Technical Report

FL No. 200002 Fluorescence Spectrophotometer

HITACHI
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Applications of spectroscopic analysis in the assessment of plastic degradation

Depending on the raw material resin and additives used, the deterioration of molded plastic products differs due to factors such as changes over time in the material itself and environmental conditions such as heat and ultraviolet (UV) light. Because of this, it is important to predict the lifetime of a molded product before releasing it to the market. Yellowness, shine, and other such parameters are generally evaluated using spectophotometer.[1)] However, there are few examples of evaluation using fluorescence spectrophotometer.

In the present study, 3D fluorescence spectra of plastic samples irradiated by UV light were acquired using a fluorescence spectrophotometer, and multivariate analysis was performed to evaluate the degree of degradation. Fluorescence spectrophotometers can perform highly sensitive nondestructive measurements without the need for complex pretreatment processes. This provides a practical method for predicting the lifetime of plastic products and for quality control.

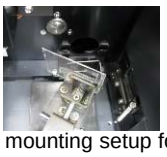
1) Examples of plastic materials and products. Latest material performance and evaluation techniques (Sangyo Gijutsu Service Center, 2014)

Evaluation Method

- ✓ The samples used were commercially available 1-mm-thick plastic pieces (PE and PET).
- ✓ Test pieces were irradiated with UV light with a wavelength of 365 nm, and the effects of UV light exposure were evaluated at fixed intervals.
- ✓ 3D fluorescence spectra were measured using an F-7100 Fluorescence Spectrophotometer equipped with an automatic filter accessory and a solid sample holder.
- ✓ Transmission spectra of samples were measured with a UH4150 Spectrophotometer, and the yellowness was calculated in accordance with JIS K 7373.
- ✓ 3D SpectAlyze® multivariate analysis software was used to perform principal component analysis.

Samples:	PE (polyethylene) and PET (polyethylene terephthalate)
Size:	5 × 5 cm, thickness 1 mm
UV light source:	SLUV-4 (AS ONE), UV light intensity 743 μW/cm^2,
Number of days exposure:	wavelength 365 nm
Equipment:	0, 3, 9, 15, 35, 65
	F-7100 Fluorescence Spectrophotometer, automatic filter accessory, solid sample holder
	UH4150 Spectrophotometer, ⌀60 integrating sphere
Multivariate analysis:	3D SpectAlyze®[2)]

2) Registered trademark in Japan of Dynacom Co., Ltd.



Sample mounting setup for the F-7100 Fluorescence Spectrophotometer

UH4150 Spectrophotometer

F-7100 Fluorescence Spectrophotometer

Changes in 3D fluorescence spectrum of plastic due to irradiation by UV light

■ 3-D fluorescence spectra of PET

Data interval : Ex 5.0 nm, Em 5.0 nm
Scan speed : 60000 nm/min
Slit width : Ex 5.0 nm, Em 5.0 nm
PMT voltage : 400 V

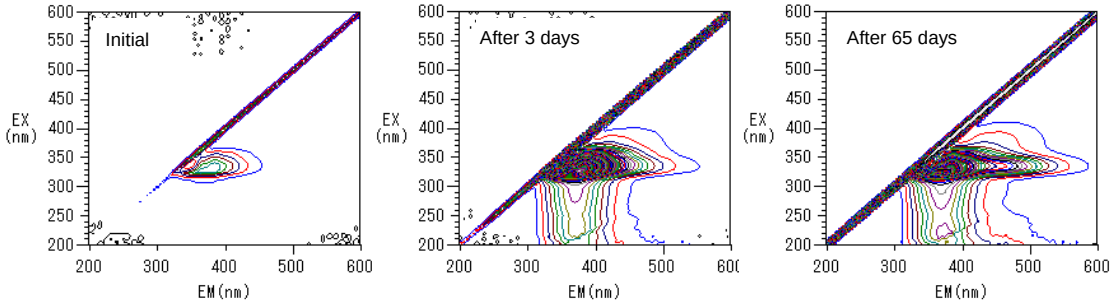


Figure 1 Changes in 3D fluorescence spectrum of PET due to irradiation by UV light

■ 3-D fluorescence spectra of PE

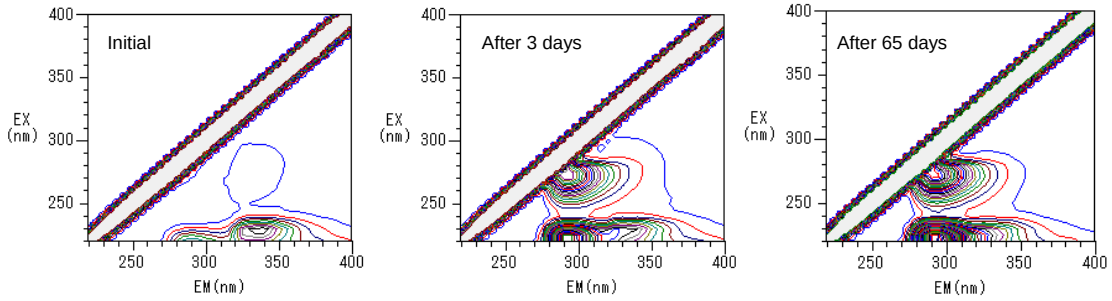


Figure 2 Changes in 3D fluorescence spectrum of PE due to irradiation by UV light

Evaluation of PET by principal component analysis

- ✓ A principal component analysis of the measured 3D fluorescence spectral data for PET was performed using 3D SpectAlyze® analysis software.
- ✓ The PC2 value increased with increasing number of days of UV exposure (Figure 3).
- ✓ From the loading plots, the 335 nm excitation wavelength is related to the period of exposure (Figure 4).
- ✓ The pre-exposure sample had the lowest fluorescence intensity at a fluorescence wavelength of 385 nm and tended to differ from the post-exposure fluorescence spectrum (Figure 5).
- ✓ For an excitation wavelength of 335 nm, the fluorescence intensity at 385 nm (A) decreases with increasing exposure time, whereas that at 470 nm (B) increases (Figures 5 and 6).

■ Principal component analysis

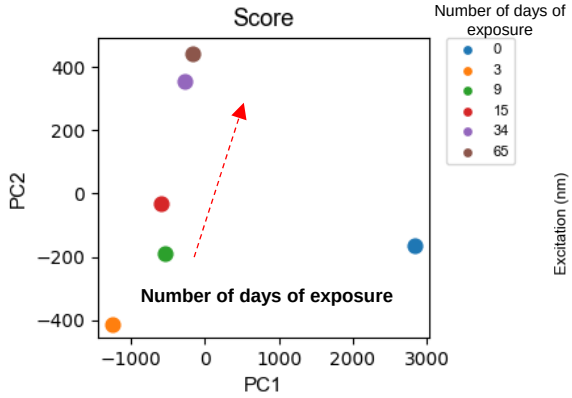


Figure 3 PET score

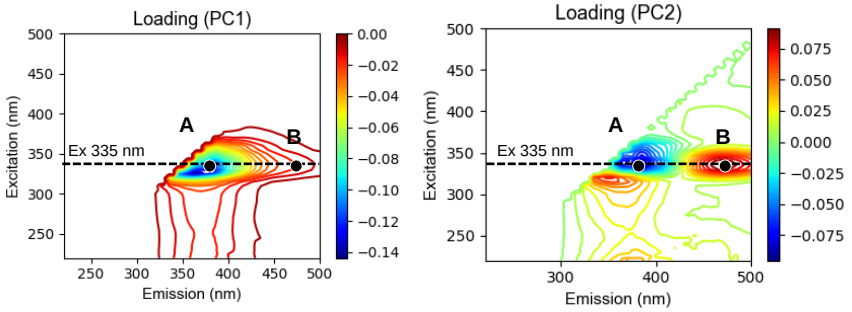


Figure 4 PET loading

■ Change in fluorescence intensity with number of days of exposure

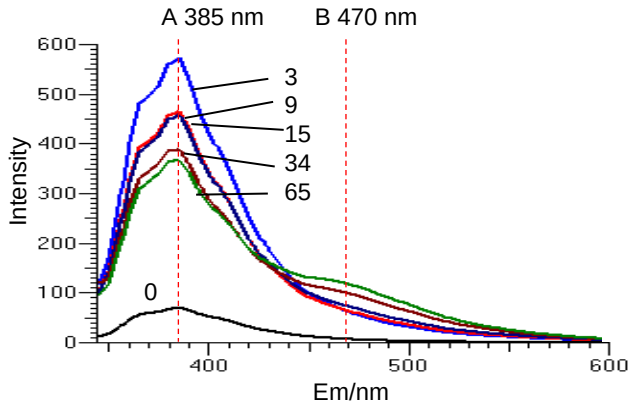


Figure 5 PET fluorescence spectrum for Ex 335 nm

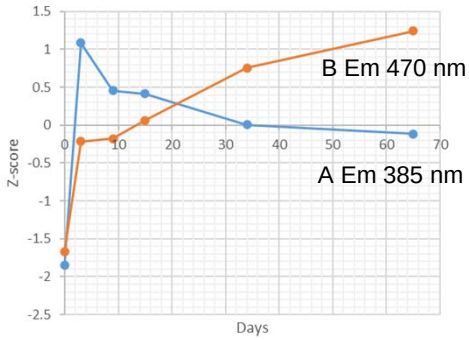


Figure 6 Change in PET fluorescence intensity for Ex 335 nm

Fluorescence intensity and yellowness

- ✓ Transmission spectra of samples were measured with a UH4150 Spectrophotometer, and the yellowness was calculated in accordance with JIS K 7373.
- ✓ Except for pre-exposure (day 0), a negative correlation was found between the fluorescence intensity and yellowness for fluorescence peak A, and a positive correlation was found for fluorescence peak B.
- ✓ It is possible that the sample surface condition changed at the initial stage due to UV light exposure.

■ Correlation between fluorescence intensity and yellowness

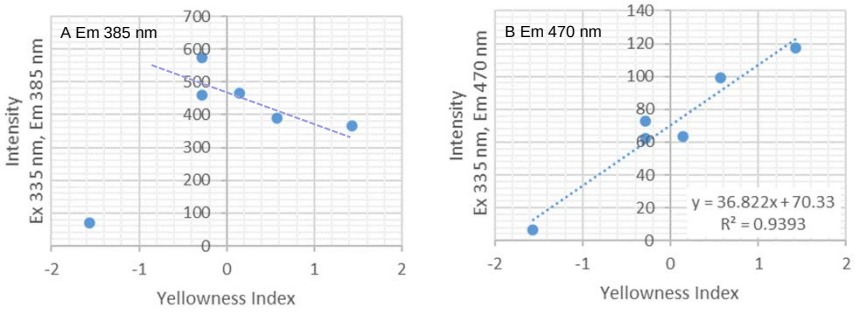


Figure 7 - Correlation between fluorescence peak intensity and yellowness for Ex 335 nm in PET

Table 1 - Fluorescence intensity and yellowness for Ex 355 nm

Days	Intensity Em 385 nm	Intensity Em 470 nm	Yellowness index
0	70.0	6.8	-1.57
3	573.6	62.2	-0.29
9	465.4	63.6	0.14
15	458.6	72.8	-0.29
34	388.4	99.0	0.57
65	367.5	117.6	1.43

Z-score used for yellowness index

Evaluation of PE by principal component analysis

- ✓ A principal component analysis of the measured 3D fluorescence spectral data for PE was performed using 3D SpectAlyze® analysis software.
- ✓ Except for pe-exposure (day 0), the PC2 value decreased with increasing exposure time from the score plot, (Figure 8).
- ✓ From the loading plots, the 230 nm excitation wavelength is related to the period of exposure (Figure 9).
- ✓ At an excitation wavelength of 230 nm, the fluorescence intensity at 290 nm (C) increases with increasing exposure time, whereas that at 340 nm (D) decreases (Figures 10 and 11).
- ✓ The variation in the fluorescence spectral intensity is different for PET and PE.

■ Principal component analysis

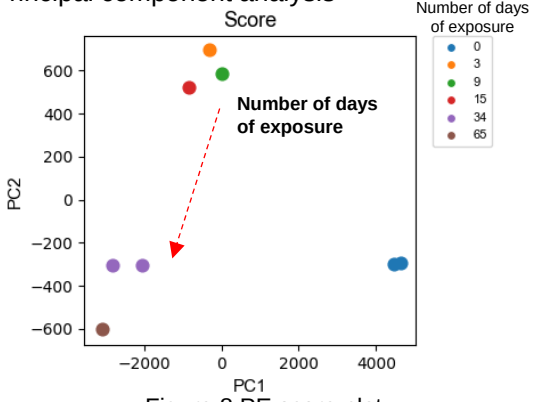


Figure 8 PE score plot

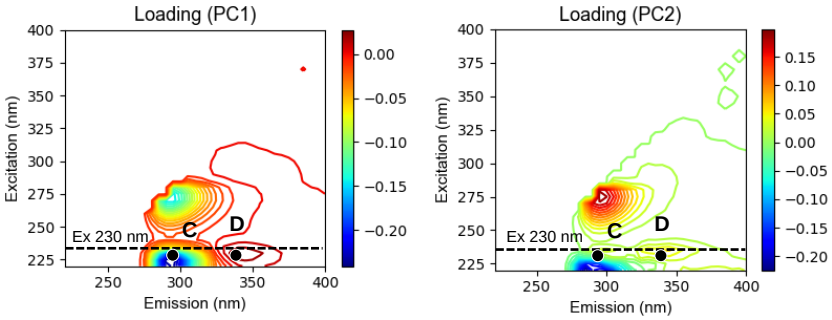


Figure 9 PE loading plots

■ Change in fluorescence intensity with number of days of exposure

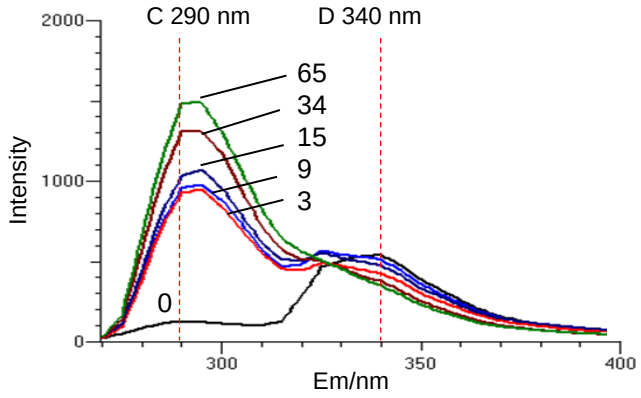


Figure 10 PE fluorescence spectra for Ex 230 nm

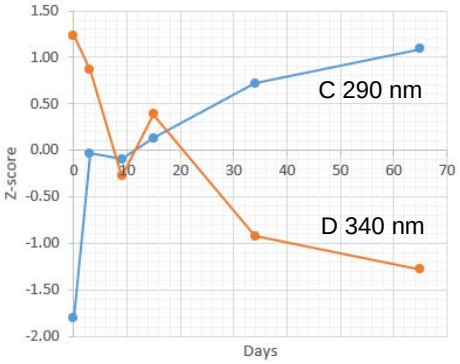
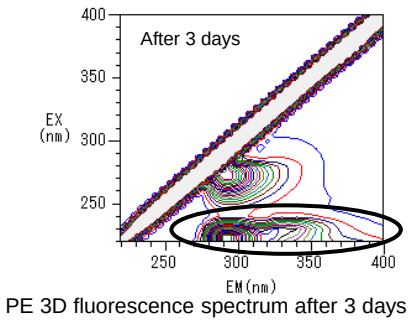


Figure 11 Change in PE fluorescence intensity for Ex 230 nm

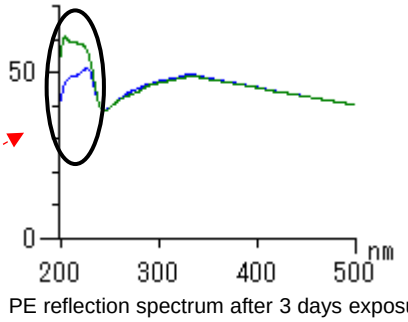
Fluorescence intensity and reflection spectra

- ✓ A UH4150 Spectrophotometer was equipped with a ⌀60 integrating sphere to measure the total reflection spectrum of the sample.
- ✓ At 200 nm to 250 nm, the reflectance after 3 days of exposure increased by about 10%.
- ✓ It is thought that changes in the sample surface condition due to UV light exposure caused an increase in the fluorescence intensity for excitation wavelengths close to 230 nm. Simultaneous reflection measurements using a spectrophotometer showed that the reflectance around this wavelength also increased.

■ Fluorescence intensity and reflection spectrum



PE 3D fluorescence spectrum after 3 days exposure



PE reflection spectrum after 3 days exposure

■ Measurement conditions

Scan speed:	300 nm/min (UV-Vis)
Slit width:	8 nm
Sampling interval:	1 nm

Number of days of exposure
0
3

Figure 12 PE 3D fluorescence spectrum and reflection spectrum

Note: The external appearance and the specifications of the products described in this technical report are subject to change for improvement. The data in this document represent an application example and are not a guarantee of performance.

[KEY WORDS]

fluorescence spectrophotometer, F-7100, fluorescence spectrum, plastic, ultraviolet light, degradation, spectrophotometer, UH4150, yellowness, 3D SpectAlyze

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