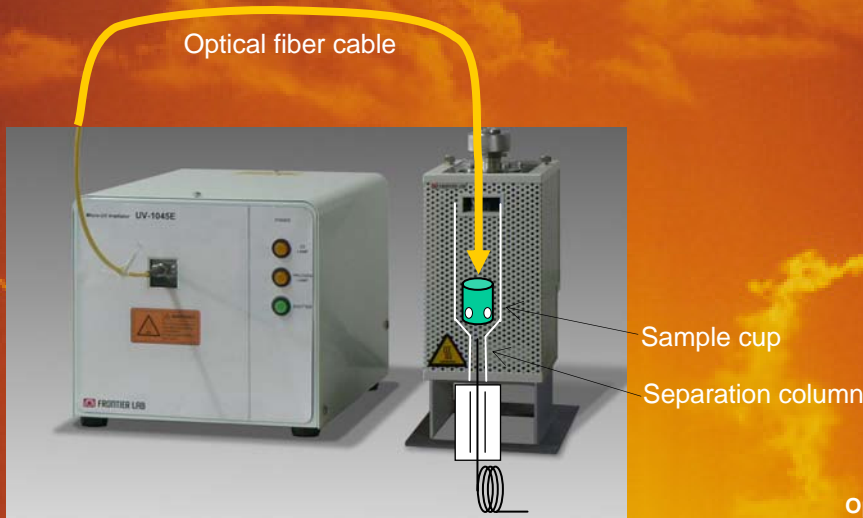


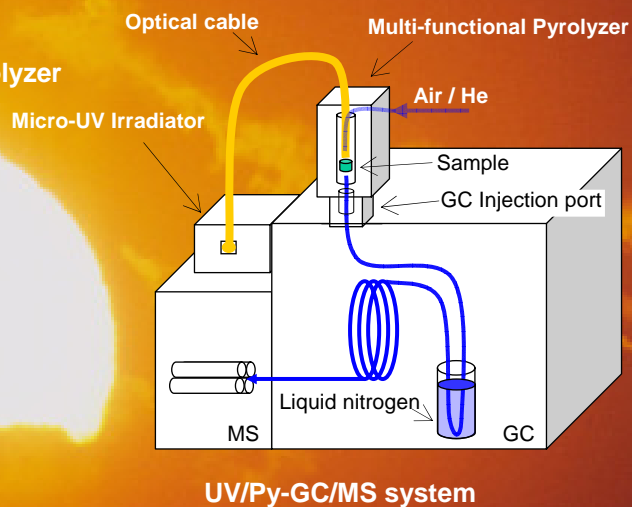
NEW!

Innovative accessory for Multi-functional Pyrolyzer **Micro-UV Irradiator : UV-1045E**

An on-line UV/Py-GC/MS system for the rapid evaluation and/or analysis of the photo / thermal - oxidative degradation of polymeric materials. The information will assist in the design and development of new, stable polymeric materials.



Interfacing the Micro-UV Irradiator to the Multi-functional Pyrolyzer



Features of the Micro-UV Irradiator (UV-1045E) – GC/MS system

Conventional techniques such as weather meters and/or atmospheric exposure tests are used for evaluating the degradation of polymeric materials. These techniques require several weeks or several months to complete and do not provide information about the chemical reactions occurring during the degradation. UV irradiation / Pyrolysis-GC/MS (UV/Py-GC/MS) is a complimentary technique providing insight into the chemistry of the degradation process.

Features of UV/Py-GC/MS --- In this system, the photo / thermal - oxidative deterioration of polymeric materials is evaluated by analyzing both the volatile degradation products and the residual degraded polymer.

1. Enables the rapid analysis of volatile compounds formed during the photo / thermal - oxidative degradation of the sample.

Trace levels of volatile compounds are formed by the UV irradiation of polymeric materials at different temperatures in an air atmosphere. The volatiles are cold trapped at the column inlet and subsequently analyzed by GC/MS.

2. Enables the analysis of the denatured, residual polymer after it has been subjected to photo / thermal - oxidative degradation.

The structural changes in the denatured polymeric material after photo / thermal – oxidative can be examined using evolved gas analysis (EGA) or Pyrolysis-GC/MS (Py-GC/MS)

Configuration of the UV/Py-GC/MS system

The system configuration of the UV/Py-GC/MS is shown in Fig. 1. In this system UV light from a D2 lamp passes into the center of the Multi-functional Pyrolyzer and irradiates the sample directly. The sample can be heated to any temperature (40-800°C) using any atmosphere during the irradiation. The volatile compounds formed during photo / thermal - oxidative degradation are cryo-trapped at the inlet of the separation column using liquid nitrogen. Upon completion of the irradiation, the Dewar is removed and the GC/MS analysis commences. In addition, the degraded polymer remaining in the sample cup can be analyzed by EGA-MS or Py-GC/MS.

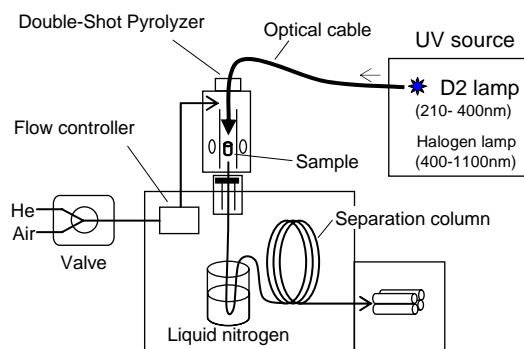


Fig. 1 System configuration of UV/Py-GC/MS

The analysis of (1) the volatile compounds formed during The irradiation of polystyrene and (2) the denatured PS

1. Analysis of volatile compounds formed during irradiation

The chromatogram of the compounds formed when PS is irradiated at 100°C in air for 1 hour is shown in Fig 2. In the case of UV-ON, styrene monomer and several oxides are observed. The peak areas of benzaldehyde (BA) and acetophenone (AP) which are the primary compounds formed are shown in Table 1. The relative standard deviation (RSD) of each peak area is less than 5% The UV data generates both qualitative and quantitative data.

2. Analysis of the degraded polymer (PS):

Analysis of the degraded polymer by EGA (Fig.3) and Py-GC /MS (Fig.4) provide additional information about the irradiated PS. In the EGA thermogram, the temperature of the PS peak apex is 25°C lower than that prior to irradiation. The onset of the PS decomposition is almost 100°C lower (380 to 280°C) after the PS is irradiated for an hour. The EGA results suggest that the molecular weight of the PS is lower. In the pyrogram, the peak area of styrene trimer in UV-ON is lower than when UV-OFF which suggests a degradation of the styrene sequence in the PS.

Py temperature: 100°C, irradiation time: 3 hour, atmosphere gas: Air, split ratio: 1/5

sample weight: 25 µg (thin film), Ultra ALLOY metal capillary column: UA1, 30m (0.25 φ) 0.25 µm, GC: 50 – 320°C (20°C/min)

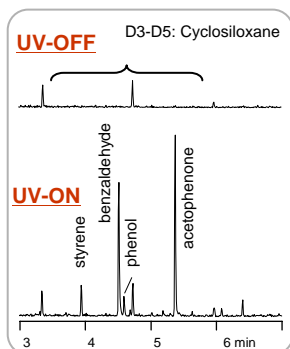


Fig.2 TIC of volatile degraded compounds

Table1 Reproducibility of the peak areas of BA and AP

	Peak area	
	BA	AP
1	321705	132627
2	316034	128345
3	339649	145381
4	347035	139562
5	341399	140803
average	333164	137344
RSD (%)	3.62	4.43

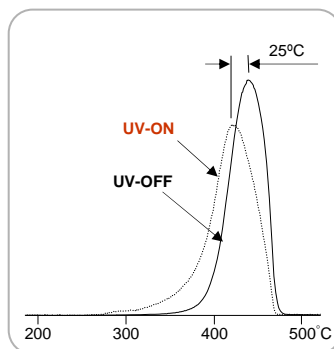


Fig.3 EGA thermogram

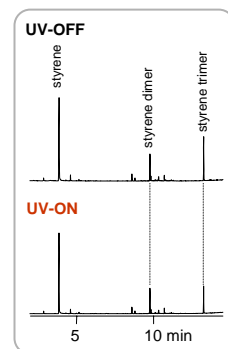
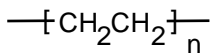


Fig.4 Pyrogram

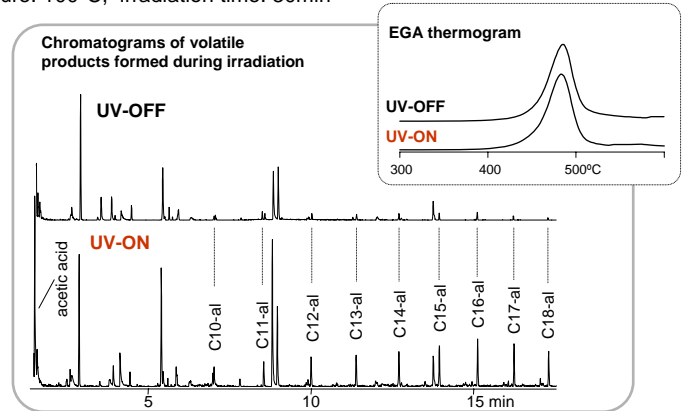
Using UV/Py-GC/MS to irradiate polymeric materials

1. High density polyethylene (HDPE) sample temperature: 100°C, irradiation time: 30min

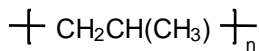


atmosphere gas: Air, sample weight: 1000 µg (powder), split ratio: 1/10, Ultra ALLOY metal capillary column: UA1, 30m (0.25mm i.d.) 0.25µm, GC oven: 40 – 320°C (20°C/min)

In the case of UV-ON, aldehyde levels are 5 – 20 higher than when UV-OFF. These compounds are generated by the oxidation of the HDPE main chain. Analysis of the denatured polymer by EGA, shows little difference between UV-ON and OFF; therefore, the degradation reaction appears to be limited to the surface of the polymer. The bulk of base polymer remains unaffected by the irradiation.

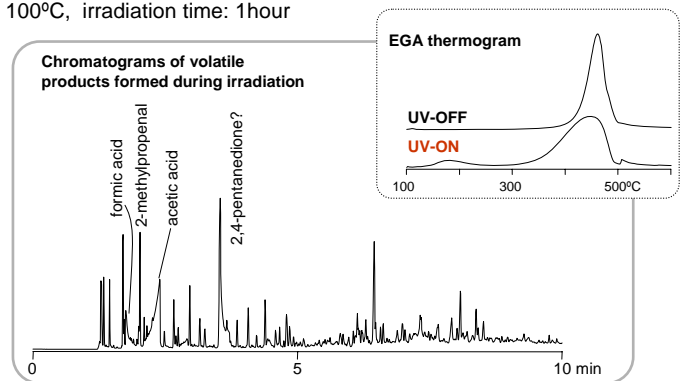


2. Polypropylene (isotactic) (PP) sample temperature: 100°C, irradiation time: 1hour

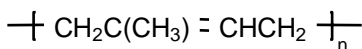


atmosphere gas: Air, sample weight: 200 µg (powder), split ratio: 1/10, Ultra ALLOY metal capillary column: UA1, 30m (0.25mm i.d.) 0.25µm, GC oven: 40 – 320°C (20°C/min)

The volatile oxidative compounds formed during irradiation are acids, aldehydes and ketones. In the subsequent analysis of the denatured polymer by EGA, a volatile thermal zone is observed at temperatures below 300°C. Furthermore, the onset of the PP decomposition is almost 100°C lower (400 to 300°C) after irradiation which suggests a reduction in the molecular weight of the PP.

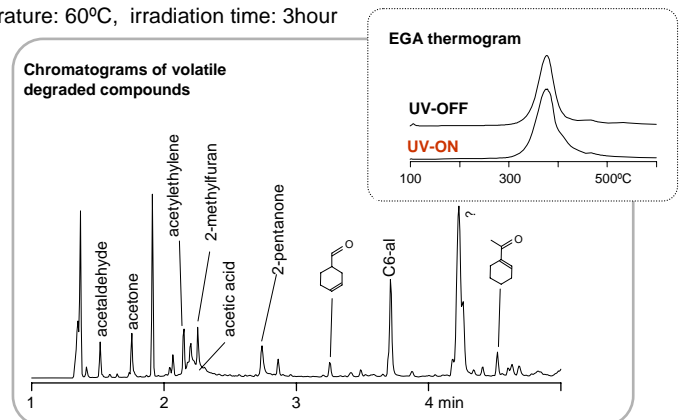


3. Natural rubber (Polyisoprene) (NR) sample temperature: 60°C, irradiation time: 3hour

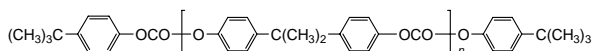


atmosphere gas: Air, sample weight: 150 µg (chip), split ratio: 1/2, Ultra ALLOY metal capillary column: UA1, 30m (0.25mm i.d.) 0.5µm, GC oven: 40 – 280°C (20°C/min)

The volatile oxidative compounds formed during irradiation are mainly acetic acid, aldehydes and ketones. The EGA thermogram shows an increase in the apex of the EGA thermal zone suggesting an increase in the molecular weight of the NR.

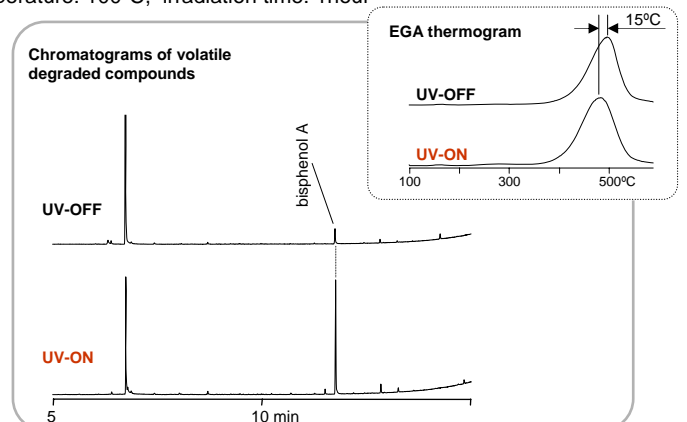


4. Polycarbonate (solvent method) (PC) sample temperature: 100°C, irradiation time: 1hour



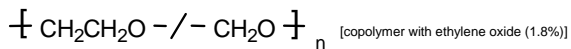
atmosphere gas: Air, sample weight: 15 µg (thin film), split ratio: 1/10, Ultra ALLOY metal capillary column: UA1, 30m (0.25mm i.d.) 0.25µm, GC oven: 40 – 320°C (20°C/min)

The decomposition of the PC main chain as indicated by the amount of Bisphenol A formed, is ten times higher than that observed prior to irradiation. The peak apex on the UV-ON EGA thermogram shifts down 15°C which suggests a decrease in the molecular weight of the polymer. In addition, the final decomposition temperature is slightly higher before irradiation (i.e., UV-OFF) which suggests an increase in the molecular weight of the PC due to the crosslinking of the polymer.



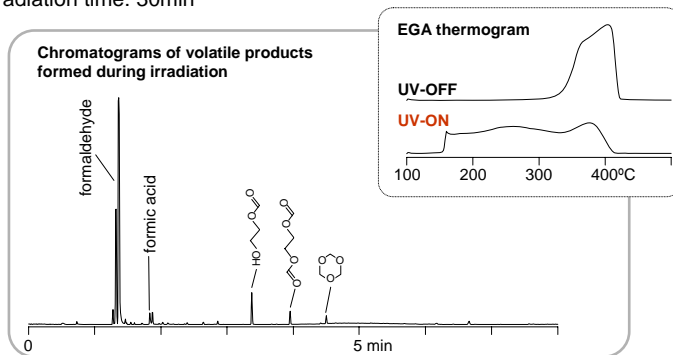
Using UV/Py-GC/MS to irradiate polymeric materials

5. Polyoxymethylene (POM) sample temperature: 150°C, irradiation time: 30min



atmosphere gas: Air, sample weight: 180 µg (powder), split ratio: 1/2, Ultra ALLOY metal capillary column : UA1, 30m (0.25mm i.d.) 0.5µm, GC oven: 40 – 280°C (20°C/min)

The volatile products formed during irradiation are mainly formaldehyde and trioxane which are the monomer and trimer of POM. Moreover, the formation of the formic acid ester of ethylene glycol is a function of the number of ethylene oxide units present in the base polymer. Analysis of the deteriorated polymer by EGA, shows an increase in the volatile fraction which may result in a decrease of the polymer's thermal stability.

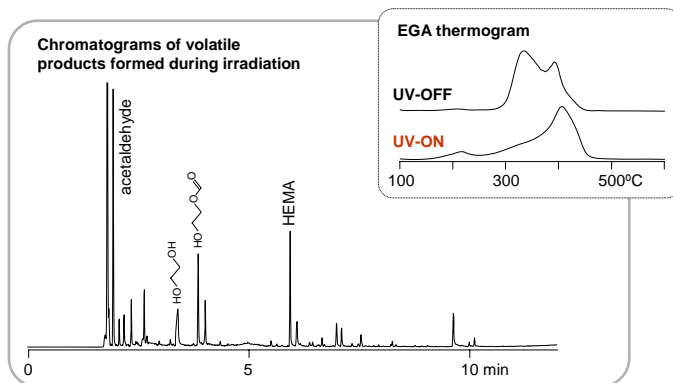


6. Poly (2-hydroxyethyl methacrylate) (PHM) sample temperature: 150°C, irradiation time: 30min

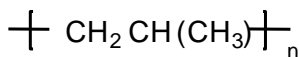


atmosphere gas: Air, sample weight: 100 µg (powder), split ratio: 1/2, Ultra ALLOY metal capillary column : UA1, 30m (0.25 mm i.d.) 0.5µm, GC oven: 40 – 280°C (20°C/min)

The volatile products formed during irradiation are mainly ethylene glycol, monoformate and hydroxyethyl methacrylate: HEMA. Analysis of the deteriorated polymer by EGA, shows that the temperature of the polymer's peak apex in UV-ON is higher than in UV-OFF. This may be attributed to a cross linking reaction which increases the molecular weight of the irradiated polymer.

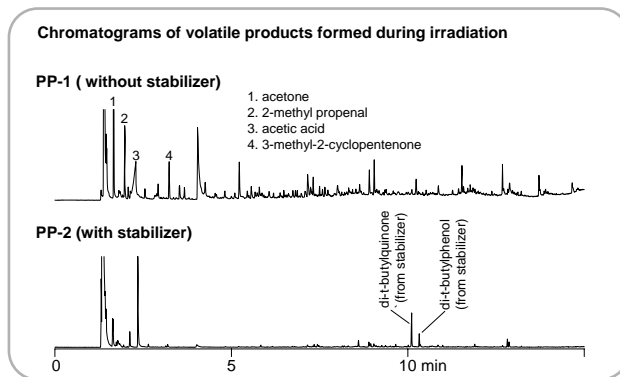


7. Stabilizer in polypropylene (PP) sample temperature: 100°C, irradiation time: 1 hour



atmosphere gas: Air, sample weight: 200 µg (powder), split ratio: 1/10, Ultra ALLOY metal capillary column : UA1, 30m (0.25 mm i.d.) 0.25µm, GC oven: 40 – 300°C (20°C/min)

PP-1 and PP-2 are two polypropylene samples. PP-1 is stabilized by incorporating Irganox1010, Irgafos168 (each 0.3 wt.%) and Adecastab LA-68LD (2.5 wt.%) into the polymer. The lower stability of PP-2 is evident by the large number of volatile compounds formed during irradiation in an oxidative atmosphere at 100°C.



Specifications:

Wave length range (at the end of cable) : 210 - 1100 nm (D2 lamp (UV) and/or halogen lamp are available)

Control of irradiation time : PC software control

Required Py-GC/MS : Double-Shot Pyrolyzer with GC/MS (Double-Shot Pyrolyzer requires no modification)

Standard accessories:

UV irradiator (contains gas switching function), optical cable, Ultra ALLOY metal capillary column, Liquid N₂ Dewar, etc.

Site preparation:

Air (cylinder air, 300-980kPa), liquid nitrogen

Please forward your inquiries via our web.

R&D and manufactured by:
Frontier Laboratories Ltd.

<http://www.frontier-lab.com/>
1-8-14, Saikon, Koriyama,
Fukushima, 963-8862 Japan