Stabilization of Polymers Against Photodegradation

Eduard Marius Lungulescu and Traian Zaharescu

1 Introduction

Due to their organic nature the most of polymers currently used in various applications in different areas of industry or household are characterized by a certain degree of stability on the environmental natural conditions leading to their degradation. By this reason the functional properties of these aged materials become improper for long term operation. The accumulation of oxidation products by various chemical reactions during light absorption quantifies this instability progress.

The absorption of natural UV radiation (from solar light) or artificial UV beam (from different UV light sources) generates excited electrons on unstable high energy entities initiating physical and chemical damage processes with the consequences on the structure changing of polymeric materials, i.e. photodegradation [1]. The photodegradation process is based on the cleavage of polymer chains followed by the formation of radicals and the building up of lower molecular weight compounds, the crosslinking (the formation of high molecular weight compounds) or the increase in unsaturation level and photo oxidation.

Certain polymeric structures, such as the configurations containing benzene rings, double bonds (C=C, C=O), hydroxyl or carboxyl groups may themselves absorb UV radiation [2]. The conjugated structures show also remarkable efficiency

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D. Rosu and Visakh P. M. (eds.), *Photochemical Behavior of Multicomponent Polymeric-based Materials*, Advanced Structured Materials 26,
DOI 10.1007/978-3-319-25196-7_6

in the absorption of UV radiation. The groups of this structural type known as chromospheres groups often induce an advanced tendency of polymers to achieve photo-induced transformations. The photodegradation of saturated polymers, such as polyethylene or polypropylene, which do not contain such UV sensitive groups in their structure, is explained by the photo-sensitizing action of impurities—double bonds, hydroperoxides, traces of catalyst, the structural irregularities (like chain branches) [1]. These impurities appear during the synthesis process of polymers. Subsequently, the processing, storage and service conditions add new and different imperfections that increase the susceptibility to photodegradation of polymeric materials.

The combined effect of sunlight and oxygen occurred during outdoor service is accompanied by altering useful properties of polymeric material. The photodegradation effect can be observed as discoloration, the decrease in molecular weight due to the chain scission, the crosslinking of susceptible substrate, if formulation allows it, and the hardening of material, the formation of oxygenated chemical groups (hydroxyl, carbonyl, carboxyl, etc.) leading to the deterioration of mechanical and dielectric properties [3–10].

2 Mechanisms of Polymer Photodegradation

The mechanisms of photochemical degradation depend peculiarly on the type of polymer, as well as on the specificity of environmental factors. Usually, whereas the applications of polymeric materials run in the presence of air and of atmospheric oxygen, the polymer degradation lead to a variety of physical and chemical effects. This damaging process is practically an oxidative photodegradation (photo-oxidation).

The main macroscopic effects induced into polymeric material by the photodegradation processes [11, 12] are related to:

– *mechanical properties*. The modification of coloration accompanies the material damage during photodegradation. For example, polystyrene exposed to sunlight turns to yellow, polyvinyl chloride becomes dark yellowish or black reddish, the change degree being proportional with the exposure time. The discoloration is often accompanied by the formation of cracks or brittle regions on material surface. In general, the mechanical properties of polymeric materials are declined as the result of photo energy absorption;
– *chemical transformations.* Besides chain scission and modification in material structuring, photodegradation produces oxygen-containing functional groups such as: ketones, carboxylic acids, peroxides, alcohols, etc.;
– *electrical properties*. Photochemical degradation alters the main electric properties such as dielectric constant, volume resistivity, breakdown tension or any other dipole concentration dependent in the sense of their deterioration by the accumulation of polar groups [13].

Table 1 The characteristics of some single chemical bond in polymers

Chemical bond	Binding energy (kcal mol^{-1})	Wavelength (μm)
O–H	110.6	259
C–F	105.4	272
C–H	98.8	290
N–H	93.4	306
C–O	84.0	340
C–C	83.1	342
C–Cl	78.5	364
C–N	69.3	410

The photochemical transformations require certain transferred radiation energy which transports equal or greater energy than the dissociation energy of molecules for the efficient absorption of solar radiation. The UV radiation processes such suitable photonic energy [14]. When a molecule absorbs a photon it is raised onto photo-activated energetic level and, consequently, it passes into an electronic excitation state. The energy of incidental UV radiation is higher enough to dissociate some chemical bonds from polymer structure, whose main features are listed in Table 1.

The energy retained polymeric molecules in the excited state can cause several chemical reactions called primary photochemical reactions i.e. free radical formation, ionization, cyclization, addition, intermolecular regrouping and fragmentation followed by a number of secondary reactions through which the former intermediates are decayed. In the case of polymers with mobile hydrogen atoms the transferred UV radiation energy is consumed for the expelling such types of hydrogen atoms and the formation of specific polymeric macroradicals which create new molecular structures.

During the oxidative degradation of the most industrial engineering polymers it was found that the specific inhomogeneities including ketones or other products containing carbonyl groups, hydroperoxide, catalyst residues become the start points for the reactions with primary fragments produced by damage initiators. The photolysis of polymers occurred in processed materials increases the sensitivity to UV radiation, the initiation threshold and the acceleration of the photodegradation process depend on the spectral structure. In Table 2 the wavelengths of UV radiation to which the sensitivity of polymers attains maximum are presented.

Basically, the photooxidation mechanism involves the creation of some excited molecules species by the interactions between photons and irradiated polymeric material, as well as with the oxygen molecules, when reactive excited species appear, such as oxygen singlet. The photochemical reactions are chained reactions of free radicals accompanied by different photo-induced physical processes, such as: fluorescence, internal conversion of exciting energy or the intermolecular energy transfer (phosphorescence). The oxygen singlet, $^1O_2$, is involved in many reactions due to its high chemical reactivity. The nature of the formed chemical species depends on the polymeric structure, environmental conditions, temperature, etc.

The photooxidation mechanism of polymers is a process similar to thermooxidation process [15]. The difference between the two oxidative degradation

Table 2 UV wavelengths to which the polymers are the most sensitive

Polymer	Wavelength (μm)
Polyester	325
Polystyrene	318.5
Polyethylene	300–320
Polypropylene	310–370
Polycarbonate	295–305 and 350–360
Polyvinyl chloride	310–320
EVA copolymer	322 and 364
Polymethylmethacrylate	290–315
Polyamide	400
Styrene-acrylonitrile copolymer	290 and 325
Polyvinyl acetate (film)	<280

processes consists in the difference of initiation stage, when photooxidation is much faster due to the photo activation and the higher volume density of intermediates.

Photooxidation takes place at ambient temperatures and it can also be produced by different artificial light sources.

The rate of photooxidation depends on the nature of polymer, on the polymeric layer thickness, on oxygen solubility and diffusion rate, as well as on the crystallinity degree or on the branching degree of macromolecular chain [11] and on the level of irradiance [16].

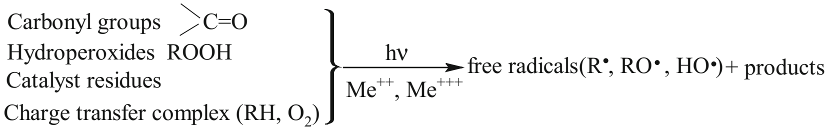
A scheme describing photooxidation processes accomplished in polymers can be represented by a certain sequence of stages [2, 15, 17]:

(a) *Chain initiation*

- Primary

$$\mathrm{RH} + \mathrm{O_2} \rightarrow (\mathrm{RH}^+ - \mathrm{O_2}) \rightarrow \mathrm{R}\cdot(\text{free radical})$$

- *secondary* (from polymers with irregular structure);



(b) *Chain propagation*

- primary:

$$\mathrm{R}\cdot + \mathrm{O_2} \xrightarrow{h\nu} \mathrm{RO_2}\cdot$$

$$\mathrm{RO_2}\cdot + \mathrm{RH} \xrightarrow{h\nu} \mathrm{ROOH} + \mathrm{R}\cdot$$

- chain branching:

$$\mathrm{ROOH} \xrightarrow{hv} \mathrm{RO}\cdot + \cdot\mathrm{OH}$$

$$2\mathrm{ROOH} \xrightarrow{hv} \mathrm{RO_2}\cdot + \mathrm{RO}\cdot + \mathrm{H_2O}$$

$$\mathrm{RO}^{\cdot} + \mathrm{RH} \xrightarrow{hv} \mathrm{ROH} + \mathrm{R}\cdot$$

$$\mathrm{HO}^{\cdot} + \mathrm{RH} \xrightarrow{hv} \mathrm{H_2O} + \mathrm{R}\cdot$$

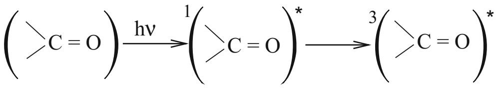
(c) *Chain Termination*

$$\mathrm{ROO}\cdot + \mathrm{RO_2}\cdot \rightarrow \text{non radical products}$$

$$\left.\begin{array}{l}\mathrm{ROO}\cdot + \text{Radical} \rightarrow \\ \mathrm{ROO}\cdot + \text{Inhibitor} \rightarrow\end{array}\right\}\text{Inactive products}$$

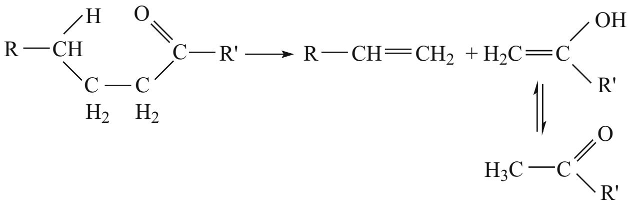
$$\mathrm{R}\cdot + \mathrm{R}\cdot \rightarrow \text{crosslinked inactive products}$$

During to the UV exposure of polyolefin the most important chromophores species are the carbonyl groups formed in presence of air [18]. These species contribute to the initiation of photodegradation reactions, produce excite states of singlet and triplet and initiate Norrish type I reactions (1), which lead to the scission of the main polymeric chain [19]



(1)

In the case of polyethylene it has been shown that about two-thirds of carbonyl species are involved in a Norrish type II reaction (2) without radical intermediates and about one third of those gives a Norrish type I reaction [19]



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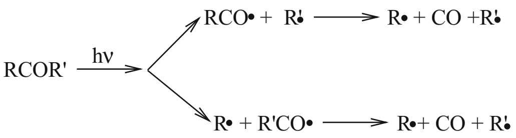


(3)

Besides carbonyl groups, hydroperoxides formed during the polymer processing play an important role in the increasing polymer sensibility on the UV radiation [20]. Other impurities such some traces of catalyst (titanium compounds) decompose the hydroperoxides and affect the thermal and photostability of polymer over time [21].

In the case of polymers the photostabilization methods are related to the mechanisms that describe the harmful effects of photonic UV radiation energy on polymer structures and they illustrate how additives (photostabilizers or antioxidants) can achieved the protection against oxidation.

The highest efficiency against the photooxidation process is obtained, if the used stabilizers fulfil certain conditions:

- To absorb efficient UV light and to present good dissipation properties of energy;
- To be stable to UV light action;
- To present low optical absorption on the visible domain.

The most known photostabilizers can be classified by their action mechanisms: UV reflectors, UV absorbers, quenchers of excited states, hydroperoxide decomposers, radical scavengers [22].

3 Photostabilization

3.1 Screening of UV Radiation

The light screening means the protection against the degrading action of solar radiation by the preventing penetration of UV radiation into polymer, the degradation process being limited only on the surface of polymer. An efficient screening of light can be carried out by using some protective coatings (compound with cellulose materials, appropriate paints and lacquerers, a. s. o., but, in time, themselves are subjected to photooxidative degradation).

Another method of photoscreening is the use of some substances to reflect UV radiation generically called UV light reflectors. The action mechanism of such substances consists in the reflection of UV light. The incidental light interacts with polymer macromolecules only in a lower proportion. The most important method used to reflect the light are: polymer surface metallization [23], coating with pigmented fluoropolymers or dispersing TiO_2 particles [24] or aluminium which can integrally reflect UV light. The pigmentation is limited by many factors such as: product colouring, dispersion issues, negative influences on functional electrical and mechanical properties. The efficiency of pigments in the protection of polymers against the progress in photodamage depends also on the nature of substrate. The iron oxide can be used as the protector polyolefin playing the role of light screener [25], but, in the same time, it catalyses the decomposition of polymeric substrate, like polyvinyl chloride exposed to UV radiations [26]. TiO_2 could have a photocatalytic effect for fibres, polyethylene insulation materials [27] and films of polypropylene [28] or epoxy resins [29]. A high amount of this TiO_2 pigment accelerates the degradation of ABS polymer.

Another method to screen the UV light is the use of ***UV absorbers***. The photostabilizers from this category can be fluorescent compounds which absorb the UV light and re-emit immediately these photons at higher wavelengths as fluorescent light. Compounds such as cumarins, naphtalimide, benzimidazolyl, diaminostilbenedisulphonate are efficient photoprotectors as UV absorbers, even at concentrations lower than 1 % [30].

One of the most efficient stabilizers as UV absorber is carbon black. The disadvantage of using black carbon is its disadvantageous color due which polymeric materials becomes nontransparent. Additionally, the black carbon generates heat which causes a thermal degradation of polymer [31, 32].

Besides organic UV absorbers already presented, inorganic compounds such as TiO_2, CeO_2, ZnO, could be used as UV absorbers [33–35].

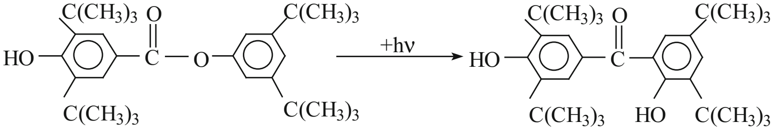
The protection mechanism involving such kind of substances used as UV absorbers is followed by many action systems:

(a) *Intersystem crossing molecules*

In these systems the stabilizer absorbing the UV light is excited to triplet state T_1 (π-π*) which either produces a photochemical rearrangement or becomes relatively inert in respect to photochemical reactions. The efficient compounds for this system can be phenol ester of benzoic acid, salicylates, butyrophenones and their substitution compounds.

Some examples of the rearrangement systems under photoexposure are presented in the following reactions:

- The rearrangement of the esters of 4-hydroxy-3-5-di-*t*-butyl benzoic acid to *o*-hydroxybenzophenone:



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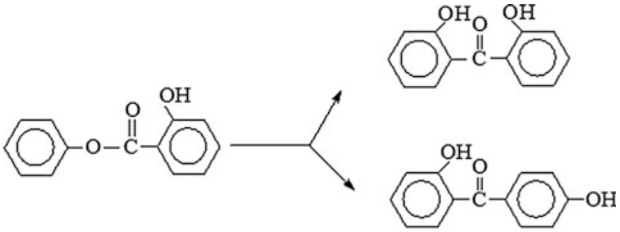
These esters have a good efficiency to the UV light stabilization of polyolefin.

- The rearrangement of the phenyl salicylate onto 2,2′-dihydroxybenzophenone and 2,4′-dihydroxybenzophenone: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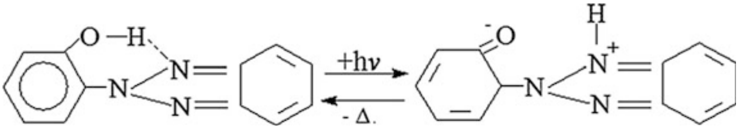
The product of 2,6-dimethylphenyl salicylate is successfully used to stabilize polypropylene. The addition of *p*-*t*-octylphenyl salicylate to polyethylene significantly increases its resistance against aging [36].

(b) *Internal conversions*

In these circumstances, the energy of absorbed light is converted into vibration energy by a radial process without spin changing i.e. S_1–S_0, S_2–S_1, the returning to the nonionic stage is possible with a presumable transformation of radiation energy into heat. The frequently used photostabilizers are *o*-hydroxybenzophenone compounds, whose photostabilization mechanism is based on a rapid tautomerization of excited states.

Another class of compounds is represented by benzotriazoles i.e. *o*-hydroxyphenylbenzotriazoles, which have a photostabilisation mechanism similar to *o*-hydroxyphenones, by rapid tautomerization of the excited states.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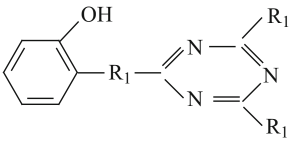
- S-triazine, such hydroxyphenyl-*s*-triazines, act by a mechanism similar to *o*-hydroxyphenones with the following considerations:
- compounds with high number of *o*-hydroxyphenile groups provide a better protection and a good absorption of UV radiations with higher wavelengths;
- various substituents, which may reduce the basicity of the *s*-triazine ring, can increase the light resistance of the compounds.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(c) *Deactivation*

This process is based on the deactivation of the different energy stages for polymer (singlet, triplet) produced by the photonic energy during solar radiation exposures. On this way, the destructive action of those energies on the polymer structure is avoided. This manner of energetic decay can be considered as the energy donation when an excitation of a stabilizer molecule (quencher) is produced:

$$\mathrm{P} \xrightarrow{h\nu} \mathrm{P_s} \longrightarrow \mathrm{P_t} \xrightarrow{\mathrm{S}} \mathrm{P} + \mathrm{S_t} \longrightarrow \mathrm{P} + \mathrm{S} + \mathrm{heat}$$

where

- P is a polymer molecule which contains chromophore groups such as [C=O];
- S is an acceptor stabilizer molecule which can have excited energy levels;
- S and T are singlet excitation stages and triplet excitation states, respectively
- The stabilizer should possess the capacity to return to the underground state $S_t \rightarrow S$.

(d) *Formation of a complex in excited stages by photo physical processes (fluorescence, internal conversion, etc.)*

$$\mathrm{P}^* + \mathrm{S} \rightarrow [\mathrm{P} + \mathrm{S}]^*$$

The stabilizers used for these mechanisms are:

- *Organometallic compounds* such as: copper acetylacetonate, zinc diethylthiocarbamate, nickel dibutyldithiocarbamate, nickel acetylacetonate, metal chelates, and many others,
- *hindered amines*
- *derivatives of piperidine*
- *derivatives offerrocene* such as benzyl ferrocene, *o*-hydroxybenzoilferoccene, etc.

3.2 Quenchers of the Excited States

The quenchers of the excited states accept energy from an excited molecule polymer before this excess of energy produces its degradation. The energy transfer can be achieved by dipole-dipole interaction (Förster mechanism [37]). Energy quenchers must have excited stages with energies lower than the excited state of polymer molecule. Once energy is transferred, the quencher returns to its ground state by emissions of fluorescence, phosphorescence and heat [38].

As additives belonging to this category of stabilizers, organometallic compounds of nickel [39] can be used such as nickel dibuthyldithiocarbamate, nickel-2,2,2-thio-bis (4-octophenolate)-*n*-buthylamine, as well as some phenolic stabilizers [40].

In principle, the difference between the UV absorbers and energy quenchers consists of the protection of absorbers in polymer by absorbing UV light, while the quenchers deactivate the excited states of the polymer molecules. In reality, it was shown that the absorbers can function also as quenchers [1].

3.3 Hydroperoxides Decomposers

Hydroperoxides represent, as it is generally accepted, ones of the most reactive species in the polymer photodegradation [41]. They can be induced during the processing of polymer, as well as during the subsequent exposure of polymers to light and heat in the presence of air. The present transitional metals accelerate the decomposition by radicalic process of the accumulation of hydroperoxides. In the case of polyolefin, the hydroperoxides photolysis leads to the formation of some carbonyl compounds and/or alcoxy radicals.

The efficient compounds in respect to hydroperoxide decomposers include nickel and sulphur—containing complexes [42]. Such substances can also act as UV absorbers and quenchers of excited states [43].

3.4 Radical Scavengers

3.4.1 Hindered amine (hindered amine light stabilizers, HALS)

The hindered amine represent the most recently type of UV light stabilizers. These products have been industrial produced since 1980, the first stabilizer being HALS-1 (Tinuvin 770, Sanol LS 770) with the chemical formula bis (2,2,6,6-tetramethyl-4-piperidinyl) sebacate. Other important HALS compounds are: bis (1,2,2,6,6-pentamethyl-4-piperinidyl) sebacate (known as Tinuvin 292), the polymeric form of the dimethyl ester of butyric acidwith 4-hydroxy-2,2,6,6-tetramethyl pyridine (HALS-2), poly[[6-[1,1,3,3-tetramethylbutyl) amino]-1,6-hexandiyl[(2,2,6,6-tetramethyl-4-piperidinyl)imino]] (HALS 3).

The HALS compounds are largely used for polyolefin photostabilisation due to their competitive costs and high performances, which permit the utilization of lower amounts than UV absorbers such as benzophenone and benzotriazole compounds. The mixtures of HALS compounds with benzophenones present some synergic photostabilization effects [11], being reported also an antirad efficiency of them [44, 45].

Other hindered amines used with good results in the stabilization promotion of polyolefin, polyurethanes, polystyrene, ABS, acrylonitrile styrene copolymers, are derivatives of piperidine such as: 2,2,6,6-tetramethylpiperidine, 2,2,6,6-tetramethyl-4-hydroxy-phosphonopiperineor by stable free radicals such as: 4-[cyan (phenylmethylene)-2,2,6,6-tetramethyl piperidinoxil], 4-(ureidoimino)-2,2,6,6,-tetramethyl-piperidinoxil, 2′,2′,6′,6′ tetramethylspiro(benzimidazoline)-2,4-piperi dinoxil.

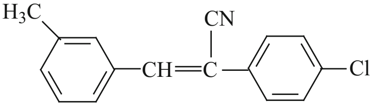
Taking into account the experimental results obtained with the hindered amines, it was possible to formulate appropriate stabilization mechanisms. They were reported as several academic approaches. Unfortunately, the mechanism of photoprotection is not fully elucidated.

The photostabilization mechanism of hindered amines consists of the scavenging free radicals [46, 47], i.e. through Denisov cycle. It was observed that these compounds absorb UV light beams with wavelengths lower than 290 nm. Several compounds such as tetramethylpiperidines act either as destroyers of free radicals reacting directly with peroxyl units or as a catalyst which forms nitroxyl radical under the action of UV light by the regeneration process:

$$>N-O^{\bullet} \xrightarrow{R^{\bullet}} >N-O-R \longrightarrow RO_2^{\bullet} + >N-O^{\bullet} \qquad (8)$$

It has been reported that other photooxidation mechanisms are also reliable concerning the complexation of transitional metals, the complexation and decomposition of hydroperoxides, the quenching of the polymer-oxygen charge transfer complexes [38].

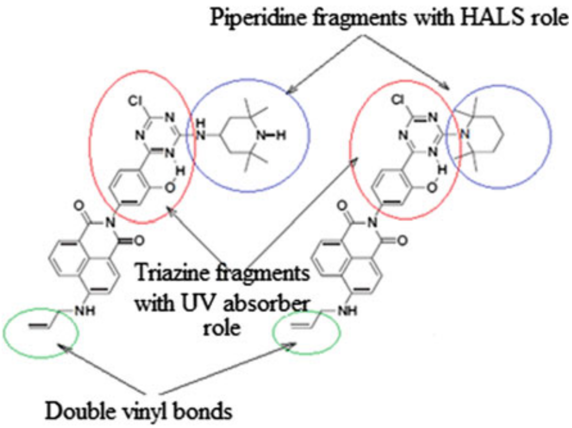
In order to assess the efficiency of a light stabilizer in its coupling with a phenolic antioxidant, multifunctional hindered amine light stabilizer or some complexes of tetramethylpiperidine with nickel were synthesized [48]. These products were successfully used for the stabilization of monofilament polypropylene and the usage range was expanded to low density polyethylene. For the PVC stabilization, some stilbene compounds such as 4-chloro-α-cyan-3-methyl-stilben (9) were also efficiently used [49].



(9)

An interesting solution for photostabilisation is the use of some substances containing structural units which combines both the properties of UV absorbers and HALS such as derivatives of 1,8-naphtalimide which contain fragments of 2-(2-hydroxyphenyl)-1,3,5-triazine and 2,2,6,6-tetramethylpiperidine previously included in the structures capable to polymerize via vinyl double bond (Scheme 1) [50]. These substances present yellow-green fluorescent emission due to the triazine

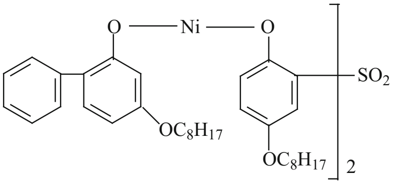
Scheme 1 Derivatives structure of 1,8-naphtalimide containing traces of HALS and UV absorber [50]



group having UV absorber role. They are efficient in the photostabilization simultaneously acting by absorption mechanism of UV radiation and by blocking oxidation of photoinduced free radicals by means of hindered amine group.

Besides the above mentioned methods, there are other photostabilization methods of polymeric materials such as:

- **the use of organometallic compounds of nickel, copper and transitional metals** such as those presented in the stabilised polymer formulas (10–17):



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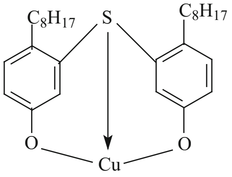
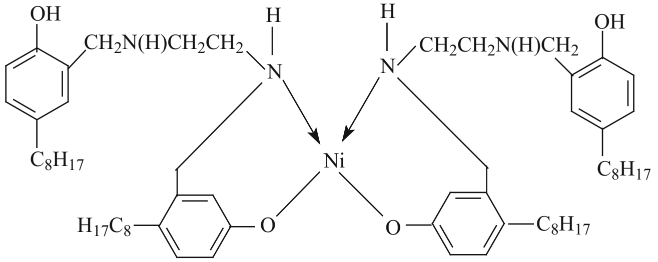
Nickel complex with bis-sulphonyl for polyolefins polyethylene



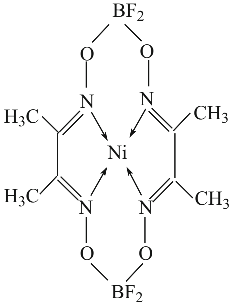
(11)

Copper complex for polyethylene



Nickel salts with N-(alkyl-hydroxybenzyl) alkylen-polyamine for polypropylene

(12)



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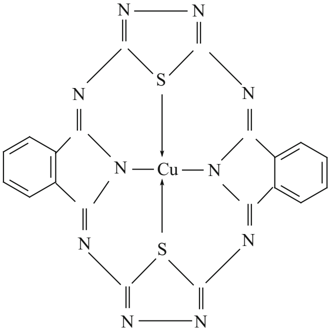
Complex of nickel-boron bifluorine-N, N-bis (dimethylglyoxime)



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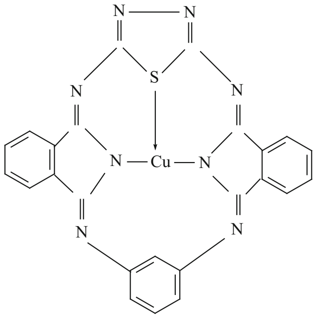
Copper complex with thiodiazoleindiole for polyamides



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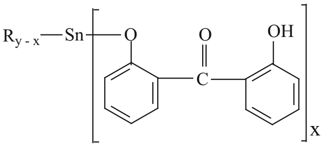
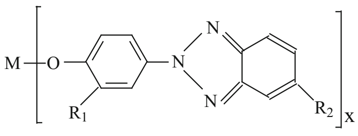
Copper complex with thidiazoleizo-indolephenylene for polyamides



(16)

o-hydroxybenzophenone – organo – tin compounds



(17)

Benzotriazole with metal

- **synergistic pairs of photostabilizers with antioxidants.**

These couples of oxidation protectors have the main role of delay on the progress of photochemical degradation by the oxidation inhibition of free radicals and by hydroperoxides decomposition. This type of compounds includes antioxidants (either for the inhibition of radical decay onto peroxyl radicals or for the decomposition of hydroperoxides), carbon black, ZnO (which is activated by UV radiation) or other compounds which are involved in the oxidation/reduction reactions.

- **polymer light resistance improving by purification and modification**

The increase of polymer light resistance can be achieved by many ways such as:

(a) *The assurance of high purity of polymer and additives*

– It is well known that the polymers can incorporate molecules or parts of other trace materials or impurities during synthesis which contribute to the decrease of

their resistance against photostabilisation: metallic impurities or compounds which catalyse the photooxidation such manganese traces.
- It is also known the catalytic effect of copper and other transition metals to the thermooxidation of many polymers [51]. The traces of other foreign groups in the polymer structure may drop down the resistance to photooxidation of polymers.

(b) *The convenient modification of polymer structure by the incorporation of some stabilizers during polymerization.*

This process eliminates the inconvenient brought about by the photostabilizer evaporation during the polymer processing or its migration during the storage and it can be achieved by:

- the attachment of photostabilizer by introducing some reactive or polymerizable groups such vinyl or allyl group by a chemical or physical process;
- the preparation of polymerizable UV absorbers which lead to the preparation of polymers containing photostabilization groups by polymerization or copolymerization of certain monomers;
- the use of the photo-rearrangement of polymers with additives. For example, there were obtained homopolymers and copolymers of phenyl 5-acryloxymethylsalicylate and phenyl 5-methacryloxymethyl-salicylate with vinyl acetate, vinylidene chloride and vinyl chlorine.

4 Stabilization Characterization of Various Polymers

4.1 Polyethylene

Polyethylene is the most common thermoplastic polymer with multiple applications: insulating materials in electrical cables, pipes, packaging (bags, film, containers, a. s. o.), medical devices and other fields because of its good chemical and stress-crack resistance besides high strength.

In order to increase the product durability under environmental conditions, especially to the UV exposure, polyethylene is stabilized by different types of additives.

There are many ways to assess the level of photodegradation in PE such: electron spin resonance (ESR), UV and FTIR absorption [52–54], gel fraction, mechanical properties measurements [52], different thermal analysis techniques (TGA [55, 56], DSC [27, 56, 57], CL [55, 58, 59]).

The most used photostabilizers for PE includes HALS compounds. These compounds are up to four times more effective than nickel chelates and up to ten times than usual UV absorbers [53, 60].

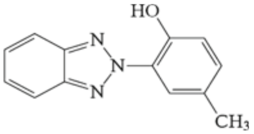
According to Malik [61] an efficient stabilizer must comply with three basic requirements: higher stability or compatibility with polymer matrix, minimal diffusion and high degree of homogeneity of active species. It is well known that in the case of polymers it is very difficult to obtain a good homogeneity of the stabilizers inside the polymer matrix. In order to decrease the diffusion of stabilizer out of polymer matrix it is necessary to use stabilizers with high molecular weight or, the currently used technique in the UV stabilization of polyolefin, the grafting of stabilizer on the polymer backbone [53, 62].

Kaci et al. [53], using a PBH-3 compound, commercially known as Sanduvor PR31, to stabilize the PE under natural weathering conditions. It was demonstrated that the grafting of the stabilizer on polymer is very fast and occurs on few days. Due to the presence of methylenic double bond on the PBH-3 structure, the grafting process occurs by a photochemical reaction.

The UV radiation ($\lambda = 210$ nm) have been used the photoinduced grafting various diazo-compounds and methyl azidocarboxylate, bearing extended mono-HAS (Hindered Amine Stabilizer) [62] on polyethylene structures. It can be noticed that the grafting process increases the polyethylene photostability, the high stability against photo-oxidation being achieved for those films supposed to bear the largest amount of bonded HAS groups close to surface.

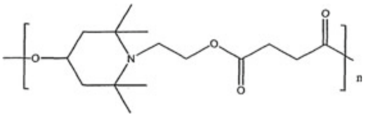
Yang et al. [54] studied the photodegradation of linear low density polyethylene (LLDPE) modified with inorganic nanofillers and/or light stabilizers compounds. They observed by FTIR spectroscopy measurements that the used nano-fillers (Al_2O_3, SiO_2 and ZnO) had positive effect on the photostabilization of LLDPE, the fillers lowering the degradation rate. However, the presence of ZnO and TiO_2 nanoparticles induces degradation more rapidly in polyethylene exposed to UV radiation. This effect was demonstrated by the increase in the rates of both carbonyl group build up and of CO_2 generation in LDPE substrate with nanoparticles of ZnO [63].

The chemiluminescence (CL) is an appropriate method to assess the effectiveness of some UV stabilizers on polyethylene exposed to UV radiation. Jipa et al. [64] studied by isothermal and non-isothermal CL the contribution to the photostability of polyethylene brought about by: an UV absorber *2-(3-methyl-6-hydroxyphenyl) benzotriazole* (Tinuvin P), and two HALS UV stabilizers: (*2,2,6,6-tetramethyl-4-pyperidyl-succinate) polyester* (Tinuvin 622) and [(*4-methoxyphenyl)-methylene]-bis-(1,2,2,6,6-pentamethyl-4-pyperidinyl)propanedioate* (Sanduvor PR31). The CL provides reliable information about the improvement in the life time of polyethylene by the stability qualification measuring oxidation induction time (OIT) by isothermal CL and onset temperature oxidation (OOT) by non-isothermal CL. An indicative parameter for photodegradation of polymers is the integrated non-isothermal CL signal (Σ_{CL}) which is proportional to the concentration of peroxides intermediates built up during the UV exposure. The minimum values of Σ_{CL} are related to the significant efficiency in oxidation stability [64].



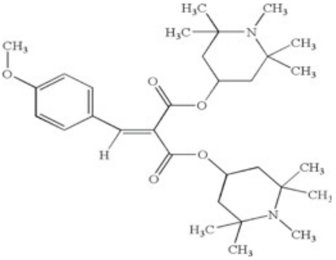
(18)

Tinuvin P



(19)

Tinuvin 622



(20)

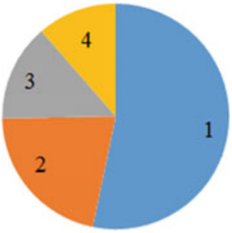
Sanduvor PR31

In Fig. 1 the decreasing order of UV stability provided by various additives is illustrated: Tinuvin 622 > Tinuvin P > Sanduvor PR 31.

The addition of HALS compounds on the PE resin can be efficiently extended to the protection against surface photo-oxidation of XLPE onto the photo-crosslinking process of PE. The FTIR and XPS data gave the evidence that the surface photo-oxidation of XLPE increase as the UV-irradiation time increases, the main formed products being identified as hydroperoxides and carbonyl groups [65].

It was proved that some compounds of transitional metals such copper stearate could retard the photo-degradation of HDPE [66] and PP [67]. Cooper stearate can acts both as UV light absorber and as radical scavenger, respectively. The stability effect of copper stearate on polyolefin was explained by two directions [67]:

Fig. 1 Comparison of Σ_{CL} for LDPE containing various UV stabilizers: *1* unstabilized, *2* Sanduvor PR 31, *3* Tinuvin P, *4* Tinuvin 622 [64]



- the photo-chemical reaction of the copper stearate takes place before of the degradation of the polymeric substrate;
- the radicals formed by Norrish type I cleavage of ketone groups react with the copper ion to form inactive groups such as terminal carbon-carbon double bonds.

Many studies carried out on polyethylene/nanoclay systems [68–70] showed that the polymer as the major component of nanocomposites degrades faster than the pristine material, when it is exposed to UV radiation. This feature was explained on the basis of interaction of organo-clays and the antioxidant used for the protection of polymer substrate. Morlat-Therias et al. observed in the study on the photochemical stabilization of LLDPE/clay nanocomposites by infrared spectroscopy [71] that the presence of organo-clay promotes a lower durability of the nanocomposites exposed to artificial or natural UV light. By the comparison of the effectiveness provided by various UV absorbers (Cyasorb UV-1164, Cyasorb UV-2337, Cytec THT 6460) and by a metal deactivator compound (i.e. Irganox MD-1024), it was observed that the use of metal deactivator is an efficient solution for the stabilization of nanocomposite. In the presence of the metal deactivator, the active metal ions are scavenged by chelation forming an inactive complex [71].

Various compounds such as thiobisphenol were reported to exhibit a pro-oxidant effect in the early period of polyethylene photooxidation, which is accelerated as their concentration is enhanced, while on the later irradiation period the carbonyl build up was retarded [72]. The retardation of the carbonyl accumulation was obtained with a compound based on dodecyl-3,3′-thiodipropionate over the whole period of ultraviolet exposure. Kinetic data showed [72] that the concentration of 0.1 w/w% of thiobisphenols determines the most effective retardation for the accumulation of carbonyl group in LDPE films.

4.2 Polypropylene

The photooxidation of polypropylene involves the initiation of free radical chain reaction by the photolysis of hydroperoxides, producing peroxyl radicals as well as alkoxy radicals. In the last decades many studies dealing with the types of stabilizers used to delay the polypropylene photodegradation were reported as well as several studied on the experimental methods for assessing their photostability effectiveness [73–78].

Rychlý et al. used infrared and UV spectroscopies to estimate and to compare the action of two antioxidants, Irganox HP 136 and Irganox 1010, by the UV stabilization of polypropylene films [78]. It was observed by the evolution of carbonyl peak at 1730 cm^{-1} that the high efficiency of Irganox Hp 136 is attained in stabilization of PP exposed to UV radiation, whose activity is quite competitive to Irganox 1010 (Table 3). The stabilization mechanism is mainly based on the scavenging of free radicals formed by UV initiation. It can be observed that the

Table 3 Values of induction time from infrared spectroscopy measurements for evolution of carbonyl absorption [78]

Samples	Induction time (h)
Pure polypropylene	100
PP + 0.10 % Irganox 1010	885
PP + 0.15 % Irganox HP 136	1214
PP + 0.30 % Irganox HP 136	1243

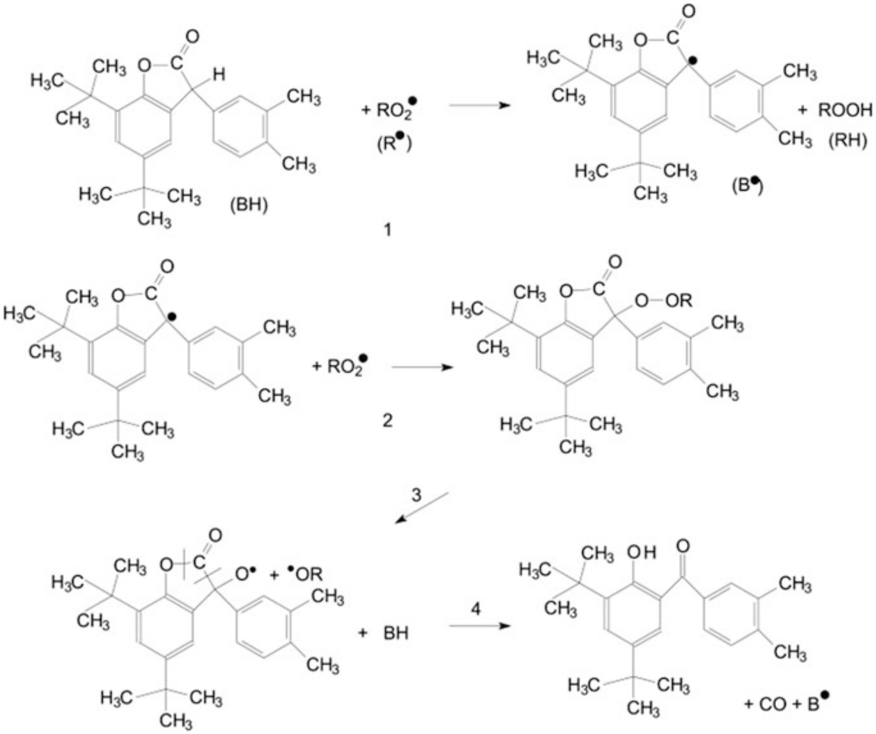


Fig. 2 The stabilization mechanism of Irganox HP 136 in polypropylene [78]

value of induction time of Iganox HP 136 at 0.15 % is similar with the oxidation induction time measured at the loading of 0.30 %.

The authors proposed a stabilisation mechanism of Irganox HP 136 by which benzofuranone lactone is converted in the oxidized PP into 2-hydroxy benzophenone derivatives, which is efficient against the effect of light (Fig. 2) [78].

Because the chemiluminescence method is a tool frequently used to qualify the stabilizing effect in polypropylene of various hindered amine, the analysis of CL kinetic parameters (oxidation induction time, oxidation rate, activation energy of oxidation, CL intensity) could provide reliable information related to the photodegradation state of polypropylene modified with different HALS compounds [76–78].

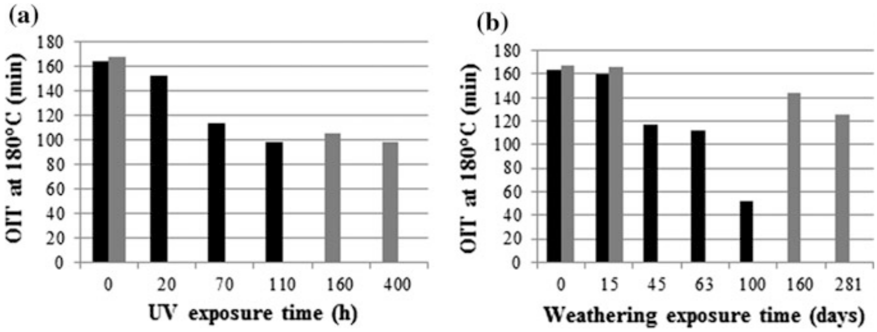


Fig. 3 Activation energy versus exposure time for iPP unstabilized (*black*) and stabilized with 0.3 % Sanduvor PR31 (*Grey*): **a** artificial UV light, **b** weathering exposure time [77]

In Fig. 3 the values of oxidation activation energy obtained from CL measurements for isotactic PP film stabilized with 0.3 % (w/w) Sanduvor PR31, exposed to UV light from both artificial and natural weathering, respectively, are presented [77].

It is generally accepted that higher values of activation energy correspond to higher stability of tested material. It can be observed that the presence of Sanduvor PR31 induces higher values of activation energy as compared to unstabilized samples.

Jipa et al. [76] studied by isothermal chemiluminescence the behaviour to photooxidation of isotactic polypropylene in the presence of some HALS (H2-H4) compounds and compared them with mercapto-1,3,5-triazinic phenolic stabilizer (antioxidant H5) and Tinuvin 770 (H1). The values of oxidation induction time (OIT) (Fig. 4) obtained from CL curves are related to the photostability of PP induced by each antioxidant. The longer the induction time, the higher the

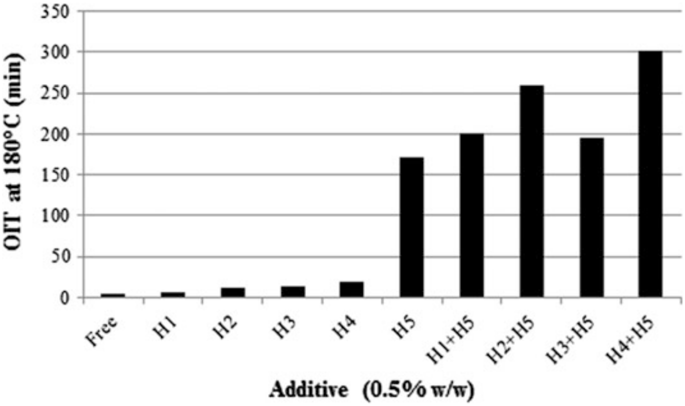


Fig. 4 CL OIT values for PP modified with various HALS compounds

stabilisation efficiency. It can be observed that H1-H4 compounds present lower photooxidative protection of PP. The most effective antioxidant is the mercapto-triazine compound. It can be also observed the synergistic activity between the H1-H4 compounds and H5 which lead to higher OIT values. This effect is due to the regeneration of phenoxy radicals provided by the hydroxylamine derivatives resulting from oxidation of piperidine [76].

The exposure to accelerated photodegradation of polypropylene plaques improved with various systems based on hindered amine stabilizers (Tinuvin 327, Tinuvin 123), UV absorbers (Tinuvin 327, Tinuvin 120) and phenolic antioxidant Irganox 1010 revealed by ESRI (Electron spin resonance imaging) a modification of nitroxide concentration profile (U-shape profile) as a function of the additives type and the manner of exposure [79]. The U shape profiles mean that almost the same nitroxide concentrations on both sides of irradiated and unexposed PP plaque surfaces were detected, but small nitroxide concentration in the inner layers was revealed. The use of a couple including UV absorber (Tinuvin 120) and HAS compound (Tinuvin 327) delays efficiently the PP photodegradation. The lack of evidence for any modification in nitroxide concentration, similarly proved in the samples without UV absorber [79] indicates the proper involvement of additives in the diminution of oxidation effects. Accordingly, the ATR/FTIR spectra recorded on the surface of PP plaque shown an increase of the absorption bands corresponding to carbonyl and hydroxyl groups with the irradiation time, the height of carbonyl peak being the same on both exposed and unexposed PP sample [79].

The use of some metal oxides i.e. rare earth oxides [33], TiO_2 [27, 29], in a proper concentration may improve the photodegradation resistance of the polymer matrix to UV exposure due to light screening effect provided by these particles. The addition of rare earth oxides, for example CeO_2 at 0.1 w/w% in PP, showed a minor effect on the changes in mechanical and thermal properties when the photodegradation of PP was accomplished [33]. The increase of the concentration of CeO_2 to 1 w/w% improves the thermal stability and mechanical properties of PP matrix. The FTIR, DSC, ATG analyses and mechanical characterization evidenced simultaneously that CeO_2 particles improve in a significant extent the resistance of PP to photodegradation [33]. The CeO_2 particles act as UV filter [27, 29, 33–35] by absorbing part of UV irradiation, reducing the UV intensity which can promote the oxidation of the PP chains.

4.3 Other Polymers

Poly(vinyl chloride) **(PVC)** is one of the most extensively investigated polymers since many years, due its large range of utilization in many application areas: automotive, pipes, electrical cables, window frames, etc.

Nevertheless, PVC suffers from poor light stability. Upon light exposure undergoes a rapid autocatalytic dehydrochlorination, which forms conjugated polyene, responsible for PVC discoloration [80–82]. The photodehydrochlorination is accompanied by modification of the mechanical properties of the PVC [82, 83]. In order to increase the PVC resistance to photodegradation are used many compounds which act as UV absorbers, HALS compounds, UV screeners a. s. o.

Rabie et al. [80] investigated the stabilizing efficiency of some diamide derivatives as photostabilisers for PVC containing dioctyl phthalate and dibutyl phthalate by evaluating the weight loss of the polymer. The unadditivated PVC weight loss, resulted from evolution of HCl during the photodegradation, increased with the UV radiation exposure time. The photostabilising efficiency of diamide derivatives was indicated by the lowering of the weight loss, reflecting a lower rate of dehydrochlorination [80].

The modification of commercial PVC by introducing of benzothiazole and benzimidazole compounds as pending groups into the repeating unit of PVC, evidenced an increase of the photostability of modified PVC, as compared to unmodified PVC [84]. The photostabilization of films of PVC could be achieved by using of some diorganotin (IV) complexes. These additives stabilize the PVC films through HCl scavenging, UV absorption or screening, peroxide decomposer and radical scavenger mechanisms [85].

The photostability of PVC-based materials for outdoor application can be substantially improved by means of some protective coatings such as: photocured urethane-acrylate clearcoats containing a UV absorber and a HALS radical scavenger which can filter the most harmful solar radiation, delaying the onset of PVC degradation [86], photo cross-linked epoxy-acrylate resins [87]. An additional benefit of this method of photostabilization subsists in the improvement of some surface properties of the coated polymer by making it more resistant to organic solvents, chemicals, abrasion and scratching [86].

Zhang et al. investigated the photostabilizing efficiency of different light stabilizers (TiO_2, Tinuvin 234, Tinuvin XT 833, Tinuvn 531, Chimasorb 944) in poly (vinyl chloride) by means of discoloration, Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM). The results show that the addition of light stabilizers can slow down discoloration of PVC, the most effective being TiO_2, due to its UV light reflective properties. However, the FITR analysis showed high carbonyl content for pure PVC and PVC modified with TiO_2 and Chimassorb 944, indicating that the photo-oxidation reactions of these UV irradiated samples are relatively serious [88].

Besides stabilizing methods presented above, there are many other compounds which can be used to delay de photodegradation of PVC among which we mention: Cadmium-stearate (II) [89], organotin compounds [90], dibutyltin maleate (DBTM) mixed with trisnitro (1,3-dihydroxyl-2-hydroxylmethyl-2-nitropropane) compounds as stabilisers [91], Schiff's bases [92], etc.

Copolymers cover the large part of polymer market, because they gather the most interesting features required by long term application. Luengo et al. [93] studied the photostabilization of poly(styrene-b-ethylene-co-butylene-b-styrene) (SEBS) modified with some hindered phenols and their combination with phosphite antioxidants by using a variety of spectroscopic methods including FTIR, UV, and luminescence spectroscopies coupled with crosslinking and hydroperoxide analysis.

The addition of a hindered phenol photostabilized the SEBS by inhibiting of discoloration, and the formation of hydroperoxides, acetophenone, and oxidation products, as well as chain scission and disaggregation of the styrene units. The combination hindered phenol-phosphite exposes high synergistic effect in the inhibition of SEBS yellowing, the reduction in the concentrations of chromophore groups and the decrease in the probability of chain scission. Consequently, higher phosphite concentration inhibits crosslinking reactions in the photo-oxidative degradation of SEBS as well as the formation of hydroperoxides groups [93].

Recently, a new method for attaining improved resistance against photodegradation of SBS copolymers (polystyrene-block-polybutadiene-block-polystyrene) was proposed [94]. The reported method consists in the modification of SBS copolymer with multiwall carbon nanotubes (MWCNT) and carbon nanotube functionalised with carboxylic groups (CNT-COOH). The ATR-FTIR spectra recorded on pristine SBS, SBS/CNTs and SBS/CNTs-COOH samples at different exposure times showed the accumulations of oxygen containing products, i.e. both carbonyl and hydroxyl species at the sample surface is considerably lower for CNTs containing nanocomposites in comparison to pristine SBS. The CNTs improve the mechanical properties of SBS nanocomposite as compared to pristine SBS: elastic modulus higher with 20 % for SBS/CNT and 35 % from SBS/CNT-COOH, ductility of the nanocomposites decreases in the same amount. This result proves that the presence of CNTs and CNTs-COOH have a beneficial effect on the photo-oxidative resistance of SBS nanocomposites by hindering the crosslinking reactions and slowing down the oxidized species formation. The CNTs stabilizing effect is attributed to their UV-light shielding properties and their radical scavenging activity [94]. The modification of EVA copolymers with carbon nanotubes evidenced the same stabilising effect of CNT, especially at higher CNT content (3–5 %) [95].

5 Conclusions

The stabilization of polymers is one of the most important questions related to the product lifetime. The proper solution for the delay of oxidation during the inevitable exposure to the joint actions of light and oxygen is the addition of compounds which present efficient activities in the scavenging and blocking reaction tendency of free radicals. The outdoor services of polymeric items require the improvement in the oxidation resistance avoiding accidents and frequent maintenance. The delay efficiency of oxidation depends strongly on the protector efficiency, whose action is macroscopically measured by the diminishing oxidation induction time and by the slowing down the progress of oxidation ageing.

The analysis of stabilizer activity must be accomplished by the incorporation of increasing amount of involved compound for the determination of concentration threshold where functional properties are not altered. The correlation between the oxidation protection and the materials durability must be considered as the key of the integrity persistence in the polymer material science.

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