Analysis of Red Phosphorus in Resins using Pyrolysis-Gas Chromatography/Mass Spectrometry

Masuo IIDA*, Kenichiro MIYATAKE and Atsushi KIMURA

Flame retardance is a very important property of polymer materials, and red phosphorus is often used as a flame retardant. Because red phosphorus contains a high level of elemental phosphorus, fire-retardant property can be obtained even when polymer materials are very lightly doped with red phosphorus. In material development, quality control, and material acceptance inspection of compound resins, it is important to qualitatively and quantitatively analyze red phosphorus contained. However, the method for analyzing red phosphorus in compound resins is not established yet, because it is very difficult to isolate red phosphorus from resins and also because red phosphorus has a low sensitivity to infrared absorption spectrometry, Raman spectrometry and X-ray diffraction. Pyrolysis-gas chromatography mass spectrometry is used mainly for analyzing organic materials, but because red phosphorus sublimes, the authors found that it shows a characteristic mass spectrum in the pyrolysis-gas chromatography mass spectrometry. This method is expected to be used for analyzing other products containing red phosphorus.

1. Introduction

Resins are used widely in applications such as protective coverings and functional components for electric wires and communication cables and adhesives for bonding these. Because flame resistance is very important to resins, various kinds of flame retardants are contained in them. There are cases where phosphorous flame retardants are used in resins. Some of well-known phosphorous flame retardants are based on either phosphate ester, halogen-containing phosphate ester, polyphosphate, or red phosphorus. Among these, red phosphorus contains a high level of elemental phosphorus, and therefore only a small amount is needed to impart resistance against flame.

In areas like material development, quality control and acceptance inspection, qualitative and quantitative analysis of red phosphorus contained in resins is important, and there are various methods of analyzing organic phosphorus flame retardants. However, the method for analyzing red phosphorus in resins has not been established yet. [(1), (2), (3), (4)] Qualitative and quantitative analysis of red phosphorus in resins is troublesome because it is difficult to separate red phosphorus from resins and collect it, and also because red phosphorus has a low sensitivity on infrared absorption spectrometry, Raman spectrophotometry and X-ray diffractometry. The authors worked on developing a method of analyzing red phosphorus in resins using a pyrolysis-gas chromatograph/mass spectrometer that requires no troublesome pretreatment. [(5)] In the past, pyrolysis-gas chromatography/mass spectrometry was exclusively used to analyze organic matter, and there had been no previous cases where solid inorganic compounds, such as red phosphorus, were analyzed using this method. However, the authors focused their attention on the fact that red phosphorus has the property of sublimation, and found that red phosphorus exhibits distinctive mass spectra in pyrolysis-gas chromatography/mass spectrometry. The authors then verified that red phosphorus in resins can be analyzed quantitatively and qualitatively through pyrolysis-gas chromatography/mass spectrometry. The results of the analysis is reported herein.

2. Experiment

When developing a method for analyzing red phosphorus in resins, the authors prepared the following samples: (1) red phosphorus (a reagent produced by Kanto Chemical Co., Inc.) and (2) a compound containing red phosphorus (ethylene-ethyl acrylate copolymer (EEA)/magnesium hydroxide/red phosphorus = 100/90/8.4). On the assumption that not only red phosphorus but also inorganic compounds such as magnesium hydroxide are added abundantly to resins in actual products, the authors used a compound containing a large amount of magnesium hydroxide in addition to red phosphorus as a sample to be examined.

These samples were analyzed using the analysis methods of infrared absorption spectrometry, Raman spectrophotometry, X-ray diffractometry and pyrolysis-gas chromatography/mass spectrometry.

In infrared absorption spectrometry, the attenuated total reflection (ATR) method was applied using a Fourier transform infrared spectrometer (Magna 560 manufactured by Nicolet Instrument Corporation). Diamond was used as the ATR crystal that comes into contact with the samples. The resolution was 4.0 cm-1, the wavelength measurement range was 4000 to 650 cm-1, and the integration frequency was 16.

In Raman spectrophotometry, the backscatter measurement method was applied using a Raman spectrophotometer (HoloProbe manufactured by Kaiser Optical Systems, Inc). The excitation wavelength was 532 nm (Nd:YAG laser pulses), the laser radiation intensity was approximately 1 mW, the resolution was 5.0 cm-

1, the wavelength measurement range was 4000 to 200 cm-1, and the integration frequency was 16.

X-ray diffractometry was carried out using an X-ray diffractometer (RINT2500 with CuK α radiation manufactured by Rigaku Corporation), at a rated output of 40 Kv, up to 200 mA.

Pyrolysis-gas chromatography/mass spectrometry was carried out by combining a pyrolysis apparatus (Double-Shot Pyrolyzer manufactured by Frontier Laboratories Ltd.) and a gas chromatography/mass spectrometer (5937N manufactured by Agilent Technologies Inc). Pyrolysis was carried out at 600˚C for 0.2 minutes. Gas chromatography/mass spectrometry was carried out under the following conditions: the column was HP-5MS (0.25 mm internal diameter, 0.25 μm thickness, 30 m length), the column He gas flow rate was 1.0 ml/min, the column temperature rise was from 50˚C to 320˚C at a rate of 25˚C/min and then retained for 5 minutes, the measurement mode was TIC mode, and the mass range was 33 to 550 m/z. The amount of the sample to be analyzed was 0.1 mg.

3. Results and Discussion

3-1 Measurement using infrared absorption spectrometry

Measurement of red phosphorus using infrared absorption spectrometry was carried out. As shown in **Fig. 1**, no infrared absorption by red phosphorus was observed and therefore it was difficult to identify infrared absorption spectrum of red phosphorus. The peak near 2200 cm-1 indicates the absorption by carbon dioxide present in the measurement atmosphere and not by red phosphorus.

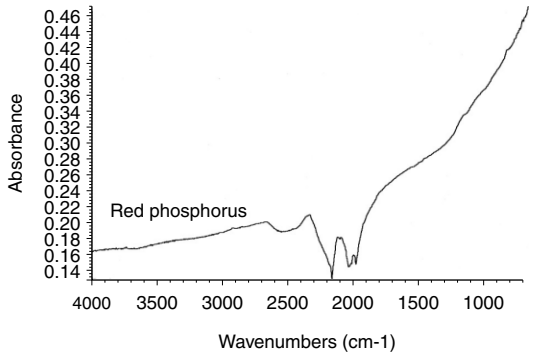

Fig. 1. Infrared absorption spectrum of red phosphorus

3-2 Measurement using Raman spectrophotometry

Measurement of red phosphorus using Raman spectrophotometry was carried out. As shown in **Fig. 2**, a Raman shift was found near 400 cm-1. The data obtained show that there is a possibility that red phosphorus is identified using Raman spectrophotometry if red phosphorus alone is measured. However, in the case of a compound, it is difficult to judge whether or not red phosphorus is contained because information from resins is dominant in the Raman spectra.

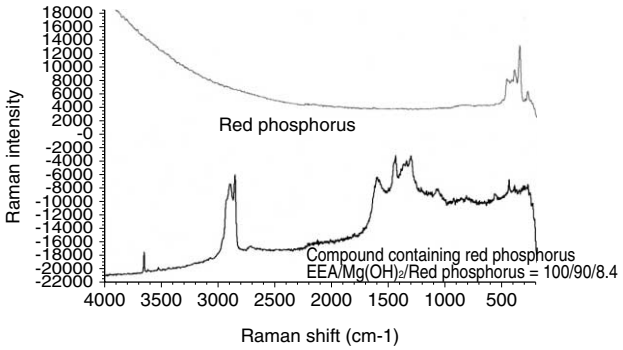

Fig. 2. Raman spectra of red phosphorus and compound containing red phosphorus

3-3 Measurement using X-ray diffractometry

The X-ray diffractometry result for red phosphorus in **Fig. 3** shows that three diffraction lines were detected. However, these diffraction lines are very broad, and therefore it is difficult to use them for qualitative analysis. It is conceivable that the broad diffraction lines were caused owing to the nonuniform strain of the crystal and the size of the crystallite. Then X-ray diffractometry was carried out on the compound containing red phosphorus. Since the compound (EEA/magnesium hydroxide/red phosphorus = 100/90/8.4) contains a large amount of magnesium hydroxide, peak information from magnesium hydroxide is dominant, and it is difficult to judge whether or not red phosphorus is contained.

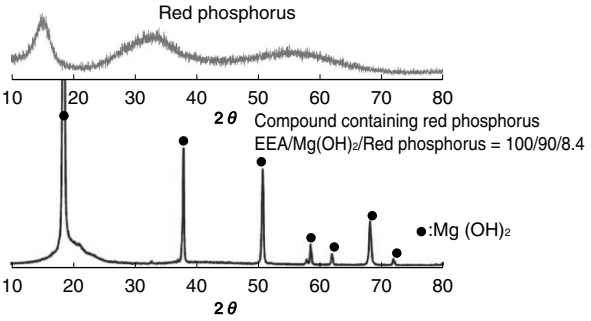

Fig. 3. X-ray diffractometry results of red phosphorus and compound containing red phosphorus

3-4 Measurement using pyrolysis-gas chromatography/mass spectrometry

Pyrolysis-gas chromatography/mass spectrometry is exclusively used to analyze organic matter, such as polymeric materials. Solid inorganic compounds, such as red phosphorus, have not been analyzed using this method. However, focusing on the fact that red phosphorus has the property of sublimation, the authors examined whether or not analysis of red phosphorus using pyrolysis-gas chromatography/mass spectrometry was possible.

Figure 4 shows the pyrolysis-gas chromatograms of

red phosphorus and the compound containing red phosphorus. In the case of red phosphorus, a peak was detected at a retention time of 4.2 minutes. As shown in **Fig. 5**, the mass spectra of this peak are observed at m/z = (31), 62, 93 and 124, and a fragment pattern indicating that red phosphorus (P_4 = 124, P = 31) was pyrolytically decomposed is obtained. Peaks were detected at intervals of m/z = 31, that is, (31), 62, 93 and 124. The reason m/z = 31 is not shown is because the mass range was set at m/z = 33 to 550 in the measurement conditions of the pyrolysis-gas chromatography/mass spectrometry for the purpose of eliminating the influence of oxygen (m/z = 32). Mass spectra exhibiting the characteristics of red phosphorus were thus obtained. Even in the case of the compound containing red phosphorus, a peak was detected at a retention time of 4.2 minutes, and it was verified that the mass spectra of this peak are observed at m/z = (31), 62, 93 and 124. The authors found that the distinctive mass spectra of red phosphorus were obtained using pyrolysis-gas chromatography/mass spectrometry and established a method for analyzing red phosphorus contained in the compound without requiring troublesome pretreatment, such as isolation and collection using solvents.

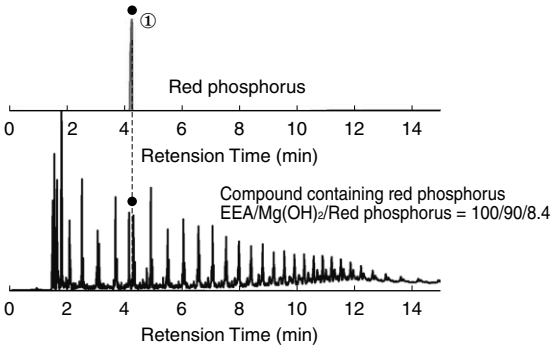

Fig. 4. Pyrolysis-gas chromatograms of red phosphorus and compound containing red phosphorus

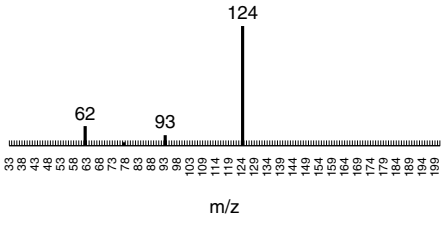

Fig. 5. Mass spectra of red phosphorus (peak ① in Fig. 4)

Figure 6 shows a flowchart for analyzing red phosphorus contained in resins using pyrolysis-gas chromatography/mass spectrometry. **Table 1** summarizes the possibility of red phosphorus analysis using various analysis methods. According to **Table 1**, red phosphorus can be analyzed using pyrolysis-gas chromatography/mass spectrometry without requiring troublesome pretreatment, such as isolation and collection using solvents, regardless of whether or not red phosphorus is present by itself or contained in a compound. The table also shows that red phosphorus cannot be analyzed using the other methods.

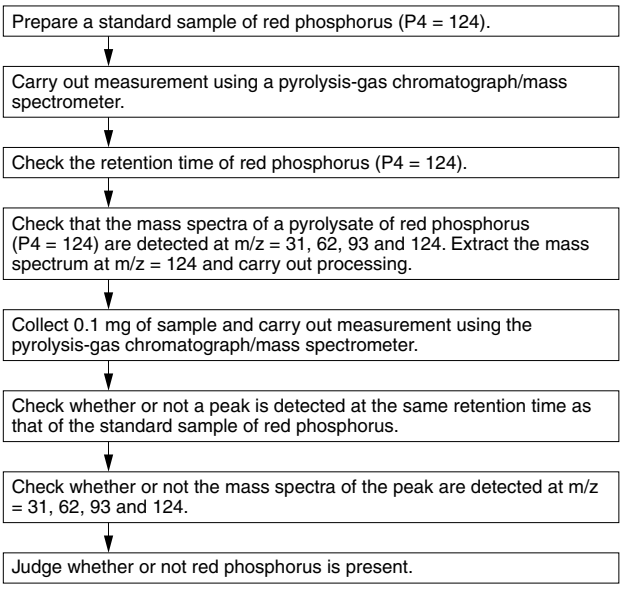

Fig. 6. Flowchart of analysis of red phosphorus in resins

Table 1. Possibility of red phosphorus analysis using various analysis methods

Analysis method	Possibility of identification	
	Red phosphorus alone	Red phosphorus in compound
Pyrolysis-gas chromatography/mass spectrometry	Possible	Possible
Elemental analysis	Not possible	Not possible
Infrared absorption spectrometry	Not possible	Not possible
Raman spectrophotometry	Possible	Not possible
X-ray diffractometry	Not possible	Not possible

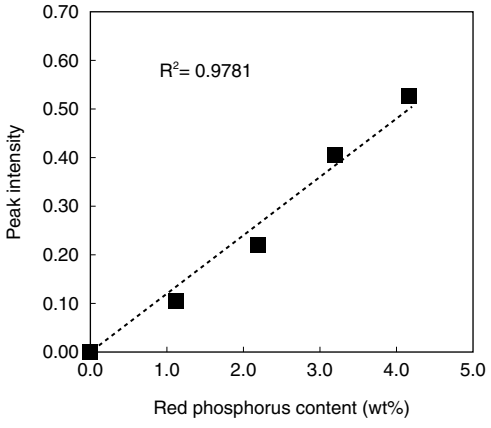

Fig. 7. Quantitative evaluation of red phosphorus using pyrolysis-gas chromatography/mass spectrometry

After clarifying that red phosphorus can be analyzed qualitatively using pyrolysis-gas chromatography/mass spectrometry, the authors also examined the quantitative analysis of red phosphorus by pyrolysis-gas chromatography/mass spectrometry. The authors prepared samples comprising EEA/magnesium hydroxide/red phosphorus in which red phosphorus was contained as described below.

EEA/magnesium hydroxide/red phosphorus
= 100/90/2.2 (red phosphorus content: 1.1 wt%)
EEA/magnesium hydroxide/red phosphorus
= 100/90/4.4 (red phosphorus content: 2.2 wt%)
EEA/magnesium hydroxide/red phosphorus
= 100/90/6.3 (red phosphorus content: 3.2 wt%)
EEA/magnesium hydroxide/red phosphorus
= 100/90/8.4 (red phosphorus content: 4.2 wt%)

As shown in **Fig. 7**, there is a high correlativity between the red phosphorus content in the resin and the peak intensity in pyrolysis-gas chromatography/mass spectrometry, and the coefficient of the correlation is 0.9781. The authors thus found that pyrolysis-gas chromatography/mass spectrometry was applicable to not only the qualitative analysis but also the quantitative analysis of red phosphorus.

Next, **Fig. 8** shows the influence of pyrolysis temperature on the detection of red phosphorus. When red phosphorus alone was measured at a pyrolysis temperature range of 300˚C to 600˚C, peaks began to be detected near 450˚C and the peak intensity became nearly constant at 500˚C and higher. This result is assumed reasonable since the sublimation temperature of red phosphorus is approximately 400˚C. According to the data obtained herein, although pyrolysis-gas chromatography/mass spectrometry is exclusively used to analyze organic matter, this method can also be used to analyze solid inorganic matter like red phosphorus, provided that it has the property of sublimation. The pyrolysis temperature of pyrolysis-gas chromatography/mass spectrometry is generally 600˚C, and resins are pyrolytically decomposed completely at this temperature. Although red phosphorus alone can be analyzed at 500˚C and higher, the pyrolysis temperature of red phosphorus in pyrolysis-gas chromatography/mass spectrometry should be 600˚C so as to prevent insufficient pyrolysis of resins.

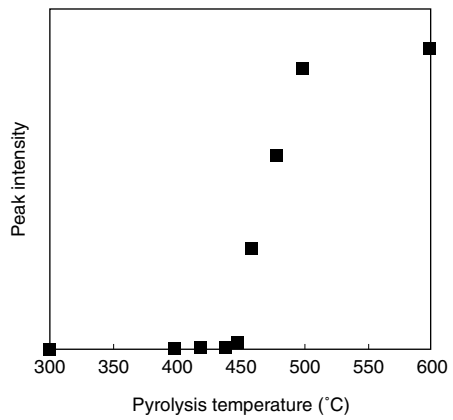

Fig. 8. Relationship between pyrolysis temperature and peak intensity

4. Conclusion

Red phosphorus is being used as a flame retardant for polymeric materials. However, no qualitative and quantitative analysis methods for red phosphorus contained in resins have been established because it is difficult to separate and collect red phosphorus from resins and also because of the low sensitivity of red phosphorus on infrared absorption spectrometry, Raman spectrophotometry and X-ray diffractometry. Pyrolysis-gas chromatography/mass spectrometry is exclusively used to analyze organic matter, such as polymeric materials, and there is no precedent in which solid inorganic compounds, such as red phosphorus, are analyzed using the method. However, focusing attention on the fact that red phosphorus has the property of sublimation, the authors found that red phosphorus exhibits distinctive mass spectra through pyrolysis-gas chromatography/mass spectrometry, and verified that red phosphorus in resins can be analyzed qualitatively and quantitatively. This analysis method can be carried out using a very small amount of sample in the order of 0.1 mg without requiring troublesome pretreatment, such as isolation and collection using solvents. This method can be used for such purposes as material development, quality control and acceptance inspection of various resin products.

References

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Contributors (The lead author is indicated by an asterisk (*)).

M. IIDA*
- Analysis Technology Research Center

K. MIYATAKE
- Assistant Manager, Analysis Technology Research Center

A. KIMURA
- Dr.Eng., Manager, Analysis Technology Research Center