Technical Guide 106

Primary Factors of Weathering

Factors of Weathering

The three main environmental stress factors of weathering are solar radiation (light energy), temperature, and water (moisture). But it is not just "how much" of each of these factors ultimately causes degradation to materials, because different types of solar radiation, different phases of moisture, and temperature cycling have a significant effect on materials on exposure. These factors, in conjunction with secondary effects such as airborne pollutants, biological phenomena, and acid rain, act together to cause "weathering."

Solar Radiation

Radiant energy that comes from the sun is made up of photons that travel through space as waves. Their energy (E) is proportional to their frequency (ν) according to the equation (Figure 1), where (h) is Planck's constant, (c) is the velocity of light in a vacuum, and (λ) is wavelength. Note from this equation that photon energy is inversely proportional to wavelength, i.e., the lowest wavelengths photons have the highest energy (Figure 2).

$$\underbrace{E}_{\text{energy}} = \underbrace{h}_{\text{Planck's constant}}\overbrace{\nu}^{\text{frequency}} = \underbrace{h}_{\text{Planck's constant}}\overbrace{c}^{\text{velocity}}/\underbrace{\lambda}_{\text{wavelength}}$$

Figure 1. Planck's Law of photon energy.

The solar radiation that reaches the earth's surface consists of wavelengths between 295 and 3000 nanometers. A nanometer (nm) is one billionth (1 x 10-9) of a meter. This terrestrial sunlight is commonly separated into three main wavelength ranges (Figure 2): ultraviolet (UV), visible (VIS), and infrared (IR). Wavelengths between 295 and 400 nm are considered the ultraviolet (UV) portion of the solar spectrum, making up between 4 – 7 % of the total radiation. Ozone in the stratosphere absorbs and essentially eliminates all radiant energy below 295 nm. Extremely sensitive instruments may detect radiation below 295 nm, but this amount is considered negligible by most experts.

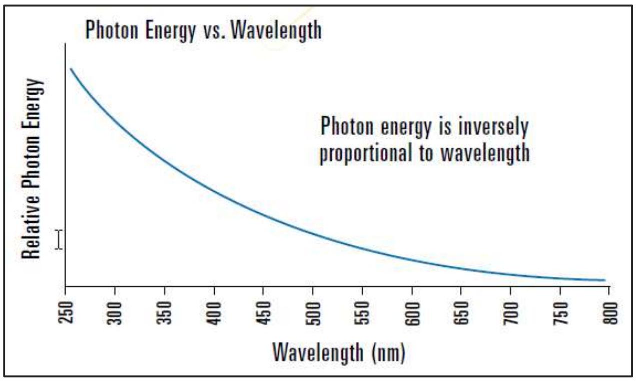


Figure 2. Relation of photon energy to wavelength.

Range Name	Wavelength Range	% of Total Solar
Ultraviolet (UV)	295 – 400 nm	6.8
Visible (VIS)	400 – 800 nm	55.4
Infrared (IR)	800 – 2450 nm	37.8

Reference Table in Accordance to CIE Pub. 85, Tab.4

Figure 3. Distribution of terrestrial solar radiation.

Ultraviolet (UV), according to ASTM G113–94, Terminology Relating to Natural and Artificial Weathering Tests of Non-metallic Materials, is radiation for which the wavelengths of the components are shorter than those for visible radiation. The spectral range for the UV, and its sub-components, are not well defined. However, the CIE (Commission Internationale de l'Eclairage) committee E-2.1.2 makes the following distinction:

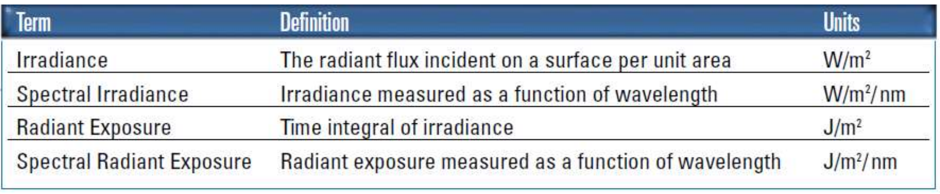
UV–A: 315 to 400 nm

UV–B: 280 to 315 nm

UV–C: < 280 nm

Visible light (the radiation the human eye can detect) is between 400 and 800 nm, making up just over half of the solar spectrum. About 40 % of the radiation from the sun is contained in the infrared portion of the solar spectrum beyond 800 nm.

There are several terms (Figure 4) that must be defined as we continue our discussion of solar radiation. Irradiance can be defined as the radiant flux incident on a surface per unit area, commonly expressed in W/m^2 (Watts per square meter). For this parameter, it is necessary to indicate the spectral range in which the measurements were taken or for which the values were calculated, such as 295-3000 nm (total solar) or 295-400 nm (total UV). If we turn our attention to narrow wavelength intervals, we obtain the spectral irradiance, measured in W/(m^{2}nm). For weathering tests, the concept of radiant exposure, which is the time integral of (spectral) irradiance, may be more important, stated in J/m^2 (Joules per square meter). Most radiant exposures are measured in either kJ/m^2 or MJ/m^2 to convert this energy into numbers to which we can more easily relate. Again, we must define the spectral range for any specified radiant exposure.



Term	Definition	Units
Irradiance	The radiant flux incident on a surface per unit area	W/m^2
Spectral Irradiance	Irradiance measured as a function of wavelength	W/m^2/nm
Radiant Exposure	Time integral of irradiance	J/m^2
Spectral Radiant Exposure	Radiant exposure measured as a function of wavelength	J/m^2/nm

Figure 4. Radiometric terminology.

On the Spectral Power Distribution (SPD) graph, the X-axis represents wavelengths of radiation found in the solar spectrum (Figure 5). On the Y-axis of the graph, irradiance at each wavelength is indicated. The curve on the graph identifies the wavelength range of natural sunlight and the irradiance associated with each wavelength of radiation. In looking at the curve for natural sunlight on the graph, we see that there is essentially no irradiance below 295 nm. Understanding SPD graphs such as this is critical when we begin to compare various artificial light sources for weathering with natural sunlight.

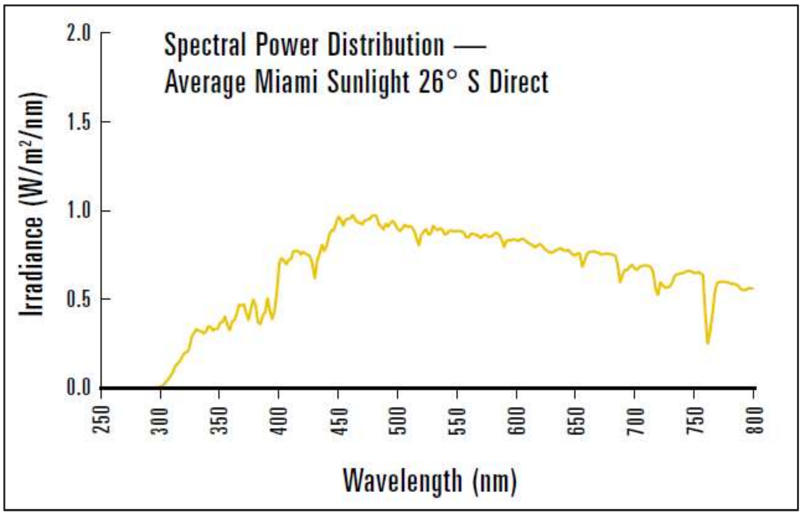


Figure 5. SPD of terrestrial solar radiation.

Climatic Effects on Solar Radiation

Direct radiation is radiant energy that reaches the earth's surface directly from the sun, excluding the scattered radiation of the atmosphere. For radiometry measurements, this is defined as radiant energy within a 6º field of view of the solar disk. Diffuse radiation is a component of radiant energy that has been scattered by the atmosphere, and therefore, reaches exposed surfaces at all angles (that are not defined as direct) in a 180º field of view. Hence, for an exposed horizontal surface, both direct and diffuse solar radiation are received. This is referred to as global solar radiation (Figure 6).

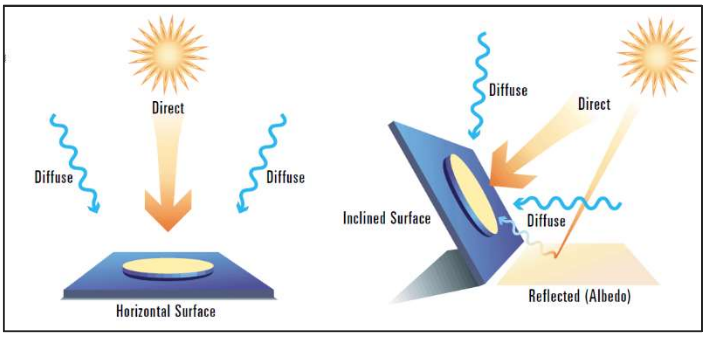


Figure 6. Direct, diffuse and albedo solar radiation.

One easy way to understand direct and diffuse radiation is if we imagine a tall building. The direct light causes the sharp shadow of the building. Diffuse radiation creates general ambient light, allowing us to see if we are standing in the shadow of that building.

As we will discuss later, it is common to expose specimens in natural conditions with some kind of tilt that will increase solar radiation received or better simulate end-use conditions. Under these conditions, the surface of a specimen still receives the direct and diffuse radiation as discussed previously. In addition, there is radiation that reflects off the earth's surface (sometimes referred to as albedo radiation) that also reaches the surface of a specimen. The amount of radiation reflected off the earth's surface is dependent on the ground covering. Bare rocks, sand, or gravel will reflect much more radiant energy than a grass-covered surface. Water or snow will reflect an even greater amount of radiant energy.

The ratio between direct and diffuse radiation reaching the earth's surface is strongly influenced by atmospheric conditions. Water vapor (humidity) and pollution will increase the amount of radiant energy found in the diffuse component. A desert climate has a much higher percentage of radiant energy in the direct component than a subtropical climate. This occurs because there is much less water vapor in the desert than in a subtropical climate. By contrast, a location with higher levels of pollution dramatically reduces the amount of direct radiant energy.

Based on Rayleigh's Law, shorter wavelengths of radiation are more likely to be scattered than long wavelengths, which makes the sky appear blue. Therefore, the percentage of UV in the direct component will always be less than that of total solar radiation. This difference can be seen in graphs comparing the percentage of direct irradiance between total solar radiation (including all regions of the solar spectrum) and the UV only (Figure 7).

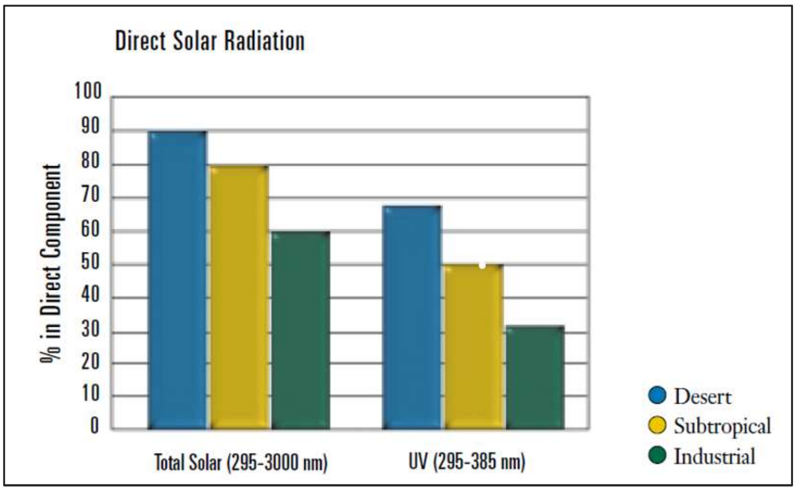


Figure 7. Direct component for total and UV solar.

The discussion of direct and diffuse radiation is important when considering radiant energy received at different orientations to the sun. Because of the high water vapor content in a subtropical climate such as south Florida, about 50 % of the UV radiation is diffused on clear days. Many days in Florida are not clear, which results in an even greater percentage of radiation in the diffuse component. To maximize solar radiation, specimens in a subtropical climate like south Florida should be exposed at a tilt angle close to horizontal, such as 5°. Conversely, a desert climate such as central Arizona would have a greater percentage of UV radiation in the direct component (as much as 75%). This means that the most radiant exposure over the course of one calendar year would be on specimens that were near the latitude angle of the exposure site, although other angles such as 5°, 45°, and 90° are common.

Seasonal variability exists in both subtropical and desert environments. The amount of variation depends on the exposure angle and climate, especially the atmospheric conditions that cause different ratios of direct and diffuse radiation. Because of the high percentage of direct radiant energy in a desert environment such as central Arizona, there is a high seasonal variation for 5° exposures at that location. Exposures conducted at 5° in south Florida are relatively constant in UV because of the scattering by water vapor. Exposures conducted at the latitude angles (which are 26° in south Florida and 34° in central Arizona) result in minimized seasonal variations, because the sun is closer to the perpendicular of these surfaces, called direct normal incidence, over the entire year. A 34°exposure is optimal for central Arizona because of the high amount of direct radiation. Overall, south Florida has less UV at 45° due to the diffusing of radiant energy by water vapor.

The Effect of Radiant Energy on Materials

While radiant exposure is an important factor in understanding the degradation of materials or determining the length of a weathering test, it really tells us only half the story. Radiant exposure tells only how much radiation has been deposited onto the surface of a material. It says nothing about how much of that radiation has been absorbed by the material or what effect, if any, it has. According to the Grotthus-Draper principle,

> ***Absorption of radiation by any component of the system is the first necessary event for photochemical reaction occurrence.***

To put this in layman's terms, "If radiation can get into a material, it potentially can cause it to change." But does this mean that a black paint will degrade in the sun because it is absorbing nearly all wavelengths of visible light? The answer to that question lies in understanding the chemical nature of the paint and which wavelengths of radiation will cause this paint to degrade. The molecular structures that constitute different polymers are susceptible to radiation they might absorb at sites called chromophores. Following another basic principle of degradation,

> ***The amount of energy absorbed by a molecule must exceed the bond energy to cause degradation.***

Simply put, if the absorbed radiation has more energy than the energy holding the molecular structure together, polymeric bonds may be broken, and degradation will begin. Note, however, that not all absorbed photons result in bond breakage, and that the energy required for photochemical reactions is unrelated to thermal bond energy. As previously discussed, we know that shorter wavelengths contain higher amounts of energy. Therefore, it is now easy to understand, when we are discussing the durability of a material, why UV, as the shortest wavelength region of radiation to reach the earth's surface, is the most important part of sunlight. For example, consider Figure 8. It has been found through experimentation that a certain polymer absorbs radiant energy and photodegrades when irradiated below 310 nm. From our spectral

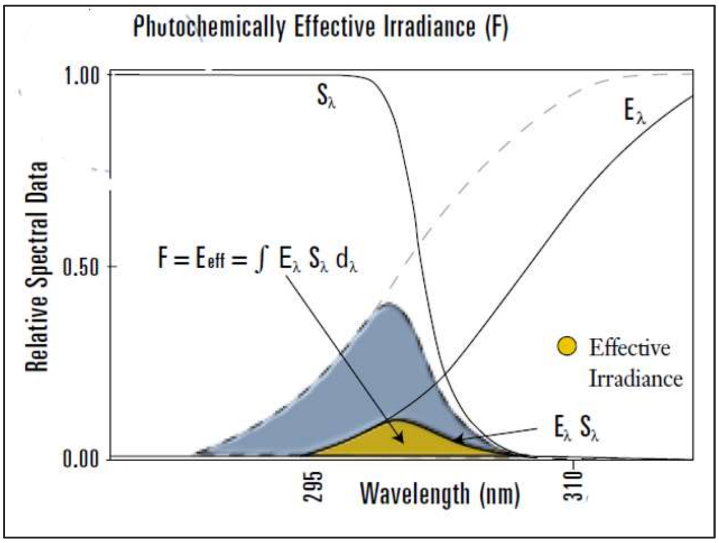


Figure 8. Relationship between spectral irradiance and spectral sensitivity.

power distribution graph, we know that natural sunlight contains wavelengths of radiation as low as 295 nm. The area under the two curves represents the effective irradiance concerning that material. The curve itself is known as the activation spectrum for that material. Do those wavelengths of radiation contain enough energy to alter chemical bonds? Will the material degrade? What type of degradation will we see? How will we know for sure? By conducting a weathering test.

To summarize, the result of the degradation characteristics of a material as a result of radiation is dependent on:

- the quality and quantity of radiant energy deposited onto the material
- the wavelengths of radiation absorbed by the material
- whether or not that absorbed radiation has enough energy to cause a chemical change, which could lead to material degradation.

We have spent time discussing the changes that occur to a polymer as a result of short wavelength radiation. Color changes, however, are only partly related to changes of the polymer matrix, such as yellowing. Often, they are caused by changes in the pigment or dyestuff used. Both pigments and dyes absorb wavelengths in the visible range (otherwise, they wouldn't be colored) and are also damaged by UV-A radiation and visible light. From a customer's perspective, color change is undoubtedly one of the most important parameters when evaluating a material's performance. For most applications, it is necessary to simulate the full spectrum of the solar radiation.

Temperature

The temperature of materials exposed to solar radiation has an influence on the effect of the radiation. In polymer degradation it is often said that light initiates, temperature accelerates, and moisture participates. Temperature often determines the rate of subsequent secondary reaction steps in polymer degradation. These secondary reactions can be often qualified using the Arrhenius equation. A general rule of thumb in chemistry assumes that reaction rates approximately double with each 10°C rise in temperature, although this doesn't usually apply to solid-state materials, and may not be seen when measuring physical or appearance changes. Also, thermochemical reactions that may be initiated at higher temperatures may not occur at all or at a very low rate at lower temperatures.

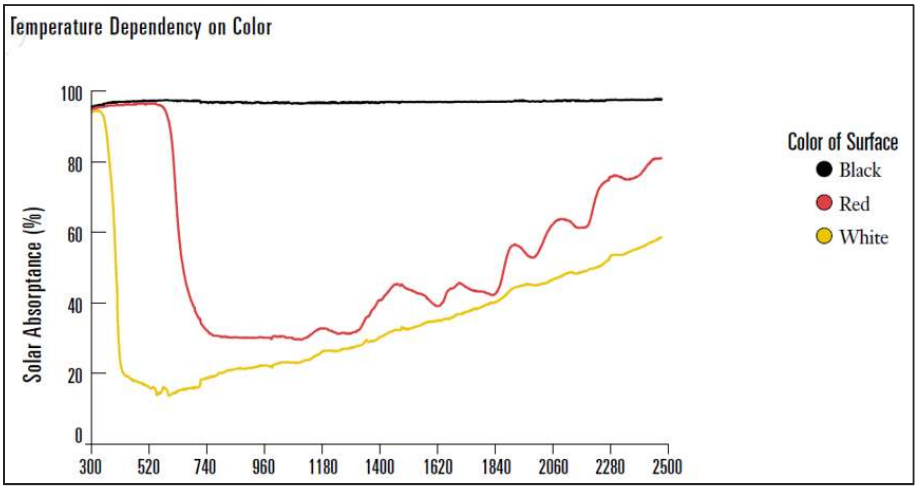


Figure 9. Specimen temperature dependency based on color.

The temperature of a material exposed to natural sunlight is determined by a number of factors. Specimen surface temperature is a function of ambient temperature, specimen solar absorptivity, solar irradiance, and surface conductance and emissivity. Therefore, in the presence of sunlight, the surface temperature of an object is usually considerably higher than the temperature of the air. Solar absorptivity in both the visible and infrared regions is usually closely related to color, varying from about 20 % for white surfaces to over 90 % for black surfaces; thus, materials of different colors will reach different temperatures on exposure (Figure 9).

This surface temperature dependency on color can have secondary (non-thermochemical) effects on materials as well. For example, as a result of different surface temperatures, mildew and other biological growth will form and accumulate at different rates on materials of different colors. White, or lighter colored materials, tend to “grow” more mildew than darker colored materials. Weathering can be both chemical and physical in nature. Temperature cycling can induce mechanical stresses which can lead to nonchemical degradation such as cracking and crazing, for example.

Much higher temperatures are obtained on painted or coated metal surfaces than in the bulk of a plastic material because the thermal conductivity and heat capacity of metals are generally higher than plastic substrates. Ambient air temperature, evaporation rates, and the convective cooling from the surrounding air during exposure all play a role in the temperature of a material, and therefore, influence degradation rates.

Water (moisture)

Water is one of the substances in our environment that is everywhere, whether in the form of humidity, rain, dew, snow, or hail. All materials used outdoors are exposed to these influences. There are two ways in which water affects materials.

Water absorption by synthetic materials and coatings from humidity and direct wetness are examples of physical effects. As the surface layers absorb moisture, a volume expansion is produced that places stress on the dry subsurface layers. Following a drying out period, or desorption of water, the surface layers will lead to a volume contraction. The hydrated inner layers resist this contraction, leading to surface stress cracking. This fluctuation between hydrated and dehydrated states may result in stress fractures (Figure 10).

The freeze-thaw cycle is another physical effect. Because water expands when it freezes, absorbed moisture in a material causes expansion and stresses that cause peeling, cracking, and flaking in coatings. Rain, which periodically washes dirt and pollutants from the surface, has an effect on the long-term rate of deterioration that is determined more by its frequency than its amount. When rain strikes an exposed surface, evaporation rocesses cool the surface rapidly, which may cause physical degradation to a material. Frozen rain, or hail, may also cause physical degradation.

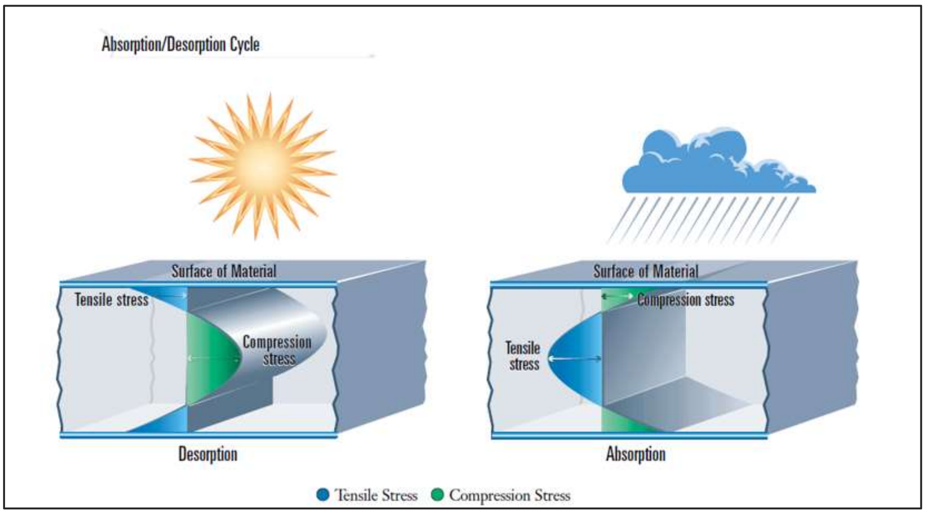


Figure 10. Tensile and compressive stresses caused by moisture absorption and desorption.

Secondary Effects

The secondary effects of weather or the atmosphere that may cause degradation cannot be underestimated. Gases and pollutants in the atmosphere, especially in the form of acid rain, may cause entirely new reactions. In highly industrialized areas, acid rain is the primary element driving the weathering process that affects a wide range of materials.

Blowing dirt and dust may have effects on the weathering process without reacting with the actual molecular structure of the material. These effects include the screening of ultraviolet radiation from the materials by dirt, which absorbs the ultraviolet portion of the spectrum. Semi-permanent “varnishes” can form on the surface of exposed materials in certain climates. Mold, mildew, and other microbiological agents may play a significant role in material degradation, particularly in tropical and subtropical climates, although they may not be generally thought of as weathering factors. Acts of Nature may not directly cause typical weathering processes to occur, but events such as El Niño, La Niña, and volcanism may affect climatic conditions which, in turn, result in different degradation rates.

Synergy

When considering the roles that solar radiation, temperature, moisture, and secondary effects play on products, we must realize that these factors work together to degrade materials. For example, if a material is exposed to only one of these factors, it is very unlikely that the degradation incurred will look anything like that of a material exposed to outdoor conditions, where all factors, and their cycles, play a role in the degradation processes.

The synergistic effects of the main factors of weathering vary, depending on materials being exposed. Even small changes to a product’s formulation, such as the addition of stabilizers, flame retardants, fillers, etc., will change the degradation characteristics of that material. The use of recycled material, impurities in the polymer matrix, and the characteristics of product processing are additional variables in weathering performance. While there are literally thousands of publications that examine the durability characteristics of pure polymers, stabilizers, and specific aftermarket products, the study of a material’s durability to weathering is not an exact science. It is safe to say that a complete understanding of the effect of weathering factors on every material will never be achieved.

Author: Allen Zielnik, Atlas Material Testing Technology LLC, May 13, 2019