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Application News

No. AD-0093

Polymer / GCMS-QP2010 Ultra PY-3030

Characterization of Rubber Materials by Multi-Functional Pyrolyzer GC-MS Approach with Pyrolyzate Library

❑ Introduction

Rubber is an elastomer material which has been used extensively in our daily life. About 26 million tones of rubbers are produced annually. There are over 200 types of synthetic rubbers which are account for about 70% of the total rubber production [1]. Synthetic rubbers are produced by polymerization of monomers. Vulcanization is a chemical process to cure rubber using sulfur and heat for better durability and desired physical properties of rubber products. In addition to sulfur, other additives such as zinc ligands and benzothiazole derivatives are used to activate and accelerate the vulcanization process. After vulcanization, antioxidant additives may also be added to enhance the rubber's longevity. Desirable properties of rubbers can be obtained by adding various types of additives in the manufacture process [2].

Due to the complexity of rubber materials, characterization of chemical properties and composition of rubber materials is tedious and costly. Rubbers mainly consist of two types of components, the polymeric backbones and the additives. The polymer backbone is commonly characterized by nuclear magnetic resonance (NMR) [3], while the additive is analyzed by thermogravimetric Fourier transform infrared spectroscopy (TG-FTIR) [4]. For a comprehensive study of the organic components in rubber materials, a multi-functional Pyrolyzer-Gas Chromatography-Mass Spectrometry system (Py-GC-MS) has been developed and used to characterize both polymeric backbone and the additives components in recent years. The Pyrolyzer uses strong heat to desorb and pyrolyze the organic compounds from rubber samples in a heating process, whereas the GCMS enables separation, detection and identification of the released compounds. In this Application News, we describe the analysis procedure of pyrolysis to characterize and identify the additives and backbone of unknown rubber samples through distinctive chromatographic fingerprints and dedicated additives-polymer MS libraries [5].

❑ Experimental

Preparation of Test Sample

Approximately 0.5mg of an unknown rubber sample was cut and weighed into an eco-cup. The eco-cup is a customized stainless cup coated with stabilizer for high temperature heating process. Then, the eco-cup was placed to the Pyrolyzer Autosampler for analysis. No other pretreatment was required. The sample preparation is illustrated in Figure 1.

Instrument and Analytical Conditions

Shimadzu GCMS-QP2010 *Ultra* was equipped with multi-Functional Pyrolyzer, PY-3030D from Frontier Lab along with an autosampler, AS-1020E. Sample analysis was carried out in two steps: Evolved Gas Analysis (EGA) and Heart Cut Analysis.

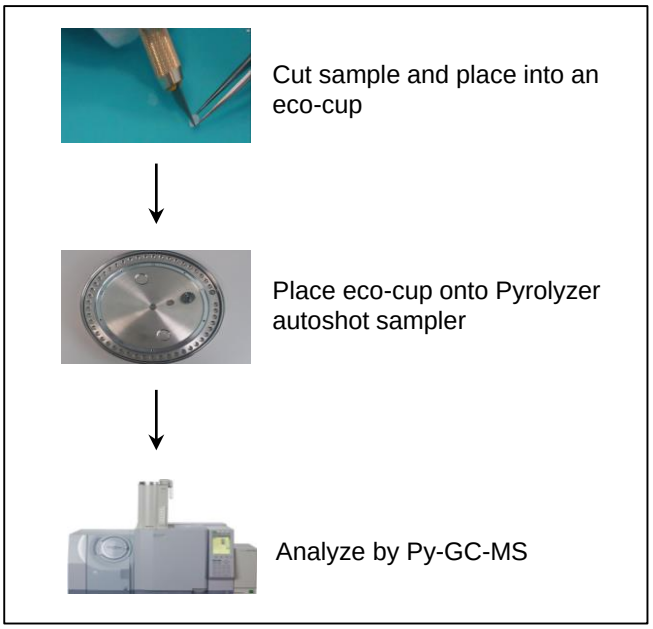


Figure 1: Preparation of rubber for Py-GC-MS analysis

Evolved Gas Analysis (EGA)

First, the EGA is carried out to obtain a thermogram of the rubber sample studied. The rubber sample was heated continuously under an helium environment from 100ºC to 800ºC. All the compounds evolved from the rubber were directed into the MS detector through a deactivated guard column connecting between the GC injection port and the MS. A thermogram of the sample was generated, from which the appropriate temperatures to extract additives and pyrolyzate of the rubber sample was revealed. The analysis condition is shown in Table 1.

Heart Cut Analysis

After suitable extraction temperatures were established through above EGA experiment, the rubber sample was heated at the temperatures of different heating regions. The compounds evolved were directed into a separation column installed in the GC-MS. In this analysis, step of the rubber sample, organic compounds were evolved mainly at two temperature regions. The details of the analysis condition was shown in Table 1. The principle of full analysis process is illustrated in Figure 2.

Table 1: Analysis parameter of Part 1 (Evolved Gas Analysis) and Part 2 (Heart Cut Analysis)

	Step 1	Step 2
Pyrolyzer		
Pyrolysis Mode	Evolved Gas Analysis (EGA)	Heart Cut Analysis
Temp. Program	100ºC → 20ºC/min → 800ºC	Zone A: 200ºC → 20ºC/min → 300ºC Zone B: 400ºC → 20ºC/min → 500ºC
Interface Temp.	300ºC	300ºC
GC		
Injection Temp.	300ºC	300ºC
Injection Mode	Split	Split
Linear Velocity	52.3cm/sec	40.0cm/sec
Split Ratio	20	20
Column	IP Direct 5.0m x 0.15mm	Ultra-Alloy5 (HT/MS) 30.0m x 0.25mm x 0.25µm
Column Oven Temp.	300ºC (35min)	40ºC (1min) → 20ºC/min → 300ºC (1min)
MS		
Ion Source Temp.	250ºC	250ºC
Interface Temp.	300ºC	300ºC
Acquisition m/z	Scan (50-400m/z)	Scan (50-400m/z)

❑ Results and Discussion

Evolved Gas Analysis (EGA) and Heart Cut Analysis

The thermogram of EGA of the rubber sample (Figure 3) indicates that main components were evolved from the sample at temperature zone A and zone B. Zone A ranges from 200ºC to 300ºC and zone B from 400ºC to 500ºC. In the lower temperature zone A, additives are evolved because of their weaker bonding with the polymer chains. Upon mild heating, the additives were thermally desorbed from the rubber sample. When the pyrolyzer temperature was elevated to above 400ºC, the rubber polymeric backbone started to breakdown into different oligomers.

Upon heating up to the respective temperature zone, the evolved compounds were directed into the GC-MS. The organic compounds were separated into individual peaks by the GC separating column and detected by the MS. Total ion chromatograms from zone A and zone B are shown in Figures 4 and 5.

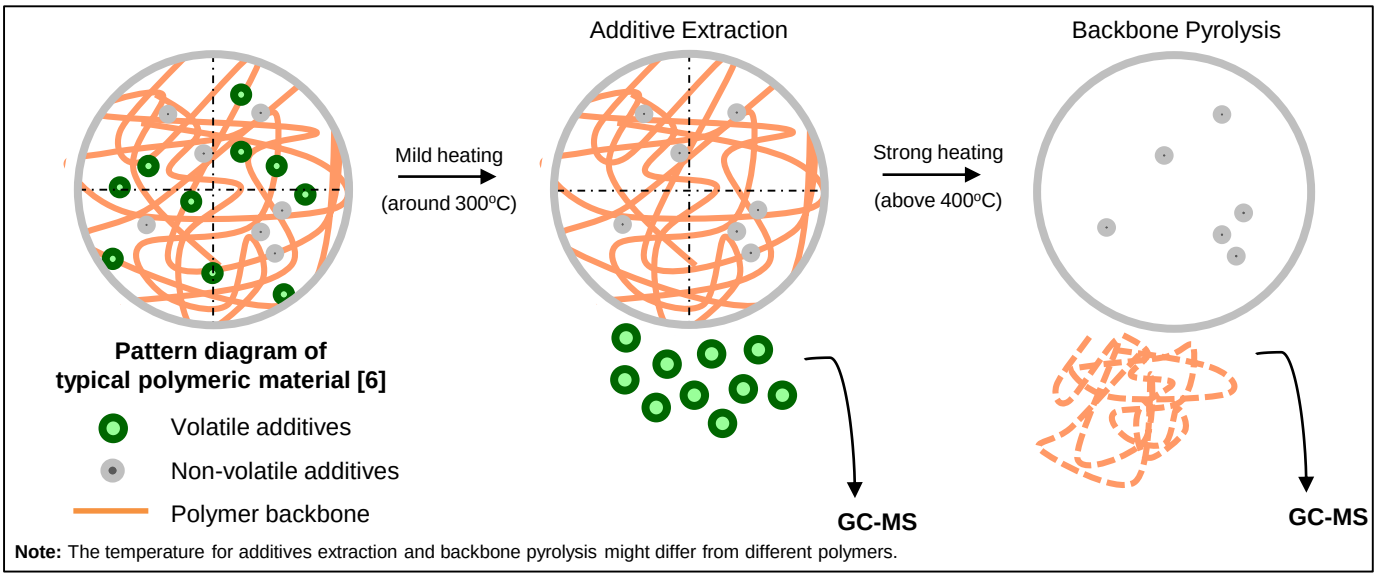


Figure 2: Principle of polymer analysis by pyrolysis on Py-GC-MS

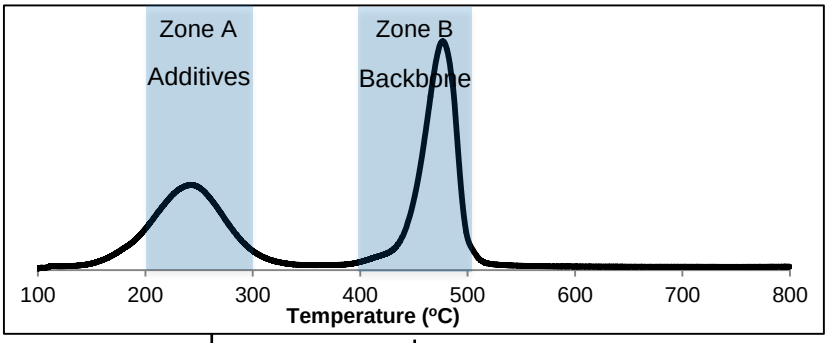


Figure 3: Thermogram of an unknown rubber sample by Evolved Gas Analysis (EGA) method

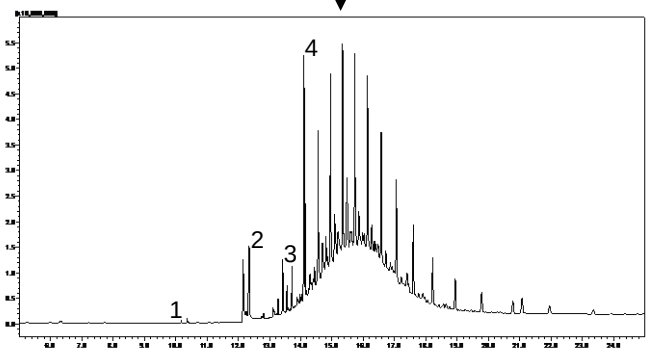


Figure 4: Chromatogram of evolved components from Zone A

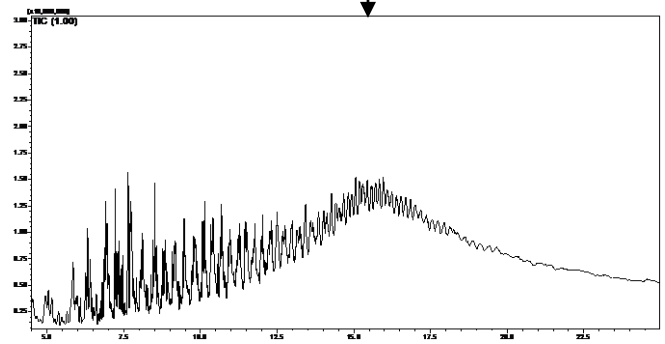


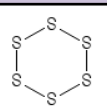
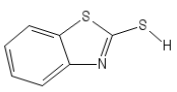
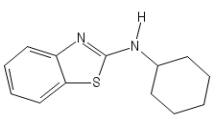
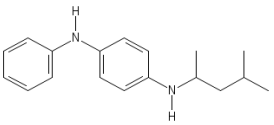
Figure 5: Chromatogram of evolved components from Zone B

PY-GC-MS results of Zone A and Zone B

The GC-MS results of Zone A reveal that vulcanization agents and antioxidants were evolved, corresponding to Peaks 1~4 in Figure 4. The identification information of the four peaks is summarized in Table 2. Sulfur (Peak 1) and 2-mercaptobenzothiazole (Peak 2), which are commonly vulcanization agents, were found in the unknown rubber sample studied. Peak 3 is identified to be N-cyclohexyl-2-benzothiazolamine, which is an inhibitor used for controlling the vulcanization process. Peak 4 is confirmed to be 1,4-benzenediamine,N-(1,3-dimethyl butyl)-N'phenyl, which is a commonly used antioxidant known as the trade name of Akcochem Antiozonant PD-2. The role of this additive is to protect rubber from degradation. Apart from these four peaks, other peaks were mainly consist of hydrocarbons.

The pyrogram of the degraded rubber in Zone B above 400°C is shown in Figure 5. The GC-MS analysis results indicate that the polymeric backbone of the rubber studied started to pyrolyze and decompose into oligomer fragments. It is worth to note that the conventional mass spectrum library of GC-MS could not be used for identification of the components due to the oligomers possessing very similar mass spectra of the hydrocarbon chains. The peak identification was investigated via the matching of chromatographic profile and mass spectrum from a F-Search Pyrolyzate library [5] developed for Py-GC-MS analysis of polymeric materials. Figure 6 shows

Table 2: List of additives found in an unknown rubber from Zone A (200°C~300°C)

Peak No.	Retention Time (min)	Compound Name	Chemical Structure	CAS No.	Application
1	9.805	Sulfur		13798 – 23 – 7	Vulcanization agent
2	12.350	2-Mercaptobenzothiazole		149 – 30 – 4	Vulcanization agent
3	13.420	N-Cyclohexyl-2-benzhiazolamine (NCBA)		28291 – 75 – 0	Vulcanization Inhibitor
4	14.090	1,4-Benzenediamine, N-(1,3-dimethylbutyl)-N'-phenyl-		793 – 24 – 8	Antioxidant

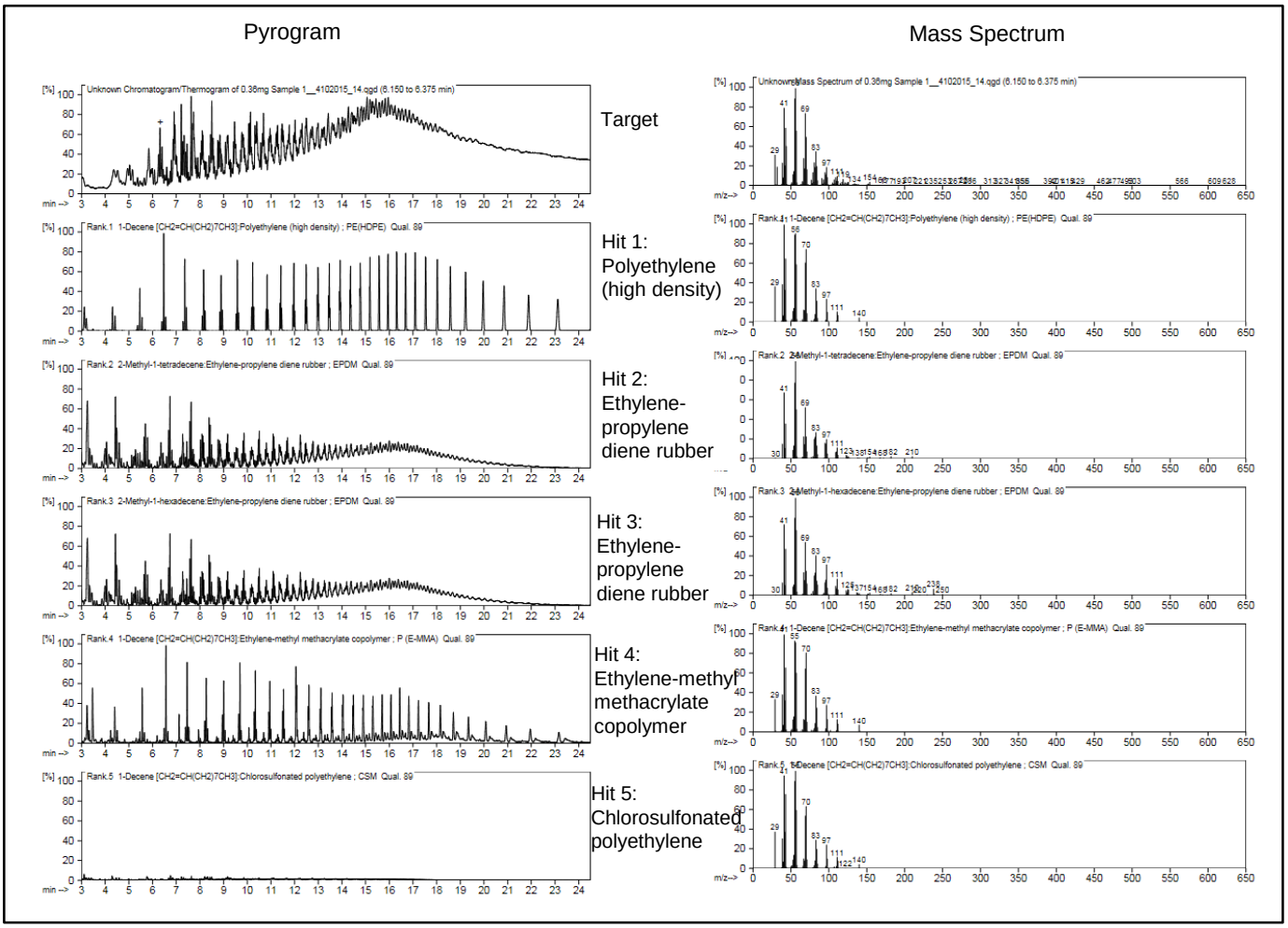


Figure 6: Top five hits obtained from F-Search Pyrolyzates library search of the unknown rubber pyrogram and mass spectrum (top)

the research result (showing the top five hits of similarity) in the Pyrolyzate library. The unknown rubber pyrogram matches perfectly Etheylene-Propylene Diene with the mass spectrum similarity of 89% (both hit 2 and hit 3).

❑ Conclusions

This study shows an approach for characterization of rubber composition by Py-GC-MS with F-Search Library. The analysis is carried out in two steps, i.e., evolved gas analysis (EGA) and heat cut analysis which generates GCMS chromatograms for two pyrolysis zones (A & B). The components from the chromatogram of Zone A (200-300ºC) are mainly rubber additives such as vulcanization agents, vulcanization inhibitors and antioxidants. The type (backbone) of the rubber studied can be identified from the chromatogram of Zone B (400-500ºC) through pyrolyzate library search for matching both pyrogram and mass spectrum.

❑ References

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