

Application News

IRSpirit™-X Series / IRXross™/IRTracer™-100 Fourier Transform Infrared Spectrophotometer

Distinction of Polyethylene and Polypropylene by Infrared Spectrum

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User Benefits

- ◆ The ATR method using the IRSpirit-TX enables easy qualitative analysis of resins.
- ◆ Polyethylene and polypropylene can be differentiated based on their infrared spectra.
- ◆ It is also possible to differentiate structural differences between low density and high density polyethylene from differences in their absorption peaks.

■ Introduction

Synthetic resins generally refer to polymers produced by polymerizing monomers made from a petroleum feedstock. Among the synthetic polymers, hydrocarbon resins are resins that consist mainly of carbon (C) and hydrogen (H). Although various types are known, polyethylene (PE) and polypropylene (PP) are representative hydrocarbon resins. PE and PP can be differentiated based on the infrared spectra acquired by a Fourier transform infrared spectrophotometer (FTIR). Furthermore, if the structures of the same PE differ slightly, those differences also appear in the acquired infrared spectra. Hence, it is possible to differentiate resins with different structures and properties, even in the same PE by distinguishing those differences.

This Application News article introduces an example in which the representative hydrocarbon resins PE and PP were measured using an FTIR, and explains the differences in their infrared spectra arising from structural differences in the resins.

■ Instruments Used and Measurement Conditions

The instruments used in these measurements were an IRSpirit-TX FTIR spectrophotometer and QATR™-S single-reflection ATR accessory. Fig. 1 and Table 1 show the appearance of the IRSpirit-X series and the measurement conditions, respectively. A diamond prism was used in the QATR-S. A background measurement was carried out with no specimen of any kind on the prism, after which the samples were firmly fixed on the prism and their infrared spectra were acquired.



Fig. 1 Appearance of IRSpirit™-X Series

Table 1 Measurement Conditions

Instruments	: IRSpirit-TX, QATR-S (diamond prism)
Resolution	: 4 cm ⁻¹
Accumulation	: 40 times
Apodization function	: Happ-Genzel
Detector	: DLATGS
Measured wavelength range	: 4000 - 400 cm ⁻¹

■ Infrared Absorption and Molecular Vibration

Under irradiation with infrared light, molecular vibration occurs in organic substances due to the interaction of the infrared light and the molecules of the substance. This vibration arises from the motion of the atoms that make up the molecule.

Fig. 2 shows the basic vibration modes. The arrows indicate the motion of each atom in the molecule, and the plus (+) and minus (-) signs show motion in the vertical (perpendicular) direction relative to the plane formed by the three atoms.

The vibration of molecules can be broadly classified as stretching vibration, in which the distance between atoms expands and contracts, and bending vibration, in which the angle between the atoms changes. Stretching vibration can be further divided into symmetric stretching vibration (v_s) and asymmetric stretching vibration (v_{as}), while bending vibration can be divided into scissoring vibration (δ), rocking vibration (ρ), wagging vibration (ω), and twisting vibration (τ). However, it is not necessarily possible to detect all of these standard vibrations as absorption. For a more detailed discussion of molecular vibration, please refer to FTIR TALK LETTER Vol. 41.

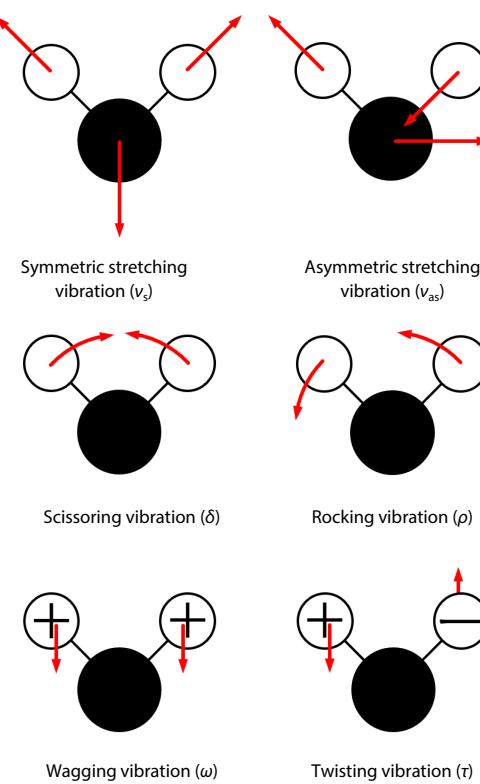


Fig. 2 Types of Molecular Vibration

■ Polyethylene and Polypropylene

Polyethylene (PE) and polypropylene (PP) are known as representative resins made up of carbon (C) and hydrogen (H). Fig. 3 shows the structural formulas of PE and PP. Both PE and PP consist of only C and H, and their structures are also similar, but as the functional group, PE and PP differ in that PP contains one CH_3 molecule per monomer, while in PE, CH_3 exists only at the chain end.

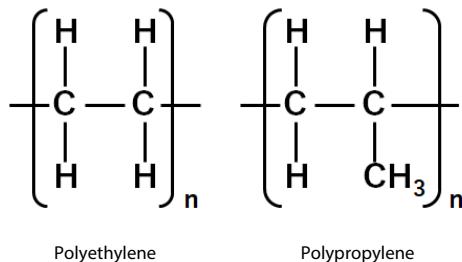


Fig. 3 Structural Formulas of Polyethylene and Polypropylene

Here, the infrared spectra of PE and PP were measured using an ATR accessory instrument. Fig. 4 shows the overlay of the measurement results. PE is shown by the red line and PP is shown by the black line. In this figure, the peak heights are aligned for easy comparison.

Differences in the absorption peaks of PE and PP can be seen in several wavenumber regions. In Fig. 4, the distinctive regions that show structural differences are indicated by the three colored boxes. Absorption related to stretching vibration of C-H can be seen in the vicinity of 3200 to 2600 cm^{-1} surrounded by the blue box, while absorption related to bending vibration of C-H can be seen in the vicinity region from 1600 to 1200 cm^{-1} surrounded by the green box. Absorption related only to PE can be observed around 720 cm^{-1} , in the region surrounded by the red box.

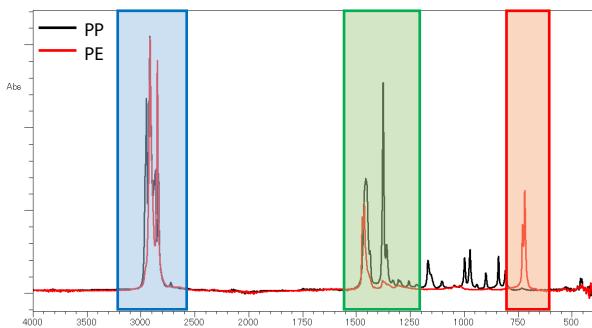


Fig. 4. Infrared Spectra of PE and PP

Fig. 5 shows an enlargement of the 3200 to 2600 cm^{-1} region (blue box) in Fig. 4.

Here, the absorption originating from stretching vibration of CH_2 , a molecule common to PE and PP, can be observed around 2930 cm^{-1} and around 2850 cm^{-1} . These two peaks show absorption associated with asymmetric and symmetric stretching vibration of CH_2 , respectively. Although a slight difference in the positions of the absorption peaks of PE and PP can be seen, this is considered to be caused by differences in the molecular structure and the functional groups adjoining CH_2 . In addition, in PP, prominent absorption peaks originating from asymmetric stretching vibration and from symmetric stretching vibration of CH_3 can be recognized around 2960 cm^{-1} and 2870 cm^{-1} , respectively.

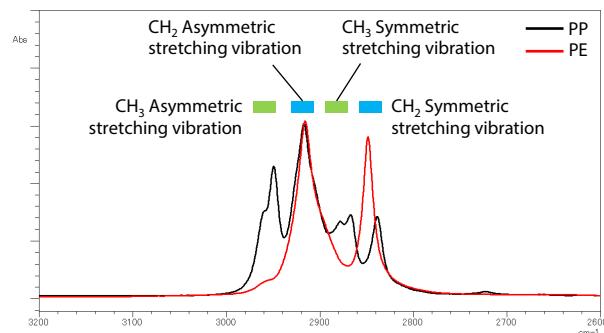


Fig. 5 Enlargement of 3200-2600 cm^{-1} Region in Fig. 4

Fig. 6 and Fig. 7 show enlargements of the 1600 to 1200 cm^{-1} (green box) and 800 to 600 cm^{-1} (red box) regions in Fig. 4, respectively.

Although peaks of both PE and PP can be seen around 1460 cm^{-1} in Fig. 6, it is known that their peak assignments are slightly different. In PE, CH_2 shows a comparatively sharp peak originating from scissoring vibration of CH_2 . However, in PP, in addition to scissoring vibration of CH_2 , a broad peak can be observed due to overlapping by the absorption peaks of CH_3 symmetric bending vibration, which is positioned on the somewhat lower wavenumber side than the scissoring vibration of CH_2 . In addition, the prominent peak around 1380 cm^{-1} , which originates from CH_3 asymmetric bending vibration seen in PP, is also a distinctive feature of PP.

On the other hand, the peak at around 720 cm^{-1} in Fig. 7 is conspicuous in PE but cannot be observed in PP. This is called the rocking vibration of CH_2 . Because stretching like that of the bellows of an accordion can be seen in $\text{CH}_2\text{-CH}_2\text{-CH}_2$, which is the main chain of PE, this is also called "accordion vibration" as another name.

As demonstrated here, if there are partial differences in the structures of resins, it is possible to differentiate the type of resin from differences in their infrared spectra, even in resins consisting of only C and H.

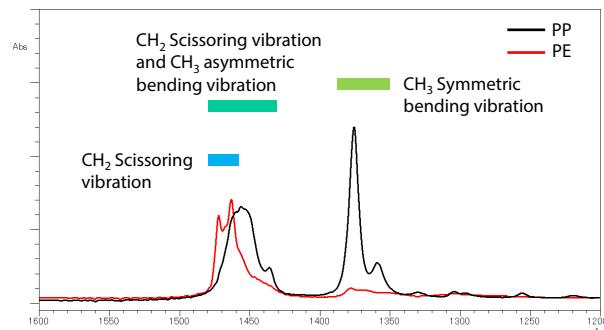


Fig. 6 Enlargement of 1600-1200 cm^{-1} Region in Fig. 4

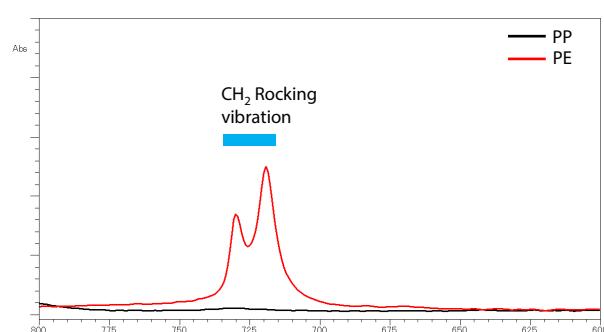


Fig. 7. Enlargement of 800-600 cm^{-1} Region in Fig. 4.

■ Low Density Polyethylene and High Density Polyethylene

Although several types of PE exist, low density polyethylene (LDPE) and high density polyethylene (HDPE) are well known. LDPE is a soft resin that displays stretchability (elasticity), while HDPE is a hard resin with poor elasticity compared to LDPE. These differences in their properties are caused by the side-chain structure. Fig. 8 shows schematic diagrams of LDPE and HDPE, where the red dots indicate terminal CH_3 groups. LDPE has a structure which contains a large number of long side chains, and its density is low because entanglement of the molecules is difficult in this structure. On the other hand, because HDPE has a structure with few side chains, molecular entanglement occurs easily, resulting in high density. Differences originating from this side-chain structure can also be observed on the infrared spectra.



Fig. 8 Schematic Diagrams of LDPE and HDPE

Fig. 9 shows an overlay of the infrared spectrum measurement results for LDPE and HDPE. The red and blue lines indicate LDPE and HDPE, respectively. The peak heights were also aligned in this figure for easy comparison. The regions where differences in the absorption peaks can be seen are indicated by the three colored boxes.

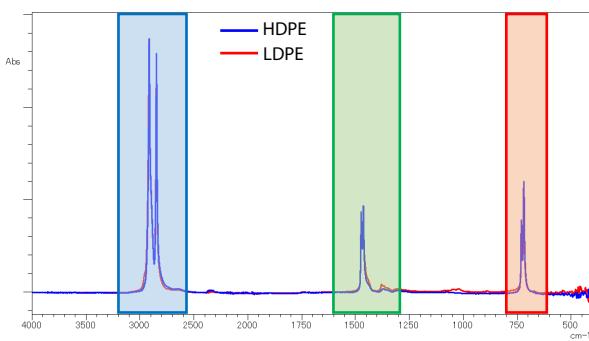


Fig. 9 Infrared Spectra of LDPE and HDPE

Fig. 10 shows an enlargement of the 3200 to 2600 cm^{-1} region (blue box) in Fig. 9. In comparison with HDPE, it can be understood that absorption of 2960 cm^{-1} originating from asymmetric stretching vibration of side-chain terminal CH_3 group appears more strongly in LDPE, which has many side chains.

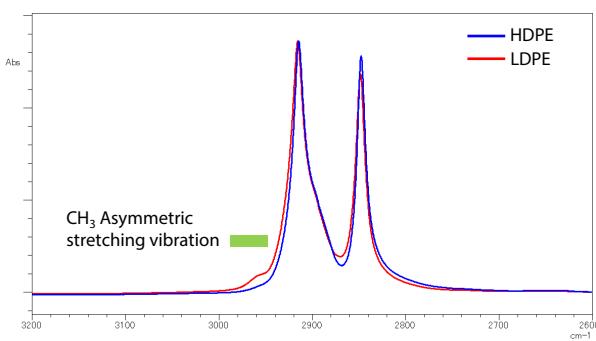


Fig. 10 Enlargement of 3200-2600 cm^{-1} Region in Fig. 9

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Fig. 11 and Fig. 12 show enlargements of the 1600 to 1200 cm^{-1} (green box) and 800 to 600 cm^{-1} (red box) regions in Fig. 9, respectively.

In the case of LDPE, strong absorption appears around 1380 cm^{-1} in Fig. 11. This is also symmetric bending vibration of the side-chain terminal CH_3 group.

Furthermore, differences can be seen between LDPE and HDPE in the peak which is divided into two peaks of CH_2 scissoring vibration at around 1460 cm^{-1} in Fig. 11 and CH_2 rocking vibration at 720 cm^{-1} in Fig. 12. In HDPE, the peak intensity on the high wavenumber side appears more strongly than that of LDPE, but this is attributable to the degrees of crystallinity of LDPE and HDPE. The crystallinity of HDPE is high because the molecules align easily due to the small number of side chains. It is known that polyethylene with high crystallinity displays a strong peak on the high wavenumber side.

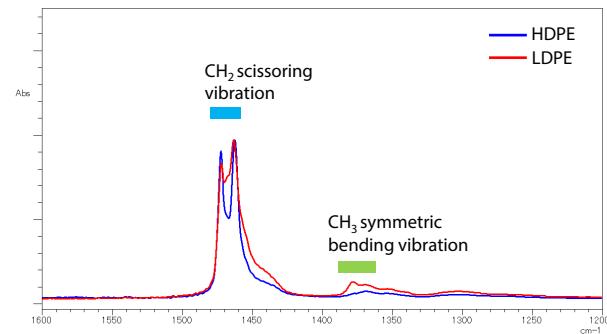


Fig. 11 Enlargement of 1600-1200 cm^{-1} Region in Fig. 9

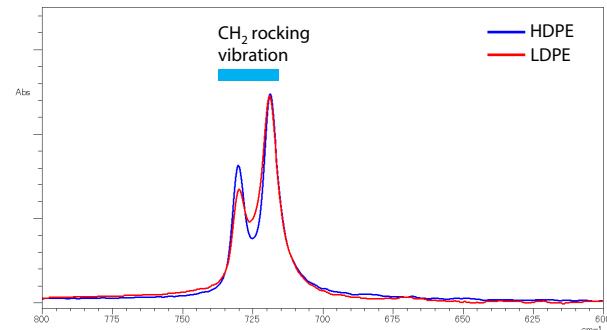


Fig. 12 Enlargement of 800-600 cm^{-1} Region in Fig. 9

■ Conclusion

This Application News article described several characteristics of the absorption peaks of polyethylene (PE) and polypropylene (PP), which are resins that consist of only carbon (C) and hydrogen (H). Various types of polyethylene exist, and this article has introduced the structural differences that appear in the infrared spectra. It is possible to distinguish structural differences, even in the same polyethylene resin, by investigating the characteristics of their infrared spectra.