

## **Chapter 4. ADDITIVES IN POLYMERS**

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## 4.1. Introduction

### 4.1.1. Role of polymer additives

Pristine polymeric materials often show poor properties and would result in a commercial failure. Additives play a very important role both in the processability of plastic materials and in their applications (Gatcher and Muller, 1990). The incorporation of additives makes polymer materials suitable for multiple applications in the plastic market: automotive, design, packaging, constructions, electronics, telecommunication (Prithchard, 1998). Additivation of molecules or particles to the virgin polymer can improve the properties of the bulk product as well as its surface. For example, polypropylene (and polyolefins in general), would not be one of the most widely employed commodity polymer without additives. It would, in fact, degrade in weeks, because of its poor thermal oxidative stability (Bockhorn et al, 1999). According to 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”. This chapter wants to give an insight on the most common additives used in plastic in the last few decades; in particular we will focus on the following additives: antioxidants, light stabilizers, UV absorbers, flame retardants, heat stabilizers, impact modifiers, plasticisers, compatibilizers, coupling agents, colorants, pigments, whiteners.

### 4.1.2. Technological aspects of polymer additives

Different effects can be achieved, such as protection from several external agents, and improvement of the material performances in mechanical, processability and miscibility behaviour. Additionally, the macroscopic appearance of material can be changed adding whiteners, dyes or pigments to the standard formulations (Bart, 2006).

Depending on the additive used, it will modify in a more or less strong way the basic polymer characteristics, its performance and durability. Traditional additives are added in powder form, although this may cause hygiene and handling problems. On the other side, only few additives are added in the liquid form (e.g. Vitamin E). Additives in the ideal physical form have a spherical product shape (500-1500  $\mu\text{m}$ ) ensuring at the same time the same performance as the original powders, high homogeneity, dispersibility and mechanical resistance. In the last years the market has experienced an increase in *additive masterbatches* (concentrates containing high level of additives already dispersed in the

polymer), e.g. color masterbatch (Kutz, 2011). Therefore an effort is usually made in the compounding techniques, because each complex material added to the pristine polymer could result in different processability characteristics. For example, handling of solid additives has been reviewed (Hubis, 2000).

A key parameter to take into account for the design of a compounding mechanism is the surface energy involved in the polymer/filler interaction. High surface energies create dispersion issues, adversely affecting mechanical properties in the final product. Ideally, additive needs to interact strongly with the polymer matrix, minimizing their surface energy. Some of these dispersion problems can be overcome adding dispersing agents to the polymer/additive formulation, typically fatty alcohols or phosphoric esters. For example, the addition of calcium carbonate, the most used additive for plastics, rubbers and paints, can be increased up to 70% without significant mechanical modifications.

Another concern is the aggregation of fillers, if added in particulate form. This is a particularly dangerous effect because it can lead to processing problems, and even damaging in the mixing machinery. The basis of aggregation is to be found in the attractive forces that can occur between similar particles, in particular adhesion forces (hydrogen bonding, acid/base interactions, other specific interactions). A way to hinder these processes is to increase shear forces, which instead lead to particle separation (Nardin and Papirer, 2006).

As all areas in polymer technology, health standards must be applied to regulate the use of additives. Most sensitive problems involve the use of halogen-containing flame retardants, heavy metals (as used in pigments and PVC stabilizer systems), and plasticizers. Nowadays the main concerns of society regarding polymer industry is focused on plastic recycling. So far, most exploited technology is incineration of plastics in order to produce consisting amounts of energy. Additivation of any particulate can affect the safety of the incineration process, releasing dangerous combustion by-products in the atmosphere. Fortunately, toxicity and safety issues lead research and development teams to study more sustainable alternatives with applications in even wider areas than those originally envisaged. Therefore, the last section of this chapter will be devoted to bio-based additives, which could guarantee a valuable and more sustainable alternative to commercial additives.

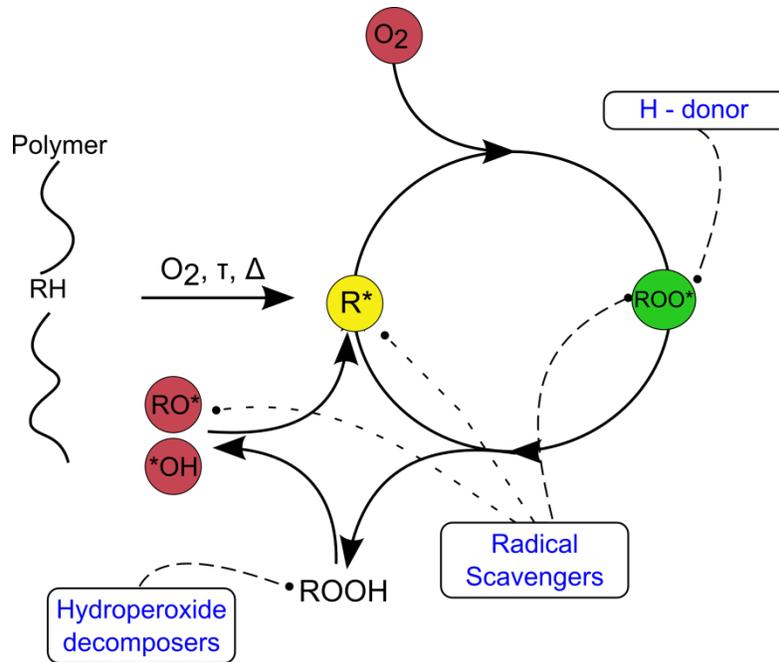
## **4.2. Protective Additives**

Many factors affect the shelf life of polymers, so in the past they were considered very unsatisfactory materials if compared to most commonly used materials, such as metals and ceramics. Main concerns regarding polymer stability and durability are now overcome with the use of polymer stabilizers, essential ingredients that can make the difference between success and failure of plastic items.

Under natural (weathering) conditions, several factors such as exposure to sunlight, day/night or seasonal temperature variation, humidity and atmospheric contamination with highly corrosive elements affect polymer stability. Ultimately, these processes lead to mechanical failure, most commonly the formation of a brittle surface layer (Rabek, 1996).

#### *4.2.1. Protection against weathering*

The phenomenon of oxidation has been investigated since the late 40s (Bolland, 1949), stating the connection between aging and oxygen absorption. Oxygen and sunlight are the principal degrading agents for hydrocarbon polymers during outdoor weathering (Scott, 1965). Autoxidation plays an important role in the transformation of organic compounds in the atmosphere (Crouse et al, 2013). In particular, hydrocarbon compounds react with molecular oxygen forming oxidation products according to the autoxidation scheme reported in Scheme 1. Free radicals form and react in the presence of oxygen to generate peroxy radicals, which further react with organic material leading to hydroperoxides (ROOH). The latter, the primary products of autoxidation are therefore the main initiators in both thermal and photo oxidation. 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 variation in the physical properties of the polymer surface (e.g. loss of gloss, reduced transparency, cracking, yellowing, etc).



**Scheme 1** – Polymer degradation in presence of oxygen and mechanism of activity ascribed to antioxidants (adapted from Zweifel, 1988).

Photo degradation is a mechanism that involves the activation of the polymeric chain by means of a light photon. Three main processes can be distinguished (Lala and Rabek, 1980):

- **photo-initiated degradation** where light is absorbed by photo-initiators, that are then photo-cleaved into free radicals, which can themselves initiate degradation on the polymeric macromolecule;
- **photo-thermal degradation** which occurs when photo-degradation and thermal degradation enhance each other accelerating the process;
- **photo-aging** usually initiated by solar UV radiation, air or other factors.

Photo oxidative degradation dominates at the surface, because the intensity of the UV fraction of sun radiation is maximum at the surface and has low penetration efficiency, if compared to Infra-red (Rabek, 1996).

### Antioxidants

Antioxidants (AO) are chemical compounds which protect polymers and plastics against thermal and photo-oxidative processes occurring during natural ageing. AO are generally classified in two groups, accordingly to their protection mechanism (Rabek, 1990):

**1. Kinetic chain-breaking antioxidants** (chain terminators, chain scavengers). They have the capability to scavenge some of even all available low molecular radicals ( $R^\bullet$ ,  $RO^\bullet$ ,  $ROO^\bullet$ ,  $HO^\bullet$ , etc) and polymeric radicals ( $P^\bullet$ ,  $PO^\bullet$ ,  $POO^\bullet$ ) by a process called chain breaking electron donor mechanism;

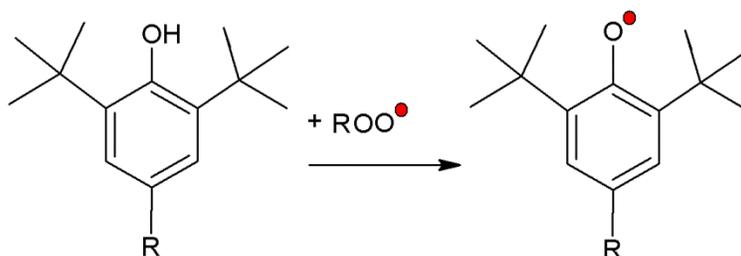
**2. Peroxide decomposers**, which decompose hydroperoxy groups ( $HOO-$ ) present in a polymer.

Antioxidants cover different classes of compounds which can interfere with the oxidative cycles to inhibit or retard the oxidative degradation of polymers (Al-Malaika and Sheena, 2006). Many classes of additives have now been developed for the prevention or reduction of the photo-oxidative degradation of polypropylene. These additives seem to operate by several mechanisms, some of which can be remarked in order of increasing practical importance: singlet oxygen quenching, UV absorption, hydroperoxide decomposition, radical scavenging. (Zweifel, 1998). A classification of commercially available antioxidants is reported in **Table 1**.

### **Primary antioxidants**

Primary antioxidants inhibit oxidation via chain terminating reactions. They have reactive OH or NH groups (hindered phenols and secondary aromatic amines). Inhibition occurs via a transfer of a proton to the free radical species. The resulting radical is stable and unable to abstract a proton from the polymer chain.

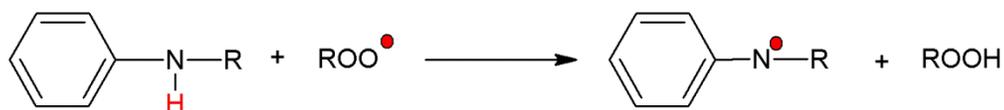
**Hindered phenols** are primary antioxidants that act as hydrogen donors. They react with peroxy radicals to form hydroperoxides and prevent the abstraction of hydrogen from the polymer backbone (Pospíšil, 1993). Often used in combination with secondary antioxidants, phenolic stabilizers are offered in an extensive range of molecular weights, product forms, and functionalities. Sterically hindered phenols are the most widely used stabilizers of this type. They are effective during both processing and long term aging, and many have the Food and Drug Administration (FDA) approvals.  $ROO^\bullet$  radicals are deactivated by hindered phenols via reaction represented in **Scheme 2** (Lutz and Grossman, 2001; Ingold and Pratt, 2014).



**Scheme 2** – Deactivation of ROO\* radicals by hindered phenols.

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

**Secondary aromatic amines** act as primary antioxidants and are the most efficient hydrogen donors. The reaction of deactivation of peroxy radicals by secondary aromatic amines is reported in **Scheme 3**.



**Scheme 3** – Deactivation of ROO\* radicals by means of secondary aromatic amines.

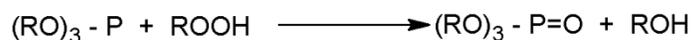
Also available in an extensive range of molecular weights and product forms, aromatic amines are often more active than hindered phenols, because of less steric hindrance. Aromatic amines, however, are more discoloring than hindered phenols, especially on exposure to light or combustion gases (gas fade) and have limited FDA approval (Pocius, 2002).

### Secondary antioxidants

Secondary antioxidants, frequently referred to as hydroperoxide decomposers, act converting hydroperoxides into non-radical, non-reactive, and thermally stable products. They are often used in combination with primary antioxidants to yield synergistic stabilization effects. Hydroperoxide decomposers prevent the split of hydroperoxides into extremely reactive alkoxy and hydroxy radicals. Organophosphorus compounds and thiosynergists antioxidants are widely used as hydroperoxide decomposers. (Shanina et al, 2002)

**Phosphites**, and in particular organophosphorus compounds, are secondary antioxidants that decompose peroxides and hydroperoxides into stable, non-radical products, accordingly

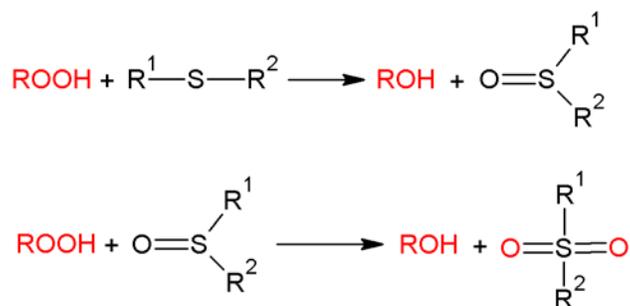
to the **Scheme 4** reported below. They are extremely effective stabilizers during processing and are normally used in combination with a primary antioxidant. Trivalent phosphorus compounds are excellent hydroperoxide decomposers. Generally, phosphites (or phosphonites) are used and react according to the following general reaction, generating phosphates. (Zweifel, 1998)



**Scheme 4** – Decomposition of hydroperoxides by means of Organophosphorus compounds.

Some of these compounds are sensitive to water and can hydrolyze, leading to formation of acidic species. By all means, the addition of an acid scavenger could minimize the effect, however, the industry has generally turned directly to hydrolysis-resistant compounds.

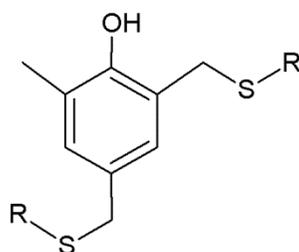
**Thiosynergists.** Among sulphur-based hydroperoxide decomposers, thioethers and esters of 3,3-thiodipropionic acid play a very important role. Also known as thiosynergists, these compounds react according to the general reaction reported in **Scheme 5** for thioethers. Hydroperoxide is typically reduced to an alcohol and the thiosynergist is transformed into a variety of oxidised sulphur products, including sulfenic and sulfonic acid (Karian, 1999).



**Scheme 5** - Decomposition of hydroperoxides by means of thiosynergists.

Although thiosynergists do not improve the melt stability of polymers during polymer processing, they are very efficient for long-term thermal aging applications. Sulfur-based hydroperoxide decomposers are mainly used in combination with hindered phenol antioxidants. The most common commercially available thiosynergists are based on either lauric or stearic acid.

**Multifunctional antioxidants (Scheme 6)** have only recently become available. Due to their special molecular design, they combine primary and secondary antioxidant functions in one compound (Collins et al, 2005).



**Scheme 6** – General structure of a multifunctional antioxidant molecule.

Having several stabilizing functions combined in the same molecule, multi-functional antioxidants eliminate the need for co-stabilizers, such as phosphites and thioethers. This not only simplifies the formulation, but it also simplifies the storage, handling, and use of the stabilizer.

**Table 1** – Classification of commercially available antioxidants.

CLASSIFICATION	CHEMICAL COMPOSITION	COMMERCIAL NAME (SUPPLIER)	APPLICATIONS
Primary Antioxidants	Phenols	ANOX <sup>®</sup> 29 ( <i>Addivant</i> ), IRGANOX <sup>®</sup> 1010 ( <i>BASF</i> ), EVERNOX <sup>®</sup> 10	PVC, PA, PP, PE, Cellulosic Polymers
		ADK STAB A040 ( <i>Adeka Corp</i> ), SONGNOX <sup>®</sup> 1077 LQ ( <i>Songwon</i> )	Cellulosic Polymers
	Amines	AMINOX <sup>®</sup> ( <i>Addivant</i> ), DUSANTOX <sup>®</sup> 86 ( <i>Dulso</i> ), ANTIOXIDANT DQ ( <i>AKrochem</i> )	Natural Rubbers
		Sipax <sup>®</sup> DLTD, BNX <sup>®</sup> 2000 ( <i>Mayzo</i> )	PA, PE, PP

Secondary Antioxidants	Phosphites	WESTON ® 705 ( <i>Addivant</i> ), ADK STAB 1500 ( <i>Adeka Palmarole</i> )	Cellulosic Polymers
		EVERFOS ® 168 ( <i>Everspring Chemicals</i> ), ADK STAB PEP-36 ( <i>Adeka Palmarole</i> ), ALKANOX ® 240 ( <i>Addivant</i> )	PVC, PS, PA, PP, PE, Cellulosic Polymers
	Thioester	Octolite 529 ( <i>Tiarco Chemical</i> )	Synthetic rubbers
		Songnox ® DSTDP ( <i>Songwon</i> ), Irganox ® PS800	PA, PE, PP, PVC, PC

### Photo-stabilizers

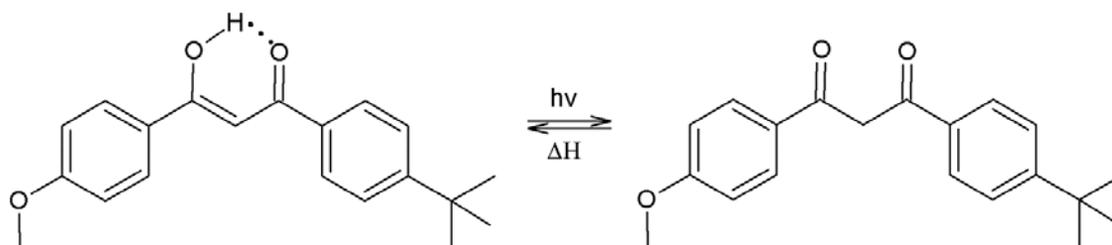
Photodegradation is degradation of a photodegradable molecule caused by the absorption of photons, particularly those wavelengths found in sunlight, such as infrared radiation, visible light, and ultraviolet light (Yousif and Haddard, 2013).

Photostabilization of polymers involves the inhibition or retardation of photochemical processes (mainly photo-oxidation) in polymers and plastics by a reduction in the rate of photoinitiation and or a reduction in the kinetic chain length of the propagation stage of the photo-oxidation mechanism. Photostabilizers (UV, light stabilizers) are additives to plastics and polymeric materials, which prevent photochemical destructive process and reaction caused by UV radiation present in sunlight (Rabek, 1996).

Photostabilizers can be classified into three main classes:

1) **UV absorbers.** The action of a UV absorber is relatively simple, as it interacts with the first step of the photooxidation process by absorbing the harmful UV radiation (300–400 nm) before it reaches the photo active chromophoric species in the polymer molecule. Therefore, the energy dissipates in a manner that does not lead to photosensitization. A UV absorber must be light stable, because otherwise it would be destroyed in stabilizing reactions. (Yousif, 2012). A very common process for energy dissipation is converting harmful UV radiation into harmless infrared radiation or heat that is dissipated through the polymer matrix. Carbon

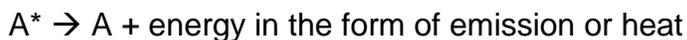
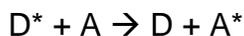
black is one of the most effective and commonly used light absorbers, as well as rutile titanium oxide which is effective in the 300-400 nm range but is not very useful in the very short wavelength UVB range below 315 nm. The activity of many **hydroxyaromatic** compounds as UV stabilizers for several polymers has been reported. This is due to their filtrating action which depends on their absorption characteristics (Ranby and Rabek, 1975; Allen and McKellar, 1980). Hydroxybenzophenone and hydroxyphenylbenzotriazole are well known aromatic UV stabilizers that have the advantage of being suitable for neutral or transparent applications (Gugumus, 1979). However, hydroxyphenylbenzotriazole is not very useful in thin parts below 100 microns. Other UV absorbers include oxanilides for polyamides, benzophenones for PVC and benzotriazoles and hydroxyphenyltriazines for polycarbonate. (Allen and Edge, 1992). Hydroxyaromatic compounds are often referred to as the classical absorbers because they were originally designed to absorb the ultraviolet portion of the sunlight spectrum in the range 290-400 nm, i.e. the region which is determinant to most polymer systems. For example, Avobenzones dissipate absorbed energy by a mechanism that involves the reversible formation of a six membered hydrogen bonded ring. The following two tautomeric forms in equilibrium provide a facile pathway for deactivation of the excited state induced by the absorption of light (**Scheme 7**):



**Scheme 7** – Energy dissipation mechanism occurring in avobenzone based UV-absorbers.

2) **Quenchers.** These compounds are able to deactivate excited states (singlet and or triplet) of chromophoric groups present in a polymer before bond scission occurs [Wiles and Carlsson, 1980]. In contrast to absorbers, quenchers do not need to have high absorption at the critical wavelength for polymer degradation. Quenching is a bimolecular process characterized by a very fast kinetics. In other words, quenching is a diffusion controlled process and is effective in polymer protection only if the sensitizer triplets have a long half-life and if the quencher is freely diffusible. (Heller, 1969). The quenching reaction may be represented by a simple reaction, reported in Scheme 8, where excited donor ( $D^*$ ) (an excited

chromophoric group in a polymer, which can be responsible for the initiation of photodegradation) is deactivated by an acceptor (quencher) (A) molecule (Rabek, 1990):

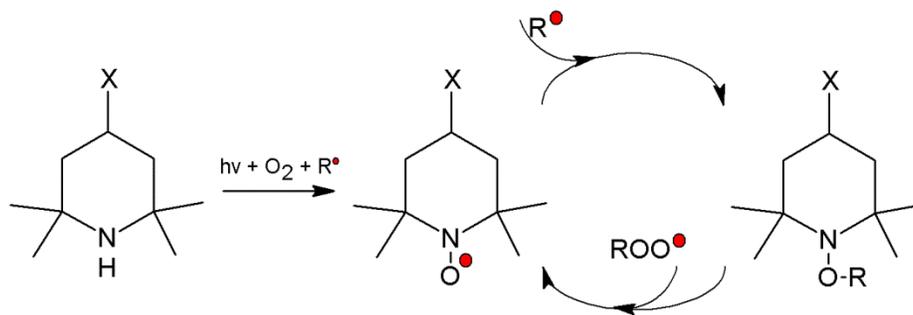


**Scheme 8** – Schematization of the quenching reaction.

The development of **metal complexes**, particularly those based on nickel, resulted in compounds with relatively low extinction coefficient in the near UV region and yet are often found superior in performance. Nickel chelates are very effective quenchers of the triplet state of carbonyl groups in polyolefins. These chelates have been tested for photostabilization of polyisobutylene, polybutadiene (Lala and Rabek, 1980), as well as polystyrene (George, 1974).

Hindered Amine Light Stabilizers (HALS) are long-term thermal stabilizers that act by trapping free radicals formed during the photo-oxidation of a plastic material and thus limiting the photodegradation process. The ability of HALS to scavenge radicals created by UV absorption is explained by the formation of nitroxly radicals through a process known as the Denisov Cycle (Hodgson and Coote, 2010).

It has been generally accepted that during UV irradiation and in the presence of oxygen (air) and radicals ( $R^\bullet$ ), hindered piperidine (e.g., 2,2,6,6-tetramethyl piperidine, which is the simplest model compound for HALS), produces hindered piperidinoxy radicals according to **Scheme 9** (Yousif et al, 2011)



**Scheme 9** – Schematization of mechanism of radical scavenging of hindered piperidine.

Although there are wide structural differences in the HALS products commercially available, all share the 2,2,6,6-tetramethylpiperidine ring structure (Bottino et al, 2004). HALS are some

of the most proficient UV stabilizers for a wide range of plastics. For example, HALS have enabled the growth of polypropylene in the automotive industry. While HALS are very effective in polyolefins, polyethylene and polyurethane, they are not useful in PVC.

As most photostabilizers behave according to a different mechanisms, they are often combined into synergistic UV absorbing additives. For example, benzotriazoles are often combined with HALS to protect pigmented systems from fading and colour changes.

3) **UV screeners.** UV screeners are materials that can reflect the damaging light from the surface of the polymer. Some examples are coatings (with paintings or by metallization) of the surface or incorporation of a pigment with high UV reflectance (Rabek, 1990). Since pigments act as highly absorbing additives, photooxidative phenomena are limited mainly to the surface of samples (Yousif, 2012). Pigments can be divided in two classes:

- inorganic pigments: titanium dioxide, zinc oxide, iron oxide (red), chromium oxide, etc;
- organic pigments: phthalocyanine blues and greens, quinacridone reds, carbazole violet, ultramarine blue.

Inorganic pigments are widely used for decorative and colour coding, but not for stabilization. In general white pigments give a better reflectance in the 300-400 nm region than coloured pigments. Not always there is a good synergy between polymer and pigment, so the match must be considered properly. (Hihara et al, 2013; Bigger and Delatycki, 1989). For further information on pigments refer to Section 4.6.

In **Table 2** a classification of commercially available photo/stabilizer is reported.

**Table 2** – Classification of commercially available photo-stabilizers.

CLASSIFICATION	CHEMICAL COMPOSITION	COMMERCIAL NAME (SUPPLIER)	APPLICATIONS
UV absorbers	Benzophenones	LOWLITE 20 ( <i>Addivant</i> ), MAXGARD® 1000 ( <i>Syrgis Berform Specialties</i> )	Adhesives (Polyolefins, Polyesters, Acrylics, PVC)
	Benzotriazoles	TINUVIN™ 1130 ( <i>BASF</i> ), SUNSORB 5411 ( <i>Everspringchem</i> ),	Adhesives (Natural Rubbers, Polyurethanes, Polyamides, Polyvinyl

		MILESTAB 1130 (MPI Chemie)	Alcohols, Epoxies, Polyolefins), Sealants
Quenchers	HALS	LOWLITE ® 19 (Addivant)	PVC, Polyurethanes, PA, PET, PBT, PMMA
		ADK STAB LA-402AF (Adeka corporation)	PE, PP
		HALS GW 622 (Beijing Additives Institute)	PA, PE, PP, Polyester, Cellulosic Polymers
	Metal Complexes	KRITILEN ® UV 17 (Plastika Kritis), Vibatan® PE UV MASTER 02566 (Viba Group)	PE (agriculture, greenhouse)

#### 4.2.2. Heat Stabilizers

Heat stabilizers are used to prevent degradation of plastics by heat, especially during processing, but also in applications. For example, they are widely used in PVC compounds. Heat stabilizers act by stopping thermal oxidation or by attacking the decomposed products of oxidation (Murphy, 1999). The autoxidation process has been reviewed in **section 4.2**. Because of its structure, PVC is particularly sensitive to heat. The largest use of heat stabilizers is indeed in the PVC industry, and PVC is by far the most needful of heat stabilizers. Another important field of application for heat stabilizer includes recycled materials, where they play the double role of inhibiting degradation and re-stabilizing post-use plastic waste. Three groups of materials can be individuated for the use as heat stabilizers, and many commercially available heat stabilizers are classified in **Table 3**:

- Metallic salts, most commonly based on barium, cadmium, lead or zinc, often used together to obtain a synergistic effect. The mixed metal salts and soaps are generally prepared by reaction of commercially available metal oxides or hydroxides with the desired C8–C18 carboxylic acids. Zinc (and cadmium) salts react with defect sites on PVC to displace the labile chloride atoms (Mesch, 1994).
- Organometallic compounds, mainly based on tin. These compounds are all derivatives of tetravalent tin, Sn(IV), and all have either one or two alkyl groups covalently bonded directly

to the tin atom. Many of the alkyltin stabilizers are considered safe to use in almost every conceivable end use for PVC (Figge, 1990).

- Non metallic organic stabilizers. Since the early 1990s there has been a significant effort to reduce or eliminate most metals, particularly lead, from PVC heat stabilizers. This crusade was launched in the name of improving both human health and environmental effects from metals that leach from PVC products. They are typically based on phosphites, improving optical characteristics such as transparency, initial colour and light fastness.

Development in recent years has centred on technical improvement, increase in processability, handling and dispersion (developing pelletized and liquid systems) and studies on toxicological properties for food contact and medical applications. For applications in contact with food, FDA regulations recommend liquid antioxidants based on natural compounds such as Vitamin E.

**Table 3** – Classification of commercially available heat stabilizers.

<b>CLASSIFICATION</b>	<b>CHEMICAL COMPOSITION</b>	<b>COMMERCIAL NAME</b>	<b>APPLICATIONS</b>
Metallic salts	Barium-Zinc	ADK STAB 666 ( <i>Adeka corporation</i> )	PVC
	Calcium-Zinc	ADK STAB 36 ( <i>Adeka corporation</i> ), INTERLITE ZP9604 ( <i>Akoros Chemicals</i> ), ZINC STEARATE SP ( <i>Baerlocher</i> )	PVC, PS, PE
Organometallic compounds	Organotin	ADK STB 129 ( <i>Adeka corporation</i> ), baeropan® M26 SF ( <i>Baerlocher</i> )	PVC
Non metallic organic stabilizers	Bisphenol type epoxy resin	ADK CIZER EP-13 ( <i>Adeka corporation</i> )	PBT, Other thermoplastics
	Hydrolyzed Polyvinyl	Elvanol® 51-05 ( <i>DuPont</i> )	PS

	Alcohol		
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#### 4.2.3. Flame Retardants

All carbon-based materials, from wood to plastics, can be combusted as long as heat and oxygen are present, and because oxygen is plentifully available, combustion is a constant force of nature on our planet. The energy is absorbed until the C-C, C-O, C-N bond in the backbone is broken and low molecular weight volatile gases are released in the atmosphere together with potentially harmful elements such as nitrogen, oxygen, sulphur, fluorine and chlorine (Morgan and Gilman, 2013). The role of flame retardant is to make the polymer formulation less flammable by interfering with the chemistry and/or physics of the combustion process. (Innes and Innes, 2003). Flame retardants (FR) can be classified in three types depending on their technology. A list of commercially available flame retardants is reported in **Table 4**.

1) **Halogen-based flame retardants**. Halogen FRs, like their name suggests, are molecules that incorporate elements from group VII of the periodic table – F, Cl, Br, and I. They can vary widely in chemical structure, from aliphatic to aromatic carbon substrates that have been per-halogenated (all hydrogens replaced with halogen atoms) or can come in inorganic form. The organo-halogen compounds find the most effectiveness as flame retardant additives for polymers (Grand and Wilkie, 2000). These work in the vapour or gas state interfering with the chemical radical mechanism of the combustion process. However, some flame retardants belonging to this class, especially brominated, are considered harmful for the environment (De Wit, 2002).

2) **Phosphorus-based flame retardants** incorporate phosphorus into their structure, and the structure can vary greatly from inorganic to organic forms, and between oxidation states (0, +3, +5) (Levchik and Weil, 2006). These FRs are also known as *char formers*, because during the burning process they produce phosphoric acids, that, reacting with the substrate produce a char that acts as a protection of the substrate itself.

3) **Metal hydrate flame retardants**. This class of FRs include typically aluminium trihydroxide ( $\text{Al}(\text{OH})_3$ ) and magnesium hydroxide ( $\text{Mg}_2(\text{OH})_4$ ). These products provide FR protection by releasing water upon heat decomposition, impacting the combustion process (Horn, 1996).

**Table 4.** Classification of commercially available flame retardants.

CLASSIFICATION	CHEMICAL COMPOSITION	COMMERCIAL NAME (SUPPLIER)	APPLICATIONS
Halogen	Brominated	GREEN ARMOR <sup>®</sup> (Albermate) BIOFR 245 (Bioray Chem) BE-51 <sup>™</sup> (Chemtura)	PA, PE, PP, PS, Cellulosic Polymers
	Chlorinates	ARYAFIN A1/62 (Aditya Birla Chem),	PVC (flexible, rigid), cables, hoses, pipes, ecc...
		CHLOREZ <sup>®</sup> 700 (Dover ICC Istitute)	Other Rubber
		DECHLORANE plus 25	PA, PP, Natural Rubber, Cellulosic Polymers
	Fluorinated	BioFR KPBS (Bioray Chem)	PC
Phosphorus	Ammonium Polyphosphates	BUDIT 380 (Budenheim) EXOLIT <sup>®</sup> AP422 (Clariant) HILEFLAME APP-201	Other thermoset PP PE, PP, Epoxy
	Other phosphorous based	BIOFR IPPP-35 EXOLIT <sup>®</sup> OP 930	PVC, PE, PA, Epoxy, PP Other Thermoplastics and Thermosets
Metal hydrate	Magnesium hydroxides	PERKALITE <sup>®</sup> A100 (Akzo Nobel)	Natural Rubber
		MAGNIFIN <sup>®</sup> H-10C	PVC (Flexible/Rigid)
		DUHOR <sup>®</sup> C-02/s	PP/PS
	Aluminum Trihydroxides	MARTINAL <sup>®</sup> OL-104LEO (Albemarle)	PVC, PE, PP, Other Rubber
		AC30 (Aluchem)	Other rubber

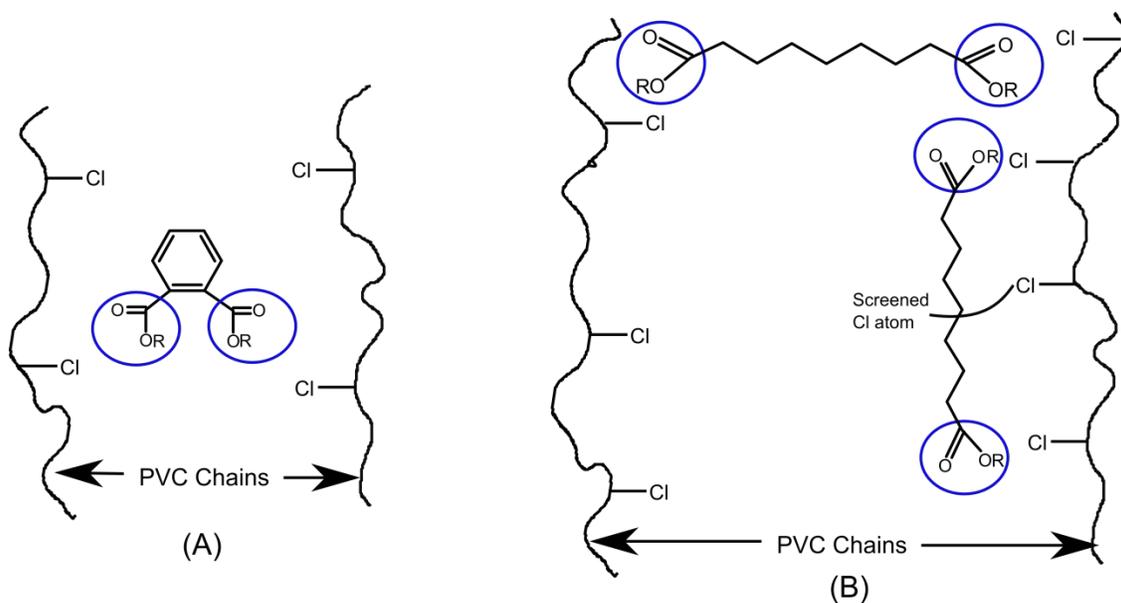
		HALTEX ® 302 (TOR Minerals)	
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### 4.3. Plasticizers

Plasticizers are organic substances of low volatility that are added to plastics compounds to improve their flexibility, extensibility, and processability. They increase flow and thermoplasticity of plastic materials by decreasing the viscosity of polymer melts, the glass transition temperature ( $T_g$ ), the melting temperature ( $T_m$ ), and the elastic modulus of finished products. (Chanda and Roy, 2007). Plasticizers are particularly used for polymers that are in a glassy state at room temperature. These rigid polymers become flexible due to strong interactions between plasticizer molecules and chain units, which lower their brittle-tough transition and extend the temperature range for their rubbery or viscoelastic state behaviour. (Štěpek and Daoust, 1983). One of the most important practical factors to take into account is the mutual miscibility between plasticizers and polymers. If a polymer is soluble in a plasticizer at high concentration of the polymer, the plasticizer is called *primary*. *Primary plasticizers* should gel the polymer rapidly in the normal processing temperature range and should not exude from the plasticized material. *Secondary plasticizers*, on the other hand, have lower gelation capacity and limited compatibility with the polymer. In this case, two phases are present after plasticization process: one in which the polymer is only partly plasticized, and another one where it is completely plasticized. For this reason these polymers do not deform homogeneously when stressed, the deformation appears only in the plasticizer-rich phase and the mechanical properties of the systems are poor (Chanda and Roy, 2007).

Poly(vinyl chloride) (PVC) is the second largest selling pure polymer in Europe, after polyethylene. However, PVC as a pure resin has very poor properties and requires the use of additives to manufacture products of acceptable quality. The need for the use of PVC additives can be thought of in two ways: negatively, such additives introduce unwanted complexity and additional price, while the use of these additives gives additional ability to tailor the properties of the final product. Plasticizers are typically organic liquids, which can be added to PVC to obtain a product with flexibility. Plasticizers for PVC can be divided into two main groups accordingly to their nonpolar part (Cadogan and Howick, 1996). The first group (**Scheme 10 - A**) consists of plasticizers, such as phthalic acid esters, having polar groups

attached to aromatic rings. An important characteristic of these substances is the presence of the polarizable aromatic ring. It has been suggested that they behave like dipolar molecules and form a link between chlorine atoms belonging to two polymer chains or two segments of the same chain. The second group (**Scheme 10 - B**) consists of plasticizers having polar groups attached to aliphatic chains and is called the polar aliphatic group. Examples are aliphatic alcohols and acid or alkyl esters of phosphoric acid. Their polar groups interact with polar sites on polymer molecules, but since their aliphatic part is rather bulky and flexible other polar sites on the polymer chain may be screened by plasticizer molecules, reducing the extent of intermolecular interactions between neighbouring polymer chains.



**Scheme 10** – Effect of different types of plasticizers on PVC chains.

Plasticizers can also be divided according to their chemical structures. In the following chart (**Table 5**) commercially available plasticizers are listed and they are divided into two main categories: **phthalates** and **non phthalates**. The most widely used class of plasticizers are indeed phthalates, and in particular phthalic acid esters. It is reported that phthalate exposure may pose health concerns. As the 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. (Heudorfa et al, 2007; Xu et al, 2010). In the general class of

non phthalates are enclosed all other chemical compounds, such as phosphoric acid esters, fatty acid esters, etc. In **Table 5**, a list of commercially available phthalates and non phthalates plasticizers is reported.

**Table 5** – Classification of commercially available plasticisers, based on their chemical structure.

Classification	Chemical Composition	Commercial Name	Applications
Phthalates	Diocetyl phthalate (DOP)	EASTMAN DOP ( <i>Eastman Chem Company</i> ) PALATINOL <sup>®</sup> DOP (BASF)	PVC (Flexible), Pipes, Hoses, Buildings, Medical PVC
	Diisononyl phthalate (DINP)	PALATINOL <sup>®</sup> N (BASF) LD-flex DINP (LG Chem)	PVC
	Diisodecyl phthalate (DIDP)	EMOLTENE <sup>™</sup> 100 KLJ-DIDP (KLJ Group)	PVC (Flexible), PVC (Flexible, rigid), Other rubbers, bioplastic, Cellulosic Polymers
	Di-n-buthyl phthalate (DBP)	PALATINOL <sup>®</sup> C (BASF) KLJ-	PVC (Flexible, rigid), Other rubbers, bioplastic, Cellulosic Polymers
Non Phthalates	Adipates	ADIMOLL <sup>®</sup> BO ( <i>Rhein Chemie Additives</i> )	Natural Rubbers, PS, PVC, (calendaring, extrusion, injection)
		PALAMOLL <sup>®</sup> 632 (BASF)	PVC (Flexible, rigid)
	Benzoates	BENZOFLEX <sup>™</sup> 2088 ( <i>Eastman chemical</i> )	PVC

		<i>company)</i> K-FLEX ® 500 ( <i>Emerald performance materials)</i>	
	Phosphates	DISFLAMOLL ® 51036 ( <i>Rhein Chemie Additives</i> ) KLJ-TCP-100 (KLJ Group)	PVC  PVC (flexible, rigid) Cellulosic Polymers
	Polyesters	ADK CIZER HPN-3130 ( <i>ADK chemicals</i> )	PVC (rigid) - Wiring, Cables, Pipes, Packaging, Magnetic tapes,
		UPC Group-UN610 ( <i>UPC Group</i> )	Cellulosic Polymers, PS.
	Trimellitates	EASTMAN™ TOTM ( <i>Eastman Chemical Company</i> )	PVC (flexible) - Wiring, Cables, Packaging, Medical, Automotive.
		MEXICHEM TOTM ( <i>Mexichem</i> )	PVC – wiring, cables

#### 4.4. Impact Modifiers

The use of brittle polymers, such as polyvinyl chloride (PVC) and polystyrene (PS), was limited prior to the development of rubber-toughened polymers in the 1930s and 1940s. PVC has been toughened by the addition of small amounts of acrylonitrile rubber (NBR) and other elastomeric materials (Seymour, 1987). The traditional purpose of impact modifiers is to absorb the impact energy by inducing plastic deformation before crack initiation and propagation can happen. The general characteristics of such additives can be summarized as follows:

- Low  $T_g$ ;
- Effectiveness with minimum amount;
- Optimum particle size and particle size distribution;

- Good adhesion to the thermoplastic matrix.

There are basically two types of structure found in impact resistant polymeric systems for rigid polymer structures, which differ in their structure and fracture mechanism (Dufton, 1998):

- Spherical elastomer particles (ABS, MBS, acrylics);
- Honeycomb, network-type dispersed elastomeric phase.

Butadiene based graft copolymers constitute one of the most used families of impact modifiers. Their success in the market is due to their low  $T_g$  ( $-80^\circ\text{C}$ ). However, the presence of double bonds in diene polymers can induce thermal and oxidative degradation at the fabrication temperatures and under UV and oxygen exposure. Therefore, these effects must be minimized by the use of suitable antioxidants (Paul and Newman, 1978).

ABS modifiers. Daly (1948) produced acrylonitrile-butadiene-styrene (ABS) compositions in 1952 by the polymerization of styrene and acrylonitrile in the presence of polybutadiene to form a graft terpolymer. Each component contributes to the effectiveness of these materials as impact modifiers: the butadiene provides the soft rubbery phase while styrene and acrylonitrile provide the polarity necessary for interfacial compatibility with the polymer in which they are used. Other side features are also important: the butadiene chain is susceptible to UV degradation and requires protection while the acrylonitrile brings hardness and chemical resistance. In this frame, ABS polymers are engineering thermoplastics exhibiting good processability, excellent toughness and sufficient thermal stability. They have found applications in many fields, such as appliance, buildings and constructions, automotive electronic and many others.

MBS modifiers. The MBS (methacrylate-butadiene-styrene) impact modifiers are similar to their ABS counterparts and are typically produced either by copolymerization of styrene and methyl methacrylate in the presence of polybutadiene or by polymerization of methyl methacrylate in the presence of a styrene butadiene rubber. Also in this case the presence of butadiene makes these materials susceptible to UV degradation and limits their use to indoor applications. The absence of acrylonitrile enhances the clarity of the products but reduces the chemical resistance. MBS modifiers provide the required toughness to obtain polymers, such as PVC, suitable for both transparent and opaque packaging applications (impact resistant bottles, packaging films and sheets electrical trunking, etc) (Titow, 1986). MBS impact modifiers demonstrated a significant impact-modifying effect at low temperatures. However, in

many cases the addition a large amount of the MBS impact modifiers is required to enhance impact strength (Tseng and Lee, 2000).

Acrylic modifiers are probably the most widely used class of impact modifiers as they overcome the problems associated with the limited weather resistance, typical of ABS and MBS. This class of modifiers are typically graft terpolymers of methyl methacrylate-butyl acrylate-styrene or methyl methacrylate-ethylhexyl acrylate-styrene. Apart from the improved light stability these materials also offer high impact strength, good heat resistance and good thermal stability (Platzer, 1972).

A list of commercially available impact modifiers is reported in **Table 6**.

**Table 6 – Classification of commercially available impact modifiers.**

CLASSIFICATION	COMMERCIAL NAME (SUPPLIER)	APPLICATIONS
ABS – based	ELIX TM 150 IG ( <i>Elix Polymers</i> )	PVC, Rigid flexible, Cellulosic polymers
	BLENDX ® 101 ( <i>Galata chemicals</i> )	PVC rigid, Cellulosic Polymers
	Baymod® A 52 ( <i>Lanxess</i> )	PVC (rigid)
MBS,MABS – based	CLEARSTRENGHT ® E950 ( <i>Archema</i> )	PC, PVC, PBT, Polyesters
	PARALOID™ BTA-702S ( <i>Dow Chemicals</i> )	PVC rigid
	Kane ace™ B382 ( <i>Kaneka</i> )	PVC (rigid), pipes, packaging, films
Acrylic – based	ADD-AIM-100 ( <i>Add chem</i> )	PVC flexible
	DURASTRENGHT ( <i>Archema</i> )	PVC rigid
	Paraloid™ EXL-2314 ( <i>Dow Chemical</i> )	PC, PA, PBT,

#### 4.5. Compatibilizers

Polymer blending is a convenient route for the development of new polymeric materials, which combine the excellent properties of more than one existing polymer. This strategy is usually cheaper and less time-consuming than the development of new monomers and/or new polymerization routes, as the basis for entirely new polymeric materials. Polymer blending usually takes place in processing machines, such as twin-screw extruders (Korning et al, 1998). However, polymers with different structures are not always thermodynamically miscible and therefore cannot form homogeneous blends. The polymer in higher concentration will form a continuous phase and the polymer with a low concentration will be dispersed in the continuous matrix. However, the intermolecular adhesion between the continuous and the dispersed phase is very weak, resulting in poor mechanical performances of the blend.

Compatibilizers are macromolecular species exhibiting interfacial activities in heterogeneous polymer blends. Usually the chains of a compatibilizer have a blocky structure, with one constitutive block miscible with one blend component and a second block miscible with the other blend component (Paul and Newman, 1978). The compatibilization method can be divided into two categories (Utracki, 2002):

1. Addition of (i) a small quantity of a component which is miscible with both phases, (ii) a small quantity of copolymer whose one part is miscible with one phase and another with another phase, (iii) a large amount of a core-shell, multi-purpose compatibilizer-impact modifier;
2. Reactive compatibilization, which uses such strategies as: (i) trans-reactions, (ii) reactive formation of graft, block or lightly crosslinked copolymer, (iii) formation of ionically bonded structures, (iv) mechano-chemical blending that may lead to chains break and recombination, thus generating copolymers.

Strong environmental pressures are pushing industries to deal with recycle of waste polymers, particularly those used in packaging applications. Polyethylene (PE) in all its commercially available forms (high density HDPE, low density LDPE, linear low density LLDPE) currently represents more than 50% of the polymer recycling market. Along with polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC) and polyethylene terephthalate (PET), PE forms the major post consumer waste products concerning polymeric materials (La

Mantia, 1993). According to the desired polymeric blend, different types of compatibilizers are commercially available (**Table 7**).

**Table 7** – Commercially available compatibilizers for targeted blends.

<b>COMMERCIAL NAME</b>	<b>SUPPLIER</b>	<b>TARGET RESINS</b>
Ken-React® CAPS® L® 12/L (20% active pellet)	<i>Kenrich Petrochemicals, Inc.</i>	HDPE/PP Blends, Post-Consumer Recycle, Comm./Eng. Thermoplastics
Ken-React® CAPOW® L® 12/H (65% active powder)	<i>Kenrich Petrochemicals, Inc.</i>	HDPE/PP Blends, Post-Consumer Recycle, Comm./Eng. Thermoplastics
Ken-React® LICA® 12 (100% active liquid)	<i>Kenrich Petrochemicals, Inc.</i>	HDPE/PP Blends, Post-Consumer Recycle, Comm./Eng. Thermoplastics
Vistamaxx® propylene-based elastomer	<i>Exxon</i>	polyisobutylene (PIB), styrene isoprene styrene (SIS), polyvinyl chloride (PVC)
Exxelor polymer resins	<i>Exxon</i>	"most commonly used polar polymers and polyolefins"
Fusabond® M603	<i>Dupont</i>	PE/ PA, PE/ EVOH, PA/ EVOH/ PE
Fusabond® E226	<i>Dupont</i>	PE/PA, EVOH or PA
Bynel® 41E710	<i>Dupont</i>	PE/EVOH or PA/EVOH/PE
Fusabond® P353	<i>Dupont</i>	PP/PA or PP/EVOH/PP
Elvaloy® PTW	<i>Dupont</i>	(Recycle Stream) Polysters/ PE
Arkema	<i>Arkema</i>	Polyamide/polyolefin
Styrennics	<i>Kraton Polymers</i>	Polypropylene / Polystyrene or PPE, Nylon / Polyethylene or Nylon / Polypropylene, Nylon / Polystyrene or PPE, Polypropylene / Polyethylene

## 4.6. Dyes and Pigments

Plastics can possess a wide range of colours and plastics designers have exploited this particular property. In fact, some uses of plastics rely completely on the availability of a multitude of colours. When making a coloured product, dry colour, liquid colour or colour concentrates may be used. *Pre-colour* is a material that has already been compounded to a desired colour. *Dry colour* is a powdered colorant, which is often difficult to handle and leads to dust problems. *Liquid colour* is a colour in a liquid base, and finally *colour concentrate* is a high loading of colorant carried in a base-resin. With regard to their solubility, colorants fall into two classes, viz. dyes and pigments (Allen, 1971). The key distinction is that dyes are soluble in water and/or an organic solvent, while pigments are insoluble in both types of liquid media. **Table 8** lists a number of commercially available dyes and pigments.

### 4.6.1. Dyes

Organic dyes are often brighter and stronger than inorganic colorants. Dyes are the best choice for a totally transparent product. Even though some dyes have poor thermal and light stability, they still appear on the market in thousands of different formulations. (Richardson and Lokensgard, 1996). Azo dyes are numerically the most important class of dyes since more than 50% of all dyes listed in the Color Index are azo dyes. Covering all shades of color, azo dyes are used for dyeing textiles, paper, leather, rubber or even foodstuffs (Fleischmann et al, 2005). Unlike most organic compounds, dyes possess colour because they (Abraham, 1977):

- 1) absorb light in the visible spectrum (400–700 nm);
- 2) have at least one chromophore (colour-bearing group);
- 3) have a conjugated system, i.e. a structure with alternating double and single bonds;
- 4) exhibit resonance of electrons, which is a stabilizing force in organic compounds.

One of their main disadvantages is the high solubility in plastics, for which reason they are very prone to move or migrate often resulting in colour macroscopically changing. For instance, a red dye may migrate into a white part causing it to turn pink. Synthetic dyes cannot be commercialized unless they pose little health risk under end-use conditions. For this reason, the raw materials employed in the manufacture of synthetic dyes should not involve compounds known to pose health risks. This would include a large group of aromatic

amines (Ahlström et al, 2005) that are either cancer-suspect agents or established mutagens in the standard Salmonella mutagenicity assay (Prival et al, 1984).

#### 4.6.2. Pigments

Pigments can be used to colour any polymeric substrate but by a mechanism quite different from that of dyes, in that surface only colouration is involved unless the pigment is mixed with the polymer before fibre or moulded article formation (Zollinger, 1987).

##### Organic Pigments

Unlike dyes, which are present in polymeric substrates as either single molecules or small clusters, pigments are applied in the form of discrete crystalline particles well dispersed in the medium (Hao and Iqbal, 1997). Therefore, they must be mixed and evenly dispersed within the resin. Organic pigments provide the most brilliant opaque colours available. However, the translucent and transparent colours achieved with organic pigments are not as brilliant as those produced with dyes. Organic pigments can be hard to disperse, they tend to form clumps of pigment particles, that behaves as *agglomerates*, that cause spots and specks in the product. (Herbst and Hunger, 2004)

##### Inorganic Pigments

Most inorganic pigments are based on metals, e.g. oxides and sulphides of heavy metals such as titanium, zinc, iron, cadmium, and chromium. The easiest way to classify the inorganic pigments is to divide them in three classes: white pigments (mostly based on titanium dioxide), black pigment (carbon blacks) and coloured pigments. (Huckle and Lalor, 1995). The migration of organic pigments does not occur easily unless the plastic material is degraded by weathering or chemical attack. However the recycling process of the artefacts containing such additives represents a major concern considering that the heavy metals may leach out of the plastic artefact, and end up groundwater, posing a health hazard. For this reason the use of some of the listed metals is restricted (Järup, 2003).

Titanium dioxide (TiO<sub>2</sub>). Classified as a hiding pigment, as a result of its high refractive index, owes its dominant position to its ability to provide high degree of opacity and whiteness (maximum light scattering with maximum light absorption) and to its excellent durability and non-toxicity. The pigment can be produced in two polymorphic forms: rutile and anatase. The

rutile form with its higher refractive index and better weathering properties is much more important than the anatase form. However the anatase exhibits lower absorption in the blue-violet region of visible light below 420 nm and is frequently used, often in conjunction with fluorescent brightening agents (Diebold, 2003).

Carbon black (CB). Carbon black is widely used as a reinforcing filler to improve dimensional stability, as a conductive filler, ultraviolet light stabilizer, antioxidant to prolong the lifetime of rubber, and a pigment or colorant (Huang, 2002). CB is by far the most important black pigment, and is the second most used in terms of volume of all pigments employed by the plastic industry, ranking behind only titanium dioxide. In applications where their role is to provide a black colour, carbon black pigments exhibit high tinctorial strength and an outstanding range of fastness property at a relatively low cost. However, carbon black can adopt a number of other important functions when incorporated into polymers. The pigments excel in their ability to protect polymers against weathering, as a result of a combination of UV absorption and their capability to function at the particle surfaces as traps for radicals formed in the photodecomposition.

**Table 8** – Classification of commercially available Dyes and Pigments for polymer colouring.

<b>CLASSIFICATION</b>	<b>CHEMICAL COMPOSITION</b>	<b>COMMERCIAL NAME (SUPPLIER)</b>	<b>APPLICATIONS</b>
Soluble dyes	Antraquinone	Oil green 5602, Plast Blue 8514 ( <i>Arimoto Chemicals</i> ) Solvent blue 63 ( <i>Ningbo precise color</i> ), Plastone GS blue GP ( <i>Wuxi Ming Hui Int. Trading</i> )	PMMA, PS, PC, Cellulosic polymers, PA, Nylon
	Azo	Oil Red 5330 ( <i>Arimoto Chemicals</i> ), Solvent Red 2BS(SRI95) ( <i>Hangzhou Chemicals</i> ), Keyplast™ Scarlet BLZ ( <i>Keystone</i> )	PS, Other rubbers
Inorganic pigments	Iron Oxide	Eupolen® PE Brown 29-1505 ( <i>BASF</i> )	PP, PE, Polyolefins

	Molybdated Lead chromate	Lufilen ® Orange 30.2505 C6 (BASF)	PP, PE (Fibers, Yarns)
	Carbon Blacks	Black Masterbatch 045 black (Changzhou Plastic Modification)	PE, LDPE (Packaging, agriculture)
		JE- BLACK JE2100 (China synthetic rubber)	PVC, other rubber
		QualiBlack M13 (Ngai Hing Hong Coltec)	HDPE, LDPE, LLDPE, food contact
	Titanium dioxide	Polywhite ® 8000 (A. Shulman)	PE, PP, food contact
		Tronox ® R-FK-2 (Tronox)	PVC, Other thermoplast
Organic Pigments	Benzimidazol one	Akafast Carmine HF3C (Akafast), Benzimidazolone Red HF2B (Haining Light Industry)	PMMA, PS, PC, Cellulosic polymers, PA, Nylon
	Quinacridone	CINQUASIA® Red B RT-790-D (BASF)	PVC, PE, PP, PS, Cellulosic Polymers
	Mono Azo	Sinfast Yellow 2008-001 (Corporation), BENZIDINE YELLOW RN (Hangzhou Dimachema)	PS, PUR, PVC

### Special Effect Pigments

May be organic or inorganic compounds. Coloured glass is used in a fine powder form and it is a heat and light stable pigment for plastic, highly effective in exterior uses because of its colour stability and chemical resistance.

Fluorescent pigments. the striking brilliance of a fluorescent colour results when a molecule absorbs visible radiation and re-emits an intense narrow band of visible light at somewhat higher wavelengths, reinforcing the colour already present due to normal visible light absorption. Fluorescent pigments are formed using solid solutions at low concentration of fluorescent dyes in transparent resin finely ground. The main use in plastics are visual impact in toys, packages of safety applications (Christie, 1994).

Pearlescent pigments. The addition of these pigments to plastics give rise to a white pearl effect and a coloured iridescence. The most important pearlescent pigments are thin platelets of mica coated with titanium dioxide, which both reflects and transmit incident light. The sense of depth is given by the simultaneous light reflection from many layers of oriented platelets. Modulating the platelets thickness colours can be produced by interference phenomena (Pfaff, 2008).

Metallic pigments. The most important effect pigments without a layer structure are by far the metal effect pigments. They consist of flakes or lamellae of aluminium (“aluminium bronzes”), copper and copper-zinc alloys (“gold bronzes”), zinc or other metals. The metallic effect is caused by the reflection of light at the surface of the pigment particles. The so observed *luster* effect is decreased when the part of the light scattered at edges and corners of the particles increases. Larger particles are better reflectors leading to higher brilliance and brightness. The metallic appearance depends also on the orientation of the metal flakes in the application system, the particle shape, the transparency of the binder matrix, and the presence of other colorants. The required particle size of the pigments depends on the intended use and can vary from few micrometers (offset printing) to medium grades (10–45  $\mu\text{m}$ , automotive coatings, gravure and flexographic printing) and coarser grades (corrosion-inhibiting systems, plastics). The thickness of the flakes can vary from smaller than 0.1–1  $\mu\text{m}$ . Bronze pigments are introduced in plastics to reproduce a gold or copper effect (Maile et al, 2005).

#### **4.7. Bio-based additives and formulations**

For more than fifty years, plastic polymers have been the most practical and economical solution for several applications, as packaging, personal care, etc, replacing more traditional materials such as paper, glass and metals in many packaging applications, due to their low cost, low density, resistance to corrosion, ready availability, and outstanding physical properties. In fact, packaging accounts for approximately 40% of all plastic consumption.

However, nowadays the biggest environmental problem around plastics is their low recycling percentage. Whereas metal is recycled for 35%, paper for 30% and glass for 18%, plastic only reaches 3–4%. In the case of plastics the other options are energy recovery and landfill disposal, and in the specific case of Europe it can be said that around 50% plastics is not recycled, hence not valorised. Therefore, biobased, biodegradable polymer formulations are increasingly studied, and a large number of biodegradable polymers is already commercially available (Malinconico et al, 2014). In this regard, substitution of oil-based, synthetic additives with natural compounds acting as processing aids (Ambrogi et al, 2011), plasticizers (Battezzato et al, 2014), stabilizers (Bridson et al, 2015) or antibacterials (Arrieta et al, 2014) is also attracting interest aiming at manufacturing bio-based and biodegradable polymer formulations.

In **Table 9**, a list of commercially available bio-based alternative to traditional polymer additives is provided. As we can notice, a good percentage of products is based on vegetable oil derivatives (soy, palm, linseed, jatropha). The use of soy in industrial products has a long history: soap, drying oils in wood finishes, adhesives, and paper sizing (Schmitz et al, 2008). Soy products (oil, protein, meal) are now being used in a wide variety of products such as plastics and elastomers, paint and coatings, lubricants, adhesives, and solvents in addition to the well-established use of soy oil to make biodiesel. The United Soybean Board maintains a current listing of commercial products utilizing soy as a raw material or ingredient (Soy Products Guide).

As we mentioned in Section 4.3, plasticizers are added to polymers to facilitate processing and improve flexibility of otherwise rigid polymers, mainly PVC. Unfortunately, unmodified vegetable oils are largely incompatible with PVC. A modified soybean oil, e.g. epoxidized soybean oil (ESBO), results more compatible and provides an alternative to petroleum-based plasticizers for with PVC resin (Benecke et al, 2004). Another example is epoxidized methyl ester of soybean oil (soy-eFAME), which can be used as the sole plasticizer for PVC and other polymers or it can be blended with ESBO (Ghosh-Dastidar et al, 2013). Soy-based plasticizers can also be utilized in bioplastics such as poly(lactic acid) and polyhydroxyalkanoates (Mekonnen et al, 2013; Xu and Qu, 2009).

**Table 9** –Commercially available bio-based additives.

<b>CLASSIFICATION</b>	<b>CHEMICAL COMPOSITION</b>	<b>COMMERCIAL NAME (SUPPLIER)</b>	<b>APPLICATIONS</b>
Light Stabilizers/ UV absorbers	Mixed metal epoxidized soybean oil blend	AKEROSTAB® LT- 4803 (Akros Chemicals)	PVC (flexible): fibers, textiles.
	Epoxidized soybean oil	Vikoflex® Epoxidized vegetable oil (Archema)	Chlorinated Rubbers, PVC (flexible, rigid): Automotive, fibres, textiles, packaging
	Epoxidized linseed oil	Vikoflex® 7190 Epoxidized vegetable oil (Archema)	PVC (rigid, flexible)
	8(2,2,6,6- tetramethyl -4- piperidyl) sebacate	CAPLIG 770	PE, PP
Heat Stabilizers	Epoxidized soybean oil	Baerostab® LSA (Baerlocher)	PVC (rigid)
	Barium salt of a technical lauric acid	Ligastab BAL (Peter Greven)	PVC
Flame retardants	Polyhydric alcohol	Charmor™ PM40 Care (Perstorp)	
	Crestl diphenyl phosphate	Kronitex ® COP (Great Lakes)	Natural rubber, PVC
Plasticizers	Esther of di-fatty acid	SYNCROFLEX™ 3019 (Croda)	PVC, Other rubbers
	Fatty acid ester	DOMPLAST BIO DEN (Domus chemicals)	Natural rubbers, Chlorinated rubber
	Acetyl 2-ethylhexyl citrate	CITOFOL® AHII (Jungbunzlauer)	PVC: wiring cables, automotive

Inorganic pigments – Titanium dioxide	TiO <sub>2</sub>	Polywhite ® 8100 ES	PE, PP
Organic pigments		Advaitya – Pigment Green 7 ( <i>Advaita Dye Chem</i> )	Other rubbers

New business development of bio-based chemicals does have its risks and difficulties. Differentiation is often focused on cost and environmental profiles which can require a significant advantage to drive change, and the barrier to entry for substitutes may be low. However, chemicals with new functionality targeting substitution of conventional materials may have advantages of long-term low cost compared to petro-based materials, enabling bio-based claims due to renewable feedstock source, and opportunities to change the end-of-life options for applications (Hatti-Kaul et al, 2007).

Therefore, a dramatic increase in adoption of bio-based additives is expected in the near future, able to boost growth in the global additives market.

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