Photolytic Degradation

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ENGINEERING PLASTICS of various types are currently used outdoors or are soon expected to be used outdoors (Ref 1, 2). In addition, new materials are continually being developed. An organic material used outdoors is exposed to a very hostile environment. Sunlight, oxygen, heat, humidity, atmospheric pollutants, and physical stresses all combine to produce changes in the chemical composition of the material. These changes may take the form of polymer molecular weight reduction due to main chain cleavage, the formation of cross links, or the formation of oxidized and other functional groups. As the chemical composition of the material changes, its mechanical properties and physical appearance change. At some point, the changes in chemical composition become sufficiently extensive to render the material unfit for its design objectives, and the material fails.

Typically, a new material is evaluated for outdoor weatherability by placing it in a location known to have a harsh environment, such as Florida, and waiting for physical failure to occur (Ref 3). Typical types of failure include yellowing, chalking, surface embrittlement, loss of tensile or impact strength, and cracking. Chemical degradation usually proceeds from the top layer; this weakened surface can serve as a site for crack initiation. Once formed, cracks can propagate rapidly into the undegraded material below, causing failure.

Although a great deal of information has been gathered by following the physical performance of materials during outdoor exposure, the information tends to be empirical and therefore not easily extrapolated to new plastics systems. For example, it is not clear whether the individual components of new materials, such as plastics alloys/blends, will weather independently, allowing the weakest component ultimately to determine the rate at which physical properties are lost, or whether synergistic or antagonistic interactions between components are to be expected. Most of the weatherability data on plastics are restricted to simple systems.

Only recently, with advances in spectroscopic techniques, have relationships begun to develop between the chemistry that takes place in materials during outdoor exposure and the loss of mechanical properties. The absence of such relationships is surprising because the photochemistry of the simpler plastics, as well as model compounds representing every type of functionality found in plastics, has been studied in great detail (Ref 4, 5). However, the photochemistry of plastics in the outdoors is very difficult to follow systematically. First, the chemistry itself is slow, with many years between the onset of exposure and failure. The amount of chemistry necessary to cause failure can actually be very small. The loss of a single bond can halve the molecular weight of a polymer chain. Finally, the chemistry occurs in the near absence of the usual laboratory controls. Light intensity and wavelength, temperature, humidity, and physical stresses, representing the more obvious variables, can span enormous ranges over the course of an experiment. Compounding this issue, failure events also tend to be stochastic and require multiple exposures to accumulate statistically reliable data. Several samples of the same plastic exposed to the same weathering will have a distribution of time-to-failure, and this must be taken into account in analyzing failure data.

Because there are few truly photostable plastics and because there is a lack of specific long-term data on many engineering plastics, it is generally assumed that these plastics require some protection in the form of stabilizers or an external coating. Although the use of coatings can eliminate concerns regarding plastic durability, coatings have their own set of durability issues and can add significantly to the cost of the final product. The photolytic instability and degradation of plastics have a direct analog in the corrosion of metals in that function is slowly degraded in the external environment by chemical reactions and must be treated as limiting the true usefulness of the materials. In the future, the full and successful outdoor use of engineering plastics will undoubtedly depend on a clear understanding of the chemical changes induced by weathering and their relationship to physical properties.

This article will provide a basic review of polymer photochemistry as it relates to the weatherability of engineering plastics. The present work considers only one aspect of weatherability chemistry, namely, the chemistry induced by exposure to sunlight in the open air. Mechanochemical, biochemical, hydrolytic, and air pollution induced degradation are not discussed. It is recognized that these other environmental factors can influence the rate of photochemistry (Ref 6). Elementary aspects that will be discussed include the light wavelengths responsible for polymer photochemistry, problems with artificial light sources, general photooxidation and specific photochemical reactions important in plastics, and factors influencing the rate of degradation. The approaches used to stabilize plastics against photochemical damage, including ultraviolet light absorbers, oxidation inhibitors, and the use of protective coatings, are also considered.

Sunlight

Ultraviolet Light. When light is absorbed by a plastic, the energy is used to promote an electron in the absorbing chromophore to an excited state. Photochemistry begins when the stored light energy is used to drive a chemical reaction. No photochemistry occurs when the light is dissipated harmlessly as heat. The rate at which reaction occurs depends on the energy content and intensity of the light absorbed, the chemical nature of the chromophore excited, and its environment.

The energy content of sunlight at ground level, as well as its intensity as a function of wavelength, is modified considerably by the presence of ozone in the earth's atmosphere. Ozone absorbs sunlight at wavelengths shorter than 290 to 300 nm (2900 to 3000 Å). The ozone cutoff has often been ignored in the design of apparatuses used to accelerate the degradation of polymers for test purposes (specifically, fluorescent sunlamp devices). This is one of the reasons why accelerated weathering results do not always correlate with outdoor exposure results. Ozone limits the energy of photons reaching ground level to a maximum of 410 to 400 kJ/mol (98 to 95 kcal/mol). In contrast, many studies of polymer photochemistry have used mercury arc light sources. This source has light at wavelengths as low as 254 nm (2540 Å) and an energy level of 470 kJ/mol (112 kcal/mol), and it may induce chemistry that does not occur outdoors.

The activation energy of most photochemical reactions in the gas phase usually lies no more than 5 to 6% above the dissociation energy of the bond being broken. Typical bond dissociation energies in plastics range between 420 and 290 kJ/mol (100 and 70 kcal/mol). Therefore, it is not surprising that ultraviolet light at wavelengths shorter than 300 nm (3000 Å) is sufficient to break bonds and to initiate degradation. Fortunately, the intensity of the light in the 290 to 300 nm (2900 to 3000 Å) region is very low; if this were not the case, few present-day plastics would be of use outdoors. Light in the 290 to 320 nm (2900 to 3200 Å) range, with 410 to 370 kJ/mol (98 to 89 kcal/mol), is estimated to account for 0.5%, at most, of the radiant energy of the sunlight at noon in southern regions. Light in the 300 to 360 nm (3000 to 3600 Å) range, with 370 to 330 kJ/mol (89 to 79 kcal/mol), is more abundant, but it is less energetic and accounts for up to 2.5% of the total radiant energy of sunlight. Light in the 360 to 400 nm (3600 to 4000 Å) range, with 330 to 300 kJ/mol (79 to 71 kcal/mol), is sufficiently energetic to break only the weakest polymer bonds, and it accounts for over half of the ultraviolet component of sunlight.

Absorption of Ultraviolet Light. Figure 1 identifies some polymers that are commonly used in engineering plastics. These polymers can be divided into two broad categories based on whether or not the monomer unit contains a chromophore that absorbs the ultraviolet component of sunlight. The division is artificial in that nonsunlight-absorbing polymers invariably contain traces of sunlight-absorbing impurities. All these polymers photochemically degrade during outdoor exposure. Transparency alone is not a good measure of the utility of a polymer in the outdoors. Much depends on the criteria assigned to constitute failure. The surface of a photodegraded material consisting of a sunlight-absorbing polymer may yellow, while its interior remains physically sound and chemically unchanged because it is screened. Conversely, absorption of ultraviolet light and subsequent photodegradation may occur throughout the bulk of a nonsunlight-absorbing polymer. However, the division is useful in categorizing the type of chemistry likely to dominate degradation.

The photodegradation of nonsunlight-absorbing polymers is dominated by free radical chain oxidation initiated by the photolysis of unwitting chromophoric impurities or chemical defects. In the photodegradation of sunlight-absorbing polymers, the direct photochemistry of specific functional groups leads to destruction of the polymer chain, with subsequent free radical chain oxidation chemistry, causing further damage. Strategies for extending the useful life of plastics in the outdoors are keyed to these differences in degradation mode.

Polymer Photochemistry

Reactions in the Excited State. The first step in any photochemical reaction is the absorption of light by a chromophore to create an excited state denoted by A^* (Ref 7):

$$A + h\nu \rightarrow A^* \qquad \text{(Eq 1)}$$

The excited state can either relax back to the ground state (through emission of a photon or heat) without any changes in chemistry or undergo chemical reaction. Two types of reactions dominate the chemistry of excited states in polymers: dissociation and hydrogen atom abstraction. Both of these processes form a pair of radicals in close proximity. The initially formed radical pair is thought to reside in a cage, surrounded by its polymer host. A number of reaction possibilities exist for radicals within the cage. They may escape the cage to become free radicals or may simply recombine. Recombination is favored in a highly viscous medium, such as a polymer, and accounts for the fact that the quantum yield for the formation of free radicals in polymers is usually very low (<1%) relative to model compounds in solution. Recombination within the cage may result either in the regeneration of the original chromophore or in a rearrangement, as illustrated by the well-known photo-Fries reaction observed in aromatic PCs (Fig. 2).

The product of this rearrangement is a phenyl salicylate ultraviolet absorber. This moiety acts to protect lower layers of PC from sunlight. In part, this accounts for the relatively good durability of the material. The PC fraction at or near the surface does yellow. In applications in which optical performance is important (for example, headlamps), this can be unacceptable, and coatings or ultraviolet absorbers are required.

The escape of cage radicals to form free radicals is illustrated in Fig. 3 by the Norrish I photocleavage of a terephthalate ester. This reaction results in the cleavage of the polymer chain and opens the possibility for free radical chain oxidation, as will be discussed shortly.

Dissociation is the predominant path for free radical formation in most of the functional groups shown in Fig. 1.

Intermolecular hydrogen atom abstraction is illustrated in Fig. 4 by the reaction of excited benzophenone, an analog of PEEK, with the hydrogen atom donor, PH. Hydrogen atom abstraction can result in the formation of polymer-polymer cross links, which will cause changes in polymer properties, especially embrittlement.

The Norrish II photocleavage of a terephthalate ester illustrates an intramolecular hydrogen atom abstraction, shown in Fig. 5, in which free radicals are not formed. This reaction results in the cleavage of a polymer chain.

Free Radical Induced Oxidation. The reactions illustrated in Fig. 2 through 5 also pertain to trace chromophores in nonsunlight-absorbing polymers. The nature of the chromophore-absorbing light is usually unknown. Typically, the chromophores are impurities, such as end groups, initiator and inhibitor fragments, and processing-related oxidation products. Specific chromophores include aliphatic and aromatic ketones, phenols, hydroperoxides, and transition metal compounds. Upon absorption of light, the excited states of these groups dissociate, or hydrogen atom abstract, (for example, the reactions shown in Fig. 3 and 4) to yield free radicals. Some species may also transfer the excited-state energy to another species, which undergoes these reactions.

Because the specific chromophore(s) is not usually known, the photoinitiation reaction is usually generalized as polymer + light → 2$Y\cdot$, as shown in Fig. 6. The photolysis of a noncovalently bound chromophoric impurity causes no direct damage to the polymer. A chromophore-base free radical, $Y\cdot$, goes on to abstract a hydrogen atom from its polymer host to produce a polymer radical. This reaction destroys the identity of the initially formed free radical, and subsequent reactions reflect the free radical chemistry of the polymer. The polymer radical may undergo a variety of transformations in which radical character is preserved. A reactive polymer radical may abstract a hydrogen atom from a neighbor to produce a less reactive polymer radical. In Fig. 7, for example, the tertiary benzylic radical is more stable than the secondary aliphatic radical.

If the resultant radical is sufficiently nonreactive, then reaction ceases. Intramolecular hydrogen atom abstraction results in the movement of a radical site down a polymer chain. Repeated intramolecular or intermolecular hydrogen atom abstraction between nearly equivalent radical sites is thought to be one of the ways in which radical sites move in polymers, for which translational motion is restricted. The formation of polymer radicals can lead to depolymerization, although this reaction is most often encountered when polymers are photolyzed at elevated temperatures (>100 °C, or 212 °F) and may not be important in the outdoors. In depolymerization, the radical site moves down a polymer chain in a stepwise fashion as monomer units are eliminated.

When oxygen is plentiful, the most likely reaction for a radical (either the primary event radical, $Y\cdot$, or polymer radical, $P\cdot$) is the reaction with oxygen. The oxygenated

(a) Polyethylene (PE)

(b) Polybutadiene

(c) Polyvinyl chloride (PVC)

(d) Polystyrene (PS)

(e) Polyvinyl acetate

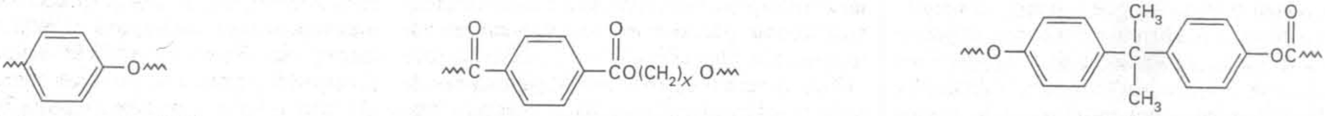
(f) Polyacrylonitrile

(g) Polymethacrylate

(h) Polyvinyl alcohol (PVAL)

(i) Polyamide (PA)

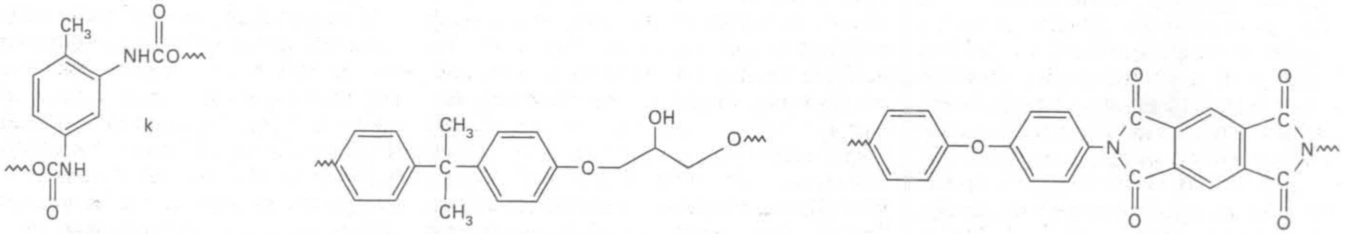
(j) Polyacetal



(k) Polyphenylene ether (PPE)

(l) Polyester

(m) Polycarbonate (PC)



(n) Polyurethane (PUR)

(o) Bisphenol A epoxy

(p) Polyimide (PI)

(q) Polyetheretherketone (PEEK)

(r) Polysulfone (PSU)

Fig. 1 Monomer units of common polymers. (a) through (j) are not sunlight absorbing; (k) through (r) are sunlight absorbing.

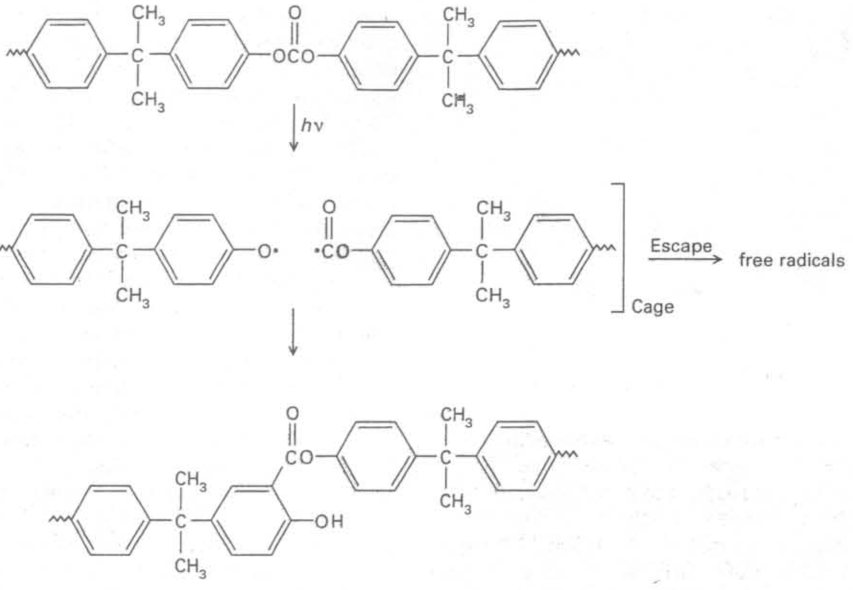


Fig. 2 Photo-Fries reaction in aromatic PC

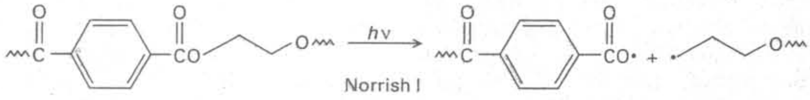


Fig. 3 Norrish I photocleavage of terephthalate ester

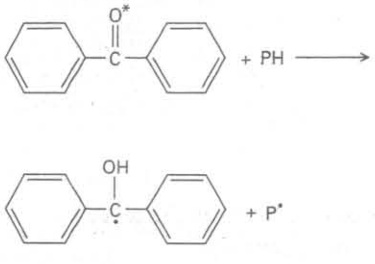
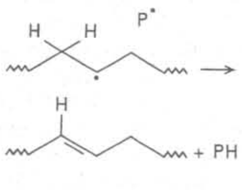


Fig. 4 Intermolecular hydrogen atom abstraction

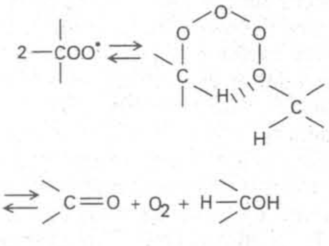
radicals, YOO· or POO·, abstract hydrogens from the polymer matrix to form a hydroperoxide and a new polymer radical. The newly generated polymer radical reacts with oxygen to complete an oxidation cycle, as illustrated in Fig. 6. This is termed propagation. A free radical will cycle or propagate through the loop, generating oxidized products, until it is terminated by reaction with another radical. Under oxygen-starved conditions, two polymer radicals can terminate either by disproportionation:



or by recombination:

$$P^{\bullet} + P^{\bullet} \longrightarrow P-P$$

Recombination results in the formation of a polymer-polymer cross link. When oxygen is plentiful, most termination reactions involve oxygenated radicals:



Subsequent reactions of peroxy radicals and hydroperoxides result in both chain scission and cross-link formation, shown in Fig. 8 and 9, respectively.

The balance between chain scission and cross linking depends on the nature of the polymer. Polymers such as polybutadienes, polyacrylates, and polystyrenes tend to form cross links upon degradation, while polymers such as polymethacrylates tend to degrade by chain scission. Oxidative-induced chain scission and cross linking occur in addition to the direct photoinduced chain scission that occurs in sunlight-absorbing polymers.

The reactions shown in Fig. 6 are a gross simplification of the reactions necessary to describe the photooxidation chemistry of even the simplest polymer. In an actual system, a variety of P· and POO· radicals will coexist. Alkoxy radicals, PO·, are also formed. The rate at which oxidation proceeds (Eq 2) is determined by the photoinitiation rate W_i, the propagation rate constant k_p (the rate constant for the hydrogen atom abstraction of PH by POO·), and the termination rate constant k_t. Equation 2 is derived using the steady-state approximation for the reactive radicals shown in Fig. 6 (Ref 8):

$$\text{Photooxidation rate} = \frac{-\mathrm{d}[\mathrm{PH}]}{\mathrm{d}t} = \frac{k_p\,[\mathrm{PH}]\,(W_i)^{1/2}}{k_t^{1/2}} \qquad \text{(Eq 2)}$$

The photooxidative chain length is the ratio of the photooxidation rate to the photoinitiation rate. The photoinitiation rate is proportional to the light intensity at the wavelength necessary to excite chromophoric impurities, as well as their concentration. As oxidation proceeds, the photochemistry of oxidation products contributes both to reaction complexity and to rate. The initial chromophores may be consumed while other chromophores are produced during the photooxidative cycle. A chromophore that is particularly important in the photooxidation of polyolefins is hydroperoxide. In polyolefins, the chromophore concentration, and therefore the photoinitiation rate, is initially very low. This leads to large photooxidative chain lengths (>100) with a slow build up of hydroperoxides. Oxidation is relatively slow during this photooxidation stage, termed the induction period. Hydroperoxides decompose either thermally or by reaction with light to form alkoxy and hydroxyl radicals. This chain branching (Fig. 6) leads to an autocatalytic increase in the photoinitiation rate and the photooxidation rate.

Hydroperoxide-driven autooxidation is less important in polymers in which the photooxidation chain length is relatively small. This is likely to be the case with sunlight-absorbing polymers. Hydroperoxide photochemistry was found to be of little importance in a cross-linked acrylic coating in which the oxidative chain length was relatively short (<10). Hydroperoxide buildup was not observed, and the rate of photooxidation was relatively constant with time. The rate of oxidation in these coatings was found to be very sensitive to the concentration of ketone end groups formed during polymer synthesis. The introduction of unwitting chromophores may play a similar role in determining the photooxidative stability of engineering plastics. Here, processing usually involves both high mechanochemical and thermal stresses, conditions that are ideal for oxidative degradation.

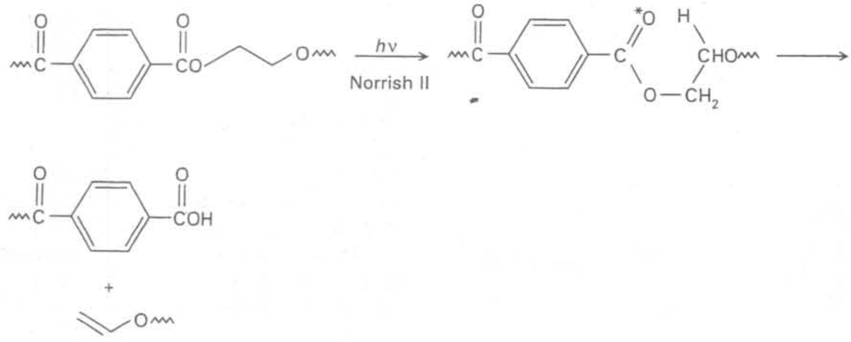


Fig. 5 Intramolecular hydrogen atom abstraction

Factors Controlling Photodegradation Rates. In addition to chromophore concentration, several other polymer variables can affect photoinitiation and photooxidation rates (Ref 9). The photooxidation rate depends on the ratio of $k_p/(k_t)^{1/2}$. The propagation rate constant, k_p, is determined by the ease of hydrogen atom abstraction from the host polymer by peroxy radicals. The ease of hydrogen atom abstraction from aliphatic alkanes is as follows: tertiary > secondary > primary. Aromatic hydrogens are much more difficult to abstract than aliphatic hydrogens. Hydrogens that are α to an ether oxygen are relatively easy to abstract. Amide hydrogens are also easily abstracted. Fluorine atoms are nearly impossible to abstract. Hydrogen atom abstractability can explain in part the different photodegradation rates of different polymers. For example, PE has better photostability than polypropylene (PP) because PP has a large concentration of easily abstractable tertiary hydrogens, while PE has only secondary hydrogens. This leads to a higher ratio of $k_p/(k_t)^{1/2}$ in PP and to more rapid photooxidation.

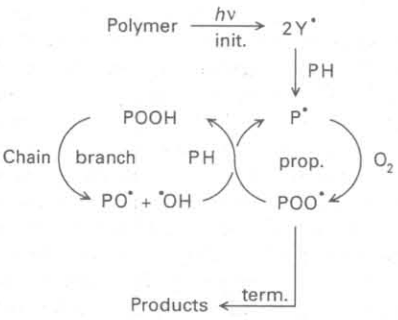


Fig. 6 Schematic of photooxidation cycle

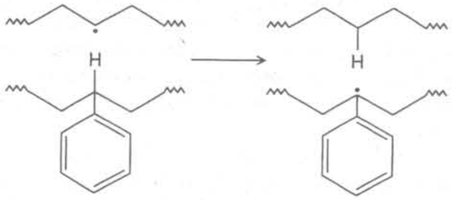


Fig. 7 Tertiary benzylic and secondary aliphatic radicals

Another very important variable in determining photooxidation rate is the rigidity of the polymer chain. The more rigid the chain, the less likely that photooxidation will occur on the chain. In semicrystalline polymers, photooxidation occurs almost exclusively in the mobile amorphous phase. Photooxidation can be very slow in the rigid crystalline phase. Therefore, increasing the crystallinity generally improves the photostability of a polymer. In amorphous polymers, the rate of photooxidation is strongly influenced by the glass transition temperature, T_g, of the polymer. For example, in a series of cross-linked acrylic copolymer coatings, the photoinitiation rate and the photooxidation rate decreased as the T_g of the acrylic copolymer increased (Ref 10). This effect can be explained as the influence of cage rigidity on free radical escape efficiency. Polymer rigidity will also affect the propagation and termination rate constants. Photoinitiation and photooxidation are also affected by service temperature. Increasing the temperature increases polymer mobility, which increases cage escape efficiency and leads to more rapid photooxidation.

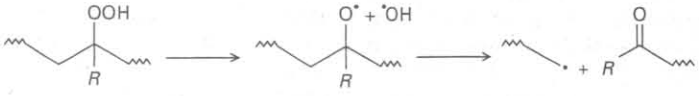


Fig. 8 Chain scission formation

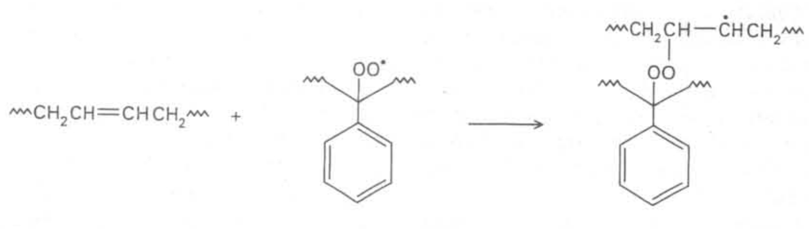


Fig. 9 Cross-link formation

Ultimate mechanical failure depends on the rate of photodegradation and on the amount of chemical damage that a particular plastic can sustain before failure. The amount of chemical damage necessary to cause failure depends on a number of factors. One factor is the type of chemical reactions that occur. For thermoplastic polymers, chain scission, which results in a decrease in polymer molecular weight, may be a more important reaction than the oxidation of a side chain, which leaves the main polymer chain intact. The basic structure of the polymer is also important. A cross-linked polymer (thermoset) can tolerate a higher level of chain scission while maintaining its structural integrity. Finally, the level of stress that the polymer is subjected to will also affect how much chemistry will cause failure. Higher levels of stress will cause the plastic to fail at lower levels of chemical change. In addition, there is evidence that higher levels of stress can actually increase the rate of photodegradation.

Protection of Plastics From Sunlight

Ultraviolet Absorbers and Excited-State Quenchers. From the above discussion, it should be clear that nearly all plastics require protection from sunlight in order to perform outdoors for long periods of time (Ref 11, 12). There are basically two strategies for stabilizing plastics against photodegradation. The first involves slowing the rate of initial photochemistry, while the second involves interfering with the propagation cycle of photooxidation. Generally, it is more difficult to inhibit degradation in sunlight-absorbing plastics than in nonsunlight-absorbing plastics. Stabilizers that interfere with the propagation cycle are not as effective in sunlight-absorbing plastics, because they cannot prevent the primary photochemical reactions.

The initiation of photochemistry is usually controlled by lowering the amount of ultraviolet light available in the plastic. This can be done by adding ultraviolet-absorbing or -scattering pigments, such as carbon black or titanium dioxide. This prevents ultraviolet light from reaching very far into

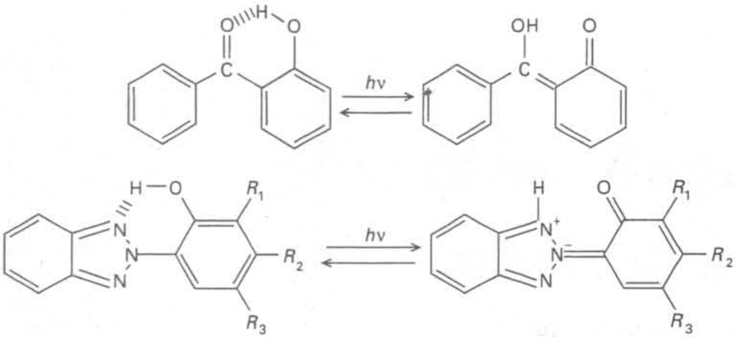


Fig. 10 Excited-state energy dissipation through internal hydrogen bond transfer

the plastic. Further reductions in ultraviolet light intensity are obtained by using ultraviolet absorbers. There are a number of classes of commercially available ultraviolet absorbers, including phenyl salicylates, *o*-hydroxybenzophenones, and *o*-hydroxyphenylbenzotriazoles. The benzotriazoles are probably the most effective ultraviolet absorbers currently available. At the 1 wt% concentration level, benzotriazole effectively reduces the intensity of sunlight below 370 nm (3700 Å) by 99%, at a depth of 40 to 50 μm (1.6 to 2.0 mils). Transmission above 400 nm (4000 Å) is high, minimizing the effects on color. The performance of an ultraviolet absorber depends on its ability to dissipate the energy absorbed without degradation. Benzotriazoles and *o*-hydroxybenzophenones rapidly dissipate excited-state energy through internal hydrogen bond transfer, as shown in Fig. 10.

For example, the lifetime of the benzotriazole excited state is less than 100×10^{-12} s, thus minimizing its excited-state photochemistry. In addition to its light-absorbing capability, the performance of an ultraviolet absorber depends on its compatibility with the polymer matrix and its long-term permanence. If the ultraviolet absorber is incompatible with the polymer, it will tend to bloom out of the polymer and be ineffective.

Another approach to reducing the initiation rate is to add materials that quench excited states. This reduces the lifetime of the excited state, thus lowering the quantum yield. The effectiveness of quenchers depends strongly on the nature of the chromophore to be quenched. Some ultraviolet absorbers can also act as excited-state quenchers. For example, *o*-hydroxybenzophenones and benzotriazoles can be effective quenchers of aromatic excited states. Nickel chelation compounds are also used as quenchers in polymers, mainly polyolefins.

Free Radical Scavengers. Ultraviolet absorbers can reduce the rate of the specific photochemical reactions, as well as the rate of free radical oxidation (by reducing the rate of initiation of radicals). One limitation of ultraviolet absorbers is that they cannot be effective at the surface of the polymer. The second basic approach to stabilization is to inhibit the photooxidation cycle through the use of antioxidants. One class of commonly used antioxidants is that of the hindered phenols. Hindered phenols react with peroxy radicals to lower the steady-state concentration of polymer-base radicals and to shorten the photooxidative chain length, as shown in Fig. 11.

Hindered phenols are primarily used to minimize thermal oxidation during processing and end-use. This limits the formation of chromophores produced by thermal oxidation. Hindered phenols are not very effective as light stabilizers, because they and their radical scavenger products can absorb sunlight and initiate free radical oxidation. Hindered phenols are generally not photostable; they do not last very long upon exposure to sunlight.

Another widely used class of stabilizer that inhibits photooxidation is the hindered amines. Typical hindered amines are shown in Fig. 12. The functional group that is important in preventing oxidation is the amine group in the tetramethyl piperidine ring. The amine is converted to a nitroxide by reaction with peroxy radicals, as shown in Fig. 13.

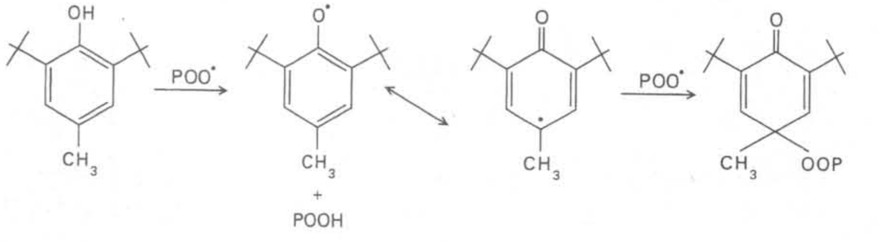


Fig. 11 Hindered phenol reaction with peroxy radicals

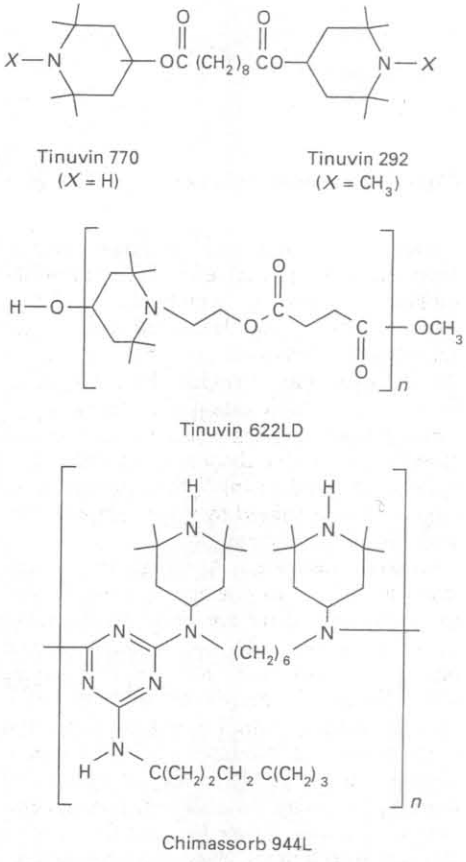


Fig. 12 Common hindered amine light stabilizers, including low molecular weight and polymer additives

Nitroxides are efficient scavengers of alkyl and other radicals to form amino ethers (>NOP). Amino ethers can also react with radicals to regenerate nitroxides. In each case, a polymer free radical is removed from the oxidation cycle. A key advantage of the hindered amines is that one hindered amine can ultimately scavenge many radicals through the nitroxide-amino ether cycle. Another advantage is that neither the hindered amine nor the amino ether reaction products absorb sunlight. Thus, they do not initiate photochemistry.

Hindered amines may also act to decompose hydroperoxides to non-free-radical products, thus limiting the possibility of chain branching. Additives containing sulfur and phosphorus are also used to decompose hydroperoxides.

Hindered amines, although excellent photostabilizers, are generally not effective as stabilizers for thermal oxidation, because amino ethers (>NOP) are not thermally stable, although some hindered amines are effective in moderate-temperature (<125 °C, or 250 °F) oven aging but not during processing. Hindered amines can greatly

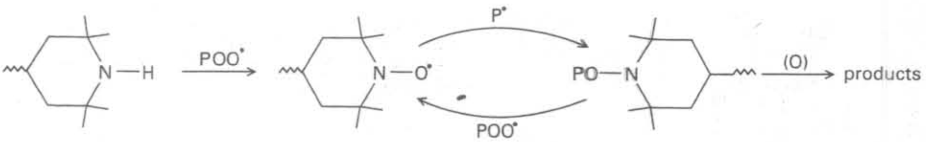


Fig. 13 Hindered amine converted to nitroxide by reaction with peroxy radicals

reduce the photooxidative chain length. They are most effective in nonsunlight-absorbing polymers in which the oxidative chain length is long. Hindered amines, together with ultraviolet absorbers to reduce the initiation rate, provide the most effective overall stabilization for many polymers, particularly polyolefins. As was the case for ultraviolet absorbers, the effectiveness of hindered amine light stabilizers is in large part determined by their compatibility with the polymer host.

External Coatings. Although photostabilizers are added to plastics to prevent photodegradation, there are some disadvantages to their use. As noted above, some photostabilizers may not be compatible with the plastic matrix or with the processing requirements. For example, it is not possible to use hindered amines in PCs, because they catalyze depolymerization during processing. In addition, photodegradation is usually limited to the first 100 to 200 μm (4 to 8 mils), even in unpigmented, nonsunlight-absorbing polymers. The stabilizers are present throughout the plastic. Therefore, most of the stabilizer is wasted (or at best serves as a reservoir) in the bulk of the plastic. Because stabilizing additives are generally more expensive than the host plastic, there is a cost penalty associated with their use. For this reason, coatings are often used to protect plastics from sunlight. There are numerous advantages to the use of protective coatings. They offer the potential for improved appearance and decoration. Coatings with ultraviolet absorbers protect the surface of the plastic as well as the bulk, provided the coating is not broken or scratched. They can be designed specifically for durability and can protect the plastic from attack by other environmental agents.

The design of coatings for plastics is rarely straightforward. Although a complete discussion of coatings is beyond the scope of this article, a few key issues should be mentioned. First, coatings often require baking for solvent removal and cure. The cure temperature must be below the heat-deflection temperature of the plastic to prevent shape changes. Some plastics, such as PCs, can craze or otherwise degrade in the presence of some solvents. The coating must not contain species that can attack the plastic. The choice of solvent in the coating formulation is critical for avoiding damage to the plastic, and for obtaining good initial adhesion. Removal of contaminants, such as mold release agents, is also important. The coating must be sufficiently durable to protect the plastic surface for the entire service life of the part. Finally, the viscoelastic properties of the coating must be matched to the plastic. For example, if a brittle coating is used over a ductile plastic, brittle failure of the plastic can occur upon impact. Basically, the coating can act as a crack-initiating site. The crack then propagates into the plastic, causing premature failure. Despite these potential problems, coatings are widely and successfully used to protect plastics from outdoor exposure.

REFERENCES

1. V. Wigotsky, Alloys and Blends Gain Market Momentum, *Eng. Plast.*, Vol 62 (No. 7), July 1986, p 19
2. V. Wigotsky, Engineering Resins Widen Performance Boundaries, *Eng. Plast.*, Vol 43 (No. 1), Jan 1987, p 15
3. M.L. Ellinger, Weathering Tests, *Prog. Organ. Coat.*, Vol 5, 1977, p 21
4. J.G. Calvert and J.N. Pitts, Jr., Photochemistry of the Polyatomic Molecules, in *Photochemistry*, John Wiley & Sons, 1966, p 366-486
5. B. Ranby and J.F. Rabek, Photodegradation and Photo-Oxidation of Particular Polymers, in *Photodegradation, Photo-Oxidation and Photostabilization of Polymers*, Wiley-Interscience, 1975, p 120-275
6. A.G.H. Dietz, H.S. Schwartz, and D.V. Rosato, Reinforced Plastic Composites, in *Environmental Effects on Polymeric Materials*, D. Rosato and R.T. Schwartz, Ed., Interscience, 1968
7. N.J. Turro, *Modern Molecular Photochemistry*, Benjamin/Cummings, 1987
8. N.M. Emanual, E.T. Denisov, and Z.K. Maizus, The Chain Mechanism of Free Radical Oxidation, in *Liquid Phase Oxidation of Hydrocarbons*, B.J. Hazzard, Trans., Plenum Press, 1967, p 1-18
9. I. Mita, Effect of Structure on Degradation and Stability of Polymers, in *Aspects of Degradation and Stabilization of Polymers*, H.H.G. Jellinek, Ed., Elsevier, 1978, p 248-294
10. J.L. Gerlock, D.R. Bauer, and L.M. Briggs, Electron Spin Resonance Determination of Nitroxide Kinetics in Acrylic/Melamine Coatings: Relationship to Photodegradation and Stabilization Kinetics, in *Polymer Stabilization and Degradation*, ACS Symposium Series No. 280, American Chemical Society, 1985, p 119
11. W. Schnabel and J. Kiwi, Photodegradation, in *Aspects of Degradation and Stabilization of Polymers*, H.H.G. Jellinek, Ed., Elsevier, 1978, p 195-246
12. G. Scott, Ed., *Developments in Polymer Stabilization*, Vol 1 to 5, Applied Science, 1979-1984