



(Photo)oxidative degradation and stabilization of flame retarded polymers



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ARTICLE INFO

Article history:

Received 25 February 2013

Received in revised form

28 June 2013

Accepted 3 July 2013

Available online 12 July 2013

Keywords:

Flame retardants

Stabilization

Antioxidants

Light stabilizers

Nanocomposites

ABSTRACT

Flame retarded polymer formulations are mainly used in long-term applications whereas antioxidants, light stabilizers and co-additives provide the requested lifetime of plastic materials. However many flame retardants influence the oxidative and photooxidative stability of polymers often in a negative way resulting in early failure and loss in value. Moreover insufficient (photo)oxidative stability of the flame retardant itself may reduce the flame retardance performance over time. Therefore, there is a need to develop adjusted stabilizer systems considering the type of flame retardant, the polymer substrate and the intended application. Therefore, the influence of flame retardants on the (photo)oxidative stability of selected polymers is reviewed and strategies to extend the lifetime of flame retarded polymers are provided. In addition, the specific requirements of the stabilization of nanocomposites as potential flame retardant components are covered.

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1. Introduction

Flame retardants comprise an attractive market share in the field of plastic additives, as the overall value approaches 5 Bill US\$. It is a fast growing area with an estimated annual growth rate of 5–6% [1]. Moreover the flame retardants market is in a dynamic phase because there is a strong trend to replace traditional halogenated flame retardants preferably through non-halogenated solutions or through more environmentally friendly halogenated products. In addition more stringent safety and flammability standards, e.g. in transport industries require new efficient flame retardant systems. As a result of these market driven requirements the number of suppliers of commercial flame retardants is continuously increasing, novel chemistries have been developed and many new products have been introduced.

Flame retarded polymers are mainly used in long-term applications whereas the extended use time allows only minor properties' loss with regard to mechanical performance, visual quality and flame retardancy. However many flame retardants influence the oxidative and photooxidative stability of polymers often in a negative way. Already during processing of flame retarded

polymers initial degradation of the flame retardant may cause accelerated degradation of the polymer chain resulting in performance loss. Moreover insufficient (photo)oxidative stability of the (organic) flame retardant may reduce the long-term and/or the flame retardance performance over time. With regard to (photo)oxidation the polymer and the flame retardant may degrade independently. A direct interaction between the polymer and the flame retardant causing acceleration or retardation is possible and there might be an indirect interaction through influence on the usual stabilizing additives. Moreover secondary chemical processes during use like hydrolysis of flame retardants may result in degradation products influencing the overall stability of the polymer formulation.

In addition many flame retardants act in the polymer as typical inorganic or organic fillers and have to be used in high loadings to achieve the requested flame retardancy. Therefore, these molecules "disturb" the polymer compound and influence the rheological properties during processing, the resulting mechanical properties of the compound (e.g. providing stiffness but loss of elasticity and/or acting as nucleating agent) and the visual appearance of the final product. Furthermore it is well known that filler interactions reduce the stability of the polymer which is even more critical if nano-sized materials are applied. Therefore, depending on the type of flame retardant selected, the polymer substrate and the intended application adjusted stabilizer systems have to be selected or developed [2,3].

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2. Flame retarded polymers and (photo)oxidative stability

The influence of flame retardants on the stability of a selected polymer depends of course on the chemical structure of the flame retardant. Bromine compounds which have been used for a long time are very well investigated. Consequently there are many potential solutions to reduce or to eliminate the weaknesses of bromine compounds in polymer formulations. Contrary to halogenated products the knowledge of phosphorus or nitrogen containing flame retardants on the (photo)oxidative stability is quite poor. In other flame retardant fields like inorganic filler type materials ($\text{Al}(\text{OH})_3$, $\text{AlO}(\text{OH})$, $\text{Mg}(\text{OH})_2$) conclusions can be drawn from the general knowledge of the interaction of fillers with polymers. Some recently introduced chemistries (alkoxyamines) combine even flame retardancy and enhanced light stability in one molecule.

2.1. Processing, long-term thermal and light stabilization of polymers containing halogenated flame retardants

Classical bromine containing flame retardants such as tetrabromobisphenol A or brominated diphenyl ethers are less thermally stable than most polymers as for example the bond dissociation energy of C–Br is only about 285 kJ/mol compared to the C–C bond with 347–356 kJ/mol, aromatic C–Br is even less and is lowered furthermore by substitution [67]. Therefore, the dehydrobromination reaction may already occur during standard polymer processing temperatures. However, it can be efficiently suppressed by the addition of typical heat stabilizers from the entire PVC processing range, such as organotin compounds (e.g. tin maleate) [4–7] or mixed metal soaps [8] whereas the same stabilization mechanisms as in the heat stabilization of PVC can be postulated.

The photooxidation of polypropylene [9] (but as well of polystyrene [10] and polyethylene [11]) is accelerated in the presence of decabromodiphenylether and antimony oxide as the fire retardant decomposes quickly under irradiation into free radicals, which attack the polymer. However, the main decomposition products of the polymer are unchanged.

In addition to the acceleration of the (photo)oxidative degradation of the polymer itself degradation of the brominated flame retardant deactivates one of the most efficient light stabilizer classes, hindered amine (light) stabilizers (HA(L)S), through the formation of an amine salt. Thus the oxidation of HALS to the nitroxyl radical is prevented which is the key intermediate in the stabilization process [12]. Furthermore, the resulting aminium salt is less thermally stable than the corresponding amine and may be further degraded during processing [13].

To eliminate the antagonistic effect of brominated flame retardants on HALS, the use of an alkoxyamine HALS with reduced basicity is the state-of-the-art solution to increase the light stability [14–16]. Several commercial products e.g. LS-1 or LS-2 (see Appendix) are available and much more structures and synthetic processes have been published in patents and patent applications [17–22]. On the basis of the weathering results it can be concluded that alkoxyamine HALS structures don't form salts with HBr and, therefore, protect the polymer from photooxidative degradation.

In summary the influence of halogenated flame retardants on the (photo)oxidative stability of polymers is known, weaknesses of interactions of light stabilizers and degradation products from the flame retardants are identified and efficient adjusted stabilizer structures to eliminate antagonistic effects are established.

2.2. Processing, long-term thermal and light stabilization of polymers containing phosphorus and melamine based halogen free flame retardants

The published data on the (photo)oxidative stability of phosphorus based (ammonium polyphosphate (APP), red phosphorus, melamine (poly, pyro)phosphates) and of nitrogen based (melamine cyanurate) flame retardants are not very numerous. The thermal stability of these flame retardants varies from 200 °C (some APP grades) to more than 300 °C (melamine polyphosphate) and determines, therefore, the potential application field. Consequently, the application of APP is limited to coatings and polyolefins, melamine cyanurate may be used in polyamide-6 and melamine polyphosphate or red phosphorus in polyamide-6.6.

Intumescent flame retardants on the basis of ammonium polyphosphate and pentaerythritol do not modify the degradation of unstabilized PP [23] i.e. the photodegradation of the polymer and of the flame retardant are independent processes [24]. UV stabilizer and HALS show light protection. The activity of HALS is somewhat reduced likely through protonation by the polyphosphoric acid [25], however the effect is less severe than with brominated compounds.

In a patent application comparison [26], it was demonstrated that halogen containing flame retardants like octabromodiphenylether (4.27% in combination with 1.22% Sb_2O_3) show significant surface degradation already after 400 h, even in presence of HALS, while ammonium polyphosphate flame retarded systems (39% of APP) are stable up to 1800 h of artificial light exposure in the presence of 0.5% HALS (LS-3), which is nevertheless lower than that achieved by the stabilized polymer without APP (>2500 h). However, in case of artificial weathering, hydrolysis of ammonium polyphosphate and formation of orthophosphates, pyrophosphates and oligophosphates may occur resulting in reduced fire retardancy as the formation of the intumescent network is disturbed [25,27].

Red phosphorus is mainly used in engineering plastics (polycarbonate, polyamide, polyester), therefore its influence on light and long-term thermal stability is less critical compared to polyolefine applications. From the stabilization point of view, it is more important to stabilize red phosphorus against phosphine formation through moisture, which is achieved by microencapsulation [28] or by adding salts such as copper acetate [29].

The influence of melamine (poly)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 [30], even a slight improvement of light stability could be detected due to a pigment effect of the flame retardant.

Stabilized polyamide melamine cyanurate formulations have been found to not lose their fire retardancy after artificial weathering however, some blooming of melamine cyanurate was detected [25].

The available results of the (photo)oxidative stability of phosphorus and/or melamine containing flame retarded polymers suggest that these flame retardants behave mostly like an inert organic filler (or even like a pigment). The thermal stability of the flame retardant determines the application field. The (photo)oxidative stability of the melamine and phosphorus based flame retardant itself seems to be not a critical parameter. However, chemical reactions during use such as hydrolysis can cause side effects which influence polymer stability and flame retardancy as secondary influence. As consumption of these halogen free flame retardants is considerably increasing, the need of more detailed investigations will become obvious.

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