

Effects of climate change and UV-B on materials †

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The outdoor service life of common plastic materials is limited by their susceptibility to solar ultraviolet radiation. Of the solar wavelengths the UV-B component is particularly efficient in bringing about photodamage in synthetic and naturally occurring materials. This is particularly true of plastics, rubber and wood used in the building and agricultural industries. Any depletion in the stratospheric ozone layer and resulting increase in the UV-B component of terrestrial sunlight will therefore tend to decrease the service life of these materials. The extent to which the service life is reduced is, however, difficult to estimate as it depends on several factors. These include the chemical nature of the material, the additives it contains, the type and the amount of light-stabilizers (or protective coatings) used, and the amount of solar exposure it receives. Concomitant climate change is likely to increase the ambient temperature and humidity in some of the same regions likely to receive increased UV-B radiation. These factors, particularly higher temperatures, are also well known to accelerate the rate of photodegradation of materials, and may therefore further limit the service life of materials in these regions. To reliably assess the damage to materials as a consequence of ozone layer depletion, the wavelength sensitivity of the degradation process, dose-response relationships for the material and the effectiveness of available stabilizers need to be quantified. The data needed for the purpose are not readily available at this time for most of the commonly used plastics or wood materials. Wavelength sensitivity of a number of common plastic materials and natural biopolymers are available and generally show the damage (per photon) to decrease exponentially with the wavelength. Despite the relatively higher fraction of UV-A in sunlight, the UV-B content is responsible for a significant part of light-induced damage of materials.

The primary approach to mitigation relies on the effectiveness of the existing light stabilizers (such as hindered amine light stabilizers, HALS) used in plastics exposed to harsh solar UV conditions coupled with climate change factors. In developing advanced light-stabilizer technologies, more light-resistant grades of common plastics, or surface protection technologies for wood, the harsh weathering environment created by the simultaneous action of increased UV-B levels due to ozone depletion as well as the relevant climate change factors need to be taken into consideration. Recent literature includes several studies on synergism of HALS-based stabilizers, stabilizer effectiveness in the new m-polyolefins and elucidation of the mechanism of stabilization afforded by titania pigment in vinyl plastics.

Introduction

Materials that are deleteriously affected on exposure to UV-B radiation include man-made polymers (plastics and rubber materials)^{1,2} as well as naturally-occurring biopolymers such as wood,³ wool⁴ skin proteins,⁵ and hair.⁶ Both natural, and man-made materials are widely used in the building industry; about a third of the plastics produced in Western Europe and in the US is used in building and agricultural applications. Some of the building products, for instance roofing materials, plastic or wood siding, window frames, glazing, water tanks, rain ware (gutters) and plastic conduit are routinely exposed to sunlight during regular use. Numerous plastic products exposed outdoors photodegrade slowly on exposure to solar radiation, steadily losing their useful physical and mechanical attributes. This degradation is accelerated by higher ambient temperatures and in some polymers by the presence of moisture and pollutants in the atmosphere. The use of plastics outdoors is feasible only because of the use of efficient photostabilizers designed to slow down this degradation process. A large body of information exists on stabilizer technologies aimed at extending the service life of plastics exposed to outdoor environments.

Stratospheric ozone depletion and the ensuing increase in UV-B levels in terrestrial sunlight will tend to reduce the service life of plastic products used outdoors. With concurrent global warming, the service lifetimes of plastics are likely to be further affected as higher temperatures generally accelerate the chemical reactions responsible for the photodamage.^{2,7} The predicted average increase in ambient global air temperatures due to global warming (1.4 to 5.8 °C above 1990 values by 2100⁸) is not expected to unduly accelerate the degradation of plastics or wood. Yet, the effect could be significant at locations with higher extreme temperatures. Also, the surface temperatures of materials exposed to direct sunlight are often much higher than the surrounding air due to heat build-up.⁹ As the relationship between the rate of degradation reactions and temperature is exponential, even a small increase in the temperature of an exposed plastic surface, already at a high temperature, can result in very significant increases in the rate of the photo damage.

In regions where climatic changes caused by global warming result in higher rainfall or humidity, the situation is even further exacerbated. In both wood¹⁰ and moisture susceptible plastics,^{11,12} photodegradation can be significantly accelerated by the presence of high humidity, particularly at the higher temperatures. The effect is well documented and higher temperatures and humidity are routinely used to accelerate the photodegradation of plastics and rubber in laboratory exposure tests.

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The geographic distribution of these modifying influences of temperature and humidity has not been fully investigated. Higher ambient temperature and rainfall due to climate change are expected in some of the same geographical regions likely to experience higher UV-B radiation. Regions that would experience particularly harsh exposure conditions, however, would include developing regions of the world that rely particularly heavily on wood and plastics for construction. Wood remains the primary material of residential construction in many parts of the developing world. Also, high volume users of plastics include many developing countries. For instance, China is presently the second largest producer of plastic resin in the world with 19 million tons produced in 2000.

Maintaining the service life of plastics products used outdoors at the same level despite harsh UV-environments due to ozone depletion and contributing climatic conditions may be possible with a combination of strategies. The use of higher concentrations of conventional UV stabilizers or the development of novel highly efficient UV-B stabilizers is the most likely response of the plastics industry. The use of surface protection, particularly in the case of wood, and substitution of materials with better UV-resistant grades of plastics, are also available strategies. These, however, add to the cost of the plastic products and in some markets can potentially affect the competitiveness of plastics as a material. A critical question, however, is whether the available photostabilizer technologies will function adequately with spectrally altered sunlight due to the stratospheric ozone loss. Materials substitution with more UV resistant plastics is feasible and candidate plastics are available for the purpose but at a significant cost. In the case of wood surfaces, paints or coatings as well as UV-B stabilizers present a feasible mitigation strategy.¹³ While some success has been reported recently for the surface modification of wood to improve UV stability,^{8,14} this is a more expensive and less satisfactory option.

A good assessment of the potential impact of stratospheric ozone depletion on the lifetimes of materials and the available strategies for mitigation requires key research information on at least the common polymers and wood. Of particular interest are: a) estimates of the increase in UV-B content expected in sunlight as well as the temperature/humidity variations due to global climate change; b) reliable wavelength sensitivity data and the dose-response relationships in the photodegradation of common polymers; and c) data on the efficacy of available UV stabilizers under spectrally altered sunlight conditions.¹⁵ The data presently available on the topic is inadequate for a reliable assessment, but additional information is slowly being published in the literature.

Recent findings

Wavelength sensitivity of photodegradation

It is important to quantify the relationship between the wavelength of UV radiation and the efficiency of degradation for common polymers. This would allow the estimation of damage to these materials under different UV environments (corresponding to various geographic locations or to different ozone-depletion scenarios) and help in the design of new light stabilizers. Published data on the wavelength sensitivity for the degradation processes in common polymers have been reviewed in recent years.¹⁶ Data are presently available for a range of common materials (including polyethylene, polypropylene, poly(vinyl chloride) (PVC), polycarbonate, polystyrene), mechanical pulp (wood), wool, human hair, and skin proteins. The general relationship between the wavelength of UV-B radiation and the efficiency of photodamage for these materials is not linear. The degradation per available unit of UV radiation decreases exponentially as the wavelength of the UV radiation increases.¹⁷ Given the high efficiency of photodamage, even

small increases in UV-B content in sunlight can potentially result in marked increases in the rates of photodegradation in common polymer materials.

An important observation is that during processing, the plastics resin is mixed with a number of other chemicals (collectively referred to as additives) to impart key properties to the plastic material. For instance, the photostabilizer additives impart UV stability to the resin; other additives such as lubricants, fillers or heat stabilizers are used to obtain different properties. However, some of these additives can also alter the UV susceptibility of the material. Therefore, the more valuable wavelength sensitivity information is that pertaining to plastics materials that have the same composition (in terms of additives and stabilizers in the formulation) as the products of interest.

In the last few years, several publications have augmented the available information on wavelength sensitivity of polymeric materials. Two such studies focused on acrylic plastics¹⁸ used in construction applications while another addressed the UV-induced damage to collagen¹⁹ a key protein in human skin. Another, reported on the light-induced yellowing of mechanical pulps exposed to solar UV wavelengths.¹⁷ The exposures were carried out at selected ultraviolet wavelengths between 270 and 400 nm and chemical changes indicative of degradation were monitored. The findings were consistent with data trends well established in the literature and summarized above. In a study on polyether-polyester elastomers, Nagai *et al.*¹² found UV-B wavelengths to be responsible for the chain-scission type damage that deteriorates the strength and elasticity of the material. Another important study was on light-induced damage to polystyrene plastics compounded with a flame retardant additive¹ that reduces the risk of fire when the plastic is used as building construction materials. Interestingly, this additive also acted as a catalyst accelerating the photodamage. Also, the waveband that resulted in the most efficient degradation shifted from UV-B into the UV-A when the flame retardant was used as an additive. An additive that shifts the most effective waveband to UV-A is generally undesirable. Although the longer UV-A wavelengths are not affected by stratospheric ozone depletion, the relatively higher fraction of UV-A, compared to UV-B, in terrestrial solar radiation is likely to increase the amount of photodamage. A drawback in these experiments on wavelength sensitivity is that the studies were generally carried out at ambient temperature and humidity.

New light stabilizers and materials

The hindered amine light stabilizers (HALS) are presently the most effective class of stabilizers available and are used particularly in polyethylene and polypropylene products intended for outdoor use. Other classes of light stabilizers such as ultraviolet absorbers are also used with plastics, particularly the aromatic polymers. The harsh exposure conditions where the spectral content of sunlight has a larger UV-B component, and the ambient temperature and/or humidity is higher, generally indicates a higher concentration of the stabilizer to be used in the plastic. Also important are effective thermal stabilizers used to protect plastics from degradation during processing. Without these, high temperature processing can introduce chromophore species into polymers making them more susceptible to photodegradation.

HALS are relatively expensive additives and are used at a low concentration (0.1 to 0.2 percent in polyethylenes in mulch film applications). The protection from light-induced damage afforded by HALS is reported to increase linearly on its concentration in the plastic (up to about 0.6 weight percent).²⁰ While reported data on the issue are limited, it is likely that these stabilizers work well under a variety of different temperatures and humidity. Very little work has been done on their effectiveness and their own stability²¹ in harsh UV environments (*i.e.* in sunlight with a higher than normal fraction of UV-B or that

containing shorter than expected wavelengths of UV-B radiation).

Recent studies do not directly address the issue of performance of stabilizers under altered sunlight conditions, but discuss how the optimum protective capacity of conventional HALS stabilizers might be exploited. Synergistic mixtures of HALS have gained increasing importance for UV stabilization of polyolefin. Synergism or antagonism between two HALS was detected by evaluating a single combination of the two HALS in propylene.²⁰ The mechanism involved, however, was not fully elucidated. The synergy depended on the particular combination of HALS and on the type of polyolefin. Similarly, combinations of UV absorbers (an oxanilide with benzophenone or benzotriazole or a hydroxyphenyltriazine) were reported to be systematically synergistic in both polyethylene and polypropylene.²² Combinations of oligomeric stabilizers with photostabilizer moieties (such as HALS) and heat stabilizer have also been tested for possible synergism.²³ While synergistic protection from photodamage was not obtained for these, some mixes showed synergistic heat stabilization in polypropylene. Other promising novel light stabilizer systems, not presently in commercial use, such as HALS reacted with pyrenes,²⁴ triazines, selenium, and selenium–triazine^{25,26} were recently studied for their potential as light stabilizers in polypropylene. While these are for the most part exploratory studies, research on fully exploiting the capability of HALS and attempting to develop even better stabilizers is an important undertaking.

With most of the 23 million tons of vinyl plastics (PVC) produced globally each year being used outdoors, and developing nations reporting an increasing demand for the material for building, their light stabilization is of particular interest. This plastic uses titania pigment (rutile titanium dioxide) as an opacifier at 10–13 weight percent in compositions meant for outdoor use in the US. The pigment absorbs UV-B radiation in sunlight and reflects visible wavelengths making it a good photostabilizer. The mechanism of protection of PVC with titania pigment was recently investigated with special emphasis on the role of water in promoting oxidative degradation.²⁷ The study compared the stabilizing effectiveness of nanocrystalline rutile powder, an anatase white pigment, and a photoactive as well as photostable grades of rutile pigment in PVC.

Using better UV-resistant varieties of plastics is an important strategy to mitigate the effects of increased UV radiation in sunlight. Metallocene-catalysed plastics (m-plastic) are slowly beginning to replace conventional polyolefins in several key applications within the last few years. The stabilizer effectiveness of existing UV stabilizer systems with the new m-polyolefins was recently reported.²⁸ The compatibility of the UV stabilizers at the concentration most commonly used in plastic film products, was found to be the same for both conventional polyolefin and the m-polyolefin. Furthermore, the synergism between two polymeric HALS reported earlier for conventional polyolefins is also found to be applicable to m-polyolefins. The main difference reported so far between the conventional and m-plastics is a small but systematic increase in lifetimes with m-plastics relative to conventional plastic, for the HALS-stabilized polyethylenes. This was reflected in the better weatherability of m-polyethylene relative to that of conventional polyethylene, in outdoor exposure studies.²⁹ These observations are important in that they suggest that the trend towards the metallocene plastics with better characteristics, does not involve a compromise on the UV-stability of the material.

Influence of temperature on UV-induced effects

The outdoor degradation of common thermoplastic materials as well as the materials for construction such as wood, or even biopolymers like collagen (making up nearly a third of the body protein in mammals) is often the result of a combination of

factors acting together. While the most important of these is the solar UV radiation, factors such as the temperature of the material and the presence of moisture shows a considerable synergistic effect on the photodegradation of materials. This is illustrated in Fig. 1.

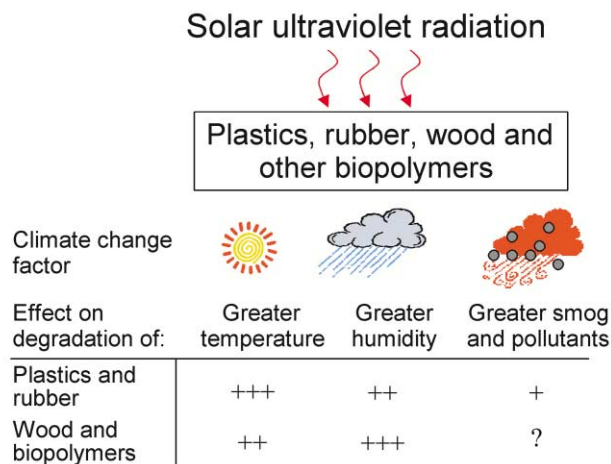


Fig. 1 The anticipated effects of climatic change factors on the degradation of materials by solar ultraviolet radiation. The + symbols indicate the amount of published research data showing climatic factors to increase UV-induced degradation. +++ = high, ++ = moderate, and + = low.

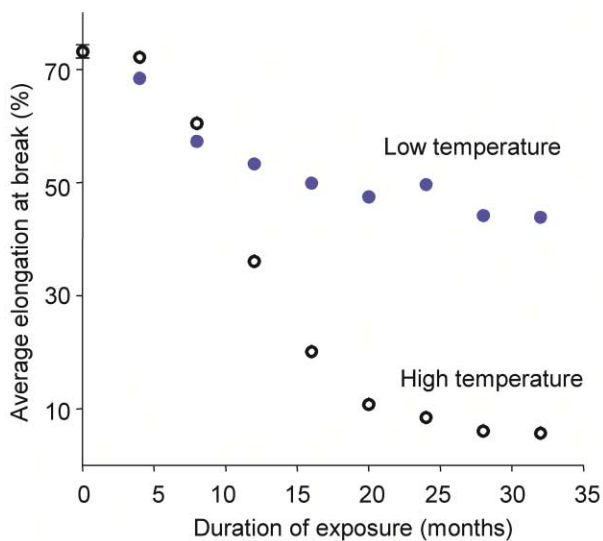
This suggests that the increase in ambient temperatures pursuant to global warming could play an important role in enhancing the rates of photodegradation in materials exposed to sunlight with higher levels of UV-B radiation. Global warming is also expected to alter rainfall and humidity in some locations, leading to longer periods of time where the material is in contact with moisture. A possible minor influence might be due to increased volatile organic compounds, VOC, emissions and NO_x/SO_x releases that would increase the tropospheric ozone levels. The NO_x/SO_x species as well as smog ozone are well documented to promote UV-induced oxidative damage of common plastics.³⁰ The oxidative damage caused by even very low levels of ozone in the atmosphere, particularly in rubber products³¹ is well documented; antiozonant additives are used in the industry to control this problem. In assessing damage scenarios associated with stratospheric ozone depletion as well as in evaluating measures available for mitigation of increased damage to materials due to increased UV-B levels, it is crucial to consider the modifying influence of climate change as well.

In a recent study,³² the weathering of polyethylene agricultural mulch films under high-UV outdoor exposure conditions at ambient temperature and at 25 °C inside a controlled temperature UV-transparent chamber, was compared. Under ambient conditions, in Dhahran (Saudi Arabia), the surface temperature of the plastic rose as high as 60 °C depending on color and thickness, because of the absorption of solar IR wavelengths. The average elongation at break of the polyethylene was periodically measured; this property is particularly sensitive to degradation in this type of material. The rate of light-induced breakdown of the polyethylene under comparable UV exposure was slower by a factor of four when the temperature was controlled at the lower temperature of 25 °C. The enhancing effect of temperature on degradation is generally the case with common plastics as evidenced by the low activation energies reported for the degradation processes.

A similar experiment was completed over a nearly-3 year period of exposure for 200-micrometer polycarbonate film, a plastic used in glazing applications because of its clarity and strength. As illustrated in Fig. 2, the rate of photodamage (measured in terms of loss in the elongation at break) was markedly lower when high temperature was excluded from the

Table 1 Loss in average elongation at break (percentage) in commercial polycarbonate sheets on exposure outdoors under different conditions

Exposure conditions		0 months	15 months	29 months
1	Ambient UV radiation Ambient temperature	73.2	36.1	6.5
2	Reduced UV radiation (white film) Ambient temperature	73.2	57.5	56.3
3	No UV radiation (black film) Higher temperature	73.2	65.4	64.3
4	Ambient UV radiation 25 °C temperature (in chamber)	73.2	54.0	49.7

**Fig. 2** The loss in the elongation at break for Lexan® polycarbonate sheets on exposure to solar radiation under desert exposure conditions at high ambient temperature (open symbols) and at 25 °C (closed symbols).

test environment. The increase in ambient temperature as a result of global warming will be much smaller than the temperature differences between the two sets of samples referred to in the figure. Yet, at least in locations experiencing extremes of temperature change, a measurable change in service lifetimes of outdoor plastics might be expected.

Table 1 compares the values for the average elongation at break of commercial polycarbonate sheets (200 micrometers in thickness) exposed outdoors under different conditions. The location of exposure, Dhahran (Saudi Arabia), receives about 180 kilolangleys of sunlight annually. The average temperature in summer is about 40 °C (with extremes of up to 60 °C recorded) and the average humidity is 60–90 percent. The control samples were exposed to sunlight outdoors while the test samples were exposed to sunlight at the same location but in a UV-transparent chamber maintained at the lower temperature of 25 °C and 50–60 percent humidity. The dramatic difference in the elongation at break of samples 1 and 4 is attributed to the enhancing effect of temperature under the same UV exposure. Also included in the Table are two other sets of samples both exposed under ambient conditions outdoors, but wrapped in either a black or a white 6 mil thick plastic film. The black film blocks out all UV (and visible light) but maintains the sample at an even higher temperature than the control sample. This is a result of the absorption of solar infrared radiation in sunlight by the black film. The white film cut down most of the UV radiation, but maintained the sample at about the same temperature as the control sample. Of the two, the sample wrapped in black film degraded slower despite the higher sample temperature (see Table 1), illustrating UV to be the dominant influence in bringing about degradation.

Influence of moisture on UV-induced effects

The presence of moisture can unexpectedly accelerate the degradation of polymers stabilized with titanium dioxide. Vinyl (PVC) extruded profile used in siding for instance, routinely uses this pigment to maintain light stability during outdoor use.

A recent study²⁷ found that neither the anatase nor rutile form of this pigment catalyzes photodegradation of the plastic under dry conditions when exposed to simulated solar radiation. But these pigments catalyzed the loss in surface gloss of the PVC (a practically relevant property) when exposed to UV radiation in the presence of moisture, illustrating the importance of moisture in promoting light-induced degradation. Another important consideration is that under high humidity soluble photostabilizers might leach out of the plastic matrix, reducing the effectiveness of the light stabilizer and leading to shorter service life. The presence of high humidity, particularly at the higher temperatures tends to increase the photodamage in polymers such as thermoplastic polyester elastomers.¹²

The accelerating effects of humidity on the UV-induced damage to wood is well known.^{10,33} This is true of changes in surface chemistry, color, and lignin content of the 80–100 micrometer layer through which UV radiation is able to penetrate into the wood. However, with plastics or wood³⁴ exposed simultaneously to both UV radiation and moisture, damage due to the radiation was clearly the dominant short-term effect. However, once the surface of wood has become more hydrophilic and oxygenated as a result of photodamage it becomes increasingly more accessible by microorganisms capable of biodegrading the wood. Common types of plastics are essentially non-biodegradable and therefore not affected by any biotic mechanism.

Conclusions

Damage to synthetic and biopolymer materials on exposure to solar radiation depends on the susceptibility of the polymer to solar UV wavelength as well as on the complexity of the weathering environment to which it is exposed. With common plastics products the inherent photodegradability of the polymer is an important factor, but the magnitude of damage is determined by the extent of processing used in the manufacturing of the product, as well as by the types of additives used in the plastics composition. The same polymer could potentially be compounded differently to have a range of different UV stabilities. However, the spectrally altered, UV-B enhanced, solar radiation that might be obtained consequent to disruption of the ozone layer, will consistently reduce the service life of these plastics relative to that under present-day sunlight environments.

The degradation potential of any UV-B environment is enhanced at higher temperatures and possibly at high ambient humidity. Changes likely to be associated with global warming are therefore expected to increase the propensity of plastic products to undergo solar UV radiation-induced degradation. This is even more so for natural materials such as wood that are porous and hydrophilic. Shortening of the outdoor lifetimes of wood and plastics used in construction can place a significant economic burden on developing regions of the world. In considering stabilization technologies it is therefore important to develop and evaluate systems that not only function under UV-B rich solar radiation environments, but also are effective under expected temperature and humidity conditions.

In mitigating the effects of increased UV-B content in sunlight on materials damage, the industry is likely to rely heavily on the use of both conventional and improved photostabilizer systems. Recently reported improvements in

synergistic mixtures of stabilizers for polyolefins and studies to better understand the stabilization mechanisms for commodity thermoplastics, are therefore encouraging in this regard. The reports on newer metallocene plastics with superior properties that can be stabilized with conventional stabilizers are also interesting for the same reason. However, the additional cost of these mitigations, especially in relation to the regions where plastics are heavily used has not been adequately assessed.

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