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Application News

No. A581

Spectrophotometric Analysis

Quantitative Analysis of Recycled Plastics Using FTIR – Mixing Ratio Calculation Method –

Plastic bottles, containers, and packaging materials are commonplace items that can be found in various aspects of our everyday lives. In Japan, such items are discarded by consumers as waste plastic but are then collected and recycled into new raw materials and products according to the Container and Packaging Recycling Law in order to reduce and recycle waste plastic.
The main four components of recycled plastics are polyethylene (PE), polypropylene (PP), polystyrene (PS), and polyethylene terephthalate (PET), which are all commodity resins. Quality standards are defined for recycled plastics and to determine the composition of components, generally a sample is dissolved in a solvent and then analyzed using a nuclear magnetic resonance (NMR) spectrometer. In place of this general method, this article introduces a screening analysis method using a Fourier transform infrared spectrophotometer (FTIR). Quantitation is possible by either the individual calculation method, in which the concentration of each component is calculated individually, or the mixing ratio calculation method, in which the concentration of each component is calculated by taking the sample as a whole as 100 %. This article studies the mixing ratio calculation method. A major feature of this method is that unlike the precision analysis using an NMR spectrometer, sample pretreatment is unnecessary and therefore speedy calculations of the composition of components are possible. For the individual calculation method, please refer to Application News No. A580.

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Analytical Conditions

The instrument used for analysis was the IRAffinity-1S Fourier transform infrared spectrophotometer combined with the Quest single-reflection ATR accessory as shown in Fig. 1. The principle of the ATR (attenuated total reflection) method is illustrated in Fig. 2 and the analytical conditions are listed in Table 1. The ATR method obtains a spectrum from a sample by first pressing the sample against the surface of a prism made of infrared transmitting material with a high refractive index and then detecting the reflected light beam that has penetrated the sample surface to a depth of a few microns.

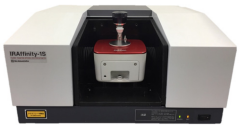

Fig. 1 The Instrument Used (IRAffinity-1S, Quest)

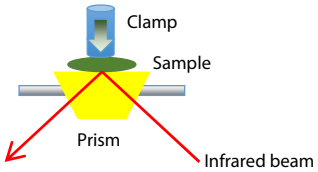

Fig. 2 The Principle of the ATR Method

Table 1 Analytical Conditions

Instrument	: IRAffinity-1S, Quest
Resolution	: 4 cm^{-1}
Accumulation Times	: 20
Apodization Function	: Happ-Genzel
Measurement Mode	: Absorbance
Detector	: DLATGS

Quantitative Analysis Using the Mixing Ratio Calculation Method

By using samples with known concentrations, calibration curves that indicate the relationship between mixing and absorbance ratios are created for PE/PP, PS/PP, and PET/PP. These calibration curves are used to calculate the mixing ratio of PE/PP, PS/PP, and PET/PP in samples with unknown concentrations and then derive ratios as PE:PP:PS:PET = A:B:C:D. The quantitation values for PE, PP, PS, and PET can then be calculated from the A:B:C:D ratio on the basis that the total is 100 wt%. The plastic-derived peak wavelengths used for quantitation are 719 cm^{-1} (PE), 841 cm^{-1} (PP), 698 cm^{-1} (PS), and 1721 cm^{-1} (PET) and the peak height ratio is used.

Characteristics of the Method

- Since quantitation values are calculated on the basis that the total of PE, PP, PS, and PET is 100 wt%, the existence of other components is not taken into account.
- Compared to the individual calculation method, effects of measurement errors due to sample shape are smaller. The method can therefore be applied to samples in pellet form as well.

Samples for Analysis

The recycled plastics in pellet form shown in Fig. 3 were measured this time. Table 2 shows the composition of the five samples that were used to create the calibration curves.

Fig. 3 Samples for Analysis

Table 2 Composition of Samples Used to Create Calibration Curves

	Composition (wt%)				
	PE	PP	PS	PET	Other
Sample 1	89	9	1	<1	1
Sample 2	74	14	3	2	7
Sample 3	21	65	4	4	6
Sample 4	20	68	10	1	1
Sample 5	14	79	4	1	2

Results of Quantitative Analysis Using the Mixing Ratio Calculation Method

The samples 1 to 5 with known concentrations were measured four times each by changing the point for measurement each time. Fig. 4 shows the calculated average infrared spectra and Table 3 lists the PE/PP, PS/PP, and PET/PP ratios for samples 1 to 5. The calibration curves indicating the relation between each mixing ratio and the absorbance ratio are shown in Fig. 5. The horizontal axes of the calibration curves indicate the mixing ratios in Table 3 and the vertical axes indicate the absorbance ratios calculated from the peak height values of the wavelengths 719 cm^{-1} (PE), 841 cm^{-1} (PP), 698 cm^{-1} (PS), and 1721 cm^{-1} (PET).

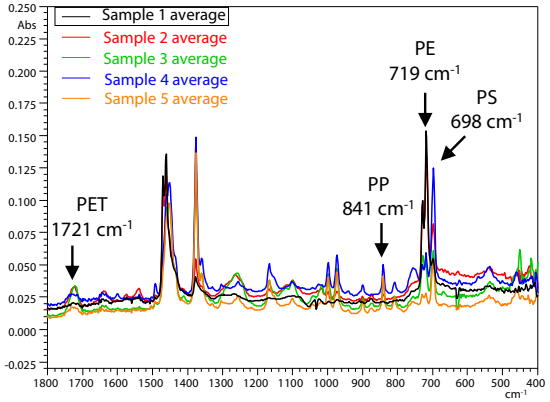

Fig. 4 Infrared Spectra of Samples 1, 2, 3, 4, and 5 (Average of four measurements)

Table 3 PE/PP, PS/PP, and PET/PP Ratios for Samples 1, 2, 3, 4, and 5

	PE/PP	PS/PP	PET/PP
Sample 1	9.89	0.11	0.11
Sample 2	5.29	0.21	0.14
Sample 3	0.32	0.06	0.06
Sample 4	0.29	0.15	0.01
Sample 5	0.18	0.05	0.01

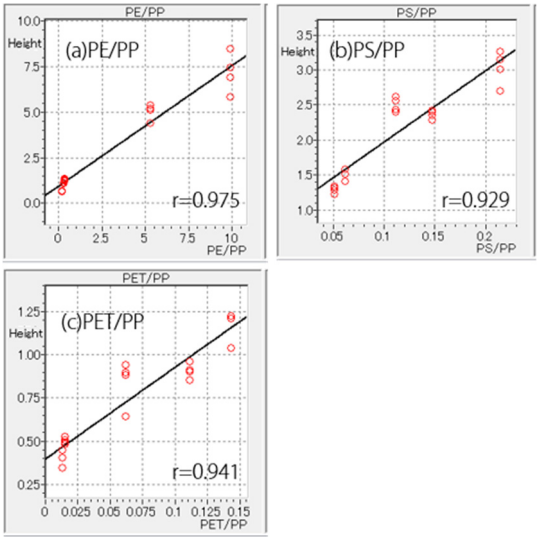

Fig. 5 Calibration Curves (a) PE/PP, (b) PS/PP, (c) PET/PP

Next, two samples with unknown concentrations were measured and mixing ratios were determined using the calibration curves shown in Fig. 5. The results are shown in Table 4. Each sample was measured five times by changing the point for measurement each time.

Table 4 Measurement Results of Mixing Ratios

Unknown 1	Measure-ment 1	Measure-ment 2	Measure-ment 3	Measure-ment 4	Measure-ment 5	Average
PE/PP	2.59	2.94	3.22	2.76	3.74	3.05
PS/PP	0.28	0.30	0.30	0.23	0.36	0.29
PET/PP	0.13	0.12	0.12	0.12	0.17	0.13
Unknown 2						
PE/PP	8.49	10.50	7.64	8.21	6.35	8.24
PS/PP	0.14	0.17	0.12	0.13	0.10	0.13
PET/PP	0.08	0.09	0.09	0.09	0.09	0.09

Using the results in Table 4, the quantitation values for PE, PP, PS, and PET were calculated according to the calculation process shown below. The results are shown in Table 5. To check the validity of the calculated composition based on measurements using FTIR, the table also lists the values obtained by using NMR as a reference.

Quantitation Value Calculation Process

Example) PE in unknown sample 1
According to Table 3: PE:PP:PS:PET = 3.05 : 1 : 0.29 : 0.13
The quantitation value of PE is:

$$100 \times 3.05 / (3.05+1+0.29+0.13) = 68.2 \text{ wt\%}$$

Table 5 Results of Quantitative Analysis Using FTIR and Reference Values Using NMR Unit: wt%

Unknown 1	Calculation Result	NMR Value
PE	68.2	56
PP	22.3	23
PS	6.6	10
PET	2.9	3
Unknown 2		
PE	87.1	89
PP	10.6	9
PS	1.4	1
PET	0.9	<1

There is a difference of up to 12 wt% between the quantitative analysis results using FTIR and the reference values obtained using NMR. Since this method does not take into account components other than PE, PP, PS, and PET, it can be expected that the difference between the obtained quantitation values and the NMR values becomes greater when the amount of such components is large.

Conclusion

This study examined simple methods for quantitative analysis of PE, PP, PS, and PET in recycled plastics using FTIR. The results suggest that for samples in pellet form, the mixing ratio calculation method described in this article may be able to obtain quantitation values that indicate a correlation with NMR values. Since the accuracy of the calibration curves greatly affects the results of quantitative analysis, further examination is necessary in selecting a typical peak that best represents each component, calculating the mixing ratio, and determining quantitation conditions.

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