TECHNICAL NEWSLETTER

# Weathering of Plastics

## Introduction

In a previous Newsletter we looked at the thermal degradation of plastics and noted that it was part of the larger issue of polymer degradation mechanisms; which could occur as a result of:

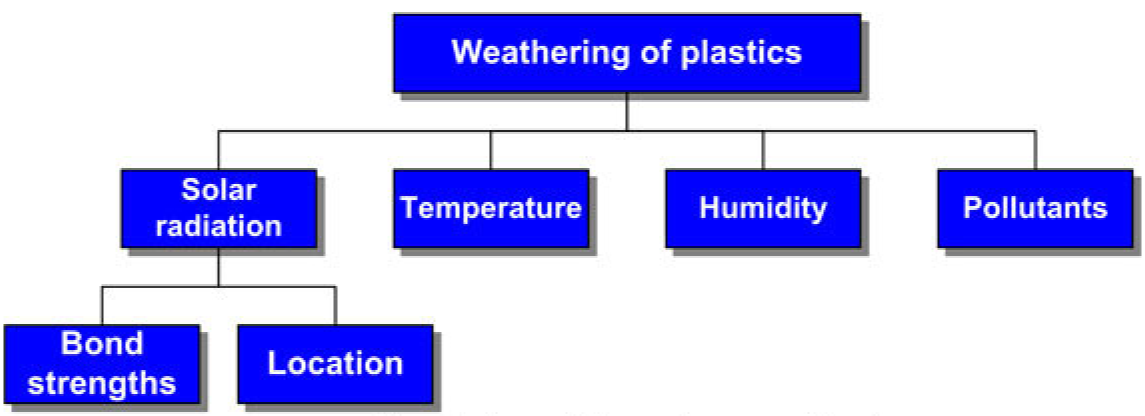
- **Heat** (thermal degradation and thermal oxidative degradation when in the presence of oxygen).
- **Light** (photodegradation).
- **Oxygen** (oxidative degradation).
- **Weathering** (generally UV degradation).

In general, the ability of a plastic to resist these degradation causes is called the ‘stability’ of the plastic and in this Newsletter we will concentrate on the process of weathering (with particular emphasis on the causes and effects of UV degradation).

The weathering behavior of a plastic is one of the most important limiting factors in assessing and selecting a plastic for outdoor applications. The selection of a material by simple mechanical properties may well be sufficient in many cases but this is ineffective if the material loses strength or discolors in service. ABS may be more than adequate mechanically for many outdoor applications but the weathering response of ABS means that it is rarely selected for such applications. Asking and adequately answering the question ‘**How long will it last in service**?’ must be a key factor in the selection of materials for external use.

## The factors influencing weathering

Response of a material to weathering is not a simple question to answer because of the complexity of the factors involved. Considering weathering involves considering the effects of solar radiation, temperature, humidity, pollutants and all the combinations of these factors. These major factors are shown in the diagram below:




The factors influencing weathering

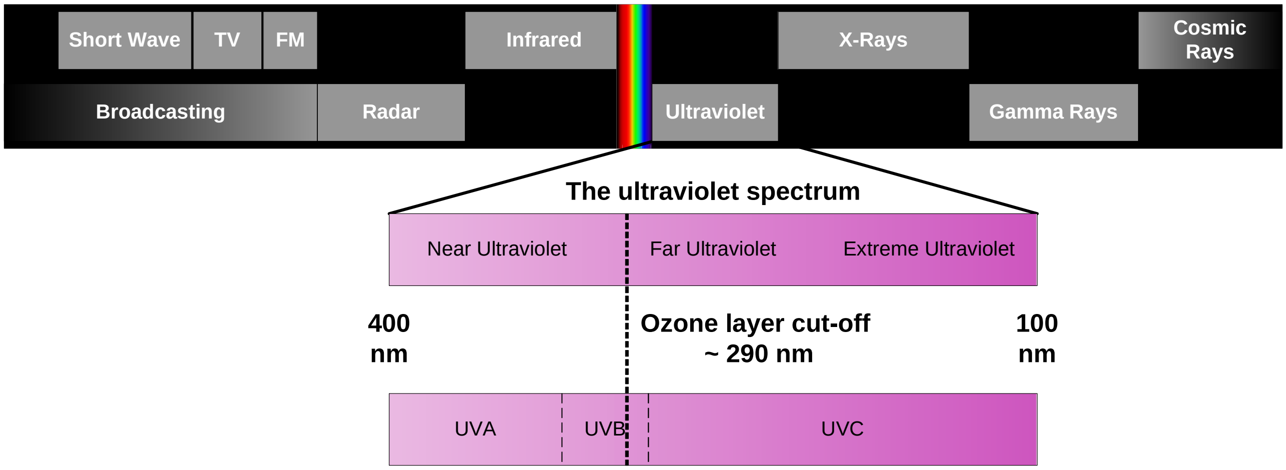
Considering weathering involves not only considering the effect of these factors on the base polymer but also the effect of these factors on all the other chemical components added to the base polymer such as colorants, plasticizers and processing aids. In this Newsletter we only have space to present an overview of this complex topic.

### Solar radiation

Composition of the solar radiation reaching the earth's surface is mainly made up of radiation in the visible and infrared areas of the electromagnetic spectrum. Approximately 43% of solar radiation is in the infrared region and has a wavelength of greater than 700 nm – this radiation does little to most plastics apart from heating the material. Approximately 52% of solar radiation is in the visible region and has a wavelength of between 400 and 700 nm – this radiation both heats the plastic and can also start photochemical reactions. The last 5% of the radiation is in the ultraviolet (UV) region and has a wavelength of between 400 and 290 nm.

The approximate lower boundary of 290 nm is due to the filtering effect of the ozone layer in the atmosphere and radiation with wavelengths of less than 290 nm is blocked by the ozone layer and prevented from reaching the earth's surface.

**The electromagnetic spectrum**




UV radiation can be classified as near, far or extreme UV but it is also possible to classify UV radiation in terms of UVA, UVB and UVC types of radiation where UVA is made up of wavelengths from approximately 320 to 400 nm, UVB is made up of wavelengths from approximately 280 to 320 nm and UVC is made up of wavelengths from approximately 100 to 280 nm. Only UVA and UVB ultraviolet rays reach the earth's surface because the ozone layer blocks the UVC radiation.

### Bond strengths

Despite the relatively low percentage of UV radiation present in the solar spectrum, this is a very damaging radiation for plastics because of the high quantum energy content.

The bonds between the atoms in many plastics have dissociation energies that are very similar to the quantum energy present in UV radiation. UV radiation in the region of 300 to 400 nm is therefore capable of breaking the bonds in the plastic to cause rapid degradation of the basic structure of the plastic. For example the $CH_3 – CH_3$ molecule can be broken apart by UV radiation of wavelengths greater than 340 nm which contains sufficient energy to break the main bond. The most damaging UV wavelength for a specific plastic depends on the bonds present and the maximum degradation therefore occurs at different wavelengths for different types of plastics, e.g. it is around 300 nm for PE and around 370 nm for PP.

**Location**

The amount of UV present in the incident solar radiation varies dramatically with location and is particularly high near the equator. Climate change processes, particularly those that deplete the ozone layer, have resulted in increasing amounts of UV radiation reaching the earth's surface and this is particularly true in the Southern Hemisphere where the 'ozone hole' in Antarctica has led to increases in the amount of UVA and UVB in Australia.

Weathering due to UV radiation can vary dramatically depending on the location of the product in the world and the intended application location should always be specified at the earliest stage. For example, PVC-U for temperate climates can be adequately stabilized against UV weathering by using around 4% $T_iO_2$ (titanium dioxide) but PVC-U for tropical climates requires around 8% $T_iO_2$ for adequate stabilization. This change has a significant effect on costs and processing of the product – using a temperate climate PVC-U mix in a tropic climate can result in significant and rapid weathering of the product.

The effect of UV radiation on humans is similar to the effect of UV on plastics (we are also carbon based) and excessive exposure to UV (particularly UVB) can lead to similar molecular damage. In the case of humans the damage can be linked to cell damage and increased rates of cancer. Increasing weathering of plastics may be the least of humanity's problems if the 'ozone hole' over Antarctica gets larger or if the ozone layer becomes further depleted. The Southern Hemisphere is already facing increased levels of UVB radiation and increasing skin cancer rates as a result of this.

**Temperature**

Weathering is a degradation process and as such is temperature dependent, i.e. it will occur more rapidly at higher temperatures. The general rule is that for every 10ºC increase in temperature the reaction rate will double. Tropical areas therefore suffer not only from increased UV exposure but also faster reaction rates because of the increased temperatures.

**Humidity**

Water is affected by UV light to produce a variety of free radicals that can both initiate and propagate the degradation process (see below for details of the need for free radicals). Most weathering processes are considerably slower in hot dry climates than in hot wet climates.

**Pollutants**

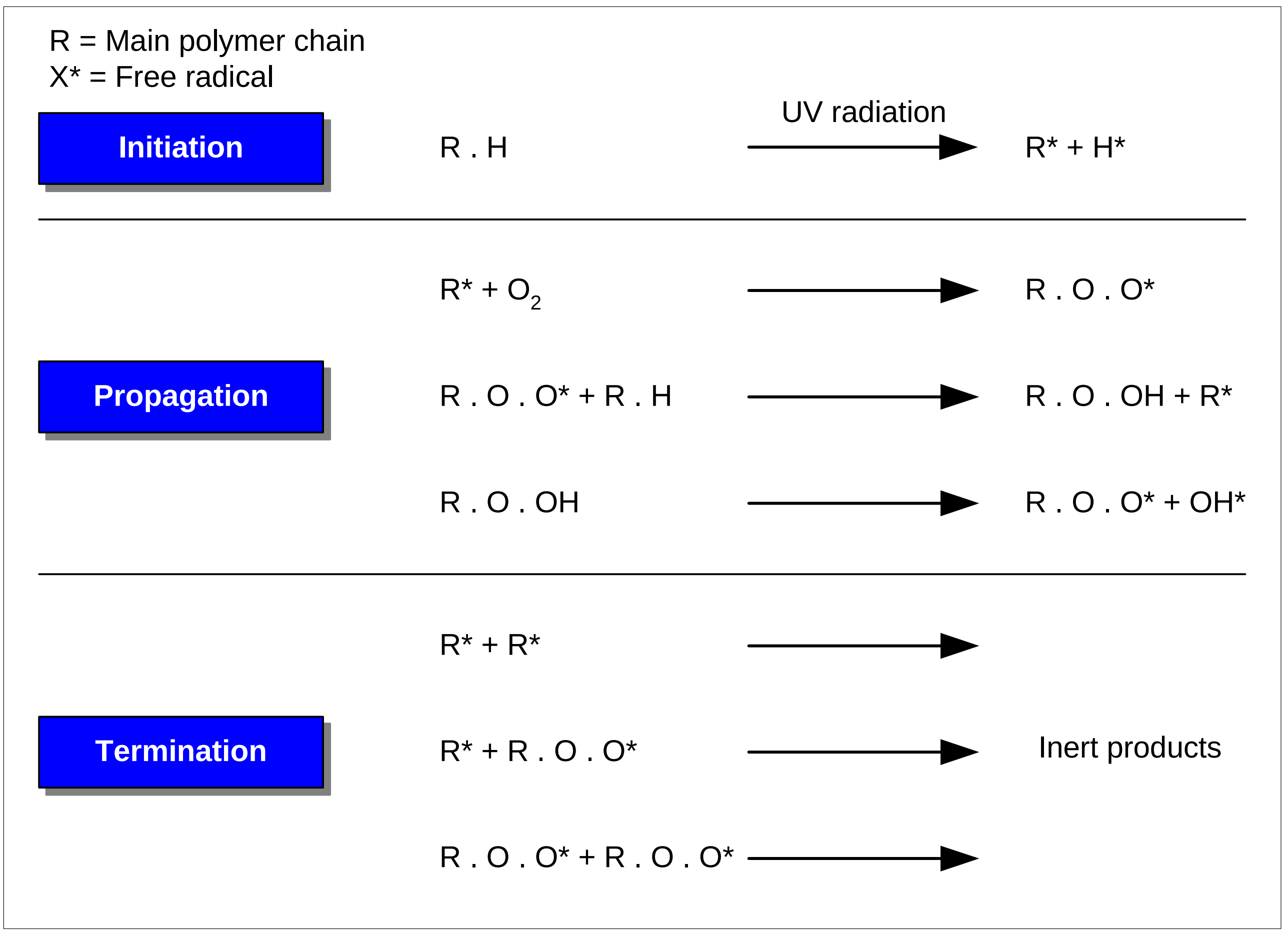
Atmospheric pollutants, including dirt and dust, will inevitably be present in outdoor applications and can have a significant effect on the weathering of a plastic. The accumulation of simple dust can trap water on the surface of the plastic to provide a continuous source of moisture but the presence of even more aggressive atmospheric pollutants such as $SO_2$ (sulfur dioxide) can create 'acid rain' or dilute sulfuric acid that can have a severe effect on the weathering resistance of plastics.

## The process of weathering by photodegradation

The process of weathering under exposure to UV is a photodegradation process that is very similar to that seen in thermal degradation; it is essentially an autoxidation process that involves the major steps of initiation, propagation, branching, and termination (for full details of this see the previous Newsletter on Thermal Degradation). In most cases the weathering process is outdoors and the incident sunlight means that the plastic is hot and some thermal degradation occurs in parallel with UV degradation.

### The mechanism

A general mechanism for photodegradation is shown below:




**The general mechanism for photodegradation and thermal degradation**

### Initiation

Initiation can be achieved by the simple absorption of UV light that has sufficient energy to break the chemical bonds in the main polymer chain. This generally does not happen with pure polymers but happens with reactive residues from processing or other additives in the plastic. Initiation creates a polymer 'free radical' (R*) and a hydrogen atom with an unpaired electron (H*). For fluoropolymers the strength of the C-F bond means that it is very hard for photodegradation to initiate.

**Propagation**

Propagation involves a variety of reactions and one of these is where the free radical (R*) reacts with an oxygen ($O_2$) molecule to form a peroxy radical (ROO*) which can then remove a hydrogen atom from another polymer chain to form a hydroperoxide (ROOH) and so regenerate the free radical (R*). The hydroperoxide can then split into two new free radicals, (RO*) + (*OH) and continue to propagate the reaction to other polymer molecules.

It is important to recognize that removing a plastic from the influence of UV will not necessarily stop photodegradation. The propagation step does not need the input of energy from UV light and can continue even after removal from the UV source.

**Termination**

The termination of photodegradation can be achieved by 'mopping up' the free radicals to create inert products. This can occur naturally by combining free radicals or can be assisted by using stabilizers in the plastic.

## Preventing weathering - absorbers and stabilizers

There are two strategies that can be used to control weathering from UV: the UV can be absorbed using a UV absorber or the degradation process can be retarded by the use of UV stabilizers. In practice it is possible to use both mechanisms to achieve a degree of synergy between the mechanisms.

**UV absorbers**

UV absorbers work by absorbing incident UV radiation and then re-emitting the absorbed energy as harmless heat. UV absorbers should absorb UV light in the 290 to 400 nm range but also be transparent to other radiation, i.e. be colorless in the visible spectrum. The amount of UV radiation absorbed is a dependent on the sample thickness and the absorber concentration and in practice high absorber concentrations are required to be effective, particularly in the surface layers where the majority of the UV radiation needs to be absorbed.

Typical UV absorbers are the hydroxyphenylbenzotriazoles and the hydroxybenzophenones. Carbon black is a good UV absorber but has obvious limitations because of the effect on color.

**UV stabilizers**

UV stabilizers work in a similar fashion to heat stabilizers and in many cases similar materials are used. They work by interrupting the photodegradation cycle to slow down or prevent the cycle from completing.

As with heat stabilizers it is possible to 'mop up' the free radicals using radical scavengers to produce another much less active free radical and slow the process down or to use a stabilizer to react with the hydroperoxide (ROOH) to produce inactive and stable products and break the cycle at the hydroperoxide propagation step.

In most cases a given plastic will incorporate a mix of stabilizers for UV and heat that is designed to work as a system to give the desired properties for the application. This mix will be designed for the specific plastic and application and will be designed to be applied at a specific concentration – over dosing stabilizers can in fact be detrimental to the plastic and the effect of the stabilizer.

## Testing for weathering

Testing for weathering is a complex process but one essential is that the testing must be carried out on the same plastic (compounded and processed) as is intended for the application. Testing using a pure plastic resin will give unrealistic results because the reactive products created during compounding and processing will not be present.

### Outdoor testing

Natural outdoor testing can be carried out in a variety of climates, e.g. hot dry Arizona testing or hot humid Florida testing. The major drawback of outdoor testing is that it takes a long time and ideally testing should be continued for the proposed application life of the product. While outdoor testing gives results for actual exposures it can sometimes be difficult to correlate the results achieved at a test site with the results that will be achieved in a different set of climatic conditions.

### Accelerated outdoor testing

It is possible to accelerate outdoor testing to reduce the time taken by concentrating the exposure to the solar radiation (EMMA and EMMAQUA). This will greatly reduce the time taken but again it can be difficult to correlate the results to varying locations and to account for the varying acceleration that is seen with various plastics.

### Laboratory testing

Pure laboratory testing involves using environmental chambers and artificial light sources such as Xenotest® and QUV® apparatus to approximately replicate outdoor conditions but with a greatly reduced test time under very controlled conditions. Laboratory testing can quickly assess the relative stability of plastics but has the major disadvantage that the quicker the test the lower the correlation to real behavior in the field.

Each test method has advantages and disadvantages in terms of control and time taken and it is common for a combination of tests to be carried out to determine the real response to actual field conditions.

## The effect of weathering

Photodegradation changes the physical and optical properties of a plastic relative to the initial specified properties. The most damaging effects are the visual effect of ‘yellowing’ and the loss of mechanical properties (from changes to the molecular weight and the molecular weight distribution).

### Yellowing

Many polymers, such as PVC, PS and PC, will suffer from yellowing when exposed to UV light for extended periods and this can result in the product becoming visually unsuitable for the application.

### Mechanical properties

Typical changes to mechanical properties caused by photodegradation are:

- Reduced tensile strength
- Reduced impact resistance
- Increased embrittlement and the possible creation of small surface cracks
- Chalking (particularly for PVC products)

The dominant mechanism of photodegradation and the degree of resistance to degradation depends on the application and the actual plastic concerned. Some families of plastics can be protected by the use of stabilizers. Others are difficult or impossible to protect against the mechanical damage induced by photodegradation, e.g. ABS can be made color fast but the mechanical properties will still suffer under the action of UV. For those plastics families where damage does occur then the property degradation can be both rapid and significant. Some families of plastics are inherently resistant to UV induced photodegradation and weathering and do not require additional stabilization, e.g. the fluoropolymers and PEI (Ultem®).

In general, the fluoropolymers processed by Zeus (such as PTFE, FEP, PFA, PVDF, THV, ETFE and ECTFE) have excellent inherent resistance to UV induced photodegradation because the exceptionally high bond strengths in the carbon - fluorine (C-F) bonds in the long chain backbone and the absence of UV absorbing structures or impurities. The energy required to break these bonds is generally not achieved by the UV radiation that reaches the earth's surface, i.e. it is below 290 nm cut-off caused by the earth's atmosphere. In particular, PTFE shows no deterioration after 30 years of continuous exposure in Florida.

## Summary

As a general rule the fluoropolymers do not require the use of additional stabilizers to protect them against UV induced photodegradation. As with resistance to thermal degradation, these polymers are amongst the best available for resistance to long-term UV induced photodegradation.

## Contact Us

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