



Analytical evaluation of the performance of stabilization systems for polyolefinic materials. Part I: Interactions between hindered amine light stabilizers and phenolic antioxidants



Susanne Beißmann^{a,*}, Michael Reisinger^a, Klemens Grabmayer^b, Gernot Wallner^b, David Nitsche^c, Wolfgang Buchberger^a

^a Johannes Kepler-University Linz, Institute of Analytical Chemistry, Altenbergerstraße 69, 4040 Linz, Austria

^b Johannes Kepler-University Linz, Institute of Polymeric Materials and Testing, Altenbergerstraße 69, 4040 Linz, Austria

^c AGRU Kunststofftechnik GmbH, Ing.-Pesendorfer-Str. 31, 4050 Bad Hall, Austria

ARTICLE INFO

Article history:

Received 4 June 2014

Received in revised form

12 August 2014

Accepted 27 September 2014

Available online 7 October 2014

Keywords:

HALS

Phenolic antioxidants

Antagonism

Degradation

Accelerated aging

Model formulation

ABSTRACT

Degradation pathways and interactions between the phenolic antioxidant Irganox 1330 and three commercially used hindered amine light stabilizers (HALS) were successfully studied by accelerated aging of model formulations in the polymer-mimicking solvent squalane. Methods based on high-performance liquid chromatography hyphenated with mass spectrometric detection (HPLC-MS) were developed for structural elucidation of transformation products and monitoring of interactions between the two chemical groups. The developed method was able to differentiate and chromatographically separate transformation products originating from the HALS including the active aminoxyl radicals. The investigations showed a strong antagonism between HALS and phenols, leading to useless consumption of both stabilizer groups, whereby tertiary amines showed less effect compared to secondary HALS. By monitoring the degradation behavior of unstabilized squalane it was possible to perform a rating of stabilization efficiencies of the different systems.

© 2014 Published by Elsevier Ltd.

1. Introduction

The importance of polymers has increased over recent years and nowadays they are deployed in nearly every aspect of our lives. Without proper stabilization, polymers are susceptible to degradation caused by reactions with oxygen or UV-light, which leads to undesirable changes in the properties of the polymer. To minimize decomposition during processing, storage and service, combinations of stabilizers belonging to different chemical groups are added to the polymer. During the lifetime of a polymeric material the stabilization system is responsible for maintaining mechanical properties like strength and toughness.

An important class of additives are so called hindered amine light stabilizers (HALS), which show a high protecting efficacy against light and radiation-induced degradation of polymers. The high efficacy is considered to originate from a complex set of reactions including scavenging of alkyl and peroxy radicals formed during oxidative attack on the polymer [1–9]. According to the Denisov Cycle [4] the parent amine is oxidized to the corresponding

aminoxyl radical, which subsequently reacts with a polymeric alkyl radical to form amino ethers. These species are able to scavenge peroxy radicals, whereby aminoxyl radicals are regenerated. HALS are often used in combination with phenolic antioxidants as they fail as processing stabilizers. Processing stabilizers are responsible for the protection of the polymer melt during the processing stage, where high temperatures are used to melt and form the material. This combination may show antagonism as well as synergism [6,10–14]. 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. Assessment of the efficacy and reaction between different groups requires accelerated tests to get results in acceptable times [15] and highly sophisticated methods to monitor the chemical changes of the additives during the accelerated aging tests. Nowadays there are various analytical tools for analyzing polymer additives. A direct analytical method for the detection of several HALS in solid polymer samples using liquid extraction surface analysis mass spectrometry (LESA-MS) was reported by Paine et al. [16,17]. Although this method provides a simple and fast

* Corresponding author. Tel.: +43 732 2468 8720.

E-mail address: susanne.beissmann@jku.at (S. Beißmann).

analysis, it does not readily allow absolute quantitation. Instead, generally stabilizers have to be extracted from the particular matrix as a first step. Of the different procedures to analyze polymer additives, chromatographic methods play a dominant role. Besides the application of pyrolysis coupled to gas chromatography (Py-GC) [18,19], high performance liquid chromatography (HPLC) in combination with ultraviolet (UV) or MS-detection is commonly applied [20–22]. Recently flow injection in combination with tandem MS without preceding chromatographic separation was reported for the fast analytical evaluation of stabilization systems [23–25]. For the quantitative determination of the aminoxyl radicals originating from the HALS formed during protection of the polymer an ESR-method is commonly employed, with the disadvantage that no structural information of the different compounds involved is provided [26–28]. In this work an HPLC method in combination with sensitive MS-detection was developed. With this method it became possible to monitor interactions between HALS and phenolic antioxidants in model formulations after exposure to heat. Commercially important low and high molecular weight HALS were selected and the aging behavior and chemical changes of the separately aged HALS were compared to the combination with a phenolic antioxidant. Structural identification of the individual compounds and their degradation products was achieved using a high mass accuracy quadrupole time-of-flight (Q-TOF) mass spectrometer together with knowledge about HALS chemistry. Thereby new insights into the stabilization mechanisms and antagonistic effects were obtained. Furthermore, the stabilizing efficacy of the different model formulations was rated according to the degradation of the polymer-mimicking aging fluid squalane.

2. Material and methods

2.1. Chemicals

The following polymer stabilizers were included in this work: Irganox 1330 obtained from Ciba (Basel Switzerland), Tinuvin 770 from BASF (Ludwigshafen, Germany), Cyasorb UV-3529 from Cytec

Industries (Woodland Park, USA), and Uvasorb HA 88 from 3V Sigma (Milano, Italy). Structures according to the data sheets are shown in Fig. 1. Squalane was obtained from Chrompack (Middelburg, Netherlands), ammonium formate from Sigma–Aldrich (Steinheim, Germany). Toluene and methanol were purchased from VWR (Fontenay-sous-Bois, France), acetonitrile from VWR (Leuven, Belgium). 18 M Ω water obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA) was used throughout the work.

2.2. Instrumentation

The chromatographic separation with UV-detection was performed on an Agilent Series 1260 Infinity HPLC system equipped with vacuum degasser, quaternary pump, autosampler, and UV-VIS diode array detector. For structure elucidation the chromatography was performed on an Agilent Series 1100 HPLC system coupled with an Agilent 6510 Q-TOF MS (Agilent, Palo Alto, CA, USA). The system was operated in the positive ion mode. The separation column was a Kinetex C18 (50 \times 3.0 mm, 2.6 μ m particle size) from Phenomenex (Aschaffenburg, Germany).

2.3. Sample preparation and aging conditions

The apolar solvent squalane was used as it is a liquid model for polypropylene [29–31]. The thermal stability of the additives dissolved in squalane was investigated. Therefore about 10 mg of the stabilizers were added separately to 1 mL of the polymer-mimicking solvent squalane. Additionally, binary combinations of the phenolic antioxidant Irganox 1330 with the hindered amines (Tinuvin 770, Cyasorb UV-3529, Uvasorb HA 88) were prepared. The solutions were heated in an ambient atmosphere to 130 $^{\circ}$ C. At various times samples were taken and the stabilizers along with their degradation products were extracted by shaking with methanol (squalane: methanol = 1:10). After separation of the layers, the methanol phase (containing intact stabilizers and degradation products) was 10-fold diluted and analyzed.

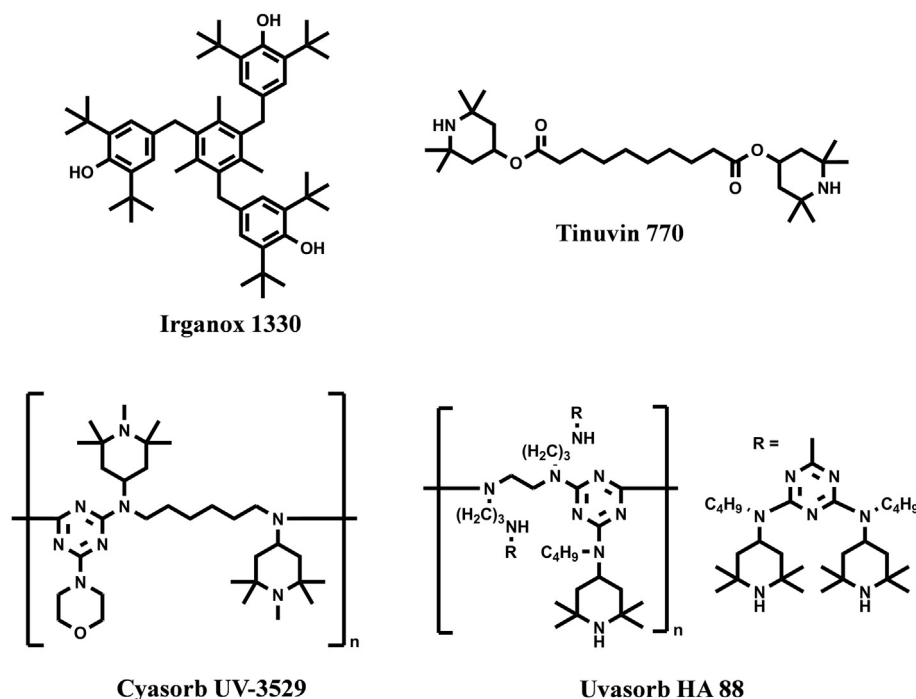


Fig. 1. Chemical structures of investigated analytes.

Download English Version:

<https://daneshyari.com/en/article/5201685>

Download Persian Version:

<https://daneshyari.com/article/5201685>

[Daneshyari.com](https://daneshyari.com)