C H A P T E R

8

Weathering of Plastics

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8.1 INTRODUCTION

Nothing lasts forever—certainly not the polymeric materials that comprise the plastics, composites, and coatings used outdoors and exposed to the weather. Understanding, managing, and predicting the degradation processes and lifetimes of these materials have presented great challenges over many decades, but great progress has been made. Nevertheless, the weatherability of plastics remains a difficult problem that results in much frustration among those who use, specify, supply, and design the materials. Meaningful accelerated weathering and service-life prediction are particularly troublesome.

Plastics are used in applications when they have some performance advantage over more traditional materials such as metal, glass, and wood. Plastics can provide low-weight, toughness, design flexibility, and lower cost. They can be colored without painting. However, most plastics are comprised of organic molecules that are not particularly resistant to the effects of sunlight, oxygen, heat, and moisture, and they undergo chemical reactions resulting in degradation of properties. In addition, all plastics do not have the same chemistry, so one may behave in considerably different ways than others when subjected to the same environmental conditions. Understanding the weathering of plastics requires understanding at least a little of their underlying chemistry.

This poses a problem for those who design products and specify the materials to make them. The materials are selected to provide certain properties at minimal cost and are expected to maintain their properties for the life of the product. If the materials can undergo changes, it becomes necessary to specify tests that simulate and quantify those changes in a reliable way. Specifications can then be set for maximum allowable change. One type of such testing, called accelerated weathering, has been practiced for nearly a century (McGreer, 2001; Nelson and Schmutz, 1926). It began as a rather crude exercise limited by the hardware available at the time, but great advances have been made. Unfortunately, many of the original techniques are still deeply embedded in current procedures, standards, and specifications. It is no wonder that many test results so poorly reflect reality.

The honest answer to most questions about polymer stability, testing, and lifetime prediction is, "it depends." It depends on the environmental conditions outdoors and in the laboratory. It depends on the underlying chemistry. It depends on the exact composition of the material. It depends on the colorants and additives. It depends on the criteria for failure. Specifying engineers must make hard binary pass/fail decisions and are not very tolerant of such soft explanations. The purpose of this chapter is to help engineers understand some of these "it depends" questions and how they should be translated to the design, testing, and specification of materials. The focus is not on the chemistry, and the interested reader is encouraged to refer to a number of recent books and chapters on the chemistry of polymer degradation and stabilization (Wypych, 2013, 2011; Gugumus, 2009; Searle et al., 2010). Generalizations will be made, but it must be understood that there will always be exceptions to any statement that can be made on this topic. Some of the discussion is aimed at helping engineers understand some of the tradeoffs involved in material design.

8.2 ENVIRONMENTAL VARIABLES

A nearly unlimited number of factors can affect the outdoor weathering of plastics, but the main factors discussed in this section are solar radiation, heat, moisture, and to a lesser extent, microbial growth. Atmospheric pollutants, thermal cycling, flexing due to wind loads, electrical loads, etc., can also affect specific materials, designs, and applications but are not discussed in any detail.

8.2.1 Solar Radiation

The sun emits radiation more or less as a 5800K black body (Goody and Yung, 1989) with absorption lines due to elements in the sun's atmosphere. The shorter wavelengths are absorbed by oxygen in the earth's upper atmosphere and by ozone in the stratosphere to produce an effective short-wavelength cutoff of ~ 295 nm at the surface. A reference solar UV spectrum can be calculated using open-source SMARTS 2.9.5 software (Gueymard) and is published as ASTM G177 (ASTM Standard G177, 2003). The calculated solar spectrum between 250 and 3000 nm is shown in Fig. 8.1, with the UV portion of the spectrum, plotted on both linear and logarithmic scales, shown in Fig. 8.2. This spectrum is for Air Mass 1 (AM 1), which is when the sun is directly overhead (zenith angle $\theta_z = 0$ degrees). $AM = 1/\cos(\theta_z)$ and shows the relative path length of the sunlight through the atmosphere. When the sun is lower in the sky (higher θ_z), the air mass is higher and more UV is absorbed by the ozone layer. Consequently, an annual average UV solar power spectrum will have less UV at wavelengths <330 nm due to higher average AM and more absorption by ozone when the sun is lower in the sky. In general, the shorter-wavelength UV is more damaging because it is more highly absorbed by the polymer or impurities and has sufficient energy to cause chemical reactions. The irradiance on a surface over the course of a year depends in nonobvious ways on the azimuth (compass angle), tilt from horizontal, and latitude (Koller, 1965).

Outdoor exposure is most easily benchmarked against standard exposure sites. Several commercial exposure sites exist near Miami, Florida and Phoenix, Arizona. These two sites are reasonable worst cases for populated sunny, hot, and humid or sunny, hot, and dry environments and are useful for product life prediction (Bauer, 2000). Solar radiation is measured continuously as total solar (290−3000 nm) and total UV (TUV, 295−385 nm) at these sites. UV radiation in much of the rest of the world is measured at 295−400 nm, so it is important to always know the range before comparing UV radiation values. Average annual values are shown in Table 8.1 for commercial exposure sites. (Atlas Material Testing Solutions).

The UV component of sunlight accounts for only about 5% of its energy, but it is responsible for most polymer degradation because it is absorbed by impurities that can initiate degradation or, in some cases, by the chemical
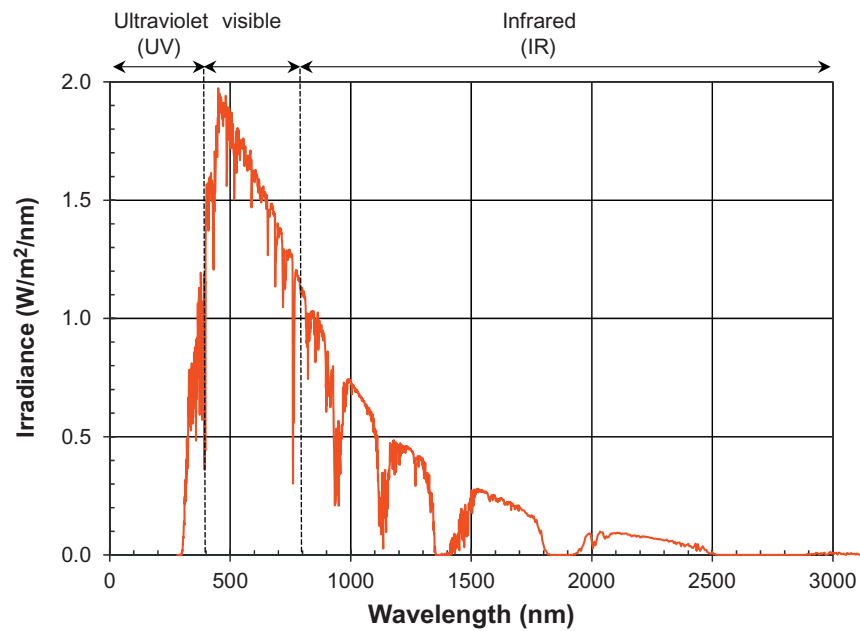
FIGURE 8.1 Solar spectrum calculated using SMARTS 2.9.5 and the parameters given in ASTM G177 for AM 1.
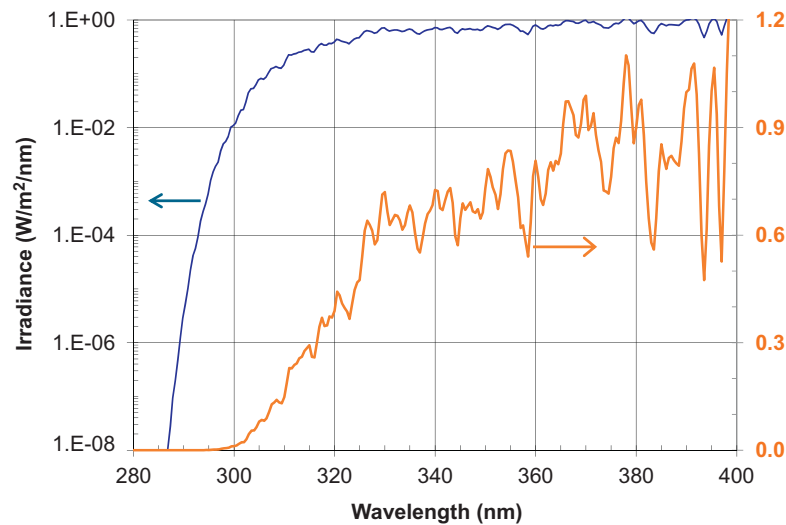
FIGURE 8.2 Solar UV spectrum calculated using SMARTS 2.9.5 and the parameters given in ASTM G177 for AM 1.

TABLE 8.1 Average Annual Solar Radiation (MJ/m^2) for South-facing Exposures Reported at Commercial Exposure Sites 1989−2016

	Miami		Phoenix	
Tilt angle[a]:	5 degrees	45 degrees	5 degrees	45 degrees
Total solar (290−3000 nm)	6311 (224)	6176 (250)	7638 (258)	8154 (343)
TUV (295−385 nm)	310 (21)	286 (22)	353 (18)	333 (22)

[a]From horizontal.
Standard deviation in parentheses.
Data from Atlas Material Testing Solutions.

structure of the polymer itself to cause direct photochemistry. The visible and infrared components of solar radiation cannot be completely ignored. Blue light (400−450 nm) can cause polymer degradation in some cases. Visible light can degrade colorants and cause unacceptable fade and color shifts. Both visible and infrared light contribute to raising the temperature of articles exposed to the sun.

There is inevitably some variability in outdoor exposures. The standard deviations for the annual solar radiation are shown in parentheses in Table 8.1. Exposures lasting less than 1 year will have greater variability due to seasonal effects, but exposures greater than 2 years will tend to have less variability as natural fluctuations average out. Exposures > 2 years are expected to be reproducible within ∼10% at the 95% confidence level (Pickett et al., 2018; Pickett and Gardner, 2005). UV radiation data are scarce for other parts of the world, but total solar radiation is available online for many places (https://climatedataguide.ucar.edu/). To a first approximation, much polymer degradation will scale to annual total solar radiation (Pickett et al., 2005).

8.2.2 Temperature

In principle, the rates of pure photochemical reactions do not depend much on temperature, but most polymer weathering is due to much more complicated chemistry than simple A → B. The degradation usually is due to reaction of the carbon atoms of the polymer with oxygen, followed by further decomposition and reaction of the initial products through many stages. Absorption of light energy serves as the first step in a branching series of reactions, each with its own temperature dependence, eventually leading to the final products. Over a small temperature range, temperature effects can be estimated from the Arrhenius Equation (8.1) where k is the rate of a reaction, A is a scaling factor related to entropy, E_a is the activation energy, R is the gas constant, and T is the temperature in kelvins. For a complex process such as weathering, the E_a is an apparent activation energy of the entire process. The ratio of the rates at two temperatures T_1 and T_2 is given by Eq. (8.2).

$$k = A \cdot \exp\left(\frac{-E_a}{RT}\right) \tag{8.1}$$

$$\frac{k_2}{k_1} = \exp\left[\frac{E_a}{R} \cdot \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right] \tag{8.2}$$

Activation energies typically are expressed as kilojoules per mol (kJ/mol) or kilocalories per mole (kcal/mol), in which case R is 8.314 J/mol/K or 1.987 cal/mol/K, respectively. Note that the equations use joules or calories, not kJ or kcal. Physicists prefer using electron volts (eV) as the energy, in which case the Boltzmann constant 8.617 E-5 eV/K is used in place of R. The effects of modestly increasing the temperature on reactions rates are shown in Table 8.2. Aromatic engineering thermoplastics (Pickett et al., 2008b) undergo weathering with E_a about 10−20 kJ/mol while E_a for aliphatic polyolefins (François-Heude et al., 2014; Audouin et al., 1988; Tocháček and

TABLE 8.2 Rates Relative to 30°C for Chemical Reactions With Various Activation Energies

	10	20	30	40	60	kJ/mol
T (°C)	2.4	4.8	7.2	9.6	14.3	kcal/mol
20	0.87	0.76	0.67	0.58	0.44	
30	1	1	1	1	1	
35	1.07	1.14	1.21	1.29	1.47	
40	1.14	1.29	1.46	1.66	2.14	
50	1.28	1.63	2.09	2.67	4.37	
60	1.43	2.04	2.92	4.18	8.55	
70	1.59	2.52	4.01	6.37	16.1	
80	1.75	3.08	5.40	9.48	29.2	
90	1.93	3.71	7.16	13.8	51.3	
100	2.11	4.44	9.35	19.7	87.4	

Vrátníčková, 2014) is in the range of 30−60 kJ/mol. The rates in Table 8.2 are benchmarked against 30°C because this is approximately the irradiance-weighted average annual temperature (effective temperature, T_{eff}) for white or clear samples at Miami and Phoenix test sites (Pickett and Sargent, 2009). Black samples have T_{eff} of approximately 45°C due to heating by the sun. Note that the "rule of thumb" of the rate doubling every 10°C does not apply in most of this regime, and that the rate increase is much greater for polyolefins with $E_a \sim$ 40 kJ/mol than for aromatic polymers with $E_a \sim$ 10−20 kJ/mol. This becomes very important when considering the problem of accelerated testing.

8.2.3 Moisture

Moisture comes in several forms for materials exposed outdoors: humidity, condensation (dew), and rain. Relative humidity (RH) is the ratio of the ambient vapor pressure of water to the saturation water vapor pressure: $RH = p_w/p_s$. RH, dew, and rain are highly variable from place to place and time to time and are especially difficult to simulate well in accelerated weathering chambers. RH and dew seem to be minor variables for most plastics, although they are key variables in the weathering of some coatings (Nichols et al., 2013). Moisture can reverse condensation reactions that are responsible for curing some coatings and that occur during the synthesis of some polymers, leading to bond breaking and loss of properties.

In considering the role of moisture, it is important to note that the proper metric is the RH *at the sample temperature* (Pickett, 2015). For example, if the ambient conditions are 25°C and 60% RH, a sample surface at 25°C is in equilibrium with 60% RH. The moisture content can be calculated from the solubility of water in the material at 100% RH (S) and Eq. 8.3. However, if the sample is heated by the sun to 50°C, the moisture in the sample surface is in equilibrium with a boundary layer of 50°C air having an RH of 15% because p_s is higher at 50°C than at 25°C, while p_w is the same. In other words, the sun bakes out the moisture. RH conversions can be done by using the Magnus equation or other equations (Alduchov and Eskridge, 1996) that approximate the saturation water vapor pressure (p_s in hPa) at a temperature (°C) as shown in Eq. (8.4). To convert from RH_1 at T_1 to RH_2 at T_2, $RH_2 = RH_1 \cdot p_{s1}/p_{s2}$.

$$[H_2O] = S \cdot RH \tag{8.3}$$

$$p_s = 10 \wedge [0.66077 + 7.5 \cdot T/(237.3 + T)] \tag{8.4}$$

Rain is highly variable from place to place, but weathering of many materials is surprisingly similar in places like subtropical Miami and desert Phoenix once UV dose and temperature are taken into account (Pickett et al., 2005). However, it is apparent that some rain (or wind) is necessary because very often samples weathered outdoors do not look the same as those exposed in artificial weathering chambers, even if the light source and temperatures are carefully matched to the outdoor location. Many times, the surface appearance is "dirty" or "chalky" after laboratory weathering while samples exposed outdoors appear much cleaner. Some of this is due to the practice of washing samples weathered outdoors but not samples from artificial weathering (Pickett, 2005). Some is also due to the fact that the gentle, misting spray in weathering chambers is more reminiscent of dew than the more aggressive washing effects of natural rain. In any case, rain (or wind) is very important for the surface appearance of weathered plastics, and artificial weathering cannot yet fully simulate its effects.

8.2.4 Microbial Growth

An often-overlooked aspect of outdoor weathering is microbial growth on the degraded surface. Microbes such as fungus and algae generally cannot digest high molecular weight (MW) polymers, but they can thrive on surfaces after the polymer has degraded into small molecules or when the surface has become sufficiently roughened to collect dirt. Plasticizers in plastics such as PVC can also support microbial growth. Materials exposed at subtropical sites such as Miami commonly have fungus on the surface after the sample has been sufficiently degraded. Such growth is less noticeable after exposures in more temperate or dry locations, but it has been observed on coatings, even in temperate environments (Schulz et al., 2003, 2004; Wachtendorf et al., 2012). Excellent images can be found in these references, and fungus on different weathered plastics looks very similar (Pickett et al., 2005). The way the growth is manifested depends on the maximum temperature of the surface, which is in turn related to the color. It is especially apparent on dark, glossy surfaces where fungus can appear as star-shaped spots 0.5−2 mm in diameter, as shown in the optical profilometer image in Fig. 8.3. Note the central area surrounded by filaments. Black samples in Florida seem to approach the thermal limit of the fungus.
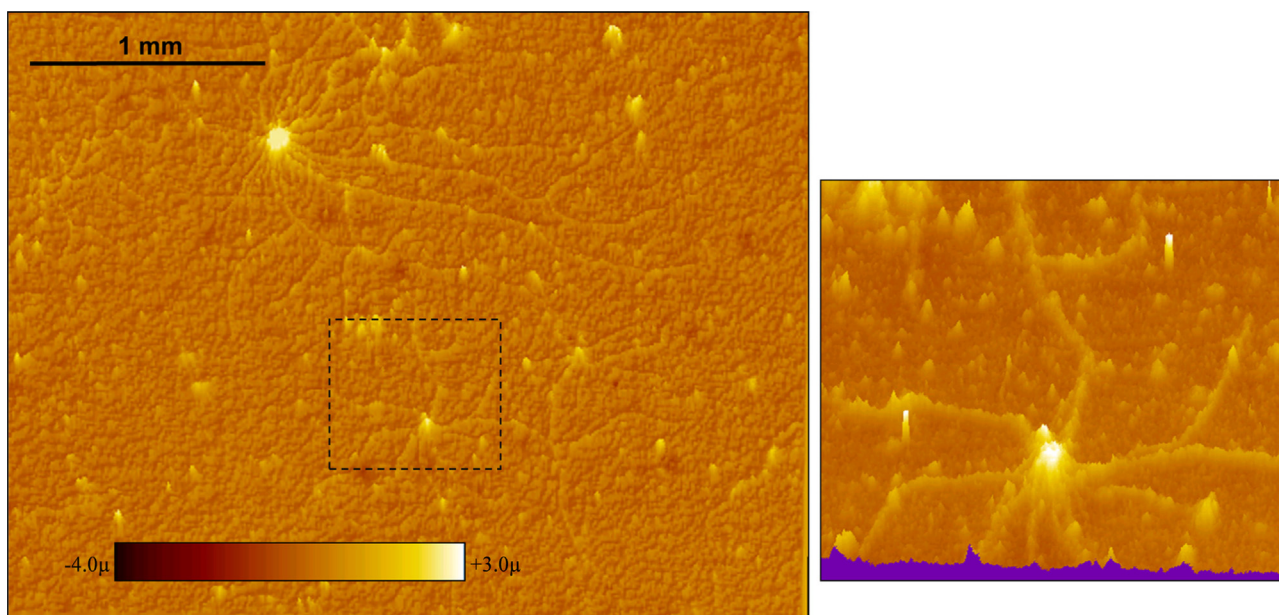
FIGURE 8.3   Optical profilometer image of bisphenol-A (BPA) polycarbonate containing 0.6% carbon black after 2 years of exposure in Miami. The image on the right is an enlargement of the area enclosed by the dashed square. *Image from W. Morris and J.E. Pickett, GE Global Research, 2000.*

Lighter colors and transparent samples can appear covered with mats of fibers because the lower temperature supports more growth. The fungus is well-adhered to the surface and requires good scrubbing to remove it, leaving behind small pits where the digestive fluids from the central region have eaten into the degraded surface (Schulz et al., 2004).

8.2.5 Other Factors

Specific materials and specific applications can suffer degradation due to other environmental factors (Pospíšil et al., 2006). Ozone is particularly destructive to unsaturated rubbers under strain because it reacts with and cleaves carbon−carbon double bonds. Strain causes the polymer chains to pull back and open cracks that allow more ozone to penetrate deeper into the material. Acid rain and nitrogen oxides affect some systems, particularly coatings (Wypych; Schulz et al., 2000), but effects on other polymers and plastics have not been discussed much in the literature.

Mechanical factors such as flexing under wind loads, thermal expansion and contraction, and freeze/thaw can be important for the durability of engineered systems like photovoltaic modules (Reese et al., 2011). Mechanical factors could also become important in initiating and driving cracks into a material as it is weakened by chemical changes caused by other environmental factors. Determining just what factors need to be included in evaluating and testing durability of specific systems should be done through a Failure Modes and Effects Analysis, taking into account both chemical and physical degradation of the material or system. This requires participation of chemists, material scientists, and engineers since no single discipline is likely to understand all the dimensions of the problem.

8.3 EFFECTS OF WEATHERING

The environmental factors described in Section 8.2 cause chemical changes to the material that change its properties. In most cases, the polymer undergoes reaction with oxygen, resulting in the chain being broken. Each polymer has its particular chemistry, but the effects can be grouped into a few broad categories.

8.3.1 Loss of Mechanical Properties

A common result of weathering is breaking of the polymer chains. Polymers are useful because their long chains entangle with each other to give structural integrity. For thermoplastics, properties such as glass transition temperature increase as the chain length (i.e., MW) increases. Ductility also often improves as the MW is increased. Because high MW also increases melt viscosity and makes processing more difficult, resin suppliers often design the polymers to have the minimum MW to achieve the desired properties. Therefore, if degradation results in cleaving the chains, the MW decreases and the desired properties can be diminished. Because the chains are long, it takes only a very small number of units to break, 1 or 2 per chain, to cause loss of ductility. Impact and flex properties often are first to go, both because they are very dependent on MW and because they are sensitive to cracks propagating from the surface during the strain caused by the event. The surface usually is more degraded than the bulk of most real systems so cracks form and are driven into the bulk. Tensile strength itself is more of a bulk property and often does not change much, even when a material has become very brittle. Caution should be used when considering retention of tensile strength as a primary measure of stability if ductility is also important in an application.

The opposite of chain scission is cross-linking, which occurs when reactive groups on one chain attack and become attached to a neighboring chain. This can turn a thermoplastic into a thermoset, resulting in decreased ductility. Polyethylene (PE) is known to undergo some cross-linking during weathering (La Mantia, 1984), but for most polymers, chain scission dominates the degradation process.

8.3.2 Erosion

After prolonged weathering, the surface of a polymer can become very highly oxidized and chopped into fragments small enough to be washed away by water or just evaporate directly into the gas phase. This is a particular characteristic of the aromatic polymers described in Section 8.4.3. Erosion commences after a delay as degradation accumulates, and unpublished work by this author has shown that rates vary from 2 to 25 μm/year, depending on the system. The delay can vary from weeks to a year or more depending on the polymer. Very slow erosion (< 4 μm/year) usually is fairly uniform, but faster rates can result in irregular surfaces causing haze in transparent articles and loss of gloss in opaque articles. Gloss loss is also a function of the pigments. Large particle size pigments such as coated rutile titanium dioxide shade the area under the particle and leave raised areas as the matrix erodes around it (Hunt et al., 1998). The erosion products and loose pigment particles are washed off during outdoor weathering from the effects of rain and wind, even in desert areas, but they can accumulate on surfaces during artificial weathering because the gentle misting sprays of weathering chambers do not have the washing power of rain. Nonaromatic polymers can also undergo erosion, but in properly stabilized aliphatic systems it usually takes a very long time to commence compared with the aromatic polymers, and severe surface degradation can be manifested as cracking, checking, and chalking.

8.3.3 Resin Yellowing

Most polymers will become at least a little yellow as they degrade. Color formation is the result of about four or more double bonds (C = C, C = O, or C = N) alternating with single bonds all in a row, called conjugation. Such structures are not very stable in the presence light and oxygen, so there is a steady state between their formation and destruction. Conjugated structures are difficult to make in polymers with a simple carbon backbone, such as the aliphatic polymers discussed in Section 8.4.2, so these kinds of polymers do not turn very yellow on their own. Additives in them can make yellow products when viewed through a thick section. On the other hand, the aromatic polymers discussed in Section 8.4.3 already have three double bonds in conjugation by virtue of the benzene ring. The rings can be oxidized to open chains with two C = C bonds in the middle and a C = O bond at each end (Factor et al., 1987). These compounds are yellow when there are substitutions on the carbons, so aromatic polymers generally become quite yellow during degradation. Certain aromatic polymers with electron-withdrawing groups on the rings, such as polyesters, are more difficult to oxidize and generate much less yellow color.

A second consideration about resin yellowing is that many polymers have yellow impurities that are generated during synthesis or high-temperature processing. These impurities can be bleached away by UV and blue light, so the first effect of weathering may be a color shift toward the blue as the yellow color bodies are destroyed (Andrady et al., 1991). Polymer yellowing can then take over and dominate the weathering behavior. Color shift often is evaluated as just the scalar of the shift in a 3D color space (as ΔE, for example), with the loss of

information about the direction of the shift. Thus, color shift sometimes is seen to increase as the impurities bleach, decrease as polymer yellowing rebuilds the yellow color that was bleached, and then increase again as polymer yellowing continues. This can be very confusing if the direction of the color shifts is not examined. This is also one of the reasons testing unpigmented resins can give very misleading results. Bleaching occurs in the bulk of the part while yellowing often occurs just near the surface. Without pigment, bleaching can predominate. When pigment is added, the bleaching deeper down is not seen while the surface yellowing is not changed much and the yellowing can dominate. It's also easy to believe that "dirty" polymer is more stable than "clean" polymer because bleaching of the impurities offsets some of the yellowing. A method to separate bleaching from yellowing is to initially expose the sample behind a UV-blocking filter until bleaching is complete, then to remove the filter to observe just the yellowing phase.

8.3.4 Colorant Fade

The degree of discoloration of the pigments and dyes used in a plastic is a function of the colorant itself and, to a lesser extent, the polymer matrix (Allen, 1994). Colorants stable in one polymer may not be stable in another. Inorganic pigments usually are the most weatherable, but the colors available from them tend to be less vibrant than the colors available from organic pigments. Dyes, which are dissolved in the polymer to give transparent colors, can give very vibrant colors but generally are less stable than pigments. Color fade often is more apparent in plastics than in paints because the concentration of colorants used in plastics typically is much lower than in paint. Lower concentration means that a small amount of chemical change makes a larger proportional difference in color. For the same reason, a colorant that appears stable in a saturated color can appear very unstable in a pastel. It is desirable to reproduce the entire UV and visible portions of the solar spectrum during accelerated weathering testing in order to reliably assess color shifts because visible light can affect the final color state.

8.4 MATERIAL FACTORS

Just as many environmental factors affect weathering in different ways, the composition and design of a material affect the weathering. Engineers make a major mistake when they consider all soft materials as "plastic" and treat them as if they were all the same. In addition, the same base resin can undergo weathering very differently depending on how it is blended, colored, stabilized, and formed. Weatherability emerges more as a *system property* than a material property. There are also some fundamental differences among classes of polymers that help in understanding how they degrade and how they respond to environmental variables.

8.4.1 "Stable" Polymers

A certain subset of polymers can be considered inherently resistant to weathering. The common features are that they absorb absolutely no solar energy and that they are difficult to oxidize. The most stable are the **polyfluorocarbons**. These polymers have fluorine atoms along the chain in place of hydrogen atoms. Any remaining hydrogen atoms along the chain in principle could still react with oxygen radicals, but they are unreactive due to the strong electron-withdrawing power of the neighboring fluorines. Being more electron-poor means being more difficult to oxidize. These polymers are relatively expensive and soft, making them unsuitable for many applications, but their stability makes them ideal for highly weatherable coatings and laminate films. A common example is **poly(vinylidine difluoride) (PVDF)** with alternating $-CH_2-$ and $-CF_2-$ units (Goldbach et al., 2016). The pure polymer can be expected to last indefinitely, but comonomers and additives used to improve processing and function are less stable than the PVDF itself. Polymers with fewer fluorines such as **poly(vinyl fluoride) (PVF)** with alternating $-CH_2-$ and $-CHF-$ units appear to be slightly less weatherable than PVDF (Raman et al., 2000). **Poly(tetrafluoroethylene) (PTFE)** has only $-CF_2-$ units and is very stable.

A second highly weatherable class is the **silicones**. Typically, the base repeat unit is $-OSi(CH_3)_2-$ so that the only oxidizable C$-$H bonds are those of a methyl group attached to silicon. These hydrogen atoms are relatively difficult to abstract and cannot undergo the typical autoxidation chain reaction efficiently. Silicones are rubbery materials widely used in sealants and gaskets with service lifetimes of many decades (Oldfield and Symes, 1996).

The third highly weatherable polymer is **poly(methyl methacrylate) (PMMA)**. It does have hydrogen atoms that are susceptible to oxidation, but it does not oxidize efficiently with solar UV. (PMMA does degrade when

exposed to shorter-wavelength UV.) The surface of PMMA will show some degradation after about 10 years of exposure in Miami, and some yellowing can occur in thick sections unless UV absorbing stabilizers are added. PMMA is quite brittle, and adding impact modifiers generally reduces its weatherability. PMMA is useful as weatherable plastic glazing and as the matrix material for coatings and laminates (Raman et al., 2000) and in solar energy applications (Miller et al., 2015). Acrylate polymers commonly used in coatings are somewhat less stable than methacrylate polymers.

8.4.2 Aliphatic Polymers

Aliphatic polymers can have straight or branched chains, and if they have rings, they are not aromatic (benzene) rings. Their major weathering characteristics are that (1) they absorb no UV emitted by the sun, so photodegradation is initiated by impurities; (2) they degrade by free-radical chain oxidation reactions; (3) their degradation products are not highly yellow; (4) degradation goes deep into the part unless the UV is blocked by pigments or additives; (5) they generally respond well to stabilizers. Most of these polymers are semicrystalline, and degradation occurs primarily in the amorphous regions.

8.4.2.1 Polyolefins

Polyolefins are the largest volume plastics and have a very long carbon chain as the backbone. **Polyethylene (PE)** is primarily just $-CH_2-$ groups while **polypropylene (PP)** has alternating $-CH_2-$ and $-CH(CH_3)-$ groups. PE, PP, and various copolymers are commonly grouped together and called **thermoplastic polyolefins (TPO)**. TPOs are semicrystalline, waxy polymers with widely varying properties depending on how they are made, structural variations, and chain length. TPOs themselves do not absorb any solar UV. Photodegradation can be initiated by a number of controversial processes, but once started, the oxidation follows a very efficient chain reaction that rapidly destroys properties. In fact, TPOs are absolutely worthless without stabilizers that delay the onset of rapid oxidation. Outdoor stabilization since the 1970s has relied on the class of hindered amine light stabilizers (HALS) that act as catalysts to terminate the oxidation chain reaction. Properly stabilized TPO can last 10 + years in use, as evidenced by the TPO toys and other artifacts in suburban backyards. The weathering characteristics of TPOs are that they undergo relatively little yellowing and retain gloss for a long time, but will suddenly become brittle when the stabilizer is depleted. Discoloration most often is due to fading of the colorants. The surface of TPOs can become cracked and chalky after prolonged exposures (Wypych, 2013, 2011).

PP is typical of many polymers that have a carbon atom with one hydrogen atom and three carbon atoms attached to it. This is called a tertiary hydrogen, and it is easily abstracted by oxygen-centered free radicals to sustain the chain oxidation process. The polymer itself has no easy way to terminate the oxidation chain, so polymers with tertiary hydrogens will last only as long as the stabilizers hold out. Oxidation causes the polymer chains to break into smaller fragments causing embrittlement. PP articles can appear perfectly good one day and be easily broken a week later. PE is a little more forgiving. Its backbone has only scattered tertiary hydrogens due to branching or comonomers. The secondary $-CH_2-$ carbon-hydrogen bonds are a little stronger and also allow easy chemistry to terminate the oxidation chain. In addition, only some of the oxidation events lead to chain cleavage.

An important variation is **polybutadiene (PBD)**, often as a block copolymer with styrene. It is used as a very effective and low-cost rubber to provide impact resistance to plastics. PBD has a carbon—carbon double bond every four carbon atoms along the chain as well as a number of tertiary hydrogens at branch points. This is called an "unsaturated" rubber. The hydrogen atoms on $-CH_2-$ groups adjacent to the double bonds, in the "allyl" position, are very susceptible toward oxidation, and oxidation is easily initiated by impurities or other factors. HALS and UV absorbers help, but even blue light can cause PBD photooxidation (Searle et al., 1989), so UV-blocking alone is not enough for long-term stability. Oxidation of PBD causes loss of its rubbery properties and leads to loss of ductility of the plastic. PBD itself generates little yellow color upon oxidation, but oxidation products can react with neighboring polymers with which it is grafted or blended to generate intense yellow colors. Unsaturated PDB rubbers can be converted to saturated rubbers that are much more stable by adding hydrogen to the double bonds, but these are generally somewhat less effective as impact modifiers. Other rubbers such as EPDM have double bonds, but they exist as side groups, and oxidation does not result in so much chain cleavage. Natural rubber also has many double bonds and must be highly filled with pigments (e.g., carbon black) and heavily stabilized to have a long life.

8.4.2.2 Poly(vinyl chloride)

Poly(vinyl chloride) (PVC) is in a class by itself (Wypych, 2015). It has a structure like PE with a chlorine atom replacing hydrogen on every second carbon. PVC itself absorbs no solar UV, but it is susceptible toward losing a chlorine atom and a neighboring hydrogen as HCl and generating a carbon−carbon double bond. The hydrogen atoms on the −CH$_2$- group adjacent to the double bond are easily oxidized, similar to PBD. Several double bonds in alternation with single bonds can be formed in a row, creating a yellow color. Upon weathering PVC can become yellow, brittle, and chalky. Fortunately it responds well to special classes of stabilizers so that properly designed systems can last decades outdoors, e.g., as vinyl siding on homes.

8.4.2.3 Polyamides and Other Aliphatic Polymers

The previous polymers in this section all have backbones comprised only of carbon atoms. Polymers containing other atoms in the backbone can have higher performance properties. Good examples are the **polyamides (PA)** or **nylons**. They have short carbon chains, usually of 6−12 units, linked together by amide groups (−C(=O)−NH−) in various ways. PAs do begin absorbing UV just at the shortest wavelength limit of solar output, so artificial weathering tests that include unnaturally short-wavelength UV can overaccelerate PA (Hu, 1998), and care must be taken in selecting accelerated weathering conditions as discussed in Section 8.5.1. Highly crystalline PA is quite weatherable, as evidenced by the persistence of discarded fishing line, but glass-filled injection molded grades are susceptible to erosion and the exposure of glass fibers after several years of weathering. PAs respond well to stabilization (Gugumus, 2009). Copper sometimes is used as a thermal stabilizer in PAs, but it can have an adverse effect on polymers that are blended with PAs.

Other aliphatic polymers are less commonly encountered as plastics. A few aliphatic polyesters (linked with −C(=O)−O− groups) are available and undergo weathering much like polyolefins (Totaro et al., 2014). Other aliphatic polyesters, polyurethanes, and polycarbonates are most often encountered as components in weatherable coatings and thermosets. UV absorbers and HALS stabilizers are effective in improving performance.

8.4.3 Aromatic Polymers

Aromatic polymers contain rings of six-carbon atoms with three double bonds, the so-called "benzene rings." There are usually some aliphatic portions as well. These structures often give very desirable physical properties such as higher heat distortion temperatures and greater strength than most aliphatic polymers. However, they fundamentally change the degradation modes and chemistry of weathering. The contrast to aliphatic polymers is shown in Table 8.3. Aromatic polymers can absorb UV that the sun emits, or the onset of absorption is very close to the limit of solar UV. This absorption can directly initiate photodegradation, and UV at unnaturally short wavelengths sometimes present in accelerated weathering tests can greatly overaccelerate degradation (Pickett et al., 2008a). The aromatic rings are easily oxidized by some of the reactive intermediates of photodegradation leading to highly colored products (Factor et al., 1987). These products act as internal UV absorbers and limit the photodegradation to relatively narrow bands (typically < 50 μm) near the surface. This protects the core from photodegradation, and physical properties sometimes can be retained indefinitely. However, the surface becomes very highly degraded within a year of Miami exposure and subject to erosion of 2−25 μm/year.

TABLE 8.3   Contrast Between Weathering Characteristics of Aliphatic and Aromatic Polymers

	Aliphatic	Aromatic
Directly absorb solar UV?	No	Yes
Initiation of degradation	Impurities	Direct absorption; sometimes impurities
Efficiency of free-radical chain oxidation	Moderate to high	Low
Effectiveness of stabilizers	Large	Modest
Thickness of degraded layer	Thick	Thin
Intrinsic yellowing	Slight to moderate	Large to severe
Surface erosion	After several years	Within 1−2 years
Self-limiting steady state?	No	Yes

This can cause gloss loss, but it also can allow the material to enter a steady state of degradation and erosion that may or may not have acceptable properties. In any case, UV absorbers and HALS generally are not nearly as effective in aromatic polymers as in aliphatic because the mechanisms of degradation are so different. Much of the common wisdom generated from studying the degradation of polyolefins simply does not apply to aromatic polymers.

Styrenic polymers such as **polystyrene** and **poly(styrene-*co*-acrylonitrile) (SAN)** are amorphous polymers that do not absorb much in the solar UV and thus often have a period of very slow degradation, possibly from free-radical oxidation of the chain, like the aliphatic polymers. However, once some degradation products are formed, they can sensitize the degradation of the aromatic rings so yellowing and erosion rapidly follow. Since polystyrene and SAN are quite brittle, they often are modified with a PBD rubber to make high-impact polystyrene (**HIPS**) and **ABS**, respectively. Photodegradation starts rapidly in the rubber phase and spreads to the aromatic polymer leading to severe discoloration (Searle et al., 1989; Jouan and Gardette, 1991). Black ABS, however, can be reasonably weatherable if properly stabilized. Replacement of the PBD rubber with a saturated or acrylic rubber improves weatherability but is usually more expensive and results in poorer low-temperature impact properties. The **ASA** plastics are SAN plus acrylic rubber and can be highly weatherable if stabilized and pigmented properly.

Polycarbonate (PC) is an amorphous engineering thermoplastic used in many outdoor applications. It undergoes erosion and yellowing after 8−12 months in Miami, but PC sheet can be protected by coextruding a cap layer of PC containing high loading of UV absorber or by a coating. These can last > 10 years with minimal discoloration or haze formation. Physical properties of pigmented or UV-stabilized PC often are retained because of the thin, self-protecting degraded layer, even in the absence of a cap layer. Its UV absorption commences at the edge of the solar spectrum, so testing with unnaturally short-wavelength UV greatly overaccelerates PC (Pickett et al., 2008a).

Polyesters such as **poly(ethylene terephthalate) (PET)** and its many variations are semicrystalline polymers that absorb strongly in the solar UV, and degradation starts quickly outdoors because of direct photochemistry. Polyesters tend to discolor less than styrenics or PC because the aromatic ring is more difficult to oxidize all the way to yellow products. Highly crystalline fibers are quite weatherable, but molded grades and films degrade rapidly in direct sunlight. Highly weatherable polyesters used in **powder coatings** have structures that absorb less UV and block some of the direct photochemistry, but there is a tradeoff with less attractive physical properties.

High-heat polymers such as **polysulfones**, **polyimides**, **aramides**, **polyetherimides**, **polyphenylene ether**, etc., absorb strongly in the solar UV and into the visible region. They invariably undergo rapid degradation outdoors leading to erosion and yellowing, but the degraded layers are generally very thin, so mechanical properties often are retained. The polysulfones are an exception because very facile photocleavage of the sulfur-carbon bond causes embrittlement.

Many **epoxy** resins used in composite materials have aromatic structures based on bisphenol-A (BPA). The aliphatic portions of the resin are susceptible to free-radical oxidation, and the intermediates formed can attack the aromatic rings, generate yellow color, and cause erosion (Monney et al., 1997; Mailhot et al., 2005). The products formed from oxidation of the aromatic rings limit UV penetration. Fiber-reinforced composites often are pigmented black so discoloration may not be noticeable, but the surface will become oxidized and erode, exposing the reinforcing fibers and allowing penetration of water into the surface.

8.4.4 Additives and Colorants

The minor components of a formulation are critical parts of the material system. The selection and amount of additives and colorants can make the difference between a highly weatherable system and one that degrades quickly. The two major classes of UV stabilizers are the UV absorbers and HALS. Other additives, particularly ones that are acidic or generate acidic products, can have negative interactions with HALS and reduce weatherability. Weathering testing should always be performed after formulation changes. As noted in Section 8.4.2, polyolefins respond well to stabilizers, but they are highly dependent on them. Cutting back on the HALS and UV-absorber loadings can cut costs, but can be expected to affect weathering performance, for example. Saving a few pennies on stabilizer can result in an article failing years earlier than necessary. This has been a greater problem in recent years because resin suppliers have fewer experts on staff, more extended supply chains, less knowledgeable support from additive suppliers, and heavy pressure to reduce costs. It is thus up to the user to understand weathering performance and how to test it realistically.

Selection of colorants is the work of specialists to attain the desired color with acceptable durability. Many colorants with excellent color and weatherability were based on toxic heavy metals and are no longer in use. Some pigments, particularly carbon black, coated rutile titanium dioxide, and iron oxides, absorb strongly in the UV and act as stabilizers (Allen, 1994). High loadings of these pigments restrict UV penetration into the surface making a thinner degraded layer, less color shift, retention of mechanical properties, and slower overall degradation. So, a material that performs very well in black might not be so good in a light blue, e.g., without further formulation changes.

8.5 ACCELERATED WEATHERING TESTING

Accelerated weathering techniques are required because no one wants to wait the years it takes to test materials outdoors for every sample. At least one environmental stress has to be taken outside its natural range in order to achieve acceleration: higher light intensity, shorter dark periods, higher temperature, etc. Different materials respond differently to these stresses, and it simply is not possible to get uniform acceleration of all materials under a single set of test conditions. Increasing temperature 10°C might accelerate one material by 25% and another by 100% as discussed in Section 8.2.2. Similarly, one material might degrade twice as fast when doubling the irradiance while another might degrade only 50% faster. Some materials are greatly accelerated by UV with wavelengths shorter than occur naturally while others are not. A good accelerated test will keep conditions as close to natural as possible while achieving predictable acceleration and without changing the mechanism of degradation. A good technologist will know what conditions are appropriate for particular classes of materials and what conditions are not.

Users of plastics want to know how a material will perform in actual use after a number of years and will want to set some sort of pass/fail specification in an accelerated laboratory test. This is fraught with difficulties (Pickett et al., 2018) among which are the problems of identifying a good test procedure and determining how long to run it. For the specifier, the goal is to reduce the risk of failure to an acceptable level, in whatever way this may be defined. In any case, the test conditions and specification need to be appropriate for the range of materials under testing and to have some predictive value to be useful. Most commonly-used accelerated weathering protocols do neither because they are rooted in the knowledge, equipment, and materials that were available 30, 50, or even 80 years ago when the protocols were first developed. Fortunately, more recent knowledge and equipment allow us to do much better.

8.5.1 Methods Not Recommended

Any light source or technique might be used for research purposes as long as the researcher understands the effects or limitations of the methods. However, techniques for general testing, material qualification, or service-life prediction must be more carefully considered. In particular, the techniques should avoid conditions known to be unreliable when better alternatives are available. Some problematic techniques are summarized in Table 8.4.

TABLE 8.4   Problematic Accelerated Weathering Methods

Method	Examples[a]	Reasons
Carbon arc	ASTM G152, G153; ISO 4892−4; various automotive	Excess UV < 295 nm
		SPD[b] unlike sunlight
Extended UV xenon arc	SAE J1960/2527; SAE J1885/2412	Excess UV < 295 nm
Borosilicate-filtered xenon arc	ASTM G155 Cycle 1; ISO 4892-2	Excess UV < 295 nm
Fluorescent UVB-313	ASTM G154; ISO 4892-3	Excess UV < 295 nm
		SPD unlike sunlight
High-intensity metal halide		Unproven reciprocity
		SPD unlike sunlight

[a]May apply to only some parts of the standard.
[b]Spectral power distribution.

When accelerated weathering exposures began in the early 20th century, the only high-intensity light source available was **carbon arc**. Testing equipment and protocols were developed using carbon arc sources, and some automotive manufacturers still specify materials using these methods. Enclosed carbon arc was used to test color fastness of fabrics, and open-flame (sunshine) carbon arc was used to test weathering of materials, particularly paints and varnishes (Ollinger, 1941). Carbon arc equipment is difficult to operate, but the major deficiency is that the spectral power distribution (SPD) is not much like sunlight, as shown in Fig. 8.4. In particular, sunshine carbon arc has excess energy at wavelengths < 295 nm, which accelerates different materials differently depending on how they absorb these wavelengths and the photochemistry that results. This makes it impossible to do legitimate side-by-side comparison of different materials and makes interpretation of results difficult. The advent of xenon arc lamps and their wide use after the 1960s made carbon arc functionally obsolete, although ASTM G154 and ISO 4892-3 standards have been maintained. There really is no good reason to continue this technique since there is no comparative value to the data.

With the advent of xenon arc weathering devices, automotive manufacturers desired highly accelerated weathering protocols. The equipment available at the time limited the irradiance of the lamps to a little less than the intensity of noon sunlight, so test developers achieved extra acceleration by using **"extended UV" filters** that provided UV at wavelengths 270−295 nm, which does not occur naturally. The spectral power distribution is shown in Fig. 8.5. For water-cooled xenon arc, this consisted of a quartz inner filter and a borosilicate outer filter (quartz/boro). For air-cooled xenon arc, a single thin borosilicate filter could be used. This method came into common use as SAE J1960 for exterior materials and SAE J1885 for interior automotive materials. As with sunshine carbon arc, the unnatural SPD makes side-by-side comparisons of different materials impossible because the short-wavelength UV accelerates different materials differently. For example, a study of a series of 110 aromatic engineering thermoplastic formulations produced a correlation of 1 year outdoors in Miami, Florida to about 1.6 ± 1.5 MJ/m^2 (at 340 nm) of SAE J1960 exposure in laboratory-accelerated weathering (95% confidence level) (Pickett, 2005). In other words, there was no predictive value from the SAE J1960 test, even for this limited range of materials. There is no technical justification in continuing its use.

A much better xenon arc filter combination was **borosilicate inner and outer filters** (boro/boro), which is specified as a "daylight" filter in ASTM G155 and ISO 4892-2 standards (ASTM Standard G155-13 2013; ISO Standard 4892-2 2013). The spectral power distribution, shown in Fig. 8.5, cuts off much of the excess UV shorter than 295 nm, but not all of it. This filter was state-of-the-art until the mid-1990s and is still in very wide use. The extra short-wavelength UV still causes different materials to be accelerated differently under the same test conditions. The study of aromatic engineering thermoplastic formulations found the correlation to 1 year of Miami, Florida to be 2.0 ± 1.3 MJ/m^2 at 340 nm at the 95% confidence level (Pickett, 2005). This is considerably better
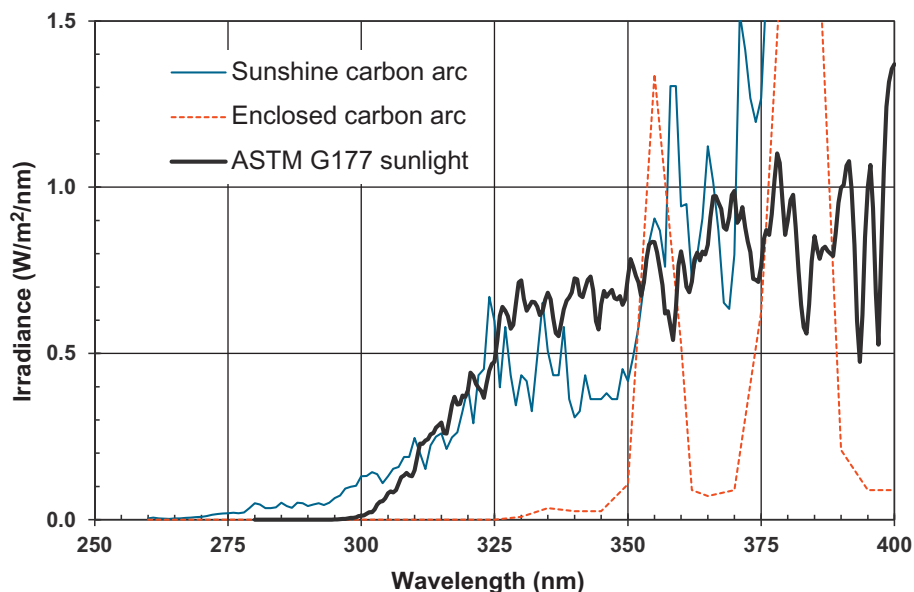

FIGURE 8.4 Spectral power distributions of two carbon arc sources (Technical Bulletin LU-0822) and ASTM G177 sunlight.
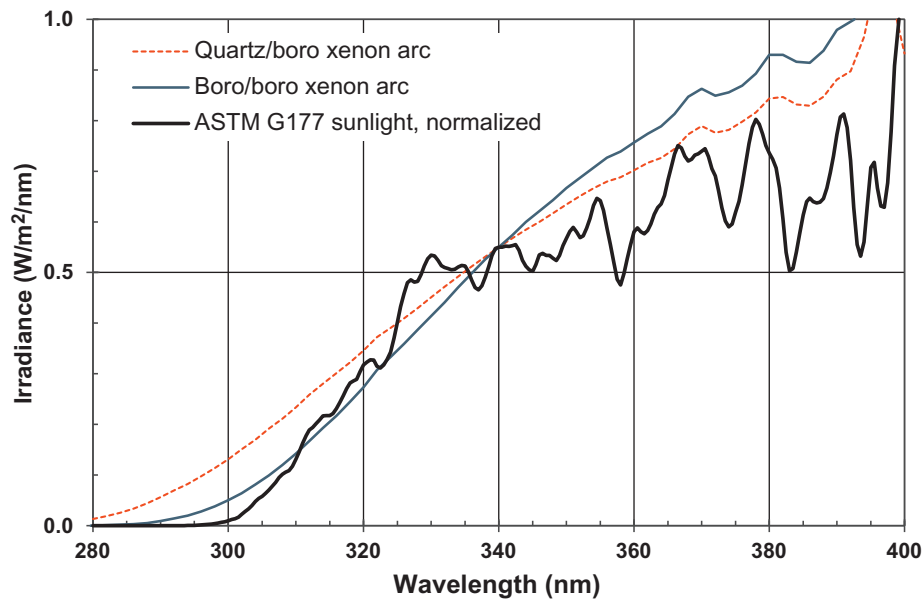
FIGURE 8.5 Spectral power distributions of xenon arc filtered with quartz/borosilicate and borosilicate/borosilicate filters compared with ASTM G177 sunlight all normalized to 0.55 W/m^2/nm at 340 nm.
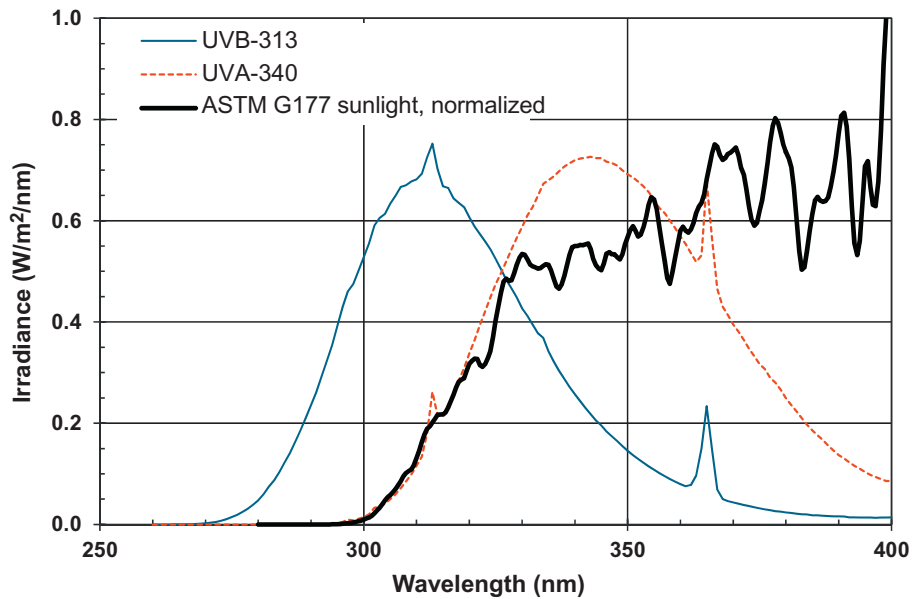

FIGURE 8.6 Spectral power distributions of fluorescent UV lamps (Technical Bulletins LU-8051 and LU-8052) compared to normalized ASTM G177 sunlight.

than using the extended UV filters, but still cannot be considered very predictive. The advent of improved filters, discussed below, renders this filter combination obsolete.

Weathering chambers using fluorescent lamps have been widely used because of their relatively low cost and ease of use. The **FS-40** or **UVB-313 lamps** that were widely used had phosphors emitting with maximum intensity at 313 nm and extending to 270 nm as shown in Fig. 8.6. The UV < 295 nm causes acceleration, but it is unreliable for the same reasons as the methods described above. ASTM G154, which is the standard practice for fluorescent lamp weathering, does not recommend using this lamp. The UVA-340 lamp has a short-wavelength cutoff closely matching sunlight and is the recommended choice for lamps in fluorescent testers.
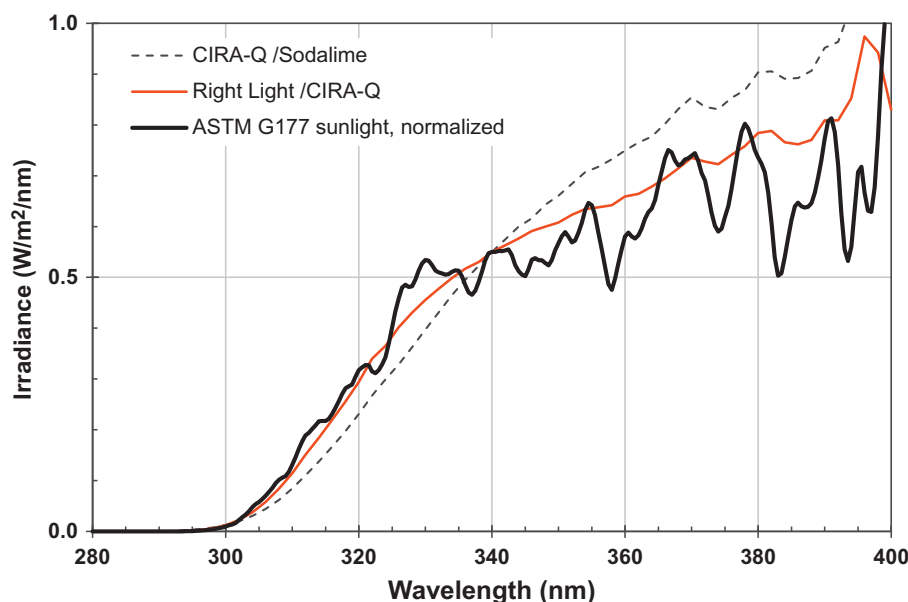
FIGURE 8.7 Spectral power distributions of xenon arc with Atlas CIRA-quartz/soda lime or Right Light[TM]/CIRA-quartz filters compared to normalized ASTM G177 sunlight. Q-Lab Daylight-Q and Daylight-F filters have SPDs similar to CIRA-quartz/soda lime and Right Light/CIRA-quartz filters, respectively.

In recent years Japanese companies have introduced **high-intensity metal halide** lamps in accelerated weathering equipment, but no US or European standards have yet been written for this kind of apparatus. High acceleration is claimed by virtue of the very high irradiance. The spectral power distributions of the lamps generally are broadened lines through the UV range 290−400 nm with little visible or infrared radiation so that temperature control can be maintained. There are two issues. First, the spectral power distribution is not like sunlight, so there is no *a priori* way to estimate the expected acceleration relative to outdoor exposure for a material. Second, the irradiance level is much higher than commonly used, and there is no guarantee that degradation rate scales with irradiance for a particular material. This property, called *reciprocity*, has been carefully studied for only a few materials and only a few of those at the irradiance levels used in this equipment. Some materials are likely to increase their degradation rate proportionally with higher irradiance, but some are known not to do so, even at modestly high irradiance (Martin et al., 2003; Hardcastle 2005; White et al., 2018). It is very important that the validity of this technique be established before it is used widely as a method to qualify materials or predict their lifetimes (Wu, 2018).

8.5.2 Recommended Methods

Tests run according to ASTM G155 Cycle 1 or ISO 4892-2 Cycle 1 with Atlas **Right Light inner and CIRA-quartz outer** or Q-Lab **Daylight-F** filters, irradiance of 0.75 W/m^2/nm at 340 nm (88 W/m^2 300−400 nm), and with regular sponge washing of the samples should give the best and fastest accelerated weathering of plastic materials within the scope of current published standard practices. This is with the proviso that the water spray does not simulate rain and that gloss and haze values are not highly predictive of outdoor weathering. The **ASTM D7869** protocol, which was developed for moisture-sensitive coatings, is acceptable, but it is slower due to lengthy dark periods, is somewhat hotter so requires greater temperature correction, and still does not fully simulate the effects of rain. The rationale behind these recommendations is discussed in the following sections.

8.5.2.1 Xenon Arc Lamp Filters

The first requirement for good accelerated weathering is accurate reproduction of sunlight. Fortunately, this problem recently has been solved with the advent of Atlas Right Light and Q-Lab Daylight-F filters. The SPDs shown in Fig. 8.7 show the very close match to ASTM G177 sunlight, especially in the most critical range of 295−350 nm. The older Atlas CIRA-quartz/soda lime and the similar Q-Lab Daylight-Q filters have very good short-wavelength cutoffs near 295 nm, but a poorer match through the rest of the UV range. The Right Light or

Daylight-F filters are required by the recent ASTM D7869 standard for accelerated weathering of transportation coatings (ASTM Standard D7869-13, 2013) and meet the requirements for "Daylight" filters under ASTM G155 and ISO 4892-2. These filters are stable during the lifetimes of the lamps. Their use is highly recommended for general testing because they (1) are the best available match to sunlight and (2) allow rational calculation of correlation to outdoor weathering as discussed in Section 8.6.1.

Elimination of unnatural short-wavelength UV reduces the acceleration of many materials, but modern equipment can be run at higher irradiance to offset the loss. Traditional weathering protocols specified irradiance levels that were limited by the technology of the time. It is now possible to run xenon arc lamps at $0.75-0.80 \text{ W/m}^2/\text{nm}$ at 340 nm ($88-94 \text{ W/m}^2$ 300−400 nm) while maintaining temperature control of the chamber and without dramatically reducing the lifetime of the lamps. With the proviso that the rates of degradation of some materials may not increase proportionally with irradiance, the use of the higher irradiance is recommended and is a part of ASTM D7869. Higher than usual irradiance is permitted by ASTM G155 and ISO 4892-2 with the agreement of the parties.

8.5.2.2 Xenon Arc Temperature Settings

The second requirement is maintaining the temperatures as close to the actual use temperatures as possible. The temperatures of samples inside of the test chambers usually are higher than the effective temperatures (Pickett and Sargent, 2009) outdoors for a variety of technical reasons, and the higher temperature must be taken into account when comparing different materials and estimating service lifetimes by the use of Eq. 8.2 as discussed Section 8.2.2. Obviously, the corrections needed and any errors introduced by the corrections are minimized when the test temperature is not much different from the use temperature. In addition, polymer yellowing has been observed to be greater at elevated laboratory test temperatures than found outdoors (Pickett et al., 2008b). The temptation to specify the maximum worst case temperature for the test should be avoided. A material has to *survive* the brief times it encounters extreme conditions, but it must *endure* something closer to the average conditions (Pickett et al., 2018). The ISO 4892-2 Cycle 1 temperatures of 38°C chamber and 65°C black standard temperatures are reasonable. (Note that black standard temperatures are 3−12°C higher than black panel temperatures under the same irradiation conditions.) Yet lower temperatures would result in more predictive, although slower, tests if the weathering chambers could maintain them.

8.5.2.3 Xenon Arc Humidity and Water Spray

The third requirement is managing moisture. Humidity does not seem to play a great role in the degradation of most plastics (Pickett, 2005), unlike the case for transportation coatings (Nichols et al., 2013). Any RH between 25% and 50% should be adequate. However, the effects of rain (and perhaps wind) are critical to the surface appearance of many plastics, especially as manifested as gloss for opaque materials and haze for transparent materials (Pickett, 2005). Unfortunately, the gentle, misting sprays of commercial weathering chambers seem to simulate the wetting effects of dew rather than the washing effects of rain. This largely remains an unresolved problem, but regular washing of the samples with a wet sponge has been found to help correlation with outdoor weathering (Pickett, 2005). Traditionally, technologists have regarded washing laboratory-weathered samples as taboo, but there really is no technical justification for this belief, especially since outdoor-weathered samples typically are washed prior to evaluation. This author highly recommends regularly washing the samples with a clean cellulose sponge and deionized water.

The traditional spray cycle of 102 minutes of light followed by 18 minutes of light + gentle spray originated nearly a century ago based on the design of equipment (Ollinger, 1941). There is no scientific rationale behind it. It may be better to have less frequent sprays of longer duration and greater force, but much more research is required to find something that adequately simulates rain. For now, the 102/18 cycle is as good as any. However, users must be aware that gloss of pigmented plastics and haze are not well-predicted by any standard accelerated weathering protocol.

8.5.2.4 Fluorescent Lamp Testers

A lower-cost testing alternative is the use of cabinets equipped with UVA-340 fluorescent tubes as described in ASTM G154 and ISO 4892-3 standards (ASTM Standard G152-12, 2012; ISO Standard 4892-3, 2013). The common exposure cycles were developed for coatings and at a time when the cabinets were not equipped with water spray nozzles. Therefore, these cycles incorporate long periods of dark condensation to simulate effects of dew. This does not seem necessary for uncoated plastics. Of the exposure cycles described in the standards, ISO 4893-3 Cycle 3 seems most appropriate for plastic materials with 5 hours of light at 50°C followed by 1 hour of dark

water spray. Users should be cautioned that color shifts may not be faithfully reproduced because of lack of longer wavelength UV and visible radiation (Pickett et al., 2008a) and that the gentle water spray may not reproduce the effects of rain on gloss loss and haze. Regular washing of the samples with a sponge and deionized water is recommended.

8.5.3 Accelerated Outdoor Testing

Commercial outdoor exposure sites in Arizona commonly offer a method of accelerated weathering using concentrated sunlight meeting the specifications of ASTM G90. Samples are exposed on a forced air-cooled platen and irradiated with sunlight focused by a Fresnel mirror. The unit can be equipped with water spray nozzles to wet the samples at night. The UV irradiance is about $6\times$ that of the ambient sunlight, so acceleration factors should be comparable to xenon arc protocols. The technique has the advantage of using natural sunlight and removing any issues about unnatural SPD of the light source or the lack of natural light/dark cycles. However, it does not subject the samples to natural rain and does subject them to elevated temperatures, which can cause issues common with laboratory accelerated testing procedures.

8.6 TEST DURATION AND CORRELATION

A basic question is always, "How many hours in the test is equivalent to a year outdoors?" This can be answered empirically, but often the answer is unsatisfactory as discussed in Section 8.5.1. A good test will properly account for most or all of its acceleration so that the number of hours it will take to apply a year's worth of photons can be calculated, corrections can be made for the effects of temperature, and the moisture effects can be properly simulated. As discussed above, the latter remains a problem with respect to surface properties, but the other two factors can be managed. It is best to consider how a test corresponds to a standard outdoor exposure site such as Miami, Florida or Phoenix, Arizona, and then estimate how Miami or Phoenix relates to actual use elsewhere (Pickett et al., 2005).

8.6.1 Temperature-adjusted UV Dose

Light sources that do not match sunlight present problems in determining a correlation to outdoors. Different materials are sensitive to different parts of the UV and visible spectrum of sunlight (Pickett et al., 2008a; Andrady, 1997; Searle, 2000; Torikai, 2000), and artificial light sources often do not reproduce the chemistry that occurs outdoors. In principle, it is possible to measure the effects of various portions of the spectrum and calculate the degradation due to the light source in each portion, but this ignores interactions and introduces many opportunities for experimental error. In practice, it is rarely successful. Only empirical correlations are possible with unnatural SPDs, and the correlations will differ among different materials. This was a very serious issue for all artificial weathering methods until the advent of the xenon arc filters described in Section 8.5.2.1 that adequately match sunlight. For this reason, the correlation discussion is applicable only to xenon arc filtered with Atlas Right Light, Q-Lab Daylight-F, or equivalent filters meeting the requirements of ASTM D7869.

It is important to understand how UV is measured and reported. Outdoor UV at test sites in the United States commonly is measured as "TUV" in the range 295−385 nm. Long-term average annual TUV radiant exposures at two common reference sites are shown in Table 8.1. Outdoor UV at other global sites may be measured and reported in the range of 295−400 nm, so it is important to know the range. Laboratory weathering equipment in the United States commonly measures UV irradiance during exposures in a 1 nm band at 340 nm while those in Europe often measure 300−400 nm.

Many users run tests based on hours rather than UV exposure. Conversion of hours to UV radiant exposure is done using Eq. (8.5) where E_R (MJ/m^2) is the radiant exposure, I_{avg} (W/m^2) is the time averaged irradiance through the entire cycle, and t (h) is the exposure time. For example, a cycle such as ASTM D7869 applies 0.00164 MJ/m^2/h on average, accounting for the dark and low irradiance periods, while ISO 4892-2 Cycle 1 run continuously at 0.75 W/m^2 irradiance applies 0.0027 MJ/m^2/h (all per nm at 340 nm).

$$E_R = 0.0036 \times I_{avg} \times t \qquad (8.5)$$

A conversion factor, F_x, is needed to convert the radiant energy measured in a test chamber to the equivalent radiant energy measured outdoors because the radiometers measure over different ranges and the SPD of even Right Light or Daylight-F filtered xenon arc emission does not exactly match sunlight at wavelengths > 370 nm. These wavelengths usually do not contribute much to photodegradation, so it is more important to accurately match shorter-wavelength UV. The values of F_x in the first column of Table 8.5 were obtained by integrating the ASTM G177 outdoor UV spectrum over the wavelength range given and dividing by the irradiance of the 1 nm band at 340 nm. The values in the second column were obtained by dividing the integrated ASTM G177 spectrum by the Right Light-filtered xenon arc spectrum integrated from 300 to 400 nm when both spectra were normalized to the same irradiance at 340 nm.

The rate of acceleration due to differences in temperature between the in-use and test-chamber conditions can be estimated by using Eq. (8.2). The outdoor equivalent UV radiant energy for a given exposure in a xenon arc chamber equipped with Right Light or Daylight-F filters is then given by

$$E_{equiv} = F_x \times E_R \times exp\left[\frac{E_a}{R}\left(\frac{1}{T_{eff}} - \frac{1}{T_{test}}\right)\right] \tag{8.6}$$

or, solving for E_R

$$E_R = \frac{E_{equiv}}{F_x} \times exp\left[\frac{-E_a}{R}\left(\frac{1}{T_{eff}} - \frac{1}{T_{test}}\right)\right] \tag{8.7}$$

where E_{equiv} is the temperature-corrected equivalent outdoor UV radiant energy, F_x is the xenon arc spectral conversion factor from Table 8.5, E_R is the measured UV radiant energy from the weathering chamber, E_a is the activation energy, R is the gas constant, T_{eff} is the effective temperature of the sample outdoors in kelvins, and T_{test} is the irradiance-averaged temperature of the sample in the weathering chamber in kelvins. Note that the E_a units are cal/mol or J/mol and not the kcal/mol or kJ/mol commonly reported in in the literature. The value for R is 1.987 cal/mol/K or 8.314 J/mol/K.

As an example of using Eq. (8.7), 1 year of 45 degrees south exposure in Miami (286 MJ/m^2 295$-$385 nm) could be simulated by $(286/72.4) \times exp[(-20000/8.314)(1/303-1/313)] = 3.1$ MJ/m^2/nm at 340 nm using the following assumptions:

1. Activation energy, $E_a = 20,000$ J/mol
2. Outdoor $T_{eff} = 30°C$ (good assumption for a white sample)
3. Sample $T_{test} = 40°C$ in the test chamber (good assumption if set temperature $= 38°C$)
4. Reciprocity is obeyed; i.e., degradation rate doubles when irradiance doubles
5. Moisture effects are either not important or properly simulated (not a good assumption for properties that depend on rain)

Obviously, this "correlation factor" of 3.1 MJ/m^2/nm at 340 nm for 1 year of Miami exposure will be different if any of the assumptions are different. Higher activation energy or greater difference between use and test temperatures will reduce the required radiant energy in the tester to simulate 1 year. For example, a white and black polyolefin with $E_a = 40$ kJ/mol would require 2.4 and 1.7 MJ/m^2/nm at 340 nm, respectively, to be the equivalent of 1 year of Miami exposure under the same conditions, assuming T_{eff} for black is 42°C and T_{test} is 60°C (Pickett and Sargent, 2009). Therefore, accurate predicted lifetimes, or even fair comparisons, require knowing the E_a of property change, which can be determined experimentally. *It is clear that testing all samples under a single set of conditions with a single correlation factor cannot be expected to produce meaningful results over a wide range of materials.* This is what makes specification and testing of plastic weathering fundamentally different from specification and testing of other physical properties (Pickett et al., 2018). We cannot avoid the consequences of weathering being due to chemical reactions.

TABLE 8.5   Values for F_x in Eqs. (8.6) and (8.7) to Convert Right Light/Daylight-F Xenon Arc Radiant Energy to Outdoor Radiant Energy

Outdoor radiometer	Xenon arc radiometer	
	340 nm	300-400 nm
295$-$385 nm	72.4	0.73
300$-$400 nm	91.8	0.93

8.6.2 Moisture Effects

As noted in Sections 8.2.3 and 8.5.2.3, most plastics are not particularly sensitive to relative humidity and wet time as long as there is some. This is not the case with many transportation coatings (Nichols et al., 2013). RH settings of 25%−50% and occasional water sprays should be sufficient and require no particular correction factors. However, the effects of rain and wind on surface properties such as gloss and haze are not reliably simulated by any current standard protocol. Regularly sponge washing the samples helps correlation, but it is not a perfect solution (Pickett, 2005). More research and development are required to improve this situation. Until then, it makes little sense to put tight specifications on these properties based on standard testing protocols, especially if the samples are not washed.

8.6.3 Kinetics

It is common practice for specifications to be written requiring less than a certain property change after a set amount of exposure to pass. This gives only one piece of information and is the least robust way to evaluate the data. Consider the hypothetical degradation curves illustrated in Fig. 8.8. Curve A shows a linear change in a property, which almost never is observed. Comparing materials would be easy if they degraded linearly because it makes no difference where the failure point and time are set. The only problem is ensuring that the slopes (the rates of degradation) are fairly accelerated for different materials. Curve B is more common. It can occur when there is underlying chemistry that takes some time to be apparent as a measurable property change. It is also common when products of the degradation reaction act as promoters of degradation, resulting in autoacceleration and an eventual plateau as a steady state is reached or all reactant has been consumed (as in bleaching of a dye). Note what happens if the curve shifts to B′, due to experimental variability or a formulation improvement. If the specified test time is near the steep part of the curve, very large differences in property change may be measured when in fact there is little difference in the durability in actual use. It is easy to become endlessly frustrated working with single points on the steep part of the curve, so it is much better to get enough data points to know the shape. Nondestructive measurements can be made as read-and-replace so it is not necessary to expose excessive numbers of samples.

For very long-term weathering, it is important to know if there is a steep curve such as Curve B that results in abrupt failure. Abrupt change can also be the result of coating failure, e.g., or the exhaustion of the stabilizers. This can increase risk. Excellent accelerated testing and service-life prediction are required to ensure that the failure event occurs after the expected lifetime of the article.

A more robust design is shown as Curve C. In this case, some degradation occurs, but the material reaches a steady state or a period of slow property change. This can be termed "graceful aging" or a "soft failure" approach. The key to the approach is keeping the initial change in property within an acceptable range. An example is coextruded polycarbonate sheet in which a thin cap layer containing a high loading of UV absorber is extruded over a thick core. The surface degrades a little fairly rapidly, but the subsequent property change is
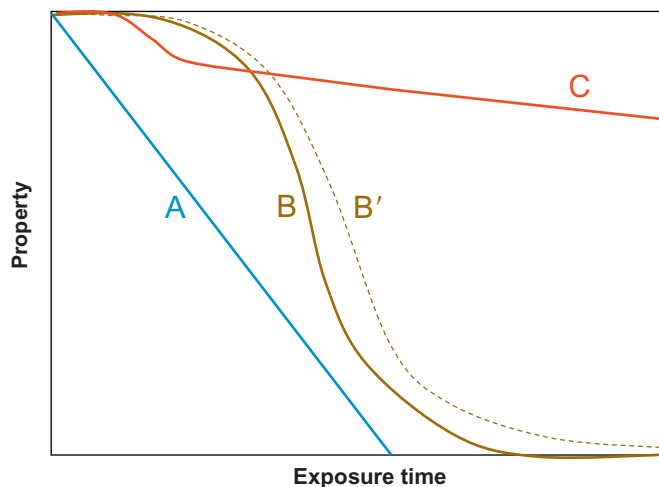

FIGURE 8.8 Some hypothetical examples of degradation kinetics.

very slow resulting in a highly weatherable system. Again, this can be understood only by taking enough data points to see the entire curve.

8.7 CONCLUSIONS

Sunlight, oxygen, heat, and moisture cause chemical reactions in plastics that result in degradation of properties. These chemical reactions cause the polymer chains to be broken into small pieces, cause formation of yellow products, and cause destruction of dyes and pigments resulting in loss of mechanical and esthetic properties. For the most part, none of these chemical processes is understood completely from start to finish, but the processes as a whole can be characterized and quantified so that the effects of environmental variables can be defined. This allows rational design of accelerated tests, including knowledge of when they are likely to give nonpredictive results. The phenomenon of weathering cannot be understood without taking into account at least some of the chemistry that underlies it.

An important material distinction must be made between the aliphatic and aromatic polymers. Aliphatic polymers tend to degrade by free-radical chain reactions, respond well to stabilizers, and undergo relatively mild discoloration. Failure often is by becoming brittle or by colorant fade. Weatherable systems using aliphatic polymers need to be carefully designed and are highly dependent on stabilizer selection and loading. Aromatic polymers tend to degrade by a combination of free-radical oxidation, direct photochemistry, and oxidation of the aromatic rings. The products are highly colored and restrict degradation to a thin surface layer that often protects the bulk from further degradation. Therefore, discoloration, surface erosion, and loss of gloss and other surface properties can occur, but mechanical properties often can be retained. In general, aromatic polymers are much more difficult to stabilize than aliphatic polymers, but highly weatherable systems can be designed.

As a consequence of the differences in degradation chemistry, the way polymers respond to environmental variables such as the SPD and intensity of light, temperature, and moisture are different. It is not possible to have a "fair" universal accelerated test that accelerates all materials to the same degree. Test conditions must be appropriate for the class of materials under consideration. Xenon arc protocols using state-of-the-art lamp filters closely reproduce the important UV wavelengths of sunlight, eliminating one of the major factors for poor test correlation. Older-generation filters and lamp types should be considered obsolete and no longer used, even though this means abandoning historic data.

The response of different materials to temperature remains an important factor but can be minimized by keeping test temperatures as close as possible to actual effective temperatures when in use. Determining the activation energies needed to correct for temperature differences is fairly straightforward, but more work needs to be done to produce more published values for more materials. More information also would be welcome on the effective temperatures of specimens during outdoor exposure and actual use.

The problem of providing moisture in accelerated testing is only partially solved. The recent ASTM D7869 protocol specifically provides for long wet periods important to the degradation of many coatings. However, humidity and surface wetting appear to be relatively minor variables in the weathering of most plastics, while simulating the effects of rain is very important for reproducing surface properties such as gloss loss and haze. This remains an unsolved problem, and accelerated weathering results for gloss and haze of uncoated plastics should not be considered reliable until more research is done and new test protocols are validated. Finally, microbial growth can affect surface appearance of naturally weathered plastics, primarily in tropical and subtropical regions. Obviously, this is not reproduced by accelerated weathering tests.

Acknowledgments

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