11

POLYMER ADDITIVES

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11.1 INTRODUCTION

Additives are essential components of plastic formulations that provide maintenance and/or modification of polymer properties, performance, and long-term use. The extension of polymer properties by additives has been playing a substantial role in the growth of plastics, and many polymer applications are accessible only in the presence of a number of ingredients, often only in small quantities, in addition to the polymer itself.

Historically, polymer additives were decisive for the development of thermoplastic material applications. On the basis of previous findings [1], the first synthetic commercial thermoplastic, celluloid, is a success story of additives, when camphor was added to intractable cellulose nitrate to make it flexible [2–4]. Plasticized poly(vinyl chloride) (PVC) was developed in the 1930s using dialkyl phthalates. The key to processing rigid PVC was the development of heat stabilizers such as metal soaps, lead salts, and organotin compounds. There, contrary to plasticizers, small quantities were sufficient to provide the required processing performance. Light stabilizers were first used in cellulose nitrate coatings on packaging to protect packaged oil and food [5]. This was soon followed by the use of benzophenones and phenyl salicylate to protect plastics from weathering [6]. The breakthrough of polypropylene (PP), a thermally very unstable material, as well as Ziegler–Natta polyolefins was possible only through the development of efficient antioxidants. Quite logically, the growth of additives parallels the growth of plastics in the last decades [7].

Additives embrace a wide area of different chemical structures used in plastics for many different purposes (Fig. 11.1). They can be classified into additives to maintain polymer properties and those to extend polymer properties. The first class comprises additives to transform plastics into the desired shape and to protect the materials from degradation by heat, oxidation, as well as mechanical and chemical attack mainly during processing and thus keeping the polymer chain and the polymer molecular weight basically unchanged. Typical examples of the "maintaining" class are antioxidants, plasticizers, heat stabilizers, processing aids, and lubricants.

Additives to extend polymer properties help prolong the service life of plastic applications and/or allow the use of plastics in additional or demanding applications. Examples of these additives are UV/light stabilizers, antimicrobials, flame retardants, and also antioxidants. By using these additives, the polymer chain and polymer molecular weight remain unchanged for an extended period or under specified use conditions (e.g., outdoor, UV light) or in further application fields (e.g., microbial attack, fire risk, electrostatic discharge, high esthetics). Other additives modify polymer bulk or surface properties, again without changing the polymer chain or molecular weight. Examples comprise nucleating agents, clarifiers, surface modifiers, as well as antifogging and antistatic agents. Additives such as chain extenders or crosslinking/branching agents react with the polymer chain and may change the polymer structure/architecture fundamentally. In addition, some additives are incorporated in polymers not with the aim of influencing the polymer itself but to protect goods through the additive-incorporated polymer. Examples are UV absorbers and oxygen scavengers to protect packaged food.

The consumption of polymer additives today is estimated in the range of 5000 kt (kilotons) corresponding to a value

Polymer properties retention

- Antioxidants
- Processing stabilizers
- Heat stabilizers
- Lubricants
- Acid scavengers

Polymer properties extension

− Service life/ extended applications

- UV / light stabilizers
- Antioxidants
- Flame retardants
- Pigments
- Optical brighteners
- Biocides/antimicrobials
- Scavengers
- (Anti)odorants
- Conductive additives
- Repellants
- Markers
- Foaming agents

− Modifying bulk/surface properties

- Antistatic agents
- Nucleating agents
- Clarifiers
- Plasticizers
- Surface modifiers
- Slip/antiblocking
- Antifogging

− Modifying polymer structure

- Chain extenders
- Crosslinking/coupling agents
- Compatibilizers
- Prodegradants

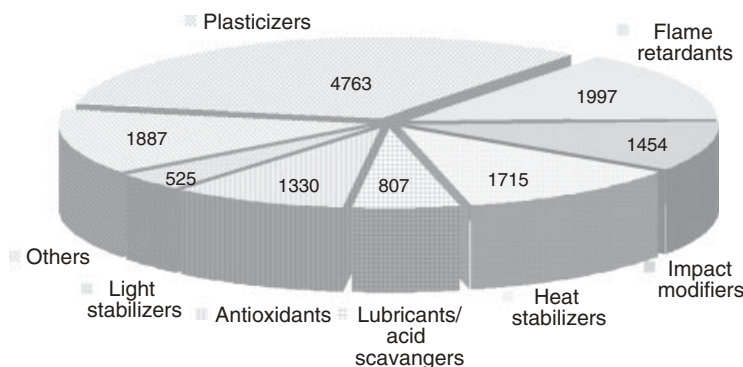**Figure 11.1**   The world of additives.

Figure 11.2   Turnover of additives (in million dollars) in 2004 [9].

of US$32 billion [8], without taking fillers and pigments into consideration. PVC is still the main polymer that consumes most additives because most of the plasticizers and heat stabilizers, representing together one-third of the additives production (Fig. 11.2), are used there [9]. Plasticizers still dominate the market but their growth is slow and the per kilogram value low. The class of flame retardants is the fastest growing market: about 6% annually [10]. Forty percent of the antioxidants and 45% of the light stabilizers are used in PP applications [11].

In the following part, the most important classes of additives (antioxidants, PVC heat stabilizers, light stabilizers, and flame retardants) are presented, as well as general information on chemical structures and mechanisms, on testing methods, and on use examples in selected polymer classes. Other important additive classes are summarized afterwards. It should be mentioned that the character of an overview on additives will simplify some aspects and will focus on some selected representative examples; for more detailed information on certain additive classes, it is necessary to refer to special literature. Another aim of the chapter is to point at recently introduced products and new developments. Fillers, reinforcing agents, and impact modifiers are outside the scope of the chapter because usually large amounts of these additives are added to the polymer and composite structures with new properties formed, which deserve a more detailed description. Colorants/pigments and optical brighteners are used to provide plastics with colorful and attractive appearance, but those products are outside the scope of this chapter as well.

11.2 ANTIOXIDANTS

Polymers, like all kind of organic materials, are sensitive to oxidation. Oxidation will take place at any time of the life-time of the polymer during thermal transformation, storage, or application. Furthermore, the combined action of light and oxygen results in photooxidation. Degradation of the polymer and irreversible changes of the polymer structure are the consequence of (photo)oxidation, resulting finally in insufficient mechanical properties, cracking, failure of the part, change in visual appearance (e.g., discoloration), etc. However, the sensitivity to oxidation depends on the chemical structure of the polymer. Polystyrene, poly(methyl methacrylate) or polyimide, and other high performance polymers are quite stable; but PP and other polyolefins such as polybutadiene are very sensitive to oxidation (Fig. 11.3).

The so-called autoxidation of polymers starts with an initiation step forming radicals, for example, from defect structures in the polymer chain. Reaction with molecular oxygen results in peroxy radicals followed by hydroperoxide formation through H abstraction, and hydroperoxides decompose into alkoxy and hydroxyl radicals (Fig. 11.4). Furthermore, the polymer chain is modified through the formation of oxygen-containing structures (carbonyls, alcohols, carboxyls) and unsaturated groups (vinyl, vinylidene, allylic). Disproportionation and depolymerization result in low molecular weight products.
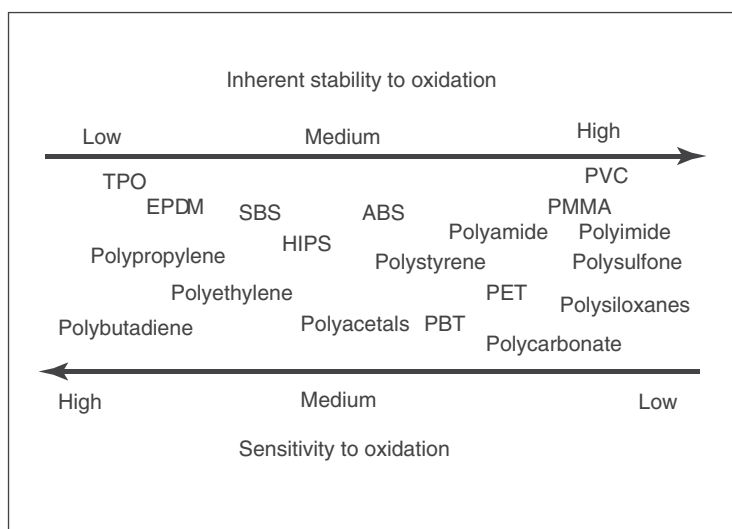

Figure 11.3 Relative sensitivity of selected thermoplastic polymers to oxidation.
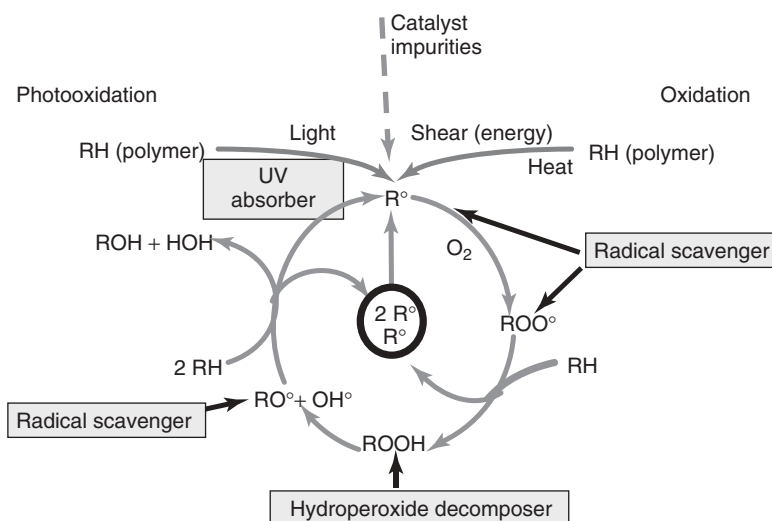

Figure 11.4 Autoxidation of polymers.

crosslinked polymer chains originate from the radical recombination of lower molecular weight fragments.

Suitable stabilizers, the so-called antioxidants, inhibit or reduce the thermo-oxidative degradation in polymers and maintain available properties during processing as well as during the product life cycle in the intended application. Antioxidants interrupt the autoxidation cycle by chemical reactions with the formed intermediates. Primary antioxidants are radical scavengers, either chain-breaking acceptors or chain-breaking donors reacting with radicals by forming thermally stable reaction products. Secondary antioxidants are hydroperoxide decomposers transforming hydroperoxides into thermally stable products.

Antioxidants are used in concentrations between 0.05% and 1% depending on the polymer structures and requirements.

11.2.1 Primary Antioxidants

Typical representatives of primary antioxidants are secondary aromatic amines and sterically hindered phenols; both classes are widely used in the protection of polymers (Figs. 11.5 and 11.6). Aromatic amines act as H donors by forming aminyl radicals, followed by coupling reactions and/or nitroxide formation and further coupling reactions.

Sterically hindered phenols react through H abstraction from the phenol group and form a phenoxyl radical,
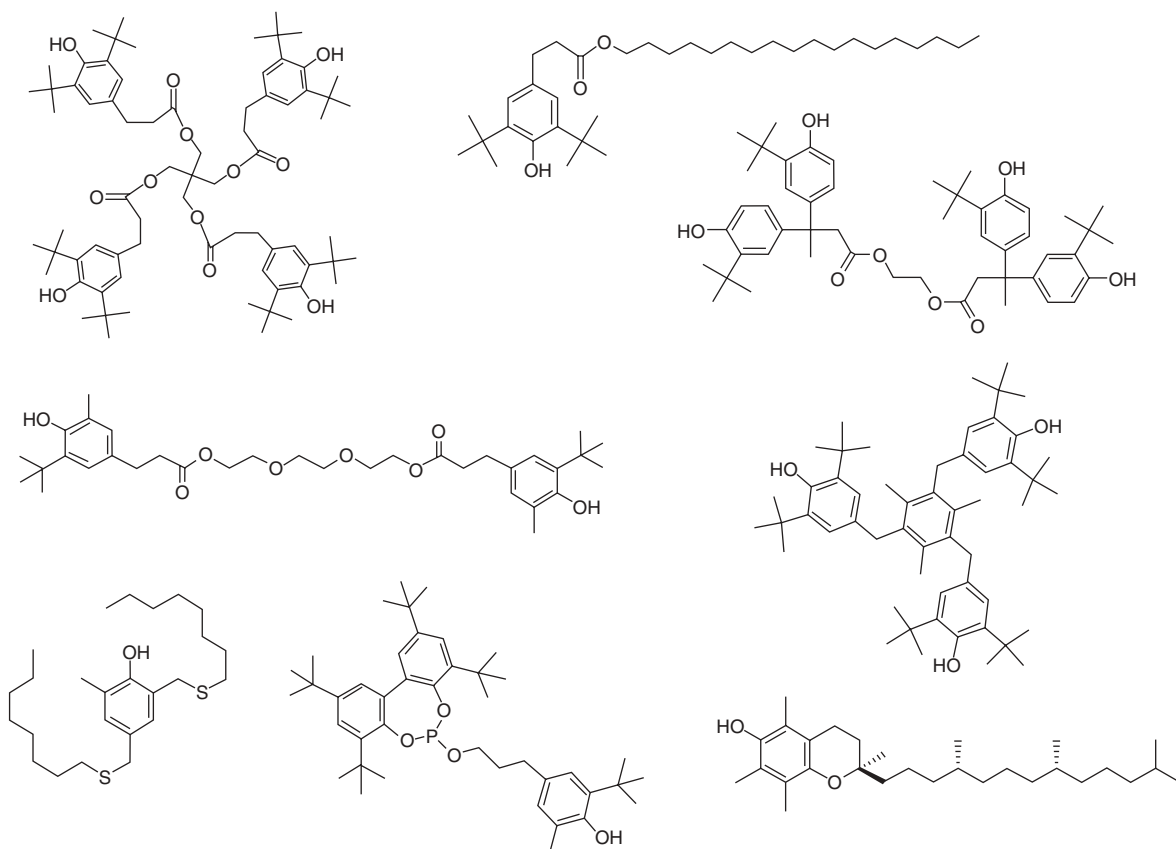
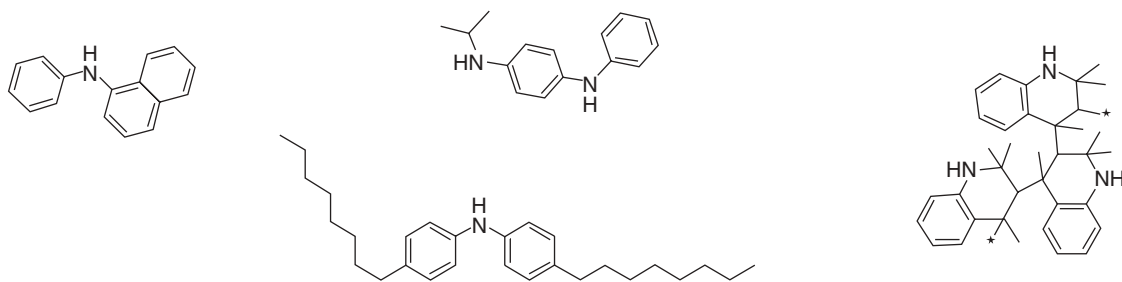**Figure 11.5** Chemical structures of phenolic antioxidants.

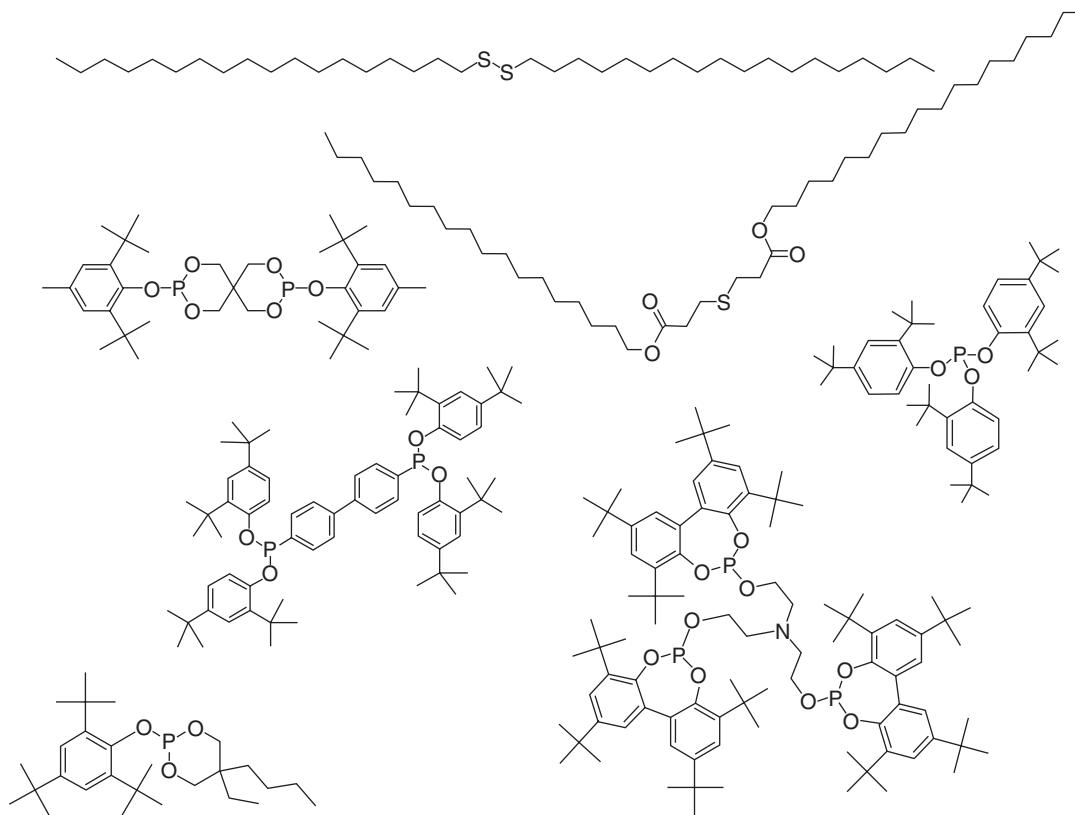**Figure 11.6** Chemical structures of aminic antioxidants.

Figure 11.7   Structures of secondary antioxidants based on phosphorus and sulfur.

followed often by a disproportionation reaction to the parent compound and quinone methide, which reacts with alkyl, alkoxy, and peroxy radicals to thermally and chemically stable products.

11.2.2   Secondary Antioxidants

Examples of widely used secondary antioxidants are phosphites, phosphonites, and sulfides (Fig. 11.7). Usually, secondary antioxidants are used in combination with primary antioxidants to benefit from a synergistic effect. The main action of phosphites and phosphonites is the oxidation to the corresponding phosphates by reacting with hydroperoxides. These P compounds are mainly used as melt stabilizers during processing. Sulfur compounds act as well as hydroperoxide decomposers via sulfur oxide and sulfenic acid formation. Sulfur compounds are preferably used in combination with phenolic antioxidants to improve the long-term thermal stability of polymers at temperature ranges between 100 and 150 °C.

11.2.3   Other Antioxidative Stabilizers

Hindered amine stabilizers, popularly known as *hindered amine light stabilizers* (*HALS*, see below), are efficient radical scavengers through an oxidation reaction to the nitroxyl radicals and hydroxylamines. The nitroxyl radical reacts with alkyl radicals to form stable alkoxyamines. Hydroxylamines are known *stabilizers* by themselves, whereas an intermediate product formed, nitrone, scavenges C radicals. Other efficient C-radical scavengers are benzofuranone derivatives and acryloyl-modified phenols. As transition-metal ions catalyze the decomposition of peroxides resulting in reactive radicals, phenolic antioxidants modified with metal complexing groups are used as metal deactivators. Moreover, optimized blends of different antioxidants are used, and as well structures with different stabilizer functions in one molecule.

Somewhat exceptionally, aliphatic polyamides are stabilized in non-color-critical applications with small amounts (20–50 ppm) of copper in the form of halogenids, for example, CuBr or CuI, or even more efficiently in combination with metallic iron [12].

11.2.4   Testing of Antioxidants

Standard test methods to analyze the thermal stability of polymers cover multiple extrusions and accelerated heat-aging. Multiple extrusions evaluate the melt-processing stability of a polymer or polymer formulation and determine

the efficiency of antioxidants or antioxidant combinations. The melt properties are usually characterized by melt mass flow rate (MFR) or melt volume flow rate (MVR) according to ISO 1133. The impact of processing temperature and shear can be analyzed in addition by measuring the mechanical properties, discoloration, molecular weight, or melt viscosity under different conditions and with optimized additive packages. Accelerated heat-aging simulates the long-term thermal stability. Samples are oven-aged at defined temperatures and conditions, and the change of selected properties, for example, visual appearance, color, mechanical values, molecular weight, is recorded over aging time. A simple version of long-term stability for quality control purposes is to determine the oxidation induction time (OIT, ISO 11357), whereas the induction time for the onset of the oxidation process is measured with differential scanning calorimetry (DSC) or differential thermal analysis (DTA). For some polymers, the carbonyl index is easily determined via infrared (IR) spectroscopy as an indication of the oxidative degradation of the polymer. Furthermore, the additive concentration may be analyzed directly, the consumption recorded, and the lifetime extrapolated; however, also the reaction products of the selected antioxidant may still be active as antioxidants, which are not analytically considered if only the initial molecular structure is determined.

11.2.5   Selected Examples

PP is a polymer very sensitive to oxidation. As outlined (Fig. 11.8), an unstabilized material does not survive a single processing step without deterioration of the properties. On the other side, small concentrations of phosphite or phenolic antioxidant can provide sufficient stability for several transformation steps, for example, extrusion and injection molding, however, depending on the processing conditions (temperature, shear). Furthermore, the common practice of using combinations of phosphites

and phenolic antioxidants results in improved processing stability.

Processing stabilization of other polyolefins such as high density polyethylene (HDPE), low density polyethylene (LDPE), and linear low density polyethylene (LLDPE), and styrenic polymers is achieved similarly by phosphite/phenolic antioxidant blends in the range of 0.1–0.2%. Polymers with unsaturated groups in the chain, such as polybutadiene, need higher concentrations of stabilizers. The influence of antioxidants during processing on engineering plastics such as poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT), or polyamide (PA) is not very pronounced; however, a certain stability improvement may be found experimentally.

In addition to processing stability, the long-term thermal stability of polymers is very important. In this case, antioxidants prolong the life of the polymer in general to an extent depending on the polymer structure and test conditions (Table 11.1). Although substantial extension of the polymer lifetime can be found in all cases, the shown values are only an indication from different experiments in order to illustrate the effect of antioxidants, as the criteria of the stabilities are not identical and the polymer grades tested may vary (manufacturing process, catalysts, testing procedure).

TABLE 11.1   Effect of Antioxidants on the Long-Term Stability of Selected Polymers

Polymer	Long-Term Thermal Stability in Days at °C, Unstabilized	Long-Term Thermal Stability in Days, 0.2% Antioxidant (AO)
Polypropylene	<1 at 135 °C	10–160
HDPE	5 at 120 °C	100 to >300
Polybutadiene	<1 at 80 °C	20–100
Polyamide-6	20 at 100 °C	40–150
PBT	3 at 160 °C	80–100
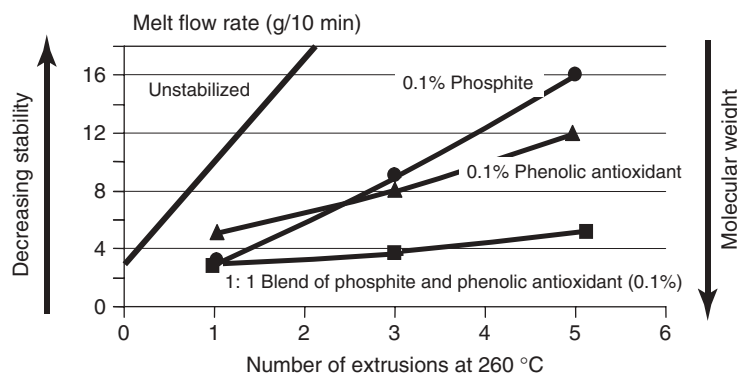
Figure 11.8   Stabilizer efficiency shown through multiple extrusion experiment.

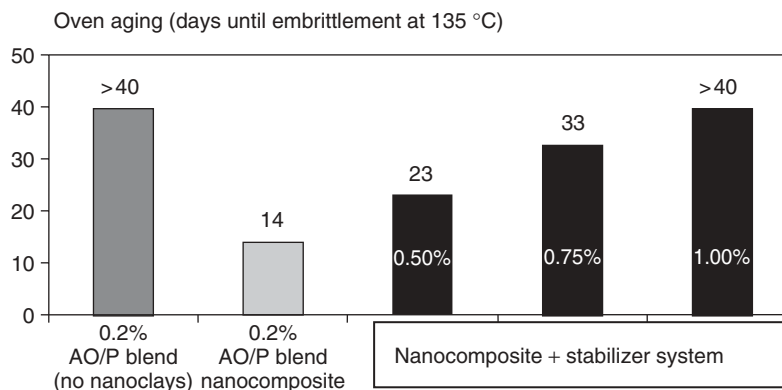Oven aging (days until embrittlement at 135 °C)

Figure 11.9 Influence of (nano)fillers on long-term thermal stability of polypropylene (P).

To select the correct stabilization package for a polymer and application further formulation ingredients have to be considered as interactions of the stabilizer with the polymer matrix and other ingredients may influence the overall stability. Fillers, pigments, carbon black, and reinforcement agents are known to interact considerably with the stabilizers. For example, a strong influence on the thermal stability is often found when fillers are added to the polymer. PP containing organically modified montmorillonite to obtain a nanocomposite degrades much faster than pure PP (Fig. 11.9). The main reason for this behavior is the adsorption of antioxidants on the filler surface [13]. To moderate the negative influence of fillers on the oxidative stability, filler deactivators or coupling agents (see below) have to be added and the overall stabilizer system concentration has to be adjusted, that is, increased [14].

11.3 PVC HEAT STABILIZERS

The principal thermal degradation reaction of halogen-containing polymers such as PVC, poly(vinylidene chloride) (PVDC), or chlorinated polyethylene (PE) is less due to autoxidation than to dehydrochlorination, that is, elimination of HCl during thermal processing. The dehydrochlorination reaction starts from polymer chain defects and results in polyene sequences and carbenium salts, both of which are responsible for the strong discoloration. Therefore, the protection of PVC by antioxidants is not very pronounced. The main mechanism to protect PVC from thermal degradation is by scavenging HCl, stabilizing initial defects of the polymer chain, as well as stabilizing the formed defects after HCl elimination. Therefore, efficient PVC heat stabilizers absorb HCl, eliminate defect structures, react with polyene sequences, and destroy carbenium salts. The compounds used today as PVC heat stabilizers are based on mixed metal salts, for example, calcium/zinc, organotin compounds, and metal-free organic-based systems. Organic

phosphites, polyols, epoxides, β-diketones, and hydrotalcites are often used as costabilizers. Historically, organic and inorganic lead (Pb) compounds have been widely used as heat stabilizers; however, these are gradually phased out in many countries because of environmental and toxicity reasons. PVC heat stabilizers are used in concentrations from below 1% (tin) up to 5% (mixed metal) depending on the formulation, lubricants, plasticizers, and costabilizers.

11.3.1 Mixed Metal Salts

Calcium/zinc mixed metal salts, for example, calcium stearate and zinc stearate and barium/zinc stabilizers (or the meanwhile phased out barium/cadmium stabilizers) are used in a synergistic way. Zinc carboxylates are capable of substituting labile chlorine atoms by forming $ZnCl_2$. $ZnCl_2$ reacts with calcium carboxylates and forms again zinc carboxylates. Although Zn compounds result in very good initial color and transparency, $ZnCl_2$ itself destabilizes PVC and catalyzes the dehydrochlorination reaction. Therefore, the ratio and concentration of Ca compounds and Zn compounds, as well as of additional costabilizers, are decisive for the performance of mixed metal salts.

11.3.2 Organotin Heat Stabilizers

Organotin mercaptide, for example, dioctyltin dithioglycolate, and organotin carboxylate, for example, dioctyltin maleate (Fig. 11.10), the latter group mainly, are used for outdoor applications because of high light stability, and act as efficient heat stabilizers by reacting with HCl under formation of alkyl-substituted tin chlorides. Furthermore, there is a direct reaction with labile chlorine atoms through substitution with more stable groups. Mercaptides can add to polyene sequences and thus interrupt the conjugation. Maleic acid derivatives may act similarly in a Diels–Alder mechanism.
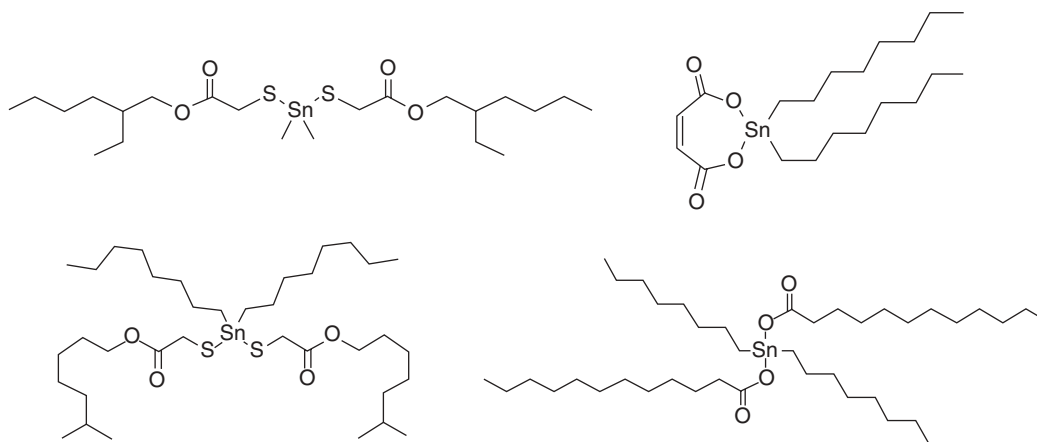
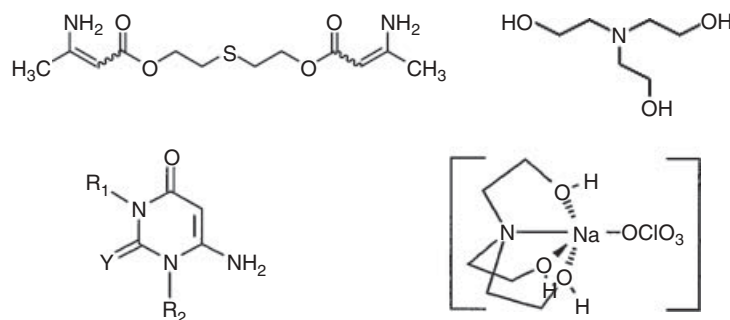**Figure 11.10** Structures of selected organotin PVC stabilizers.

Figure 11.11 Structures of organic-based PVC stabilizers.

11.3.3 Metal-Free Heat Stabilizers

In recent years, metal-free stabilizer systems have been developed because of environmental concerns of traditional lead and tin stabilizers. Chemically regarded nitrogen-based molecules are used, for example, β-aminocrotonates, dihydropyrimidines [15], trialkanolamines, as well as their reaction products and salts, for example, the perchlorate salt [16], etc. (Fig. 11.11). Owing to their good compatibility with other stabilizers, organic-based stabilizers are predestinated to be used in PVC recycling in case restabilization is needed [17].

11.3.4 Costabilizers

The most important costabilizers in PVC formulations used mainly in combination with mixed metal salts are alkyl-aryl-phosphites to improve early color. Epoxy compounds, for example, epoxidized fatty esters such as epoxidized soy bean oil, react directly with HCl or substitute labile chlorine atoms, for example, in the presence of zinc ions. Furthermore, the epoxidized fatty esters act as plasticizers. Polyols such as pentaerythritol or dipentaerythritol and β-diketones act as complexing agents and deactivate the negative effect of the formed zinc chloride. Hydrotalcites

and zeolites scavenge HCl. Contrary to tin and lead systems, mixed metal stabilizers based on Ca/Zn (or Ba/Zn) are usually complex mixtures of compounds, contributing to heat stability and optimized lubrication to provide smooth processing.

11.3.5 Testing of PVC Heat Stabilizers

The stability of PVC formulations is tested, for instance, according to ISO 305 by static heat tests, where test specimens are aged at constant temperature and mainly color changes (e.g., Yellowness Index) are recorded. Alternatively, to assess the performance of heat stabilizers, the time until the dehydrochlorination reaction takes place can be measured, for example, through pH change (ISO 182). Combined thermal and shear stress is analyzed via dynamic tests such as two-roll mill processing or multiple extrusion.

11.3.6 Selected Examples of PVC Heat Stabilization

As explained already, there is a distinct synergism between Ca/Zn stabilizers. Whereas Zn salts show a very good initial color, the time until HCl formation (discoloration) upon heating is considerably short. Ca salts offer a very
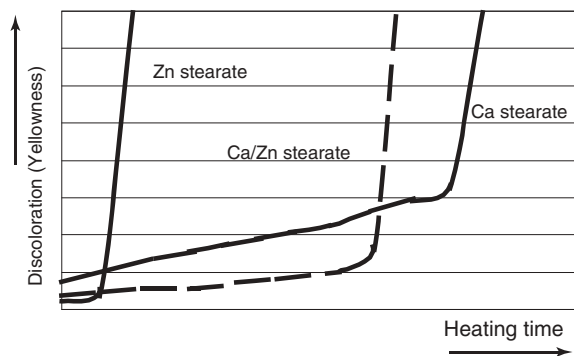
Figure 11.12 Scheme of the synergistic activity of Ca/Zn PVC heat stabilizers.

much extended stability but a less attractive initial color. Therefore, the combination of both salts is the method of choice (Fig. 11.12).

As an alternative to the widely used Ca/Zn stabilizers, organic-based stabilizers can replace technically traditional heat stabilizers. Maintenance of the initial color and transparency is supported efficiently (Fig. 11.13) [18].

11.4 LIGHT STABILIZERS

Although many polymers are sensitive to (sun)light alone, the combination of light and ubiquitous oxygen causes photooxidation. Through the action of light, free radicals are formed depending on the polymer structure and the energy of the light. These radicals can react with oxygen via peroxy radicals to form hydroperoxides (Fig. 11.4) and initiate the autoxidation cycle. Polyolefins such as PP and PE, or elastomers, are very sensitive to photooxidation, resulting in fast degradation (PP chalking) or crack formation, discoloration, and loss of mechanical properties. Polystyrene, styrene acrylonitrile polymer (SAN), antioxidant-stabilized

polyamide and polyester, and heat-stabilized PVC and poly(methyl methacrylate) are comparatively very stable. The light stability of a polymer formulation is furthermore influenced by light absorbing pigments, fillers, or carbon black, and the thickness of the parts. To protect polymers from the negative influence of light, UV absorbers, quenchers, and free-radical scavengers, namely, HALS, are used. Quenchers are based on Ni compounds and, therefore, they are phased out in many countries for environmental reasons. Light stabilizers are used in the range of 0.1–1% depending on the formulation, use area, and the required lifetime.

11.4.1 UV Absorbers

UV absorbers absorb UV radiation and dissipate it as heat in order to avoid photosensitization of the protected polymer. The UV absorber of choice should have high absorption coefficients and high inherent light stability. Chemical structures comprise mainly benzophenones, benzotriazoles, hydroxyphenyltriazines, cinnamates, diphenylcyanoacrylates, and oxanilides (Fig. 11.14).

Depending on their structure, polymers show different absorption maxima in the UV range; therefore, the UV absorber of choice should correspond to those or cover as broad a UV range as possible. Furthermore, combinations of different UV absorbers can be used or combinations of a UV absorber and HALS.

11.4.2 Hindered Amine Light Stabilizers

HALS hardly absorb UV light but act most likely as radical scavengers and hydroperoxide decomposers. Chemical structures are mainly based on piperidines. Sterically hindered piperazines are known as well (Fig. 11.15). Secondary amines are the most common structures, but alkylamines or, more recently, alkoxyamines are commercially
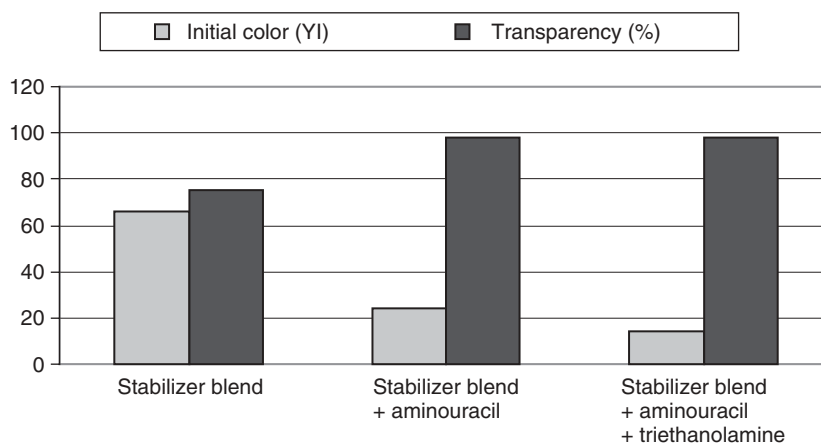

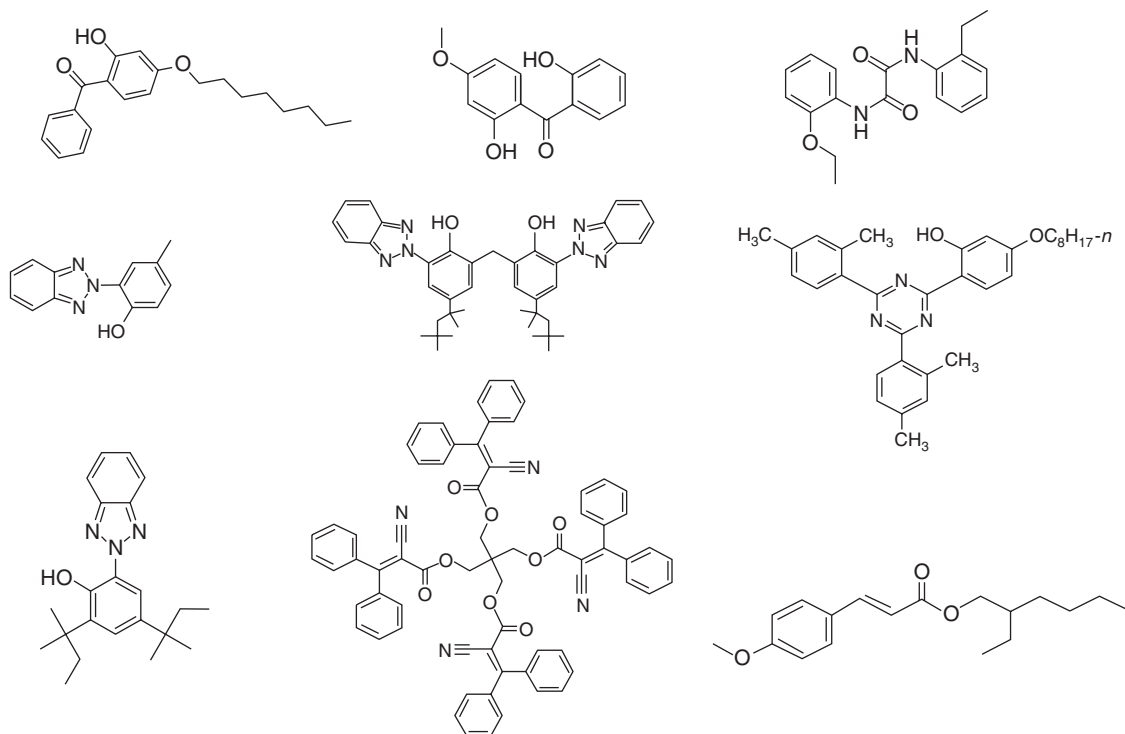**Figure 11.13** Stabilization efficiency of organic-based PVC heat stabilizers.

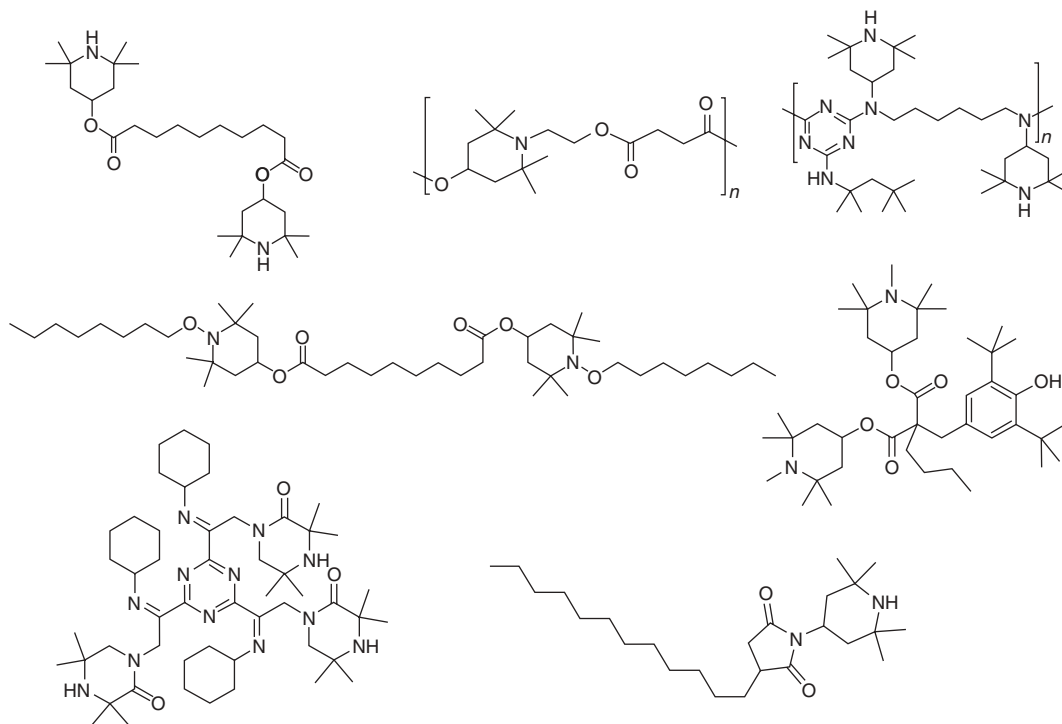**Figure 11.14**   Chemical structures of UV absorbers.

Figure 11.15   Chemical structures of hindered amine light stabilizers (HALS).
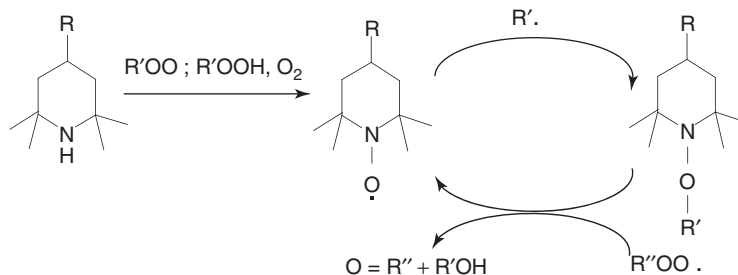
Figure 11.16   Simplified mechanism of HALS action.

available. A simplified cyclic mechanism of the stabilization through HALS starts with the oxidation to the nitroxyl radical, scavenging of an alkyl radical, reaction of the resulting alkoxyamine with a peroxyradical, and reformation of the nitroxyl radical (Fig. 11.16). To balance migration and performance, low or high molecular weight (oligomeric) products or their blends are applied.

11.4.3   Testing of Light Stabilizers

Photooxidation is tested by UV exposure or artificial or natural weathering. Natural weathering or outdoor weathering is carried out in high radiation areas to get an accelerating effect and is influenced by the season and humidity (e.g., Florida, humid or Arizona, dry). Artificial weathering is carried out in suitable devices, where light sources close to sunlight in their spectrum or lamps with high UV intensity are used. Change of the properties, for example, visual appearance such as chalking, crazes, gloss, and/or mechanical properties such as tensile strength, elongation, and impact strength are measured in relation to the exposure time or radiation energy (e.g., according to ISO 4582).

11.4.4   Selected Examples of Light Stabilization

Depending on their chemical structure, polymers show a different sensitivity to light and, therefore, a different stability with regard to maintaining mechanical or surface properties, to crack formation, and to discoloration [19]. Addition of light stabilizers shows always improvements in maintaining the properties, but to greater or lesser extents. The improvements shown (Table 11.2) can only be a rough and very general indication, as it is a compilation of different experiments, different failure criteria, and expert knowledge [19]. Although the performance of light stabilizers depends on the polymer, the grade, the application, the composition, and the exposure, there is mostly a definite relationship to the stabilizer concentration as shown for PP tapes in natural and artificial weathering (Fig. 11.17) [20]. Combination of different light stabilizers results often in a synergistic improvement as shown for different polymeric HALS (Table 11.3) [21].

11.5   FLAME RETARDANTS

With the exception of halogen-containing polymers and a few inherently flame-retarded high performance polymers, most polymers can be easily incinerated. Therefore, flame or fire retardants are added to polymer formulations in order to reduce the risk of fire, for example, for electro/electronic or construction applications. Flame retardants do not transform the polymer into a nonburning material but delay the incineration, may reduce the freed energy and decompose into easily burning gases or the damage caused by the fire. In addition to halogen-containing additives, halogen-free flame retardants are being increasingly developed. The latter are often based on inorganic hydroxides, such as $Al(OH)_3$ or $Mg(OH)_2$, or phosphorus or nitrogen compounds. Closely related to flame retardants are smoke suppressants, which are added to the polymer to reduce the generation of smoke in case of fire. Typical examples are ammonium polyphosphates and molybdates, the latter mainly used in PVC formulations. Flame retardants are often used in concentrations of 10–60% with respect to the polymer.

11.5.1   Halogenated Flame Retardants

Despite some environmental concerns, halogenated flame retardants still play an important role. With the exception of a few chlorinated products (e.g., chlorinated paraffins), these flame retardants contain usually molecules with several bromo groups (Fig. 11.18). Bromo compounds are active during combustion in the gas phase, whereas HBr reacts with OH and H radicals under formation of less reactive halogen radicals. The flame retardancy of bromo compounds is often synergistically improved by the addition of antimony oxide Sb_2O_3.

11.5.2   Inorganic Flame Retardants

Aluminum trihydroxide (ATH), aluminum oxidhydroxide (boehmite), and magnesium dihydroxide (MDH) decompose at elevated temperatures endothermically with the formation of water. Therefore, these flame retardants act

TABLE 11.2   Effect of Light Stabilizers on the Lifetime of Polymers

| Polymer	Polymer Degradation Induced by Light	Light Stability, Unstabilized under Artificial Weathering Conditions, h	Light Stability, 0.5% UV-A or HALS Added
Polypropylene	Loss of gloss	500	1500 h (UV-A)
	Chalking		1500 h (carbon black)
	Crazes		10,000 h (HALS)
Loss of mechanical properties			
HDPE	Crazes	1000–1500	5000 h (UV-A)
	Loss of mechanical properties		>30,000 h (HALS)
LDPE/LLDPE	Crazes	>500	1500 h (UV-A)
	Loss of mechanical properties		20,000 h (HALS)
ABS	Yellowing	200	1500 h
	Loss of mechanical properties		
PC	Yellowing	<2000	>15,000 h (5% UV-A)
PMMA	Yellowing	20,000	>20,000 h (UV-A + HALS)
	Loss of transmission		
Polyamide-6	Loss of mechanical properties	500	3000 h (AO)
	Yellowing		4000 h (AO + HALS + UV)
PVC	Yellowing	500	4000–6000 h (UV-A)
	Loss of mechanical properties		
PET/PBT	Yellowing	1000–2000	10,000 h (UV-A)
	Loss of mechanical properties		
SBR/BR	Crack formation	300	2000 h (UV-A)
	Yellowing		
PUR	Yellowing	200–3000	1000–10,000 h (HALS)
	Crack formation		
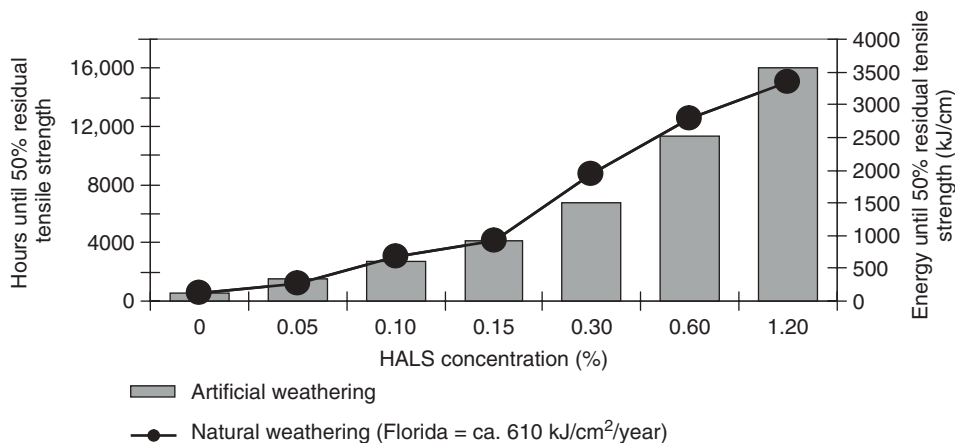
Figure 11.17   Influence of HALS concentration on the lifetime of polypropylene.

in the condensed phase by removing heat and diluting the burning gases. To generate sufficient water for this mechanism, the quantity to be used is high and mostly above 50% of the compound to be flame-retarded. More recently, nanocomposites from layered silicates [22] and carbon nanotubes (CNTs) [23] have been proposed as flame-retardant components acting through barrier formation at the surface and thus insulating the polymer from the flame source.

11.5.3   Phosphorus- and Nitrogen-Containing Flame Retardants

Red phosphorus itself can be used as an efficient flame retardant, as well as organic phosphorus compounds, for example, ammonium polyphosphate, bisphenol-A-diphenylphosphate, or resorcinol diphenylphosphate, or phosphorus-containing salts, for example, the aluminum salt of diethylphosphinate (Fig. 11.19). Phosphorus-containing

flame retardants act often through the formation of a barrier layer in the condensed phase or through P-radical species in the gas phase.

Melamine and melamine derivatives, such as melamine cyanurate or melamine polyphosphate, are representatives of nitrogen-containing flame retardants (Fig. 11.20). Melamine is an inert diluent and removes heat through decomposition; melamine polyphosphate provides an isolating barrier through an intumescent mechanism.

TABLE 11.3 Synergistic Behavior of Different HALS Structures in Light Stabilization of Polypropylene

HALS	Hours of Artificial Weathering until 50% Residual Tensile Strength
Without	450
0.3% Polymeric main chain HALS	3200
0.3% Polymeric side chain HALS	3600
0.15 + 0.15% Blend of both HALS structures	4500

More recently, alkoxyamines and azo compounds were proposed as flame retardants for thin-film PP applications [24, 25], where an activity is found already at concentrations as low as 0.5%.

11.5.4 Testing of Flame Retardancy

There are many often country- and application-specific tests to be passed for flame-retarded plastic formulations. Some standard test methods evaluate the limiting oxygen index (LOI, for example according to ISO 4589), in which a test specimen is burned in a mixture of oxygen and nitrogen. The higher the oxygen content to support burning, the more resistant the material is. LOI values range from 15% (polyoxymethylene, POM) to 95% (poly(tetrafluoroethylene), PTFE) and for most commodity polymers it ranges between 17% and 25%; above 27%, the self-extinguishing behavior can often be expected [26]. One further common test is the Underwriter Laboratory (UL) 94 test, where a sample is ignited at the bottom, burned vertically, and is classified, according to flame time, dripping, ignition of the underlying cotton, in to V-0 (best classification), V-1, V-2, and NC (not classified).
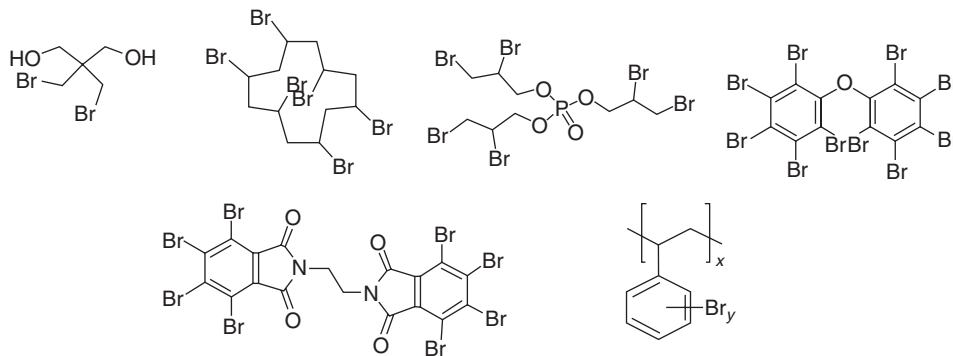

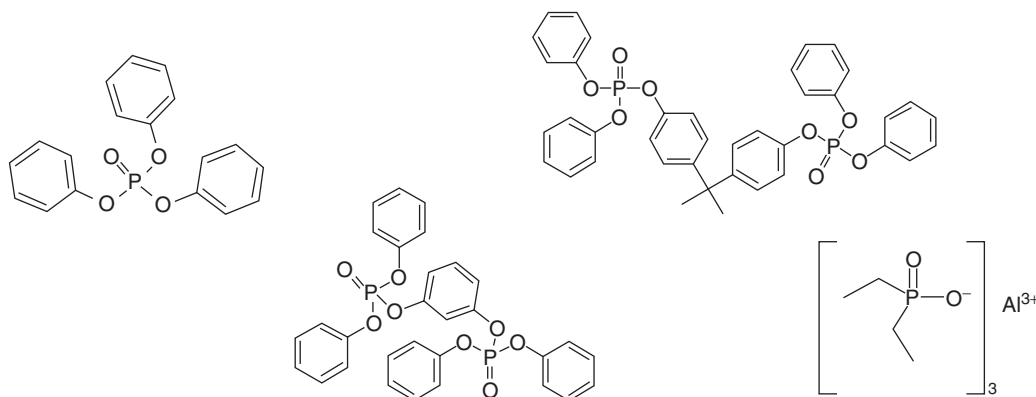**Figure 11.18** Chemical structures of brominated flame retardants.

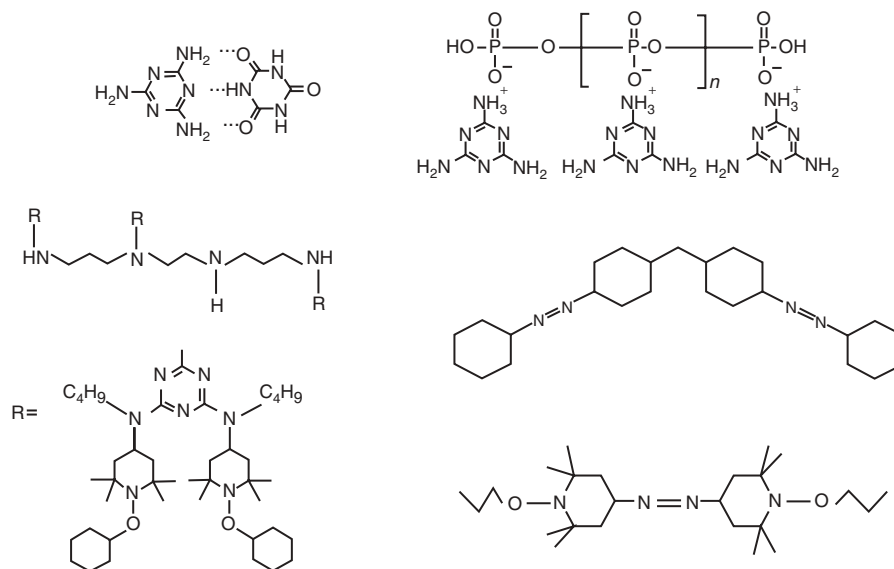**Figure 11.19** Structures of phosphorus-based flame retardants.

Figure 11.20 Chemical structures of nitrogen-containing flame retardants.

11.5.5 Selected Examples of Flame Retardancy

The activity of flame retardants depends on the inherent flammability of the polymer, on the degradation behavior of the polymer substrate, on the influence through further formulation ingredients, and on the degradation mechanism of the flame retardant. Moreover, the choice of a suitable flame retardant is related to the fire standards to be fulfilled. For example, unreinforced polyamide-6.6 is easily flame-retarded by adding 6–8% of melamine cyanurate to achieve a UL 94 V-0 rating. Glass-fiber-reinforced polyamide-6 achieves only a V-2 rating at around 20% of melamine cyanurate, whereas 25% of melamine polyphosphate may result in V-0. However, often synergistic combinations between different flame retardants are used from cost–performance reasons, for example, nitrogen and phosphorus compounds together. For instance, the combination of diethylaluminum phosphinate and melamine polyphosphate results in a V-0 classification of glass-fiber-reinforced polyamide 6.6 at a total concentration of 12–15% [27]. Furthermore, the combination of halogen-free flame retardants with a low concentration of halogen allows the achievement of flame retardancy at very low concentrations; for example, the combination of 0.2% aluminum hypophosphite, 0.3% melamine hydrobromide, and 0.1% 2,3-dimethyl-2,3-diphenylbutane results in a V-2 classification of PP [28]. On the other extreme, V-0 classification when using magnesium dihydroxide needs a concentration above 60% [29]. Intumescent formulations based on ammonium polyphosphate and pentaerythritol (3 : 1) achieve a V-0 classification of PP at 30% loading [30].

11.6 PLASTICIZERS

Plasticizers in the form of additives (the so-called external plasticizers) act as processing aids, reduce the melting and processing temperature of the polymer, and modify the polymer properties, for example, reducing the elastic modulus and making it more flexible and softer. PVC formulations consume most of the plasticizers. Plasticizers can be considered chemically as (weak) solvents for PVC. Phthalates such as di-2-ethylhexyl-phthalate or dibutyl phthalate represent still the major part of PVC plasticizers despite environmental concerns and bans in some applications such as children's toys in Europe. Alternative chemistries are based on phosphates, adipates, citrates, cyclohexane-1,2-dicarboxylates, terephthalates, and trimellitates (Fig. 11.21). Furthermore, oligomeric/polymeric plasticizers or plasticizers grafted to the PVC backbone via a thiol group can be seen as a new approach for plasticized PVC to cope with migration [31]. Within the trend of materials from renewable resources, plasticizers based on isosorbide esters have been introduced recently [32]. Technical performance of plasticizers is related to their gelation capacity, compatibility, volatility, water solubility, aging resistance, and light stability. Plasticizers are used in concentrations between 10% and 40%.

Technical criteria of plasticized PVC comprise the gelation behavior (measured as the temperature to fuse the plasticizer/PVC mixture), which varies between 80 and 180 °C depending on the plasticizer activity and the performance at high (processing) and low temperature. For example, adipate plasticizers allow use at lower temperatures than
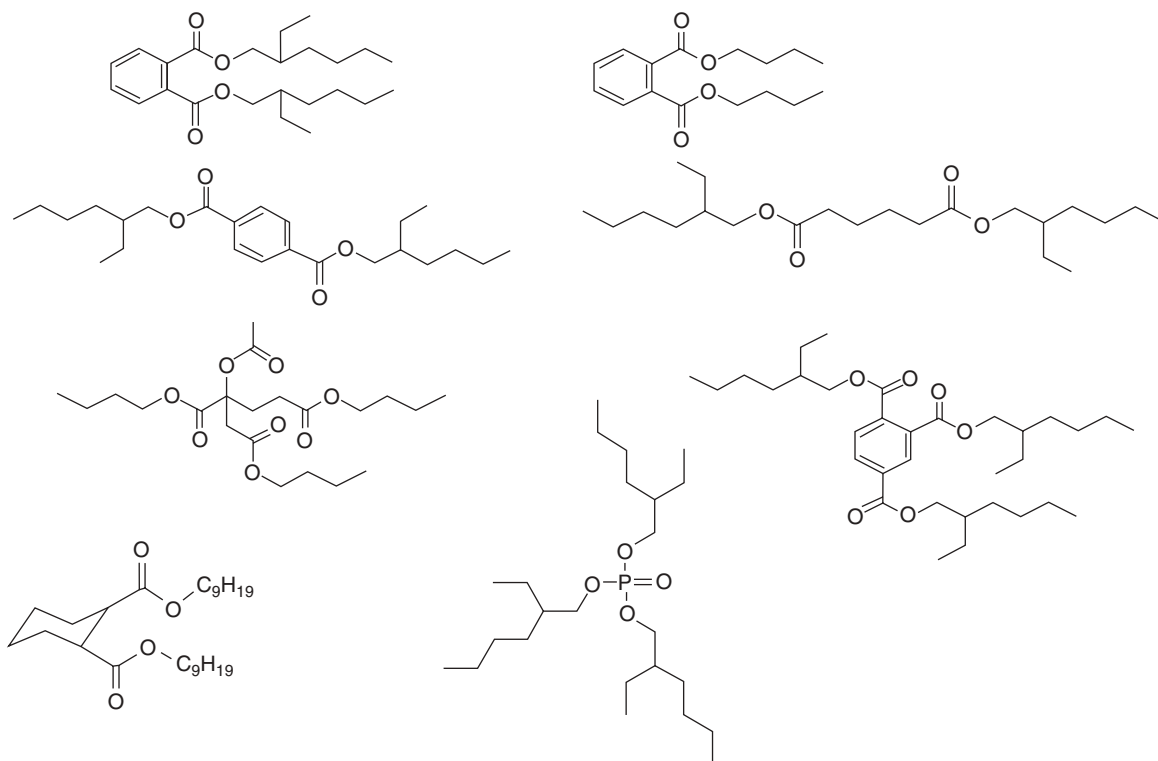
Figure 11.21 Chemical structures of plasticizers used in PVC.

phthalates. Interestingly, already rather small concentration changes show a considerable influence on properties; for example, increasing the plasticizer concentration from 37% to 42% decreases the glass-transition temperature from −7.5 to −21.5 °C (unplasticized PVC: 70–90 °C) [33].

The so-called antiplasticizers are used in PET bottle manufacturing to enhance the gas barrier. The proposed additives comprise aromatic hydroxy and carboxylic group containing benzene and naphthalene compounds, for example, methyl-4-hydroxybenzoate or 1,3-dihydroxynaphthalene [34].

11.7 SCAVENGING AGENTS

Scavenging agents are added to polymer formulations to remove unwanted byproducts, impurities, degradation products, or molecules inducing degradation of the polymer, for example, to scavenge water by reactive molecules such as carbodiimides in order to avoid hydrolytic degradation of the polymer or of other additives. The class of scavengers comprises mainly acid scavengers, aldehyde scavengers, and additives to reduce odor in recyclates.

11.7.1 Acid Scavengers

Acid scavengers or antacids are often used in base stabilization packages of polyolefins to neutralize acidic

byproducts from polymerization catalyst residues, namely, HCl. These byproducts may cause corrosion on processing equipment, reduce overall thermal stability of the polymer, and catalyze hydrolysis. Representative acid scavengers are acid salts such as calcium stearate, zinc stearate, calcium lactate, and also hydrotalcites and zinc oxide. Concentrations range mostly between 0.1% and 1%. The acid scavenger of choice depends on catalytic residues, that is, the polymerization process, acceptance of discoloration, and the required processing stability. For color-critical applications, aluminum–magnesium hydrotalcites are often preferred.

11.7.2 Aldehyde Scavenger

The main application fields of aldehyde scavengers are PET (more specifically water bottles made from PET), and polyacetals such as POM or polymers synthesized from formaldehyde such as urea–formaldehyde resins.

Any melt-processing of PET generates acetaldehyde in small concentrations caused through an elimination reaction from the terminating ethylene glycol unit. Acetaldehyde influences the taste of bottled water and, therefore, minimizing the content of acetaldehyde in the final product is mandatory. In addition to engineering approaches for optimized production, a number of molecules are known to play the role as active acetaldehyde scavengers, for example,
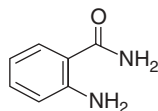
Figure 11.22 Structure of anthranilamide used as acetaldehyde scavenger in PET.

nitrogen compounds such as polyamides, amines, hydroxyl-amine, polyols including polyvinyl alcohol, zeolites, and cyclodextrins. Anthranilamide seems to be one of the preferred molecules (Fig. 11.22) [35, 36].

Thermal degradation of polyoxymethylene and polyacetals results in the formation of formaldehyde, which is furthermore catalyzed by oxidation of formaldehyde to formic acid. In addition to antioxidants and acid scavengers, formaldehyde scavengers are used in polyacetal formulations. Formaldehyde scavengers of choice are nitrogen compounds, for example, melamine derivatives such as benzoguanamine, urea derivatives such as allantoin, hydrazides, imides, and polyamide.

11.7.3   Odor Reduction

Some polymers, for example, recycled polymers, suffer often from odor problems caused by contaminations or degradation products. Additives that claim to reduce odor include zeolites [37] and silicates [38]. Recently, zinc ricinoleate-based additives were described to reduce odor of recyclates by absorbing low molecular weight amines and sulfuric substances [39].

11.8   ADDITIVES TO ENHANCE PROCESSING

To obtain a high production capacity of polymers processed in the melt, wear, and machine energy should be at a low level. As the polymer melt is usually of high viscosity, additives can be used to reduce the melt viscosity and internal and external friction. The most important class of additives to enhance processing is lubricants. Internal lubricants are soluble in the polymer melt and reduce the melt viscosity, whereas external lubricants are insoluble, form a film between metal surfaces of the processing equipment and the polymer melt, reduce friction, and show a slip effect. Chemically regarded lubricants are often hydrocarbons, for example, PE waxes, metal salts of long-chain acids, for example, calcium stearate or salts of montan waxes, and amide waxes, for example, erucamide or oleic acid amide. Their main use is in PVC, polyolefins, and some engineering plastics, and their concentrations may vary from below 1% up to several percentage.

Fluoropolymers (e.g., copolymers of vinylidene fluoride and hexafluoropropylene) and silicone-based (e.g., poly-dimethylsiloxanes) additives are often referred to as *processing aids*, preventing melt-fracture, for example, the so-called sharkskin. Fluoropolymers are applied in concentrations between 0.01% and 0.1%.

11.9   ADDITIVES TO MODIFY PLASTIC SURFACE PROPERTIES

A number of additives do not aim at modifying the properties of bulk polymers but target to influence specific surface properties. These primarily surface-active additives include slip and antiblocking agents to facilitate separation of individual films, antistatic agents to modify the surface resistivity, and antifogging agents to avoid water condensation on polymer films in the form of droplets. Other surface-modifying additives influence the roughness and the gloss of the polymer surface. Also, plasticizers and lubricants can influence the surface aspect of shaped plastic parts. Surface-active additives with hydrophilic or hydrophobic character can change the polarity of a polymer: for example, a hydrophilic surface-active agent can create a hydrophilic surface on a hydrophobic polyolefin.

11.9.1   Slip and Antiblocking Agents

Often, polymer films show a tendency to stick together, which makes it difficult to separate individual films in processing steps, for example, for packaging applications.

Slip agents are related to lubricants, as amide waxes, such as erucamide or oleamide, are typical representatives. Through migration of the slip agent to the film surface, a lubricating layer is formed that facilitates the separation of adjacent films. Antiblocking agents fulfill a similar target, but they are based on inorganic materials, for example, silica, talc, zeolites. Concentrations of slip or antiblocking agents are in the range of 0.1–0.3%.

11.9.2   Antifogging Agents

Antifogging agents help to avoid the formation of water droplets on polymer films originating from temperature differences; instead, the water droplets spread in a continuous transparent film. As the antifogging agent migrates to the surface, the surface energy of the plastic film is increased and the surface energy of the water droplet is reduced. Main applications are in agriculture/greenhouse films (to avoid reduced light transmission, burning of plant leaves through lens effect, and water drips on the plants) and in packaging films, for example, to keep esthetics of packaged food. Chemically, antifogging additives are often glycerol esters, sorbitan esters, or ethoxylated fatty alcohols, and their concentrations are in the range of 1–3%.

11.9.3   Antistatic Agents

Polymers are generally good insulators, but they can build up high electrostatic charges. Static electricity may cause handling problems of plastic goods, dust contamination, and risk of electrical discharges. Antistatic additives dissipate electrostatic charges and, therefore, reduce these potential problems. Chemically regarded, antistatic agents are based either on organic migrating compounds, on inherently antistatic polymers, or on conductive fillers. Surface migrating organic compounds cover the plastic surface and pick up water from the surrounding environment, creating a conductive pathway. Often, fatty acid esters, typically glycerol monostearate, ethoxylated alkylamines, ethoxylated alcohols, alkylsulfonates, and ammonium salts are used.

Inherently, antistatic polymers are block-copolymer elastomers, for example, block polyetheramides. These can form a permanent conductive network within the host polymer matrix, thus dissipating electrical charges, independent of water uptake [40]. Electrically, conductive fillers comprise carbon black, graphene, carbon nanotubes (CNTs), carbon nanofibers, metal powders such as copper, and conductive polymers, for example, polyaniline, polypyrrole, or polythiophene [41, 42]. In addition to the activity as antistatic agents, these molecules may be used as components for electromagnetic shielding. Concentrations of antistatic agents vary from 0.1% to 15% depending on the chemistry used, as well as the required performance and permanency.

11.10   ADDITIVES TO MODIFY POLYMER CHAIN STRUCTURES

Some additive classes are intended to modify in a controlled way the molecular weight and/or molecular weight distribution of the polymer or to create branched or crosslinked structures often in the course of a processing step, for example, by reactive extrusion. The modification of the molecular weight can be in both directions: chain extenders and branching and crosslinking agents will increase the overall molecular weight, whereas prodegradants will decrease the molecular weight. Consequently, many polymer properties, for example, the mechanical and rheological characteristics, are influenced, as these are directly linked to the molecular weight and to the polymer architecture.

11.10.1   Chain Extenders

Polycondensation polymers such as polyesters or polyamides carry functional end groups, which can be used to build up the molecular weight by reaction with suitable additives that are capable of reacting with these end groups. As there are ideally two end groups per chain, a linear molecular weight increase should be possible if difunctional additives are used. Higher functionalities will result in branching and crosslinking depending on the functionality and additive concentration.

Polyester chains exhibit either -COOH or -OH end groups, and polyamides either -NH$_2$ or -COOH end groups. In principle, any difunctional additive that reacts at the processing temperature with those chemical groups and with sufficient thermal stability may be used. The proposed chemistries include diepoxides, bis-oxazolines, diisocyanates, dianhydrides, bis-acyllactams, bis-maleimides, dicyanates, carbodiimides, diesters, etc., sometimes combined with catalysts to accelerate the reaction. Depending on the starting polymer and careful selection and adjustment of the type and concentration of the reactive additives, the basis for manufacturing tailor-made products is provided. Concentrations vary from 0.1% up to several percent.

As an example of molecular weight increase of polyamides, the decrease of the MVR (increase in molecular weight) in relationship to the reactive additive concentration is shown for diepoxides, catalyzed by a phosphonate (Fig. 11.23) [43].

Because of a lack of functional end groups, chain extension of polymerization polymers such as polyolefins or polystyrene is limited. In case double bonds are present in the polymer, for example, in PE, these may be used for some branching and crosslinking during processing in the presence of radical generators, such as peroxides or hydroxylamine esters [44]. A limited chain extension of PP can be achieved by combining radical generators and multifunctional acrylates [45].

11.10.2   Controlled Degradation

To reduce the molecular weight of PP, radical generators are used to cleave the polymer chain during processing and to adjust molecular weight and molecular weight distribution, for example, fiber applications. As radical generators, peroxides are used in general. Hydroxylamine
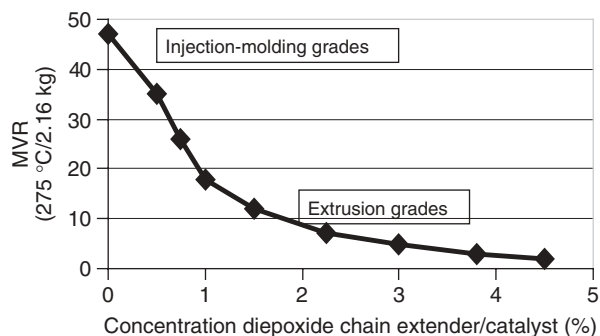
Figure 11.23   Molecular weight increase of polyamide-6.6 by chain extenders.

esters or azoalkanes have been proposed more recently for this purpose [46, 47]. The concentrations of radical generators for controlled degradation can be up to 1%.

11.10.3 Prodegradants

As an alternative to the use of biodegradable polymers, prodegradants have been developed to promote (photo)oxidative degradation of polyolefins, for example, of agricultural or packaging films, in a considerably short time, that is, after the use season. Ideally, the degradation time can be programmed. Increased photooxidative degradation is achieved by adding photosensitizers such as carbonyl-containing species, for example, diketones [48]. Additives for oxidative degradation are based on metal salts, for example, iron, cerium, or cobalt fatty acid salts [49, 50].

11.10.4 Cross-Linking Agents

crosslinking of polymers results in a three-dimensional network and is common in thermosetting resins (curing, hardening) and in rubber processing (vulcanization). crosslinking of thermoplastic polymers, mainly PE, is used in wire and cable insulation as well as in pipe and foam applications. Chemical compounds to achieve crosslinking are radical generators used sometimes in combination with graftable monomers. The radical generators are usually organic peroxides such as alkyl/aryl peroxides (dicumylperoxide), peroxyester, or diaroyl peroxides (dibenzoyl peroxide). By cleavage of the peroxy group, free radicals are formed, abstracting hydrogen from the polymer. The formed macroradical recombines with another macroradical, forming finally, after several reaction steps, the three-dimensional network. If reactive monomers are present, the macroradical may react with the monomer in a grafting reaction in competition to recombination. The latter is used, for example, in wire and cable insulation, when organofunctional silanes, for example, vinyltrialkoxysilanes are grafted on PE in the presence of peroxides. The silane-functionalized PE is crosslinked in a consecutive step by water. Another monomer to be grafted radically on polyolefins is maleic acid anhydride; the resulting modified polymers are used as adhesion promoters and compatibilizers between different polymers, polymer and metal, polymer and fillers, or polymer and reinforcement agents.

As an alternative to organic peroxides, carbon-carbon (CC) initiators, for example, dimethyl diphenylbutane, hydroxylamine esters [51], or unsymmetric azo compounds [47] can be used for crosslinking reactions especially at higher processing temperatures.

Concentrations of crosslinking agents depend on the required crosslinking density, the application, and the production process, and vary between 1% and 10%.

11.11 ADDITIVES TO INFLUENCE MORPHOLOGY AND CRYSTALLINITY OF POLYMERS

Some additive classes influence the overall mechanical and optical properties through inducing morphology changes. Nucleating agents, clarifiers, and antinucleation agents are used to influence the crystal growth of semicrystalline polymers. The morphology of polymer blends and the distribution of polymers, fillers, and reinforcements in a polymer matrix are adjusted with the help of compatibilizers, dispersants, and coupling agents.

11.11.1 Nucleating Agents/Clarifiers

Crystallization of semicrystalline polymers (e.g., PP, PE, PET, PBT, PA-6, and PA-6.6) can be influenced during processing through the addition of nucleating agents. Nucleating agents accelerate the crystallization rate and thereby reduce the cycle time during injection molding and increase the number of formed crystals, thus influencing the morphology as well as mechanical and optical properties. Nucleating agents that induce low haze and high transparency, for example, in PP, are called *clarifiers*. Clarifiers for PP are usually based on dibenzylidene sorbitols and its derivatives, for example, bis(3,4-dimethyl-dibenzylidene) sorbitol. Nonsorbitol structures are, for example, composed of aramides [52] or phosphates [53]. Nucleating agents for PET, PBT, and PA consist often of alkali metal salts (e.g., sodium benzoate) or phosphates (e.g., sodium 2,2'-methylene-bis-(4,6-di-*tert*-butyl-phenyl)phosphate) (Fig. 11.24); however, talc or carbon black show a nucleation effect also. The concentrations of nucleating agents used can be below 0.1% (nonsorbitol clarifiers), but are often in the range of 1–3%.
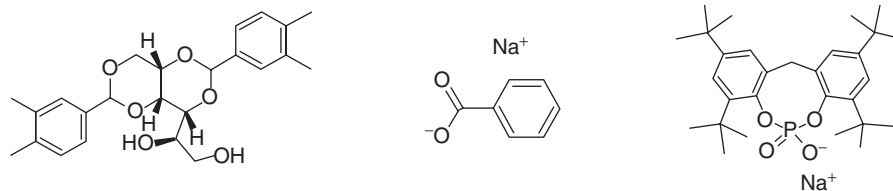

Figure 11.24 Chemical structures of nucleating agents.

Antinucleation agents reduce the crystallization rate of polymers: for example, addition of 1% SAN or polystyrene to PET reduces haze during blow-molding [54, 55].

11.11.2   Coupling Agents/Compatibilizers

Polymers of different structures are in general not miscible thermodynamically and, therefore, do not form homogeneous blends. The polymer in the highest concentration forms a continuous phase, and the polymer with a lower concentration is dispersed in the continuous matrix. The intermolecular adhesion between the continuous and the dispersed phases is very weak, resulting in insufficient mechanical properties of such a blend. Compatibilizers modify polymer interphases by reducing the interfacial tension in the melt, stabilizing the dispersed phase against growth during annealing ("morphology stabilizers"), and increasing the adhesion at phase boundaries, resulting finally in improved overall properties. Compatibilizers are polymers with structures similar to those the polymers to be compatibilized. They can be reactive, that is, carrying functional groups, or nonreactive [56, 57]. Examples of reactive compatibilizers include acrylic acid-grafted or maleic acid anhydride-grafted PE or PP or glycidyl(meth)acrylate copolymers. A typical nonreactive compatibilizer is styrene-(ethylene/butylene) styrene triblock copolymer. The concentrations of compatibilizers have to be in the range of 5–15% to show the requested effects.

Like compatibilizers, coupling agents are used to improve the adhesion of fillers and reinforcements, for example, glass fibers or carbon fibers to the polymer matrix [58]. The coupling agent consists of a part that is compatible to the polymer and another part that is reactive to the filler or reinforcement. Examples of coupling agents are fatty acids (e.g., stearic acid), calcium, zinc, or magnesium stearate, and amino-, epoxy-, methacryl-functionalized silanes. More sophisticated coupling agents are based on complex titanates and zirconates [59]. Optimized concentrations of coupling agents depend on the filler/reinforcement surface area and are in the range of 0.2–5%.

11.12   ANTIMICROBIALS

Antimicrobials or biocides protect plastics from attack on the surface by microorganisms, for example, fungi, yeasts, bacteria, and algae, and are used in outdoor applications in public areas (e.g., wood–plastic composites, liners for pools, bath mats, appliances), in hygienic household and consumer applications such as textiles, and in medical devices [60, 61]. Biocides are based on organic, often surface migrating, molecules, or inorganic compounds releasing silver, copper or zinc ions. Examples

for organic biocides are 10,10′-oxybisphenoxyarsine, 2-*n*-octyl-4-isothiazolin-3-one, both mainly used as antifungals in flexible PVC, 2,4,4′-trichloro-2′-hydroxy-diphenylether (Triclosan), and quaternary ammonium salts, for example, polysiloxanes with functional ammonium groups [62]. Silver-releasing antimicrobial compounds include silver salts, colloidal silver, nanosilver, silver complexes such as Ag zeolite sometimes in combination with Zn, and silver glasses. The concentrations used of antimicrobials are in the range of 0.2–2%.

11.13   ADDITIVES TO ENHANCE THERMAL CONDUCTIVITY

Thermally conductive compounds are mainly used in the electronic industry to remove heat from electronic components. Additives to be used are ceramics (e.g., aluminum nitride, or boron nitride) or carbon-based additives (e.g., graphite, carbon fibers, or CNTs) or even metal fibers [63, 64]. The concentrations used are quite high and can easily be in the 50% range.

11.14   ACTIVE PROTECTION ADDITIVES (SMART ADDITIVES)

Some additives are incorporated in polymers not to protect or influence the polymer itself but to act on the surroundings in an active way: protection of packaged goods, plant growth in greenhouses, or heat management in buildings.

11.14.1   Content Protection

The incorporation of additives in packaging to protect packaged goods is a technique often called *active packaging*. Examples include the use of UV absorbers to protect food from discoloration and food ingredients, for example, vitamins, from degradation and to extend the shelf-life. The UV absorbers are based on the same chemical classes as used for protecting plastics as described above.

Oxygen scavengers remove oxygen residues from the packaging by a chemical reaction and transform them into stable products. Therefore, the packaged good is protected from oxidation, and undesirable taste, odor, or appearance caused by oxidation of the food is eliminated. Chemical compounds to act as oxygen scavengers include polybutadiene or copolymers with cyclohexene or with allylic groups in combination with transition-metal catalysts based on cobalt or zinc (e.g., cobalt acetate or zinc acetate) or photocatalytic initiation [65]. Alternative oxygen scavengers are based on the oxidation of iron activated by moisture.

Other additives to be used in food packaging include ethylene scavengers (e.g., potassium permanganate) on silica, CO_2 scavenger (e.g., calcium hydroxide reacting to calcium carbonate), and CO_2- generating additives (e.g., ferrous carbonate). Further additives to be used for content protection incorporated in plastics provide antimicrobial effects, for example, silver or ethanol release, antioxidant release, flavor release, flavor absorption, and moisture control [66].

11.14.2 Productivity Enhancer

The growth of plants in greenhouses and some potential plant diseases caused by pests and fungi may be controlled by incorporating fluorescent dyes or pigments in greenhouse films. These dyes are able to modify the spectrum of outside solar radiation and convert UV light into visible red light. The changes in the radiation transmission can result in significant modification of plant architecture and shape, as the photosynthetic process strongly depends on the total amount of light that plants receive in photosynthetic active radiation (400–700 nm). For example, the yields of tomatoes and the number of rose flowers were significantly increased when a film with a red fluorescent dye was used in the greenhouse [67].

11.14.3 Heat Control

IR absorbers and reflectors are used to limit the heat development in rooms (e.g., in greenhouses) and are incorporated in agricultural films or in glazing. Typical materials range from kaolin (aluminum silicate) or other silicates and hydrotalcites [68] in agricultural films to dyes (e.g., phthalocyanines or anthraquinones). Furthermore, dyes with near-IR absorption are added to enhance laser welding of polymers.

11.15 ODOR MASKING

Odor from contaminants or degradation products, instead of being scavenged (see above), may be masked by fragrance-releasing agents, for example, with fruit or flower scent. In some cases, to manage odor it may be advantageous to use combinations of maskants, odor absorbers, and/or neutralizers.

11.16 ANIMAL REPELLENTS

Plastic application materials such as cables are destroyed by animals and especially by rodents. Therefore, additives may be incorporated to eliminate potential damage to these materials. Additives of choice to repel rodents are substances with a bitter taste, for example, denatonium benzoate, with a spicy taste (capsaicin, hot pepper), and/or with an unpleasant odor for animals (Fig. 11.25). Other substances repel birds, for example, natural oils or methyl salicylate [69].

11.17 MARKERS

Identification of polymers may be important for the manufacturer to establish the identity and the source and to differentiate own products from those of other suppliers (e.g., in the case of identifying the cause of damage) or to separate different polymers for recycling reasons. Target is the use of very small quantities of additives as markers or tracers. Proposed additives of choice may be fluorescent dyes [70], hapten compounds [71], or rare-earth metals [72] in the ppm range.

11.18 BLOWING AGENTS

Blowing agents are used in manufacturing foams. Chemical blowing agents are additives that decompose thermally within the foam production process, liberate gases, and create the foamed structure. Product classes comprise azo compounds (e.g., azodicarbonamide, hydrazides, tetrazoles), monosodium citrate, but also inorganic carbonates, for example, sodium hydrogen carbonate (Fig. 11.26).
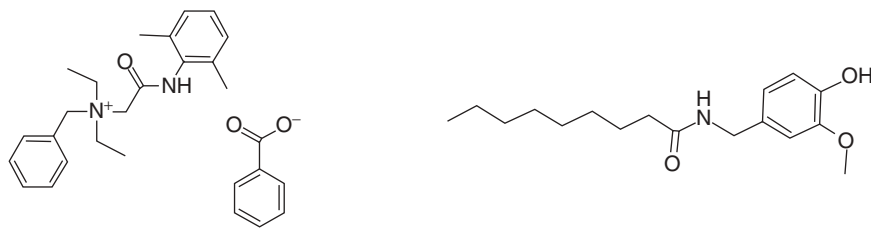

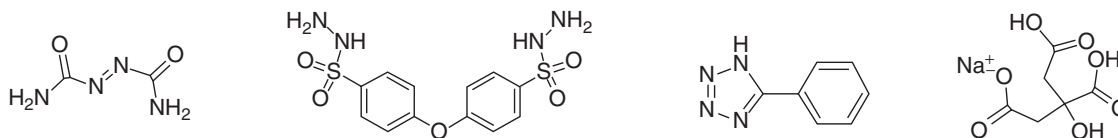**Figure 11.25** Chemical structures of animal repellents.

Figure 11.26 Chemical structures of blowing agents.

11.19 SUMMARY AND TRENDS IN POLYMER ADDITIVES

Additives are essential components in polymer formulations to maintain and to extend polymer properties. Many additive classes, for example, antioxidants, heat stabilizers, and light stabilizers, are seen today as commodities and standard products, available from different manufacturers and applied in many use areas. These additives will grow in parallel to the growth of plastics. New additive developments in the traditional areas address more stringent or new requirements, mainly in niche applications. Optimized combinations of different additives acting through different mechanisms result often in an optimized solution for a specific requirement. The art of formulation is in the knowledge on the synergisms and antagonisms of the considered additives.

Furthermore, modification of polymer properties through additives contributes decisively to the use of commodity plastics in demanding applications that have been the traditional field of engineering plastics.

A further driver for developing new additives is the increasing awareness of the environment, of carbon footprint, and of energy savings, resulting in environmentally friendly additive solutions shown, for example, through the developments of halogen-free flame retardants and metal-free PVC stabilizers as well as green manufacturing processes. Moreover, (bio)additives based on renewable resources may grow in the future.

Owing to the trend in plastics to be produced in larger volumes and fewer grades, the importance of additives in plastics will not only sustain but also increase. Typical additive examples comprise surface or interphase modifiers, nucleating agents, and reactive additives, providing tailor-made molecular weight, polymer structures, morphologies, as well as rheological and/or surface behavior. Smart additives allow plastics to enter new applications, new effects, and new functionalities of high value.

In a nutshell, plastic additives are and will be essential components in polymer formulations to support the further growth of plastics. Also they do and will provide innovative solutions for the resin producer and the plastic converter, and better value for the user of the plastic article.

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