

P

Photostabilization of Polymers

Riham R. Mohamed

Faculty of Science–Chemistry Department, Cairo University, El-Giza, Egypt

Keywords

Photostabilizers; Polymers; Thermooxidation; Degradation; UV radiation

Introduction

The photodegradation of polymers has been studied from the early years due to its commercial production. Most plastics are affected by exposure to sunlight in conjunction with other natural weathering forces such as oxygen, water, and heat. Almost all synthetic polymers require stabilization against adverse environmental effects. The consequences of photodegradation depend on the nature of the polymer and can cause polymer chain scission and cross-linking leading to changes at the molecular level. These irreversible processes eventually change the physical or visual properties of polymer to such extent that the end product cannot serve its purpose (Bolland and Gee 1946). It is necessary to find means to reduce or prevent damage induced by environmental components such as heat, light, or oxygen (Rabek and Ranby 1974a, b). The

photostabilization of polymers may be achieved in many ways. The following stabilizing systems have been developed, which depend on the action of the stabilizer: (1) light screeners, (2) UV absorbers, (3) excited state quenchers, (4) peroxide decomposers, and (5) radical scavengers; of these, it is generally believed that excited state quenchers, peroxide decomposers, and radical scavengers are the most effective (Yousif et al. 2013). Research into degradation and aging of polymers is extremely intensive and new materials are being synthesized with a preprogrammed lifetime. New stabilizers are becoming commercially available although their mode of action is sometimes not thoroughly elucidated. They target the many possible ways of polymer degradation, thermolysis, thermooxidation, photolysis, photooxidation, radiolysis, etc. with the goal for increasing the lifetime of a particular polymeric material; two aspects of degradation are of particular importance: storage conditions and addition of appropriate stabilizers. A profound knowledge of degradation mechanisms is needed to achieve the goal (Yousif and Haddad 2013).

Definitions and Historical Aspects of Photodegradation of Polymers

One of the defects of using polymers is that they degrade when they are used in high-temperature conditions or in outdoor applications. When

polymers are used in outdoor applications, the environment negatively influences their lifetime. This process is called weathering (Zweifel 1998; Wypych 2008).

Degradation of macromolecules denotes all processes which lead to a decline of polymer properties. It may eventually involve physical processes, such as polymer recrystallization or denaturation of protein structures. Chemical processes related to degradation may lead to a reduction of average molar mass due to macromolecular chain bond scission or to an increase in molar mass due to cross-linking, rendering the polymer insoluble.

Aging of polymers is usually associated with long-term changes of polymer properties under the conditions of weathering and may involve any of the above processes (Strlič and Kolar 2005).

A wide variety of synthetic and naturally occurring high polymers absorb solar ultraviolet radiation and undergo photolytic, photooxidative, and thermooxidative reactions that result in the degradation of the material (Valkoa et al. 2001). This is a serious problem with economic and environmental implications and therefore a large effort is focused on understanding the changes that occur at the molecular level and the degradation kinetics. Following different routes, UV radiation causes a photooxidative degradation which results in breaking of the polymer chains, produces radicals, and reduces the molecular weight, causing deterioration of mechanical properties and leading to useless materials, after some time (Bottino et al. 2003).

Exposure to ultraviolet (UV) radiation may cause the significant degradation of many materials. Damage by UV radiation is commonly the main reason for the discoloration of dyes and pigments, weathering, yellowing of plastics, loss of gloss and mechanical properties (cracking), sunburnt skin, skin cancer, and other problems associated with UV light. The manufacturers of paints, plastics, contact lenses, and cosmetics have a great interest in offering products that remain unaltered for long periods under conditions of light exposure (Goldshtein and Margel 2011). Most of the common polymers used in such applications contain photostabilizers to

reduce photodamage and to ensure acceptable lifetimes under outdoor exposure conditions.

Solar radiation reaching the surface of the Earth is characterized by wavelengths from approximately 295 up to 2500 nm. The solar radiation classified as UV-B (280–315 nm) has an energy of 426–380 KJ mol⁻¹. Fortunately, the higher energetic part of UV-B (280–295 nm) is filtered by the stratosphere and does not reach the Earth's surface. UV-A (315–400 nm) has energy between 389 and 300 KJ mol⁻¹ and is less harmful for organic materials than UV-B; visible radiation has a wavelength of 400–760 nm and infrared 760–2500 nm (Pospisil and Nespurek 2000).

Photooxidation of organic materials is a major cause of irreversible deterioration for a large number of substances. It is responsible not only for the loss of physical properties of plastics and rubber but also for foodstuffs (Grassie and Scott 1985). In most polymers, photooxidative degradation may be induced by UV radiation or catalytic process (or both) and can be accelerated at elevated temperature.

Factors Causing the Photodegradation

Generally, many factors are responsible for causing photodegradation of polymeric materials. They may be divided into two categories (Schnabel 1981):

- I. *Internal impurities*, which may contain chromophoric groups that are introduced into macromolecules during polymerization processing and storage; they include:
 - (a) Hydroperoxide
 - (b) Carbonyl
 - (c) Unsaturated bonds (C = C)
 - (d) Catalyst residue
 - (e) Charge-transfer (CT) complexes with oxygen
- II. *External impurities* – which may contain chromophoric groups – are:
 - (a) Traces of solvents, catalyst, etc.
 - (b) Compounds from a polluted urban atmosphere and smog, e.g., polynuclear hydrocarbons such as naphthalene and

- anthracene in polypropylene and polybutadiene
- (c) Additives (pigments, dyes, thermal stabilizers, photostabilizers, etc.)
 - (d) Traces of metals and metal oxides from processing equipment and containers, such as Fe, Ni, or Cr

Photodegradation

Photodegradation is degradation of a photodegradable molecule caused by the absorption of photons, particularly those wavelengths found in sunlight, such as infrared radiation, visible light, and ultraviolet light. However, other forms of electromagnetic radiation can cause photodegradation. Photodegradation includes photodissociation, the breakup of molecules into smaller pieces by photons. It also includes the change of a molecule's shape to make it irreversibly altered, such as the denaturing of proteins, and the addition of other atoms or molecules. A common photodegradation reaction is oxidation. Photodegradation in the environment is part of the process by which ambergris evolves from its fatty precursor. Photodegradation also destroys paintings and other artifacts. Light-induced polymer degradation, or photodegradation, includes the physical and chemical changes caused by irradiation of polymers with ultraviolet or visible light. In order to be effective, light must be absorbed by the substrate (polymeric system). Thus, the existence of chromophoric group in the macromolecules is a prerequisite for the initiation of any photochemical reaction (Schnabel 1981).

Ketones, quinines, and peroxides are initiators for different reaction degradation or chemical modification occurring in organic compounds (Kaczmarek et al. 1999). They absorb light up to about 380 nm, which causes their excitation or cleavage to radicals. One may initiate polymer degradation and other transformations by abstraction of hydrogen atom from a macromolecule (PH) and formation of polymer alkyl radical (P^\bullet) (Rabek 1996).

Photodegradation may occur in the absence of oxygen (chain breaking or cross-linking) and the presence of oxygen (photooxidative) degradation. The photooxidative degradation process is induced by UV radiation and other catalysts (or both) and can be accelerated at elevated temperatures. The term photodegradation might be distinguished from photooxidation of the polymer. In the latter, oxygen is involved in the process, while in the former light energy ($E = h\nu$) only is responsible for the photodegradation.

Photostabilization Mechanisms in Polymers

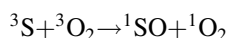
It is well known that all commonly used plastics degrade under the influence of sunlight. Almost all synthetic polymers require stabilization against the adverse effects; with the development of synthetic resins, it became necessary to find ways and means to prevent, or at least reduce, the damage caused by the environmental parameters such as light, air, and heat. That is why the photostability of polymers is one of the most important considerations for application. Photostability can be achieved through the addition of special chemicals, light stabilizers, or UV stabilizers that have to be adjusted to the nature of the resin and the specific application considered. The photostabilization of polymers involves the retardation or elimination of photochemical process in polymers and plastics that occur during irradiation. There are several different methods of photostabilization, and the choice of method is dependent on the type of polymer and field of applications. The most important methods of photostabilization are the screening or absorbing of UV radiation by stabilizing agents and the use of antioxidants, which react with the polymer radicals, stopping the degradation process by forming inactive products (Ruoko 2012).

Two mechanisms have been proposed to explain the photooxidation of polymers in conformity with similar observations made on low molecular weight compounds. One proceeds through direct reaction of singlet oxygen with the substrate while the other involves the

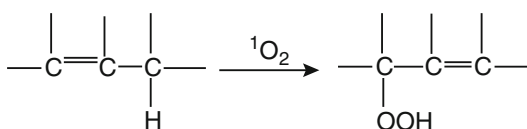
production of radicals and subsequent reaction with oxygen (Yousif and Haddad 2013).

The Singlet Oxygen Mechanism of Oxidation

It has been clearly demonstrated that many photosensitized oxidation reactions proceed with participation of oxygen in an electronically excited singlet state. The photochemical production of singlet oxygen is mainly due to quenching of the excited triplet state of suitable sensitizers:

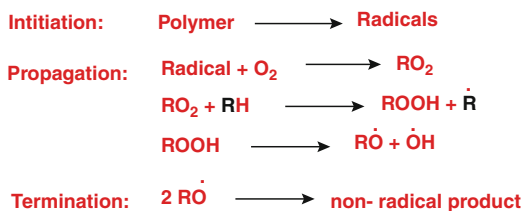


Singlet oxygen exhibits several specific reactions, and the one that has been most often invoked in the photooxidation of polymers is the formation of a hydroperoxide by oxidation of an olefin containing allylic hydrogen, which could further decompose and lead to chain scission and formation of a terminal of carbonyl group.



The Free Radical Mechanism of Oxidation

The radical mechanism of photooxidation of polymers proceeds through a chain reaction similar to that of homogeneous liquid phase oxidations.



Ultraviolet Stabilizers

Ultraviolet stabilizers: *they are additives for plastics and other polymeric materials which prevent the photodegradation or photocrosslinking caused by ultraviolet light.*

The UV absorber and screener operate by absorbing the incident UV radiation, preventing it from reaching the bulk of the polymer and converting the energy thus acquired into a less damaging form such as heat, or they may act as radiation reflecting or scattering (preferably coating) (Decker and Biry 1996) on the surface of the polymer, thus delaying discoloration and delamination. An important disadvantage of UV absorbers is the fact that they need a certain absorption depth (item thickness) to provide good protection to a polymer. Therefore, the protection of polymer surfaces of thin items such as films or fibers is only moderate (Gugumus et al. 1987).

The amount of an absorber required to provide economical protection in a plastic is governed by several factors such as:

- (i) Thickness of the plastic
- (ii) Tolerance of color
- (iii) Effect of high concentration of absorber in plastics
- (iv) Compatibility of the absorber in the plastic

The most common UV stabilizers are UV absorber and light screeners, quenchers, hydroperoxide decomposers, radical scavengers, and singlet oxygen (¹O₂).

Ultraviolet stabilizers can be classified according to their mechanisms of action in the photostabilization process into (Yousif and Haddad 2013):

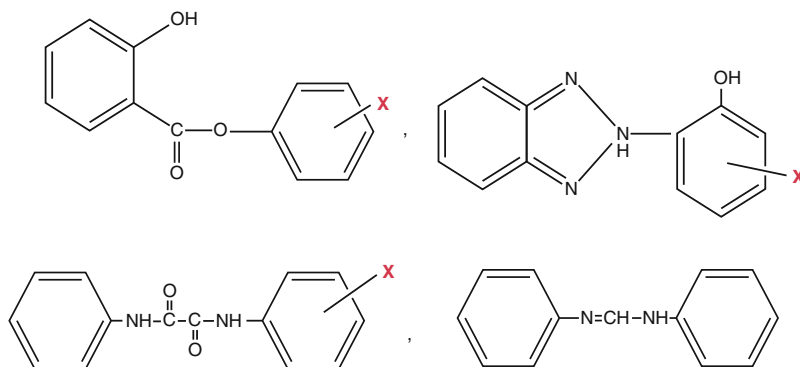
- (i) UV absorbers and light screeners
- (ii) Quenchers
- (iii) Hydroperoxide decomposers
- (iv) Radical scavengers
- (v) Singlet oxygen (¹O₂) quenchers

The UV stabilizer can be classified according to their chemical nature into (Rabek 1987):

- (i) Pigments
- (ii) Metal chelates
- (iii) Carbon black
- (iv) Salicylates (Fig. 1)
- (v) Salicylanilides

Photostabilization

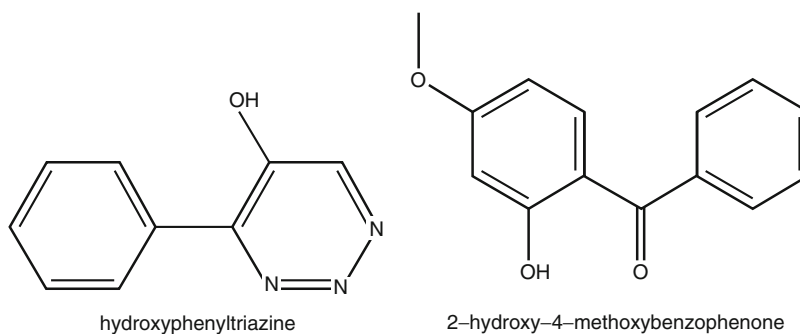
of Polymers, Fig. 1 Some phenolic and non-phenolic UV absorbers; Hydroxy phenyl benzoate hydroxy-phenyl benzotriazoles and oxanilide



Some phenolic and non-phenolic UV absorbers; Hydroxy phenyl benzoate hydroxyphenyl benzotriazoles and oxanilide

Photostabilization

of Polymers, Fig. 2 Some examples of Photostabilizers



hydroxyphenyltriazine

2-hydroxy-4-methoxybenzophenone

- (vi) Hydroxyphenyl benzotriazoles
- (vii) Hydroxy benzophenones (Fig. 2)

Mode of Action of UV Absorber

The action of a UV absorber is relatively simple; it interacts with the first step of the photooxidation process, meaning that it absorbs the harmful UV radiation before it reaches to the photoactive chromophoric species in the polymer molecule (300–400) nm. Thus, the energy dissipates in a manner that does not lead to photosensitization. A UV absorber must be light stable, because otherwise it would be destroyed in stabilizing reactions.

Hydroxybenzophenones and hydroxyphenyl benzotriazoles (Fig. 2) are the most extensively studied UV absorbers. Generally, after photons are absorbed by the chromophores, molecules rise to a higher excited state by spin inversion of singlet state. The singlet states may change to triplet states by intersystem crossing (ISC) or

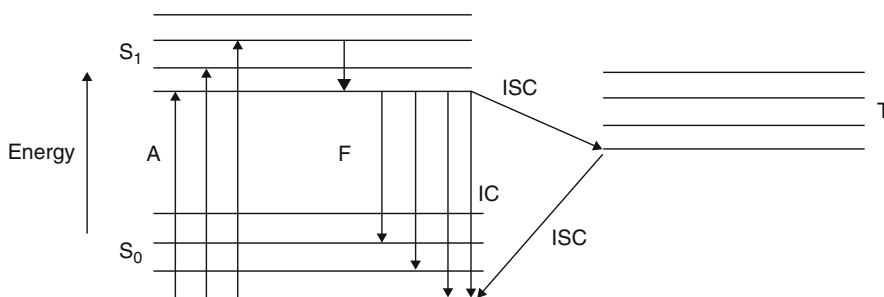
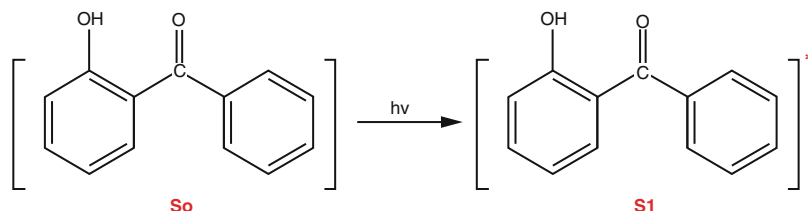
return to a lower excited state by internal conversion (IC) (these are radiationless processes). Excited states have the ability to lose the excitation energy by some radiation processes such as fluorescence or phosphorescence or by energy transfer to another molecule (Figs. 3 and 4).

Concerning the energy transformation in hydroxybenzophenones, it has been shown with 2-hydroxybenzophenone (Allen 1983) that on exposure to light, it is transformed into the enol form which turns back into its initial form on losing thermal energy to the medium. On the basis of spectroscopic data, it is concluded that the energy transformation involves exclusively a fast radiationless transition.

The photostabilizing process of O-hydroxybenzophenone has been the subject of many investigations (Collell and Amer 1968). The most probable process involved is the utilization of the energy of the absorbed photon to intramolecular proton transfer during which a

Photostabilization of Polymers,

Fig. 3 Excitation of β -Hydroxybenzophenone with UV radiation



Photostabilization of Polymers, Fig. 4 Intersystem crossing (ISC) and internal conversion (IC)

quinone structure is formed. Urethane and silylated derivatives of hydroxybenzophenones are effective photostabilizers; they can act as (Patel 2007):

- (i) Light screeners
- (ii) Excited state quenchers of chromophoric groups present in polymers
- (iii) Radical scavengers
- (iv) Hydroperoxide decomposers

The photostabilizing effect of many aromatic compounds to be UV stabilizer for several polymers has been reported due to their filtrating action which depends, in turn, on their absorption characteristics (Rabek and Ranby 1975).

Pigments

Pigments are insoluble inorganic or mineral and organic compounds of complex structure, such as powder metal (aluminum) which is an excellent reflector to UV light. Fe_2O_3 , Fe_3O_4 , ZnO , and TiO_2 are inorganic pigments of excellent potency

as UV screeners. Organic pigments such as azo- and anthraquinone display good UV light absorption. Pigments used as additives are incorporated into polymers, coatings, inks, etc. for:

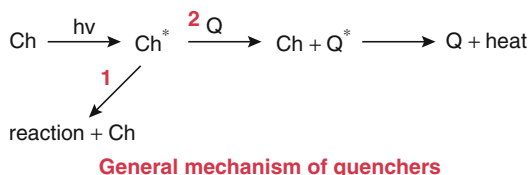
- (i) Cost reduction
- (ii) Reinforcement
- (iii) Hardening
- (iv) Improving slip and skid resistance
- (v) Color effect
- (vi) Storage stability

A pigment as a light screener should be:

- (i) Light stable for long-term performance without fading
- (ii) Heat stable to withstand polymer processing conditions
- (iii) Migration resistant
- (iv) Low cost and nontoxic

The influence of pigments in polymer photostability is not completely understood. If an absorbing pigment is introduced into a polymer, it acts as an inner screen for photo products.

If these products are not photooxidized, they accumulate in the polymer matrix. Since pigments act as highly absorbing additives, photooxidative phenomena will be limited mainly to the surface of samples (Yousif et al. 2012).



Carbon Black

Carbon black is one of the most efficient and widespread light absorbers. It consists of very fine particles fused together to form primary aggregates. Carbon black contains different functional groups such as carbonyl, hydroxyl, quinone, ether, etc. Carbon black absorbs UV radiation more efficiently than conventional colored pigments; carbon black is an efficient light stabilizer for polymers (Winslow et al. 1969). Thus, the UV stabilization efficiency of carbon black increases as the particle size decreases. An optimum concentration of carbon black is 3–5 %. Higher than this concentration, the polymer loses its tensile strength and other mechanical properties (David and Hsuan 2003).

Quenchers

Quenchers deactivate excited states (singlet and/or triplet) of chromophoric groups in polymers before bond scission can occur by *two methods* (Wiles and Carlsson 1980):

1. Energy transfer process
2. Chemical and/or physical deactivation

The excited state of a chromophore (Ch) (such as dyes, pigments, antioxidant products, carbonyl groups, and a variety of impurities or pollutants such as polynuclear aromatic compounds) may react but it can also transfer its excess electronic energy to a quenching entity (Q) as shown below.

Radical Scavengers

The scavenging of radical intermediates is another possibility for polymer stabilization, analogous to that used in thermal degradation. Quinones react with alkyl radicals to form radicals that do not initiate polymer oxidation. The radical scavengers operate by interfering with the propagating step in the oxidative chain and this can be achieved by two routes:

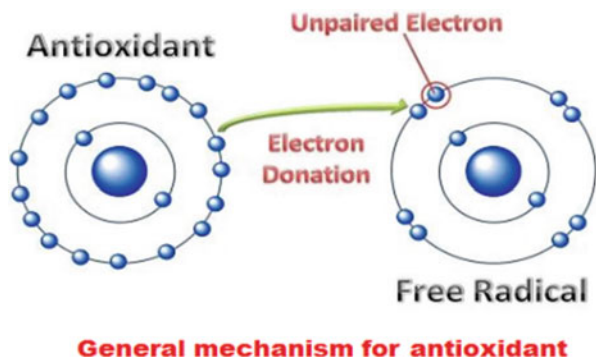
- (i) Reaction with propagating radicals (P° , PO° , POO°)
- (ii) Reaction with resulting hydroperoxides which are the source of chain branching through the propagating process (Feldman 2002)

Antioxidants

The development of the auto-oxidation theory, in which the propagating radicals, alkyl, alkyl peroxy ($\text{R}\cdot$, $\text{ROO}\cdot$), and the hydroperoxide (ROOH), are the key intermediates, has led to a comprehensive theory of antioxidant action. The two major antioxidant mechanisms are shown: the chain-breaking donor (CB-D) and chain-breaking acceptor (CB-A). Also an antioxidant can act by preventive inhibition processes. Many reducing agents, e.g., hindered phenols and aromatic amines, which reduce the $\text{ROO}\cdot$ to hydroperoxide in CB-D step, have already been empirically selected and used for rubbers and by this time also for the newer plastics industry (Cheremisinov 1997). Oxidizing agents, e.g., quinones, which have been shown to be able to retard oxidation, can function as antioxidants (via a chain-breaking acceptor process), if they can

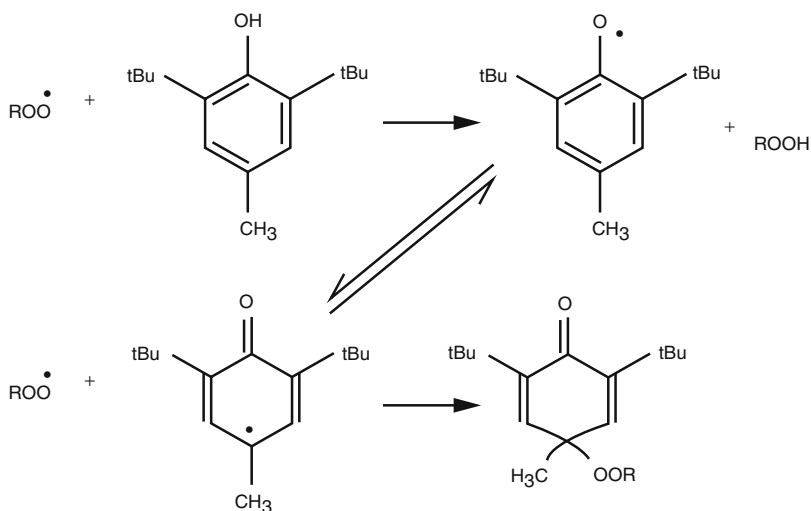
Photostabilization of Polymers,

Fig. 5 General mechanism for antioxidants



Photostabilization of Polymers,

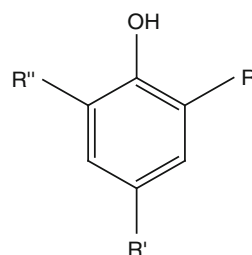
Fig. 6 Mechanism of hindered phenolic antioxidants



compete with oxygen for alkyl radicals (Watson 1953) (Fig. 5).

Phenolic Antioxidants

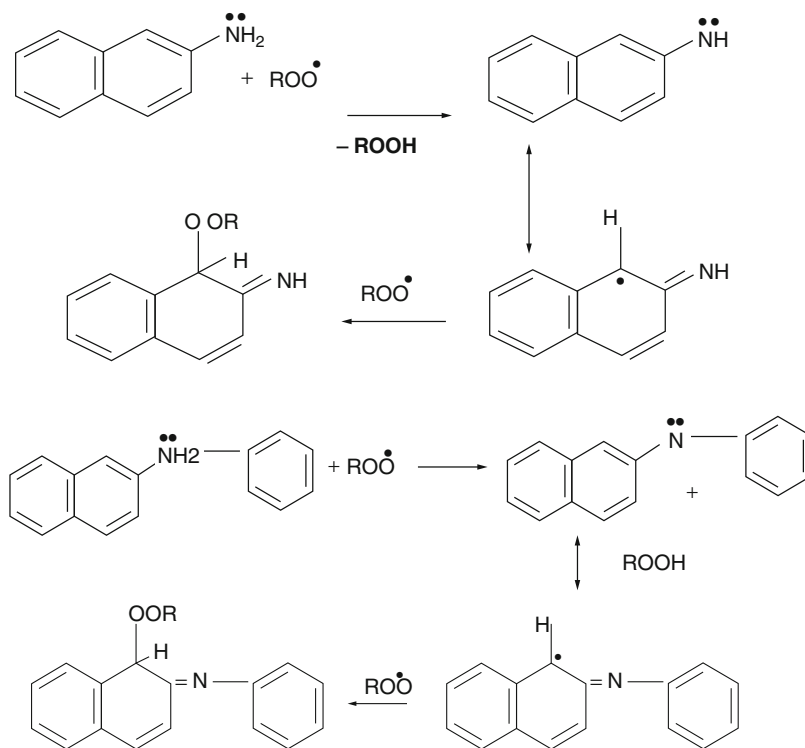
It was found that sterically hindered phenols are quite efficient as antioxidants. Moreover, it was found that the tri-alkylated phenols are more efficient than mono- or di-alkylated phenols. Thus, the phenolic antioxidant could be represented by the following general structure:



As R, R', and R'' are either similar or different alkyl groups.

The efficiency of the phenolic antioxidant is based on its potency to trap two peroxy radicals

Photostabilization of Polymers,
Fig. 7 Mechanism of aromatic amine antioxidants



for each molecule of the phenol derivative as represented below (Fig. 6).

Aromatic Amine Antioxidants

Some of the aromatic amines are considered to be good antioxidants. From these materials, we can nominate β -naphthylamine and its derivatives as well as the derivatives of *p*-phenylenediamines (Fig. 7).

As shown in the above equations, hydroperoxides (ROOH) are the primary molecular photooxidation products and the most dangerous chromophore in the photodegradation of polymers. Their deactivation by a hydroperoxide-decomposing antioxidant (HDAO) or hindered amine light stabilizer (HALS) reduces ROOH homolysis and, consequently, chain initiation and chain transfer.

Conclusion

In recent years, the use of polymeric materials has rapidly increased, but it is well established that

rapid photodegradation of these materials is possible when they are exposed to natural weathering. Most of the commonly used polymers contain photostabilizers to reduce photodamage and to ensure acceptable lifetimes under outdoor exposure conditions. The photostabilization of polymers may be achieved in many ways. The following stabilizing systems have been developed, which depend on the action of the stabilizer: light screeners, UV absorbers, excited state quenchers, peroxide decomposers, and radical scavengers; of these, it is generally believed that excited state quenchers, peroxide decomposers, and radical scavengers are the most effective.

References

- Allen NS (1983) Photostabilising action of ortho-hydroxy aromatic compounds: a critical review. *Polym Photochem* 3:167–187
- Bolland J, Gee G (1946) Kinetic studies in the chemistry of rubber and related materials. III. Thermochemistry and mechanisms of olefin oxidation. *Trans Faraday Soc* 42:244–252

- Bottino FA, Cinquegrani AR, Pasquale G, Di LL, Pollicino A (2003) Chemical modification, mechanical properties and surface photooxidation of films of polystyrene. *Polym Test* 12:405–411
- Cheremisin NP (1997) Handbook of engineering polymeric materials. Marcel Dekker, New York, chapter 8
- Collell E, Amer J (1968) Physiological and pathophysiological aspects of ceramide. *J Chem Soc* 90:1012–1019
- David SL, Hsuan YG (2003) Assessing the photodegradation of geosynthetics by outdoor exposure and laboratory weatherometer. *Geotext Geomembrane* 21:111–122
- Decker C, Biry S (1996) Light stabilization of polymers by radiation cured acrylic coatings. *Prog Org Coat* 29:81–87
- Feldman D (2002) Polymer weathering: photo-oxidation. *J Polym Environ* 10:163–173
- Grassie N, Scott G (1985) Polymer degradation and stabilization. Cambridge University Press, London
- Goldshtein J, Margel S (2011) Synthesis and characterization of polystyrene/2(5-chloro-2H-benzotriazole-2-yl)-6-(1, 1-dimethylethyl)-4-methyl-phenol composite microspheres of narrow size distribution for UV irradiation protection. *Colloid Polym Sci* 289:1863–1874
- Gugumus F, Gachter R, Muller H (1987) Plastics additives, 2nd edn. Hanser, Munich, pp 97–185
- Kaczmarek H, Kaminska A, Swiatek M, Sanyal S (1999) Photoinitiation degradation of PS in the presence of low molecular organic compounds. *Eur Polym J* 36:1167–1173
- Patel P (2007) Additive primer, blown films, cast films and extraction coating. In: Plack conference, pp 16–20
- Pospasil J, Nespurek S (2000) *Prog Polym Sci* 25:1261–1335, Addcon World 17–18 Oct 2006 conference, Cologne, Germany
- Rabek JF, Ranby B (1975) Photodegradation, photooxidation and photostabilization of polymers. Wiley, New York
- Rabek JF (1987) Mechanism of photophysical process and photochemical reaction in polymers. Wiley, New York
- Rabek JF (1996) Polymer photodegradation of polymers: physical characteristic and applications. Springer, Berlin/Heidelberg
- Rabek JF, Ranby B (1974a) Studied on the photooxidation mechanism of polymers, photolysis and photooxidation of polystyrene. *J Polym Sci* 12:273–291
- Rabek JF, Ranby B (1974b) Polymer photophysics and photochemistry: an introduction to the study of photoprocess of macromolecules. *J Polym Sci A* 12:273–281
- Ruoko TP (2012) UV light induced degradation of polyethylene and polystyrene—spectroscopic and DSC study. MSc thesis, Tampere University of Technology
- Schnabel W (1981) Polymer degradation: principle and practical applications. Chapter 14. Hanser Int, München
- Strlič M, Kolar J (2005) Aging and stabilization of papers. Distributed by the National and university Library, Turjaška 1, 1000 Slovenia
- Valkoa L, Kleinb E, Kovarikb P, Simonb P (2001) HPLC stanovenie sacharidov v procese modelovaného zrýchleného starnutia papiera. *Eur Polym J* 37:1123–1133
- Watson WF (1953) Principles of polymer engineering rheology. *Trans IRI* 29:29–32
- Wiles DM, Carlsson DJ (1980) Photostabilisation mechanisms in polymers: a review. *Polym Degrad Stabil* 3:61–72
- Winslow FH, Matreyek W, Trozzolo AM (1969) Particle size distribution and morphology of in situ suspension polymerized toner. *Am Chem Soc Polym Prepara* 10:1271
- Wypych G (2008) Handbook of material weathering, 4th edn. Chemtec Publishing, Toronto, p 211
- Yousif E, Salimon J, Salih N (2012) New stabilizer for polystyrene based on 2-thioacetic acid benzothiazol complexes. *J Appl Polym Sci* 125:1922–1927
- Yousif E, Hameed A, Salih N, Salimon J, Abdullah BM (2013) New photostabilizers for polystyrene based on 2,3-dihydro-(5-mercapto-1,3,4-oxadiazol-2-yl) phenyl-2-(substituted)-1,3,4-oxazepine-4,7-dione compounds. *Springerplus J* 2:1–8
- Yousif E, Haddad R (2013) Photodegradation and photostabilization of polymers, especially polystyrene: review. *Springerplus J* 2:398–430
- Zweifel H (1998) Stabilization of polymeric materials. Springer, Berlin/Heidelberg