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Evaluation of Polyethylene Terephthalate (PET) Degradation by Molecular Weight Distribution Measurements

Introduction

Polyethylene terephthalate (PET) is a polymer widely used in food containers and synthetic fibers. Exposure to ultraviolet light and repeated recycling can cause PET to degrade, affecting its physical properties. Quantitative evaluation of these changes is important for product development and quality control. Gel permeation chromatography (GPC) provides a means of assessing polymer degradation by measuring changes in molecular weight distribution. Hexafluoroisopropanol (HFIP) is commonly used as the eluent for GPC analysis of PET; however, its high cost makes reducing solvent consumption an important consideration. Semi-micro GPC offers an approach to lowering solvent consumption while shortening analysis times.

In this application note, PET test samples were exposed to irradiation in a xenon accelerated weathering tester, and the resulting changes in molecular weight distribution were evaluated using an HFIP-compatible semi-micro GPC system equipped with an RI-4035 refractive index detector and a high-performance analytical GPC column while the changes in color were measured using a UV-Visible spectrophotometer. Data analysis was performed using the molecular weight distribution calculation program in ChromNAV. A calibration curve generated from polymethyl methacrylate (PMMA) standards was used to determine the molecular weight distribution of the degraded PET samples on a PMMA-equivalent basis.

Keywords

Polyamide 6, PA6, gel permeation chromatography, GPC, molecular weight distribution, molecular weight calibration curve, Polyethylene terephthalate, PET, polymethyl methacrylate, PMMA, hexafluoroisopropanol HFIP, refractive index detector, RI detector

Experimental

LC System		LC Conditions	
Pump:	PU–4185	Column:	GPC LF-404
Autosampler:	AS–4150*		(4.6 mm I.D. x 250 mm L, 6 µm)
Column oven:	CO–4060	Eluent:	5 mM sodium trifluoroacetate in HFIP
Detector:	RI–4035	Flow rate:	0.15 mL/min
* with option units		Column temperature:	40 °C
		Injection volume:	20 µL

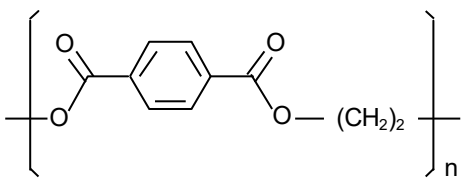


Fig. 1 *Structure of polyethylene terephthalate (PET)*

UV–Vis System

Instrument:	V–750 UV-Vis spectrophotometer
Accessories:	ISV–922 Integrating sphere unit
	VWCD-960 Color evaluation (color diagnosis) program

UV–Vis Conditions

Measurement range:	340 nm to 800 nm
Light source:	D_2/WI
Data interval:	1 nm
Bandwidth:	5 nm
Response:	0.24 sec
Scan speed:	400 nm/min
Accumulations:	1

Sample

Standard samples for creating molecular weight calibration curve

Polymethyl methacrylate (PMMA) mixed sample

(two samples prepared for different molecular weight peaks (M_p))

Standard sample 1: M_p 772,000; 51,900; 6,900; 645

Standard sample 2: M_p 211,000; 21,700; 2,200

Each sample was dissolved and diluted in the mobile phase to 0.025 % (w/v)

Test samples for evaluation

PET test pieces (approximately 10 mm x 10 mm x 2 mm, Standard Test Piece Co., Ltd.)

Results

Figure 2 illustrates the photodegradation test procedure. PET test samples were irradiated using a xenon accelerated weathering tester (SOLARBOX 1500e, manufactured by Cofomegra, provided by JASCO INTERNATIONAL Co., Ltd.) at an irradiance of 60 W/m^2 and a temperature of 65 °C. Three samples were sequentially introduced into the weathering tester at different times to achieve total irradiation times of 10 days, 5 days, and 1 day for samples 1, 2, and 3, respectively. Following irradiation, the degraded surface layer of each sample was removed using a plane slicer (Slice Master KS-10, provided by JASCO Engineering Co., Ltd.) and dissolved in mobile phase to a concentration of 0.1 % (w/v) for GPC analysis.

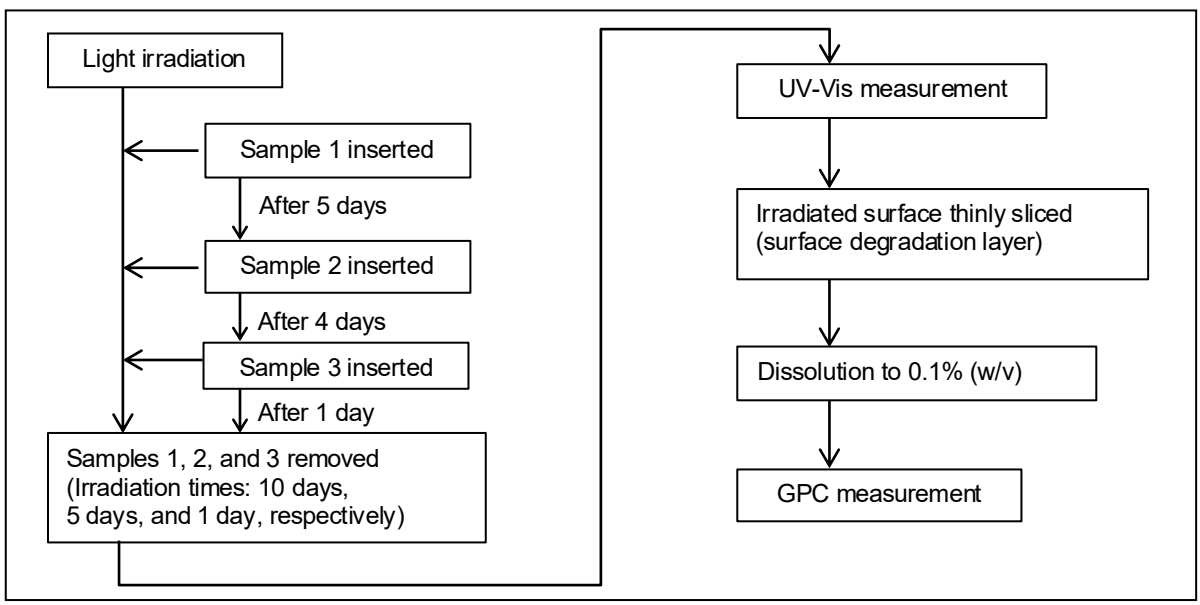


Fig. 2 *Photodegradation test procedure*

The PET test samples changed color from transparent to yellow following irradiation, as shown in Figure 3. The PET test samples were measured using a V-750 UV-Visible spectrophotometer to calculate the color (L*, a*, b*) and yellowness index (YI) to quantitatively evaluate the degree of degradation. Figure 4 shows the chromaticity coordinates of the PET test samples.

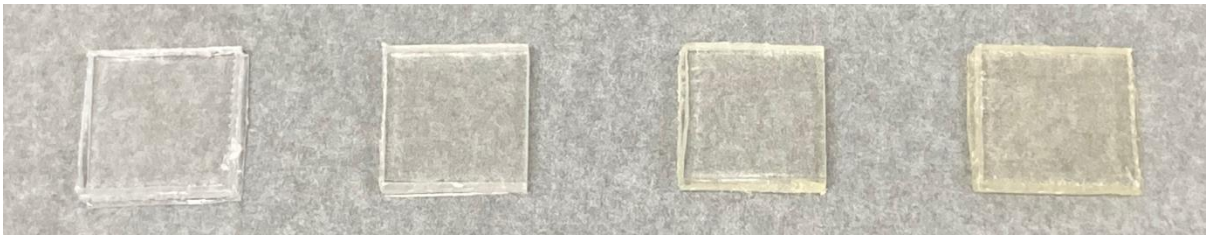


Fig. 3 *Color change in PET test samples following irradiation*

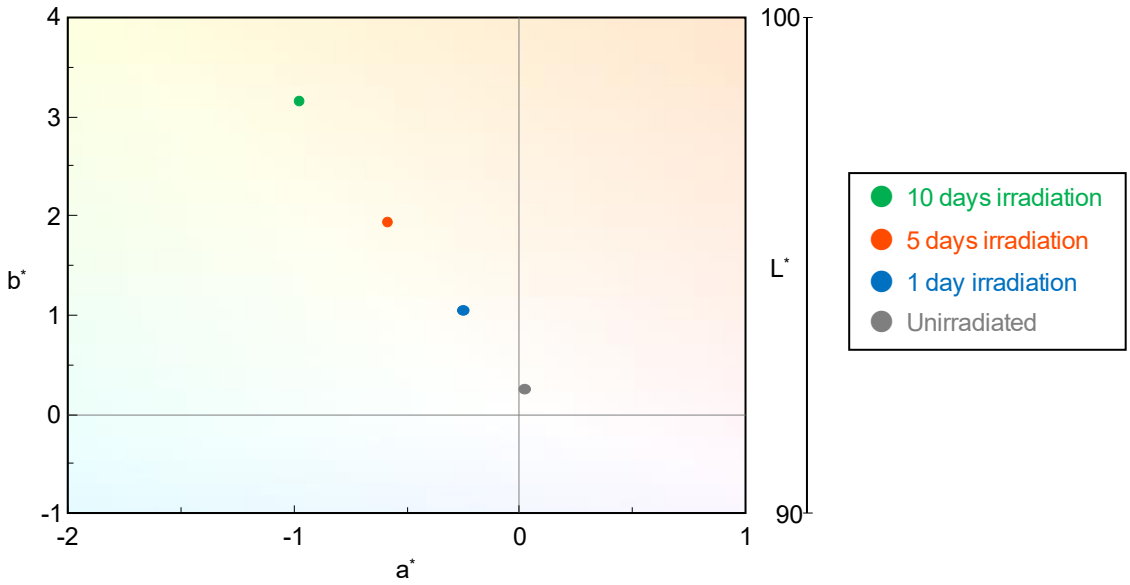


Fig. 4 *Chromaticity coordinates of the PET test samples*

Table 1 summarizes the calculated results for color (L*, a*, b*) and yellowness index (YI), and Figure 5 shows the change in b* and YI with irradiation time.

Table 1. *Calculated chromaticity results for PET test samples*

Sample	L^*	a^*	b^*	YI
Unirradiated	95.6	0.03	0.24	0.49
1 day irradiation	95.5	-0.3	1.04	1.80
5 days irradiation	95.5	-0.6	1.93	3.22
10 days irradiation	95.4	-1.0	3.15	5.23

YI: JIS K 7373:2006 (Light source: D65, View angle: 2 degrees)
Color matching function: JIS Z 8781-1:2012 (View angle: 2 degrees, Data interval: 1 nm)

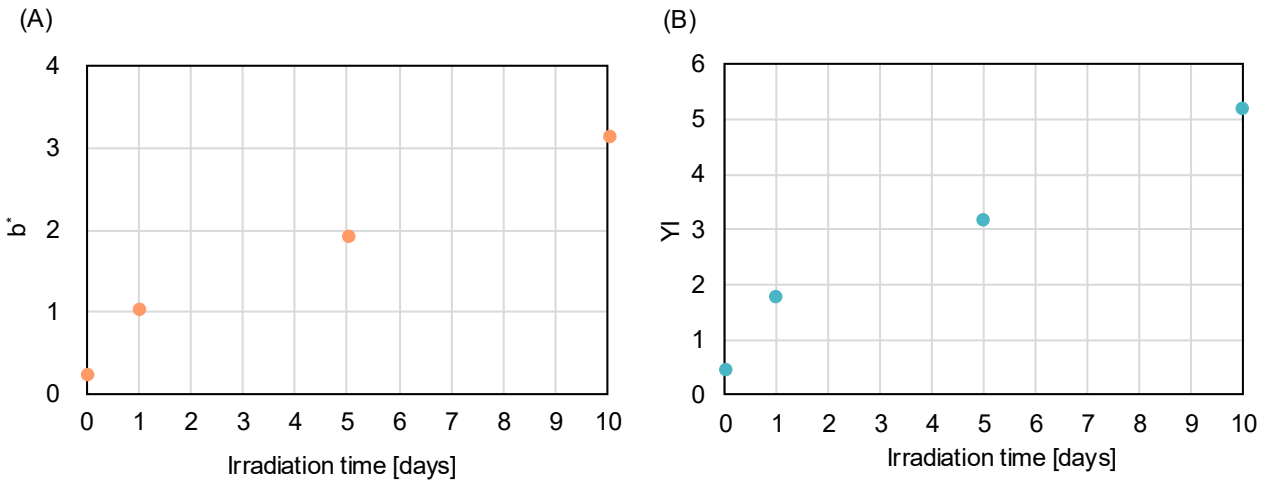


Fig. 5 *Changes in b* and YI with irradiation time*
(A) b; (B) YI*

The values of b* and YI increased with irradiation time, confirming the color change of the PET test samples from transparent to yellow. This color change is thought to result from irradiation-induced changes in the chemical structure of PET, which contains aromatic rings with conjugated double bonds, leading to the formation of new conjugated systems.[2]

Figure 6 shows the chromatograms of the two PMMA standard samples used for the molecular weight calibration. The resulting calibration curve is shown in Figure 7.

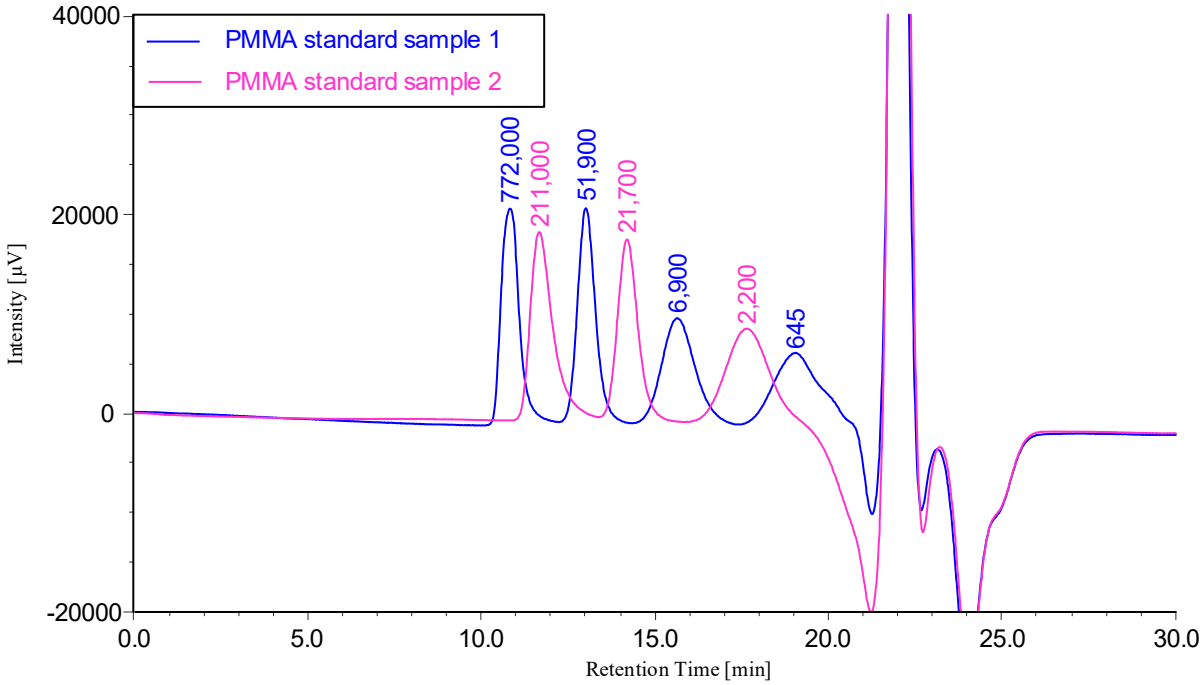


Fig. 6 *Chromatograms of the two PMMA standard samples*
(The values above the peaks represent the M_p for the PMMA standard samples)

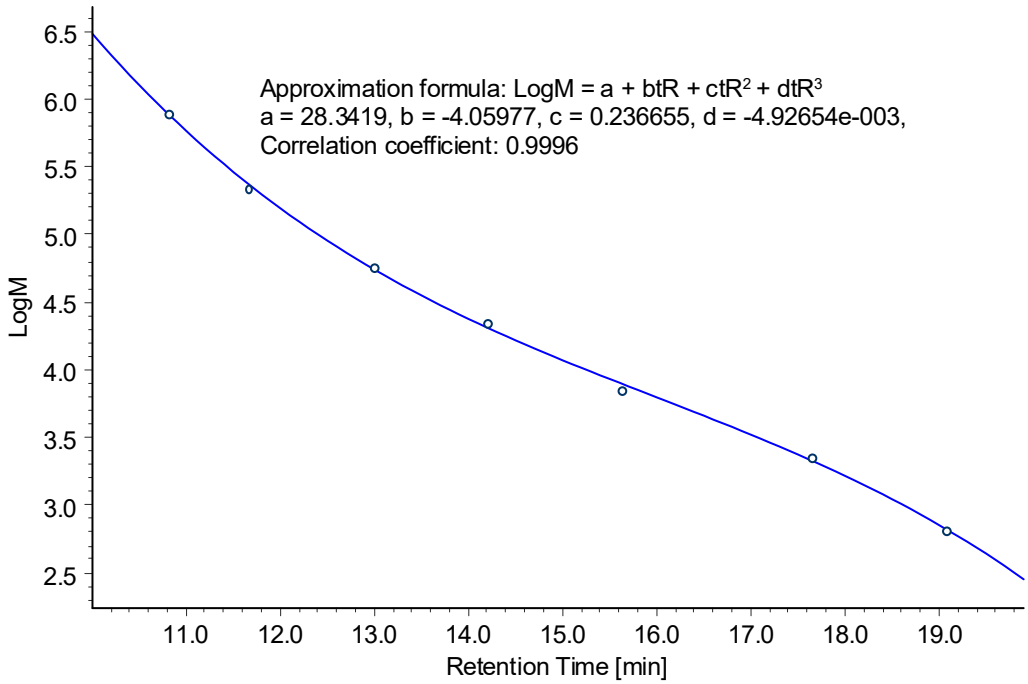


Fig. 7 *Molecular weight calibration curve created using PMMA standard samples*

Figure 8 compares the chromatograms of the three irradiated PET samples with that of an unirradiated sample. The corresponding differential molecular weight distribution curves are shown in Figure 9. Molecular weight is plotted on a logarithmic scale to facilitate comparison of the distributions. As irradiation time increased, the peak molecular weight (M_p) decreased, while the high molecular weight tails of the molecular weight distribution increased. These changes indicate that irradiation affected both the position and shape of the molecular weight distribution.

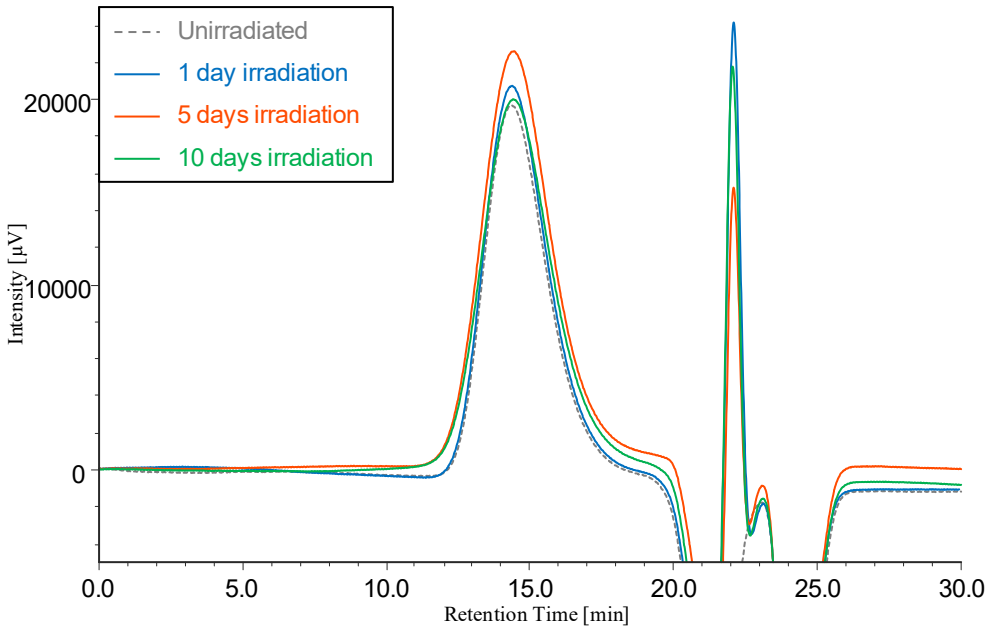


Fig. 8 *Chromatograms of the PET test samples*

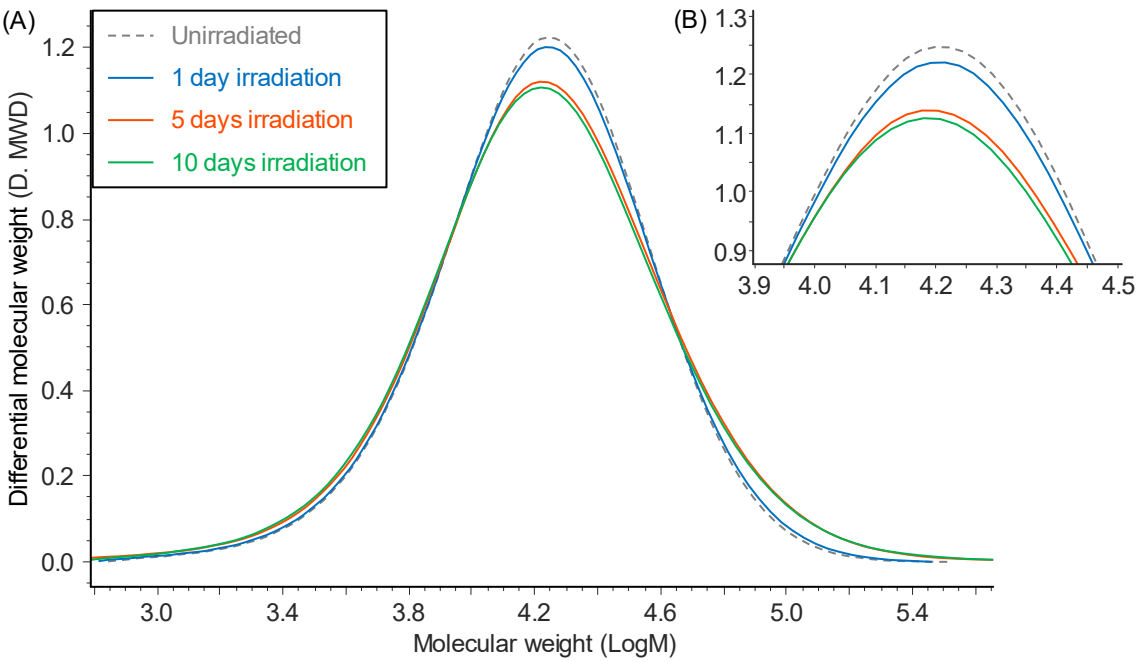


Fig. 9 *Differential molecular weight distribution curves of the PET test samples (A) Full curves; (B) Enlarged view of the peak molecular weight (M_p)*

Table 2 summarizes the calculated PMMA-equivalent average molecular weight values of the PET test samples. Figure 10 shows the changes in number-average molecular weight (M_n) and weight-average molecular weight (M_w) with irradiation time. As the irradiation time increased, M_p and M_n decreased, whereas M_w increased. This suggests that main chain scission and intermolecular crosslinking occur simultaneously under light irradiation.

Table 2. *PMMA-equivalent molecular weight calculation results of the PET test samples*

Sample	M_p	M_n	M_w	M_w/M_n
Unirradiated	18,039	10,756	19,994	1.86
1 day irradiation	17,825	10,571	20,356	1.93
5 days irradiation	17,511	10,136	22,421	2.21
10 days irradiation	17,035	10,028	23,174	2.31

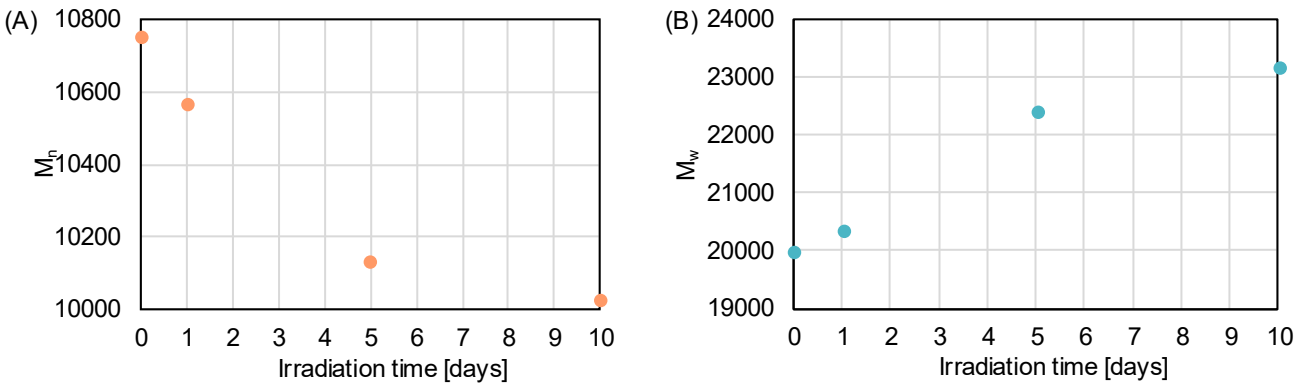


Fig. 10 *Change in average molecular weight with irradiation time*
(A) Number-average molecular weight (M_n); (B) Weight-average molecular weight (M_w)

Conclusion

In this application note, the photodegradation of PET test samples irradiated in a xenon accelerated weathering tester was evaluated by combining UV-Visible color measurements with semi-micro GPC analysis of the molecular weight distribution The UV-Vis results indicated a color change from transparent to yellow with increasing irradiation time, as reflected by increases in the color (b*) and yellowness index (YI). GPC analysis revealed decreases in M_p and M_n and an increase in M_w, with increasing irradiation time, suggesting that main chain scission and intermolecular crosslinking occur simultaneously during irradiation. Together, UV-Visible measurements and GPC analysis provide complementary quantitative indicators of changes in PET test samples associated with photodegradation.

References

1. JIS K 7373, Plastics - Method for Determining Yellowness and Yellowing (2024)
2. Nagano Prefecture Industrial Technology Center Technical Report: N. Shimosato, “Study on Color Changes Due to Photodegradation of Industrial Materials", No. 16, pp. E13–E17 (2021)

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