

Ethylene Propylene Diene Monomer Rubber Analysis by using Pyrolysis-GCxGC-MS

Product used : Mass Spectrometer (MS)

【Introduction】

Recently, we developed a new gas chromatography/high resolution time-of-flight mass spectrometer (GC/HR-TOFMS) system which allows using multiple ionization techniques not only electron ionization (EI) but also field ionization (FI) and photo ionization (PI).

FI is a soft ionization technique that is well suited for hydrocarbons analysis because it generates molecular ions with minimal fragmentation for all compounds, including saturated hydrocarbons. PI is an also soft ionization technique that provides high sensitivity and molecular ion information for compounds with ionization energies below the maximum practical photon energy (10.8 eV) of the deuterium lamp used in our current design.

In this study, pyrolysis(Py)/GCxGC/HR-TOFMS system was applied to investigate the pyrolysis products of Ethylene-propylene–diene rubber (EPDM).

【Result and discussion】

To evaluate the potential of Py/GCxGC, we compared the chromatographic peak separation between regular 1DGC and 2DGC (Fig.1) measured by EI. In the 1DGC data, a lot of co-elute components were observed and they were difficult to identify clearly. In the 2DGC data, these compounds were separated with 2nd GC dimensions and we observed approximately 1,023 compounds in the EPDM sample using an automatic peak search function for the GCxGC/EI data.

Table 1 Measurement condition

【Pyrolysis condition】

Pyrolysis Temp.: 650 °C

【GCxGC condition】

1st column: BPX5(SGE), 30m x 0.25mm, 0.25um

2nd column: BPX50(SGE), 2m x 0.1mm, 0.1um

Oven temp.: 50 °C (1 min) -> [5 °C/min]

-> 320 °C (10 min)

Inj. Temp.: 300 °C

Inj. Mode: Split mode (100:1)

Column flow: 1.8 mL/min

Modulation period: 5 sec

【MS condition】

Ion source: EI/PI combination ion source

EI/FI combination ion source

Ionization: EI+, 70 eV, 300 uA

PI+, D₂ lamp: 115-400 nm
(10.8 eV@115 nm)

FI+, -10kV, 8mA/10msec

Mass range: *m/z* 35-650

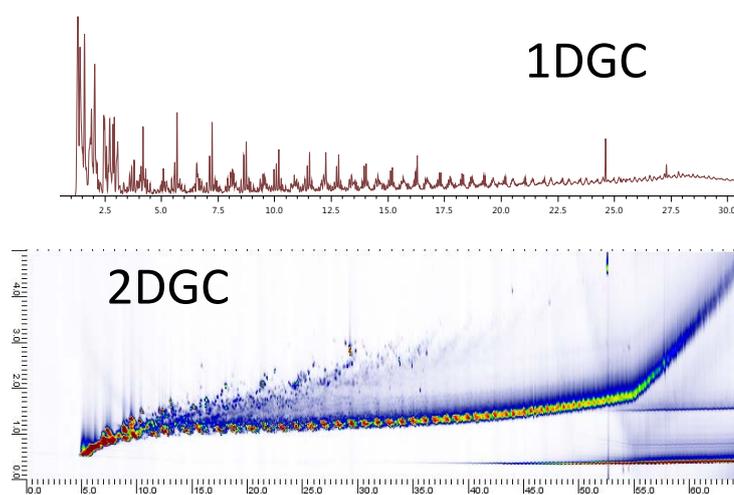


Fig.1 Comparison of the 1DGC and 2DGC TICs

We got excellent chromatographic separations not only EI method but also soft ionization methods, PI and FI (Fig.2). We identified pyrolysis products using NIST EI database search (Fig.3).

On the other hand, there were many un-known components which cannot be identified using EI database with lower match factor. In this case, we estimated these chemical formulas from the accurate *m/z* values of these molecular ions in FI and PI mass spectra. For example, we showed accurate mass analysis about compound A. We got 6 candidate for the molecule formula. The measured *m/z* and isotopic pattern is most similar with C₂₃H₂₆N₂. So, we suspected that this compounds is Polymerized 2,2,4-trimethyl-1,2-dihydroquinoline which is used as **Rubber Antioxidant TMQ**

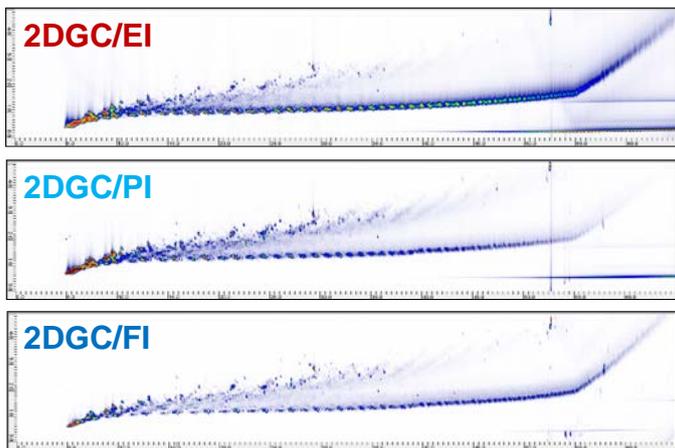


Fig. 2 GCxGC/EI, PI and FI TICCs

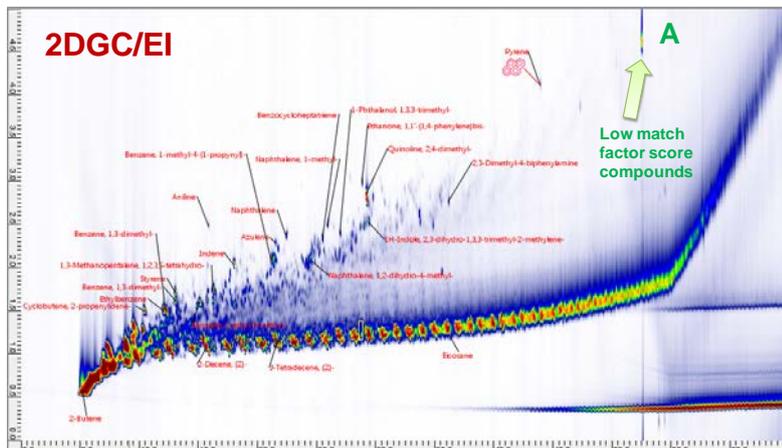
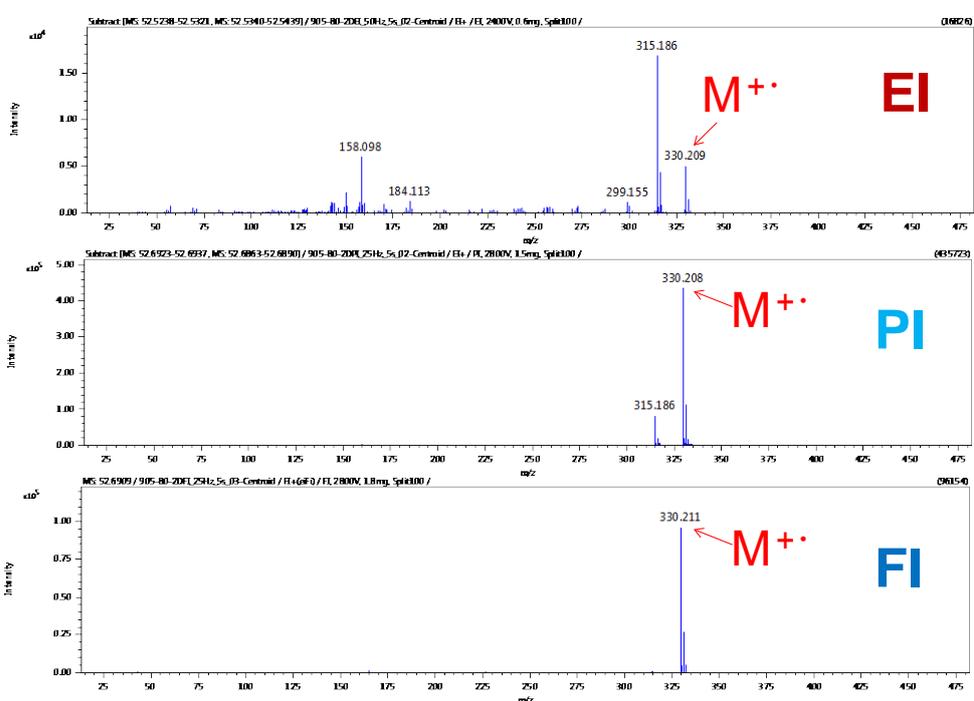


Fig. 3 GCxGC/EI qualitative analysis result



Mass	Formula	Calculated Mass	Mass Error [mDa]	DBE
77.0395	C6 H5	77.0386	1.0	4.5
91.0554	C7 H7	91.0542	1.2	4.5
115.0548	C9 H7	115.0542	0.6	6.5
143.0740	C10 H9 N	143.0730	1.0	7
158.0975	C11 H12 N	158.0964	1.1	6.5
184.1133	C13 H14 N	184.1121	1.2	7.5
222.1287	C16 H16 N	222.1277	0.9	9.5
299.1546	C21 H19 N2	299.1543	0.3	13.5
315.1855	C22 H23 N2	315.1856	-0.1	12.5
330.2088	C23 H26 N2	330.2091	-0.3	12

Mass	Formula	Calculated Mass	Mass Error [mDa]	DBE
315.1860	C22 H23 N2	315.1856	0.4	12.5
330.2085	C23 H26 N2	330.2091	-0.6	12

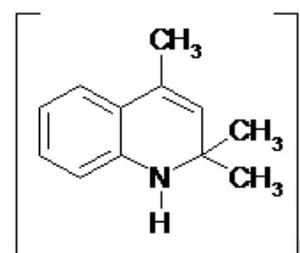
Mass	Formula	Calculated Mass	Mass Error [mDa]	DBE
330.2111	C23 H26 N2	330.2091	2.1	12

Fig.4 Mass spectra and accurate mass analysis for the compound A on the 2DGC TICC.

【Conclusion】

- We can get excellent GCxGC separations for EI and soft ionizations, PI and FI.
- EI database search is still first step for the GC/MS qualitative analysis.
- Soft ionizations and accurate mass analysis is useful for the compound identification.

The combination of PY/GCxGC/HRTOFMS and multiple ionization technique is a quite useful for qualitative analysis of the pyrolysis products of rubbers.



TMQ

