE: high-density polyethylene. PCA: photoconductive antenna.).

The main specifications of the system are as follows: a spectrum range of 0.1 ~ 3.5 THz with a spectrum resolution is 12.5 GHz, a signal to noise ratio better than 70 dB at the lower
frequency end, and about 30 dB at the high-frequency end, an observation window range of 0 ~ 80 ps, with 0.1 ps resolution, a rapid scanning rate of 1 kHz, and a focal spot of 1.2 cm in diameter.

The PMI foam samples were purchased from Evonik Specialty Chemicals (Shanghai) Co., Ltd. The models are Rohacell 51HF, 71HF, 51WF and 71WF. We used the same thickness 10 mm to investigate the relationship of scattering with different microstructure diameters.

In a second experiment, we examine the power spectral density (PSD) as a function of the foam thickness, where the THz wave attenuation and the -75dB stop frequencies were analyzed. The PMI foam sample thicknesses considered were 3mm, 6mm, 12.5mm, 25mm, 25.4mm, 37.9mm, and 50.8mm.

Table 1 summarizes the major attributes of the selected samples, including material type, manufacturer, models, and density. The microstructure, density and thermal conductance data of the foam materials are summarized or concluded from the manufacturer specifications. The Micro-structure Scanning electron microscope photographs were shown in Fig.3.

Table 1. The micro-structure diameters and density of four Models PMI samples summarized from the manufacturer specifications [11].

<table>
<thead>
<tr>
<th>Model</th>
<th>Material type</th>
<th>Micro-structure diameter(μm)</th>
<th>Density(kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rohacell 51hf</td>
<td>PMI</td>
<td>~120</td>
<td>±20%</td>
</tr>
<tr>
<td>Rohacell 71hf</td>
<td>PMI</td>
<td>~160</td>
<td>±20%</td>
</tr>
<tr>
<td>Rohacell 51wf</td>
<td>PMI</td>
<td>~460</td>
<td>±20%</td>
</tr>
<tr>
<td>Rohacell 71wf</td>
<td>PMI</td>
<td>~550</td>
<td>±20%</td>
</tr>
</tbody>
</table>
4 Results and discussion

THz–TDS measurements provide simultaneous information about the amplitude and phase of the THz after interacting with the samples under study. The slice thickness in mm for each sample investigated by THz-TDS method was measured at ten different positions and the average value is used as the nominal thickness. The experiments were implemented within the sample chamber purged with nitrogen gas to avoid water vapor absorption and the humidity is well below 5%. One reference waveform $E_{\text{reference}}(t)$ is measured without the sample or with a sample of known dielectric properties, and a second measurement
$E_{\text{sample}}(t)$ is performed, in which the THz radiation interacts with the sample. In the present case, $E_{\text{reference}}(t)$ was obtained with nothing in the beam path, and $E_{\text{sample}}(t)$ was the signal through different samples. The time domain waves of reference and four models PMI samples with 10mm thickness are shown in the Fig.4 and the PSD are shown in Fig.5.

Based on the power spectral density curves in Fig.5, we can distinguish the same thickness PMI samples with different microstructure diameters. According to the Table 1, the microstructure average diameters of the four model PMI foam samples are about 120 $\mu$m for 51hf, 160 $\mu$m for 71hf, 460 $\mu$m for 51wf and 550 $\mu$m for 71wf, respectively. We
obtained the absorption coefficient using the Formula (21) and shown in Fig.6.

![Absorption coefficients of four PMI samples with 10mm thickness.](image)

**Fig.6 Absorption coefficients of four PMI samples with 10mm thickness.**

The strongest absorption occurs with 71WF, and that smaller the microstructure — smaller the absorption. Using Eq.(21), we obtain the refractive index shown in Fig.6. Straightforward calculations give almost constant values (close to the index of refraction of air) for the refractive index of 1.0271 for 51HF, 1.0379 for 71hf, 1.0412 for 51WF and 1.0549 for 71WF. For all the samples, the refractive index increases slightly with increasing frequency [12]. It can be seen from the PSD that the attenuation of 71WF beyond 1THz is more than -100dB, so its refractive index for frequencies higher than 1 THz cannot be
obtained in the normal way. However, there is no reason to expect it to change drastically from its values below 1THz. The small variation of the computed refractive index (1.5%, greater than experimental uncertainty) may arise either from sample inhomogeneities or irregular microstructures in the multisampling arrangement. The absorption coefficients of 51HF and 71HF remain less than the value of 2 cm\(^{-1}\), and for 51WF and 71WF they remain less than the value of 5 cm\(^{-1}\) for frequencies up to 2 THz. The accuracy is 1.5% for the refractive index and 4.5% for the absorption coefficient. The physical origin of the small refractive index of the foams is principally due to the low average mass density of the material and the extinction is thought to be due to scattering rather than absorption. This latter reasoning is corroborated by the fact that the extinction coefficient changes with the diameters of the PMI microstructures and the density of the material, as shown in Fig.8.

![Absorption Coefficient vs Diameter](image)

**Fig.8** The absorption coefficient at 0.2THz, 0.5THz, 1THz and 1.5THz with different diameters under the different frequencies (0.2THz, 0.5 THz, 1 THz, 1.5THz)

The higher the frequency, the stronger the influence of the diameter of the micro structure on the absorption coefficient. The impact of the material density on the refractive index is shown in Fig.9.
And when the thickness is different, which microstructure diameter will influence the stop frequency on -75dB PSD more seriously. It’s shown in Fig.10.

The relationship between the sample thickness and the transmitted power is an exponentially decaying one according to the Beer-Lambert Law, and the decay rate for a given PMI foam sample is higher when the diameter of the microstructure of the sample is
larger (see Figure 8).

We analyze the cause of this result is related to the PMI foam microstructure scattering of THz radiation. As the size of the microstructured particles are comparable to the wavelengths of the THz radiation in the spectral region under consideration, it is appropriate to invoke the Mie scattering theory, which was briefly introduced in Section 2.

The main feature of the theory deals with the extinction by a single or a number of spheres, which we now apply to the present situation of microstructured PMI samples. For convenience, we have recast equations (11a) and (12a) respectively in the following forms [8] [13]

\[
a_m = \frac{\left[ \frac{1}{n} g(u) + \frac{m}{x} \right] j_m(x) - j_{m-1}(x)}{\left[ \frac{1}{n} g(u) + \frac{m}{x} \right] [j_m(x) + i y_m(x)] - [j_{m-1}(x) + i y_{m-1}(x)]}
\]

(11b)

\[
b_m = \frac{\left[ n g(u) + \frac{m}{x} \right] j_m(x) - j_{m-1}(x)}{\left[ n g(u) + \frac{m}{x} \right] [j_m(x) + i y_m(x)] - [j_{m-1}(x) + i y_{m-1}(x)]}
\]

(12b)

where

\[
g(u) = -\frac{m}{u} + \frac{j_{m-1}(u)}{j_m(u)}
\]

(23)

First, we use Eq. (9) to calculate \(S(\lambda, D)\). Then we bring the result into the Eq.(10), which, combined with Eq.(8), along with the particle size distribution function given by Eq. (19), will result in the extinction coefficient. The distribution functions of diameters of the spheres diameter used in the calculation are parametrized by \(\eta = 1.02\) and \(\sigma = 0.2\) for 71WF, \(\eta = 1.155\) and \(\sigma = 0.6\) for 51WF, \(\eta = 1.045\) and \(\sigma = 0.2\) for 71HF, \(\eta = 1\) and \(\sigma = 0.2\) for 51HF. These are obtained according to the manufacturer’s specifications as well as our independent microscopic observations. Our simulation results, along with
experimental data for comparison, are shown in Fig.10, where it is obvious that if the diameters are smaller than 200 µm, the extinction coefficient does not change rapidly within the wave band under consideration. Otherwise, the extinction coefficient will change rapidly, such as in the case of 71WF and 51WF.

![Graphs showing extinction coefficient vs frequency for different PMI samples.](image)

**Fig.11** The experimental data and numerical simulation using Mie theory for the extinction coefficient of the PMI samples.

(a) 51HF(η = 1, σ = 0.2) (b) 71HF(η = 1.045, σ = 0.2) (c) 51WF(η = 1.155, σ = 0.6) (d) 71WF(η = 1.02, σ = 0.2)
The above simulation process was carried out using MATLAB programming [14-16]. As can be seen that the application of Mie theory to explain the extinction phenomenon of THz wave propagating through PMI foams is quite reasonable, with the theoretical predictions fairly consistent with measurements, affirming our original hypothesis that the extinction results mainly from scattering rather than absorption. [17-20]

5 Conclusions

We have carried out a systematic experimental investigation of PMI foams of various thicknesses in terms of their THz transmission spectroscopic properties and dielectric properties in order to assess the applicability and merits of THz as a NDT tool for such polymer materials. In this, we have determined both the index of refraction and the optical extinction coefficient of a class of PMI foam. In general, we found that the former is very close to that of air, a results expected based on the porous and light-weight nature of these materials. On the other hand, the extinction showed a pronounced frequency dependence which was correlated with the micro-particle (thought to be main constituent of the material) size that can only be rationalized with the Mie scattering theory. This hypothesis was demonstrated to be valid through a careful simulation, in which we consider dielectric spheres whose diameters follow a log-normal distribution are scatterers of the incident THz radiation. Both the size/wavelength and material density dependence of the THz transmission spectroscopic characteristics found experimentally were recreated by the Mie scattering model. The work presented here should be useful in guiding further studies of THz spectroscopic imaging techniques as effective NDT tools for composite structures having PMI foams as components, or for online quality control during the manufacture process of these and similar materials.
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