ELSEVIER

Polymer Degradation and Stability 76 (2002) 441–448

Polymer Degradation and Stability

www.elsevier.com/locate/polydegstab

A molecular study towards the interaction of phenolic anti-oxidants, aromatic amines and HALS stabilizers in a thermo-oxidative ageing process

Julien Barret, Pieter Gijsman*, Josefien Swagten, Ronald F.M. Lange*,[1]

DSM Research, PO Box 18, 6160 MD Geleen, The Netherlands

Received 9 November 2001; received in revised form 21 January 2002; accepted 27 January 2002

Abstract

The molecular interactions of phenolic anti-oxidants, aromatic amines and HALS stabilizers are successfully studied by heating the stabilizers under oxidative conditions in polar and non-polar solvents. The polar solvent bis(2-methoxyethyl)ether is used to mimick polar engineering plastics like e.g. TPE-U's, whereas the non-polar solvent squalane or 2,6,10,15,19,23-hexamethyltetracosane is used to mimick polypropylene. The oxidation rate is followed by the analysis of samples taken in time using various analytical techniques as e.g. IR, HPLC–PDA, GC–FID, GC–MS and LC–MS. A general occuring interaction between sterically hindered phenols and aromatic amines, i.e. regeneration of the aromatic amine by the sterically hindered phenol, is demonstrated by varying the molecular structure of the phenol as well as the polarity of the system. Studies using mixtures of a HALS with structurally different sterically hindered phenols visualized a general antagonistic effect between the phenols and the HALS, in which the HALS consumes the phenol. In all stabilizer combinations using the sterically hindered phenols studied here, a stabilization of the resulting quinone form is observed which can, dependent on the molecular structure of this quinone, lead to solubility issues in polymers.

Keywords: Molecular; Interaction; Phenolic anti-oxidant; Aromatic amine; HALS

1. Introduction

Sterically hindered phenols, aromatic amines and hindered amine light stabilizers (HALS) are so called primary stabilisers and are frequently used in the thermo-oxidative and UV stabilization of polymers [1–3]. The actions of these individual stabilizers are well known and the use of these stabilizers increase the lifetime of polymers significantly, making these polymers suitable for applications where severe requirements are demanded. To increase the lifetime of polymers even further, a combination of stabilizers is frequently applied [1–3]. Mixing of stabilizers are also common practice to protect the polymers from different environmental attacks. Phenolic anti-oxidants and aromatic amines are generally applied in thermo-oxidative stabilization whereas HALS are used to prevent thermo-oxidative and mainly UV degradation [1–3]. The synergistic or antagonistic effects in a mixture of stabilizers are often determined by characterizing the loss of mechanical properties in time [4]. Studies concerning interactions of different stabilizers on a molecular scale are rare [5]. Recently, we reported about the interaction of the sterically hindered phenolic anti-oxidant 1,3,5-trimethyl-2,4,6-Tris(3,5-di-*t*-butyl-4-hydroxybenzyl) benzene, **1a**, with the aromatic amine 4,4′-bis(α,α-dimethylbenzyl)diphenylamine, **2a**, in a polyether mimicking solvent bis(2-methoxyethyl)ether [6]. It was demonstrated by using various analytical techniques that **2a** was regenerated by **1a**. In addition, it was found that the quinone structure of the oxidized sterically hindered phenolic anti-oxidant is only stable in the absence of radical species. This results, for the **1a**–**2a** system in the stabilisation of the highly conjugated and hence low soluble oxidized **1a**. Curious about the generality of this **1a**–**2a** interaction, we performed additional experiments

* Corresponding authors.
E-mail address: pieter.gijsman@dsm.com (P. Gijsman).
[1] Present address: BASF Aktiengesellschaft, ZKS/B1, 67056 Ludwigshafen, Germany.

0141-3910/02/$ - see front matter
PII: S0141-3910(02)00047-2

using different phenolic anti-oxidants and amine containing stabilizers in different polymer mimicking solvents. Here we describe a detailed molecular study dealing with the interactions of the sterically hindered phenolic anti-oxidants 1,3,5-trimethyl-2,4,6-tris(3,5-di-*t*-butyl-4-hydroxybenzyl)benzene, **1a**, and octadecyl-3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionate, **3a**, the aromatic amine 4,4′-bis(α,α-dimethyl-benzyl)diphenylamine, **2a**, and the HALS bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate, **4a**, using several analytical techniques as e.g. IR, HPLC–PDA, GC–FID, GS–MS and LC–MS. To enhance the analysis of the ageing process and to investigate the interaction in different environments, both the polyether mimicking solvent bis(2-methoxyethyl)ether and the polypropylene mimicking squalane or 2,6,10,15,19,23-hexamethyltetracosane has been used.

2. Experimental

The thermo-oxidative stabilizers 1,3,5-trimethyl-2,4,6-Tris(3,5-di-*t*-butyl-4-hydroxybenzyl)benzene, **1a**, octadecyl-3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionate, **3a**, and bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate, **4a**, where obtained from Ciba Specialty Chemicals, whereas the 4,4′-bis(α,α-dimethylbenzyl)diphenylamine, **2a**, was obtained from Uniroyal. The stabilizers were used as received. The bis(2-methoxyethyl)ether ($CH_3OCH_2CH_2OCH_2CH_2OCH_3$) and 2,6,10,15,19,23-hexamethyltetracosane (squalane) were obtained from Aldrich.

The ATR spectra were recorded on a Perkin-Elmer Spectrum One FT–IR Spectrophotometer equipped with a Universal ATR. The crystal was a ZnSe/Diamond composite. Absorptions were corrected for baseline variations by using the non-varying ether absorption at 1453 cm^{-1} as reference for bis(2-methoxyethyl)ether. The carbonyl index is defined as the absorption of the carbonyl at 1725 cm^{-1} divided by the absorption at 1453 cm^{-1}. The carbonyl intensity at 1755 cm^{-1}, which is less intense and omitted for clarity, shows the same behaviour as the depicted absorption at 1725 cm^{-1}. For squalane the non-varying absorption at 735 cm^{-1} is taken as the reference. Here the carbonyl index is defined as the absorption of the carbonyl at 1718 cm^{-1} divided by the absorption at 735 cm^{-1}.

The HPLC measurements were performed with a Waters HPLC/PDA, equipped with a Chromsep ODS-2 column and a Photo Diode Area detector, using a gradient of acetonitrile and water as the eluent. The amounts of the thermo-oxidative stabilizers and their oxidation products were calculated using an internal standard. The response factors of **1a**, **1d**, and **2a** (Scheme 1) were determined with the help of the pure products in known concentrations. The response factors for the oxidation products **1b** and **1c** were calculated using the determined response factors of **1a** and **1d** in the formula $f_{1b}=f_{1a}+(f_{1d}-f_{1a})/3$ and $f_{1c}=f_{1a}+2\ (f_{1d}-f_{1a})/3)$, respectively. The response factors of the oxidation products **2b** and **2c** were assumed to be equal to the response factor of **2a**.

GC–MS analysis was performed on a MD800 bench top mass spectrometer (Fisons Instruments). Gas chromatographic separation was done on a 25 m×0.25 mm I.D. fused silica capillary column with 0.12 μm CP SIL5 CB stationary phase using helium as the carrier gas at a constant flow of 1 ml min^{-1}. The following temperature program was used: 1 min 40 °C isothermal, followed by an increase of 10 °C min^{-1} to 180 °C and from there on with 4 °C min^{-1} up to 325 °C. The sample was injected on-column at a temperature of 60 °C. EI mass spectra were obtained in full scan mode, scanning from 20 to 600 amu. Data were processed using MassLab 1.3 software. GC–FID analysis was performed on a HP5890 instrument. Gas chromatographic separation was done on a 25 m × 0.32 mm I.D. fused silica capillary column with 0.13 μm CP SIL5CB stationary phase using N_2 as carrier gas at a constant pressure of 8.7 psi. The same temperature program as described for the GC–MS analysis is used. For GC–FID an on-column injection was performed at a temperature of 50 °C. The temperature of the FID was 350 °C. The amounts of the thermo-oxidative stabilizers and their oxidation products were calculated using an internal standard method. The response factors were determined with the help of the pure products in known concentrations or calculated as described for the HPLC method.

LC–APCI–MS data were obtained on a PE SCIEX API150 single quadrupole mass spectrometer (PE SCIEX, Toronto, Canada), coupled to an HP1100 liquid chromatograph. Unit resolution was used for all measurements. Positive as well as negative ion APCI–MS was used. The source temperature was 350 °C. Spectra were recorded over a mass range of 120–1500 amu at a fragmentor voltage of 50 V. Chromatographic separations were performed on a 150×4 mm Chromsep ODS-2 column (Chrompack, Middelburg, The Netherlands). The column was maintained at a temperature of 50 °C throughout the analysis, which was performed using a gradient elution starting with water/acetonitrile (40/60), going to 100% acetonitrile in 13.3 min. This condition was kept until 32 min. The flow rate was 1 ml/min. A UV detector was used in series with the MS. A UV signal was recorded at a wavelength of 220 nm. The detailed chromatographic GC and HPLC-data are available on request.

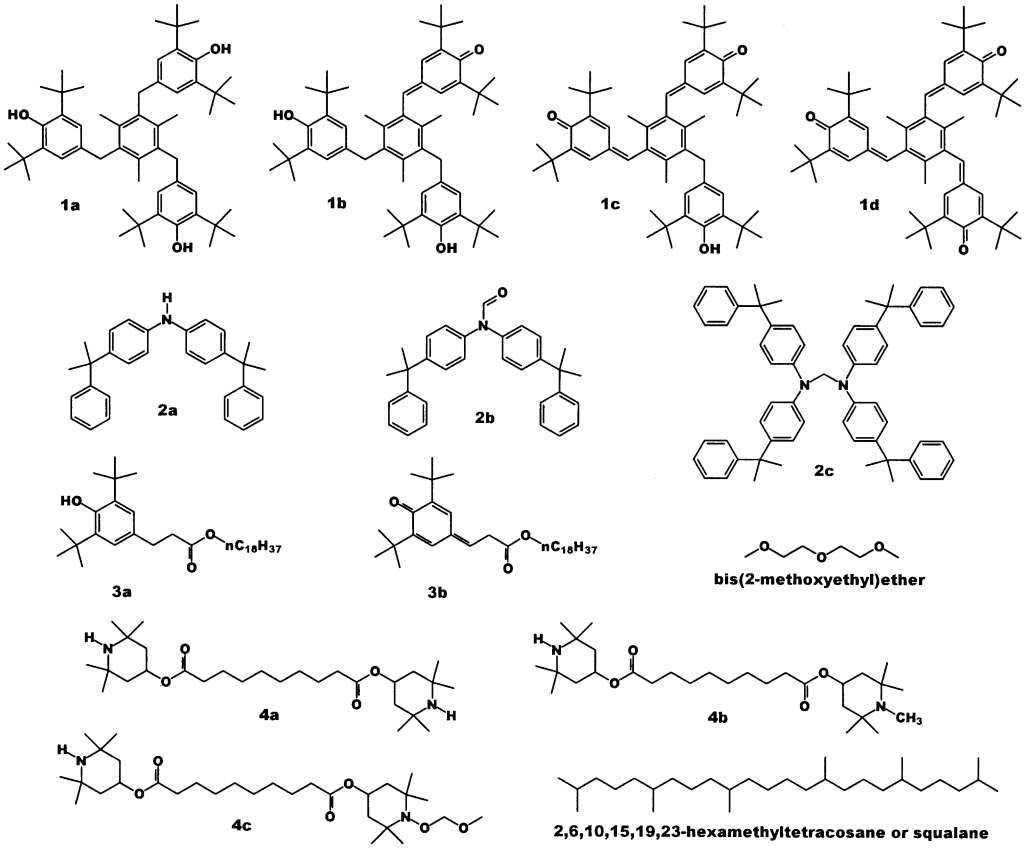
General ageing procedure: the thermo-oxidative stabilizers, 1 g (1.3 mmol **1a**, and hence 3.9 mmol phenolic units, 1.9 mmol **3a**, 2.5 mmol **2a**, and 2.0 mmol **4a**, and hence 4.0 mmol amine units) were added to 19 g bis (2-methoxyethyl)ether or squalane in an open 100 ml erlenmeyer flask equipped with a condenser and heated

on an oil bath in an ambient atmosphere at 120 °C. At various times 0.5 g of samples were taken and analyzed.

3. Results and discussion

To study the interaction of the different stabilizers in squalane and bis(2-methoxyethyl)ether, the conversion products of these different stabilizers have been determined using HPLC–PDA, GC–FID, GS–MS and HPLC–MS. For sterically hindered phenols like **1a** and **3a** it is generally assumed that in the first stabilization step the phenolic hydrogen is donated to a radical species. In a second step an α-hydrogen is donated leading to a quinone structure [7–9]. Following this stabilization mechanism, and ignoring side reactions, **1a** is subsequently converted to **1b**, **1c** and finally to **1d**, whereas **3a** is converted to **3b** (Scheme 1). Looking at the highly conjugated structure of **1d** it is expected that further radical reactions are possible leading to a variety of products. The oxidation sequence of the aromatic amine **2a** is less clear. In the first step the amine hydrogen is donated. The resulting **2a**-radical is subsequently stabilized by the aromatic system leading to a large number of mesomeric structures, and hence to a variety of different degradation products [10]. Although not all degradation products could be determined here, the major two degradation compounds of **2a** in squalane and bis(2-methoxyethyl)ether, i.e. compounds **2b** and **2c**, could be identified by the combination of HPLC–PDA, LC–MS, GC–FID and GC–MS. Compound **2b** is the (oxidized) formaldehyde adduct of **2a**, whereas compound **2c** is a methylene bridged dimer of **2a**. The generally assumed stabilising ability of HALS, like **4a,** are believed to be based on the formation of nitroxyl radicals, which are able to react with a polymer radical, and hence eliminate this polymer radical [1–3]. In subsequent steps this nitroxyl radical is regenerated. Due to the presence of numerous structurally different polymeric radicals, which all can react with **4a**, the analysis of the **4a** conversion products is significantly hampered. As shown in Scheme 1, two degradation products, i.e. **4b** and **4c**, are formed they could be identified by GC–FID and GC–MS.

As mentioned in the introduction, an interaction between the phenolic anti-oxidant **1a** and the aromatic amine **2a** was observed in a polyether mimicking solvent bis(2-methoxyethyl)ether [6]. To investigate the generality of this interaction, analogous experiments have been



Scheme 1. Structural formulas of the sterically hindered phenolic anti-oxidants 1,3,5-trimethyl-2,4,6-Tris(3,5-di-*t*-butyl-4-hydroxybenzyl)benzene, **1a**, and octadecyl-3-(3,5-di-*t*-butyl-4-hydroxyphenyl)propionate, **3a**, and their oxidation products **1b–d** and **3b**, the aromatic amine 4,4′-bis(α,α-dimethylbenzyl)diphenylamine, **2a**, its formaldehyde adduct, **2b**, and its dimer **2c** together with the HALS bis(2,2,6,6-tetramethyl-4-piperidyl)-sebacate **4a** and its degradation products **4b** and **4c**. For completeness the structures of squalane and bis(2-methoxyethyl)ether are shown.

performed in the polypropylene mimicking solvent squalane. The thermo-oxidative stabilizers **1a** and/or **2a** were heated in the intrinsic thermo-oxidative labile squalane in an ambient atmosphere at 120 °C. At various degradation times samples were taken and analysed. To determine the stability of the squalane and the action of the stabilizers IR measurements were recorded focusing on the formation of carbonyl functionalities, here for squalane at 1718 cm^{-1} [11]. A dramatic increase in the carbonyl absorption of the non-stabilized squalane is immediately observed after starting the experiment. This in contrast to the **1a** and/or **2a** containing solutions, which show only a small initial increase of this carbonyl absorption. Obviously no significant additional oxidation of the squalane occurs pointing to the stabilizing ability of **1a**, **2a** and the **1a**–**2a** mixture. The absence of an increased carbonyl intensity indicates that, even after 7000 h, stabilizing species are present in the solution. Due to analytical issues no experiments with reduced stabilizer concentrations in order to reduce the oxidation time have been performed. The analytical data obtained by HPLC of a heated mixture of **1a** dissolved in squalane in time are depicted in Fig. 1. As expected, a gradual decrease of **1a** is observed whereas almost from the start the concentration of the first oxidation product **1b** and at about 600 h the concentration of the second oxidation product **1c** increases and subsequently decreases. The third oxidation product **1d** is formed at about 2500 h. The stabilizing ability of the phenol containing **1c** is indicated by the absence of a significant increase of the carbonyl intensity in the IR spectra at a time when **1a** and **1b** are absent. Although **1d** is, due to its highly conjugated structure, easily oxidized, its stabilizing ability is thought to be less important compared to **1c**. The cumulative relative concentration of **1a**–**d** in Fig. 1 does not equal 100% due to the fact that the response factors of the compounds **1b** and **1c** are unknown and are estimated, in combination with the instability (and restricted solubility) of **1d**.

The analytical data concerning the stabilization of squalane by **2a** are shown in Fig. 2. A decrease of the concentration of **2a** is observed together with a simultaneously increase of the formaldehyde adduct **2b** and the dimer **2c**, which are obviously the main oxidation products of **2a**. Compound **2b** is also detected by the formation and increase of a carbonyl absorption at 1690 cm^{-1} in IR. The almost instant formation of compound **2b** and **2c** in squalane, formed by a reaction of **2a** with formaldehyde [6], is noticeable since it is generally assumed that low molecular oxidized products like formaldehyde are not formed in the beginning of a polyolefine oxidation cyclus [1]. However, the results obtained here confirm the almost instant formation of formaldehyde during polypropylene oxidation as has been suggested in an earlier report [12]. Analogous to the results obtained with **1a**, no significant increase of the carbonyl intensity in IR is observed due to the presence of stabilizing species, here **2a**, in the mixture.

Based on the initial rate of the decrease of stabilizing species in time it is concluded that the stabilizers **1a** and **2a** are roughly equally effective to stabilize the squalane towards oxidative degradation. Comparing the molar amounts of the individual stabilizers present in the reaction mixture, i.e. 1.3 mmol **1a** (and hence 3.9 mmol phenolic units) and 2.5 mmol **2a**, it is suggested that aromatic amines are more effective in the thermo-oxidative stabilization of squalane compared to sterically hindered phenols.

The analytical data obtained by HPLC concerning the stabilization of squalane by a mixture of **1a** and **2a** is shown in Fig. 3. Analogous to the experiments performed in bis(2-methoxyethyl)ether [6], an interaction of **1a** and **2a** is clearly observed. The course of the decrease and formation of the different products is comparable to that discussed for the individual **1a** and **2a** alone.

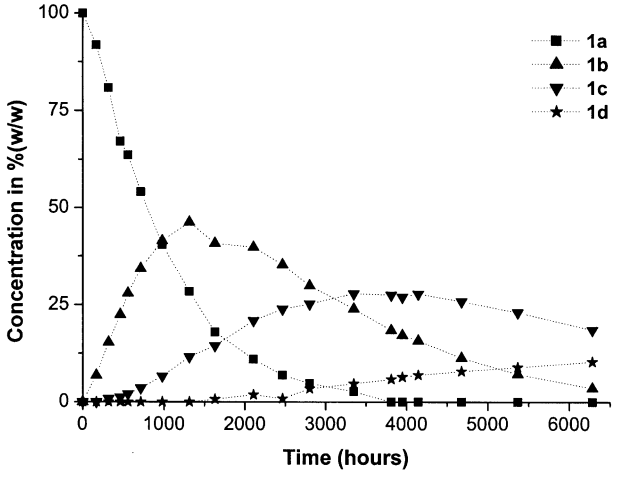


Fig. 1. Relative concentration of **1a**–**d** dissolved in squalane in time at 120 °C as determined using HPLC.

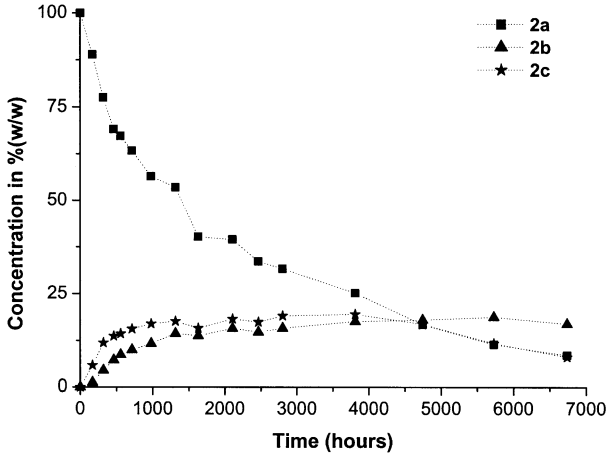


Fig. 2. Relative concentration of **2a**–**c** dissolved in squalane in time at 120 °C as determined using HPLC.

However, the rate of decrease and formation, together with the amounts formed, is significantly different. Focusing on compound **2a** a significantly higher concentration over the complete time range is observed in the **1a**–**2a** mixture. Combined with this indicated longer lifetime of **2a**, the formation of **2b** and **2c** is also delayed. In contrast to **2a** an accelerated decrease of **1a** is observed in the **1a**–**2a** mixture. The concentration of **1a** becomes zero at about 700 h compared to about 3800 h for **1a** alone. Linked to this, the formation and decrease of **1b**–**d** is accelerated too. Compounds **1b** and **1c** are both formed from the beginning and the concentrations become already zero at about 700 and 1600 h, respectively. In analogy with the experiments performed in bis(2-methoxyethyl)ether, the largest effect is obtained for compound **1d**. Next to its earlier appearance in the **1a**–**2a** mixture at about 400 h compared to about 2500 h for **1a** alone, the relative concentration is increased from about 15% (w/w) alone to 30% (w/w) in the mixture. The different concentration levels of **1d** in squalane compared to the experiments performed in bis(2-methoxyethyl)ether (concentration of **1d** is increased from 3% (w/w) alone to 85% (w/w) in the mixture) [6] can be explained with the intrinsic stability of the solvent and the solubility of **1d** in these solvents. The highly conjugated **1d** is susceptible towards radical reactions. Due to the increased oxidative stability of squalane compared to bis(2-methoxyethyl)ether, a lower concentration of radical species is present which results in the increased concentration of **1d** in squalane compared to bis(2-methoxyethyl)ether. However, due to the decreased solubility of **1d** in squalane, the concentration of **1d** in the **1a**–**1d** mixture is limited to 30% (w/w).

In summary it can be concluded that the observed regeneration of the aromatic amine **2a** by the phenolic anti-oxidant **1a** is of a general nature since this effect was both observed in the polar engineering plastics mimicking solvent bis(2-methoxyethyl)ether [6] as well as in the non-polar polyolefine mimicking solvent squalane or 2,6,10,15,19,23-hexamethyltetracosane.

It was shown that the interaction of the sterically hindered phenol **1a** and the aromatic amine **2a** seems to be independent of the environment. To investigate the generality of this interaction with regard to the molecular structure of the phenolic anti-oxidant, compound **3a** is used in combination with **2a** in both bis(2-methoxyethyl)ether and squalane. Analogous to the results obtained with **1a** and the **1a**–**2a** mixture, an initial increase of the carbonyl intensity, which is then constant in time, is observed in IR using both **3a** and the **3a**–**2a** mixture in squalane. HPLC experiments using **3a** in squalane alone (Fig. 4) show the expected gradual decrease of **3a** and the formation and subsequent decrease of the oxidized **3b**, both concentrations being almost zero at about 6500 h. The data obtained using the **3a**–**2a** mixture in squalane are depicted in Fig. 5. Here too, an interaction of the phenolic anti-oxidant and the aromatic amine is clearly observed. Compound **3a** is less stable in the **3a**–**2a** mixture whereas the initial stability of compound **2a** is increased compared to the use of **2a** alone. The interaction is even better noticed by observing the formation of the degradation products. In the **3a**–**2a** mixture, the oxidised **3b** is formed earlier and is obtained in higher concentrations, whereas the oxidation products of **2a** appear later and in a lower concentration.

The results obtained using the stabiliser **3a** and the **3a**–**2a** mixture in bis(2-methoxyethyl)ether are shown in the Figs. 6–8, whereas the data obtained using only **2a** have been reported earlier [6]. The almost neglecting difference between the significant increase of the carbonyl absorption observed in IR (Fig. 6) of bis(2-methoxyethyl)ether and bis(2-methoxyethyl)ether containing stabiliser **3a** alone points to a minimal stabilising ability

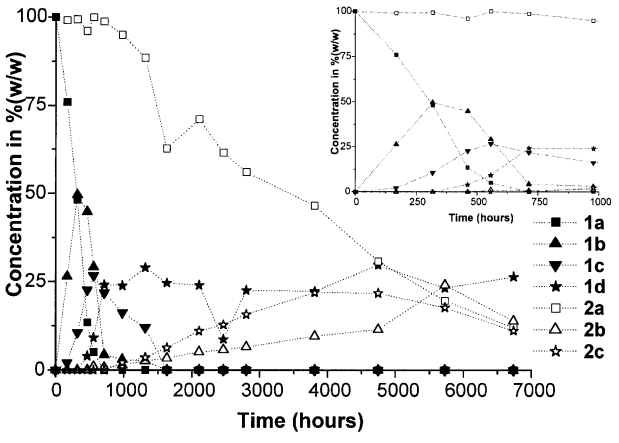


Fig. 3. Relative concentration of a mixture of **1a**–**d** and **2a**–**d** dissolved in squalane in time at 120 °C as determined using HPLC.

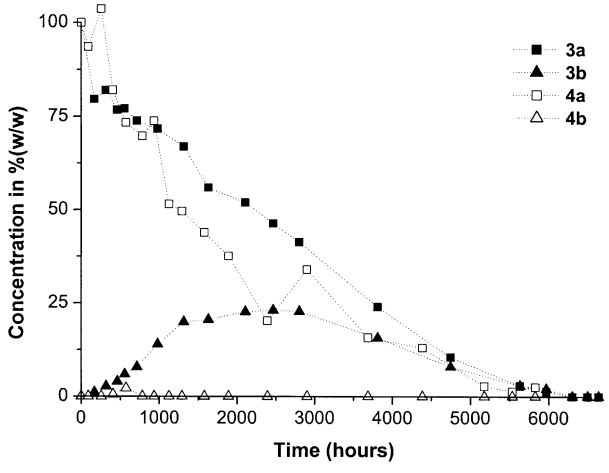


Fig. 4. Relative concentration of **3a**, **3b**, **4a** and **4b** dissolved alone in squalane in time at 120 °C as determined using HPLC (**3**) and GC (**4**).

of **3a** in bis(2-methoxyethyl)ether. The HPLC results obtained using **3a** alone (Fig. 7) show the expected decrease of **3a** and formation of the quinone **3b**. At about 150 h the concentration of **3a** is zero, which coincides with the increase of the carbonyl absorption as observed with IR. The observed low stabilizing ability of **3a** alone towards bis(2-methoxyethyl)ether is unexpected. As reported earlier, a two-fold molar excess of sterically hindered phenol functionalities of stabilizer **1a** compared to the concentration of **3a** used here, is able to stabilise a bis(2-methoxyethyl)ether solution for about 700 h. No satisfying explanation was found to explain this effect. In contrast to the action of **3a** alone, a **3a**–**2a** mixture is able to stabilize the bis(2-methoxyethyl)ether. No significant increase of a carbonyl absorption is observed up to about 4500 h. As depicted in Fig. 8, here too, an interaction of the phenolic **3a** with the amine **2a** is observed. The lifetime of **2a** is increased from about 700 to about 2000 h, whereas the formation of the main degradation product **2b** is delayed. In contrast to the previous experiments no decreased lifetime of the phenolic anti-oxidant was found. The lifetime of **3a** is increased from about 150 to about 900 h in the **3a**–**2a** mixture. This effect can be explained by assuming that stabilizer **3a** alone is only consumed via a radical mechanism. In the **3a**–**2a** mixture these radicals are neutralized by **2a**, which increases the lifetime of **3a**, whereas **3a** is regenerating and hence extending the lifetime of **2a**. As for the **1a**–**2a** system, the quinone **3b** is also stabilized and obtained in a higher concentration in the **3a**–**2a** mixture. However, due to the increased solubility of the quinone **3b** compared to **1a**, no solubility issues have been observed for **3b**.

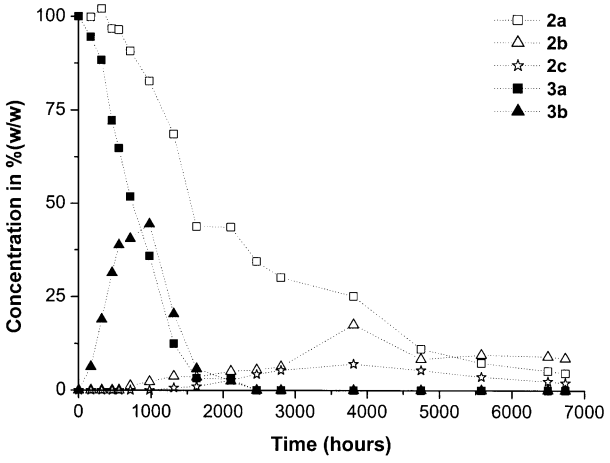


Fig. 5. Relative concentration of a mixture of **3a**, **3b** and **2a**–**c** dissolved in squalane in time at 120 °C as determined using HPLC.

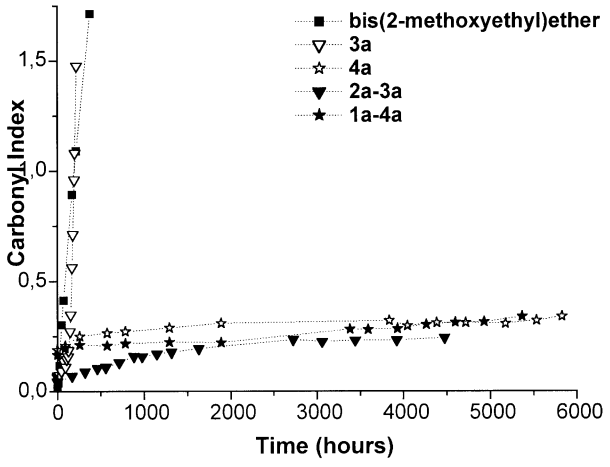


Fig. 6. The carbonyl intensities at 1725 cm^{-1}, as obtained by oxidation of bis(2-methoxyethyl)ether and the bis(2-methoxyethyl)ether containing the various stabilizers and mixtures thereof, versus ageing time.

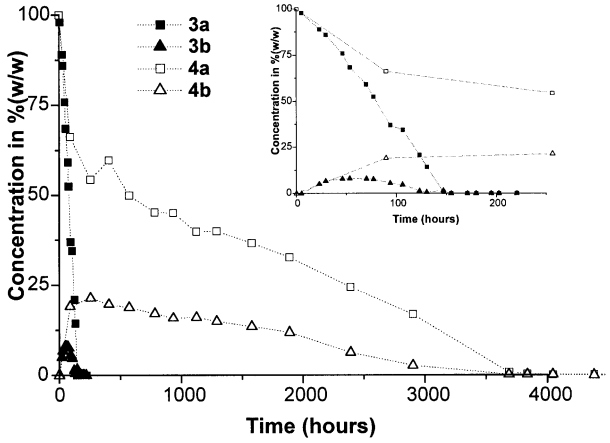


Fig. 7. Relative concentration of **3a**, **3b** and **4a**, **4b** alone dissolved in bis(2-methoxyethyl)ether in time at 120 °C as determined using HPLC (**3**) and GC (**4**).

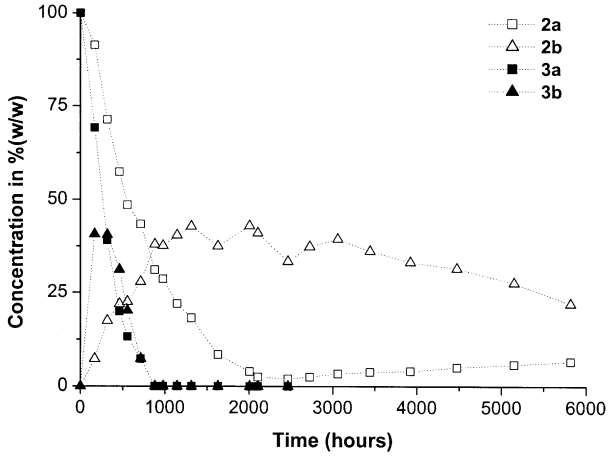


Fig. 8. Relative concentration of a mixture of **3a**, **3b** and **2a**, **2b** dissolved in bis(2-methoxyethyl)ether in time at 120 °C as determined using HPLC.

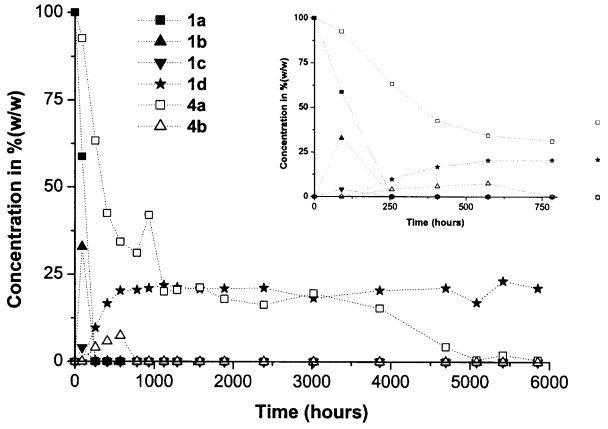


Fig. 9. Relative concentration of a mixture of **1a–d** and **4a**, **4b** dissolved in squalane in time at 120 °C as determined using HPLC and GC.

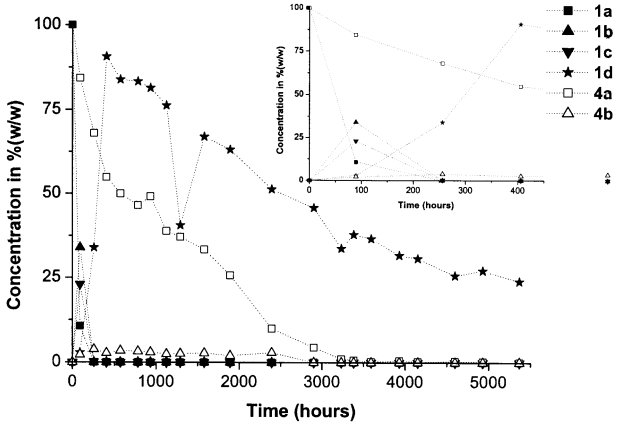


Fig. 10. Relative concentration of a mixture of **1a–d** and **4a**, **4b** dissolved in bis(2-methoxyethyl)ether in time at 120 °C as determined using HPLC and GC.

From the results obtained with the stabilisers **1a**, **2a** and **3a** in bis(2-methoxyethyl)ether and squalane it can be concluded that the interaction between sterically hindered phenols and aromatic amines is general with regard to the molecular structure of the phenol and the polarity of the environment. To extend this study to the frequently in combination with other thermo-oxidative stabilizers used amine containing HALS, IR and GC experiments using **4a** have been performed. The lack of a significant increasing carbonyl absorption in IR demonstrates that compound **4a** is able to stabilize squalane at the conditions used. The results obtained with GC (Fig. 4) shows the expected gradual decrease of **4a** in time. As mentioned in the introduction, HALS are converted to nitroxyl radicals. These nitroxyl radicals react with radical species and are subsequently regenerated. Due to the large number of structurally different radical species present, a large number of peaks appear in the GC spectrum, hampering the identification of the degradation products of **4a** significantly. Only degradation compound **4b** could be identified, which is only present in small amounts. The HPLC and GC results of the **1a**–**4a** mixture are depicted in Fig. 9. It is observed that both **1a** and **4a** are consumed faster in the **1a**–**4a** mixture than alone. In addition, the resulting degradation products of **1a** appear earlier, again with an increased concentration of **1d**. This behaviour is explained by the assumption that the **4a** nitroxyl abstracts the phenolic hydrogen of **1a**, which results in the conclusion that an antagonistic effect exists between HALS and phenolic anti-oxidants. Both synergistic and antagonistic effects are reported in literature for combinations of sterically hindered phenolic antioxidants and HALS [4,5,13]. The antagonistic effect is explained by the interaction of stabilizer radicals or by the possibility that the phenol prevents the conversion of the HALS to the stabilizing nitroxide. The effect observed here points to the last explanation.

Analogous results as obtained in squalane were obtained in bis(2-methoxyethyl)ether. As shown in Fig. 6, only a small initial increase of the carbonyl absorption is observed in bis(2-methoxyethyl)ether. No significant increase is noticed up to 5500 h showing the stabilizing ability of **4a**. The analytical data obtained by GC of a heated mixture of **4a** alone dissolved in bis(2-methoxyethyl)ether show the expected gradual decrease of **4a** in time (Fig. 7). In the **1a**–**4a** mixture both **1a** and **4a** are less stable compared to the individual stabilizers, which points to the same antagonistic effect as described above. Here again, the largest effect is obtained for degradation product **1d**, reaching a concentration of about 90% (w/w) in about 400 h. An analogous behaviour as described for the **1a**–**4a** mixture was found, both in squalane and bis(2-methoxyethyl)ether, for the **3a**–**4a** mixture (results not shown here). An additional degradation compound, **4c**, could be identified in the **3a**–**4a** mixture using bis(2-methoxyethyl)ether as the solvent. In summary it is concluded that a general (antagonistic) interaction exist between phenolic anti-oxidants and HALS. This interaction is independent of the molecular structure of the phenolic anti-oxidant and the polarity of the solvent (Fig. 10).

4. Conclusions

The molecular interactions of phenolic anti-oxidants, aromatic amines and HALS stabilizers are successfully studied by heating the stabilizers under oxidative conditions in polar and non-polar solvents. The polar solvent bis(2-methoxyethyl)ether is used to mimick polar engineering plastics like e.g. TPE-U's, whereas the non-polar solvent squalane or 2,6,10,15,19,23-hexamethyltetracosane is used to mimick polypropylene. The oxidation rate is followed by the analysis of samples taken in time using various analytical techniques as e.g.

IR, HPLC–PDA, GC–FID, GC–MS and LC–MS. The sterically hindered phenols, the aromatic amine and HALS used are 1,3,5-trimethyl-2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl)benzene, **1a**, octadecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate, **3a**, 4,4′-bis(α,α-dimethylbenzyl)diphenylamine, **2a**, and bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate **4a**, respectively. A general occurring interaction between sterically hindered phenols and aromatic amines, i.e. regeneration of the aromatic amine by the phenol, is demonstrated by varying the molecular structure of the phenol as well as the polarity of the system. This is in agreement with results reported previously [6]. Studies using mixtures of the HALS **4a** with the sterically hindered phenols **1a** and **3a** in the polar and non-polar solvents visualized a general antagonistic effect between the phenols and the HALS, in which the HALS consumes the phenol. In all stabilizer combinations using the sterically hindered phenols studied here, a stabilization of the resulting quinone form is observed which can, dependent on the molecular structure of the quinone, lead to solubility issues in polymers.

Acknowledgements

The authors acknowledge the fruitful discussions with many colleagues at DSM Research and want to thank G. Meijers for assistance with the experimental set-up and H. Henderickx for performing the LC–MS measurements.

References

[1] Zweifel H. Stabilization of polymeric materials. Berlin: Springer Verlag, 1998.
[2] Gachter R, Muller H. Plastic additives handbook. Munich: Hanser Publishers, 1990.
[3] Pospisil J, Klemchuk PP. Oxidation inhibition in organic materials, vol. I. Boca Raton, Florida: CRC Press, Inc, 1990.
[4] Allen NS, Hamid Ali, Loffelman FF, MacDonald Patrick, Rauhut M, Susi PV. Plastics and Rubber Processing and Applications 1985;5:259.
[5] Pospisil J, Klemchuk PP, editors, Oxidation inhibition in organic materials, Boca Raton, FL: CRC Press, 1990. p 173–192.
[6] Barret J, Gijsman P, Swagten J, Lange R. Polym Degrad Stab 2002;75:367
[7] Koch J. Angew Makromol. Chemie 1971;20:7.
[8] Koch J. Angew Makromol Chemie 1971;20:21.
[9] Pospisil J. Adv Pol Sci 1995;124:87.
[10] Pospisil J, Klemchuk PP, editors. Oxidation inhibition in organic materials, vol. 1. 1990. p 51–4.
[11] IR C=O squalane.
[12] Gijsman P. In: Al-Malaika S, Golovoy, A, Wilkie, CA, editors. Specialty polymer additives. Oxford: Blackwell Science, 2001. p 67–90.
[13] Rychla L, Rychly J, Fodor Z, Barabas K, Iring M, Tudos F. Int J Polym Mater 1990;13:227.