Thermal Stability of Polymer Additives: Comparison of Decomposition Models Including Oxidative Pyrolysis

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The thermo-oxidative stability of widely used polymer additives has been investigated. A comparative analytical approach with classic and innovative decomposition models for polymer additives was conducted and the results supported using quantum-chemical calculations. Unique pyrolysis products of the analytes were compiled utilizing pyrolysis online coupled to gas chromatography followed by mass spectrometric detection (Pyr–GC–MS). The pyrolysis was either performed under inert conditions or in an oxygen-containing atmosphere. Squalane was applied as polymer-mimicking liquid next to low density polyethylene (LDPE) and polyamide 6 (PA 6) as matrices for 10 selected additives. The additives included in this study range from antioxidants and plasticizers to processing aids. These were selected to address a range of application in consumer products and to cover different chemical classes. The toxicological relevance of additives and potential breakdown products was considered. Consequently, degradation of sterically hindered antioxidants, diarylamines, and a trimealllic acid derivative was investigated. The findings were used to predict the behavior of consumer products made of polymeric materials containing additives. The level of Antioxidant 2246 [2-tert-butyl-6-[3-tert-butyl-2-hydroxy-5-methylphenyl][methyl]-4-methylphenol] and one of its predicted decomposition products was determined in baby bottle nipples made of natural rubber [2-tert-butyl-4-methyphenol] utilizing the complementary technique of gas chromatography coupled to tandem mass spectrometry (GC–MS/MS). This study provides a comprehensive characterization of important polymer additives and enables the prioritization of degradation products for further risk assessment. J. VINYL ADDIT. TECHNOL., 25:E12–E27, 2019. © 2018 The Authors. Journal of Vinyl and Additive Technology published by Wiley Periodicals, Inc. on behalf of Society of Plastics Engineers.

INTRODUCTION

In addition to exposure to moisture or UV-light, thermal impact on polymeric material is a well-known tool for stimulating material aging [1,2]. Over time, the physico-chemical properties of the material can change dramatically. Because of the wide application of polymer additives in everyday products, their stability in long-term usage is of special interest. Once embedded the additive is exposed to atmospheric oxygen through all stages of the polymer life cycle [3]. While addition of antioxidants prevents the polymer from being oxidized, numerous nonintentionally added substances (NIAS) may be formed as a consequence of the interaction of the antioxidant with oxygen. Oxidation products of additives and NIAS contribute to the overall decomposition pattern for the material. From a legal perspective, an NIAS is classified as “an impurity in the substances used or a reaction intermediate formed during the production process or a decomposition or reaction product” [4] for food contact materials. Consequently, degradation products can be part of consumer products and consumers may be exposed to these compounds. Depending on the level present and toxicological and migration properties, degradation products might present risk for consumers. Three different accelerated aging protocols were conducted using a qualitative analytical approach to assess the potential risks associated with the presence of degradation products of polymer additives. In a long-term study, squalane was used as an artificial polymer matrix. The decomposition of antioxidants was investigated at moderate temperatures for about 3 weeks according to a previously reported protocol [5]. Furthermore, aging resistance of polymers can be tested by exposing it to hot air (700°C) for several days [6]. To simulate this accelerated aging, pyrolysis was used in this study. Pyrolysis has been reported to be a suitable tool for the study of thermal degradation of polymers [7]. It was shown previously that thermal degradation of polymers under different atmospheric conditions led to different degradation products [8,9]. There is still a lack of knowledge about the application of pyrolysis in the field of additive aging. This is especially true for aging under atmospheric conditions [10]. Because of the rather low concentrations and the possible interference from degradation products from the complex original polymeric matrix, pyrolysis of additives in consumer products poses particular
analytical challenges [11]. The online coupling of pyrolysis to gas chromatographic separation as it was applied in this study allows a direct transfer of pyrolysis products to the mass spectrometric detector (Pyr-GC–MS) with negligible loss. To differentiate between thermal effects and oxidative impacts on degradation of polymers and additives, pyrolysis of custom-synthesized polymers and of pure additives was conducted in an inert and in an oxygen-containing atmosphere. The respective degradation patterns were utilized for comparison with those from pyrolysis of polymers containing additives. It was intended to emphasize the role of oxygen not only in the polymer decomposition but also in the additive degradation process. Computational chemistry may be used to predict expected products from decomposition and reaction products [12]. In this study, the degradation of additives was monitored by visualization of the average local ionization energy (ALIE) [13] of additives and by applying the Fukui function for radical attack ($f^p$) on the chemical structure of selected additives. The identification of degradation products is useful for the preparation of a comprehensive risk assessment. Exemplarily, for risk assessment of polymeric food contact materials, the presence of NIAS with a molecular weight of up to 1000 Da must be considered [14]. Larger molecules are unlikely to be absorbed in the gastrointestinal tract [15]. A similar consideration is important for polymeric consumer products which contact skin. Components with a molecular weight up to 500 Da are likely to overcome the natural human skin barrier [16]. Therefore, dermal exposure may lead to an increased individual body burden of smaller decomposition products. There is evidence of skin penetration for all additives discussed in this work [17]. These are able to migrate out of a polymer matrix and to overcome the human skin barrier during contact ex vivo to varying extents. Therefore it is of particular importance to further classify the additives with respect to degradation properties and the potential for the formation of typical decomposition products.

**EXPERIMENTAL**

**Materials**

**Tested polymers.** The polymers included in this study were characterized by their typical pyrogram patterns and respective mass spectra of pyrolyzates [18]. Custom-synthesized polymeric material entailing individual additivation was purchased from Clariant (Gersthofen, Germany). LDPE and PA 6 were used as matrix for the 10 additives tested. LDPE powder (SABIC® 1922Z900) and PA 6 powder (Aquamid® AQ 500 L) was used as the matrix. The additivation was subdivided into two recipes (LDPE 1/PA 6 1: NBBS, α-MSD, Irganox 1081, Irganox 1222, Santonox; LDPE 2/PA 6 2: Nonox A, Neozon D, Antioxidant 2246, Tinuvin P, TOTM). Raw LDPE material with following specifications was used: a melt volume index (MVI) of 22 g/10 min, melting temperature (10°C/min) of 107°C, a heat deflection temperature of 83°C and a density of 919 kg/m$^3$ [19]. The raw PA 6 material was used with a melting point of 222°C and a density of 1.13 g/cm$^3$ [20]. To increase the homogeneity of the final material, compounding was performed by preparing a master batch of polymer pellets containing the respective additives. Pellets of the master batches and pure LDPE or PA 6 respectively were extruded followed by injection molding to specimens with the size of 60 × 60 × 1 mm and a scheduled final concentration of each additive of 10 g/kg. The LDPE samples were processed with a rotation speed of 300 rpm and the following temperature zones ($T_1–T_{1(Dio)}$): $T_1$: 170°C, $T_2$: 180°C, $T_3$: 180°C, $T_4$: 180°C, $T_5$: 185°C, $T_6$: 190°C, $T_7$: 190°C, $T_8$: 200°C, $T_9$: 200°C, $T_{1(Dio)}$: 200°C. The compounding conditions for PA 6 samples are hereafter listed: rotation speed of 230 rpm and the following temperature zones: $T_1$: 200°C, $T_2–T_{1(Dio)}$: 230°C. Additionally, two conventional baby bottle nipples made of natural rubber from different manufacturers were analyzed.

**Chemicals.** 2-tert-Butyl-4-(5-tert-butyl-4-hydroxy-2-methylphenyl)sulfanyl-5-methylphenol (Santonox, CAS 96–69-5), 2,6-di-tert-butyl-4-(diethoxyphosphorylmethyl)phenol (Irganox 1222, CAS 976–56-7) and 2-tert-butyl-6(3-tert-butyl-2-hydroxy-5-methylphenyl)methyl-4-methyl phenol (Antioxidant 2246, CAS 119–47-1) were purchased from abcr GmbH (Karlsruhe, Germany). Squalane (CAS 111–01-3) was purchased from Sigma-Aldrich (St. Louis, MO), as well as all the remaining additives included in this study (N-butylbenzenesulfonamide: NBBS, CAS 3622–84-2; 2,4-diphenyl-4-methyl-1-pentene: α-MSD, CAS 6362–80-7; N-phenylphthalalen-2-amine: Neozon D, CAS 135–88-6; N-phenylphthalalen-2-amine: Nonox A, CAS 90–30–2; tris (2-ethylhexyl)benzene-1,2,4-tricarboxylate: TOTM, CAS 3319–31–1; 2-tert-butyl-6-(3-tert-butyl-2-hydroxy-5-methylphenyl)sulfanyl-4-methylphenol: Irganox 1081, CAS 90–66–4; 2-(benzotiazol-2-yl)-4-methylphenol: Tinuvin P, CAS 2440–22–4). Standard substances with a purity of ≥97% were utilized as stock solution mixture in acetonitrile with a final concentration of 10 μg/ml each.

The following isotopic labeled substances were used as internal standards: $p$-cresol-d$_8$, $p$-terphenyl-d$_{14}$, di-(2-ethylhexyl)-phthalate-d$_{12}$, 2-aminonaphthalene-d$_7$ (all from CIL: Cambridge Isotope Laboratories, Inc. Tewksbury, MA), acetonophenone-d$_8$, 2-isopropyl-d$_7$-thioxanthene-9-one, benzophenone-d$_{10}$ (all from Sigma-Aldrich), and di-n-nonylphthalate-3,4,5,6-d$_4$ (Dr. Ehrenstorfer GmbH, Augsburg, Germany). A stock solution of internal standards with a concentration of 10 μg/ml each in acetonitrile was prepared. Solvents for GC analyses and for sample preparation (acetonitrile, acetonitrile, methanol, ethyl acetate and toluene) were purchased from Sigma-Aldrich (St. Louis, MO) or Merck KGaA (Darmstadt, Germany).

**Apparatus and techniques**

**Pyr-GC–MS. Pyrolysis conditions.** Pyrolysis was performed using a platinum filament localized in a thermal desorption unit (TDU) mounted with a Pyrolyzer Module for TDU onto a Cooled Injection System (CIS) equipped
with liquid nitrogen cooling and a MultiPurpose Sampler (MPS2-XL; all items from Gerstel, Mülheim, Ruhr, Germany). This set-up was connected to a gas chromatograph coupled with the mass selective detector 7890A-5975C GC/MSD System (Agilent, Santa Clara, CA) and maintained as described previously [20]. Pyrolysis of polystyrene was performed regularly at 500°C for 0.33 min to assure an appropriate performance of the system by evaluating the signal intensity for styrene mono-, di-, and tri-mer. A constant ratio of the monomer-signal to the trimer-signal was implemented as quality requirement and a value of 3.4 ± 0.5 was indicative of a successfully performed pyrolysis. The pure additives as well as the polymers were placed directly into pyrolysis tubes (Gerstel). Specimens of the polymers were randomly taken from a sample supply that has been previously cut to size, mingled and homogenized. Synthetic air was used (20% O_2 in N_2, both gases with purity ≥99.999%, Linde, Pullach, Germany) for an in situ oxidation and helium as the carrier gas (purity ≥99.999%, Linde). To this end, a solvent vent method was applied and 60 ml/min synthetic air passed into the Pyr-TDU-CIS complex using a pneumatic gas regulator (Gerstel) with a helium vent flow of 10 ml/min. A vent pressure of 15 kPa was applied. According to Gerstel specifications, the concentration of synthetic air during pyrolysis was 83.6%, amounting to a final oxygen concentration of 16.7% [20]. Inert pyrolysis was carried out with similar parameters as used for oxidative pyrolysis. The synthetic air was replaced using pure helium with a vent flow of 70 ml/min instead. The pyrolysis took place subsequently with a standard initial temperature of 700°C to cause fragmentation of additives and also to obtain information on polymer decomposition patterns [21]. To investigate the effect of varying thermal energy on semi-volatile components and matrix in real samples 300°C, 600°C, and 800°C were applied to the material of baby bottle nipples additionally. These samples are intended for use as eating utensil and of particular interest as a consequence [22,23]. Infants are potentially exposed to additives and decomposition products via multiple routes. Components can be taken up orally either directly or via migration into the food. The following parameters were also used: lead time of 0.10 min, initial time of 0.33 min and follow-up time of 1.00 min. The TDU temperature was ramped starting with an initial temperature of 50°C, followed by 720°C/min up to 320°C and a final hold for 1.4 min. The CIS initial temperature was held at −120°C using cryo cooling to capture the volatile pyrolysis products for 4.0 min. This was followed by a ramp of 12°C/min up to 320°C and a final hold for further 3.0 min.

Parameters for gas chromatographic separation and mass spectrometric detection. Chromatographic separation was performed using column-back-flush with an HP-5MS GC column (30 m x 0.25 mm i.d., 0.25 μm df, Agilent, New Castle, DE) equipped with a pre-column (10 m x 0.25 mm i.d., Phenomenex, Aschaffenburg, Germany). Helium as the carrier gas was used as follows with a continued back-flush flow program: initial flow of ~1.39 ml/min for 3 min to rinse out the oxygen from the Pyr-TDU-CIS complex, then with a rate of 10 to 1.00 ml/min. The GC oven was heated to 50°C for 6 min, ramped with 10°C/min to 320°C and held for an additional 3 min. MS analyses were carried out by collecting total ion chromatograms in the full scan mode and the mass range of 30–500 amu.

The material of baby bottle nipples was identified and the effect of different temperatures on pyrograms of the complex matrices was studied. A GC method without backflush mode was used for that reason on the same Pyr-GC–MS device as described in chapter 2.2.1.1.

Squalane model aging and examination of degradation products. Six of the additives were tested under ambient air conditions at 130°C in line with a previously reported aging protocol utilizing squalane as a polymer-mimicking solvent [5]. To this end, 10 mg of the following additives were placed discretely into a 2 ml vial with 1.0 ml squalane matrix respectively and mixed thoroughly using a Vortex test tube mixer (neoLab, Heidelberg, Germany): Neozon D, Nonox A, Antioxidant 2246, Santonox, Irganox 1222 and Irganox 1081. These additives have been selected to investigate analytes which are structurally related and representative for phenol and arylamine based antioxidants. Pure squalane without additives was used as negative control. Each set-up was prepared in duplicates. The vials were sealed using a layer of aluminum foil followed by a cap with a PTFE septum. The mixtures underwent accelerated aging for 18 days at 130°C in an oven (type 720 FED; Binder, Tuttingen, Germany). The subsequently applied liquid–liquid extraction procedure was performed as follows: the squalane mixtures were quantitatively transferred into test tubes with ground glass joints, applying five rinsing steps to the vial with 1 ml acetonitrile each. Subsequently, two liquid–liquid extraction steps using a total of 9 ml acetonitrile each were conducted by adding the acetonitrile to the squalane samples followed by intensive shaking. The acetonitrile phases were collected and combined in a flask after phase separation and filled to an exact volume of 50 ml. The resulting extracts were analyzed for the additives as well as for degradation products by operating a 7000A mass spectrometric detector coupled to a 7890 GC in full scan mode and the mass range of 30–500 amu.

Quantification of additives and degradation products using tandem mass spectrometry coupled to gas chromatographic separation (GC-ESI-MS/MS). A multiple reaction monitoring (MRM) method was established to quantify the polymer additives and degradation products and to identify these with high selectivity [17]. The analytical system for GC-ESI-MS/MS operation was formed by a GC7890A-MS7000A set-up (Agilent, Santa Clara, CA, USA) equipped with an electron impact ion source at 70 eV and helium as the carrier gas (purity ≥99.999%, Linde).

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The extraction protocol for additives in polymeric material was optimized according to previously reported ultrasonic assisted treatment, where the comminuted material is submerged in solvents and exposed to ultrasonic waves [24]. To this end, the material was cut to a size of maximum 1 mm edge length using a scalpel. Investigated solvents were toluene, methanol, ethyl acetate and acetonitrile. The extraction durations varied up to 2 h and the extraction temperature was adjusted up to 50°C to optimize the efficiency of the protocol. Final extractions were conducted by submerging approximately 15 mg of LDPE or natural rubber in 10 ml toluene and exposing it to ultrasonic treatment for 1 h at 22°C. Ultrasonic treatment in methanol at 50°C for 1 h proved to be the most efficient way of extracting the additives from PA 6. The quantification focused on Antioxidant 2246 and its degradation products, as this additive was identified in the material of baby bottle nipples. Additionally, the phenol based degradation products are of special toxicological relevance in this context [25]. The transitions for the compounds were set to m/z = 177 → 119, 177 → 91 and collision energy (CE) of 15 V for Antioxidant 2246; m/z = 108 → 91 CE 35, 108 → 57 CE 40 for cresol; m/z = 164 → 149 CE 15, 164 → 121 CE 30 for 2-tert-butyl-4-methylphenol; m/z = 122 → 107 CE 15, 122 → 91 CE 30 for 2,4-dimethylphenol and m/z = 136 → 121 CE 15, 136 → 91 CE 30 for 2,4,6-trimethylphenol.

**Data acquisition and analysis**

Pyrolysis data were acquired with MSD ChemStation software E.02.02. (Agilent Technologies) and converted from ChemStation data files using MassHunter GC/MS Translator (version B.07.00, Agilent). The data were further processed using MassHunter Workstation software applying a deconvolution algorithm. To filter compounds, only peaks with at least 5000 counts of absolute area were taken into consideration and mass criteria of 500 counts of only peaks with at least 5000 counts of absolute area were applying a deconvolution algorithm. To ther processed using MassHunter Workstation software Translator (version B.07.00, Agilent). The data were further processed using MassHunter Workstation software (Qualitative Analysis version B.06.00 and Quantitative Analysis version B.05.00, Agilent). Where full scan data were concerned, a deconvolution algorithm was applied in the same way as used for pyrolysis data.

All optimizations have been done with ORCA 4.0.1.2 [26] using B3LYP-D3/def2-TZVP [27–29] in combination with the chain-of-spheres approximation [30] (COSX). To avoid larger computational efforts only crude conformational analyses have been performed for TOTM and NBBS. Consequently, the main conformations used for the calculations have been chosen arbitrarily based on an educated guess and keeping in mind that the conformations will have a negligible effect on the investigated properties. Fukui functions and the average local ionization energies (ALIE) [13] were obtained from multiwfn [31]. A combination of VMD [32] and PovRay was used to graph the ALIE and the f0 surfaces.

**RESULTS AND DISCUSSION**

**Decomposition of additives**

The intended fragmentation of the pure additives was investigated under oxidative or inert conditions to identify specific breakdown products. Furthermore, matrix effects were studied by embedding the additives in two different polymers (LDPE, PA 6) prior to pyrolysis. The polymer types were chosen because of their common application in consumer products and to investigate two materials with different polarity. Additionally, the polymer-mimicking solvent squalane was used for long-term aging studies and kinetics. The apolar triterpene is a liquid model for polypropylene [33]. It is comparatively easy to prepare mixtures with additives which substantially simplifies the aging protocol. The time consuming polymer design can be circumvented and therefore it presents a more versatile technique. The main decomposition products of 10 additives (Fig. 1) in seven matrix-specific decomposition protocols were investigated and the results compiled in Table 1. The products are listed according to their substance of origin. If a reaction product was derived by decomposition of more than one additive, the additional source and table number are listed below the individual entry. The protocol, which led to the specific fragmentation, is indicated with an x. The majority of breakdown products of additives were formed during oxidative pyrolysis. This was true for the phenolic compounds under study as well as for the plasticizers TOTM and NBBS and the processing agent α-MSD.

**TOTM.** TOTM (Table 1, No.1) is used in polymeric material as a substitute plasticizer for example, di(2-ethylhexyl)phthalate (DEHP). It shows about 30 times less leaching properties and is attributed to lower toxicity than DEHP due to its higher molecular weight [34]. However, investigations on degradation of this plasticizer are of particular importance because both DEHP and TOTM were proved to leach out of polyvinylchloride tubes from medical devices to blood in vitro [35]. TOTM underwent
manifold degradation applying accelerated aging protocols. In total, about 25 degradation products of TOTM were identified. DEHP was ascertained among the direct decomposition products of TOTM in five of six investigated aging protocols (Table 1, Nos.1, 25). Respective negative controls were critically evaluated and the presence of impurities of DEHP excluded. This finding is of particular concern, as DEHP is strongly associated with teratogenic and endocrine-disrupting effects [36]. DEHP was formed during pyrolysis of the pure additive in both inert and oxidative mode. Additionally, the phthalate could be qualified in the tailor-made polymers PA 6 and LDPE entailing TOTM. The formation of DEHP was accompanied by formation of the respective isophthalate bis(2-ethylhexyl)benzene-1,3-dicarboxylate (DOIP) (Table 1, No.26). The 1,4-dicarboxylate derivative was not formed however in
| No. | Source | IUPAC name | CAS No. | Molecular formula | Exact mass | Additives w/o matrix | Additives embedded in matrix |
|-----|--------|------------|---------|-------------------|---------------|---------------------|-----------------------------|
|     |        |            |         |                   |               | 700°C 20 s                   | 700°C 20 s                  |
|     |        |            |         |                   |               | Oxidative pyrolysis | Inert pyrolysis | LDPE ox. pyrolysis | PA 6 ox. pyrolysis | PA 6 in. pyrolysis | Squalane extracts |
| 1   | TOTM   | tris(2-ethylhexyl) benzene-1,2,4-tricarboxylate | 3319–31-1 | C_{14}H_{27}O_{6} | 546.4 | x | x | x | x | x | 18 days |
| 2   | TOTM   | (E)-butene-2 | 624-6-6 | C_{6}H_{10} | 56.1 | x | x | x | x | x | 130°C |
| 3   | TOTM   | cyclopropylmethanol | 2516-33-3 | C_{8}H_{14}O | 72.1 | x | x | x | x | x | 130°C |
| 4   | TOTM   | (2S)-2-methylxirane | 16088-62-3 | C_{8}H_{14}O | 58.0 | x | x | x | x | x | 130°C |
| 5   | TOTM   | butanal | 123-72-8 | C_{6}H_{12}O | 72.1 | x | x | x | x | x | 130°C |
| 6   | TOTM   | (E)-2-methylbut-2-enal | 1115-11-3 | C_{8}H_{14} | 84.1 | x | x | x | x | x | 130°C |
| 7   | TOTM   | (Z)-heptene-2 | 6443-92-1 | C_{8}H_{16} | 98.1 | x | x | x | x | x | 130°C |
| 8   | TOTM   | (E)-3-methylhept-3-ene | 7300-03-0 | C_{8}H_{14} | 112.1 | x | x | x | x | x | 130°C |
| 9   | TOTM   | (E)-Octene-2 | 13389-42-9 | C_{8}H_{16} | 112.1 | x | x | x | x | x | 130°C |
| 10  | TOTM   | 3-methylidene heptane | 1632-16-2 | C_{8}H_{14} | 112.1 | x | x | x | x | x | 130°C |
| 11  | TOTM   | (E)-Octene-4 | 14850-23-8 | C_{8}H_{16} | 112.1 | x | x | x | x | x | 130°C |
| 12  | TOTM   | (E)-3-methylhept-2-ene | 3404-75-9 | C_{8}H_{16} | 112.1 | x | x | x | x | x | 130°C |
| 13  | TOTM   | 5-hexylidihydro-2(3H)-furanone | 2865-82-9 | C_{8}H_{10}O_{2} | 114.1 | x | x | x | x | x | 130°C |
| 14  | TOTM   | heptan-3-one | 106-35-4 | C_{7}H_{14} | 98.1 | x | x | x | x | x | 130°C |
| 15  | TOTM   | 1-(2-methylcyclopenten-1-yl) ethanone | 3168-90-9 | C_{8}H_{14}O | 124.1 | x | x | x | x | x | 130°C |
| 16  | TOTM   | 2-ethylhex-2-enal | 645-62-5 | C_{8}H_{16} | 126.1 | x | x | x | x | x | 130°C |
| 17  | TOTM   | 5-ethyl-1-cyclopentene-1-carboxaldehyde | 36431-60-3 | C_{8}H_{16} | 124.1 | x | x | x | x | x | 130°C |
| 18  | TOTM   | 2-ethylhexanal | 123-05-7 | C_{8}H_{16}O | 126.1 | x | x | x | x | x | 130°C |
| 19  | TOTM   | (E)-5-methylhept-3-en-2-one | 5090-16-4 | C_{8}H_{16}O | 126.1 | x | x | x | x | x | 130°C |
| 20  | TOTM   | 2-ethylhexan-1-ol | 104-76-7 | C_{8}H_{16}O | 130.1 | x | x | x | x | x | 130°C |
| 21  | TOTM   | 2-ethylhexyl benzene | 5444-75-7 | C_{8}H_{16}O_{2} | 234.2 | x | x | x | x | x | 130°C |
| 22  | TOTM   | 1,4-trimethylbenzene | 95-63-6 | C_{10}H_{12} | 120.1 | x | x | x | x | x | 130°C |
| 23  | TOTM   | 2-methylbutyl 4-hydroxybenzoate | 8452-60-8 | C_{12}H_{14}O_{2} | 208.1 | x | x | x | x | x | 130°C |
| 24  | TOTM   | bis(2-ethylhexyl) hexanediol | 103-23-1 | C_{12}H_{24}O_{3} | 370.3 | x | x | x | x | x | 130°C |
| 25  | TOTM   | bis(2-ethylhexyl) benzene-1,2-dicarboxylate | 117-81-7 | C_{12}H_{16}O_{2} | 390.3 | x | x | x | x | x | 130°C |
| 26  | TOTM   | bis(2-ethylhexyl) benzene-1,3-dicarboxylate | 137-89-3 | C_{12}H_{16}O_{2} | 390.3 | x | x | x | x | x | 130°C |
| 27  | NBBS   | N-butylibenzenesulfonamide | 3622-84-2 | C_{10}H_{16}N_{2}O_{3}S | 213.1 | x | x | x | x | x | 130°C |
| 28  | NBBS   | benzene | 71-43-2 | C_{6}H_{6} | 78.1 | x | x | x | x | x | 130°C |
| 29  | NBBS   | 1-(benzenesulfonyl)pyrrole | 16851-82-4 | C_{10}H_{16}N_{2}O_{3}S | 207.0 | x | x | x | x | x | 130°C |
| 30  | NBBS   | N-ethyl-N-methylbenzenesulfonamide | 16950-19-0 | C_{12}H_{16}N_{2}O_{3}S | 199.1 | x | x | x | x | x | 130°C |
| 31  | NBBS   | 2-(benzenesulfonyl)acetonitrile | 7605-28-9 | C_{12}H_{16}N_{2}O_{3}S | 181.0 | x | x | x | x | x | 130°C |
| 32  | NBBS   | N-butylibenzylbenzenesulfonamide | 1907-65-9 | C_{12}H_{16}N_{2}O_{3}S | 227.1 | x | x | x | x | x | 130°C |
| 33  | α-MSD  | 2,4-diphenyl-4-methyl-1-pentene | 6362-80-7 | C_{14}H_{30} | 236.2 | x | x | x | x | x | 130°C |

(Continues)
| No. | Source       | IUPAC name          | CAS No. | Molecular formula | Exact mass | Additives w/o matrix | Additives embedded in matrix |
|-----|--------------|---------------------|---------|-------------------|------------|----------------------|-------------------------------|
| 34  | α-MSD        | benzene             | 71–43-2 | C₆H₆              | 78.1       | x                    | x                            |
|     | cf.28 NBBS   |                     |         |                   |            |                      |                              |
|     | cf.43 Neozon D |                    |         |                   |            |                      |                              |
|     | cf.59 Nonox A |                    |         |                   |            |                      |                              |
| 35  | α-MSD        | styrene             | 100–42-5 | C₈H₈              | 104.1      | x                    |                              |
|     | α-MSD        | benzaldehyde        | 100–52-7 | C₆H₆O            | 106.0      | x                    |                              |
| 37  | α-MSD        | 1-phenylethanone    | 98–86-2 | C₆H₆O            | 120.1      | x                    |                              |
| 38  | α-MSD        | 1,1,3-trimethyl-1-phenyl-2H-indene | 3910–35-8 | C₁₈H₂₀        | 236.2      | x                    |                              |
| 39  | α-MSD        | 2,4-diphenyl-4-methyl-2(E)-pentene | 22768–22-5 | C₁₈H₂₀       | 236.2      | x                    | x                            |
| 40  | α-MSD        | (2,3-dimethyl-3-phenylbutan-2-yl) benzene | 1889–67-4 | C₁₈H₂₀         | 238.2      | x                    | x                            |
| 41  | α-MSD        | 1,4-diphenylbenzene | 92–94-4 | C₁₈H₂₀         | 230.1      | x                    |                              |
| 42  | Neozon D     | N-phenylnaphthalen-2-amine | 135–88-6 | C₁₆H₁₃N   | 219.1      | x                    | x                            |
| 43  | Neozon D     | benzene             | 71–43-2 | C₆H₆             | 78.1       | x                    | x                            |
|     | cf.28 NBBS   |                     |         |                   |            |                      |                              |
|     | cf.34 α-MSD  |                    |         |                   |            |                      |                              |
|     | cf.59 Nonox A |                    |         |                   |            |                      |                              |
| 44  | Neozon D     | aniline             | 62–53-3 | C₆H₆N            | 93.1       | x                    |                              |
|     | cf.61 Nonox A |                    |         |                   |            |                      |                              |
|     | cf.64 Nonox A |                    |         |                   |            |                      |                              |
| 46  | Neozon D     | 3-phenylfurane      | 13679–41-9 | C₁₆H₁₃O | 144.1      | x                    |                              |
| 47  | Neozon D     | N-phenylamine       | 122–39-4 | C₁₂H₁₃N         | 169.1      | x                    |                              |
| 48  | Neozon D     | 1-phenylbenzofuran  | 63317–69-1 | C₁₈H₁₃O   | 244.1      | x                    |                              |
| 49  | Neozon D     | 1-(2-hydroxynaphthalen-1-yl) naphthalen-2-ol | 602–09-5 | C₂₀H₁₆O₂      | 286.1      | x                    |                              |
| 50  | Neozon D     | benzene             | 3781–67-7 | C₁₈H₁₃N         | 243.1      | x                    |                              |
| 51  | Neozon D     | benzene             | 207–06-9 | C₂₀H₁₆         | 252.1      | x                    |                              |
| 52  | Neozon D     | dinaphtho[1,2-b:1',2'-d]furane | 207–93-2 | C₂₀H₁₆O        | 268.1      | x                    |                              |
| 53  | Neozon D     | 3,4-dihydro-1,2,5,6-dibenzoazulene | 63077–00-9 | C₂₀H₁₆N₂ | 269.1      | x                    |                              |
| 54  | Neozon D     | benzene             | 188–55-6 | C₂₀H₁₆N₂        | 280.1      | x                    |                              |
| 55  | Neozon D     | 2-naphthalen-2-yl-3,5-diphenyl-1H-pyrole | 170238–88-7 | C₂₀H₁₆O₅ | 345.2      | x                    |                              |
| 56  | Nonox A      | N-phenylnaphthalen-1-amine | 90–30-2 | C₁₆H₁₃N      | 219.1      | x                    | x                            |
| 57  | Nonox A      | prop-2-yl-2-ethyl nitrite | 1070–71-9 | C₁₆H₁₃N | 51.0       | x                    |                              |
| 58  | Nonox A      | (E)-but-2-enedinitrile | 764–42-1 | C₆H₈N₂         | 78.0       | x                    |                              |
| 59  | Nonox A      | benzene             | 71–43-2 | C₆H₆             | 78.1       | x                    | x                            |
|     | cf.28 NBBS   |                     |         |                   |            |                      |                              |
|     | cf.34 α-MSD  |                    |         |                   |            |                      |                              |
| 60  | Nonox A      | ethinylbenzene      | 536–74-3 | C₆H₆          | 102.1      | x                    |                              |
| 61  | Nonox A      | amines              | 62–53-3 | C₆H₆N          | 93.1       | x                    |                              |
|     | cf.44 Neozon D |                    |         |                   |            |                      |                              |
| 62  | Nonox A      | 1H-indene           | 95–13-6 | C₆H₆          | 116.1      | x                    | x                            |
| 63  | Nonox A      | N-propan-2-ylamine  | 768–52-5 | C₆H₆N         | 135.1      | x                    |                              |
| 64  | Nonox A      | naphthalene         | 91–20-3 | C₁₀H₈         | 128.1      | x                    |                              |
|     | cf.45 Neozon D |                    |         |                   |            |                      |                              |
| 65  | Nonox A      | biphenylene         | 259–79-0 | C₁₂H₈        | 152.1      | x                    |                              |
| 66  | Nonox A      | naphthalene-1-carbonitrile | 86–53-3 | C₁₁H₇N       | 153.1      | x                    |                              |
| No. | Compound                         | Molecular Formula | Molecular Weight | Structure | Notes                        |
|-----|----------------------------------|-------------------|------------------|-----------|------------------------------|
| 67  | Nonox A 9-methylidenefluorene    | C_{14}H_{10}      | 178.1            | x         |                              |
| 68  | Nonox A 4H-cyclobuta[1,3]phenanthrene | C_{13}H_{10}     | 170.1            | x         |                              |
| 69  | Nonox A N-phenyl-p-phenylenediamine | C_{12}H_{12}N_{2} | 184.1            | x         |                              |
| 70  | Nonox A pyrene                   | C_{10}H_{10}      | 202.1            | x         |                              |
| 71  | Antioxidant 2246 2-tert-butyl-6-[(3-tert-butyl-2-hydroxy-5-methyl[phenyl)methyl]-4-methylphenol | C_{23}H_{32}O_{2} | 340.5            | x         |                              |
| 72  | Antioxidant 2246 2-methylphenol   | C_{8}H_{10}O      | 108.1            | x         |                              |
| 73  | Antioxidant 2246 4-methylphenol   | C_{8}H_{10}O      | 108.1            | x         |                              |
| 74  | Antioxidant 2246 (E)-3-phenylprop-2-enal | C_{10}H_{10}O    | 132.1            | x         |                              |
| 75  | Antioxidant 2246 2-methyl-1-benzofuran | C_{10}H_{10}O    | 132.1            | x         |                              |
| 76  | Antioxidant 2246 2,4-dimethylphenol | C_{8}H_{12}O      | 122.1            | x         |                              |
| 77  | Antioxidant 2246 2,4,6-trimethylphenol | C_{10}H_{14}O    | 164.1            | x         |                              |
| 78  | Antioxidant 2246 4,7-dimethyl-1-benzofuran | C_{10}H_{10}O    | 146.1            | x         |                              |
| 79  | Antioxidant 2246 2-propan-2-ylphenol | C_{8}H_{10}O      | 136.1            | x         |                              |
| 80  | Antioxidant 2246 2-ethyl-4,5-dimethylphenol | C_{10}H_{12}O    | 150.1            | x         |                              |
| 81  | Antioxidant 2246 2-methoxy-1,3,5-trimethylbenzene | C_{10}H_{12}O    | 150.1            | x         |                              |
| 82  | Antioxidant 2246 (E)-3-methyl-4-phenylbut-3-en-2-one | C_{11}H_{12}O    | 160.1            | x         |                              |
| 83  | Antioxidant 2246 2,2′-methanediyl-bis(4-methylphenol) | C_{15}H_{16}O_{2} | 228.1            | x         |                              |
| 84  | Antioxidant 2246 2-tert-butyl-4-methylphenol | C_{11}H_{12}O    | 164.1            | x         |                              |
| 85  | Antioxidant 2246 2-tert-butyl-4,6-dimethylphenol | C_{12}H_{12}O    | 178.1            | x         |                              |
| 86  | Antioxidant 2246 5-[(2-methylpropyl)-1,3-benzodioxole | C_{11}H_{12}O    | 178.1            | x         |                              |
| 87  | Antioxidant 2246 2-methoxy-1,3-di(propan-2-yl)benzene | C_{10}H_{12}O    | 192.2            | x         |                              |
| 88  | Antioxidant 2246 2,6-bis[(3-tert-butyl-2-hydroxy-5-methyl[phenyl)methyl]-4-methylphenol | C_{21}H_{16}O_{3} | 460.3            | x         |                              |
| 89  | Santonox 2-tert-butyl-4(4-tert-butyl-4-hydroxy-2-methylphenyl)sulfinyl-5-methylphenol | C_{22}H_{20}O_{2}S | 358.2            | x         |                              |
| 90  | Santonox 2-methylphenol           | C_{8}H_{10}O      | 108.1            | x         |                              |
| 91  | Santonox 3-methylphenol           | C_{8}H_{10}O      | 108.1            | x         |                              |
| 92  | Santonox 2-methyl-1-benzofuran    | C_{10}H_{10}O     | 132.1            | x         |                              |
| 93  | Santonox 2,4-dimethylphenol       | C_{8}H_{12}O      | 122.1            | x         |                              |
| 94  | Santonox 2,4,6-trimethylphenol    | C_{10}H_{14}O     | 164.1            | x         |                              |
| 95  | Santonox 4,7-dimethyl-1-benzofuran | C_{10}H_{10}O    | 146.1            | x         |                              |
| 96  | Santonox 1-(4-methoxyphenyl)propan-2-one | C_{10}H_{12}O    | 164.1            | x         |                              |
| 97  | Santonox 2-methoxy-4-methyl-1-propan-2-yl benzene | C_{11}H_{12}O    | 164.1            | x         |                              |
| 98  | Santonox 2-tert-butyl-5-methylphenol | C_{11}H_{12}O    | 164.1            | x         |                              |
| 99  | Santonox 5-[(2-methylpropyl)-1,3-benzodioxole | C_{11}H_{12}O    | 178.1            | x         |                              |
| 100 | Santonox 1-methoxy-3-methylsulfanylbenzene | C_{8}H_{9}OS    | 154.1            | x         |                              |
any of the investigated decomposition protocols. Interestingly, the aging protocols applied revealed differences in the strength of the C-C bonds from benzene to the carboxylate groups which are in excellent accordance with the Fukui calculations for radical attack of TOTM. The bonds in position 1 and 4 appeared to be significantly more reactive than in position 2 as indicated by the red spheres in the Fukui depiction (Fig. 2a).

NBBS. NBBS is a plasticizer used in films, transparent paper coatings and nylon (polyamide) [37,38]. The use of NBBS is the subject of controversial discussion because of its neurotoxic activity [38]. Benzene was identified as an unspecific decomposition product of NBBS, because the aging of 3 more additives resulted in the formation of benzene (Table 1, No.28: NBBS, α-MSD, Neozon D, Nonox A). The most specific decomposition product of NBBS was N-ethyl-N-methylbenzenesulfonamide (Table 1, No.30). The ψ Fukui function and the ALIE surface of NBBS revealed no clearly preferred area for a radical methylation among the aromatic carbon atoms (cf. Supporting Information, Figure S1) but pointed to an increased reactivity for the nitrogen. Although, it was formed during pyrolysis of the pure additive through radical methylation, this degradation product could not be identified in matrix based accelerated aging. It is likely that initially formed methyl radicals also reacted competitively with the matrix.

α-MSD. The processing aid α-MSD is commonly used in polyolefin crosslinking (e.g., LDPE) [39]. Several α-MSD-specific decomposition products were identified by stimulating aging of this additive. For example, styrene was a specific main product of α-MSD decomposition in four of the six aging protocols applied (Table 1, Nos.33, 35). The formation of the cyclic saturated isomer No.38 (1,1,3-trimethyl-3-phenyl-2H-indene) is triggered by thermal impact and so is the rearrangement of the carbon double bond to form isomer No.39 (2,4-diphenyl-4-methyl-2(E)-pentene) [40]. Both were detected in two or five aging protocols, respectively. Free radicals can add to the double bond of α-MSD and form intermediate adducts. Cumyl radicals are expelled as a consequence [41,42]. Decomposition product No.40 ((2,3-dimethyl-3-phenylbutan-2-yl)benzene) is formed by combination of two cumyl radicals during pyrolysis of the pure additive and during pyrolysis of LDPE entailing α-MSD.

Neozon D and Nonox A. The arylamines act as radical scavengers by donating hydrogen. Because of this, they are added to polymers as antioxidants to terminate radical chain mechanisms. The positive mesomeric effect of the arylgroups increases the antioxidative efficiency of these secondary aromatic amines [43]. Nonox A is an antioxidant highly esteemed for high temperature applications [44]. Previously reported studies revealed high thermal stability of Nonox A with an onset decomposition temperature of 225°C determined by thermogravimetric analyses [44].
Phenolic antioxidants. Phenolic antioxidants are used in polymers because of their radical chain breaking properties. They compete with the polymeric matrix for the radicals that occur during aging. Especially chain-carrying peroxyl radicals are responsible for material aging [46]. Hence, accelerated aging of the pure phenolic antioxidants (Antioxidant 2246, Santonox, Irganox 1222/1081 and Tinuvin P) led to a multitude of decomposition products under oxidative conditions, among them several cresol derivatives. Depending on the chemical structure of the respective antioxidant of origin either o-cresol, m-cresol or p-cresol was formed. Cresols can be absorbed through the skin, the gastrointestinal or respiratory tract and are metabolized in the liver. The toxicological relevance of these components has been proven in several previously reported studies [47]. It was shown that exposure to cresol mixtures led to positive developmental and reproductive toxicity tests in rats and mice and to an impaired liver function [48]. Additionally, all cresols appeared to be eye irritants. Oxidative pyrolysis turned out to be the most efficient method for stimulating aging of phenolic antioxidants in this study.

A main application field of Antioxidant 2246 is the pre-stabilization of natural rubber latex. For latex that is to be further processed to pacifiers, baby bottle nipples or teething rings, it is the only stabilizer allowed to be added to the fresh latex milk to an extent of 0.4% [22]. On account of the fact that the material undergoes numerous heating stages during its life cycle, it is important to know potential degradation products of the additive for further risk assessment. The main degradation products of Antioxidant 2246 were 2-tert-butyl-4-methylphenol and 2-tert-butyl-4,6-dimethylphenol (Table 1, Nos.84, 85). Both products might be harmful to health if swallowed or in contact with skin [49]. They were formed in four or six of seven tested aging protocols, respectively. Their increased occurrence can be explained by the symmetrical structure of Antioxidant 2246 and cleavage of the methylene bridge. It was found that the C—C bond strength in methylene bridges of methanediyldiphenols is weakest in o-o' position (Fig. 1). The same argumentation is applicable for the other symmetrical sterically hindered antioxidants Santonox and Irganox 1081 (Table 1, Nos.89, 106). Accelerated aging of the sulfur containing antioxidant Irganox 1081 resulted in the smallest amount of degradation products. This is indicative of a comparatively high thermo-oxidative stability that was determined for the Irganox 1081 previously [17]. The additional electron pairs of sulfur lead to a more stable delocalized electron system. The most reactive site of this antioxidant is located at the sulphur atom according to ALIE and Fukui calculations (Supporting Information Figure S1 lowest ALIE at sulphur surface). Consequently, this site will be initially oxidized during aging.

The 4-methyl group of 2,6-dialkyl-4-methylphenols can often be selectively oxidized to an aldehyde group [25]. The oxidation of 2,6-di-tert-butyl-4-methylphenol by oxidizing agents to 3,5-di-tert-butyl-4-hydroxybenzaldehyde has been described earlier [50]. In this study, the oxidized...
form was identified as main degradation product of Irganox 1222 (Table 1, No.104).

The UV-stabilizer Tinuvin P showed the least degradation of all tested additives under study in general. The benzotriazole ring is very stable and few examples are reported of it being cleaved during a reaction [51]. Nevertheless, the ALIE surface of Tinuvin P revealed one significantly more reactive carbon atom in o-position referring to the hydroxyl group (Supporting Information Figure S2). No prominent areas for radical attack were determined according to the nearly equally distributed Fukui $f^0$ surface. Toluene was the only decomposition product identified during accelerated aging of Tinuvin P using pyrolysis. Unlike previously discussed degradation products, toluene is a rather unspecific fragmentation product, so its formation cannot be attributed exclusively to the presence of Tinuvin P in polymers.

Comparison of inert and oxidative pyrolysis using the example of two polymers

Generally, fewer decomposition products of additives were identified when they were pyrolyzed at 700°C embedded in LDPE or PA 6. This analysis was also performed to investigate the effect of additivation on the typical polymer decomposition, however. Fig. 3 shows pyrograms of the tailor-made polymers entailing Tinuvin P (109), Nonox A (56), Neozon D (42), Antioxidant 2246 (71), and TOTM (1). The typical peaks of polymer decomposition products are highlighted in the pyrolyzates in addition to the distinct additives. The homopolymer peaks of different carbon numbers are noticible and are formed by dienes, alkenes and alkanes in inert pyrolysis of LDPE (Fig. 3c). It was demonstrated that LDPE is sensitive to oxidation by synthetic air, because the typical triplet peak is accomplished by a ketone and an epoxide peak in the oxidative pyrolysis mode (asterisks in Fig. 3a). This pattern is typical for pyrolysis of LDPE aged under oxygen [52] and absent under inert conditions (Fig. 3c). Moreover, comparison of both LDPE pyrolyzates revealed that additivation with the stabilizers Nonox A, Neozon D, Antioxidant 2246 and Tinuvin P up to 10 g/kg each was not sufficient to completely suppress the formation of polymer oxidation products [53]. PA 6 appeared to be more resistant to oxidation. The polymer PA 6 proved to be more stable to thermo-oxidative degradation than LDPE, because the matrix peak pattern of PA 6 did not change significantly as a function of the pyrolysis mode applied (Fig. 3b and d). This observation is in accordance with the respective thermal decomposition temperature of the tested polymers. While LDPE decomposes under inert conditions at around 290°C, PA 6 starts to decompose at approx. 340°C [54]. In both pyrolysis modes $\varepsilon$-caprolactam was identified as characteristic and main PA 6 pyrolysis product [55,56].

Additives in consumer products—Identification via pyrolysis combined with GC–MS/MS quantification

Everyday consumer products were investigated in respect of the results of the aging protocols. Most consumer products consist of unique and complex polymer mixtures. Samples composed of a standardized polymer were investigated in order to reduce the complexity of the matrix to a minimum and to focus on the additivation. The great toxicological relevance to oral and dermal exposure was a further selection criterion. On this basis, two baby bottle nipples made of natural rubber were analytically characterized in detail. The raw material of natural rubber
is latex milk which chemically consists of polyisoprene. Therefore, isoprene and isoprene oligomers were expected to be found in the material characterization process utilizing pyrolysis. Antioxidants are commonly added to the latex milk for prestabilization and processing aids for vulcanization purposes. These aspects were considered in

FIG. 4. The pyrograms of a baby bottle nipple were modified using a deconvolution algorithm and the resulting total compound chromatograms (TCC) at three temperatures (300°C, 600°C, 800°C) are depicted. Natural rubber-specific peaks are highlighted [7]: M: isoprene, T: toluene, X: xylene, D': 2,4-dimethyl-4-vinylcyclohexene, D: dipentene, trimers to hexamers of isoprene. Two additives were identified: DBA: dibenzylamine, 71: Antioxidant 2246 (cf. Table 1). The extracted spectrum of (71) is depicted top left. Major ion traces are highlighted with the respective chemical structure. If the structure is also present in the degradation Table 1, the corresponding number is added in squares: 72/73: 2/4-methylphenol, 76: 2,4-dimethylphenol, 84: 2-tert-butyl-4-methylphenol, 85: 2-tert-butyl-4,6-dimethylphenol, 83: 2,2'-methanediyl-bis(4-methylphenol).

FIG. 5. Chromatograms of GC-MS/MS in MRM (multiple reaction monitoring) mode: a: toluene extract of a baby bottle nipple, b: standard chemicals at 250 ng/ml in acetonitrile. Antioxidant 2246 (71) and the degradation product 2-tert-butyl-4-methylphenol (84) were quantified.
the evaluation of analytical data. The material was pyrolyzed at different temperatures of 600°C and 800°C (Fig. 4). Analysis of semivolatile components was conducted by applying a subpyrolysis temperature of 300°C [57]. The typical peaks representing degradation products of natural rubber were identified and highlighted in the pyrograms. The presence of dibenzylamine (DBA) was also ascertained. DBA is known to occur from thermal degradation of the rubber vulcanization agent zinc dibenzylthiocarbamate [58]. Moreover, Antioxidant 2246 was identified in the pyrograms (Fig. 4) and quantified using GC–MS/MS in MRM mode. Fig. 5 shows representative MRM chromatograms of the toluene extract of a baby bottle nipple (A) next to the chromatogram of a standard chemical mixture in acetonitrile (B). The presence of Antioxidant 2246 and of its degradation product 2-tert-butyl-4-methylphenol was confirmed by this complementary method according to the good match of retention time and quantifier/qualifier ion intensity ratio. A content of $2.7 \pm 1.0$ mg/kg Antioxidant 2246 and $0.37 \pm 0.06$ mg/kg 2-tert-butyl-4-methylphenol was determined in the material of baby bottle nipples from Manufacturer 1. The

![Image](https://via.placeholder.com/150)

FIG. 6. GC-MS/MS in scan mode: the total compound chromatograms (TCC) of extracts from aged Antioxidant 2246 (71) in squalane are displayed after deconvolution algorithm. a: chromatogram of (71) after 30 min in squalane (Sq) at 130°C. b: chromatogram of (71) after 18 days in squalane at 130°C. Identified degradation products are highlighted by their number according to Table 1: 84: 2-tert-butyl-4-methylphenol, 85: 2-tert-butyl-4,6-dimethylphenol, 87: 2-methoxy-1,3-di(propan-2-yl)benzene. The isolated spectra are depicted alongside the corresponding peaks. Matrix derived peaks are asterisked (acetonitrile, siloxane (0), squalane, alkanes).

![Image](https://via.placeholder.com/150)

FIG. 7. GC-MS/MS in scan mode: the total compound chromatograms (TCC) of extracts from aged Santonox in squalane (Sq) are displayed after deconvolution algorithm at three different time points at 130°C each. a: chromatogram of Santonox (89) after 30 min, b: 7 days, c: 18 days. The identified degradation product is highlighted by the number 98: 2-tert-butyl-5-methylphenol according to Table 1. The respective spectra were extracted and depicted alongside the peaks. Matrix derived peaks are asterisked (Sq: squalane).
Accelerated aging of phenolic antioxidants in squalane

The TCC of squalane extracts are depicted for two representative additives (Figs. 6 and 7). The extracts were taken at different time points of accelerated aging. In all chromatograms, the matrix-derived peak of squalane (Sq) showed highest intensity. A main peak for Antioxidant 2246 (Fig. 6) and Santonox (Fig. 7) was noticeable at the beginning of the experiment after 30 min at 130°C (A) next to the squalane peak. These additive signals clearly decreased in the course of the experiment (B, C). In case of Santonox, the additive pattern changed to one main decomposition product only. This decomposition product has been identified as tert-butylated cresol derivative, and its occurrence increased steadily over time (Fig. 7b and c No.98). Unlike Santonox, the pattern of Antioxidant 2246 ultimately changed to numerous smaller peaks (Fig. 6a and b). The latter were accomplished by several asterisked matrix-related peaks, which partially caused an overlay (Fig. 6 Nos.0 and 87). Fig. 6 therefore points out the advantages of deconvolution treatment at the example of full scan chromatograms. Despite the chromatographic overlay, the individual peaks and corresponding spectra could be isolated after applying the chromatogram deconvolution algorithm and used for identification purposes. Two cresol derivatives were confirmed as the main degradation products of Antioxidant 2246 (Fig. 6, Table 1 Nos.84 and 85) and an anisole derivative (Fig. 6, Table 1 No.87). These were also major decomposition products as predicted by pyrolysis studies.

CONCLUSIONS

When it comes to identification of decomposition products of additives, the use of custom-synthesized polymeric material offered an advantage compared to the use of consumer products. The resulting decomposition products cannot be unmistakably assigned to additives of origin in consumer products considering the unknown composition of the polymeric material. Because degradation products like DEHP, could have been intentionally added as an ingredient to the product, it is important to exclude this using custom-synthesized polymers in aging protocols. Its occurrence is thereby evidently additive-derived (here TOTM-derived). Both, analytical evaluations and quantum-chemical calculations, predicted the formation of DEHP and DOIP from TOTM. It should be considered as a consequence for further studies that TOTM is potentially converted into DEHP and the isophthalate under thermo-oxidative impact. Investigations of additives in the polymers provided the most realistic matrix set-up, but the polymer design is challenging and time-consuming. The use of squalane as polymer-mimicking liquid is therefore a feasible alternative. With the squalane set-up, it is possible to treat the additives separately in the matrix with smaller volumes. One disadvantage, however, is that it requires complex sample preparation, including several extraction steps. Compared to this, pyrolysis of the pure chemicals is a more artificial system but needs fewer preparation steps and is applicable to assess the variety of individual breakdown products. The pyrolysis and the squalane model have limitations because these protocols cannot provide information about potential reaction products of additives with the polymer or with other polymer components. These systems are useful for attributing specific decomposition products to additives of origin.

Besides matrix-related effects, the choice of technical implementation had an impact on the decomposition of additives. Online oxidative pyrolysis was especially useful for mimicking the aging of LDPE material and pure phenolic based antioxidants, whereas inert pyrolysis can be used to assess more degradation products of arylamines. It is essential to take the aging conditions in reality into consideration when an artificial system is applied to additives for predictive purposes. From this perspective, the decomposition models with oxygen supply may be used to mirror the actual aging conditions of additives. Complementary techniques should be applied to support the results. Therefore the analytical findings were checked for plausibility using ALIE surfaces and the Fukui function. The quantum-chemical data were in agreement with experimental observations. Degradation products of occasional additives can be identified using the discussed protocols and prioritized with respect to toxicological concerns for further risk assessment. The results may also be used to develop a targeted analytical approach as shown for Antioxidant 2246 and 2-tert-butyl-4-methylphenol. In this study, Antioxidant 2246 was identified in the pyrograms of baby bottle nipples and quantified using GC–MS/MS. Its decomposition product 2-tert-butyl-4-methylphenol was also present in the material as predicted by pyrolysis of the pure substance and by accelerated aging in squalane. Alkylphenols are readily absorbed from oral administration in vivo [59]. Consequently, a facilitated uptake of degradation products compared to the substance of origin can be expected and may present risk for infants in this case. In summary it can be concluded, therefore, that information on additive-specific degradation patterns must have an impact on the use of additives in polymeric consumer products.
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