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Phenols and Aromatic Amines as Thermal Stabilizers in Polyolefin Processing

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Summary: Scavenging of C- and O-centered free radicals is mandatory in processing stabilization of polypropylene. Phenolic antioxidants act principally as O-radical scavengers only. Aromatic amines, *N,N'*-disubstituted 1,4-phenylenediamines (PD) and 4,4'disubstituted diphenylamines (DPA), scavenge both C- and O-centered radicals and have consequently a broader activity spectrum. PD cannot be used, however, in polypropylene because of formation of strongly discoloring and staining sacrificial transformation products. Such products formed from DPA have even more discoloring properties. A good processing stability and acceptable extent of discoloration can be achieved by blends of phenols with 4,4'-di-*tert.*octyl DPA. The effect is considered as a beneficial cooperation between the two chain-breaking antioxidants involving interactions with amine-based transformation products.

Introduction

Polyolefins degrade when subjected to melt processing for a short time at high temperatures under strong mechanical forces and in the presence of trace amounts of oxygen dissolved in the polymer mass. In-chain and terminal carbon-centered radicals (macroalkyls) are formed in the primary step of the oxidation process. Chain scission and autoreactions of macroalkyls (disproportionation, recombination) resulting in branching, crosslinking and changes in unsaturation and molecular weight are expressed in changes of the melt viscosity of polyolefins. Oxygen present during processing oxidixes alkyl radicals to alkylperoxyl radicals ROO·. Hydroperoxides are formed transiently and thermolyse at the processing temperatures to alkoxyl radicals, sources of carbonyl species, though most of the oxygenated products are present in trace amounts only. However, these have to be considered as inherent impurities that can trigger the subsequent photodegradation of polyolefins under weathering[1] and contribute to discoloration of the polymer.

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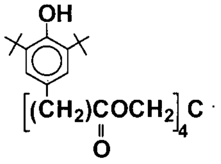
Radical-scavenging (chain-breaking) and secondary antioxidants are used to prevent or reduce the damaging effect of carbon- and oxygen-centered radicals and hydroperoxides formed as a consequence of the degradation reactions during processing [2,3]. In order to have a better understanding of the performance and the fate (sacrificial transformation) of chain-breaking antioxidants (CB-AO) during melt processing, a number of such antioxidants were used in polypropylen based on: phenols differing in the extent of their steric hindrance and substitution at the *para*-position (**1**, **2**), a phenol containing sulfanyl bridge (**3**), 4,4'-disubstituted diphenylamine, DPA (**4**) and 1,3,5-triazine-based *N,N'*disubstituted 1,4-phenylenediamine, PD (**5**), as well as combinations of amines and phenols.



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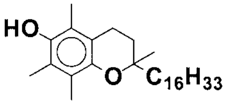

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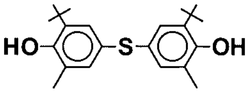

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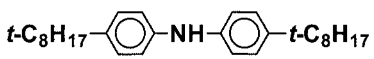

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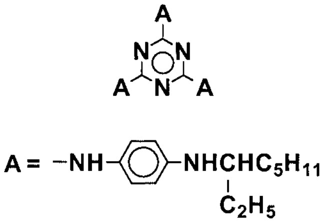

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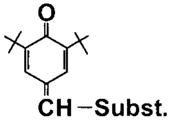
Materials and Methods

The phenol antioxidants **1**, **2**, and **3** (4,4'-thiobisphenol), and the amine antioxidants **4** (4,4'-di-*tert.*octyldiphenylamine) and **5** (1,3,5-triazine-based phenylenediamine) were dry-blended with unstabilised general-purpose molding grade polypropylene (PP) Mosten® 55302900. Polymer processing was carried out in closed chamber of an internal mixer for 10 min at 200 °C (1st pass, under nitrogen or air) and 230 °C (2nd to 5th passes, under nitrogen). Melt flow rates were determined at 130 °C. Polymer plaques, 2 mm thick, were prepared by compression molding at 190 °C and oxidised at 140 °C. Processed and oxidised PP samples were extracted in order to determine the presence of discoloring transformation products formed from the antioxidants.

The Potential of Chain-breaking Antioxidants as Processing Stabilisers

Macroalkyls ($P^{\cdot}$) are formed as primary radicals during the high-temperature processing operation and they participate in changing both the molecular weight and melt viscosity of the polymer (PP). Trace amounts of oxygen account for the oxidation of macroalkyl radicals to macroalkylperoxyl radicals and hydroperoxides[2-5]. In order to protect PP from melt degradation, an effective scavenging of the primary radicals, i.e. macroalkyls, is required[2,3]. The real potential of the CB-AO's (phenols and aromatic amines) to deactivate macroalkyls must be considered. Conventional phenolics and aromatic amines do not react, however, in their original chemical form with alkyls. Both types of CB-AO's are effective scavengers of O-centered radicals, in particular, macroalkylperoxyls [2,3,5]. This results in sacrificial transformation of the CB-AO[3,4,6,7], accompanied by changes of their original structure and losses of concentration of the parent additive. Consequently, the performance and the chain-breaking activity are modified.

There is a crucial difference in the properties of transformation products of phenolic and aromatic amine CB-AO's with respect to their contribution to the integral stabilisation process[3,4,6,7]. Principal final transformation products of phenolic antioxidants have quinone methides (QM) structures [3,4,6], compounds with the general structure **6**. These compounds are formed from mononuclear and polynuclear phenolics of the benzyl- and propionate-types[4,6]. The 'Subst' in **6** constitutes the rest of the QM molecule and may contain another QM moiety and/or an unchanged original phenolic moiety (such complicated products arise from polynuclear phenols, such as **1**. QM compounds, which have absorption maxima λ_{max} at 420-460 nm and log ε ~1.2-1.8, are sources of weak discoloration of the polymer matrix. QM may contribute to the integral stabilising effect ascribed to phenolics, because of their weak scavenging ability of alkyls[4,6,8]. 2,6-Disubstituted 1,4-benzoquinones (**7**) are another source of low extent of discoloration arising from phenolics. Bezoquinones **7** have absorption maxima λ_{max} at 420-440 nm and log ε ~ 1.2-2.1. They are formed in trace amounts by thermolysis of transiently arising peroxycyclohexadienones XOO-CHD **8** (X = H or alkyl), another transformation product of phenolic antioxidants[3,4]. Due to steric effects, substituted benzoquinones **7** have a negligible alkyl-scavenging potential.



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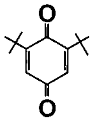

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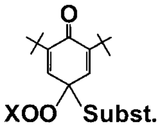

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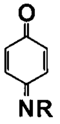
Thiobisphenols, such as **3**, are bifunctional antioxidants having both chain-breaking and hydroperoxide decomposing activity[9]. Both mechanisms contribute effectively to decreasing the extent of degradation during processing of PP. Scavenging of ROO$^\cdot$ radicals by the phenolic part of the thiobisphenol results in non-discoloring or very low discoloring products containing sulfur species. In trace amounts, discoloring oxidized coupling products of the diphenoquinone type can be formed from phenolic fragments released by thermooxidative degradation of thiobisphenols. The sulfidic part of thiobisphenols accounts for deactivation of the hydroperoxides[9].

Aromatic amines (**40** and diamines (**5**) are characteristic of a multistep sacrificial transformation chemistry[7]. Nitroxides or nitrones are formed from appropriately 4,4'disubstituted diphenylamines (type **4**). Both transformation products are low discoloring species that are able to scavenge alkyl radicals. Discoloring quinone mono-imines **9** (QMI) can be formed from DPA (**4**) only in trace amounts and under very harsh conditions that do not take place during PP degradation. Formation of **9** requires fragmentation of the amine **4** in the nitrone stage.



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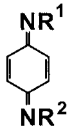

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Quinone diimines **10** (QDI) are common final sacrificial transformation products of mono-nuclear PD, polynuclear PD (such as **5**) or polymer-bound PD[7]. QDI (**10**) *N*-substituted by a secondary alkyl group undergo acid catalyzed hydrolysis with ease, and are transformed into QMI **9**. Both QMI and QDI arising from PD are highly discoloring and staining species, as they absorb light in the visible region (λ_{max} = 420-580 nm, log ε = 2.1-3.5). Oxidative and hydrolytic transformations of PD is accompanied by coupling and cyclization reactions, that account for the formation of colored N-heterocyclic polynuclear systems[3,4,7].

Discoloration of the polymer matrix by quinone imines **9** and **10** cannot be avoided by any structural change in the PD molecule. This strong disadvantage of PD is compensated by ability of quinone imines to scavenge effectively alkyl radicals. As a result, the integral stabilization effect of aromatic diamines in a polyolefin matrix is higher than that of phenolic antioxiants. This advantage cannot be, however, exploited practically in polyolefins, where discoloration due to PD/QDI effect is not acceptable.

Exploitation of the Potential of Chain-breaking Antioxidants when Used in Combinations: Phenols and Aromatic Amines

The mechanism for the antioxidant (phenolics and aromatic amines) interactions with ROO˙ radicals gives rise, in the first step, to the formation of phenoxyl and aminyl radicals, rerspectively. The phenoxyl radicals are prone to scavenge another ROO˙, but its the final transformation products, the low-discoloring quinone methides, offer only a weak alkyl-scavenging potential[3,4,6]. Aminyl radicals of the DPA series are sources of nitroxides which are strong scavengers of alkyl radicals, thus increasing the integral stabilization performance of DPA. The discoloration of DPA-doped PP was found to be low. However, a suitably substituted DPA (**4**) influences the yellowness index of oven aged (150 days of oven aging at 140 °C) compression molded PP plaques to an extent similar to that of the effective phenolic antioxidants **1** and **2**, when used at comparable molar concentrations (Fig. 1).

Surprisingly, in spite of its ROO˙/R˙ scavenging potency which was confirmed in model experiments, DPA (**4**) when used as the sole additive provided a lower protection for PP melt than did the phenols **1**, **2** and the thiobisphenol **3** (Fig. 2). Evidently, the oxygen deficient conditions that prevail during PP processing were not effective enough to transform the DPA into alkyl-scavenging species, and only the alkylperoxyl-scavenging potency was fully exploited.

In contrast, PD (**5**) which was also confirmed to act as ROO˙/R˙ scavenger, via a cooperative action between the parent PD and the formed QDI (**10**), protects PP well against processing degradation (Fig. 2). However, PD does discolor the PP matrix to an unacceptable extent (Fig. 1). In addition its transformation product, QDI, has also staining properties.

It should be noted that the thiobisphenol **3** offers less efficient protection to PP during processing than do both phenols **1** and **2**, in spite of its potential hydroperoxide deactivating power. Furthermore, the influence of **3** on the yellowness index of PP is favourable (Fig. 1). We checked the presence of discoloring quinone methides, quinone imines and other discoloring transformation products (mostly formed as yellow or amber spots on thin layer chromatograms) in extracts of PP after the 5th extrusion (at 230 °C) under nitrogen and, and after a model extrusion at 200 °C in an air atmosphere for comparison. The presence of oxygen accounts for a strongly enhanced formation of discoloring compounds; their chemical character is comparable to that of compounds formed under a limited access of oxygen. Thin layer chromatography revealed spots of discoloring products formed from **1**, **2**, **4** and **5**. Some of the products were difficult to identify due to the lack of model compounds that are necessary as standards.

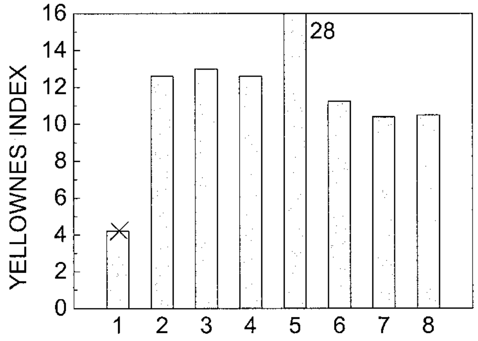

Fig. 1. Changes of the yellowness index of 2 mm compression molded plaques of the general-purpose molding-grade PP Mosten® 55302900 processed at 200 °C and oven aged for 150 days at 140 °C. Concentration of additives: 0.02 mol kg^{-1}. 1 control, 2 Irganox® 1010 (**1**), 3 Ronotec® 2001 (**2**), 4 DPA **4**, 5 PD **5**, 6 thiobisphenol **3**, 7 1:1 blend of phenol **1** with DPA **4**, 8 1:1 blend of phenol **2** with DPA **4**.

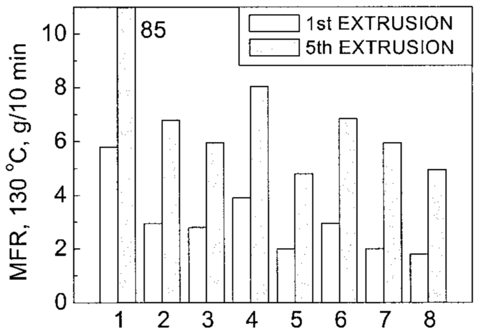

Fig. 2. Effect of phenols and aromatic amines on melt stability of the general-purpose molding-grade PP Mosten® 55302900 (MFR of the stabilizer-free PP: 1.2). 1st extrusion 10 min/200 °C /nitrogen, following passes at 230 °C. Concentration of additives: 0.02 mol kg^{-1}. 1 control, 2 Irganox® 1010 (**1**), 3 Ronotec® 2001 (**2**), 4 DPA **4**, 5 PD **5**, 6 thiobisphenol **3**, 7 1:1 blend of phenol **1** with DPA **4**, 8 1:1 blend of phenol **2** with DPA **4**.

Application of a combination of the low-discoloring phenols **1** and **2** and the amine **4** in 1:1 blends at a total additive concentration of 0.02 mol kg^{-1}, revealed a beneficial effect on the processing stability (Fig. 2). The influence was more evident with the biological hindered phenol α-tocopherol (**2**) than with the physically persistent phenol **1**. In spite of the detection of discoloring compounds in extracts of processed and oxidised PP samples, a rather beneficial effect, in terms of decreasing extent of discoloration, of stabiliser blends containing DPA (**4**) was surprisingly observed in PP after oven aging (Fig. 1). Any combination of phenols **1** and **2** with PD (**5**) did not reduce the discoloration arising from QDI (**10**).

We suggest an involvement of some beneficially co-operating processes under the assumption that the mechanism of interaction between the antioxidants in the blends and ROO$^\cdot$ (formed via Eq. 1) is analogous to that of the individual stabilisers (phenols = ArOH, aromatic amines = >NH). Aminyls (>N$^\cdot$), nitroxides (>NO$^\cdot$), nitrones (≡N→O), quinone imines (QI), Eq. 2, and various coupling products, Eq. 3, are formed from the amines. Phenols are transformed via phenoxyls (ArO$^\cdot$) into peroxycyclohexadienones (XOO-CHD) **8**, quinone methides (QM) **5** and benzoquinones (BQ) **7**, Eq. 4.

Phenols interact with the aminyls (>N$^\cdot$) and nitroxides (>NO$^\cdot$) Eqs. 5, 6. As a result, part of the secondary amine function (>NH) is regenerated, Eq. 5, or a new chain-breaking (ROO$^\cdot$ scavenging) function, a hydroxylamine >NOH, is formed, Eqs. 6, 7. This enhances the integral performance of the phenol-amine blend, by exploiting the combined ROO$^\cdot$/R$^\cdot$ scavenging potential. The sequence of interactions with the phenol reduces in the DPA series the amount of coupling products prone to be oxidized into highly discoloring polynuclear systems, Eq. 3. This mechanism cannot be exploited in the PD series because of a fast formation of QI **9**, **10** from the respective aminyls and their unacceptable discoloring and stainig effect.

As a consequence of interactions between phenols and the diphenylamine **4**, and/or its free-radical transformation products, the phenolic component is consumed faster than the amine component[7,10]. The colored transformation products of both components accumulate gradually in the PP matrix[3,4,6-8,11].

A rather beneficial effect of thiobisphenols (represented by compound **3**) for PP processing, and low discoloration after oven aging, cannot be effectively exploited when used in combinations with aromatic amines. Thiobisphenol **3** deactivates alkylhydroperoxides which accounts for the formation of related sulfoxides HO-Ar-SO-Ar-OH and sulfones HO-Ar-SO_2-Ar-OH, Eq. 9[9]. However, the phenolic sulfinic, sulfenic and sulfonic acids HO-Ar-SO_nH (n = 1-3) which are formed amongst other products, Eq. 9, deactivate the aromatic amines. The chain-breaking activity of thiobisphenols is described by Eq. 10.

$$\mathrm{R\cdot} + \mathrm{O_2} \longrightarrow \mathrm{ROO\cdot} \tag{1}$$

$$\mathrm{>NH} \xrightarrow{\mathrm{ROO^\cdot}} \mathrm{>N\cdot} \xrightarrow{\mathrm{ROO^\cdot}} \mathrm{>NO\cdot},\ \mathrm{\equiv N{\rightarrow}O},\ \mathrm{QI} \tag{2}$$

$$\mathrm{>N\cdot} \longrightarrow \text{N-N and C-N coupling} \xrightarrow{\mathrm{ROO^\cdot}} \text{Products} \tag{3}$$

$$\mathrm{ArOH} \xrightarrow{\mathrm{ROO^\cdot}} \mathrm{ArO\cdot} \longrightarrow \text{XOO-CHD, QM, (BQ)} \tag{4}$$

$$\mathrm{ArOH} \xrightarrow{\mathrm{>N^\cdot}} \mathrm{ArO\cdot} + \mathrm{>NH} \tag{5}$$

$$\mathrm{ArOH} \xrightarrow{\mathrm{>NO^\cdot}} \mathrm{ArO\cdot} + \mathrm{>NOH} \tag{6}$$

$$\mathrm{>NOH} \xrightarrow{\mathrm{ROO^\cdot}} \mathrm{>NO\cdot} \tag{7}$$

$$\mathrm{>NO\cdot},\ \mathrm{\equiv N{\rightarrow}O},\ \mathrm{QI} \xrightarrow{\mathrm{R^\cdot}} \text{Products} \tag{8}$$

$$\text{HO-Ar-S-Ar-OH} \xrightarrow{\mathrm{ROOH}} \text{HO-Ar-SO}_n\text{-Ar-OH, HO-Ar-SO}_n\text{H} \tag{9}$$

$$\text{HO-Ar-SO}_n\text{-Ar-OH} \xrightarrow{\mathrm{ROO^\cdot}} \text{HO-Ar-SO}_n\text{-Ar-O}\cdot \longrightarrow \text{Products} \tag{10}$$

Conclusions

Processing stabilisation of PP requires scavenging of both C- and O-centered radicals. *N,N'*-disubstituted 1,4-phenylenediamines (PD) and 4,4'-disubstituted diphenylamines (DPA) are the only conventional chain-breaking antioxidants that possess both scavenging activities due to the involvement of the parent amine structure as well as products of its sacrificial transformation. However, discoloring and staining by quinone imines **9** and **10** arising from phenylene diamines[7] cannot be tolerated in PP. An appropriate substitution of diphenylamine in positions 4,4' restricts the formation of discoloring quinone imines. Nitroxides and nitrones arising by oxidative transformation of DPA, scavenge alkyl radicals and enhance the overall stabilisation. A good processing stability and reduced discoloration can be achieved in blends of the phenolic antioxidants **1** and **2** and the disubstituted DPA (**4**). This is due to a beneficial co-operation between the two antioxidant classes and involvement of the amine transformation products, resulting in reduction of the formation of aminyl coupling products, the source of polynuclear discoloring compounds. Thiobisphenols contributing by a similar chain-breaking mechanism to that of the phenols **1** and **2** may partially deactivate the aromatic amines as a consequence of traces of acid transformation products formed in the thermal transformation and oxidation of sulfoxides, products of deactivation of alkylhydroperoxides of the thiobisphenols[9]. The bleaching effect of organic phosphites that reduce the extent of discoloration in processed polymers which are doped with phenolic antioxidants **1** and **2** and their quinone methinoide transformation products[2-4,12], was not effective with transformation products of aromatic amines.

Acknowledgement

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