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Polymer additives

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1 Introduction

1.1 Role of polymer additives

In the present era, every activity of our life revolves around polymers and plastic materials. However, pristine polymeric materials possess unsuitable properties for such a wide range of commodity and specialty applications. The properties of a macromolecule can be tailored by incorporation of additives in their formulation, to improve both their processability and end-use [1]. Natural rubber, extracted from a *hevea* tree, was already in use by the Mayans long before the discovery and colonization of the Americas to fabricate balls or to waterproof clothes and shoes. In 1755, the French engineer and botanist François Fresneau published what is acknowledged as the first paper about rubber (submitted to the *Académie Royale des Sciences*) [2], reporting that crude rubber possessed the valuable properties of elasticity, plasticity, strength, durability, electrical non-conductivity and water resistance; however it hardened in winter, softened and became sticky in summer, it was not resistant to solvents and smelled bad. Natural rubber, named *latex* for its milky appearances, did not find its application until Charles Goodyear discovered that the addition of sulphur dramatically improved its properties, in a process called plastic vulcanization [3]: this was the first example of how additives can dramatically improve polymer properties. Polymer research and development necessarily evolves in parallel with additives technologies, especially if we consider that plastics are progressively more involved in sophisticated applications. Polymer formulations have to be accurately designed to meet the critical requirements that engineers face every day in key sectors, such as Automotive, Aeronautics, Smart Devices, Healthcare and Energy Production and Storage. According to the definition given by the European Community, an additive is “a substance which is incorporated into plastics to achieve a technical effect in the finished product, and is intended to be an essential part of the finished article.” With this chapter, we want to provide an insight into key functional additives for the end-use application of plastics. This means leaving out both structural additives (such as fibres, fillers, etc.) and processing aids (such as slipping agents, lubricants, etc.). According to the *Allied Market Research* report, the global plastic additives were valued for $41.4 billion in 2013 and are expected to generate revenue of $57.8 billion by 2020. Also, in terms of volume, it was estimated at 12,619.8 KTons in 2013 and is expected to reach 17,071.7 KTons by 2020. The top six categories of additives with higher market demand were recognized to be plasticizers, flame retardants (FRs), impact modifiers, antioxidants, antimicrobials and UV stabilizers [4].

The European Union industrial policy is pushing industrial and academic world toward the development of sustainable alternatives to fossil-fuel based products declaring the bio-based products sector to be a priority area with high potential for future growth, reindustrialization, and addressing societal challenges [5]. In this frame, bio-based polymers have shown a steady growth over the past years, and obviously this trend has involved the search for additives “green” and not oil-based, to obtain all bio-based polymer formulations. For this reason, in this chapter, for each class of polymer additive, novel bio-based alternatives will be mentioned.

1.2 Additives incorporation in polymer formulation

The additives for polymer formulation are commonly found in several forms, either in solid (powders, flakes, beads, granulate, spheres, emulsions) or, more rarely, in liquid state. The final shape of the additive is influenced by the production method, namely extrusion, pelletizing, grinding, spraying or flaking.

A greater awareness of the drawbacks related to fine dust and particulate characterizes modern safety protocols; for this reason, the current trend involves modification of traditional manufacturing technologies, to

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provide more environmentally acceptable products endowed with greater safety, and easier to handle and mix [6]. Top challenges of polymer compounding are dust reduction, dispersion quality enhancement and dosing optimization. Ideally, additives should possess spherical form (with diameters ranging between 500 and 1,500 µm), they should ensure high homogeneity and dispersibility, suitable mechanical resistance and no segregation in the polymer matrix [7].

Over the last 15 years, additive masterbatches (i. e. concentrates containing a higher level of additives dispersed in the parent polymer) have become very popular alternatives to pure additives and have found a very wide range of applications, e. g. FRs, impact modifiers, antimicrobials, colour masterbatches, etc. The use of concentrated additive masterbatches has several advantages, if compared with pure additives, in terms of better dosability, ease of handling, homogeneous mixing, safety, additive protection and improvement of performance. Masterbatches overcome the problems of pure additives that usually require specific handling and weighted choice of processing conditions to optimize mixing/dispersing/dissolving processes.

As mentioned before, only a few additives (vitamin E is one of them) are introduced into the polymer in their liquid state, because liquids usually require different handling approach, often incompatible with high-temperature mixing technologies. A novel technique of incorporation of viscous liquids and low-melting additives in the polymer has recently been reported [8]. The technique involves the introduction of highly concentrated liquid or temperature-sensitive additives (e. g. antistatic agents, lubricants, antioxidants, UV stabilisers, pigments and fragrances) in high-porosity carriers, namely low density polyethylene (LDPE), which allows for a very good dispersion, thanks to its spherical shape.

The incorporation of additives in the polymer matrix can be carried out in different stages of the polymer processing: during polymer production inside the reactor, during the processing stage of the finished polymer pellets by mixing or blending. Additives can also be directly applied to the surface of the finished product. The handling of solid additives has largely been reviewed [9]. For example, stabilizing additives are typically introduced during the manufacturing stage of the raw material, while high-performance additives (e. g. FRs) are introduced during the compounding stage. For specialty applications, reactive compounding techniques are employed to chemically bind reactive additives to the polymeric backbone. Virtually, from very few basic plastic types, the range of recipes and formulations is virtually inexhaustible [7].

2 Plasticizers

Plasticizers have been used as polymer additives since the nineteenth century; however, the human kind has known the plasticizing effect of water for thousands of years. As a matter of fact, the first clay figure found in Europe dates back to 24,000 BC, making pottery most likely the first human activity involving plasticizers. The Council of the International Union of Pure and Applied Chemistry (IUPAC) defined a plasticizer as a substance or material incorporated in a material (usually a plastic or elastomer) to increase its flexibility, workability or distensibility. By this definition, a plasticizer may reduce the melt viscosity, lower the temperature of a second order transition or lower the elastic modulus of the product.

Poly(vinyl chloride) (PVC) is the third most widely produced synthetic plastic polymer, after polyethylene and polypropylene (PP). Unmodified PVC is mainly employed in the construction industry (e. g. pipes, door and window components, etc.) where its natural rigidity is needed. However, the addition of organic molecules, known as plasticizers, can provide increased flexibility, extensibility and processability [10].

In 2014, the global plastic market involved 8.4 MTons of plasticizers, of which 80–90 % was employed in the PVC industry. The physical action of plasticizers produces a reduction of Young’s modulus, density, melt viscosity and glass transition temperature of the polymer, while they enhance the final product flexibility, deformation at break and toughness [11, 12]. For this reason, flexible PVC can be used in many applications where it can replace rubber and polyolefins, such as electrical cable insulation, inflatable products, packaging, etc.

The mechanism of plasticization involves the formation of secondary bonds between plasticizer and polymer chains, where they act like “spacers,” increasing the distance of neighbour chains, hindering their interaction and increasing their mobility.

2.1 Mechanism of plasticisation

The concept of polymer plasticization has been adequately explained, starting from 1930s, with several theories. The classical theories are very elementary, as they were developed in the first part of twentieth century, when the knowledge on polymers was still limited.

- The LUBRICITY THEORY was developed by Kilpatrik [13] and Houwink [14] among others, in the 1940s. Plasticizers were defined as molecules with one segment strongly attracted by the polymer and another acting as lubricant. The plasticizer molecules hinder polymer–polymer interactions (van der Waals forces) between neighbour polymer chains causing a decrease in mechanical rigidity, and the plasticized formulation results in a more flexible and deformable material.
- The GEL THEORY was introduced by Aiken in parallel with the lubricity theory [15]. According to this theory, the plasticized polymer exists in an intermediate state between solid and liquid, so-called *gel state*, characterized by relatively weak secondary attractive forces. These bonding forces acting between plasticizer and polymer are easily overcome by applied external stresses, allowing the plasticized polymer to flex, elongate or compress.
- The FREE VOLUME THEORY was developed later on [16] to explain the decrease in glass transition temperature of plasticized polymers. Free volume is typically defined as the difference in specific volume between temperature T and reference temperature of absolute zero. Free volume is caused by motion of polymer end or side groups, or internal polymer motions. Unplasticized PVC at room temperature (below its glass transition temperature) shows limited motions of any kind and results in a very hard and rigid material. As plasticizers are added to the polymer, free volume is increased and various movements in the polymer chains are suddenly allowed, lowering the glass transition.
- MECHANICISTIC THEORY OF PLASTICIZATION considers the association between polymer and plasticizer as impermanent and variable. While the association can be formed and disrupted, the “strength” of each association depends on the type and quantity of plasticizer added to the formulation. The “antiplasticization” effect is therefore explained, considering that at high plasticizer loadings, plasticizer–plasticizer interactions are dominant over polymer–plasticizer interactions.

2.2 Classification of plasticizers

Gel theory allows plasticizers to be classified in *primary* and *secondary*, basing on the quality of the polymer–plasticizer interaction, which is strictly related to the leaching and/or migration of plasticizer molecules from polymer matrix. *Primary plasticizers* have solubility parameters close to those of polymer and are able to rapidly gel the polymer in the temperature range used during the processing step. In this case, they have a scarce tendency to “bleed” from the plasticized material. On the contrary, *secondary plasticizers* have lower gelation capacity and limited compatibility with the polymer. Therefore, after plasticization process, two separate phases can be distinctly identified: the partially plasticized polymer and the completely plasticized polymer. If a stress is applied to these materials, the resulting deformation will appear inhomogeneous, because the actual deformation occurs only in the plasticizer-rich phase. In addition to the loss of mechanical properties, another key issue of diffusion of the plasticizer is its intrinsic toxicity, which may represent a hazard for the outside environment [17]. Therefore, primary plasticizers can be used as the sole component of the plasticizer formulation, while secondary plasticizers are blended with primary ones to improve the final material properties, but are never employed alone.

The classification of plasticizers is most commonly based on their chemical composition in two classes: phthalates and non phthalates. It is now widely recognized that phthalate exposure may constitute a hazard for human health. As phthalate plasticizers are not chemically bound to PVC, they can leach, migrate or evaporate into indoor air and atmosphere, foodstuff, other materials, etc. Consumer products containing phthalates can result in human exposure through direct contact and use, indirectly through leaching into other products, or general environmental contamination [18, 19].

2.2.1 Phthalate plasticizers

Phthalate plasticizers are basically phthalate esters whose chemical structure is represented in Figure Figure 1. Phthalates are colourless liquids, their solubility in oil, hexane and most organic solvents makes them unfortunately/likely soluble in some body fluids such as saliva or blood plasma. Two of the most commonly used plasticizers for PVC are diethylhexyl phthalate (DEHP) and diisononyl phthalate (DINP). Considering their chemical structures, reported in Table Table 1, it can be easily understood why DEHP, which remains the most used plasticizer in medical applications, has been substituted by DINP in children healthcare products. DINP is formed by longer hydrocarbon chains, possesses higher molecular weight, and therefore presents lower solubility and slower migration rates.

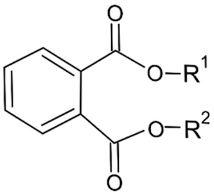
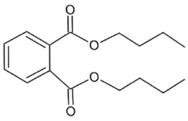
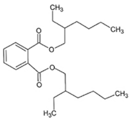
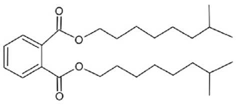
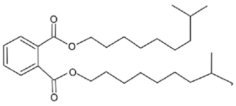
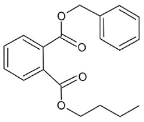


Figure 1: Chemical structure of a phthalic ester.

Table 1: Common phthalates with acronym, chemical structure and primary applications.

Phthalate name	Abbreviation	Substituting group	Applications
Di-*n*-butyl phthalate	DBP		PVC, PVA and rubber
Diethylhexyl phthalate	DEHP		PVC (dolls, shoes, raincoats, clothing, medical devices, plastic tubing and intravenous storage bags)
Diisononyl phthalate	DINP		PVC (Teethers, rattles, balls, spoons, toys, gloves, drinking straws)
Diisodecyl phthalate	DIDP		PVC (electrical cords, leather for car interiors and PVC flooring)
Benzyl butyl phthalate	BBP		PVC, polyurethane, polysulfide (vinyl flooring, sealants, adhesives, car care products, automotive trim, food conveyor belts, food wrapping material and artificial leather)

The health risks related with the use of DEHP in PVC medical devices were reviewed by Tickner et al. [20]; moreover, DEHP has been shown to affect the development of the male reproductive system of laboratory animals [21].

However, the plasticizing efficiency is inversely proportional to chain branching. In other words, the plasticizing effect is stronger for shorter chains since the branched structure accounts for an increase in viscosity. In Table Table 1, the most commonly used phthalate plasticizers are listed, together with the chemical structure and main application.

2.2.2 Non-phthalate plasticizers

Other chemical compounds, potentially employed as phthalate replacement, are generally classified as non-phthalate plasticizers. In this class are included phosphoric esters, citric esters, adipates or sebacates, trimellitic esters and benzoates. Some of the listed compounds (such as adipates) are already widely used in PVC artefacts, others are solely used in niche products because their high price would not allow their use in commodity applications. Most of these alternative plasticizers are not well studied with regard to their potential effects on human health and the environment. Although many of these alternatives show promising application potential, significant exposure may lead to adverse health effects [22].

2.3 Bio-based plasticizers

To date, several bio-based plasticizers were tested as PVC secondary plasticizers. For example, Lim et al. [23] reported the use of palm oil-based alkyd in PVC as a co-plasticizer to dioctyl phthalate (DOP) and DINP, resulting in an enhancement of mechanical and thermal properties of the formulation. Bouchareb and Benaniba [24] also reported good results in the use of epoxidized sunflower oil as secondary plasticizer for PVC in combination with DEHP. Some plasticizer formulations based on esters of di-fatty acids have been patented [25] and are commercially available (e. g. Syncroflex TM by Croda).

Leaving aside PVC applications, natural-based products have been widely reviewed as plasticizers for biopolymer films of different nature, such as polysaccharides (starch, cellulose, pectins, chitosan, etc.), microbial polyhydroxyalcanoates (PHAs) and polyhydroxybutyrates (PHBs) and polylactic acid (PLA). In addition to water, the most commonly used plasticizers are glycerol, polyols (such as sorbitol or xylitol) and vegetable oils [26].

3 Flame retardants

In the presence of heat and oxygen, all organic materials engage in a process called combustion, which constitutes the "living" force of nature on our planet. Not only combustion is at the basis of energy production of every living cell, in a controlled process known as cellular respiration, but also the ability to control fire was a dramatic change in the habits of early humans, the first of many ways by which mankind has exploited a combustion reaction in its favour. Combustion of fossil fuels is currently the chief source of energy for humanity; however, man has learned some harmful effect of fossil fuel combustion.

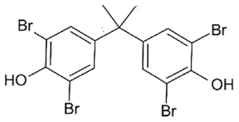
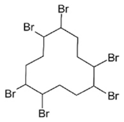
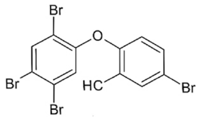
Like other organic substrates, polymers usually burn. Combustion of hydrocarbon macromolecules leads to the scission of polymeric chains in smaller units, which eventually are small enough to become volatile and be released in the atmosphere. These small units, formed by elements such as nitrogen, oxygen, sulphur, fluorine and chlorine, are potentially harmful [27]. For this reason, FRs are added to polymer formulations. Over 175 different FRs are on the market today and fall into three major chemical groups: halogenated, organophosphorous and inorganic [28].

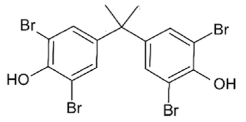
3.1 Halogenated FRs

Chlorine and bromine are the only halogens used as FRs in synthetic plastic formulations, since fluorine and iodine are unsuitable for this application. Brominated flame retardants (BFRs) are by far the most widely used FRs, because they are more effective, cost less and have wider application. From an environmental point of view, however, BFRs are highly resistant to chemical, biological and photolytic degradation and are capable of long-range migration and bioaccumulation in living tissues. As a matter of fact, contamination of terrestrial and marine environment with BFRs has been widely documented [29] and traced back even to deserted location such as the Arctic [30].

BFRs can vary widely in chemical structure, from aliphatic to aromatic carbon substrates that have been per-halogenated (all hydrogens replaced with bromine atoms). In Table Table 2, the five classes of BFRs most commonly found in polymer formulations are listed, together with their chemical structure.

Table 2: Common brominated flame retardants (BFRs) with acronym, chemical structure and primary applications.

Name	Abbreviation	Chemical structure
Tetrabromobisphenol-A	TBBP-A	
Hexabromocyclododecane	HBCD	
Poly-brominated diphenyl ethers (BDEs)	Penta-BDE	

	deca-BDE	

The mechanism of action of these FRs takes place in the gas state, induced by the high combustion temperatures. The molecules react with the radicals formed during the combustion process, according to the following reactions:

Step 1. High-energy OH and H radicals are formed by chain branching;
Step 2. The halogenated FR breaks down:
$RX \rightarrow R + X$ (where X is either chlorine or bromine)
Step 3. The halogen radical reacts with hydrogen from the polymer chain to form hydrogen

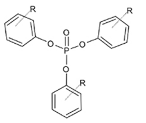
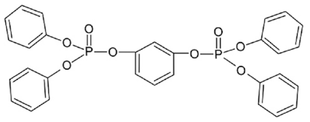
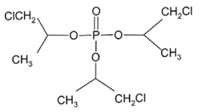
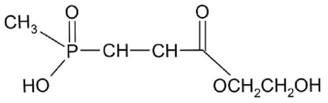
halide:
$X + RH \rightarrow R + HX$
Step 4. Hydrogen halide interferes with the chain mechanism, high-energy H and OH

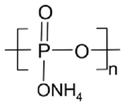
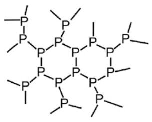
radicals are replaced with low-energy X radicals.
$HX + H \rightarrow H_2 + X$
$HX + OH \rightarrow H_2O + X$
Step 4. The hydrogen halide is regenerated by reaction with hydrocarbon:
$X + RH \rightarrow R + HX$

3.2 Phosphorus-based FRs

This class of FRs incorporates phosphorus into their structure (PFRs), which can vary according to phosphorus oxidation states (0, +3, +5) [31]. The mechanism of action of PFRs in gas phase is very similar to that of BFRs. Once again, hydrogen and hydroxyl radicals can be replaced by less energetic radicals or combined to form harmless gaseous products. However, differently from BFRs, PFRs are also able to act in condensed phase by enhancing char formation, yielding intumescence (foaming-up) or formation of inorganic glasses [32]. In fact, PFRs are most commonly known as *char formers*, because during the burning process they produce phosphoric acids, which, reacting with the substrate, produce a char that acts as a protection of the substrate itself. Most used PFRs are reported in Table Table 3, their main area of application is in polyamides, polyesters, polyolefins and polystyrene (PS) formulations, especially in electrical and electronic insulation components [33].

Table 3: Common phosphorous-based flame retardants (PFRs) with acronym, chemical structure and primary applications.

Name	**Acronym**	**Chemical structure**
Triaryl phosphates	–	
Resorcinol bis(diphenylphosphate)	RDP	
Tris(chloropropyl) phosphate	TCPP	
Phosphinic acid derivatives	–	

Ammonium polyphosphate	APP	
Red phosphorous	–	

3.3 Inorganic FRs

Inorganic flame retardants (IFRs) typically include aluminium and magnesium hydroxide ($Al(OH)_3$ and $Mg_2(OH)_4$). The mechanism of action of these compounds deeply differ from organic FRs. IFRs, in fact, cannot evaporate by effect of the combustion heat; however, they can decompose in non-flammable gases (mostly water [34]) by endothermic reactions [35]. Currently, aluminium hydroxide is the most commonly employed IFR, due to low cost and good compatibility with most plastic materials, especially PVC and PE. $Al(OH)_3$ decomposition occurs between 180 and 200 °C according to the endothermic reaction reported below:

$$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_2O$$

The endothermic decomposition of aluminium hydroxide primarily leads to the cooling of polymer and the formation of a protective layer of aluminium oxide. Moreover, the formation of water vapour decreases the oxygen concentration near the surface, hindering the combustion reaction.

Magnesium hydroxide ($Mg_2(OH)_4$) has the same flame retardancy effect of aluminium hydroxide, but a different range of decomposition temperature (300–330 °C); therefore, it can be employed in engineering polymers, such as PPs and polyamides (PA), which are usually processed at higher temperatures.

3.4 Bio-based FRs

Most of the commercially available FR formulations have adverse effect in the environment, because their chemical components are capable of leaching and bio-accumulation, contaminating water and fields and polluting the atmosphere.

In most cases, IFRs that contain minerals very common in nature, such as aluminium and magnesium hydroxide, are actually produced through synthetic procedures using bauxite as a rough material. It was estimated that the total volume of natural IFRs ranged around 37 TTon/year (2010), constituting only about 5 % of all mineral filler FRs [36].

It has been found that the addition of natural zeolites to thermoplastic polymers provides a synergistic effect on traditional FRs [37]. However, a more sustainable approach is pushing towards all bio-based formulations. Das and Karak [38] suggested that the incorporation of nanoclays in a vegetable oil-based epoxy resin would provide self-extinguishing properties. The most extensively studied nanoclays in use are based on montmorillonite, exfoliated and added to the polymer matrix in flaky shapes [39].

Another natural material involved in FR formulations is cellulose. Not only cellulose is the world’s most abundant, renewable, inexpensive and biodegradable polymer, it is also prone to chemical modification. Phosphorus can be covalently attached to the cellulose chain, forming phosphorylated cellulose derivatives whose flame retardancy action takes place during heating, dehydrating the polysaccharide molecules and promoting the consequent char formation [40].

4 Impact modifiers

Most plastic materials suffer from excessive brittleness; in other words they break without significant deformation when subjected to a stress. Unmodified PVC or PS are brittle at room temperature, polyamides and polyolefins instead are ductile at room temperatures and become brittle at low temperatures. An impact modifier is needed whenever the polymer does not meet impact requirements in the specific application.

Rubber toughening of PVC was introduced in the 1930s and 1940s and involved the addition of small amounts of acrylonitrile–butadiene copolymer elastomer (NBR) and other elastomeric materials [41]. The traditional purpose of impact modifiers is to absorb the impact energy by inducing plastic deformation before craze or crack propagation can occur.

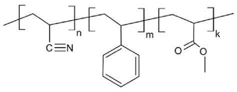
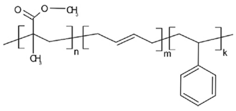
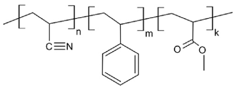
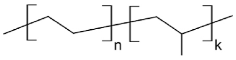
In general, impact modifiers are elastomeric or rubbery in nature, with a lower modulus compared to the polymer matrix and a low glass transition temperature (T_g). The rubbery phase should also show good compatibility to the host polymer and a fine particle size distribution.

Impact modifiers can be either incorporated in the polymerization reaction (e. g. acrylonitrile-butadiene-styrene (ABS) block copolymers [42]) or incorporated as solid particulate in the processing step as particles. In Table Table 4, the most common impact modifiers are listed with their relative contribution to the global market [43], while chemical composition of the most common classes of impact modifiers, with their chemical structure and commercial trade names are listed in **Table 5**.

Table 4: Global market contribution of the most common impact modifiers.

Impact modifier	Contribution to global market
ABS – acrylonitrile-butadiene-styrene terpolymers	45 %
MBS – methacrylate-butadiene-styrene terpolymers	
Acrylics	30 %
Elastomers	10 %
CPE – Chlorinated polyethylene	10 %
Others	5 %

Table 5: Chemical composition of the most common classes of impact modifiers, their chemical structure, commercial name and suppliers available in the market.

Class of impact modifiers	Chemical composition	Chemical structure	Trade name (Supplier)
Butadiene-based modifiers	Acrylonitrile-butadiene-styrene		Blendex® 333 (Galata Chemicals)
	Methacrylate-butadiene-styrene		Paraloid™ EXL-2678 (Dow Chemical)
Acrylic modifiers	Acrylonitrile-styrene-acrylate		Shinepoly™ LP2068 (Shine Polymer Technology)
Elastomers	Ethylene-propylene copolymer		Elvaloy® HP 4051 (Du Pont)

4.1 Butadiene based graft copolymers

Butadiene based graft copolymers constitute alone 45 % of the global impact modifiers market. Their success in mainly due to their very low T_g (−80 °C). On the other side, one of the main drawbacks is their sensitivity to thermal and oxidative degradation, due to the presence of double bonds in diene polymers. During processing step and final application, the polymer undergoes severe temperature stress and UV and oxygen exposure; therefore, the formulations should include also suitable antioxidants (see Section 5) [44].

4.1.1 ABS modifiers

By far the most used graft terpolymer, ABS earns its unique properties by the combinations of the three components: soft rubbery effect is provided by butadiene while acrylonitrile and styrene give the terpolymer the polarity needed for compatibilization to the polymer matrix. As mentioned before, the butadiene chain is susceptible to UV degradation and requires protection while the acrylonitrile brings rigidity and chemical resistance. ABS is very reliable in a wide range of temperatures (between −20 and 80 °C), it is very light and prone to be injection moulded and extruded, as well as 3D printed. For these reasons, ABS has found a wide range of applications in engineering polymers in buildings and constructions, automotive, electronics and many others. A drawback of ABS impact modifiers stands in the development of carcinogenic chemicals and ultrafine particles during the process and final disposal [45, 46].

4.1.2 MBS modifiers

Similar to ABS, MBS (methacrylate-butadiene-styrene) impact modifiers are produced according to two different procedures: copolymerization of styrene and methyl methacrylate in the presence of polybutadiene or polymerization of methyl methacrylate in the presence of a styrene butadiene rubber. Once again, butadiene makes these materials susceptible to UV degradation and limits their use to indoor applications. The presence of methacrylate instead of acrylonitrile provides a unique transparency to the polymer but at the same time reduces its chemical resistance. MBS modifiers are mainly applied in PVC in transparent and opaque packaging applications such as impact resistant bottles, packaging films and electrical covers [47]. MBS impact modifiers demonstrated a significant impact-modifying effect at low temperatures. However, in many cases, the addition of a large amount of the MBS impact modifiers is required to enhance impact strength [48].

4.2 Acrylic modifiers

PVC formulations directed to outdoor applications require special attention in order to achieve long-time structural and aesthetical properties. In this frame, acrylic modifiers are probably the most widely used impact modifiers as they overcome the problems associated with the limited resistance to weathering phenomena, typical of ABS and MBS. The typical chemical structure of this class of modifiers is that of a graft terpolymer of methyl methacrylate-butyl acrylate-styrene or acrylonitrile-styrene-acrylate. Other advantages of such formulations are the high impact strength, good heat resistance and good thermal stability [49].

4.3 Elastomers

The impact strength of polyolefins can be optimized by introducing in the homopolymer formulations a wide variety of elastomers such as ethylene-propylene copolymer (EPM) or ethylene-propylene diene terpolymer (EPDM). The investigation on macroscopic and morphological properties of PP/impact modifiers blends dates back to the 1970s [50].

5 Antioxidants and UV stabilizers

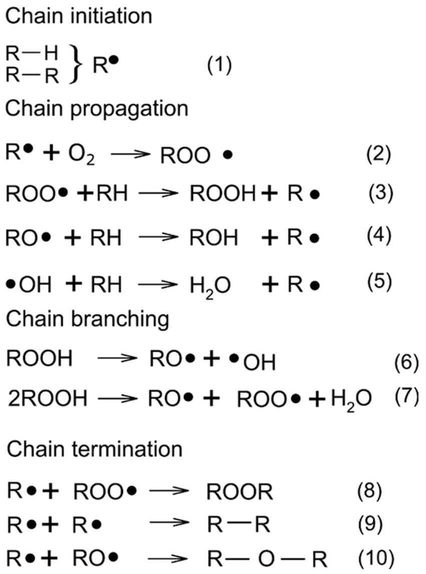
5.1 Antioxidants

The resistance of polymeric materials to weathering is a key issue if we take into account the wide range of applications in which plastic products are exposed to outdoor environment. Weathering does not simply result in aesthetic decay, such as discoloration, but also changes in mechanical properties. Weathering phenomena includes mainly thermal- or UV light-induced oxidative phenomena, as well as day/night or seasonal temperature variation, humidity and atmospheric contamination with highly corrosive elements [51].

Starting from the 1940s, the phenomenon of polymer degradation *via* oxidation has been the centre of scientific research in parallel with the spread of polymeric materials in many specialty and commodity applications. The degradation process involves the oxygen-induced formation of reactive oxygen species (ROS), also known as free radicals, which eventually leads to the modification of the macromolecular structure by chain scission or crosslinking. This process is frequently called autoxidation because it proceeds by an autoaccelerated radical chain mechanism.

In the initiation step, a hydrogen atom is extracted by an excited oxygen or a free radical from the hydrocarbon chain, forming an organic radical. Further reaction of organic radicals with oxygen leads to the formation of polymer hydroperoxides (ROOH). Consequently, hydroperoxides and their decomposition products are responsible for the changes in molecular structure and molar mass of the polymer, which are manifested in practice by the loss of mechanical properties (e. g. impact, flexure, tensile, elongation) and by the variation in the physical properties of polymer surface (e. g. loss of gloss, reduced transparency, cracking, yellowing, etc.).

During autoxidation, the radical reaction cyclically goes through four steps: initiation, propagation, branching and termination, as described in Figure Figure 2. During the initiation step (Figure Figure 2-1), the primary alkyl radical is formed from polymer interaction with molecular oxygen [9]. The formed polymeric radical P• further reacts with molecular oxygen forming the peroxy intermediate radical POO• (Figure Figure 2-2**)**. The rate-determining step in autoxidation can be identified in the abstraction of a hydrogen, corresponding to the disruption of a C-H bond, which stabilizes the formed peroxy radical POO•(Figure Figure 2-3). Chain termination is promoted, in oxygen deficiency conditions, by combination of the various radical species shown in Figure Figure 2 – 8, 9 and 10.


Chain initiation

$\left.\begin{array}{l}R-H\\R-R\end{array}\right\} R^\bullet \quad (1)$

Chain propagation

$R^\bullet + O_2 \longrightarrow ROO^\bullet \quad (2)$

$ROO^\bullet + RH \longrightarrow ROOH + R^\bullet \quad (3)$

$RO^\bullet + RH \longrightarrow ROH + R^\bullet \quad (4)$

$^\bullet OH + RH \longrightarrow H_2O + R^\bullet \quad (5)$

Chain branching

$ROOH \longrightarrow RO^\bullet + {}^\bullet OH \quad (6)$

$2ROOH \longrightarrow RO^\bullet + ROO^\bullet + H_2O \quad (7)$

Chain termination

$R^\bullet + ROO^\bullet \longrightarrow ROOR \quad (8)$

$R^\bullet + R^\bullet \longrightarrow R-R \quad (9)$

$R^\bullet + RO^\bullet \longrightarrow R-O-R \quad (10)$

Figure 2: General diagram of autoxidation (Polymer additives handbook, Zweifel).

Oxidative degradation in polymers can be inhibited by addition in the polymer formulation of proper stabilizing additives, called antioxidants (AOs). In Figure Figure 3, the cyclical degradation mechanism is schematized, highlighting the reactive species (polymer and peroxy radicals, and hydroperoxides) susceptible of the intervention of such additives in different steps of the reaction .

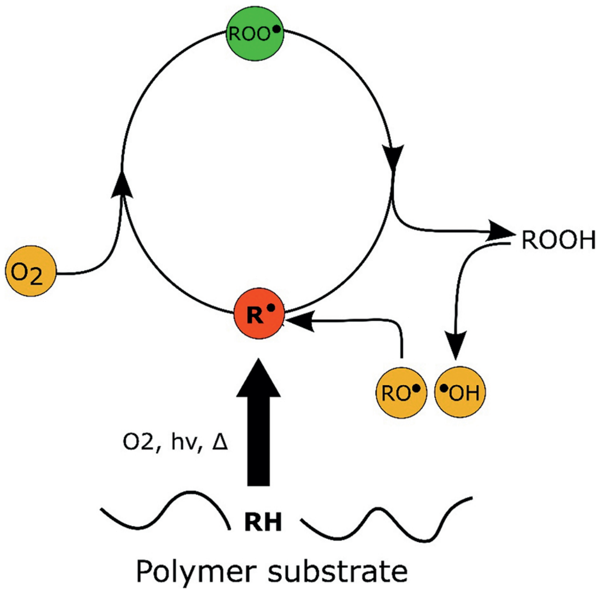


Figure 3: Autoxidation mechanism as represented in Zweifel, 1988.

AOs are generally classified into two groups, according to their protection mechanism [52]:

- Primary antioxidants also known as chain-breaking antioxidants. These AOs are able to scavenge free radicals via a process called chain-breaking electron donor mechanism. Two classes of primary AO can generally be identified: radical scavengers (chain-breaking acceptors) and H-donors (chain-branching donors).
- Secondary antioxidants are able to decompose hydroperoxides (POOH) forming inert secondary products and therefore are also known as hydroperoxide decomposers.

5.1.1 Radical Scavengers

The reaction of radical scavenging induces the immediate disruption of the autoxidation mechanism. It is extremely difficult to scavenge alkoxy (RO•) or hydroxyl (•OH) radicals because they are extremely reactive [53]; therefore, the mechanism of action of radical scavengers is focused on the stabilization of carbon centred alkyl radicals (R•). Lactones and acrylated bis-phenols are the most effective classes of scavengers.

Lactones are a class of cyclic esters suitable as alkyl radical scavengers, in particular benzofuranone derivatives are very effective even in low concentrations [54]. Their mechanism of actions is described in Figure Figure 4.

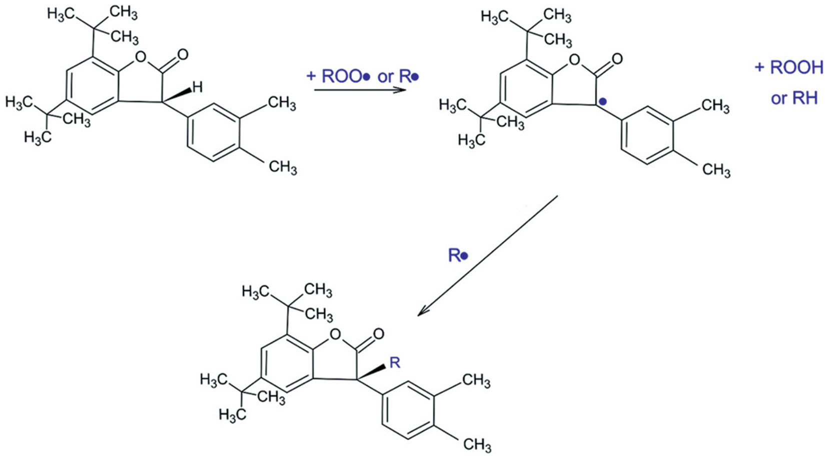


Figure 4: Radical scavenging activity of benzofuranone derivatives.

Other very effective radical scavengers are the acrylated bis-phenols; this class of stabilizers are widely used in styrene copolymers (such as SBS), preventing the degradation or crosslinking that often occurs during the processing steps. Their mechanism of action is similar to the one studied in hindered phenols, and is schematized in Figure Figure 5.

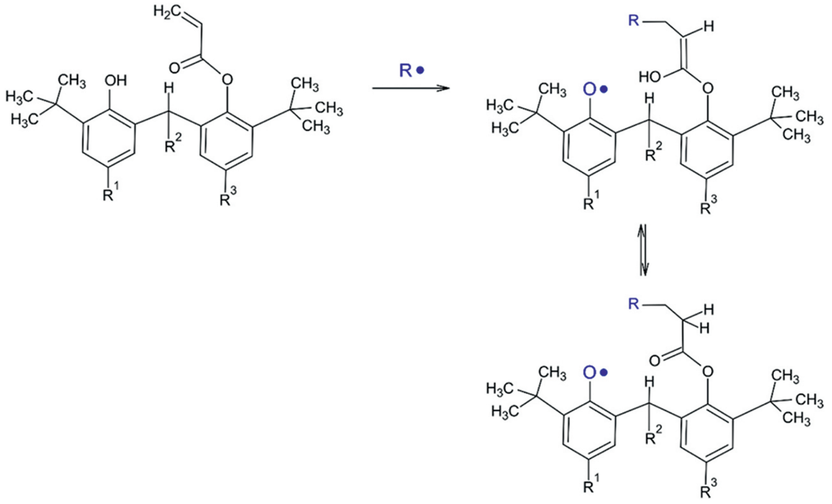


Figure 5: Radical scavenging activity of acrylated bis-phenols.

5.1.2 H-donors

Usually containing aromatic or phenolic rings, these antioxidants donate a hydrogen atom (H) to the free radicals formed during oxidation. H-donor therefore becomes a radical itself but is able to reach stabilization via resonance delocalization of the electron within the aromatic ring [55]. In case further abstraction of a hydrogen from polymeric backbone results hindered, the H-donor is considered suitable as polymer additive [56]. Two of the most effective H-donor compounds are aromatic amines and hindered phenols. Aromatic amines, in particular secondary aromatic amines and diamines, are the most efficient hydrogen donors; however, their application in plastics is limited for their carcinogenic effect known since the 1970s [57]. The reaction of deactivation of peroxy radicals by secondary aromatic amines is reported in Figure Figure 6.

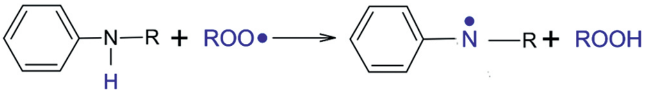


Figure 6: Deactivation of ROO* radicals by means of secondary aromatic amines.

The safety issues related to the aromatic amines make hindered phenols the most widely used stabilizers for polymers. The antioxidant effect of natural phenols, such as α-tocopherol (vitamin E), is widely reported in literature [58].

Often used in combination with secondary antioxidants, phenolic stabilizers are offered in an extensive range of molecular weights, product forms and functionalities. They are effective during both processing and long-term aging, and many have the Food and Drug Administration (FDA) approvals. The reaction of radical deactivation involving hindered phenols is represented in Figure Figure 7 [59].

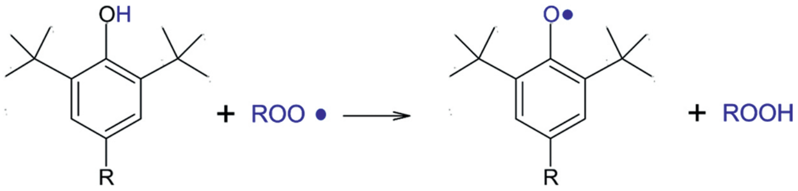


Figure 7: Deactivation of ROO* radicals by hindered phenols.

The phenoxy radicals generated are very stable due to their ability to build numerous mesomeric forms.

5.1.3 Hydroperoxide decomposers

Hydroperoxide decomposers belong to the class of secondary antioxidants; these compounds are able to convert the hydroperoxide radicals into non-radical stable products. Their use in combination with primary antioxidants often yields synergistic stabilization effects. According to their general mechanism, the hydroperoxide group (ROOH) is reduced to an alcohol group (ROH) while the decomposer is oxidized. The most widely used classes of hydroperoxide decomposers are organic compounds containing phosphorous and sulphur, respectively, called organophosphorous and thiosynergists.

Organophosphorus compounds are extremely effective stabilizers during polymer melt processing and are commonly used in formulations containing a primary antioxidant, especially hindered phenols. The reaction of organophosphorous antioxidants is reported in Figure Figure 8. Accordingly, phosphites or phosphonites are oxidized to phosphates, while hydroperoxides are reduced [60].

Figure 8: Decomposition of hydroperoxides by means of organophosphorus compounds.

One of the main drawbacks of these compounds is their easy hydrolysis in contact with water that eventually leads to the formation of acidic species. The application of these additives is therefore limited to applications that do not involve metal parts. To overcome this issue, acid scavengers are usually added to the formulation or the organophosphorous compound is replaced with another hydrolysis-resistant additive.

Thiosynergists are sulphur-based organic molecules, typically thio-esters. According to their mechanism of action, reported in Figure Figure 9, the thiosynergist molecule is transformed into a variety of oxidized sulphur products (e. g. sulfenic and sulfonic acid), while hydroperoxides are reduced to alcohols in an overstoichiometric reaction [61].

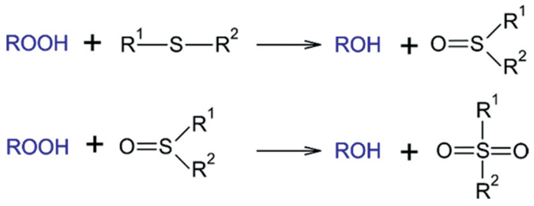


Figure 9: Decomposition of hydroperoxides by means of thiosynergists.

Thiosynergists, different from the organophosphorous compounds, are very efficient for long-term thermal aging applications.

5.2 UV stabilizers

For polymers employed in outdoor applications, the absorption of photons from sunlight radiation (e. g. wavelengths ranging from 100 nm to about 1 mm including ultraviolet, visible and infrared radiation) is inevitable and eventually leads to the oxidative degradation of photosensitive molecules [62]. The mechanism, called photooxidation, is triggered by light and proceeds similarly to what reported in Section 5 for oxidation of polymers.

The stabilization of polymers against the adverse effect of sunlight involves the inhibition or retardation of photochemical processes in polymers and plastics. This retardation can be achieved by reducing the rate of photoinitiation or the kinetic chain length of the propagation stage of the photooxidation mechanism. Visible and infrared light are rather unharmful; therefore photostabilization of polymer items involves the protection against destructive reactions mainly caused by high-energy UV radiation [63]. UV stabilizers can be classified into three main classes:

5.2.1 UV absorbers

UV absorbers interact with the first step of the photooxidation process by absorbing the harmful UV radiation (300–400 nm) before it reaches the photosensitive moieties in the polymer. In other words, these compounds are able to provide energy dissipation before photosensitization can occur. UV absorbers are characterized by excellent light stability; therefore, they are modified but not destroyed in the stabilization process [64]. Energy dissipation mechanism reckon on the conversion of harmful UV radiation into harmless infrared radiation or heat that is dissipated through the polymer matrix. Carbon black is one of the most effective and commonly used light absorbers, as well as rutile titanium oxide which is ineffective for radiation below 315 nm, the so-called UV-B radiation.

Compounds with good filtrating action, such as hydroxyaromatic UV stabilizers (such as hydroxybenzophenone and hydroxyphenylbenzotriazole), are successfully used and their absorption characteristics are widely reported in the literature [65, 66]. Other UV absorbers include oxanilides for polyamides, benzophenones for PVC and benzotriazoles and hydroxyphenyltriazines for polycarbonate [67].

Schematization of the energy dissipation mechanism of the β-diketone avobenzone UV absorber is reported in Figure Figure 10. The reaction involves the reversible formation of a six-membered hydrogen bonded ring and the equilibrium between the two tautomeric forms provides a facile pathway for deactivation of the excited state induced by the absorption of light.

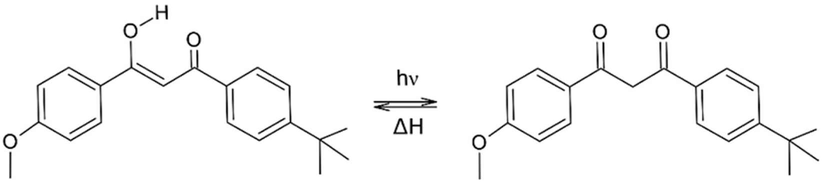


Figure 10: Energy dissipation mechanism occurring in avobenzones UV absorbers.

5.2.2 Quenchers

This class of UV absorbers provides deactivation of photosensitive groups in their excited state (singlet and or triplet) before the disruption of molecular bonds can occur [62]. Quenching is a diffusion-controlled process and is effective in polymer protection only if the photosensitive moiety in its triplet state has a long half-life and if the quencher is freely diffusible [68]. The quenching reaction is represented in Figure Figure 11, where an excited chromophoric group in a polymer (donor, D*), responsible for the initiation step in the photodegradation of the polymer, is deactivated by an acceptor molecule (quencher, A) [69]:

$$D^* + A \longrightarrow D + A^*$$

$$A^* \longrightarrow A + \textit{Energy} \quad \textit{(heat or light emission)}$$

Figure 11: Schematization of the quenching reaction.

Metal complexes, particularly those based on nickel, are very effective quenchers for their relatively low extinction coefficient in the near UV region. Nickel chelates, for example, are able to quench the triplet state of carbonyl groups in polyolefins. These chelates have been tested for photostabilization of polyisobutylene, polybutadiene [70] as well as PS [71].

5.2.3 Hindered Amine Light Stabilizers

Hindered amine light stabilizers (HALS) mechanism of action involves trapping of free radicals formed during the photooxidation of a polymeric material, hindering the propagation of the photodegradation process [72]. The ability of HALS to scavenge radicals created by UV absorption is explained by the formation of nitroxyl radicals through a process known as the Denisov cycle, reported in Figure Figure 12 [73]. During UV irradiation, when oxygen (from air) and radicals ($R^\bullet$) are made available, hindered piperidine, the model compound for HALS, is able to produce hindered piperidinoxy radicals, which are able to further trap other radicals in a cyclic reaction.

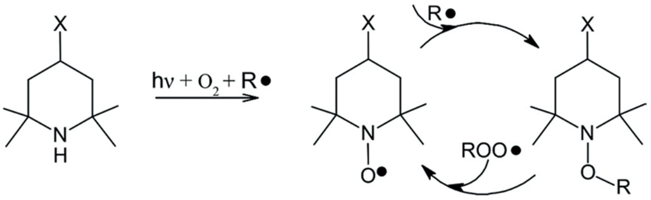


Figure 12: Schematization of mechanism of radical scavenging of hindered piperidine.

Currently, a wide range of HALS products are commercially available; however, they all share the 2,2,6,6-tetramethylpiperidine ring structure [74]. HALS are some of the most effective UV stabilizers for commodity and specialty plastics.

5.3 Natural antioxidants

It is widely recognized that synthetic antioxidants are very effective and highly stable. However, one of the main drawbacks is their derivation from oil-based products, together with their potentially harmful interaction with the human metabolism, especially in food contact applications. Bio-based materials are able to provide a valid alternative source for antioxidants. The search for safe and effective naturally occurring antioxidants has been mainly focused on tocopherols, vitamin C, carotenoids and phenolic compounds [75].

These products have shown very different mechanism of oxidative inhibition; however, they all react stabilizing ROS species, secondary products of plant photosynthesis, making them unharmful.

Tocopherols, for example, are Vitamin E constituents exclusively synthesized by plants, present in seed oil, leaves and other green parts [58].

Tocopherols can act both by a chain-breaking donor and acceptor mechanism, as well as singlet oxygen ($^1O_2$) quenchers. The two mechanisms mentioned above have not been completely elucidated; however involvement of quinone structures has been proposed by Cuppett et al. [76], while Clough et al. [77] claimed about formation of tocopherol hydroperoxide derivative as an intermediate product. These two reaction schemes are reported in Figure Figure 13 and Figure Figure 14, respectively.

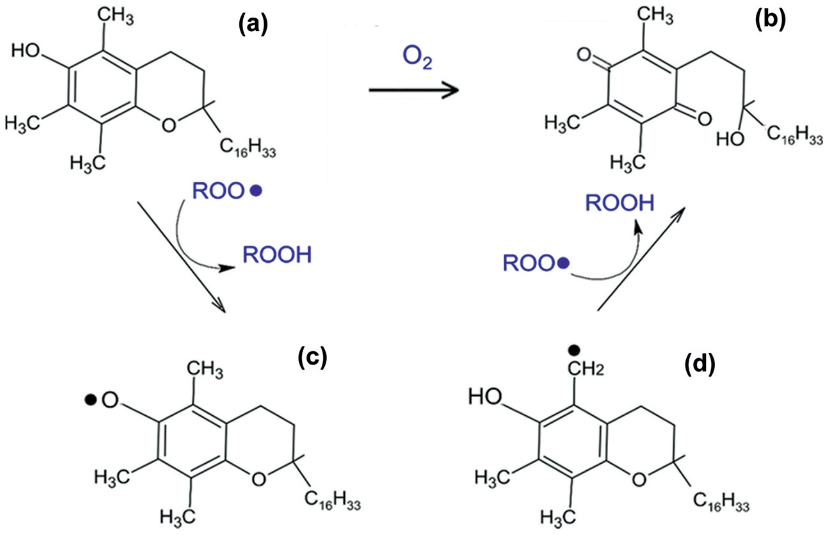


Figure 13: (a) α-tocopherol oxidation to (b) α-tocopheryl quinone through semi-quinone intermediates (c,d).

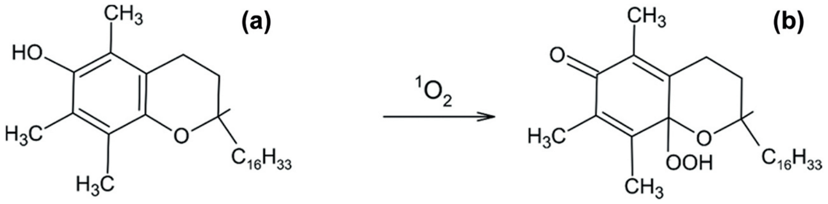


Figure 14: Singlet oxidation of (a) a-tocopherol to (b) hydroperoxydienone [76].

Up to this date, the antioxidant activity of several natural products has been reported in both commercial polymers, such as PE [78] and PP [79] as well as bio-based polymers, such as PHB [80], MaterBi [81] or PLA [82, 83]. Successful attempts prove that the substitution of oil-based products with their natural and renewable counterparts will indeed be possible in the future and has the potential to reach industrial scale.

6 Antimicrobials

Under favourable conditions, plastic materials support the growth of microorganisms such as viruses, bacteria and fungi (yeasts and moulds) [84]. Even those plastics that would not normally promote microbial growth can be used in environments that sustain microorganism life or proliferation, for example water or fertile soil [85].

In the modern era, where plastic recycling or disposal is a serious issue, biodegradation can represent a desirable feature. However, bio-stability and prevention of health hazards during both shelf life and final use of plastic artefacts are key factors to take into account in engineering polymer formulations. To overcome these problems, antimicrobial additives are added to the polymer formulation. It is necessary to underline that not all the antimicrobial additives are biocides, i. e. have the ability to kill bacteria or fungi, but many of them are simply biostatic agents, able to hinder the reproduction of the microorganisms.

Antimicrobial additives are mostly used in medical fields and food packaging applications. Therefore, the main requirement of antimicrobial (AM) additives is low toxicity to human and environment in both processing and end-use stages. Moreover, ideal AM additives have to be compatible with processing aids and other additives involved in plastic formulation and should not affect the properties or aesthetic appearances of the final artefact.

There are several ways to classify AM additives; however, they can generally fit in two general classes based on their chemical composition and mechanism of action: organic and inorganic AM agents [86].

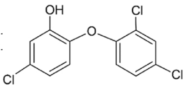
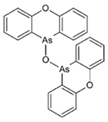
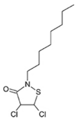
6.1 Organic antimicrobial agents

Organic antimicrobial agents are typically small molecules able to migrate over time from the bulk to the polymer surface to introduce an antimicrobial effect at the polymer surface. The variable interaction between the organic AM molecules and the polymer matrix represents the pushing force for migration.

One of the advantages of polymer-based antimicrobial systems is that the migration of the AM molecule on the surface can be controlled, so that microbial growth kinetics and antimicrobial activity at the product's surface can be properly modeled. However, the migration of the AM additives eventually leads to their leaching out of the polymer. For this reason, organic AM agents fit application in disposable items rather than durable goods with longer lifespans. Another drawback of these compounds is the limited food contact approval for organic based systems. Once again, the primary concern is their mobility and solubility in food simulants; therefore inorganic based technologies are generally considered more suitable for direct food contact. Organic AM systems are also thermally unstable; many compounds decompose in the typical processing temperature range and in other cases a temperature increase may cause excessive mobilization and consequently high loss rates of AM agents from the plastic.

The most common organic AM agents are organometallic compounds, in particular arsenic-based materials, such as oxybisphenoxarsine (OBPA), are acknowledged as very efficient and cost-effective. As a matter of fact, the use of arsenic-based compounds dates back to the 1930s in the United States. where the *Bordeaux mixture* was first employed in bio-stabilization of plastic materials. On the other hand, arsenic is universally perceived as hazardous material; for this reason the spread of arsenic-based compounds will always receive poor trust from the market. The demand for alternative formulations, such as the isothiazoline family or triclosan (chlorinated diphenyl ether), is growing rapidly [86]. Successful application of organic AM systems is soft PVC. Pristine PVC owns an intrinsic resistance to microbial attacks; however, plasticizers, fillers, pigments and other carbon-based additives used in PVC formulations become nutrients for microorganisms, especially when the final product is employed in wet environments such as shower curtains, paddling pools, etc. For this reason, AM organic agents are commercially available in formulation dissolved in other additives, such as plasticizers. Table Table 6 shows examples of organic antimicrobial products, together with their chemical structure and composition, supplier and typical applications.

Table 6: Organic antimicrobial agents listed with their chemical composition and structure, suppliers and applications.

Trade name	Chemical composition	Chemical structure	Supplier	Applications
Triclosan	5-chloro-2-(2,4-dichlorophenoxy)pheno		Spec-Chem Industry	Chopping boards, kitchen utensils, sponges, gloves, medical devices, toys, food containers.
Intercide® ABF-2 BBP	Solution of OBPA in DIDP plasticizer carrier		Akcros Chemicals	Flooring, roofing, coated fabrics, wall covering and leather cloth, PVC flexible films, foils and sheets.
Vinyzene™ IT-4000 DIDP	4,5-dichloro-2-n-octyl-isothiazolinone in DIDP plasticizer carrier		Dow Chemical	PVC Decking, Fencing, Fabrics (Fibres/Textiles/Carpets), Refrigerators inserts, films and sheets

6.2 Inorganic antimicrobial agents

Inorganic antimicrobial agents exploit metal ions for their intrinsic biocidal activity. The main difference between organic and inorganic AM agent is that the latter do not have the possibility to migrate but they are immobilized in the polymer matrix. The antimicrobial effect of silver ions has long been recognized, dating back to the Ancient Rome. Not only inorganic AM agents are capable of inhibiting microbial growth, but they are also very effective biocides.

Their mechanism of action involves the binding of the metal ion to the cell membrane of the microorganism, causing an unbalance in the diffusion in and out of the cell. Once inside the cell, the ions start a process of enzymatic denaturation, targeting thiol groups on the proteins, which rapidly leads to the loss of cell functional ability and eventually to cell death [87]. In order to be incorporated in the polymer matrix, the highly mobile metal ions are bonded to a delivery system, which allows minute quantities of ions to be released through a process of ion exchange at the plastic’s surface, as depicted in Figure Figure 15 for the case of zeolites loaded with silver ions.

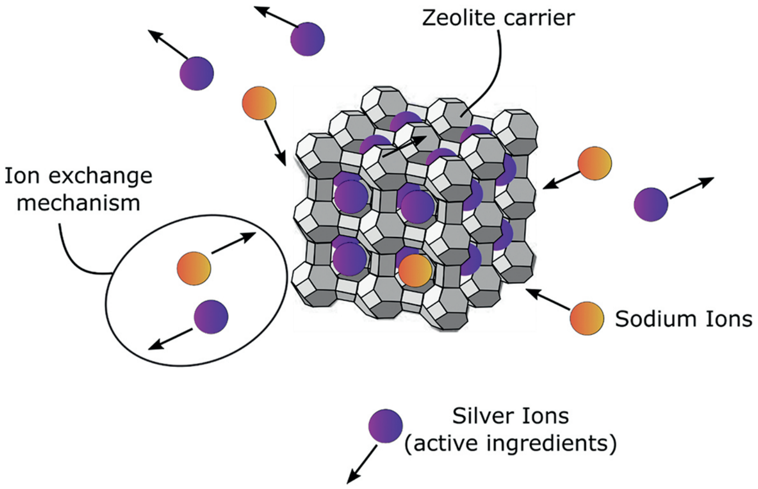


Figure 15: Ion exchange mechanism in antimicrobial zeolites loaded with silver ions.

The main advantage of such a mechanism is that the ions are continuously made available over the lifetime of the plastic artefact. Moreover, inorganic systems are characterized by a very good thermal stability that makes them suitable in a wide range of application in different polymer formulations.

The inorganic AM market currently includes releasing systems based on ceramic glasses, doped titanium dioxides or zeolites as carriers. One current trend in inorganic AM polymer additives is the used of nano-sized particles as carriers and delivery systems. Their high aspect ratio (lamellae, flakes, spheres) could offer a higher ion release rate but brings on adverse issues such as possible toxicity, excessive discoloration resulting from rapid oxidization and the increased complexities of producing nano-scale active grades. Currently, nano-silver is not recognized by the US Environmental Protection Agency and its application is therefore forbidden [88].

6.3 Natural antimicrobial additives for polymers

The concerns related to the use of arsenic-based products and nanotechnologies as antimicrobial additives for plastics, especially in food-packaging applications, have pushed academic and industrial world towards the development and rediscovery of plant extract as antimicrobial agents. Since prehistoric times, man has learned to exploit different spices and herbs, not only for food flavouring but also for their antiseptic and medicinal properties. Among others, basil is a popular culinary herb used extensively for many years in food flavouring. Its essential oil is known to have very powerful antimicrobial activity [89], and possible applications in food packaging have been forecasted [90]. Naturally derived antimicrobial agents are becoming increasingly more important in antimicrobial packaging as they present a perceived lower risk to the consumers. Other than plant extracts, bacteriocins and enzymes are also used in antimicrobial packaging. Natural antimicrobials belonging to the above-mentioned classes are listed in Table Table 7, together with examples of targeted microorganism [91].

Table 7: Classification of natural antimicrobial agents.

Class	Composition	Targeted microorganism	Reference
Bacteriocins (especially Nisin)	Peptidic antimicrobial compounds synthesized by different bacteria	*Listeria innocua* *Listeria monocytogenes* *Salmonella* spp.	Hoang et al. (2010) [92] Jin (2010) [93] Santiago-Silva et al. (2009) [94].
Enzymes (lysozyme)	Naturally occurring enzyme produced by humans and many animals, it has activity against bacterial cellular structures	*Alicyclobacillus acidoterrestris*	Buonocore et al. (2005) [95]
		Micrococcus lysodeikticus	Appendini and Hotchkiss (1997) [96]
Phytochemicals (essential oils and plant extracts)	Oregano or Citrus essential oils	*E. coli*, *Salmonella enterica* and *L. monocytogenes*	Muriel-Galet et al. 2013 [97]
	Basil essential oil	*E. coli*	Suppakul et al. (2003b) [90]
	Grapefruit seed extract	*E. coli* and *L. monocytogenes*	Luther et al. (2007) [98]

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