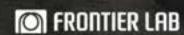


2023 최신분석기술 온라인 세미나 시리즈

자동차 내장재 및 타이어 분석을 위한 Pyrolysis-GC/MS 솔루션

2023. 03. 30 (목) 영인과학



Products for Automobile Applications

The automotive industry is constantly evolving due to government regulations, changing consumer demands, and improvements in technology.

The industry faces many challenges including lowering greenhouse gas emissions, boosting aerodynamics, increasing fuel economy, delivering the optimum strength-to-weight ratio, and ensuring safety.

The industry is also in the midst of a revolution with the global surge in electric vehicle production and demand as well as the rise in semiand fully-autonomous (self driving) vehicle technologies.

This constant evolution creates a landscape of continuous challenges and opportunities for improvements through advanced materials and innovative design.

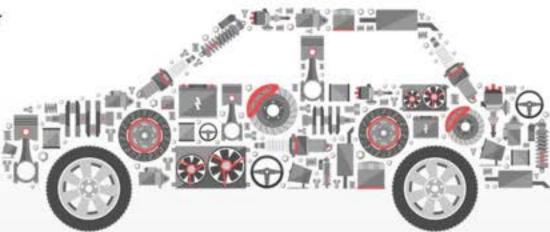


Polymer products for automotive applications



High Performance Polymers for Automobile Industry

- After packaging, building, and construction, the automotive industry is the third largest consumer of polymers.
- Polymers deliver the characteristics of high-impact resistance, reduced noise and vibration, structural integrity design flexibility, low density, and high durability. Each feature is vital to the industry for use in automobiles, over-the-road trucks, and off-highway equipment.
- Within the market, some typical applications include air conditioning, braking, safety, steering, suspension, shock absorption, thermal management, and fuel systems.
- Additionally, the automotive sector uses polymer products for drivetrain and transmissions, electronic control units (ECU), clutches, torque converters and differentials, interior and exterior components, panel, and so much more.



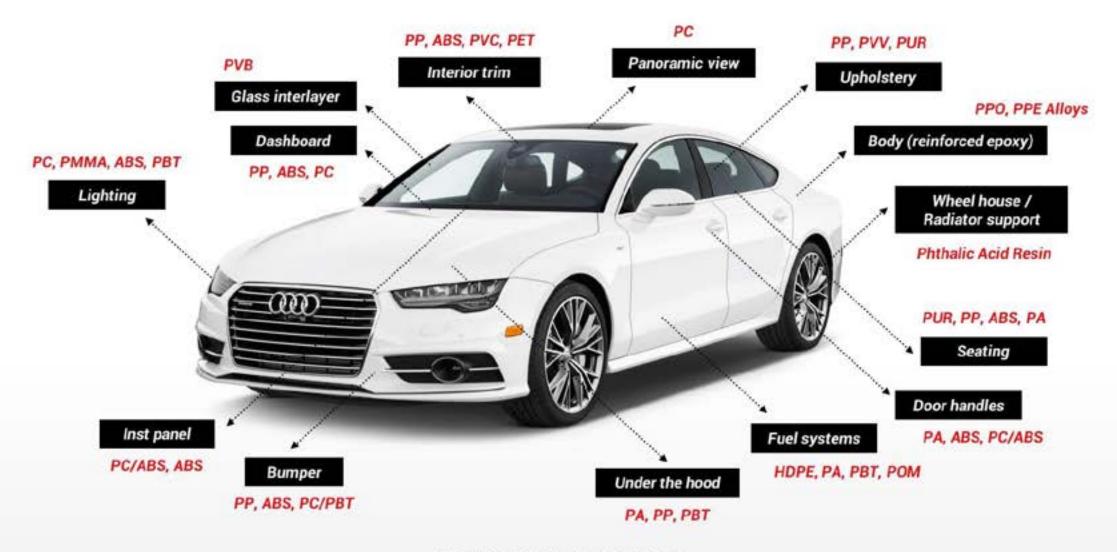
High Performance Polymers for Automobile Industry

Here is a sample of the many products manufactured using high-performance polymer products for the automotive industry;

- Oxygen sensor grommets
- PTFE seals
- O-Rings
- Bearings and thrust bearings
- Low-drag mudflaps
- Suspension cylinder seals
- Bushings
- Diaphragms
- Sensor covers
- Rubber-to-metal bonded seals
- Wiring hardness and housing
- Battery sealing for pressure relief valves
- Buffer rings and back-up rings
- Rotary seals
- Friction and wear-resistant components
- Custom-made gaskets
- Custom-molded parts



Plastics Applications in Automotive Parts



High Performance Polymers for Automobile Industry

The average vehicle uses about 150 – 300 kg of plastics and plastic composites versus 1,163 kg of iron and steel – currently it is moving around 15 – 20% of total weight of the car, over 2,000 parts and components of all shapes and sizes.

Although up to 13 different polymers may be used in a single car model(see Table 1), just three types of plastics make up to about 66% of the total plastics used in a car;

- Polypropylene(PP), 32%
- Polyurethane(PU), 17%
- PVC, 16%

Table 1: Plastics used in a typical car

Component	Main types of plastics	Avg. weight in car (kg)
Bumpers	PS, ABS, PC/PBT	10
Seating	PUR, PP, PVC, ABS, PA	13
Dashboard	PP, ABS, SMA, PPE, PC	7
Fuel systems	HDPE, POM, PA, PP, PBT	6
Body (incl. panels)	PP, PPE, PU	6
Under-bonnet components	PA, PP, PBT	9
Interior trim	PP, ABS, PET, POM, PVC	20
Electrical components	PP, PE, PBT, PA, PVC	7
Exterior trim	ABS, PA, PBT, POM, ASA, PP	4
Lightning	PC, PBT, ABS, PMMA, PU	5
Upholstery	PVC, PUR, PP, PE	8
Liquid reservoirs	PP, PE, PA	1
Total		105

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Rubber Products in Automobile



Rubber Raw Materials



Additives

- Vulcanizing agent
- · Vulcanization accelerator

2023 영민과학 최신분석기술 세미나 시리즈 ②

- Accelerator activator
- · Antioxidant, etc.

Compounding agent	Compound
Filler	Carbon black, Metal powder
Crosslinker	Polyamines, Polyols
Vulcanization accelerator	Amines, Thiazoles
Plasticizer	Phthalates
Antioxidant	Aromatic amines, Phenols
Anti-scorching agent	Aromatic acids

Characterization of these material is important (Py-GC/MS)

- Product Verification and Conformity
- · Reverses Engineering
- Failure Analysis

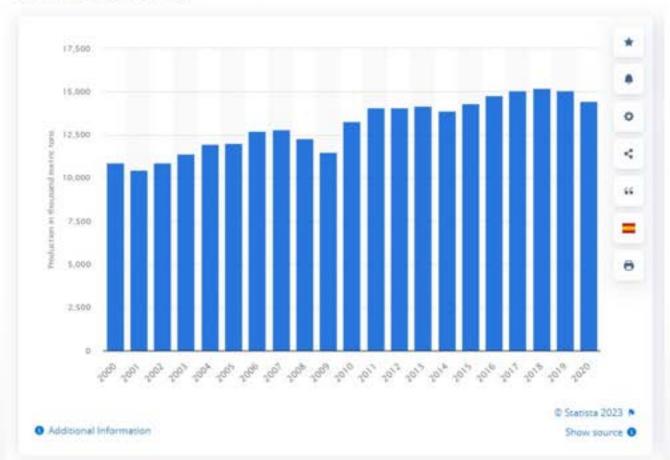


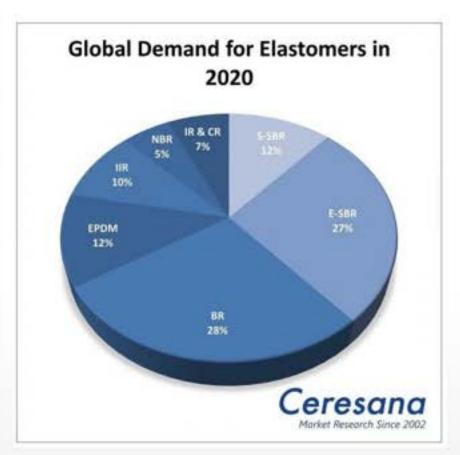


Annual Rubber Production and Usage

Synthetic rubber production worldwide from 2000 to 2020

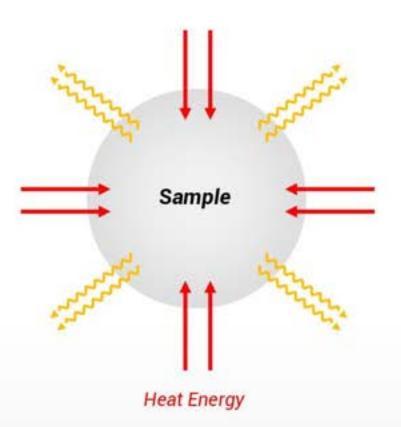
(in 1,000 metric tons)







Information from Polymeric Materials by Heating

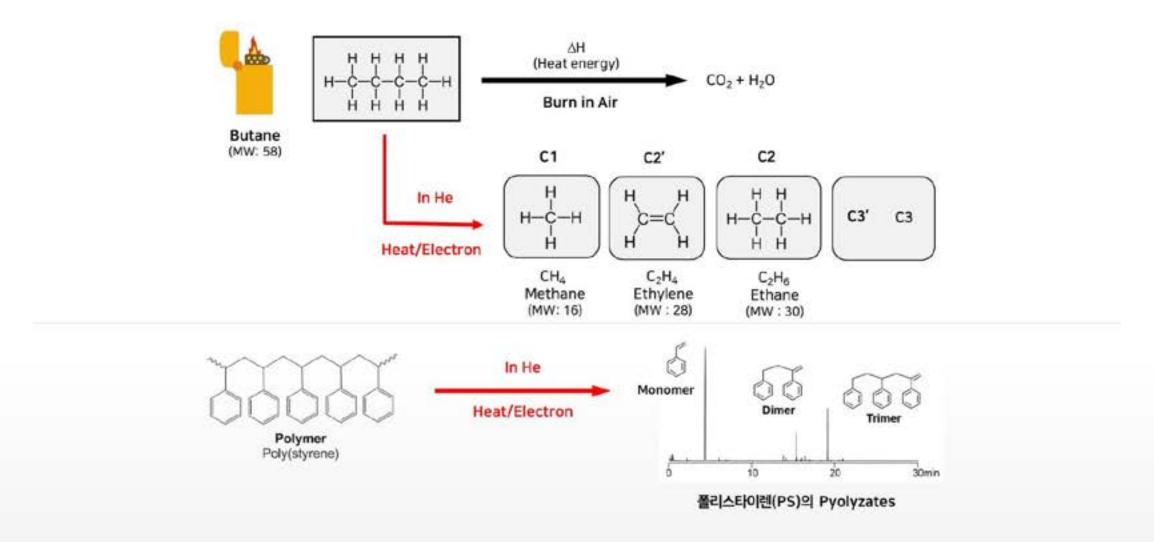


Analytical Pyrolysis Defined

- Pyrolysis is a thermochemical decomposition of organic material at elevated temperatures without the participation of oxygen. It involves the simultaneous change of chemical composition and physical phase, and is irreversible. The word is coined from the Greek-derived words pyr "fire" and lysis "separating".
- Think of analytical pyrolysis as breaking apart or manipulating organic molecules in a controlled and predictable manner using the precise use of heat.

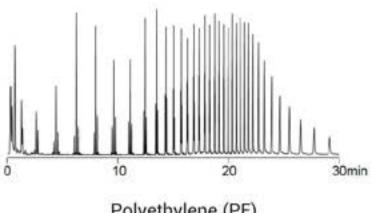


Pyrolysis of Polymeric Materials and Pyrolyzates

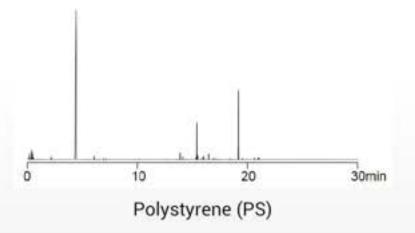


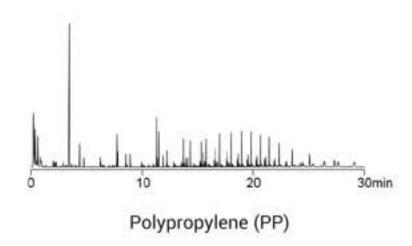


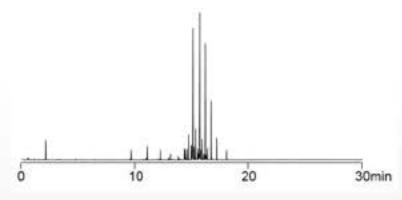
Typical Pyrograms of Different Polymers



Polyethylene (PE)



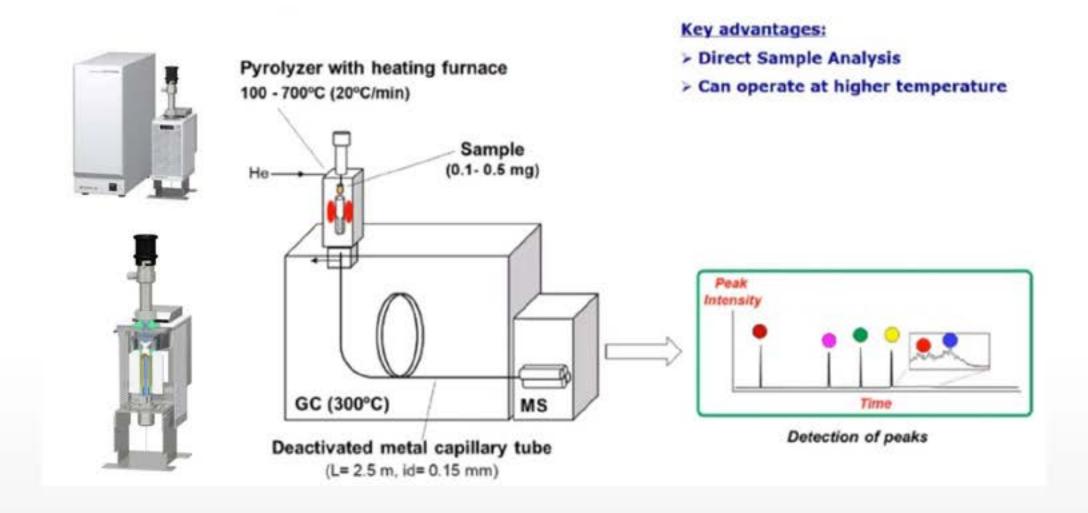




Higher methacrylate copolymer

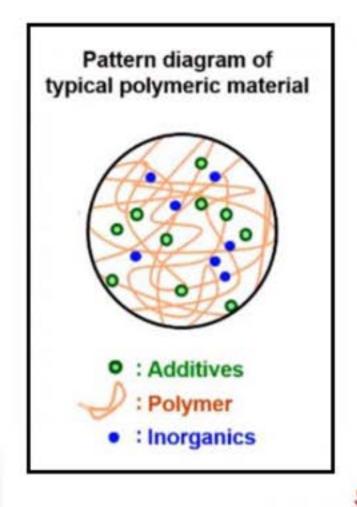


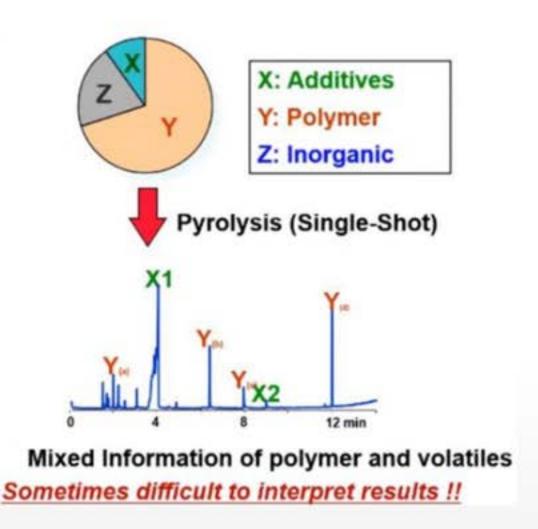
Py-GC/MS Working Principle





Polymeric Materials and Pyrolysis





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Py-GC/MS Working Principles

STEP 01 Sample Preparation



Solid samples Using a cutter knife



Solid samples Using a cryogenic mill



Film samples Using Micro-puncher



Liquid sample Using a micro syringe

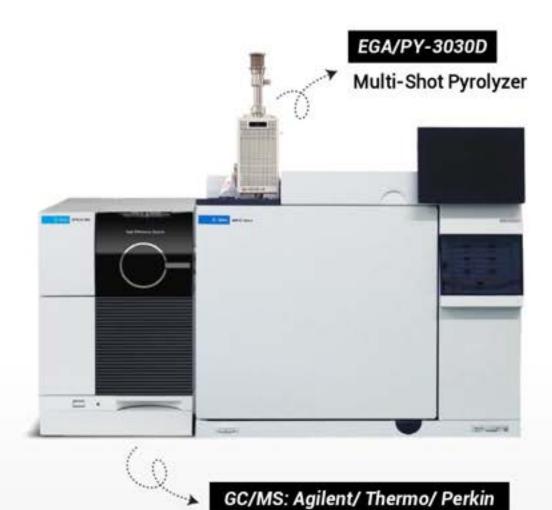




2023 영민과학 최신분석기술 세미나 시리즈 ②



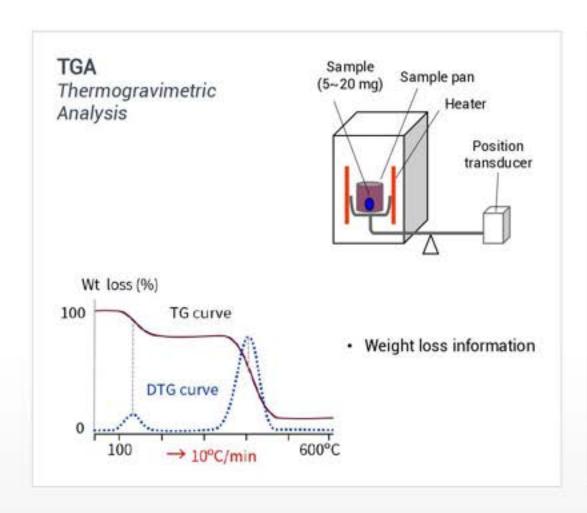
4 Analytical Techniques & Method Mapping

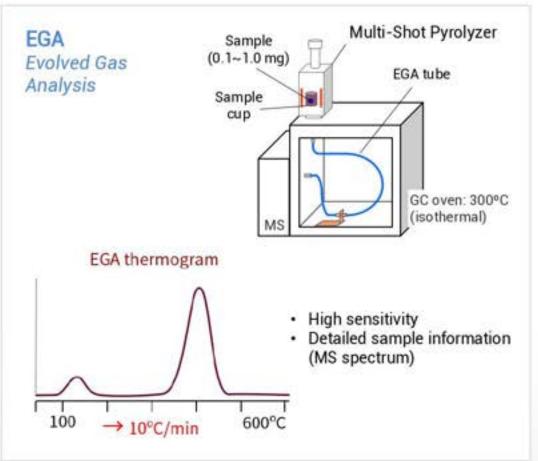


- 1. Evolved Gas Analysis (EGA-MS)
- 2. Single-Shot Analysis (PY, Flash Pyrolysis)
- 3. Double-Shot Analysis (TD/PY)
- 4. Heart-Cut/EGA-GC/MS Analysis (Multi-Shot Analysis)



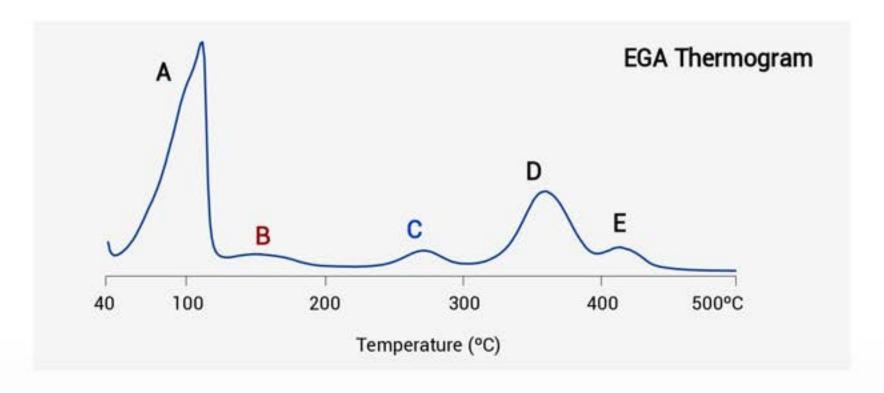
Evolved Gas Analysis (EGA-MS)







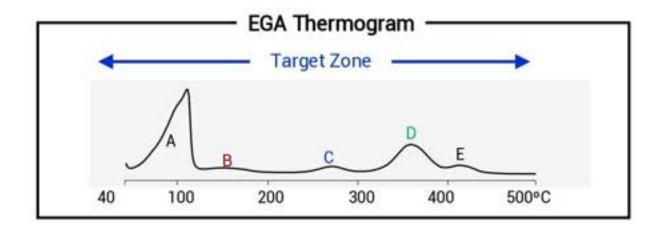
Evolved Gas Analysis (EGA-MS)

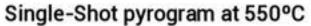


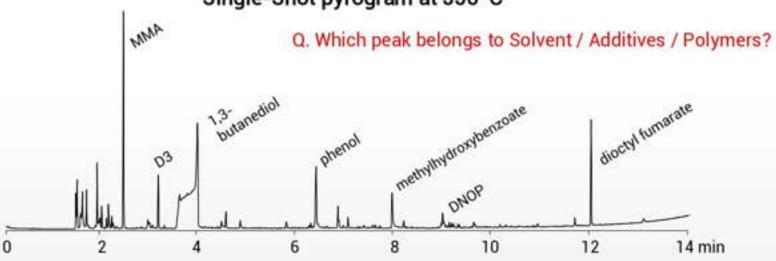
- > How many peaks?
- Each temperature?



Single-Shot Analysis

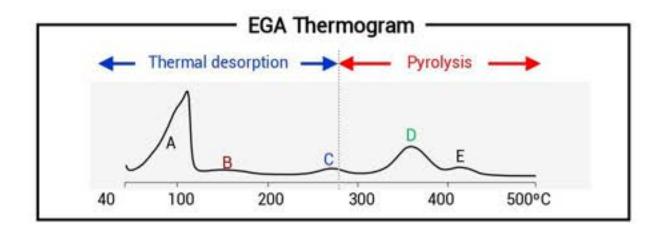


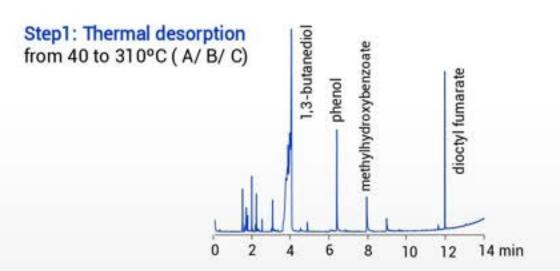


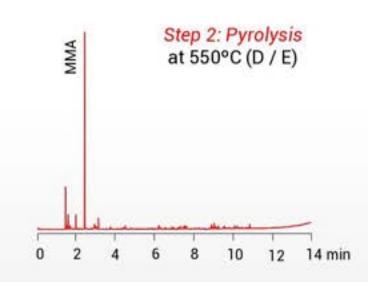




Double-Shot Analysis

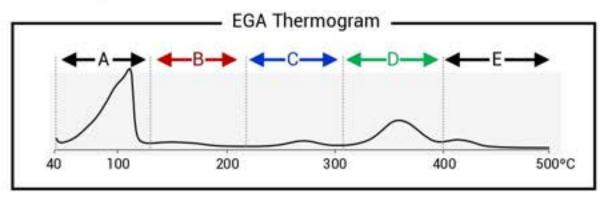


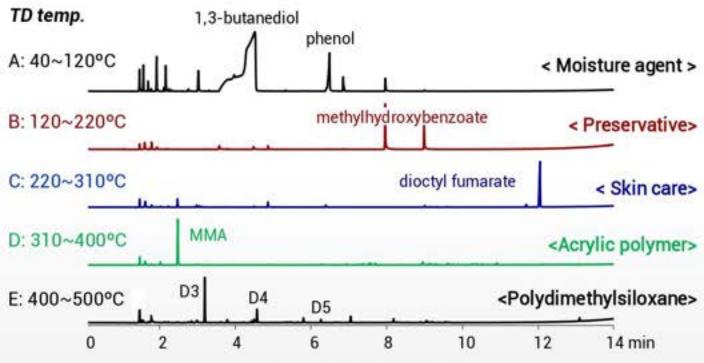






Heart Cutting EGA-GC/MS Analysis







Py-GC/MS Applications for Automotive Market



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A. Polymer Processing

B. Additives

C. Paints & Coating

D. Rubbers

E. Adhesives

F. Weatherability Tests







A. Polymer Processing

PMMA(Acrylic) is a transparent thermoplastic; Applications: Windows, displays, screens

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

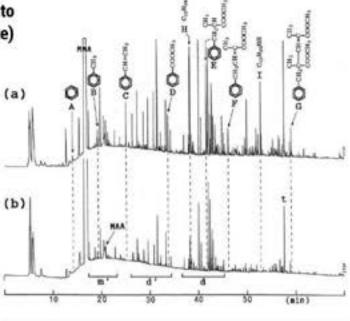


Fig. 1 Pyrograms of poly (methyl methacrylate): prepared in toluene with 0.3% of benzoyl peroxide and 1.5% of dodecanethiol; and thermally polymerized in bulk without any polymerization reagent.

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

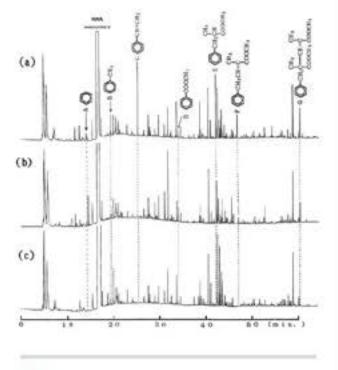


Fig. 1 Pyrograms of PMMA samples obtained at 460°C (a) polymerized in toluene,

- (b) polymerized in benzene, and
- (c) polymerized without any initiator.

A. Polymer Processing

Polybutylene Terephthalate(PBT) has good chemical resistance and electrical properties, hard and tough material with water absorption, very good resistance to dynamic stress, thermal and dimensional stability.

Applications: Fog lamp housings and bezels, sun-roof front parts, locking system housings, door handles, bumpers, carburetor components, etc.

Analysis of the Constituent Monomers of Polybutylene Terephthalate (PBT)

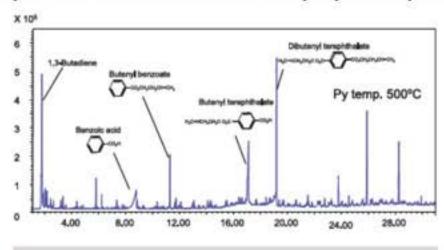


Fig. 1 Pyrogram obtained by flash pyrolysis of PBT

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.

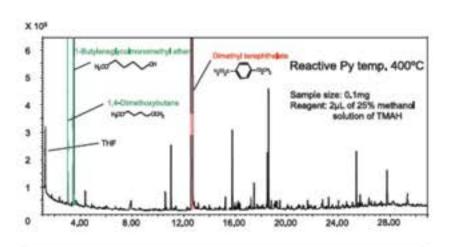
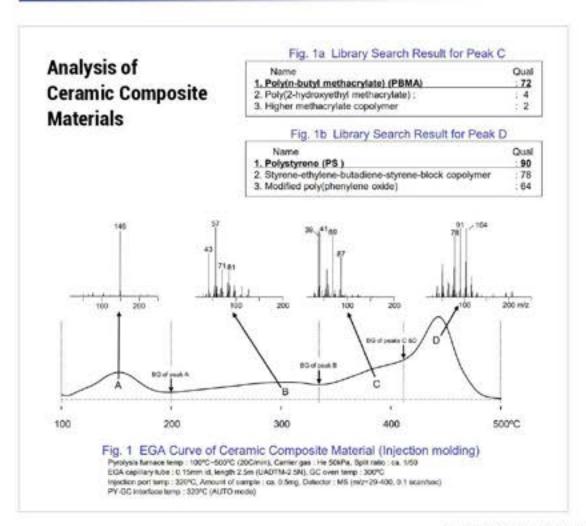
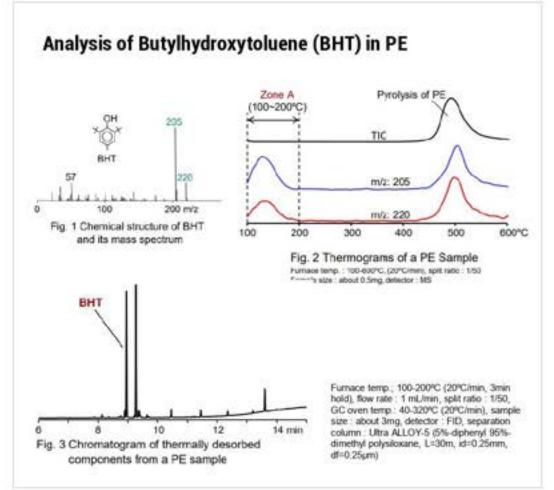


Fig. 2 Pyrogram obtained by reactive pyrolysis of PBT Carrier gas: He, Injection port pressure: 103kPa, Split ratio: 1/60, Separation column: Ultra ALLOY+-5 (5% diphenyldimethylpolysiloxane) L=30m, Id=0.25mm, df=0.25mm, GC oven temp: 38°C-300°C (20°C /min)



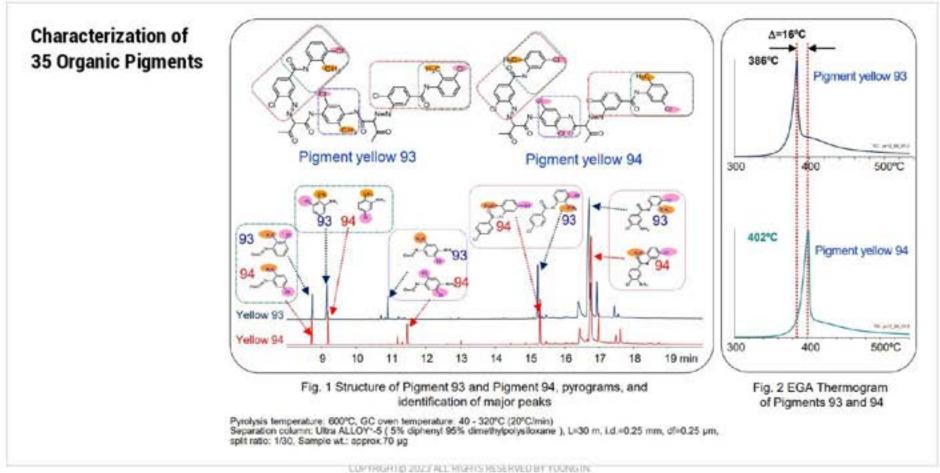
B. Additives





C. Paints & Coating

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.





C. Paints & Coating

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.

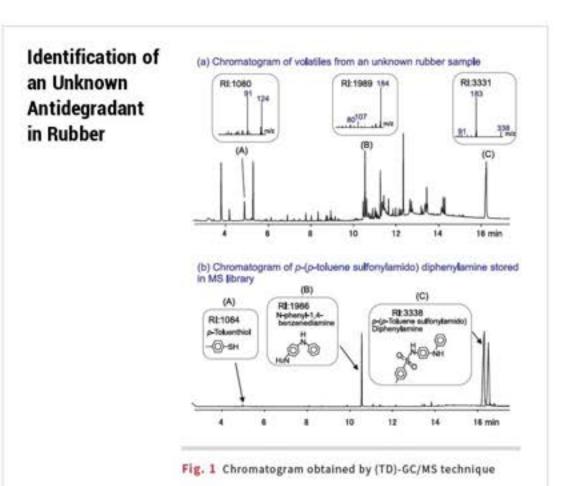
Analysis of Toxic Gases Released from Polyvinylidene Chloride (PVDC) Film tributyl aconitate tributyl acetylcitrate Zone B Zone C Zone A. acetic acid CITROFLEX A-4 butanol Zone A (40~200°C) (200-240°C) (240~500°C) (40-200°C) HCL Zone B (200-240°C) dichlorobenzene 100 200 300 400 500°C chlorobenzene benzene/ trichlorobenzene Zone C Fig. 1 EGA Profile of Polyvinylidene (240-500°C) Chloride Pyrolysis temp: 40~600°C (30°C/min), carrier gas: He Interface: deactivated metal capillary column (length: Fig. 2 Analysis Results of Zones A, B, and C of Polyvinylidene Chloride 2.5m, id: 0.15mm) Carrier gas. He, column flow rate: 1milinin; Split injection, separation column; Ultra ALLOY-5 (5% diphenyl dimetryl polysiloxane). Injection port pressure: 50kPa length: 30m, id: 0.25mm, film thickness: 0.25µm, GC oven temp: 40°C (1min hold) = 320°C (20°C/min), injection port temp: 320°C, Cryo trap temp: -196°C, sample: 0.25cm² Reference: Hosaka et.al., 49th Japan Analytical Society Meeting (2000)



D. Rubbers

Rubber Materials: Tires, Seal, O-rings

Polymer main chain Analysis of Compounded Rubber Volatile components Fig. 1 Evolved gas curve of a compounded rubber Pyrolysis temp.: 100-700°C (20°C/miri), Carrier gas : He 50kPa, Split ratio : ca. 1/20 E6A capitlary tube: 0.15mm ld, 2.5m (UADTM-2.5N), GC oven temp.: 360°C Injection temp.: 320°C, Sample: ca. 5g, Detector: MS (m/z=29 400) a. Thermal Description (100~300°C, (20°C/min) 2-mercapto thioberusothiazole , Nocrac 6C 2-methyl thicbenzothiszele Isoprene -dimer (limonene) b. Pyrogram (550°C) bulisciene 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 polysilaxane), 30m, 0.25mm id, 0f: 0.25m GC oven temp.: 40-300°C (20°C/min), Sample: Sg, Detector: MS (m/z=29-400, 2 scans/sec)

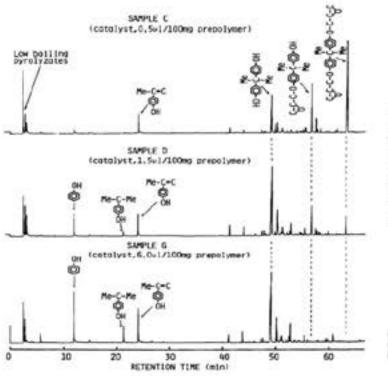


D. Rubbers

Curing process of epoxy resins has been often studied by IR, FT-IR, or NMR by looking at the spectral changes of chemical species formed during the course of curing process. DSC has also been used to study the curing reactions by evaluating the heat of reaction. On the other hand, high resolution Py-GC is another technique that can be applied for studying systems with insoluble species and various additives.

Results showed 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.

Studies on Curing Process of Epoxy Resins by Py-GC - Cured with 1-Benzyl-2-Methyl Imidazole (1B2MZ) -n



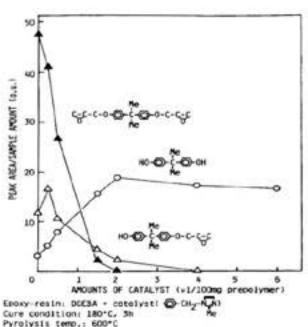


Figure 1. High-resolution pyrograms of epoxy resins cured with various amounts of imidazole catalyst at 180°C for 3h.

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

*Contents excerpted from H. Nakagawa, S. Wakatsuka, S. Tsuge, T. Koyama, Polymer. J. No. 1, pp 9-16 1992.

F. Weatherability Tests

UV curable resins are used in a wide spectrum of applications including microelectronics packaging adhesives in electronics and optical parts, etc. The curing reaction generates volatile compounds from the resin, which corrode metal surfaces and deteriorate product quality; therefore, there is a need for qualitative and quantitative analysis of such volatiles.



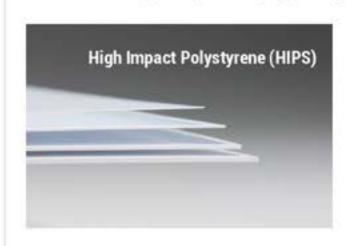
Analysis of Volatiles Released from a UV Curable Resin Without UV irrad. With UV irrad. x 1 Magnified Without UV irrad. With UV Irrad. 7 min Fig. 1 Analysis of volatiles released from UV curable acrylic

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)

F. Weatherability Tests

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.

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



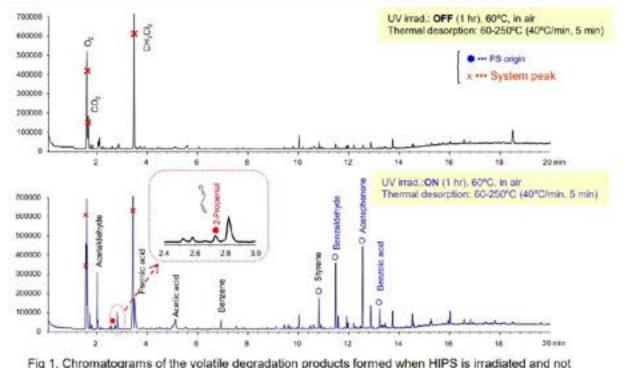


Fig 1. Chromatograms of the volatile degradation products formed when HIPS is irradiated and not

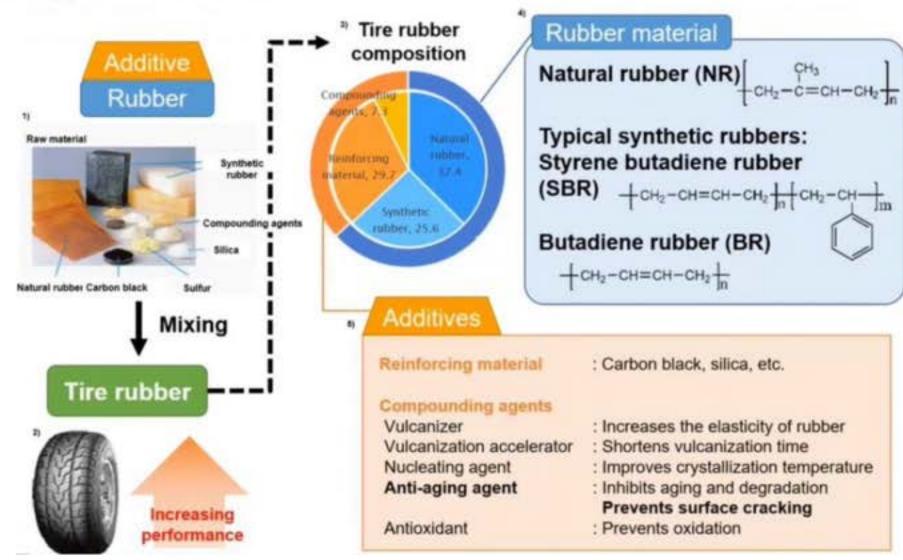
<UV irradiation* Micro UV irradiator : UV-1047Xe, irradiation: 1 fr, furnace temp.: 50°C, atmosphere gas: 10 mL/min Air, split ratio: 1/10 <GC/MS> Separation column: Utra ALLOY'-1 (polydimethylsiloxane, L=30 m, i.d=0.25 mm, d=0.5 µm), GC oven temp.: 40°C(6 min)-240°C(20°C/min). GC injection temp.: 250°C, carrier gas: 50 m/min He, split ratio: 1/50

Application

for Rubber Tires



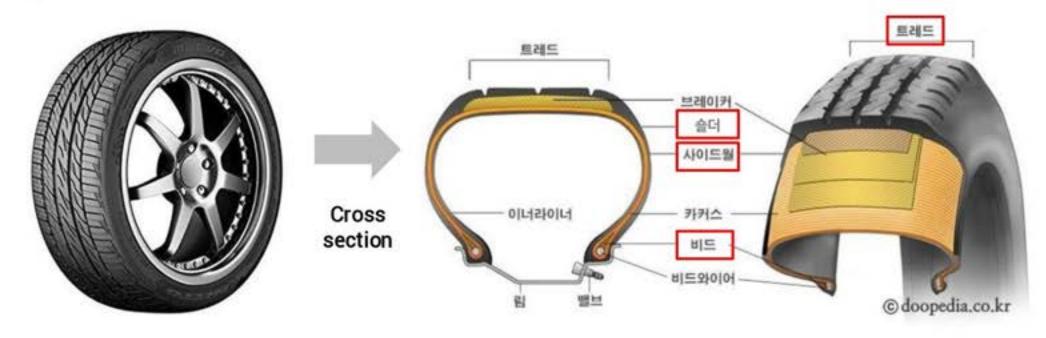
Py-GC/MS Application for Tire Rubber



ackground About Pyrolysis Py-GC/MS Principle Application for Application for Rubber Tires



Background and Goal



Roles differ depending on parts

- · Tread: Protects the inside from impact
- · Shoulder: Dissipates heat during driving
- · Sidewall: Protects the inside and prevents stretching
- . Bead: Fix the tire to the wheel



Tire rubber composition varies depending on each of the part.

Our Goal: Analysis of rubber components and additives contained in each part of tire by pyrolysis



Collecting Samples



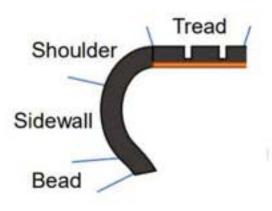
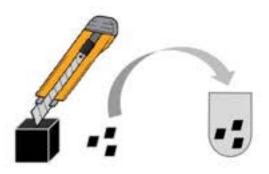
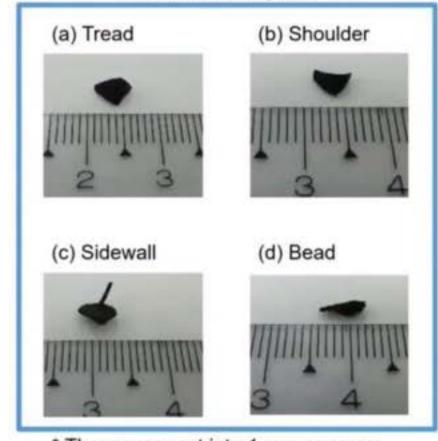


Fig. 1 Cross section of tire

Sampling

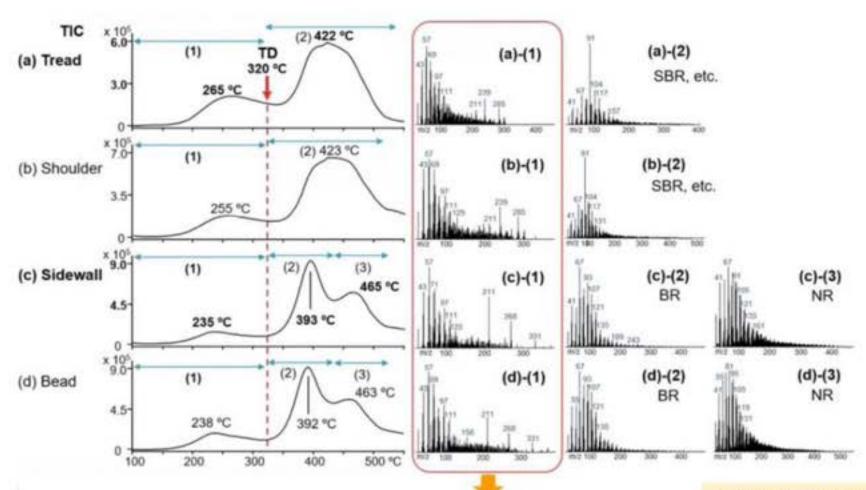


Photos of samples



* These were cut into 1 mm squares.

EGA Thermogram and Averaged Mass Spectrum of Tire Rubber



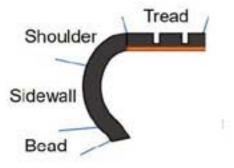


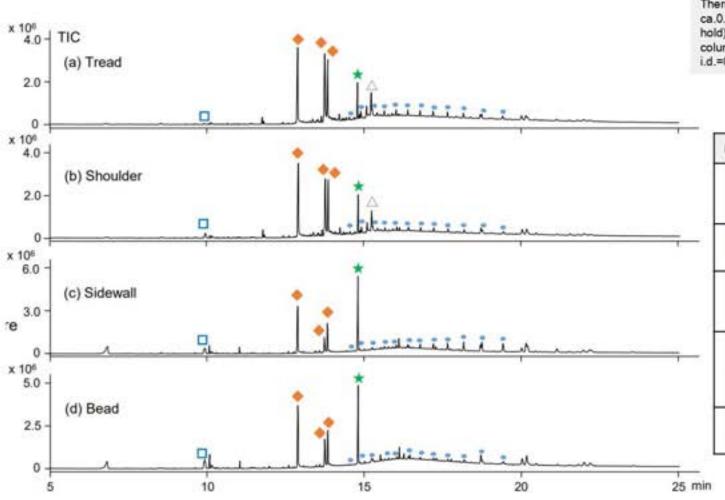
Fig. 1 Cross section of tire

- Pyrolysis of rubber starts at 320 ℃
- TD-GC/MS temperature set as 100 to 320 ℃

Additives



Additives Analysis of Tire Rubber by TD-GC/MS

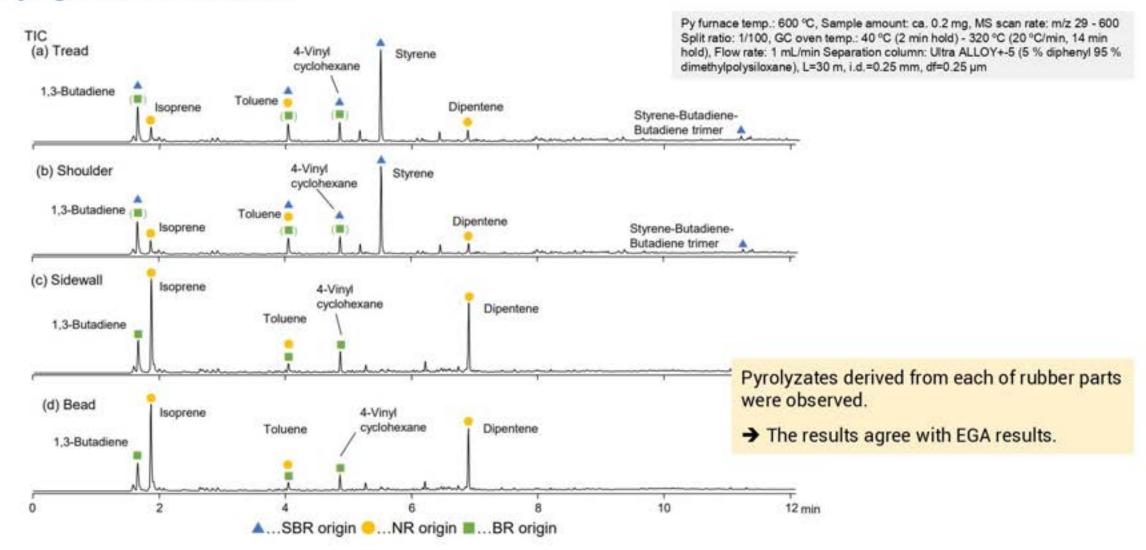


Thermal desorption temp.: 100 - 320 °C (20 °C/min, 1 min hold), Sample amount: ca.0.2 mg, MS scan range: m/z 29 - 600, Split ratio: 1/20, GC oven: 40 °C (2 min hold) - 320 °C (20 °C/min, 14 min hold), Column flow rate: 1 mL/min, Separation column: Ultra ALLOY+-5 (5 % diphenyl-95 % dimethylpolysiloxane), L=30 m, i.d.=0.25 mm, df=0.25 μm

Mark	Chemical	Role	Structure
	DCHA	Vulcanization accelerator	
•	PLA	Fatty acids	~~~~
*	6PPD	Antiaging agent	
Δ	DHA	Nucleating agent	mo follow
•	Wax		C23 - C34



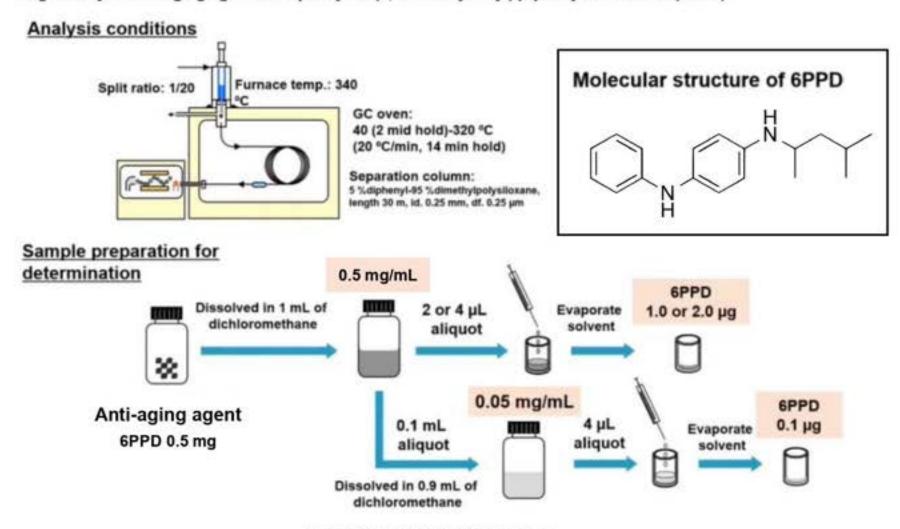
Pyrograms of Tire Rubber





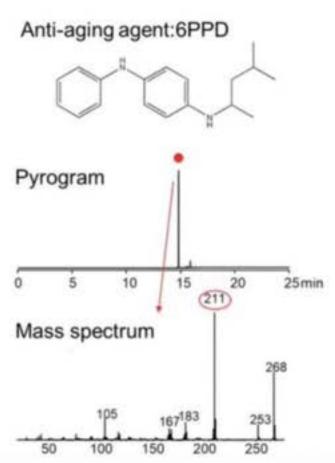
Quantitative Analysis of Additives in Tire Rubber

Target analyte: Anti-aging agent : N-phenyl-N'-(1,3-dimethylbutyl)-p-phenylenediamine (6PPD)

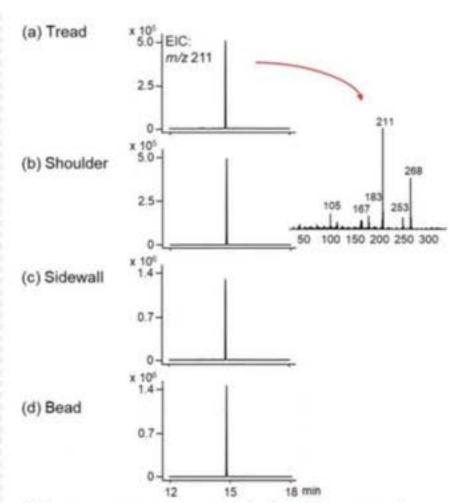




EIC of 6PPD in Tire Rubber



EICs with m/z 211 were obtained from TD chromatograms of tire rubber parts.



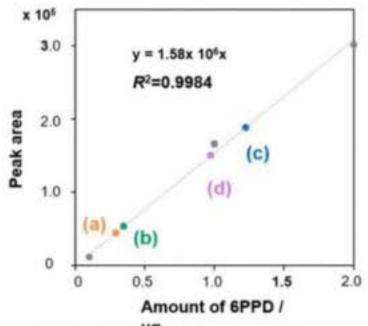
·The average areas were calculated by measuring three times each.



Quantitative Results and Reproducibility

Calibration Curve

6PPD [µg]	Average area (n=3)	RSD [%]
0.1	128,534	0.25
1.0	1,661,627	2.29
2.0	3,017,483	0.53



Samples

	μg				
	Average area (n=3) (/0.2 mg of tire sample)	RSD [%]	6PPD [µg] (/0.2 mg of tire sample)	6PPD content [ppm]	
(a) Tread	446,716	0.58	0.29	1,452	
(b) Shoulder	536,792	4.75	0.35	1,744	
(c) Sidewall	1,883,990	1.04	1.22	6,122	
(d) Bead	1,498,021	1.51	0.97	4,868	

- Rubbers and additives were found to be different depending on parts of the tire.

	Rub	ber	Additive	
Tread	SBR	NR	Vulcanization accelerator, fatty acid, anti- aging agent, and nucleating agent	
Shoulder	SBR	NR	Vulcanization accelerator, fatty acid, anti- aging agent, and nucleating agent	
Sidewall	BR	NR	Vulcanization accelerator, fatty acid, and anti-aging agent	
Bead	BR	NR	Vulcanization accelerator, fatty acid, and anti-aging agent	

- The amount of anti-aging agent (6PPD) was elucidated for each part of the tire.

Quantification result	6PPD content (ppm)
Tread	1,452
Shoulder	1,744
Sidewall	6,122
Bead	4,868

영인과학 2023 최신 분석기기 세미나

상반기 세미나 일정 (예정)

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일 자	장 소	주 제	응 용
2023-02-23	On-line	Pyrolysis-GC/MS를 이용한 플라스틱 및 고무의 열분해 특성 연구	Plastic, Rubber
2023-03-30	On-line	자동차 내장재 및 타이어 분석을 위한 Py-GC/MS 활용 가이드	Automobile
2023-04-19	Off-line	대체 단백질 식품 향 분석을 위한 GERSTEL 전처리 솔루션	Food, Flavor
2023-04-19	Off-line	Py-GC/MS를 이용한 미세플라스틱 분석 솔루션	Microplastics
2023-04-20	Off-line	미량 수분 분석을 위한 새로운 GC 검출기 LUMA	Water, Pharma
2023-04-20	Off-line	바이오 이미징용 전자현미경(SEM) 소개	Biology
2023-05-25	On-line	탄소중립을 위한 그린 에너지, 수소 분석 토탈솔루션	Energy, Battery
2023-06-29	On-line	대기 악취 채취부터 GC/MS 분석까지! Entech 대기 분석 토탈 솔루션	Ambient Air, VOCs



2023 KOREA LAB

제17회 국제연구·실험 및 첨단분석장비전

2023.4.18*~21*
KINTEX 1

영인과학 전시 품목

- GERSTEL 다목적 시료 전처리 시스템(DHS, SPME, TDU, ODP(관능 검출기) 외)
- AC 황검출기
- Frontier Lab 미세플라스틱 전처리 솔루션(동결 시료 분쇄기, MP 여과 시스템 외)
- Entech Instruments 대기/악취 분석 솔루션(캐니스터, 캐니스터 오토 샘플러 외)
- VUV Analytics GC용 UV 검출기(VGA, LUMA)
- 모듈싸이 주사 전자 현미경(SEM)

영인과학 신제품·우수제품 소개 세미나

4/19. WED. 11:00 AM	대체 단백질 식품향 분석을 위한 GERSTEL 전처리 솔루션	
4/19. WED. 15:00 PM	Py-GC/MS를 이용한 미세플라스틱 분석 솔루션	***
4/20, THU. 14:00 PM	미량 수분 분석을 위한 새로운 GC 검출기 LUMA	
4/20. THU. 15:00 PM	바이오 이미징용 전자현미경(SEM) 소개	



최신 첨단분석솔루션을 직접 체험하세요! **영인과학 솔루션 분석 기기실**

















대기/악취 분석 자동화 시스템



Q&A

파이롤라이저 관련 문의 마케팅팀 이 혜 민 과장 02-519-7494, hyemin@youngin.com



THANK YOU