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Research Article

Weatherability of Polypropylene by Accelerated Weathering Tests and Outdoor Exposure Tests in Japan

Kenichi Shimizu,[1,2] Yuuki Tokuta,[1,2] Akihiro Oishi,[1,3] Takashi Kuriyama,[1,4] and Masao Kunioka[1,3]

[1] *Polymer Subcommittee in the Industrial Technology Cooperative Promotion Committee, Umezono 1-1-1, Tsukuba, Ibaraki 305-8560, Japan*
[2] *Tokyo Metropolitan Industrial Technology Research Institute, Aomi 2-4-10, Koto-ku, Tokyo 135-0064, Japan*
[3] *National Institute of Advanced Industrial Science and Technology (AIST), Higashi 1-1-1, Tsukuba, Ibaraki 305-8565, Japan*
[4] *Yamagata University, Jonan 4-3-16, Yonezawa, Yamagata 992-8510, Japan*

Correspondence should be addressed to Masao Kunioka; m.kunioka@aist.go.jp

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As a joint study of the Polymer Subcommittee in the Industrial Technology Cooperative Promotion Committee, in which members are Japanese local governmental research institutes and National Institute of Advanced Industrial Science and Technology (AIST, Japan), carried out from 2010 to 2012, polyethylene reference sample (PE-RS) pieces and six types of polypropylene (PP) were subjected to accelerated weathering tests and outdoor exposure tests, resulting in the following findings. (1) The PE-RS was subjected to eight 100 h exposure tests in the same test machine. The accelerated weathering test machines of the participating institutes had high reproducibility. (2) The PE-RS CI values were greater when the temperature in the chamber was greater during accelerated weathering tests, and there was a high correlation with the average temperature in the outdoor exposure tests at 20 places in Japan. (3) By comparing the change in PP strength by normalizing the degradation environment using the PE-RS CI values, the accelerated weathering test with results showing the highest correlation with the outdoor exposure test results was the one with the xenon arc lamp at an irradiance of 60 W/m^2 and a BPT of 63°C.

1. Introduction

Because plastics have lower specific gravities and are more easily moldable compared to metals and ceramics, their applications as device components have expanded, allowing components to become lighter and leading to cost reductions. In the future, as weight and cost reductions continue, the opportunities for plastics to be used in harsh environments will multiply. Materials used in outdoor locations are placed under harsh conditions, being exposed to sunlight and temperature changes. Therefore, evaluating the weather resistance of these materials is extremely important for their safe use. Outdoor exposure tests are the most useful for observing the changes that occur in plastics when exposed to real environmental conditions. However, currently, rapid product development is often desired, so accelerated weathering tests using accelerated weathering test machines are required.

Accelerated weathering tests are methods of exposure testing that attempt to rapidly reproduce the changes that occur in materials on outdoor exposure tests; methods include irradiation from an artificial light source and this may be accompanied by water spraying and cyclic experimental conditions, including changes in temperature, relative humidity, and irradiation energy [1–3]. Several light sources are available, including xenon arc lamps [4–6], open-flame carbon arc lamps (i.e., sunshine carbon arc lamp type) [7], ultraviolet carbon arc lamp type [8], ultraviolet fluorescent lamp type [9], and metal halide lamp type [10]. Furthermore, specifications have been stipulated concerning the test machines or test methods for all of these types of light sources

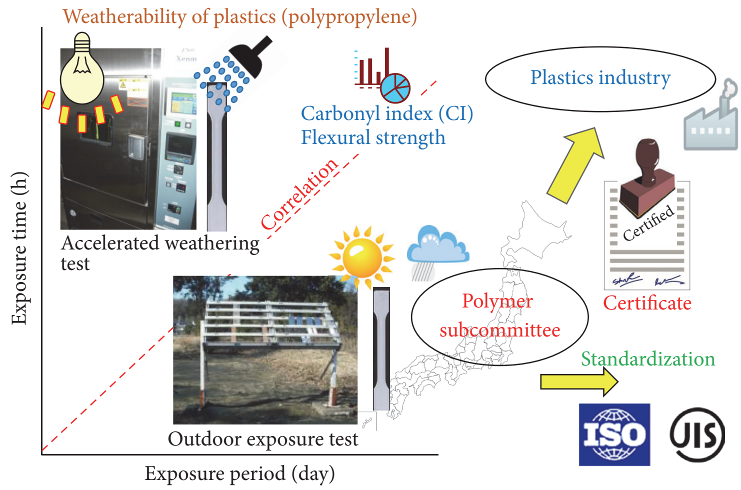

Figure 1: Aims of joint study in Polymer Subcommittee.

other than metal halide lamps. Each type of lamp has a characteristic spectral irradiance that affects the degradation of polymer materials differently. In Japan, the open-flame carbon arc lamp type is commonly used, but at present the xenon arc lamp type, the ISO standard, is also used widely [11]. In addition, xenon arc lamps with high light intensities have been developed in recent years and are used in some tests.

When selecting an appropriate accelerated testing method based on the International Standard (ISO) 4892-1 [12] (same as the Japan Industrial Standard (JIS) K7350-1), reproducibility for confirming the quality of required properties of different batches, acceleration degree for confirming the satisfying required property, and correlation between outdoor exposure and weathering test machine for confirming the lifetime outdoors for plastic product are very important. Many data of weathering test for adhesives and other outdoor applications were published [13–15]. Thus, the objective of this joint study was to perform accelerated weathering testing and outdoor exposure testing of a polyethylene reference sample (PE-RS) [16–19] and six types of polypropylene (PP) at public research organizations under the Polymer Subcommittee in the Industrial Technology Cooperative Promotion Committee (Japan) to obtain findings regarding the reproducibility and acceleration of the accelerated weathering testing and the correlation between the accelerated weathering testing and outdoor exposure testing as indicated in Figure 1.

The Polymer Subcommittee was founded about 50 years ago under the Industrial Technology Cooperative Promotion Committee to develop the technical level of participating members (41 research institutes) including local governmental research institutes, public research organizations, and National Institute of Advanced Industrial Science and Technology (AIST, Japan), for polymer product characterization by information exchange and cooperative research projects. A variety of accelerated weathering test machines have been introduced in the public research organizations under the Polymer Subcommittee in the Industrial Technology Cooperative Promotion Committee (Japan) as indicated in Figure 2, and these range widely in operating conditions. Using the accelerated weathering test machines already in operation in these public research organizations is advantageous because exposure test data can be obtained from a variety of test machines and test conditions in a relatively short time.

2. Materials and Methods

2.1. Test Pieces

2.1.1. Polyethylene Reference Sample (PE-RS). Test pieces purchased from the Japan Weathering Test Center (JWTC) were used without alteration. Figure 3 shows the outward appearance of the PE-RS (45 × 15 × 0.2 mm) mounted in a plastic flame of slide folder.

2.1.2. Polypropylene (PP). Six types of pellets supplied from Sumitomo Chemical Co., Ltd., were formed into multipurpose test pieces as indicated in JIS K7139 (2009) which is modified from ISO 20753 (2008) [20], via injection molding at Yamagata University before being used. Sample test pieces (Type A1, parallel part: 80 mm; thickness: 4 mm) were used as indicated in Figure 3(b). Table 1 indicates the attributes of the PP types used. Melt flow rates (MFR) of PP were measured by Melt Indexer (Toyo Seiki Seisaku-sho Ltd., Japan) at 230°C and 2.16 kg [21]. Melting temperature and heat of fusion were measured by DSC-60 (Shimadzu Co., Japan) at increasing rate of 10°C/min [22]. Test specimens were prepared using a 55-ton injection machine (J55E-C3, Japan Steel Works Co.). The mold had dumbbell-shaped cavity with 10 mm width, 4 mm thickness, and 159 mm length. The barrel temperature of PP homopolymer and copolymer was set from 190 to 210°C and 170 to 200°C, respectively, with same mold temperature of 40°C.

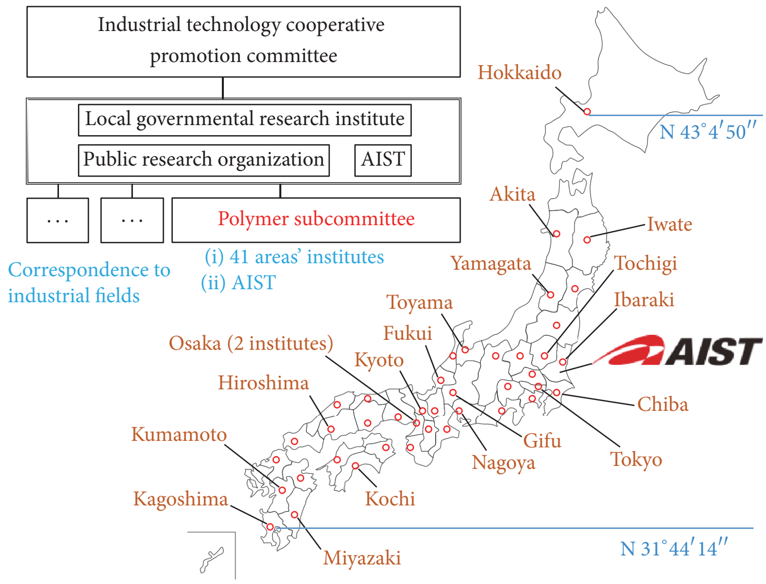

Figure 2: Participation members (∘) of Polymer Subcommittee in Industrial Technology Cooperative Promotion Committee. Participation members of outdoor exposure test in Table 3 are located at indicated place names. AIST is National Institute of Advanced Industrial Science and Technology.

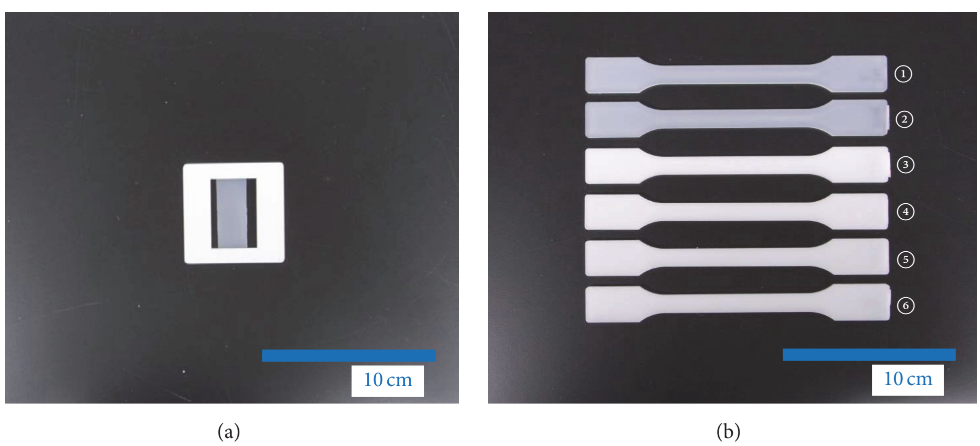

Figure 3: Polyethylene reference sample (PE-RS) (a) and polypropylene (PP) homopolymer and PP copolymer samples (b) as indicated in Table 1.

Table 1: Attributes of polypropylene (PP) used in weathering experiments.

Code	Molecular structure	Additive formulation	MFR[c], g/10 min	Melting temperature, °C	Heat of fusion, J/g
①	PP homopolymer	Standard[a]	7.4	166	122
②	PP homopolymer	Weather resistant[b]	7.1	167	112
③	PP copolymer	Standard[a]	3.3	166	94
④	PP copolymer	Weather resistant[b]	3.4	166	105
⑤	PP copolymer	Standard[a]	8.5	167	100
⑥	PP copolymer	Weather resistant[b]	8.8	167	101

[a]Antioxidant was melt-mixed.
[b]Antioxidant and light stabilizer were melt-mixed.
[c]Melt flow rate (MFR) was measured at 230°C and 2.16 kg.

Table 2: Exposure conditions for 100-hour accelerated weathering tests.

Number	Irradiance/(wavelengths) (W/m^2/(nm))	BPT[a] or BST[b] (°C)	Chamber temperature (°C)	Water spray time per total irradiation (min/(min))
1	30/(300–400)	63 ± 3^a	38	—
2	50/(300–400)	63 ± 2^a	38	—
3	60/(300–700)	65 ± 2	38	—
4	60/(300–400)	65 ± 2^b	38	18/(120)
5	60/(300–400)	63 ± 2^a	38	18/(120)
6	60/(300–400)	63 ± 3^a	38	18/(120)
7	60/(300–400)	63 ± 3^a	38	18/(120)
8	60/(300–400)	63 ± 3^a	42	18/(120)
9	60/(300–400)	65 ± 2^a	52.8	—
10	60/(300–400)	63 ± 2^a	52-53	—
11	390/(300–700)	63 ± 3^a	42	12/(60)
12	390/(300–700)	63 ± 3^a	38	18/(120)
13	100/(300–400)	65 ± 2^b	38	18/(120)
14	100/(300–400)	65 ± 2^b	38	18/(120)
15	100/(300–400)	65 ± 2^b	38	18/(120)
16	100/(300–400)	63 ± 2^a	43	
17	180/(300–400)	63^a	21	
18	180/(300–400)	63 ± 3^a	28	18/(120)
19	180/(300–400)	63^a	28	2/(300)
20	180/(300–400)	63 ± 3^a	—	18/(120)
21	180/(300–400)	63 ± 3^a	33	18/(120)
22	180/(300–400)	63 ± 1^a	38	18/(120)
23	180/(300–400)	83 ± 2^a	41	
24	255/(300–700)	63 ± 3	40	18/(120)
25	255/(300–700)	63 ± 3^a	42	18/(120)
26	255/(300–700)	63 ± 3^a	42	18/(120)
27	255/(300–700)	63 ± 3^a	43	18/(120)
28	500/(300–700)	63 ± 3	40	—
29	500/(300–700)	63 ± 3	40.6	—
30	563/(300–700)	63 ± 3	38	—
31	1000/(300–400)		63	—
32		—	40	—

BST: black standard thermometer temperature. BPT: black panel thermometer temperature.

2.2. Exposure Tests

2.2.1. 100 h Accelerated Weathering Test. The PE-RS samples were sent to the 20 institutions listed in Appendix A, and exposure tests were conducted for 100 hours in 31 accelerated weathering test machines owned by these institutions. Also, as a control, PE-RS was exposed for 100 h in a thermostatic chamber set to 40°C. The main exposure conditions of the accelerated weathering test machines are indicated in Table 2. The accelerated weathering test machines included 21 xenon arc lamp machines for numbers one to 23 (23 samples), four open-flame carbon arc lamp type machines for numbers 24 to 27, three ultraviolet carbon arc lamp type machines for numbers 28 to 30, and one metal halide lamp type machine for number 31. The exposure conditions and handling of periods when the test machines were halted were determined by the participating institutions according to circumstances. All institutes calibrate the intensity of illumination using certified illuminometer once a year and black panel temperature (BPT) using black panel thermometer continuously during weathering tests.

2.2.2. 800 h Accelerated Weathering Test. Samples of PE-RS and three types of PP were sent to the 10 institutions listed in Appendix B, and exposure tests were conducted for 800 h within the accelerated weathering test machines owned by these institutions. The main exposure conditions of the accelerated weathering test machines are listed in Table 3. Each PE-RS was exposed for 100 h, while the PP samples were removed for five tests, respectively, after 100, 200, 300, 500, and 800 h had elapsed. The exposure conditions and handling of periods when the test machines were halted were determined by the participating institutions according to

Table 3: Exposed PP test pieces and conditions for 800 h accelerated weathering tests.

Institution	Test pieces	Machine name	Manufacturer	Irradiance (measurement wavelength range) (W/m^2/(nm))	BPT (°C)	Chamber temperature (°C)	Chamber humidity (%)	Water spray time per total irradiation time (min/(min))
A	1, 4, 5	7.5 kW Super Xenon Weather Meter SX75	Suga Test Instruments	60/(300–400)	83	—	50	—
B	2, 3, 6	Metaling Weather Meter SUV-W151	Iwasaki Electric	1000		50	50 (RH)	—
C	1, 4, 5	Super Xenon Weather Meter SX75	Suga Test Instruments	60/(300–400)	63	38	50	18/(120)
D	2, 3, 6	Low-Temperature Cycle Weather Meter WEL-75XS-LHP-BEc	Suga Test Instruments	390/(300–700)	63 ± 3	42[a]	50 (set value)	12/(60)
E	1, 4, 5	Super Xenon Weather Meter SC750-WA	Suga Test Instruments	180/(300–400)	63	No control (26[b] 35[c])	50	18/(120)
F	2, 3, 6	Super Xenon Weather Meter SX75	Suga Test Instruments	180/(300–400)	63 ± 1	33 ± 1	50 ± 10 (RH)	—
G	2, 3, 6	Super Xenon Weather Meter (2-Tank Independent Type) SX2D-75	Suga Test Instruments	180/(300–400)	63 ± 1	38 ± 1[b]	50 ± 5 (RH)[c]	18/(120)
H	1, 4, 5	Atlas Weatherometer Ci3000	Atlas	60/(300–400)	63 ± 2	38 ± 3	50	18/(120)
I	2, 3, 6	Super Xenon Weather Meter SX75	Suga Test Instruments	180/(300–400)	63 ± 3	—	50	18/(120)
J	1, 4, 5	Super Xenon Weather Meter SX75-WAP	Suga Test Instruments	180/(300–400)	63	28 ± 3	60 (RH)	2/(300)

[a]Reported by manufacturer. [b]During spray. [c]During irradiation. RH: relative humidity.

Table 4: Features of lamps for weathering test machine.

Lamp type	Mechanism	Characteristic of spectral distribution	Standard[a] related to plastics
Xenon arc	Light by passing electricity through ionized Xenon gas in glass tube	Extremely resembling sunlight in UV and visible part	ISO 4892-2 (same as JIS K7350-2) [23]
Open flame carbon arc	Carbon arc in open air	Resembling sunlight UV-B (280–315 nm) and severalfold intensity in UV-A (315–400 nm)	ISO 4892-4 (same as JIS K7350-4) [24]
Ultraviolet carbon arc	Carbon arc in glass tube	Major peak at 388 nm, minor peaks at 358 and 415 nm	JIS B7751 [25], ASTM D5031 [26]
Metal halide lamp	Light by passing electricity through ionized mercury and metal halide gases in quartz glass tube	20–30 times UV (270–450 nm) as compared to sunlight	None

[a]ISO: International Standard, JIS: Japan Industrial Standard, and ASTM: American Society for Testing and Materials.

circumstances. Features of lamps for weathering test machine are indicated in Table 4.

2.2.3. Outdoors Exposure Test. Samples of PE-RS and three types of PP were sent to the 20 institutions listed in Appendix C, and exposure tests were conducted for two years on exposure platforms owned by these institutions. The exposed test pieces and main exposure conditions at each institution are indicated in Table 5. Each PE-RS was exposed for one month, while the PP samples were removed for five tests, respectively, after 3, 6, 9, 12, and 24 months had elapsed.

2.3. Degradation Measurement

2.3.1. Carbonyl Index (CI). The methods described in the specification [16–19] were followed. Specifically, a Fourier transform infrared spectrometer (FTIR, Thermo Scientific Nicolet-6700) was used to measure the infrared absorption spectrum of the postexposure PE-RS sample films (thickness 0.2 mm) in the range from 2200 cm^{-1} to 1600 cm^{-1} on transmission mode at a typical average of 24 scans, and the CI was calculated from the absorbances at around 1715 cm^{-1} (peak of carboxyl group produced by oxodegradation) and 2020 cm^{-1} (peak of methylene group (standard)), according to

$$\mathrm{CI} = \frac{A_{1715}}{A_{2020}}. \tag{1}$$

Here, A_{1715} and A_{2020} indicate the absorbances of the peaks around 1715 and 2020 cm^{-1}, respectively.

2.3.2. Observation of Surface Texture. The central area of parallel part of as-mold and postexposure PP test pieces was observed by a scanning-white-light interferometer (Zygo, New View 6200). It was used at $20 \pm 1^{\circ}$C. A 50x objective lens was used with a 0.5x zoom lens; the horizontal resolution was 0.88 μm, and the z-axis scan length was 150 μm.

2.3.3. Flexural Strength. To calculate the flexural strength (maximum value) of the PP test pieces before and after exposure, a micrometer and a universal testing machine (Autograph AG-10TD) were used; the measurements followed the ISO 178 (same as JIS-K7171 (2008)) [27] protocol. Triplicated samples were measured at by three points bending with 64 mm lower span gap and 2 mm/min head insertion speed. The postexposure PP test pieces were placed in the test machine so that the exposed surface was the surface under tension.

2.3.4. Weather Data Acquisition. The relevant dates and closest observation points to the locations of the institutions performing the exposure were selected from data provided by the Japan Meteorological Agency, which is publically available on the Internet [28]. Monthly average temperature, precipitation, and insolation time data were acquired for the period from September 2011 to August 2013.

3. Results and Discussion

The carbonyl index (CI) quantitatively represents the combined effects of temperature and UV rays on the samples. PE-RS, supplied by JWTC, was standardized with respect to the material, production method, outward appearance, dimensions, absorbance ratio to measure CI in an outdoor exposure test, and an experimental light source exposure test. The CI of PE-RS increases linearly with increasing exposure time in a uniform exposure environment and increases with temperature.

Figure 4 shows the CI of the PE-RS sample exposed for 100 h in accelerated weathering test machines. The numbers on the horizontal axis match those in Table 2. Comparing the CI of samples under different exposure conditions, the CI was greater when exposed in the accelerated weathering test machines (numbers 1–31) compared to when exposed in a thermostatic chamber at 40°C (NO. 32), confirming that CI of PE-RS increases due to the combined effects of temperature and light irradiation. Meanwhile, sample numbers 10, 23, and 31 had larger CI values, and these were exposed to either higher temperatures in the chamber or higher black panel temperatures, confirming that the CI of the PE-RS is

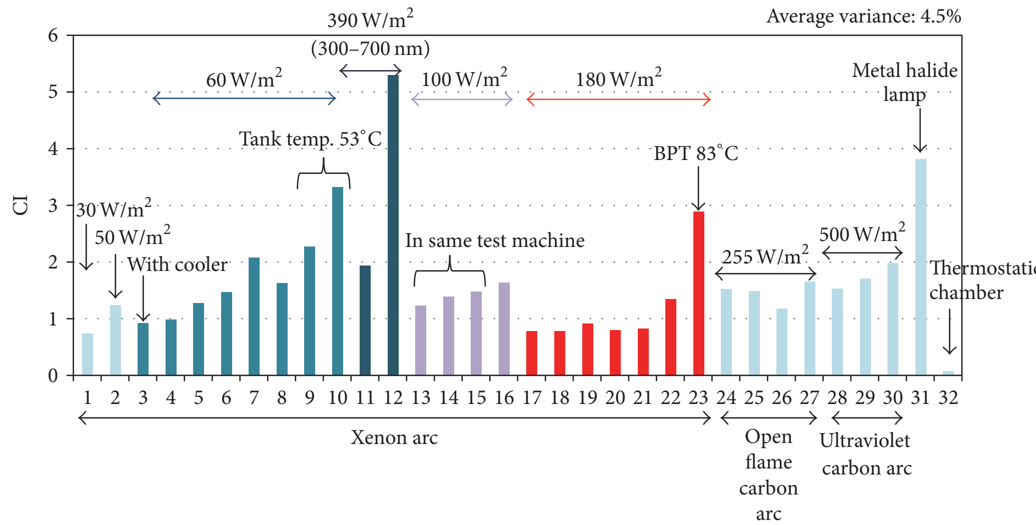

Figure 4: Carbonyl index (CI) of PE-RS exposed for 100 h in an accelerated weathering machine.

Table 5: Outdoor exposed PP test pieces at place (latitude and longitude) with conditions for outdoor exposure tests.

Institution	Latitude	Longitude	Test pieces	Compass bearing	Elevation[a]
Hokkaido	N43°4′50″	E141°20′15″	①, ④, ⑤	South	C
Akita Prefecture	N39°43′	E140°6′	①, ④, ⑤	South	B
Iwate Prefecture	N39°40′29″	E141°7′55″	②, ③, ⑥	South	C
Yamagata Prefecture	N38°14′	E140°17′	②, ③, ⑥	South	C
Toyama Prefecture	N36°36′34″	E136°54′56″	①, ④, ⑤	South	C
Tochigi Prefecture	N36°19′8″	E139°34′14″	①, ④, ⑤	South	A
Ibaraki Prefecture	N36°16′42″	E139°53′4″	②, ③, ⑥	—	—
Fukui Prefecture	N36°7′0″	E136°12′10″	②, ③, ⑥	South	A (26°)
Tokyo	N35°37′6″	E139°46′46″	②, ③, ⑥	South	C
Chiba Prefecture	N35°36′45″	E140°9′5″	①, ④, ⑤	South	C
Gifu Prefecture	N35°21′5″	E136°44′33″	①, ④, ⑤	South	E (90°)
Nagoya City	N35°7′10″	E136°53′20″	②, ③, ⑥	South	A (25°)
Kyoto City	N34°59′32″	E135°44′41″	①, ④, ⑤	South	E
JCII (Osaka)	N34°40′13″	E135°34′12″	②, ③, ⑥	—	—
Osaka Prefecture	N34°26′37″	E135°26′41″	①, ④, ⑤	South	B
Hiroshima Prefecture	N34°13′38″	E132°35′10″	②, ③, ⑥	South	D (5°)
Kochi Prefecture	N33°34′23″	E133°34′44″	②, ③, ⑥	South	C
Kumamoto Prefecture	N32°47′5″	E130°46′1″	②, ③, ⑥	—	—
Miyazaki Prefecture	N32°2′15″	E131°15′19″	①, ④, ⑤	South	A (22°)
Kagoshima Prefecture	N31°44′14″	E130°42′54″	①, ④, ⑤	South	C

[a]Elevation: A; Latitude – 10°, B; 30°, C; 45°, D; 5–10°, E; other.

strongly affected by temperature. In a comparison between experimental conditions, the open-flame carbon arc and ultraviolet carbon arc lamps resulted in nearly equivalent CI values; these correspond to the 60–100 W/m^2 range with the xenon arc lamp type. Notably, the xenon arc lamp at 180 W/m^2 and a black panel thermometer temperature (BPT) of 63°C (numbers 17–22) resulted in smaller CI values than at an irradiance of 60 W/m^2 and a BPT of 63°C (numbers 3–10). We believe that this is because the PE-RS samples as indicated in Figure 3 were white, resulting in lower visible light absorbance compared to the black panel. In addition, the temperature of the accelerated weathering test machine chambers was controlled until the BPT became a specific temperature during light irradiation at fixed irradiance, leading to the temperature in the chamber being maintained at a lower level compared to the high irradiance conditions and resulting in the PE-RS temperature being lower in the case of irradiation at 180 W/m^2 than that at 60 W/m^2.

Additionally, during irradiation at 60 W/m^2 and BPT 63°C (numbers 3–10) and at 180 W/m^2 and BPT 63°C with a xenon arc lamp, the CI differed by up to a factor of two, despite the exposure conditions being very similar. However, aside

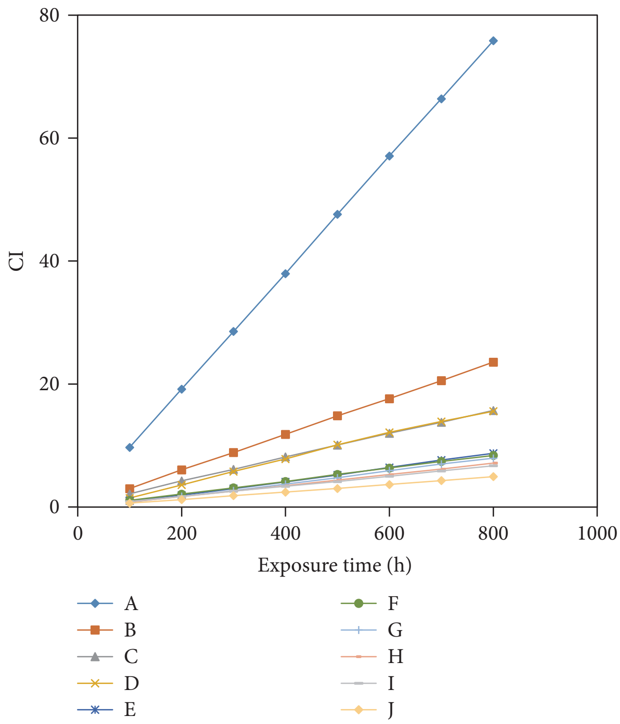

Figure 5: Cumulative CI values for PE-RS during eight repetitions of 100 h exposure in an accelerated weathering test machine. A–J are institution codes (detailed machine condition) as indicated in Table 3.

from these conditions, there were no significant differences between samples within the same test machines (see samples 13, 14, and 15). Also, for sample 12, the CI value was large; however, it was determined that, for this test, exposure time may have been longer than originally suggested.

Figure 5 shows the cumulative CI values for PE-RS during eight repeated 100-hour exposures. The CI values increased proportionally with exposure time in all of the exposure test machines, with a correlation coefficient of at least 0.999 in each case. This indicates that the exposure test machines produced highly reproducible data. The greatest and smallest cumulative CI values for the PE-RS samples after 800 hours of exposure were 8.74 and 4.94 for the five institutions using a xenon arc lamp type at 180 W/m^2 and a BPT of 63°C, respectively, and 15.70 and 7.15 for the three institutions using a xenon arc lamp type at 60 W/m^2 and a BPT of 63°C, respectively. In common with the 100 h exposure tests, there was a maximum twofold difference between machines. In addition, the average values were, respectively, 7.34 (180 W/m^2) and 12.80 (60 W/m^2).

Figure 6 shows the relationship between PP flexural strength and exposure time obtained from accelerated weathering tests. PP flexural strength rose in the initial stages of exposure, but under each set of exposure conditions, once flexural strength began to decrease, it decreased monotonically with increasing exposure time. Bending tests are believed to be an appropriate test to evaluate the degree of PP degradation; however, when evaluating degradation using strength tests, the relationship between exposure time and a decrease in strength is not always monotonic in other polymers.

Figure 7 shows a representative example of surface texture changes in a PP sample exposed in an accelerated weathering test machine. As is evident from Figure 7, the most prominent change in surface texture on exposure was cracking in the direction perpendicular to the flow direction, and the number of cracks increased with increasing exposure time. In general, cracks concentrate stress, leading to brittle fracturing. Consequently, the fracture strength value ceases to be stable. However, once numerous cracks have developed, the cracks open during bending tests, easing the concentration of tensile strain at the tips of the individual cracks and, thus, increasing bending, leading to a more ductile stress-strain curve. In fact, the postexposure test samples rarely suffered from brittle failure in the elastic region during bending tests. In addition, the opening of numerous cracks dissipates strain energy, decreasing the test force. Thus, changes in surface texture can be inferred to be intimately involved in the result of a monotonically decreasing flexural strength.

However, changes in flexural strength during initial degradation are low, and so detecting early degradation is difficult. As a result of verifying the bending strength values and the surface texture, the strength decrease started at an exposure time of approximately 200–500 h for the standard-formulation PP (samples①, ③, and ⑤), and the only sample that started to decrease in flexural strength at 100 h was sample ⑤ from exposure institution A, in which cracks had clearly developed (see Figure 7). In contrast, for the weather-resistant PP formulations (②, ④, and ⑥), a decrease in the bending test only arose under the high irradiance conditions of a xenon arc lamp type at 180 W/m^2 and the metal halide lamp accelerated weathering test machines; there was no decrease in flexural strength after 800 h under 60 W/m^2 conditions, even at the high temperature (BPT conditions of 83°C).

Figure 8 indicates the two-year cumulative CI values and locations of the exposure institutions from the test exposing PE-RS outdoors monthly for two years. However, this excludes data from institutions at which the PE-RS was lost for some reason (e.g., as a result of a storm) resulting in less than two years' worth of CI data. The greatest two-year cumulative CI value was 29.76, measured in Kumamoto. The lowest value was 19.09 in Hokkaido. In addition, the average value at the 16 institutions that obtained two years' worth of data was 24.01. In a simple comparison of these values and the results of the 800 h accelerated weathering test, the exposure conditions in the accelerated weathering test machine resulting in a PE-RS CI value equivalent to that after one year of outdoor exposure were a xenon arc lamp type at 180 W/m^2 and a BPT of 63°C for 1309 h or 60 W/m^2 and a BPT of 63°C for 750 h.

Figure 9 shows an example of the relationship between the number of exposure days and the cumulative CI value. The PE-RS CI exhibited periodicity by increasing greatly from spring (April) through summer (August) and a reduced rate of increase from fall (September) through winter (March);

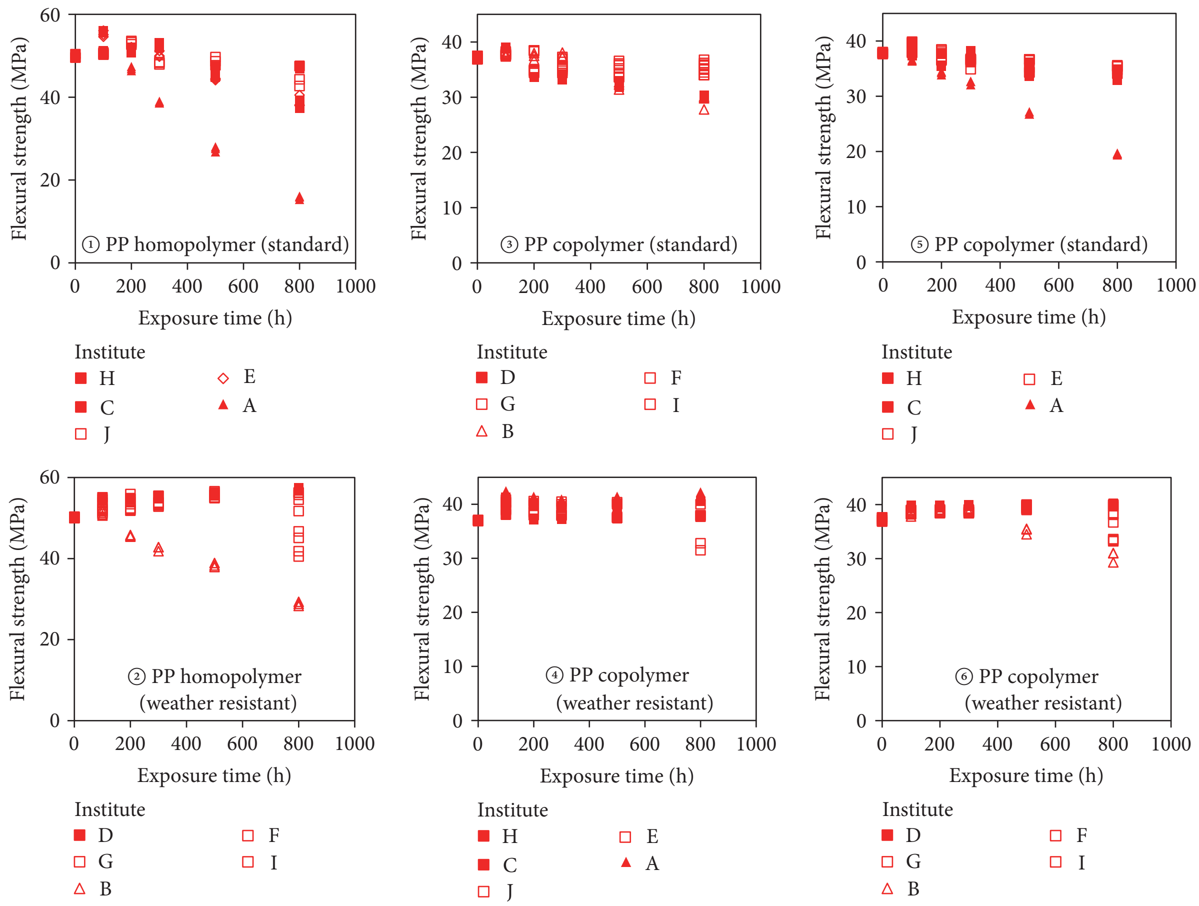

Figure 6: Relationship between PP flexural strength and exposure time in accelerated weathering test machine. ①–⑥ are sample codes as indicated in Table 1. A–J are institution codes as indicated in Table 3. ■: xenon 60 W and 63°C or parity condition, □: xenon 180 W and 63°C, ▲: xenon 60 W and 83°C, and △: metal halide lamp.

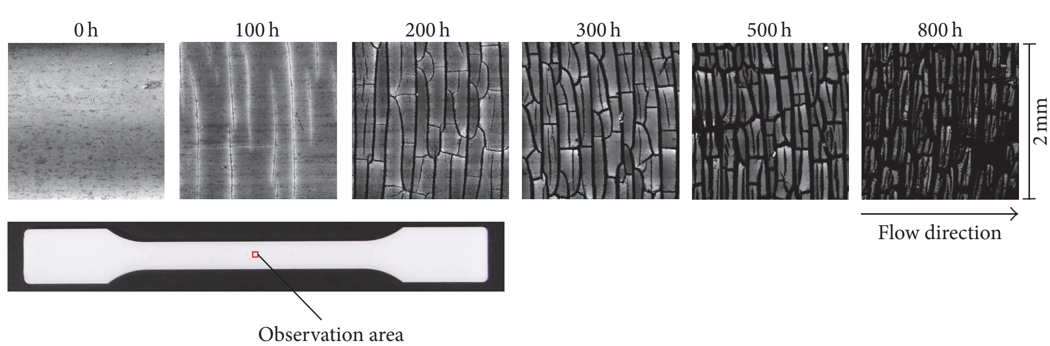

Figure 7: Surface texture changes in PP exposed to accelerated weathering test machine (institution A as indicated in Table 3, test piece code ⑤ as indicated in Table 1).

however, at the same time, the CI increased monotonically with increasing exposure time. Additionally, Figure 10 shows the relationship between each weather factor and two years of cumulative CI values. The correlation coefficients between the PE-RS CI value during the outdoor exposure test and the average temperature, cumulative precipitation, and cumulative insolation time were 0.712, 0.217, and 0.241, respectively. Thus, average temperature had the highest correlation coefficient among the three weather factors. This trend matches the results of a Polymer Subcommittee joint study conducted from 2002 to 2004 [29]. This confirmed that the CI value for PE-RS CI is strongly affected by temperature.

Figure 11 shows the relationship between PP flexural strength and outdoor exposure time. The flexural strength of PP with the weather-resistant formulations (samples ②, ④, and ⑥ in Figure 11) did not decrease during the 24-month period. In contrast, the standard-formulation PP flexural strength rose for six months and then decreased after

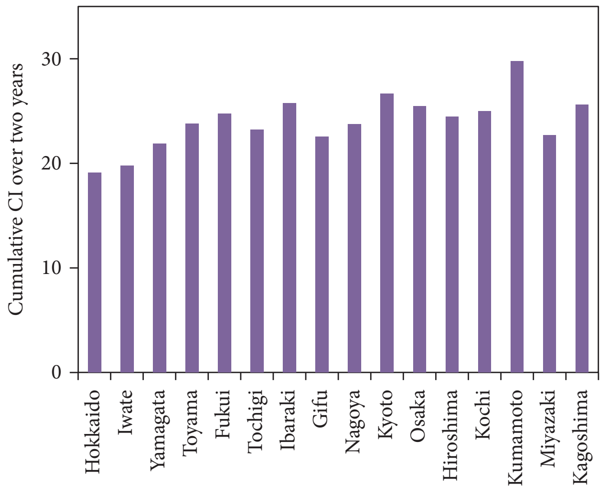

FIGURE 8: Cumulative PE-RS CI values at locations of exposure institutions as indicated in Table 5.

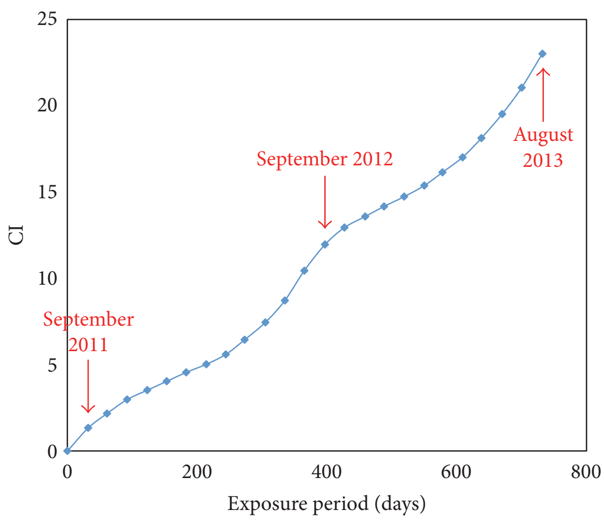

FIGURE 9: Example of cumulative PE-RS CI value and outdoor exposure (days) in Tochigi Prefecture.

nine months of exposure for a subset of samples and after twelve months of exposure for all samples, further decreasing after 24 months. The average tendency can be said to be an increase in flexural strength during the initial stage of exposure, followed by a monotonic decline with increased exposure time once decrease begins. This tendency matches the results of exposure in the accelerated weathering test machines. Nevertheless, the bending tests of the samples exposed for nine months, when the decline in flexural strength begins, resulted in a relatively large number of samples that underwent brittle failure; consequently, flexural strength was widely scattered. This tendency is not seen due to exposure in accelerated weathering test machines. One factor behind this result is believed to be the concentrated stress at the few crack tips developing during the initial stages and the cracks deeper in outdoor exposure tests compared to in accelerated weathering testing machines. It is showed by FTIR analysis for successive microtomed PP specimen after 12-month outdoor exposure test and 400 h accelerated weathering test that the CI depth profiles are different from each other and the CI from 40 to 200 μm depth is larger in outdoor exposure tests compared to in accelerated weathering testing [30].

Figure 12 illustrates the changes in PP flexural strength due to outdoor exposure testing and accelerated weathering testing based on the PE-RS CI values. The CI is an index that represents the combined effect of temperature and ultraviolet rays on the degradation of plastic. Using the CI, it is possible to compare changes in PP flexural strength in different exposure environments. In the outdoor exposure testing of standard-formulation PP (samples ①, ③, and ⑤ shown in Figure 12), the flexural strength began to decrease at a CI of around 6 to 8, after which point there tended to be a monotonic decrease with increasing CI. In the accelerated weathering testing, due to insufficient plot points at the large CI region, it was somewhat difficult to identify a tendency towards a lower flexural strength with respect to CI under different conditions. Still, as shown for sample ① in Figure 12, the rate of decrease in flexural strength with respect to CI can be arranged into three lines. Namely, these are the lines corresponding to the xenon arc lamp type at 180 W/m^2 and a BPT of 63°C, at which the rate of decrease in flexural strength with respect to CI was the greatest; the line corresponding to the xenon arc lamp type at 60 W/m^2 and a BPT of 83°C, at which the rate of decrease was the smallest; and the line corresponding to the xenon arc lamp type at 60 W/m^2 and a BPT of 63°C, at which the rate of decrease was intermediate to above. It is even more difficult to identify a decreasing trend for samples ③ and ⑤ in Figure 12, but if there is another line corresponding to the metal halide lamp type in addition to the three decreasing trends stated above, the PP flexural strength in the region of large CI due to outdoor exposure testing appears to be on a line at the outside of the line corresponding to the xenon arc lamp type at 60 W/m^2 and a BPT of 63°C, and among the accelerated weathering tests in this joint study, these conditions can be considered to have the highest correlation with the outdoor exposure tests. However, there was the difference that, under the conditions of accelerated weathering tests, the flexural strength decrease began at a lower CI than the outdoor exposure testing.

In the outdoor exposure tests of PP with the weather-resistant formulation (②, ④, and ⑥ in Figure 12), the flexural strength did not decrease, although the CI value reached approximately 30 due to two years of outdoor exposure and 75 due to 800 h accelerated weathering test of the xenon arc lamp type at 60 W/m^2 and a BPT of 83°C (not plotted in the figure). Meanwhile, we confirmed a drop in flexural strength at a CI of no greater than 10 under 1000 W/m^2 conditions using the metal halide lamp and 180 W/m^2 conditions using the xenon arc lamp type weathering machines. Consequently, accelerated weathering tests with high irradiance are superior in terms of rapidly obtaining a pass/fail determination for the weather-resistant formulations, but they correlated poorly with outdoor exposure testing compared to the accelerated weathering testing using a xenon arc lamp at 60 W/m^2.

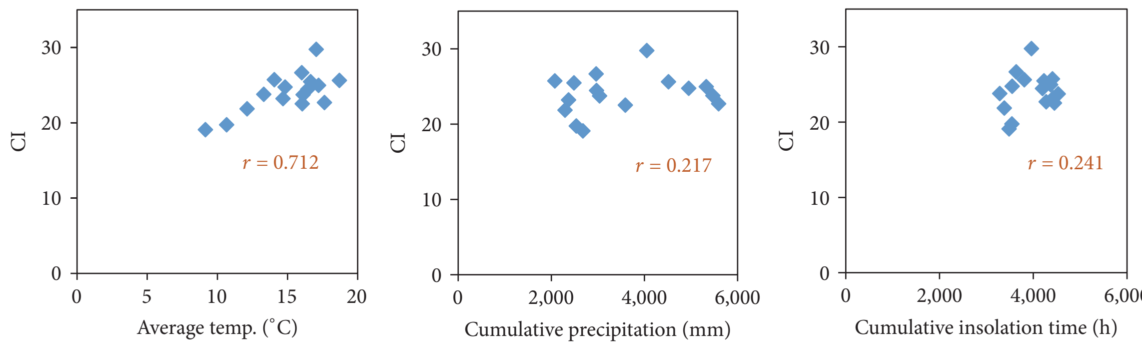

FIGURE 10: Relationship between weather factors and CI.

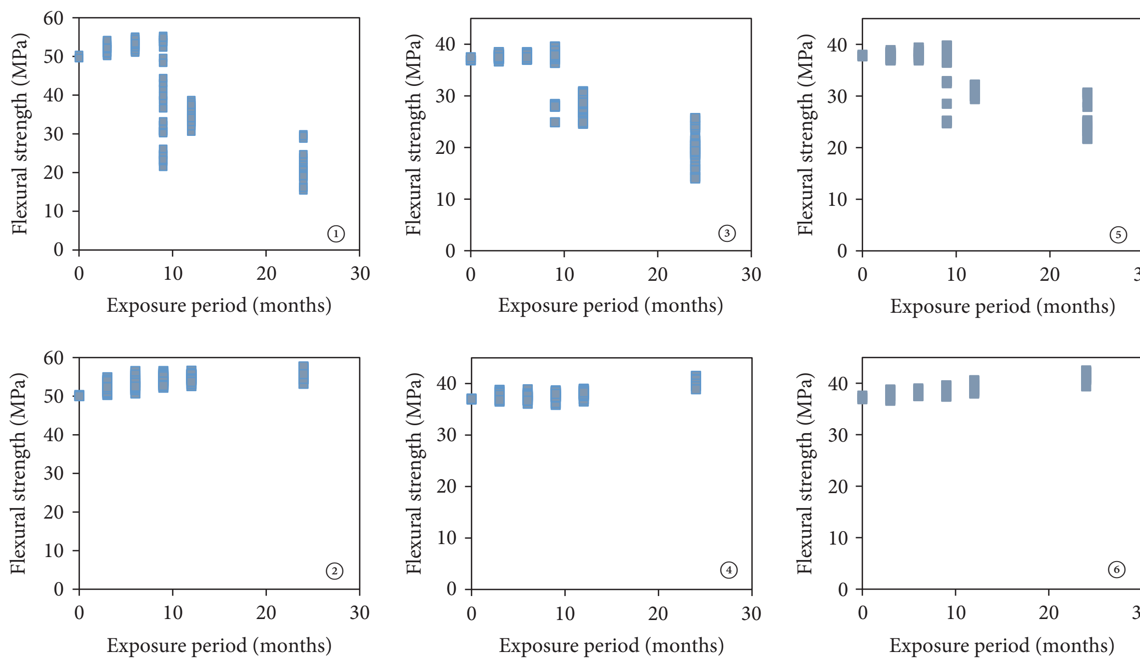

FIGURE 11: Relationship between outdoor exposure period and PP flexural strength. ①–⑥ are sample codes as indicated in Table 1. 3–10 square plots looks bar by lapping.

4. Conclusions

In this joint study of the Polymer Subcommittee from 2010 to 2012, accelerated weathering tests and outdoor exposure tests were performed on polyethylene reference samples (PE-RS) and six types of polypropylene (PP). (1) In case of reproducibility, PE-RS was subjected to eight 100 h exposure tests in the same test machine. Consequently, from the measured carbonyl index (CI) of the PE-RS sample, the correlation factor between the CI value and the exposure time was found to be 0.999, indicative of the high reproducibility of measurements carried out in the accelerated weathering test machines. (2) In case of acceleration, the PE-RS CI values were greater when the temperature in the chamber was greater during accelerated weathering tests, and there was a high correlation with the average temperature in the outdoor exposure tests. From these results, the effect of temperature on the PE-RS CI values was confirmed to be relatively large. Due to this property, the PE-RS CI values were greater when using a xenon arc lamp with a power density of 60 W/m^2 than that with a 180 W/m^2 power density. In contrast, in both the 800 h accelerated weathering test and the two-year outdoor exposure test, weather-resistant PP decreased in strength on exposure to 1000 W/m^2 and 180 W/m^2 irradiation, indicating that high-energy light irradiation was effective for screening the weather-resistant formulations. (3) In case of correlation, comparing the PE-RS CI values during the outdoor exposure tests and during the accelerated weathering tests showed that the exposure time in the accelerated exposure tests resulting in a PE-RS CI value equivalent to one year of outdoor exposure was 750 h at an irradiance of 60 W/m^2 with a black panel thermometer temperature (BPT) of 63°C, and it was 1309 h at an irradiance of 180 W/m^2 with a BPT of 63°C. By comparing the change in PP strength by normalizing the degradation environment using the PE-RS CI values, the accelerated weathering test with results showing the highest

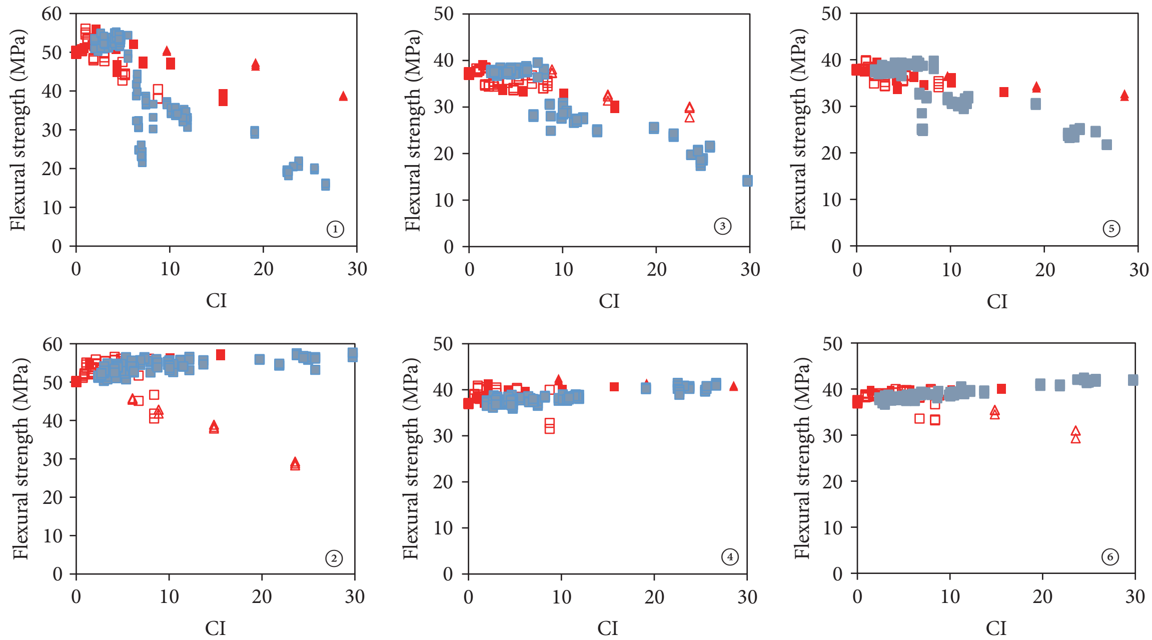

FIGURE 12: Changes in PP flexural strength resulting from outdoor exposure test and accelerated weathering test machines on the basis of PE-RS CI. ①–⑥ are sample codes as indicated in Table 1. ■: outdoor exposure; others; same as Figure 6.

correlation with the outdoor exposure test results was the one with the xenon arc lamp at an irradiance of 60 W/m^2 and a BPT of 63°C. The flexural strength was decreased with the surface defects of the standard-formulation PP due to the molecular weight decreasing of PP with the increase of the CI.

Appendix

A. Institutions Participating in 100 h Accelerated Weathering Tests

(i) Industrial Research Institute of Shizuoka Prefecture

(ii) Yamagata Research Institute of Technology

(iii) Toyama Industrial Technology Center, Human Life Technology Research Institute

(iv) Mie Prefecture Industrial Research Institute

(v) Kanagawa Industrial Technology Center

(vi) Kochi Prefectural Industrial Technology Center

(vii) Kyoto Municipal Institute of Industrial Technology and Culture

(viii) Technology Research Institute of Osaka Prefecture

(ix) Industrial Research Center of Shiga Prefecture

(x) Industrial Technology Center of Okayama Prefecture

(xi) Northeastern Industrial Research Center of Shiga Prefecture

(xii) Chiba Industrial Technology Research Institute

(xiii) Iwate Industrial Research Institute

(xiv) Osaka Municipal Technical Research Institute

(xv) Industrial Technology Institute of Ibaraki Prefecture, Textile Technology Office

(xvi) Hokkaido Research Organization (HRO), Industrial Technology Research Department, Industrial Research Institute

(xvii) Industrial Technology Center of Tochigi Prefecture, Southern District Technology Support Center

(xviii) National Institute of Advanced Industrial Science and Technology, Research Institute for Innovation in Sustainable Chemistry

(xix) Japan Chemical Innovation and Inspection Institute (JCII), Highpolymer Test & Evaluation Center, Osaka Office

(xx) Tokyo Metropolitan Industrial Technology Research Institute (11 machines)

B. Institutions Participating in 800-Hour Accelerated Weathering Tests

(i) Yamagata Research Institute of Technology

(ii) Industrial Technology Center of Okayama Prefecture

(iii) Toyama Industrial Technology Center, Human Life Technology Research Institute

(iv) Kyoto Municipal Institute of Industrial Technology and Culture

(v) Technology Research Institute of Osaka Prefecture

(vi) Chiba Industrial Technology Research Institute

(vii) Osaka Municipal Technical Research Institute

(viii) Hokkaido Research Organization (HRO), Industrial Technology Research Department, Industrial Research Institute

(ix) National Institute of Advanced Industrial Science and Technology, Research Institute for Innovation in Sustainable Chemistry

(x) Japan Chemical Innovation and Inspection Institute (JCII), Highpolymer Test & Evaluation Center, Osaka Office

(xi) Tokyo Metropolitan Industrial Technology Research Institute

C. Institutions Participating in Outdoor Exposure Tests

(i) Akita Industrial Technology Center

(ii) Hokkaido Research Organization (HRO), Industrial Technology Research Department Industrial Research Institute

(iii) Industrial Technology Center of Tochigi Prefecture, Southern District Technology Support Center

(iv) Hiroshima Prefectural Technology Research Institute, Western Region Industrial Research Center

(v) Japan Chemical Innovation and Inspection Institute (JCII), Highpolymer Test & Evaluation Center, Osaka Office

(vi) Toyama Industrial Technology Center, Human Life Technology Research Institute

(vii) Industrial Technology Institute of Ibaraki Prefecture, Textile Technology Office

(viii) Tokyo Metropolitan Industrial Technology Research Institute

(ix) Iwate Industrial Research Institute (local incorporated administrative agency)

(x) Technology Research Institute of Osaka Prefecture

(xi) Chiba Industrial Technology Research Institute

(xii) Kagoshima Prefectural Institute of Industrial Technology

(xiii) Kumamoto Industrial Research Institute

(xiv) Industrial Technology Center, Gifu Prefectural Government

(xv) Industrial Technology Center of Fukui Prefecture

(xvi) Miyazaki Prefecture Industrial Technology Center

(xvii) Kochi Prefectural Industrial Technology Center

(xviii) Kyoto Municipal Institute of Industrial Technology and Culture

(xix) Yamagata Research Institute of Technology

(xx) Nagoya Municipal Industrial Research Institute

Competing Interests

The authors declare no conflict of interests.

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