RESINATE

UV PROPERTIES OF PLASTICS: TRANSMISSION AND RESISTANCE



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RESINATE

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INTRODUCTION

We are all no doubt aware of the main effect of ultraviolet (UV) radiation on ourselves. How many of us have ended up with a red face after a day out in the sun? Our skin is not the only organic structure to suffer from UV exposure. Organic polymers are also affected to varying degrees by exposure to sunlight (which includes ultraviolet radiation). There are many parameters that affect the level of UV exposure. Fortunately, there are several ways of providing resistance to the effects of UV exposure for both humans and polymer plastics.

UV RADIATION AND THE ELECTROMAGNETIC SPECTRUM

UV light is part of the electromagnetic (EM) spectrum. The EM spectrum is composed of waves produced by charged particles as they travel through air or space. EM waves at very short wavelengths (high frequencies) are referred to as electromagnetic radiation. EM waves at long wavelengths (low frequencies) are called electromagnetic fields. Visible light, the part of the EM spectrum with which we are all familiar, trends from red to violet in color as the EM wavelengths become shorter. Visible light, however, represents only an extremely small portion of the entire EM spectrum. Ultraviolet (*beyond* violet) light is higher in energy compared to visible light. UV is followed in energy by x-rays and gamma rays as the EM wavelengths become shorter (**Fig. 1**). It is the UV wavelength range, though, that possesses the energy that is of most concern regarding organic molecules found in polymer plastics and in living things.



A secondary worry regarding UV light and its effects is that because UV light emanates from the sun, it generally cannot be avoided. UV effects are also particularly related to the intensity of the exposure. Factors such as stratospheric ozone, clouds, altitude, the position of the sun (height; time of day and time of year), and reflection each play a role in the UV effects upon polymers. Elevated temperature and humidity additionally accelerate the effects of the UV radiation. The complexity of the effects is apparent when examining global UV exposures (**Fig. 2**).



THE MAIN EFFECTS ON POLYMERS EXPOSED TO UV

Effects of UV upon plastics notwithstanding, UV radiation has been grouped into three wavelength ranges based upon their characteristic biological effects (**Table 1**). For plastics, all types of UV radiation can cause a photochemical effect within the polymer structure. This effect can either be a benefit or lead to degradation of the material. Compared to our skin, for example, higher energy UVC is more likely to affect plastics. Despite extensive study, some of the mechanisms surrounding UV effects upon plastics are still not entirely understood. To this end, considerable efforts have been put forth towards manipulating UV effects to improve polymer properties as well as mitigate the degradative effects of UV light.

Table 1: UV Radiation Types		
DESCRIPTION	WAVELENGTH RANGE (nm)	COMMON EFFECT
UVA	320 - 400	skin tanning
UVB	280 - 320	skin burning
UVC	100 - 280	germicidal

Degradation

There are several obvious effects of UV light upon plastics. A primary visible effect of UV exposure is a chalky appearance of the plastic material. This effect is often accompanied by a color shift on the material surface. The surface of the plastic also becomes brittle. These effects are predominantly in the uppermost layers of the material and are unlikely to extend to depths greater than 0.5 mm (0.02"). However, stress concentrations caused by the highly brittle nature of some commodity plastics may well lead to a complete failure of the component.

UV effects upon plastics are not difficult to find in our everyday surroundings. Polypropylene (PP) monkey bars (also known as a *jungle gym*) found in a children's playground provide a good demonstration of UV effects. After a few years outside, the extruded pipes retain their full color, yet the injection molded clamp parts become white and cracked. Other examples where the effects of UV exposure can easily be seen include stadium seats, outdoor furniture, greenhouse films, window frames, and automotive parts. Thus, whether a plastic product will be used primarily indoors or outside becomes an important consideration.

Some plastics are exposed to much harsher radiation levels than those on earth. The Hubble Space Telescope (HST) and the International Space Station (ISS) are two prime examples. These orbiting facilities require plastics that can survive the demands of outer space. In these environments, there is no planetary atmosphere to filter out harmful rays from the sun, including UV light. Fluoropolymers such as fluorinated ethylene propylene (FEP) and polyimides like Kapton® are plastics which have been successfully used for HST and ISS applications. Plastics intended for unique UV environments should be evaluated for their performance in these settings before use.

Benefits

UV light can also be useful in certain applications. The photochemical effects of UV radiation upon polymers can result in improvements in the plastic material. Many of us benefit from UV radiation-cured protective polymeric coatings such as the polyurethane acrylates on the exterior of automobile components. A more local benefit for many people is the UV radiation in counter top purifiers or water coolers which are often assisted by the good transmission properties of FEP tubing and its ability not to degrade under UV exposure. Melt-processable FEP is also used as a protective coating on UV lamps for electric fly killers because the coating gives excellent light transmission (only about 4% loss for a 0.25 mm film). There are also many applications for UV curing of inks on plastic substrates. Not solely associated with plastics is UVC radiation. This comparatively shorter wave length (higher energy) UV light can be used for surface sterilization – including for some plastic components.

Another useful interaction of UV radiation and plastics is with fluorescent whitening agents (FWA). In natural light, many polymer products can seem to have a yellow appearance. By adding a FWA, the UV light absorbed is emitted in the blue region of visible light (400-500 nm wavelength) instead of in the yellow region. Compared to other additives, FWAs only need to be added in very small amounts, typically 0.01 - 0.05% by weight. UV light, thus, is not always destructive and can be manipulated to bring about desired effects.

INTERACTION OF UV RADIATION AND PLASTICS

So how does the energy of UV radiation get into the polymers and organic materials that it affects? UV radiation is absorbed by plastics (and living things) as photons – quanta of energy which can excite atoms, molecules, and more importantly - electrons. When sufficient UV energy is absorbed, free radicals – unpaired outer shell electrons of atoms – can be generated spurring a chain reaction within the polymer material leading to degradation. Fortunately, many pure plastics cannot absorb UV radiation, but the presence of catalytic residues and other impurities can act as receptors to cause degradation. Only a very small amount of impurity may be needed for degradation to occur. In polycarbonate, as little as trace parts per billion of sodium will initiate color instability. In the presence of oxygen, the free radicals form hydrogen peroxides that can break the double bonds of the polymer backbone chain leading to a brittle material. This process is often called photo-oxidation. However, in the absence of oxygen there will still be degradation due to cross-linking processes; this is the effect seen in plastic fasteners used on the HST and ISS. It is incumbent upon the user to understand the nature of their polymer plastic in addition to the presence of impurities or other fillers for UV environments where component failure could be catastrophic.

To help guide the use of plastics with respect to UV exposure, reference texts exist outlining recommended and discouraged materials. Unmodified plastics that are regarded as having unacceptable resistance to UV include polyoxymethylene (POM or acetal), polycarbonate (PC), acrylonitrile butadiene styrene (ABS), and nylon 6/6. Other plastics such as polyethylene terephthalate (PET), polypropylene (PP), high density polyethylene (HDPE), polyether sulfone (PES), poly(*p*-phenylene oxide) (PPO), polybutylene terephthalate (PBT); and nylons 6, 11, and 12 are regarded as fair with respect to UV tolerance. A PC/ABS alloy is also graded as fair. Good resistance to ultraviolet rays can be achieved from polymers extruded by Zeus such as polytetrafluoroethylene (PTFE), polyvinylidene difluoride (PVDF), fluorinated ethylene propylene (FEP), perfluorinated alkoxy alkanes (PFA), and polyether ether ketone (PEEK). The only plastics found with excellent UV resistance are the imides, polyetherimides (PEIs) and polyimides (PIs) such as those used on the HST. It is highly encouraged to consult a reference guide when selecting materials for components that may be exposed to UV light.

Many fluoropolymers have proven to be especially tolerant with respect to UV exposure. PTFE, for example, has particularly good UV resistance because of its very strong carbon-fluorine (C–F) bonds along its polymer backbone. These bonds are more than 30% stronger than the carbon-hydrogen (C–H) bonds that surround the C–F backbone which forms the helical structure of PTFE. Most fluoropolymers, too, do not have the light absorbing chromophore impurities in their structures that can act as initiators for photo-oxidation. These UV traits of PTFE as well as some other fluoropolymers make them attractive for outdoor use.

HOW TO AVOID UV DEGRADATION

There are several ways of avoiding UV degradation in plastics. Agents known in industry as UV stabilizers, blockers, and absorbers can mitigate the damaging effects of UV exposure. For many outdoor applications, the simple addition of carbon black (at about 2% by weight) will provide the protection for the plastic molecular structure by the blocking process. Other pigments such as titanium dioxide (TiO_2) – the same material found in sunscreen – can also be effective against UV radiation upon plastics. Organic compounds such as benzophenones and benzotriazoles are typical absorbers which selectively absorb the UV radiation and re-emit at a less harmful wavelength, primarily as heat (**Fig. 3**). Benzotriazole-type absorbers can be used at low concentrations (below 0.5% by weight) and have low color. For applications where the polymer plastic cannot be substituted, using a UV-mitigating agent can be a good alternative.



Another principal method to protect plastics against UV degradation is with a stabilizer. Hindered amine light stabilizers (HALS), usually derivatives of tetramethylpiperidine (TMP), are generally large complex molecules; they do not absorb UV energy (**Fig. 4**). Instead, they react with, or *scavenge*, the radicals that are formed from the absorption of photonic energy of other atoms within the polymer. In this way, HALS prevent further degradative reactivity of free radicals and stop the chain reaction. Another benefit of HALS is that they are usually regenerated giving them long chemical life and high efficiency.



In practice, various types of additives are used and frequently in combinations. These additives can be compounded into the original polymer to produce a special UV grade of plastic. In some instances, it may be preferable to add antioxidants to some plastics to avoid photo-oxidation. On the other hand, care must be taken that the chosen antioxidant does not act as a UV absorbent which would enhance the degradation

process. A final consideration for UV protecting additives is that they must not affect the plastic's properties in an undesirable way.

TESTING OF COMPONENTS

Weathering of components is most often associated with outdoor product use because of the exposure to UV light from the sun. There can also be similar UV radiation effects from indoor strip fluorescent lighting. For those applications, exposed surfaces should be resistant to UV degradation and adverse coloring. Intentional accelerated aging is a common technique for assessing long term damage with products exposed to artificial light from various sources. The exposure often takes place at an elevated temperature and can be cycled with periods of high humidity. Testing regimes such as these have become useful not only for selecting the best plastic for outdoor (or indoor UV) use but also for estimating plastic component lifetimes and maintenance requirements.

There are several standards which regulate the type and levels of illumination regarding plastics. ASTM D 2565, for example, addresses standards for xenon arc exposure of plastics for outdoor uses. Other guidelines (with abridged descriptions given) include ASTM D 4329 (fluorescent lamp), ASTM D 4459 (as for 2565 with Indoor Applications), SAE J1960 (automotive exteriors with xenon arc), ISO 4892-2 (xenon arc), and ISO 4892-3 (fluorescent). None of these protocols, however, gives a required standard for the properties of the exposed plastic product at the end of the exposure period.

Several major industries have derived their own criteria for assessing UV radiation effects upon plastic products. Weathering of Plastic Pipes (Report TR18/99) by the Plastic Pipe Institute, for example, warns of the large differences in environment regarding UV exposure for different locations in the USA. Another example is the standard for plastic lumber which states that the hardness of the outer skin must not have changed by more than 10% after 500 hours of exposure. There are also standards for UV exposure in indoor applications. This is especially relevant for plastics used in fluorescent light casings where their light spectrum contains UV wavelengths. An obvious UV-induced discoloration will result if a non-stabilized polymer is used. For certain applications or industries where there are no standardized property specifics regarding UV exposure, it may be useful for those entities to derive their own specifications.

SUMMARY

Sunlight is part of the electromagnetic (EM) spectrum which contains all wavelengths of EM radiation. Sunlight contains a UV component that may be detrimental to some plastics. For products that will be exposed to direct sunlight, designers and engineers must consider test standards for the products' performance which may be adversely effected or otherwise changed by UV exposure. To achieve the desired long-term product properties, appropriate polymer formulation must be determined at the outset. Additives to the polymer melt process can provide UV protection. For larger volume production, additives can be pre-compounded into the resin. Fluoropolymers such as FEP, PFA, PTFE, and other resins extruded by Zeus offer good UV resistance and generally do not require additives for UV protection. Choosing the right polymer and UV-mitigating agent can produce long-lasting plastic products even when exposed to UV light.

ABOUT ZEUS

Zeus is the world's leader in polymer extrusion technologies. For over 50 years, Zeus has been serving the medical, aerospace, energy exploration, automotive, and fiber optics industries. Headquartered in Orangeburg, South Carolina, Zeus employs approximately 1,800 people worldwide and operates multiple facilities in North America and internationally. You can find us at <u>www.zeusinc.com</u>.

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