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Accelerated weathering parameters for some aromatic engineering thermoplastics. Part 2: Polycarbonate copolymers, polyarylate and ABS



James E. Pickett^{a,*}, Olga Kuvshinnikova^{b,*}, Li-Piin Sung^c, Brett D. Ermi^d

^a Consultant, Schenectady, NY 12304 United States

^b SABIC-HPP, 1 Noryl Avenue, Selkirk, NY 12185 United States

^c National Institute of Standards and Technology, Gaithersburg, MD 20899 United States

^d SABIC-HPP, 1 Lexan Lane, Mt. Vernon, IN 47620 United States

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ABSTRACT

Understanding the responses of materials to environmental variables is essential for performing meaningful accelerated weathering and service life prediction. Samples of polycarbonate-*b*-resorcinol polyarylate copolymer (RPA), poly(acrylonitrile-*co*-butadiene-*co*-styrene) (ABS), and two polycarbonate copolymers with silicone or aliphatic diacids were exposed in the NIST (National Institute of Standards and Technology) SPHERE (Simulated Photodegradation via High Energy Radiant Exposure) to determine the effects of ultraviolet intensity (UV irradiance), temperature, relative humidity (RH), and UV wavelength on yellowing and gloss loss and were compared to other aromatic polymers. All showed proportional response to irradiance (i.e., reciprocity) except ABS, which deviated notably at elevated temperatures. The activation energy for ABS yellowing was higher than other aromatic polymers (31 kJ mol⁻¹ \pm 2 kJ mol⁻¹) while RPA had a slightly negative activation energy (-5 kJ mol⁻¹ \pm 3 kJ mol⁻¹), reflecting differences in their photodegradation mechanisms. These two polymers also exhibited faster degradation when the RH was \leq 10 % compared to \geq 50 % RH. Wavelength effects varied among the polymers. The results indicate that predictive accelerated weathering should be performed with UV sources that accurately reproduce sunlight, at temperatures as close as possible to use conditions, and with RH > 10 %.

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1. Introduction

Predictive accelerated weathering of materials generally requires at least three steps: 1) defining the environmental exposure conditions, 2) finding the responses of the materials to the environmental factors, and 3) designing appropriate laboratory exposure conditions [1]. The first step can be accomplished by examining climatic data from benchmark exposure sites such as near Miami, Florida, near Phoenix, Arizona, or the south of France, for example [2]. To achieve acceleration, at least one of the environmental factors must be taken out of its natural range, but different materials respond differently to increased light intensity (irradiance) and temperature, among other variables. The effects of increasing the environmental stress on materials must be understood and quantified to do rational service life predictions. Importantly, because of the different responses to the increased stresses, not all

https://doi.org/10.1016/j.polymdegradstab.2020.109330 0141-3910/© 2020 Elsevier Ltd. All rights reserved. materials will have the same acceleration factor to a given set of testing conditions. This has been understood by experts in the field for quite some time (for example, Ref. [3,4]), but it is not well understood by many users of accelerated weathering data who often assume that all materials are accelerated equally.

The effects of irradiance, ultraviolet (UV) wavelength, temperature, and relative humidity (RH) on color shift and gloss loss were reported in Part 1 of this work [5] for four commercially important engineering thermoplastics: bisphenol-A polycarbonate (PC), poly(butylene terephthalate) (PBT), a PC/PBT blend, and poly(styrene-*co*-acrylonitrile) (SAN), all pigmented with 3 % (by mass) of coated rutile TiO₂. The two selected properties are important in end-use applications and are easily measured by precise, non-destructive methods. Exposures were carried out in the NIST (National Institute of Standards and Technology) SPHERE (Simulated Photodegradation via High Energy Radiant Exposure), where exposure conditions are carefully controlled on individual samples. In general, these polymers exhibited good reciprocity (a linear, directly proportional increase in degradation rate with increased irradiance), activation energies in the range of 16 kJ mol⁻¹ to 20



^{*} Corresponding authors.

E-mail addresses: dr.james.pickett@gmail.com (J.E. Pickett), olga.kuvshinnikova@ sabic-hpp.com (O. Kuvshinnikova).

kJ mol⁻¹ for yellowing and 9 kJ mol⁻¹ to 16 kJ mol⁻¹ for gloss loss, and little effect of humidity when > 10 % RH. Response to UV wavelength was different for all of the polymers tested.

The results of a second series of exposures on other commercially important aromatic thermoplastics are reported here as Part 2 of the work. These materials are two PC copolymers with silicone or aliphatic diacids (as unpigmented, transparent specimens), a block copolymer of PC with poly(resorcinol iso/terephthalate) (RPA), and poly(acrylonitrile-*co*-butadiene-*co*-styrene) (ABS). The PC copolymers behaved much like pigmented PC from Part 1, but the latter two polymers, pigmented with 3 % (by mass) of coated rutile TiO₂, were different from the other polymers.

2. Experimental

2.1. Materials

All compositions are as percentages by mass. PC-1 is a block copolymer of bisphenol-A polycarbonate with ca. 20 % poly(dimethyl siloxane) [6]. PC-2 is a random copolymer of bisphenol-A polycarbonate with approximately 15 % bisphenol-A ester of a long-chain aliphatic diacid [7]. The PC copolymers were unpigmented and were unstabilized except for \leq 0.1 % of a phosphite processing stabilizer to reduce the initial yellowing due to oxidation during extrusion and molding. The phosphite has no effect on weathering. RPA (resorcinol polyarylate) is a block copolymer of bisphenol-A polycarbonate with ca. 20 % of the polyester of resorcinol and 1:1 isophthalic:terephthalic acids. It was pigmented with 3 % of coated rutile TiO₂ and also contained \leq 0.1 % of a phosphite processing stabilizer to reduce initial color. ABS is poly(acrylonitrile-co-butadiene-co-styrene) and was also pigmented with 3 % of coated rutile TiO₂. The ABS was formulated with no stabilizers. Samples were extruded and then injectionmolded as high gloss color chips (3.2 mm thick) that were cut down to octagons ca. 19 mm across to fit the NIST sample holders.

2.2. UV exposures

Detailed descriptions of the NIST SPHERE and all experimental details can be found in Part 1 [5]. The spectral power distribution of the lamps and transmission spectra of the band pass filters are also shown in Fig. 8. Sample specimens were held in a sample wheel and covered with either quartz disks, neutral density filters, or band pass filters with an air gap between the filter and the specimen. Exposure from the filtered metal halide lamps is reported as MJ m⁻² over the range of 295 nm to 400 nm, and typical full irradiance through a quartz disk was nominally 150 W m⁻². Incident irradiance was measured at each location of the sample wheel using a spectroradiometer, integrated over 295 nm to 400 nm. Irradiance on the samples was calculated using those measurements and the measured transmission of the filters, and is shown in Table S-1 of the Supporting Information. The SPHERE does not operate with dark or water spray cycles.

2.3. Experimental design

The same experimental design was used as in Part 1. Reciprocity and temperature effect experiments were run at 35°C, 55°C, and 70°C with nominal 100 %, 90 %, 70 %, or 50 % irradiance, controlled by individual neutral density filters. A replicate sample of PC-1 at nominal 100 % irradiance was included, and its results were indistinguishable from the other PC-1 sample. Humidity effect experiments were run at 55°C and < 1 % (nominal 0 %), 10 %, 50 %, and 75 % RH at nominal irradiance of 100 %, 70 %, and 50 %. Wavelength effects experiments used narrow band pass filters

centered at 306 nm (6 nm full width at half height, FWHH) and 326 nm (10 nm FWHH) and a wide band filter centered at 354 nm (28 nm FWHH). All data not shown in the body of the report are summarized in the Supporting Information.

2.4. Measurements

Samples were removed periodically, gently washed with deionized water, and measured for 60 degree gloss as described in ASTM D523 [8] and CIE color (L* a* b*) using a portable spectrophotometer with integrated gloss measurement (spectroguide sphere gloss meter, BYK-Gardner USA, Columbia, MD). Color shift is expressed as described in ASTM D2244 [9], $\Delta E = \sqrt{(L^* - L_0^*)^2 + (a^* - a_0^*)^2 + (b^* - b_0^*)^2}$, where L_0^*, a_0^*, b_0^* are the initial color values. All color and gloss data were the average of four measurements measured from different orientations on the same samples. Error bars in the graphs represent one standard deviation from four measurements on the same specimen, and the error bars are smaller than the size of the symbols. Note that measurement uncertainties for different specimens from the same batch on the same exposure conditions are smaller than 2 % according to previous experiments [3].

2.5. Data analysis

The data were analyzed in the same way as Part 1 of the study [5]. Relative rates were obtained using the x-axis shift factor method to superpose data [10]. The reference curve was defined to have a shift factor (i.e. relative rate) of 1. Only the initial slopes were used when the entire curves could not be made to superpose. All superpositions are shown either in the text or in the Supporting Information. Arrhenius activation energies were obtained by plotting the natural logarithm of the relative rates vs. 1000/T where T is the thermodynamic temperature in kelvin. The slope was multiplied by the negative of the gas constant, $R = 8.314 \text{ J} \text{ mol}^{-1} \text{ K}^{-1}$, to give the activation energy in units of kI mol⁻¹. Slopes and standard errors of the slopes were determined using the LINEST regression function in Microsoft EXCEL. The standard error was then multiplied by the t value for the 95% confidence level (2 tailed) for the appropriate degrees of freedom to give the confidence intervals shown in the tables. Wavelength effects were visualized by plotting the relative rates (expressed as response per MJ m⁻² of transmitted UV radiation) on a logarithmic scale vs. the centers of the transmission windows of the band bass filters. Humidity effects were judged qualitatively.

3. Results and discussion

3.1. Irradiance effects: reciprocity

Accelerated weathering testing generally involves increasing the irradiance (intensity) of the UV radiation, decreasing the amount of dark time, or both. Very high irradiance (such as with lasers) on short time scales can cause two-photon processes, such as exciting an excited triplet state, that do not occur significantly at natural irradiance levels. Moderately high irradiance over long time scales can cause changes in mechanism due to thermally-controlled processes being unable to keep up with the photochemistry. These may be chemical reaction steps or physical phenomena such as diffusion of oxygen [11]. Unstabilized polyolefin photooxidation can be dependent on the square root of the irradiance due to the kinetics of free radical chain oxidation [4,12,13]. Since the response is material-dependent, it is important to know whether or not the photodegradation rates of particular polymers are directly proportional to irradiance, a property termed "reciprocity."



Fig. 1. Color shifts for (a) PC-1, (b) PC-2, (c) RPA, (d) ABS copolymers exposed at four irradiance levels: nominally 100 % to 50 %, 70 °C, and 10 % RH.

Fig. 1 shows color shifts of the four copolymers exposed in the SPHERE at 70°C, 10 % RH, and four irradiance levels. Data obtained at 35°C and 55°C are shown in Figs. S-1 and S-2 of the Supporting Information. The results show that the color shift (mostly yellowing, positive shift in b*) depends primarily on the radiant energy and not the rate at which it is applied. That is, the materials generally seem to obey reciprocity. However, the ABS results at 50 % irradiance seem to lie slightly above the other irradiance levels. Gloss loss data for RPA and ABS exposed at 70°C are shown in Fig. 2, which shows excellent reciprocity. Gloss is not well-defined for transparent samples such as PC-1 and PC-2, and these data were not analyzed.

A more quantitative approach to evaluate reciprocity is to determine the relative rates of color shift when plotted as a function of exposure time and to compare the rates vs. irradiance. Relative rates can be determined by applying shift factors to the exposure axis to cause superposition of the data [10], and these graphs are shown in Figs. S-3 to S-5 of the Supporting Information. The shift factors are plotted vs. relative irradiance in Fig. 3, and the resulting slopes for each polymer and temperature are shown in Table 1. All of the polymers exhibited good reciprocity with slopes near 1.0, except ABS color shift, and the ABS non-reciprocity becomes important only at high temperature. PC, PBT, PC/PBT blend, and SAN were found to exhibit good reciprocity in Part 1 of this study [5]. Non-reciprocity of ABS also had been found in earlier experiments [14]. Analysis according to the Schwarzchild law [15] is in Table S-2 of the Supporting Information.

3.2. Temperature effects: activation energy

Temperature is an important variable for accelerated laboratory weathering because the temperatures in the exposure chambers generally are higher than the effective temperatures outdoors [16]. As described in Part 1 [5], if the temperature difference and activation energy (E_a) are known, any temperature effect can be corrected using the Arrhenius equation.

Relative rates of color shift and gloss loss at 35° C, 55° C, and 70° C were found using the shift factor method for each of the four irradiance levels, shown in Figs. S-6 and S-7 of the Supporting Information. The shift factors are shown in Table S-3 of the Supporting Information. The resulting Arrhenius plots are shown in Figs. 4 and 5, and the activation energies calculated from the slopes are summarized in Table 2. The E_a for color shift of transparent PC-1 and PC-2 copolymers are essentially the same as for the white pigmented PC from Part 1 of the study. By contrast, the E_a for RPA color shift appears to be slightly negative, while the E_a for ABS is significantly higher than the other aromatic polymers. The E_a for RPA gloss loss also is slightly negative while for ABS it is in line with other aromatic polymers.

The unusual negative E_a for RPA can be attributed to the photochemistry of polyarylates, which is dominated by a photo-Fries rearrangement [17,18,19]. Polyarylates, especially terephthalates, absorb strongly in the range < 320 nm, so direct photochemistry is facile. By-products also are formed from this reaction that lead to discoloration and erosion of the polymer. Direct photochemistry



Fig. 2. Gloss loss for (a) RPA and (b) ABS copolymers exposed at four irradiance levels: nominally 100 % to 50 %, 70 °C, and 10 % RH.



Fig. 3. Reciprocity plots for (a) color shift and (b) gloss loss. The dashed line denotes hypothetical perfect reciprocity (slope = 1). Note that ABS (triangles) generally lies above the line in panel a. Slopes for individual datasets and combined temperatures are shown in Table 1.

Table 1

Slopes of relative rate vs. relative irradiance for individual polymers and temperatures shown in Fig. 3.

	PC-1	PC-2	RPA	ABS	RPA	ABS
	ΔΕ	ΔΕ	ΔΕ	ΔΕ	Δ Gloss	Δ Gloss
35 °C	1.08	1.14	1.18	0.86	1.04	0.86
55 °C	0.96	1.04	1.02	0.85	1.01	0.89
70 °C	0.90	1.02	1.00	0.67	0.98	0.93
combined*	0.98 ± 0.09	1.06 ± 0.06	1.05 ± 0.08	0.79 ± 0.09	1.01 ± 0.10	0.90 ± 0.06

*Each of the entries in the first three rows of Table 1 are the slopes of four points from the four neutral density filters used in the experiments (see Figs. S3, S4, S5.) The "combined" are the slopes from the 12 points combined for all three temperatures. The standard error and the t value for 10 degrees of freedom were used to calculate the 95 % confidence limits.

usually does not have a significant activation energy because the photon provides the energy needed to cause the reaction, but it is not clear why it should actually be slightly negative for RPA.

ABS copolymer has a SAN continuous phase and polybutadiene (PBD) domains. The 12 kJ mol⁻¹ higher E_a for ABS color shift compared with SAN is attributed to chemistry of the PBD rubber phase, since the SAN continuous phase is identical to the SAN from Part 1 of this study. Photooxidation is facile in the PBD phase, but PBD itself generates little discoloration. Radicals, such as hydroxyl radicals, formed during PDB oxidation can migrate to the SAN phase and oxidize aromatic rings to generate color [20]. The E_a for PDB photooxidation has not been reported to our knowledge. PBD undergoes a free radical chain photooxidation, and free radical chain

photooxidation of polypropylene, for example, has reported E_a in the range of 28 kJ mol⁻¹ to 58 kJ mol⁻¹ [21,22], so it is not surprising that ABS has a higher E_a for color shift than SAN. It is surprising that the difference is not exhibited for gloss loss where the E_a is in line with most other aromatic polymers. Gloss loss requires chain scission and erosion of the continuous phase, and this may be driven by inherent SAN photooxidation chemistry.

3.3. Humidity effects

Samples were exposed at full irradiance under quartz disks (*ca.* 150 W m⁻²) at 55°C and 0 %, 10 %, 50 %, and 75 % RH. Results for color shift and change in 60° gloss are shown in Figs. 6 and 7, re-



Fig. 4. Arrhenius plots of relative rates of color shift for (a) PC-1, (b) PC-2, (c) RPA, (d) ABS copolymers exposed at four irradiance levels shown in parentheses; three temperatures: 35 °C, 55 °C; and 70 °C, and 10 % RH.



Fig. 5. Arrhenius plots of relative rates of gloss loss for (a) RPA and (b) ABS copolymers exposed at four irradiance levels shown in parentheses; three temperatures: 35 °C, 55 °C; and 70 °C, and 10 % RH.

spectively. Results obtained at 70 % and 50 % irradiance are nearly identical and are shown in Figs. S-8 and S-9 of the Supporting Information. The rates of color shift for PC-1 and PC-2 copolymers were independent of RH, but the plateau values for Delta E were higher at higher humidity. PC containing white TiO_2 pigment exhibited no effect at all of RH on either rate or final value of Delta

E in Part 1 [5], and it is not clear why RH affects the plateau values in this study.

RPA exhibited unexpectedly fast rates of color shift and gloss loss at *ca*. 0% RH but only slightly faster rates at 10 % RH compared to 50 % and 75 % RH. RPA exhibits a two-stage photo-yellowing process before reaching a steady state plateau. The initial jump is



Fig. 6. Color shifts for (a) PC-1, (b) PC-2, (c) RPA, (d) ABS copolymers exposed at four relative humidity levels: ca. 0 %, 10 %, 50 %, and 75 % RH at 55°C and full irradiance.



Fig. 7. Gloss loss for (a) RPA and (b) ABS copolymers exposed at four relative humidity levels: ca. 0 %, 10 %, 50 %, and 75 % RH at 55°C and full irradiance.

due to the formation of slightly yellow benzophenones from the photo-Fries rearrangement of the polyarylate blocks near the surface of the specimen [18]. This is very fast and appears to be independent of RH. The second stage probably has contributions from yellowing due to photooxidation of the PC blocks as well as slower photo-Fries reactions driven by longer wavelength UV deeper into the surface. RH dependence of this stage must be due to interactions between the polyarylate and polycarbonate components since

neither alone seems to be very sensitive to RH, but investigating the nature of this was beyond the scope of the study. It is interesting to note that the RH dependence occurs both for color shift and gloss loss, so the effect is probably on the actual oxidation chemistry and not just on the structure of the chromophores that may be formed.

ABS also exhibited faster rates of color shift and gloss loss at RH \leq 10 %, as was seen for SAN in Part 1 of the study. Therefore,

Table 2

Activation energies (kJ mol⁻¹) and 95 % confidence range for color shift and gloss loss.

Polymer	ΔE	Δ Gloss	Reference
PC-1	24 ± 1	-	This work
PC-2	21 ± 1	-	This work
RPA	-5 ± 3	-9 ± 2	This work
ABS	31 ± 2	15 ± 1	This work
PC	21 ± 2	13 ± 1	[5]
PBT	16 ± 4	16 ± 3	[5]
PC/PBT	21 ± 3	9 ± 1	[5]
SAN	19 ± 1	16 ± 1	[5]



Fig. 8. Typical incident spectral power distribution of the SPHERE (right scale) and transmission spectra of the band pass filters used in the wavelength experiment.

the RH effect likely is due to chemistry in the SAN phase and not in the PBD rubber. The terminal color shift showed no clear trend with RH. At this point, the specimens were eroding quickly, so variability in the effectiveness of sample washing may contribute to the variability in color. Again, the mechanism of the RH dependence was not part of this study, but like RPA, humidity affects both color shift and gloss loss and so is probably related to the underlying oxidation chemistry.

The results show that RH cannot be ignored in accelerated weathering experiments. Samples exposed at ambient RH and elevated temperatures will experience RH less than ambient, as calculated by the Magnus or related equations [23]. For example, with laboratory air conditions of 50% RH at 23°C, a sample heated to 50°C by radiant energy (which is not uncommon) experiences an RH of only *ca.* 11% unless humidity is controlled within the exposure chamber. The very dry conditions apparently can affect degradation rates and steady-state color shifts, so the RH should be controlled to higher values for predictive testing.

3.4. Wavelength effects

Specimens were exposed behind interference band pass filters at 55° C and 50 % RH. The typical incident spectral power distribution (SPD) of the SPHERE and transmission spectra of the filters are shown in Fig. 8. The actual SPD for the specific locations and transmission of the particular filters were used to determine radiant exposures for the specimens. Results for color shift are shown in Fig. 9 with the exposure axis multiplied by shift factors in an effort to superpose the data. The shift factors were determined by superposing the data in the initial linear portions of the curves. Gloss did not change significantly during the exposure period and could not be analyzed. The data for PC-1 copolymer superposes well, and the data for PC-2 copolymer also superposes except for a slight shift in the 306 nm data. However, the color shifts for the transparent samples were quite small so there is some uncertainty in the superpositions. The polymers studied in Part 1 [5] also superposed very well, suggesting that the actual yellowing mechanisms were unchanged throughout this wavelength range for these polymers. (Note that the mechanism of PC changes dramatically at wavelengths < 295 nm [24], but that range was not part of this study.)

By contrast, the data obtained in the different wavelength ranges could not be made to superpose for RPA and ABS copolymers: initial rates and later rates would not superpose at the same time. This indicates that the mechanisms, either chemical, physical, or both, are dependent on the UV wavelength in this range. RPA is especially unusual in that exposure to longer wavelength UV results in more color shift than exposure at 306 nm. In this case, the primary source of color is the photo-Fries reaction that converts the aryl ester to a benzophenone [18,19]. The ester absorbs strongly at 306 nm, somewhat less at 326 nm, and much less at 354 nm. Exposure to 306 nm UV results in a thin band of the UV absorbing benzophenone near the surface that limits the conversion [19]. Thus, conversion is rapid, but it does not proceed very far. The RPA absorbs 326 nm UV less strongly, so it penetrates more deeply into the surface and results ultimately in more conversion. The conversion is still limited by the fact that the benzophenone product absorbs very strongly near 326 nm so conversion is still confined to a narrow band, but thicker than from 306 nm exposure. UV passing through the 354 nm filter is much more weakly absorbed by both the aryl ester and the benzophenone product. These wavelengths of UV therefore penetrate much more deeply into the surface and result in a thicker degraded layer and more color shift. For RPA, the different wavelengths affect the locus of the photochemistry and probably not the photochemistry itself.

ABS presents yet another case. The exposures using the 306 nm and 326 nm filters can be made to superpose quite well, but the exposure behind the 354 nm filter has a different shape. The initial period up to *ca.* Delta E = 4 can be made to superpose on the shorter wavelength exposure data, but the later degradation does not. Data for SAN from Part 1 of the study are also shown in Fig. 9d. In the absence of PBD, SAN degradation is much slower, and data from all three wavelength ranges superpose well. The unusual wavelength response, therefore, is due to PBD. The activation spectrum of ABS has been shown to have contributions extending into the visible portion of the spectrum [14,25], so some effect on PBD at longer UV wavelengths is expected. However, the later photoyellowing after the PBD has been consumed apparently is not driven as efficiently by the longer wavelength UV.

The shift factors in Fig. 9 can be considered as the relative rate contribution per unit energy in the wavelength range transmitted by the filter. Thus for PC-1, 1 MJ m⁻² in the range 340 nm to 368 nm is only 0.007 × as effective as 1 MJ m⁻² in the range 303 nm to 309 nm in causing color shift (yellowing). All of the shift factors from this study are shown in Table 3 and are plotted in Fig. 10. The two transparent PC copolymers of this study agree with the white PC of Part 1. All of the polymers except RPA show a generally exponential relationship between yellowing rate and wavelength through the range of 303 nm to 368 nm with the slopes of the log plots shown in Table 3.

4. Implications for testing and service life prediction

The purpose of this study was to understand the effects of environmental variables on aromatic polymers in order to design predictive accelerated weathering conditions and interpret the results. A key variable missing from the study is the effect of rain, which is known to affect the surface appearance of eroding materials, including aromatic polymers [26]. Since the SPHERE has no capabil-



Fig. 9. Color shifts for (a) PC-1, (b) PC-2, (c) RPA, (d) ABS and SAN copolymers exposed behind band pass filters at 55°C and 50 % RH. The exposure (dose) has been multiplied by the factors shown in the legend in an attempt to superpose the data.

Table 3

Logarithm of the relative rate contribution to yellowing for wavelength ranges per unit energy.

Polymer	$306\pm3~nm$	$326\pm5nm$	$354\pm14nm$	Slope*	Intercept*	Reference	
PC-1	0	-0.721	-2.154	-0.045 (0.004)	13.93 (1.39)	This work	
PC-2	0	-0.796	-2.221	-0.047 (0.031)	14.31 (1.02)	This work	
RPA**	0	0.255	-1.398	N/A	N/A	This work	
ABS**	0	-0.620	-1.456	-0.030 (0.0003)	9.27 (0.10)	This work	
PC	0	-0.824	-2.071	-0.043 (0.0009)	13.24 (0.30)	[3]	
PBT	0	-1.046	-2.469	-0.051 (0.0004)	15.72 (0.14)	[3]	
PC/PBT	0	-1.301	-2.921	-0.061 (0.002)	18.53 (0.66)	[3]	
SAN	0	-0.678	-1.886	-0.040 (0.003)	12.14 (0.85)	[3]	

*log₁₀(rate contribution) vs. wavelength; standard deviation in parenthesis. **initial rates.

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ity for water spray, this variable will have to be investigated separately. A discussion of expected correlation factors can be found in Part 1 of this study [5]. Irradiance, temperature, and RH were discussed extensively in Part 1, so this discussion focuses on UV wavelength.

4.1. UV source wavelength

The UV source of an artificial weathering chamber is characterized by two important factors: its spectral power distribution (SPD) and its intensity (irradiance). The SPD is particularly important, and its effects are not intuitive. It is well known that inclusion of UV with wavelengths < 295 nm can over-accelerate some polymers due to a change in degradation mechanism at these UV wavelengths [27], so such sources are undesirable for general exposure testing. The effect of an SPD greatly different from the solar SPD at wavelengths \geq 295 nm is less clear.

A semi-quantitative estimation of the effects can be made by multiplying the SPD of UV sources by the relative wavelength sensitivities from Fig. 10. (The limitations of Fig. 10 are the low number of data points per polymer and the fact that the filters did not extend to < 300 nm.) The sensitivity relative to 306 nm, S_{λ} , of a polymer to a particular wavelength, λ , is given by Eq. (1) where *s* and *b* are the slope and intercept from Table 3. The rate contribution, k_{λ} , of a wavelength is obtained by multiplying S_{λ} by the irradiance at that wavelength, I_{λ} , and the wavelength interval (in this case $\Delta \lambda = 1$) from the SPD of the source (Eq. (2)), which is then summed over the wavelength range to give a rate, *k*. This is



Fig. 10. Plot of relative rates of color shift *vs.* center of band pass filter transmission for all the data shown in Table 3. Error bars represent \pm 20%, the maximum estimated uncertainty from the superposition method.



Fig. 11. Spectral power distributions of UV sources in this analysis. Data from [29,31,32].

not an actual degradation rate, but it can be used to compare the relative degradation rates of a polymer exposed to the various UV sources when normalized by the total irradiance of the UV source over this wavelength range. This is comparable to the "effective UV dose" described by Kempe [28].

$$\log_{10}(S_{\lambda}) = s\lambda + b \tag{1}$$

$$k_{\lambda} = S_{\lambda} \cdot I_{\lambda} \cdot \Delta \lambda \tag{2}$$

$$k = \sum_{\lambda=295}^{400} k_{\lambda} \tag{3}$$

In this analysis, the rates were normalized to the rate calculated for an outdoor sunlight SPD [29]. The metal halide lamp SPD is from Fig. 8. The xenon arc SPD is from a source complying with ASTM D7869 [30,31] (e.g. Atlas Right Light® or Q-Lab Daylight-F filters), and the UVA-340 SPD is for a weathering chamber equipped with fluorescent UVA-340 lamps [32]. The SPD of these sources are shown in Fig. 11. The effects were calculated for three polymers with different slopes in Fig. 10: ABS, PC-1, and the PC/PBT blend. The results in Table 4 show the initial yellowing rates relative to outdoor exposure per unit radiant energy measured 295 nm to 400 nm. Note that the relative rates account only for differences in SPD and do not take into account any temper-

Table 4

Initial yellowing rates per MJ m^{-2} (295 nm to 400 nm) of exposure to several UV sources relative to outdoor sunlight, standard deviation in parenthesis.

	Metal halide	Xenon arc*	UVA-340
ABS	0.71 (0.01)	0.89 (0.01)	1.44 (0.02)
PC	0.89 (0.03)	0.86 (0.02)	1.43 (0.04)
PC/PBT	1.19 (0.06)	0.86 (0.04)	1.41 (0.07)

*filtered according to ASTM D7869



Fig. 12. Relative rates of color shift normalized to rate behind 326 nm band pass filter.

ature effects. They also do not take into account UV with wavelengths < 295 nm, which will accelerate PC and its blends. Ideally, all of the values should be 1.0 if the sources accurately reproduced the degradation caused by sunlight. That is, 1 MJ of UV in the device should produce the damage caused by 1 MJ of UV from sunlight.

The analysis in Table 4 shows that the filtered xenon arc and UVA-340 sources are expected to degrade all three polymers equally relative to sunlight. That is, the acceleration factors due to UV exposures will be the same for the polymers. This is because the SPD of the sources closely match the SPD of sunlight for wavelengths 295 nm to 340 nm, where the polymers show greatest sensitivity. The UVA-340 lamp has its output concentrated toward shorter wavelengths, so it is more effective (relative rates > 1) in creating degradation than sunlight when comparing broad-band irradiance 295 nm to 400 nm. The filtered xenon arc lamp closely approximates outdoors (rates \cong 1). They are slightly less than 1 because there is more output at wavelengths > 350 nm relative to sunlight, which does not contribute much to the degradation but is included in the radiant energy measurement.

By contrast, the metal halide lamp is not expected to degrade the different polymers equally relative to outdoors. Counterintuitively, this is not due to the large output 350 nm to 390 nm, but rather to the relatively large output < 315 nm (and does not take into account the unnaturally short wavelength UV < 295 nm). This is seen more clearly if the rates in Fig. 10 are normalized to the rates behind the 326 nm filter as shown in Fig. 12. ABS is relatively more sensitive to long wavelength UV than PC or PC/PBT, but the rate contributions are fairly small at these wavelengths. PC and the PC/PBT blend are much more sensitive at shorter wavelengths than ABS. Thus, the high output in the shorter wavelength UV of the metal halide lamp drives the color shift of these polymers proportionally more than it drives ABS. Therefore, an acceleration factor for PC/PBT will be at least $1.19/0.71 = 1.68 \times$ higher than ABS. In reality, it will be higher yet because UV < 295 nm has not been accounted for.

Because different polymers have different responses to the SPD, either a UV source closely matching the SPD of sunlight should be used, or the action spectrum of the polymer must be determined to correct for differences between the source and sunlight. In other words, side-by-side comparisons are legitimate for these polymers when exposed to sunlight (by definition), xenon arc conforming to ASTM D7869, or UVA-340 lamps, but not when exposed to metal halide lamps. Other xenon arc filters and other sources that allow UV with wavelengths < 295 nm also should be avoided. Since acquisition of good action spectra is very difficult, it is prudent to compare different materials only with UV sources that closely match sunlight.

4.2. UV irradiance

In this study, we have found that color shift and gloss loss generally have little dependence on irradiance up to ca. 150 W m^{-2} over the range 295 nm to 400 nm. Maximum irradiance of outdoor sunlight is estimated to be between 64 W m^{-2} and 75 W m^{-2} over this range [29,33], so reciprocity can be assumed for irradiance to at least $2 \times$ maximum sunlight. The exception is ABS color shift where extrapolation from high irradiance underestimates the degradation rate at lower irradiance. However, the results in Fig. 1d show that the differences in exposure to failure (say, Delta E = 5) appear relatively small comparing 100 % and 50 % irradiance. Both correctly predict that white ABS undergoes rapid yellowing. Therefore, it seems reasonable to have irradiance up to $2 \times \text{maximum}$ sunlight in a predictive artificial weathering procedure, with the caveat that ABS color shift will be under-predicted. This corresponds to filtered xenon arc up to an irradiance of *ca*. 1.4 W m^{-2} nm⁻¹ at 340 nm.

4.3. Temperature

The wide range of E_a reinforces the conclusions from Part 1 [5] that the temperature in the artificial weathering device should be as close as possible to the actual use temperature (or effective temperature) so that different materials are accelerated similarly. Otherwise, empirical activation energies need to be determined and corrections made using the Arrhenius equation. By coincidence, the higher E_a of ABS yellowing causes the higher temperature of most accelerated weathering chambers to at least partially offset its non-reciprocity.

4.4. Moisture

Several materials such as ABS, RPA, and SAN exhibit different degradation behavior at RH \leq 10 % compared with higher RH. The cause of this is not known. Since such dry conditions are very rarely encountered in actual use, least 30 % to 50 % RH (at the sample temperature) is desirable in an artificial weathering device to insure not changing the degradation chemistry. Higher RH may be required to simulate wetter environments.

Simulation of rain is an important factor not included in this study. Aromatic polymers erode during weathering at rates of 3 μ m to 25 μ m per year in Miami, Florida [34]. Eroded material and particulate pigments are effectively washed away by rain, even in desert regions such as Phoenix, Arizona. However, the gentle water spray of most weathering chambers does not reproduce the washing effects of rain, leading to surface appearance unlike outdoor weathering for some aromatic polymers [26]. Adequate reproduction of the effects of rain is under study but remains an unsolved problem.

5. Conclusions

Weathering acceleration factors were determined for transparent PC copolymers, RPA, and ABS. There were both similarities and significant differences from the aromatic polymers previously studied. The PC copolymers and RPA exhibited reciprocity with irradiance up to at least 2 × peak solar irradiance while ABS color shift exhibited non-reciprocity, especially at 70°C. The non-reciprocity for ABS is caused by the polybutadiene rubber, since a similar formulation of SAN without the rubber did exhibit reciprocity. The effect on the actual failure time is relatively small, however. ABS gloss loss was very nearly reciprocal with irradiance. In general, irradiance is not a critical variable for accelerated weathering of these aromatic polymers, at least at irradiance $\leq 2 \times$ peak sunlight.

The effects of UV wavelength for the PC copolymers were very similar to those previously found for the white pigmented PC. Sensitivity toward yellowing increases exponentially as wavelength decreases through the range 306 nm to 354 nm. Effects for wavelengths < 300 nm were not investigated in this study but are known to be significant for PC and its blends. The degradation curves for RPA and ABS at the three wavelength bands could not be made to superpose indicting changes of mechanism with wavelength. In the case of RPA, this probably had to do with the thickness of the degraded layer: highly absorbed shorter wavelengths probably cause a high conversion of arylate to yellow-colored benzophenone units in a thin band while more penetrating longer wavelengths cause slower conversion in a thicker band and ultimately more color shift.

Temperature effects on color shift of the PC copolymers were much like those previously determined for white pigmented PC, with E_a in the range of 22 kJ mol⁻¹ \pm 2 kJ mol⁻¹. Surprisingly, the RPA copolymer had zero or slightly negative E_a , probably because the color shift and degradation were driven by direct photochemistry on the polyarylate units. The E_a of ABS color shift was higher than the other aromatic polymers at 31 kJ mol⁻¹ \pm 2 kJ mol⁻¹. This is due to chemistry of the polybutadiene component since the E_a of SAN is at least 10 kJ mol⁻¹ lower. Because these polymers exhibit a broad range of E_a , different corrections must be made for the elevated temperature found in most artificial test chambers. It is recommended that the temperatures be set as closely as possible to the actual use temperatures or outdoor "effective temperatures" [16] to minimize the corrections and subsequent possible errors.

Moisture effects became apparent only at RH \leq 10 %, suggesting that operating accelerated weathering equipment with at least 30 % to 50 % RH is prudent. Certainly, very dry conditions with < 10 % RH are to be avoided to simulate most exposure environments. The origin of the faster degradation at low RH for SAN, ABS, and RPA is not known and warrants further study.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. The authors declare the following financial interests/personal relationships which may be considered as potential competing interests. This work was funded by SABIC-HPP and was part of a NIST consortium project. O. Kuvshinnikova and B. Ermi are employees of SABIC-HPP, and J. Pickett is a consultant under contract with SABIC-HPP, which is a manufacturer of these and similar polymers. None of the materials in this work are actual commercial products offered for sale. L.-P. Sung is a U.S. Government employee and has no financial interest in this work.

CRediT authorship contribution statement

James E. Pickett: Conceptualization, Formal analysis, Writing review & editing. **Olga Kuvshinnikova:** Conceptualization, Supervision, Resources, Writing - review & editing. **Li-Piin Sung:** Conceptualization, Methodology, Investigation, Data curation, Resources, Writing - review & editing. **Brett D. Ermi:** Supervision, Funding acquisition.

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Supplementary materials

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