

Accelerated Photo-Oxidation of Polyethylene. I. Screening of Degradation-Sensitizing Additives

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Synopsis

Numerous simple compounds have been shown to be capable of accelerating the photo-oxidation of polyethylene upon exposure to wavelengths near 300 nanometers. Probable mechanisms of photo-initiation by the principal classes of degradation-promoting additives are discussed.

INTRODUCTION

Modification of thermoplastics to enhance their susceptibility to environmental photodegradation has been proposed as a means of reducing labor requirements in the use of agricultural films and of minimizing litter problems related to the careless disposal of plastic packaging materials.¹⁻¹⁸ Intentional partial photodegradation by exposure to artificial light sources could also be considered as a means of introducing chain defects or sensitizing groups which would increase the susceptibility of plastics to subsequent environmental deterioration; this might be carried out immediately after fabrication of plastic films or molded articles, or at the stage of disposal/reclamation of waste plastics. *Thermal* oxidation of polyolefins has been shown to enhance their susceptibility to photodegradation.¹⁹⁻²²

While there have been numerous reports of the enhancement of photodegradability by selective modification of polymer structure or by incorporation of specific additives, there have been few reported attempts to compare the effectiveness of a wide variety of possible sensitizing additives. The present paper summarizes the results of one such attempt in the specific case of low-density polyethylene.

IDENTIFICATION AND SELECTION OF DEGRADATION-SENSITIZING ADDITIVES

In order to have maximum utility in practical applications, an additive or additive system for polyethylene should have the following characteristics: (1) effective sensitization of photo-oxidative degradation of the polymer; (2) no adverse effect on the thermal-oxidative stability of polyethylene, so that the additive can be incorporated prior to melt processing; (3) minimal effect on color and transparency of the polymer; (4) preferably, the wavelength of maximum photosensitivity should be in the range of 300 to 330 nm, so that degradation

would be rapid in sunlight but slow under normal indoor illumination; (5) the additive(s) should be readily incorporated in molten polyethylene and should remain well dispersed in the polymer as the melt solidifies.

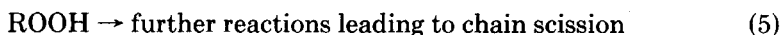
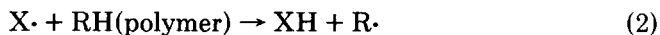
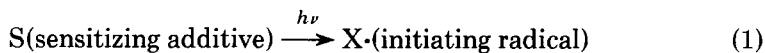
In view of the second and third requirements, two otherwise promising classes of additives—peroxidic compounds and organic dyes—were excluded from consideration. For the same reasons, metallo-organic additives were not examined in great detail, though a few representative metallo-organic compounds were included in this study. In view of present concerns over toxicity and environmental contamination, most halogenated compounds were also excluded from consideration.

A search was made for readily available organic compounds having ultraviolet absorption maxima in the range 250 to 350 nm. Such compounds, and those having related chemical structures, received the major emphasis. In order to ensure homogeneity of the additive/polymer composition, initial "screening" studies were performed on films cast from warm xylene. Films containing 1–5% by weight of selected additives were exposed for 24 hr in air to light from an unfiltered ultraviolet source having peak emission at 305 nm. The extent of photo-oxidative degradation was then ascertained from the increase in intensity of the aliphatic carbonyl peak (at ca. 1710 cm^{-1}) in the infrared spectrum of the film. Additives causing substantial increases in carbonyl intensity are listed in Table I; unless otherwise specified, each additive was employed at a level of 2% by weight.

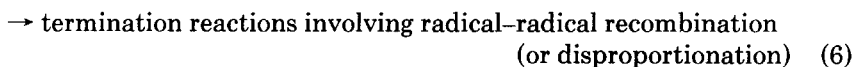
DISCUSSION

In considering the results shown in Table I, it must be remembered that we are intentionally examining degradation only in one specific wavelength range (near 300 nm). Such a well-established photosensitizer as benzophenone proved to be relatively ineffective under these conditions, a result which is readily understood since benzophenone does not exhibit strong UV absorption in this wavelength range.

Abundant evidence indicates that the photo-oxidation of polyolefins is a free-radical chain reaction in which molecular oxygen participates.^{23–28} Hence, we ascribe the action of degradation-promoting additives to the acceleration of such a free-radical process, probably by facilitating the initiation step (initial formation of radicals capable of abstracting hydrogen atoms from the polymer chain):



$\text{R}\cdot, \text{RO}_2\cdot, \text{X}\cdot$



Let us attempt to examine the first step in greater detail. The polymer itself does not possess light-absorbing groups other than those present as chain defects or impurities, which are responsible for the initiation of photo-oxidation of the additive-free polymer. Hence, we assume that photodegradation begins with absorption of light by the additive, with conversion of the additive to an excited state:



In some cases, two excited states are likely to be involved—an excited singlet formed directly by photochemical excitation and a longer-lived triplet formed from the singlet as a result of intersystem crossing.

The excess energy of the excited additive S^* may be lost in any of several ways: by reemission of radiation (fluorescence or phosphorescence), by radiationless conversion to the ground state with the evolution of heat, by transfer of electronic energy to other molecules, or by chemical reaction. There are four principal alternative mechanisms by which the deactivation of S^* can lead to the formation of free radicals:



Reaction (8) involves a direct hydrogen atom abstraction from the polymer by the excited state of the sensitizer. The photoreduction of benzophenone²⁹⁻³¹ is a well-known process in which such a hydrogen abstraction step occurs.

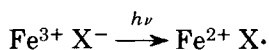
In reaction (9), the excited state decomposes unimolecularly to form a pair of radicals. Examples of this process include the Norrish Type I reaction of aliphatic ketones^{31,32} and the photodissociation of peroxides^{33,34} and benzoin derivatives.³⁵⁻³⁷

Reaction (10a) involves transfer of a single electron from S^* to a suitable acceptor A. Alternatively, S^* could also accept a single electron from a suitable donor molecule, reaction (10b). If S, A, and/or D are ions, the products of such electron transfer processes need not be charged species. The photopolymerization of vinyl monomers in the presence of ketone-amine mixtures^{36,38,39} and the photopolymerization of N-vinylcarbazole in the presence of electron acceptors^{40,41} are examples of reactions in which similar photoexcited electron transfer processes are believed to occur.

In alternative (11), the excitation energy of S^* is transferred to another molecule Z, whose excited state is capable of forming free radicals either directly or indirectly. Species Z is usually molecular oxygen, in which case Z^* is "singlet oxygen."^{42,43} The sensitized photo-oxygenation of olefins⁴⁴⁻⁴⁶ provides an example of a reaction which appears to involve singlet oxygen; subsequent reaction of the singlet oxygen with the olefin yields a hydroperoxide which is capable of undergoing further decomposition to form radicals. Mechanisms involving singlet oxygen have been proposed for the photo-oxidative degradation of many polymers including unsensitized polyethylene.⁴⁷⁻⁵³

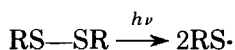
The majority of degradation-promoting additives listed in Table I are aromatic ketones or quinones. The photo-initiating activity of these compounds is probably due, in most cases, to a direct hydrogen abstraction reaction between the excited state of the additive and the polymer molecule, reaction type (8). Initiation mechanisms of this type have been proposed by other workers who have recently examined the photodegradation of polyolefins⁵⁴⁻⁵⁷ and poly(vinyl chloride)⁵⁸ in the presence of aromatic ketones. Similar hydrogen abstraction mechanisms have also been proposed to account for the activity of quinones and their derivatives in promoting photodegradation of polystyrene and cellulosic materials.⁵⁹⁻⁶² The ability of such photo-initiators to abstract aliphatic hydrogen atoms is further demonstrated by their activity in promoting photochemical crosslinking,⁶³⁻⁶⁸ photo-induced graft polymerization,^{55,63,64,67} and photopolymerization of vinyl monomers in the presence of solvents capable of acting as hydrogen atom donors.^{36,69-71}

The degradation-promoting activity of many organic derivatives of transition metals is believed to result from photo-excited ligand-to-metal electron transfer, e.g.,

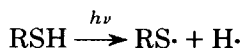


The ligand-derived radical X·, or another radical derived from X·, presumably serves as the autoxidation-initiating species. Such radical-forming photo-initiation processes have been proposed in a number of publications dealing with the photochemistry of transition metal derivatives.^{13,21,64,72-85} Although this is frequently viewed as an example of photo-excited electron transfer, reaction type (10b), it can also be regarded as a photochemical homolytic scission of a covalent metal-ligand bond, reaction type (9). If the transition metal is in a low oxidation state (e.g., ferrous iron), initiation may be preceded or accompanied by thermal or photochemical oxidation of the metal, with oxygen (or a periodic impurity) acting as the oxidizing agent.⁸⁶⁻⁸⁹

Organic disulfides such as benzyl disulfide and phenyl disulfide are believed to function by photolytic scission of the sulfur-sulfur bond:^{64,90-92}



The mode of action of the other organic sulfur compounds listed in Table I is less clear; they may be capable of undergoing specific radical-forming photolytic scission processes, or they may participate in energy transfer or electron transfer processes. The initiating activity of 2-mercaptobenzothiazole can be rationalized by assuming a photolytic scission of the S-H bond:⁹³⁻⁹⁸



Similar photolytic processes involving homolytic cleavage of N-H bonds⁹⁹⁻¹⁰¹ could be advanced to account for the photo-initiating activity of such compounds as thiocarbanilide and N-phenyl- β -naphthylamine. However, this is not the only mechanism worthy of consideration, particularly since other aromatic amines lacking N-H bonds are also active. Interaction of the excited state of the amine with oxygen via energy transfer, electron transfer, or hydrogen atom

transfer may be involved; apparent precedents for such processes exist in the photochemistry of aromatic amines^{102,103} and dyes.^{45,46,49,92,104-113}

It is interesting to note that Table I contains several additives which would be expected to function as antioxidants in thermal autoxidation; examples include *N*-phenyl- β -naphthylamine and 1,4-naphthalenediol. This suggests that a single additive can serve both as an inhibitor of thermal oxidation during polymer processing and as an initiator of subsequent photochemical autoxidation. Similar observations have recently been reported by others.^{13,114,115}

TABLE I
Additives Causing Substantial Acceleration of Polyethylene Photodegradation

Aromatic Carbonyl Compounds	Anthraquinone-2-carboxylic acid
<i>p</i> -Anisyl benzyl ketone	2- <i>tert</i> -Butylanthraquinone ^a
9-Anthraldehyde	2-Chloroanthraquinone ^a
Benanthrone	2-Ethylanthraquinone ^a
Benzoin	1-Methoxyanthraquinone ^a
Benzoin Acetate	2-Methylanthraquinone ^a
4'-Benzoyloxypropiophenone	2-Methyl-1,4-naphthoquinone
4,4'-Bis(diethylamino)benzophenone	Phenanthrenequinone
4,4'-Bis(dimethylamino)benzophenone	Phenyl- <i>p</i> -benzoquinone
Chalcone	Aromatic Amines
Decanophenone	4,4'-Methylenebis(<i>N,N</i> -dimethylaniline)
Deoxybenzoin	<i>N</i> -Phenyl- β -naphthylamine
Deoxyanisoin ^a	Triphenylamine
<i>p</i> -Diacetylbenzene	Metallo-Organic Compounds
Dibenzalacetone	Cobalt octoate (1%)
Dibenzocycloheptadiene ^a	Ferric octoate (1%) ^a
1,4-Dibenzoylbutane	Ferrous stearate (1%)
4-Dimethylaminobenzophenone	Manganous stearate (1%)
Flavanone	Organosulfur Compounds
Flavone ^a	Benzyl disulfide
<i>p</i> -Hydroxypropiophenone	2-Mercaptobenzothiazole
Laurophenone	2,2'-Methylenebis(benzothiazole)
4-Methoxybenzophenone ^a	Phenyl disulfide
4'-Methoxychalcone	Thiocarbanilide
β -Naphthyl methyl ketone	Miscellaneous Additives
<i>p-n</i> -Octyloxybenzaldehyde	Azobenzene
4,4'-Oxydibenzophenone ^a	<i>m</i> -Diphenoxybenzene
10-Thioxanthone ^a	Fluorene
1,3,5-Triacetylbenzene	Leucomalachite Green
2,4,7-Trinitro-9-fluorenone	Linoleic acid (5%)
Xanthone	1,4-Naphthalenediol ^a
Quinones	<i>trans</i> -Stilbene
Anthraquinone ^a	

^a Accelerating effect particularly pronounced.

Certain specific additives listed in Table I could be regarded as precursors for other, more active degradation-promoting additives. For example, the activity of leuco-Malachite Green may be attributed to its facile conversion to Malachite Green during film formation or the early stages of photo-oxidation.¹¹⁶ Similarly, we might regard linoleic acid as the precursor of the corresponding hydroperoxide. While we have no definite evidence to substantiate such mechanisms, these observations suggest the possible use of "latent sensitizing additives" which

are converted to the active degradation-promoting additives during polymer processing or subsequent environmental exposure.

More detailed studies of the accelerated photo-oxidation of polyethylene in the presence of selected additives will be reported in the succeeding paper of this series.

EXPERIMENTAL

Materials

An additive-free grade of low-density polyethylene (Sinclair-Koppers Super Dylan WPD-367F) was employed. Additives were laboratory or commercial chemicals of the highest available purity, used without further purification; in most cases these were reagent-grade laboratory chemicals.

Sample Preparation

Additive-containing films were cast from a warm xylene solution containing 10% by weight of polymer plus the calculated amount of additive. Weighed amounts of polymer, additive, and reagent-grade xylene were transferred to a glass beaker, which was placed on a combination hot plate-magnetic stirrer and covered with a bell jar fitted with gas inlet and outlet tubes and a cold-finger condenser. A nitrogen atmosphere was maintained while the contents of the beaker were warmed and stirred until a homogeneous solution was obtained. A portion of this solution was then cast onto a large glass microscope slide with the aid of a doctor blade having a fixed clearance of 75 mils; the microscope slide had previously been warmed to a temperature of ca. 60–80°C by means of a miniature hot plate. Warming was continued during the time (approximately 2–3 min) required for film formation. This procedure yielded films of a thickness (2–3 mils) convenient for direct analysis by infrared spectrophotometry.

Ultraviolet Exposure

Additive-containing films were exposed for a period of 24 hr, in air, to unfiltered radiation from a set of four circular PCQ-X1 photochemical lamps of 3-in. diameter (Ultra-Violet Products, Inc.) These lamps are phosphor coated to produce primary emission at 305 nm.

The sample was placed in the center of a four-lamp array which in turn was surrounded by a cylindrical Alzac reflector. The total output energy of the system was 5.6 watts. The distance from lamp to sample was approximately 1.5 in.

Infrared Measurements

Infrared spectra of unexposed and exposed additive-containing films were obtained on a Perkin-Elmer Model 237B double-beam grating infrared spectrophotometer equipped with a mechanical attenuator for the reference beam. The extent of photo-oxidative degradation of exposed films was ascertained from the intensity of aliphatic carbonyl peaks at ca. 1710 cm^{-1} . Unexposed films and exposed additive-free films exhibited no significant absorption in this region. The resolution of the spectrophotometer was sufficient to separate clearly the

carbonyl absorption of photo-oxidized polyethylene from that of aromatic carbonyl compounds examined as additives. Exposed 3-mil films containing those additives listed in Table I were found to exhibit an aliphatic carbonyl absorbance of 0.04 or greater; the absorbance was 0.20 or greater in the case of those additives designated by superscript a.

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