



Cite this: *Photochem. Photobiol. Sci.*, 2015, **14**, 170

Consequences of stratospheric ozone depletion and climate change on the use of materials

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Materials used in the exterior of buildings and in construction are routinely exposed to solar UV radiation. Especially in the case of wood and plastic building materials, the service life is determined by their weather-induced deterioration. Any further increase in ground-level solar UV radiation, UV-B radiation in particular, will therefore reduce the outdoor service life of these products. Any increase in ambient temperature due to climate change will also have the same effect. However, the existing light-stabilizer technologies are likely to be able to mitigate the additional damaging effects due to increased solar UV radiation and maintain the outdoor lifetimes of these materials at the present levels. These mitigation choices invariably increase the lifetime cost of these products. A reliable estimate of what this additional cost might be for different products is not available at the present time. Personal exposure to UV radiation is reduced both by clothing fabrics and glass windows used in buildings and automobiles. This assessment describes how the recent technical advances in degradation and stabilization techniques impact the lifetimes of plastics and wood products routinely exposed to solar UV radiation and the protection to humans offered by materials against solar UV radiation.

Received 20th October 2014,
Accepted 20th October 2014

DOI: 10.1039/c4pp90038c

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Introduction

Wood and plastics are used extensively as construction materials. Of the 280 million tons of plastics produced globally [2011 data], about 23% is used in building construction, the second largest market for plastics after packaging applications.¹ Rigid poly(vinyl chloride) [rPVC] is the dominant plastic used in building applications. Polymers are also used extensively in architectural and industrial coatings. Wood is used widely in building construction, often as the principal structural element. Annually, ≈ 1.8 billion m³ of industrial roundwood [all industrial wood in the rough] is harvested worldwide. Materials for construction used in exterior applications require long-term durability that is delivered by stabilized plastics and coated or treated wood.

Some of the materials used in agricultural and transportation applications are also regularly exposed to solar radiation, rain, and pollution but are expected to have service lives that span several decades. Those used as coatings on automobiles or on aircraft exteriors in particular are exposed to

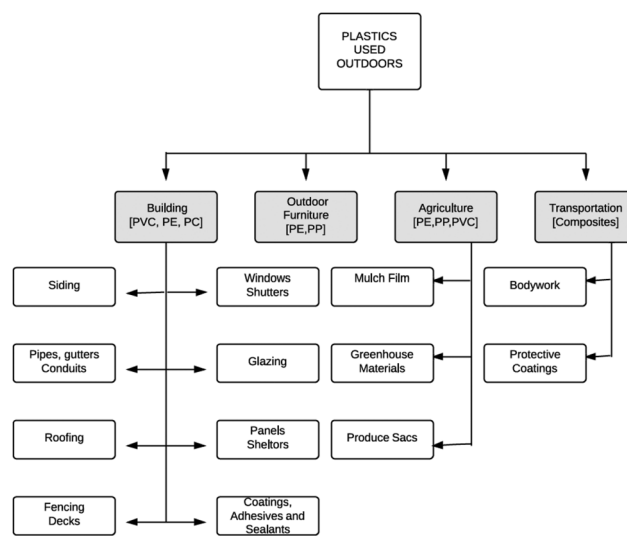


Fig. 1 Uses of plastic materials in outdoor applications. PE = polyethylene; PP = polypropylene; PVC = poly(vinyl chloride); PC = polycarbonate.

high heat and UV radiation fluxes on a routine basis. Their outer clear-coat layers responsible for finish and gloss is often compromised by exposure to UV radiation. Fig. 1 shows the main uses of plastics in outdoor applications.

Plastics and wood absorb solar UV radiation and are inherently susceptible to damage, especially at high ambient

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temperatures. The primary cause of weathering damage to wood and plastics is from solar UV-B radiation that is efficiently absorbed by chromophores generally present in these materials. High humidity, temperature, and pollutants in air often accelerate light-induced degradation. With plastics, the damage ranges from uneven discoloration or surface changes to cracking and loss of material strength.² With wood products, weathering degradation also renders the surface hydrophilic, facilitating subsequent moisture absorption and surface biodegradation.³

Depletion of the stratospheric ozone layer to any extent increases the fraction of UV-B (290–315 nm) in the solar radiation reaching the Earth's surface. Potential latitude-dependent increases in UV-B radiation can significantly shorten the service life of wood and plastics used outdoors, especially at locations where the ambient temperatures are relatively high. Levels of UV radiation are expected to decrease globally in the decades ahead (see Bais *et al.*⁴), but there is still concern about its impact on materials due to the interactive effects with climate change. Climate change is widely expected to result in an increase in the average global temperature by 1.1–6.4 °C by the end of the century and there is an international effort to keep the increase under 2 °C.⁵ Any increase in ambient temperatures exacerbates the damage as weathering reactions in both wood and plastics proceed at faster rates at the higher temperatures.⁶ Intrinsic factors such as additives or impurities of trace metals (including pro-oxidant additives to make the plastic photodegradable)⁷ also tend to accelerate the rate of light-induced photo-damage to both classes of materials.

The use of efficient UV stabilizers in compounding of plastics and effective surface coatings or treatments of wood, allows them to be successfully used in long-term outdoor applications such as in cladding, panels, fencing, or decking. Even at concentrations as low as <0.1% by wt, light stabilizers, such as the Hindered-Amine Light Stabilizers [HALS] can control light-induced damage in plastics to yield service lives of several decades. Existing stabilizer and coating technologies are likely to be able to mitigate additional damaging effects from small potential increases in UV-B radiation in the solar spectrum reaching the Earth.⁵ Either greater concentrations of stabilizers in plastics or the use of more efficient surface treatments for wood will have to be employed to mitigate these effects. Intensive industrial research effort is focused on discovering better and lower-cost light stabilizers for specific classes of plastics used in building⁸ and improved surface coatings for preserving wood against weathering. New materials, additives or new variants of existing plastics that are more weather-resistant emerge in the marketplace regularly.

Polymeric materials are also used to protect humans against exposure to solar UV radiation. These include clothing made of synthetic fibers and plastic glazing used in buildings (and vehicles) to filter out the UV radiation. The effective use of these limits exposure and therefore the adverse health impacts of UV radiation on humans. This paper assesses the relevant literature published since the last report in 2010.

Plastics use in building

Unlike with biota, that may show a limited capacity to adapt to increased UV-B radiation levels and where evolution of new traits is relatively slow, man-made materials can be designed to withstand new, harsher, solar UV radiation environments. Plastics, for instance, can be formulated with either greater levels of conventional stabilizers or more efficient novel stabilizers, to ensure a minimal loss in their service life. A substitution of materials with different, more UV-resistant classes of plastic or non-plastic material is a second strategy. Surface coatings and modifications of wood can also be designed for better resistance to solar UV radiation. However, invariably, it is the economics of their use that will dictate the specific mitigation strategy adopted. Regardless of the technology choice, it will inevitably add to the lifetime cost of using either class of materials.

Durability of materials outdoors is determined primarily by the dose of solar UV radiation, especially the proportion of UV-B radiation the material will be exposed to. As the dose of UV-B is latitude and altitude dependent, the durability of a given material will vary widely with the geographic location. The certified lifetime for a plastic material assessed at one location cannot be assumed to be the same for another with a different UV environment. Global UV-A and UV-B radiation maps (for Nov. 1, 1978 to June 30, 2000) estimated from TOMS data, corrected for the effect of cloud,⁹ (Fig. 2) illustrates the wide range of UV-B radiation environments encountered at different locations around the World. However, these must be viewed with caution. Firstly, they are generally based on data

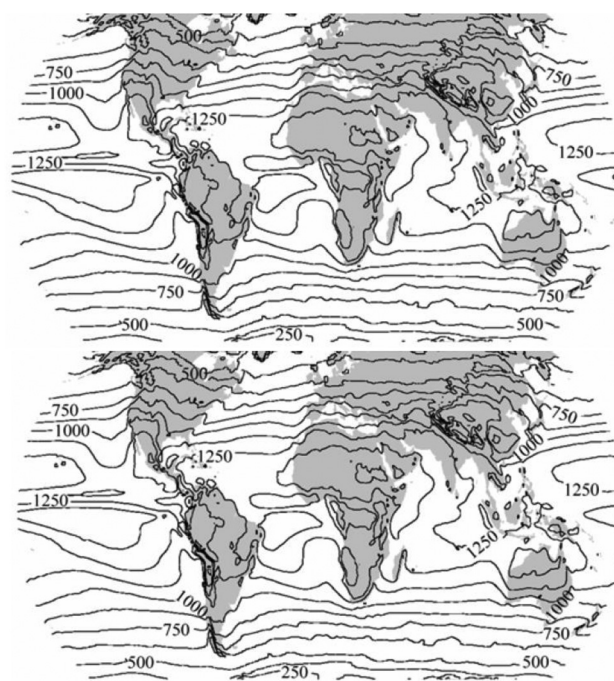


Fig. 2 A global map of the annual un-weighted mean dose of UVA (above) and UVB (below) in units of $\text{kJ m}^{-2} \text{day}^{-1}$. Reproduced with permission from Lee-Taylor.⁹



from a single satellite overpass each day, and amounts of cloud at that time may not be representative of a true average. Secondly, satellite estimations of UV tend to be too high under polluted conditions.⁴

The main uses of plastics in building construction include plastic pipes, siding, windows, soffit, fascia, rainwater goods and decorative panels and a majority of these are made of rigid PVC (rPVC). In fact, 76% of the PVC produced globally is used in the construction of buildings. The most popular cladding in residential housing in North America is rPVC siding produced by a profile extrusion process. In this application, the useful lifetime of the product is generally determined by uneven discoloration and loss of impact strength from photo-damage by solar UV radiation.

Polycarbonate [PC] glazing used in architectural window panels as well as continuous windows and domes is similar to or better in performance than the conventional glazing in several characteristics.¹⁰ One important advantage of these is their lower thermal conductivity, k , relative to glass. The value of k for PC glazing panels are as low as 1.2–1.9 W m⁻² (25 mm thickness), but new technology such as PC/aerogel composites¹¹ can bring this value down to 0.5 W m⁻² (25 mm section). In these products as well, discoloration induced by solar radiation, determines their useful lifetime.

The present push towards sustainable materials in construction has led to some reassessment of the use of PVC materials in buildings.¹² Despite its dominance in the building sector and excellent performance in construction, PVC is perhaps the worst choice of a plastic in terms of environmental merit.¹³ Not only does the production of PVC result in potential emission of toxic monomers and precursors to air but it is also compounded into soft products with phthalate plasticizers that are potent endocrine disruptors. Nevertheless, no imminent move away from its use in buildings is apparent. Alternative plastics that can replace PVC in construction such as polyolefins are available, but at a greater lifetime cost. The susceptibility of these alternatives to solar UV radiation will also influence their lifetime costs.

PVC in building and construction

Improvements in rigid PVC technology aimed at making it more environmentally acceptable, better performing, and with lower lifetime costs, are being made on a continuing basis. In the face of competition from alternative materials, PVC technology has advanced considerably. The lighter micro-foamed PVC siding¹⁴ and the emerging (polystyrene) foam-backed PVC siding with greater insulation efficiency are examples of such improvements.

Most of the PVC products are processed as extruded profiles. Recent introduction to the market of a new processing aid¹⁵ as well as an acrylic impact modifier¹⁶ for PVC extrusion products (in profile, window, and siding applications) is a significant improvement in the technology. The new additives allow PVC to be extruded at a lower temperature with reduced risk of degradation and atmospheric emissions. On heating, PVC breaks down emitting hazardous corrosive HCl gas

making it difficult to process. Typically, either tin-based or lead-based heat stabilizers are used to allow thermal processing of rPVC. A new thermal stabilizer¹⁷ with a lower tin content (19%) was recently commercialized for use in the same types of PVC products used in building. Improved processibility and superior thermal stabilization of PVC are afforded by the use of new stabilizers, which also are claimed to impart superior weatherability to the plastic material. Lower thermal degradation during processing improves the service lifetimes of rPVC products as it reduces the buildup of UV-absorbing functionalities in the polymer. No long-term UV-stability data for PVC compounds that incorporate these newer additives are as yet available. However newer tin-maleate stabilizers effectively control yellowing due to weathering of the material. Other manufacturers¹⁸ have also introduced their own novel PVC additives for the same set of building products.

The solar UV-B-induced degradation of rPVC is catalyzed by ZnO used as a filler in the plastic.¹⁹ The findings have implications only in the management of plastic waste as outdoor PVC products are generally formulated to be resistant to UV radiation. The wavelength sensitivity and activation spectra for typical injection molded rPVC formulations are known. Similar data for solvent-cast sheets of PVC, manufactured for graphic arts applications, were recently published and the merit of the material as a UV dosimeter discussed.²⁰ The data on wavelength sensitivity as well as activation spectra determined for solvent-cast plastic generally agreed with those already published for injection molded rPVC.^{21,22} This shows that the wavelength sensitivity of these materials is governed primarily by the nature of the polymer rather than the additives or processing-related factors. In accelerated weathering of plastics under laboratory conditions, it is essential to use a light source with a spectrum similar to that of sunlight. For example, mercury vapor lamps cannot be used as a substitute for a xenon source.²³ Recent advances in PVC technology have contributed to improved service lifetimes of the material exposed to solar UV-B radiation and the anticipated effects of climate change.

Wood-plastic composites

The 2010 global market for wood-plastic composites (WPC) was 2.3 million tonnes and, given the short-term projected growth rate of 13.8%, per year this is expected²⁴ to grow to 4.6 million tonnes by 2016. WPCs are essentially thermoplastic composites (of PE, PP, PVC, and polystyrene (PS)) highly filled with powdered wood. Often, post-consumer plastics are used in their manufacture. Embedding wood fibers in a polymer matrix restricts absorption of moisture and hence avoids fungal growth and biodegradation of the wood fraction.²⁵ A higher-grade product results when a single type of plastic such as virgin PP is used^{26,27} and the compounding and/or processing operations are carefully controlled²⁸ to obtain good dispersion of the wood filler.

To improve miscibility of the hydrophilic wood and hydrophobic plastics in fabricating WPCs, compatibilisers are often employed.^{29,30} Good adhesion between the phases was



reported, for instance, with maleic anhydride grafted PE and PP.^{28,31} A continued search for good adhesion-promoters or compatibilisers for specific wood/plastic systems is critical for future growth of this technology. Alternatively, the wood fraction can be chemically functionalized (e.g., acetylated;³²) for better compatibility. Low processing temperatures (<200 °C) have to be used in processing WPCs because the wood component can otherwise thermally degrade. However, WPCs based on waste plastics and wood powder can be processed using conventional equipment into “plastic lumber” that can be handled and worked on using tools designed for wood. WPC is promoted as a ‘green’ (environmentally friendly) material as it uses waste wood and often post-consumer plastics as well.^{33–35}

Lignin in the wood fraction of WPC absorbs solar UV radiation and undergoes photo-degradation³⁶ leading to delignification of the wood particles at the surface of the WPC material.³⁷ Photodegradation is reported to cause discoloration and breakdown of the filler in PP/wood³⁸ and PE/wood WPCs.³⁹ These changes render the surfaces hydrophilic, encouraging fungal growth, and biodegradation of the cellulose rich tissue.⁴⁰ Absorption of water by wood particles under freeze–thaw cycles causes swelling/shrinkage of the fibres that also destabilizes WPC creating voids or empty spaces in the matrix. These recent findings on WPC parallel that which is already known of the mechanisms of degradation for wood species. Understanding all the degradation pathways involved for WPCs is critical to developing better UV-B stabilizers for the material. The main advantage of WPC is that hydrophilic wood fibres that absorb water and are prone to biodegradation are embedded in plastic protecting them from solar UV radiation and environmental biodegradation.

The color, mechanical properties and durability of WPCs vary with the species of wood fiber used. For instance, in WPCs made of high density polyethylene [HDPE] with Douglas Fir and HDPE-hybrid Poplar wood discolored the least (>15%) on exposure to solar-simulated radiation (xenon lamp) compared to HDPE composites with wood species such as White oak and Ponderosa pine.³⁹

As expected, the plastic component of WPC also undergoes light-induced degradation. Of the common thermoplastics used in WPCs, polystyrene⁴¹ is the most susceptible. There is some evidence that the presence of wood in PVC-based WPCs may also promote photodegradation of the plastic matrix.⁴² Naturally, the same light stabilizers used with plastics are also effective in protecting WPCs; for instance, the use of HALS stabilizers in wood-HDPE^{42,43} and light absorber (benzotriazole type) in wood-PVC⁴⁴ composites have been successful. The extent of protection afforded depends on the level of the stabilizer and its dispersion in the polymer matrix.⁴⁵ Whether there is an advantage in using a single stabilizer known to be effective in both wood and plastics, to protect WPC is not clear at this time.

Fig. 3 shows the effect of brown-rot fungi acting on a sample of WPC biodegrading the particles of wood exposed at the surface of the composite. A thin layer of plastic (or a cap

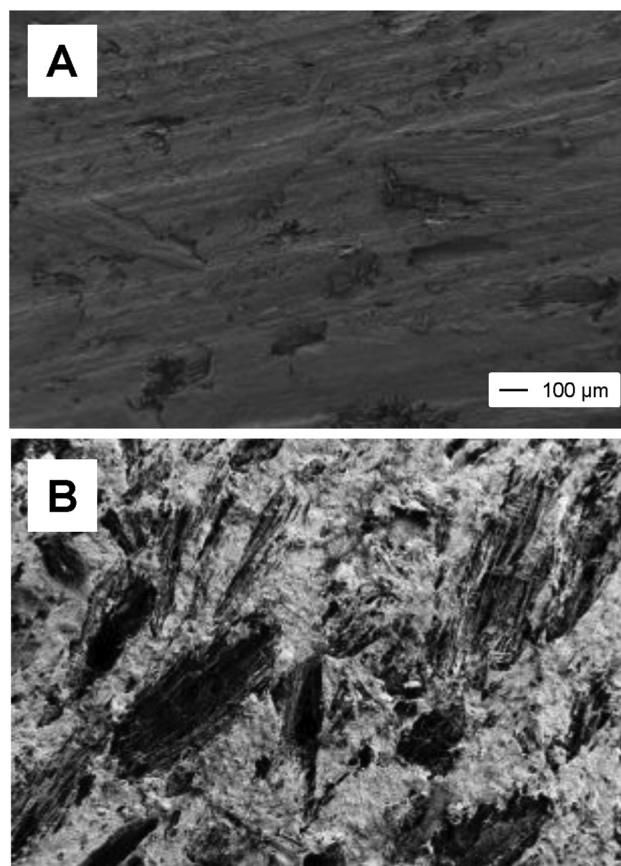


Fig. 3 Scanning electron micrograph of a WPC (white oak (60%)/HDPE (40%) control sample (A) and after exposure to *Gloeophyllum trabeum* (Brown rot fungi) for 12 weeks (B). Reproduced with permission from Fabiyi *et al.*³⁹

layer) extruded on to the WPC surface may help seal in these exposed wood particles at the surface, discouraging biodegradation.⁴⁶ With a HDPE cap layer, the rate of discoloration from exposure to solar UV radiation was reduced by ≈50% and access of the wood fibers to moisture was also substantially reduced.⁴⁷ Blending UV absorbers with a HALS in the HDPE cap layer can further enhance photostability.⁴⁸ While several studies have established the effectiveness of cap-layer technology, its techno-economic feasibility in specific product categories remains to be demonstrated.

Biodegradable and compostable plastics such as poly(lactic acid)⁴⁹ or poly(3-hydroxybutyrate)⁵⁰ have been studied for their potential use in WPC. The perceived sustainability of these potentially fully biodegradable WPCs that return all the carbon into the carbon cycle is attractive. However, the greater cost of these specialized plastics will likely preclude commercialization of such WPCs in spite of the claimed but questionable environmental advantage of biodegradability.

Emerging issue of weathering and microplastics

Weathering of plastics outdoors produces micro-scale plastic fragments that have serious environmental consequences.⁵¹ Microplastics (fragments in the size range of 1 mm to 1 µm)



are primarily believed to be derived from weathered, brittle plastic litter and are widely accepted to be a serious ecological concern, especially in the marine environment.^{52,53} The surface cracking of highly weathered plastics is the likely origin of microplastics.⁵¹ Plastic particles, regardless of size, concentrate persistent organic pollutants (POPs).⁵⁴ dissolved in the ocean water at very low concentrations. The distribution coefficients (K) of a compound between the plastic and water phase is the ratio of its equilibrium concentration in the plastic and in seawater. For common POPs, values of the K between sea water and plastics are large, ranging from 10^4 to 10^5 in favor of plastic. This means the equilibrium concentration of a POP species can be several orders of magnitude greater in the plastic debris compared to in seawater. Because of their small size, some of the microplastics are ingested by zooplankton and other marine species,⁵⁵ thus providing a pathway for POPs to enter the marine food web.⁵⁶ The specific compounds of concern include endocrine disruptors (EDs) such as PCBs, BPA, phthalates, and residual polymer catalysts.

Polypropylene (PP) is commonly found in urban litter and is an important generator of microplastics *via* surface photo-degradation. The wavelength sensitivity of the surface cracking of PP stabilized by HALS has been reported recently.⁵⁷ The same logarithmic dependence of photodamage on the wavelength of exposure, already reported for various measures of damage, such as discoloration or mechanical properties, was also confirmed for surface cracking. This is the first reported action spectrum for crack formation and is relevant as microplastics originate from surface cracks. However, quantifying surface cracking was indirect and not entirely satisfactory, being based on a correlation between carbonyl index (a spectroscopic quantity) and the degree of cracking. Extrinsic fluorescence techniques using Rhodamine dye, recently used for the first time to study microstructural changes in polymers during UV degradation,^{58,59} hold more promise for quantification of weathering-induced microcracking of plastics.

Higher degrees of crystallinity obtained under extensive weathering are one of the main reasons for embrittlement. On weathering of semi-crystalline plastics (such as PE or PP), it is the amorphous regions that oxidize first because of the lesser solubility and diffusion rates of oxygen in the crystallites. This was recently confirmed for PE⁶⁰ using dielectric relaxational spectroscopy, a technique not hitherto used for this purpose. In contrast, Ojeda² reported that polypropylene samples underwent a decline (>12%) in crystallinity during natural weathering. The latter observation has not been satisfactorily explained although impurities or accumulation of product during degradation has been suggested as the cause. Research is needed to clarify the relationship between crystallinity changes and exposure to UV radiation during weathering.

Plastics in solar photovoltaic applications

While plastics are also being evaluated as solar thermal absorbers,⁶¹ it is the photovoltaic (P-V) applications that are of

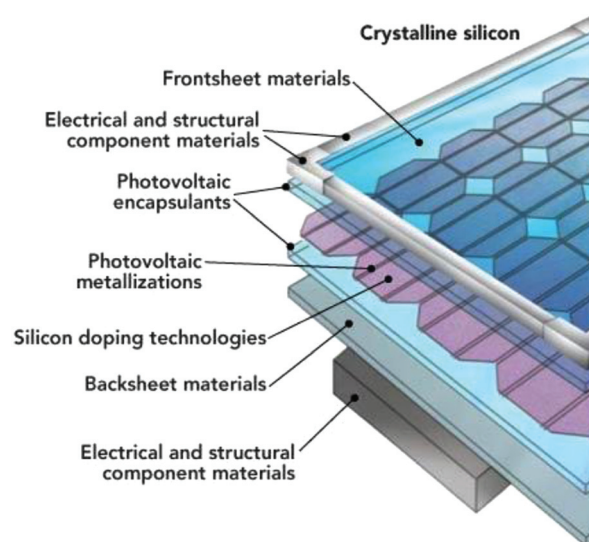


Fig. 4 Structure of a P-V module showing the back sheet and front sheet material placement. Source: Courtesy of DuPont.

greater commercial interest.^{62,63} Research emphasis appears to be divided between the solar UV-damage to light-harvesting semiconductor polymers in organic P-V devices^{47,64,65} and that of plastic encapsulants used to protect silicon P-V modules.

Recent designs of P-V modules utilize plastics extensively. Generally, two plastic protective laminates or sheets in the modules are affected by solar radiation (Fig. 4). Light transmitted through the transparent front panel reaches the exposed parts of the front sheet and the front surface of the back sheet, discoloring and weakening these after long durations of exposure. The back sheet is often constructed of a multi-layered laminate designed for the service life of the module (20–25 years). These sheets are made of a poly(vinyl fluoride) (PVF) outer layer, a thicker inner core of poly(ethylene terephthalate) (PET) with titanium dioxide (for opacity), and a PVF surface layer (or a PE/EVA tie layer). Of the plastics evaluated over the years, PVF has been selected as the best suited for the application. Long-term exposure can result in discoloration and loss of strength in these sheets and, although accelerated test methods are available^{64,66,67} they are inadequate to reliably predict their service lifetimes. PE and PET degrade under solar UV exposure and undergo yellowing and cracking. The back surface of the back sheet is also affected by diffused UV radiation that, along with high temperatures⁶⁸ cause initial damage within ≈ 5 years of outdoor exposure.⁶⁹

There is an urgent research need to (a) develop weather resistant encapsulants as well as accelerated test methods to assess the long-term (>20–30 years) service lifetimes of P-V modules, reliably. Any increase in UV-B radiation and/or temperature due to climate change will clearly accelerate the degradation, but techniques and standards to reliably quantify the effects reliably are still being developed.⁷⁰ The lifetime of protective plastics is a determining factor in implementing large-scale economical P-V technology.



Plastics in greenhouse covers

Plastic films and laminates are the leading greenhouse cladding materials used worldwide. Thin plastic films are sometimes used on conventional glass cladding to modify the spectral quality of light reaching the crops.⁷¹ Plastic panels have different transmission rates for photosynthetically active radiation (PAR, 400–700 nm) and sometimes the plastics incorporate dyes or modifiers⁷² to change the transmitted spectrum of solar radiation. The photostability of the dye is a concern in this technology and has not been explored as yet in detail.

Rigid plastics (>10 year service life) commonly used in greenhouses are fibre-reinforced polyester panels, polycarbonate (PC), and acrylics. Flexible cladding (3–4 years of service life) is generally made from PE, ethylene copolymers, and PVC; although PET is also sometimes used. Both classes of cladding undergo discoloration and loss of PAR transmission with weathering during use.⁷³

Nanofillers have been evaluated in low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE) greenhouse films to improve mechanical properties and to reduce transmission of UV. Nanoscale oxides of titanium, zinc oxide, and silica were evaluated for this purpose.⁷⁴ Nano-zinc oxide fillers improve weatherability of the films *via* UV-absorption or shielding, without affecting their transparency for PAR wavelengths. With certain varieties of crops, some degree of transparency to UV radiation might be needed to ensure a greater quality produce (see Bornman *et al.*⁷⁵) and plastic films can be designed to accommodate this need. The market for durable greenhouse films is large enough for speciality chemical companies (Clariant, Switzerland) to offer tailor-made light stabilization solutions designed for greenhouse films.⁷⁶ While the potential for durable but UV-resistant greenhouse films based on nano-composites clearly exists the lifetime cost of their use has not been reported.

Dependence of solar UV radiation damage to greenhouse films on the dose of solar UV-B radiation is of interest in developing lifetime assessments. Dehbi and colleagues^{77,78} reported a U-shaped (nonlinear) dependence of yellow discoloration with duration of exposure for LDPE greenhouse films, in both natural and accelerated weathering. However, this form of dose–response behaviour is unexpected and atypical and is likely an artifact of the layered structure of the film. Oreski and colleagues⁷⁹ investigated the weathering changes in stabilized EVA copolymer greenhouse films (200 μm) and showed that only a thin surface layer was degraded. Even in thinner films (30 μm) of EVA, the mechanical properties were not significantly affected at 1000 h of accelerated weathering exposure at 60 W m^{-2} of UV irradiance (300–400 nm) at 40 °C. Present-day stabilizer technology is clearly adequate for greenhouse film applications. Energy costs of maintaining greenhouse temperatures vary with the choice of cladding. In a new modelling study, Al-Madhour and colleagues⁸⁰ found that the low emissivity of PVC is a better choice than LDPE in conserving heat in greenhouses. The search continues for a single plastic material that combines long-term resistance to solar UV radi-

ation, transmittance of PAR, and thermal insulation, and is ideally suited for greenhouses.

Nanofiller in photostabilisation of plastics

The bulk of reported work on nanofilled polymers involves polymer-based coatings, especially clear coats used in protecting exterior surfaces from solar UV damage (these are assessed below).

Redhwi^{81,82} studied three nano-composites of LDPE (with Clay, ZnO, and Silica at 5% (wt)) and found that natural resistance of the plastic to weathering was not compromised by the presence of the nanofillers except in the case of nanosilica. In studies on nanocomposite systems, surface-modified rutile titania (40–100 nm) in LDPE⁸³ was reported to control the loss in tensile properties relative to unfilled samples in accelerated weathering studies. Nanofillers generally need to be either surface-treated or a compatibiliser must be used in the formulation to ensure that high levels of dispersion are achieved throughout the material. While some work has been carried out on this topic, further information is needed across the wide range of filler and/or plastics. The stability of the compatibilisers or modifiers to UV radiation also has not been studied in sufficient detail.

In general, the inclusion of nanoscale fillers should impart increased photostability to polymer coatings (including wood topcoats) and bulk polymers. Because variables, such as the particle size distribution and dispersion effectiveness are involved, quantitative effects are difficult to compare even for the same nanofillers in identical polymer matrices. Different combinations of these have been used in different studies. It appears that, in some systems at least, nanofillers yield at least the same level of protection as conventional fillers, but at a lower volume fraction and can therefore be an economical choice. However, further work is needed to elucidate the conditions under which they act as photostabilizers.

Kingston *et al.*,⁸⁴ recently reviewed the potential for release of nanofillers from several nano-composites filled with multi-wall carbon nanotubes (MWCNT) and concluded that the potential for release of MWCNT with typical intended consumer use is expected to be small. It is not known if weathering of the composite surfaces facilitates the release of nanofiller particles from filled-coatings or composites. Release of nanoscale fillers from composites during their use is an emerging environmental concern and is being investigated.

Temperature effects in solar UV-damage of materials

At higher ambient temperatures the light-induced degradation rates of materials accelerate. In the case of wood, heat alone often does not result in significant degradation; yet higher temperatures accelerate the photo-degradation process. In modelling effects of temperature in weathering studies, ambient temperatures are typically used. However, because of the absorption of solar radiation, especially the infrared radiation, the surface temperature of the sample is often higher by as much as 10–20 °C (depending on the material) and should be used in more realistic weathering models. A sophisticated



heat transfer model that allows the estimation of sample surface temperatures from metrological data (without resorting to expensive field measurements) has been developed and validated.⁸⁵ Its availability will not only refine the modelling of damage estimates but also contribute to the assessment of stabilizers.

The surface cracking of light-stabilized PP exposed to xenon lamp radiation was recently reported.⁵⁷ In this first quantitative study of light-induced crack formation, the activation energy estimated for this process was 20 kJ mol⁻¹. However, models based on the Arrhenius equation⁸⁶ or the reciprocity rule are inadequate in describing the case of concurrent light-induced and thermal (photothermal) degradation of PP.⁸⁷ The lack of a satisfactory general quantitative model is a major drawback in predicting the rates of degradation and service life in plastics exposed to solar UV radiation where heat build-up also increases the temperature of the material. This deficiency is particularly apparent in P-V device technology.

The temperature dependence of UV radiation-induced photodegradation was recently demonstrated experimentally *via* the exposure of wood from conifers and deciduous species to UV-B.⁸⁸ However, as a mercury vapor lamp that also emits UV-C radiation was used as the source in this study, the results are not pertinent to natural weathering. Increases in temperature from 30 °C to 80 °C increased the light induced color changes by 33–57% in pine, spruce, ash, and poplar wood,⁸⁹ and the effect is more pronounced at greater humidity.⁹⁰ The high temperatures used in the laboratory accelerated weathering tests reported by Persze and Tolvaj,⁸⁹ do not correspond to realistic temperatures of storage or use of wood.

Wood as a building material

In North America 25% of the windows are made of wood with nearly 9 million units made in 2010. The overriding market trend for building materials in general is the increasing demand for “green” or sustainable materials of construction.^{12,91–93} Exposed wood products are common in buildings, and these are generally surface-coated to ensure durability. A wide range of protective finishes such as paints, varnishes, stains, or water repellents are used for this purpose.⁹⁴ Recent life-cycle analyses (LCA) confirm wood to be an environmentally friendly building material.^{95,96}

Photodegradation of wood

Lignin in wood is a potent chromophore that readily absorbs UV radiation and undergoes ready photodegradation. This results in rapid color changes,^{90,97,98} lignin degradation^{97,99,100} and loss in microtensile strength.¹⁰¹ As with plastics, the oxidative degradation process in wood also increases the carbonyl index (the relative spectral signal from carbonyl groups in its infra-red spectrum) as a result of lignin degradation.¹⁰² The fundamental measures in weathering are the efficiency of the photoprocess, the photodamage/mole of available photons and the action spectrum.¹⁰³ The action spectrum for yellowing of mechanical pulp (newsprint paper) under exposure to simulated solar radiation was re-investigated recently in a rigorous

laboratory study.¹⁰⁴ The action spectrum for yellowing showed a logarithmic dependence of yellowing efficiency on wavelength as previously reported for newsprint paper.¹⁰³ These recent findings are in line with and confirm the known data on photodamage to wood.

As with plastics, solar UV radiation typically penetrates only the surface layer of wood. Photodegradation of surface layers monitored by microtensile measurements^{101,105} shows the damage is limited to about a 250 μm layer for Spruce wood exposed to simulated sunlight. Scanning electron microscopy showed some cellular damage at greater depths, but this was not supported by tensile property changes.

The role of wood extractives in UV stabilization

Extractives are naturally-occurring compounds that can be extracted from wood using common solvents such as acetone, ether and methanol. Natural wood extractives, being good absorbers of solar UV radiation, protect the wood from photodegradation.¹⁰⁶ Extractives in wood generally include phenolic compounds, stilbenes, and flavonoids that act as antioxidants and light stabilizers. Nzokou and Kamden¹⁰⁷ found the extractives to act as antioxidants and a stabilizer against degradation by UV radiation, during artificial weathering of *Prunus serotina*, *Quercus rubra*, and *Pinus resinosa*. Chang and colleagues¹⁰⁶ also showed that extractives slow down the rate of wood degradation in *Cryptomeria japonica* and *Acacia confuse* heartwood. Wood/LLDPE composites prepared with extractive-free wood (extractives removed by solvent extraction) showed poorer UV radiation stability compared to un-extracted wood fiber.³ In contrast to the above, Sharratt and colleagues;⁵⁶ however, reported that discoloration of Scots pine (*Pinus sylvestris*) exposed to simulated sunlight exposure, was unaffected by the presence of extractives. Consistent with this observation of UV-stabilizer activity of extractives, textile dyes derived from plants have very good UV-protective properties.¹⁰⁸

Drawbacks of extractives as stabilizers, however, are their water solubility and ready leachability from wood. While heat treatment, at least in the case of *Merbau* heartwood, appears to help prevent this,¹⁰⁹ a general solution to the problem is not available. Wood extractives, depending on the species, could be a new source of light stabilizer that can be further developed and refined to guard both wood and WPCs against damage caused by solar UV radiation.

Stabilizing wood against UV radiation

Improved protection of wood against solar UV radiation is afforded by coating the surface with layers containing light stabilizers¹¹⁰ such as HALS (or synergistic combinations of stabilizers¹¹¹) or inorganic fillers. Coating and surface modifications (as with cap layers already referred to in connection with WPC) also reduced moisture pick-up and therefore increased the fungal resistance¹¹² of wood.

A wide range of protective surface coverings or finishes such as paints, varnishes, stains, or water repellents¹¹³ are now commercially available. Transparent coatings that are not UV stabilized merely protect the wood against moisture but are



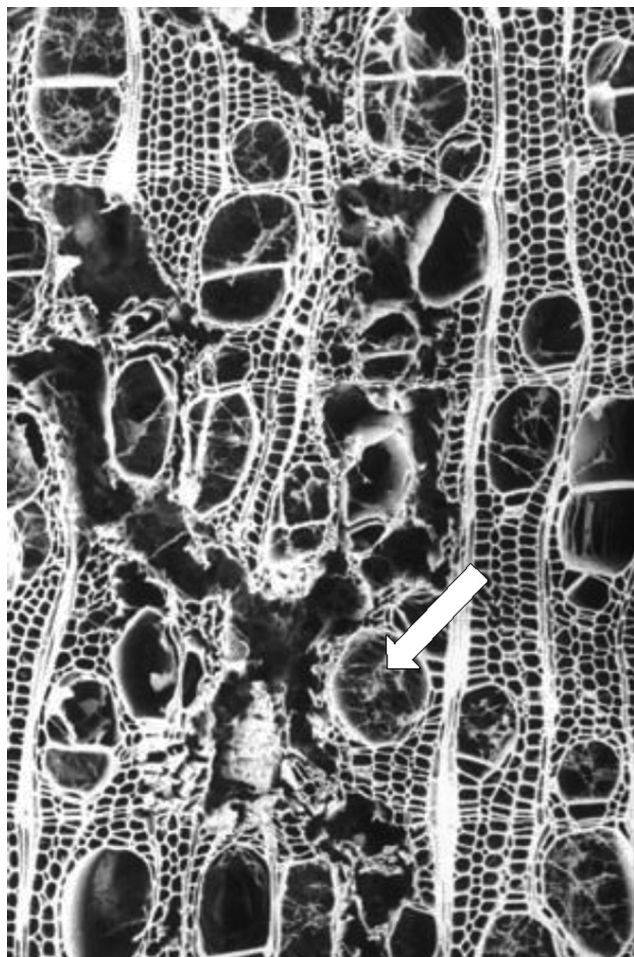


Fig. 5 Cross section of Oak Wood being biodegraded by white rot fungi. Biodegraded cells and fungal hyphae within other cells can be seen (100 \times). Reproduced with permission from Robert A. Blanchette, Pathology and Wood Microscopy Research Laboratory, University of Minnesota, MN (USA).

not effective in controlling light-induced damage.¹¹⁴ In such finishes, the interface (between wood and the coating) is degraded by UV-B radiation transmitted through the coating. This influences the coating performance.¹¹⁵ However, coatings that are hydrophilic (e.g., waterborne acrylic) must also be avoided as they promote the diffusion of water into the wood.¹¹⁶ Moisture in wood can facilitate biodegradation by fungi such as white-rot fungi (see Fig. 5).

Using conventional light stabilizers in clear coats on wood can be an effective stabilization technique. For instance, the generation of carbonyl groups by photodegradation of the underlying wood, is reduced by incorporating 2% of a conventional light absorber (Tinuvin-1130 or hydroxyphenylbenzotriazole) in the polyurethane surface coatings.¹¹⁷ Treatment of Yellow Cedar wood surface with a low molecular weight phenol formaldehyde resin, containing 2% Lignostab-1198, a HALS, improved the weathering resistance.⁹⁴ A low-cost wax coating was also found to control light-induced yellowing of Norway spruce wood.¹¹⁸ Of the waxes studied, high loadings

(wax content 11.7%) of emulsion of Montan wax was the most effective.

The effectiveness of clear coats can be further improved by photostabilizing the underlying wood substrate itself prior to the application of coatings.^{114,115,119} Chemically bonding UV absorbers to the wood is effective for many wood species.^{113,120} Pretreatment with a reactive UV-absorber 2-hydroxy-4(2,3-epoxypropoxy)-benzophenone with epoxy functionalized soybean oil improved photostability of Scots pine wood.¹²¹ Surface modifications involving UV stabilizers may hold promise in protecting high-cost wood species from photodamage.

Changing the surface layer of the wood substrate by chemical reaction (as opposed to using a protective clear coat) can also retard photodegradation.¹²² This can be cost-effective, as only a thin surface layer of wood needs to be chemically altered. Esterification using an anhydride reagent is a popular route to surface modification. Bhat *et al.*¹²³ reported that acetylation of *Acacia mangium* and *Acacia* hybrid woods with succinic anhydride better controlled UV-induced discoloration and mechanical loss compared to surface propylation. However, esterification only partially controls photo-yellowing and lignin degradation in Rubberwood.¹¹⁰ In contrast to unmodified wood, esterified wood showed photo-bleaching.^{110,124} Aromatic esters [via vinyl benzoate reaction] also performed satisfactorily in controlling discoloration.¹²⁵ A novel process for benzoylation of wood meal was reported,¹²⁶ but the method uses ionic liquids (salts that are liquids <100 °C) and is therefore likely to be too expensive for commercial use. The same is true of surface treatment approaches that rely on silylation (using methoxysilanes), despite their effectiveness in stabilizing wood, being as yet too expensive for commercial use.¹²⁷

Of the approaches available, the use of clear coats that are impervious to moisture but stabilized with conventional HALS or other stabilizers is the most effective (and also the most economical) approach for wood. It is also relatively environmentally friendly compared to other methods.

Use of nanofillers to protect wood against UV radiation

A majority of the studies reviewed suggest that nanoscale fillers in the topcoat or wood surface improve the UV stability of wood. While the economic feasibility of using nanofillers in wood coatings is not clear as yet, their performance is equal or better than conventional fillers at comparable volume fractions is supported by recent research. Three strategies for stabilization have been reported: incorporating nanofillers in topcoats, applying nanofiller directly to wood, and generating nanofillers in the wood.

Photostabilization of water-based polyurethane coatings intended for use on wood substrates, with 10 nm ceria (CeO₂) nanoparticles^{128,129} at a level of 0.4–1.4% has been reported. Nano-ceria was also reported to stabilize PP.¹³⁰ A similar improvement in controlling discoloration (and other surface damage such as reduction in gloss) was obtained with 7 nm nano-silica particles¹³¹ at 1–5 wt% incorporated into the poly-



urethane coating. The same was reported for 50 nm nano-ZnO¹³² in the same class of coating and for a 20 nm grade of the nanofiller at 1–2 wt% in an acrylic wood stain.¹³³ However, using 0.5–1.0 wt% of 20 nm rutile, a crystalline form of nanotitania, in similar coatings showed a decrease in photostability compared to base polymer, in terms of discoloration under accelerated weathering.

Acrylic water-based coatings for wood, containing nanotitania (NT) as well as nano-ZnO¹³³ have also been evaluated for control of discoloration, loss of gloss, and carbonyl group formation indicative of degradation. Fufa *et al.*^{134,135} found NT in the topcoat of wood cladding to be only marginally better than the base coating (with no NT) in controlling discoloration and carbonyl formation in Norway spruce. However, a very low fraction of only 1 wt% (based on solids) of filler was used in that study. A 50 µm thick clear coat with 1.14 wt% of NT filler afforded a much higher level of protection compared to that from a comparable coating with benzotriazole light absorbers.¹³⁶ Direct deposition of rutile nanoparticles on hardwood surface (without a coating) is also an option; this is achieved by hydrothermal processing.¹¹⁸ Such coatings are thicker and higher in concentration of NT particles, yielding excellent resistance against discoloration. Nanoparticles can also be chemically generated *in situ* on wood and bamboo surfaces¹¹⁸ and this greatly enhances the material's photostability. This was demonstrated with Chinese hardwood where the *in situ* generation was followed by silylation treatment to increase hydrophobicity. Wang and colleagues¹³⁷ studied NT coatings on Chinese fir wood followed by silylation. However, such two-step processes, especially those involving silylation, are likely to be too expensive for large-scale commercial use.

Role of fabric in protection against UV radiation

Personal protection afforded by clothing against the damaging effects of solar UV radiation is considerable and depends on fiber composition, (natural, synthetic or mixed fibers), fabric construction (porosity, weave and thickness) and dyeing (natural or synthetic dyes) and their UV-absorbing properties.¹³⁸ In addition, outdoor uses of fabric such as in tents, awnings, shading and sunshade fabrics also provide a protective role to humans from solar radiation. Clothing is in fact one of the best ways of protecting people against solar UV radiation¹³⁹ as even where the fabric materials themselves undergo limited UV-induced degradation they continue to provide excellent protection. The effectiveness of fabrics in this regard is quantified using the “ultraviolet protection factor” or UPF of the fabric. UPF is the ratio of the minimum erythemal dose of solar UV radiation for skin protected by fabric to that unprotected.¹⁴⁰ The percentage of effective UV radiation transmittance at each UPF value range is given in Table 1. For instance a cotton T-shirt provides a UPF of 3–5 (dry) and even lower when wet while denim has a UPF 1700. Dark colored fabrics have a higher UPF compared to light-colored ones.¹⁴¹

Several features of fabric determine its UPF: (a) the porosity of the material or how open the structure is will be inversely

Table 1 The relationship between UPF and fraction of erythemally effective UV transmitted through the material. (From Australian/New Zealand Standard: AS/NZS 4399 (1996). Sun Protective Clothing: Evaluation and classification.)

UPF range	UV radiation protection category	Effective UV radiation transmission (%)
15–24	Good protection	6.7–4.2
25–39	Very good protection	4.1–2.6
40–50, 50+	Excellent protection	<2.5, <1%

proportional to the UPF; (b) the absorption of UV by the fabric material; (c) dyes, chemical reactants,⁴³ or UV stabilizers¹⁴² applied to the fabric; and (d) moisture level of the fabric.¹⁴³

Of these, the porosity or tightness of the weave is the dominant factor in obtaining UV radiation protection, followed by the ability of fibers to absorb UV radiation. Grifoni *et al.*¹⁴⁴ compared the UV protection afforded by natural-fiber fabrics (cotton, hemp, flax and ramie) and concluded that thicker fabrics with denser weaves (with a cover factor, CF > 94%) such as drapery fabrics usually showed UPF > 50. Cover factor is the ratio of the area covered by the yarns to the whole area of the fabric. Cotton fabrics afforded excellent protection from UV radiation as confirmed in other studies.¹⁴² Lighter textile-grade fabrics, however, showed high UPF values only when the porosity was low (Cover factor > 94%). Different natural fibers have about the same UV absorbance, and the difference in the performance of corresponding fabrics is mostly determined by cover factor and dyeing. Commercial sun-protective garments (UPF 50+ that transmit <1% of UV radiation) perform by reducing their porosity or “open areas” in the weave of the fabric and using UV absorbers. Even these, when wet (with water filling the spaces) do not scatter but transmit UV, reducing their effective UPF value.

The UPF of different fabric materials varies as follows: Cotton > Polyester > Nylon > Elastane¹³⁸ Chemical modification of fiber surfaces can increase the UPF ratings. A particularly successful approach is the use of inorganic oxides (including nanoscale particles¹⁴⁵ or zinc oxide in polyester^{146,147} and in cotton¹⁴⁸ and with titania-silica,¹⁴⁹ alumina or nanosilica¹⁵⁰ particles in cotton, yielded very high UPF values in the hundreds (UPF > +50). While the untreated thick (tightly woven) fabric often has high UPF values to afford excellent protection, the use of surface modification technologies allows even a lighter-weight fabric to deliver the same high level of UV protection.

Layer-by-layer (LBL) deposition of nanolayers of three brightener compounds also increased the UPF of cotton fibers (UPF > 40) and improved durability in laundering as well.¹³⁷ Optical whiteners absorb UV radiation and re-emit as blue radiation (typically 420–470 nm). LBL has also been used to deposit nano-alumina on cotton.¹⁵¹ Despite the impressive performance of LBL technologies, they are expensive and are not near commercialization at this time. Chitosan metal complexes have also been used as organic stabilizer coatings on textile fibers but whilst these improve the antibacterial pro-



Table 2 Percentage transmission of UV-A radiation by different types of glazing materials

Type of glazing	Thickness ^a (mm)	Percentage transmission
<i>Residential windows</i>		
Double glazed clear glass	3.0/3.0	57
Double glazed tinted glass	3.0/3.0	20–33
Double glazed laminated glass	3.0/6.0	0.5
Double glazed UV-blocking glass	3.0/3.0	0.1
<i>Automobile windows</i>		
Laminated windshield glass	—	2–3
Tempered glass in rear and side window	—	33–48
Grey privacy glass	—	8
Moon-roof glass	—	2

^aThe two numbers refer to the two sheets of glass in double-glazed windows.

properties significantly they only provide a moderate improvement in UPF.¹⁵²

Glazing and protection against UV radiation

Window glass (glazing) filters out the solar UV-B radiation but allows some UV-A radiation to pass through; the transmitted fraction depends on the type of glazing used. In buildings and in automobiles where some of the solar radiation is screened by glass, sunlight reaching into the cabin can still cause discoloration of materials and bleaching of dyes. In spite of the lower efficiency of UV-A wavelengths (compared to UV-B) in discoloration, the relatively greater amounts of the former in the terrestrial solar spectrum can still affect exposed fabric and other materials. Individuals, however, are protected from the UV-B radiation by almost all the different types of glass used on residential, commercial and automobile applications. Reported values for transmission of UV-A by different glazing are summarized below (Table 2¹⁵³).

Thermal performance of windows can be improved dramatically by incorporating monolithic or granular aerogel in the interspace between panes in double-glazed windows.¹⁵⁴ According to Buratti¹¹ the rate of heat transfer decreased by 23% in aluminium-framed windows using aerogel technology. An associated benefit is that the presence of aerogel also cuts down the radiation transmitted, especially UV-A and UV-B radiation in sunlight.

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