

# Identification of pour point depressant by terahertz time-domain spectroscopy

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The frequency-dependent absorption coefficients and refractive indexes of three selected pour point depressants (PPDs) are extracted within the spectral range of 0.2–2.5 THz using terahertz time-domain spectroscopy (THz-TDS). The selected PPDs are also characterized by the middle-infrared spectrum. The experimental results reveal that PPD is more sensitive in the THz range than that in the middle-infrared range. Moreover, the different compositions of PPD can be identified according to their different spectral features in the THz range. Due to its properties of better repeatability, shorter testing time, and easier operation, THz-TDS can be used as a complement for identifying the chemical compositions of PPD.

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Pour point depressant (PPD) is a kind of petroleum additive, which is added in minute quantities to diesel to prevent it from freezing under low temperature. The long hydrocarbon paraffin chains in diesel tend to interact with the polymer alkyl groups in PPD, which act as crystallization nuclei dangling from the polymeric matrix. Thus, larger numbers of crystallization nuclei correspond to less free paraffin hinder fluidity with the reduced temperature, resulting in a lower pour point. Different kinds of PPD have varying sensitivities to different kinds of diesel, and for the same copolymer composition, the increase in size of the alkyl group improves the performance of the additive. Thus, it is important to choose a suitable one for certain diesel. At present, all kinds of PPDs in the market are esters, such as polyvinyl acetate (PVA), polymethacrylate (PAMA), and crotonate; these are dissolved in organic solvent and are analyzed by infrared (IR) spectroscopy, a process which is complicated and time-consuming.

For rapid testing of petroleum products, much attention has been paid to terahertz time-domain spectroscopy (THz-TDS), which can effectively obtain the molecular vibration mode and amplitude, phase, and structural information of the organism<sup>[1–8]</sup>. In this letter, the optical properties of PPDs have been studied in both the IR and THz regions. The results demonstrate that THz spectroscopy has more information and better identification of samples, allowing it to supplement the IR spectrum.

The THz spectrometer in the transmission mode is used to investigate the optical properties of samples. A spectrum physics regenerative amplifier system produces 800-nm pulses of 100-fs duration with 1-kHz repetition rate. The source beam is split into two portions, corresponding to THz generation and probe beams, respectively. THz-TDS is based on a ZnTe emitter for THz generation and electro-optic sampling<sup>[9]</sup>. The THz radi-

ation is detected by free-space electro-optic sampling in a <110> ZnTe crystal. Then, the signal is collected by a lock-in amplifier with the phase locked to an optical chopper<sup>[10]</sup>. The path with THz radiation is enclosed and purged with dry nitrogen. THz-TDS allows us to measure both the phase and the amplitude of the THz pulses propagating through the sample and reference, respectively. The frequency-dependent refractive index and absorption coefficient are extracted from the derivation of Fresnel law. By comparing the reference and the sample pulse, as well as the use of a numerical fast Fourier transform (FFT), the refractive index and the absorption coefficient can thus be calculated<sup>[11]</sup>.

Three kinds of commercial PPDs from USA (M-PPD), Germany (G-PPD), and China (C-PPD) were collected. The main ingredient of G-PPD and C-PPD is PVA, and that of M-PPD is PAMA. The 0.3-cm-thick PPD samples in the liquid phase were sealed in polyethylene cells, which were transparent for visible light and had low refractive index and THz absorption. Figure 1 shows

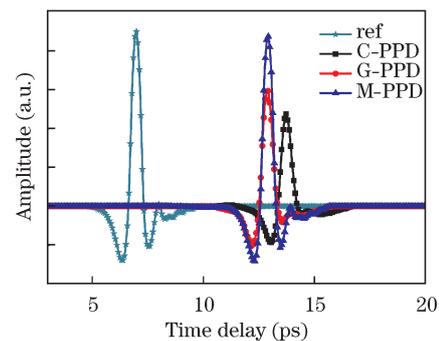


Fig. 1. THz pulses of reference in the free cell (star line), C-PPD (square), G-PPD (circle), and M-PPD (triangle).

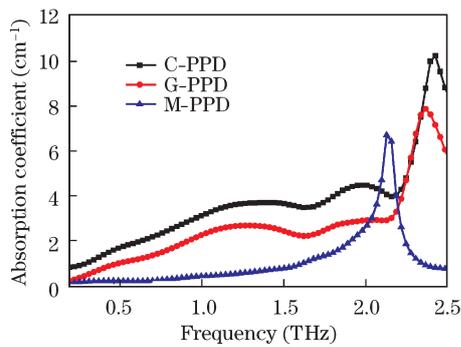


Fig. 2. Absorption coefficients of PPDs in the 0.2–2.5 THz region.

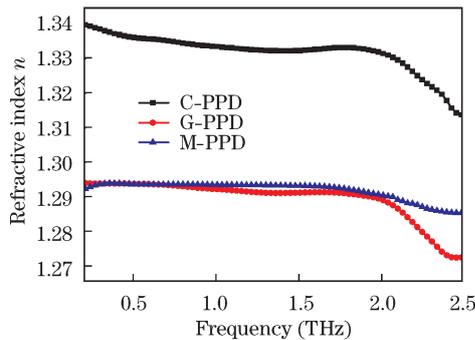


Fig. 3. Refractive indices of PPDs in the 0.2–2.5 THz region.

the time-domain spectra of the three PPDs. The left line is the reference pulse of the free space without sample and the other lines are the THz signals passing through the PPDs, showing drops in amplitude and delays in time, which indicates the difference in physical and chemical properties of the samples.

As shown in Figs. 2 and 3, the three PPDs show different absorption coefficients and refractive indices in the spectral range from 0.2 to 2.5 THz under nitrogen at room temperature. In Fig. 2, the absorption peaks can be found at 2.14, 2.37, and 2.41 THz for M-PPD, G-PPD, and C-PPD, respectively. In addition, G-PPD shows a similar absorption curve but a different absorption coefficient from C-PPD, indicating that the component is the same while the content is different. The results are in accordance with the components of samples and demonstrate that different molecules have different vibration modes and frequencies, from which the different PPDs can be identified in the THz region. The fundamental dynamic properties of fluid, such as rotation, translation and random diffusion, are related to the viscosities, densities, temperature, and molecular sizes or flexibility of the constituent molecules<sup>[12]</sup>. In the liquid phase, various types of vibration occur, wherein the characteristic frequencies are described as intra-molecular and intra-molecular vibrations. These vibrations give rise to characteristic frequencies<sup>[13]</sup>.

The average refractive indices of M-PPD, G-PPD, and C-PPD are 1.29, 1.29, and 1.33, respectively (Fig. 3). Although G-PPD and C-PPD show similar refractive curves because of their similar components, their refractive indices were different. On the contrary, G-PPD has the same refractive index with M-PPD. The results reveal that the optical properties

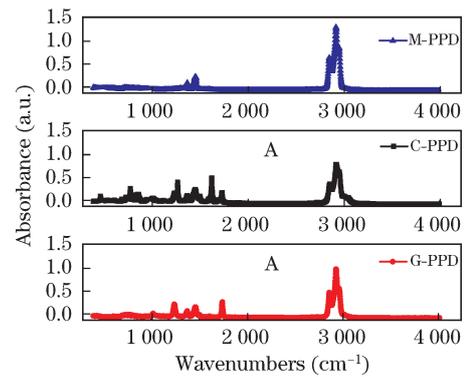


Fig. 4. Middle-IR spectra of selected PPDs.

of the samples are determined not only by the composition but the content, and THz-TDS can be a useful way to identify them.

Figure 4 shows the IR spectroscopy of the three samples, showing distinct absorption peaks and coefficients in the range of 400–4 000  $\text{cm}^{-1}$ . It is difficult to identify whether G-PPD has a similar composition with C-PPD or a different component compared with M-PPD. PPD is a mixture consisting of ester dissolved in organic solvent made of naphtha. The naphtha may have some different groups with the ester, and the different naphtha can be used in a different PPD. For the disturbance of solvent, the G-PPD and C-PPD have different absorption features in the IR region. In addition, the vibration frequency of naphtha in the THz region was calculated using the GAUSSIAN 03 software package. The B3LYP method was used in conjunction with the 6-31G (d) basis set. The result show that naphtha has low absorption in the THz region, and that only the absorption properties of ester in PPDs can be detected by THz-TDS. This is the reason why the same or various compositions in PPD can be discerned distinctly within the range of 0.2–2.5 THz.

In conclusion, the spectral characteristics of PPDs with different components have been studied in both the 0.2–2.5 THz and 400–4 000  $\text{cm}^{-1}$  IR regions. The results indicate that the THz spectra can obtain more information than IR spectra and that PPDs can be discerned distinctly by THz-TDS. The investigations have also demonstrated that THz-TDS can be an excellent supplement to the IR spectrum for PPD detection and identification and has a potentially significant application in the analysis of PPDs.

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