PolyCE

Post-Consumer High-tech Recycled Polymers for a Circular Economy
Project Duration: **01/06/2017 - 31/05/2021**

Deliverable No.:	**5.1**
Deliverable Title:	**Material matrix with the predominant polymers and their additives in PCR polymers from WEEE**

Version Number:	**001**
Due Date for Deliverable:	**28/02/2018**
Actual Submission date:	**26/02/2018**
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Deliverable Type: **R**
    R   = Document, report
    DEM = Demonstrator, pilot, prototype, plan designs
    DEC = Websites, patent filing, press & media actions, videos, etc.

Dissemination Level: PU
    PU   = Public
    CO   = Confidential, only for members of the consortium, including the Commission Services

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Summary

This deliverable comprises a systemic categorization of the plastic types present in WEEE at EoL. This will form the basis for the technical strategy development for re-use of these PCR.
A previous study by IZM on plastics types in televisions – a representative product category for WEEE – showed that the predominant polymers are ABS, PC, PC-ABS blends and HIPS. Within this WP, this list will be checked against the broader product scope within WEEE and accounted polymers will be classified according to their type (polyolefins, polyamides, styrenics, polycarbonates) and the additives they typically contain (UV-stabilizers, flame retardants, pigments, fillers, plasticizer). A systematic estimation will be made of the degree to which these additives remain functional, based on the chemical nature of their function. For example, an oxygen scavenger type stabilizer can only perform its function once, as it relies on bonding with oxygen present faster than the master polymer, thus protecting the polymer matrix. Once it has bonded, its functionality is gone and new stabilizer will have to be added for re-use. On the other hand, most plasticizers retain their functionality, as they are short mobile polymer chains that position themselves between the longer chains of the master polymers. No primary bonds are made and the plasticizer remains active when recycled. To this end, a determination table is made, containing data of all additives (anti-oxidants, fire retardants and fillers), that will be used in further tasks as a guide for restabilization and improvement of properties through compounding. The table is a condensed version of the report included below.

Content

1   Introduction

The production of plastics has risen from 1,5 million tonnes in 1950 to a stunning 335 million tonnes in 2016 (60 Mt for Europe). After China, the leader on global plastic materials production which accounts for 29% of the global plastic materials production, Europe and NAFTA closely follow with 19 and 18% of the global amount respectively. Here, in Europe, almost 80 % of the plastic demand is concentrated in six of the larger European countries and Benelux with Germany taking the lead having a demand of 24,5% (followed by Italy with 14,2% and France with 9,6%). Together they account for a demand good for 49,9 Mt plastics, designated for market sectors of which packaging (39,9%), building and construction (19,7%), automotive industry (10%) and electrical and electronic equipment (EEE, 6,2%) account for the largest demands (see Figure 1-1 [1]).
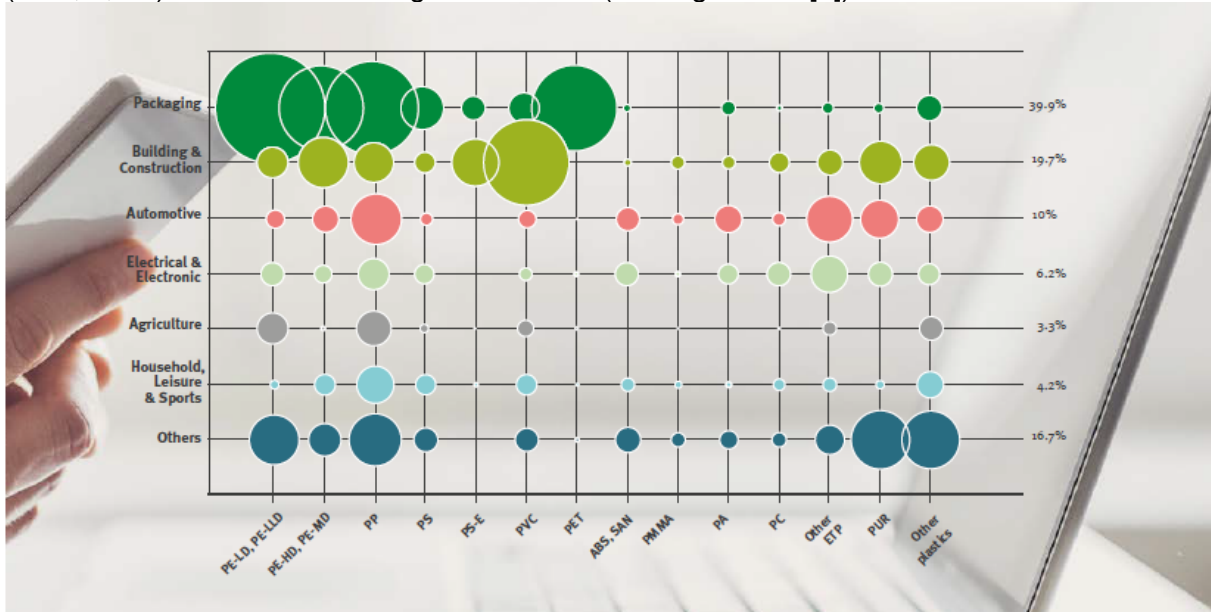

Figure 1-1: European plastics demand by segments and polymer types in 2016, source: PlasticsEurope Market Research Group (PEMRG) and Conversion Market & Strategy GmbH [1]

The electrical and electronic equipment sector or EEE sector is growing at an increasing pace due to our rapid economic growth and growing demand for consumer goods [2]. The rapid development of the EEE technology combined with the lower life cycle of most present-day products poses a significant issue as far as their disposal is concerned. In 2014, a world production of 41,8Mt of WEEE (Waste EEE) was estimated of which 11,6 Mt in Europe. This amount is expected to increase even more up to 50 Mt in 2018 [3]. In view of this environmental problem concerning the management of these WEEE a legislation was drafted to improve reuse, recovery and recycling of WEEE. Thanks to the European Directive (2000/53/EC) and the WEEE directive (2002/96/EC) at least 70-80% of materials of end-of-life vehicles (ELV) and WEEE have to be recovered in the form of materials and/or energy [4], [5]. This means that a large amount of polymers reenters the market for reprocessing. A study by Achilias et al. [4] demonstrates that a typical WEEE fraction contains 20-30% plastics. The WEEE plastics are composed of different resins such as the styrenics (PS, HIPS, ABS, SAN), polyolefins (HDPE, LDPE, PP), engineering plastics (PC, POM, PUR, PA and PVC) and thermosets. The general composition of the plastic fraction itself is depicted in Figure 1-2. As can be seen from this graph the main constituents of the WEEE plastic fraction are ABS, high impact polystyrene (HIPS), polycarbonate (PC), PC/ABS and polypropylene (PP). For this reason these will form the main research topics in this study. To better understand and anticipate the performance of the products made by these recycled materials further investigation in regards to the changes in properties of these materials during recycling still has to be done. The main problem with these materials is the large

variability in the product composition due to the presence of polymer mixtures, additives or contaminations. A close intermingling of materials, as well as their use in sometimes very small quantities makes it quite infeasible to separate these streams entirely. Furthermore, WEEE can contain hazardous pollutants like heavy metals, polychlorinated biphenyls or PCBs or brominated fire retardants (BFR). The restriction of hazardous substances or RoHS Directive (and by extension the REACH Directive (EC 1907/2006)) deals with these hazardous substances and determines which ones are to be phased out or severely limited in their concentration levels in order to minimize the impact of WEEE on the environment [6]. Conventionally, these waste streams are separated as they are not suitable for mechanical recycling. The separation of the non-hazardous products from the recyclable products itself can occur via XRF, FTIR or solution based via the patented Creasolv® process [7], [8].
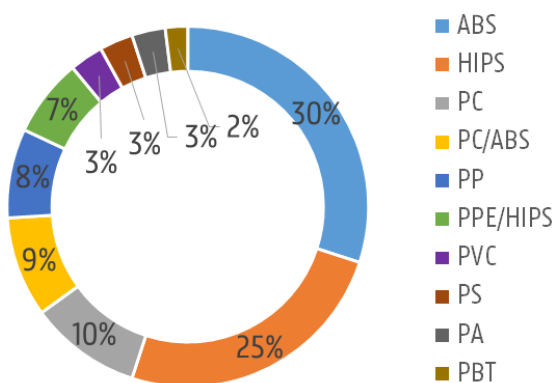

Figure 1-2: Typical WEEE composition according to Achilias et al. [4]

In addition, it is well known that polymers are subject to degradation, both by daily use as during processing of the materials [9]. In its everyday use, polymers are susceptible to photo-degradation, oxidation, leaching of various additives (e.g. plasticizers) and other weathering phenomena. These effects are dependent on the lifetime of the plastic and can furthermore be exalted during melt reprocessing operations. This is reflected in changes of material properties such as mechanical, crazing, cracking, discoloration, phase separation or delamination [10]. As a result, the properties of the recycled materials are typically worse than that of the virgin material.

In view of these facts, a good sourcing method is indispensable in the conversion process of waste raw materials into new plastic products. Proper collection schemes must be optimized in order to acquire valuable raw materials of reasonable purity in EE appliances and ELV. Cleaning, regrinding and sorting of the waste stream are strict necessities in order to purify the stream. Furthermore, separation based on color can astonishingly enhance the value of these recyclables. Next, post-consumer plastics are unusable in the form they are collected; the material must be processed again by e.g. extrusion to commercial grade pellets. To ensure that the material will not further decay by the processing method a restabilization must occur through additivation. The most commonly used additives used for this purpose are stabilizers such as antioxidants and light stabilizers, chain extenders or repair systems and compatibilizers like impact modifiers [11].

The PolyCE project aims to construct a circular plastics value chain in which WEEE plastics are recycled and restabilized for specific applications. This report will summarize the possible additives that can be found in WEEE plastics and how these polymers can be stabilized for further use. In a first chapter, the antioxidants are discussed, both thermo-oxidative as photo-oxidative stabilizers are discussed in this regard. Next, some attention is drawn to the importance of compatibilizers to coop with possible cross contaminations that one can encounter while reprocessing WEEE plastics and chain extenders to as a possible way to

repair the damage in polymer chains by degradation. Further, fire retardants are elaborated with their mechanism and problematics as there exists a prominent shift nowadays to the non-halogenated flame retardants. Finally, possible fillers are discussed in order to enhance certain properties of the WEEE plastics and in so, compensate or improve the difference in properties compared to their virgin alter ego.

2 Anti-oxidants, UV-and thermal stabilizers

Additives are universally incorporated in plastics. In end-of-life plastics a certain amount of degradation has occurred in the plastics depending on their use and lifetime. The residual level of stabilizers is usually depleted or insufficient on its own and must be replenished in order to protect the recycled material from further oxidative damage. Most of the additives for restabilization of the recyclates are based on hindered phenols, hindered amines, phosphites or sulfites and co-stabilizers like acid scavengers [11], [12].

Pospíšil et al. [13] made an extensive overview on the stabilization of recycled plastics by upgrading them in a melt blending process with suitable additives. They stress the importance of the history of the plastic as the application determines the amount of weathering the material has undergone. Structural changes take place by reprocessing, heat ageing or weathering that differentiate the WEEE plastic from its original virgin form. The gravity of the changes is dependent on the service time of the plastic and the aggressiveness of the environment. Careful selection and analysis of the plastic waste is incumbent for reuse into new applications. Traces of halogenated flame retardants, metals from printing inks or pigments, surfactants or fillers can sensitize degradation.

Determining the amount of stabilizers in the recycled polymers remains a challenge. Most commonly analyses are performed on the residual content of phenolic antioxidants and phosphite or sulfite co-stabilizers and light stabilizers. Successful analyses of residual additives using extraction methods like Soxhlet extraction, microwave-assisted/accelerated solvent extraction or supercritical carbon dioxide (sc-CO_2) coupled with analytical techniques like high-performance liquid chromatography (HPLC), coupled gas chromatography/selective ion mass spectrometry (GC-MS), Fourier transform infrared spectroscopy and supercritical fluid chromatography as well as the oxidation induction time (OIT) [8], [13], [14].

2.1 Thermo-oxidative stability

Polymers undergo auto-oxidation which can be described as an autocatalytic free-radical chain mechanism exhibiting the initiation, propagation and termination reactions. The general oxidation pathway as described in the literature [15]–[18] is written in Equation 1 to 9. Radicals can be formed by heat, mechanical shear, light or impurities. The high mechanical forces, especially on the more entangled (amorphous) polymer molecules, are said to lead to C-C chain scission giving macro alkyl radicals [12]. These can then rapidly react with oxygen forming peroxy radicals (Equation 2) which can in turn abstract a hydrogen atom from the polymer chain forming hydroperoxides (Equation 3). The latter can subsequently decompose into two new free radicals (Equation 4) which can initiate further reactions (Equation 5Equation 7&Equation 9). The general oxidation pathway together with possible inhibition pathways are depicted in Figure 2-1. Antioxidants can inhibit oxidation in two ways: either by terminating the primary oxidants (i.e. primary antioxidants or radical scavengers) or by decomposing the formed hydroperoxides, these are known as secondary antioxidants or hydroperoxide decomposers (Equation 10-Equation 12).

The main operating principle of the primary antioxidants rests on the transfer of the radical to a stable molecule that does not react further with the polymer. This is typically done through hydrogen atom donation from a stable molecule -usually hindered phenols or hindered amines- to the peroxy, alkoxy or hydroxyl radical. The phenoxy radical in this case is stable

due to its ample resonance states (see Figure 2-2) and does therefore not abstract any hydrogen atoms from the polymer chains. The activity of the Hindered Amine Stabilizers (HAS) is based on their ability to form nitroxyl radicals which are in turn efficient radical scavengers. The secondary antioxidants undergo oxi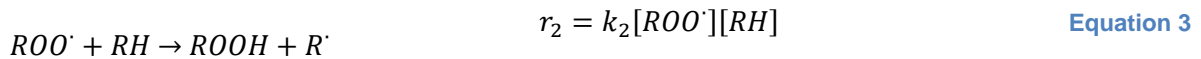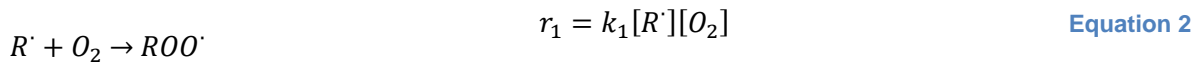dation/reduction reactions with the hydroperoxides forming stable products like harmless alcohols therefor inhibiting further propagation reactions. The latter type includes phosphites, sulfites and thioesters. Typically, a combination of primary and secondary antioxidants is used for a synergistic effect with superior performance. Metallic impurities such as titanium, aluminum, chromium or iron (noted as M^{n+} in Figure 2-1) can act as a source for alkyl radical formation during processing and life cycle of the product. Therefore these metals should be deactivated prior to use.

Initiation
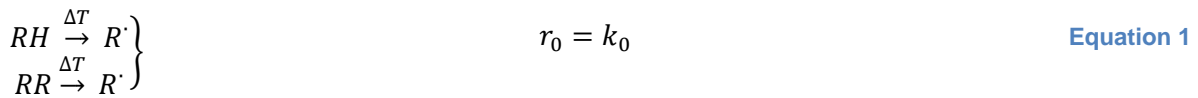
$$RH \xrightarrow{\Delta T} R^{\cdot} \brace RR \xrightarrow{\Delta T} R^{\cdot}$$

$r_0 = k_0$ **Equation 1**

Propagation

$R^{\cdot} + O_2 \rightarrow ROO^{\cdot}$

$r_1 = k_1[R^{\cdot}][O_2]$ **Equation 2**

$ROO^{\cdot} + RH \rightarrow ROOH + R^{\cdot}$

$r_2 = k_2[ROO^{\cdot}][RH]$ **Equation 3**

Oxidation

$ROOH \rightarrow RO^{\cdot} + HO^{\cdot}$

$r_3 = k_3[ROOH]$ **Equation 4**

$RO^{\cdot} + RH \rightarrow ROH + R^{\cdot}$

$r_4 = k_4[RO^{\cdot}][RH]$ **Equation 5**

$HO^{\cdot} + RH \rightarrow H_2O + R^{\cdot}$

$r_5 = k_5[HO^{\cdot}][RH]$ **Equation 6**

Chain scission

$RO^{\cdot} \xrightarrow{\beta-scission} R' = O + R'''$

$r_6 = k_6[RO^{\cdot}]$ **Equation 7**

Termination

$2ROO^{\cdot} \rightarrow R = O + O_2 + ROH$

$r_7 = k_7[ROO^{\cdot}]^2$ **Equation 8**

$RO^{\cdot} + RO^{\cdot} \rightarrow ROOR$

$r_8 = k_8[RO^{\cdot}][RO^{\cdot}]$ **Equation 9**

Inhibitor reactions

$ROO^{\cdot} + InH \rightarrow ROOH + In^{\cdot}$

$r_9 = k_9[ROO^{\cdot}][InH]$ **Equation 10**

$RO^{\cdot} + InH \rightarrow ROH + In^{\cdot}$

$r_{10} = k_{10}[RO^{\cdot}][InH]$ **Equation 11**

$HO^{\cdot} + InH \rightarrow H_2O + In^{\cdot}$

$r_{11} = k_{11}[HO^{\cdot}][InH]$ **Equation 12**
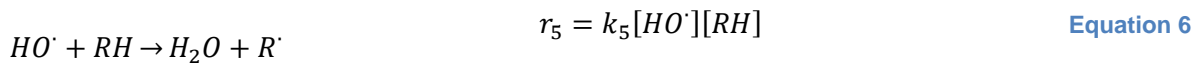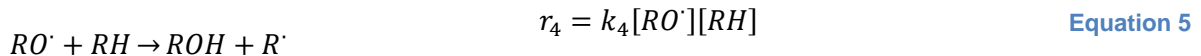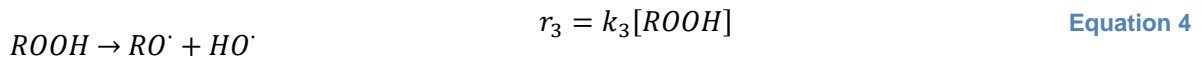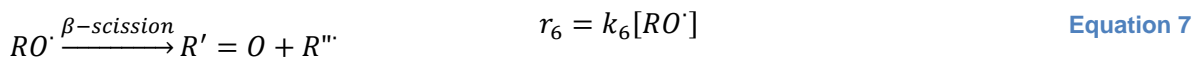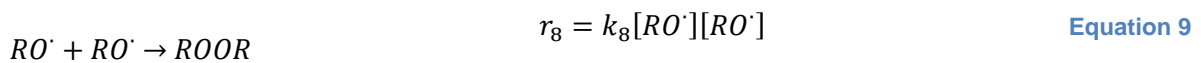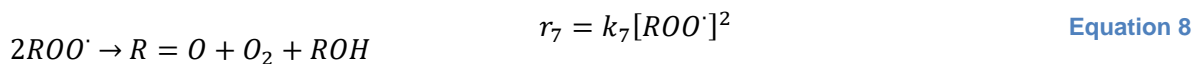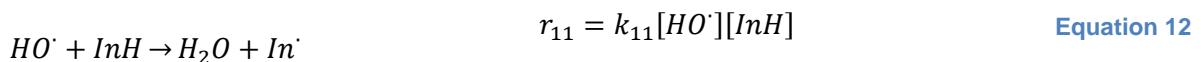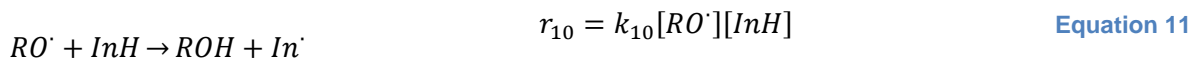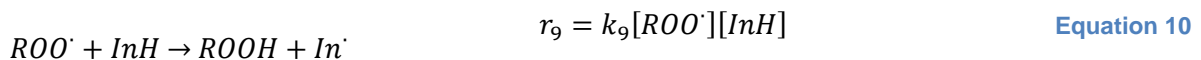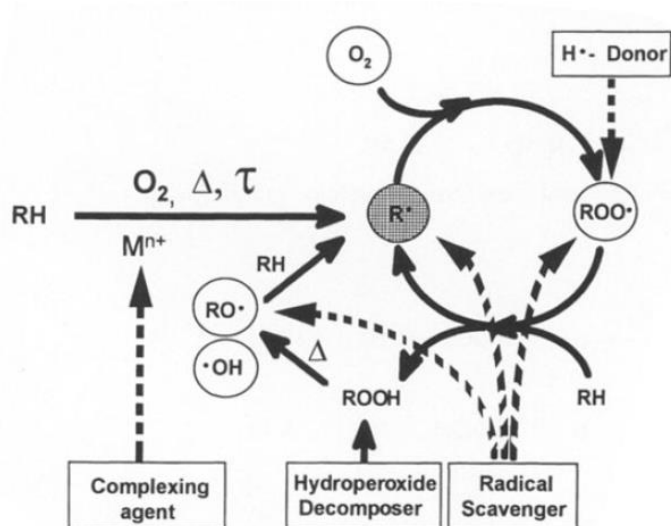
Figure 2-1: The cycle of auto-oxidation and its inhibition pathways according to H. Zweifel [12]
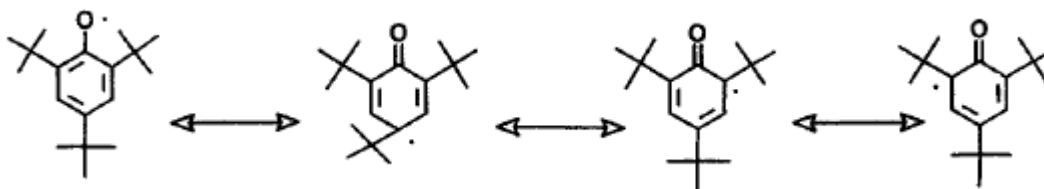
Figure 2-2: Resonance states of a fully hindered phenoxy radical

Neal J. Earhart [16] reports on the use of 2-2'-methhylene bis(4-methyl-6-t-butylphenol) and octadecyl 3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate (ODBHP) as common primary AO and tris(nonylphenyl)phosphite (TNPP) and thioesters as dilaurylthiodipropionate (DLTDP) and distearylthoidipropionate (DSTDP) as secondary AO in ABS resins. These are common anti-oxidants which have also been known to be used in other thermoplastics and elastomers like PC and EPDM [15]. Most common UV-stabilizers and anti-oxidants are also noted in the 'UV degradation and Stabilization' handbook (2nd edition) by George Wypych [19] and 'Stabilization of polymeric materials' by Hans Zweifel [12].

The use of the hindered phenols has in the last decade called the attention to the possible health and environmental hazards linked to the decay of these products. As a result the focus has shifted somewhat to natural anti-oxidants as potential stabilizers for polymer materials. Kirschweng et al. [17] has done extensive research on the subject summarizing the main classes of natural anti-oxidants: the carotenoids, flavonoids, curcuminoids, lignins and tannins, polyphenols and phenolic polymers which have a smaller risk of forming harmful byproducts during their use than their synthetic counterparts. However, the use of natural anti-oxidants is still in its infancy, the only currently used product being α-tocopherol, a substance used in UHMWPE for stabilization of medical devices [17].

2.2 Photo-oxidative stability

Most commercial polymers like PP of PE do not absorb VIS light as their absorption bands are below the lower limit of 200 nm for visual light. Unsaturations and the presence of other chromophore moieties present in polymer chains however makes them prone to photo-oxidation and the induced radical reactions that follow in the presence of oxygen. For

example, the polybutadiene phase in ABS, HIPS, rubber modified PVC or ABS-PC blends, are prone to photo-oxidative degradation due to their tendency to absorb UV-VIS radiation because of the C=C double bounds present in the structure. Furthermore, other chromophores like the aromatic group present in the SAN fraction (also present other commodity polymers like PS, PC & PET) and carbonyl functions in PA, PC, PET, PMMA and others absorb in the UV-region promoting the photo-oxidation [12]. In the presence of oxygen this effect often result in discoloration and embrittlement with subsequent loss of impact properties due to light-induced reactions such as photolysis of the hydroperoxides [20]. With increasing temperature, photo-oxidation may overlap with thermo-oxidation in which case both phenomena may contribute significantly to the overall degradation process. In the case of thermo-oxidative degradation hydroperoxide groups are formed which absorb in the UV region leading to internal conversions with the formation of carbonyl groups and accompanied chain scission [12]. Furthermore, any contaminants like catalyst remnants or atmospheric pollutants such as aromatic hydrocarbons that are absorbed in the polymer can further contribute to the photo degradation of the polymer.

There are several ways to impede the photon induced degradation which are depicted in Figure 2-3. UV-absorbers incorporated in the polymer can absorb the penetrating light and deactivate it by transforming it to thermal energy in a radiationless process. They are typically characterized by high extinction coefficients in the 300-400 nm spectral range. Most currently used UV-absorbers are o-hydroxybenzophenones, 2-(2-hydroxyphenyl)benzotriazole, 2-(2-hydroxyphenyl)-1,3,5-triazine, oxanilides, salicylates and cinnamates. Their principle mechanism is based on an intramolecular hydrogen bond transfer, this process is called Excited State Intramolecular Proton transfer (ESIPT) and is depicted in Figure 2-4 for o-hydroxybenzophenone. It is postulated that the benzophenones can also deactivate through the formation of a triplet state by an Inter System Crossing (ISC). The UV-absorber in this case remains functional as long as the tautomerisation can take place. As these are phenolic structures, they are therefore also capable of undergoing reactions with the peroxy radicals and act as hydrogen atom donors (i.e. radical scavengers), losing their UV-absorbing functionality.
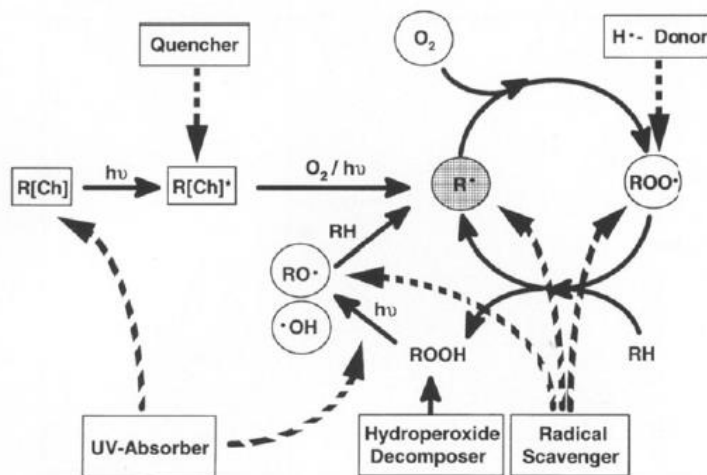

Figure 2-3: General scheme of inhibition of photon induced degradation according to Hans Zweifel [12]
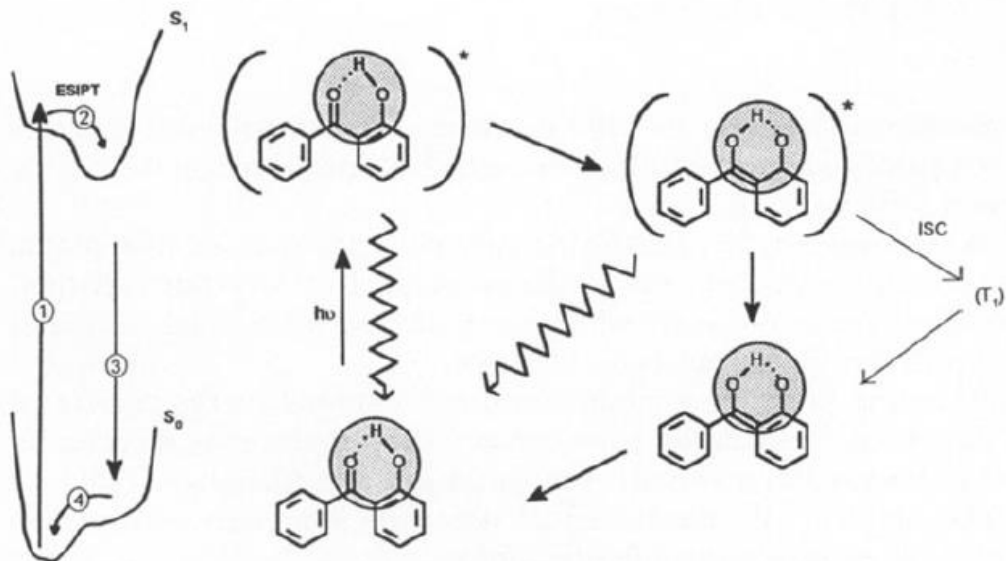
Figure 2-4: Energy states involving o-hydroxybenzophenones with harmless dissipation of energy by intramolecular proton transfer [12]

On the other hand, quenchers can deactivate the excited chromophores such as carbonyl groups or other impurities formed by thermo-oxidation. Nickel-chelates are one of the most investigated groups in this regard. Thought their absorption in the 300-400 nm region is quite small; their main function is based on an energy transfer process of the excited chromophores to the quencher which then deactivates by a radiation-free process.

Finally, analogous to the thermo-oxidative radical scavengers, radical scavengers like Hindered Amine Stabilizers (HAS) and hydroperoxide decomposers can be used for the inhibition of the auto-oxidation radical chain reaction. Sterically Hindered Amines also known as sterically Hindered Amine Light Stabilizers (HALS) are very efficient stabilizers against photo induced oxidation. Often, because these structures display a phenolic character, combinations of UV absorbers with sterically hindered amines as scavengers of peroxy radicals are used for maximum effect. One should be aware of possible antagonistic effects when combining thiosynergists with HAS. These secondary AO cause hydroperoxide decomposition forming sulfuric acids which in turn can form ammonium salts with the sterically hindered amines. The formation of these salts should be avoided as it drastically reduces the photo stabilizing effect [12]. Similarly, halogen containing flame retardants can form halogen containing acids by light induced reactions which in turn form ammonium salts. Finally, Kulich et al. state [20] the best protection against photo-oxidation to apply a protective coating a of weatherable polymer like polymethylmethacrylate (PMMA) or acrylonitrile-styrene-acrylate (ASA).

3 Impact modifiers and chain extenders

Almost all post-consumer waste streams suffer from the same problems; pure post-consumer mono streams are rarely found, meaning lots of impurities from residual waste and cross contaminations from other polymers are ever-present. Additionally, due to the degradation phenomena these waste plastics typically show a lower elongation at break and a reduced impact resistance. The presence of incompatible polymer components, be it of the same polymers of different molecular weight due to degradation or contaminations by polymers of different type, causes poor dispersion of the components. This results in low interfacial adhesion which negatively affects the physico-mechanical properties. To improve the interfacial adhesion compatibilizers can be added which minimize the interfacial tension

through the presence of branched or block copolymers whose segments can interact physically or chemically with the individual components. These molecules maneuver between the immiscible blends by preferentially locating themselves at the interface of both phases and in doing so increase the compatibility through interpenetration and entanglements at the polymer/polymer interface [21], [22]. In doing so, a uniform (and small) distribution of the dispersed phase is obtained with a stable morphology. By adding an elastomer as impact modifier to the recycled polymer, the impact resistance is increased, preventing severe crazing and propagation of cracks. The underlying mechanism being the dissipation of stress through the elasticity of the elastomers [23]–[26]. Three main compatibilizers groups can be distinguished based on their composition and interactions with the heterogeneous blend:

1. *A block or branched copolymer: built out of different polymer segments of which one is more compatible with the matrix phase whilst the other is more compatible with the dispersed phase (Figure 3-1, left). In this case the easiest and more conventional way is the use of a block copolymer consisting of the polymer chains of either blends, e.g. a block copolymer of PP and PE in mixed PP/PE blends. The elastomer chain can also consists of a block-copolymer chain like styrene-ethylene-butylene-styrene (SEBS) or a polyolefin chain (POE).*
2. *Non-reactive polymers containing polar groups: in this case the interfacial tension is reduced by the secondary intermolecular interactions such as Van de Waals, dipoles or hydrogen bonding interactions (Figure 3-1, middle). Examples of such compatibilizers are polymethyl methacrylate (PMMA) and polycaprolactone (PCL).*
3. *Reactive polymers which have a reactive group that will covalently bond to the dispersed phases' functional groups whilst the polymer backbone is compatible with the matrix phase. Well known examples are polypropylene grafted with maleic anhydride (PP-g-MA) or PP grafted with glycidyl methacrylate (PP-g-GMA). Acrylic acid has also been known to give good compatibility [21], [22], [26] (Figure 3-1, right).*
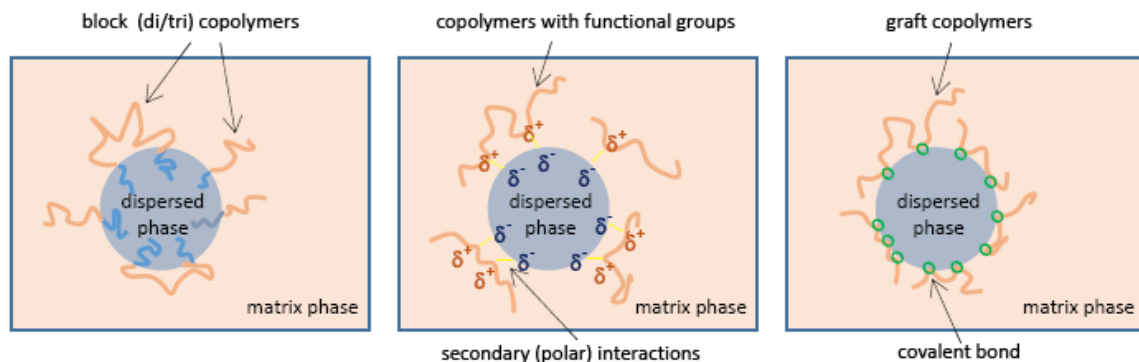
Figure 3-1: (left) block copolymers, (middle) copolymers with functional monomers and (right) graft copolymers. Illustration thanks to [27]

Van Bruggen et al. [26] studied the use of a SEBS-g-GMA compatibilizers on a blend of PP/PET. The compatibilization mechanism is represented in Figure 3-2 to elucidate the micrographs in the study indicating PP/PET with and without compatibilizers in Figure 3-3. The effect of the interactions brought about by the compatibilizers can be seen in the micrographs in Figure 3-3 with a reduction in the PET spheres from 1-3 µm diameter without compatibilizers to a diameter below 1 µm with compatibilizer. The change in morphology has its effect on the mechanical properties [26]. More specifically to the field of WEEE, Van Damme et al. [23] investigated the use of SEBS-g-MA on rABS and, based on a study of H. Yang [28], examined the use of rPP as impact modifier. The use of recycled polymers to

optimize the recycled polymers' properties sheds an interesting light on reducing the ecological footprint even more. Chain extenders were examined by Wang et al. [29] as an alternative to upgrade the recycled ABS. Thermoset fractions present in WEEE like the phenolic or epoxy resins in circuit boards can currently only be mechanically recycled by pulverization and subsequent use as filler or deactivator in both thermosetting and thermoplastic resins [12], [30]. The addition of compatibilizers with an elastomeric segment has a counter side however; rubber toughening of polymers frequently goes together with a reduction of modulus and tensile strength. Luckily, the percentage added elastomer only needs to be a small fraction in order to obtain adequate impact resistance without a major effect on tensile strength and modulus. Figure 3-4 demonstrates this for a specific case in which rABS is stabilized using different weight percentages for SEBS or rPP as impact modifiers [23].
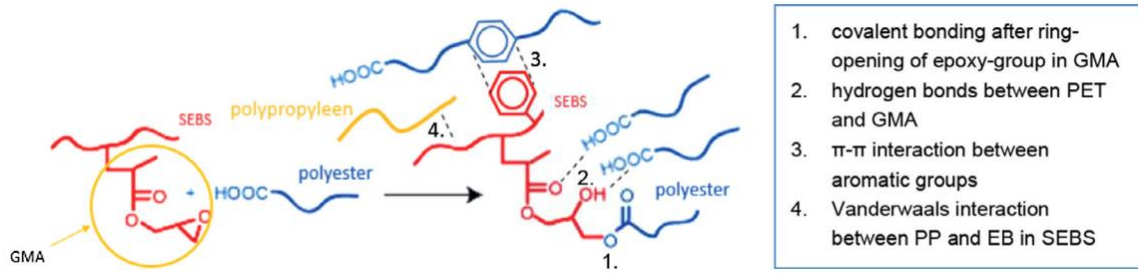
Figure 3-2: Interactions between the SEBS-g-GMA compatibilizer (red) and the PP (yellow)/ PET (blue) blend [22]

1. covalent bonding after ring-opening of epoxy-group in GMA
2. hydrogen bonds between PET and GMA
3. π-π interaction between aromatic groups
4. Vanderwaals interaction between PP and EB in SEBS

Figure 3-3: Left: Incompatible PP/PET 85/15 blend without compatibilizer. Right: the same PP/PET 81/15 blend with 2,5 wt.% SEBS-g-GMA [26]
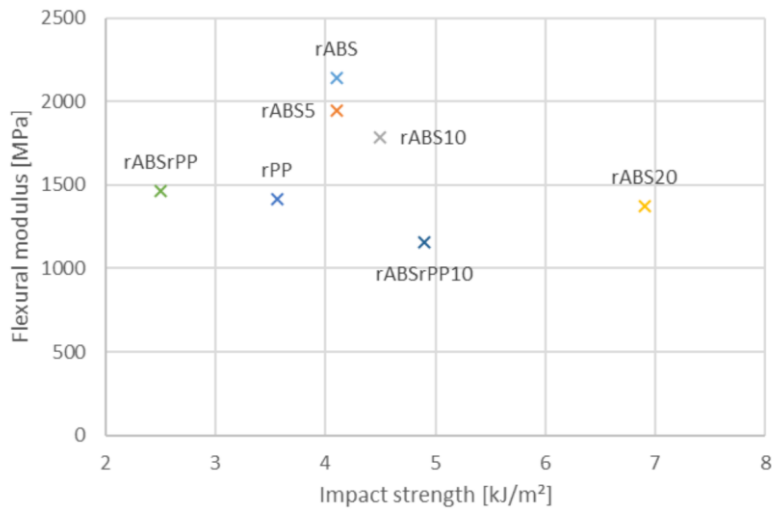
Figure 3-4: Increasing impact strength with decreasing flexural modulus for rABS from WEEE and ELV stabilized with either SEBS or rPP. The weight percentage for SEBS is always indicated after the 'ABS' annotation while rPP was always added in 50 wt.%. Data from from [23]

At the end-of –life of EEE, plastics have undergone all sorts of structural changes due to their environment. This is also reflected in the rheology of the plastics, i.e. the viscosity. A decrease or increase in viscosity is therefore a good indication of degradation of the polymer by chain scission or chain deformations. These alterations are the cause for the different processing conditions of the WEEE plastics compared to their virgin alter ego. In order to restore these affected by chain scission and restore the characteristics, chain extenders can be used. It is a process fairly known in the PET recycling process yet the principle can also be used for other condensation polymers such as polyamides, polyurethanes, polycarbonates and their blends. Most used additives in this regard are the dianhydrides, bis(oxazolines), bis(hydrooxazine), carbodiimides, diepoxides and diisocyanates molecules [31], [32] yet multi-functionalized extenders also exist to increase the effectiveness of the reaction [33]. These typically operate by connecting the end groups of two polymer chains, reforming one large chain. This process can also be adopted for the vinyl polymers using radical polymerization with a monomer and suitable initiator like a peroxide through reactive extrusion or by electron beam irradiation in solid phase, albeit this process is less controlled for the formation of cross-linked and branched polymers [27], [34].

4 Case studies

4.1 Acrylonitrile-Butadiene-Styrene

ABS is a two phase system consisting of a thermoplastic styrene acrylonitrile (SAN) continuous phase and a dispersed elastomeric butadiene (PB) phase. The latter being responsible for the high impact properties associated with ABS materials. In the continuous phase the styrene component contributes to the rigidity and processability of the material while the acrylonitrile component contributes to the chemical resistance [20]. As the SAN phase is fairly brittle, it is the rubber phase that accounts for the impact toughness, the extent of which is dependent on the phase volume fraction, particle size and distribution and structure. Typical commercial ABS resins have a rubber con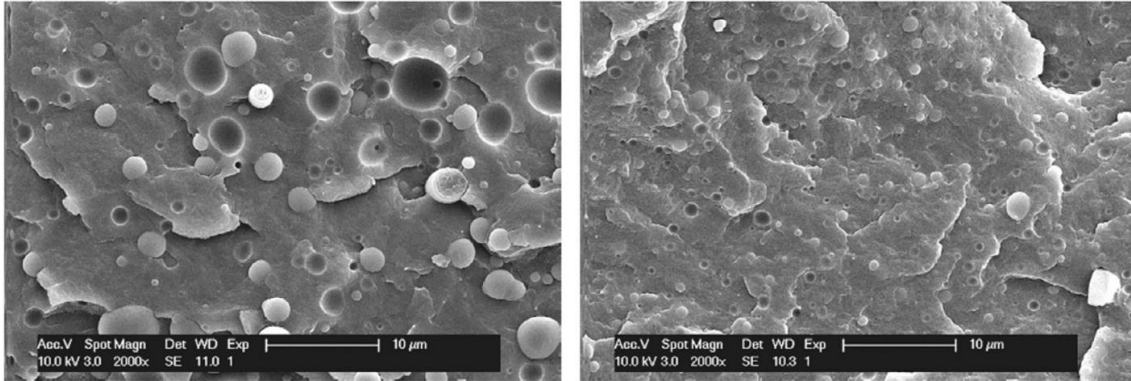tent of 10 – 35 wt.% and particle sizes ranging from 50 to 2000 nm [20]. The effect of the SAN matrix composition also has a significant influence on the material properties. Kulich et al. [20] summarize these properties in an extensive review remarking that the AN content plays an important role in stress-cracking resistance which improves with a higher content of the latter. Additionally, a higher AN content improves creep and fatigue resistance as well as crazing resistance. Typical ABS resins contain a SAN phase with 20-30 wt.% AN content. Here, attention should be drawn to the AN content in the grafted SAN as a difference of more than 5% in AN content between the grafted SAN and matrix SAN could result in immiscibility and thus partial phase separation. The rubber particles itself furthermore have an effect on surface gloss with a decreasing gloss noticed for large particles or agglomerates of small particles. Standard ABS grades are opaque because of a mismatch in refractive indexes between the SAN and PB phase yet can be made transparent by matching these refractive indexes through the use of comonomers like methyl methacrylate.

There are three basic mechanisms for the thermo-oxidation of ABS: (1) degrafting caused by the oxidation of the SAN-PB graft site (Figure 4-1**b**), (2) chain scission in the PB phase (Figure 4-1**a)** and (3) peroxide-induced crosslinking of the PB [16], [35], [36]. Degradation by chain scission is said to occur to a large extent by β-scission of an alkoxy radical (see Figure 4-1) and by thermo-mechanical degradation.
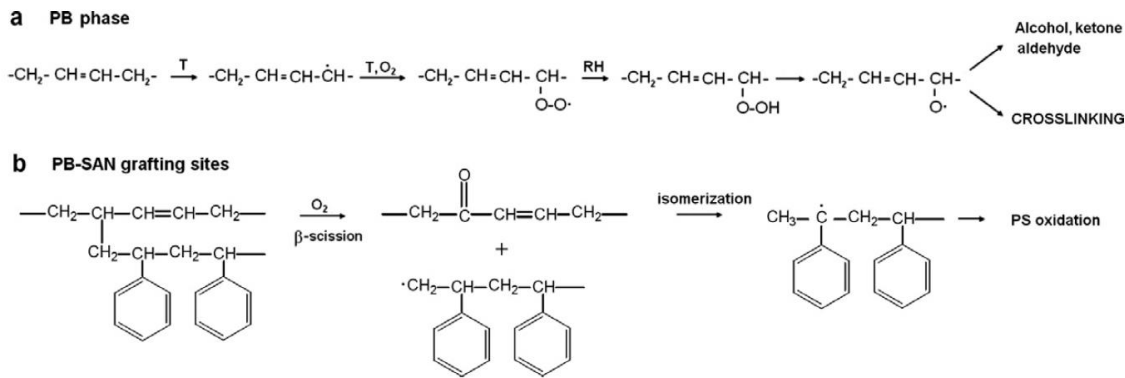
Figure 4-1: β-scission of an alkoxy radical created by oxidation of the C=C double bond in the PB phase [35]

Photo-oxidative degradation is said to occur most prominently at the PB phase at the outermost layer of the sample causing embrittlement of the rubber and possible scission of the SAN matrix [20]. Specifically for multiphase polymers like ABS and HIPS, Kulich et al. [20] warns on the partition of the stabilizers between the different phases which may cause a concentration difference influencing the actual effectiveness of the additives. As the PB component is significantly more prone to oxidation [37], the use of rubber-bound stabilizers is sometimes used to permit a good distribution through the phases and concentration in the rubber phase [20].

Stabilization of ABS against photo-oxidative degradation is preferably performed using a combination of UV-absorbers and sterically hindered amines. In this regard H. Zweifel [12] reports on the use of Tinuvin P with Chimassorb 119 or combinations of Tinuvin 571 with Tinuvin 765 leading to better resistance against discoloration. The thermo-oxidation can be retarded significantly by the use of the Tinuvin 571 benzotriazole anti-oxidant in combination with Irganox PS 800 thiosynergist as depicted in Figure 4-2.
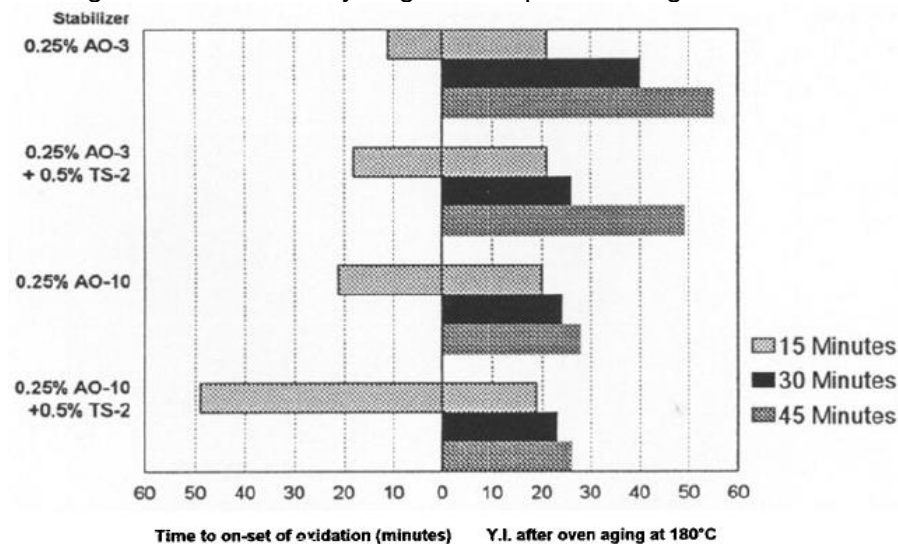
Figure 4-2: Anti-oxidant influence on the thermal stability of ABS using DTA measurements at 180 °C isotherm on air and Y.I. by oven ageing at 180 °C. A0-10: Tinuvin 571, TS-2: Irganox PS 800

The influence of additives on the low behavior of ABS has been described by Blyler et al. [38] who claimed a reduction in viscosity was due, firstly by trapped volatile components like unreacted styrene and water the total of which can amount up to 4%. They confirmed this by reprocessing the ABS through melt processing with a vented twin-screw extruder to let the volatile components escape (see Figure 4-3). The result after rheology testing being a more

viscous ABS resin with a viscosity increase up to 35 %. Scaffaro et al. [35] nuances these findings by their investigation on the influence of reprocessing cycles on virgin ABS and ABS blends and attribute the consumption of antioxidants and stabilizers during reprocessing as cause to a decrease in viscosity, leaving the ABS less protected and more prone to degradation. The degradation of the polybutadiene leads in this case to a degrafing of the SAN after multiple reprocessing cycles at high temperatures. This decrease in molecular weight is accompanied by a noticeable decrease in viscosity. This is in agreement with other scientific literature [9], [16], [20].

Secondly, the viscosity was further lowered sizably by the addition of calcium stearate reducing the viscosity by about 25 at 100 s^{-1} shear rate and a fatty acid amide lowering the viscosity by about 30 %. The viscosity curves are depicted in Figure 4-3.
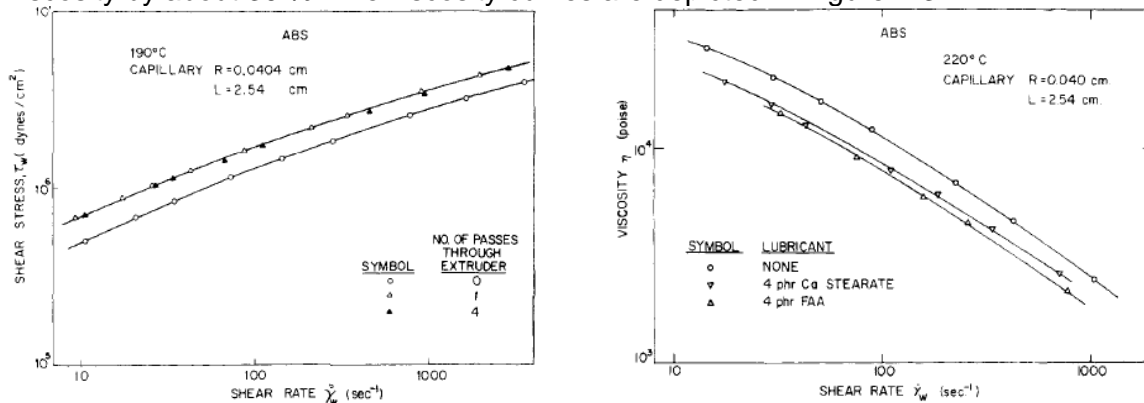
Figure 4-3: Left: increase in viscosity due to loss of volatile components by extra extruding step using vents before measurement. Right: decrease of viscosity by adding the lubricants calcium stearate or fatty acid amides.

4.2 High impact polystyrene

High impact polystyrene (HIPS) is a composite material consisting of a polystyrene base and a polybutadiene dispersed phase. The product enjoys the benefit of both the dimensional stability of polystyrene and the increased impact strength and toughness that is accompanied by the butadiene content [4]. As a result, degradation is said to occur by chain scission at the PS phase (Figure 4-4) and oxidative degradation of the elastomer phase. Achilias et al. [4] describes the thermal decomposition of the HIPS to occur primarily in the PB phase of the HIPS. Degradation is accompanied with yellowing and loss of mechanical properties.
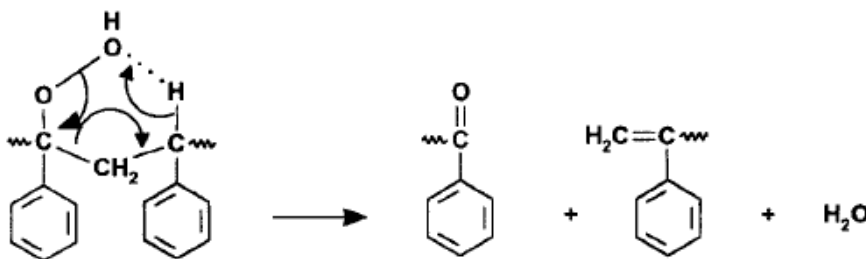
Figure 4-4: Oxidative degradation of polystyrene [12]

F. Gugumus [39] investigated the effect of phenolic anti-oxidants on the molecular weight of PS through multiple extrusions and concluded that the degradation can be substantially retarded by the addition of the phenolic anti-oxidant available under the trade name Irganox 1076. A significant effect was noticeable at 0,1 wt.% (see Figure 4-5). Analogous to the ABS materials, UV-absorbers of the benzotriazole type in combination with sterically hindered amines (HAS) proved to have a beneficial effect on discoloration noticed via the Yellowness

Index (see Figure 4-6). In this regard combinations of the Tinuvin P and Tinuvin 770 were found to have the best effect at 0,1 wt.% each [12]. It should be mentioned that phosphite-phenol combinations are typically beneficial to stabilization during melt processing suppressing discoloration. Finally, in order to further prevent crosslinking of the butadiene phase R. Mathis et al. [40] found that the addition of a C-radical scavenger, Irganox 3052, in combination with the anti-oxidant Irganox 1076 and secondary anti-oxidant Irgafos TNPP inhibits crosslinking of the butadiene phase substantially.
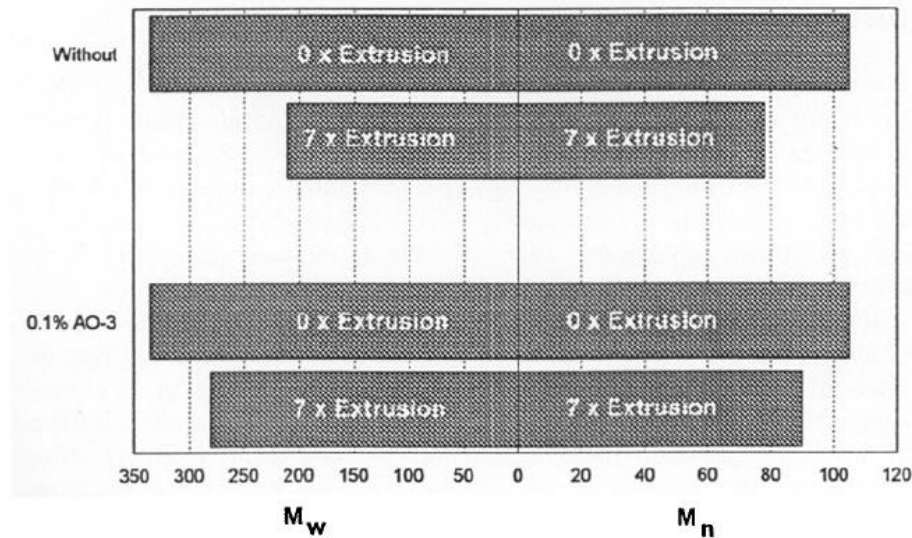
Figure 4-5: Stabilization of PS tested by multiple extrusions at 170 °C with and without stabilizer [12], [39]
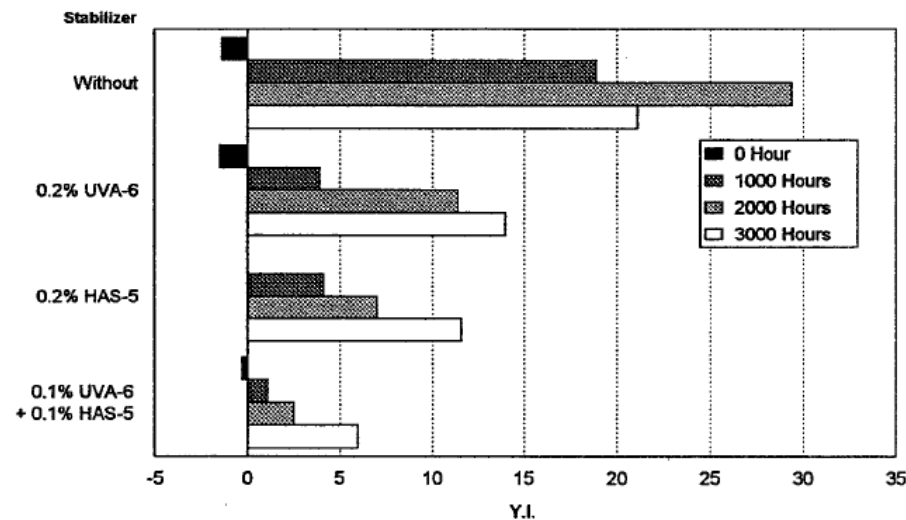
Figure 4-6: Yellowness Index of polystyrene after exposure to light using a Weather.O.Meter WRC 600, dry, b.p. temp. 55°C (sample size 2mm injection molded plaques) showing the synergistic effects of UV-absorbers and HAS [12]

4.3 Poly(bisphenol A carbonate)

Poly(bisphenol A carbonate) (PC) is an engineering plastic which is the third most abundant plastic in the WEEE plastics. It features a dimensionally stable, transparent, high impact resistance and ductility at ambient temperature or below. The vast majority of PC are based on bisphenol A or BPA and have a glass transition temperature in the range of 140-155°C. The bulky structure of the polymer chain is responsible for this as it restricts the conformational changes. The polymer exhibits a good thermal resistance and can be heated

at high temperatures (320 °C) for an extended time with only minimal degradation [41]. Because of its aromatic structures in the polymer backbone, absorption in the UV-region around 255 nm takes place which can lead to photoyellowing, crosslinking and formation of cracks resulting in embrittlement. Water uptake place an accelerating role in this reaction as it increases the detrimental effect of hydrolysis [42]. Furthermore thermo-oxidative degradation can lead to a complex series of reactions resulting in slight yellowing of the polymer requiring stabilization to prevent this (Figure 4-7). The equilibrium water content at 60% relative humidity is 0,26 wt.%. It is therefore important to carefully dry PC prior to processing as basic or acidic impurities in the substrate can cause degradation of the polymer backbone by partial hydrolysis [41].

In order to stabilize polycarbonate one should ensure no acid traces are present. The use of acid acceptors like epoxides in combination with phosphite stabilizers like Irgafos 168 has proven to produce positive effects because of its better resistance against hydrolysis (see Figure 4-8 [12]). H. Zweifel [12] points out that a combination of the phenolic anti-oxidant Irganox 1076 with the phosphite stabilizer Irgafos 168 gives the best results in terms of long term thermal stabilization, as depicted in Figure 4-9. The use of HAS should be avoided in this class of polymer as bases can intensely accelerate hydrolysis of polycarbonate. Protection from photo-oxidation is thus only carried out via the use of UV-absorbers in higher concentration. In this regard, because of the high processing temperatures of PC (up to 330°C), UV-absorbers of low volatility have to be chosen. In this regard Tinuvin 1577, a hydroxyphenyl-triazine, was found to be most effective (see Figure 4-10) [12]. Conventionally, UV protection is effected by coextrusion of a thin film with a high concentration (typically 2 wt.%) of UV-absorbers.
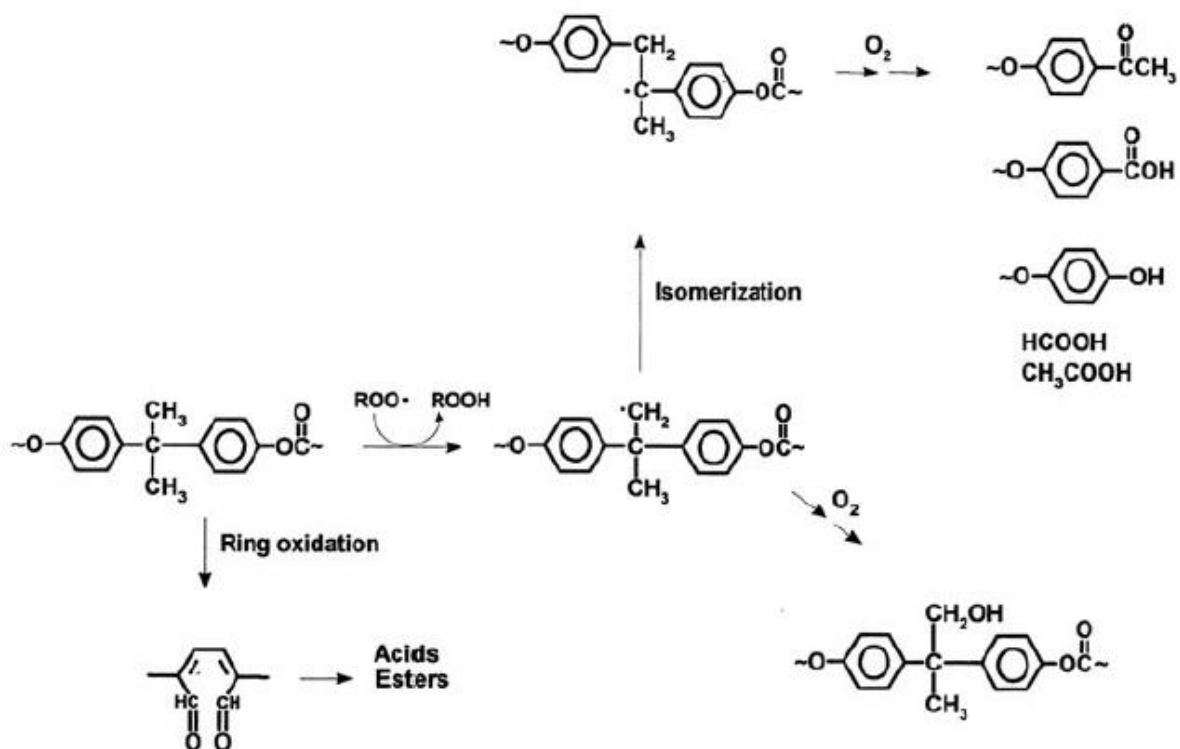
Figure 4-7: PC thermo-oxidative degradation leading to a series of complex reactions [12]
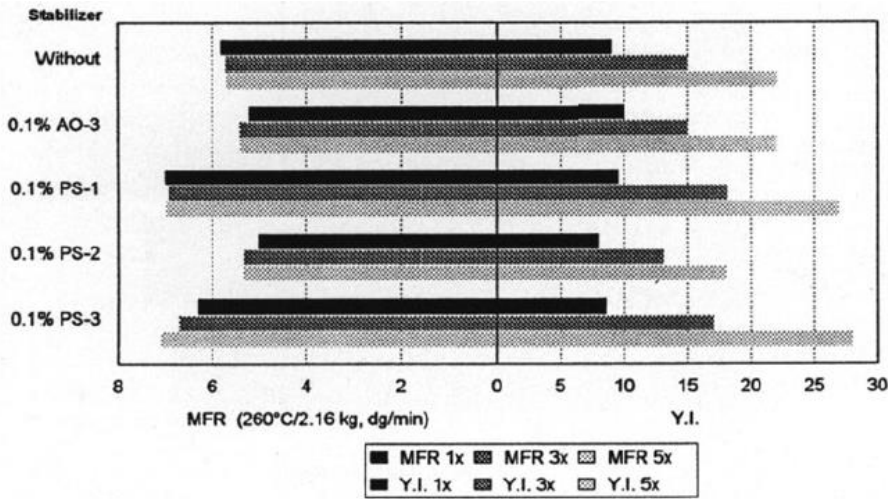
Figure 4-8: Effect of different stabilizers on melt flow of PC measured by MFR (260°C/2,16kg dg/min), and discoloration measured by Y.I. after multiple extrusions at 330 °C. AO-3: Irganox 1076, PS-1: Irgafos TNPP PS-2: Irgafos 168, PS-3: Ultranox 626
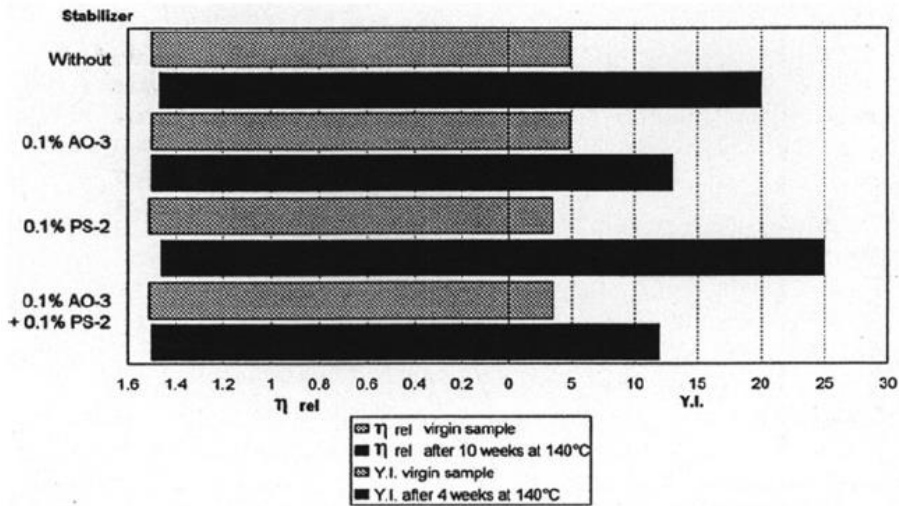
Figure 4-9:Synergistic effect of the phenolic antioxidant Irganox 1076 (AO-3) with the phosphite stabilizer Irgafos 168 (PS-2) measured by Y.I. by exposure to circulating air oven at 140 °C and relative viscosity measurements in CH$_2$Cl$_2$ [12]
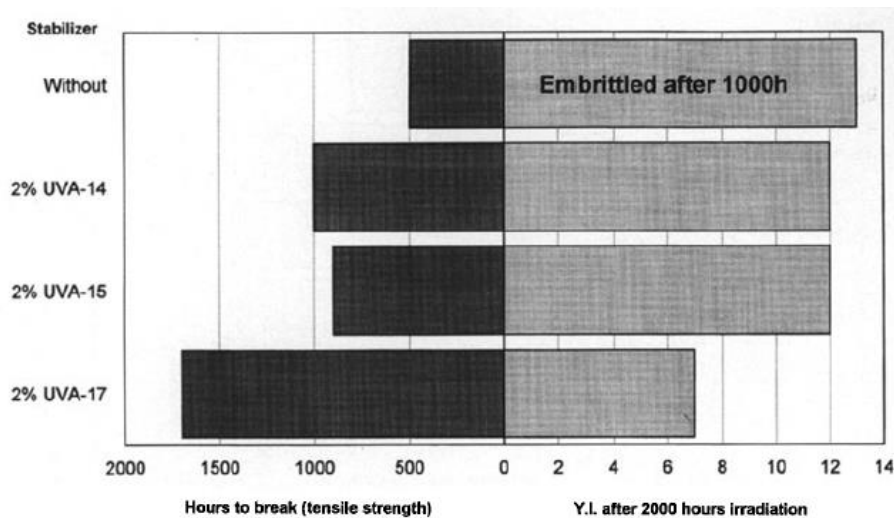
4.4 Polypropylene

Polypropylene is one of the most widely used polymers because of its low monomer and manufacturing price and widespread availability. It is a semi-crystalline polymer which is commonly available under its atactic (aPP), syndiotactic (sPP) and isotactic (iPP) form. Both iPP and sPP exhibit polymorphism meaning that, depending on the crystallization conditions, different crystal forms can be obtained. The % crystallinity has an influence on degradation as oxygen is generally only soluble in the amorphous phase of the semi-crystalline polymers causing oxidation to occur primarily there. Similarly, additives are present predominantly in the amorphous phase of the polymer. As a result, the local concentration of stabilizers can be several times higher than the original stabilizer concentration as the stabilizers are rejected into the amorphous phase during crystallization [12].

A vast number of PP grades are available with varying molecular weight, tacticity, filled grades and grades with varying stabilizations already performed upon. Unstabilized polypropylene is very prone to degradation under the influence of heat, mechanical shear and UV radiation [12]. The polymer undergoes chain scission causing a reduction in molecular weight and associated reduced properties of the polymer. Polypropylene is especially sensitive to the formation of hydroperoxides through intramolecular hydrogen abstraction in a six membered transition state (see Figure 4-11). The resulting peroxides can then react forming a carbonyl function through β-scission. This mechanism is said to be general for polymers with branched alkanes as repeating units and therefor also occurs in polystyrene [12].
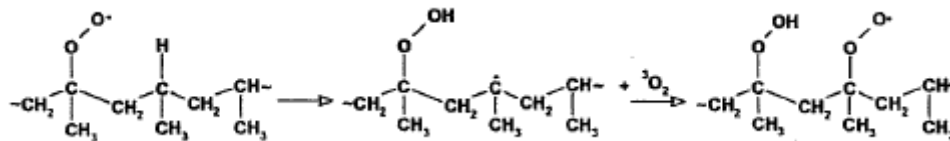
Figure 4-11: Reaction of PP with peroxides by intramolecular hydrogen abstraction in a six membered transition state resulting in the formation of hydroperoxides [12]
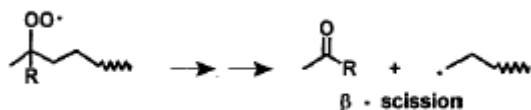
Figure 4-12: β-scission of the peroxide alkyl radical by the formation of a carbonyl moiety [12]

Synergistic effects have been noticed by the use of phosphoric anti-oxidants in conjunction with phenolic anti-oxidants for the processing stability of polypropylene (see Figure 4-13 [43]). Phosphite stabilizers play and important role in processing stability of polypropylene in melt while the phenolic anti-oxidants act on the long term thermal stability of the polymer. H. Zweifel [12] reports on the influence of the hindered phenols on the melt flow during multiple extrusions as an indication for melt stability of the polymer and found a significant improvement in stability through the use of BHT, Irganox 1010 and α-Tocopherol or Vitamin E (Figure 4-14). Though BHT and α-Tocopherol display the best melt processing stability, for long term thermal stabilization they are too volatile and diffuse more easily from the polymer matrix. For this reason H. Zweifel [12] goes on displaying the synergistic effect of Irganox 1010 with Irgafos 168 using comparable multiple extrusion experiments (see Figure 4-15). Irganox 1010 has a higher molecular weight which results in low volatility and a slow diffusion rate making it a more suitable candidate for long term thermal stabilization.

In contrast to the stabilization during melt processing, the phosphite stabilizers exert almost no significant influence on long term thermal ageing. More so, Zweifel et al. [12], [44] have shown that the phosphite stabilizer Irgafos 168 has completely hydrolyzed to its respectable phosphate after a short period making the phenol stabilizer entirely responsible for the long term thermal stability of the polymer. A possibility for enhancing the long term thermal stabilization is by adding a thiosynergist to a system stabilized primarily by phenolic anti-oxidants. In this regard, Irganox PS 802 has shown to exert a synergistic effect when used with Irganox 1010 (see Figure 4-15).

In order to bind residues of acids created during polymerization or by degradation of stabilizers, acid acceptors (a.k.a. antacids) are added during processing. The use of antacids can affect degradation both positively as negatively as shown in Figure 4-16. Depending on the polymer, catalyst used during polymerization and its deactivation afterwards, as well as the stabilizer combinations used can be determining factors in this process [12].
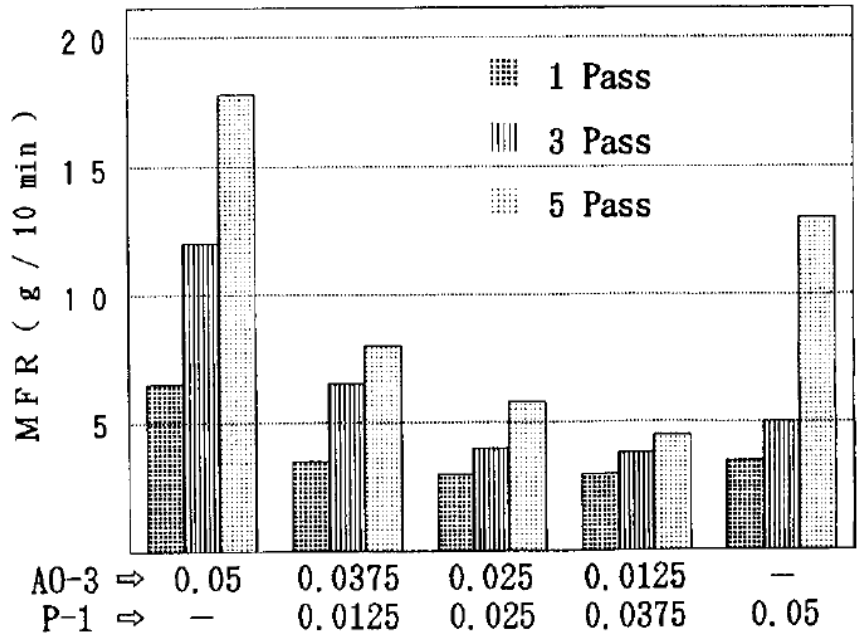
Figure 4-13: Synergistic effect of using Irganox 1010 (AO-3) and ADK STAB PEP-36 (P-1) on thermal stabilization of polypropylene [43]
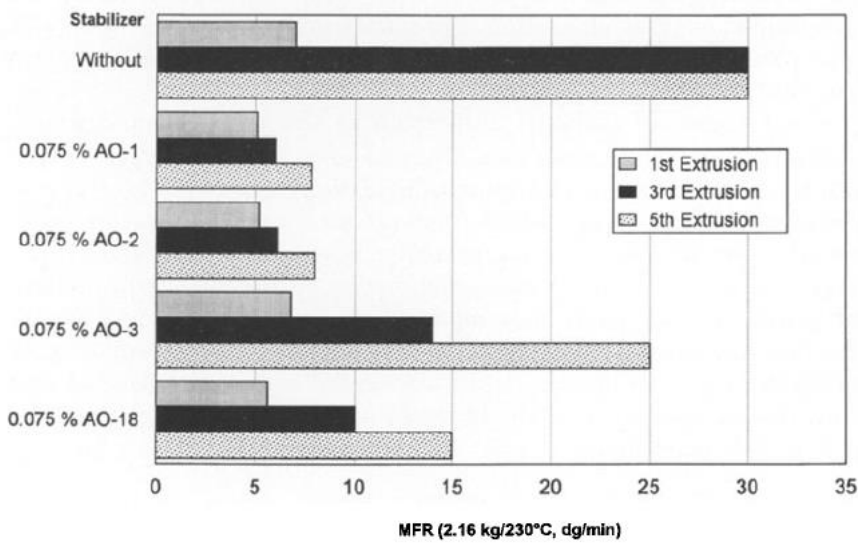
Figure 4-14: Influence of the phenolic anti-oxidants α-Tocopherol (AO-1), BHT (AO-2), Irganox 1076 (AO-3) and Irganox 1010 (AO-18) on the MFI of a polypropylene homopolymer during multiple extrusion at 270 °C [12]
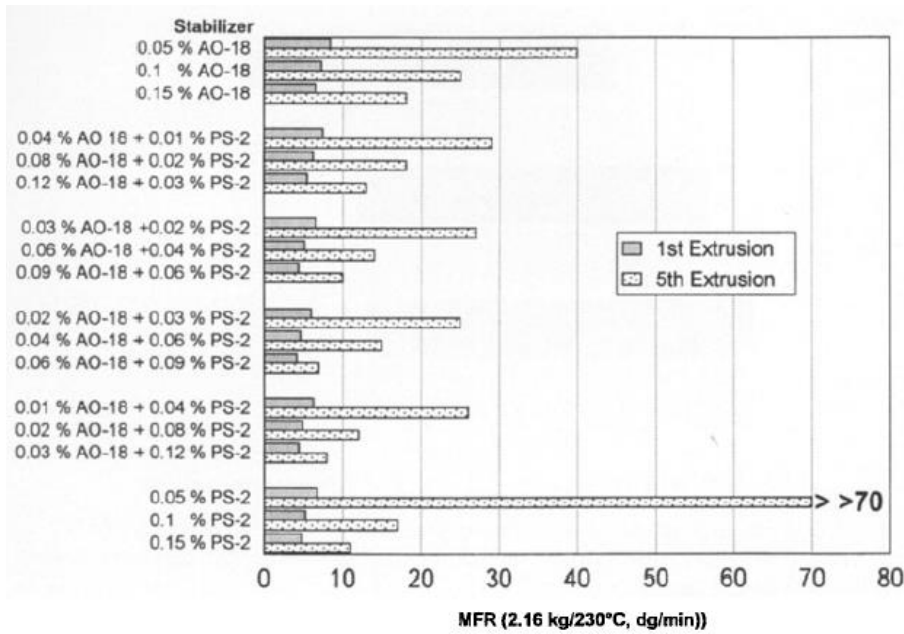
Figure 4-15: Optimal composition of Irganox 1010 (AO-18) and Irgafos 168 (PS-2) depicted by melt flow, MFR, of a PP-homopolymer during multiple extrusions at 280 °C [12]
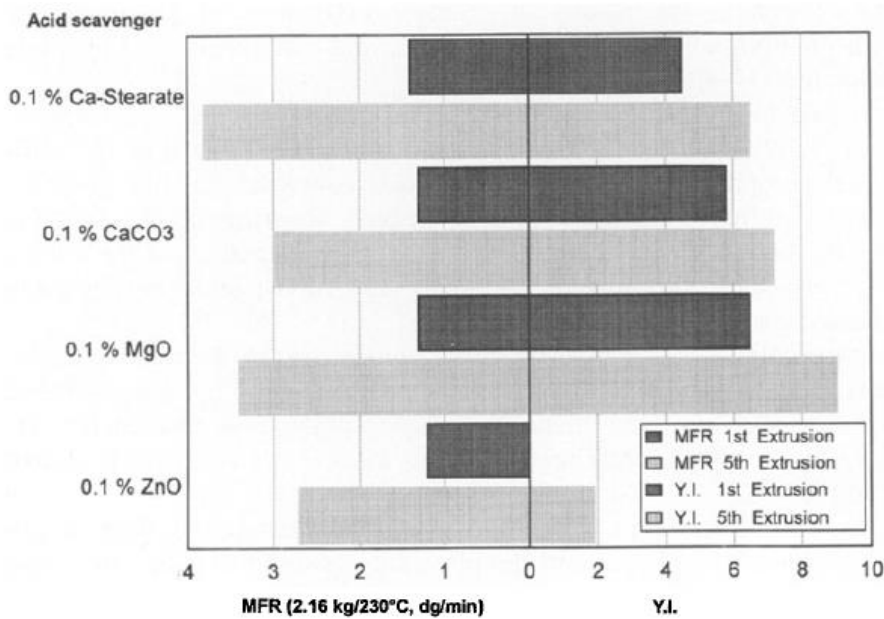
Figure 4-16: Influence of antacids on the melt flow and discoloration through measurement of Y.I. and MFR on a PP-homopolymer at 280 °C. Samples contain 0,05 wt.% Irganox 1010 and 0,1 wt.% Irgafos 168
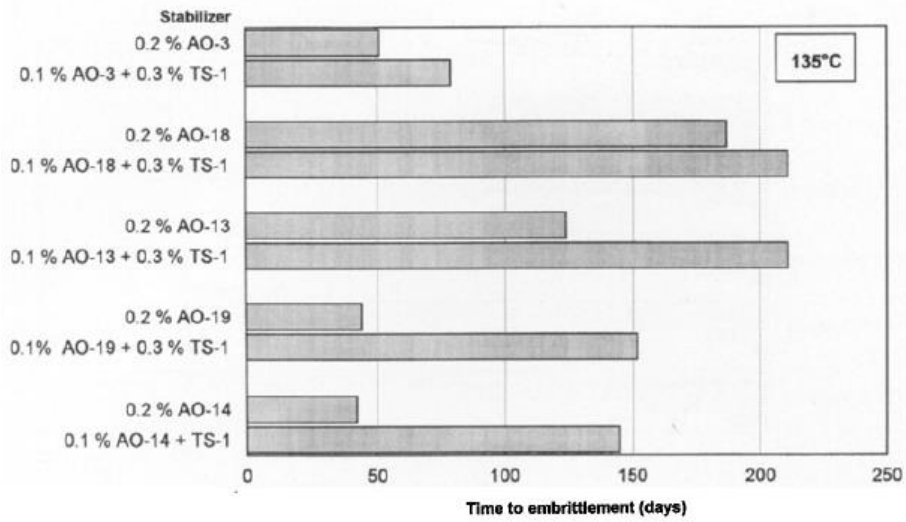
Figure 4-17: Synergistic effect of a sulfite stabilizer with the phenolic antioxidant for long term thermal stabilization of a PP-homopolymer at 135°C. Samples contain 0,1 wt.% Ca-stearate and are exposed to a circulating air oven [12]

5 Flame retardants

Over the last 50 years, there has been a continuous change in the materials used for construction and content of buildings and transport, including electric and electronic appliances, with an increasing dependence on synthetic polymers and their composites with different reaction-to-fire properties. Compared with natural materials (wood, wool, cotton, leather, etc.), widely used synthetic polymers such as polyethylene (PE), polypropylene (PP), polyamide (PA), polystyrene (PS), Acrylonitrile butadiene styrene (ABS), Polycarbonate (PC) or polyurethane (PU) burn more quickly, and generate more smoke. To reduce this hazard, additives known as Flame/Fire retardants have been developed. The use of these additives has become crucial everywhere and are extensively used in key electrical and electronic application areas like housings, cables, connectors and switches, printed wiring boards.

This report aims to find the best flame retardant solutions for application in E&E sector. Therefore, a bibliographic and market study was carried out. This chapter includes a review of current flame retardant technologies and additives, considering also different topics of special interest from an end of life (EOL) perspective such as environmental, health, recyclability and long-term stability issues.

5.1 Flame retardants, mechanism of action

Fire retardant (FR) is a compound which is added to a matrix, usually polymeric, in order to retard a fire by cancelling, during a certain period, a triangle fire setting (heating, oxidizer and fuel) (Figure 5-1), thus disturbing the fire development. The development of fire-retarded polymers is undertaken to reduce the likelihood of unwanted fires. If the first item exposed to an ignition source does not ignite or propagate flame, a fire might never start. If ignition does occur, FR products usually reduce the spread of flame or the rate of burning compared to non-FR products. There are different type of effects typically associated with FR polymers: the flame poisoning, cooling, diluting type flame retardants and the solid phase mechanism flame retardants.
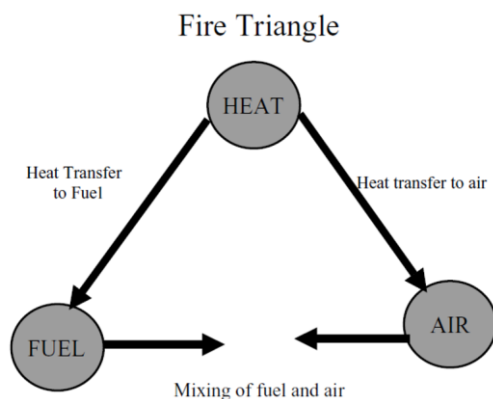
Figure 5-1: The combustion triangle

5.1.1 Gas phase mechanism—flame poisoning

The flame retardants that act in the gas phase are free radical scavengers that bond the oxygen or hydroxy radicals present in the gas phase. Halogenated chemicals act in this fashion by themselves or in combination with antimony trioxide: in this case, the antimony oxyhalides are the active free radical scavengers. Some phosphorus chemicals such as triphenyl phosphate (TPP) and phospinates are known to have some gas phase action.

The acting principle in the use of halogenated materials as flame retardants is the interruption of the radical chain mechanism in the gas phase. The following scheme describes the reactions occurring:

1. *Release of halogen radicals (X* : Cl* or Br*) from the flame-retardant R-X at the beginning of combustion process:*
   $$R - X \rightarrow R^* + X^*$$
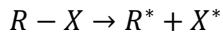
2. *Formation of halogen hydroxides (HX)*
   $$RH + X^* \rightarrow HX + R^*$$
3. *Neutralization of energy-rich radicals present in the combustion evolving gas.*
   $$HX + H^* \rightarrow H_2 + X^*$$
   $$HX + OH^* \rightarrow H_2O + X^*$$
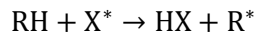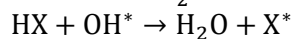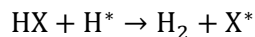
The replacement of energetic radicals by less energetic ones reduce the heat generation and contribute to stop the combustion cycle

5.1.2   Cooling

Flame retardants that decompose in endothermic reactions will cool the combustion environment and therefore slow down reaction pathways. The hydrated minerals alumina trihydrate and magnesium hydroxide act in such a fashion by releasing water in endothermic decomposition reactions.
$$Al(OH)_3 + Energy \rightarrow Al_2O_3 + H_2O$$
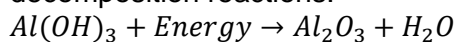
5.1.3   Dilution of oxygen concentration

The active concentration of oxygen in the gas phase is the driving force for the combustion of carbon radicals and creation of more oxygen and hydroxy radicals that propagate decomposition. The release of inert gases in a fire environment dilutes the active oxygen concentration and decelerates the reaction pathways. An example of this effect is the decomposition of nitrogenated compounds like melamine.

5.1.4   Solid phase mechanism

These mechanisms occur in the condensed phase, in the exposed area of the material in combustion by:

1. Charring
   Silicon- or phosphorus-containing chemicals have the possibility to initiate, at elevated pyrolysis temperatures, cross-linking reactions in the polymer matrix that create an effective barrier to heat transfer and diffusion of gases, thereby providing effective flame retardancy. These reactions resemble the reactions present in the formation of glass and are catalyzed by acidic conditions and certain cations.
2. Intumescence
   The term refers to the formation of a porous carbonaceous char by the combined action of a carbon source, a blowing agent/gas released, and a catalyst necessary to set the reaction in motion. Examples of such systems are combinations of alcohols (carbon source), ammonium compounds (releasing NH3 as the blowing agent), and phosphorus compounds where the phosphoric acid formed during pyrolysis acts as the reaction catalyst. The strength of the char and its structure are critical in achieving the desired flame-retarding performance.

The choice of a flame-retardant additive depends on the best mechanism that can be exploited and put in action for the specific polymer matrix. As an example, charring cannot occur in polypropylene, but is readily possible in polycarbonate and polyphenylene oxide. Table 5-1 shows the mechanism of action of flame retardants used in various polymers.

Table 5-1: Polymers and flame retardants' preferred mechanism

Polymer	Heat sink	Condensed phase	Vapor phase
Polyolens	X	Minor	X
Styrenics			X
Nylon		X	X
PC		X	X
PC/ABS		X	
PBT & PET			X
PPO/HIPS		X	
PVC		X	X
Polyurethane foam	X	X	X
Epoxy			X
Unsat polyester	X		X

5.2 Classes of commercial flame retardants

In 2003, the Restriction of Hazardous Substances Directive RoHS (Directive 2002/95/EC) was adopted by the European Union. This restricts the use of certain hazardous substances in E & E equipment. It limits the use of six hazardous materials, including BFRs (Brominated flame retardants), in the manufacture of various types of electronic and electrical equipment, Additionally, the Waste Electrical and Electronic Equipment Directive (WEEE) 2002/96/EC require the separation of plastics in E & E waste containing BFRs prior to recycling. This situation has driven the European market to look for alternative non- halogenated compounds. Nowadays, antimony oxide and halogenated flame retardants account for 21% of the total flame retardant market (498.000 metric tons) Figure 5-2.

Flame retardants have to give solutions for several applications with different materials involved, FRs need to match polymer properties and specific processing requirements. Figure 2 illustrates the variety of polymer types (plastics) used in Europe. This variety explains why so many different FR technologies are necessary in E&E and other applications [45]. Considering the actual situation, both regulatory and marketwise, halogenated flame retardants have been considered of minor interest for this report and will not be studied in detail.
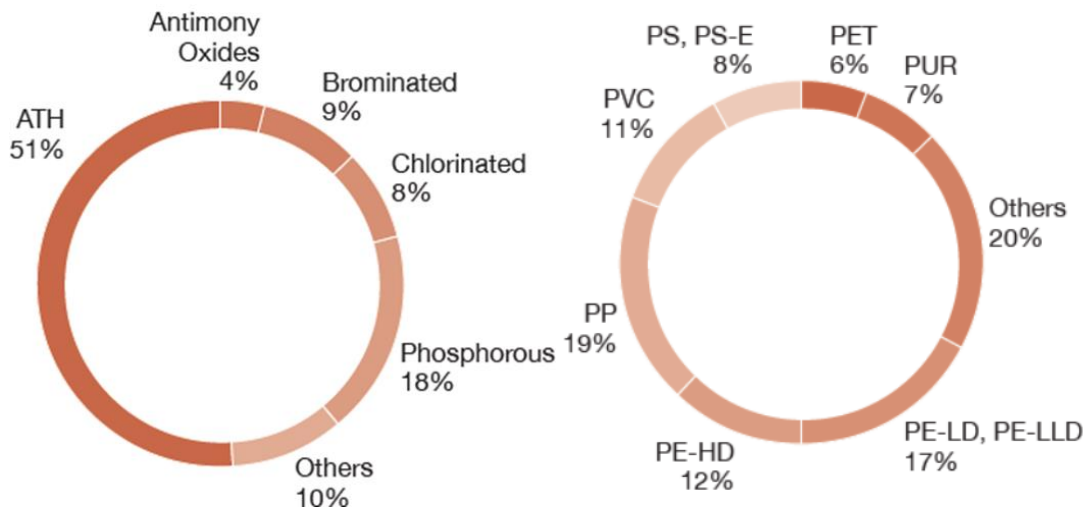
Figure 5-2: Consumption of flame retardants in Europe by categories (left) and plastic consumption in Europe by resin type (right) in 2015

5.2.1   Halogenated compounds.

Even though a wide variety of flame retardants have been developed, halogenated compounds, due to their cost, availability, and extensive industry experience have been the most frequently employed for enhancing the flame retardancy of polymers. Halogen-based flame retardants interfere with the combustion cycle primarily through free-radical scavenging mechanisms, inhibiting the flame propagation in the vapor phase. Halogenated flame retardants can react with the highly radical species, OH· and H· (produced during polymer combustion), hampering the chain decomposition and, thus the burning of the polymer. This effect is a consequence of the generation of hydrogen halides (MX $\rightarrow$ HX + M·, where X is halogen and M is the residue of the flame-retardant molecule) or, if the flame-retardant molecule does not contain hydrogen, of halogen atoms (MX $\rightarrow$ X· + M·) during the degradation (upon heating) of the halogenated compounds. Hydrogen halides (produced also through the reaction between halogen atoms and the polymer, (RH + X· $\rightarrow$ HX + R·), are considered to be the actual flame inhibitors as they react with the polymer degradation radicals (HX+ H· $\rightarrow$ X· + H_2 and HX + OH·/X· + H_2O), leading to much less active species [46], [47]. Typical representatives of halogenated flame retardants are chlorine-, bromine-, fluorine-, and iodine containing compounds:

5.2.1.1   Chlorinated Paraffins.

Chlorinated paraffins contain a maximum of 75 to 76 percent chlorine and are manufactured via chlorination of a paraffin hydrocarbon. Thermal degradation occurs via a dehydrochlorination reaction and starts at 180°C.

5.2.1.2   Brominated Materials.

There is no universal brominated flame retardant suitable for all plastic resins and applications. Considering the mechanism of action of brominated materials and the wide range of thermoplastics in use, this is readily explainable. Bromine acts in the gas phase and must be delivered there; it should be made available at the same temperature at which the thermoplastics pyrolysis occurs and the free radical segments diffuse and are available in the gas phase to combine with bromine. Some examples of Brominated flame retardants are Tetrabromophthalic Anhydride (TBPA), Hexabromocyclododecane (HBCD),

Tetrabromobisphenol A (TBBA), Tribromophenol derivatives, dibromostyrene derivatives or brominate polystyrenes, brominated alcohol derivatives and specialty brominated compounds.

5.2.2 Antimony Trioxide

Antimony trioxide is synergistic with most halogenated compounds, allowing a decreased amount of halogenated compound to be used to achieve equivalent flame-retardant performance compared to using the halogenated compound on its own. Antimony oxide is nonvolatile, but antimony oxyhalide (SbOX) and antimony trihalide (SbX_3), which are formed in the condensed phase by reaction with the halogenated flame retardants, are volatile and facilitate transfer of the halogen and antimony into the gas phase where they function as radical scavengers [48].

5.2.3 Non- Halogenated flame retardants.

Alternative to halogenated flame retardants have been developed in the last years and different chemistries are now available. These chemistries are designed to respond to current expectations in terms of sustainable fire safety with environmentally friendly flame retardants. The main chemicals used as FR are commonly classified as:

5.2.3.1 Inorganic

This category comprises mainly metal hydroxides like aluminum hydroxide and magnesium hydroxide, boehmite, brucite, hydromagnesite, huntite, and mixed metal hydroxyl carbonates. Other compounds like e.g. zinc borate or B_2O_3, are used to a much lesser extent. In this category can be also included novel nanoparticles: Modified montmorillonites, sepiolites and so on.

5.2.3.2 Phosphorus-based flame retardants

These include organic and inorganic phosphates, phosphonates and phosphinates as well as red phosphorus, thus covering a wide range of phosphorus compounds with different oxidation states.

5.2.3.3 Nitrogen-based flame retardants

These are typically melamine and melamine derivatives (e.g., melamine cyanurate, melamine polyphosphate, melem, melon). They are often used in combination with phosphorus based flame retardants.

5.2.3.4 Char promotors

Carbon-based polyalcohols such as pentaerythritol, starch, urea resins and lignin derivates, are normally used in combination with other flame retardants.
Despite its own effect, phosphorous, nitrogen and char promoters form part of the Intumescent flame retardants systems that is an example of a typical mechanism for non-halogenated flame retardants. The combustible material is separated from the fire or heat source by an insulating foam which forms at the surface. Intumescent flame retardant systems can be applied to decrease flammability of thermoplastic polymers such as polyethylene, polypropylene, polyurethane, polyester- and epoxy resins.
There is not a universal flame retardant (as there is not a universal plastic, or a universal metal usable everywhere for every application). Each material has its own properties and compatibilities. This applies to flame retardants too.

5.2.4 Metal hydroxides

The function of metal hydrates as flame retardants is based on physical and chemical processes. To inhibit combustion, they must possess a significant endothermic decomposition at a temperature exceeding the polymer melt processing temperature, typically between 180 and 300 ˚C. Additionally, they should have a small particle size and surface area with optimum particle morphology to enable their use at high filler levels without affecting the polymer rheology during processing and mechanical properties of the final composite. Below it is shown the involved processes of a metal hydroxide filled polymer in case of a fire. In the presence of an ignition source – a flame or a hot object – the thermal decomposition of the metal hydroxide into metal oxide and water according to the reactions (1) to (3) takes place:

1. $2Al(OH)_3 \xrightarrow{1075 \text{ kJ/kg}} Al_2O_3 + 3H_2O$
2. $2AlOOH \xrightarrow{700 \text{ kJ/kg}} Al_2O_3 + H_2O$
3. $Mg(OH)_2 \xrightarrow{1220 \text{ kJ/kg}} MgO + H_2O$
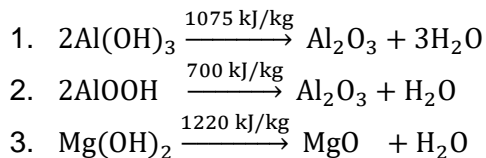
During this process, energy is detracted from the ignition source, as the decomposition is an endothermic reaction. At the same time, the released water vapor cools the surface of the polymer and particularly dilutes the concentration of burnable gases in the surrounding area. The remaining metal oxide residue has a high internal surface where sooty particles, respectively polycyclic aromatic hydrocarbons are absorbed. Additionally, the oxide residue is very stable due to their melting point which is about 2000 – 3000 °C and acts as a barrier, disabling the further release of low molecular weight decomposition products as well as a heat barrier protecting the polymer against further decomposition. The maximum processing temperatures range from 200 °C (ATH) to 300 °C for MDH and 320 °C for AOH. Unfortunately, both ATH and MDH share the disadvantage of higher loading levels for FR efficacy (over 50 % of filler) which typically interferes with physical properties of the system. This can often be overcome with careful formulation development. Examples include the use of surface treatments, especially for MDH and the selection of proper base resin with adequate melt flow index. Processing conditions should also be properly adjusted to ensure a good result.

Today, ATH is widely used as a flame retardant in many types of polymers and a host of grades varying in particle size distribution and particle shape are available to suit particular applications, typical polymer grades treated with ATH include EVA-cop; PE, PVC rigid or Thermoplastic elastomers and thermosets polymers [49]–[53].

Boehmite, AlO(OH), a natural aluminum hydroxide, have a decomposition temperature significantly higher than ATH while the enthalpy of decomposition and volatile release are significantly less than for ATH and MDH hydroxides. Therefore the fire retardant effect is not as marked as these other hydroxides in most low-temperature decomposing polymers and boehmite finds most application where the high thermal stability is important, including a higher number of polymers, ABS, PP, PC, PC/ABS, HIPS; PE, PVC, PA,PBT, PET, EVA-cop, or thermoplastic elastomers.[49], [51], [54]–[56].

The principal advantage of magnesium hydroxide over ATH is its greater thermal stability, with decomposition starting at 300 ˚C. This makes it more suitable where high processing temperatures are required, principally in thermoplastics such as polypropylene and polyamides. It is also much more chemically reactive than ATH, and this limits its suitability in one of the main markets, unsaturated polyesters. Typical polymers treated with MDH are EVA-cop, PA, PP, PE or Thermoplastic elastomers [49], [51], [57]–[59].

Other metal hydroxides with a flame retardant effect include kaolin, Calcium hydroxide, Hydromagnesite, brucite, huntite. Brucite is essentially magnesium hydroxide in a naturally occurring form. Hydromagnesite is a natural mineral usually found with huntite ($3MgCO_3Mg(OH)_2$, $3H_2O$) + $Mg_3Ca(CO_3)_4$. Mixed metal hydroxycarbonate compounds are like hydrotalcite with varying amounts of magnesium and aluminum interspersed in layers. These less frequently used types of metal hydrate FRs have been studied, but their

commercial usage is small in comparison with ATH and MDH. ATH is by far the largest volume FR and has been so for many years. ATH is low cost FR and is easy to use.

5.2.5 Boron compounds

Borates are another family of inorganic additives with flame retardant properties. Boron compounds such as boric acid (BA) and sodium borates are well-known flame retardants for cellulosic products. However, the use of boron salts such as zinc borates, ammonium pentaborate, melamine borate, boron phosphate, metal borophosphate, and borosiloxane as flame retardant in plastics and rubbers has become prominent only in recent years. Among them, zinc borates such as $2ZnO\text{-}3B_2O_3\text{-}3.5H_2O$ are the most frequently used. Their endothermic decomposition (503 kJ/kg) between 290 and 450°C liberates water, boric acid and boron oxide (B_2O_3). The B_2O_3 formed softens at 350 °C and flows above 500 °C leading to the formation of a protective vitreous layer. In the case of polymers containing oxygen atoms, the presence of boric acid causes dehydration, leading to the formation of a carbonized layer. This layer protects the polymer from heat and oxygen. The release of combustible gases is thus reduced. Zinc borate is well-known as smoke suppressant [49], [60]–[64].

5.2.6 Phosphorous compounds

5.2.6.1 Mechanism of action

In the last years a set of phosphorus-containing flame retarded systems have been developed, which are produced according to green chemistry and are favored environmentally because they are safe during their production and use; furthermore, they are not harmful at the end of their life.

Phosphorus based FRs involve phosphorus that can be stable in different oxidation degrees states, such as phosphate, phosphonate, phosphinate and phosphine or phosphine oxide, Figure 5-3.
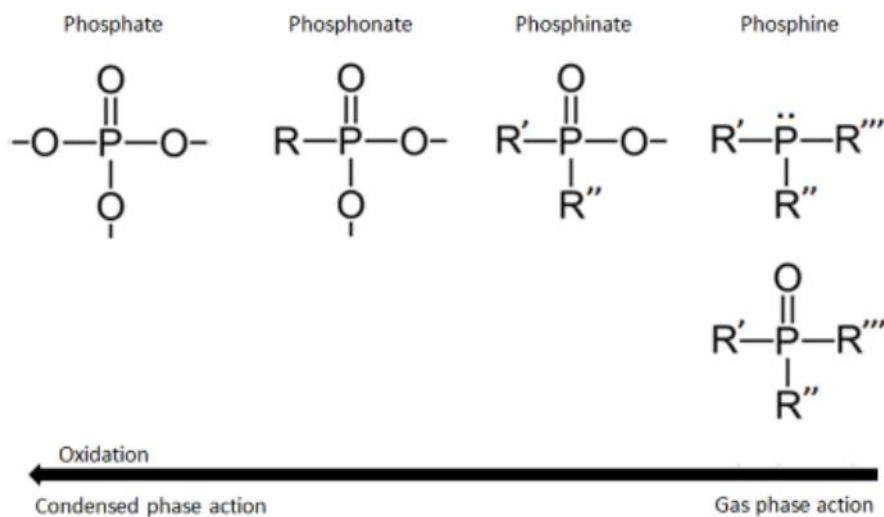
Figure 5-3: Different grade of oxidation of organophosphorus compounds

The choice of the phosphorus-based FR depends on different parameters such as the polymer matrix and the final application. Even though it is well-known today that the major action of those FR occurs in the condensed phase, it is also admitted that the less oxidized phosphorus-based FRs (phosphinate, phosphine) can act in the gas phase as flame poisoning agents. In this case hydrogen and hydroxyl radicals are replaced by less effective radicals or are turned into harmless components by radical recombination in the gas phase.

The efficiency of P in the gas phase is reported to be similar or even superior to hydrogen halides like HBr. Although detailed investigations of the flame area, such as identifying the intermediate products and monitoring concentrations of the different products are quite rare, the main principle seems to be understood. It is believed that the PO-radical plays the major role. Furthermore, the resulting flame retardancy effects are obvious, including a clearly decreased heat release due to a reduced heat release rate (HRR)/mass loss rate value during flammability and fire tests. Some possible key reactions are proposed in the equations below.

$$PO^. + H^. \rightarrow HPO$$
$$PO^. + OH^. \rightarrow HPO_2$$
$$HPO \quad + H^. \rightarrow H_2 + PO^.$$
$$OH^. + H_2 + PO^. \rightarrow H_2O + HPO$$
$$HPO_2^. + H^. \rightarrow H_2 + PO_2$$
$$HPO_2^. + OH^. \rightarrow H_2O + PO_2$$
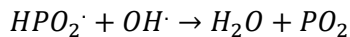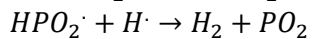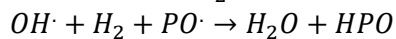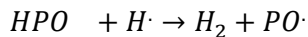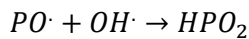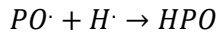
Another general action of phosphorous flame retardants is related to the presence as main component in Intumescent FRs combined with a nitrogen-containing additive and a further synergist which forms char or inorganic residue in the condensed phase when ignited, inhibiting the pyrolysis process necessary to feed the flames.
The main reactions involve high oxidation of phosphorus compounds to promote phosphoric acid (H_3PO_4) releasing, acting in the condensed phase by Diels Alder cyclisation process, thus generating the polycyclic aromatic carbonaceous solid structure (Figure 5-4). Then, the combustible source is protected from the thermal source and oxygen penetration.
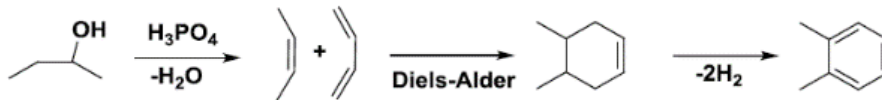
Figure 5-4: condensed phase action of phosphorous based FR - Diels-Alder cyclisation

Simultaneously to the charring effect, if an important quantity of gases is released (nitrogen synergist), the char swells thus increasing the thermal barrier effect. A complete Intumescent system is so a system which allows the material to expand and generate the thermal shield protecting the polymer against the heat [65]–[68].
Typically, the principal ingredients of intumescent system are the following:

- *Inorganic acid or material yielding acidic species - e.g.: For this application high oxidation degree of phosphorus is used, such as phosphoric acid, ammonium polyphosphate etc.*
- *A char former or carbon source, basically a primary hydroxyl rich compound such as pentaerytritol*
- *A blowing agent that decomposes to release a lot of inert species in the gas phase, mostly based on nitrogen derivatives e.g.: melamine, urea, guanidina etc.*

Like in every flame retardant, intumescent systems have to be designed for every application, polymer matrix and generally have to fulfil:

- *The additive must be thermally stable at polymer processing temperature (often greater than 200 °C).*

- *The thermal degradation process of the polymer, which gives large amounts of volatile products and possibly leaves a charred residue depending on the chemical structure of the polymer, must not adversely interfere with the intumescence process.*
- *The additive must form the protective foamed char over the entire surface of the burning polymer, in spite of being diluted within the polymer itself.*
- *The additive must not impair the physical and chemical properties of the polymeric material. In particular, it should not interact adversely with fillers or other additives such as stabilizers, which ensure protection of the polymer during processing and outdoor exposure.*
- *Low water solubility as well as low hygroscopic character could also be required if the host matrix requires such properties.*

By the way, the current market offer allows the formulator to prevent any of the above problems since FR producers exhibit large ranges of ready-to-use intumescent systems for various final applications. Apart from the traditional components of intumescent systems, some additional compounds, can be added to enhance the properties, thus resulting in synergistic effect such as smoke suppressant (inorganic elements) or elements like nanoparticles that reinforce the char structure. Figure 5-5 shows the different modes of action involving phosphorous based flame retardants.
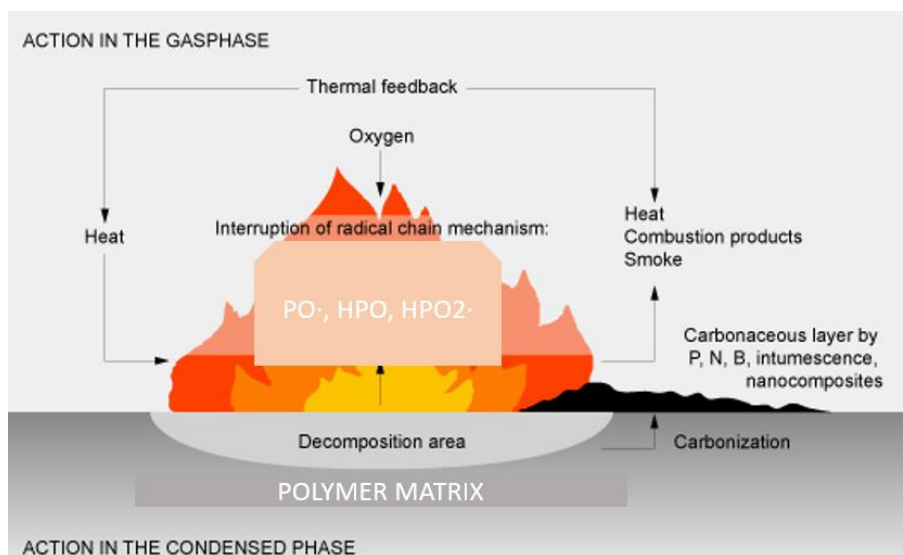
Figure 5-5: Flame retardant effect involving phosphorous compounds. Radical chain poisoning and condensed phase: charring , intumescence

5.2.6.2 Phosphates
1) Ammonium polyphosphate
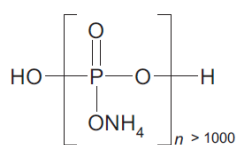
Figure 5-6: Ammonium polyphosphate

Ammonium polyphosphate (APP) (Figure 5-6) is an inorganic salt of polyphosphoric acid and ammonia. APP is used in FR systems for installation equipment (cables, cable ducts,

sealants), timber (boxes, doors), and other applications in E & E sector, mainly with polyolefins and thermoset resins [49], [69]–[71]. Additionally, APP is currently used primarily as a component in intumescent paints and coatings [49], [68], [72], [73].

The properties of APP depend on the number of monomers in each molecule and the structure of the polymeric chains. Shorter chains (n < 100) are more water sensitive, more soluble, and less thermally stable than longer chains (n > 1000) [74]. Commercial products differ in molecular weight, particle size, solubility, and surface coating. Processing of APP in plastics is limited by its thermal stability of about 250 ˚C. Encapsulated grades, normally with thermosetting aminoplast coatings, prevent hydrolysis during formulation, processing, or use, and simultaneously provide better dispersibility.

2) Ethylene diamine phosphate
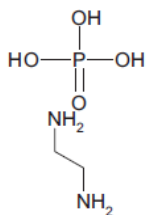
Figure 5-7: Ethylene diamine phosphate

Ethylene diamine phosphate (Figure 5-7) is a white powder with a melting point of 250 ˚C. This compound is self-intumescent and does not need any char-forming synergists [68], [75], [76]. It was introduced as FR for polyolefins, EVA, and PVC.

3) Melamine polyphosphate
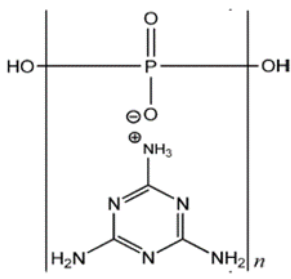
Figure 5-8: Melamine polyphosphate

Melamine salts derivatives (Figure 5-8) have higher decomposition temperatures melamine polyphosphate (MPP), 360 ˚C) in comparison to melamine (250 ˚C) alone and is less soluble in water. Melamine phosphate and melamine pyrophosphate are mainly used in intumescent coatings and in glass-filled polyolefins and PAs. Additionally, it finds application in PET, PBT, or HIPS/PPO [49], [68], [77]–[80].

MPP is characterized by its good thermal stability, under thermal stress, melamine derivatives decompose endothermically (heat sink) and release inert nitrogen gases (e.g. ammonia) that dilute oxygen and the flammable gases in the flame. Often phosphoric acid is also formed as a decomposition product and promotes the formation of insulating char on the surface of the polymer.

4) Phosphoric acid aryl esters for plastics enclosures

The use of plastics in housings for Electric & Electronic sector is very extended. This application has a huge potential for recycling and circular approach, therefore this topic is considered in more detail in this report.

Electronic enclosures are a market segment which includes primarily the enclosures of consumer and information technology equipment such as televisions, desktop or notebook computers, monitors, printers, copiers, household appliances, etc. Different types of polymer resins such as high impact polystyrene (HIPS), acrylonitrile butadiene styrene (ABS) copolymers, polycarbonate-ABS blends (PC/ABS), and polyphenylene ether-HIPS blends (PPE/HIPS) and polycarbonate (PC), are used for this application.

International standards provide that the plastic materials used for these housings usually should meet high fire safety standards such as UL 94 V or similar flame retardant specification. In general, it is not possible to meet these requirements with the pure polymer resins. Therefore, flame retardants are added to the polymer compound. Halogen free phosphates based flame retardants are of growing importance in this electronic enclosures segment, because the electronics industry tends to move to more sustainable flame retardants. In addition to the required level of fire safety, the used polymer resins have to meet additional criteria such as: (1) Processability, in this case a high melt flow, which allows a high throughput is preferred. (2) Thermal stability, if a higher Heat Deflection Temperature (HDT) is required. (3) Mechanical properties, in particular a high impact strength is requested. (4) Hydrolytic stability, if a high resistance against degradation caused by moisture is stipulated. (5) Recyclability, the used polymer resins must be suitable for easy separation and they should be recyclable with standard processes. And (6) RoHS and WEEE directives to which the plastics should comply.

Figure 5-9 shows principle aryl phosphates used as flame retardants. Resorcinol bis(diphenyl phosphate) (RDP) and bisphenol A bis(diphenyl phosphate) (BDP) are mixtures of oligomers with two to five phosphorus atoms, but with their molecular weight distribution shifted mainly toward the diphosphates. RDP has higher phosphorus content than BDP and is therefore more efficient as a FR. On the other hand, BDP is more thermally and hydrolytically stable than RDP. Resorcinol bis (di-2,6-xylenyl phosphate) (RXP) has a higher hydrolytic stability than RDP and BDP due to the steric hindrance by the 2,6-xylyl groups. Triphenyl phosphate (TPP) is the most volatile aryl phosphate.
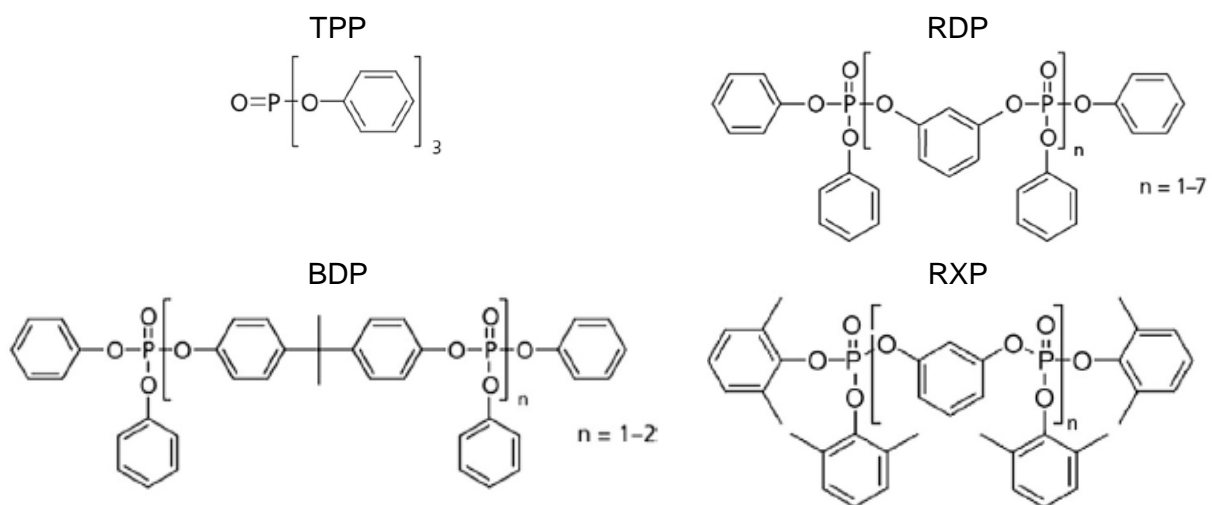
Figure 5-9: Main aryl phosphates used as flame retardants

Other compounds include Cresyl diphenyl phosphate - (diphenyl tolyl phosphate), Tricresyl phosphate (TCP), Triethyl phosphate (TEP), Tris-(2-ethylhexyl) phosphate or Trixylyl phosphate (TXP).

The effect of aryl phosphates in fire retardancy, mechanical and thermal properties of polymeric blends have been extensively studied in polymers that include HIPS/PPO, PC/ABS, PC, PA, PBT, PET, and thermoplastic elastomers [49], [55], [56], [81]–[85]. Specially, Aryl phosphates are suitable halogen-free FRs for PC/ABS blends. The required loadings depend on the ratio of PC and ABS in the blend. In commercial PC/ABS blends where the ABS content normally does not exceed 25% it is possible to achieve a UL 94 V 0 rating with these products at 8 – 15 wt.% loading in combination with a co-additive. The co-additive usually retards the dripping. A common anti-dripping agent is PTFE with loadings up to 0,5 wt.%. The effect of the addition of different aryl-phosphates in the physico-chemical properties of recovered post-consumer PC/ABS blends have been studied in the CloseWEEE project [86].

5) Red phosphorus

Red phosphorus is thermally stable up to 450 ˚C and is not spontaneously flammable. Red phosphorous act in the gas phase by flame poisoning effect, it breaks down during the process of fire to form P_2-molecules that are active species. Red phosphorus is a very effective FR for glass fiber-reinforced PAs, PBT and is used in thermosets and polyolefins for wire and cable applications as well [49], [56], [68], [87]. Intense red color prevents its use in non-colored applications. Additionally, the emission of toxic phosphine gas can be created by the reaction of phosphorus with traces of water and oxygen. Therefore, suppliers provide red phosphorus in encapsulated or chemically stabilized compounds.

6) Phosphonates
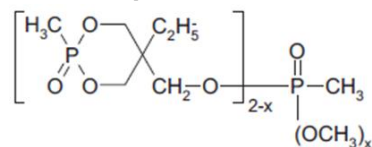
Figure 5-10: Organic phosphonate

Phosphonates or phosphonic acids (Figure 5-10) are organic compounds containing C-$PO(OH)_2$ or C-$PO(OR)_2$ groups (where R = alkyl, aryl). Its activity in flame retardance have been reported for different authors [88]–[90]. Normally they are more efficient FRs than phosphates, but raw materials for phosphonates are more expensive than for phosphates. Recently a novel phosphonate-containing PC designed for the use in PC and PC/ABS, epoxy resins, and polyesters have been developed by FRX Company and is present in the market [68], [91], [92]. Other phosphonate derivates, Dimethyl/ Trimethyl methyl phosphonate, have been reported to be flame retardant actives for PU foams, PE, PP, EVA-cop and PA [49], [56], [68].

7) Phosphinates
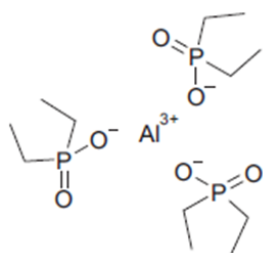
Figure 5-11: organophosphinate aluminium salt

Phosphinates are compounds with the formula $OP(OR)R_2$. Several families of phosphinates have been developed and are commercially available. Especially relevant are the aluminum salts of organophosphinates/Hypophosphites (Figure 5-11) with special application in PA and Polyesters, alone or with other synergist like melamine derivates. Other studied polymers include PBT, PP, PC, PC/ABS and Thermoplastic elastomers. This flame retardants are effectives both in condensed and gas phase (flame poisoning) [49], [78], [93]–[97].

Special attention must be taken during polymer processing with phosphinates. The release of phosphine gas ($PH3$, CAS-No. 7803-51-2), which is very toxic and highly flammable with garlic like smell, can be promoted at elevated temperatures. Synergy effect of Aluminum phosphinates + melamine polyphosphate (MPP) is appreciated in the formation of residue in the condensed phase and release of melamine and phosphinic acid in the gas phase. The aluminum phosphate acts as a barrier for fuel and heat transport, whereas the melamine results in fuel dilution and the phosphinic acid results in flame inhibition.

8) Reactive Phosphorous flame retardant

Epoxy resins that are fire retarded with conventional additives are of poorer physical properties than the unmodified ones; therefore, in many cases, the use of reactive comonomers is preferred. With this approach, the flame retardant is incorporated in the polymer chain so the general properties (mechanical, stability and so on) are improved. The most versatile method involves incorporating phosphorus-containing compounds that react easily with the OH groups of the resin, resulting during fire in high char yield. Extensive reviews on phosphorus-containing flame retardants for epoxy resins have been previously published by Jain et al. [98] in 2002, by Levchik et al. [99] in 2004, by Döring et al. [100] in 2010 and Marosi et al [101] in 2016. Other Reactive phosphorus FRs are mainly used in polyethylene terephthalate (PET) fibers and polyurethane (PU) foams.

Despite their disadvantages, the additive fire retardants dominate the market for this applications because most of the available reactive solutions are too complicated and expensive.

5.2.7 Nitrogen based flame retardant

Well-known nitrogen based flame retardants have an application as part of an intumescent system, melamine, urea, guanidine are examples of this. Nitrogen containing flame retardants alone only find limited application in polymers, e.g. melamine in polyurethane foams and melamine cyanurate in polyamides. Specifically developed systems based on melamine and derivatives are used in intumescent systems that have already been reviewed in this work, such as ammonium polyphosphate (APP) and melamine (poly)phosphate. Most of the above-mentioned salt structures of melamine and related substances act in the condensed phase through endothermic decomposition of the flame retardant, dilution of the burning gases through the formation of inert gaseous molecules, and through char formation.

1) Melamine cyanurate
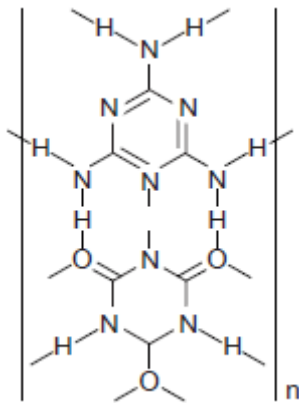
Figure 5-12: Melamine cyanurate

Melamine cyanurate (MC, Figure 5-12) is especially suited for unfilled and mineral filled polyamides. UL V0 can be achieved with 10 to 15% in unfilled PA and up to 20% for UL V2 in low glass filled PA 6. It is known that the effectiveness of MC is higher in PA66 than in PA6. Flame retardant mechanisms may be chemical and/or physical. The majority of the mechanisms described for MC are physical. The sublimation of melamine (ΔH_{subl} = 960 J/ g) and the degradation of cyanuric acid (ΔH = 7.1kJ/g) and melamine (ΔH = 15.5 kJ/g) are endothermic process, which may result in flame retardancy due to the formation of heat sinks. The decomposition of MC also leads to the formation of inert gases that dilute the fuel gases. According to a different postulated mechanism, MC leads to increased dripping, resulting in the withdrawal of fuel from the flame and thus flame retardancy [102], [103]. MC is often used as synergist in combination with other phosphorus based FRs [49].

2) Monomeric N-alkoxy hindered amines

A somewhat different activity mechanism was found by using alkoxyamines (NOR) as flame retardants. Those compounds forms radical species during decomposition. It was demonstrated that alkoxyamines alone can achieve flame retardancy, e.g. in polypropylene fibers and films. Meanwhile, various structures and process patents have been published that claim alkoxyamines to be efficient flame retardants [104], [105]. Moreover, the addition of alkoxyamines as an FR synergist can improve the efficiency of conventional flame retardants, whereas all kinds of flame retardants and synergistic mixtures, e.g. brominated compounds, phosphorus compounds.

The activity of the alkoxyamine as a flame retardant is based on the thermolysis of nitroxyl ethers, which leads to the formation of either alkoxy and aminyl radicals or alkyl and nitroxyl radicals (Figure 5-13). Aminyl and alkoxy radicals are very reactive and cause, on the one hand, degradation of polypropylene (and crosslinking of polyethylene). On the other hand, they are involved in the free radical chemical reactions during the combustion process [106].
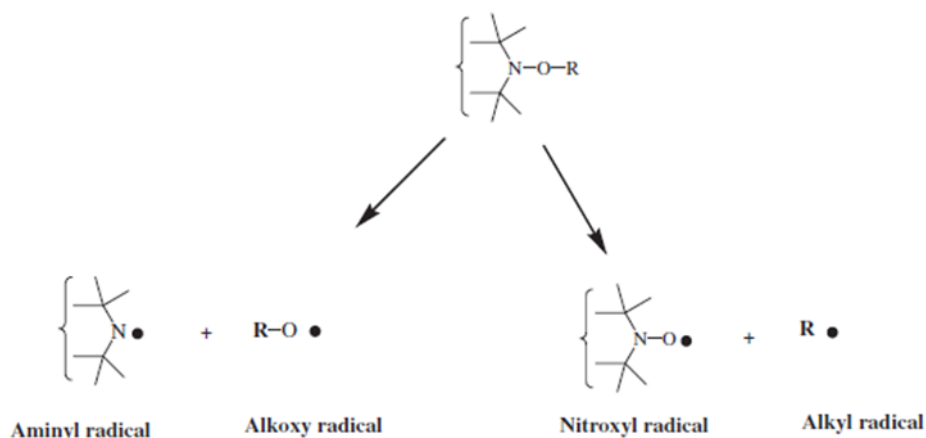
Figure 5-13: Radical decomposition of alkoxyamines

3) Triazines derivates
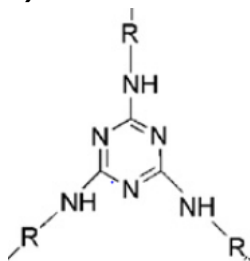
Figure 5-14: Triazine derivate

Inert large molecular weight PPM triazines (Figure 5-14) are nitrogen blowing agents particularly recommended where small molecular weight state-of-the-art nitrogen synergists fail either in processing or in performance such as due to sublimation, liberation of toxic ammonia by self-condensation, mould deposits, and plate-out from or interaction with the polymer itself [107].

5.2.8 Sulphur based flame retardant

Sulfur compounds have been appointed recently as promising flame retardant for polymers [108]–[112]. To date, no sulfur based additives are being commercialized as flame retardant, except expandable graphite that include sulfuric acid in the interlamellar space of graphite layers [113], [114]. Expandable graphite is a synthesized intercalation compound of graphite that expands or exfoliates when heated. This material is manufactured by treating flake graphite with various intercalation reagents that migrate between the graphene layers in a graphite crystal and remain as stable species. If exposed to a rapid increase in temperature, these intercalation compounds decompose into gaseous products, which results in high inter-graphene layer pressure. This pressure develops enough force to push apart graphite basal planes. The result is an increase in the volume of the graphite of up to 300 times, a lowering of bulk density, and approximately a 10-fold increase in surface area. The generated intumescent layer protects the polymeric material below. Phosphorous-sulphur compounds (disulphides) are being used currently in textiles (Viscosa)[108].

5.2.9 Nanofillers as flame retardants

Nanometric particles when individualized and properly dispersed in polymer matrices are known to contribute to the enhancement of polymer properties. Polymers reinforced with as

little as 2% to 5% of these particles via melt compounding or in-situ polymerization exhibit dramatic improvements in thermo-mechanical properties, barrier properties and flame retardancy. They enable a considerable reduction of the filler loading rate as the interfacial area between the polymer and the nanofiller is greatly increased.

More precisely, the contribution of each type of nanoparticle to flame retardancy varies and strictly depends on its chemical structure and geometry. Nanoparticles could be differentiated according to their geometry. Nanocomposites can be classified into three categories according to the number of dimensions of the nanofillers (<100 nm) dispersed in polymers: (1) lamellar, (2) nanotubular, and (3) spherical polymer nanocomposites. Examples are:

1. *Layered materials: such as nanoclays (e.g., montmorillonite: MMT), which are characterized by one nanometric dimension.*
2. *Fibrous materials, such as carbon nanotubes and sepiolite, which are characterized by elongated structures with two nanometric dimension.*
3. *Particulate materials, such as polyhedral oligosilsesquioxane (POSS) and spherical silica nanoparticles, which are characterized by three nanometric dimensions.*

The two types of nano-fillers that have been most widely discussed and the first to break into commercial use are nanoclays and carbon nanotubes. Both are chemically modified with surface treatments in order to achieve the fine dispersion and resin coupling required to derive maximum benefit. Both of these nanofillers have demonstrated improvements in structural, thermal, barrier and flame-retardant properties of plastics. Carbon nanotubes also enhance electrical conductivity.

1) Nanoclays

Nanoclays effects are observed when are properly dispersed in the polymer matrix. Spontaneous intercalation between the layers of phyllosilicates (Clays) is limited to small molecules, and hydrophilic polymers such as polyethylene oxide. In order to render these hydrophilic phyllosilicates more organophilic, the hydrated cations in the interlayer can be exchanged with cationic surfactants such as alkylammonium or alkylphosphonium to lower the surface energy, thus improving the wetting by the polymer matrix. The phyllosilicates modified with organic surfactant is usually referred to as modified clay or organoclay.

It is generally agreed that the combustion behavior of polymer nanocomposites strictly depends on the interface between polymer condensed phase and the gas phase. The function of the organoclay and other nanofillers as flame retardant synergist is basically to form a stable and strong char (barrier) on the polymer surface in case of a fire. This barrier prevents the exposure of further low molecular decomposition products, thus stopping the "refueling" of the fire and works as a thermal insulation preventing further polymer degradation. In particular, a reduction of the heat release rate is generally observed as a consequence to a lower fuel feed rate, often without substantial modifications of the total heat evolved [115], [116].

Nanocomposites studies have revealed that increased carbonaceous char yields in the presence of silicates is promoted in PA, PC polymers with an intrinsic charring ability. A detailed study of the flame-retardant mechanism of polymer-clay nanocomposites showed that a clay reinforced carbonaceous char is formed during combustion also for nanocomposites which base polymer matrix that normally produce little or no char when burned alone, such as polyethylene (PE), polypropylene (PP), poly[ethylene-co-(vinyl acetate)] (EVA) polystyrene (HIPS) , or acrylonitrile-butadiene -styrene (ABS) copolymer [49], [56], [117]–[122].

Montmorillonite and sepiolite organically modified are commercially available as flame retardant additives. Those nanoparticles are normally used with phosphorus-based fire retardant as part of an intumescent flame retardant system. Phosphorus-based fire retardants and nanofillers both act as barriers during combustion; therefore, adding nanofillers to composites containing phosphorus-based fire retardants will reinforce the barrier effect [123], [124].

For wire and cable applications organoclays are normally used in combination with traditional flame retardants such as ATH and MDH because compounds containing only organoclays are not fulfilling the required flame retardancy. The main purpose of combining nanofillers with metal hydroxides is to reduce the metal-hydroxide load without deteriorating flame retardancy. So far the usage of organoclays is nearly entirely within EVA based cable compounds, with filling levels in the range of 3-5%. The content of the traditional flame retardant in these compounds can be reduced down to 50% versus 60-65% in absence of the organoclay for moderate and standard flame retardant requirements. To fulfil higher classifications of Reaction to Fire cables, the total loading including nanocomposite synergists are in the range of 65% [125], [126].

Recently, Layered double hydroxides (LDH) has been synthetized and appointed as potential flame retardants, this material as a hydrated material (very similar to $Mg(OH)_2$ or $Al(OH)_3$) is of particular interest because of its potential to release water under firing conditions. Therefore LDH can have a dual action as a nanofiller that could retard the combustion process, as well as a FR agent via its endothermic decomposition during polymer degradation [127].

5.2.10 Bio-based flame retardants

Today, new flame retardants, based on renewable resources, are attracting great interest, due to their availability and the growing awareness of environmental issues linked to the increased use of fossil feedstock. Furthermore, the development of flame retardant systems from renewable resources is suitable for supporting the increasingly use of bio-based polymers in many technical fields, maintaining thus their sustainability and preserving their good environmental impact.

As explained before, one category of flame retardants widely used for protecting polymers against fire is that of char-forming materials. These materials swell (intumesce) during degradation (combustion), creating a shield that protects the substrate. Thus, research and development of new intumescent bio based flame retardants has been focused on finding ways to increase this char-forming tendency, since there is a strong correlation between char yield and fire resistance.

The char formation during the burning of wood is well known. When exposed to heat, the temperature of the wood surface increases, the water adsorbed in the wood starts to be released and the decomposition of the wood constituents, i.e. lignin, cellulose and hemicelluloses, begins around 160–180 ˚C. At 350–360 ˚C, ignition of the wood can occur in the presence of a spark, and the accelerated degradation leads to the formation of a charred layer which acts as an insulator for the underlying wood. The decomposition of suberin (waxy substance composed of polyaliphatic and polyaromatic domains interlinked by glycerol), cellulose and lignin promote the formation of char. These bio-based compounds owe their advantages as flame retardant additives to their molecular composition and structure providing them inherent ability to produce thermally stable charred residues when exposed to fire.

Starch, cellulose, and lignin have been found to be easy oxidized by oxygen in the presence of copper salts and alkali. The basic products of oxidation are salts of polyoxyacids. Such salts can be used as components of flame retardant system [128].

1) Cellulose

Cellulose has the advantage of being easily functionalized, since it contains a high amount of hydroxyl functions. The chemical modification of cellulose is an interesting way to tailor cellulose properties and enhance its fire-retardant behavior. The phosphorylation of cellulose is the most extensively explored modification for improving its char-forming ability, and hence its fire retardant properties [129], [130]. The incorporation of the phosphorylated cellulose propionate derivatives into PLA resulted in a UL 94 V-2 rating [131].

2) Starch

Starch has been mainly used as a carbon source in intumescent flame retardant systems [132]. Oxidized starch has also been proven to have a high Flame retardant ability. Studies of thermal decomposition of oxidized starch (at dynamic heating between 25 and 950 °C) have shown that the formation of foam coke occurs at the very early stages of decomposition (at 150-280 °C) as a result of the reduction of polymer viscosity (transition from the glassy state to that of a viscous fluid) and the chemical reactions of decarboxylation and dehydration. Reactions of intermolecular dehydration/decarboxylation promote the formation of the sewed spatially mesh structure, and the stabilization and hardening of the foam coke.

3) Lignin

The thermal degradation of lignin begins between 150 °C and 275 °C and continues up to 700 °C with the formation of stable charred residues. Its main steps correspond to a first mass loss, below 180 °C, resulting from water release and condensation reactions, and to a second mass loss in a broad temperature range, from 150 °C to 800 °C, resulting from lignin structure decomposition and leading to the formation of highly stable carbonaceous structures [133].

The incorporation of 15 to 20 wt.% lignin into polypropylene (PP) [128] has proven to be effective in improving its fire behavior. The use of lignin as the carbonization agent instead of pentaerytrytol PER, in intumescent systems, is a suitable solution for enhancing the amount of bio-based materials, while maintaining fire retardant performances in PLA [134].

The phosphorylation of lignin is being increasingly studied [135], generally in order to improve its flame retardant properties. Phosphorylated lignin, which has both a thermally stable aromatic structure and phosphorous groups, usually exhibits a much higher char forming potential [136], which can be attributed to the dehydration effect of the phosphoric acid compounds generated during thermal degradation, and has been proved effective for polymers like ABS and PLA.

4) Other Bio-based flame retardants

Chitosan, the fully or partially deacetylated form of chitin, is one of the very few natural polymers which has a primary amino group along its backbone. Modified chitosan has been studied as flame retardant for Epoxy, PLA and PU resins [137].

DNA represents a potential as a bio-based flame retardant acting as an all-in-one intumescent flame retardant system for polymeric materials. Indeed, it contains the three typical components of these systems, each nucleotide is composed of a nitrogen-containing nucleobase, i.e. cytosine, guanine, adenine, and thymine, a five-carbon sugar, i.e. deoxyribose, and a phosphate group. Therefore it is able to form an intumescent char

when exposed to heat [138]. Under the action of temperature, the phosphate groups produce phosphoric acid, which constitutes the acid source; the deoxyribose units act as the carbonization agent by decomposing with auto-crosslinking process, giving rise to the formation of aromatic structures, and the nitrogen-containing bases act as the blowing agent by releasing ammonia. Its effect have been shown in polymers like EVA and PET. Proteins, such as casein, hydrophobins, or whey protein, have been shown to present some interest as flame retardants, mainly for cotton fabrics. The presence of such protein-based coatings on cotton fabrics induces a premature cellulose thermal decomposition, thus favoring the char forming pathway, instead of the depolymerization with further production of volatiles, thanks to the release of acidic species, such as phosphoric or sulfuric acid [139].

5.3 Flame retardants, end of life and recycling related issues.

5.3.1 Environmental, health and regulatory issues.

The discussions about halogenated flame retardants started, when some brominated flame retardants (BFRs) became a topic of environmental concern in the early 1990ies., when it was discovered that some BFRs could form halogenated dioxins and furans under severe thermal stress or when they were burnt in accidental fires or uncontrolled combustion [140]. Findings in the environment and biota and the suspicion that some flame retardants bio accumulate in organisms have added to these concerns [141]–[144].

Public concern has been translated to European legislation and those has had an important effect in E&E sector in Europe. In 2003, the Restriction of Hazardous Substances Directive (RoHS) was adopted by the European Union. This restricts the use of certain hazardous substances in E & E equipment (Directive 2002/95/EC). It limits the use of six hazardous materials, including BFRs (Brominated flame retardants), in the manufacture of various types of electronic and electrical equipment, and is closely linked with the Waste Electrical and Electronic Equipment Directive (WEEE) (Directive 2002/96/EC), which sets collection, recycling, and recovery targets for electrical goods and is part of a legislative initiative to solve the problem of huge amounts of toxic electronic waste. The maximum concentrations of PBBs and PBDEs allowed are 0.1 wt.% of homogeneous material, without separate collection and treatment.

The RoHS procedure has now combined with EU Registration, Evaluation, Authorization and restriction of Chemicals (REACH), to become a new regulation EC/2006/1907. REACH addresses the production and use of chemical substances and their potential impacts on both human health and the environment, regulating manufacture and use of all man-made non-polymeric chemical substances. The 10-year phased implementation of REACH started in 2007. BFRs were one of the first categories investigated by REACH and the investigation was almost complete within 2 years. The use of penta-PBDE and octa-PBDE was severely restricted, while deliberations on deca-PBDE still continue.

With the gradual pressure over the use of polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) as flame retardants, an urgent demand for alternative FRs has been increasing. Due to their technical characteristics, organophosphorus compounds (OPs) are suitable substitutes for brominated flame retardants (BFRs) and have been extensively used worldwide in a variety of industries, including plastics, furniture, textile, electronics, construction, vehicle and petroleum industries. Therefore a new focus has been stablished on the environmental and health profile of phosphorous compounds. As explained before, many of the OPs are frequently present as additives rather than chemically bonded to diverse materials, therefore several studies related to the occurrence and environmental behaviors of OP have been carried out. The occurrence and environmental behaviors of OPs in diverse matrices (e.g., dust, air,

water, sediment, soil and biota) have been reviewed, but there is insufficient knowledge related to the toxicity of OPs, and only a few reports of adverse effects have been published. The criteria for persistent organic pollutants (POPs), i.e., persistence, bioaccumulation, toxicity and LRAT, is being investigated to determine whether OPs are new candidates for the POPs (Persistent Organic Pollutants) list and proper substitutes for BFRs and to consider whether regulations are reasonable and required [145].

Recently, some non-halogen flame retardants has been included in annex 14 and 17 of REACH as substances of "Very High Concern" (SVHC): inorganic ammonium salts and trixylylphosphate (TXP). The restriction of inorganic ammonium salts relates to the regrettable use of inappropriate materials in cellulosic building insulation material which caused the emission of ammonia in the past, mainly in France. Therefore, the restriction is very specific for this application. TXP is an aryl phosphate which can be used in E&E applications. However, other alternatives to this substance exist, should it become an SHVC.

In addition to public regulations, other environmental requirements can affect the development of flame retardant market. As an example, ecolabels have been introduced since the 1970's as voluntary measures in order to promote environmentally conscious products. The idea is that the consumer can make a conscientious decision for such products, and the manufacturers can demonstrate compliance with environmental standards if they are labelled according to an accepted and respected scheme. Worldwide there are about 25 ecolabel organizations and schemes. Although the framework for the operation of ecolabel schemes is governed by regulation, their actual use is voluntary. Individual schemes develop and publish environmental performance criteria for product groups (for example, TVs, furniture, etc.), which have to be met to qualify for an ecolabel.

The European Ecolabel is the most widespread scheme, established in 1992 to encourage businesses to market products and services that are more environmental friendly, and aims to substitute hazardous substances with safer ones [146]. Traditionally, many ecolabel systems have prohibited the use of most halogenated flame retardants in their criteria for electronic products (e.g. EU label, Blue Angel in Germany, Nordic Swan in Scandinavia, and TCO in Sweden). Often, the flame retardants which are used in products need to be declared to the Eco labelling organization. Ecolabels are also relevant for green public procurement, because e.g. in Europe ecolabel criteria can be included in public calls for tender.

5.3.2 Recycling

Recyclability of plastics containing flame retardants is a key factor to improve life cycle and carbon foot print of electric & electronic sector. In 2014 about 12% of all used FRs in Europe where for electronic and appliances and another 20% for wires and cables. Largest use is in Building and construction (37%). At the end of their use phase, flame retarded polymers become part of waste streams and may be subjected to recycling activities.

Over the past decade, the fate of electronic waste and the contained hazardous materials have gained increasing political attention and have led to the WEEE and RoHS Directives in Europe. Specifically, the European WEEE (Waste Electrical and Electronic Equipment, 2002/96/EC) Directive is an example of regulations which force producers to consider the full life-cycle of manufactured goods. Plastic components not recycled directly are stripped of hardware, washed, granulated and recycled back into the market for use in a similar or completely different application. The WEEE directive bans recycling of composites containing hazardous heavy metals and brominated flame retardants back into the feed steam. Therefore, current waste technology prefers not to have halogenated additives in this feed stream as it may limit or "poison" the subsequent generation of products. Although the U.S. and other regional markets do not have similar regulations, many manufacturers/fabricators are global producers and prefer to standardize their products using similarly sourced

materials. By de facto, these companies force these regulations and the practice of recycling components becomes a design consideration in the life-cycle of products.

Unfortunately, despite the favorable regulatory framework in Europe, certified recycling companies often operate on a commercial basis and compete mainly on cost to obtain a share of the collected WEEE stream. As a result, recyclers often face supply uncertainties and strive to reduce processing costs. Furthermore, direct cooperation between manufacturers or retailers and recyclers is a rare phenomenon. Consequently, recyclers seldom have access to information about material content of the products they process. Under these boundary conditions, disassembly is merely performed in very specific reuse oriented cases or when the removal of hazardous substances is required by legislation [147].

Currently, a substantial amount of WEEE is treated in size reduction based processes. In such treatments, following magnetic and eddy current separation, a plastic dominated mix remains. From this plastic mix the non-FR HIPS and ABS can be separated for reapplication by means of sink float techniques. The remaining fraction contains a mix of different types of heavy plastics and plastics with PFRs, BrFR or Glass Fibers (GF). Because of the mostly black color and the density overlaps between these higher density plastics, they cannot be separated by commonly used separation techniques [148]. As a result, the most adopted End-of-Life (EoL) treatments for FR plastics in Europe are incineration with energy recovery, co-combustion in cement kilns or land filling [32]. Even when plastic housings are disassembled, they are rarely sorted out from other plastic components, because the (black) plastic and FR type used in these components often cannot be identified easily. For this reason, many FR housing plastics are shredded after disassembly and processed in a similar way as in a size-reduction based recycling strategy [149].

Main work to date in recycling has been directed to the study of treatment of current WEEE streams. Flame retardants in WEEE have been studied by a variety of authors [150]–[152] who revealed the presence of additive and reactively bound FR. The latter are mainly used in resins of printed circuit boards, whereas additive FRs are mainly found in thermoplastics. Relevant polymer fractions in WEEE have a rather high share of flame retarded types, including BFR polymers [153].

5.3.2.1 Recycling of thermoplastics: Case studies

Laboratory tests have demonstrated that different FR plastics can be recycled and that the degree of deterioration of mechanical properties of the plastics and flame resistance strongly depends on the applied type of FR and stabilizer compounds [154]–[157]. One of the most extended recycling process for post industrial waste is recompounding, that mainly include the reprocessing of production waste in the same production line. Compared to virgin polymers, recompounded polymers have been exposed to thermal-oxidative stress more than once, and therefore, their physic mechanical properties may have been deteriorated, as reported in several studies. Post-consumer waste material need a preprocessing step before being available for a new cycle of compounding. Several sorting processed have to be carried out in order to separate different polymer fractions and reduce the level of impurities. Shredding; Float; Electrostatic, sieves, spectroscopy detection or solvent based recycling process [158]. Considering the difficulties of complete separation in polymer type, prior research has also assessed the miscibility of different plastics [159]. However, most of these tests were performed with virgin material on a lab scale and little is known on the feasibility of separating FR plastics from the evolving and complex mix of plastics present in WEEE for the purpose of closed loop recycling.

1) Styrenics

BFRs (TBBPA, PBDE, and TBPE) in thermoplastics are mainly used in acrylonitrile butadiene styrene (ABS) and polystyrene (PS). Technically, some commercial

halogenated flame retarded polymers can be recycled without substantial loss of quality in HIPS and ABS polymers [160].

PC/ABS; HIPS/PPO composites are used extensively for housing components in computer and office equipment, so this polymers are becoming more significant in the plastic waste stream. Phosphorous-based FRs are applied in this blends. A specific study of recyclability of FR PC/ABS blends including triaryl phosphate flame retardants (TPP, RDP, BDP) have shown that:

- *Used at typical recycling rates (20% recyclates), all bis-phosphate FRs used in this study meet the industrial standards.*
- *A retention of flammability & impact properties and a stable melt viscosity was noticed*
- *Where hydrolytic stability is an issue, stabilizers can be used.*
- *Polycarbonate is sensitive to acidic conditions.*
- *Different phosphate esters have different hydrolytic stabilities.*
- *All phosphate esters decompose to acid species especially after exposure to high heat and humidity.*
- *Bis-phenol A bridged phosphate (BDP) FRs are less susceptible to hydrolysis but will show PC polymer degradation eventually while polyphosphonate co-carbonates show good hydrolytic stability because they the phosphorus is bound in the backbone.*
- *RDP analogs displayed instability earlier in the testing exposure regime but upon the addition of stabilizers, substantial improvements are seen.*

Summarizing, phosphorous based flame retardants RDP and BPADP shows a reduction of flame efficiency in PC/ABS after humid aging, including a loss of mechanical properties. This is not observed in HIPS/PPO blends, where test carried out at lab scale indicated good retention of properties [154], [155], [161].

In other work, Peeters et al. [162]–[164] has investigated the recyclability of FR plastics coming from LCD Displays, including PC/ABS, HIPS/PPO, ABS and ABS/PMMA, with two recycling scenario: a) disassembly and plastic identification and b) size reduction of waste steams with automated sorting and density based separation process. Disassembled samples shows a reduction of mechanical properties between 10 and 25 % compared with virgin polymers, and flammability performance dropped from V0 to V1, but still the recovered polymers fulfill with the requirements of TV application. However in the size reduction approach and considering the concentration of impurities in the PFR PC/ABS fraction and the results of the miscibility tests, it can be concluded that closed loop recycling of this plastic fraction is only possible when the mechanical and flame retardant properties are enhanced by diluting the impurities and/or by adding compatibilizers. This conclusion is confirmed in the work carried out by Vazquez et al. (ABS/HIPS blends) [165] or Wang et al. (ABS) [29].

2) Polyolefines

The polyolefin fraction of a mixed plastic waste is one of the most valuable for thermomechanical recycling. Recyclable polyolefin fractions can mostly be obtained from automotive, electrical and electronic equipment, and packaging waste. Using a self-reinforcing approach Bocz et al. [166] have development an environmentally friendly composite from secondary raw materials with improved mechanical properties and reduced flammability at the same time, using an APP based intumescent flame retardant additive. In other work, the influence of melamine phosphate on stabilized polypropylene in multiple extrusion experiments has been found to be negligible; moreover, there was no antagonistic effect with HALS in artificial weathering experiments [167]; even, a slight

improvement could be detected due to a pigment effect of the flame retardant. Recycling of melamine cyanurate polyamide compounds, APP polypropylene, and melamine phosphate-polypropylene seems to be feasible with minor properties loss [168], [169].

3) Solvent-based recycling techniques

Solvent-based plastic recycling processes make use of selective organic solvents that are able to dissolve a target polymer whereas non-target polymers of the input fraction do not interact with the solvent. Such approaches enable an efficient cleaning of dissolved target polymers from undissolved polymers, foreign materials, and even codissolved contaminants. After the polymer purification, the solvent is separated from the polymer solution again and reused within the process. A specialized plant concept has been developed and optimized at the Fraunhofer Institute IVV, in Germany, namely the CreaSolv process. Creasolv process is able to eliminate by 98,4% of Brominated flame retardants in WEEE polymers. This technology have been used in the CLOSEWEEE project for cleaning of flame retardant ABS fractions. The recovered ABS is suitable for new E&E applications [86]. However, the CreaSolv process is not yet available on an industrial scale.

5.3.3   Stabilization of flame retardants

5.3.3.1   Phosphorous and nitrogen

One approach to improve flame retardants from a circular perspective is to increase the life time of flame retardant effect in the polymer matrix. In this field several works have been carried out in order to increase processing and long-term thermal and light stabilization of phosphorus and nitrogen-based halogen free flame retardants.

Antioxidants inhibit or reduce the thermo-oxidative degradation in polymers and maintain inherent properties during processing as well as during the product life cycle in the intended application. Antioxidants interrupt the autoxidation cycle by chemical reactions with the formed intermediates. To protect polymers from the negative influence of light, UV-absorbers e.g. benzophenones, benzotriazoles and free radical scavengers in the form of hindered amine light stabilizers (HALS) are used.

The published data on the photo-oxidative stability of phosphorus-based (ammonium polyphosphate, red phosphorus, and melamine(poly, pyro)phosphates) and of nitrogen-based (melamine cyanurate, alkoxyamines) flame retardants are not very numerous. For example, Intumescent flame retardants based on ammonium polyphosphate and pentaerythritol do not modify the degradation of unstabilized PP; the photo-degradation of the polymer and of the flame retardant are independent processes. However, the intumescent flame retardant may influence the light stabilized material. There, the activity of HALS is somewhat reduced likely through protonation by the polyphosphoric acid [170]; however, it is less severe than with brominated compounds. On the other side, the efficiency of an UV-absorber is increased through the polyol present in the flame-retardant combination. In a patent application comparison, it was demonstrated that halogen-containing flame retardants like octabromodiphenylether (OBDE) show significant surface degradation already after 400 h, even in the presence of HALS, while ammonium polyphosphate flame-retarded systems are stable up to 1800 h of artificial light exposure in the presence of 0,5% HALS (LS-4), which is nevertheless lower than that achieved by the stabilized polymer without APP [171]. However, in case of artificial weathering, hydrolysis of ammonium polyphosphate may occur and result in reduced fire retardancy as the formation of the intumescent network is disturbed already after exposure with an incident energy of 210 kJ/cm^2, a value which corresponds to less than 1 year of outside use in mid Europe.

Red phosphorus is mainly used in engineering plastics (polycarbonate, polyamide, polyester), therefore its influence on light and long-term thermal stability is less critical. From

the stabilization point of view, it is more important to stabilize red phosphorus against phosphine formation through moisture, which is achieved by microencapsulation or by adding salts such as copper acetate.

The processing stability of melamine cyanurate containing polyamide is claimed to be improved by addition of sulfates, e.g. magnesium sulfate or metal acetates e.g. magnesium acetate [172].

More recent flame retardant systems mainly for polypropylene/polyolefins thin section applications, such as films or fibers, consist of alkoxyamine structures, which are related to hindered amine light stabilizers. These alkoxyamine flame retardants can be used alone or in combinations with other flame retardants.

An even more efficient molecule with combined flame retardancy and light stabilizer activity was identified in azo-alkoxyamine flame retardants (Azo-NOR); very low concentrations (0,5%) provide flame retardancy to polyolefin films even after extended weathering time [173].

5.3.3.2 Inorganic flame retardants

It is well known that inorganic fillers show, independent of the structures, experimentally a negative effect on the (photo-)oxidative stability of the polymer; however, to a various extent. Interactions between the stabilizer and the filler and adsorption/ desorption mechanisms are mainly responsible for this influence. The surface area of the filler and pore volumes, surface functionality, hydrophilicity, thermal and photosensitization properties of the filler, and transition metal ion content (manganese, iron, titanium) have been found as potential elements of the interaction [174]. Mechano-degradation through the filler forms additional radicals during processing resulting in additional consumption of stabilizers. Furthermore, efficient stabilization of polymers becomes even more complicated when additionally, to natural inorganic fillers other materials, such as carbon black, or pigments, such as TiO_2, are incorporated in the formulation.

The influence of silica (SiO_2) on the oxidative and photo-oxidative stability of polypropylene is correlated to the metal ion (Fe, Al, Ti) content of impurities present in natural silica. Most of the silica act as photosensitizers and accelerate the degradation of the polymer even at low concentrations. Therefore, to achieve the requested processing and long-term properties, the adsorption effect of the filler and the effect of filler impurities must be compensated. One simple solution is to increase the stabilizer level to the necessary extent. So, the selection of an adjusted stabilizer or stabilizer combination for the selected filler polymer pair is decisive.
Layered silicates have been extensively evaluated as flame retardant components, but the stabilization of the resulting nanofillers implies additional challenges. Layered silicates from natural sources (e.g. montmorillonite) contain metal ions as contaminants, which act in the same way as in other fillers but might be more homogeneously distributed and, therefore, their presence is more crucial to the polymer stability than metal ions in micro sized fillers.

Layered silicates as such are only compatible to hydrophilic polymers such as EVA, PA or TPU. As explained, to improve the compatibility of layered silicates to most polymers to allow intercalation or exfoliation, a modification step is necessary to make the filler organophilic. Modification of the clay is usually achieved by cation exchange with a long chain amine or a quaternary ammonium salt. The amount of organic material within the clay can be up to 40% and, therefore, the stability of this organic part cannot be neglected. At processing temperatures during extrusion or for injection molding of most polymers the thermal stability of the ammonium salts is very limited. Most of the ammonium structures tend to undergo Hofmann elimination resulting in volatile olefins and amines. The thermal degradation of

ammonium salts starts already at 180°C and is furthermore reduced by catalytically active sites on the aluminosilicate layer [175].

Some nanocomposites manufactured by hydrophobic polymers such as polyolefins often require on top of the organic modification of the filler an additional compatibilizer e.g. polypropylene-g-maleic anhydride (PP-g-MAH), which is used in concentrations of 5-25%. These lower molecular weights modified polypropylene materials possess usually an inferior stability compared to the parent polymer and, therefore, comprise a further reason for a potential insufficient long-term performance of polymer nanocomposites.

As expected, nanocomposites based on montmorillonite show compared to unfilled materials a dramatic loss in processing and long-term stability [176], [177], e.g. the long-term thermal stability of a stabilized polypropylene at 135°C has been found to decrease from more than 40 days to only 15 days in the presence of 5% organically modified clay. An even more serious problem is the photo-oxidative stability of nanocomposites. Polypropylene montmorillonite based nanocomposites (stabilized with antioxidant) degrade much faster under photo-oxidative conditions than pure polypropylene [178], [179]. This behavior is attributed to the active species of the clay generated by photolysis or photo-oxidation e.g. from alkylammonium modifiers and by interactions between antioxidant, montmorillonite and maleic anhydride modified PP.

Apart from layered silicates similar photooxidation acceleration was found e.g. for nanodispersed hydrotalcite in polypropylene [180], for $CaCO_3$ and SiO_2 nanoparticles [181], for EPDM nanocomposites synthesized from layered double hydroxides (LDH) [182] and for boehmite, modified by long-chain alkyl benzene sulfonic acid in isotactic PP and in syndiotactic PP [183].

Most flame retardants influence the photo-oxidative stability of the polymer substrate directly through acceleration of the degradation process or indirectly by interacting with the antioxidants and light stabilizers. Whereas the behavior of brominated flame retardants is well understood, the impact of halogen free flame retardants on the photooxidation of polymers is investigated in very few examples only.

Phosphorus and nitrogen based flame retardants seem to influence the (photo)oxidative stability of polymers less than brominated compounds and they show no or less antagonism with hindered amine light stabilizers. Some recently developed flame retardants combine flame retardancy and light stabilizer functionality. Adjustment of stabilization of plastics containing fillers either used for mechanical reasons or as flame retardant is necessary to achieve sufficient long-term properties. Filler deactivators can play a decisive role in this respect. Overall, the (photo)oxidative stabilization of non-halogen flame-retarded polymers stays a complex field as the polymer, the flame retardant system, and the additives (processing stabilizers, antioxidants, light stabilizers a.o.) have to be considered together. As not much is known about the interactions of the different components, cost performance and optimization of flame-retarded formulations is still a challenge

6 Nanomaterials

In ISO/TS 80004, nanomaterial is defined as a "material with any external dimension in the nanoscale or having internal structure or surface structure in the nanoscale", with nanoscale defined as the "length range approximately from 1 nm to 100 nm". This includes both nano-objects, which are discrete piece of material, and nanostructured materials, which have internal or surface structure on the nanoscale; a nanomaterial may be a member of both these categories [184].

On 18 October 2011, the European Commission adopted the following definition of a nanomaterial: "A natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm – 100 nm. In specific cases and where warranted by concerns for the environment, health, safety or competitiveness the number size distribution threshold of 50% may be replaced by a threshold between 1% to 50% [185].

The reason why these types of materials caught the attention of scientists, regulators and industries producing advanced materials, is due to the fact that their functionality depends on their size. Auffan et al.3 concluded that there is a critical size that is considerably smaller than 100 nm at which properties of particles change. They identified this critical size of about 20–30 nm by relating the exponential increase in the number of atoms localized at the surface to the size of nanoparticles. This excessive increase in surface energy of nanoparticles results in crystallographic changes [186], [187] and subsequently effects their interfacial reactivity [187], [188].

The presence of nanoparticles in a polymer system provides an opportunity to alter many of the base properties of the system. The extent of alteration and the potential of these materials to exhibit superior properties are dependent on two major aspects: interface between polymer and matrix and confinement of polymer matrix chains at the nano-level.

The interface is a region with altered chemistry, altered polymer chain mobility, and altered crystallinity [189]. With the same volume fraction of filler, the higher radius of curvature of nanoparticles ensures that more polymer is involved in the interfacial regions. This huge interfacial area created by well-dispersed nanoparticles is shown to influence the surrounding polymer matrix, fundamentally influencing the glass transition temperature, T_g and mechanical properties of the matrix [190].

It is known that under conditions of nanoscopic confinement, conformation of chains and segmental mobility are highly affected, suppressing the conventional spherulitic superstructures and resulting in growth of structures with specific crystal orientations. Various reasons are considered for the formation of interfacial zones ranging from chemisorption (e.g. interaction of polar groups with inorganic fillers), to geometric confinement [191]–[193]. Geometric (spatial) confinement specifically hypothesizes that nanoparticles like carbon nanotubes might be treated as macromolecules as their diameters are similar to the radius of gyration of a polymer. Their highly curved surfaces result in strong geometric confinement (by allowing preferential orientation of lamellae) even if (lattice) matching between polymer chain and the filler (graphitic sheet) is absent. This is termed 'soft epitaxy' [194], [195]. While in the case of large diameter particles, as the surface curvature is small, the polymer behaves as if it is on a flat surface and, therefore, require crystallographic lattice matching for preferential lamellae organization.

However, there are many other studies that reported the absence of soft epitaxy despite a uniform dispersion of nanoparticles with sizes similar to or less than individual lamellae. This suggests the complexity in analysing an interface as it is affected by even the slightest

change of shape, size and surface modification (influencing the surface energy) of the particles along with their dispersion/inter-particle distances.

Regardless of these discrepancies about interfacial zones, it is rather more important to identify whether their presence would enhance the filler-polymer interfacial strength and ultimately result in improved mechanical properties. Though mostly positive results are reported in the literature on stiffness and strength of polymer nanocomposites, toughness/ductility is often dramatically reduced (in line with the scaling/dimension arguments) [196]. Nevertheless, their promising potential is realized, in particular with functional and physical properties. These include optical, magnetic, thermal, energy scavenging, biosensing, gas/water barrier, anti-microbial, and biodegradability. As discussed earlier, it is also important to understand how the nanoparticles are dispersed and distributed (inter-particle spacing) in a polymer matrix as many intrinsic properties of polymers are influenced by this [197].

Characteristics such as molecular structure, chemical composition, melting point, boiling point, vapour pressure, flash point, pH, solubility, and water octanol partition coefficient have to be determined for nanomaterials in the same manner as they are for larger non-nanomaterials. In addition, nanomaterial characterization places special emphasis on parameters such as size/size distribution, porosity (pore size), surface area, shape, wettability, zeta potential, adsorption isotherm (adsorption potential), aggregation, distribution of conjugated moieties and impurities [198].

Many methods have been used for evaluating manufactured nanomaterials, including techniques in optical spectroscopy, electron microscopy magnetic resonance, X-ray scattering and spectroscopy, and zeta-potential measurements [199].

6.1 Characterization techniques for nanomaterials

6.1.1 Scanning electron microscopy (SEM)

In contrast to optical microscopy, which uses light sources and glass lenses to illuminate specimens to produce magnified images, electron microscopy (EM) uses beams of accelerated electrons and electrostatic or electromagnetic lenses to generate images of much higher resolution, based on the much shorter wavelengths of electrons than visible light photons. SEM is a surface imaging method in which the incident electron beam scans across the sample surface and interacts with the sample to generate signals reflecting the atomic composition and topographic detail of the specimen surface [200]–[202]. The incident electrons cause emissions of elastic scattering of electrons, referring to backscattered electrons, inelastic scattering of electrons named low-energy secondary electrons, and characteristic X-ray light called cathodoluminescence from the atoms on the sample surface or near-surface material [201]. Among these emissions, detection of the secondary electrons is the most common mode in SEM and can achieve resolution smaller than 1 nm [201]. The size, size distribution and shape of nanomaterials can be directly acquired from SEM; however, the process of drying and contrasting samples may cause shrinkage of the specimen and alter the characteristics of the nanomaterials [200], [203]. In addition, while scanned by an electron beam, nonconductive specimens tend to acquire charge and insufficiently deflect the electron beam, leading to imaging faults or artifacts. In these cases coating an ultrathin layer of electrically conducting material onto the biomolecules is often required [200]. An exception is environmental SEM(ESEM), through which samples can be imaged in their natural state without modification or preparation [199], [204]. Because the sample chamber of ESEM is operated in a low-pressure gaseous environment of 10–50 Torr and high humidity, the charging artifacts can be eliminated, and coating samples with a conductive material is no longer necessary [204].

6.1.2 Transmission electron microscopy (TEM)

As the most frequently used technique for characterizing nanomaterials, TEM provides direct images and chemical information of nanomaterials at a spatial resolution down to the level of atomic dimensions (< 1 nm) [205]. In the conventional TEM mode, an incident electron beam is transmitted through a very thin foil specimen, during which the incident electrons interacting with specimen are transformed to unscattered electrons, elastically scattered electrons or inelastically scattered electrons [206]. The magnification of TEM is mainly determined by the ratio of the distance between objective lens and the specimen and the distance between objective lens and its image plane [206]. The scattered or unscattered electrons are focused by a series of electromagnetic lenses and then projected on a screen to generate an electron diffraction, amplitude-contrast image, a phase-contrast image or a shadow image of varying darkness according to the density of unscattered electrons [206]. In addition to the high spatial resolution of TEM that enhances the morphological and structural analyses of nanomaterials, a wide variety of analytical techniques can be coupled with TEM for different applications; for example, chemical analyses of electron energy loss spectroscopy and energy dispersive X-ray spectroscopy can quantitatively investigate the electronic structure and chemical composition of the nanomaterials, respectively [204], [205]. Overall, both TEM and SEM can reveal the size and shape heterogeneity of nanomaterials, as well as the degrees of aggregation and dispersion. TEM has advantages over SEM in providing better spatial resolution and capability for additional analytical measurements. A significant tradeoff is that a high vacuum and thin sample section are required for electron-beam penetration in TEM measurement [200]. Sample destruction are common to all EM techniques. In general, high resolution EM imaging enables examination of a minute part of the specimen over a certain period of time and results in poor statistical sampling. Also, abundant artifacts are generated due to 3D specimens being probed by the 2D TEM technique in transmission view, leading to no depth sensitivity for a single TEM image. Another limitation is that specimens have to be thin enough to transmit sufficient electrons to produce images; in particular cases, the specimen thickness of less than 50 nm is required while doing high-resolution TEM or electron spectroscopy. The extensive preparation of thin specimens increases the possibility of altering sample's structure and makes TEM analysis a very time consuming process. Another big concern is that TEM specimens can be damaged or even destroyed by intense, high-voltage electron beams.

6.1.3 Scanning tunnelling microscopy

STM uses quantum tunnelling current to generate electron density images for conductive or semi conductive surfaces at the atomic scale [207], [208]. Adapting the generic principle for all SPM techniques, i.e. bringing a susceptible probe in close proximity to the surface of an object measured to monitor the reactions of the probe [209], the essential components of an STM include a sharp scanning tip, an xyz-piezo scanner controlling the lateral and vertical movement of the tip, a coarse control unit positioning the tip close to the sample within the tunnelling range, a vibration isolation stage and feedback regulation electronics [210]. As the tip–sample separation is maintained in the range of 4–7 Å, a small voltage applied between the scanning tip and the surface causes tunnelling of electrons by which variation of the responding current can be recorded while the tip moves across the sample in the x–y plane to generate a map of charge density [211]. Alternatively, keeping the responding current unchanged by adjusting the tip height through the use of feedback electronics can generate an image of tip topography across the sample [211]. The high spatial resolution of STM benefits the characterization of nanoscale biomaterials such as size, shape, structure, and states of dispersion and aggregation. STM is a preferred tool for investigating conductive atomic structures of, for example, carbon nanotubes, fullerenes and graphene.

6.1.4 Atomic force microscopy (AFM)

Unlike STM, AFM does not require oxide-free, electrically conductive surfaces for measurement and is a SPM imaging tool consisting of a micro-machined cantilever (typically made of silicon or silicon nitride) with a sharp tip at one end to detect the deflection of the cantilever tip caused by electrostatic and van der Waals repulsion, as well as attraction between atoms at the tip and on the measured surface [212]. The oscillating cantilever then scans over the surface of specimen to generate an image with a vertical resolution of around 0.5 nm [204]. Like SEM and TEM techniques, AFM can be used for investigating the size, shape, structure, sorption, dispersion and aggregation of nanomaterials — the different scanning modes employed in AFM studies include noncontact mode (also called static mode), contact mode and intermittent sample contact mode (also called dynamic mode and tapping mode) [213].

6.1.5 Dynamic light scattering (DLS)

Several physicochemical characteristics of nanomaterials including hydrodynamic size, shape, structure, aggregation state, and biomolecular conformation can be explored using radiation scattering techniques [199]. DLS, one of the most popular light scattering modalities, can probe the size distribution of small particles, molecules or polymers at the scale from submicron down to one nanometer in solution or suspension using a monochromatic light source, e.g. a laser. The principle of DLS is to monitor the temporal fluctuation of the elastic scattering intensity of light, i.e., Rayleigh scattering, induced from the Brownian motion of the particles/molecules of a size much smaller than the incident light wavelength, at a fixed scattering angle [214]. The intensity fluctuation trace comprises a mixture of the constructive and destructive interferences of the scattered light, through which the particle size can be derived from analysis of the motion-dependent autocorrelation function using the Stokes– Einstein equation. For physicochemical characterization of nanomaterials, the main strengths of DLS include its non-invasive manner, short experiment duration (in minutes), accuracy in determining the hydrodynamic size of monodisperse samples, and capabilities of measuring diluted samples, analyzing samples in a wide range of concentrations and detecting small amounts of higher molecular weight species, along with lower apparatus costs and more reproducible measurement than other methods. However, DLS has limited utility for analysis of samples with heterogeneous size distributions, and resolving the dimensions of a mixed sample population varying in size less than a factor of three; moreover, DLS is unsuited to accurately measuring the sizes of non-spherical nanomaterials because spherical nature of particles is already assumed in the analysis [214].

6.1.6 Raman scattering (RS)

RS is a widely-used tool for structural characterization of nanomaterials and nanostructures that provides submicron spatial resolution for light-transparent material without the requirement of sample preparation, making it suitable for in situ experiments [215]. The principle of RS is to measure the inelastic scattering of photons possessing different frequencies from the incident light after interacting with electric dipoles of the molecule. The process of RS results in frequency differences between the incident photons and the inelastically scattered photons associated with the characteristics of the molecular vibrational states, during which the inelastically scattered photons emitting frequencies lower than the incident photons refer to the Stokes lines in Raman spectrum and the inelastically scattered photons emitting frequencies higher than the incident photons are named Anti-Stokes lines. RS is generally considered to be complementary to IR spectroscopy, i.e., vibrational modes that are Raman active should be IR inactive, and vice versa, for small symmetrical molecules, because Raman transitions result from nuclear motion modulating the polarizability of the molecules, rather than a net change in the dipole moment of the molecules. However, while the conventional RS technique provides indirect characterization

of nanomaterials, such as average size and size distribution through analysis of the spectral line broadening and shift, it lacks the spatial resolution necessary to delineate different domains for application in nanotechnology [215]. By adapting the concept of confining the light field in Raman nearfield scanning optical microscopy to overcome diffraction-limited resolution, a recently emerging technique, tip-enhanced Raman spectroscopy (TERS), utilizes an apertureless metallic tip instead of an optical fiber to gain the surface enhancement of the Raman signals (the SERS effect) [216]. In contrast to conventional RS, SERS and TERS provide topological information of the nanomaterials, in addition to their structural, chemical and electronic properties, which conventional RS provides [217].

6.1.7 Infrared spectroscopy (IR)

Typically, a molecule may absorb IR radiation if it possesses a time variant dipole moment and its oscillating frequency is the same as the frequency of incident IR light [201]. The absorption of IR radiation transfers energy to the molecule, inducing a corresponding covalent bond stretching, bending or twisting, which, in the case of a normal mode, is described by a stationary state of molecular vibrational Hamiltonian. Molecules without dipole moments, e.g. diatomic molecules N_2 and O_2, do not absorb IR radiation [201]. Generally in a molecule, the vibrations involve various coupled pairs of atoms or covalent bonds, each of which must be considered as a combination of the normal modes; therefore, the IR spectrum, illustrating absorption or transmission versus incident IR frequency, can offer a fingerprint of the structure of the molecule of interest. Furthermore, FTIR has also been extended to study nano-scaled materials, such as confirmation of functional molecules covalently grafted onto carbon nanotubes [218]. A recently developed technique called attenuated total reflection (ATR)–FTIR spectroscopy uses the property of total internal reflection in conjunction with IR spectroscopy to probe the structure of adsorbed/deposited species at a solid/air or solid/liquid interface, while avoiding the drawbacks of sample preparation complexity and spectral irreproducibility in conventional IR [201]. In an ATR–FTIR system, the total internal reflectance, occurring within the equipped internal reflection element (IRE) crystal, which has a high refractive index at certain angles, forms evanescent waves that extend from the IRE crystal–sample interface into the sample with penetration depth of micrometers (0,5–5 μm), and the intensity of the evanescent waves decays exponentially from the interface [201]. ATR–FTIR can provide IR absorption spectra to investigate, for example, changes in surface properties as well as identification of chemical properties on the polymer surface when sample on the IRE–sample interface absorbs the evanescent IR waves with frequencies matching the vibrational modes of the sample. Although ATR–FTIR spectroscopy can be implemented to study the surface features of nanomaterials, it is not a very sensitive surface-analysis method at nanometer scale because the penetration depth of ATR–FTIR has the same order of magnitude as the incident IR wavelength.

6.1.8 Nuclear magnetic resonance (NMR)

In contrast to imaging and diffraction techniques affording structural information at long-range order, i.e. the crystalline property, NMR is sensitive to the local environment to resolve the structures of amorphous materials, polymers and biomolecules that lack long-range order [41]. In addition to evaluating the structures and compositions of the species, NMR spectroscopy provides tools to investigate dynamic interactions of the species in different conditions — the relaxation, molecular conformation and molecular mobility can be evaluated through different dynamic measurements using specifically designed rf and/or gradient pulse sequences [219]. NMR spectroscopy has been implemented to determine several physiochemical characteristics of nanomaterials, including structure, purity and functionality in dendrimers, polymers and fullerene derivatives, as well as conformational changes occurring in the interactions between ligands and nanomaterials. Pulsed field gradient NMR has been implemented to evaluate the diffusivity of nanomaterials, through which the sizes and interactions of species under investigation can be calculated [220]. NMR is a non-

destructive/non-invasive technique that requires little sample preparation. However, the low detection sensitivity of NMR, in contrast to optical techniques, requires a relatively large amount of the sample for measurement. It can also be time consuming if a certain level of signal-to-noise ratio is necessary for spectral analysis.

6.1.9 Zeta potential

In an ionic solution, the surface of a charged particle is firmly bound to opposite charged ions, forming a thin liquid layer named the Stern layer, which is encompassed by an outer diffuse layer consisting of loosely associated ions. These two layers compose the so-called electrical double layer [221]. Given the tangential motion driven by an external force or Brownian motion of the charged particle, the movement of the charged particle shears ions migrating with the charge particle in the diffuse layer from ions staying with the bulk dispersant outside the layer. The electric potential on the shear surface is called zeta potential, which is usually determined by measuring the velocity of the charged species towards the electrode in the presence of an external electric field across the sample solution. The zeta potential with a value of ±30 mV is generally chosen to infer particle stability, through which the absolute value greater than 30 mV indicates a stable condition, whereas a low zeta potential value of less than 30 mV indicates a condition towards instability, aggregation, coagulation or flocculation. Among the methods of evaluating zeta potential, the technique of electrophoretic light scattering (ELS), which can simultaneously measure the velocities of many charged particles in liquid, is most commonly used [222], [223]. However, it still suffers the electroosmotic effect that reduces precision and reproducibility of the measurement. Although measuring the zeta potential of suspended particles after dilution reduces difficulty of light penetration into the sample solution, it is worth noting that zeta potential is a property sensitive to environmental changes including pH and ionic strength. Therefore, a precise, repeatable zeta potential measurement in a diluted solution cannot reflect the true value in a concentrated suspension [223].

6.1.10 X-ray Diffraction (XRD)

In a variety of X-ray spectroscopic modalities, XRD is a primary tool for completely resolving the tertiary structures of crystalline materials at the atomic scale. The diffraction of X-ray can be simply described as the reflection of a collimated beam of X-rays incident on the crystalline planes of an examined specimen according to Bragg's law [224]. Typically, XRD, based on wide-angle elastic scattering of X-rays, is a tool for characterizing crystalline size, shape and lattice distortion by long-range order, but is limited to disordered materials [225]. Although XRD is a well-established technique and has frequently been used to determine the material structure at the atomic scale, difficulty in growing crystals and the ability of getting results only from single conformation/binding state of the sample limit the applications of XRD technique [226]. Another disadvantage of XRD is the low intensity of diffracted X-rays, particularly for low atomic number materials, compared with electron diffractions.

6.1.11 Small angle X-ray Scattering (SAXS)

In contrast to XRD, whose applications are limited to crystalline materials, SAXS provides information of several characteristics by examining either crystalline or amorphous materials from polymers, proteins to nanomaterials [227]. In SAXS, a portion of an incident X-ray beam elastically scattered from the sample forms a scattering pattern on a two-dimensional flat X-ray detector perpendicular to the direction of the incident X-ray beam. By analyzing the intensity of the scattered X-ray collected within the scattering angle, ranging from 0.1 to 3°, SAXS can evaluate the size/size distribution, shape, orientation, and structure of a variety of polymers and nanomaterial-bioconjugate systems in solution. The features of small-angle scattering in SAXS lead to the capability of studying non-repeating structures; therefore, perfect crystallized structures are not required, which simplifies sample preparation and makes SAXS a non-destructive method. On the other hand, SAX measurements provide

holistic information about the structure, which exhibits the averaged characteristics rather than local probes of individual grains. This feature can be a disadvantage if high resolution is required. On the other hand, recent progress in SAXS can achieve higher resolution measurements by introducing synchrotron as the high-energy X-ray source. Other X-ray spectroscopic techniques, such as X-ray absorption spectroscopy, can yield information about chemical state and symmetries of the absorption site through analysis of the X-ray absorption near edge structure spectra, and provide structural information, including coordination numbers and inter-atomic distance to ligands and neighbouring atoms from the absorbing element through investigation of the spectra of extended X-ray absorption fine structure (EXAFS) without the requirement of long-range order in the measured species [228]. Both XRD and EXAFS can provide the averaged structural information of a nanomaterial, resulting from a long-range order and a local order of samples examined, in the manner of elastic and inelastic X-ray interaction with the samples, respectively.

6.2 Classification of nanostructured materials (NSMs)

In the past two decades, hundreds of novel NSMs have been obtained; therefore, the need in their classification is ripened. NSMs as a subject of nanotechnology are low dimensional materials comprising of building units of a submicron or nanoscale size at least in one direction and exhibiting size effects [229]. The first classification idea of NSMs was given by Gleiter [230] and was further explained by Skorokhod et al. [231]. However, Gleiter and Skorokhod's scheme was not fully considered because of 0D, 1D, 2D, and 3D structures such as fullerenes, nanotubes, and nanoflowers were not taken into account. Therefore, Pokropivny and Skorokhod [232] reported a modified classification scheme for NSMs, in which 0D, 1D, 2D and 3D NSMs are included.

6.2.1 0D NSMs

A major feature that discriminates various types of nanostructures is their dimensionality. The word ''nano''stems from the Greek word ''nanos''. This word ''nano'' has been assigned to indicate the number 10-9, i.e., one billionth of any unit. In the past 10 years, significant progress has been made in the field of 0D NSMs. A rich variety of physical and chemical methods have been developed for fabricating 0D NMSs with well-controlled dimensions. Recently, 0D NSMs such as uniform particles arrays (quantum dots), heterogeneous particles arrays, core–shell quantum dots, onions, hollow spheres and nanolenses have been synthesized by several research groups [233]–[237].

6.2.2 1D NSMs

In the last decade, 1D NSMs have stimulated an increasing interest due to their importance in research and developments and have a wide range of potential applications. It is generally accepted that 1D NSMs are ideal systems for exploring a large number of novel phenomena at the nanoscale and investigating the size and dimensionality dependence of functional properties. They are also expected to play an important role as both interconnects and the key units in fabricating electronic, optoelectronic, and EEDs with nanoscale dimensions. 1D NSMs such as nanowires, nanorods, nanotubes, nanobelts, nanoribbons, and hierarchical nanostructures have a profound impact in nanoelectronics, nanodevices and systems, nanocomposite materials, alternative energy resources and national security [238].

6.2.3 2D NSMs

2D nanostructures have two dimensions outside of the nanometric size range. In recent years, a synthesis 2D NSMs have become a focal area in materials research, owing to their many low dimensional characteristics different from the bulk properties. In the quest of 2D NSMs, such as junctions (continuous islands), branched structures, nanoprisms, nanoplates, nanosheets, nanowalls, and nanodisks, considerable research attention has been focused over the past few years on their development. 2D NSMs with certain geometries exhibit

unique shape-dependent characteristics and subsequent utilization as building blocks for the key components of nanodevices [239]–[241]. In addition, a 2D NSMs are particularly interesting not only for basic understanding of the mechanism of nanostructure growth, but also for investigation and developing novel applications in sensors, photocatalysts, nanocontainers, nanoreactors, and templates for 2D structures of other materials [242].

6.2.4 3D NSMs

Owing to the large specific surface area and other superior properties over their bulk counterparts arising from quantum size effect, 3D NSMs, have attracted considerable research interest and many 3D NSMs, such as nanoballs (dendritic structures), nanocoils, nanocones, nanopillers and nanoflowers, have been synthesized in the past 10 years. It is well known that the behaviour of NSMs strongly depend on the sizes, shapes, dimensionality and morphologies, which are thus the key factors to their ultimate performance and applications. Therefore it is of great interest to synthesize 3D NSMs with a controlled structure and morphology. In addition, 3D nanostructures are an important material due to its wide range of applications in the area of catalysis, magnetic material and electrode material for batteries. Moreover, the 3D NSMs have recently attracted intensive research interests because the nanostructures have higher surface area and supply enough absorption sites for all involved molecules in a small space. On the other hand, such materials with porosity in three dimensions could lead to a better transport of the molecules [243]–[250].

6.3 Polymer nanocomposites

The very first applications of fillers in polymer industry have had, as a main goal, to reduce the price of the final material. However, it soon became clear that fillers such as some inorganic materials (talc, glass fibers, carbon black, calcium carbonate, several oxides and hydroxides) could significantly improve the polymer matrix characteristics, particularly from a mechanical point of view. Most of these inorganic fillers have been used at a micron size scale, leading to some drawbacks: a high loading is usually required for a modest improvement in properties; the high loading can, in turn, cause a problems in melt flow and processing due to the higher viscosity of the system. Furthermore, the use of high density fillers can lead to a heavier composite. The nature of the interfacial interactions between the filler and the polymeric matrix is another key point in the development of a performing composite [251].

Obviously, the influence of filler's particles size had been studied thoroughly since the beginning of their application to polymer industry and the importance of this parameter soon became clear. It is not surprising that the smaller the particles, the better (potentially) is the possibility of a homogeneous dispersion in the polymer matrix, but a very important role is also played by the interaction of filler and polymer at a molecular level: the possibility of tailoring the characteristics of filler particles through a chemical functionalization in order to achieve a better compatibility is another interesting aspect of the problem.

The developments in the field of nanosciences led to a completely new approach in the world of composite materials, the use of concepts such as *nanofillers* and *nanocomposites* became widespread both in the academic world as well as in the industrial research environment.

Nanomaterials are widely studied as fillers for polymeric matrices, in particular there are examples of 3D, 2D and 1D nanostructures that have been reported to improve one or more properties of the pristine materials such as: mechanical resistance, scratch resistance, fire retardancy, thermal stability, electrical conductivity. In this short review, we focused in particular on mechanical properties enhancements through the use of nanofillers. Informations are grouped following the nature of the polymeric matrix.

6.3.1 Polyethylene (PE) and Polypropylene (PP) nanocomposites

Layered double hydroxide (LDH) are inorganic materials with a 2D highly tunable brucite-like layered crystal structure and are promising candidates for the development of new

nanocomposites, they've been studied both in the original form that in modified alternatives, Charifou et al. performed the optimization of the morphology, thermal, and mechanical properties of polypropylene through the addition of modified LDH by a calcination/rehydration process and the use of two different surfactant molecules (sodium dodecylsulfate, SDS and sodium dodecylbenzensulfonate). The analysis of the nanocomposites samples were performed by thermal gravimetry (TG), XRPD, FT-IR, and, of course, a mechanical properties study. The nanocomposites prepared from modified nanofillers exhibited improved thermal stability; significant increase of the tensile modulus was obtained by adding PP-g-MA in the nanocomposite prepared from SDS modified LDH; nanocomposites based on the simultaneous use of PP, SDS-LDH, and PP-g-MA exhibited the most interesting combination of transparency, thermal and mechanical properties. On the other hand, the high amount of modifying agent beared by the modified fillers associated to the high content of interfacial area developed in PP/SDS-LDH nanocomposite led to the lowest tensile modulus [252].

Natural and modified nanoclays are an important class of nanofillers and they have been evaluated for a wide series of polymers for the production of valuable nanocomposites. Lapshin et al. studied the effect of a natural montmorillonite (Cloisite 20A) modified with a quaternary ammonium salt on the properties of HDPE and PP. In this study, an ultrasound assisted process have been used to prepare nanocomposites. It was found that, upon the addition of 2.5% additive, elongation at break and toughness improved and that the intercalation/exfoliation of nanofillers resulted improved by the ultrasounds treatment. As a drawback, it has been noted that the ultrasounds application may lead to a partial degradation of the polymer matrix [253].

The effect of nanofillers had been evaluated also in the case of recycled (the recycling process had been simulated through multiple extrusions) polypropylene [254]: nanoparticles of calcium carbonate ($CaCO_3$, an inexpensive filler obtained from limestone), appear promising for improving the mechanical characteristics of recycled PP. The study showed an increase in Young's modulus for both virgin and recycled PP and an increase in impact strength for recycled PP with 10% $CaCO_3$ NP loading. On the contrary, a decrease in impact strength for virgin PP with 10% $CaCO_3$ NP loading had been observed.

Calcium carbonate nanoparticles, after $CaCO_3$ surface modification with isopropyl tri-(dioctylpyrophosphato) titanate (JN114), had been used also in combination with high density polyethylene (HDPE) and linear low density polyethylene (LLDPE) and showed some interesting features [255]. Electron microscopy techniques, such as scanning electron microscopy (SEM) and transmission electron microscopy (TEM) indicated the positive effect of the surface modification applied to particles in order to improve the interaction with the polymer matrix, this aspect may be correlated with the improvement in mechanical properties (tensile fracture strength, tensile elastic modulus and Izod impact strength) that have also been observed. As drawback, a decrease in the value of melt flow index (MFI) in direct proportion to the increase in the amount of $nCaCO_3$ can be seen as a potential obstacle in terms of nanocomposite industrial workability.

Metal oxides, such as alumina (Al_2O_3), have been investigated in the form of nanoparticles with a surface pre-treatment (using a silane coupling agent) for the production of LDPE nanocomposites [256]. In this study, the addition of 1wt.% of nanoalumina has successfully enhanced the tensile and elongation at break LDPE nanocomposite, whereas Conc. > 1 wt.% of alumina nanoparticles had caused agglomeration and uneven distribution of NP, leading to poorer mechanical properties.

The influence of LDHs materials has been studied also in combination with graphene and graphene related compounds, in order to investigate possible synergies from these two families of nanofillers. Daud et al. [257] reviewed some of the developments in their synthesis

and applications (i.e. oxygen evolution reactions, supercapacitors, hybrid sensors, adsorption, catalysis, water purification, and flame retardant materials).

Carbon based nanomaterials represent an important class of nanfillers and their use is constantly growing over the last decades. Also carbon nanomaterials, as for any other nanostructures, follow the ordinary grouping into 0D, 1D, 2D and 3D families; examples of carbon nanostructures are respectively fullerenes, carbon nanotubes, graphene and graphite. Any of these kind of nanomaterials possess interesting properties and applications. Expanded graphite (EG) of different particle sizes, 5–7 μm (EG5) and 40–55 μm (EG50) has been studied as a suitable filler material in combination with HDPE, leading to an improvement of mechanical properties: tensile strength of HDPE increased 18.7% and 8.5% with 40 wt.% EG5 and EG50; the storage modulus and the relaxation transition peak of EG5-HDPE and EG50-HDPE is also increased respect to HDPE. On the contrary, upon the increase in filler content up to 10% the tensile strengths of the EG5-HDPE and EG50-HDPE nanocomposites decrease [258].

The effect of multi-wall carbon nanotubes (MWCNTs) has been studied in concentration 1-5 % by Stan et al. for the production of PP nanocomposites. Yield strength and yield strain, stress at break and strain at break measurements showed an increase of Young modulus of the injection molded PP/MWCNTs nanocomposites with increasing carbon nanotube content. Clearly, the results in nanocomposites production depend not only on the nature of nanofillers and polymers but also on processing parameters. For example, studies have been performed to verify the effect of the injection molding parameters (melt temperature and injection pressure) and strain rate on the mechanical properties. Also metamodeling techniques, including the Taguchi method and the analysis of variance (ANOVA), have been applied in this case study [259].

6.3.2 Polycarbonate (PC) nacomposites

Polycarbonates nacomposites have been investigated from a point of view of enhanced mechanical properties through the use of silica nanoparticles as nanofillers. In particular, scratch resistance have been observed to improve significantly upon the addition of up to 5% nano-silica [260].
The behavior of PC-silica nancomposites have been studied also from the point of view of thermal stress, through the use of techniques such as Thermomechanical Analysis and In-situ Temperature Assisted SAXS [261].
As observed for nanocomposites based on other polymers and nanofillers, also in the case of PC-silica NC the amount of filler has been found to be crucial. The effect of silica amount, in the range 1–5 wt.%, on the morphology, mechanical properties and thermal degradation kinetics of polycarbonate was investigated[81]. In this study, several techniques were used to fully understand the behavior of the PC-silica system, also at a molecular level: nanoparticles and composites were characterized using transmission electron microscopy (TEM), X-ray diffractometry (XRD), dynamic mechanical analysis (DMA), thermogravimetric analyses (TGA), and 13C cross-polarization magic angle spinning nuclear magnetic resonance (13C{1H} CP–MAS NMR).
Also TiO_2 had been investigated as a suitable nanofiller with the aim of increasing the mechanical resistance (especially tensile strength and hardness) of nanocomposites films [262].

6.3.3 Polystyrene (PS) and High Impact Polystyrene (HIPS) nanocomposites

Polystyrene is a polymer with a wide field of application and it is manufactured on a very large scale. The brittleness of polystyrene considerably limits its use in some applications. The toughness of polystyrene can be improved by copolymerization or blending with a butadiene elastomer or other rubberlike polymer. This polymer is known as the high-impact polystyrene (HIPS).

Nanofillers have been studied both for the production of PS-nanocomposites and HIPS copolymers nanocomposites. The effect of carbon nanoparticulates (CNPs) for example, clusters loading on polystyrene-CNPs nanocomposites mechanical properties have been investigated. The mechanical properties of carbon nano-tubes composites are largely dependent upon the quantity of CNTs in the system, the dispersion and alignment of the tubes, and the interfacial bonding between the carbon nano- tubes and the matrix [263].

Several additives have been evaluated by Dujkova et al. [264] for the study of HIPS nanocomposites: micromilled calcite Omya EXH 1sp (Calplex), modified silica Aerosil R812 (Degussa), organosilicate nanotubes Halloysite (Sigma-Aldrich) and organically modified layered clay nanofillers Nanofil 5 and Nanofil SE3010 (Südchemie). The use of analytical techniques such as XRD, TEM microscopy, resilience and hardness Shore D measurements, water vapor permeability and gas permeability for nitrogen and air measurements, showed that there is an improvement in water vapor barrier effetct for almost all filled samples , fillers Nanofil 5 and Aerosil R812 showed an improvement of overall barrier properties besides pure HIPS matrix. A drawback is represented by the significant decrease in resilience for all samples .

6.3.4   ABS (Acrylonitrile/Butadiene/Styrene) nanocomposites

The effect of graphene (in concentration 2.5 – 7.5 %) as a suitable nanofiller for the production of Acrylonitrile Butadiene Styrene (ABS) nanocomposites has been studied by Sharma et al., analyzing in particular the advantage of solution blending method over other methods such as melt mixing and in-situ polymerization. The authors observed in the former case a better dispersion of graphene nanofiller. Moreover Young's Modulus for compression for ABS exhibited maximum increase at 2.5 wt.% Graphene loading (38 % enhancement), at higher loading graphene nanofiller resulted to be less dispersed in polymer matrix [265].

The study of organicaly modified montmorillonite (OMMT) in concentration of 5% has been performed by Modesti et al. [266] through X-ray diffraction (XRD), transmission electron microscopy (TEM), dynamic-mechanical analyses (DMA), thermal gravimetric analyses (TGA), and fluorescence spectroscopy (FS) of optical probes. The preparation of nanocomposites have been achieved through melt blending process, low temperature solvent based techniques and ultrasonic-mixing assisted solution processes. The authors found that, regarding thermal stability during processing, particularly good results are obtained for imidazolium salts based modifiers. The good thermal stability observed for imidazolium modified clays suggested in fact their huge potential in the preparation of nanocomposites suitable for elevated processing and/or operating temperatures; OMLS exerted a reinforcing action on the polymer matrix in terms of stiffness.

6.3.5   Polyurethanes (PU) nanocomposites

Montmorillonites (MMT) have been used also in the study of PU nanocomposites. For example, a natural Vietnamese montmorillonite, modified through the intercalation of polyethylene oxide (PEO) and polyvinyl alcohol (PVA), was used to synthesize a PU/clay nanocomposite [226]. The obtained nanocomposites have been characterized by several analytical techniques: TEM, XRD, FT-IR, TGA, DSC, Dynamic Mechanical Analysis Properties (DMA) and Water Adsorption Measurement. The analysis showed that the introduction of inorganic components into organic materials can partially enhance their thermal resistance compared to that of pristine PU. Young's modulus of material enhancement confirms the good dispersion of clays in PU matrix. When the addition of organoclay reached more than 1%, the water absorption function of clay became dominant, leading to slightly higher water absorption and resulted in the decrease of Young's modulus.

Hydrophobic nanoparticles and nanocomposite of 1,4-hexamethylene diisocyanate (HMDI)-modified PU have been synthesized by Pradhan et al. using castor oil and an organically modified montmorillonite (CLOISITE 30B). Polyurethanes and their nanocomposites have been characterized by methods like FTIR, SEM, XRD, TGA, and mechanical testing [254]. Investigation have been carried out also on PU blended with other polymers: for example polyurethane (PU) and polyvinyl chloride (PVC) doped with low different content of single walled-carbon nanotubes (SWCNTs) were studied [267]. In this study a direct solution mixing process was used and the resulting nanocomposites have been analyzed trough XRD, HR-TEM microscopy, FT-IR, thermogravimetric analysis and tensile strength analysis. The PU/PVC was grafted successfully to the SWCNTs surface as indicated by the formation of core-shell structure. This result lead to several improvement respect to pristine material: the tensile strength and elastic modulus increased compared with the pure blend, the thermal stability of the prepared nanocomposites increase with increasing SWCNTs content.

Sohrabi et al. [268] studied the effect of alumina (Al_2O_3) nanoparticles on a blend of thermoplastic polyurethane (TPU) / acrylonitrile butadiene styrene (ABS) using analytical techniques such as SEM-EDAX analysis, mechanical characterizations, dynamic mechanical thermal analysis (DMTA), impact tests, shape memory test. The mechanical properties analysis revealed several interesting features of the obtained nanocomposites. The tensile strength and impact resistance increased for alumina nanoparticles concentration of 1%; the shape memory investigation showed that the shape recovery and fixity of neat TPU/ABS blend improve significantly by presence of alumina nanoparticles. The tensile strength and impact resistance decreased significantly when the content of alumina nanoparticles was more than 1 wt.%.

6.4 Prolabin & Tefarm additives

Prolabin&Tefarm (P&T) exploits its vast experience in synthesis and applications of lamellar solids to develop a wide range of fillers able to improve polymer nanocomposites characteristics in terms of mechanical properties, thermal stability, barrier properties, oxidation and UV resistance. Among nanofillers layered inorganic solids possess unique properties to be active as filler of polymeric nano-composites (Figure 6-1):

- *Exfoliation into single layers*
- *Thickness of the layers at nanometric scale (about 1 nm)*
- *High aspect ratio*
- *Functionalization of the layers increases the compatibility with the polymer*
- *Layered solids may intercalate polymeric chains into the interlayer region*
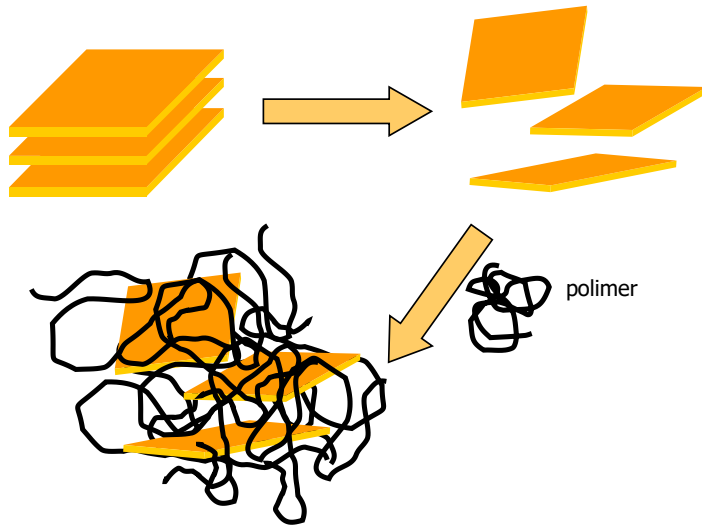
Figure 6-1: Lamellar solids exfoliation process and polymer nanocomposite formation

Hydrotalcite α-zirconium phosphate
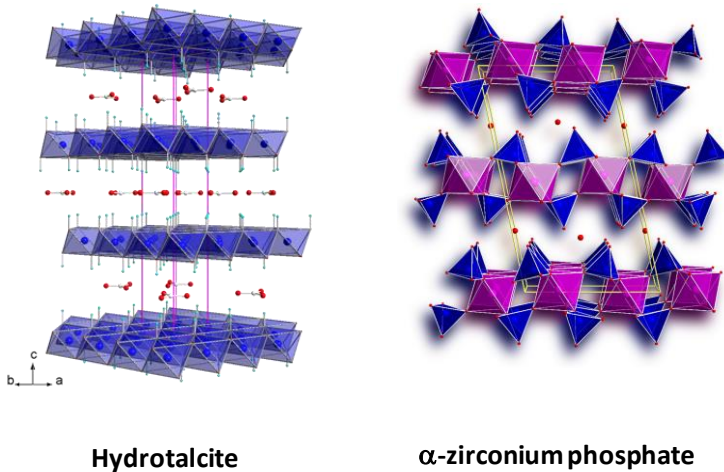
Figure 6-2: Hydrotalcite and α-zirconium phosphate typical structure

Among layered materials, hydrotalcites and phosphates (Figure 6-2) and phosphonates of tetravalent metals compare favorably with organically modified natural clays for many features:

- *Purity*
- *Composition and stoichiometry*
- *Reproducibility*
- *Crystal size and aspect ratio*
- *Wider possibility of layer modification*
- *Higher ion exchange capacity*
- *Storage and release of biologically active species*
- *Preparation is inexpensive*
- *Scalable procedures for industrialization*

For these reasons, hydrotalcite and α-zirconium phosphate (Figure 6-2) are two of the most promising class of lamellar compounds, Prolabin & Tefarm developed a series of

hydrotalcites and α-zirconium phosphates, intercalating different ionic species in these versatile ion-exchange materials.

6.4.1 Selection of P&T additives

In Table 6-1, a selection of P&T hydrotalcite, zirconium phosphate and montmorillonite additives are reported. The intercalation of anions with different properties (especially in terms of hydrophilicity/hydrophobicity) allows to tune the properties of the additive and to optimize the compatibility with polymers and other co-formulants.

The reported additives have been selected on the base of P&T experience in the field of polymer nanocomposites, nevertheless, the pronounced tunability of these systems (obtained through both ion exchange and surface modification) opens the possibility of a wide "application-designed" approach to the synthesis of new compounds.

Table 6-1: Prolabin&Tefarm additives selection

Additive	Short name	CAS numbers	P&T code
Magnesium Aluminum Hydrotalcite carbonate	MgAl-carbonate	11097-59-9	PT-Clay 100
Zinc Aluminum Hydrotalcite carbonate	ZnAl-carbonate	202938-68-9	PT-Clay 200
Zinc Aluminum Hydrotalcite Stearate	ZnAlSte	202938-68-9; 822-16-2	PT-Clay 307
Magnesium Aluminum Hydrotalcite Stearato	MgAlSte	11097-59-9; 822-16-2	PT-Clay 311
Zinc Aluminum Hydrotalcite Dodecylsulfate	ZnAl-DS	202938-68-9; 151-21-3	PT-Clay 313
Magnesium Aluminum Hydrotalcite Dodecylsulfate	MgAl-DS	11097-59-9; 151-21-3	PT-Clay 317
Zinc Aluminum Hydrotalcite Phenylphosphonate	ZnAl-PP	202938-68-9; 66778-08-3	PT-Clay 331
Magnesium Aluminum Hydrotalcite Phenylphosphonate	MgAl-PP	11097-59-9; 66778-08-3	PT-Clay 337
Zirconium Phosphate	ZrP	13772-29-7	PT-Clay 409
Zirconium Phosphate Octadecylamine	ZrP-octa	13772-29-7; 124-30-1	PT-Clay 419
Zirconium Phosphate propylamine	ZrP PrN	13772-29-7; 107-10-8	PT-Clay 421
Zinc Aluminum Hydrotalcite Acrylate	ZnAl-acrylate	202938-68-9; 7446-81-3	PT-Clay 439
Organically modified Montmorillonite	MMT-2MTA1	68953-58-2; 14808-60-7	PT-Clay 501
Organically modified Montmorillonite	MMT-2MTA2	68953-58-2; 14808-60-7	PT-Clay 502

P&T additives have been already tested in polymer applications, in particular, MgAl Hydrotalcite have been found a valuable additive for polyolefins based polymer matrices. For example, in isotactic polypropylene (PP) with a flexural module of 1390 MPa and an elongation at break of 50% and an Izod impact strength of 3KJ/m^2, the addition of a P&T Magnesium Aluminum Hydrotalcite (MgAl-STE) lead to an increase of 15-30% in flexural modulus, with an invariant ultimate strain and a slight reduction of elongation at break. Moreover, the use of P&T Zirconium Phosphate organically modified with octadecylamine (ZrP-octa) to produce a low density polyethylene (LDPE) nanocomposite, led to an increase both in tensile strength at break (+3%) and in elongation at break (+0,5%) in an aging test conducted at 100 °C for 13 days. This results indicate the beneficial effects in terms of thermal stability of the nanocomposites. In addition to the improvement in mechanical properties.

In Table 6-2, a selection of P&T additives suitable for polymer nanocomposites applications are reported along with a suggested matching of polymer/additives based on the experience of P&T and on the expected chemical compatibility.

Table 6-2: Prolabin&Tefarm additives for polymer applications

Functionalized clays specially advised for the dispersion in a suitable polymer																
Product	LLDPE	LDPE	PP	PVC	EVA	PU	PA6	PA66	PBT	PLA	PET	PVA	EPOXY	ACRYL	PS/ABS	WPC
PT-Clay 100		√	√	√		√										√
PT-Clay 200		√	√	√		√										√
PT-Clay 307	√		√	√	√	√							√	√		√
PT-Clay 311	√		√	√	√	√							√	√		√
PT-Clay 313		√										√				
PT-Clay 317	√	√	√	√					√	√	√	√				
PT-Clay 331	√	√								√					√	
PT-Clay 337		√													√	
PT-Clay 409		√					√	√	√	√	√	√				
PT-Clay 419	√	√	√	√	√	√	√	√	√	√	√		√	√	√	√
PT-Clay 421												√	√	√		√
PT-Clay 439														√		

In addition to the polymer-compatibilization effect, the intercalated species may also play other fundamental active roles: several additives have been developed to exploit anti-oxidant and UV-protection performances and they are reported in table 3.

Table 6-3: Prolabin&Tefarm anti-oxidant and UV-protection additives

Additive	Short name	CAS numbers	P&T code
Zinc Aluminum Hydrotalcite Salycilate	ZnAl-salycilate	202938-68-9; 69-72-7	PT-Clay 601
Zinc Aluminum Hydrotalcite Cinnamate	ZnAl-cinnamate	202938-68-9; 140-10-3	PT-Clay 602
Zinc Aluminum Hydrotalcite para-Hydroxy Benzoate	ZnAl-pOHBenzoate	202938-68-9; 99-96-7	PT-Clay 603
Zinc Aluminum Hydrotalcite Coumarate	ZnAl-coumarate	202938-68-9; 501-98-4	PT-Clay 604

6.4.2   Mechanism of action of P&T additives

The core components of P&T additives is represented by lamellar solids as reported before. This kind of compounds are able, under appropriate condition, to undergo an exfoliation process, leading to the formation of platelets of nanometric thickness thus forming a nanomaterial that could be classified a 2D.
The nanoplatelets deriving from the exfoliation process have many of the advantageous properties of nanomaterials in general:

- Extreme surface area
- Better dispersibility
- Higher interfacial interaction when mixed with polymer
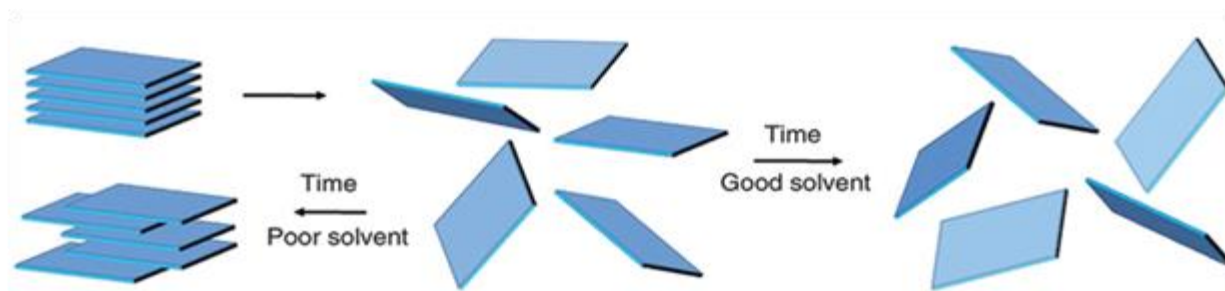
Figure 6-3: Exfoliation and possible re-aggregation of a lamellar solid

After the exfoliation have been achieved, the stability of the platelets depends on many factors like the nature of the solvent (or better, of the environment), the tendency of the platelets to re-aggregate, etc. (Figure 6-3). To obtain a proper dispersion of nanoplatelets in the polymer matrix all these aspects must be taken into account. Nonetheless, nanofillers in general and lamellar nanofillers in particular have already proved to be promising additives for the development of innovative and functional nanocomposites.
Among the many advantages of nanofillers use there are:

- *A lower amount is required respect to micron size fillers (in some cases 3-5 % of a suitable nanofiller could replace 20-30% of a classical filler)*
- *The lower loading of polymer lead to a lighter composite with mechanical properties equal (or, in some case better) with respect to the traditional material*
- *There are reported examples of synergistic effect between traditional fillers and nanofillers, thus opening the possibility of replacing only a fraction of the micro-sized fillers (this aspect is important also from an economic point of view)*

6.4.3 Safety of P&T additives

There is some concern about the use of nanomaterials in consumer products. This is due to the possibility that some of the nanoparticles may be released into the environment and/or be assimilated by living organism and ultimately by humans. The human toxicity and the ecotoxicity of some nanomaterials are currently under careful scrutiny.

From the point of view of P&T additives, both hydrotalcites and zirconium phosphate have so far been proven to be highly bio-compatible, both from the point of view of human safety and the environmental perspective.

Moreover, in the case of polymer applications, it seems extremely improbable that the nanoparticles may be easily spread over the boundary of the polymeric matrix.

7 Annex

Additives Database
Turntable.xlsx

8 References

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