



UV Damage to Polymers

The chemical pathways by which common polymers photodegrade are fairly well known, but various aspects of the mechanisms involved remain unelucidated. However, it is important to take into account very significant influence of compounding additives in modifying these pathways (Gugumus, 1993). Typically, these are pigments, extenders, photostabilizers and thermal stabilizers. For instance, the effect of flame-retardant additives on the photodegradation of several common polymer compositions was reported recently (Torikai et al. 1998, 1993a-c). Virtually all plastics products are manufactured using extrusion, injection molding, or extrusion blowing. The processing of polymers using heat and high shear into useful end products introduces impurities and reaction products that make them susceptible to photodegradation. Because of these complications, the extrapolation of research findings on UV-induced degradation of pure polymer resins to compounded and processed products of the same polymer, is often unreliable. Photodegradation data generated on the actual polymer formulations used in practice, processed in the conventional manner are the most useful for assessment of damage.

The many concurrent chemical processes taking place in polymers exposed to UV radiation result in several different modes of damage, each progressing at a different rate. It is usually the critical first-observed damage process that determines the useful service life of the product. For instance, poly(vinyl chloride), PVC, window frame exposed to sunlight undergoes discoloration, chalking, loss of impact strength, and a reduction in tensile properties as well as a host of other chemical changes. It is, however, the discoloration (or the uneven yellowing) of the window frame that generally determines its service life [Ho, 1984]. The consumer may demand its replacement based on this criterion alone. In most developing countries, however, these products often continue to be used despite changes in appearance or even stages of damage becomes apparent. With continued use, however, other damage such as chalking and eventually loss of impact resistance (leading to cracking) can occur making the product even more unacceptable. The two critical modes of photodamage applicable to most natural and synthetic materials are yellowing discoloration and loss in mechanical integrity.

Yellowing Discoloration. Both natural biopolymer materials and synthetic polymers undergo UV induced discoloration, usually an increase in the yellowness on exposure. Lignocellulosic materials such as wood and paper readily undergo light-induced yellowing (Hon et al., 1991). While both cellulose and lignin constituents of wood can photoyellow, it is the latter that is mostly responsible for the phenomenon. Lignin, which comprises 29-33% by weight of softwood, contains numerous chromophores that efficiently absorb UV radiation (Heitner, 1993). As much as 80-95% of the absorption coefficient of wood can be ascribed to the lignin fraction. The complex photochemistry of yellowing in lignin-containing materials is not completely understood; the present understanding of the process was succinctly summarized recently (Forsskåhl et al., 1993) and at least four pathways of photodamage have been recently discussed. The practical interest in discoloration relates specially to newsprint paper made of groundwood pulp that yellows rapidly on exposure to sunlight. Action spectra for photoyellowing of these pulps have been reported, and a recent study (Andrady et al., 1991) confirms the solar UV wavelengths to cause yellowing while the wavelengths in the region of 500 nm to 600 nm was shown to photobleach the pulp. The cellulose fraction in wood also undergoes a free radical mediated degradation on exposure to wavelengths < 340 nm.

The photodamage to wool has serious economic implications in large producer countries. Exposure of wool keratins to sunlight is well known to cause yellowing, bleaching, and main-chain scission of the proteins (Lennox et al., 1971). Launer (Launer, 1965) established that visible radiation in sunlight causes photobleaching

of wool while the UV wavelength causes photoyellowing. Based on Lennox data (Lennox et al., 1971), the most effective yellowing wavelengths were in the UV-A region (340 -420 nm). As ozone layer depletion results in an increase in both UV B as well as UV A content of sunlight, wool appears to be a material that might be particularly affected.

Preliminary data on the photostability of Chitosan, another commonly found biopolymer, were recently reported (Andrady et al., 1996). While not used commercially in high volume, the biopolymer occurs widely in nature in fungal cell walls, crustacean exoskeleton and in insect tissue. Ultraviolet radiation in the wavelength range 250 nm to about 340 nm was reported to cause changes in the average molecular weight as determined by solution viscosity as well as the absorbance (at 310 nm) in chitosan derived from crab shells. The damaging role of UV-B in creating free radicals in human hair has also been reported (Jahan et al., 1987) but no quantitative spectral sensitivity data are available.

Of the synthetic polymers, poly(vinyl chloride), PVC, is best-known for its tendency to undergo photoyellowing. The photothermal mechanisms leading to the formation of conjugated polyenes that causes yellowing, is well understood (Decker, 1984; Gardette et al., 1991). An opacifier (generally rutile titania) is used to slow down the rate of yellowing in white profiles widely used in siding, window frames and pipes (Titow, 1984). The reaction is localized in the surface layers of the polymer specially in opaque formulations used in building applications. The activation energy for dehydrochlorination is reported to have a temperature coefficient of 8-18 kJ mol⁻¹ suggesting this process to be readily enhanced at high temperatures (Owen, 1984). As with wool and paper, while the UV-wavelengths cause yellowing of PVC the visible radiation >400 nm tend to cause photobleaching. Several possible photobleaching mechanisms are reported in the literature but the process is little understood.

A second polymer used in building applications, mainly as glazing, is polycarbonate. When irradiated with short wavelength UV-B or UV-C radiation polycarbonates undergo a rearrangement reaction (referred to as a photo-Fries rearrangement). At low oxygen levels this reaction can yield yellow-colored products such as o-dihydroxy-benzophenones (Rivaton et al., 1988). But when irradiated at longer wavelengths (including solar visible wavelengths) in the presence of air, polycarbonates undergo oxidative reactions that result in the formation of other yellow products (Factor et al., 1987). However, neither the detailed mechanisms nor the specific compounds responsible for the yellow coloration have been fully identified (Factor, 1995). Monochromatic exposure experiments on the wavelength sensitivity of several degradation processes of bisphenol A polycarbonates have been reported recently (see Table 7.2).

Polystyrene, widely used in both building and packaging as expanded foam, also undergoes light-induced yellowing. The presence of air retards the process and the origin of the coloration is again not clear. It is variously attributed to conjugated polyene, various oxygenated species, or products of ring-opening reactions (Rabek et al., 1995).

Table 7.2 Spectral sensitivity data from monochromatic exposure experiments.

Material Type	Damage Studied	B	r ²	Ref
1. Poly(vinyl chloride)				
1.1 rigid compound - 0% TiO ₂	Yellowing	-0.035	0.95	1
- 0% TiO ₂		-0.048	0.99	
- 2.5% TiO ₂		-0.058	0.98	
- 5.0% TiO ₂		-0.073	0.99	
1.2 plasticized compound	Stiffness change	-0.02	0.83	2
2. Polycarbonate				
2.1 rigid sheets	Yellowing	-0.082	0.99	3
2.2 films	Quantum Yield of	-0.044	0.99	4

	chain scission			
	Change in Absorbance	-0.059	0.88	5
3. Poly(methyl methacrylate)	Quantum Yield of chain scission	non-linear		6
4. Lignocellulose				
3.1 mechanical pulp	Yellowing	-0.011	0.99	7
5. Chitosan				
5.1 Chitosan films	Absorbance at 310 mm. (260 -320nm)	-0.017	0.89	8
	Viscosity	non linear		
6. Wool	Yellowing	-0.025	0.95	9

Note: r is the correlation coefficient

References 1- [Andrady, 1989] 2- [Warner et.al., 1966] 3- [Andrady et.al., 1992]

4- [Torikai et.al., 1993a] 5- [Fukuda et.al. 1991] 6- [Mitsuoka et.al., 1993]

7- [Andrady et.al. 1991] 8- [Andrady et.al., 1996] 9- [Lennox et.al 1971]

Loss of Mechanical Integrity. The loss of strength, impact resistance, and mechanical integrity of plastics exposed to UV radiation is well known. These changes in bulk mechanical properties reflect polymer chain scission (and/or cross linking) as a result of photodegradation. Changes in solution viscosity and the gel permeation characteristics of polymers have been used (Torikai et.al., 1993) to establish molecular changes during photodegradation.

With polyethylene and polypropylene, the loss of useful tensile properties on exposure to solar radiation is a particular concern. These are used extensively in agricultural mulch films, greenhouse films, plastic pipes, and outdoor furniture. Polyethylene films exposed to solar UV-B radiation readily lose their extensibility and strength (Hamid et al. 1991, 1995) as well as their average molecular weight (Andrady et. al., 1993). General features of the mechanism of photodegradation in both polyethylene and polypropylene is fairly well understood (Allen, 1983; Rabek, 1995). The mechanism is one of thermooxidative or photooxidative degradation rather than of direct photolysis, and is catalyzed by the presence of metal compounds. The free radical pathways that lead to hydroperoxidation and consequent chain scission are fairly well understood (Shlyapnikov et al., 1996). Of the polymers used worldwide, polyethylene enjoys the largest annual volume. Research interest in understanding and controlling the photodegradation process of this polymer is therefore continuing. Efficient classes of light stabilizers such as the hindered amine light stabilizers (HALS) are used to ensure that adequate lifetimes are obtained in polyolefin products intended for outdoor use under a wide range of UV environments.

Poly(vinyl chloride) PVC, is used widely in building applications where the impact strength of the material is an important requirement. The projected consumption of PVC in the near future (1995 -2010) is much higher in the developing world and in countries in transition. Estimated demand for Asia alone is more than that for the US, Canada and the European community combined (Gappert, 1996). Exposure to solar UV radiation is well known to decrease the impact strength of the polymer (Decker, 1984). As the surface layers of the plastic material degrades the titanium dioxide powder used as an opacifier is gradually released and may even form a surface layer loose enough to be rubbed off. This is responsible for "chalking" of extensively exposed PVC siding materials. Both the tensile strength and the extensibility of rigid PVC samples also decrease with the duration of exposure to solar UV radiation and the material finally embrittles (Decker, 1984). Similar changes also take place on exposure of plasticized PVC formulations used in membrane roofing applications and cable coverings (Matsumoto et al., 1984).

Other common polymers shown in Table 7.1 also undergo a loss in mechanical strength on photodegradation. A rapid change in the mechanical integrity of polystyrene caused by extensive chain scission during the photodegradation has been reported (Ghaffar et al.,1976).



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