

Additives for polyolefines: chemistry involved and innovative effects

Abstract

Because many synthetic resins suffer from photo degradation, the investigation of ways to inhibit or at least retard this type of degradation has been a major effort to the industry. Hindered amine light stabilizers (HALS) represent the most important development in light stabilization for many polymers, and in this presentation an overview of stabilization fundamentals will be provided together with some recent advances in this field. Performance data reported will show the benefit in using HALS as light stabilizing systems for plastic. The presentation will end with new directions into new additive technology that allows shelf-stable plastic packaging of oxygen sensitive ingredients and potential for extended shelf-life.

Introduction

Light and oxygen induce degradation reactions in plastics that may not only modify them visually but also exert a detrimental influence on mechanical and physical properties. The inhibition of these degradation reactions has considerable technical and economical importance, otherwise the possible applications of many plastics would be drastically reduced. Consequently, with the development of synthetic resins it became necessary to look for ways and means to prevent, or at least reduce, the damage caused by the environmental parameters light, air and heat. This has been achieved through the addition of special chemicals, light stabilizers or UV stabilizers, that have to be adjusted to the nature of the plastic and the specific application considered.

During its life, a polymer is subjected to a variety of damaging stresses. This includes high temperatures and shear rates from the multiple melt compounding steps as the product is transformed from reactor powder to pelleted product to formulated compound to finished article. In addition to temperature and shear, catalyst residues, oxygen and other types of impurities might also play a role in promoting further degradation of the polymer.

Degradation of polymers starts with free radicals which are initiated via C-C and C-H bond scission. Once the free radical cycle is initiated, the resultant carbon centered free radicals not only react with other polymer molecules, but also freed on the oxygen that is entrained in the system, leading to the formation of peroxy radicals as described in CycleII. Oxygen centered radicals can react further with the polymer leading to the formation of more carbon centered free radicals, which feed back into CycleI. The reactions leading to free radicals being formed on the polymer backbone results in chain linking and/or chain scission reactions in an effort to quench the free radicals; see Figure1.

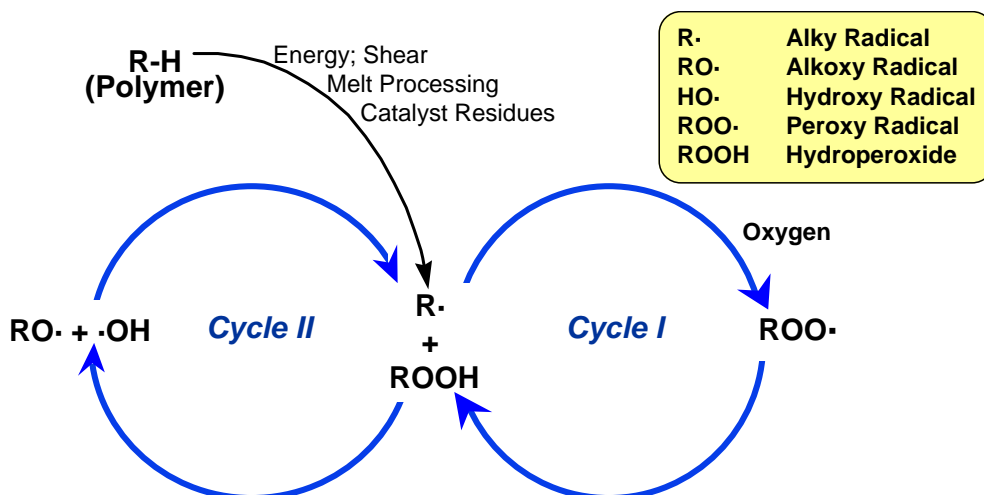


Figure 1. Auto-oxidation cycle of polyolefins

The only way to prevent or at least reduce polymer photo-oxidation is to use appropriate antioxidants. Hindered phenolic antioxidants, typically in combination with an organic phosphate can be used to meet most requirements of a given end-use application. The role of the phenolic antioxidant is to scavenge oxygen centered free radicals, such as alkoxy, hydroxyl and peroxy type species, while the role of the phosphate is to decompose the hydroperoxides into relatively inert products; see Figure 2.

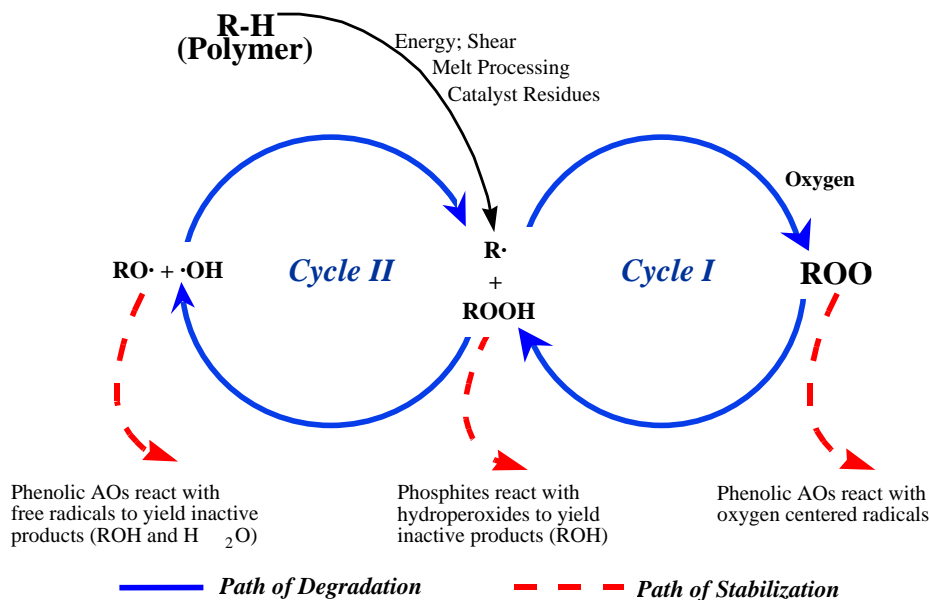


Figure 2. Auto-oxidation cycle for polyolefins and antioxidants role

Hindered amine light stabilizers (HALS) represent the most important development in light stabilization for many polymers. HALS are extremely efficient stabilizers against light-induced degradation of most polymers; they do not absorb UV radiation, but act to inhibit degradation of the polymer, thus extending its durability. Significant levels of stabilization are achieved at relatively low concentrations.

HALS' high efficiency and longevity are due to a cyclic process wherein the HALS are regenerated rather than consumed during the stabilization process; see Figure 3. They also protect polymers from thermal degradation and can be used as thermal stabilizer.

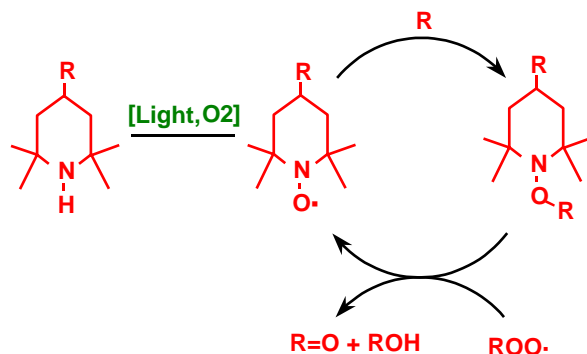


Figure 3: HALS photo-oxidation cycle

The first commercial representative of this class is bis (2,2,6,6-tetramethyl-4-piperidyl) sebacate; many other molecules have appeared on the market all based on the piperidine chemistry. The last developments are driven by the need of having less alkaline HALS; in fact the alkalinity of original HALS often represents a drawback since they interact with some acidic by-product that could come into contact with the final plastic article containing the HALS (such as selected pesticides in agriculture application, high loadings of brominated flame retardants, etc); such interactions could lead to diminished activity. The alkalinity of piperidiny groups can be arranged into four classes: secondary amines (N-H) with higher alkalinity; methylated tertiary amines (N-CH₃) with similar alkalinity; alkylated tertiary amines (N-R) with intermediate alkalinity; and tertiary aminoethers (N-OR) with the least alkalinity. Some examples of HALS and their pK_a are reported in Figure 4.

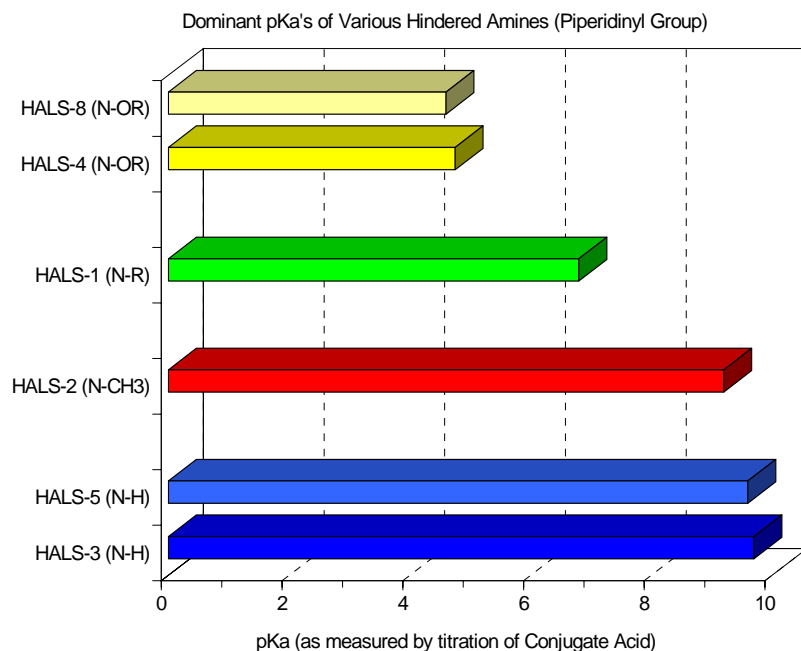


Figure 4: Dominant pKa's of the piperidinyl group of various HALS

Impact of Polymer Processing Aids on the performance of HALS

Polymer Processing Aids (PPA) are often used in the production of blow extruded films to improve the melt extrusion, together with HALS that will ensure enough duration once the film is exposed to natural aging.

In this work the interaction between HALS and PPA has been studied.

PPA used in LLDPE blown films are based on fluoroelastomers in combination with high molecular weight polyethylene glycol, and they are used to eliminate the melt fracture during blown film extrusion. On the other hand HALS have been shown to prolong the amount of time necessary to eliminate melt fracture.

In this study the combined effect of the two classes of additives has been studied on zn-LLDPE blown films, 90 micron in thickness; the resin used was Dowlex 2045 ethylene-octene: Concentration levels: 900 ppm for PPA and 1500 ppm and 3000 ppm in all experiments.

The following general trend was observed (mechanical properties were monitored up on artificial weathering as well as color index on gas fading aging):

More performance HA-8 > HA-6 > HA-7 > HA-3 > HA-1 Less performance
 NOR NR+NH NR+NCH₃ NH NR

We observed a slight negative impact of PPA on the performance of hindered amines (except HA-8) with 15-20% reduction in time to 50% retention of physical properties. Gas fade induced discoloration and oven aging at 60°C were measures as well to understand the impact of HALS on post-extrusion discoloration. The following trend was observed:

More discoloring HA-3 > HA-6 > HA-7 > HA-8 > HA-1 Less discoloring
 NH NR+NH NR+NCH₃ NOR NR

Active Food Packaging Materials – Oxygen Scavengers

A substantial cause for food losses is product decay caused by oxygen inside the packaging, leading either to consumer complaints at the retailer or, much more often, to direct disposal by the consumer. Even low concentrations of oxygen, namely 1-200 mg/kg, can adversely affect flavor and color of a wide range of foods. The residual levels of oxygen found in most packaging systems are much higher than this. For that reason, not only has the access of oxygen to the packed goods to be avoided but also oxygen levels in the headspace of the packaging have to be reduced as part of the packaging process.

The industry needs effective packaging to pack the food safely for transport and storage while maintaining the food quality, along with increasing demands of the consumer for fresher, minimally processed, more convenient and safer food. The consumers expect to be informed about the origin, treatment and quality/safety of the food. It would even be desirable to expand the current possibilities to track and trace food products from the point of sale to the point of consumption

Oxygen scavenging technologies, in combination with other techniques, can meet the increasing performance demands being placed on the package. In this section, we will discuss how to best use scavengers in packaging applications and the factors one needs to consider when designing packaging incorporating this technology.

Scavenger Form: in the past when most of durable food was contained in metal cans and glass bottles, which are naturally perfect barriers to oxygen, oxygen scavengers were not needed. With the increased use of plastic, which is by nature to some extent permeable to oxygen, there is an increased need to address the impact of permeated oxygen on product quality.

For many food products, even a small amount of oxygen present can be sufficient to adversely affect product quality. It is in these instances that one would consider the use of oxygen scavenging technology.

Currently scavengers can be introduced as either a separate entity (sachet) within the package or integrated as part of the package. The following forms are available:

Sachets

Small pouches introduced in the package; they contain a species that is highly reactive with oxygen

In-package systems

With this option the scavenging system is intended to be part of the package system with no impact on the physical characteristics of the package itself.

Scavenging Systems

Iron based systems: fine particulate of iron is introduced into the package where it reacts with oxygen in the presence of moisture

Oxidizable polymers: the oxygen scavenging reaction is catalyzed by a transitional metal salt; polymers like polybutadienes, polyamides, and copolymers incorporating unsaturated pendant groups are often used as oxidizable components. These systems may or may not require a triggering mechanism (such as UV radiation).

Photo reducible compound: the third general category of oxygen scavengers involves the use of UV radiation to photo-reduce a susceptible compound to create an oxygen reactive species. An example of this type of system can be found in CSIRO's oxygen scavenging system in which anthraquinones, upon UV exposure, form hydroxyquinones which can then react with molecular oxygen. One advantage to this type of system is that it does not require a catalyst for an effective scavenging rate to occur. Secondly, the oxygen reactive species is formed at the time of packaging, so there are no significant shelf-life issues for the scavenger.

When designing a package some considerations have to be done. The amount of oxygen that will be scavenged has to be determined as well as the intended shelf life of the package. Capacity of the oxygen scavenging system, rate of oxygen absorption and carrier resin have also to be taken into consideration. The package construction has to be designed so that barrier materials, like EVOH, Nylons, etc, are used to prevent oxygen from entering the package from outside, see Figure 5.

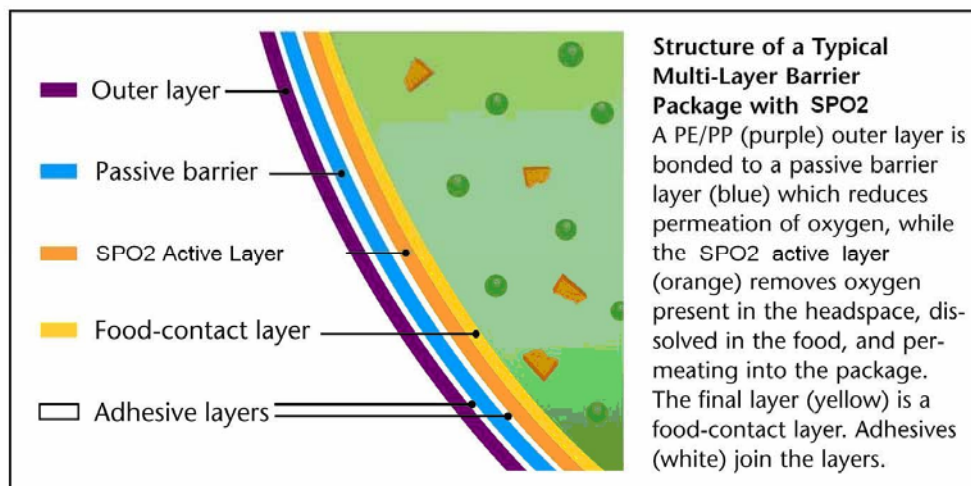


Figure 5. A Typical Multilayer Package Structure with SPO2 for Retort Applications

