Determination of Additives in Polymeric Material by Pyrolysis-GC/MS/FPD Analysis

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ABSTRACT Polymeric materials include various additives according to the demand characteristics required. It is important to conduct the qualitative and the quantitative analysis of these additives for the purposes of the product design and the quality control. On the other hand, the demand characteristics of polymeric materials have become more sophisticated and complicated in recent years, leading to the improvement and the development of additives, thus, increasing the number of cases where the conventional technology is not sufficient for the analysis. Through the usage of pyrolysis-GC (Gas Chromatograph)/MS (Mass Spectrometer) /FPD (Flame Photometric Detector) system with purged splitter installed at the end of the column during the analysis of additives in polymeric materials, which enables the simultaneous detection through MS and FPD, we were able to more easily identify the additives which included phosphorus and sulfur in their structure, as compared with the conventional pyrolysis-GC/MS method. Consideration to the determination of the precision was also given, and it was found that the results were better than those using MS detectors.

1. INTRODUCTION

Polymeric materials include various additives according to the demand characteristics required, for instance, the improvement of the formability, the physical property, the functionality or the durability. It is important to conduct the qualitative and the quantitative analysis of these additives for the purposes of the product design and the quality control. On the other hand, the demand characteristics of polymeric materials have become more sophisticated and complicated in the recent years, leading to the improvement and the development of additives, increasing the number of cases where the conventional technology is not sufficient for the analysis. For example, the pyrolysis-GC/MS analysis is a very useful method for additives in polymeric materials, because pretreatment like the solvent extraction is not necessary and enable the direct measurement of a small sample. However, it has some difficulties in identifying the original additives according to decomposing of the additives on pyrolysis condition, or masking the additive component from the decomposed materials by a matrix polymer.

When using pyrolysis-GC(Gas Chromatograph)/MS (Mass Spectrometer) /FPD (Flame Photometric Detector) system with a purged splitter installed at the end of the column during the analysis of additives in polymeric materials, we can enable the simultaneous detection through MS and FPD. Since we were able to identify more easily additives which included phosphorus and sulfur in their structure, we would like to introduce the analysis in detail[1].

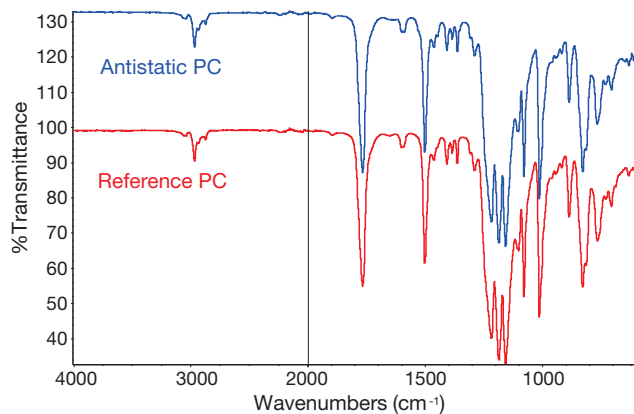## 2. ANALYSIS OF AN ANTISTATIC AGENT IN POLYCARBONATE BY THE CONVENTIONAL METHOD

We analyzed an antistatic polycarbonate pellet in the marketplace to identify the additives in the polymer by the conventional method of infrared spectrometry and the reactive pyrolysis-GC/MS.

2.1 Infrared Spectrometry

The infrared absorption spectrum measured by the attenuated total reflection (ATR) method using Fourier-transform infrared spectrometer (Nicolet Magna 550) with a single bounce ATR attachment (SensIR Technologies DuraScope)

The result is shown in Figure 1 and there is no difference between the antistatic polycarbonate and the reference polycarbonate. We could not identify absorption spectrum derived from an antistatic agent.

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Figure 1 Infrared spectrum of an antistatic polycarbonate resin. (Upper: Antistatic PC, Lower: Reference PC)

1：4-tert-Butylphenyl methyl ether；2：Bisphenol-A dimethyl ether；
3：Methyl phenyl ether

Figure 2 Reactive pyrolysis-GC/MS chromatogram of antistatic polycarbonate resin.
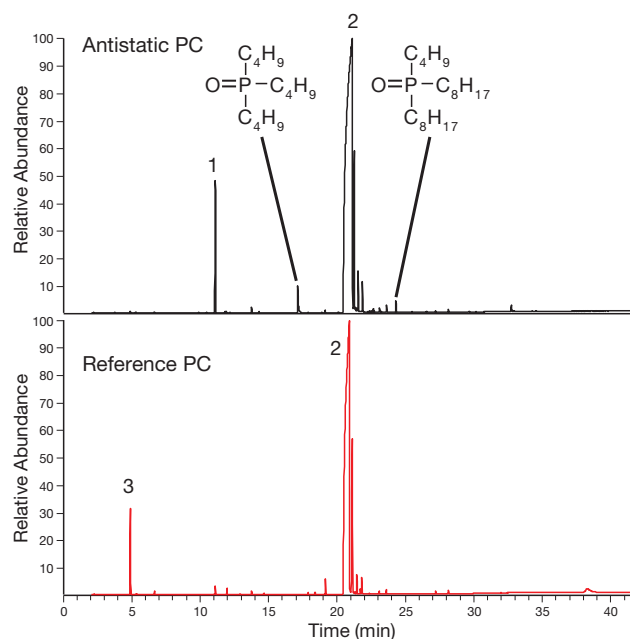
2.2　Reactive Pyrolysis-GC/MS Analysis

It is difficult in general to detect or to identify components derived from additives on pyrolysis-GC/MS analysis of polymeric materials, because a lot of thermal decomposition occurred from the matrix polymer masks small quantity of the components derived from the additives. On the other hand, additives in the polycondensation resins like polycarbonates, polyesters and polyurethanes are inclined to detect easily the component derived from the additives on reactive pyrolysis-GC/MS with hydrolysis reagents like methyl esterifying reagents. Since ester bond or urethane bond in the matrix polymer are decomposed primarily by the reagents and the decompositions derived from the matrix polymer are only monomer derivatives, it is easy to identify the component derived from the additives[2)-5)].

We tried the pyrolysis-GC/MS analysis on the antistatic polycarbonate to identify the antistatic agent. Alkaline methylation reagent (20% Tetramethylammonium hydroxide methanol solution (TMAH)) was added in a powdered sample pellet(around 0.1 mg) and the analysis condition is shown in Table 1.

Table 1　Conditions of pyrolysis-GC/MS analysis.

Apparatus	Gas Chromatography-Mass spectrometry (GC/MS); JMS-Q1050GC of JEOL Ltd. Pyrolyzer; PY-3030D of Frontier Laboratories Ltd.
Pyrolysis temperature	400℃
Column	UA-+5 of Frontier Laboratories Ltd. (Length: 30 m, Inner diameter: 0.25 mm, Film thickness: 0.25 μm)
GC Temperature	40℃ (4 min) → 10℃ /min → 320℃ (Hold)
Carrier Gas	He, 1.0 ml/min. (Constant flow)

Total ion chromatogram(TIC) of pyrolysis-GC/MS analysis on the antistatic PC and the reference PC is shown Figure 2.

Bisphenol-A dimethyl ether of a monomer derivative from polycarbonate, phenol and 4-tert-Butylphenyl methyl ether of polymer end component were detected for both of the antistatic polycarbonate and the reference polycarbonate.

With respect to the antistatic polycarbonate, Tri-butyl phosphine oxide at 17.1 min. and phosphine compound like Butyl dioctyl phosphine oxide at 24.3 min. were detected but derivatives from the surface active agent like the higher fatty acid salt generally used as an antistatic agent was not detected.

According to the result, the phosphine compound, trialkyl phosphonium oxide, was presumed to be derived from the antistatic agent, however it was not identified whether the compound is a component of the agent or a reaction product of the antistatic agent with TMAH.

## 3.　ANALYSIS WITH A REACTIVE PYROLYSIS-GC/MS/FPD

3.1　Experiment

Trialkyl phosphine oxide was detected with a reactive pyrolysis-GC/MS. In order to analyze whether it was the antistatic agent itself or the reaction product of the antistatic agent with TMAH, we tried to detect the agent with a pyrolysis GC/MS without TMAH called simple pyrolysis-GC/MS, and since the agent contained phosphine, a Flame Photometric Detector (FPD), which detects phosphine and sulfur highly selectively and sensitively, was combined to use with the pyrolysis GC/MS . This is a simultaneous analysis with pyrolysis-GC/MS/FPD[6)-9)]. Eluted material from the GC is divided into MS detector

and FPD through the purged splitter installed at the end of the column and analyzed simultaneously.

3.2　Result and Discussion

Pyrolysis-GC/MS/FPD chromatogram of the antistatic polycarbonate is shown in Figure 3.

1：4-tert-Butylphenol ；　4：Bisphenol-A
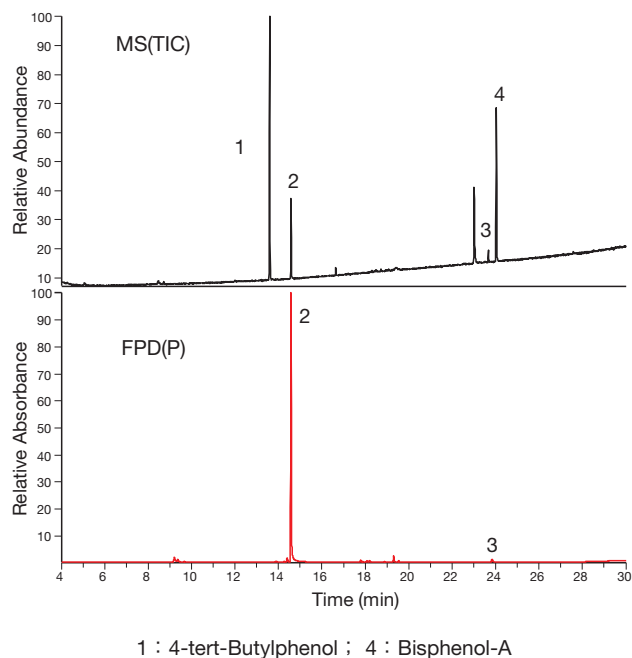
Figure 3　Pyrolysis-GC/MS/FPD chromatograph of an antistatic polycarbonate resin.

A peak at 13.6 min. of 4-tert-butylphenol based on an end group of polycarbonate and another peak at 24.0 min. of bisphenol-A were detected in the MS chromatograph (TIC).

On the other hand, a strongly reported peak 2 at 14.6 min. in the FPD chromatogram was detected and identified a Tributyl phosphine according to MS spectrum analysis on a corresponding peak of TIC, as shown in Figure 4.
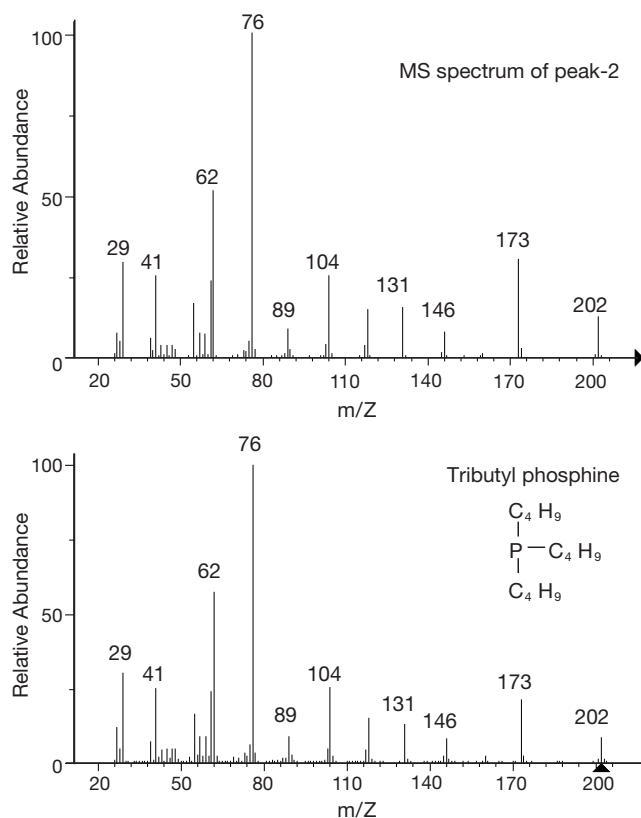

Figure 4　Identification result of peak-2.

Peak 3 at 23.8 min. of FPD was identified Butyl-dioctyl phosphine as the identification for the peak 2.

According to these results, we presumed that the antistatic agent in the polycarbonate was quaternary phosphonium salt, in detail tetraalkyl phosphonium salt, shown in Figure 5.

Since the tributyl phosphineoxide detected by the reac-
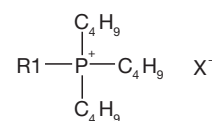
R1：Alkyl group ；　X：Anion

**Figure 5　Estimated structure of the antistatic agent.**

tive pyrolysis-GC/MS analysis was not detected by the simple pyrolysis-GC/MS analysis, we concluded that the tributyl phosphineoxide was occurred through a reaction of the quaternary phosphonium salt shown in Figure 5 or tributyl phosphine by pyrolysis of the phosphonium salt with TMAH.

A structure of the fourth alkyl group in the estimated structure of Figure 5 was unknown. In order to determine the structure, two kinds of tetra-alkyl phosphonium salt, tetrabutyl phosphonium (manufactured by Tokyo Chemical Industry Co., Ltd.) and tributylmethyl phosphonium bis (trifluoromethanesulfonyl) imide (manufactured by Tokyo Chemical Industry Co., Ltd.) were checked by the pyroly-

sis-GC/MS/FPD analysis. The result is shown in Figure 6 and Figure 7.
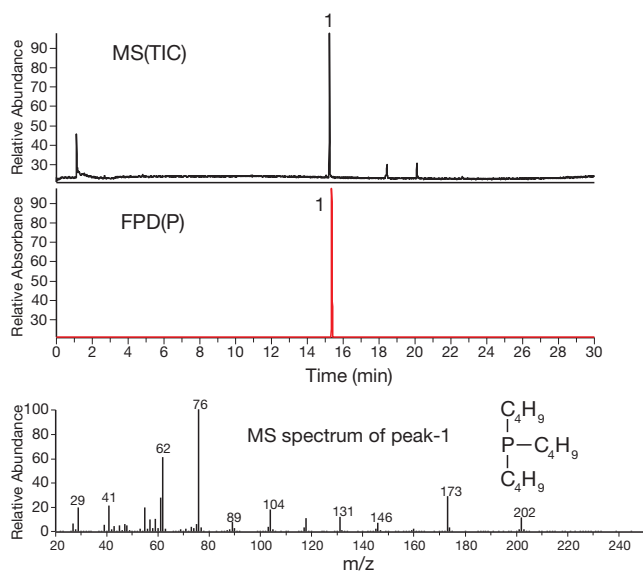
Figure 6 Analytical result of the tetrabutylphosphonium bromide with pyrolysis-GC/MS/FPD.
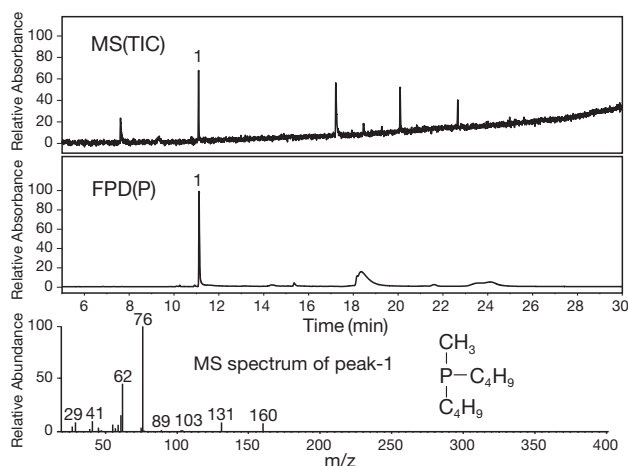
Figure 7 Analytical result of the tributylmethlphosphonium bis(trifluoromethanesulfonyl) imide with pyrolysis-GC/MS/FPD.

We had only a peak at 15.2 min. of tributyl phosphine for tetrabutylphosphonium bromide. On the other hand, we did not detect any tributyl phosphine for tributylmethylphosphonium bis (trifluoromethanesulfonyl) imide but detected at 11.1 min. methyl-dibutyl phosphine which substituted one out of three alkyl group of tributyl phosfine in the methyl group.

In order to get a structure in which phosphine bonded with three of alkyl group having same structure as tributyl phosfine, four of alkyl group bonded with phosphine have to be of the same structure. According to the above results, we presumed that the antistatic agent in the antistatic polycarbonate was tetrabutylphosphonium salt compound.

4. QUANTATIVE ANALYSIS OF AN ANTI-STATIC AGENT WITH A PYROLYSIS GC/MS/FPD

It is known to detect phosphorus additives (Phosphorus antistatic agent) highly selectively and sensitively by the simultaneous analysis with pyrolysis-GC/MS/FPD and to identify a structure of the additives. We further tried a quantitative analysis of the structure identified additives in the polymer because it is important to know the content of the additives from the product design and the quality control perspective.

Since phosphorous compounds are detected highly selectively and sensitively by the simultaneous Pyrolysis-GC/MS/FPD analysis, the quantitative analysis of the tetra-alkylphosphonium salt compound was tried.

4.1 Experiment

Tetrabutylphosphonium bromide was selected as a model compound and its methanol solution with a range of concentration were prepared. The different concentrated methanol solution of 1 μL was obtained in a sample cup and analyzed with the pyrolysis-GC/MS/FPD.

With respect to the quantitative evaluation, we made a linearity test for a calibration curve of peak area of tributyl phosphine to sample mass between FPD and MS detector.

An area peak of MS chromatogram that is a fragment of m/z=76 which is the highest intensity of MS spectrum is used for the calibration curve of the MS detector.

4.2 Result and Discussion

Figure 8 a) and b) show the calibration curve of the FPD and the MS detector respectively. Correlation coefficient (R^2) of the calibration curve for the FPD data was 0.9990 indicating a very good linearity. However, the correlation coefficient for the MS detector calibration curve was 0.9984 and it was a worse linearity than FPD.

According to the result, we understood that FPD had an advantage on the quantitative measurement for the tetrabutyl phosphonium salt compound.
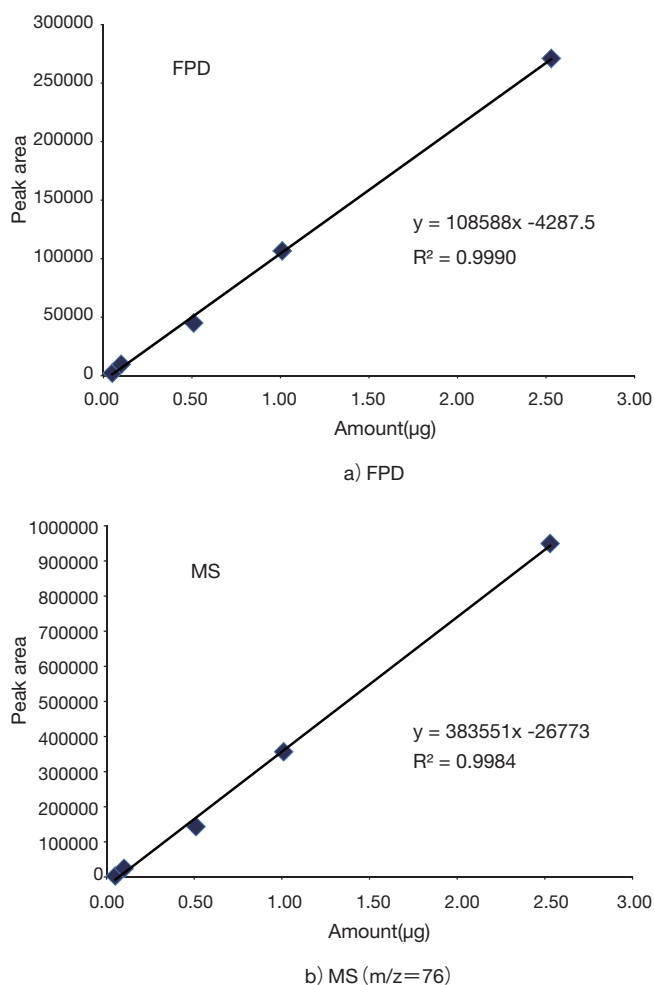
a）FPD

$y = 108588x - 4287.5$

$R^2 = 0.9990$

b）MS（m/z＝76）

Figure 8   Quantitative accuracy of the tetrabutylphosphonium bromide by pyrolysis-GC/MS/FPD analysis.

## 5.   ANALYSIS OF THE CURING AGENT IN A VULCANIZED RUBBER

5.1   Experiment

We investigated to identify a curing agent in a vulcanized rubber by the pyrolysis-GC/MS/FPD analysis.

Analysis condition for the vulcanized rubber was the same as the antistatic agent analysis except that the FPD setting was changed to detect the sulfuric compound, and pyrolysis condition was also changed.

5.2   Result and Discussion

Figure 9 shows a result of the thermal desorption-GC/MS/FPD at 300℃ for the sample rubber. According to the data for the MS detector, α-methyl styrene, acetophenone and α-cumyl alcohol were detected from 8 min. to 10 min. which were decomposed residue of dicumyl peroxide. This result would suggest the rubber to be vulcanized using peroxide.
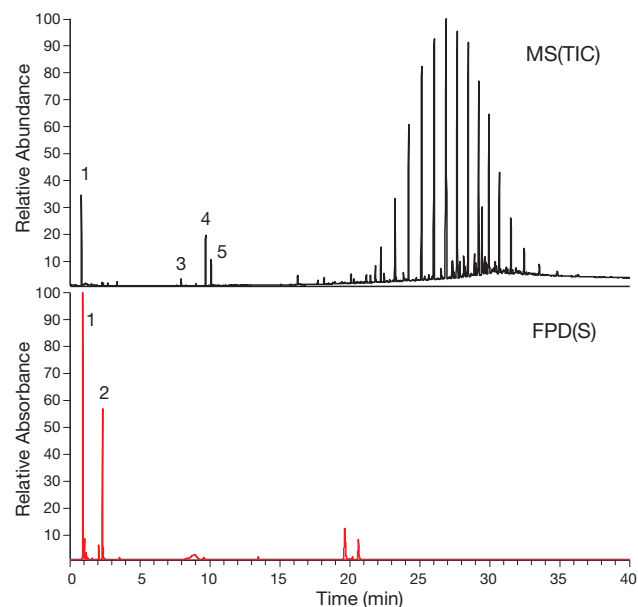

1：Methyl mercaptan； 2：Dimethyl disulfide； 3：α-Methyl styrene；
4：Acetophenone； 5：α-Cumyl alcohol

Figure 9   Result of the thermal desorption-GC/MS/FPD analysis for the vulcanized rubber.

However peak 1 at 0.9 min. and peak 2 at 2.3 min. were detected and the MS spectrum corresponding to these two peaks identified methyl mercaptan for peak 1 and dimethyl sulfide for peak 2.

Thermal residue of the rubber at 300℃ was pyrolyzed at 600℃ and analyzed with pyrolysis GC/MS/FPD. The result is shown in Figure 10 and sulfur dioxide at 1.1 min. and another two of peaks near 9.6 min. were detected.

We analyzed the 9.6 min. peak in detail with the MS spectrum and identified 2,5-cyclopenta[2,3-b]thiophene with a molecular weight of 122.
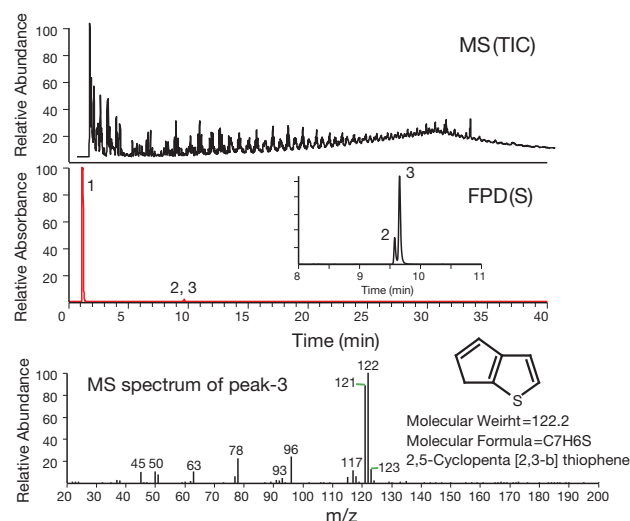
1：Sulfur dioxide； 2：2,4-Cyclopenta [2,3-b] thiophene；
3：2,5-Cyclopenta [2,3-b] thiophene

Figure 10 Result of the thermal desorption-GC/MS/FPD analysis for the vulcanized rubber.

It is reported that on pyrolyzing a sulfur vulcanized ethylene propylene diene rubber (EPDM) with ethylidene norbornene (ENB) as third component, the compound component is derived from crosslink of ENB with sulfur[10)-12)].

According to the above result and C-S bonded material detected on heating at 300℃, the rubber sample was presumed vulcanized with inorganic sulfur.

Since sulfur curing and peroxide curing are not used in combination in general, the residue of the peroxide compound detected in Figure 9 was presumed a trace on contacting other peroxide cured material.

In the case of analysis for cured rubber, the conventional analysis using only the MS detector does not identify the decomposition corresponding to the sulfur cured rubber because of its masking by the decomposition of the matrix polymer. However analysis in combination with the MS and the FPD detect a decomposition of sulfur cured rubber easily, rapidly and accurately.

6. CONCLUSION

We succeeded to analyze phosphorus and sulfur additives in polymeric materials selectively and sensitively with pyrolysis-GC/MS/FPD.

With the pyrolysis-GC/MS/FPD, with purged splitter installed at the end of the column during analysis of additives in polymeric materials, we can enable the simultaneous detection through the MS and the FPD.

We can identify the structure of the compounds more easily than the conventional method and can make quantitative analysis highly selectively and more accurately.

Since phosphorus and sulfur additives are used not only in the polymeric materials mentioned above but in many product of coated materials on wire & cable, rubber splicer and end splicer of power cable, and a regulation for environmental loading will be tightened, we would like to apply this analysis to material development, quality control and solution for environmental regulation and also to improve analysis technology.

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