

PHOTOOXIDATION OF HIGH POLYMERS

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Abstract - The oxidative photodegradation of polyolefins involves a combination of radical and nonradical processes. Singlet oxygen has an important role in the initiation step forming hydroperoxides which, in turn, decompose to radicals and ultimately lead to Norrish chain scission reactions. Both UV absorbers and light screens reduce the photooxidation rate, but only the light screens affect the overall product distribution. Mixtures of light screens and hydroperoxide decomposers show synergistic behavior.

INTRODUCTION

Prevailing views on the oxidative photodegradation of polymers have changed since 1968 in several important respects. One of the more noteworthy developments was the recognition that 2-hydroxybenzophenones and related stabilizers were effective deactivators(1) as well as ultraviolet light absorbers. Another was the sudden interest in singlet oxygen(2,3) as a probable intermediate in degradation. Still another was the unusual sensitivity of some polymer surfaces to photooxidation(4). The evidence leading to these and other advances has been gathered primarily from the polyolefin studies outlined in this critical view.

Relative resistance to weathering

Unprotected polymers vary widely in deterioration rates during outdoor exposure as indicated in Table 1. In general, high stability involves high bond energies and an absence of sensitizing groups absorbing wavelengths greater than 290 nm. Since polytetrafluoroethylene meets both criteria it is not surprising that films of this polymer show virtually no change in physical properties during weathering in Florida over a period of several decades. Perhaps more significant is the low rate of carbonyl formation in poly(vinyl fluoride), about two orders of magnitude less than that of poly(vinyl chloride) under the same exposure conditions. Unlike its fluorine-containing analog, poly(vinyl chloride) darkens rapidly from loss of hydrogen chloride by the well-known sequential reaction that forms conjugated unsaturation. Other polymers that darken in sunlight are polystyrene and related systems containing aromatic groups. Minor exceptions are some of the aromatic polycarbonates(5) and polyesters which undergo Fries-type rearrangements that form stabilizing 2-hydroxybenzophenone structures.

TABLE 1. Relative stability to photooxidation

<u>High</u>	Polytetrafluoroethylene Poly(methyl methacrylate) Polydimethylsiloxane	
<u>Medium</u>	Polycarbonate Poly(ethylene terephthalate)	
<u>Low</u>	Polyolefins Natural Rubber Cellulose Polyoxymethylene	Polystyrene Polyamides Polyacrylonitrile Poly(vinyl chloride)

The principal polymers of commercial importance, cellulose derivatives, natural rubber, the polyolefins, polystyrene and poly(vinyl chloride) are, by curious coincidence, the least stable to weathering processes. All polymers with abundant hydrogens on allylic or tertiary carbon atoms are especially vulnerable to attack by oxygen, whereas other types such as poly(methyl methacrylate) with inert primary and relatively inaccessible secondary hydrogens are far more stable. Consequently, the majority of photooxidation studies have concerned the reactive hydrocarbon polymers.

Weathering behavior of polyolefins

In the absence of stabilizers, thin films of polyolefins become brittle during outdoor exposure for one summer season in temperate or tropical regions. Although polyethylene and polypropylene are almost completely transparent to wavelengths greater than 290 nm, most oxidation occurs at or well within one micron of the film surface(4,6). Number and weight-average molecular weights decrease continuously in both polypropylene(7) and linear polyethylene(8); however, the weight-average molecular weight of branched polyethylene passes through a maximum at the outset of photooxidation as shown in Fig. 1.

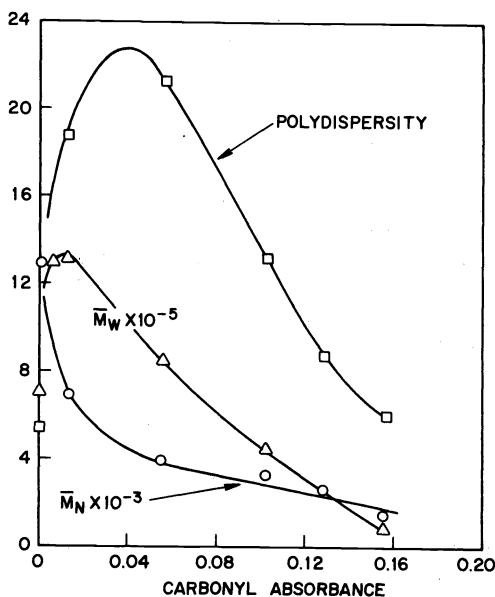
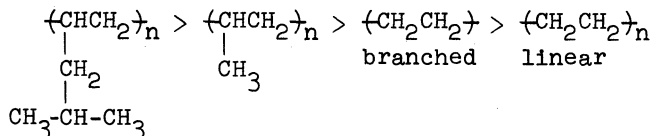


Fig. 1. Change in molecular weight and molecular weight distribution of branched polyethylene (density, 0.92) during outdoor exposure in New Jersey for one year. Carbonyl absorbance is proportional to oxygen uptake.

The oxidation rate of the branched polymer increases fourfold over the temperature range from 10° to 50°C(4), but is not significantly affected by the concentrations of ozone or nitrogen and sulfur oxides ordinarily found in the atmosphere. Thermal and photooxidation rates of polyolefins vary similarly with chemical structure(9) and morphology:



In particular, rates depend directly on the concentration and accessibility of reactive hydrogens on secondary and tertiary carbon atoms. Evidently, oxygen completely permeates the low density crystalline phase in poly(4-methylpent-1-ene) but is excluded from the more compact core regions in polyethylene crystallites(10).

Photooxidation products

Adams(7) photolyzed polyethylene and polypropylene under conditions simulating natural weathering processes and reported the variations in product distributions listed in Table 2.

TABLE 2. Product distribution in photooxidized polyethylene and polypropylene

Functional Group	Total Functional Groups %	
	Polyethylene ^a	Polypropylene ^b
Vinyl	59	22
Acid	26	17
Ketone	3	8
Aldehyde	0	8
γ -Lactone	6	6
Ester	6	39

^a after 720 hours exposure in weather-ometer

^b after 335 hours exposure in weather-ometer

Vinyl content was greater in polyethylene whereas carbonyl concentrations were higher in polypropylene. Autoxidation of polyethylene at 100°C forms no vinyl groups but tenfold more ketonic carbonyl groups than are formed by photooxidation at room temperature. A much higher hydroperoxide concentration, measured by the Mitchell method(11), developed in the thermally oxidized polymer than in the photooxidized films as shown in Fig. 2. Hydro-

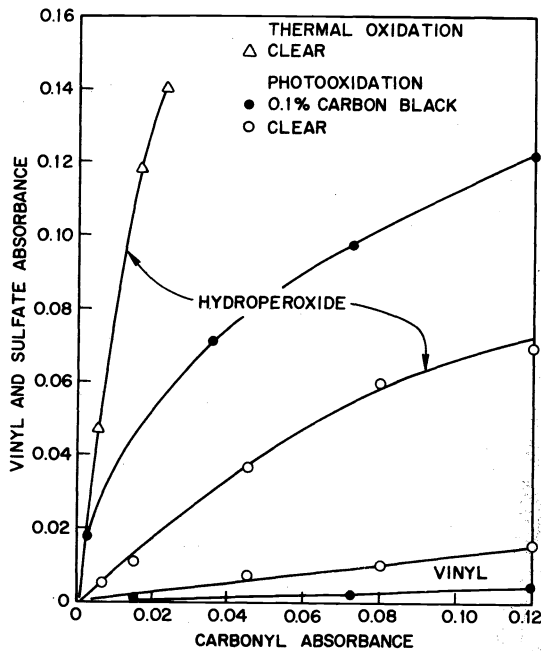


Fig. 2. Relative increase in hydroperoxide concentration during autoxidation of branched polyethylene (Δ) at 100°C. Change in both hydroperoxide and vinyl concentration during photooxidation (wavelength, 310 nm) of the same polymer (density, 0.92) in the clear form (\circ), and containing 0.1% of a 20 nm particle size furnace black (\bullet).

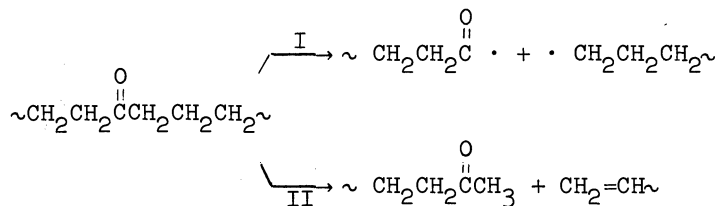
peroxide concentration rose rapidly at the outset and then leveled off in both the autoxidation and photooxidation of polyethylene. The sharp maximum observed by Scott(12) using different analytical and oxidation procedures was not observed in these studies. The Mitchell method makes use of the observation that sulfur dioxide reacts rapidly at room temperature with hydroperoxide groups in polyethylene leading to the formation of two strong sulfate bands in the infrared spectrum. Measurements were made immediately after exposure to the sulfur dioxide because the sulfate bands disappeared slowly at room temperature. Sulfate groups were not found

in other polyolefins.

The mechanism of oxidative photodegradation

Since saturated hydrocarbons do not absorb ultraviolet radiation of wavelengths greater than 200 nm, a level well below the shortest wavelength (290 nm) penetrating the atmosphere, it has been assumed that sensitizing impurities or molecular imperfections were responsible for the exceptionally low weather resistance of polyolefins. Catalyst residues, hydroperoxide, oxygen complexes and carbonyl groups(13) formed by reaction with oxygen during high temperature molding or extrusion operations are possible initiators. The remarkable reactivity of ultrathin surface regions has been ascribed (4) to products of ozonolysis and/or sensitizing deposits of polynuclear aromatic contaminants in the atmosphere(13).

Early investigators(14,15) concluded that vinyl groups were formed in polyethylene by Norrish II scission reactions and that the overall



degradation process consisted of a radical chain mechanism with high initiation and termination rates and a short kinetic chain length. The conclusion was consistent with the relative ineffectiveness of conventional radical chain stoppers as stabilizers in outdoor applications. In later studies of the photolysis of ethylene-carbon monoxide copolymers, Guillet(16) concluded that the homolytic cleavage process (I) was responsible for only ten percent of the chain breaks at room temperature and was even less important at lower temperatures.

Eventually, when its importance in photochemistry had been confirmed, singlet oxygen ($^1\Delta_g, ^1O_2$) was postulated as an intermediate in the oxidative photodegradation of polyethylene(2) according to the following scheme:

1. $^3(>C=O)^* + O_2 \rightarrow >C=O + ^1O_2$
2. $^1O_2 + CH_2=CHCH_2\sim \rightarrow HOOCH_2CH=CH\sim$
3. $HOOCH_2CH=CH\sim \xrightarrow{h\nu} \text{radical products}$

Norrish II scissions involving the n- π^* excited states of adventitious ketonic groups in the polymer chain form acetyl and vinyl groups in adjoining sites. When these groups are accessible to molecular oxygen the acetyl groups can act as photosensitizers forming singlet oxygen (reaction 1) immediately adjacent to a companionate vinyl group. The proposal is in accord with known reactions and lifetimes(17) of singlet oxygen in a solid. Nevertheless, the process may be quite inefficient because Guillet showed that the quantum yield for the Norrish II reaction declined with an increase in the length of the alkyl chains bonded to the ketonic group. In addition, the oxidative photodegradation rate of an ethylene-carbon monoxide (1%) copolymer with an enormously higher ketone concentration was merely twice that of a branched polyethylene containing no significant carbonyl concentration(4).

Consequently, Scott(12) proposed that hydroperoxides were the most significant sensitizers in photooxidation processes. His suggestion prompted the experiment whose results are shown in Fig. 3.

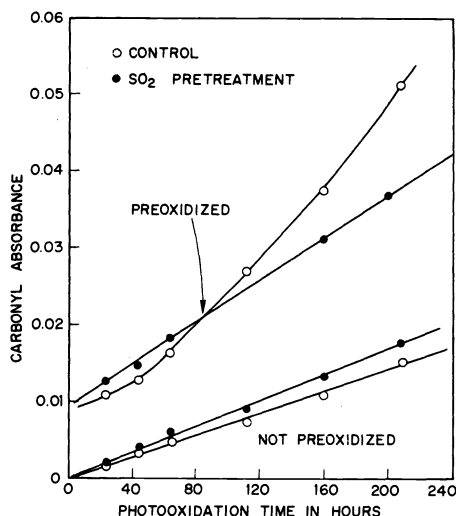


Fig. 3. Photooxidation rates of oxidized and unoxidized branched polyethylene before (O) and after (●) treatment with sulfur dioxide.

Unoxidized and oxidized films of branched polyethylene were exposed to sulfur dioxide to destroy any hydroperoxide that might be present and were then photooxidized. Although some autocatalytic activity was exhibited by the untreated preoxidized film, the results indicate that hydroperoxides are also rather ineffective sensitizers. They decompose slowly in nitrogen at 100°C or during photolysis with 310 nm radiation at room temperature.

If the Trozzolo-Winslow mechanism(2) is correct, any participation of singlet oxygen in the weathering process is limited mainly to the initiation step and contributes only in an indirect way to the chain scission process. Therefore, changes in molecular weight (Fig. 1) would result from random attack along molecular chains by alkoxy or peroxy radicals formed in step 3 of the Trozzolo-Winslow scheme. However, if the average kinetic chain length of these radical reactions was as short as Burgess suggested, the main function of photostabilizers would be suppression of the initiation step rather than interruption of the radical chain process.

Stabilization mechanisms

As a rule, photostabilizers are grouped into three categories: deactivators, ultraviolet light absorbers, and light screens. Carbon blacks are classified as light screens because the weathering rates of black films vary directly with particle size and inversely with concentration and degree of dispersion (18) and, in fact, the most weather-resistant black films of polyethylene do show negligible change in brittle temperature after one year of outdoor exposure(19). Figure 4 provides still further evidence for

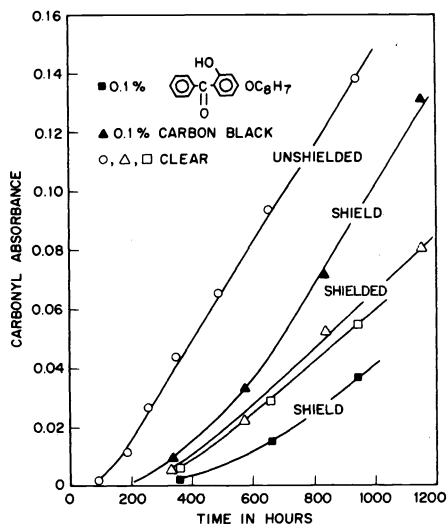


Fig. 4. Photooxidation rates of 5 mil branched polyethylene films under 310 nm radiation. Specimens containing no additive (O), 0.1% furnace black (▲), and 0.1% ultraviolet stabilizer (■) were exposed to direct radiation. Shielded specimens containing no additive were exposed to the radiation passing through either the black film (Δ) or the film containing the ultraviolet stabilizer (□).

screening activity since the black film oxidized faster than the underlying film containing no additives. Although it evidently functions simply as a light screen, the carbon clearly has another effect that has not been reported previously. For example, it reduced the rate of vinyl formation and accelerated hydroperoxide production especially in the early stages of oxidation (see Fig. 2). It also afforded a carbonyl band in the infrared spectrum of a black film of photooxidized polyethylene which closely resembled that of the autooxidized polymer (20). Finally it should be noted that the thiobisphenol in Fig. 5 suppressed the hydroperoxide

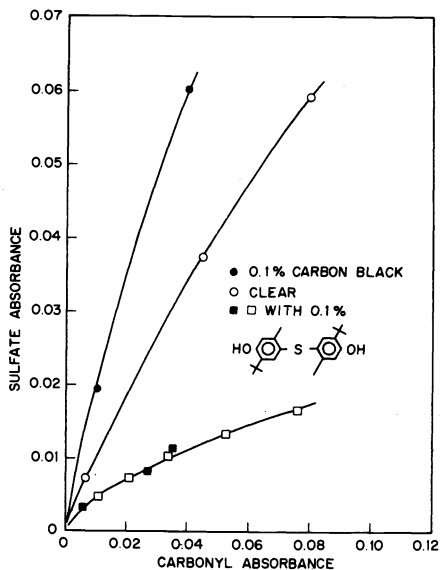


Fig. 5. Relative hydroperoxide concentrations at various stages in photooxidation of clear and black films of branched polyethylene with and without a thiobisphenol antioxidant.

concentration in both clear and black films, and the combination of carbon black and phenol in the studies shown in Fig. 6 exhibited distinctly synergistic behavior.

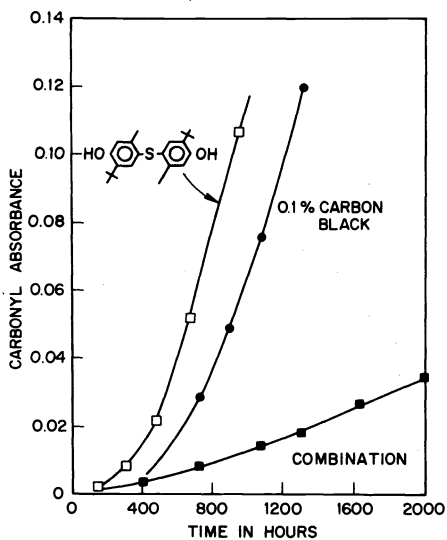
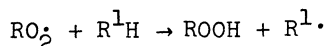
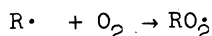


Fig. 6. Synergism in the photostabilization of branched polyethylene by carbon black and thiobisphenol.

Besides its regular role as a light screen, carbon black seems to increase the overall kinetic chain length of the radical reaction, thereby producing more hydroperoxide. Since ultrafine carbon particles seldom absorb sufficient radiation to become thermal initiators of radical reactions, it is likely that the particles promote the following propagation step by suppressing the radical chain termination rate:



The 2-hydroxybenzophenone acts entirely differently. Although it has been traditionally described as an UV absorber, it was even more effective as a deactivator in holding the oxidation rate of the nonblack shield film in Fig. 4 to about half that of the unstabilized shielded specimen. A substituted oxanilide gave similar results. Evidently these "so-called" UV absorbers function largely as deactivators, merely reducing the initiation rate without interfering significantly with the radical chain termination step (Fig. 7). Most likely they stop few radical chains if the kinetic

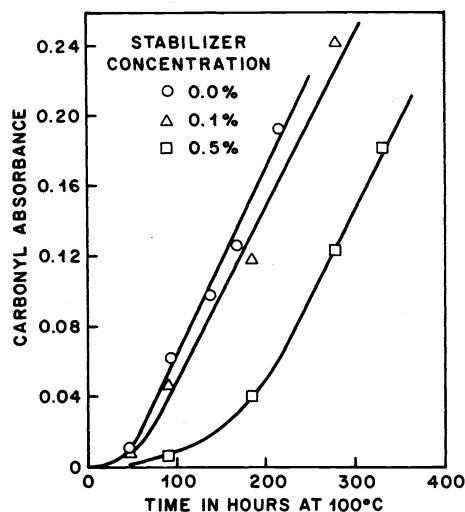


Fig. 7. The effectiveness of the *o*-hydroxybenzophenone of Fig. 4 as a stabilizer against oxidation in the absence of ultraviolet radiation.

chain length in the propagation step is as short as Burgess has suggested. Also, since photoreactions proceed far more rapidly in thin surface layers, an UV absorbing mechanism cannot be an important stabilization process(1). That would leave deactivation of singlet oxygen and various sensitizing species as the principal role of organic photostabilizers. The various sensitizers include dyes(21) and pigments in addition to other types already mentioned. Pappas(22) has obtained strong evidence for the formation of singlet oxygen and hydrogen peroxide during irradiation of titanium dioxide and zinc oxide. These reactive products from both pigments have been associated with chalking in paints. In view of these results it is strange that zinc oxide in the presence of zinc dialkyldithiocarbamates becomes an excellent photostabilizer for polyolefins(23).

CONCLUSIONS

Most photooxidation reactions in polyolefin films occur in or on ultrathin surface layers in which photosensitizers are apparently concentrated. These highly localized reactions have been simulated by photooxidizing films sensitized by polynuclear aromatics or by pretreatment with ozone. The initiation step probably involves a combination of different photosensitizers that form hydroperoxides through a singlet oxygen intermediate. Eventually, the hydroperoxides decompose to radical species which lead to chain scission by the Norrish mechanisms. These radical reactions presumably have high initiation and termination rates and a short kinetic chain length. Ultra-

violet absorbers reduce the initiation rate but have no noticeable effect on the overall radical reaction mechanism, whereas light screens lead to distributions of oxidation products similar to those obtained in autoxidations.

The relative importance of ketones, hydroperoxides and other oxidation products as sensitizers for the oxidative photodegradation of polyolefins is still largely unknown. Even less is known about other familiar polymers such as polystyrene(24) and poly(vinyl chloride)(25) which discolor during weathering.

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