

Application Note

No. 14

UV Degradation Analysis of Material for Solar Cell Modules Using GC/MS and FTIR

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Electrics and Electronics

1. Introduction

Materials for solar cell modules are expected to maintain their performance for over a decade despite the harsh environmental conditions such as high temperatures and ultraviolet irradiation to which they are subjected outdoors. However, there is concern that UV-induced degradation may occur in materials used in modules such as ethylene-vinyl acetate (EVA) which is a copolymer used as a clear encapsulation film.

This article introduces three example analyses: analysis of EVA film subjected to intense UV irradiation using a UV (ultraviolet) -Py (double-shot pyrolyzer) / GC-MS (gas chromatograph mass spectrometer) system, evolved gas analysis by mass spectrometry (EGA-MS) of EVA film which was degraded by UV irradiation in the same way as with the above, and analysis of the same using a Fourier transform infrared spectrophotometer (FTIR).

EVA: ethylene-vinyl acetate copolymer

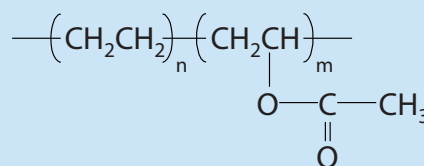


Fig. 1 Structural formula of ethylene-vinyl acetate (EVA) copolymer

2. UV degradation of EVA film using a UV-Py/GC-MS system

The UV-Py/GC-MS system shown in Fig. 2 was made by combining a micro-UV irradiator (UV-1047 Xe) manufactured by Frontier Laboratories Ltd., and the GCMS-QP2020 gas chromatograph mass spectrometer manufactured by Shimadzu Corporation. Compared to conventional weather testing methods such as outdoor exposure testing and weatherometer testing, this system enables rapid UV degradation of EVA film.

In addition, this UV-Py/GC-MS system is capable of performing GC/MS analysis of volatile degradation products which are generated due to UV irradiation.

Degradation samples can be analyzed employing evolved gas analysis by mass spectrometry (EGA-MS), a method available with the Py/GC-MS, and by using a Fourier transform infrared spectrophotometer (FTIR) to elucidate the changes in the resin structure that are induced by UV irradiation.

Fig. 3 shows the procedure for UV degradation of EVA film using the UV-Py/GC-MS system.



**Fig. 2 UV-Py/GC-MS system
(UV-1047Xe+PY-3030D+GCMS-QP2020)**

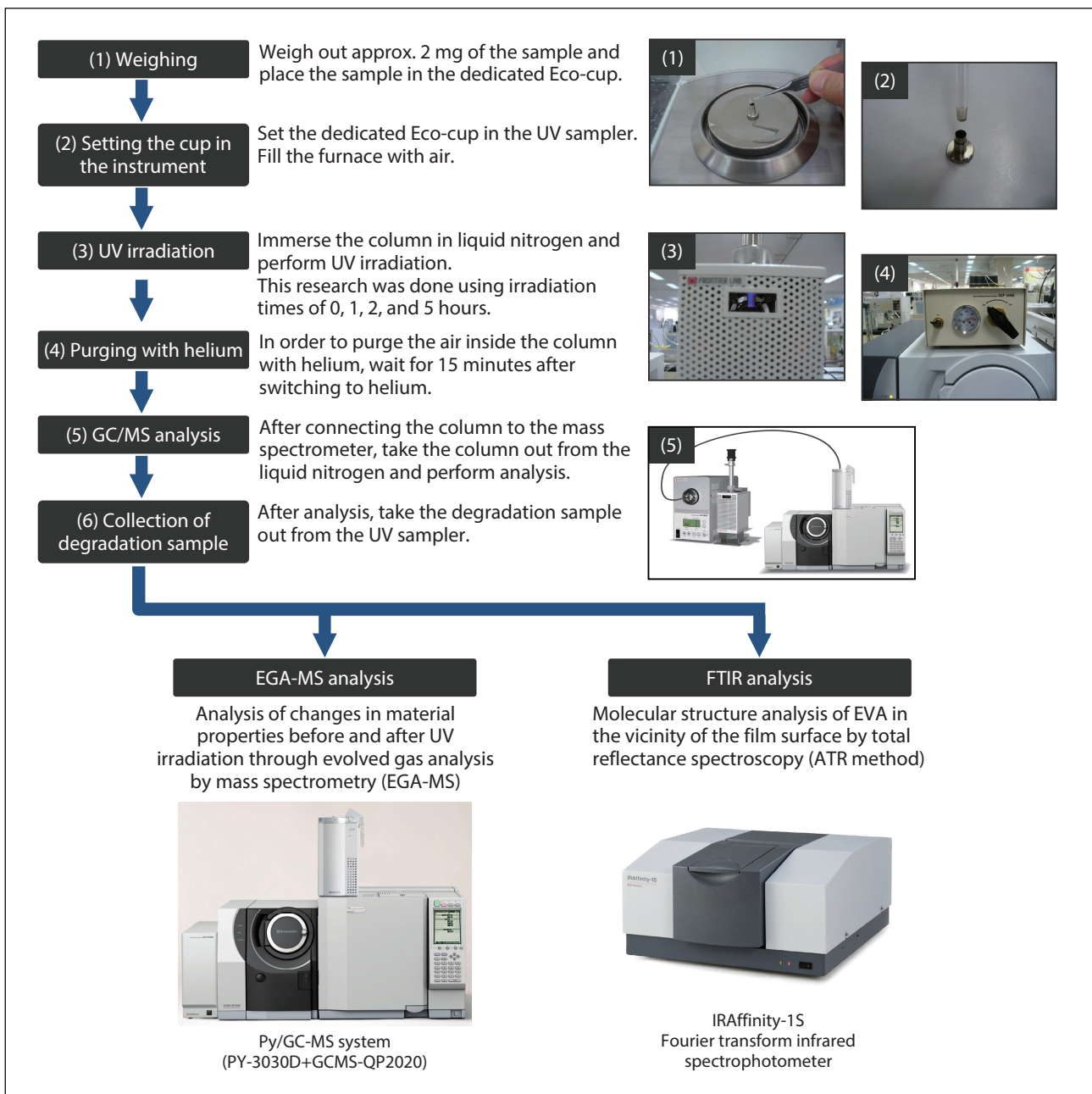


Fig. 3 Measurement flow for UV-Py/GC-MS analysis

3. Analysis of volatile degradation products using the UV-Py/GC-MS system

3-1 Overview

Volatile degradation products generated through UV irradiation were analyzed using the UV-Py/GC-MS system.

Whereas evaluation of gas generated during degradation is not possible if employing methods such as outdoor exposure testing or weatherometer testing, evaluation of such gas is possible if using a UV-Py/GC-MS system.

Fig. 4 shows the schematic of the UV-Py/GC-MS system.

Analysis is done with this system by first setting the sample inside the furnace that is filled with air and then cooling the inlet of the column using liquid nitrogen. After performing UV irradiation for the set time, the evolved gas generated during the light-induced degradation of the sample is collected.

Subsequently, the air in the instrument is purged with helium and the column is connected to the mass spectrometer. After taking the column out from the liquid nitrogen, the evolved gas collected in the cooled section of the column is analyzed.

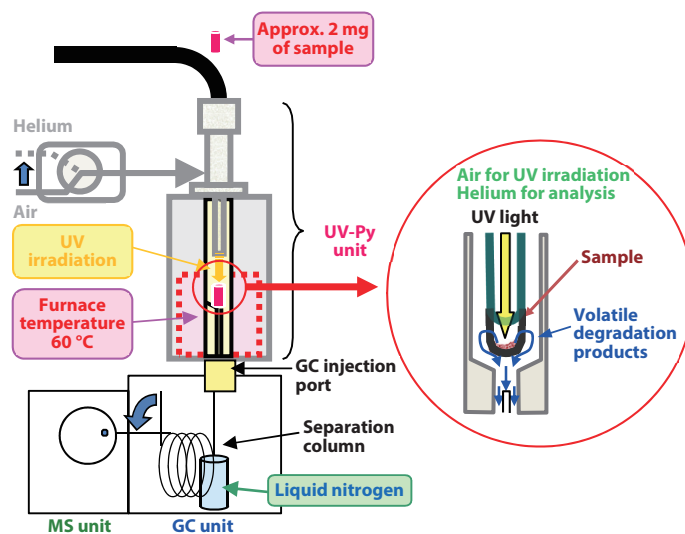


Fig. 4 Schematic of the UV-Py/GC-MS system

3-2 Analysis conditions

Table 1 lists the analysis conditions for volatile degradation products using the UV-Py/GC-MS system.

Table 1 Analysis conditions for volatile degradation products using the UV-Py/GC-MS system

Instrument	
<Conditions for the UV-Py>	
Irradiation time	0 hr, 1 hr, 2 hr, 5 hr
Helium purging time	15 min
Pyrolyzer furnace temperature	60 °C
Atmospheric gas	Air
<Conditions for the GC>	
Column	Ultra ALLOY-1 (30 m L. × 0.25 mm I.D. df=0.5 μm) manufactured by Frontier Laboratories
Injection port temperature	300 °C
Column temperature	40.0 °C → 20.0 °C/min → 300.0 °C (5.00 min)
Injection mode	Split mode
Carrier gas	Helium
Carrier gas pressure	50 kPa
Split ratio	40:1
<Conditions for the MS>	
Ion source temperature	200 °C
Interface temperature	300 °C
Measurement mode	SCAN
Measurement range	<i>m/z</i> 29-1090
Event time	0.5 sec

3-3 Analysis results

The result of analyzing the volatile degradation products generated through UV irradiation (0, 1, 2, 5 hours) using the UV-Py/GC-MS system is shown in Figs. 5 to 8.

Underlined compounds in the figures are compounds which are considered to be volatile degradation products of EVA.

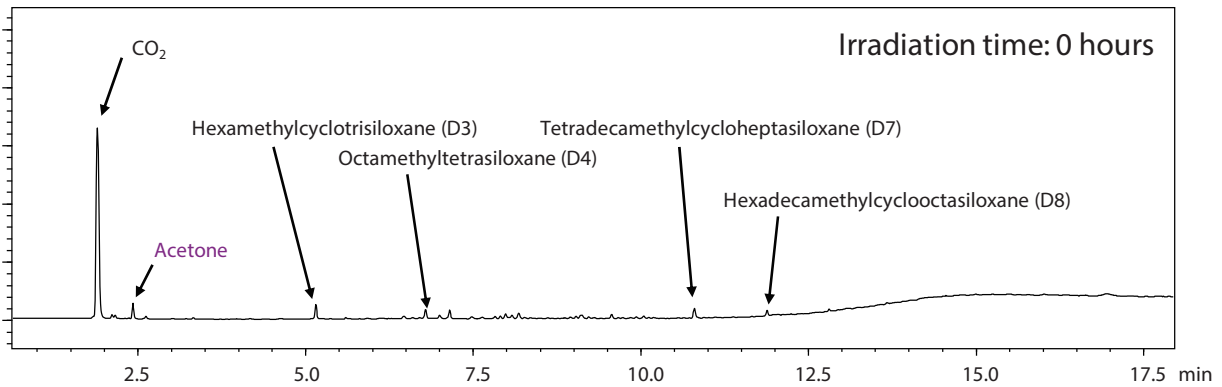


Fig. 5 UV-Py/GC-MS analysis results of volatile degradation compounds generated through UV irradiation (0 hours)

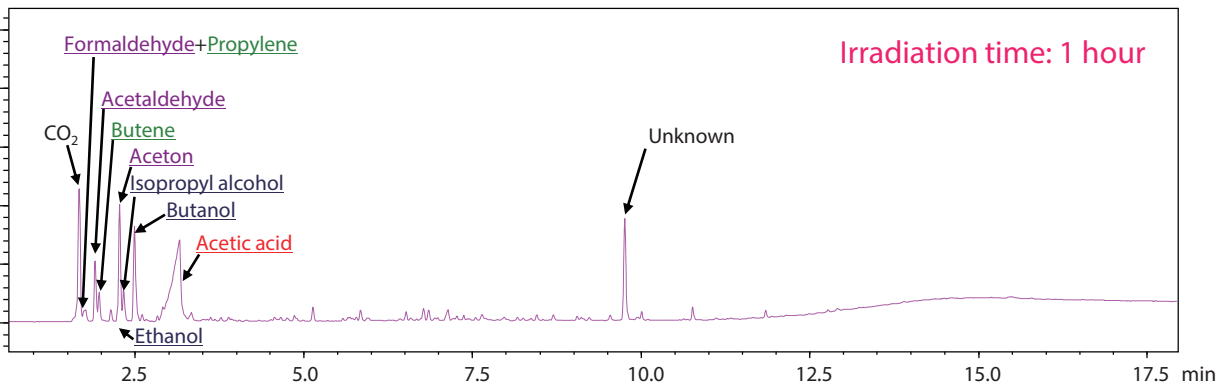


Fig. 6 UV-Py/GC-MS analysis results of volatile degradation compounds generated through UV irradiation (1 hour)

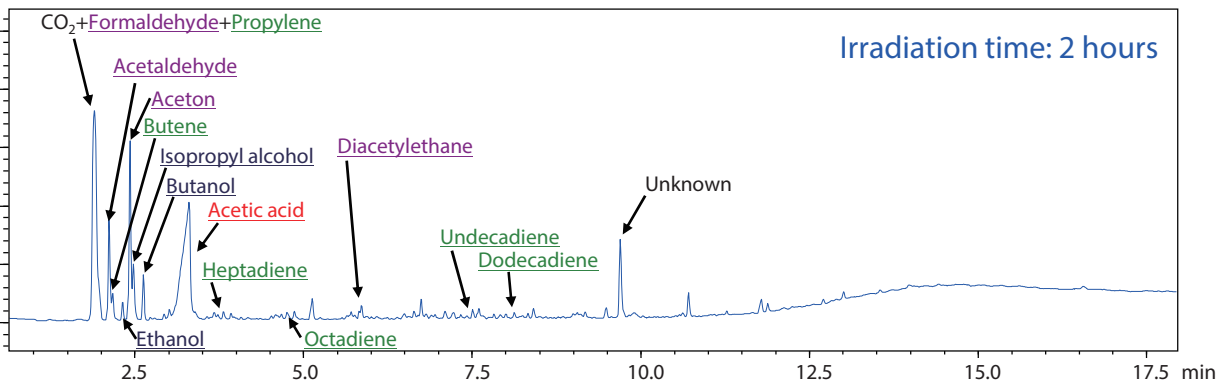


Fig. 7 UV-Py/GC-MS analysis results of volatile degradation compounds generated through UV irradiation (2 hours)

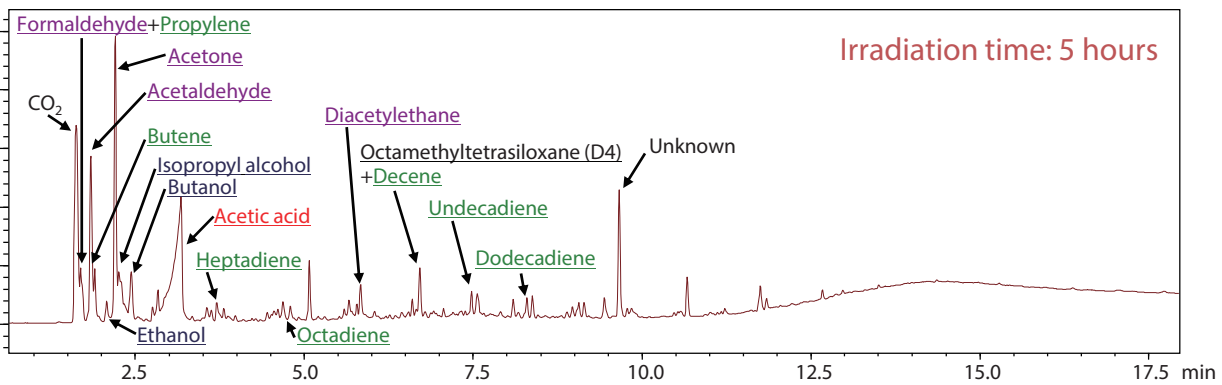


Fig. 8 UV-Py/GC-MS analysis results of volatile degradation compounds generated through UV irradiation (5 hours)

3-4 Expected light decomposition reaction of EVA

Based on Figs. 5 to 8, we can assume that compounds that have a greater peak area under a longer UV irradiation time are a product of light decomposition.

Since the EVA film used for analysis hardly contained any additives, we were able to observe the light

decomposition of the EVA film itself and therefore infer the light decomposition reaction as shown in Fig. 9.

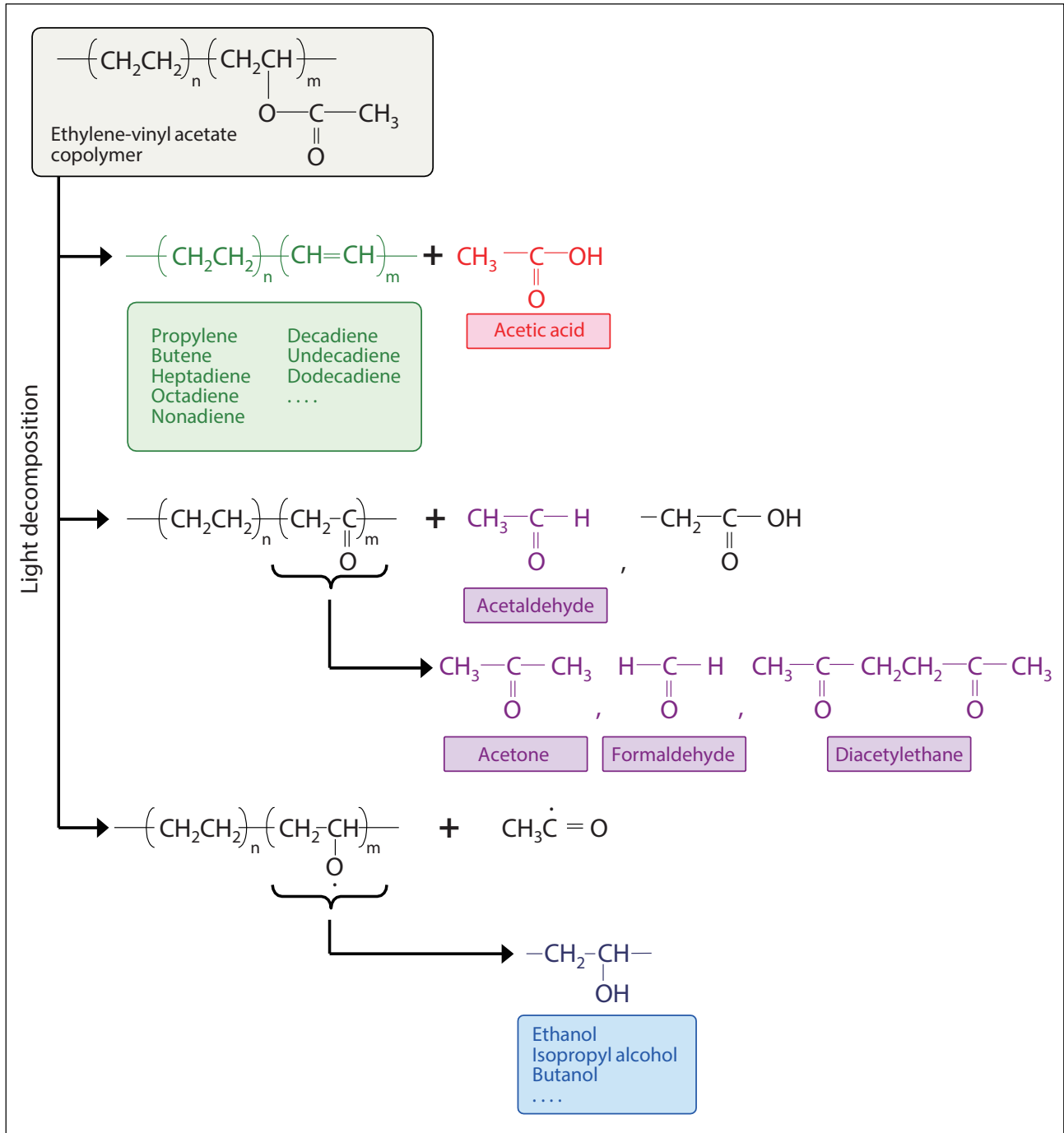


Fig. 9 The light decomposition reaction of EVA inferred based on measurement results

4. Analysis of UV-irradiated EVA through evolved gas analysis by mass spectrometry (EGA-MS)

4-1 Overview

Changes in the properties of EVA film from before and after UV irradiation were analyzed through evolved gas analysis by mass spectrometry (EGA-MS), which is a method that is available with a Py/GC-MS configuration.

Fig. 10 shows the schematic of the EGA-MS system.

Analysis by the EGA-MS method is done by connecting the outlet of the pyrolyzer with the GC detector using the inactivated tube (Ultra ALLOY, 2.5 m L. × 0.15 mm I.D.) installed inside the GC oven and then detecting, in real time, the various substances that are generated from the sample through heating.

By comparing the thermal decomposition temperatures of the degraded EVA film, it is possible to reveal the degree of cleavage reactions on the main chain that are caused by UV irradiation.

4-2 Analysis conditions

The conditions for analyzing UV-irradiated EVA by EGA-MS are listed in Table 2.

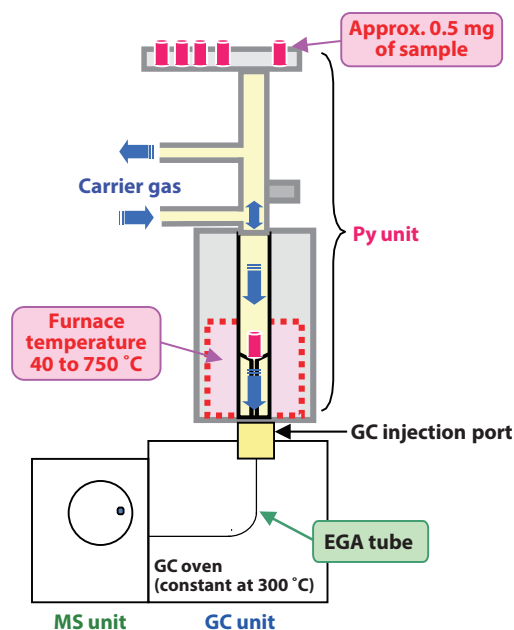


Fig. 10 Schematic of the EGA-MS system

Table 2 Analysis conditions for EGA-MS

Instrument	
<Conditions for the Py>	
Pyrolyzer furnace temperature	40.0 °C (2.00 min) → 20 °C /min → 750.0 °C (2.50 min)
Interface temperature	Auto (Upper Temp. 320 °C)
<Conditions for the GC>	
Column	Ultra ALLOY-DTM (2.5 m L. × 0.15 mm I.D., no liquid phase) manufactured by Frontier Laboratories
Injection port temperature	320 °C
Column temperature	Constant at 300 °C
Injection mode	Split mode
Carrier gas	Helium
Carrier gas pressure	120 kPa
Split ratio	40:1
<Conditions for the MS>	
Ion source temperature	250 °C
Interface temperature	320 °C
Measurement mode	SCAN
Measurement range	m/z 29-1090
Event time	0.5 sec

4-3 Analysis results

The EGA-MS analysis results of EVA film degraded by UV irradiation per each irradiation time are shown in Fig. 11.

The thermal decomposition temperature for each of the UV irradiation times is listed in Table 3.

We can see that a longer UV irradiation time results in a slightly lower thermal decomposition temperature for peak (2), meaning that the molecular weight is decreasing. This indicates that light decomposition is

occurring on the main chain of the EVA film due to UV irradiation.

In addition, the difference in the absolute intensity of the thermal decomposition of the main chain (peak (2)) between each UV irradiation time was subtle. From this, we can assume that light decomposition is occurring only on the surface of the EVA film and not the entirety of the film.

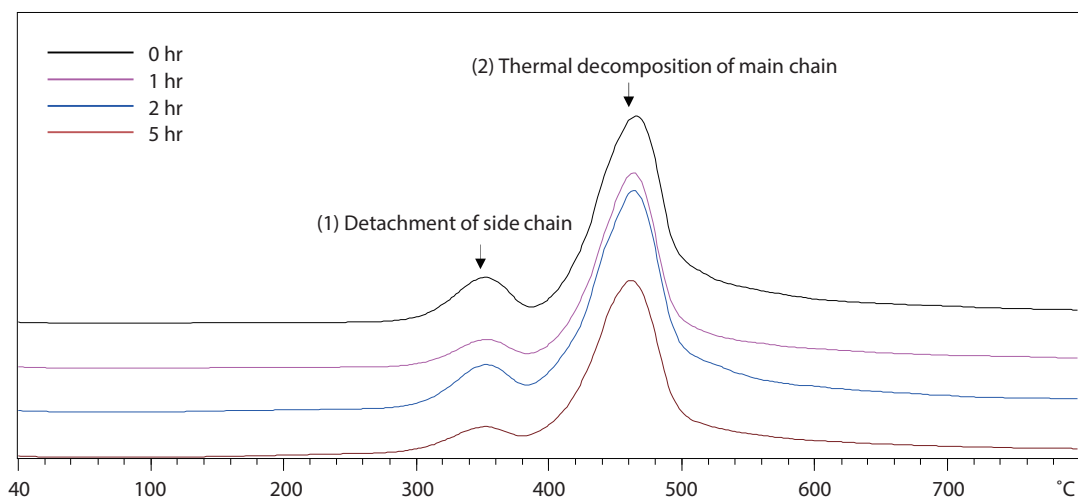


Fig. 11 EGA-MS analysis results of EVA film degraded under different UV irradiation times

Table 3 Thermal decomposition temperature of main chain under different UV irradiation times

UV irradiation time	0 hr	1 hr	2 hr	5 hr
Thermal decomposition temperature (°C)	465.5	463.7	463.9	461.9

5. Analysis of UV-irradiated EVA using a Fourier transform infrared spectrophotometer (FTIR)

5-1 Overview

Structural changes that occur in compounds through degradation can be analyzed using a Fourier transform infrared spectrophotometer (FTIR). Although the samples used in this research were only about 2 mm square in size, the surface spectrum of these samples can be measured easily by using the single reflection ATR accessory.

This section introduces the results obtained by installing the DuraSAMPLIR II, which is a single reflection ATR accessory, on Shimadzu's IRAffinity-1S Fourier transform infrared spectrophotometer and measuring samples which were UV-irradiated for 0, 2, and 5 hours respectively.



Fig. 12 IRAffinity-1S



Fig. 13 DuraSAMPLIR II

5-2 Analysis results

The spectra obtained by measuring the samples which were UV-irradiated for 0, 2, and 5 hours respectively are superimposed in Fig. 14. Changes with regard to functional groups can be observed: a decrease of the $>C=O$ group originating from acetate in the vicinity of 1735 cm^{-1} , an increase of the $>C=O$ group originating from ketone and aldehyde in the vicinity of 1716 cm^{-1} , and an increase in the peak intensity of the $-OH$ group in the vicinity of 3300 cm^{-1} . Fig. 15 (a), (b), and (c) depict these peak changes by plotting them against the UV irradiation time. Each

graph is based on the peak at 1465 cm^{-1} (CH_2 and CH_3 bending), with graphs (a) and (b) plotting the peak intensity ratio and graph (c) plotting the peak area ratio. For each sample, both the front and back sides are measured and plotted respectively.

These results indicate that the side chain structure of EVA changed at the sample surface due to UV irradiation, thereby generating compounds containing the $-OH$ group or the $>C=O$ group originating from aldehyde or ketone.

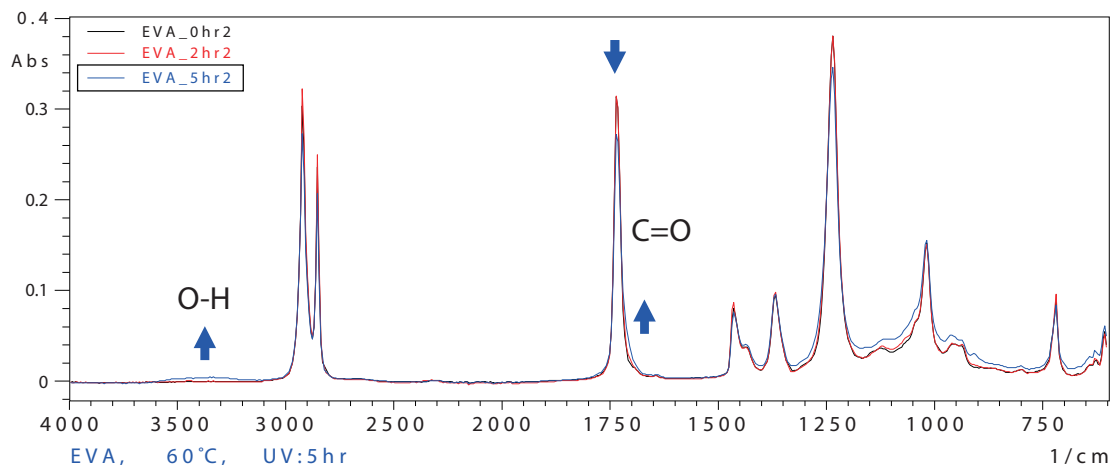


Fig. 14 IR absorbance spectra of EVA film before and after UV irradiation

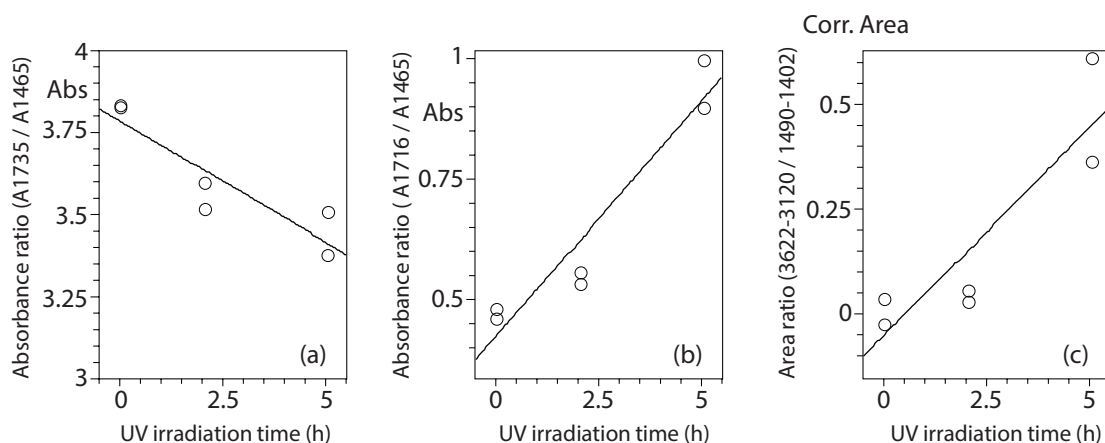


Fig. 15 Changes in functional groups (a) acetate, (b) ketone and aldehyde, and (c) O-H due to UV irradiation

6. Summary

We clarified the volatile degradation products which result from EVA film due to UV irradiation by measuring EVA film using a UV-Py/GC-MS system. We also were able to estimate the decomposition behavior of the main and sub chains through evolved gas analysis by mass spectrometry (EGA-MS) according to changes in

the UV irradiation time and evaluate changes in functional groups based on the results obtained through FTIR. Both of these methods are effective in investigating the decomposition behavior of resin structures induced by UV irradiation.

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