Description	*The Art of Stabilization – Analytical Evaluation of Stabilizer Systems*
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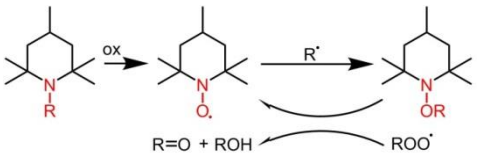
Introduction

Without proper stabilization, polymers are susceptible to degradation caused by reactions with oxygen or UV-light, which lead to undesirable changes in the properties of the polymer. A stabilization system is normally added to the polymeric material, which is responsible for maintaining mechanical properties like strength and toughness. Unfortunately, it is not yet fully clear which combination of stabilizers provides the best performance for a specific application. Furthermore, interactions between different stabilizer classes have to be carefully investigated as they may lead to exploitable synergistic or avoidable antagonistic effects.

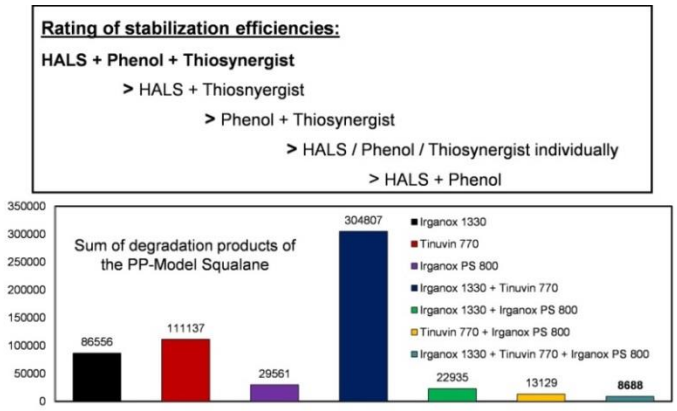
Stabilizer Systems



Suitable stabilizer systems have been developed to inhibit or slow down thermal oxidation of polymeric materials. The most important classes of additives suitable for long-term heat protection of polymers are phenolic antioxidants, thiosynergists and so called hindered amine light stabilizers (HALS), which show a high protecting efficiency against light and heat-induced degradation of polymers. The high efficiency of HALS is considered to originate from a complex set of reactions including scavenging of alkyl and peroxy radicals formed during oxidative attack on the polymer. According to the Denisov Cycle (Figure shown above) the parent amine is oxidized to the corresponding nitroxide radical, which subsequently reacts with polymeric alkyl radicals. HALS are often used in combination with primary and secondary antioxidants as they fail as processing stabilizers. This combination may show antagonism as well as synergism. Due to these unpredictable synergistic or antagonistic effects in complicated mixtures used in real polymer materials, the rating of stabilizer efficiencies is rather complicated. Obviously the investigation of interactions between stabilizers from different chemical classes is very important as they can be critical to their functionality.

Analytical Evaluation of Stabilizer Systems

Analytical evaluation of individual degradation pathways of additives is of major importance to get an idea about the suitability of individual stabilizers for certain applications.



Stabilization mechanisms of the most important additive groups for long-term heat protection of polymers were investigated. A highly sensitive HPLC-MS method was developed to detect and identify stabilizers and their degradation pathways. To elucidate the long-term heat protection efficiency of different stabilizer formulations and the possible chemical reactions between different stabilization classes, several antioxidant systems consisting of HALS in combination with a phenolic antioxidant or a thiosynergist were subjected to aging tests in squalane (mimicking a polyolefin), and decomposition rates as well as chemical changes in the molecular structure of the additives were monitored. Additionally ternary mixtures, including all three stabilizer groups were tested. Stabilization efficiencies were rated upon the observed protection of the PP-mimicking squalane. Results visualized a strong antagonistic effect between phenolic antioxidants and HALS. The reaction mechanism between HALS and thiosynergists as proposed in the literature also would suggest a strong antagonism, as acidic degradation products of the thiosynergist deplete the protection efficiency of the HALS. In the present study no antagonistic effects were observed and combination of these two stabilizers was rather favourable to extend the service life of the polymer. Of all investigated formulations the ternary combination HALS/phenol/thiosynergist showed the highest protection efficiency for the polymeric material.

Summary and conclusions

In the present study the potential of HPLC coupled to highly sensitive MS detection could be clearly demonstrated for detection and identification of HALS and their degradation products. By comparing degradation products derived from squalane using different additive packages, stabilization efficiencies could be rated. The best performance was given with the ternary mixture HALS / thiosynergist / phenol, followed by the mixture HALS / thiosynergist. These results suggest a synergistic effect between these stabilizer groups, which was not reported in the literature until now. A strong antagonistic effect between phenolic antioxidants and HALS was observed. Both stabilizer groups were consumed faster if used in combination compared to the separately aged solutions, and once the concentration of the effective form of the stabilizers drops below a critical value there is a rapid chemical change of the polymer.

The developed analytical method and newly acquired knowledge of individual complex degradation pathways and interactions between chemical groups are of significant importance to avoid antagonistic effects in additive formulations.

Recommended literature

Beissmann S, et al. Monitoring the degradation of stabilization systems in polypropylene during accelerated aging tests by liquid chromatography combined with atmospheric pressure chemical ionization mass spectrometry. Polym Degrad Stabil. 2013;98:1655-61.

Beißmann S, et al. Analytical evaluation of the performance of stabilization systems for polyolefinic materials. Part I: Interactions between hindered amine light stabilizers and phenolic antioxidants. 2014; manuscript submitted to the Journal of Polymer Degradation and Stability.

Beißmann S, et al. Analytical evaluation of the performance of stabilization systems for polyolefinic materials. Part II: Interactions between hindered amine light stabilizers and thiosynergists. 2014; Manuscript submitted to the Journal of Polymer Degradation and Stability.