

Atlas Technical Guide 102

Basics of Polymer Degradation in Weathering

Atlas Material Testing Technology

Rev 1, December 18, 2019



Basics of Polymer Degradation in Weathering

1. Introduction

Polymers are used in a wide variety of products due to their versatile properties, ease of processing, and relatively low cost. Some are used in short duration products such as consumer goods packaging while others require extended outdoor weather durability and performance for decades. Both the chemical nature of the base polymer, as well as the effect of additives, contaminants, and processing, ultimately determine the product's service life in any given environment.

2. Terminology and Definitions

The term polymer is used to describe the repeating base unit (-mer); polyethylene is simply repeating ethylene units. However, most polymers are not used in their native state, but rather have various additives included into a formulation. These can include color and appearance additives such as colorants, a wide variety of property performance or processing enhancing additives, and protective additives such as ultraviolet and heat stabilizers to retard degradation. These compounded materials are typically called plastics or, alternatively, resins.

Polymeric materials consist of a wide range of chemistries and properties. Organic (carbon containing) polymers are the most abundant and can be naturally made (such as biopolymers) or synthetically produced. Polymers can be divided into two broad categories, thermoplastics and thermosets. The key differentiator is that thermoplastics can be reheated and reshaped repeatedly. This quality also makes thermoplastics recyclable. They are further separated by their degree of crystallinity (amorphous, semi-crystalline or crystalline), temperature range and physical properties into commodity polymers (such as polyethylene and polyvinylchloride) and higher performing engineering resins. A key property of thermoplastics is that the polymer chains do not form covalent bonds with one another.

Thermosetting polymers cannot be reheated and reshaped. They contain polymers that cross-link together (like a 2-part epoxy) during the curing process to form an irreversible chemical bond, making thermosets ideal for high-heat applications such as electronics and appliances. Many film-forming paints and coatings are thermosets.

Then there are rubbers and elastomers, which combine some of the characteristics of thermoplastics and thermosets. Curing is typically at an elevated temperature, which creates long-chain polymers interconnected by crosslinks. However, these crosslinks create an elastic structure and provide recovery characteristics to the finished material and are also stable under heat and pressure. Lastly, there are various biopolymers such as proteins.

3. Polymer Degradation in Weathering

In outdoor weathering product is exposed to a variety of environmental stresses, which constantly vary and change in both short diurnal (daily) and longer term (seasonal, annual, etc.) timeframes. These parameters also vary with weather and geography, which viewed on a long-term basis comprises climate. However, there are indoor environments, such as building or automotive interiors (or any specific surface use environment) where products can also degrade from exposure to environmental stresses.

It should be noted that items made from polymers can deteriorate from both stress-induced chemical changes as well as physically induced changes. In other words, weathering is often a combination of both damaging changes to the chemistry of the polymer formulation (for example, the breaking of polymer bonds from ultraviolet radiation) as well as from mechanical stresses induced by the changes in the environment (e.g., thermomechanical expansion and contraction from daily cycles in temperature) or from product service-use induced stresses (such as from mechanical constraint of an installed window frame).

4. Main Stress Factors in Weathering

The most important environmental stress factors in the weathering of polymeric products are light, heat and moisture.

4.1 Light

Light^{Note 1}, or more accurately, terrestrial solar radiation (that which reaches the earth’s surface) is composed of a continuous spectrum of wavelengths ranging from the ultraviolet (UV), through the visible (Vis) wavelengths and into the infrared (IR) region (Figure 1)^{Note 2}. The UV region is further subdivided into the UV-C (found only outside the earth’s atmosphere), UV-B (with wavelengths below ~300 nm being filtered out by the ozone layer) and the UV-A region.

The exact solar spectrum varies with factors as diverse as sunspot activity to atmospheric humidity levels, so reference standard spectra have been created by international bodies to “define” standard outdoor solar radiation; this is important as these standards define the spectral target for solar simulators and artificial weathering devices. (Figure 2) shows the spectra for direct solar radiation (solid line) and for sunlight as filtered through 3 mm and 6 mm window glass, which filters out some of the lower wavelength UV-B and UV-A, when testing to interior conditions.

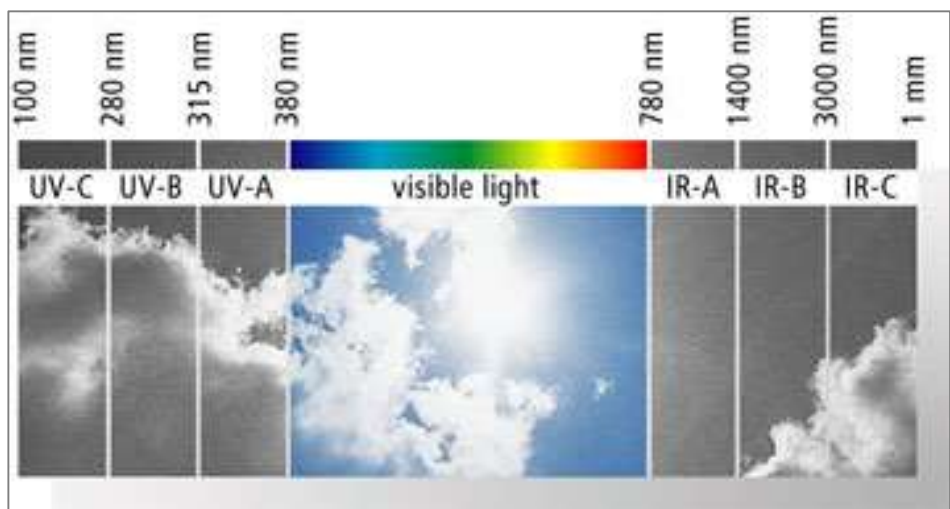
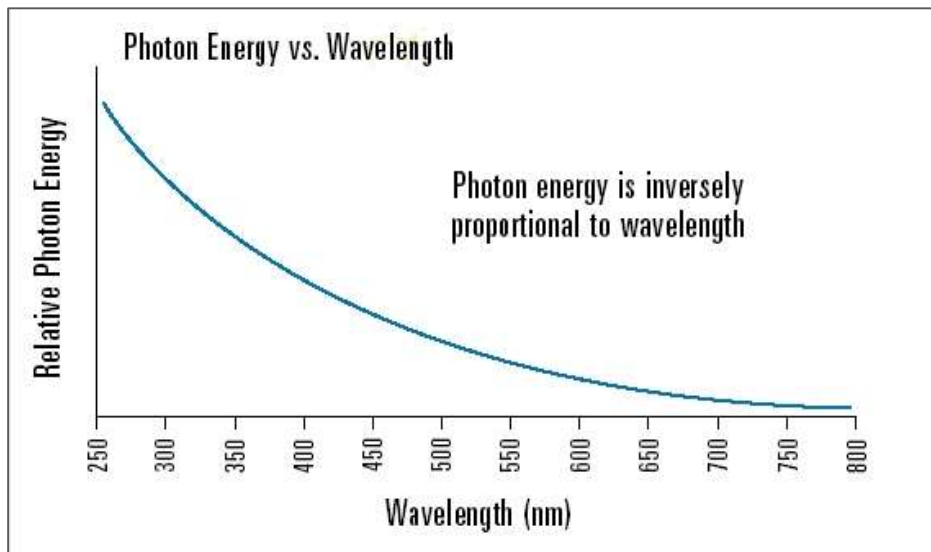


Figure 1. Terrestrial solar radiation bands by wavelength.



In polymer degradation we are very concerned with the UV region. Planck's photon energy equation states that the energy contained in a photon is inversely proportional to wavelength (Figure 3). That means that some photons have the energy to break apart chemical bonds in a polymer, and this is a necessary first step in most photodegradation mechanisms. In short, not all photons, and therefore wavelengths, are equal in their effect. An important cautionary implication is that the use of wavelengths, particularly in the

Figure 2. Spectral Power Distributions of window-glass filtered sunlight (dashed lines) versus direct sunlight.

low-UV not present in terrestrial solar radiation, may induce photo-degradation that would not otherwise occur outdoors, or skew the photochemistry and produce unpredictable results.

This is not to imply that only high-energy, low wavelength UV is important in polymer photo-degradation. In fact, many polymers (due to various chemical bonds) have wavelength sensitivity across the UV and into the visible wavelengths. A brief list of several polymers and their wavelength sensitivity is shown in Figure 4 [1].

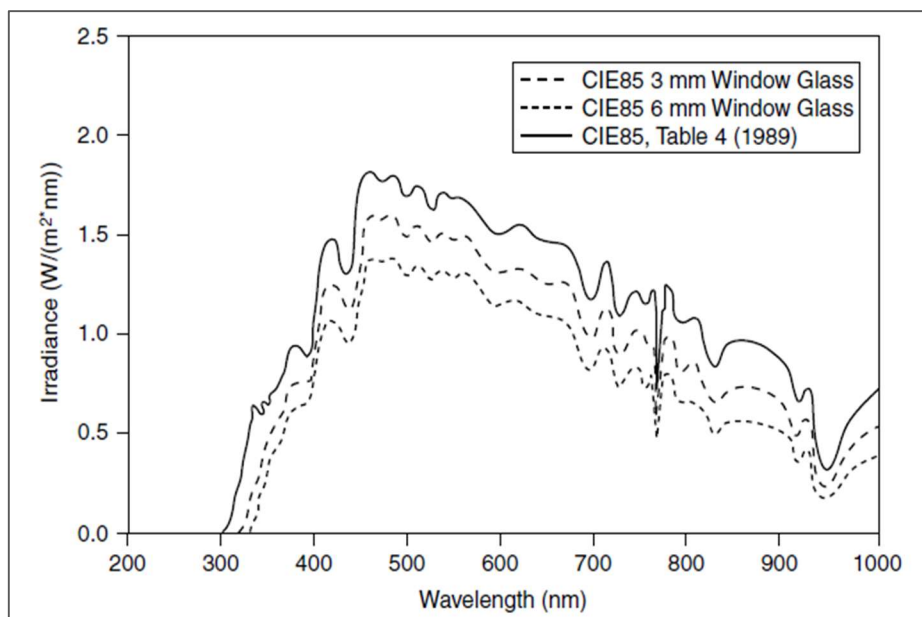


Figure 3. Photon energy v. photon wavelength relationship.

Pure polymers mostly exist only in college textbooks, and defects arising from synthesis or thermal processing, such as side chain branching, oxidation reactions, hydroperoxide formation, residual monomers and catalysts, etc., are often the initiating sites of photodegradation. Technical polymers also often contain many additives: plasticizers, heat and UV stabilizers, processing aids, flame retardants, etc., which can also be initiation sites for photodegradation. The C-C and C-H bonds in pure polyethylene, for example, do not absorb UV in the wavelengths present in terrestrial solar radiation, and therefore should be photostable outdoors. Yet we find that unstabilized PE quickly photo-degrades due to the inherent defects and inevitable contaminants present in all commercial

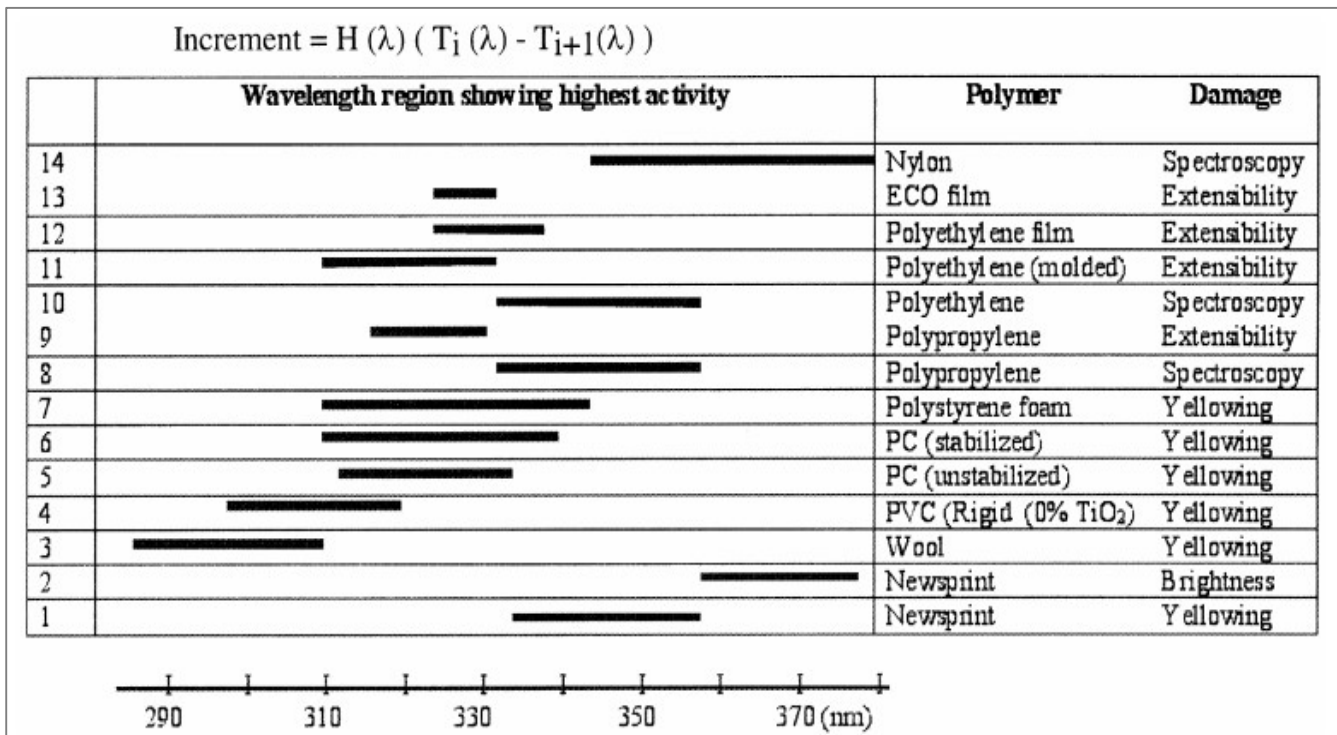


Figure 4. Wavelength sensitivity of some common polymers.

formulations. Other polymers, due to the nature of their chemical bonds and relatively high purity, such as PMMA, poly(methyl-methacrylate), often used in architectural skylights and aircraft canopies, can resist photodegradation for decades. In general, the higher performing engineering resins possess higher inherent stability than do most commodity polymers such as polyolefins (e.g., polyethylene, polypropylene, polyvinyl chloride, etc.).

As an additional note, the literature on weathering sometimes shows a table of bond energies vs. photon energy and associated wavelengths, with the implication that higher energy short wavelengths below the bond energy may or will cause bond breakage while those above cannot. However, this is incorrect as thermal bond dissociation energy and thermal bond strength are unrelated to the photon energy required to raise a molecule to the excited state necessary in photolytic degradation processes.

4.2 Heat

Heat is often a key factor in both physical and chemical weathering. While at high temperatures pyrolysis and thermal oxidation can occur, at more typical weathering exposure temperatures heat can accelerate the secondary non-photonic reactions, such as oxidation and free-radical reactions, and often adds an “additional” acceleration from that of the radiation exposure alone. These secondary reactions often cause much of the polymer damage.

The glass transition temperature (T_g) of amorphous polymers is the point at which polymers transition from a hard, vitreous, brittle, glassy state to a viscous, rubbery state. Above the T_g there is greater oxygen diffusion and mobility of small molecular weight species. The apparent rate of degradation typically increases above the T_g . While the T_g is sufficiently high for most thermoplastics to not be of concern, many thermoset resins used in coatings are in the range of some service environments and accelerated weathering test methods. A few degrees difference can reverse the rank order and magnitude of difference between these polymers in some accelerated tests.

Thermal cycles can place mechanical stress on polymeric products from expansion/contraction, or when difference in the coefficients of thermal expansion (CTE) are different, particularly in laminated materials. Thermal cycles can also affect surface and absorbed moisture or introduce moisture condensation or freeze/thaw physical stress. Physically constrained systems, such as door and window profiles, can warp to relieve the stress of thermal expansion from solar load, especially in combination with high ambient air temperatures.

4.3 Moisture

Moisture takes many forms in weathering, such as a vapor in atmospheric humidity, as various forms of precipitation or condensation when surface temperatures fall below the dew point temperature. Moisture uptake can swell (increase in hydrodynamic volume) some polymers (e.g., polyamides, such as nylon, and many coatings). This results in mechanical stress with cycles of absorption/desorption, the

rate being increased at higher temperatures. Water can also leach low molecular weight species, transport gases such as oxygen, fuel microbial growth such as mildew, act as a solvent or initiate hydrolysis degradation reactions. In the case of condensation polymers, for example, a water molecule is removed during the polymerization process. If replaced, the polymer bond is broken and reverts to its original constituents. Hydrolysis reactions follow the general form of $RX + HOH \rightarrow ROH + HX$. Hydrolysis degradation is not limited to condensation polymers, however. Generally, heteroatoms (atoms other than C or H in the polymer backbone), especially in heterocyclic compounds (ring structure containing atoms of at least two different elements), are more susceptible to hydrolysis.

Moisture effects, both chemical and physical, are often underestimated and under-represented in historical standard laboratory weathering test methods. However, both gaseous and liquid water are key factors in polymer degradation, making hot/humid-moist climates, such as exposure benchmark subtropical south Florida, among the most severe for the outdoor weather durability of polymers. Moisture can also influence the degradation of non-polymers, such as some dyes in lightfastness tests.

5. Synergistic Effects

As can be seen from the above, the three main weathering stress factors of heat, light and moisture are not completely independent. An increase in solar heating, perhaps due to test specimen color, will increase surface temperature. This, in turn, may affect moisture absorption/desorption as well as provide thermal acceleration of chemical reactions and provide thermomechanical stress. In most cases there is synergy between these stress factors. Depending on the unique stress sensitivities of any given specimen, a combination of stress factors, such as elevated temperature and moisture, may have a greater synergistic effect than each factor does individually. The

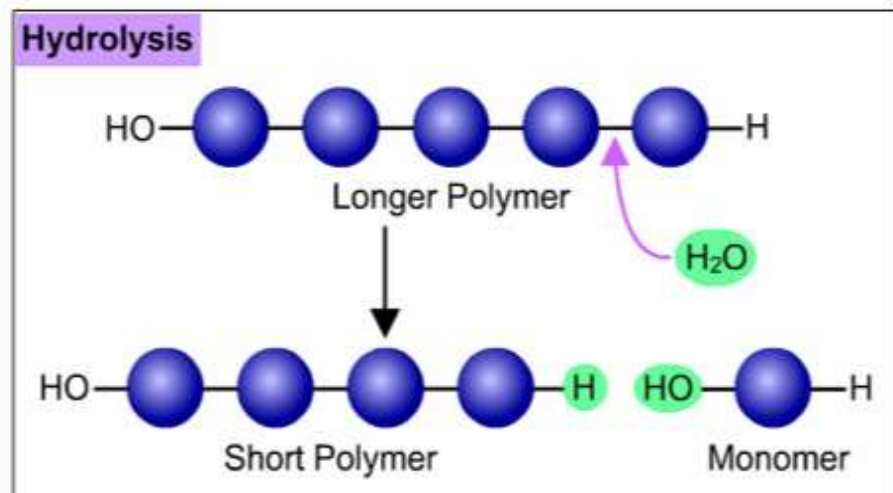


Figure 5. Polymer degradation by hydrolysis.

effect and synergistic relationship of the primary stress factors can often be identified for a specific material by conducting a Design of Experiments such as a full-factorial experimental sequence, to both help determine the best test conditions as well as interpret test results. For example, is there a moisture and temperature interaction effect which should be considered? Or, is light/dark cycling with temperature variations required reproduce field failures?

Note that estimates of accelerated test “equivalence” to outdoor exposure based only on “equivalent” radiant energy do not take temperature, moisture and other stress factors into consideration, nor do they account for specific test material stress sensitivity. This requires correlation studies between natural and accelerated tests for specific test materials and property changes. Also, note that radiant energy equivalence is not correlation; correlation requires comparing the accelerated test to the outdoor or service environment real-time results to achieve the same type and amount of a specific property change for a specific material formulation or product.

6. Secondary stress factors in weathering

There are many additional environmental stress factors, as well as service-use specific factors, which can be involved in polymer degradation. Biological agents, wind and sand erosion, pollutants (dry deposition, gases, acid rain), ozone, dust/dirt retention, wind and snow load, chemicals such as cleaning agents or fuels, etc., can also be important stress factors. These secondary factors are not included in most accelerated or artificial weathering tests. Weathering can involve both chemical changes to constituents as well as physical weathering not involving chemical changes. Mechanical stresses, such as tensile, shear, compressive, bending or torsional forces can affect polymer degradation from this physical perspective. Sealants, for example, should generally be exposed while under mechanical stress as the weathering behavior is different when unstressed. In the case of films, extruded or injection molded polymers, the additional stress may need to be applied in weathering tests in the same direction (e.g., machine or transverse direction) of in service use due to polymer molecular orientation.

Polymer degradation and stabilization

While there is considerable literature available on polymer degradation mechanisms, much of this information is of limited use to the weathering investigator as (a) the tests are often conducted on specially prepared formulations or were (b) tested under conditions which are not typical of outdoor weathering exposures. Further, academic tests often are not representative of typical commercial formulations, and do not

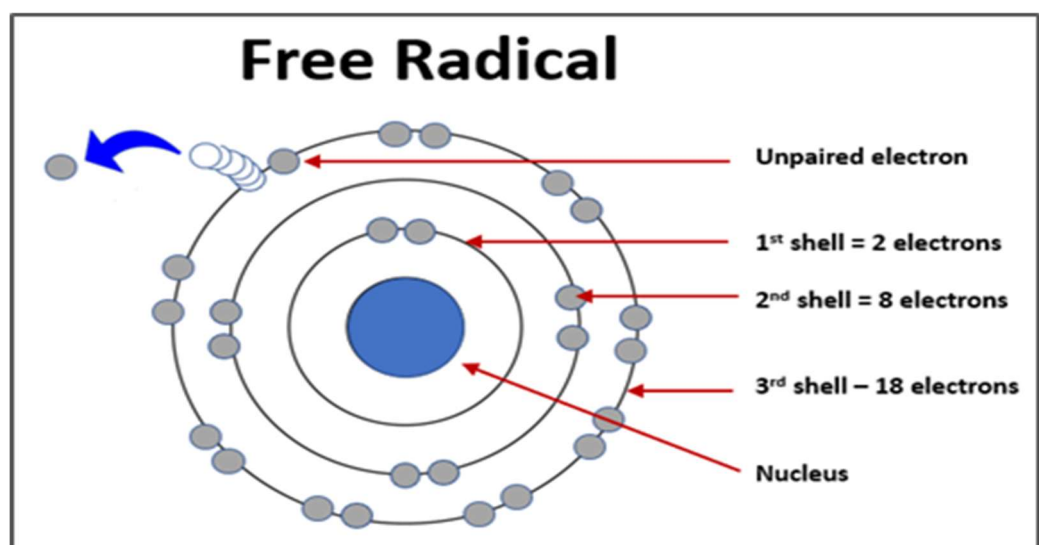


Figure 6. Free radicals contain an unpaired electron, making them highly reactive.

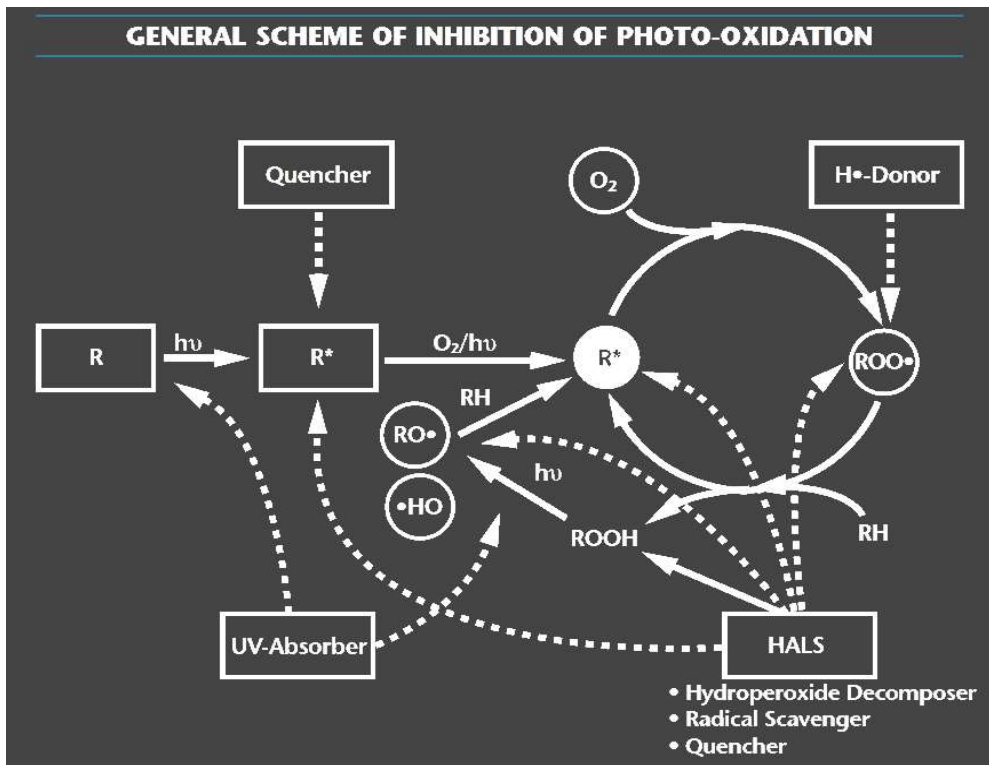


Figure 7. General polymer autocatalytic photooxidation degradation and inhibition mechanism.

account for secondary post processing effects, such as injection molding, thermo-welding, etc., which can affect degradation.

Even if you do feel that a detailed knowledge of the specifics of polymer degradation is necessary, an understanding of the general degradation mechanism for most polymers is beneficial to understand how best to test and interpret test

results. Of course, many polymers have specific degradation pathways that deviate from this scheme. Bisphenol-A polycarbonate (PC), for example, has a distinct sensitivity to UV wavelengths <300nm, and

often yellows in artificial weathering tests which contain wavelengths lower than the terrestrial cut-on, but remains clear on outdoor exposure. And poly(vinyl chloride) (PVC) undergoes competing photo-yellowing and photo-bleaching reactions. However, a detailed coverage of specific polymer degradation is beyond the scope of this document.

Most polymers degrade via a general autocatalytic photooxidation mechanism, This photo-initiated process is dominated by free radical chemistry. A free radical is an atom, molecule, or ion that has an unpaired valence electron (Figure 6) in an outer orbit. Usually, these unpaired electrons make free radicals highly chemically reactive towards other substances, including polymer chains, or will recombine with other free radicals to pair electrons. These recombinations may form stable or semi-stable products, but sometimes possess undesirable properties. This general mechanism is pictured in Figure 7 [2], and some of the main reactions which occur in this process are detailed in Figure 8 [3].

First, a photon, usually of a UV wavelength and therefore of high energy, is absorbed by a chromophore in the molecule. A chromophore is a site on a molecule able to absorb radiation due to the nature of its bonds. It can be part of the polymer backbone, a functional group or an impurity or defect. Chromophores define the wavelength sensitivity of a molecule. Note that some additives and contaminants in the formulation may also absorb photons and transfer that energy to the polymer or may catalyze degradation reactions.

This added energy, if sufficiently high, raises the molecule to an excited state. While usually harmlessly dissipated, this energy is sometimes released by breaking (scission) a chemical bond, resulting in the formation of reactive free radicals. Next, the free radicals may react with oxygen forming peroxy radicals. These can “abstract” a hydrogen atom from another polymer molecule to obtain the missing electron. This results in the formation of a

hydroperoxide (ROOH) compound, leaving a new polymer radical (due to the lost hydrogen atom). Hydroperoxides are relatively unstable and break apart with moderate thermal or photon energy into two new (alkoxy and hydroxy) radicals. While thermal energy can decompose sensitive hydroperoxides into free radicals, heat energy generally follows a different pathway to form different radicals and most polymer degradation in weathering is the result of higher energy states resulting from photon irradiation.

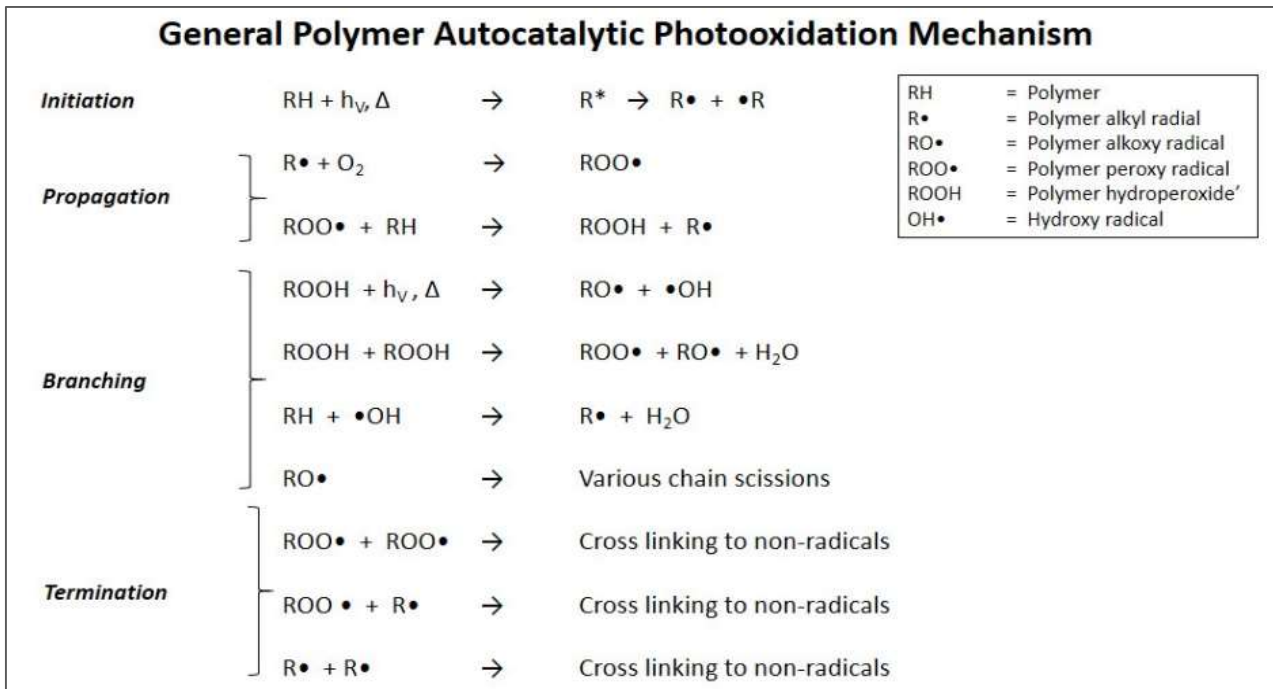


Figure 8. General mechanism of polymer autocatalytic photodegradation. The process is dominated by free radical reactions. Note that some polymers do not explicitly follow this mechanism.

Free radicals will continue to degrade the polymer and generate more radicals in the process. Radicals can also react with one another, forming stable compounds, but often ones with undesirable characteristics such as color. Polymer radicals can crosslink to both radical and non-radical species and cause polymer embrittlement. This is an autocatalytic process and can continue even without additional photon energy. Note that photons only need to initiate the process; once begun, the oxidative and radical reactions are primarily thermally governed by Arrhenius behavior. This is a primary reason why only using radiant energy to equate an accelerated or artificial weathering exposure to outdoor performance frequently fails to correlate for property change as the radiant energy method does not account for these secondary mostly non-photonic reactions. Figure 6 also shows the primary stabilization techniques and their point of action. These primarily include UV absorbers, excited state quenchers, proton donors such as antioxidants, and free-radical scavengers such as hindered amine stabilizers, among others.

Coverage of polymer stabilization is beyond the scope of this presentation, however two important points regarding UV-absorbers will be made. First, UV absorbers are destroyed as they act, so their concentration and protection decrease with exposure. Secondly, following the Beer-Lambert law regarding light absorption, there is essentially zero protective at the light exposed surface where most of the degradation occurs.

The degree of temperature dependence of a chemical reaction depends on a parameter called the activation energy (E_a) of that reaction. It is the energy that must be put into a system for the reaction to occur, as shown in Figure 9. The rate of reactions with a low value of E_a are more substantially increased with higher temperatures than those with high E_a energy barriers.

The temperature dependence of the degradation rate kinetics is one reason why using radiant energy dose to determine an accelerated test time, or calculating correlation coefficients based only on radiant energy, is often misleading. The kinetic effects of temperature typically provide an increased degradation acceleration over that produced by photons alone. It also explains why it is important to know and to use realistic test specimen temperatures as the post-initiation secondary reactions, which are responsible for much or most of the polymer degradation, mostly follow Arrhenius temperature behavior.

Fortunately, when the E_a is unknown as it often is, basing artificial/accelerated weathering tests only upon a radiant energy (dose) value usually will tend to *overestimate* the test duration as compared to a similar outdoor exposure property change and *underestimate* actual service life. This is because most laboratory weathering tests are at higher specimen temperatures than most outdoor service conditions, and any degradation rate increase resulting from this increased temperature is not factored in when basing exposure duration only on radiant energy dose.

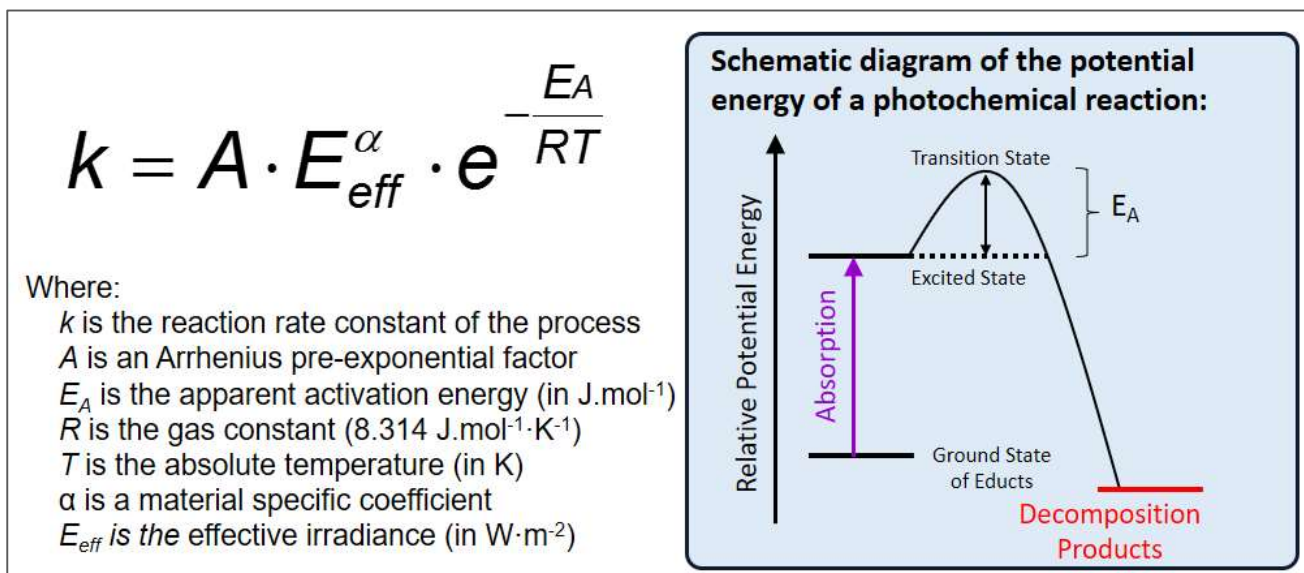


Figure 9. Modified Arrhenius equation showing the temperature dependence of a photolytic reaction.

7. Polymer stability

Of course, specific polymers may undergo other degradation mechanisms and pathways. Also, as there may be multiple pathways, different polymer properties may change at different rates. Further, some polymers, such as bisphenol-A polycarbonate have competing reactions, , such as photo isomerization (Photo-Fries rearrangement) causing photo-yellowing and a counter photo-oxidation of the yellow products resulting in photo-bleaching, the balance of which can be altered by the test conditions. With polyvinyl chloride (PVC), a dehydrochlorination (HCl elimination) reaction is followed by C=C conjugation of the backbone leading to polyene sequence (alternating C-C and C=C) formation and the development of a yellow coloration. As the C=C bond count increases, the discoloration progresses from yellow to orange-red to brown and, finally, to black.

Most commercial polymers are stabilized to improve their durability. These often include UV-absorbers, hindered amine free radical scavengers, antioxidants, excited state quenchers, hydroperoxide destroyers, etc., as shown in Figure 7. These can greatly extend the useable service life and performance of polymers. However, UV absorbers, for example, are self-sacrificial and will become exhausted, at which point degradation rapidly progresses. This can

lead to errors when extrapolating short term test data to longer term performance based on early degradation rates. Also, UV stabilizers essentially provide little to no protection at the exposed surface, where appearance properties are primarily impacted. Physical performance, such a tensile strength, will typically progress much more slowly as degradation must work its way deeper into the bulk of the material for mechanical properties to be affected.

In short, the more that is known regarding the degradation mechanism of a specific polymer, the better can choices be made regarding how to properly test, such as the selection or development of a test method with all its associated parameters.

Note 1. The term *light* technically refers only to the region of electromagnetic energy detectable by the human eye, approximately 390-700nm. The term *terrestrial solar radiation* should be used to refer to the spectral energy which reaches the earth's surface. However, terms such as sunlight, daylight, etc., are commonly used with the understanding that it refers to all wavelengths, not just the visible portion.

Note 2. The near-infrared region, particularly the near infrared (NIR) region of approximately 700 to 1100 nm is mostly responsible for solar heating effects. Photons at these wavelengths are of insufficient energy to raise molecules to excited states leading to bond scission and free radical formation but may cleave thermally sensitive bonds such as hydroperoxides.

8. References

- [1] A. L. Andradý, S. H. Hamid, X. Hu, A. Torikai, Effects of increased solar ultraviolet radiation on materials, *Journal of Photochemistry and Photobiology B: Biology* 46 (1998) 96-103.
- [2] Ciba Specialty Chemicals, Light Stabilizers for Polyolefins brochure.
- [3] E. Yousif, R. Haddad, Photodegradation and photostabilization of polymers, especially polystyrene: review, *SpringerPlus* (2013) 2:398

Author: Allen Zielnik, Atlas Material Testing Technology LLC, March 1 2018

Atlas Material Testing Technology | 1500 Bishop Court | Mount Prospect, Illinois 60056, USA
www.atlas-mts.com

© 2022 Atlas Material Testing Technology LLC. All Rights Reserved. ATLAS and ATLAS logo are registered trademarks of Atlas MTT LLC. AMETEK logo is registered trademark of AMETEK, Inc.