

Additives in Action – What Makes Polymers Better?

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Abstract

A general overview on several aspects of modern polymer chemistry and the driving force of its development is created. The ‘evolution’ of polymers is strongly attached to additives which are special chemicals and applied to improve the properties of the final polymeric products. Additives with the highest demand (plasticizers, flame-retardants, biocides/antimicrobial agents, antistatic agents, antioxidants, UV stabilizers, and colorants) and their most important properties along with examples are discussed. It is neither a systematic nor a comprehensive review, but an effort to help others to understand of this highly important research area which affect our daily life.

Keywords: plasticizers; antioxidants; flame retardants; colorants; biocides; antistatic agents; UV stabilizers; review.

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1. Introduction

The 'evolution' of polymers

Polymeric materials are older than human civilizations. The first polymers used were natural products, early biopolymers, especially cotton, starch, proteins, and wool (Burford, 2019; Feldman, 2008). Modern polymer science was born in the need to create new materials to cover the increasing demand of civil and military purposes (Feldman, 2008). It tends to be more interdisciplinary than most sciences, combining chemistry, chemical engineering, physics, biology, and other fields as well (Furukawa, 2007). Beginning early in the twentieth century, the first fully synthetic polymers (plastics) were made (Billmeyer, 1984; Feldman, 2008). These gained countless applications and expedited the development, and thus, the 'evolution' of synthetic polymer chemistry has begun. Nowadays, synthetic polymers are essential to the life of modern man, as they are used in industrial and agricultural fields (Binder, 2019; Milani et al., 2017), air and water supply (Pendergast and Hoek, 2011; Ulbricht, 2006), medical devices, and implants which enhance the quality of life (Agarwal et al., 2008; Bose et al., 2020; Ratner et al., 2004). Energy generation and storage (Vilela et al., 2012), communications and electronic devices (Tomlinson et al., 2014), and other applications of synthetic polymers are also important (Abdessalam et al., 2017; Terlikowski et al., 2019). Despite their many advantages, most of the synthetic polymers are not compatible with the environment, because they cannot be included into the natural recycling system (Campanale et al., 2020; Scott, 1999). Recent developments focus on to make the production and also the plastic products 'greener' by improving recyclability, biodegradability, using renewable resources in the synthesis, adding biomolecules to the formulations, and replacing partly or fully the synthetic polymers with bio-based alternatives (Iwata, 2015; Mülhaupt, 2013; Scott, 2000; Sheldon and Norton, 2020; Yin and Yang, 2020). However, environmental issues have not been considered at the early days of polymer science as the most important aspect was to replace various materials (metal, ceramic, *etc.*) with cheaper and more easily accessible ones which have similar or better properties (*e.g.* mechanical strength). To achieve this, a number of factors that affect the properties of polymers had to be addressed. The resistance of the polymeric materials to the external factors such as, exposure to sunlight, UV light, temperature, humidity, and air pollution, microorganisms, is a fundamental issue which have to be taken into consideration during preparation and applications (Ambrogi et al., 2017). These factors

do not only cause esthetic degradation in the product like discoloration, but also leads to potential deterioration of mechanical or other properties (Kockott, 1989; Pickett, 2020; Simon et al., 2021). To overcome many of the problems pure polymeric materials are facing, including stability and durability, and to achieve the desired properties, additives are widely used in polymer production (Marturano et al., 2017). These molecules can be incorporated into the formulation of the base polymers, and thus, improve processability, prolong the lifespan, and enhance physical and chemical behavior of the final product (Harper, 2006; Vanyorek et al., 2020). An excellent example of the use of additives is rubber, which is in its natural state, despite of many good properties such as flexibility, strength, durability, lack of electrical conductivity, and good resistance to water, also possess many undesirable qualities, including hardening in winter and increased adhesion in summer as well as its bad smell (Posadas et al., 2016). The first well known example of successful additive application was Charles Goodyear's discovery, by which he was able to drastically improve the properties of natural rubber by vulcanization (adding sulphur to the material) and thus, rubber became the versatile material it is known for today (Calzonetti and Laursen, 2010; Goodyear, 1844). This moment has been an important milestone not only for the rubber industry but for polymer science as well. From this point, the development and research of polymers cannot be separated from additive technologies (Allen and Edge, 2021). This flourishing cooperation is also shown by recent estimates, which states that the market value (~60 billion) and the production volume (~17MTons) of additives are both reached remarkable levels (Marturano et al., 2017). Under the European Union law additives are considered as “substances which are incorporated into plastics to achieve a technical effect in the finished product” and these “are intended to be present in the finished articles” (“EUR-Lex - 32002L0072 - EN - EUR-Lex,” n.d.). The accurate design of polymer formulations, which includes additives as well, is inevitable to achieve the necessary properties of the final products to meet the requirements of various industries (healthcare, energy production, automotive *etc.*) relying on the specific polymeric materials (Nouman et al., 2017). Although, additives are typically just a small portion of the final product, their impact on the polymer properties and stability is considerable (Ambrogi et al., 2017; Marturano et al., 2017). Polymer additives are commonly used in the solid-state (flakes, granulate, powders, *etc.*) (Marturano et al., 2017). The use of liquid additives is less common because they require special methods of treatment, especially the ones that are of high concentrations, sticky, or sensitive to temperature (Marturano et al., 2017). Once additives are added, the polymer mixture

is referred to as a master blend and is processed accordingly. It has to be noted, that by using these chemicals, the lifetime of polymer products can be significantly prolonged, but also makes it difficult to recycle the final product. Furthermore, these species could migrate from the polymers into the environment which could be hazardous towards living organisms (Bhunia et al., 2013; Brocca et al., 2002; Cano et al., 2002; Cherif Lahimer et al., 2017; Hahladakis et al., 2018). Thus, the development of sustainable alternatives to conventional polymer formulations and the search for “green” or “bio” additives is inevitable (De Paoli and Waldman, 2019). In addition to alter physical-chemical properties, additives employed to decrease costs, and get better aesthetic qualities as well (Defonseka, 2020). There are several options when it comes to additives and each one offers a specific improvement to the polymer’s functionality, stability or improves its properties. Additives with the highest demand are plasticizers, flame-retardants, biocides/antimicrobial agents, antistatic agents, antioxidants, UV stabilizers, and colorants. In the following sections, the most important properties of these additives will be discussed.

2. Plasticizers

One of the biggest market segments of additives are plasticizers, especially for PVC (polyvinyl chloride) (Czogala et al., 2021). The base polymers are often rigid and do not have the necessary flexibility and rheology, or flow properties which are needed for the processing. Plasticizers change the physical properties (*e.g.* Young’s modulus, melt viscosity, flexibility, toughness) of the polymers, by acting as ‘spacers’ which form secondary bonds with the polymer chains and thus, increase the distance between neighboring structural elements and hinder their self-interaction which increase their mobility (Chanda and Roy, 2007; Shaari and Kamarudin, 2019; Štěpek and Daoust, 1983). Plasticizers minimize shear during the blending steps of polymer production and improve impact resistance in the final plastic film. Plasticizing of a polymer can be done by inserting the plasticizer into the polymer internally or externally (**Figure 1**).

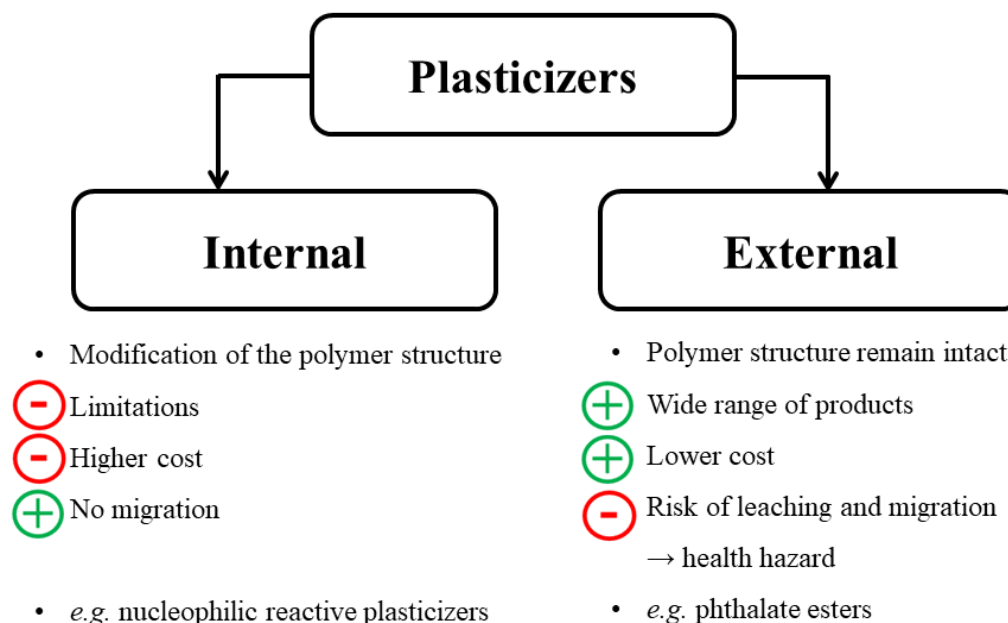


Figure 1 Classification of plasticizers and the corresponding positive and negative aspects.

Internal plasticization means that the monomers of the polymer are prepared and mixed along with the monomers of the plasticizers during the copolymerization process so that the plasticizer becomes part of the polymer structure (Godwin, 2011). There are two types of internal plasticizers, the first attached to the polymer via nucleophilic substitution, while the second is attached through a click reaction using its alkyne group (Bodaghi, 2020; Ma et al., 2020). On the other hand, external plasticizers are mixed to the polymer resin as external additives and in case of PVC, these chemicals are usually phthalate or phosphate esters (**Figure 2**).

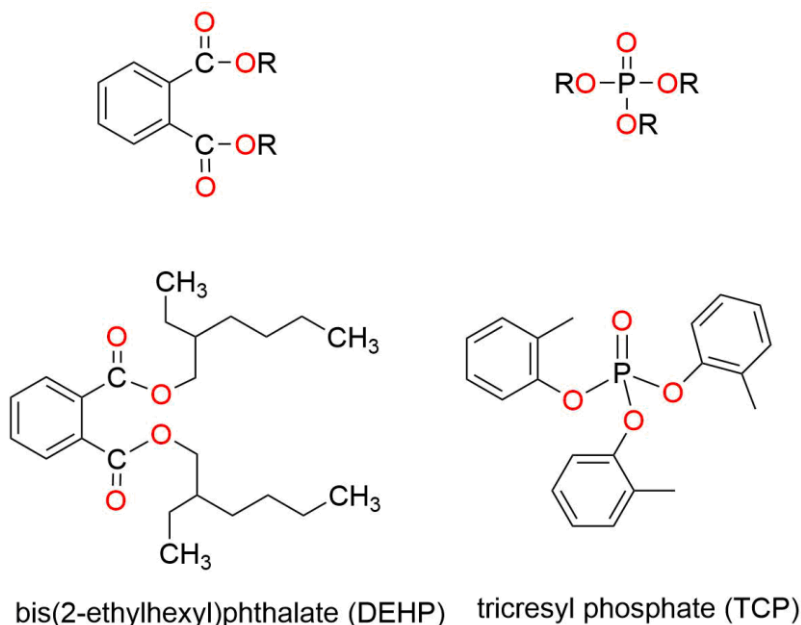


Figure 2 General structures of phthalate and phosphate esters applied as plasticizers along with specific examples *bis*(2-ethylhexyl) phthalate (DEHP) and tricresyl phosphate (TCP).

Thanks to the plasticizers, PVC can be applied in a wide variety of products from flooring to wire and cable covers, sealants and many more. However, as these external plasticizers are not covalently bonded to the corresponding polymer, products containing these molecules can lead to environmental contamination through the migration or evaporation of the plasticizers outside of the polymeric material (Guo and Kannan, 2012; Heudorf et al., 2007). Bio-based plasticizers such as palm oil-based systems, epoxidized sunflower oil, and esters of di-fatty acids have also been tested as co-plasticizers in combination with phthalates (Bouchareb and Benaniba, 2008; Lim et al., 2015; Rao et al., 2014). Other commonly used bio-plasticizers are vegetable oils and polyols (such as glycerol, sorbitol or xylitol) (Vieira et al., 2011). There were attempts to use molecular dynamics (MD) simulations to propose new green plasticizers instead of conventional phthalate esters (Özeren et al., 2020b, 2020a, 2019).

3. Flame retardants (FRs)

Flame retardants (FRs) are added to polymer formulations to prevent the undesirable combustion of the product. There is a wide variety of FRs (>175) which based on their origin and chemical composition and can be divided into four groups such as organo-phosphorous (*e.g.* triaryl phosphates, resorcinol bis(diphenylphosphate), red phosphorous, ammonium polyphosphate,

tris(chloropropyl) phosphate, phosphinic acid derivatives), inorganic (*e.g.* aluminium and magnesium hydroxide), halogenated (*e.g.* tetrabromobisphenol-A (TBBPA), hexabromocyclododecane, poly-brominated diphenyl ethers), and bio-based molecules (*e.g.* phosphorylated cellulose) (Alaee and Wenning, 2002) (**Figure 3, Figure 4**).

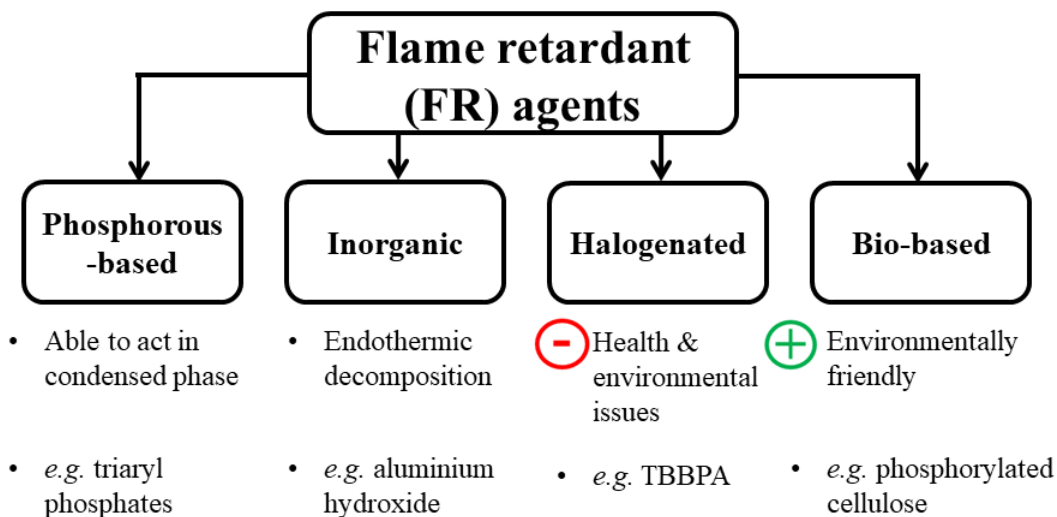
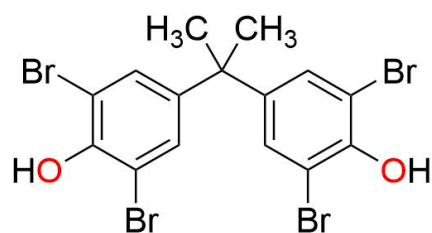
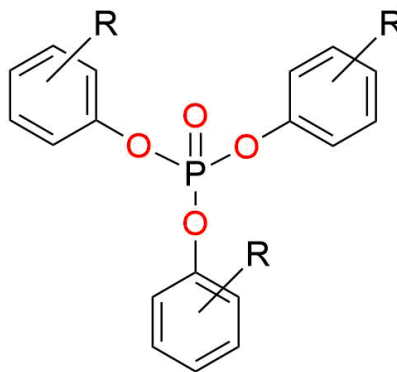


Figure 3 Classification of flame retardant (FR) additives applied in polymeric materials.

The organo-halogen compounds are considered highly effective flame retardant agents (De Wit, 2002). However, some of these, especially the brominated fire retardants, are considered harmful for the environment and thus, novel halogen-free approaches are developed (Hull and Kandola, 2009; Lee et al., 2021). To design or find better and more eco-friendly FR additives, it is important to understand the mechanism of action of conventional compounds. Therefore, computational tools such as reactive MD simulations have also been used to study at the molecular level the effect of aluminium (tri)hydroxide as flame retardant additive in polyethylene (Vaari and Paajanen, 2018). Bio-based molecules are more and more important as flame retardant agents as environmental and health issues pushed decision makers and the polymer industry to replace conventional compounds with natural alternatives (Villamil Watson and Schiraldi, 2020; Xu et al., 2021; Zhao et al., 2021).



Tetrabromobisphenol-A
TBBPA



Triaryl phosphates

Figure 4 Examples of halogenated (tetrabromobisphenol-A, TBBPA) and phosphorous-based (triaryl phosphates) flame retardant (FR) additives applied in polymer formulations.

4. Antimicrobial (AM) agents

Various substances have been used by mankind to prevent infection, despite the existence of microorganisms, such as bacteria and fungi, was not known for a long time. Antimicrobial (AM) agents are mostly used in applications, where bio-stability and prevention of the growth of microorganisms are key factors to consider (Jones, 2009). Commonly used AM additives can be organic (*e.g.* triclosan, oxybisphenoxarsine), inorganic (*e.g.* silver), or natural (*e.g.* nisin, lysozyme, phytochemicals (*e.g.* cinnamaldehyde) (Irkin and Esmer, 2015; Randazzo et al., 2018)) biocide or biostatic agents (Jones, 2009) (**Figure 5, Figure 6**).

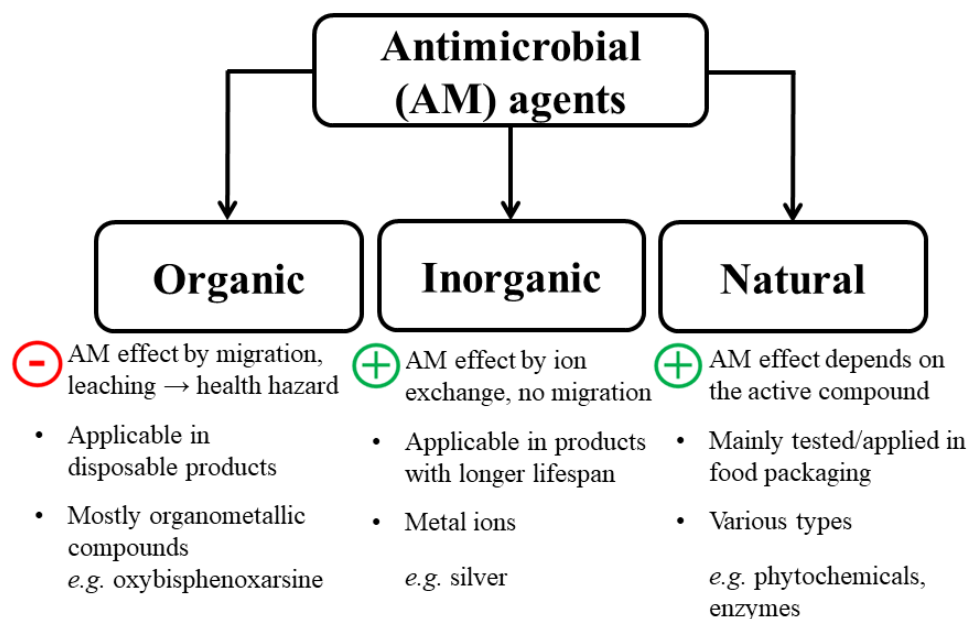


Figure 5 Classification of antimicrobial (AM) additives applied in polymer formulations.

These additives utilized mostly in medical and food packaging applications and thus, low toxicity is a key feature (Marturano et al., 2017). Furthermore, AM agents are becoming more common due to the rising trend in implantable medical products (Velu et al., 2020). These chemicals protect the plastics from microbial deterioration and reduce the potential of a microbiological attack (Turner et al., 2020). Future applications of natural AM additives include, but not limited to biodegradable and edible food packaging which will further stress the importance of low toxicity (De Paoli and Waldman, 2019; Irkin and Esmer, 2015; Latos-Brozio and Masek, 2019).

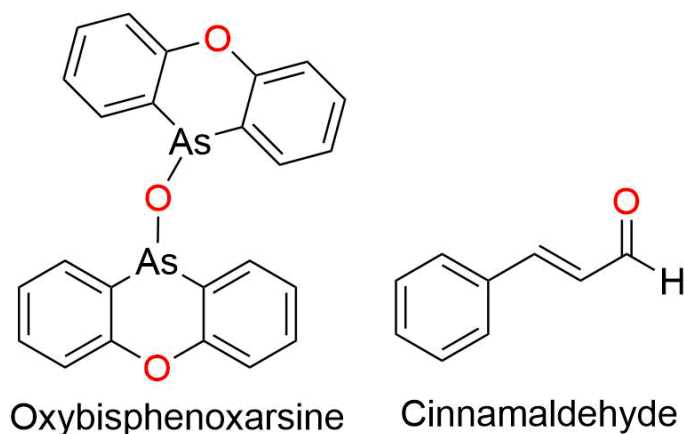


Figure 6 Specific examples of organic (oxybisphenoxarsine, OBPA) and natural (cinnamaldehyde) antimicrobial (AM) additives applied in polymer formulations.

5. Antistatic (AS) agents

Polymers have a great insulation property, unless prone to generate and retain the static charges. One of the main disadvantages of this effect is the sticking of dust particles (which have an opposite polarity) on the surface of polymeric materials, which can significantly reduce the aesthetic value of the final product. Furthermore, sparks generated due to electrostatic effects carry the risk of an accident. Antistatic (AS) agents are applied to modify this property, and added to the surface or directly into the polymers structure (**Figure 7**) (Costa et al., 2009; Grob and Minder, 1999; Wypych and Pionteck, 2016).

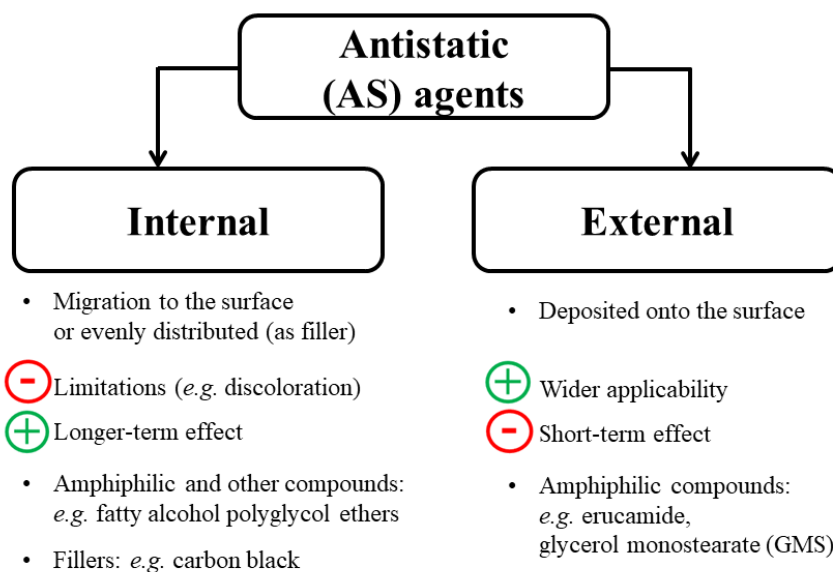


Figure 7 Classification of antistatic (AS) additives applied in polymer formulations.

AS additives applied on the surface of the polymers are amphiphilic surfactants which can be non-ionic (*e.g.* fatty amine polyglycol ethers), anionic (*e.g.* phosphoric acid alkyl esters), cationic (*e.g.* quaternary ammonium compounds), and amphoteric structures (Höfer, 2012). Their hydrophobic parts interact with the surface of the polymer while the hydrophilic groups of the surfactants can adsorb water and thus, a conductive layer will be created which can dissipate the arising electrical charge.

On the other hand, internal antistatic agents have to migrate to the surface of the material to achieve high efficiency or alter the conductivity of the entire material (*e.g.* with conductive fillers) (Heuer and Rolf Wehrmann, 2011; Sengun et al., 2020). There are some disadvantages of these additives

which strongly determine their applicability such as in case of thermoplastics and polycarbonate polymers internal surfactants can affect the density and their efficiency is not remarkable. Furthermore, the application of internal AS additives could lead to discoloration (or change of color) of the polymer and haze in transparent plastics (Grossman, 1993).

Bio-based alternatives are also extensively studied and one great example of such AS additive is erucamide (*cis*-13-docosenoamide), which is extracted from natural oils (canola and rapeseed) and derived from *cis*-13-docosenoic acid (**Figure 8**) (Catarino-Centeno et al., 2021; De Paoli and Waldman, 2019). Interestingly erucamide can act as a lubricant and slip agent as well, due to its structure (long hydrophobic chain), which influences the free volume and fosters polymer chain movement (Chen et al., 2007).

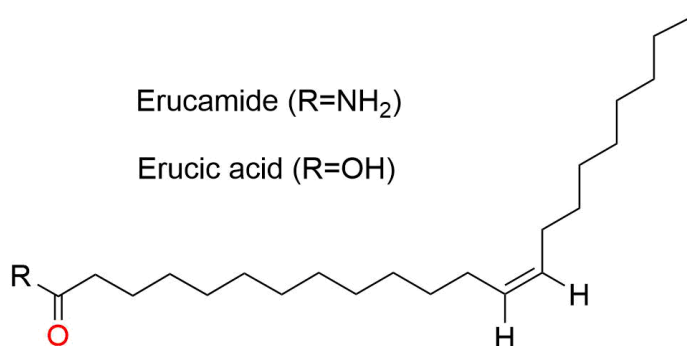


Figure 8 The 2D structures of erucic acid and its antistatic derivative erucamide.

6. Antioxidants (AO) and UV stabilizers (UVS)

Antioxidants (AO), and UV stabilizers (UVS) are utilized as additives to prevent thermal- and UV light-induced oxidation of polymers. The oxidation could lead to the modification of the macromolecular structure which causes an unwanted change in the properties of the polymeric material. Antioxidants and UV stabilizer could inhibit the oxidative degradation of polymers by various protection mechanisms (*e.g.* radical scavenging, UV absorbance).

AOs can be divided into two groups, *primary* and *secondary* antioxidants, depending on their mode of action (Rabek, 1990). *Primary* antioxidants could be radical scavengers (chain-breaking acceptors) or H-donors (chain-branching donors), while the *secondary* antioxidants are hydroperoxide decomposers (**Figure 9**) (Ambrogi et al., 2017; Marturano et al., 2017; Scott, 1988).

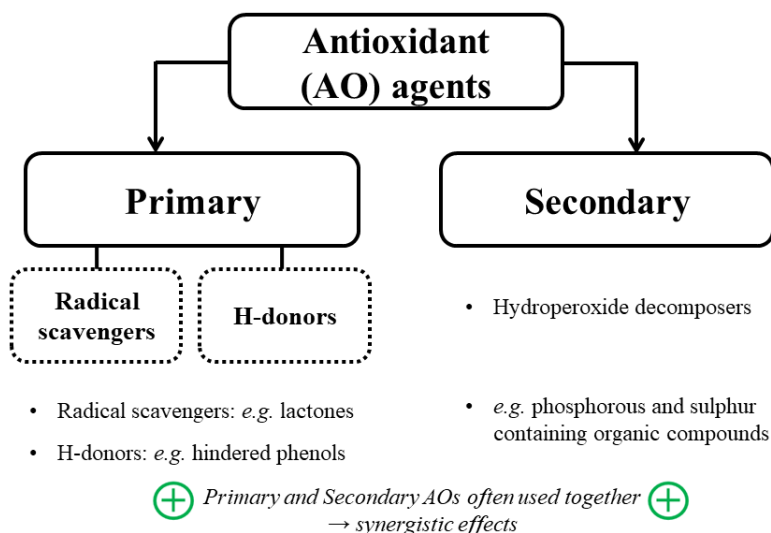


Figure 9 Classification of antioxidant (AO) additives applied in polymer formulations.

The most effective alkyl radical scavengers are lactones (*e.g.* benzofuranone derivatives) and acrylated bis-phenols (Marturano et al., 2017), while aromatic amines (AAs) and hindered phenols are the most effective H-donor type *primary* antioxidants (**Figure 10**).

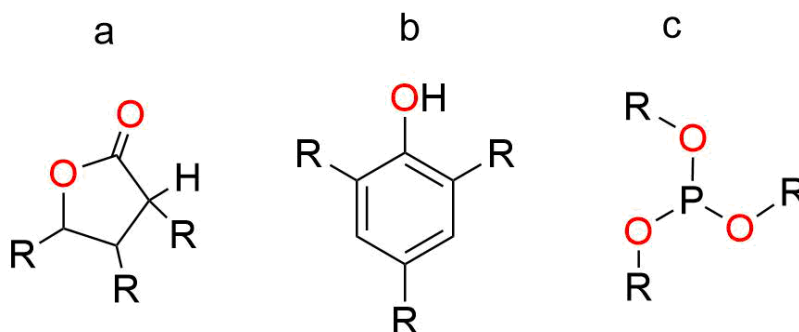


Figure 10 General examples of primary (**a** – lactone skeleton, **b** – hindered phenol) and secondary (**c** – phosphite) antioxidant (AO) additives applied in polymer formulations.

However, the application of AAs in plastics is not recommended since these molecules exhibit well-known carcinogenic effects (Kriek, 1974). Therefore nowadays, hindered phenols are the most widely used antioxidants in polymer formulations. Phenolic antioxidants are effective during both processing and long-term aging and their scavenging activity will lead to the formation of very stable phenoxy radicals (Ingold and Pratt, 2014). Primary antioxidants are often used in combination with secondary AOs which lead to synergistic effects. The most important secondary antioxidants phosphorous and sulphur containing organic compounds which are able to convert

hydroperoxide radicals into non-radicals (ROH, alcohol) (Chien and Boss, 1972; Schwetlick, 1983). Even though synthetic AO additives are highly stable and effective, their potential adverse impact on the environment and human health encouraged the use of bio-based and “green” alternatives. Natural compounds such as vitamin C, tocopherols, carotenoids and phenolic structures have been studied and found to be viable alternatives of synthetic AOs in polymer formulations (Kirschweng et al., 2017; Rigoussen et al., 2018; Shahidi, 1997). Although natural antioxidants are promising, but their industrial scale applications are still scarce and thus, the future has yet to be written.

Polymer degradation could also occur through photooxidation which could be triggered by UV light. This deteriorative process could be prevented by using UV stabilizers (UVS). There are three main categories of UVS: UV absorbers (UVAs), quenchers, and hindered amine light stabilizers (HALS) (**Figure 11**) (Shalaby, 1979).

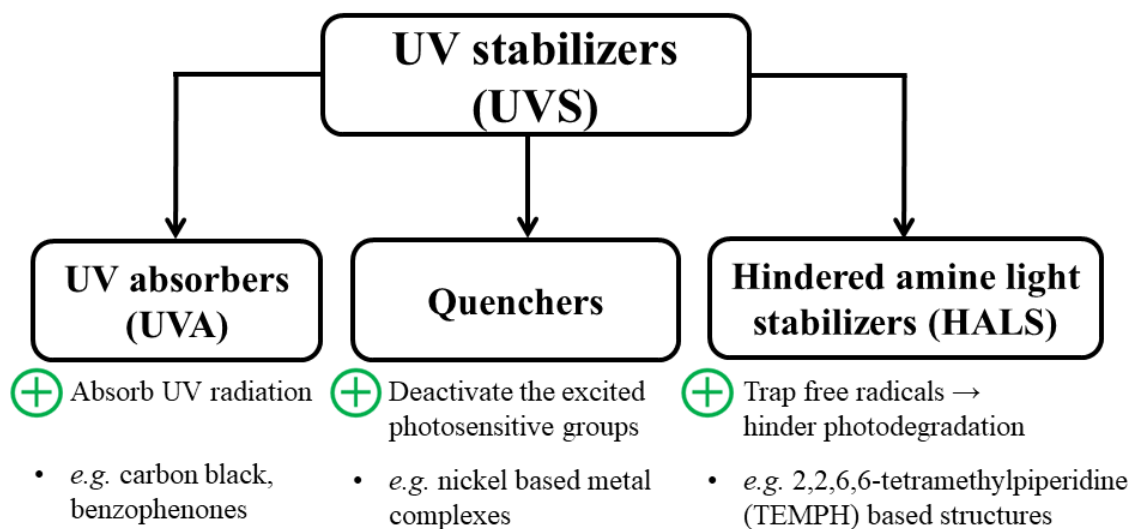


Figure 11 Classification of UV stabilizers (UVS) applied in polymer formulations.

UVAs absorb the harmful UV radiation and protect the photosensitive parts of the polymer. Carbon black, rutile titanium oxide and hydroxyaromatic UV stabilizers (*e.g.* oxanilides, benzophenones, benzotriazoles, hydroxyphenyltriazines) are commonly used additives to prevent photooxidation (**Figure 12**).

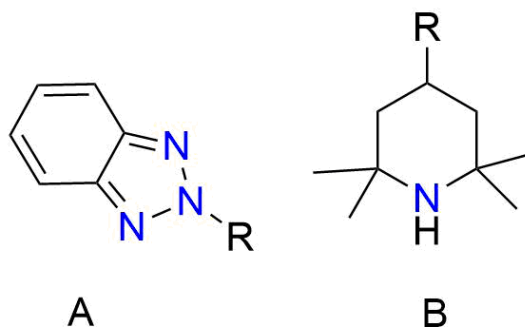


Figure 12 General examples of UV stabilizers (UVS) applied in polymer formulations.

A – benzotriazole based UV absorber (UVA), **B** – 2,2,6,6-tetramethylpiperidine based hindered amine light stabilizer (HALS).

Quenchers can deactivate the excited photosensitive groups of the polymer before bond cleavage occurs (Yousif and Haddad, 2013). Nickel based metal complexes are one of the most effective group of quenchers. The most effective UV stabilizers are HALS which can trap the free radicals formed during the photooxidation and thus, they can hinder photodegradation (Gijsman et al., 1993). Most of the hindered amine light stabilizers which are used in the polymer industry contain a common structural unit, 2,2,6,6-tetramethylpiperidine (Bottino et al., 2004; Twigg et al., 2019).

7. Colorants

Colorants refer to those chemicals which can alter the color of a material. These additives are widely applied in clothes, paints, plastics, photographs, etc. (Pavithra et al., 2019; Pfaff, 2019). The desire to make a product nicer or more colorful is as old as human civilizations. Therefore, the production of colorants and especially lightfast colorants was a valuable secret. The development of synthetic procedures reduced the price of colorants and thus, colorful textiles are available to the wider public. Almost all plastic formulations include colorants to improve the aesthetic values of the products (Maier and Calafut, 1998). There are two main types of colorants applied, pigments and dyes (**Figure 13**). The main difference arises from their solubility, as dyes dissolves in the materials they are added to, while pigments do not.

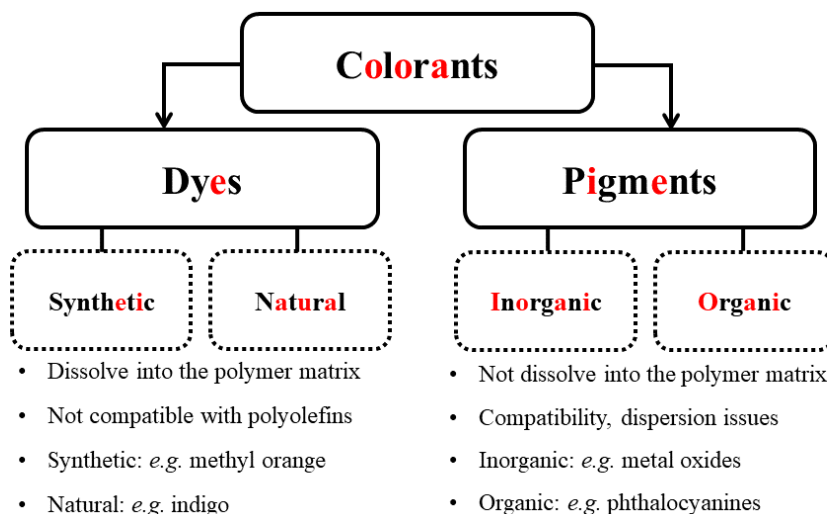


Figure 13 Classification of colorants applied in polymer formulations.

In the applications, thermal and UV stability issues have to be solved. Dyes are either natural (*e.g.* indigo) or synthetic (*e.g.* methyl orange) in terms of their source (**Figure 14**).

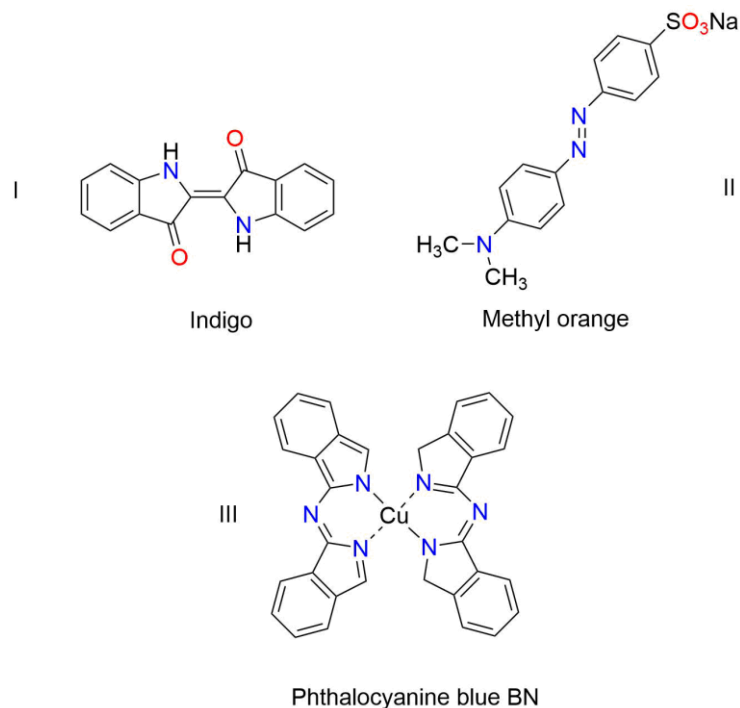


Figure 14 2D structures of specific of colorants applied in polymer formulations.

I – indigo (natural dye), **II** – methyl orange (synthetic dye), **III** – phthalocyanine (organic pigment)

The compatibility of dyes with polyolefins is low, due to the potential migration of the molecules (Maier and Calafut, 1998). Besides the classical applications in textile industry, these compounds are gaining importance in electronic devices as part of organic light emitting diodes (OLED), liquid crystal (LC) displays, optical data storage and others (Fleischmann et al., 2015).

Pigments can be inorganic, such as metal oxides and sulfides, or organic (*e.g.* phthalocyanines or carbon black) (**Figure 13, Figure 14**) (Maier and Calafut, 1998). The structure of pigments will not be altered physically, or chemically by the material to which they are added (Pavithra et al., 2019). Therefore, pigments have to be well dispersed in the polymer matrix to avoid the formation of agglomerates which decrease the mechanical properties of the polymeric product. Thus, the pigments' compatibility with the polymer and any other additives is a sensitive factor during the design of formulations (Maier and Calafut, 1998).

8. Conclusions

Pure polymeric materials are facing several problems, including stability and durability issues, and to achieve the desired properties, additives are widely used in polymer production. To improve processability, prolong the lifespan, and enhance physical and chemical behavior of the final product additives are incorporated into the formulation of the base polymers. Therefore, the development and research of polymers cannot be separated from additive technologies. The focus of this review are additives with the highest demand: plasticizers, flame-retardants, biocides/antimicrobial agents, antistatic agents, antioxidants, UV stabilizers, and colorants. An overview on several aspects of modern polymer chemistry and the driving force of its development is also presented. It is neither a systematic nor a comprehensive review, but an effort to give a glimpse into this important segment of polymer science and technology.

Acknowledgments

This research is supported by the European Union and the Hungarian State, co-financed by the European Regional Development Fund in the framework of the GINOP-2.3.4-15-2016-00004 project, which aimed to promote the cooperation between the higher education and the industry. BF thanks the support by the ÚNKP-20-4 New National Excellence Program of The Ministry for Innovation and Technology from the source of the National Research, Development and Innovation Fund (Hungary).

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