Invited Paper

Characterizations of high-density polyethylene by terahertz time-domain spectroscopy

Tong Zhang, Siqi Zhang, Zhiyuan Zheng *, Jingya Zhu, Bochao Guan, and Haochong Huang
School of Science, China University of Geosciences (Beijing), Beijing, 100083, China
* Email: zhyzheng@cugb.edu.cn

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Abstract: The optical properties of high-density polyethylene (HDPE) in the terahertz band are characterized by terahertz time-domain spectroscopy (THz-TDS). The results show that the THz-TDS can effectively distinguish the particle size of HDPE and filler content of HDPE. And it can also be used to characterize the adsorption characteristics of HDPE. These indicate that it can improve the performance of HDPE, industrial production and even environmental pollution of micro-size of HDPE.

Keywords: High-density polyethylene, Terahertz spectrum, Filler, Absorption coefficient, Microplastics

Doi:

1. Introduction

High-density polyethylene (HDPE) is one of the most versatile and widely used thermoplastics because of its unique properties, such as high impact strength, excellent chemical resistance and processability [1, 2]. Due to these characteristics, different grades of HDPE are commonly used in rigid applications, such as corrosion-resistant cables, films, pipes, packaging, containers and medical appliances. However, the interaction among linear molecular chains is weak, so its mechanical properties are poor and it is easy to deform when heated [3], which limits its applications. To meet the growing demand for improved properties in existing and emerging applications, new grades of HDPE with different physical and chemical properties have been developed. Such new HDPE composition can be achieved by modifying the resin structure or by adding a certain amount of additives to HDPE [4, 5]. Furthermore, HDPE gradually appears in the natural environment in the form of micro plastic, which affect the physiology and productivity of organisms [6], and adsorbs pollutants [7, 8]. Therefore, there is an urgent need to differentiate the particle size for handle them separately. These phenomena require appropriate analytical tools, which can more accurately distinguish different HDPE compositions and sizes. At present, infrared spectroscopy [5, 9, 10], Raman spectroscopy [11], X-ray diffraction [10] and Scanning electron microscope [12] are mainly used to identify the composition and properties of HDPE. However, these methods can only obtain the radiation intensity information of the materials, and even damage the samples. Other parameters such as phase and refractive index can not be obtained.

In recent years, terahertz spectroscopy with a longer band than infrared can fill the gap in this field. Terahertz time-domain spectroscopy (THz-TDS) has become an important tool for identifying material components and analyzing material characteristics [13-16] owing to its advantages of being non-contact, non-invasive, strong penetrability and high sensitivity [17-19]. HDPE is often used and tested as a substrate material in the terahertz range [20, 21], Stefan Sommer et al [22] distinguished the crystalline state of HDPE by refractive index, and the adsorption characteristics of HDPE have been studied by Gas chromatography [8], liquid chromatography [23, 24], etc. But the research on optical properties of HDPE composites and adsorption is rare in the terahertz range. Based on THz-TDS, this paper focuses on the study of high-density polyethylene. After characterizing the spectral properties of HDPE particle size, the spectral lines of different ratios of calcium carbonate, kaolin and talcum are investigated. Finally, the adsorption of HDPE, as one of the pollution sources of microplastics, is preliminarily explored.

2. Materials and method

2.1. Method

The terahertz time-domain spectroscopy (THz-TDS) system produced by Daheng New Era Science and Technology Co., Ltd. is used in this experiment. The parameters of femtosecond laser at the front end of the system are as follows: the central wavelength is 800 *nm*, the pulse width is 100 *fs*, the repetition rate is 80 *MHz*, and the average energy is 500 *mW*. The detection pulse propagates through a mechanical delay line (in steps of 0.005 *mm*) to vary the delay time. A total of 600 *points* are recorded to obtain time-domain waveforms. The signal generator uses a photoconductive antenna to generate terahertz electric field pulse signal. The photoconductive antenna and detector are installed in a closed space with a sealed cover. The terahertz path is purified with dry air to keep the relative humidity at (2 ± 0.3) %, so as to avoid the influence of terahertz absorption of moisture in the air on the experimental data. More detailed principles are given in reference [16].

2.2. Materials

The HDPE used in the experiment is purchased from the market in different particle size of powders less than 28 *μm*, 75 *μm*, 120 *μm* and 178 *μm* respectively. Before testing, HDPE powders with different sizes are pressed in a 10 *MPa* tablet press for two minutes to obtain test samples with a diameter of 13 *mm* and a thickness of 1-2 *mm*. The fillers involved in the experiments are commercially purchased calcium carbonate, kaolin and talcum with particle size less than 75 *μm*. The three kinds of fillers are mixed and pressed with 75 *μm* HDPE in different mass ratios and tested at 23 ℃. No other binders are mixed in the experiments to avoid effects. The liquid measurements in the experiments are filled using a liquid tank with a liquid thickness of 0.1 *mm*.

3. Data analysis and discussion

3.1. Characterization of HDPE particle size

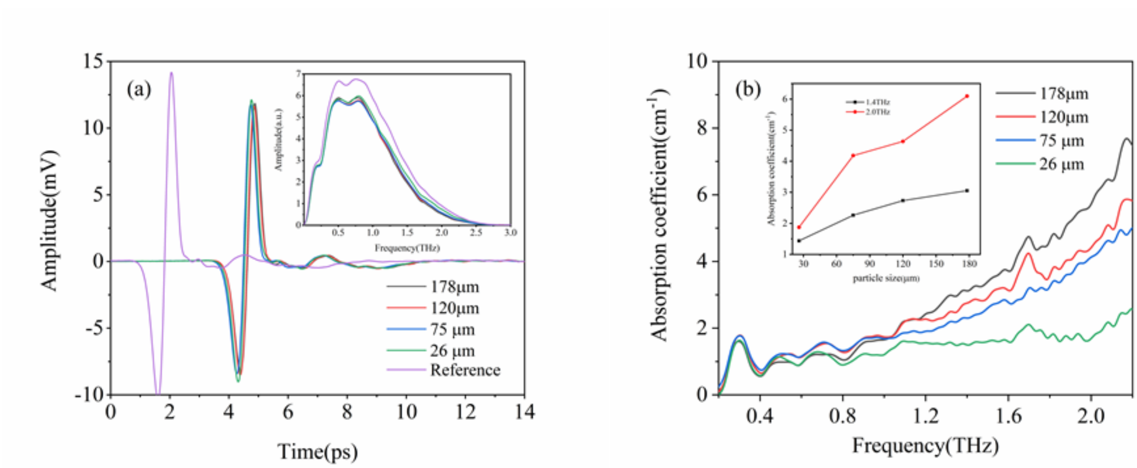


Fig. 1 Terahertz spectra of HDPE particles of different sizes, (a) time-domain spectrum and (b) absorption coefficient. The illustrations show the correlation curves of (a) frequency-domain spectrum and (b) particle size-absorption coefficient at 1.4 and 2.0 *THz*.

The time-domain amplitude, frequency-domain amplitude, and absorption coefficient of HDPE with a particle size of 28 *μm*, 75 *μm*, 120 *μm* and 198 *μm* at different terahertz frequencies are shown in Fig. 1. The reference line in Fig. 1 (a) refers to the spectral line measured without placing the sample. The purpose of measuring the reference line is to facilitate comparison with the sample line and the later data processing. Fig. 1 (a) illustrates the time-domain spectral line. It can be noticed that the sample spectral line lags behind the reference spectral line obviously. This is due to the optical path difference caused by the thickness of the sample, which makes the test curve lag behind the reference line. The time-domain amplitudes of different particle sizes have little difference, and the illustration is the frequency-domain spectrum obtained by Fast Fourier transform of the data in Fig. 1 (a). This indicates that one of the advantages of the terahertz time-domain spectroscopy technology is that the amplitude in the wideband frequency-domain can be obtained simultaneously by measuring the electric field intensity varying with time and then fast Fourier Transform.

Fig. 1 (b) shows that the absorption coefficients of different particle sizes are quite different. With the increase of particle size, the absorption coefficient also shows an upward trend, especially in the range of 0.8-2.2 terahertz range. The main reason for this difference is the relationship between the particle size and the terahertz wavelength. The current research shows that the absorption coefficient obtained from the time-domain spectrum comes from intrinsic absorption and scattering absorption. As shown in formula (1):

$$A(\omega) = \alpha abs(\omega) + \alpha sca(\omega) \tag{1}$$

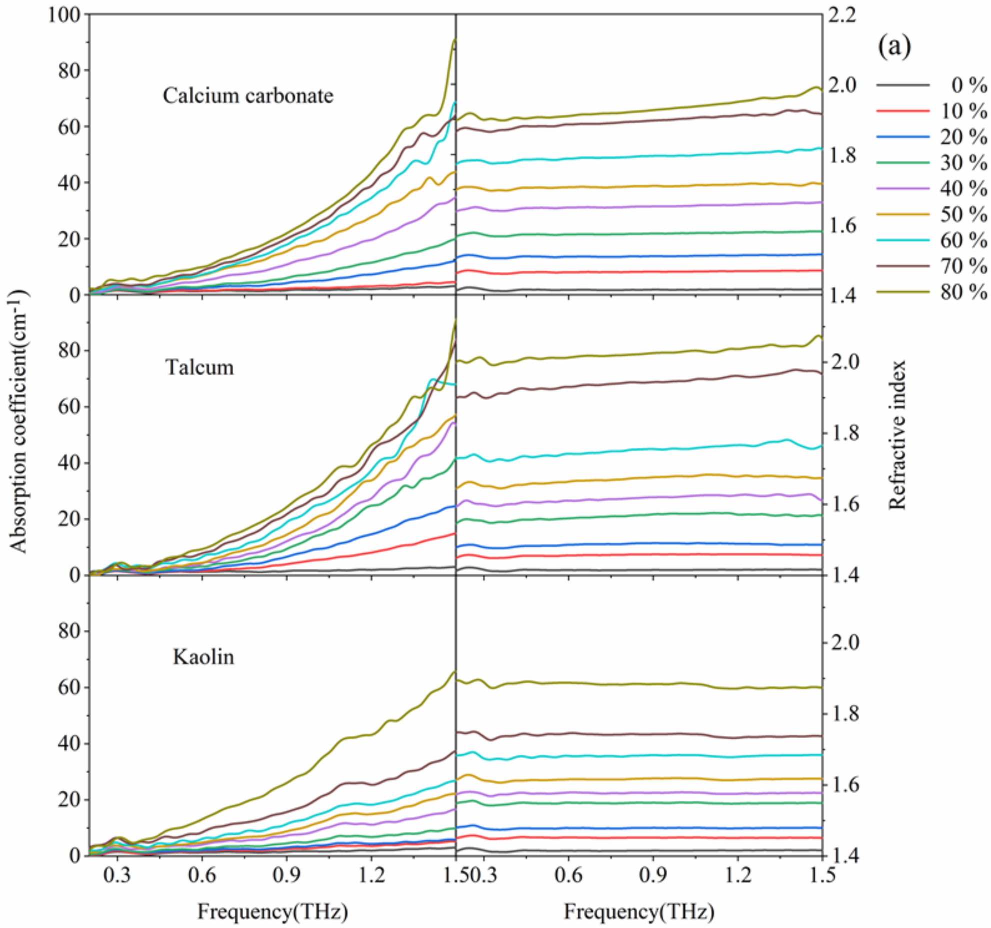
Where, $A(\omega)$ is the total absorption coefficient, $\alpha abs(\omega)$ is the intrinsic absorption coefficient and $\alpha sca(\omega)$ is the scattering absorption coefficient. The scattering absorption is mainly determined affected by the particle size. When the particle size of the medium is much smaller than the wavelength of the incident light, the scattering is Rayleigh scattering [25] and the scattering light intensity is shown as formula (2):

$$I = \frac{\pi^4 d^6}{8\lambda^4 r^2}\left(\frac{n^2-1}{n^2+2}\right)^2 (1+\cos^2\theta) I_0 \tag{2}$$

Where, d is the diameter of the particle, λ is the wavelength of the incident light, r is the distance between the incident light and the particle, n is the refractive index of the particle, θ is the scattering angle and I0 is the incident light intensity.

When the particle size is close to or larger than the wavelength of the incident light, the scattering is Mie scattering [26]. In Fig. 1 (b), the terahertz radiation range is 0.2-2.2 terahertz, corresponding to the wavelengths of 1500 μm-136 μm. In the experiment, the particle size of 178 μm is closer to the terahertz wavelength of the current frequency, so the scattering phenomenon plays a dominant role. The inset in Fig. 1 (b) shows the correlation curves of the absorption particle sizes produced for the selected stable 1.4 and 2.0 terahertz waves, showing the variation of the absorption coefficient with particle size between high and low frequencies, and it is more intuitive to see that the scattering phenomenon is more pronounced for particles of 178 μm as the frequency increases.

3.2. Characterization of fillers in HDPE



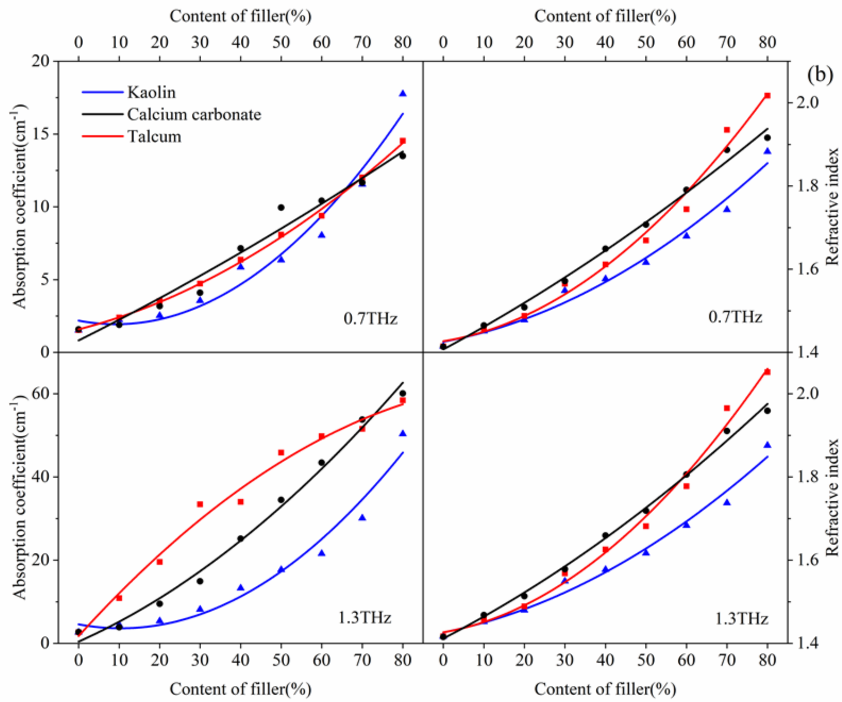


Fig. 2 (a) Terahertz spectra of absorption coefficients and refractive indices of $CaCO_3$-HDPE, Talcum-HDPE and Kaolin-HDPE blends with calcium carbonate, talc and kaolin concentrations ranging from 0% to 80%. (b) The effect of $CaCO_3$, Talcum and Kaolin concentrations on the absorption coefficients and refractive indices measured at 0.7 and 1.3 *THz*.

Calcium carbonate ($CaCO_3$), kaolin and talcum are three common fillers in the plastics industry. $CaCO_3$ is widely used because of its low price, good stability and non-toxicity. It can improve the impact strength, thermomechanical properties, elastic modulus and tensile properties of HDPE significantly [27, 28]. Talcum powder is a kind of mineral with non-toxic, tasteless, low hardness, less wear to mechanical equipment, strong smoothness and so on. It is often used to improve the ductility, mechanical and thermal properties of HDPE [29]. Kaolin is one of the most widely used clay materials. It is a layered silicate of hydrous silicate composed of a variety of minerals and therefore has good chemical stability, insulation and fire resistance properties. It is usually used to fill HDPE to improve its rheological behaviors and mechanical properties [30]. Therefore, the spectral characterization of these three representative fillers has great practical significance. Fig. 2(a) shows the terahertz spectral lines of absorption coefficient and refractive index obtained by mixing HDPE with 0-80% filler respectively.

It can be seen from Fig. 2(a) that their absorption coefficients and refractive indices show a trend of increasing with the increase of filler content. At high frequencies, the difference of absorption coefficient is more obvious, where talcum has the greatest influence on the absorption coefficient and kaolin has the least. However, the refractive index changes little with the frequency, except that each filler makes the refractive index different. For example, the refractive index of calcium carbonate is about 1.93, while that of talcum and kaolin at 80% are 2.02 and 1.88, respectively. This indicates that in the modification of HDPE, due to little difference in the refractive index among the three fillers, only the price and performance of the fillers are considered. It is noteworthy that the characteristic peak of kaolin at 1.1 *THz* disappears with decreasing content, which can also be used as a criterion to judge the interaction between kaolin and HDPE. Fig. 2(b) clarifies the variation of refractive index and absorption coefficient of blends at both high (1.3 *THz*) and low (0.7 *THz*) terahertz, which can be used to quantify the concentration of filler in samples with the same type of filler but unknown the history. The fitting curve of absorption coefficients for kaolin-filled HDPE is different from those of $CaCO_3$ and talcum, with lower concentrations of kaolin having less effect on the absorption coefficient of HDPE. These results will facilitate terahertz techniques such as distinguishing and comparing the content and type of fillers in HDPE, which is useful for quality control in the plastic industry

3.3. Adsorption characteristics of HDPE

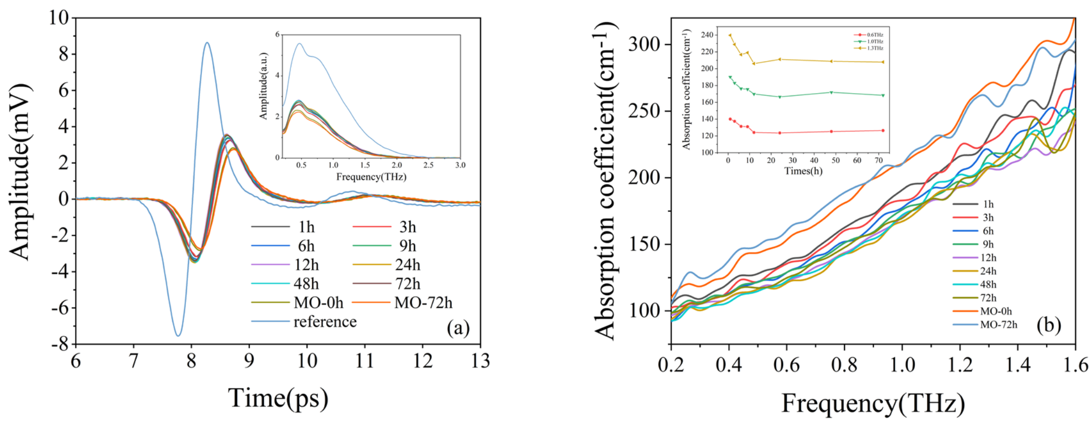


Fig. 3 (a) Time-domain spectra (the illustrations is frequency-domain spectrum), (b) The frequency-dependent absorption coefficients of the MO solution (excluding HDPE) at 0, 72 hours and the MO solution after adsorption by HDPE at different hours. The illustrations is time dependent absorption coefficient correlation curves at 0.6, 1.0 and 1.3 *THz* in fig. 3(b).

Plastic products are widely used in life because of their many advantages. These plastics break down into tiny particles under the action of nature. Generally, plastic particles smaller than 5 *mm* are called microplastics [31]. In recent years, microplastics have been detected in the atmosphere [32], seawater [33] and even in living organisms [34]. Microplastics with large specific surface area and strong hydrophobicity can adsorb heavy metals and organic pollutants from seawater

[24, 35]. In this section, HDPE solutions before and after adsorption are characterized by terahertz time-domain spectroscopy using methyl orange as the adsorbed organic material. Methyl orange solution with a concentration of 50 *mg / L* is selected as adsorption solution, and 0.1 *g* HDPE with a particle size of 120 *μm* is added into 25 *ml* methyl orange solution. The concentration changes of methyl orange solution after standing for a period of time are measured and compared. Fig. 3(a) shows the time-domain spectra (the inset shows the frequency-domain spectra), MO-2h and MO-72h indicate the curves of methyl orange solution after 72h shaking, and it can be seen that the changes are very small, which proves the validity of the experiment. From the frequency-absorption coefficient curve in Fig. 3(b), it can be seen that the absorption coefficient of the solution decreases with increasing time after the addition of HDPE. However, by 12 hours, the absorption coefficient no longer decreases. In order to clearly compare the relationship between times and absorption coefficient, the inset of Fig. 3(b) shows the correlation curves of absorption coefficients at 0.6, 1.0 and 1.3 *THz* where the frequency difference is large, and it can be seen that the absorption coefficient decreases more significantly with time at high frequencies. Therefore, it can be inferred that the adsorption behavior of HDPE leads to the decrease of methyl orange concentration and absorption coefficient.

4. Conclusion

High-density polyethylene (HDPE) is characterized by THz-TDS. Temporal spectra and absorption coefficients of HDPE are related to the particle size of the samples, especially when the particle size is comparable to the terahertz wavelength. In addition, the refractive indices and absorption coefficients of three fillers, calcium carbonate, talcum and kaolin, which are widely used in the plastic industry, are measured and the results are fitted after mixing according to different mass ratios. The results reveal that three kinds of fillers show similar variation rules, which can be used for quantitative monitoring of fillers in chemical production. In addition, HDPE with particle size less than 5mm has the function of adsorbing organic compounds. Terahertz spectroscopy can characterize the adsorption performance, and it also provides a new means for the detection and characterization of microplastics in environmental pollution.

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