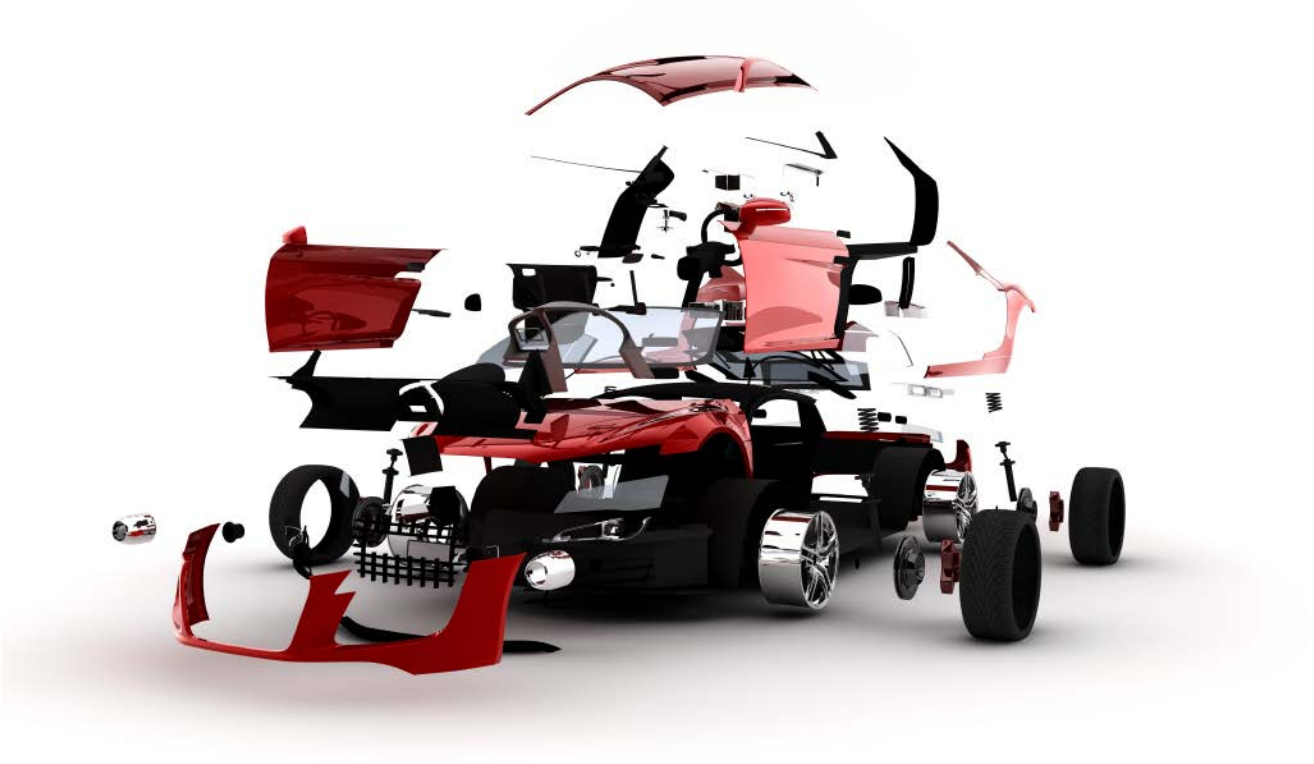
Material Characterization in the Automotive Industry Using Multi-Mode Pyrolysis GC/MS:

A COMPREHENSIVE GUIDE FOR PYROLYSIS GCMS TECHNIQUE AND ITS USE IN THE AUTOMOTIVE INDUSTRY



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Why Pyrolysis GC/MS?

Automotive manufacturers are always seeking new technologies and developments that increase production efficiency and the quality of the produced vehicle's parts.

Many analytical protocols used to analyze automotive components require multi-step sample preparation prior to chromatographic analysis. These procedures often include solvent extraction, filtration, and concentration. These traditional techniques are cumbersome, time-consuming, and suffer from analyst-to-analyst variability while producing data of limited value.

Samples are analyzed "as is" when using the Frontier pyrolyzer. No sample preparation is needed. Eliminating the solvent extraction process enhances the precision of quantitative analysis while virtually prevent sample contamination and improves analytical efficiency. These are three of the primary reasons many manufacturing and polymer development laboratories serving the automotive industry utilize the Frontier Pyrolyzer.

The Frontier Multi-Shot Pyrolyzer can be configured in a number of different ways, so that a sample can be characterized using various analytical techniques, including evolved gas analysis, thermal desorption, flash pyrolysis, double-shot, Heart-Cutting of individual EGA thermal zones and reactive pyrolysis. Initially, such diversity may be perceived as a complicated decision process: what analytical mode will give us the most insight into the nature of the sample in the least amount of time? To assist, Frontier scientists have created a "method map". An overview of the "method map" is provided on page 38.

Analytical Problems and Frontier-Based Solutions

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A-1

Analysis of Polymerization Reagents Incorporated into Poly (Methyl Methacrylate) Chains

Problem: Is there a way to characterize polymerization reagents incorporated into poly(methyl methacrylate) chains by Py-GC?

Solution: PMMA samples were prepared both with and without polymerization reagents. A pyrolyzer was attached to a GC with an FID or a flame photometric detector (FPD). Identification of peaks on the pyrograms was done using a GC-MS with both EI and CI sources.

Results: Figure 1 shows the pyrograms of samples prepared both (a) in the presence and (b) in the absence of polymerization reagents at 460˚C. Since PMMA tends to depolymerize mostly into the original monomer at elevated temperatures around 500˚C, the main pyrolysis product on the pyrograms (>90%) was the MMA monomer. As noted, peaks A through I are not observed on the pyrogram (b). Therefore, they can be assigned to the fragments of the polymerization reagents incorporated into the polymer chain.

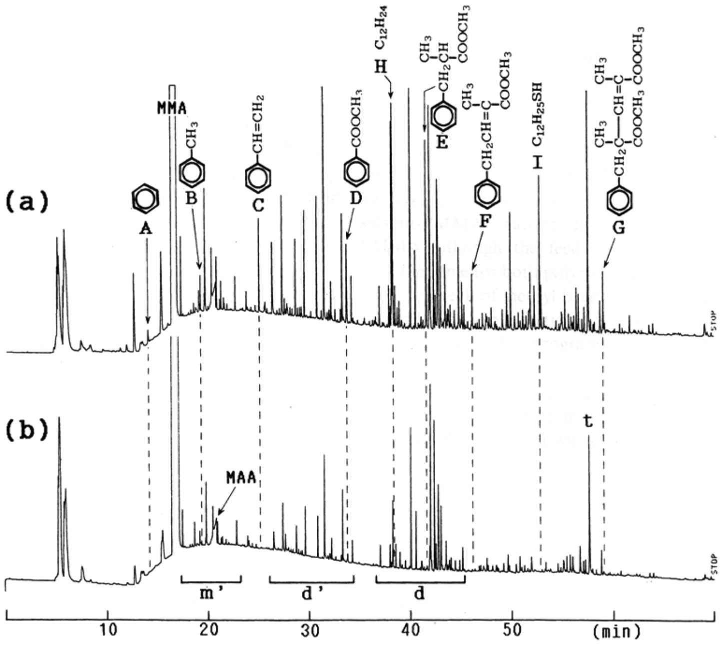


Fig. 1 Pyrograms of poly (methyl methacrylate): prepared in toluene with 0.3% of benzoyl peroxide and 1.5% of dodecanethiol; and thermally polymerized in bulk without any polymerization reagent.

Ref: Multi-functional Pyrolyzer® Technical Note, PYA1-036E

A-2

Analysis of the End Groups in Radically Polymerized Poly (Methyl Methacrylate)

Problem: Has the end groups in radically polymerized poly(methyl methacrylate) been studied by Pyrolysis-GC?

Solution: PyGC technique was used to characterize the end groups of PMMA samples which had been radically polymerized in toluene with BPO. 0.5mg of the polymer sample was pyrolyzed at 460˚C under nitrogen.

Results: Fig. 1 shows the pyrograms of PMMA samples polymerized with 0.3% of BPO as the initiator in toluene, in benzene, and thermally polymerized without any reagents, respectively. Generally, the main pyrolysis product (>95%) is the MMA monomer formed. Among these, several peaks (A through G) on the pyrogram (a) are identified as the products having a phenyl ring, all of which are scarcely observed on the pyrogram (c). Also, peaks B (toluene), C (styrene) and F are exclusively observed in (a). Therefore, these three products should be derived mainly from the solvent fragments incorporated into the chain ends through the chain transfer to toluene.

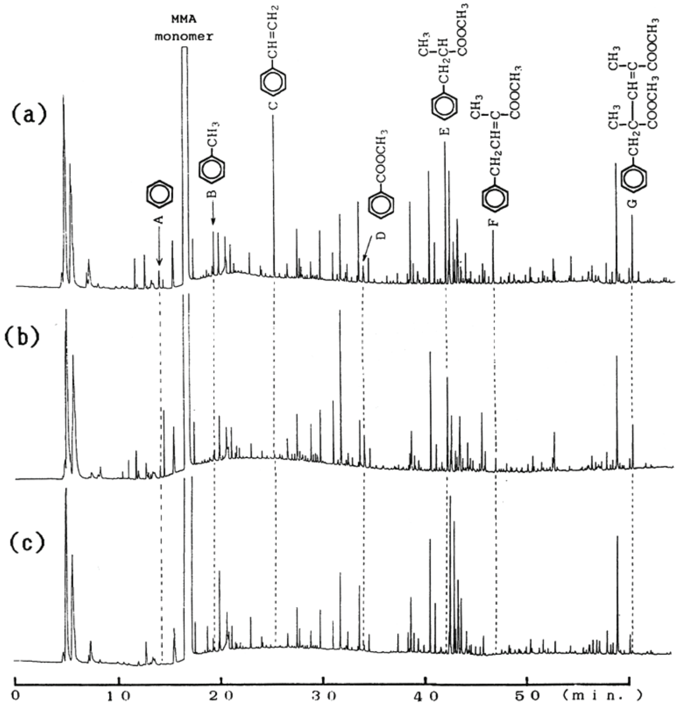


Fig. 1 Pyrograms of PMMA samples obtained at 460°C
(a) polymerized in toluene,
(b) polymerized in benzene, and
(c) polymerized without any initiator.

Ref: Multi-functional Pyrolyzer® Technical Note, PYA1-038E

A-3

Analysis of the Constituent Monomers of Polybutylene Terephthalate (PBT)

PROBLEM: Is there a simple analytical method to observe the constituent monomers of polybutylene terephthalate (PBT)?

SOLUTION: When analyzing condensation polymers such as polybutylene terephthalate (PBT) by Py-GC technique, reactive pyrolysis in the presence of tetramethyl ammonium hydroxide (TMAH) gives constituent monomer of methyl ester.

RESULTS: Fig. 1 shows a pyrogram obtained by flash pyrolysis of PBT, and Fig 2 shows a pyrogram obtained by reactive pyrolysis in the presence of TMAH. Flash pyrolysis technique gave products arising from decomposition and decarboxylation of ester group, but no monomer. On the other hand, reactive pyrolysis gave PBT constituent monomer of dimethyl derivatives of terephthalic acid and mono and dimethyl derivatives of 1,4-butanediol.

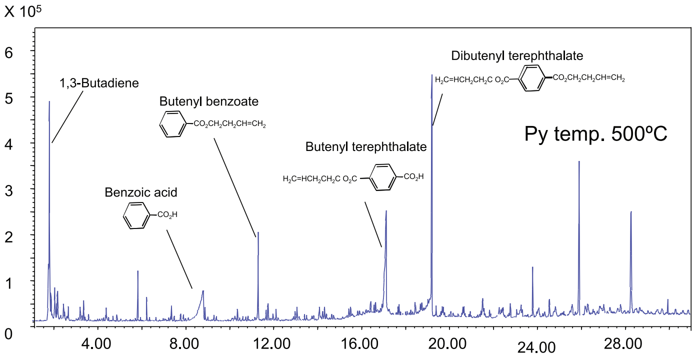


Fig. 1 Pyrogram obtained by flash pyrolysis of PBT

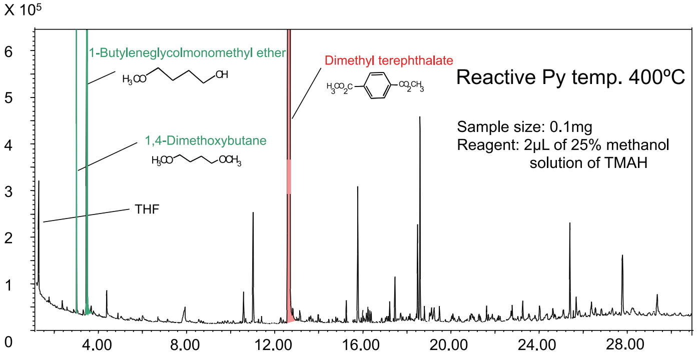


Fig. 2 Pyrogram obtained by reactive pyrolysis of PBT

Carrier gas: He, Injection port pressure: 103kPa, Split ratio: 1/60, Separation column: Ultra ALLOY+-5 (5% diphenyldimethylpolysiloxane) L=30m, Id=0.25mm, df=0.25μm, GC oven temp: 38°C~300°C (20°C /min)

Ref: Multi-functional Pyrolyzer® Technical Note, PYA2-005E

A-4

Investigation of Sequence Distributions of Polyacetal (PA)

PROBLEM: Is there a technique to obtain information about the sequence distributions of polyacetal (PA)?

SOLUTION: Multi-component copolymers of PA, containing 1-9 mol% of oxyethylene units [(-OCH2CH2-)(E)] against the main chain oxymethylene units [(-OCH2-)(F)], are analyzed. The PA sample combined with solid cobalt sulfate (CoSO · 7H2O) catalyst is frozen and pulverized. About 100 µg of the powder sample is placed in the sample cup prior to reactive pyrolysis GC/MS at 400°C.

RESULTS: The pyrogram from the reactive pyrolysis GC/MS for the PA sample is shown in Fig.1. A series of cyclic ethers consisting of E and F units are observed. This reflects the sequence structures of E units in the original polymer chain. From the relative peak intensity of these cyclic ethers, it is possible to estimate the E unit content in the polymer sample as well as the sequence distributions.

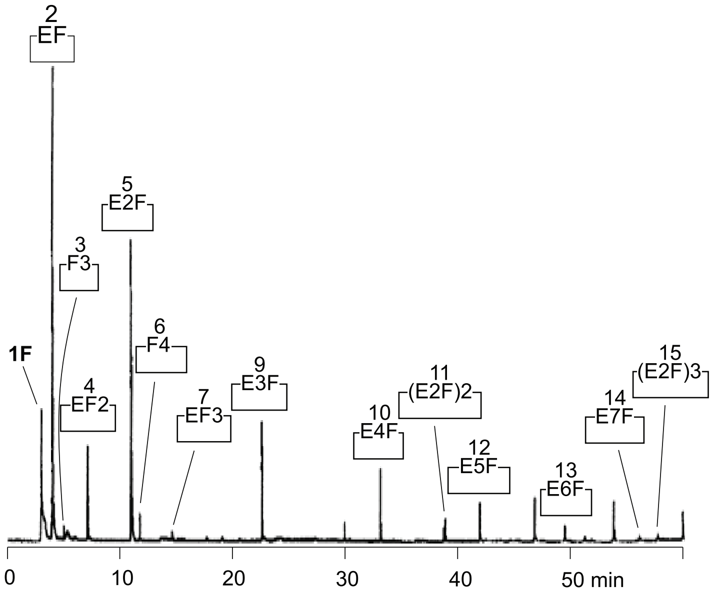


Fig. 1 Pyrogram of copolyacetal by reactive pyrolysis

Pyrolysis temp.; 400°C, GC oven temp.: 50°C-(5°C/min)-300°C, Carrier gas flow rate: 50 ml/min, Separation column: poly(methylphenylsiloxane) L=50 m, id=0.25 mm, di= 0.25 um, Column flow rate: 1.0 ml/min

Ref: Multi-functional Pyrolyzer® Technical Note, PYA2-013E

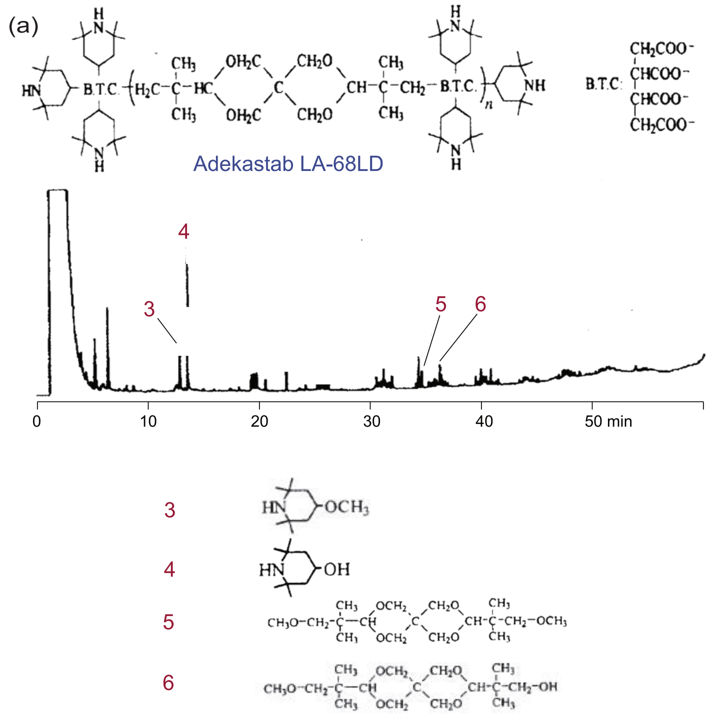
A-5

Determination of a Polymeric Hindered Amine Light Stabilizer (HALS) in Polypropylene (PP)

PROBLEM: How is hindered-amine light stabilizer (HALS) in polypropylene (PP) analyzed?

SOLUTION: Adekastab LA-68LD [MW=1900] as a high molecular weight HALS, and Irganox 1010 and irgafos 168 as antioxidants were added to a PP polymer sample. Then TMAH is added and the PP is analyzed by reactive thermal desorption GC (RTD-GC).

RESULTS: Fig. 1 shows a typical chromatogram of a PP sample containing 10,000 ppm of HALS obtained by RTD-GC in the presence of TMAH at 300°C. On this chromatogram, the reaction products originated from piperidine (peaks 3 and 4) and spiro ring (peaks 5 and 6) moieties in the original HALS molecule were clearly observed without interferences from pyrolyzates of the substrate PP polymer backbone. The precision was as good as 5% RSD or less.



i, j Peaks derived from Irgafos 168

k Peaks derived from Irganox 1010

Fig. 1 Typical pyrogram of a polypropyrene sample obtained by RTD-GC

Ref: Multi-functional Pyrolyzer® Technical Note, PYA2-017E

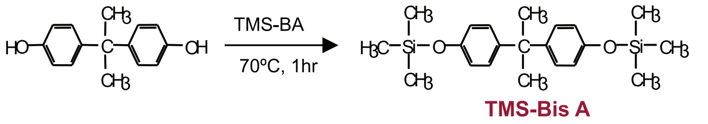
A-6

Determination of Residual Bisphenol A in Polycarbonate

PROBLEM: What is the best analytical method to determine the residual bisphenol A in polycarbonate (PC)?

SOLUTION: When thermal desorption (TD)-GC/MS is used, a small amount of Bis A is also generated as a decomposition product of PC making the determination difficult. Here, Residual Bis A is converted to a thermally stable trimethylsilyl derivative. A 10 mg of the PC sample is placed in a vial along with 700 µL of dichloromethane. 300 µL of N,O-bis(trimethylsilyl)acetamide (TMS-BA) is then added. The vial is heated at 70°C for 1 hour. 10 µL of the reaction mixture was placed in a sample cup for TD-GC/MS analysis.

RESULTS: Scheme 1 shows the reaction products from the TMS-derivatization of Bis A. Fig. 1 shows the chromatogram obtained by TD-GC/MS of the reaction products. As shown in Scheme 1, hydroxyl groups at both ends of Bis A were TMS-derivatized. Using an absolute calibration curve obtained using standard Bis A reagent, the concentration of Bis A in PC was found to be 1,170 ppm, with very good reproducibility (RSD=4.7%, n=5).



Scheme 1 TMS-derivatization of Bisphenol A

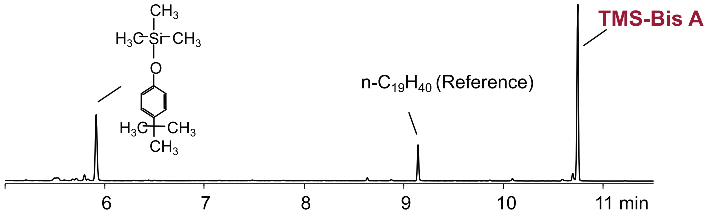


Fig. 1 Chromatogram of TMS-derivatized PC sample obtained by TD-GC/MS

Pyrolyzer furnace temp.: 100-300°C (100°C/min), GC oven temp.: 100-300°C (20°C/min, 5 min hold)
Separation column: Ultra ALLOY-5 (5% diphenyl 95% dimethylpolysiloxane, L=30 m, id.=0.25 mm, df=0.25 µm), Carrier gas flow rate: 1.0 mL/min, split ratio: 1/50

Ref: Multi-functional Pyrolyzer® Technical Note, PYA2-020E

A-7

Determination of Average Molecular Weight of Polycarbonate by Reactive Py-GC

PROBLEM: How can the average molecular weight of polycarbonate be determined?

SOLUTION: A polycarbonate (PC) sample synthesized using the solvent method (SM) was used. About 50 µg of a freezer-milled PC sample was subjected to reactive Py-GC at 400°C in the presence of 1 µL of 25wt% TMAH methanol solution.

RESULT: Figure 1 shows a pyrogram of the PC sample obtained at 400°C in the presence of TMAH. In this pyrogram, p-tert-butylanisole (peak A) and the dimethylether of bisphenol-A (peak B), derived from the end groups and the main chain of the PC sample are clearly observed. Because both terminals in the SM-PC molecules are completely end-capped with p-tert-butylphenoxy groups, the average molecular weight of the sample (Mn) can be estimated from the two peak intensities (Equations 1 and 2): where DP is the degree of polymerization, IA and IB are the intensities of peaks A and B, respectively, and the divisors 10.2 and 15.4 are effective carbon numbers (ECN) of the respective compounds for a flame ionization detector. The values of 254 and 326 in Eq. 2 are the MWs of the monomer unit and the two end groups, respectively.

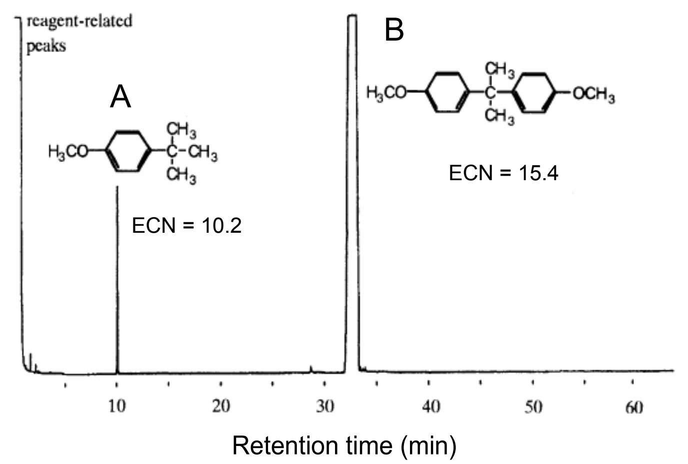


Fig. 1 Pyrograms of PC sample obtained at 400°C in the presence of TMAH

Pyrolysis temp.: 400°C, GC oven temp.: 50°C- (4 °C/min)-300°C
Separation column: Poly(dimethylsiloxane), Length 25mm, 0.25mm i.d., Film thickness 0.25µm
Carrier gas flow : 50 ml/min, Column flow: 1.3 ml/min, Detector: FID

$$DP = \frac{I_B/15.4}{(I_A/10.2)/2} \qquad (1)$$

$$\overline{M}_n = DP \times 254 + 326 \qquad (2)$$

Ref: Multi-functional Pyrolyzer® Technical Note, PYA2-015E

A-8

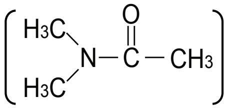
Analysis of Corrosive Gases Produced During Polyimide Curing Process

PROBLEM: Is it possible to analyze compounds out-gassing during the curing of polyimide?

SOLUTION: Microgram quantities of the sample containing bisphenyl tetracarboxylic acid di-anhydride (BPDA) and sulfonyl bisbenzamine (3,3-DDS) are placed in a sample cup. EGA is performed during the thermal polymerization of the mixture.

RESULT: Fig.1 shows that polyimide is synthesized when the mixture is heated using a two step process. Fig.2 presents the thermograms for various out-gassing compounds formed during the preparation of polyimide. This result demonstrates that DMAA* and CO2 are formed during the first heating process and SO2 and aniline are generated during the second heating process.

**DMAA: Dimethylacetamide*



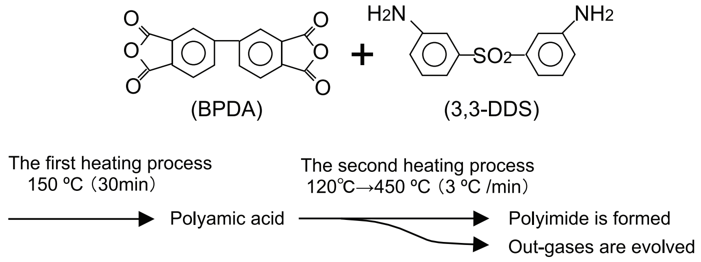


Fig. 1 The synthetic process of polyimide

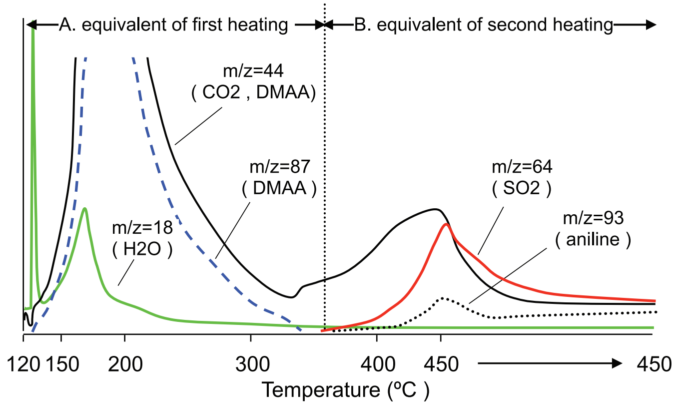


Fig. 2 Thermogram with mass chromatogram in the process of polyimide synthesis

Ref: Multi-functional Pyrolyzer® Technical Note, PYA3-002E

B-1

Analysis of Ceramic Composite Materials

PROBLEM: Is there an example in which a ceramic composite material was analyzed by the Multi-Shot Pyrolyzer? If so, please describe.

SOLUTION: A ceramic composite material was analyzed by EGA-MS technique using analytical conditions summarized in Fig. 1. Peaks on the thermogram were identified by library search using EGA-MS library.

RESULT: Fig. 1. shows the EGA curve and average spectra of peaks A, B, C, and D observed for the composite material. Background (BG) noise has been subtracted from the average spectra. Figs. 1a and 1b show the results of library search on the spectra using Frontier Lab F-Search system with EGA-MS library. Peaks C and D were found to be PBMA and PS, respectively. Peak A and B are considered to be of low boiling compounds because of their lower elution temperatures. Upon searching the normal MS library (Wiely 275), peak A was judged to be a phthalate, and peak B, saturated hydrocarbons. Library search with a combination of the MS library and EGA-MS library as shown here is extremely useful as the primary search method to determine the composition of an unknown polymer.

Ref: Multi-functional Pyrolyzer® Technical Note, PYA1-010E

Fig. 1a Library search result for peak C

Name	Qual
1. Poly(n-butyl methacrylate) (PBMA)	**72**
2. Poly(2-hydroxyethyl methacrylate) :	4
3. Higher methacrylate copolymer	2

Fig. 1b Library search result for peak D

Name	Qual
1. Polystyrene (PS)	**90**
2. Styrene-ethylene-butadiene-styrene-block copolymer	78
3. Modified poly(phenylene oxide)	64

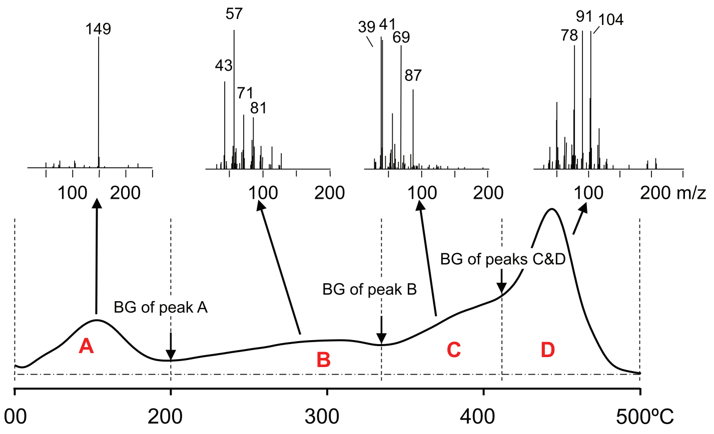


Fig. 1 EGA curve of ceramic composite material (Injection molding)

Pyrolyer furnace temp: 100°C~500°C (20C/min), Carrier gas : He 50kPa, Split ratio: ca. 1/50

EGA tube: id.=0.15 mm, L=2.5m (UADTM-2.5N), GC oven: 300°C, Injection port temp : 320°C, Sample: ca. 0.5 mg, Detector: MS (m/z=29-400, 0.1 scan/sec), PY-GC interface: 320°C (Auto)

B-2

Analysis of Butylhydroxytoluene (BHT) in PE

PROBLEM: How can an antioxidant in a polymer be analyzed while avoiding interferences by the polymer backbone?

SOLUTION: The quantitative analysis of butylhydroxy-toluene (BHT, Fig. 1), an additive commonly used as antioxidant for PE, using TD-GC/MS is illustrated here. First, evolved gas analysis (EGA-MS) was performed in temperature range 100~600°C to determine the thermal property of the sample.

RESULT: The thermogram of the PE sample, obtained by EGA-MS, is shown in Fig. 2. In the TIC chromatogram, only a single peak, emanating from the pyrolysis of PE, is observed. Extracted ion chromatograms: m/z 205 and 220 which are characteristic ions for BHT, are observed in the temperature range 100-200°C. This defines the thermal desorption conditions (100-200°C at 20°C/min, 3 min hold) for determining BHT in PE.

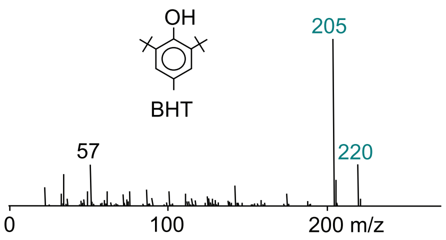


Fig. 1 Chemical structure of BHT and its mass spectrum

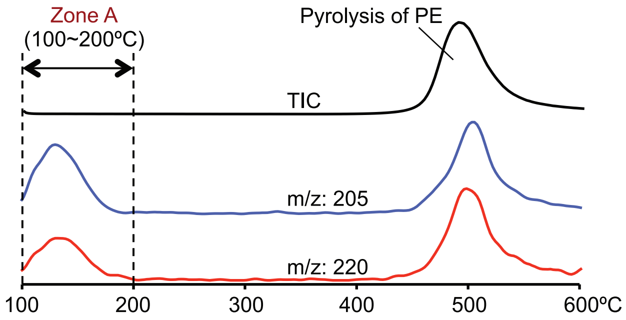


Fig. 2 Thermograms of a PE sample

Pyrolyzer furnace temp. : 100-600°C, (20°C/min), Split ratio : 1/50, sample size : about 0.5mg, detector : MS

Ref: Multi-functional Pyrolyzer® Technical Note, PYA1-055E

B-3

Identification of the Additives in Polystyrene

PROBLEM: How are the additives in polystyrene (PS) identified using the Multi-shot pyrolyzer system?

SOLUTION: A Multi-shot pyrolyzer (model 3030D) is installed on a GC/MS. Both the deactivated metal capillary tube (EGA) and the metal capillary separation column (TD) are interfaced to the MS using a vent-free GC/MS adaptor. 50 µL of a 20 mg/mL dichloromethane solution is added to a sample cup and the solvent is allowed to evaporate prior to analysis. The analytical conditions are provided in the figure captions. F-Search additive library can be used to identify unknown additives in PS. The library includes both chromatographic and mass spectral data for 358 additives.

RESULT: (EGA)-MS was utilized to determine the thermal desorption zone of the volatile additives - see Fig. 1. This thermal zone (100-300°C) was analyzed using TD-GC/MS. Each peak was tentatively identified using the F-Search additive library. Ten “additive” were identified based on mass spectral match quality and retention indices.

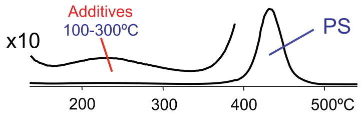


Fig. 1 Library search results

Py furnace temp.: 100 - 700°C (20°C/min), GC oven temp.: 300°C, EGA tube: UADTM-2.5N(L=2.5 m, i.d. 0.15 mm), column flow rate: 1 mL/min He, split ratio: 1/50, sample: 0.1 mg

TD-GC/MS: total ion chromatogram

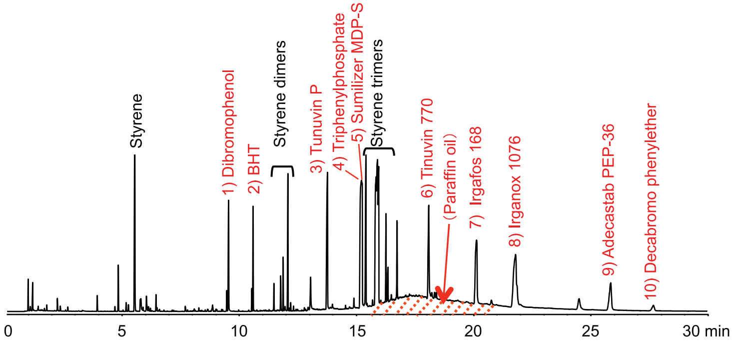


Fig. 2 Library search results

Pyrolyzer temp.: 100 - 300°C (20°C/min, 5 min), GC oven temp.: 40°C (2 min) - 320°C (20°C/min), separation column: Ultra ALLOY+-5 (5% diphenyl 95% dimethylpolysiloxane) (L=30 m, i.d.=0.25 mm, df=0.05 µm), column flow rate: 1 mL/min He, split ratio: 1/20, scan rate: 2 scans/sec, scan range: 29 - 810 (m/z), sample: 1 mg

Ref: Multi-functional Pyrolyzer® Technical Note, PYA1-066E

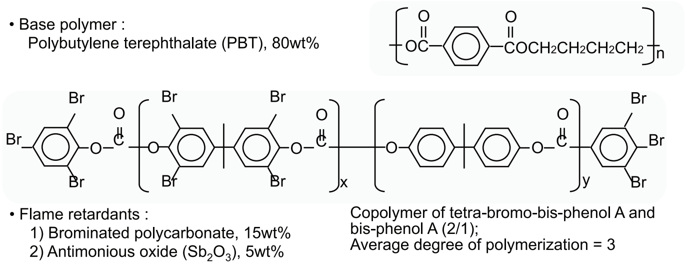
B-4

Analysis of Flame Retardants in Polybutylene Terephthalate (PBT) Using EGA-Atomic Emission Detector (AED) Terephthalate (PBT)

PROBLEM: Have flame retardants in polybutylene terephthalate (PBT) been analyzed by the Multi-Shot pyrolyzer in EGA mode?

SOLUTION: An example described here is elucidation of flame retardant mechanism of brominated polycarbonate (15%) and antimonious oxide (5%) (Fig. 1) added, as flame retardants, to PBT using Multi-Shot Pyrolyzer.

RESULT: Fig. 2 shows evolved gas curves of Sb, Br, and C contained in the flame retardant PBT. By the catalytic action of Sb2O3, brominated compounds are eluted at lower temperatures than flammable gases such as butadiene and butylene terephthalate produced during the thermal decomposition of PBT, thus it is considered that the flame retardants inhibits the ignition of PBT at the early stage of decomposition. As shown here, observing the elution of targeted elements in the evolved gases by atomic emission detector (AED) provides an insight into the effect of flame retardants.


- Base polymer :
  Polybutylene terephthalate (PBT), 80wt%
- Flame retardants :
  1) Brominated polycarbonate, 15wt%
  2) Antimonious oxide (Sb_2O_3), 5wt%

Copolymer of tetra-bromo-bis-phenol A and bis-phenol A (2/1);
Average degree of polymerization = 3

Fig. 1 . Base polymer and structure of flame retardant

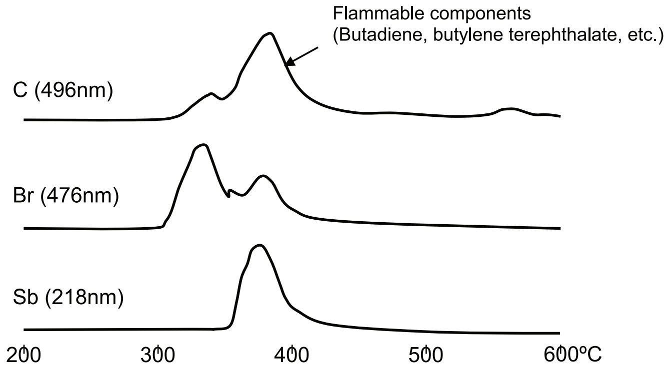


Fig. 2 Thermal decomposition of flame retardant PBT observed by evolved gas analysis (EGA)
(Detector : AED(Atomic Emission Detector), Atmosphere gas : He)

Ref: Multi-functional Pyrolyzer® Technical Note, PYA3-003E

B-5

Analysis of Flame Retardant Polybutylene Terephthalate (PBT)

PROBLEM: What is the best way to obtain the thermal properties of a flame retardant polybutylene terephthalate (PBT)?

SOLUTION: The chromatograms were obtained by programmed heating of the pyrolyzer furnace from 60 to 700°C, followed by GC analysis of resultant evolved gases that were trapped at the head of GC column.

RESULT: Fig. 1 shows chromatograms of evolved gases from flame retardant PBT. In addition to decomposed products from PBT, brominated phenols, thermal decomposition products of brominated PC, and SbBr3, produced from brominated PC and antimonious oxide, were also detected. Fig. 2 shows evolved gas curves obtained using MS as a detector (TIC) and mass chromatograms of characteristic ions of species A~E (shown in Fig 1). Dibromo phenol was detected at 350°C; while flammable gases, hydrogen bromide, and antimony bromide, were detected at 380°C. Thus, in evolved gas analysis using MS, obtaining characteristic ions of target species provides an insight into thermal properties of polymeric materials.

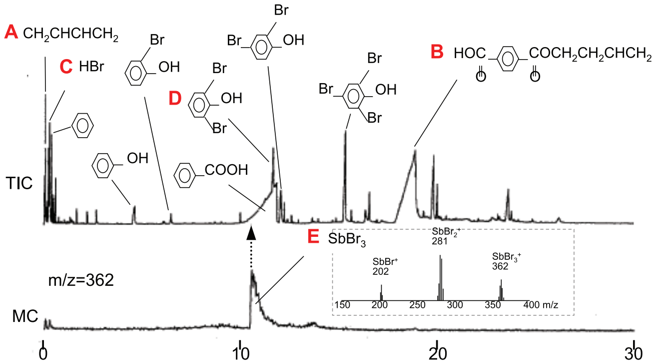


Fig. 1 Chromatograms of thermal decomposition products of flame retardant PBT

Components evolved in 60~700°C range in He were trapped in Liq. N2, then analyzed by GC/MS

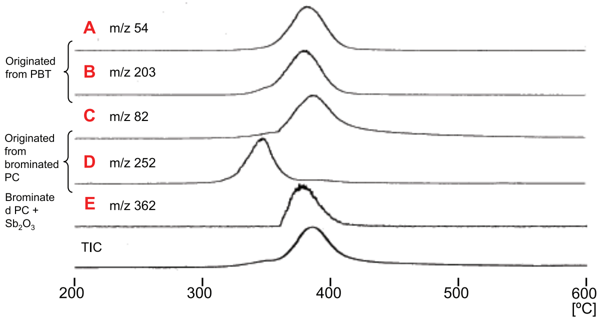


Fig. 2 EGA curves of flame retardant PBT by EGA-MS

Ref: Multi-functional Pyrolyzer® Technical Note, PYA3-004E

C-1

Characterization of 35 Organic Pigments

PROBLEM: Organic pigments are widely used in the automotive manufacturing. The analysis and structure elucidation of organic pigments is challenging because they are not only insoluble in organic solvents but also many of them have similar structures. Is there any analytical technique that can characterize these pigments?

SOLUTION: Py-GC/MS enables the analysis of organic pigments directly; no pretreatment such as solvent extraction is necessary. EGA (evolved gas analysis)-MS: 100→600°C at 20°C/min and pyrolysis-GC/MS at 600°C were performed on 35 organic pigments. F-Search was used to create the organic pigment library and process the MS sample data.

RESULT: The results obtained by the EGA and Py-GC/MS analysis of Pigment yellow 93 and Pigment yellow 94 are shown in Figure 1 and 2. The molecular structures of these two pigments have similar structures. This data was used to construct a database which can be used to identify unknown pigments which have similar structures. When analyzing samples containing multiple pigments, the Py-GC/MS is extremely useful since the pyrolyzates of each pigment can be separated, identified, and quantitated.

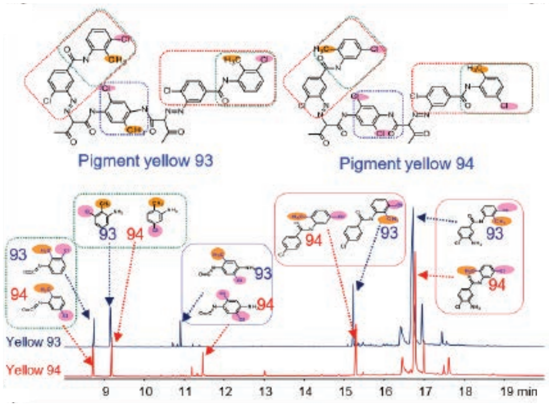


Fig. 1 Structure of Pigment 93 and Pigment 94, pyrograms, and identification of major peaks

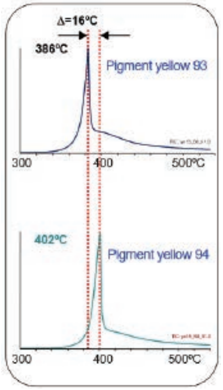


Fig. 2 Thermal decomposition of flame retardant PBT observed by evolved gas analysis (EGA)

(Detector : AED(Atomic Emission Detector), Atmosphere gas : He)

Ref: Multi-functional Pyrolyzer® Technical Note, PYA1-079E

C-2

Analysis of Shellac by Reactive Py-GC

PROBLEM: Shellac is a thermosetting resin this is used in automotive gasket, polishes, rubber, and electrical insulators. Is there a simple analytical method for analyzing Shellac?

SOLUTION: The reactive Py-GC in the presence of tetramethylammonium hydroxide (TMAH) was applied to the compositional analysis of shellac. Eight shellac samples from India and Thailand were used. Samples were cryo-milled into a fine powder (<60 mesh). About 90µg of sample and 2µL of TMAH solution were introduced into the pyrolyzer for pyrolysis at 400°C.

RESULT: Figure 1 shows typical pyrograms of Indian shellac at 400°C with and without addition of TMAH. In Figure 1a, only weak and broad peaks of terpenic acids and wax components were observed, while in Fig 1b, a series of sharp peaks due to the methyl derivatives of shellac constituents were observed with better resolution and higher sensitivity. With these results shown, this technique was found to provide simple and quick compositional analysis of shellac.

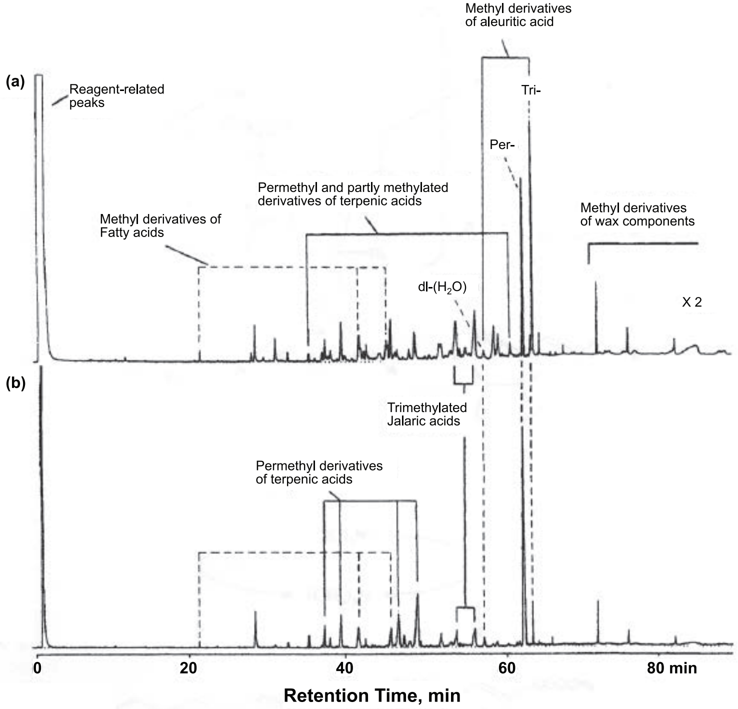


Fig. 1 Typical pyrograms of Indian Shellac obtained at 400˚C
(a) In the absence of TMAH, (b) In the presence of TMAH solution

Ref: Multi-functional Pyrolyzer® Technical Note, PYA2-008E

C-3

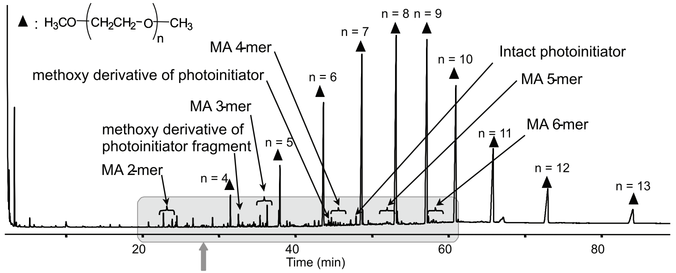
Characterization of Network Structure of UV-Cured Acrylic Ester Resin

PROBLEM: Is there a way to characterize the network structure of UV cured acrylic ester resin?

SOLUTION: About 100 µg of the powder of a UV-cured resin prepared from polyethylene-glycol diacrylate and morpholino-type photoinitiator (IRGACURE 907) is subjected to reactive Py-GC at 400°C in the presence of 4 µL of TMAH in methanol (25%).

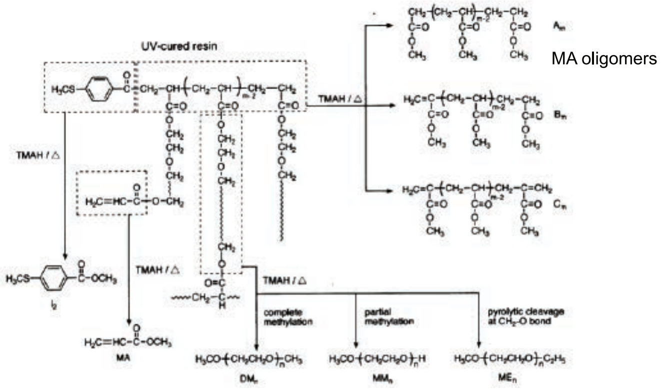
RESULT: Fig. 1 shows a typical pyrogram of the UV-cured resin. In this pyrogram, minor but distinct peaks of various methyl acrylate (MA) oligomers directly reflecting the cross-linked structures are observed along with a series of methoxy derivatives of ethylene glycol oligomers. The derivatives originate from the main chain after chemolysis at the acrylate linkages (Scheme 1). The relative peak intensities of the various MA units enable the analyst to determine the chain length distribution of the network junctions contained in the UV-cured resin.

Ref: Multi-functional Pyrolyzer® Technical Note, PYA2-016E



Various minor peaks characteristic of crosslinked network structure.

Fig. 1 Typical pyrogram of UV-cured resin prepared from polyethyleneglycol diacrylate and morpholino-type photo-initiator.
Pyrolysis temp.: 400°C, GC oven temp.: 35°C (6 min)-(5 °C/min)-340°C
Separation column: Poly(5% diphenyldimethylsiloxane), L=30 m, id=0.25 mm, df=0.25 µm



Scheme 1 Formation pathway of typical products of UV-cured resin after reactive pyrolysis

C-4

Analysis of Toxic Gases Released from Polyvinylidene Chloride (PVDC) Film

PROBLEM: Is there an easy way to analyze hazardous compounds out-gassing from PVDC film used in automotive manufacturing?

SOLUTION: A piece of polyvinylidene chloride film (0.25 cm2, 0.5 mg) is placed in the sample cup and analyzed by EGA-MS and Heart-Cutting EGA-GC/MS method.

RESULT: The EGA thermogram of the film is presented in Fig. 1. Each zone is analyzed separately using a Heart-Cutting EGA-GC/MS technique. The results of the analyses are shown in Fig. 2. The data indicates that a number of additives and pyrolyzates of the polymer back bone are present in each EGA zone.

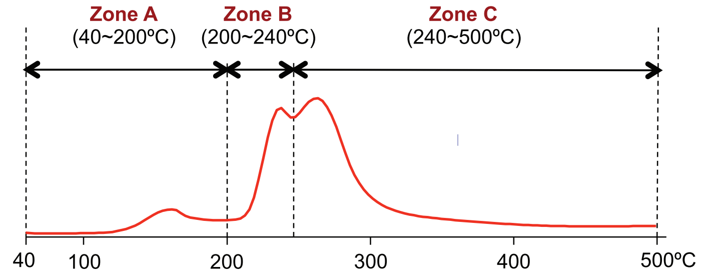


Fig. 1 Thermogram of food wrap film

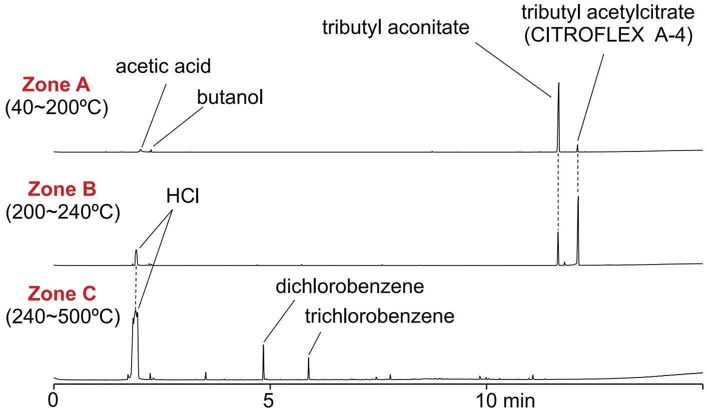


Fig. 2 Chromatograms for zones A through C by Heart-Cutting EGA-GC/MS method

Ref: Multi-functional Pyrolyzer® Technical Note, PYA1-023E

C-5

Analysis of Chitin, an Amino Polysaccharide

PROBLEM: Chitosan derived from chitin is used as the outer coating to protect the paints on cars. How can chitin be analyzed?

SOLUTION: Partially deacetylated chitin was commercially obtained. The average degree of N-acetylation (DA) of the chitin was determined by 1H NMR and Py-GC equipped with Multi-Shot pyrolyzer (pyrolyzer temp., 450°C, He carrier gas). The extent of ester group introduction was estimated by 1H NMR and Py-GC.

RESULT: The polymer reaction of 1 with ethyl acrylate to the D-glucosamine residue was carried out at 40°C (Fig. 1). The results are summarized in Table 1. Hydrolysis of pendant ester groups of the product was observed in phosphate buffer solution, while 2 (Fig. 1) was successfully obtained in the solvent containing methanol (run No's. 2 and 3 in Table 1). It was found that the Michael addition proceeded exclusively at the amino groups of 1. Degrees of substitution (DS) to the amino group of the D-glucosamine residue of 2 were determined by 1H NMR. DS values determined based on -NHCH2- were further supported by quantitative analysis of Py-GC technique. The Py-GC is a powerful and convenient methodology to determine chemical structures without considering physical structures and physical properties of polymers (Table 1).

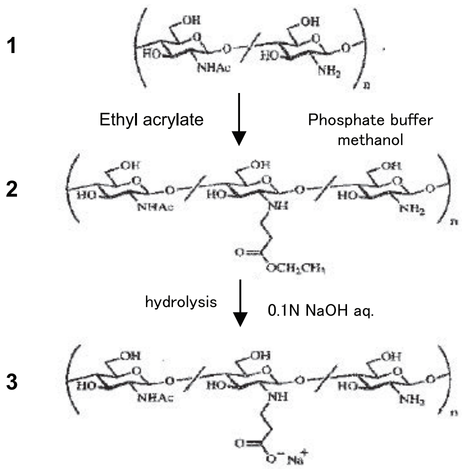


Fig. 1 Synthesis of N-selective ester functionalized chitin derivative and water-soluble carboxyethylchitin

Run No.	1		Product polymer			
	mg	-NH2 of **1** mmol	Yield mg (%)	Degrees of substitution		
				^{1}H NMR Based on $-CO_2CH_2CH_2-$	^{1}H NMR Based on $-NHCH_2-$	Py-GC
1	250	0.68	189 (-)	-	0.63	0.69
2	250	0.68	160 (52)	3.2	1.07	0.92
3	250	0.68	178 (59)	1.7	0.87	0.85
4	100	0.24	71 (-)	-	0.68	-

* Reaction condition: Temperature, 40°C; time. 240hr

Table 1 Synthesis of N-(2-ethoxycarbonylethyl)chitin (2) of partially deacetylated chitin (1) to ethyl acrylate

Ref: Multi-functional Pyrolyzer® Technical Note, PYA1-043E

C-6

Thermal Analysis of a Blend System Based on Chitin Polysaccharide

PROBLEM: Is there an example of thermal analysis of a blend system based on chitin, polysaccharide?

SOLUTION: EGA-MS and EGA-MS were applied to the characterization of a chitin-graft-poly(2-methyl-2-oxazoline)/PVA blend system. Chitin-graft-poly(2-methyl-2-oxazoline) was prepared according to the established procedure.

RESULT: Fig. 1 shows the EGA thermogram of chitin derivative/PVA blends obtained by EGA-MS. The TIC curve of PVA shows two-stage degradation. The thermal degradation of the blends samples also occurs in two stages, reflecting the degradation of both constituent polymers. The thermal degradation products were identified by EGA-MS. Fig. 2 shows the TIC of (a) the eluted products cold-trapped during the first degradation stage from 240 to 340°C and (b) those eluted during the second stage from 340 to 480°C for the B(60/40) sample. The major products such as water and various unsaturated and aromatic aldehydes as shown Fig. 2a may be formed during the first degradation stage through dehydration of PVA followed by scission of the resulting polyene chains. On the other hand, various degradation products originating from the chitin derivatives are formed during the second degradation stage as shown in Fig. 2b.

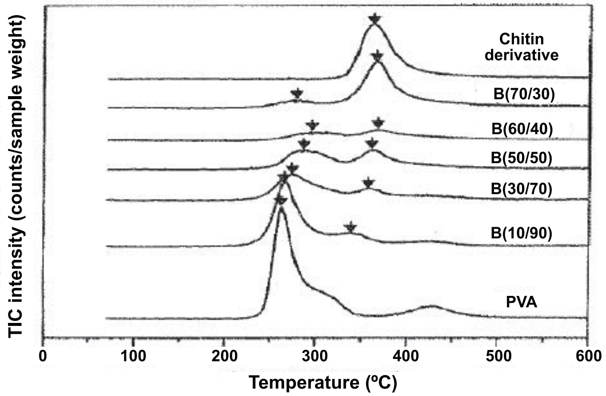


Fig. 1 EGA thermograms of chitin derivative/PVA blend samples obtained by EGA-MS

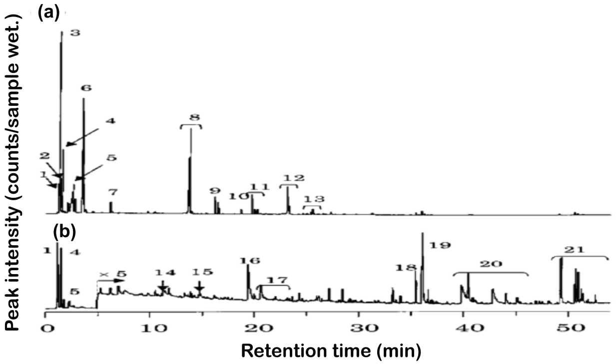


Fig. 2 TICs of degradation products generated from B(60/40) in temperature zones (a) 240- 340°C and (b) 340-480°C

Ref: Multi-functional Pyrolyzer® Technical Note, PYA3-008E

D-1

Determination of Antioxidants in NBR Rubber

PROBLEM: What is the best method to quantitate additives in rubber?

SOLUTION: A piece of an acrylonitrile-butadiene rubber sample (NBR) weighing about 1 mg is placed in a sample cup. The sample was analyzed using EGA and thermal desorption-GC/MS.

RESULT: The EGA thermogram of the NBR sample, containing various types of additives, is shown in Fig. 1 This suggests that the volatile components are desorbed in zone A. Fig. 2 shows the (TD)-GC/MS chromatogram of zone A fraction. Table 1 shows the results that the reproducibility of the relative peak intensities for two types of antioxidants is less than 2% RSD.

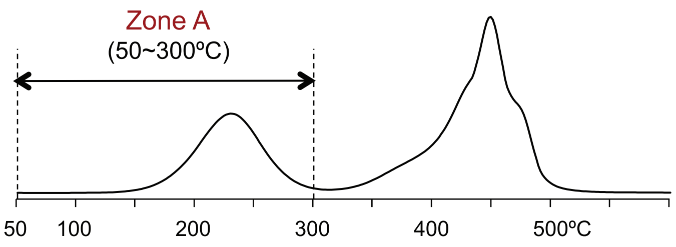


Fig. 1 EGA thermogram of NBR

Table 1 Reproducibility of Area Ratios (vs ISTD) of NBR additives

n	NOCRAC 810-NA	NOCRAC 6C
1	0.113 0.139	
2	0.118 0.140	
3	0.119 0.144	
4	0.122 0.143	
5	0.124 0.140	
6	0.123 0.144	
7	0.123 0.144	
8	0.124 0.143	
Aver.	0.122 0.143	
RSD	1.98 % 1.27 %	

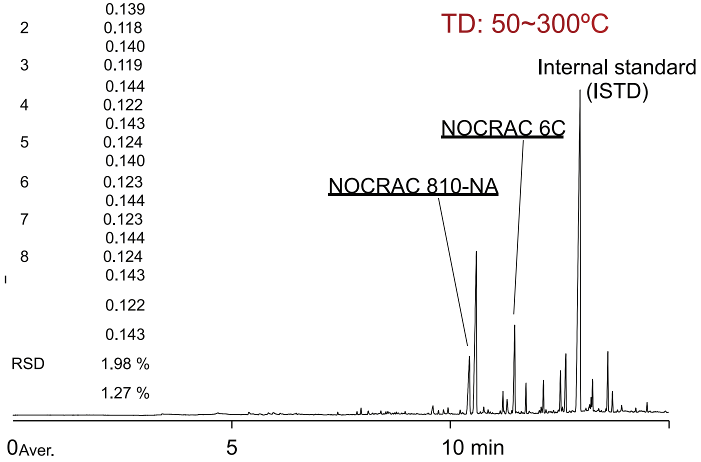


Fig. 2 Chromatogram for Zone A by (TD)-GC/MS analysis

NOCRAC810-NA: N-Phenyl-N'-isopropyl-p-phenylenediamine
NOCRAC 6C: N-Phenyl-N'-(1,3-dimethylbutyl)-p-phenylenediamine

Ref: Multi-functional Pyrolyzer® Technical Note, PYA1-005E

D-2

Analysis of Compounded Rubber

PROBLEM: How can a compounded rubber be analyzed using Multi-Shot pyrolyzer? What information can be obtained?

SOLUTION: A compounded rubber is analyzed by Multi-Shot pyrolyzer operating in double-shot mode, i.e., evolved gas analysis (EGA), followed by flash pyrolysis.

RESULT: Fig. 1 shows an EGA thermogram of a compounded rubber. Weak peaks are observed in 100~300°C zone due to the thermal desorption of additives. In 300~500°C zone, a broad peak due to thermal decomposition of the rubber is observed. From this result, thermal desorption was performed from 100 to 300°C (20°C/min), and then flash pyrolysis was done at 550°C. Fig. 2 shows results of analysis. In the chromatogram of thermal desorption shown in Fig. 2a, cyclic siloxanes (D3~D6) originated from silicon coupling agent, benzothiazole (vulcanization accelerator), higher aliphatic acid (vulcanizing agent), and waxes (antioxidants) were observed. Because isoprene and limonene were mainly observed in the pyrogram shown in Fig. 2b, the major component of this sample is natural rubber.

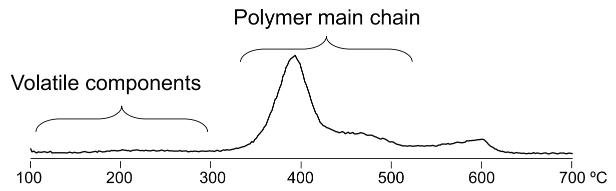


Fig. 1 Evolved gas curve of a compounded rubber

Pyrolysis temp.: 100~700°C (20°C/min), Carrier gas : He 50kPa, Split ratio : ca. 1/20 EGA capillary tube : 0.15mm id, 2.5m (UADTM-2.5N), GC oven temp.: 300°C Injection temp.: 320°C, Sample : ca. 5g, Detector : MS (m/z=29-400)

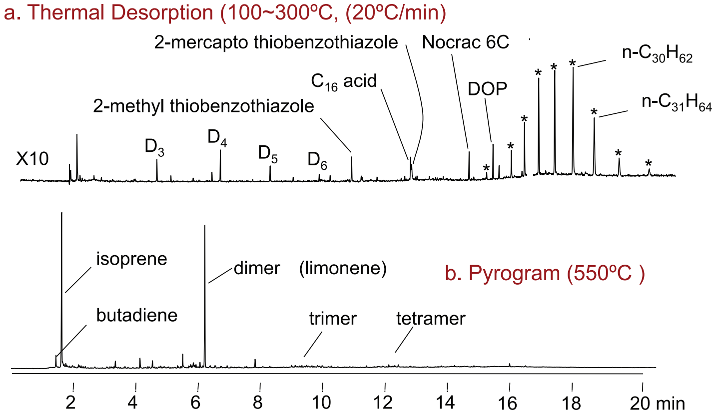


Fig. 2 GC/MS analysis of compounded rubber by double-shot technique

Column flow rate : 1ml/min (fixed flow rate), Split ratio: 1/20 Separation column: Ultra ALLOY+-5 (5% diphenyl polysiloxane), 30m, 0.25mm id, Df: 0.25m GC oven temp.: 40~300°C (20°C/min), Sample : 5g, Detector: MS (m/z=29-400, 2 scans/sec)

Ref: Multi-functional Pyrolyzer® Technical Note, PYA1-015E

D-3

Compositional Analysis of Isoprene-Butadiene-Styrene Blend Rubber

PROBLEM: Is there a simple method to analyze the chemical composition of a blended rubber sample?

SOLUTION: About 200 µg of a rubber mixture, composed of polybutadiene(PB)-polyisoprene (PI)- polystyrene (PS), is placed in a sample cup and pyrolyzed at 550°C.

RESULT: Fig.1 shows the pyrogram for the blend rubber sample. The monomers of each component, which are butadiene, isoprene and styrene, are the main pyrolyzates. The calibration curves between relative peak intensities for the specific peaks and the ratio of PB to total weight of the sample shows a fairly good linear relationship with a correlation coefficient greater than 0.99. The calibration curve for the PB composition in the blended sample is shown in Fig.2. Using this calibration curve, a fairly accurate determination of the component is possible within 3% of accuracy.

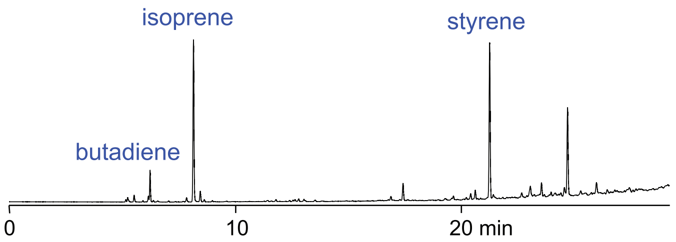


Fig. 1 Fig. 1. Pyrogram of a blend rubber

Pyrolysis temp.: 550°C, detector: FID, sample: standard sample A Separation column: Ultra ALLOY+-5 (5% diphenyl 95% dimethylpolysiloxane) Length: 60m, id: 0.25 mm, film thickness: 1.0 m GC oven temp.: 50°C (7 min hold) – 280°C (10°C/min), carrier gas: He Injection port pressure: 175 kPa, split ratio: 1/60, sample size: ca. 200 g

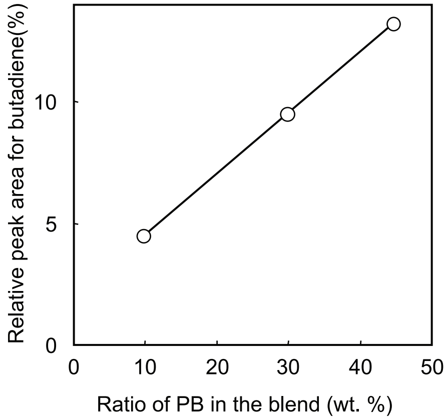


Fig. 2 Calibration curve for PB in the blend

Ref: Multi-functional Pyrolyzer® Technical Note, PYA1-047E, ISO 7270-2

D-4

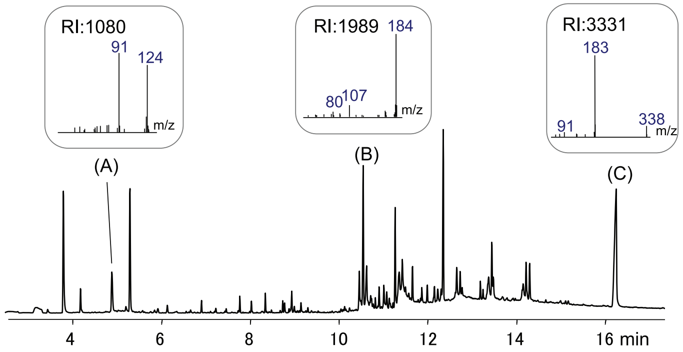
Identification of an Unknown Antidegradant in Rubber

PROBLEM: Is there any library search system that allows for the identification of unknown antidegradants used in rubber?

SOLUTION: The additive library for F-Search (mass spectra library search engine) contains data for commercially available 32 typical antidegradants. The library consists of mass spectra of major peaks on chromatograms obtained by thermal desorption (TD)-GC/MS method, chemical names, and retention indexes. Analysis of a rubber that contains ca. 1% of unknown antidegradant is described here.

RESULT: Fig. 1(a) shows the chromatogram of a rubber sample containing an unknown antidegradant obtained by (TD)-GC/MS and mass spectra for major peaks A, B and C. Major peaks were identified by comparison of mass spectra obtained by library search with their similarity and retention indexes (RI) as shown in Fig. 1(b). Further, from the chromatogram in the library shown in Fig. 1 (b), the antidegradant candidate related to these three compounds was estimated to be p-(p-Toluene sulfonylamido) diphenylamine.

(a) Chromatogram of volatiles from an unknown rubber sample



(b) Chromatogram of *p*-(*p*-toluene sulfonylamido) diphenylamine stored in MS library

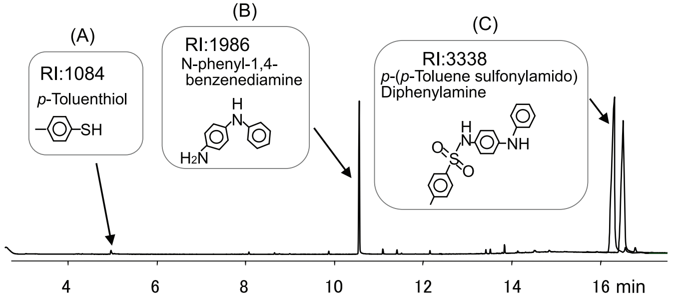


Fig. 1 Chromatogram obtained by (TD)-GC/MS technique

Ref: Multi-functional Pyrolyzer® Technical Note, PYA1-057E, ISO 10638

D-5

Analysis of Rubber Composition with EGA and EGA Polymer MS Library

PROBLEM: What analytical technique can be used to analyze a rubber of unknown components??

SOLUTION: The EGA-MS technique is a combination of evolved gas analysis (EGA) and mass spectroscopy (MS) using Multi-functional Pyrolyzer, and is very useful as a primary analytical tool for unknown polymeric samples.

RESULT: An example on the right is the analysis of a rubber with unknown composition. Shown in Fig. 1 are the EGA thermogram of the rubber and mass spectra of peaks A and B observed. Peak A is considered to arise from additives due to low elution temperatures. To obtain further information, components in peak A need to be analyzed by GC/MS. Peak B is originated from thermal decomposition of the polymer backbone. Table 1 shows the result of library search on the average spectrum of peak B using EGA-MS Library. Polynorbornene and acrylonitrile-butadiene rubber were found as candidate polymers. EGA and library search with EGA-MS Library provide information on the amounts and desorption temperatures of the additives contained in a sample, and is very useful for analysis of unknown materials as a primary technique.

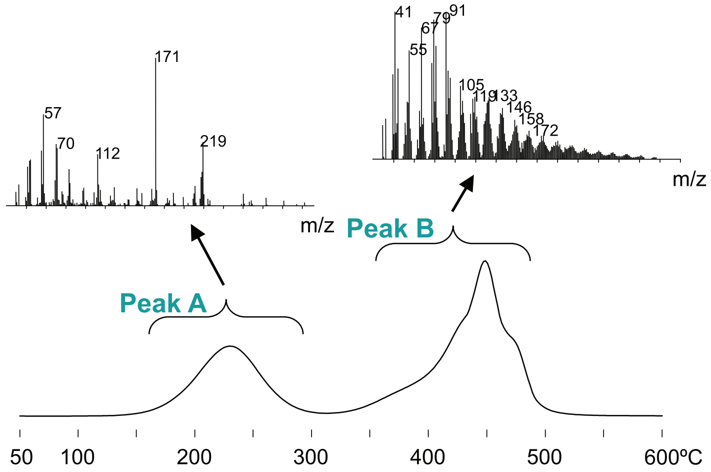


Fig. 1 EGA thermogram of a rubber and averaged Mass Spectra

Furnace temp.:50~600ºC (10ºC/min), Carrier gas : He 60ml/min, Split ratio :ca.1/50 EGA tube : id=0.15 mm, L=2.5 m (UADTM-2.5N), GC oven temp. : 300ºC Sample :ca. 0.5 mg, MS scan range: m/z=29-400, Scan speed: 0.1 scans/sec PY-GC interface temp.: 320ºC (AUTO mode)

Name	Match Qual
1. Polynorbornene	49
2. Polynorbornene	43
3. Acrylonitrile-butadiene rubber (NBR)*	43

* It was further analyzed by Py-GC/MS and was identified to be NBR.

Table 1 Result of library search on Peak B

Ref: Multi-functional Pyrolyzer® Technical Note, PYA3-006E

E-1

Composition Analysis of Adhesive

PROBLEM: Is there an example showing the composition of adhesive?

SOLUTION: The EGA-MS library search is a combination of Evolved Gas Analysis, a thermal analysis technique using Multi-Shot Pyrolyzer, and mass spectrometry; and is very useful as a primary searching technique for unknowns.

RESULT: An example shown is analysis of an adhesive with unknown composition. Shown in Fig. 1 are the EGA curve of an adhesive and its averaged spectra obtained from zones A, B, and C with the background (BG) subtracted. Peak A was considered to arise from a low boiling component by its elution temperature, and was found to be a compound shown in Fig. 1 (a) by a normal MS library search (Wiley275). Wiley275 library search was also performed on peak B, and found mainly to be of acetic acid. Table 1 shows library search results by EGA-MS LIB with F-Search performed on peak C, and various vinyl polymers were found. Because peak B contains acetic acid, the material should contain vinyl acetate. As shown in this example, EGA-MS technique and library search with EGA-MS LIB are extremely useful as a primary library search technique.

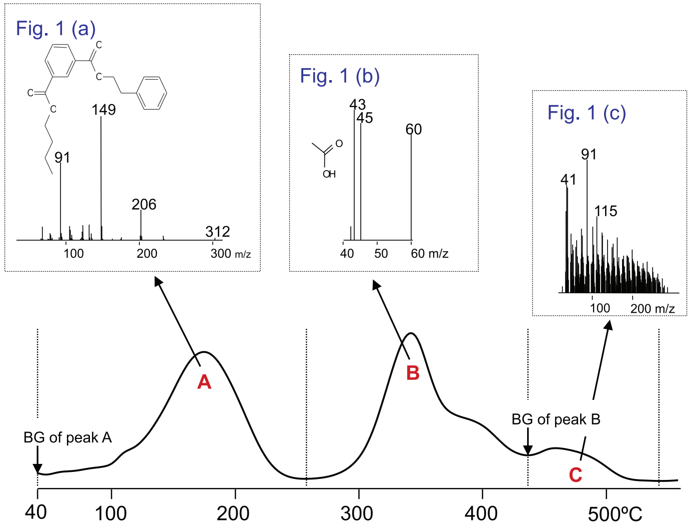


Fig. 1 EGA curve of the adhesive

Pyrolyzer furnace temp.: 100°C~600°C (20°C/min), Carrier gas: He 50kPa, Split ratio: ca. 1/50 EGA capillary tube: 0.15mm id, 2.5 m (UADTM-2.5N), GC oven temp.: 300°C isothermal Injection temp.: 320°C, Amt. of sample : ca. 1.0mg, Detector : MS (m/z=29-400, 0.1scan/sec PY-GC interface temp.: 320°C (AUTO mode)

Name	Qual.(%)
1. Poly (vinyl chloride) ; PVC:	62
2. Poly (vinyl acetate) ; PVAc	**60**
3. Poly (vinyl alcohol) ; PVA	43

Table 1 Library search result of Peak C

Ref: Multi-functional Pyrolyzer® Technical Note, PYA1-013E

E-2

Analysis of Rubber Composition with EGA and EGA Polymer MS Library

PROBLEM: How can the compositional analysis of an adhesive be performed using Multi-Shot pyrolyzer?

SOLUTION: EGA-MS is a useful technique to determine the composition of each peak observed in the EGA thermogram. In this technique, components in each temperature zone are introduced into a GC column and temporary trapped at the front of the column using Selective Sampler and MicroJet Cryo-Trap. They are then separated and identified with GC/MS.

RESULT: In the EGA thermogram of an adhesive described in the previous page, three peaks, A, B, and C are observed (see Fig. 1). Fig. 2 shows chromatograms of three temperature zones obtained by GC analysis. Peak A was found to contain a phthalate ester, while peak B was found to contain acetic acid, butyl acetate, and butyl acrylate. Acetic acid is considered to arise from polyvinyl acetate (PVAc), and butyl acrylate from thermal decomposition of polybutyl acrylate. Peak C contained a variety of aromatic compounds derived from thermal decomposition of polyene structure of the polymer backbone.

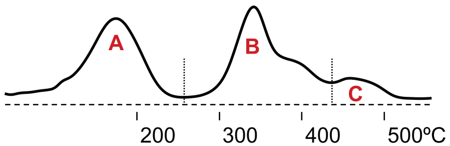


Fig. 1 EGA Curve of an adhesive

See the previous page for analytical conditions

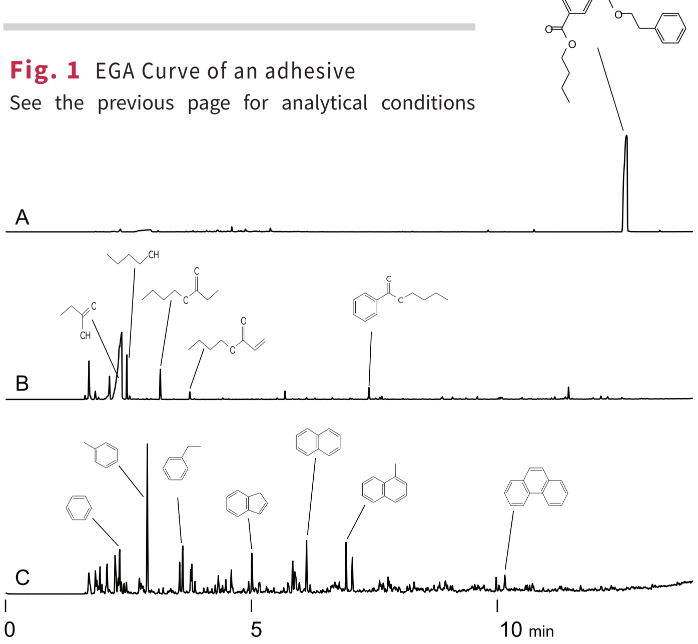


Fig. 2 Chromatograms of temperature zones of EGA thermogram

Pyrolysis temp.: 40°C~600°C (20°C/min), Column flow rate: 1ml/min, Split ratio: 1/50 Separation column : Ultra ALLOY+-5 (5% diphenyl polysiloxane), 30m, 0.25mm id, df=0.25μm GC oven temp.: 40°C~320°C (20°C/min), Sample: 0.8mg, Detector: MS (m/z=29-400, 2scans/sec

Ref: Multi-functional Pyrolyzer® Technical Note, PYA1-014E

E-3

Analysis of Epoxy Resin Curing Process

PROBLEM: Has the curing process of epoxy resin been studied using Py-GC technique?

SOLUTION: Samples of a diglycidyl ether of bis-phenol A (DGEBA, Mn≈340) prepolymer with various amounts of 1-Benzyl-2-Methyl Imidazole (1B2MZ) were cured at 180˚C for 3 hours and were analyzed by Py-GC at 590˚C.

RESULT: Figure 1 shows typical pyrograms of DGEBA cured with various amounts of 1B2MZ at 180˚C for 3 hrs. Relationships between intensities of observed peaks and the amounts of catalysts added are shown in Figure 2. It was found that the yields of the pyrolyzates with epoxide groups decreased with increase of the degree of cure, while those of various phenols, characteristic of prepolymer skeleton increased. The results observed corresponded well to the those deduced from Tg measurements by DSC.

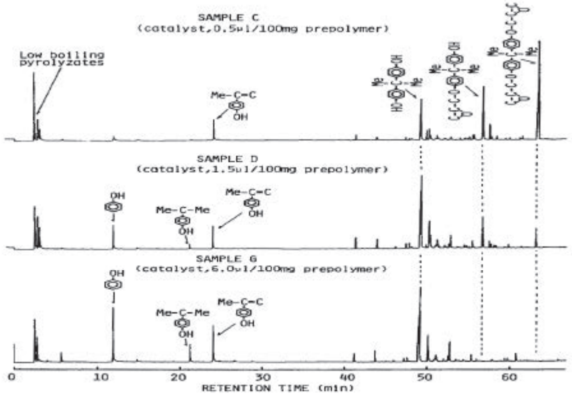


Fig. 1 High-resolution pyrograms of epoxy resins cured with various amounts of imidazole catalyst at 180°C for 3h.

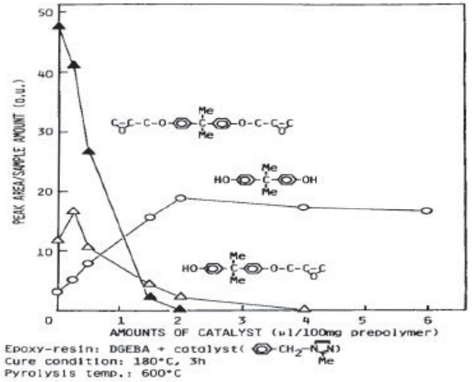


Fig. 2 Changes of characteristic products from epoxy resins as a function of catalyst amount.

Ref: Multi-functional Pyrolyzer® Technical Note, PYA1-034E

F-1

Analysis of Volatiles Released from a UV Curable Resin

PROBLEM: Have volatiles released from a UV curable resin been analyzed using UV/Py-GC/MS?

SOLUTION: A dry film of an acrylic UV curable resin was analyzed by ultraviolet light (UV) irradiation/ pyrolysis-GC/MS technique. A small disc-shaped sample (3 mm in dia., 350 µg) was used. The UV irradiation was conducted in He atmosphere at 60°C for 10 min using a micro UV irradiator (UV-1047Xe) which uses a Xe lamp as a light source.

RESULT: Chromatograms of volatile components released from the resin with and without UV irradiation and their magnified view are shown in Fig. 1. Without UV irradiation, decomposed polymerization initiator was only observed, on the other hand, upon UV irradiation various organic compounds including 300 ppm of methyl methacrylate (MMA) against the original sample weight were observed. As shown here, the UV/Py-GC/MS technique allows you to analyze volatiles released from a UV curable resin during its curing process without complicated treatments.

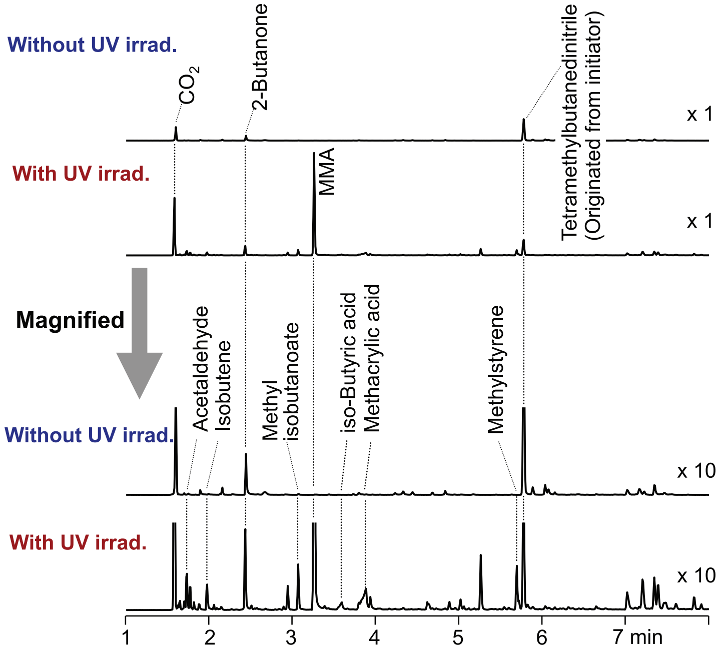


Fig. 1 Analysis of volatiles released from UV curable acrylic dry film

Micro UV irradiator: UV-1047Xe, separation column: Ultra ALLOY+-1 (dimetylpolysiloxane), L=30 m, id=0.25 mm, df=0.5 µm, atmosphere gas: He, Column flow rate: 1 ml/min, split ratio: 1/10, sample size: 350 g (3 mm diameter disc), GC oven temp: 40 ~ 300 °C (20 °C/min)

Ref: Multi-functional Pyrolyzer® Technical Note, PYA5-001E

F-2

Study of Photo/Thermal/Oxidative Degradation of Polycarbonate

PROBLEM: Has the photo/thermal/oxidative degradation of polycarbonate (PC) been studied? If so, please describe.

SOLUTION: The photo/thermal/oxidative degradation of PC was examined using a UV irradiation/ pyrolysis (UV/Py)-GC/MS. The UV irradiation of the sample was performed at 100°C in air for 1 hour. When finished, the air in the system was purged with helium (He). The volatiles formed were then analyzed (Fig 2). The irradiated PC was analyzed by reactive pyrolysis with TMAH.

RESULT: Fig. 1 illustrates the expected degradation paths of PC. It is reported that the scission of the carbonate bond and the formation of a branched structure via rearrangement are the major degradation pathways. Therefore, BisA, should be the primary volatile degradation product and the degraded polymer should have branched structures. Fig. 2, shows the intensity of BisA peak increased by a factor of 10 when irradiated. This indicates that the scission of carbonate bonds in the polymer chain occurred repeatedly. Fig. 3 shows the Rx/PY results on the degraded polymer. With UV irradiation, peak A, a branched structure, was easily observed.

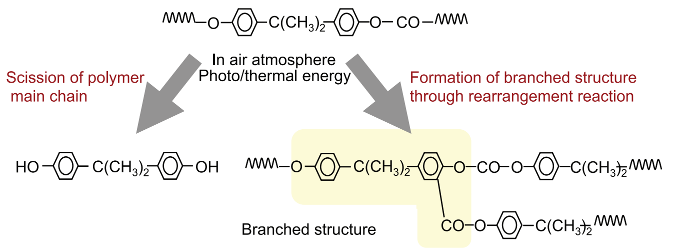


Fig. 2 Expected photo/thermal/oxidative degradation reactions of PC

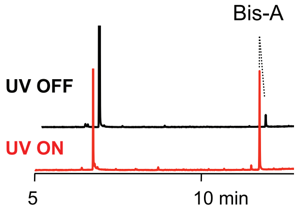


Fig. 2 Chromatograms of volatiles released from PC

Column: UA+-1(L 30 m, id. 0.25 mm, df 0.25 m), Flow rate: 1 ml/min, Split ratio: 1/10, Sample: ca.15 g (thin film), GC temp.: 40 - 300°C (20°C/min), Thermal desorption (TD) temp.: 100 - 350°C (20°C/min)

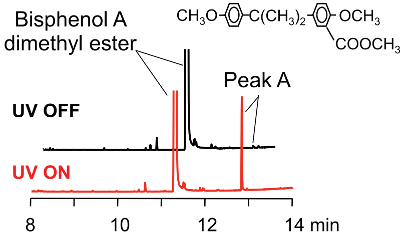


Fig. 3 Pyrograms obtained by reactive pyrolysis of the degraded PC

Py furnace temp.: 400°C, Reagent: TMAH (25 wt. % in methanol, 3 L), Split ratio: 1/50, other conditions identical to those in Fig. 2.

Ref: Multi-functional Pyrolyzer® Technical Note, PYA5-002E

F-3

Analysis of the Photo/Thermal/Oxidative Degradation Products of High Impact Polystyrene (HIPS)

PROBLEM: Is there a way to analyze volatile degradation products from high impact polystyrene (HIPS) in photo/thermal/oxidative degradation tests?

SOLUTION: Volatiles released from HIPS when it is exposed to UV radiation can be analyzed using the micro UV irradiator with a xenon (Xe) lamp. 10 µL of a dichloromethane solution (2 mg/mL) of HIPS was placed in a sample cup. The HIPS sample was irradiated for one hour at 60°C in air. Volatile degradation products were cryo-trapped at the head of the separation column. When the UV irradiation was finished, the air was purged with helium and the irradiated sample was thermally desorbed (60-250°C). The GC/MS analysis of the trapped vapors was then conducted.

RESULT: Fig. 1 shows the chromatograms of the volatile degradation products from HIPS with and without UV irradiation. Benzaldehyde, acetophenone, and benzoic acid are the PS degradation products formed during the irradiation. 2-propenal is also observed. It is the volatile degradation product of butadiene present in HIPS.

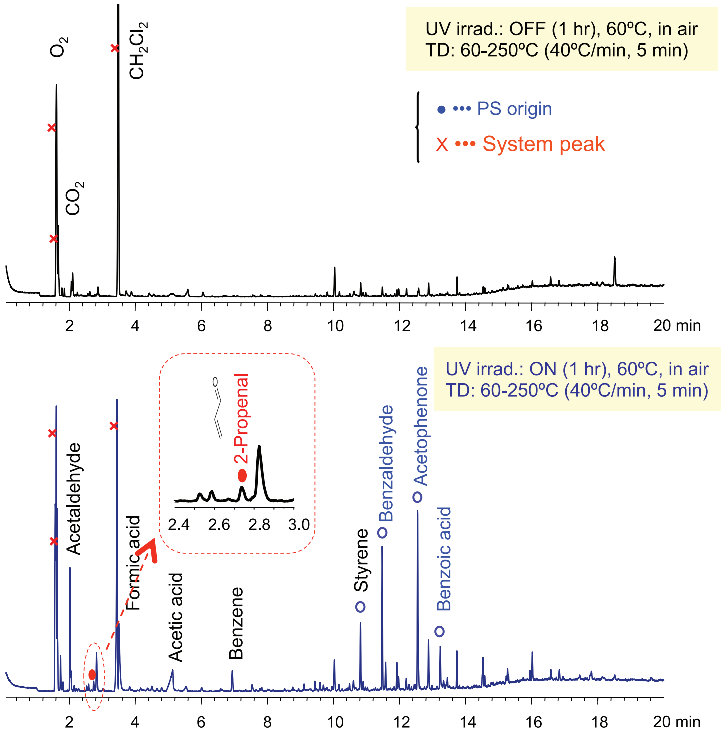


Fig. 1 Chromatograms of the volatile degradation products formed when HIPS is irradiated and not irradiated.

<UV irrad.> Micro UV irradiator: UV-1047Xe, irrad.: 1 hr, furnace temp.: 60°C, atmosphere gas: 10 mL/min Air, split ratio:1/10 <GC/MS> Separation column: Ultra ALLOY+-1 (polydimethylsiloxane, L=30 m, i.d.=0.25 mm, df=0.5 m), GC oven temp.: 40°C(5 min)-240°C (20°C/min), GC injection temp.: 250°C, carrier gas: 50 ml/min He, split ratio: 1/50

Ref: Multi-functional Pyrolyzer® Technical Note, PYA5-003E

F-4

Analysis of Degraded High Impact Polystyrene in Photo/Thermal/Oxidative Degradation Tests Using EGA-MS

PROBLEM: Have volatiles released from a UV curable resin been analyzed using UV/Py-GC/MS?

SOLUTION: A dry film of an acrylic UV curable resin was analyzed by ultraviolet light (UV) irradiation/ pyrolysis-GC/MS technique. A small disc-shaped sample (3 mm in dia., 350 µg) was used. The UV irradiation was conducted in He atmosphere at 60°C for 10 min using a micro UV irradiator (UV-1047Xe) which uses a Xe lamp as a light source.

RESULT: Chromatograms of volatile components released from the resin with and without UV irradiation and their magnified view are shown in Fig. 1. Without UV irradiation, decomposed polymerization initiator was only observed, on the other hand, upon UV irradiation various organic compounds including 300 ppm of methyl methacrylate (MMA) against the original sample weight were observed. As shown here, the UV/Py-GC/MS technique allows you to analyze volatiles released from a UV curable resin during its curing process without complicated treatments.

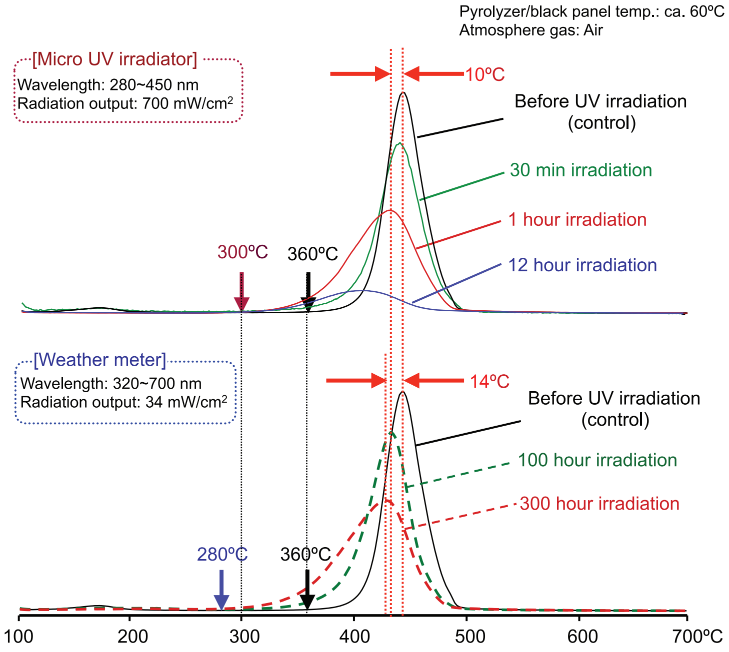


Fig. 1 Thermograms obtained before and after irradiation by UV/Py-GC/MS (top) and Xe weather meter (bottom).

Pyrolyzer temp.: 100 - 700°C (20°C/min), GC oven temp.: 300°C, UADTM-2.5N (L＝2.5 m、i.d. ＝0.15 mm), Carrier gas flow rate: 1 mL/min; He, split ratio: 1/50, sample:20µg

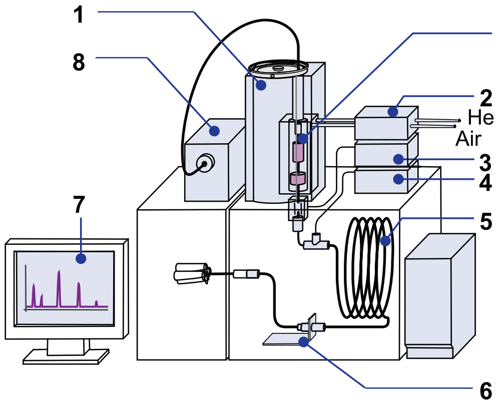
Ref: Multi-functional Pyrolyzer® Technical Note, PYA5-004E

What is Py-GC/MS Technique?

Pyrolysis GCMS is a powerful and straightforward technique that utilizes a Frontier Pyrolyzer as a programmable temperature inlet to a Gas Chromatography-Mass Spectrometer (GCMS) system. The material of interest (liquid or solid) is uniformly heated in an inert atmosphere. Volatile organics evolve at temperatures below 300 °C. At higher temperatures, covalent bonds break and the complex structure is degraded into smaller (stable and volatile) molecules which are referred to as pyrolyzates. The pyrolyzates formed and their relative intensities provide insight into the structure of the original material.

The Frontier Pyrolyzer is interfaced directly to the GC inlet. The sample is placed in a small deactivated cup which is, in turn, positioned in a micro-furnace. The temperature of the sample is carefully controlled (±0.1 °C) to ensure that the sample-to-sample thermal profile is identical. Frontier's well-engineered technology ensures that the sample is maintained at ambient temperature, in an inert atmosphere, prior to pyrolysis; thus eliminating evaporation, thermal degradation, and thermosetting before analysis.

The technical data in this monograph were obtained using one or more of the listed accessories. Each accessory is described in more detail in the system configuration section.

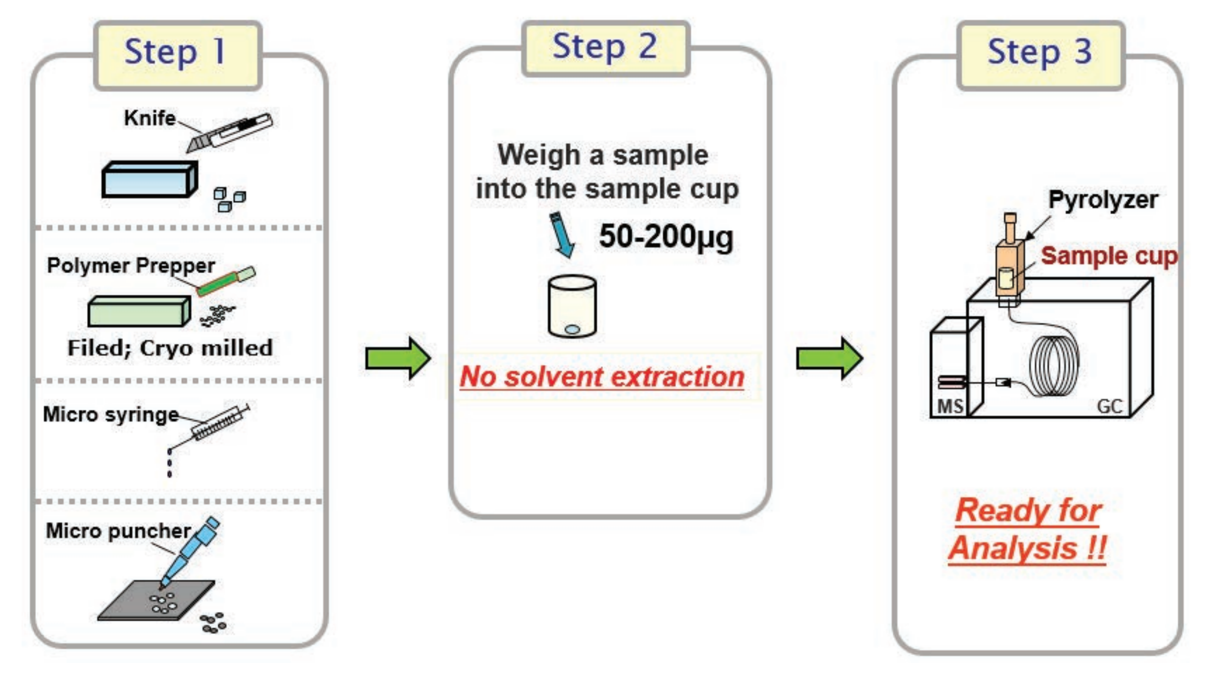


Multi-Shot Pyrolyzer (EGA/PY-3030D)

1. Auto-Shot Sampler (AS-1020E)
2. Carrier Gas Selector (CGS-1050Ex)
3. Selective Sampler (SS-1010E)
4. MicroJet Cryo-Trap (MJT-1035E)
5. Ultra ALLOY® metal capillary column
6. Vent-Free GC/MS adapter
7. F-Search system (search engine and libraries)
8. Micro UV irradiator (UV-1047Xe)

Easy Sample Preparation

This technology allows multiple analysis on a single sample. There is no need for solvent and sample preparation as the sample is simply introduced into the GCMS by the Frontier Pyrolyzer.

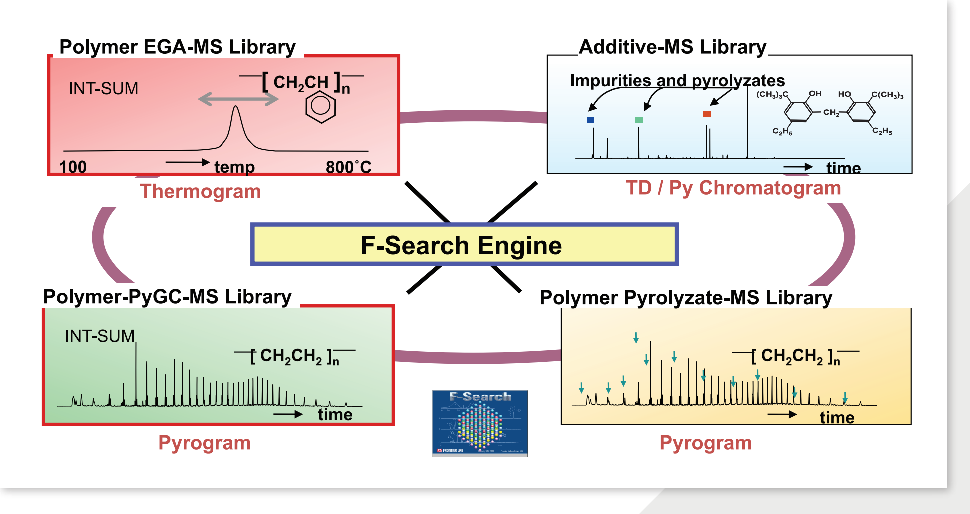


F-Search Engine

SIMPLIFYING AND IMPROVING THE ACCURACY OF DATA INTERPRETATION

Polymeric materials often contain a variety of additives such as antioxidants, UV absorbers, etc. to assist during the production phase and determine the physical and chemical characteristics of the final product. These compounds are identified using commercial mass spectral (MS) libraries; however, these general-purpose MS libraries contain very few entries for pyrolyzates and additives which severely limits their utility for polymer characterization.

Frontier Laboratories developed a search engine and libraries called F-Search. The ions associated with hundreds of polymers, their degradation products (i.e., pyrolyzates) and hundred of additives are used to identify and thus characterize the sample as it is heated in the Py. The libraries include both chromatographic and mass spectral data. There are four unique libraries which allow users to select among them for specific purposes. The ability to create in-house specialty libraries is incorporated into the standard software. Updating these libraries is straightforward.

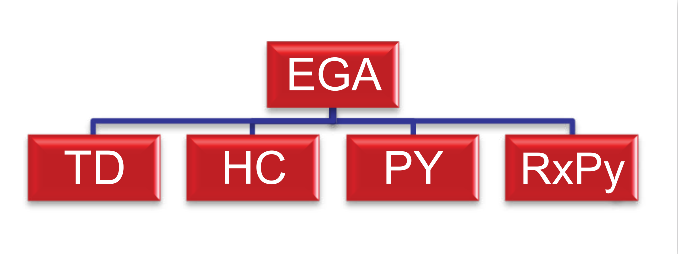


"Method Map" for Material Characterization

Frontier Lab has developed a sequence of tests referred to as the "method map" to chemically characterize samples using the EGA/PY-3030D Multi-Functional Pyrolyzer System in conjunction with a benchtop GC/MS. This sequence is applicable when characterizing virtually any organic material from volatiles to high molecular weight polymers.

The **"method map"** provides scientists with two simple steps for determining the organic composition of any unknown material:

i. The first step is to perform an **Evolved Gas Analysis (EGA)**. In this technique, the sample is dropped into the furnace which is at a relatively low temperature (ca. 40-100 ˚C). The furnace is then programmed to a much higher temperature (ca. 600-800 ˚C). Compounds "evolve" from the sample as the temperature increases. A plot of detector response versus furnace temperature is obtained.



ii. The second step is to use the EGA thermogram and selected ion chromatograms (EIC) to define the thermal zones of interest and then perform one or combination of the following techniques:

Use the links below for more information.

Thermal Desorption (TD)

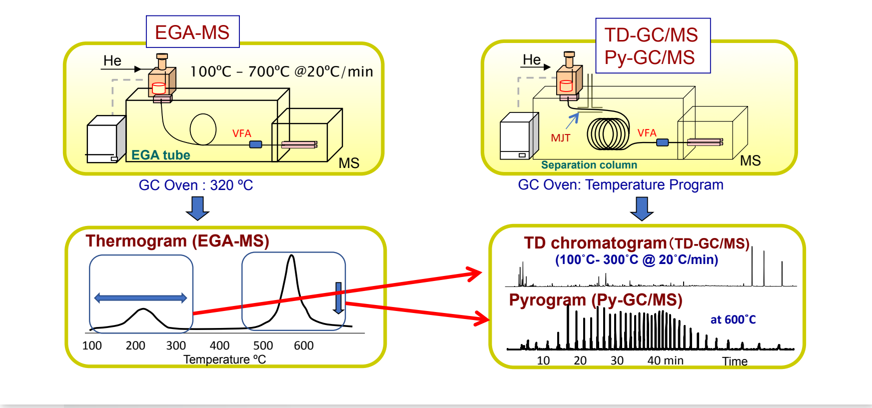
Flash Pyrolysis (Py)

Heart Cutting (HC)

Reactive Pyrolysis (RxPy)

EGA & "Method Map"

EGA CONFIGURATION: No column is used; a short, small diameter (1.5m X 0.15mm id) deactivated tube connects the injection port to the detector. All thermal zones (interface temperature, GC injection port, column oven and detector cross-over) are held at elevated temperatures to prevent condensation. The figure below shows the EGA-MS configuration and a typical EGA thermogram.



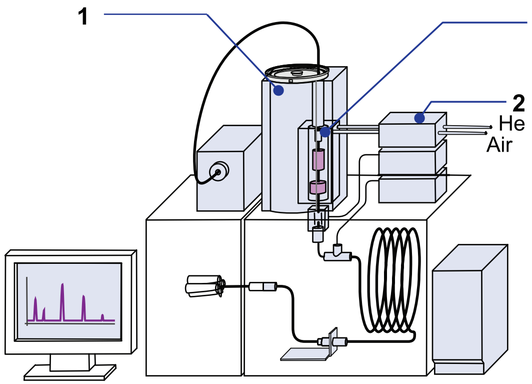
Following EGA, the instrument is re-configured. The EGA tube is replaced by an analytical column. The Frontier Vent-Free Adaptor enables this to be done easily and quickly; there is no need to vent the MS. MS vacuum equilibrium is re-established within a few minutes, and the exposure of the ion source to oxygen is minimized.

In this example, a double-shot analysis (TD of the thermally stable and the volatile components followed by Py of the residual sample in the cup) was performed to characterize the two thermal zones shown on the EGA thermogram. One sample is analyzed two times; the sequence is fully automated.

As shown in the Figure, information about the organic 'volatiles' in the sample is generated by simply introducing the sample at 300˚C, only the compounds evolving below 300˚C will evolve from the sample and be transported to the head of the column. If there is interest in both the volatile fraction and the higher boiling compounds, this can be done in two steps, and it may be necessary to add a micro-cryo trap. Thermal desorption is performed over time, e.g., 100 to 250 ˚C at 20 ˚C /min takes 7.5 minutes. The micro-cryo trap re-focuses the volatile analytes of interest at the head of the column so that the full separating power of the column can be utilized.

If there are more than two zones in the obtained EGA thermogram, Heart-Cutting (HC) technique, which utilizes an accessory called a Selective Sampler, slices the thermal zones out of the sample and separate the components chromatographically with detection by MS.

Py-GC/MS
System Configuration



Multi-Shot Pyrolyzer (EGA/PY-3030D)

Use these links for more information.

1. Auto-Shot Sampler (AS-1020E)
2. Carrier Gas Selector (CGS-1050Ex)

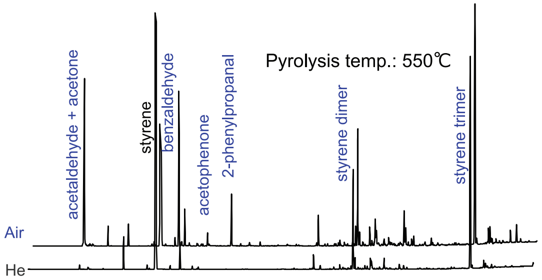
1. Auto-Shot Sampler (AS-1020E)

Up to 48 samples can be automatically analyzed using any of the analytical modes (e.g., TD, Py, Double-Shot, Heart-Cutting. Etc) with enhanced reliability.

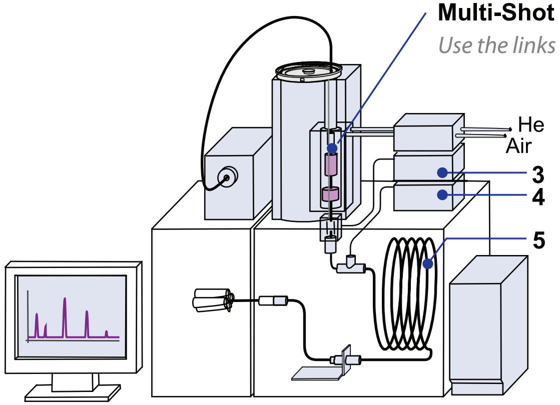
Pyrolyzer is located in the housing of Auto-Shot Sampler.

2. Carrier Gas Selector (CGS-1050Ex)

The device allows switching of the gas, e.g., He and air, surrounding the sample during analysis.



Pyrograms of polystyrene obtained in air and He



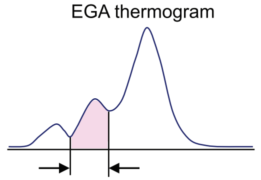
Multi-Shot Pyrolyzer (EGA/PY-3030D)

Use the links below for more information.

3. Selective Sampler (SS-1010E)
4. MicroJet Cryo-Trap (MJT-1035E)
5. Ultra ALLOY® metal capillary column

3. Selective Sampler (SS-1010E)

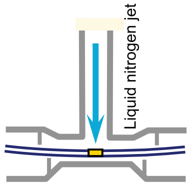
Any temperature zone as defined by the EGA thermogram, that is Heart-Cutting either manually or automatically, can be introduced to a separation column.

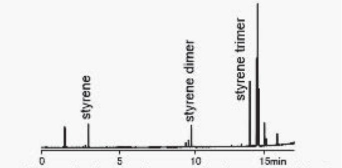


Any temperature zone can be heart-cut for GC/MS analysis.

4. MicroJet Cryo-Trap (MJT-1035E)

By blowing liquid nitrogen jet to the front of separation column, volatile compounds are cryo-trapped while maintaining the temperature at -196°C using only one third of the amount of liquid nitrogen required for competitors products. It supports automated analysis.

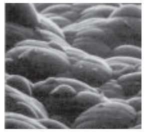




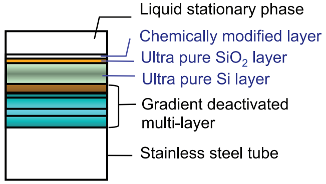
Thermal desorption analysis of residual oligomers in polystyrene using MJT-1030Ex.

5. Ultra ALLOY® Metal Capillary Column

By multi-layer gradient deactivation treatment, these separation columns have high flexibility, high temperature, and contamination resistances.

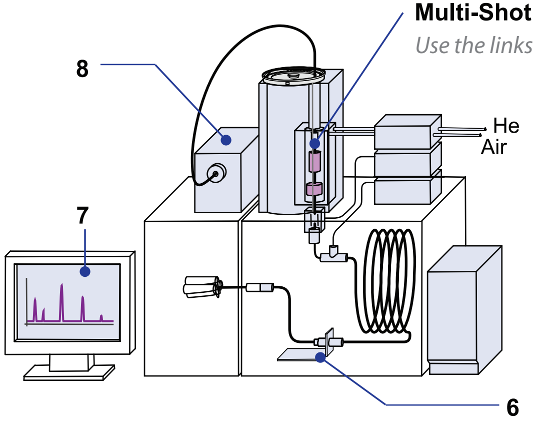


SEM image of inner surface of stainless steel tube after deactivation treatment.



Multi-Shot Pyrolyzer (EGA/PY-3030D)

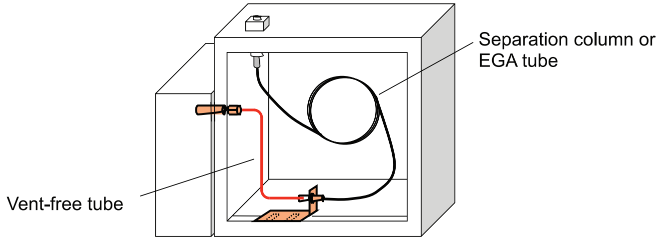
Use the links below for more information.



6. Vent-Free GC/MS adapter
7. F-Search system (search engine and libraries)
8. Micro UV irradiator (UV-1047Xe)

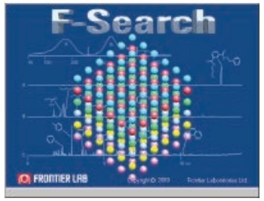
6. Vent-free GC/MS Adapter

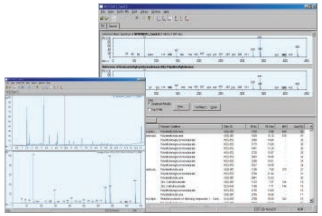
Without venting MS, separation column and/or EGA tube can be switched.



7. F-Search System (Libraries and Search Engine)

This software system supports identification of polymers and additives from data obtained by evolved gas analysis, thermal desorption, or pyrolysis GC/MS analysis.

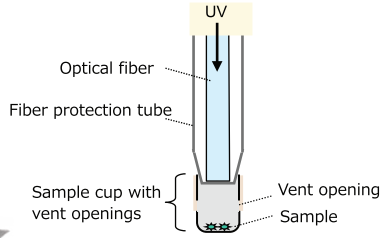




Chromatogram and result of mass spectral search

8. Micro-UV Irradiator (UV-1047Xe)

With a strong Xe UV light source, photo, thermal, and oxidative degradation of polymers can rapidly be evaluated.



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ENVIRONMENTAL	VOLATILES, POLLUTANTS, PESTICIDES
FORENSIC AND SECURITY	FORENSIC EVIDENCES
INKS AND PAINTS	PIGMENT, RESIN, SOLVENT, DEFOAMER, WAX, PHOTOCOPY TONER
PAPER AND FIBERS	WOODS, PULP, COATINGS, SIZING AGENTS
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