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DETERIORATION MECHANISMS IN WEATHERING OF PLASTIC MATERIALS

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SOMMAIRE

La détérioration de la plupart des matériaux de plastique commence à la surface extérieure et peut se révéler par la décoloration, le piquage, l'exsudation des composants, la proéminence des fibres et les microfissures. Les effets nuisibles du vieillissement consistent en une série de processus complexe où prédomine l'action combinée de la lumière ultraviolette et de l'oxygène. Lorsque l'éne peut pas être libérée par u d'un lien chimique, ce qui ite mener à un ou plusieurs xygène. Une détériorati de se rompre par le rappo midité et de température. nt la perte des propriétés a uite par le rapport cont élérée par les radiations

A. Blaga[1]

Deterioration Mechanisms in Weathering of Plastic Materials

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ABSTRACT: Deterioration of most plastic materials starts at the outer surface and may take the form of discoloration, pitting, exudation of ingredients, fiber prominence, and microcracking. The deleterious effects of weathering consist of a complex set of processes in which the combined action of ultraviolet (UV) light and oxygen are predominant. When the energy of an excited group or segment of a molecule cannot be released through a photophysical process, it causes the dissociation of a chemical bond to produce free radicals. This event, with or without the participation of oxygen, can lead subsequently to one or more chemical changes. Light-initiated degradation makes the plastic more susceptible to fracture by stress fatigue induced by changes in humidity and temperature; the resulting surface microcracks cause a loss in mechanical properties. Fiber prominence can be produced by stress fatigue alone, but its formation is accelerated by UV irradiation.

KEY WORDS: deterioration mechanisms, photo-oxidative degradation, photodegradation, weathering, plastic materials, plastic, polymers, chemical processes, physical processes, environmental stress fatigue, surface microcracks, cracks, building materials, durability

Deterioration of plastic materials can be described as an irreversible change in some of their properties which is detrimental to their usefulness. Although their properties may change slightly during processing, the most significant deterioration of plastics occurs during exposure to the service environment. Conditions during the processing of plastic compounds are relatively severe but they are of short duration and usually involve the action of oxygen. Although plastic compounds are usually well protected against thermal oxidation, sensitizing groups are generally formed in a small fraction of the molecules. These impurities, as well as some compounding

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ingredients, can initiate, or often accelerate, deterioration of the plastic material during use. Some deterioration of polymers may occur even during synthesis, but protection at that stage is generally impractical since stabilizers that inhibit deterioration usually retard polymerization.

Although the temperatures or mechanical stresses, or both, are usually lower during service than during fabrication, the time of exposure is considerably longer. In addition, the conditions usually go through cycles, in contrast to the more constant conditions of fabrication.

One of the most severe service environments is the out-of-doors, an environment where an important proportion of plastics is used. The deterioration of plastics usually starts at the outer surface and penetrates gradually into the bulk of the material. The deterioration takes the form of discoloration, pitting, reduction in gloss, crazing or cracking, erosion, exudation or leaching of ingredients, embrittlement, fiber prominence (in glass reinforced plastics), and deterioration of mechanical properties [*1-7*].[2] Other consequences of aging are opacification, reduction in light transmission and impairment of electrical properties [*8-10*]. The deterioration of plastics generally involves both chemical and physical processes, the chemical reactions usually preceding the physical processes.

This paper presents a review of the state of knowledge on the deterioration of plastics, with emphasis on the breakdown induced by exposure to natural weathering.

Chemical Processes

The deleterious effects of weathering on plastic materials generally has been ascribed to a complex set of processes in which the combined action of UV light and oxygen are predominant. The overall light-initiated process in the presence of oxygen generally is referred to as oxidative photodegradation or photo-oxidation.

Photodegradation

To undergo a photochemical reaction, a material must absorb light energy [*11-13*]. Light energy is absorbed in discrete amounts known as quanta or photons; the energy (ϵ) of a quantum or photon is an inverse function of the wavelength (Fig. 1) and is given by $\epsilon = hc/\lambda$, where h, c, and λ are the Planck constant, light velocity, and wavelength, respectively. Only radiation of wavelength greater than approximately 290 nm normally reaches the earth's surface; radiation of shorter wavelength is absorbed by the ozone layer in the upper atmosphere [*13*].

When a polymer molecule, A_0, absorbs UV light by a group, it is acti-

[2]The italic numbers in brackets refer to the list of references appended to this paper.

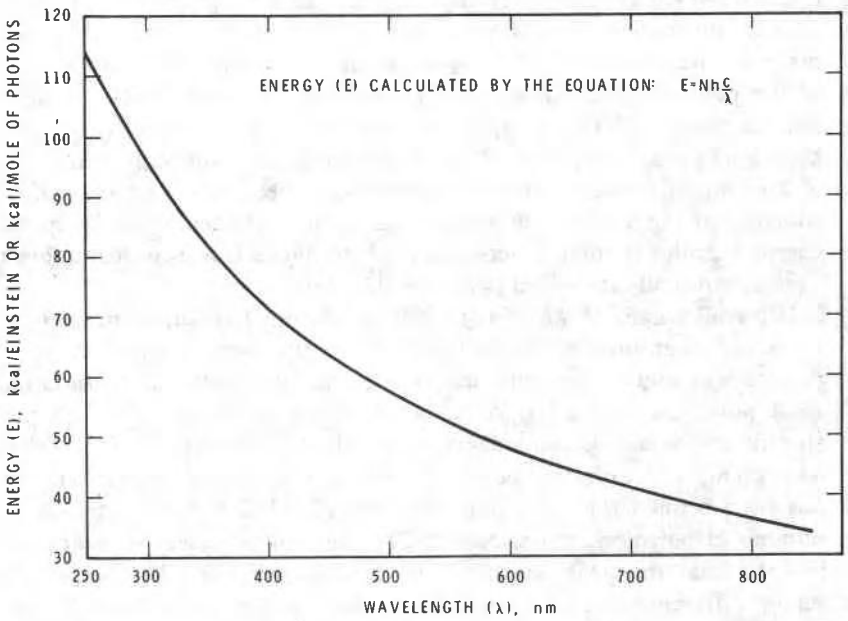

FIG. 1—*Relation between energy and wavelength.*

vated to an electronically excited state, A^*. The excited molecule may release its absorbed energy by re-emitting it at longer wavelengths as fluorescence, phosphorescence, or heat; or it may transfer it to another molecule, B_o, during a collision, thereby returning to its ground state [*11-14*]:

$$A^* \rightarrow A_o + \text{fluorescence or phosphorescence}$$

$$A^* \rightarrow A_o + \text{heat}$$

$$A^* + B_o \xrightarrow[\text{transfer}]{\text{Energy}} A_o + B^*$$

When the absorbed energy is not dissipated by any of these photophysical processes, it will initiate photodegradation.

Energy transfer from a group (donor) to another group (acceptor) located in the same molecule (intramolecular transfer) or in a different molecule (intermolecular transfer) is an important step in photodegradation and photostabilization of polymeric materials [*13,15,16*]. Intermolecular energy exchange processes between electronically excited impurity groups and another group or weak link in the polymer are believed to account for the photo-initiated degradation during weathering of hydrocarbon polymers

[*1,2,17*], which absorb practically no terrestrial UV light [*12,13*]. Impurities may be substances introduced at any stage of the life cycle of the plastic material. Another kind of impurity group present in most plastics is part of the polymer itself; it includes peroxy (-O-O-) links, carbonyl (C=O), and carboxyl (COOH) groups. The transfer of absorbed energy from one absorbing group to another along the chain is also important, since the site of absorption and the site of bond breaking need not, and often do not, coincide. If the acceptor segment or group in a molecule can dissipate the energy harmlessly, then it acts as a photostabilizer (for example, quenching agents, internally stabilized polymers) [*15,18*].

Ultraviolet light of wavelength 290 to 410 nm has quantum energies of the same magnitude (99 to 70 kcal/mol) as the bond strength in common polymers (Table 1) and thus may cause the photoinitiated degradation of most polymeric materials. As a bond or group absorbs only quanta of specific energies, the photodegradation of plastic materials is wavelength dependent. The extent of degradation as a function of wavelength, which has been termed the activation spectrum [*20*] has been determined for a number of polymeric materials [*19-21*]. Data on a variety of clear plastics indicate that the peak sensitivity is at approximately 330 nm, with only minor differences between materials. The stability of plastics to natural weathering, as stated, is complicated by the presence of additives which may act as photosensitizers; these ingredients have absorption maxima quite different from those of the polymers. Furthermore, decomposition products of the basic polymers or of the additive, or both, also can cause a significant shift in wavelength sensitivity [*17*]. The groups or bonds that absorb UV light may be part of the polymeric molecule (for example, in polyesters, polyamides) or introduced during processing. Absorbing groups

TABLE 1—*Comparison of bond strengths and wavelengths of quanta with corresponding energy* [12,13].

Chemical Bond	Bond Energy, kcal/mol	Wavelength (λ) of Quantum Having the Same Energy, nm
O-H	111	259
C-F	105	272
C=O	100	286
C-H[a]	99	290
N-H	93	306
C-O	84	340
C-C	83	342
C-Cl	79	364
C-N	70	410

[a] Typical value for C-H bonds in CH_3 or CH_2 groups of hydrocarbons; the bond strength varies widely, however, depending on the intramolecular environment [*12*].

include carbonyls, carboxyls, peroxides, hydroperoxides, and carbon-carbon double bonds, usually in conjugation with other double bonds; they may be catalyst residues.

Photoinitiated degradation of polymeric materials involves numerous general processes that are largely similar to those occurring in heat-induced degradation. The initiation steps differ considerably, however, and thus suitable laboratory methods had to be devised that would elucidate these mechanisms [*12*].

Photo-oxidation

The degradation of polymeric materials in the outdoor environment is believed to involve a very complex reaction sequence. For example, the sequence may be initiated by light and propagated by oxidative reactions; thermal processes induce subsequent steps whose rates may be affected by the presence of moisture or the participation of pollutants.

The absorbed UV light energy causes the dissociation of bonds (mostly C-C and C-H) in the molecules of one or more of the constituents of a polymeric material by a homolytic process to produce free radicals as the primary photochemical products. This event, with or without the participation of oxygen, can lead subsequently to one or more of the following chemical changes: cleavage into smaller molecules (chain scission), crosslinking, elimination of small molecules (for example, hydrochloric acid, carbon dioxide, carbon monoxide, water), formation of double bonds in the main chain, depolymerization, and photohydrolysis. Light of different wavelengths of the solar spectrum can produce different chemical changes simultaneously in the same polymeric material [*21*].

In common with other free radical reactions, oxidative photodegradation of polymeric materials involves processes of initiation, propagation, and termination [*12*]. As the strength of carbon-hydrogen (C-H) bonds increases in the following order: $\geqslant CH$, $>CH_2$, $-CH_3$, hydrogens at branch points in a polymer are attacked more readily than those of methylene groups which, in turn, are less resistant than those in methyl groups. The most frequently occurring photoinduced chemical degradation processes in polymeric materials are chain scission and crosslinking, with concomitant formation of oxygen-containing functional groups such as carbonyl, carboxyl, hydroxyl, and peroxides. The formation of these groups can be assessed easily by infrared spectroscopy [*12,22–24*].

It is believed that carbonyl photocleavage reactions may be the major cause of photodegradation [*12,18,25,26*] in a wide variety of carbonyl-containing polymers, as well as in most hydrocarbon polymers that always contain at least traces of carbonyl functions as a result of thermal oxidation during processing. If a ketone carbonyl group is located in the main molecular chain or on adjacent carbons of a side chain, the degradation may

occur by two well known scission mechanisms, Norrish I and Norrish II [*26–30*]:

Norrish I $\sim CH_2\text{-}CH_2\text{-}CO\text{-}CH_2\text{-}CH_2\sim \xrightarrow{h\nu} \sim CH_2\text{-}\dot{C}H_2 + \cdot CO\text{-}CH_2\text{-}CH_2\sim$

Norrish II $\sim CH_2\text{-}CH_2\text{-}CH_2\text{-}CO\text{-}CH_2\sim \xrightarrow{h\nu} \sim CH{=}CH_2 + CH_3\text{-}CO\text{-}CH_2\sim$

Both of these processes produce a decrease in the molecular weight, resulting in deterioration of physical properties. The radicals formed by the Norrish I process may react with oxygen to produce hydroperoxides, which are decomposed rapidly by UV light [*12,23*]. If this decomposition occurs by a homolytic cleavage, the new radical that is formed would, in turn, initiate new oxidative chain reactions, resulting in an increased amount of UV-absorbing oxidation products such as hydroperoxides, ketones, carboxylic acids, and aldehydes. The process rapidly reaches the maximum rate, accounting for the initial rate being higher in photo-oxidation than in thermally induced oxidation.

Photo-oxidation of Common Polymers

Polyethylene has been studied extensively because of the simplicity of its molecular structure and its commercial importance [*12,13,17,25*]. Briefly, the mechanism of its photoinduced degradation [*31*] consists of four steps: (1) absorption of light by ketone carbonyl groups (formed during processing), (2) Norrish Type II cleavage involving the excited state of carbonyl groups and producing vinyl groups, (3) formation of an excited oxygen molecule, and (4) reaction of the excited oxygen molecule with the vinyl groups to yield hydroperoxides. Further free radical reactions of the hydroperoxides would lead to additional carbonyl groups that can undergo Type II cleavage.

Polypropylene, the other important polyolefin, is more susceptible to photo-oxidation because its repeat unit, $\text{-}CH_2\text{-}CH(CH_3)\text{-}$, bears labile hydrogen atoms attached to tertiary carbons. The photodegradation mechanism is very similar to that of polyethylene [*12,32*].

Most of the other common polymers share, to some degree, the photo-oxidation reactions of the two polyolefins. However, they usually contain in their molecules one or more characteristic functional groups that contribute to the overall process. The photodegradation of polystyrene results in a characteristic yellowing and deterioration of mechanical properties. The color has been attributed to the formation of quinonoid (quinomethane) structures [*1,33*] by oxidation of phenyl groups at the para position or to polyenes (conjugated carbon-carbon double bonds) in the polystyrene molecular backbone [*12*].

Studies of poly(vinyl chloride) weathering have shown that this plastic

darkens due to the formation of polyene structures by a zipper-like elimination reaction of hydrogen chloride [*12,24*]; severe darkening of the polymer occurs well before any changes in mechanical strength take place. Although the effects of photodegradation processes are similar to those found in thermal degradation, the oxidative chain scission or crosslinking processes, or both, play a more important role [*24,34,35*].

Photodegradation of polymers, such as polyesters and polyamides, is complicated by the presence of hydrolyzable bonds [*36–39*]. The mechanism of their photodegradation has not yet been explained fully. Unsaturated polyesters become yellow under the influence of UV radiation and degradation occurs with scission of the main chain and crosslinking [*36*]; the yellowing is especially intense in polyesters that have benzene nuclei in their molecules. The hydrocarbon segments linked by the ester or amide groups in the molecule are susceptible to the same type of photo-oxidative processes as those occurring in hydrocarbon polymers.

Current theory of photodegradation provides a good basis for understanding the practical problems regarding the instability of most commercial polymeric materials when exposed out of doors. However, there are some discrepancies and gaps that suggest that the present theory is either incorrect or incomplete, and that additional work is necessary to explain fully the mechanism of these processes [*40*].

Physical Processes

Although much work has been done on the deterioration of polymeric materials, the emphasis was on the study of photodegradation; the role of water (moisture) and heat, two important environmental factors, has been largely neglected. Moisture, as a physical agent, exerts an important influence on the deterioration of most plastics by causing them to swell and shrink. It may also leach out soluble products of photodegradation and certain additives. Water sometimes may enter secondary photochemical reactions, for example, hydrolysis of photoactivated polymers such as polyesters and polyamides.

Thermal effects during weathering are determined by the actual temperature of the materials, especially at the exposed surface where most of deterioration occurs. The temperature of the exposed surface and that within a plastic component (for example, sheeting) are determined by the intensity of incident solar radiation, wind conditions, color, angle of exposure, thermal characteristics of the polymeric material, ambient air temperature, and type of backing material. The difference between the temperature of the exposed surface of a plastic panel and that of the ambient air ($\Delta t_{s,a}$) can be relatively large. A $\Delta t_{s,a}$ of 26 C deg (47 F deg) was reported for a backed, black poly(vinyl chloride) panel exposed in a horizontal position at Ottawa, Canada, during a clear June day [*41*]. A

maximum surface temperature of 62°C (140°F) was recorded for the same type of panel exposed in a vertical position facing west at the same location. During a summer day, under certain conditions, temperature differences larger than 30 C deg (54 F deg) may exist within a plastic sheet sample 3.2 mm (0.125 in.) thick [*42*].

Although the temperatures associated with plastics exposed in the outdoor environment are considerably lower than those prevailing during processing, the long-term thermal effects on the overall process of deterioration are important. Temperature affects the rate of secondary reactions involved in deterioration. However, more important effects are the thermally induced expansion and contraction imposed on a plastic-based material structure.

The combined effect of moisture and temperature cycles can cause severe deterioration in the form of surface cracks in plastic structures. This deterioration is accelerated greatly by the action of solar radiation. A mechanism, based on DBR/NRC studies [*43–45*] of the surface deterioration of polycarbonate and glass fiber reinforced polyester (GRP) sheeting materials will be discussed briefly. In outdoor weathering, cyclic variation of humidity causes absorption and desorption of moisture, and this, in turn, results in alternate swelling and shrinking of the surface material; cyclic variation of temperature induces alternate volume expansion and contraction.

Owing to gradients in moisture content and temperature in the plastic material and to the presence of flaws, the cyclic dimensional changes that occur are not uniform in the direction normal to the sheet or in a given plane parallel to the surface. Hence they cause a variable, nonuniform stress that results in stress fatigue. Such stress can be relatively large, depending on the environmental conditions and the nature of the plastic structure [*43,45*]. The effect of physically induced stress fatigue is particularly important in composites where dissimilarities in properties of the main components (matrix and reinforcement) are large, for example, in GRP. When GRP sheet is exposed to humidity-temperature cycling [*43*], cracks occur in the glass-resin interface region after only a relatively small number of cycles (Fig. 2*a*), indicating the intensity of the stresses involved. Prolonged exposure produces gradual fragmentation and spalling of the resin. Exposure to radiation, in addition to temperature and humidity cycling, in artificial or natural weathering, accelerates surface deterioration in the later stages of the process, by rendering the resin more brittle as a consequence of post crosslinking (induced by UV light). Eventually, the glass filaments become delaminated completely (Fig. 2*b*), resulting in a large number of glass fibers above the surface [*6*].

When deterioration in the glass-resin interface has reached an advanced stage, as evidenced by extensive fiber prominence, the exposed surface develops randomly oriented, single microcracks which propagate gradually and intersect to form a network (Fig. 2*c*). This occurs because the resin in

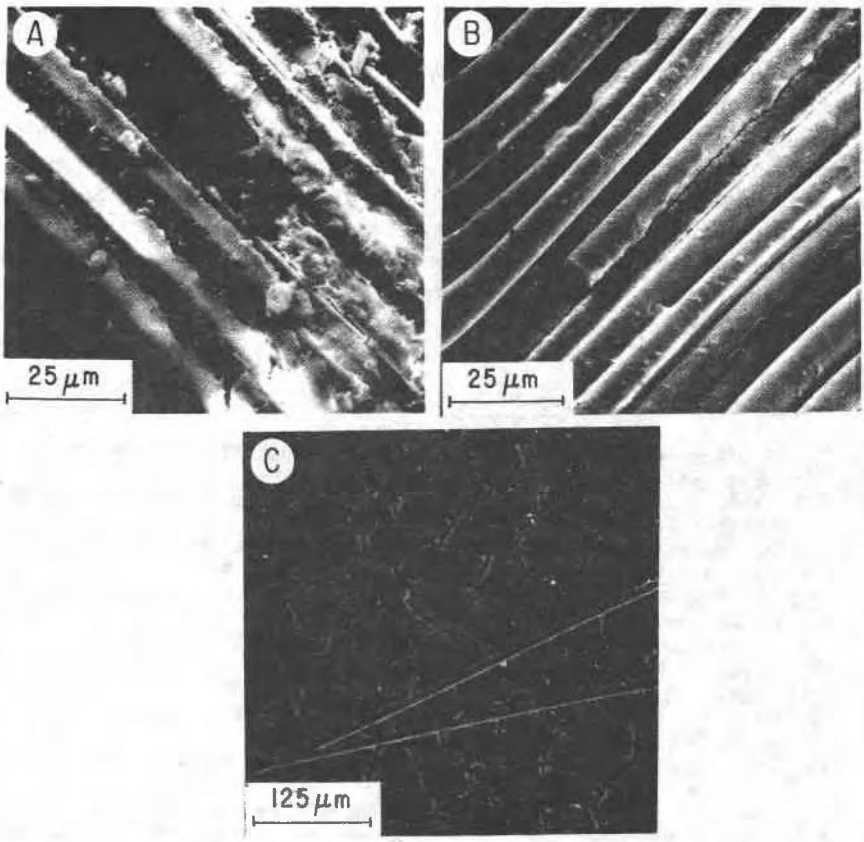

FIG. 2—*SEM photomicrographs of GRP sheet subjected to various exposures:* (a) *subjected to 40 humidity-temperature cycles.* (b) *aged in weathering machine for 600 cycles, and* (c) *weathered outdoors for 12 years.*

the exposed surface of the GRP sheet undergoes gradual shrinking as a result of post crosslinking induced by UV light. This shrinking produces permanent tensile stresses in the surface matrix, with gradients from the surface inwards. When the surface resin reaches a certain degree of rigidity as a result of post crosslinking, it can no longer deform reversibly under the action of stress-fatigue and thus undergoes fracture. The cracks grow from the surface inwards and are V-shaped, indicating that the stresses are tensile and decrease with distance from the surface.

Physically induced stress-fatigue, in conjunction with radiation, produces surface microcracking by an essentially similar mechanism [*45*], in standard UV-stabilized, unreinforced polycarbonate sheeting, a thermoplastic material. However, the UV light causes a decrease in molecular weight in the polymer of the exposed surface region [*5*] by a process of photo-oxidative

chain scission [*46*]. A decrease of the molecular weight results in a lowering of the total attractive forces (secondary forces) between neighboring polymer chains, and this, in turn, lowers the resistance of the resin to fracture. When the fatigue limit at a given microscopic site becomes lower than the environmentally induced stress fatigue, fracture of the resin material occurs, producing single cracks which gradually grow into a network, similar to that occurring in GRP under equivalent conditions. Although the surface microcracks are confined to the surface of the exposed side (5 to 10 μm deep), they cause a relatively large reduction in certain mechanical properties [*5*].

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