Physically Persistent Stabilizers by Functionalization of Polymers

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SUMMARY: The durability of polymers exposed to harsh application conditions is reduced by physical losses of stabilizers. Their physical persistence can be improved by increasing their molecular weight, without changing the action mechanism. Funtionalization of conventional polymers by grafting with monomers bearing stabilizing moieties during reactive processing, grafting during mastication, and phototriggered grafting are particularly suitable methods for synthesis of polymer-bound stabilizers. Properties and examples of application of stabilizer-functionalized polymers are given.

Polymer degradation and factors influencing their stabilization

Plastics, rubbers and coatings are exposed during processing and/or household, medical and engineering applications to chemical and physical deteriogens, many times under very aggressive conditions (high temperature, solar radiation, oxidizing atmosphere). This accounts for polymer degradation characterized by chemical transformations and loss of useful physical and mechanical properties limiting their lifetime. Hence, a suitable stabilization by antioxidants, antiozonants, photoantioxidants and UV absorbers is mandatory. The efficiency and durability of stabilization are determined by the inherent chemical efficiency of stabilizers and their physical persistence preventing losses caused by volatility in the high-temperature environment and under air flow or intensive irradiation and/or by leaching into extracting media. Chemical reactivity of stabilizers accounts for their sacrificial consumption[1]. The low physical persistence of stabilizers limits the exploitation of their inherent chemical efficiency, because the effective concentration in the polymer matrix drops[2]. As a consequence, polymer articles are no longer effectively protected and their durability diminishes. Moreover, extraction of stabilizers from packaging materials by food components or stabilizer leaching in medical application of plastics have environmental impacts.

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Chemical and physical aspects of polymer stabilization

Both the primary aspects (inherent chemical efficiency) and secondary aspects (physical relations between a stabilizer and the polymer matrix) encountering the stabilizer-polymer system have to be considered equally[1-4]. The inherent chemical efficiency, activity mechanisms and sacrificial transformations were analyzed in details[1]. The physical aspects of polymer stabilization were determined more recently[4]. A theoretical model of physical losses of additives and experimental results define principal physical requirements dictated by the additive loss control[4]: High solubility in the polymer matrix

Minimal diffusion through the matrix

Homogeneous distribution of the active moiety in the matrix.

Stabilized polymer articles are exposed in practical applications to a multitude of chemical and physical deteriogens changing in their intensity and sequence, mostly in cyclic processes. This can significantly influence theoretical expectations dealing with polymer and stabilizer durability.

Chemical approaches to enhanced physical persistence of stabilizers

The problem involves reduction of volatility and extractability of additives by chemical modification, without substantial changes of the efficiency or activity mechanism of the resulting stabilizer. Some methods are available to solve the problem[2, 3]:

- Application of nonvolatile salts and metallic complexes of stabilizers. This approach involves some solubility and compatibility problems arising in the polymer matrix.
- Synthesis of „high-molecular-weight" stabilizers (arbitrarily, 500 to ~2000 g/mol). This approach represents a good balance between efficiency, solubility and physical persistence of stabilizers and is mostly commercially used in stabilization of commodity and engineering polymers.
- Application of oligomeric and polymeric stabilizers for polymers exposed to extreme physical stresses. The systems can be prepared[2]:
  - ◊ By polyreactions (polymerization, polyaddition, polycondensation). These synthetical approaches are very effective. Some application problems arise due to inhomogeneity in distribution of the stabilizing moieties on the polymer chain leaving a great part of the

polymer matrix unprotected. Compatibility limits may arise if the polymeric stabilizers are used as additives for conventional polymers.

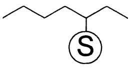
◊ Synthesis of stabilizers by polymer functionalization („reactions on polymers“). This concept of synthesis of polymer-bound stabilizers is very promising, fits physical requirements on stabilizer persistence and exploits conventional technological equipment. Two principal approaches are available: Functionalization of polymers bearing reactive groups with low-molecular-weight compounds carrying stabilizing moieties, and functionalization of conventional polymers with monomers carrying stabilizing moieties, mostly during reactive processing and without synthesis of expensive pre-functionalized polymers.

Structures of polymer-bound stabilizers prepared by polymer functionalization

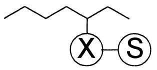
Polymer-bound stabilizers should be considered as functional polymers for special applications. Concentration, mode of binding and distribution of the stabilizing moieties in the functionalized macromolecule are of importance. Polymer-bound stabilizers are mostly used as masterbatches[2, 4, 5].

Generally, attachment modes of the stabilizing moiety **S** to the polymer backbone involve following possibilities[2]:

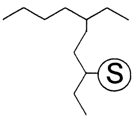
Direct bonding



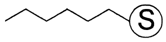
By means of a spacer **X**



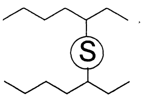
By side-chain functionalization



By end-capping



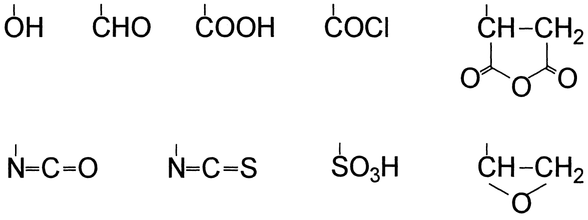
As a functionalized crosslink



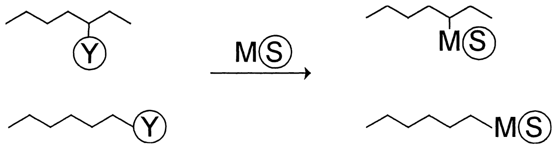
Polymer-bound stabilizers by polymer functionalization

Polymer-bound stabilizers are prepared by a chemical modification of conventional or specialty polymers by addition, substitution or elimination reactions[2, 3]. A more expensive approach exploits reactions of low-molecular-weight compounds (monomers) bearing stabilizing moieties with reactive sites (functions) located along the polymer chain or with the end-reactive groups in a post-polymerization treatment[2, 3].

Prepolymers with reactive groups **Y** and an appropriate molecular weight distribution are used for functionalization. Examples of pendant or terminal groups **Y** include:



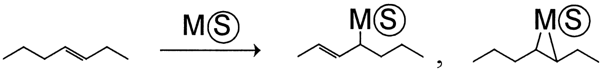
Functionalization with a monomer **MS** bearing a stabilizer moiety **S** results in a bound-in system.



However, formation of by-products during functionalization, and residual non-functionalized groups Y may introduce undesirable side effects, in photoprocesses (during polymer weathering) in particular. This difficulty must be considered. Any elimination of undesirable structures is practically impossible. Moreover, the method is a rather high cost-performance approach to polymer-bound stabilizers. Its application may be considered only in cases justifying the price of the synthesis.

The main attention has been paid to functionalization of commodity polymers by grafting during customary operations, such as melt processing of polyolefins and mastication or vulcanization of rubbers[2-5]. This post-polymerization modification of saturated and unsaturated commodity polymers and some engineering polymers with a low-molecular-weight reactant carrying a stabilizing moiety during a conventional processing operation is possible due to thermally and mechanochemically initiated or catalyzed reactions. A variety of reactants was effectively used.

Functionalization of diene based rubbers and elastomer-modified plastics (e.g., acrylonitrile-butadiene-styrene polymer, ABS) with nitroso compounds, nitrones, tetrazoles, diazooxides, azides, thiols or disulfides bearing stabilizing functions (generally **MS**, **M** = reactive part of the molecule, **S** = stabilizing function) exploits reactivity of C=C double bonds and/or rubber-born carbon-centered free radicals[2]. Stabilizing functions **S** (antioxidant, light-stabilizing, flame retardant, biostabilizing) are irregularly distributed along the polymer chain. Their concentration is determined by the amount of the low-molecular-weight reactant.



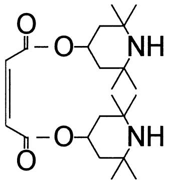
Functionalization of polymers with the saturated carbon-chain backbone, such as polyolefins or polystyrene, is more difficult than that of polymers with unsaturated backbone. Free radicals P·, generated by initiators, and/or catalysis by Lewis or protonic acids in polymer-analogous Friedel-Crafts alkylation reaction are exploited for the synthesis[2].

Functionalized masterbatches are formed and used for stabilization of virgin polymers having the same basic structure and/or - with some compatibility problems - for blending with polymers having a different chemical structure. For example, a stabilizer-functionalized ethylene-propylene-diene terpolymer (EPDM) is suitable for blending with diene-based rubbers.

Grafting of conventional polymers by functionalized monomers during reactive processing

This approach represents a cost-performance effective method for functionalization of carbon-chain polymers with antioxidants, photoantioxidants or UV absorbers[4-7]. Conventional extruder or mixer technologies are used. Mechanochemical initiation is sufficient for reactive grafting of diene-based polymers or elastomer-modified plastics. Organic peroxides, such as di-

*tert.*butylperoxide or dicumylperoxide have to be used as sources of free radicals initiating grafting in reactive processing of polyolefins. Stabilizer moiety bearing monomers able to copolymerize with the polymer, such as **1** - **3**, react with a high grafting efficiency (75 to 90 %) (Ref. 4, 5). The principal side reaction, homopolymerization of functionalized monomers, is suppressed using **1** - **3**. Homopolymerization during reactive processing of polyolefins is the main process in monoacrylates **4** and **5**, accounting for a low-yield grafting (10 - 40 %). Monomers of this type should be eliminated in grafting processes, not only because of the low yield of polymer functionalization. Homopolymers have mostly a lower stabilizing efficiency than the polymer-bound analogue, when compared on molar base of effective groups[2].



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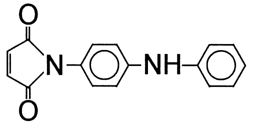

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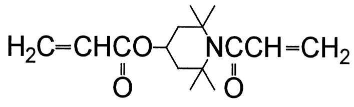

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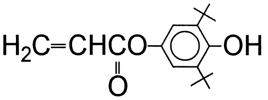

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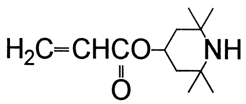

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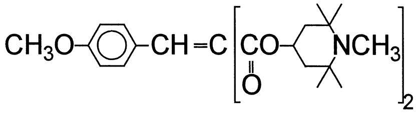
Homopolymerization of hindered amine stabilizer (HAS) **5** during reactive processing of polypropylene can be effectively suppressed by co-grafting with HAS **3** and trimethylolpropane triacrylate, yielding a 90 % stabilizer-grafted polymer[6].

Grafting of conventional polymers by phototriggered processes

Surface modification of unsaturated and saturated polymers by photo-grafting initiated by photosensitizers transferring the absorbed light energy to the polymer is exploited. Free radicals are formed on and in the surface layer of the irradiated polymer. For example, an effective photo-grafting takes place on polypropylene films immersed in solutions of acrylates **4** or **5** irradiated in the presence of benzophenone initiator[2].

A specially designed benzylidene malonate-based HAS **6** represents a recent contribution to effective photo-grafting[4, 7].



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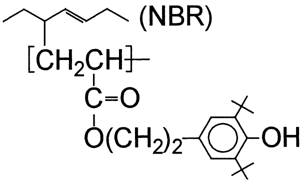
The malonate **6** can be homogeneously distributed in the polymer melt during the processing step, and initiates grafting in the 100 μm surface layer during the subsequent outdoor exposure[4, 6]. The chromophoric part of the modified HAS **6** absorbs light at λ_{max} 308 nm and utilises the absorbed energy for photo-grafting. The latter takes place during approximately 300 h outdoor exposure.

The photo-graftable stabilizer **6** is applicable for commodity and some engineering plastics, paints and coatings.

Examples of polymer-bound stabilizers synthesised by polymer functionalization

Various stabilizers were prepared by functionalization of polymers. They involve phenolic and amine antioxidants, photoantioxidants based on HAS and UV absorbers. Using two different functionalized monomers, polymers containing HAS and UV absorber moieties can be obtained. Selected examples show effective systems: antioxidants **7** and **8**, HAS **9** and **10**, and UV absorbers **11** and **12** (abbreviations used for matrix polymers: NBR = acrylonitrile-butadiene rubber, PE = polyethylene, PO = polyolefin, PP = polypropylene, AES = acrylonitrile-EPDM-styrene polymer).



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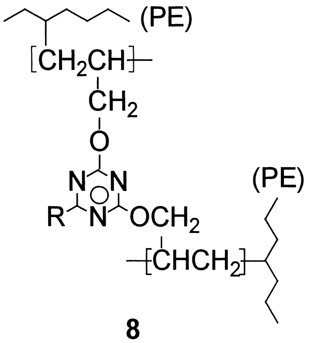

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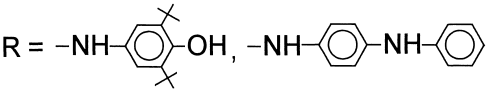

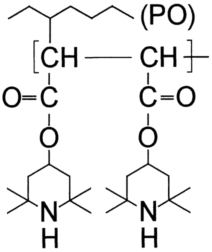

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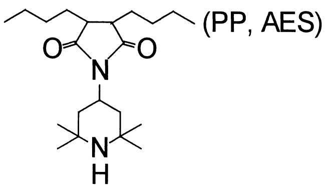

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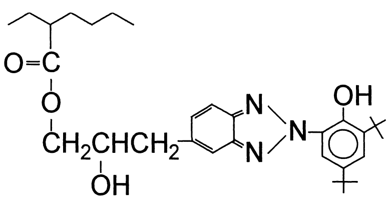
Stabilizer-functionalized specialty polymers: expectations, properties, requirements

- For a high *performance* of polymer-bound stabilizers, an even distribution of stabilizing moieties in the polymer matrix, and, in the case of masterbatches, a good compatibility with the host polymer are necessary conditions. This overcomes compatibility problems in semicrystalline polymers accounting for a slow long-term separation of phases and formation of stabilizer oversaturated domains.
- Stabilization *mechanism* of polymer-bound stabilizers: it has been generally accepted that the physical and chemical mechanisms of antioxidants and photoantioxidants (HAS) are the same as that characteristic of conventional stabilizers[1-3]. Photophysical measurements performed with polymeric UV absorbers based on phenolic benzotrazoles and benzophenones confirmed a full identity between activity mechanisms of monomeric and

polymeric species[8]. It was shown, moreover, that polymeric UV absorbers are more resistant than the related monomers to interrruption of intramolecular hydrogen bonds in matrix polymers with a high content of hydrogen acceptors.



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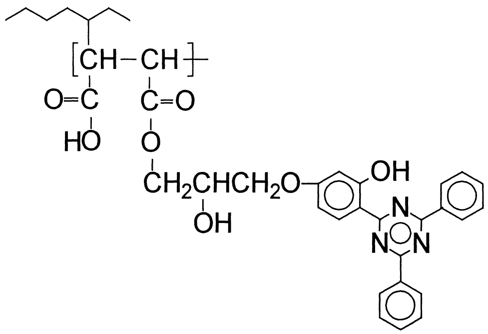

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- Polymer-bound stabilizers are expected to have no adverse *effect on basic polymer properties*. This is fulfilled with grafted stabilizing moieties. They do not disrupt crystalline domains in semicrystalline polymers, if the graft content is lower than 20 %. Incompatibility problems may arise with stabilizer homopolymers and/or copolymers with high content of polar stabilizing moieties blended with commodity nonpolar polymers.
- Excellent *physical persistence* is obtained with polymer-bound stabilizers.
- A *limited performance* of polymer bound stabilizers is observed when some stabilizer migration (especially in the case of antiozonants) and/or high surface localization (as in antiozonants and UV absorbers) are necessary conditions for effective stabilization.

Examples of application of polymers under an increased danger of physical loss of stabilizers

High physical loss of stabilizers by volatilization makes polymers more vulnerable to ageing than stabilizer-sacrificial transformation[1, 2]. Losses of stabilizers by extraction are detrimental not only for the long-term stability of the polymer matrix: the danger of contamination of package contents or of intoxication of biological materials by stabilizers leaching from packaging materials and/or various medical implants or aids is very high. Therefore, stabilizers with extreme physical persistence are necessary in long-term use of plastic materials and protective coatings under hot air and solar radiation exposure, in polyolefins used as pipes in contact with streaming hot water, as packaging materials for fat-containing food and/or alcohols or organic acids containing liquids, in polymers applied as implants or replacements in surgery or in any contact with body fluids, optical aids, in dry-spinning and high-temperature post-spinning treatment of fibres, dry cleaning and/or repeated cyclic attacks of detergent solutions and subsequent hot-air drying of textiles, in polymeric parts of washing machines, rubber articles in contact with hot oil, gasolines containing polar additives, aromatic hydrocarbons or hydraulic fluids or in special applications of polymers in solar energetics and space.

Conclusions

The commercial interest in polymer-bound stabilizers for polyolefins, some engineering polymers and rubbers has been concentrated on systems prepared by functionalization of commodity polymers using reactive processing and photo grafting, i.e. techniques having a rather favourable cost-performance ratio. Binding of the stabilizer molecule proceeds without any adverse influence on the processing technology and basic polymer properties. The polymer-bound stabilizers can be used as masterbatches for various conventional polymers. Some of them can serve potentially as inherently stabilized polymers, applied under demanding conditions, e.g., in medical applications.

Mechanistic data and information on the stabilization performance and durability (physical persistence) are available.

The principal application potential of polymer-bound stabilizers is in automotive and aerospace industries, biocompatible replacements in human medicine and environmentally friendly packaging materials.

There is a need for a better understanding of the influence of the molecular architecture of the polymer-bound stabilizers and of physical interactions with the host polymer matrix.

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