



Budapest University of Technology and Economics

Some aspects of the degradation and stabilization of Phillips type polyethylene

Ph.D. Thesis

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Chapter 1

Introduction

Polymers and plastics constitute an important part of our life for many decades now. We use them at home, many parts of cars are made from them, but often even the active component of electric and electronic devices are produced from or at least contain plastics. Polyethylene occupies an important position even among commodity plastics. It is produced and used in the largest quantity in Hungary, but also everywhere else in the world. The importance of polyethylene is shown by the latest statistical data issued by the Hungarian Association of the Plastic Industry showing that 142,500 tons of PE was used in Hungary in 2009 out of a total of 780,700 tons. Moreover TVK also produced 460,500 tons of polyethylene in the same year. These data prove unambiguously that PE is important as a structural material, and also represents a large economical potential.

Several factors led to the success and widespread use of polyethylene. First of all it is cheap, as it is produced in large quantities in huge plants. However, its low density, flexibility, aesthetic appearance and other properties make it ideal as packaging material. Easy processing with very large productivity decrease the price of products made from polyethylene even further. PE can be and is processed practically with all thermoplastic processing technologies including extrusion, injection molding, blow molding, rotational molding, etc., but the largest amount of products are prepared by extrusion. The polymer is subjected to the effect of heat, shear and oxygen in all thermoplastic processing technologies. As an effect of these factors chemical reactions take place in the processing machine with a number of consequences. Although polyethylene is a simple polymer with an apparently well defined structure, its molecular structure often contains irregularities. The actual structure of PE depends on the polymerization technology used for its production. Polymerization under high pressure with radical initiation results in low density polyethylene with a large number of branches, while catalytic processes usually yield linear chains with more regular structures. However, even the catalyst used for the production changes chain structure, chromium catalyst used in the Phillips process create a double bond at the end of each chain, while the concentration of unsaturations is at least an order of magnitude smaller in Ziegler type polymers. Double bonds and other chain irregularities are potential reaction sites on which chemical reactions take place during processing. These reactions modify the chain structure of the polymer and also the properties of the final product. It is obvious that the polymer must be protected against such changes, which needs stabilizers.

The degradation and stabilization of polymers and especially that of polyethylene is studied for a long time. Basic processes were revealed and efficient stabilizer packages developed. The combination of a hindered phenolic primary antioxidant and a secondary, processing stabilizer, very often a phosphorous compound is routinely used for the stabilization of polyethylene. Apparently all problems were solved and the attention of the polymer community turned towards more exciting areas like nanocomposites, bio-related materials, biodegradable polymers, self assembled structures, self

healing polymers, etc. The number of research groups working in this area also decreased, only a few centers studying polyethylene degradation and stabilization remained active. However, the knowledge on this field is still needed today and probably also in the future. Small changes in the polymerization technology modify the structure of the polymer leading to inferior stability and processing problems. New additives are needed to increase efficiency, decrease price and most of all to address environmental and health issues. This latter aspect is demonstrated well by the controversy related to the use of phenolic antioxidants. Several years ago Brocca et al. [1] found that phenolic antioxidants dissolve from PE pipes into drinking water and hinted at the possibility that some of the metabolites might even create a hazard for health. The paper created much excitement among polymer, additive and pipe producers and the question has not been resolved yet to this day. Banning phenolic antioxidants would create very large problems in the plastic industry, as no replacement has been found yet.

The Department of Applied Polymer Chemistry and Physics (DAPCP) at the Institute of Materials and Environmental Chemistry, CRC, HAS and the Laboratory of Plastics and Rubber Technology (LPRT) at the Budapest University of Technology and Economics (which has been working in the frame of a Joint Laboratory since 1994) both have long traditions in the study of the degradation and stabilization of polymers, mainly PVC and polyolefins. Already in the 50ies and 60ies the mechanism of degradation as well as stabilization was studied at the university (Juhász, K.K.) and in the institute (Iring, M., László-Hedvig, Zs., Kelen, T., Tüdös, F.). A new era started when the experts of Clariant visited the Joint Laboratory and offered cooperation in this field. TVK joined in the collaboration which went on for more than 15 years when the management of Clariant decided to abandon research and development activities related to plastic additives. During these more than 15 years the three partners studied various problems related to the degradation and stabilization of polyethylene from the simple optimization of additive packages through the development of new concepts in stabilization (transitional metal stabilizers, phthalides, unsaturated and conjugated compounds, etc.) to the investigation of the behavior of stabilizers under the effect of extractive media. The research resulted in several papers, a patent, a number of MSc and a PhD thesis, and considerable knowledge in this field.

In recent years the research focused on two main issues, on the effect of extractive media and on the study of the mechanism of phosphorous secondary antioxidants. The main results are compiled in this thesis, which is the next step in our continuing effort in the field of degradation and stabilization. One of the chapters focuses on basic correlations of reactions during the soaking of polyethylene in water, while the rest discusses the effect and mechanism of various phosphor containing compounds. The results of the experiments and the analysis of the data showed that the scheme and mechanism generally accepted in the community [2] might not be valid and may depend on the structure of the antioxidant. This thesis clearly demonstrates the success of the group in this field. Considering the general trends, further studies are suggested to focus on the environmental issue of polyolefin stabilization.

Chapter 2

Background

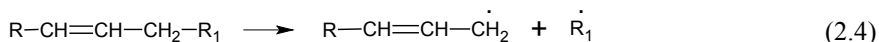
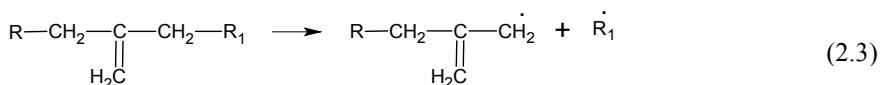
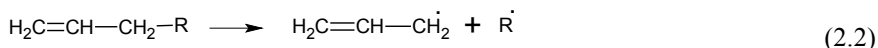
2.1. Degradation of polyethylene

2.1.1. Thermal degradation

Saturated hydrocarbons are thermally stable materials, e.g., hexadecane is stable up to 390°C in inert atmosphere. Polyolefins start to decompose at lower temperatures under the same conditions because some weak sites, like unsaturated groups and branching points decrease the dissociation energy of C–C bonds [3]. The thermal degradation of linear polyethylene in oxygen-free environment starts with random scission of the polymer chains (Reaction 2.1) followed by random intermolecular hydrogen abstraction and subsequent β -scission [4].



According to Holström and Sörvik [3,5-7] the thermal degradation of polyethylene is a radical process, and it starts with the scission of C–C bonds in allylic position:

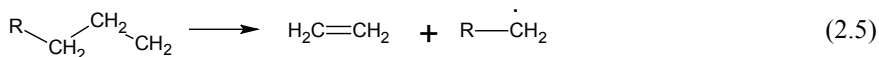


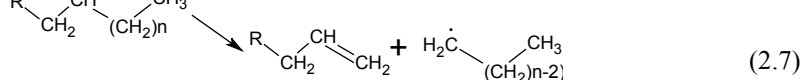
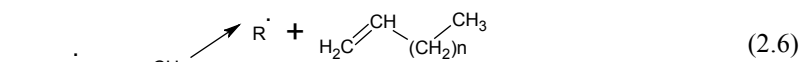
The primary radicals formed in the initiation reaction participate in the following further reactions under thermal conditions:

- depolymerization through β -scission,
- intramolecular hydrogen transfer,
- intermolecular hydrogen transfer.

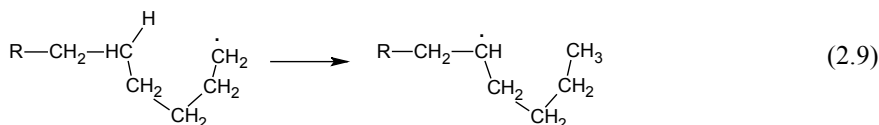
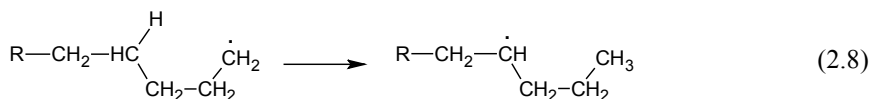
Decomposition reactions follow the intramolecular and intermolecular hydrogen transfer in the thermal degradation of polyethylene.

β -scission of the radicals results in the formation of small molecular fragments, further alkyl radicals and vinyl groups:

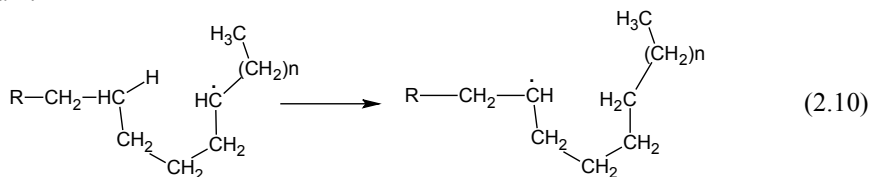




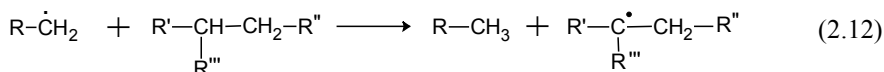
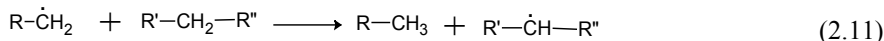
Some of the primary radicals are expected to isomerize by intramolecular hydrogen abstraction (back-biting) and to form secondary radicals, which are more stable. Intramolecular hydrogen transfer can occur from the fourth or fifth carbon atom to the first one [8-14]:



In the case of 5 → 1 hydrogen transfer the reaction can proceed inside the polymer chain:

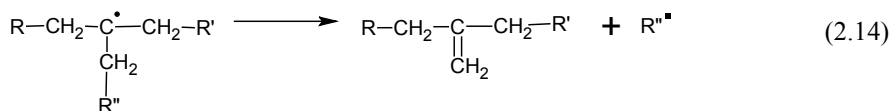
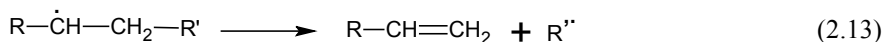


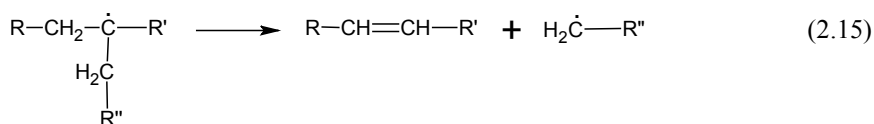
Hydrogen transfer can occur also in intermolecular reactions:



where R, R' and R'' are alkyl groups; R''' is hydrogen or alkyl group

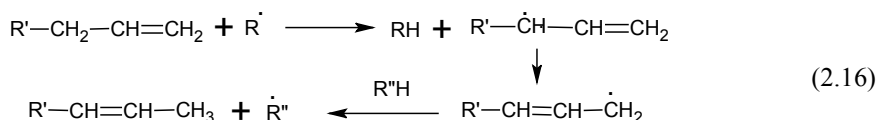
The intermolecular hydrogen abstraction can be followed by β-scission. The reactions of secondary radicals lead to the formation of vinyl groups, while those of tertiary radicals result in the formation of vinylidene and vinylene groups [3,5,7,15]:



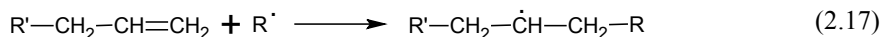


Holström and Sörvik [3] considered the intermolecular hydrogen abstraction followed by β -scission (Reactions 2.13-2.15) the most important propagation reactions in the degradation of polyethylene. These reactions result in a significant decrease of the average molecular mass and yield volatile products. On the basis of activation and bond dissociation energies Kuroki et al. [4] claimed that back-biting reactions (2.8)-(2.10), and intermolecular radical-transfer reactions (2.11) and (2.13) are much more likely to occur than depolymerization reactions (2.5) – (2.7).

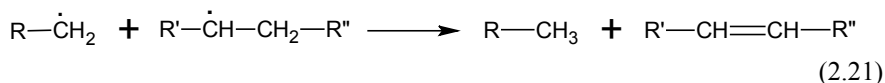
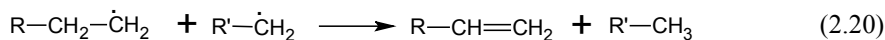
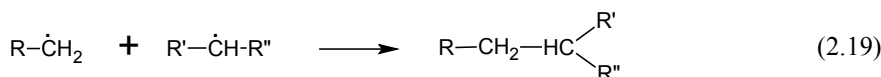
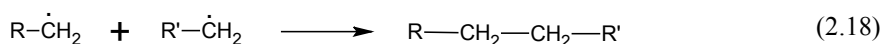
Intermolecular hydrogen abstraction followed by isomerization of a vinyl group results in the formation of vinylene group [3,5,6]:



Walling et al. [16,17] observed in solvents that alkyl radicals add to olefins leading to the formation of secondary radicals:



Recombination (2.18 and 2.19) and disproportionation (2.20 and 2.21) are the most important termination reactions of thermal degradation.



Holström and Sörvik [3] observed that the tendency to disproportionation increases with increasing temperature. From the *trans*-vinylene group/long chain branches content ratio of high density polyethylene Kuroki et al. [4] concluded that the probability of the recombination termination reaction between primary and secondary macroradicals is 2-5 times larger than that of the disproportionation reaction. Although both types of termination reactions have zero activation energy, termination reactions are diffusion

controlled in practice and the rate constant depends on the rate of diffusion of macroradicals in the media. If either of the radicals diffuses outside the field of reaction created by the surrounding polymer segments (cage), propagation (depolymerization, intra- and intermolecular radical transfer) and termination reactions take place, leading to the formation of volatiles and a decrease in molecular mass. Thus both the molecular mass increase and the degradation reactions become dependent on the rate of diffusion, in relation to the viscosity of the media, of the two radicals outside the cage.

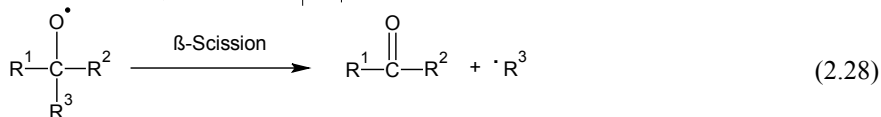
2.1.2. Thermo-oxidative degradation

The oxidation of hydrocarbons is a free radical-initiated autocatalytic chain reaction [2]. The reaction is slow at the start and accelerates with increasing concentration of the resulting hydroperoxides. The process can be regarded as proceeding in three distinct steps: chain initiation, chain propagation, and chain termination.

Chain initiation:



Chain propagation:

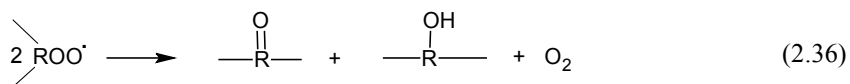


Chain branching:



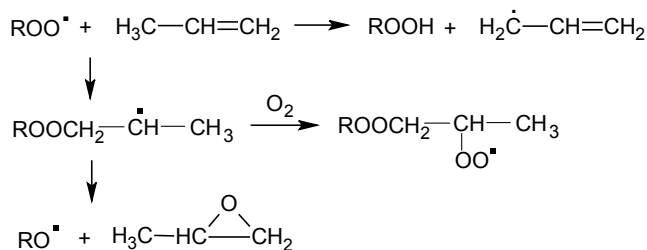
Chain termination:





Many schemes were proposed for the initiation step, but the origin of the primary alkyl radical $R^{\bullet}$ is still controversial [2]. It can be formed as an effect of heat, shear, catalyst residues, radical initiators, and/or impurities in the monomer. The alkyl radicals react with molecular oxygen practically without activation energy forming peroxy radicals (reaction 2.23). The rate constant for the reaction of most alkyl radicals with oxygen is of the order of 10^7 - $10^9 \text{ mol}^{-1}\text{s}^{-1}$.

The peroxy radicals form hydroperoxides upon abstraction of hydrogen from the polymer chain (reaction 2.24), which requires the breaking of a C-H bond, i.e. needs activation energy. Therefore this is the rate-determining step in autoxidation. The rate of the abstraction reaction decreases in the following order: hydrogen in α -position to a C=C double bond (allyl) > benzyl hydrogen and tertiary hydrogen > secondary hydrogen > primary hydrogen. Primary and secondary peroxy radicals are more reactive in hydrogen abstraction than the analogous tertiary radicals [18,19], and the most reactive are acylperoxy radicals [20]. The peroxy radicals oxidize olefins according to Scheme 2.1 in which the oxidation of double bond is considered the most important reaction by Brill and Barone [21].



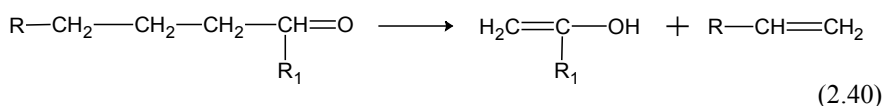
Scheme 2.1 Reaction of peroxy radical with olefins [21]

Hydroperoxides decompose fast to reactive oxy and hydroxyl radicals. The rate of decomposition increases with rising temperature [2]. Metal ions [22] and ultraviolet radiation [23] catalyze hydroperoxide decomposition. The reactions with metal ions are described by reactions (2.37)-(2.39):



Oxy and hydroxyl radicals formed in the decomposition of hydroperoxides are far more reactive than peroxy radicals, and lead to the branching of the reaction chain, i.e. auto-acceleration of the degradation process [2]. β -scission of oxy macro-radicals yields carbonyl groups and other free alkyl radicals [2,24,25].

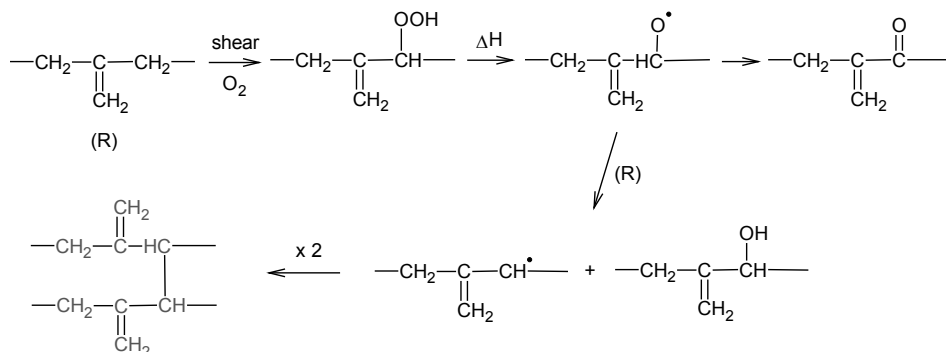
Chain termination occurs by recombination or disproportionation of radicals. At high oxygen concentrations and moderate temperatures chain termination proceeds by the recombination of peroxy radicals according to reaction (2.36) [26]. If the concentration of $R^{\bullet}$ radicals is much higher than that of peroxy radicals (characteristic for polyethylene processing), chain termination is caused by recombination with other available radicals according to reaction (2.32) and (2.33). The disproportionation of alkyl radicals according to reaction (2.35) leads to the formation of an unsaturated group but does not result in a decrease of molecular mass. The chain termination processes do not stop the thermo-oxidative reactions. The reaction products formed in the recombination reaction of peroxy radicals participate in further reactions. Norrish-II type breakdown of ketones results in the formation of vinyl and hydroxyl groups under irradiation [22]:



The melt processing of polyethylene takes place in oxygen poor environment under shear. The high mechanical forces lead to C-C chain scission resulting in macro-radicals [27]. The oxygen dissolved in the polymer reacts with the alkyl radicals forming peroxy radicals, subsequently hydroperoxides and new alkyl radicals. These hydroperoxides decompose rapidly to the corresponding alkoxy and hydroxyl radicals. The latter can form inactive products (ROH and H_2O) and further alkyl radicals through hydrogen abstraction, while β -scission leads to the scission of the macromolecule [2]. The number of weak sites in the polymer chain, the type and amount of catalyst residues, as well as the processing conditions affect significantly the rate and direction of reactions [22,28-30]. At high concentrations of unsaturated groups (Phillips type polyethylene) crosslinking reactions predominate during processing [2,22,29], while at low unsaturated group contents (Ziegler-type and metallocene polyethylenes) the direction of the reactions depends both on the number of vinyl groups and the processing conditions [22,30-33]. Transition metal impurities, including catalyst residues, accelerate the decomposition of hydroperoxides leading to detrimental effects [22,33].

The unsaturated group content in polyethylene influences all the thermal and thermo-oxidative degradation processes, as well as the photochemical stability. Chirinos-Padrón et al. [22] observed that 20% difference in unsaturation has a drastic effect

on the degree of cross-linking, which they explained by thermal decomposition and subsequent reactions of allylic hydroperoxides according to Scheme 2.2.



Scheme 2.2 Cross-linking reactions of polyethylene [22]

Other authors attributed long chain branching and cross-linking of polyethylene occurring during processing to the addition of alkyl radicals to olefin groups (reaction 2.17) [e.g., 34-38]. Johnston et al. [38] observed that the number of unsaturated groups decreases when cross-linking dominates and it increases when thermal scission is the main reaction. They calculated activation energy of about 18 kJ/mol for addition of alkyl radicals to vinyl groups and 91 kJ/mol for β -cleavage of alkyl radicals to form vinyl groups. Similar reactions were observed for vinylidene groups as for vinyl groups, but they did not find correlation between the formation of *trans*-vinylene groups and the reduction in vinyl content during the processing of polyethylene. The formation rate of *trans*-vinylene groups increased with temperature and correlated closely with carbonyl formation.

The processing conditions of polyethylene influence significantly the mechanism of thermo-oxidative degradation. The increase in the concentration of oxygen increases the rate of chain branching reactions, i.e. the concentration of radicals and the formation of small, mobile, reactive radicals like $\cdot\text{OH}$ and $\cdot\text{OOH}$ [5,6]. The termination reactions are controlled also by the concentration of oxygen in the system [2,39,40]. Recombination with alkyl radicals predominates at low oxygen contents (reactions 2.32-2.34), while oxidation and breaking of polymer chains become more and more dominating with increasing oxygen concentration due to the reactions of peroxy radicals (reaction 2.36). An increase in shear stress increases the number of initiation steps [2,29]. According to the study of Holström and Sörvik [7] the raise in temperature increases also the number of initiation steps. At high concentration of unsaturated groups recombination reactions predominate in the usual processing temperature range (180-280 °C), but at low level of unsaturation the overall direction of reactions depend on the temperature. Below 230 °C branching of polymer chains dominates, while at higher extrusion temperatures chain scission is the dominating reaction [2]. Johnston et al [38] developed a simplified kinet-

ic model to estimate the temperature above which a polyethylene with a given concentration of vinyl groups shows predominant scission during melt processing.

The stability of polyethylene under long-term thermo-oxidative conditions (during application) depends very much on temperature, the oxygen content, and the ease of peroxide formation [2]. Because of the complex reactions of autoxidation no definite relationship could be established between oven aging time and service lifetime. Oxygen is consumed by different oxidation reactions. If sufficient amount of oxygen is steadily supplied by diffusion (the sample is in equilibrium with oxygen saturation), the oxidation proceeds uniformly through the sample. If, however, oxidation reactions locally consume more oxygen than can be resupplied by diffusion into the polymer bulk, the autoxidation slows down or can practically stop. The β -scission of alkoxy radicals (reaction 2.28) can lead to the loss in mechanical properties of the originally ductile polymer. The transition from ductile to brittle behavior is related to a critical molar mass, M_c . The main feature of polymer embrittlement due to oxidative degradation can be explained in terms of fracture mechanics [41]. In the course of diffusion-controlled aging micro cracks are formed on the surface. Crack propagation under stress can reach the ductile core or proceed across the sample.

Henry et al. [42] observed that the thermo-oxidative degradation of LDPE at elevated temperature (75-92 °C) is faster in most aqueous environments (water, solution of sodium salts, basic buffer of pH 10 containing sodium hydroxide and sodium bicarbonate) than in air, but an acidic buffer of pH 3 (prepared from hydrochloric acid and potassium hydrogen phthalate) retards oxidation. The acceleration of oxidation is initially a surface phenomenon. HDPE shows similar behavior to LDPE, but the magnitude of the effect of aqueous environment is smaller. The effect of aqueous solution is discussed in terms of nucleophilic attack by peroxy anions on hydroperoxides. Hydroperoxides are acidic with a pK of 10-12 depending on structure. In basic solution a large fraction of the hydroperoxide exist in the form of polyolefin anion, which is a strong nucleophile. The nucleophilic attack of a peroxy anion on hydroperoxide produces a free radical intermediate which decomposes to various products (alcohol, ketone, etc.). The process depends on pH and ionic strength. The ratio of peroxy anion and hydroperoxide defines the equilibrium constant and the pH:



The rate of nucleophilic attack has a maximum at a pH close to the pK of the hydroperoxide. At a low pH, the rate falls with increasing acidity, while at a very high pH the rate falls with increasing basicity. For neutral salt solutions, the rate increases with increasing ionic strength of the solution, because the decrease in the activity coefficient for ionic species shifts the equilibrium in reaction (2.41) to the right, which increases reaction rate at pH's less than the pK of the hydroperoxide. According to this theory the stability of polyolefins in aqueous environment can be improved by suppressing the production of peroxy anions.

2.2. Stabilization of polyethylene against thermo-oxidative degradation

The melt stabilization of polyethylenes has primary importance in practice. The nascent polymer is subjected to heat, shear and low level of oxygen already in the pelletizing process. As a consequence, several chemical processes take place simultaneously resulting in considerable changes in the chemical structure of the polymer. The direction and the extent of the reactions depend on the chemical structure of the polymer (number of unsaturated groups, type of co-monomer, number and distribution of long chain branches), the type and amount of catalyst residues, the composition of the additive package, as well as the processing conditions (temperature, concentration of oxygen, intensity of shear forces) [28,29,43,44].

Stabilizers are chemical substances which are added to polymers in small amounts (at most 1-2 w/w%) and are capable of trapping emerging free radicals or unstable intermediate products (such as hydroperoxides) in the course of autoxidation and to transform them into stable end products. The possible path of inhibition thermo-oxidative degradation is shown in Fig. 2.1 [2].

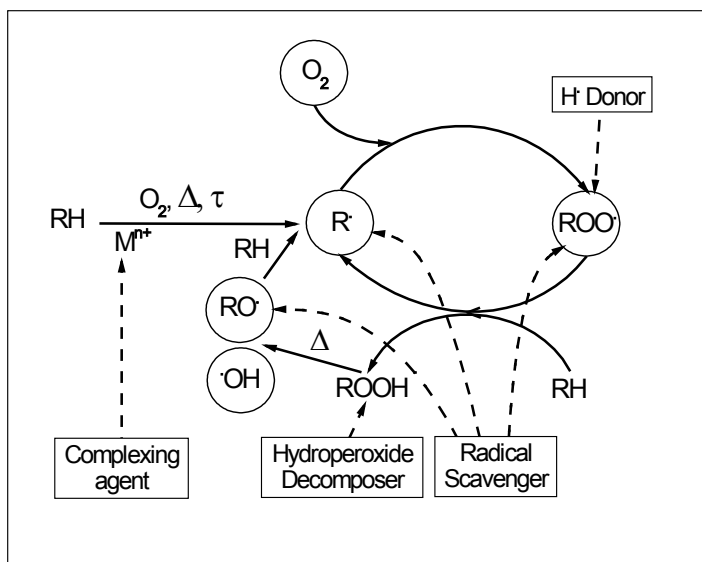


Figure 2.1 General scheme of inhibition of thermo-oxidative degradation [2]

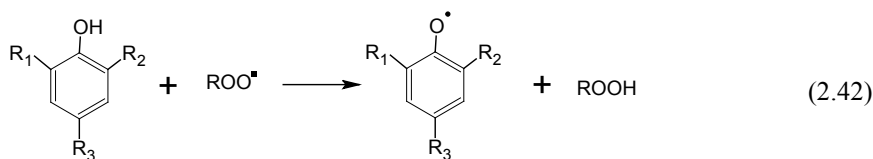
Metallic impurities originating mainly from catalyst residues are a source of the formation of alkyl radicals both under processing conditions and during the life cycle of the end product. Suitable deactivation of the active form of these catalysts is, therefore, mandatory after polymerization. In the application of polymers in direct contact with

metal (cable insulators) the use of metal deactivators improves the lifetime of the polymer [45].

In principle, scavenging the primary macroradicals, $R^\bullet$, would stop autoxidation, but it can hardly be avoided, as the rate of reaction of molecular oxygen is very high. Under oxygen-deficient conditions alkyl radical scavengers (chain breaking acceptors) could contribute significantly to the stabilization of the polymer, but only a few compounds are reported in the literature which are capable of doing that [46-50]. The rate-determining step in autoxidation is the abstraction of a hydrogen from the polymer backbone by the peroxy radical forming the hydroperoxide (reaction 2.24). If a substantially more easily abstractable hydrogen is offered by a suitable hydrogen donor (InH) to the peroxy radical, then the reactions will compete. H-donors are known as chain breaking donors. Suitable H-donors do not react further by abstraction of a hydrogen from the polymer backbone. Scavenging of the $RO^\bullet$ and $HO^\bullet$ radicals – which are far more reactive than the peroxy radicals – is practically not possible by using radical scavengers. Hydroperoxide decomposers (HD) are used as co-stabilizers to avoid chain branching during autoxidation. They decompose hydroperoxides forming “inert” reaction products. Chain breaking acceptors and H-donors are also referred to as primary antioxidants, while hydroperoxide decomposers are classified as secondary antioxidants.

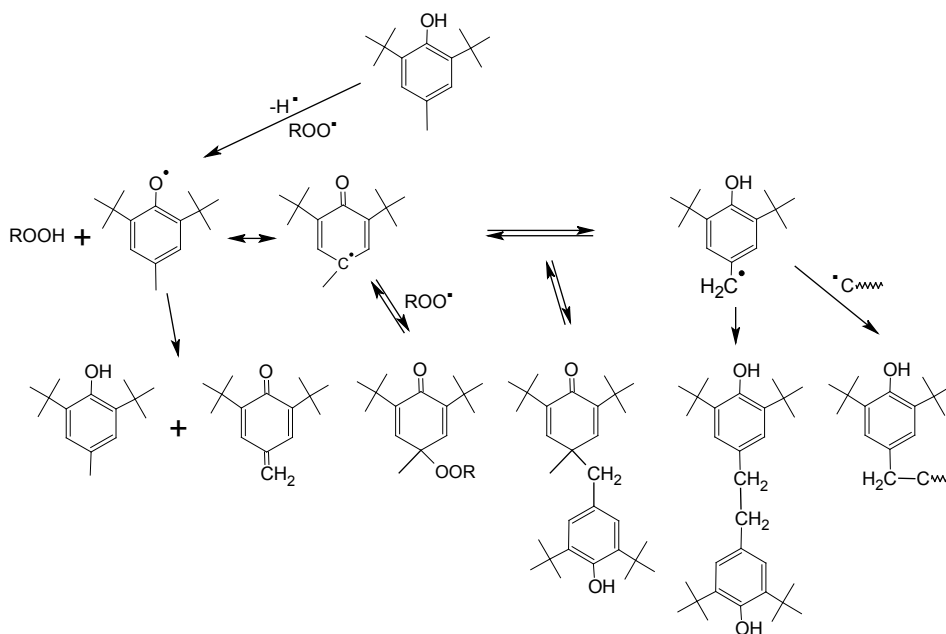
2.2.1. H-donors and radical scavengers

Phenolic antioxidants are the most widely used and extensively investigated stabilizers for polymers [e.g., 33,51-56]. Hindered phenols act as free-radical scavengers and prevent or interrupt oxidation reactions. They are trapping peroxy radicals efficiently. The key reaction is the formation of hydroperoxide by transfer of a hydrogen from the phenolic moiety to the peroxy radical and the formation of a phenoxy radical according to reaction (2.42) [55,57,58].



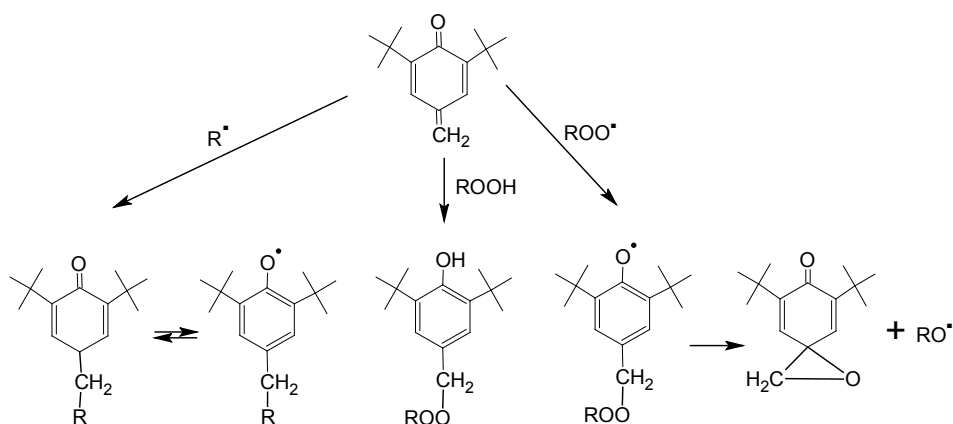
The steric hindrance by substituents, e.g. tertiary butyl groups in the 2- and/or 6-position, influences the stability of the phenoxy-radical or the mesomeric cyclohexadienonyl-radicals. Sterically hindered phenols can be classified according to the substituents in 2-, 4-, and 6-positions. The rate of hydrogen abstraction from phenol increases with decreasing steric hindrance in 2- and 6- positions [59,60], but physical effects have to be taken also into account, as the decrease in steric hindrance increases the ease of hydrogen-bonding of the phenolic hydroxyl groups [61]. The substituents in 2- and 6-positions influence significantly also the reactivity of the phenoxy radicals formed in reaction (2.42) [59,60]. Bulky substituents prevent the reaction of the phenoxy radical with the polymer and suppress dimerization of two phenoxy radicals. The sterically hindered phenols are not only effective hydrogen donors, but undergo numerous further

chemical reactions that contribute to the inhibition of autoxidation. Sterically “fully hindered phenols” have *tert*-butyl groups in 2-, 4-, and 6-positions compared to the phenyl group, i.e. have no H-atom on the C-atom vicinal to that in these positions. The contribution of fully hindered phenols to stabilization is essentially the stoichiometric reaction between the phenol and the peroxy radical. “Partially hindered phenols” have hydrogen atoms on the C-atom vicinal to at least that in 4- (or 2- or 6-)position and participate in several reactions (Scheme 2.3) resulting in C-C coupling products and quinone methides. The latter react with alkyl, alkoxy and peroxy radicals according to Scheme 2.4 [2].



Scheme 2.3 Reactions of sterically partially hindered phenols [2]

Although some thermo-oxidative degradation products of polyethylene have discoloring effect, strong discoloration of the polymer stabilized with phenolic antioxidants originates mainly from the reaction products of the stabilizer. The color development can be attributed to the formation of conjugated diene compounds, arising as a consequence of trapping of alkylperoxy radicals by phenolics [62]. The discoloration depends on the structure and concentration of the phenolic transformation products. The principal contribution to polymer discoloration is due to the formation of quinone methides. Their discoloring effect is reduced in propionate-type phenolics, as a consequence of intramolecular rearrangement of a part of the primarily formed quinone methide, and is due to oxidative dimerization resulting in nonconjugated dimeric quinone methides.



Scheme 2.4 *Reactions of quinone methides [2]*

Secondary aromatic amines and aromatic diamines are extremely efficient H-donors. They react with peroxy radicals and the primary reaction products can further react similarly to phenols [63]. Various coupling products are formed which discolor the polymer strongly; therefore their application is essentially limited to carbon black filled polymers (e.g. rubbers).

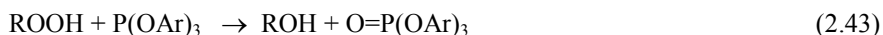
Sterically hindered amines are efficient stabilizers against thermal and photooxidative degradation of polyolefins. Therefore they are designated both as Hindered Amine Stabilizer (HAS) and Hindered Amine Light Stabilizer (HALS) [2]. The activity of these amines as antioxidants is based on their ability to form nitroxy radicals. The reaction rate of nitroxy radicals with alkyl radical is only slightly lower than that of alkyl radicals with oxygen [64,65]. The mechanism of nitroxy radical formation and the function of nitroxy radicals are controversial in the literature [e.g., 66-68]. The reaction of an alkyl radical with the $\text{N-O}^\bullet$ radical leads to the formation of hydroxylamine ether (NOR'). This reacts with a peroxy radical ($\text{R}''\text{OO}^\bullet$) resulting in the formation of alkyl peroxide ($\text{R}'\text{OOR}''$) and the reformation of the nitroxy radical [2]. It is important that the nitroxy radicals are formed in the course of polymer's autoxidation, and HAS are not able to prevent the oxidation of hydrocarbons, which takes place at high temperatures [68]. Therefore appropriate melt stabilization of the polymer is required to achieve sufficient stability.

2.2.2. Hydroperoxide decomposers

The hydroperoxides formed in thermo-oxidation of polyethylene decompose to reactive $\text{RO}^\bullet$ and $^\bullet\text{OH}$ radicals resulting in autoxidation chain reactions. The rate of decomposition depends strongly on temperature. Hydroperoxide decomposers can prevent this homolytic split of the hydroperoxide group.

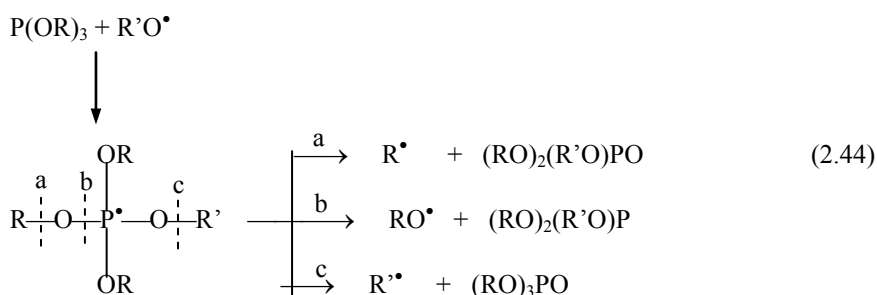
Organophosphorous compounds are efficient hydroperoxide decomposers under the processing conditions of polyolefins. Hindered aryl phosphites and phosphonites are used in large quantities generally in combinations with a hydrogen donor primary antioxidant [2]. Due to the versatility of their reactions phosphines are also promising candidates for polyolefin stabilization [69,70]. While the reaction mechanism of hindered phenols is widely investigated, less attention has been paid to that of phosphorous stabilizers.

The stabilizing action of phosphites and phosphonites is attributed to three basic mechanisms: decomposition of hydroperoxides, reactions with peroxy and alkoxy radicals [71]. The phosphorous compound reacts with hydroperoxides by reducing them to alcohols in a non-radical process, while it oxidizes simultaneously to the corresponding five-valent derivative [71-78]:



The oxidation of phosph(on)ites by hydroperoxides is a fast reaction. The rate is affected by the chemical structure of the stabilizer, and it decreases with increasing electron-acceptor ability and bulk of the groups bound to the phosphorus atom in the order: phosphonites > alkyl phosphites > aryl phosphites > hindered aryl phosphites [71,76].

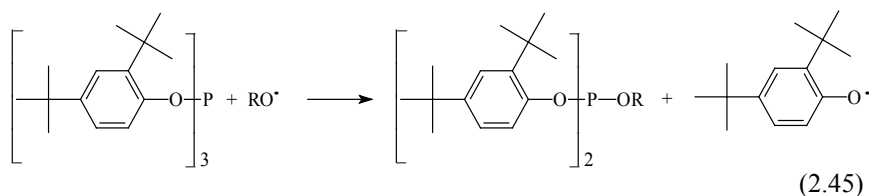
Besides decomposing hydroperoxides the organophosphorous compounds are involved in a variety of free radical reactions [71,79,80]. The reaction between trialkyl phosphites and alkoxy radicals (reaction (2.44)) yields oxidized and non-oxidized phosphorous derivatives and alkyl radicals [17,73,79]. The multiplicity in behavior of phosphite esters toward alkoxy radicals is explained by the formation of a common four-coordinate phosphorus-centered radical intermediate [16,79-81], which fragments to yield the most stable radical [79]:



According to Bentrude et al. [80] the strength of the R'-O and P-O bonds in the probable intermediate determines the ratio of α -scission (reaction (2.44b); displacement or substitution) and β -scission (reaction (2.44c); oxidation) processes.

When sterically hindered aryl phosphites react with oxy radicals by substitution sterically hindered phenoxy radicals are released, therefore they can also act as antioxi-

dants to some extent [71,82,83].

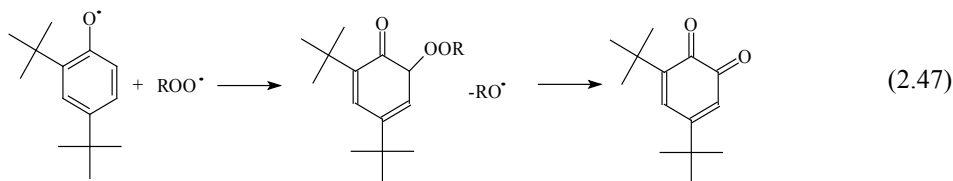


Cyclic sterically hindered arylene phosphites are less efficient antioxidants, while non-sterically hindered aryl phosphites and aliphatic phosphites have a slight pro-oxidative effect [82].

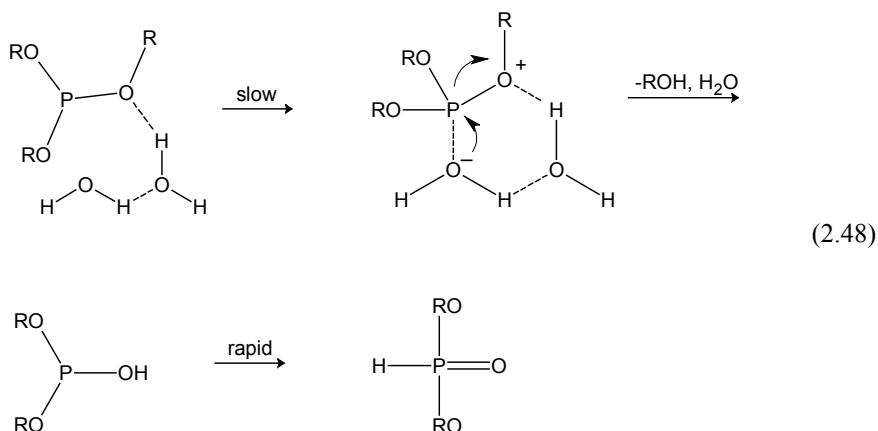
Aliphatic [84,85] and sterically hindered aryl [71,83] phosphites react with alkylperoxy radicals yielding the corresponding phosphates and alkoxy radicals:



The alkoxy radicals react further with the phosphite molecules according to reaction (2.44), but recombination of the alkylperoxy and phenoxy radicals can be also expected resulting in the formation of a quinoidal structure [83,86,87] with the potential discoloration of the polymer:



The rate constant of the reaction of peroxy radicals with hindered aryl phosphites are 10-100 times smaller than the analogous values for hindered phenols at temperatures <100 °C [88]. At high temperatures (under the processing conditions of polyolefins) hindered aryl phosphites exhibit an antioxidative efficiency, which resembles or even surpasses that of hindered phenols. This may result from the hydrolysis of phosphites under these conditions, yielding hydrogen phosphites and phenols, which are active species in high temperature oxidation. In the later stages of reactions the initially formed monohydrogen phosphites are further hydrolyzed to phosphorus acid [78,89-93]. The hydrolysis is an autocatalytic reaction, which is accelerated under acidic conditions [78,91,92]. The acid-catalyzed hydrolysis involves a protonation step at the phosphorus atom followed by the nucleophilic attack of water to produce equivalent amounts of alcohol/phenol and phosphonates. Acid scavenger additives, like hydrotalcite, improve the hydrolytic stability of phosphites [78]. In neutral environment the hydrolysis of an aliphatic phosphite obeys a third order rate law involving two water molecules [91].



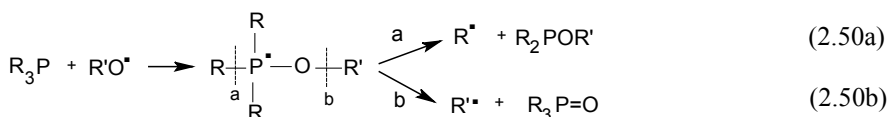
Phosphites are not sensitive to direct attack by oxygen at room temperature. The autoxidation of low molecular mass aliphatic tertiary phosphites require heat and catalyst or radical or photoinitiation [84]. Phosphites oxidize to the corresponding phosphates by ozone and singlet oxygen at temperatures higher than 200 °C [94]. On the basis of calorimetric experiments, Neri et al. [74] assumed that phosphites could react directly with molecular oxygen by a charge transfer mechanism at high temperatures.

Phosphines had not been investigated in polyethylene as stabilizers before patenting bis(diphenylphosphino)-2,2-dimethylpropane [69] and the studies conducted at the Joint Laboratory in cooperation with Clariant [70]. The reactions of various phosphines have been studied extensively in solutions. Trisubstituted phosphines react with hydroperoxides yielding phosphine oxides together with the corresponding alcohol [e.g.: 95-99]:



The mechanism of this reaction is similar to that of hydroperoxides with trisubstituted phosphites and is described by the attack of the phosphorous compound on the hydroxyl oxygen of the hydroperoxide resulting in the formation of a four-coordinate phosphorus-centered intermediate, which yields the products by a simple proton transfer [97].

Peroxy radicals oxidize trisubstituted phosphines in a direct reaction [96] by similar mechanism as the oxidation of trialkyl phosphites (reaction 2.46). The oxidation of phosphines by alkoxy radicals is a result of oxygen-transfer through the formation of a common four-coordinate phosphorus-centered intermediate [17,79,100]:



The configuration, configurational stability, and lifetime of intermediate radicals depend on the nature of the substituents on phosphorus and the configurational requirements imposed by the substituents [100]. The ratio of α -scission (reaction 2.50a; displacement) to β -scission (reaction 2.50b; oxidation) of the intermediate radical is delicately balanced and varies greatly with the nature of R and R' [101]. To the first approximation the relative strength of the R'-O and P-R bonds in the radical intermediate determines the ratio of α -scission to β -scission [80,102]. Kochi and Krusic [79] observed that the behavior of trialkylphosphites toward alkoxy radicals differs from that of trialkylphosphines. In the first case β -scission predominates, while displacement is the characteristic reaction with trialkylphosphines. According to the authors the scission of P-O bond occurs when the displaced oxy radical is resonance stabilized.

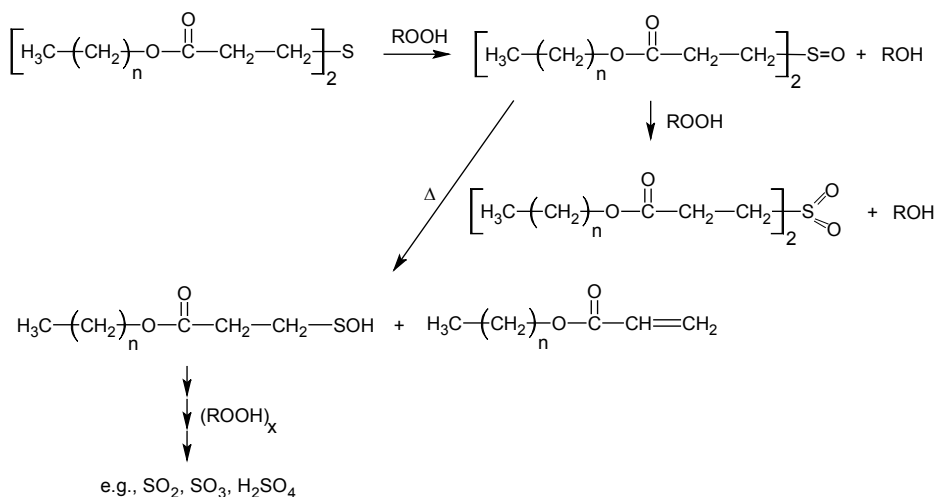
Trialkylphosphines and trialkylphosphites are effective reducing agents of peroxide bonds [16,17,103]. According to Walling et al. [16,17] the reaction of di-*tert*-butyl peroxide with triphenylphosphine follows the same path as the reaction with phosphites. The peroxide undergoes thermal dissociation and the radicals react with the phosphorus derivative. Contrary to that Greatrex and Taylor [103] concluded that the trivalent phosphorus of triphenylphosphine inserts into peroxide bonds yielding reactive phosphorane intermediates, which undergo nucleophilic substitution or elimination reactions.

Buckler [85] investigated the reaction of tributylphosphine with molecular oxygen in different solvents in the temperature range of 20 and 80 °C using different rate of air or oxygen flow. He concluded that autoxidation of the phosphine is a rapid, clean, exothermic reaction. Tertiary phosphine oxides and phosphinic acid esters are the major products. Changes in the oxygen concentration in the gas stream, the flow rate, the initial phosphine concentration and the temperature do not affect significantly the relative amounts of the major products. The medium in which the process is carried out plays the determining role. The ratio of phosphine oxide to phosphinic acid ester increases steadily as the solvent becomes more polar. Small amounts of diphenylamine and hydroquinone inhibit effectively the autoxidation of tributylphosphine and similar tertiary phosphines. On the basis of the experimental results the author proposed a reaction mechanism. According to that the oxygen reacts with a hydrocarbon radical with radical chain mechanism rather than directly at phosphorus. The relative amounts of phosphine oxide and phosphorus ester produced are determined by competitive reactions. The author concluded that the polar factors in the attacking radical and phosphorus substituents determine the course and rate of these reactions.

Because of their high reactivity, phosphites and phosphonites are used as stabilizers during melt processing (temperatures up to 300 °C). As long term stabilizers their contribution to the stabilization of the end product is small [2].

Organosulphur compounds such as sulfides, dialkyl dithiocarbamates or thiodi-propionates are efficient hydroperoxide decomposers [2]. Their effect is based on the ability of sulfenic acids to decompose hydroperoxides. In the first step the sulfide reacts stoichiometrically with a hydroperoxide molecule forming an oxide (Scheme 2.5). Sulfenic acid is formed through thermal decomposition of the intermediate sulfoxide. Further possible reactions are the formation of sulfone or oxidation with hydroperoxides,

leading to sulfuric acid and other sulfur-containing oxidation products.



Scheme 2.5 *Hydroperoxide decomposition with thiodipropionate esters [2]*

Intermediates with β,β -sulfinyldipropionate structure are particularly reactive in the formation of sulfenic acid. Therefore compounds like di-stearyl or di-lauryl dithiodipropionate are mainly used as hydroperoxide decomposers in long time applications. They contribute to the extension of the lifetime of plastics in the course of use at temperatures up to 150 °C. During processing they do not contribute to the stabilization, as the formation of sulfoxides and the subsequent oxidation products is a relatively slow process [104].

2.2.3. Practical aspects of polyethylene stabilization

A single antioxidant is used for the stabilization of polymers very seldom. Generally blends of stabilizers with differing functions, e.g., hydrogen donors (phenols or amines) with hydroperoxide decomposers (phosphites, phosphonites or thiodipropionates) are used. Most of the antioxidant combinations exhibit a synergistic effect [2]. Phenols contribute to the stabilization of the polymer during processing and long term thermal aging. Phosphorous compounds protect the polymer during processing, while thioesters, in addition to phenols, contribute to long term thermal stabilization.

We talk about antagonism, if the observed effect is smaller than the contribution of the individual components. Antagonistic effects were observed in combinations of phenolic antioxidants and sterically hindered amines, which was ascribed to the interaction of additives [105,106]. Vyprachtický et al. [107], however, emphasized the complexity of reactions in the interaction of phenols and HALS stabilizers. A decrease

in the efficiency of additives was observed also in other systems, as a result of interaction; e.g., interferences of antiblocking agents with hexafluoropropylene-vinylidene fluoride copolymer processing aid [108], stabilizing efficiency of compounds containing silica antiblocking agents [109,110], color strength of HALS/pigment systems [111]. Studies conducted in the Joint Laboratory [112] to explore the effect of additive interactions on polymer stabilization revealed that the loss of antioxidant efficiency depends on the involvement of functional stabilizing groups in the association, as well as on the strength and ratio of self- and inter-association of stabilizing molecules. Although the practical importance of additive synergism and antagonism is large, the number of publications on the latter phenomenon is very limited.

Processing stabilization of polyethylene has not only theoretical but also practical importance. While the effect and reaction mechanism of phenolic antioxidants are well documented, the role and effect of phosphorous stabilizers are less known. The processing stabilizing efficiency of an aryl phosphite and phosphonite antioxidant was compared in a metallocene type polyethylene (mPE) in the presence of the same phenolic antioxidant at the Joint Laboratory [70]. Quantitative relationship was established between the degree of oxidation of the phosphorous stabilizer and changes in the properties of mPE. Significant differences were observed in the effect of the two phosphorous antioxidants on the characteristics of mPE. The results revealed that simultaneous breaking and enlargement of polymer chains occur during processing, their overall direction depending essentially on the chemical structure of the phosphorous stabilizer. The phosphonite hinders the recombination of macroradicals more efficiently than the phosphite molecules. Significant discoloration and increase in viscosity of the polymer starts only after decreasing of the residual concentration of the phosphonite to a low critical value. In the case of the phosphite the properties of the polymer change considerably already at high residual concentration of the antioxidant.

The service life of plastic pipes and the factors influencing it have been the subject of considerable interest for some time. Pipes are used in the most diverse application areas including water, waste water and sewer pipes, floor, wall and ceiling heating systems, warm and hot water solar systems and natural gas supply [113]. Their guaranteed service life is 50 years in most cases. The lifetime of pipes is usually predicted by using internal pressure tests, in which the pipe is subjected to different internal stresses and the time to rupture is measured [114]. In accordance with most literature sources, Gedde and Ifwarson [115] claim that chemical processes play a role only in the last stage of testing, when the complete consumption of stabilizers leads to brittle fracture. The detailed study of the failure of pipes in a pressure test showed that many different mechanisms contribute to rupture, e.g. the diffusion of additives and oxygen, degradation reactions, etc. [116]. These processes depend on the polymer, the additive package, the surrounding environment and other conditions; another study showed that chlorine-containing water significantly decreases the lifetime of polyethylene water pipes [117].

Additives may evaporate, the surrounding media may leach them or they may react chemically. According to Gedde et al. [118-121] the consumption of stabilizers by chemical reactions can be neglected, the largest loss is usually caused by leaching [118,119]. Pfahler [122,123] also showed that in the presence of water the migration

and loss of Hostanox O3 was always smaller than that of Hostanox O10. The larger molecular weight of O10 should have led to a slower loss of the additive, if chemical reactions had not taken place. Accordingly, the use of additives with lower molecular weight usually leads to shorter lifetimes, because of faster evaporation or leaching [124]. Gedde et al. [120,121,125] claim that the time dependence of stabilizer loss and chemical degradation can be divided into three stages: precipitation and segregation of the additive, leaching, and auto-oxidation of the polymer. Segregated additives, which form a separate phase in the polymer, do not contribute to stabilization and OIT decreases as a consequence. On the other hand, Dörner et al. [126] did not find such a stepwise decrease of stabilizer content and OIT, while Calvert and Billingham [127] could not prove the existence of additive droplets in the polymer. These results clearly indicate that the hydrolytic and chemical stability, solubility and diffusion of additives are crucial factors in the determination of the lifetime of polyolefin pipes. In the first part of testing chemical reactions are not supposed to play any role in the failure of the pipe. However, we know that oxygen, stabilizers and the polymer always react with each other leading to stabilizer consumption and to the modification of the chemical structure of the polymer.

2.3. Summary, aim of the research

Numerous literature sources prove that considerable work has been done on the degradation and stabilization of polyolefins. Nevertheless, several questions are completely unclear or have not been dealt with at all. Among others the hydrolytic stability of antioxidants and its possible effect on the lifetime of products brought into contact with extractive media have never been sufficiently investigated and explained. In the framework of a larger project, we studied processes taking place during the storage of HDPE in water, the consumption of the additives and the consequent changes in the structure of the polymer. In the first part of this large project we focused our attention on changes in the properties of the neat polymer in the hope that the results may serve as a basis for the study of more complicated systems containing a stabilizer or even a stabilizer package (Chapter 4).

The stabilization mechanism of phenolic antioxidants is widely discussed in the literature. Less attention is paid to the processing stabilizing mechanism of phosphorous secondary antioxidants. The chemical reactions of phosphites and phosphonites are considered similar in the literature. The reaction mechanisms of various phosphorous derivatives (phosphites, phosphonites and phosphines) determined in solvents at ambient and elevated temperature show differences only in the reactions with oxy radicals. Phosphines yield esters in a higher portion than phosphites due to the predomination of displacement reactions. The mechanisms of the reactions with hydroperoxide and peroxy radicals were found similar for the three types of phosphorous compounds. On the other hand the studies on the stabilization of polyethylene revealed that not only the efficiency but also the reaction mechanism of various phosphorous stabilizers are strongly influenced by their chemical structure. Phosphines had not been investigated as polyolefin stabilizers previous to the research of the Joint Laboratory conducted in cooperation with Clariant. The aim of the larger project run at the Joint Laboratory is the

determination of the effect of the chemical structure of phosphorous antioxidants on the mechanism of processing stabilization in polyethylene. In the frame of the present work we investigated three phosphorous stabilizers (phosphites, phosphonites and phosphines) in Phillips type polyethylene. Their melt stabilizing efficiency was compared (Chapter 5), their role in melt stabilization was determined (Chapter 6), and correlation was established between their consumption during processing and the properties of the polymer (Chapter 7). In addition, high temperature reactions of a phosphite stabilizer with reactive species accelerating the degradation of polyethylene during processing were investigated by model reactions (Chapter 8). Similar model reactions are run with phosphine and phosphonite stabilizers, but their results are out of the scope of this thesis and will be reported elsewhere.

Chapter 3

Experimental

3.1. Materials

3.1.1. Polymers

The experiments were carried out with ethylene/1-hexene copolymers of the Tisza Chemical Work (TVK), Hungary, polymerized by Phillips catalyst. The polymers were obtained in the form of powder without any additive. The effect of long-term aging in water on the characteristics of additive-free polyethylene (Chapter 4) was investigated with Tipelin PS 380 grade, recommended for pipe extrusion by the producer. The efficiency and the reaction mechanism of various antioxidant combinations were studied in Tipelin FB 472 (Chapter 5) and Tipelin FA 381 (Chapters 6 and 7) grades recommended for film extrusion. The number (M_n) and mass (M_w) average molecular masses, the polydispersity, density and melt flow index (MFI) of the investigated polymer powders are summarized in Table 3.1.

Table 3.1

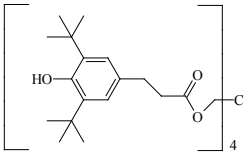
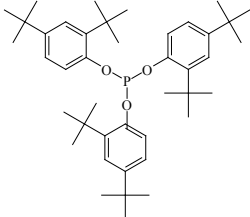
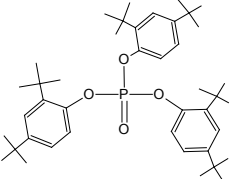
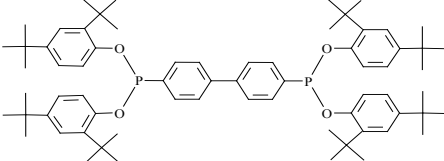
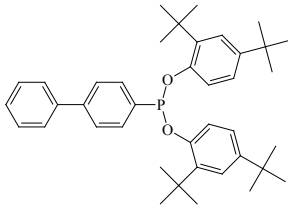
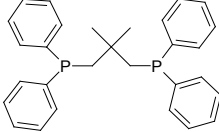
The characteristics of ethylene/1-hexene copolymer powders polymerized by Phillips catalysts

Characteristic	Polyethylene grade		
	PS 380	FA 381	FB 472
M_n (g/mol)	14500	15450	13800
M_w (g/mol)	129950	116500	111000
Polydispersity	8.96	7.54	8.04
Density (g/cm ³)	0.938	0.938	0.948
MFI (g/10 min at 190 °C, 2.16 kg)		0.50	0.80
MFI (g/10 min at 190 °C, 5.00 kg)	1.40		

3.1.2. Additives

Irganox 1010 (*Ciba*) was used as phenolic antioxidant. Three phosphorous secondary antioxidants supplied by Clariant were studied: a hindered aromatic phosphite (Hostanox PAR 24; DTBPP), a hindered aromatic phosphonite (Sandostab P-EPQ; consisting of di- and mono-phosphonites) and an aromatic-aliphatic phosphine (Pep-fine). The chemical structure of the investigated antioxidants is given in Table 3.2 together with the oxidized form of the phosphite (DTBPPO) supplied also by Clariant for the model experiments.

Table 3.2
Chemical composition of the antioxidants studied

Commercial name	Chemical composition	Molecular mass (g/mol)
Irganox 1010		1178
Hostanox PAR 24 (DTBPP)		646
Oxidized Hostanox PAR 24 (DTBPPO)		662
Sandostab P-EPQ Di-phosphonite		1034
Mono-phosphonite		594
PEPFINE		440

3.1.3. Reagents, solvents and gases

Cumene hydroperoxide (CHP; Luperox CU90) of 88 % purity, dicumyl peroxide (DCP; Luperox DCP) of ≥ 99 % purity and azobisisobutyronitrile (AIBN) of 98 % purity were purchased from Aldrich for the model experiments (Chapter 8).

N-heptane (for liquid chromatography, >99.3 % purity), acetone (for liquid chromatography, >99.8 % purity), 2-propanol (gradient grade for liquid chromatography, >99.9 % purity), acetonitrile (gradient grade for liquid chromatography, >99.9 % purity), and H_2O (for liquid chromatography) were used for chromatographic analyses. The solvents were purchased from Merck.

Argon gas of 99.999 %, nitrogen gas of ≥ 99.5 %, and oxygen gas of ≥ 99.5 % purity were applied for the model reactions and the thermal and thermo-oxidative analyses.

3.2. Sample preparation

In the study of long-term aging in water (Chapter 4) additive-free PS 380 grade polyethylene was processed by multiple extrusions on a Rheomex S 3/4" 25 L/D single screw extruder attached to a HAAKE Rheocord EU-10 V driving unit. The extruder was equipped with a screw of constant pitch and 3:1 compression ratio. Screw speed was 50 rpm. The die was fitted with a single orifice of 4 mm diameter. The temperature of the heating zones was set to 260 °C in all extrusion steps. Extruded strands were cooled in water and palletized continuously. Dried pellets were fed into the extruder in subsequent extrusion steps. Samples were taken for investigation after the first, third and sixth extrusion steps. Plates with a thickness of 1 mm were molded at 190 °C with 5 min melting and 2 min compression time. Dumb-bell specimens of 120 x 10 x 1 mm dimensions were cut from the plates for tensile testing and these or the remaining scrap material was used for other studies. The samples were stored in closed glass containers of 750 ml capacity in 700 ml distilled water at 80 °C for 1 year. Specimens obtained in each extrusion step were stored in the same container. Samples were withdrawn at regular intervals, wiped, weighed and characterized by standard techniques.

In the stabilization studies FB 472 grade polyethylene (Chapter 5) was homogenised with the additives in a Thyssen Henschel FM/A10 laboratory high-speed fluid mixer at 600 rpm. Six consecutive extrusions were carried using the same processing unit and conditions as for PS 380. Samples were taken for testing after each extrusion step. FA 381 grade polyethylene and the additives (Chapter 6 and 7) were homogenized in a high-speed mixer (Rheinstahl Maschine) at a rate of 500 rpm. The additive-free and the stabilized polymers were pelletized on a Tanabe VS 40 type extruder by six consecutive extrusions setting the temperature of each zone to 260 °C and using a rotor speed of 50 rpm. Samples were taken after each extrusion step. Blown films were prepared using a Tanabe VS 30 extruder at 175, 195, 195, 195, 195 °C barrel temperatures, 40 rpm screw speed and 1:4 blow ratio. Plates of 1 mm and films of 100-200 μm thickness were compression molded from the pellets at 190 °C using a Fontijne SRA 100 machine with 5 min melting and 2 min compression time.

3.3. Methods

The chemical structure of the polymer, the consumption of phosphorous antioxidants during the processing of polyethylene and the products of the model reactions of DTBPP were analyzed by Fourier Transform Infrared (FT-IR) spectroscopy on a Mattson Galaxy 3020 (*Unicam*) type spectrophotometer in the wavenumber range of 4000–400 cm^{-1} using 2 cm^{-1} resolution and 16 scans. Five parallel spectra were recorded on each film. The structure of the nascent polymer powder was studied by Diffuse Reflectance Fourier Transform Infrared (DRIFT) spectroscopy and the recorded spectra were evaluated according to the method described in Reference 128. The number of the functional groups in processed polyethylene was determined from the absorbance spectra recorded on compression-molded polymer films by the internal standard method according to Equation (3.1):

$$C = \frac{K}{\rho} \left(\frac{A_{inv}}{A_{ref}} \right) \quad (3.1)$$

where C is the concentration of a given functional group, K is its absorption coefficient, ρ is the density of the polymer (g/cm^3), A_{inv} and A_{ref} are the intensities of the investigated and the reference absorption bands, respectively.

The absorption coefficients and the characteristic wavenumber of the absorption bands analyzed are summarized in Table 3.3. For determining the absorption coefficients of methyl and vinyl group vibrations a series of Phillips type ethylene/1-hexene copolymers with various butyl branching and unsaturation was investigated. The absorption coefficient of the methyl vibration was determined with the help of ^{13}C NMR spectroscopy, while that of the vinyl group by using ^1H NMR spectroscopy.

Table 3.3

Infrared absorption coefficient (K), and wavenumber of the investigated (A_{inv}) and reference (A_{ref}) absorption bands used for the calculation of the number of functional groups and the concentration of phosphorous antioxidants in polyethylene by Equation (3.1)

Functional group/type of antioxidant	Unit	K	Wavenumber (cm^{-1})	
			A_{inv}	A_{ref}
Methyl	1/1000C	4.9370	1378	1034
Vinyl	1/1000C	0.5000	908	2018
Vinylidene	1/1000C	0.5654	888	2018
<i>Trans</i> -vinylene	1/1000C	0.4342	965	2018
Carbonyl	mmol/molPE	0.03826	1780-1690*	2018
Phosphite [P(III)-O-C]	ppm	4871	850	2018
Phosphonite [P(III)-O-C]	ppm	4955	850	2018
Phosphine [P(III)-C]	ppm	36561	1027	2018

* Integrated intensity in the range of 1780-1690 cm^{-1}

The absorption coefficients of the vinylidene and the *trans*-vinylene groups were derived from the values given by deKock and Hol [129]. The number of methyl groups was determined by compensation method [128,130]. The concentration of the unsaturated groups was derived by the procedure described in Reference 128. The bands at 908 cm^{-1} (vibration of the vinyl group) and 890 cm^{-1} (vibrations of the vinylidene group and the butyl branches) were separated by curve fitting. The concentration of the vinylidene group was calculated from the intensity of the band at 890 cm^{-1} according to the method given by Lomonte [131]. The concentration of the carbonyl groups was calculated from the integrated absorption intensity (T_{CO}) of the vibration appearing in the range of $1780\text{--}1690\text{ cm}^{-1}$ with the absorption coefficient given in Reference 132.

FT-IR methods were developed for the quantitative analysis of the phosphorous compounds in polyethylene. The P(III)-O-C vibration of phosphite and phosphonite gives an absorption band at 850 cm^{-1} [133]. This band is well separated from the absorption bands of the unsaturated groups of polyethylene. The calibration was carried out with n-octane solutions. The oxidation of the P(III) compounds during the extrusion of the polymer results in a decrease in the intensity of this band and simultaneous appearance of P(V)-O-C bands in the spectrum. The P(V)-O-C bands of the phosphite absorb at 894 cm^{-1} and 966 cm^{-1} , as can be seen in Figure 3.1. Unfortunately, the former band overlaps the absorption of vinylidene groups of polyethylene at 888 cm^{-1} , and the latter one the *trans*-vinylene absorption at 965 cm^{-1} . The pentavalent P-O-C bands of phosphonite absorb at 888 cm^{-1} , giving rise to the intensity of vinylidene group absorption, and at 938 cm^{-1} , isolated from the absorption bands of the unsaturated groups (Fig. 3.2).

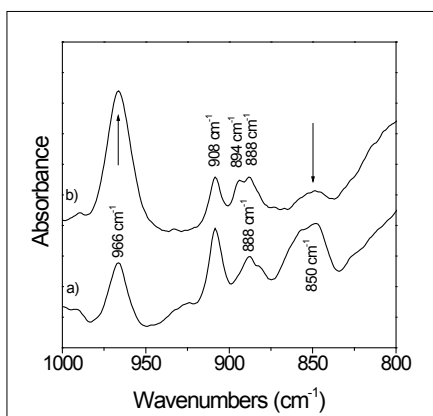


Figure 3.1 FT-IR spectra of polyethylene stabilized with the phosphite measured after the first (a) and sixth (b) extrusions.

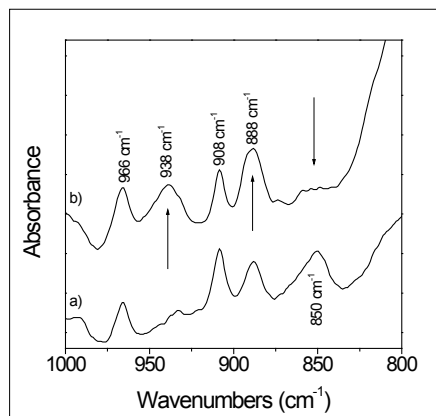


Figure 3.2 FT-IR spectra of polyethylene stabilized with the phosphonite measured after the first (a) and sixth (b) extrusions.

The concentration of the residual phosphine was determined by two methods. The trivalent P-C bond of the investigated phosphonite absorbs at 1027 cm^{-1} (Fig. 3.3),

resulting in a weak band. This band was used for quantitative analysis in FB 472 grade polyethylene (Chapter 5). The calibration was carried out with n-octane solutions.

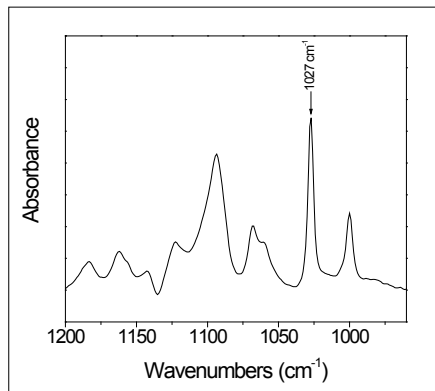


Figure 3.3 FT-IR spectrum of the phosphine.

As the P(III) bands of the investigated phosphine are either weak or overlap the bands of polyethylene, an absorption band of the P(V)=O groups was used for analysis in further investigations (Chapters 6 and 7). The P(V)=O group absorbs at 570 and 550 cm^{-1} and both bands are well separated from the vibrations of the polymer, therefore they can be used for quantitative analysis. Polyethylene samples containing oxidized phosphine in different concentrations (0–700 ppm) were used for calibration.

The following linear relationship was obtained between the relative intensity of the absorption band at 570 cm^{-1} and the concentration of oxidized phosphine mixed to the polymer:

$$\frac{A_{570}}{A_{2018}} = (2.247 \cdot 10^{-2} + 1.53 \cdot 10^{-4} C_{PhnO}) \cdot \rho \quad (3.2)$$

where A_{570} is the intensity of the absorption band of P(V)=O group at 570 cm^{-1} , A_{2018} is the intensity of the reference band at 2018 cm^{-1} , C_{PhnO} is the concentration of oxidized phosphine (ppm), and ρ is the density of the polymer.

High performance liquid chromatography (HPLC) was applied for the analysis of the residual amount of hindered phenol in the polymer after processing. The antioxidant was separated from the polymer by a dissolution-precipitation method. 1 g of polymer was dissolved in 40 ml of toluene under refluxing using an oil bath of 140 °C followed by precipitation with 75 ml of methanol and filtering. The toluene/methanol solvent mixture was evaporated in vacuum and the residue was dissolved in a mixture of n-heptane/acetone (80/20). The chromatographic measurements were carried out using the Elite LaChrom 2000 series HPLC system including a quaternary pump, a diode array detector, a column oven and injector. The analytical column was Merck, Lichrospher 100 RP18 (250 mm x 4.6 mm ID, 5 μm particle size). The column temperature was set to 40 °C. Injection volume was 10 μl . Detection wave number was 230 nm. The gradient profile of eluents is given in Table 3.4. The EZChrom Elite program for LC system was used to acquire and process the chromatographic data.

Table 3.4

Gradient profile of eluents used for the quantitative analysis of the reactions products of DTBPP by HPLC

Time		Eluents		
(min)	Water (%)	2-propanol (%)	Acetonitrile (%)	Gradient
0-5	15	5	80	
5-18	15 → 0	5 → 30	80 → 70	linear
18-37	0	30	70	
37-39	0 → 5	30 → 5	70 → 80	linear

The rheological properties of the polymer were characterized by different methods. MFI was measured according to the ASTM D 1238-79 standard at 190 °C with 2.16 kg load using a Göttfert MPS-D MFI tester. Dynamic viscosity and creep compliance measurements were carried out using a Physica USD 200 type Universal Dynamic Spectrometer. The dynamic viscosity measurements were performed at 210 °C in the range of 0.1 – 600 s⁻¹. Creep compliance was determined at 190 °C, 500 Pa mean stress and 300 s creep/600 s recovery phase times using a Physica UDS 200 type Universal Dynamic Spectrometer. The various components of compliance were derived by Equation (3.3) in the creep phase and by Equation (3.4) in the recovery phase:

$$J_t = J_0 + J_m \left[1 - \exp\left(-\frac{t}{\lambda}\right) \right] + \frac{t}{\eta_0} \quad (3.3)$$

$$J_t = J_{\max} - J_0 - J_m \left[1 - \exp\left(-\frac{t}{\lambda}\right) \right] \quad (3.4)$$

where J_t is the creep compliance at time t , J_0 , J_m and $J_{\max}$ are the instantaneous, the viscoelastic, and the maximum compliances, respectively, λ is the mean retardation time, and η_0 is the creep viscosity. The elastic (J_e) and viscous (J_v) compliances, as well as the relative values $J_e/J_{\max}$ and $J_v/J_{\max}$ were calculated after 600 s recovery time.

The molecular mass and mass distribution of the polymer was determined by GPC at 160 °C in 1,2,4-trichlorobenzene using a PL-GPC-210 type apparatus of Polymer Laboratories. The crystalline structure of the polymer was characterized by thermal analysis. DSC measurements were carried out using a Mettler TA 3000 system. DSC traces were recorded in nitrogen atmosphere with a heating rate of 10 °C/min between room temperature and 220 °C on 5 mg samples. Subsequently the samples were cooled down with the same rate to determine crystallization characteristics and then they were heated again. Melting characteristics measured in the second run were used for analysis to eliminate possible differences in the thermal history of the samples.

The color of the samples was measured by a Hunterlab Colourquest 45/0 apparatus. Yellowness (YI) and whiteness (WI) indices were calculated as characteristic parameters. The residual stability of the stabilized samples was characterized by the oxidation induction time (OIT) measured in oxygen at 200 °C using a Perkin Elmer DSC-2

apparatus. The tensile properties were measured on dumb-bell specimens using a Zwick 1445 equipment at 50 mm gauge length and 100 mm/min cross-head speed. Tensile yield stress (σ_y) and strain (ϵ_y), as well as tensile strength (σ) and elongation-at-break (ϵ) were derived from recorded force vs. elongation traces. The mechanical strength of films was determined by two methods. The Elmendorf tear strength was measured in parallel and perpendicular directions to the flow according to the ASTM D 1922-67 standard. Dart drop tests were carried out according to the ASTM D 1709-67 and 3029-72 standards.

In the study of the stabilizing mechanism of the phosphite (DTBPP) by model experiments (Chapter 8) the thermal and thermo-oxidative stability of the antioxidant were studied using a Mettler TA 4000 Thermal Analyzer. Differential scanning calorimetric (DSC) measurements were carried out in the DSC-30 cell in nitrogen flow of 50 ml/min and in oxygen flow of 100 ml/min at a heating rate of 10 °C/min. Thermogravimetric (TGA) measurements were run in the TG-50 cell in nitrogen and oxygen flow of 100 ml/min, as well as in air without gas flow using a heating rate of 3.5 °C/min. The model experiments were carried out according to the methods summarized in Table 3.5 using a round bottom flask equipped with a magnetic stirrer, a reflux condenser and a gas inlet.

Table 3.5
Reaction conditions of the model experiments of DTBPP

Reagent		Gas	Reaction temperature (°C)	Model reaction
Type	Amount (mol/mol DTBPP)			
-	-	Ar	200	Thermal stability measurement
-	-	Ar	240	Thermal stability measurement
-	-	O ₂	200	Reaction with oxygen
-	-	O ₂	240	Reaction with oxygen
AIBN	0.78	Ar*	200	Reaction with carbon centered radicals
AIBN	0.08	O ₂	200	Reaction with peroxy radical
DCP	0.48	O ₂	200	Reaction with oxy radical
CHP	0.84	Ar	200	Reaction with hydroperoxide

* Cleaned and dried

The thermal stability of the phosphite and its reaction with molecular oxygen were investigated at 200 and 240 °C in argon and oxygen gas, respectively. 1 g of DTBPP was placed into the reaction flask purged with the corresponding gas then heated to the reaction temperature under stirring and held at this temperature for 1 min. The reaction with carbon-centered radicals was investigated by mixing 1 g of DTBPP with 0.2 g of AIBN under argon cleaned from oxygen by bubbling through pyrogallol followed by drying on CaCl₂. The reagents were mixed at ambient temperature and

purged with argon gas for 10 min before heating up to 200 °C under continuous stirring. Because of the high melting temperature of DTBPP two methods were applied: the reaction flask with the reagents was a) heated gradually up to 200 °C; b) immersed into an oil bath of 200 °C. The reaction was carried out at 200 °C for 1 min. The reaction with peroxy radicals was investigated by mixing DTBPP with 2 w/w% AIBN at ambient temperature, heating up to 200 °C in oxygen atmosphere using continuous stirring, and holding at this temperature for 1 min. The reaction with oxy radicals was studied by mixing the antioxidant with 20 w/w% DCP under oxygen, immersing the reaction flask into an oil bath of 200 °C and holding it at this temperature for 1 min under continuous stirring. DTBPP was reacted with CHP at 200 °C in argon atmosphere by dropping 430 µl CHP into 2 g of the molten antioxidant under continuous stirring. The procedure took about five minutes. After the reactions the products were cooled to ambient temperature by removing the flask from the oil bath then analyzed by Fourier Transform Infrared (FT-IR) spectroscopy without dissolution. The substance was dissolved in a mixture of n-heptane/acetone 80/20 and investigated by high performance liquid chromatography (HPLC) and HPLC coupled with a mass spectrometer (HPLC-MS). Note: besides the main product gaseous substances were also formed in each reaction carried out at high temperatures as revealed by the materials condensed in the cooler.

To analyze the reaction products of DTBPP 2-3 mg of sample was mixed with 780 mg of KBr powder then compressed to a wafer or spread onto the surface of a KBr wafer depending on its physical state. FT-IR measurements were carried out according to the method used for polymer films (see above). The characteristic group absorption bands were determined from the spectra. The P(III)-O-C group absorbs at 850 cm⁻¹, the P(V)-O-C group at 966 cm⁻¹, the (C)O-H vibration appears in the range of 3500-3100 cm⁻¹, while the (P)O-H vibration have two broad bands at 2700-2600 cm⁻¹ and 2300-2100 cm⁻¹ [133]. The HPLC-MS measurements of DTBPP and its reaction products were carried out using a Perkin Elmer 200 series HPLC system equipped with a binary pump, a UV-VIS detector, a column oven and an autosampler. The experiments were carried out by gradient method on a Merck Lichrospher 100 RP18 (250 mm x 4.6 mm ID, 5 µm particle size) analytical column at 40 °C with an injection volume of 10 µl and flow rate of 1 ml/min. The gradient profile of eluents is given in Table 3.6. The chromatograms were recorded at 230 nm. Mass spectrometric measurements were performed on an Applied Biosystems 3200 QTrap tandem mass spectrometer equipped with a Turbo V ion source in positive Atmospheric Pressure Chemical Ionization (APCI) mode. A needle current of 4 µA and evaporation temperature of 500 °C were applied. Tandem mass spectrometry (MS/MS) was used for the identification of the chemical structure of the reaction products.

The HPLC measurements were done using the Elite LaChrom 2000 system. The same analytical column and experimental conditions were applied as used for the HPLC-MS measurements except for the eluents. The conditions of the HPLC measurements are described above and the method is given in Table 3.4. External calibration was done with both DTBPP and DTBPPO.

Table 3.6

Gradient profile of eluents used for the qualitative analysis of the reactions products of DTBPP by HPLC-MS

Time (min)	Eluents		
	2-propanol (%)	Acetonitrile (%)	Gradient
0-5	10	90	
5-10	10 → 40	90 → 60	linear
10-20	40	60	
20-22	40 → 90	60 → 10	linear
22-23	90	10	
23-25	90 → 10	10 → 90	linear
25-30	10	90	

Chapter 4

Dominating reactions in the degradation of HDPE during long term ageing in water

4.1. Introduction

As described in Chapter 2.3, the efficient stabilization of polyethylene pipes raises many questions. The hydrolytic stability of antioxidants and its possible effect on the lifetime of products brought into contact with extractive media were investigated in the framework of a larger project at the Joint Laboratory. To understand the processes taking place during storage of HDPE in water, first we focused our attention on changes in the properties of the neat polymer. In the subsequent sections first we present our observations, possible explanations, supporting evidence, and finally an analysis of the chemical reactions, which may lead to the observed changes.

4.2. Observations

The effect of storage in water was studied on polyethylene samples extruded 1, 3 and 6 times, compression molded to plates then stored in closed glass containers in distilled water at 80 °C for 1 year (for details see Chapter 3). Changes in the mass of the specimens are plotted against soaking time in Fig. 4.1. All samples absorb some water, which is rather strange and difficult to explain. Moreover, the polymer extruded once exhibits a maximum in its mass as a function of time. Polyethylene is completely apolar, water does not dissolve in or enter into any kind of interaction with it. Moreover, water molecules form H-bridges with each other, thus their affinity towards PE must be very low. Two other samples have larger mass than the rest, the one extruded 3 times and soaked for 3 months, as well as the polymer extruded 6 times and stored for 9 months in distilled water. These points are indicated by circles in this and in all subsequent figures. Although we have difficulties in explaining the maximum in the mass of the polymer extruded once, the latter two points can be regarded only as deviations resulting from experimental error. Rather interestingly, a similar maximum was observed in the MFI of the soaked samples (Fig. 4.2). This is even more surprising, since in multiple extrusion experiments routinely used for the evaluation of additive packages the MFI of Phillips polyethylene practically always decreases with increasing number of extrusions. A decrease in viscosity is observed very rarely. We may assume that chain scission reactions dominate under the conditions of soaking, but the small MFI, which was observed at longer soaking times (see 9 and 12 months), is extremely strange. Nevertheless, the changes in the two properties discussed in this paragraph seem to be in accordance with each other, even if we cannot explain them.

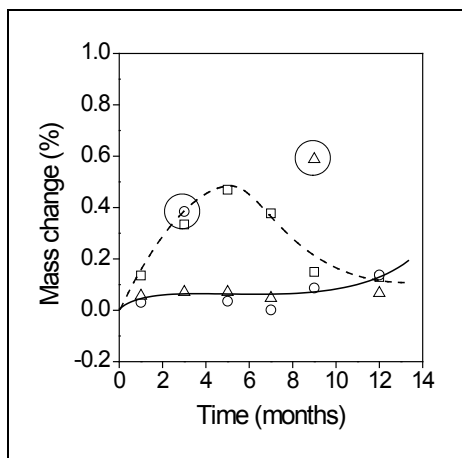


Figure 4.1 Mass increase during the soaking of Phillips HDPE in distilled water; (□) 1, (○) 3, (△) 6 extrusions. Symbols in circles indicate deviating points.

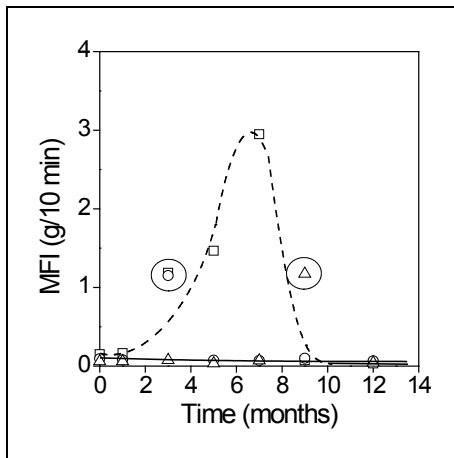


Figure 4.2 Changes in the MFI of neat HDPE during soaking in distilled water at 80 °C; (□) 1, (○) 3, (△) 6 extrusions.

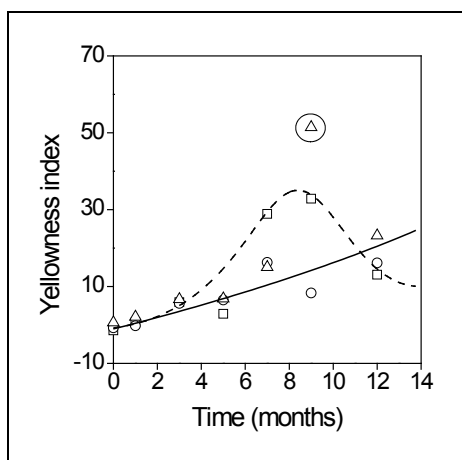


Figure 4.3 Maximum in the color of the polymer extruded once developing during soaking in water. See the lack of extreme at larger number of extrusions; (□) 1, (○) 3, (△) 6 extrusions.

Although much less pronounced, but a maximum appears also in the time dependence of the color of the neat polymer extruded once (Fig. 4.3). The change in color indicates the occurrence of chemical reactions during soaking. These reactions must result in the change of molecular mass and other properties as well. Such reactions are usually initiated by oxygen at weak sites on the polymer chain [6]. Samples extruded once and several times might have different chemical structures, the former containing a larger number of weak sites. We know that PE powder adsorbs more oxygen than granules [43] and that in the first extrusion different reactions take place than during the rest of the processing steps [35, 134]. Such weak sites can be oxygen containing groups other than carbonyl, like hydroperoxides or ethers. These weak sites react; probably decompose already in the second extrusion, thus the structure of the polymer changes and its stability increases.

Some properties change in the opposite direction with time. The molecular mass of the samples slightly decreases generally, but a very pronounced minimum appears in the molecular mass of PE extruded once (Fig. 4.4). Although not shown in Fig. 4.4, but we must note here that deviating points can be observed occasionally also in the time dependence of the molecular mass of samples extruded 3 or 6 times similarly to the change of mass, MFI or color (see Figs. 4.1–4.3). As shown in Fig. 4.5, a very strong minimum appears also in tensile yield stress, and the same tendency appears in other tensile properties as well. The standard deviation of the determination of mechanical properties is significant, thus the identification of deviating points is rather difficult in Fig. 4.5. Nevertheless we can safely claim that the small yield stress values of the samples extruded 3 times and soaked for 3 months as well as that of the one extruded 6 time and stored for 9 month strongly deviate from the general tendency and might be regarded as deviating points.

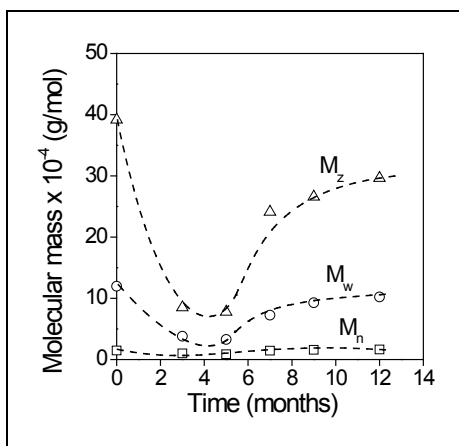


Figure 4.4 Changes in the molecular mass of the polymer as a function of soaking time. The sample was extruded once. ($\square$) M_n , ($\circ$) M_w , (Δ) M_z .

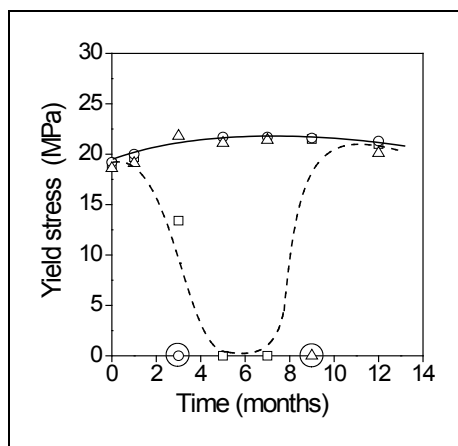


Figure 4.5 Effect of processing history and storage time on the tensile yield stress of HDPE soaked in distilled water; ($\square$) 1, ($\circ$) 3, (Δ) 6 extrusions.

4.3. Questions, hypothesis

The results presented in the previous section (see Figs. 4.1–4.5) seem to agree completely with each other. Two common features can be observed in the time dependence of practically all properties: extremes can be observed in the characteristics of samples extruded once, while the properties of samples with a longer processing history (3 and 6 extrusions) change much moderately, but a few deviating points can be observed practically always. Although the change in mass is totally unexpected, the increase in MFI might be explained by chain scission, which is supported by the decrease in molecular mass and the deterioration of mechanical properties. Since the existence of

minimums and maximums is deduced only from a few points, they also might be deviating points, the result of erroneous measurements. We cannot decide on this issue without the repetition of experiments, which is impossible to do because of the length of the study.

Although we might ignore the contradictory nature of some of the changes, a completely clear and concise explanation cannot be given for the observations presented in the previous section. These contradictions and the difficulties in understanding some of the phenomena, like the maximum in water absorption, raise several basic questions. These must be answered in order to find a plausible explanation. Through a more thorough consideration of the results, possible processes and correlations, as well as a result of a detailed analysis, the following main questions emerged:

- Do the extremes observed in some properties represent real tendencies or the corresponding values are the result of erroneous measurement?
- Does the polymer extruded once behave differently from those processed several times? In the case of a positive answer, what is the reason for the difference?
- What are the dominating processes taking place during the soaking of the neat polyethylene?
- What are the most important reactions occurring and how does the molecular structure of the polymer change as a result?
- Is there any correlation between these changes, the structure of the polymer and the properties of PE?
- If the assumed tendency does not exist, what is the reason for the deviating values?

The key to finding a plausible and coherent explanation lays in answering the first question correctly. The existence of the extremes and the different behavior of the polymer extruded once and several times, respectively, seem to be the most important questions. Depending on a positive or negative answer, respectively, two explanations or hypotheses may be developed:

- a) During the first processing step the polymer develops weak sites, mostly oxygen containing groups, which decompose during storage leading to increased MFI. Since the water contains limited amount of oxygen, alkyl radicals form later, chain extension occurs leading to increased molecular mass and strength [33-35]. Samples extruded several times do not behave this way, because the more severe processing history destroys most of the weak sites.
- b) The extremes do not exist, but they are the apparent result of deviating points similarly to those occurring at larger number of extrusions. These values result from conditions different from those prevailing in the majority of the containers. Chemical reactions occur during storage, but changes in structure and properties are continuous. Properties are determined by the chain structure of the polymer.

Because of the length of the study, the experiments cannot be repeated very easily. The questions presented above can be answered and the hypotheses verified only through the thorough analysis of the results. The most important considerations of this analysis are presented in the following section.

4.4. Analysis, verification

If the first hypothesis is valid and the extremes observed in properties really exist, they must result from changes in the chain structure of the polymer. The most important reaction of Phillips polyethylenes is the addition of alkyl radicals to the chain-end vinyl groups resulting in long chain branches [34-36]. Naturally, different reaction or reactions may dominate under the conditions of storage in water. However, if extremes exist in properties, similar extremes must appear on the time dependence of functional groups as well. However, the vinylidene group content of the polymer decreases continuously with time (Fig. 4.6) and the same tendency can be observed also for vinyl and *trans*-vinylene groups. Extremes cannot be observed in the correlation and the only common feature with other properties is the existence of some deviating points. The changes in the chemical structure of the chains do not seem to support the first hypothesis.

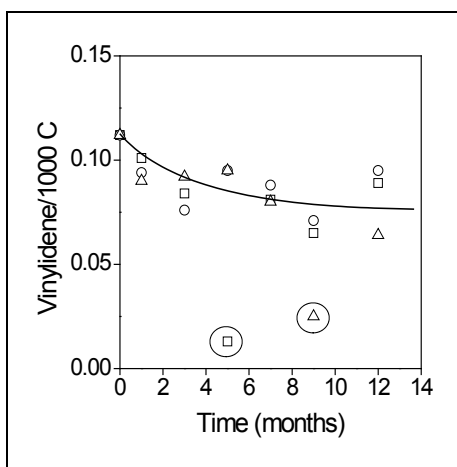


Figure 4.6 Dependence of the vinylidene group content of neat HDPE on the number of extrusions and storage time; (□) 1, (○) 3, (△) 6 extrusions.

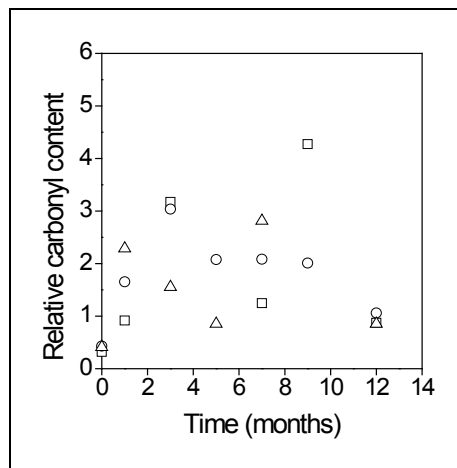


Figure 4.7 Lack of any tendency in the carbonyl content of HDPE stored in water on the time of soaking or on processing history; (□) 1, (○) 3, (△) 6 extrusions.

A crucial element of the first hypothesis is the formation of oxygen containing groups other than carbonyls and their decomposition or transformation. This should explain the extremes in properties after the first processing step and all changes as a function of time and processing history. According to the hypothesis, the amount of oxygen containing groups should show a maximum as a function of soaking time at least for samples extruded once. Fig. 4.7 does not agree with this assumption, no tendency can be observed in carbonyl content as a function of time. We may argue naturally that chain scission is caused by peroxides and hydroperoxides and not by carbonyls,

but our attempt to prove the effect of such compounds failed completely. Oxygen containing groups play an important role in other parts of the hypothesis as well. They are supposed to explain the increase in the mass of the samples and the maximum in it. However, no correlation whatsoever can be found between mass change and carbonyl content (not shown). These observations further strengthen the lingering doubt that the different behavior of the polymer after the first extrusion, as well as the extremes in properties might result from irregular storage conditions and not from the consumption of oxygen and the “healing process” described in the first hypothesis.

On the other hand, we found very strong correlations among practically all functional groups measured in the polymer. A few are presented in the following figures. Vinylidene content is plotted against the number of vinyl groups in Fig. 4.8. The correlation is very close and similar correlations can be found among other unsaturated groups as well, even if the relationship is not always that close. It is even more surprising that a close correlation exists between the vinyl and methyl group content of the polymer (Fig. 4.9). In multiple extrusion experiments methyl content usually does not change much, while during the storage in water it covers a relatively wider range.

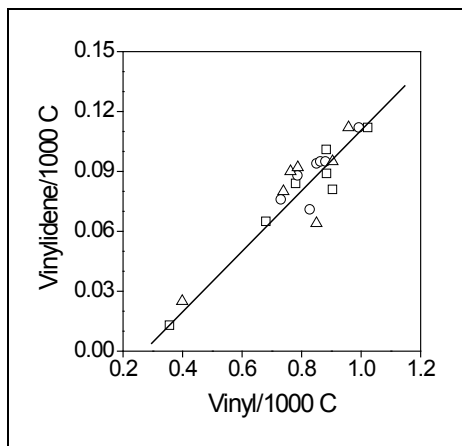


Figure 4.8 Close correlation between the vinyl and vinylidene content of HDPE stored in water for various length of times; ($\square$) 1, ($\circ$) 3, (Δ) 6 extrusions.

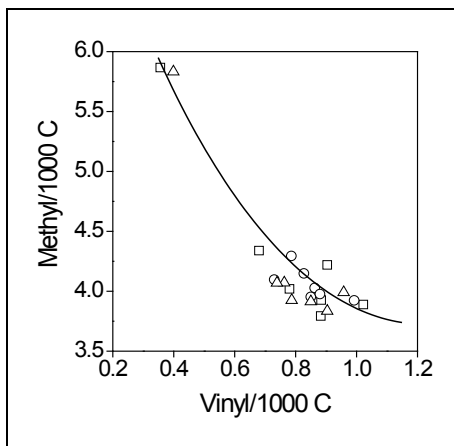


Figure 4.9 Correlation between the methyl and vinyl content of neat polyethylene stored in distilled water at 80 °C; ($\square$) 1, ($\circ$) 3, (Δ) 6 extrusions.

The very close correlation of Fig. 4.10 between the vinyl content of the polymer and the relative concentration of carbonyls is also rather astonishing especially if we consider Fig. 4.7 and the large scatter of the points in it. One might say that the correlation is so close because the two deviating points at small vinyl content dominate it. However, as the inset in the figure shows, the function remains the same even when those two points are omitted and the correlation is presented in the narrower range where most of the values are located.

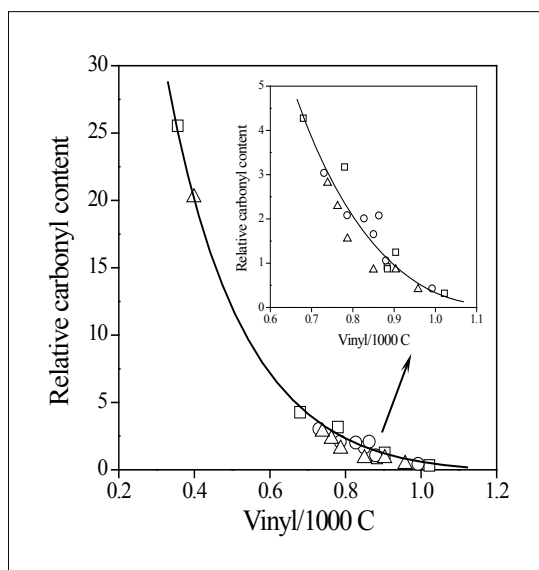


Figure 4.10 Strong relationship between the vinyl and carbonyl content of HDPE independently of the number of extrusions and storage time; ($\square$) 1, ($\circ$) 3, (Δ) 6 extrusions. The inset shows the right hand side of the correlation in larger magnification to prove its general validity.

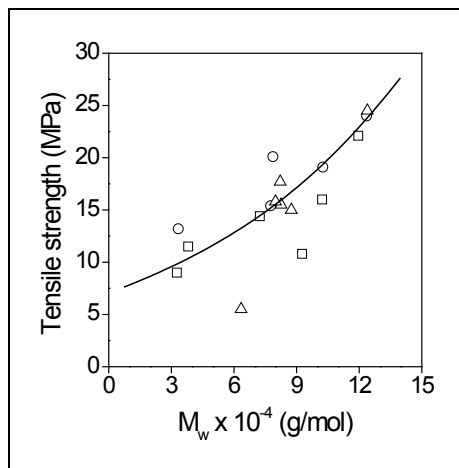


Figure 4.11 Structure-property correlations in neat HDPE stored in distilled water for various lengths of time; ($\square$) 1, ($\circ$) 3, (Δ) 6 extrusions.

These correlations unambiguously prove that most chemical reactions are related to each other and one or two reactions dominate all changes in structure and properties. Carbonyls seem to play an important role in the processes taking place during the soaking of the samples, indeed. The chemical changes determine all properties including molecular mass, crystalline structure, rheological and mechanical properties. The relation of properties to structure is proved by the close correlations between molecular mass and the heat of fusion (not shown), as well as between molecular mass and tensile properties. The latter is presented in Fig. 4.11. Although the scatter of the points is relatively large, especially if we compare it to that seen in Fig. 4.10, the tendency is clear.

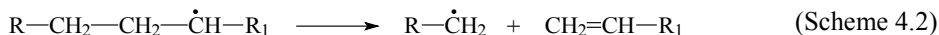
We must take into consideration here also the relatively large standard deviation of the determination of both properties.

4.5. Dominating reactions

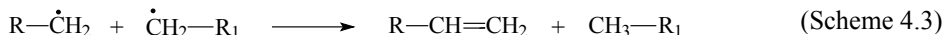
The correlations presented in the previous section prove unambiguously that most chemical reactions, or more exactly the changes in most functional groups, are related to each other. However, it is rather difficult to define the reactions, which actually take place during storage. An enormous number of reactions are proposed in the literature [2,135] and we can easily support any changes or just the opposite with them. We present here a few schemes and try to select those, which might be in accordance with our results. We may assume that if oxygen is present, it is involved in the initiation of degradation [e.g., 136,137]:



Peroxide radicals may decompose, abstract hydrogen from chains, add to unsaturated groups or take part in a number of reactions. The alkyl radical is also very reactive. It can decompose with the formation of unsaturated groups [3,5,7]:

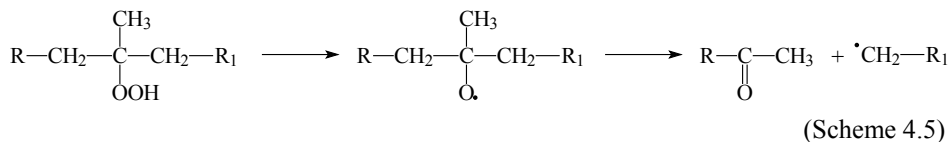
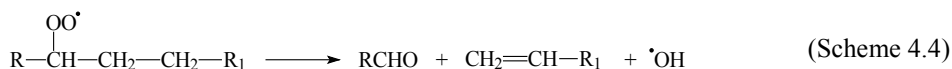


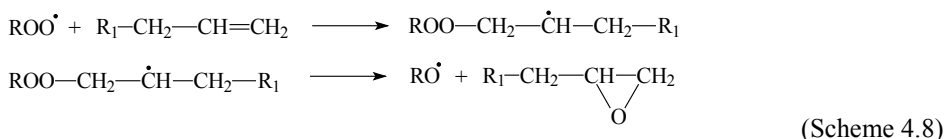
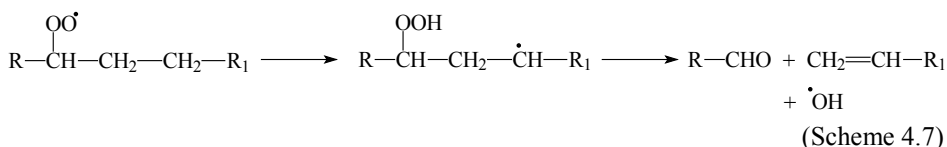
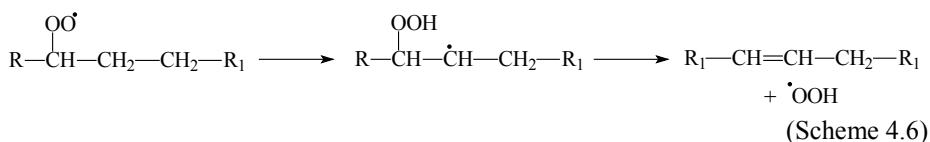
or it can react with another alkyl radical by disproportionation resulting in the formation of vinyl groups:



One of the most important reactions of the alkyl radical is the addition to unsaturated groups, mainly to vinyl groups, that leads to long chain branching [34-37]. However, alkyl radicals react preferentially with oxygen, if this latter is present.

Peroxides and hydroperoxides formed in the reaction of alkyl radicals and oxygen take part in numerous reactions leading to the formation of alcohols, carbonyls and unsaturated groups. Many reactions have been proposed in the literature and only a few of them are presented here:





However, if we investigate these reactions more closely we must conclude that most of them cannot take place under our conditions or cannot be the dominating one. Only reactions or combination of reactions can be accepted, which simultaneously satisfy the following conditions:

- decrease in the number of all unsaturated functional groups,
- increase of methyl content,
- increase of carbonyl content.

Both of the reactions presented for the alkyl radicals (Schemes 4.2 and 4.3) lead to the formation of double bonds. In the soaking experiments all unsaturations are consumed throughout the soaking period (see e.g. Fig. 4.6), while the number of methyl groups slightly increases. Several reaction schemes are proposed, which predict the increase of methyl groups, but most of them do not include the consumption of unsaturations and/or do not lead to the increase of carbonyl groups [3,5,6]. In view of these observations, the only reaction, which we can accept, is the addition of the radical to double bonds leading to its consumption. We supported the first hypothesis and explained the “healing” effect with this reaction [35-37,134].

The dominating reaction of alkoxy radicals is intermolecular hydrogen abstraction [138]. Most of these reactions lead to the formation of unsaturated, as well as carbonyl or other oxygen containing groups. Messey et al. [139] deduced from their XPS study on LDPE samples soaked in water that chain scission did not take place under their conditions, which clearly contradicts our results. These must be also rejected because of two reasons: the number of unsaturated groups decreases, on the one hand, and the concentration of unsaturated and carbonyl groups changes in the opposite direction, on the other. The only reactions, which satisfy these criteria, are the last two reactions (Scheme 4.8). The only problem with those reactions is the formation of an epoxy group, which is not very stable. Naturally, it can further react or oxidize to aldehyde or other carboxyl derivatives.

The last reaction scheme is strongly supported also by Fig. 4.10, in which carbonyl content is plotted against the vinyl group concentration of the polymer. We must

call attention here to the fact, that not a single deviating point is seen in the correlation, but neither in the other figures correlating various functional groups with each other. Moreover, values obtained for the polymer, which was extruded once also fit the correlation perfectly. Based on this close correlation and on the complete lack of deviating points, we must come to the conclusion that extremes in properties do not exist and the polymer extruded once does not behave differently from the rest of the samples.

After a thorough evaluation and reevaluation of the experimental data, as well as taking into consideration all the aspects of the experiments we may draw several conclusions. We can definitely state that the dominating chemical reaction is the oxidation of the polymer, which is accompanied by chain scission and the formation of carbonyl groups. Oxidation proceeds mainly through unsaturations and especially through vinyl groups. This reaction leads to a close correlation of most of the functional groups measured including methyl, unsaturated and carbonyl groups. Changes in properties are determined by the modification of chain structure, properties are closely related and the correlations can be explained unambiguously. The extremes observed in properties, as well as other deviating points result from irregular experimental conditions. The tightness of the seal on the containers, consequently the amount of oxygen present may have changed as well as other conditions, like the amount of water, temperature, etc. could have varied leading to different extent of oxidation, changes in chain structure and properties.

4.6. Conclusions

All reactions taking place during the storage of HDPE in distilled water are related to each other; the correlation of all functional groups formed in them is surprisingly close. The amount of oxygen present determines the direction of reactions; larger oxygen content leads to chain scission, to an increase of methyl content, and to the formation of carbonyl groups. Most of these reactions go through double bonds, their number decreases during storage. In spite of the large number of reactions proposed in the literature, only one or two dominating reactions determine changes in the chain structure of the polymer and thus the properties of the final product. Any variation in the conditions of storage is reflected in the properties of the polymer. Stabilizers used under extractive conditions must be stable against hydrolysis and should trap oxygen centered radicals.

Chapter 5

Melt stabilization efficiency of phosphorous antioxidants in polyethylene

5.1. Introduction

According to the literature sources [34,140,141] the processing stabilizing efficiency of phenolic primary antioxidant/phosphorous secondary antioxidant stabilizer packages depends on the type, amount and ratio of the additives, as well as on the type of the polymer and the processing conditions. Owing to the numerous concurrent and competitive reactions occurring during the processing of polyethylenes, which are affected by all these parameters, the individual reaction steps are not known and the efficiency of the different additive packages cannot be predicted exactly. Although a few dominating reactions may exist as shown in the previous chapter, there are not known either. As a consequence, the aim of the present work was the study of the melt stabilizing efficiency and reaction mechanism of different phosphorous compounds in polyethylene. The effect of a phosphite, a phosphonite and a phosphine secondary antioxidant on the processing stability of the Tipelin FB 472 grade Phillips type polyethylene was compared in the presence of a hindered phenol primary antioxidant. The oxidation of the phosphorous compounds was followed by FT-IR spectroscopy, and changes in polymer properties were related to the consumption of the secondary antioxidant.

5.2. Effect of processing

Three phosphorous antioxidants were studied by multiple extrusions in the concentration of 700 ppm in the presence of 700 ppm hindered phenolic antioxidant. The type and chemical structure of the antioxidants, as well as the conditions of sample preparation are given in Chapter 3. The extent of oxidation of the phosphorous antioxidants during the extrusion of polyethylene was determined after each processing step. The IR absorption intensity of the trivalent P-O bands of the phosphite and the phosphonite was compared with the pentavalent P-O absorption. Linear correlation was established for both compounds, as shown in Fig. 5.1, where the relative absorption intensities measured at 850 and 966 cm^{-1} for the phosphite are plotted. Changes in the concentration of P(III) compounds as a function of the number of extrusions reveal (Fig. 5.2) that the processes taking place in the first step differ from those in subsequent extrusions. The major part of the phosphonite is consumed, and a significant amount, about 40 %, of the other two additives also reacts already in the first processing step. The consumption of the phosphorous antioxidants is much slower in further processing operations, and proceeds with different rates for the phosphonite, and for the phosphite and phosphine, respectively.

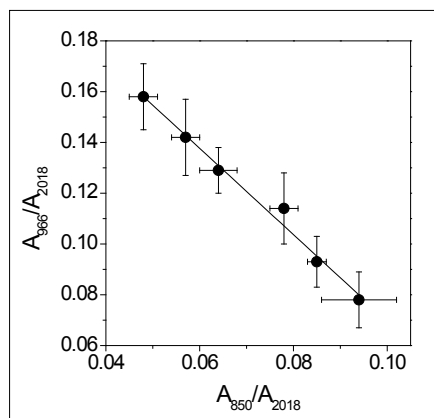


Figure 5.1 Correlation between changes in the P(III)-O-C (850 cm^{-1}) and P(V)-C-O (965 cm^{-1}) relative absorption bands of phosphite.

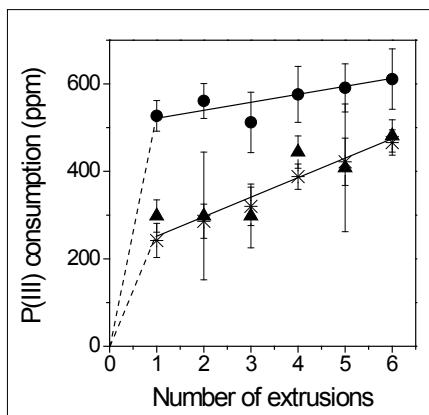


Figure 5.2 Changes in the residual amount of P(III) compound (• phosphonite, * phosphite, ▲ phosphine) in polyethylene as an effect of multiple extrusions.

In addition, the chemical structure of the polymer changes more significantly in the first extrusion than in the subsequent processes, and the modification of the structure is much affected by the type of the phosphorous compound added. Methyl group concentration decreases in the presence of the phosphite and the phosphonite during the extrusion of the polymer powder then remains essentially constant in further processing operations (Figure 5.3). In the presence of phosphine no change can be observed in the methyl content of the polymer.

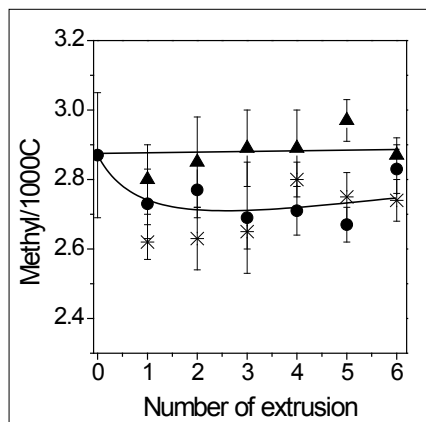


Figure 5.3 Changes in the methyl group content of polyethylene as an effect of multiple extrusions in the presence of different phosphorous stabilisers (• phosphonite, * phosphite, ▲ phosphine).

The number of vinyl groups decreases even more significantly in the first processing step than the content. 1.5 vinyl/1000C concentration of the nascent polymer powder drops to the values of 1.03 – 1.05 vinyl/1000C depending on the type of phosphorous stabilizer (Figure 5.4). The decrease is the largest in the presence of the phosphonite and the smallest with the phosphite. In further processing operations the change in vinyl content is more moderate and its extent is affected strongly by the type of the phosphorous secondary antioxidant (Figure 5.4). The phosphine hinders most effectively the decrease and the changes are the most extensive in the presence of the phosphite.

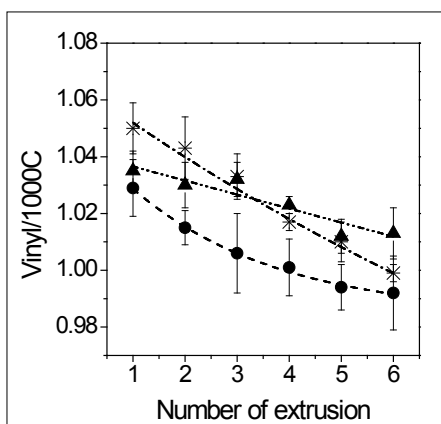


Figure 5.4 Changes in the vinyl group content of polyethylene as an effect of multiple extrusions in the presence of different phosphorous stabilisers (● phosphonite, * phosphite, ▲ phosphine).

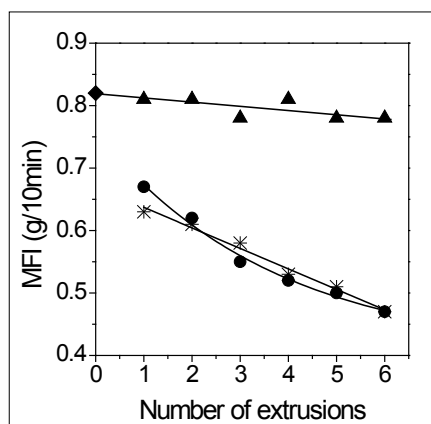


Figure 5.5 Changes in the melt flow index of polyethylene as an effect of multiple extrusions in the presence of different phosphorous stabilisers (● phosphonite, * phosphite, ▲ phosphine).

Modification of the chemical structure is accompanied by changes in the polymer properties. Viscosity increases, gradual discoloration occurs and residual thermo-oxidative stability decreases with the increasing number of extrusions. All these changes depend strongly on the type of the phosphorous secondary antioxidant indicating different chemical reactions of the polymer during processing. With increasing number of extrusions the melt flow index decreases (Figure 5.5) which is in accordance with the increase in low frequency viscosity. The MFI of the nascent polymer powder mixed with 4000 ppm BHT to achieve maximum stabilization is 0.82 g/10min, which is maintained close to constant over the six consecutive extrusions when the polymer is stabilized with 700 ppm Irganox 1010 and 700 ppm phosphine.

Under these conditions the phosphonite and the phosphite are found to be less efficient melt stabilizers, in their presence the MFI decreases considerably in the first extrusion.

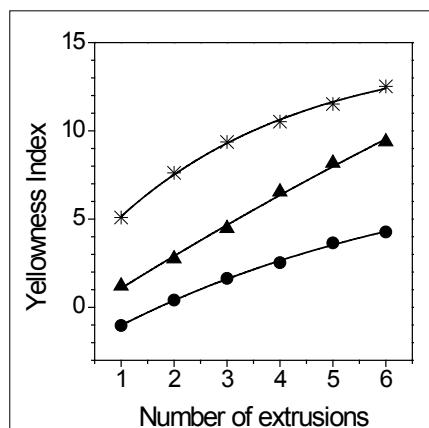


Figure 5.6 Colour changes of polyethylene as an effect of multiple extrusions in the presence of a hindered phenol and a phosphorous stabiliser (● phosphonite, * phosphite, ▲ phosphine).

Although the MFI (and the low frequency complex viscosity) shows similar changes for these phosphorous additives, some differences can be observed. In the first extrusion MFI decreases and viscosity increases to a greater extent with the phosphite than with the phosphonite but after the second extrusion this order is reversed.

In the course of polyethylene processing the efficiency in color retention does not correspond to the order of the melt stabilizing efficiency of phosphorous antioxidants. As shown in Figure 5.6, the phosphonite protects most efficiently the color of the polymer and surpasses the color stabilizing efficiency of the phosphine, and especially that of the phosphite. These results confirm that different chemical reactions occur during the processing of polyethylene in the presence of various phosphorous compounds.

5.3. Antioxidant consumption and polymer properties

The dissimilarity of the mechanism and/or the rate of chemical reactions taking place during the processing of polyethylene in the presence of various phosphorous compounds is confirmed by comparing the changes in polymer properties with the consumption of the secondary antioxidant. As can be seen in Figure 5.7, the correlation between the concentration of vinyl groups and residual P(III) compounds is similar for the phosphite and the phosphine but different for the phosphonite. The three phosphorous compounds also affect differently the rheological properties of the polymer (Figure 5.8). MFI and low frequency complex viscosity do not change with the consumption of the phosphine. This additive is an extremely efficient melt stabilizer even at as low concentrations as 200 ppm. Comparing the performance of the phosphonite and the phosphite we find a stronger melt stabilizing efficiency for the former than for the latter. The concentration of the phosphonite, however, decreases to a critical level already in the first extrusion, which may result in a fast decrease of MFI in subsequent processing operations. Therefore, this effect should be taken into account while developing formulations in order to achieve satisfactory processing stabilization also under extreme conditions.

The color retention of the polymer changes also dissimilarly with the consumption of the three phosphorous stabilizers. The yellowness index is plotted against the amount of residual P(III) compound in Figure 5.9. The color stabilizing efficiency of the phosphonite is satisfactory even below its critical concentration, while the phosphite does not protect the polymer from discoloration even at large residual P(III) contents.

When the residual oxidative stability (OIT) of the polymer is plotted against the remaining amount of P(III) compounds (Figure 5.10), rather good correlation can be observed between the two quantities indicating that OIT is independent of the type of phosphorous compound. Considering that the effect of the various phosphorous stabilizers are compared in the same polymer in the presence of the same primary antioxidant, this result could indicate similar stabilizing efficiency for the investigated phosphite, phosphonite and phosphine in oxygen rich environment.

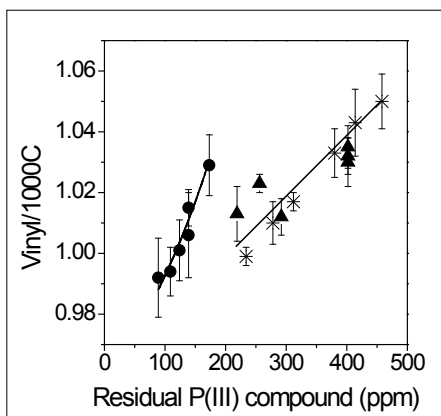


Figure 5.7 Correlation between the concentration of residual P(III) compounds (• phosphonite, * phosphite, ▲ phosphine) and the vinyl content of polyethylene.

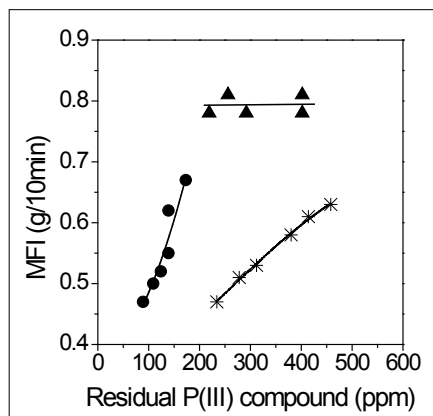


Figure 5.8 Correlation between the concentration of residual P(III) compounds (• phosphonite, * phosphite, ▲ phosphine) and the melt flow index of polyethylene.

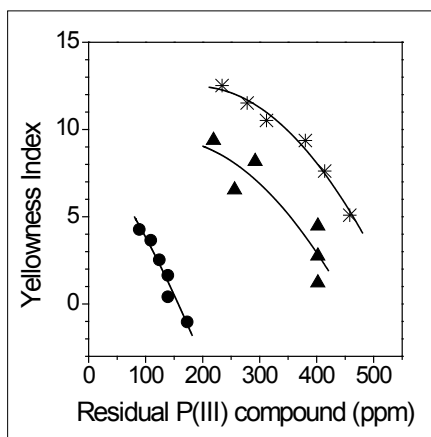


Figure 5.9 Correlation between the concentration of residual P(III) compounds (• phosphonite, * phosphite, ▲ phosphine) and the discoloration of polyethylene.

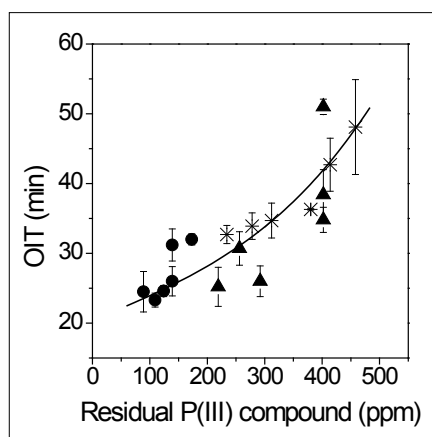


Figure 5.10 Correlation between the concentration of residual P(III) compounds (• phosphonite, * phosphite, ▲ phosphine) and the oxidation induction time of polyethylene.

5.4. Discussion

The results of the present study confirm the earlier conclusions that the degradation and stabilization reactions taking place in the first extrusion differ from those occurring in the subsequent processing of ethylene/1-hexene copolymers [134]. The chemical structure of the polymer undergoes the most significant change during the processing of the nascent polymer powder and further processing operations cause less modification both in the chemical structure and the properties.

While the stabilization mechanism of phosphites, phosphonites and phosphines is described quite similarly in the literature [2,54,71,73,74,82,85,94,103, 142-147], their reactions result in different changes in the chemical structure and properties of polyethylene during processing. The main effect of phosphorous compounds is explained by the decomposition of hydroperoxides and peroxides, as well as reactions with alkoxy and alkyl radicals. Similar effect was observed for the three phosphorous compounds only in pure oxygen atmosphere (OIT measurements), where the formation of these reactive groups is ensured. The processing of polyethylene by extrusion, however, takes place in oxygen poor environment where the formation of reactive oxygen-containing groups is limited. The reactions are shifted towards the formation of alkyl radicals, which results in the recombination of macroradicals and the formation of long chain branches in the absence of stabilizers [e.g. 34,37,148,149]. The results of our experiments show that under these conditions the chemical structure of phosphorous compounds strongly affects the direction of the reactions. The investigated alkyl-aryl phosphine hinders most efficiently the recombination of alkyl radicals during processing (indicated by the stability of the rheological properties) in spite that the concentration of vinyl groups decreases (Figure 5.11). The reaction of this latter is assumed to lead to the formation of long chain branches in an additive free polymer [34,37]. The two other phosphorous antioxidants hinder the recombination of macroradicals less efficiently but even they do not act in the same way.

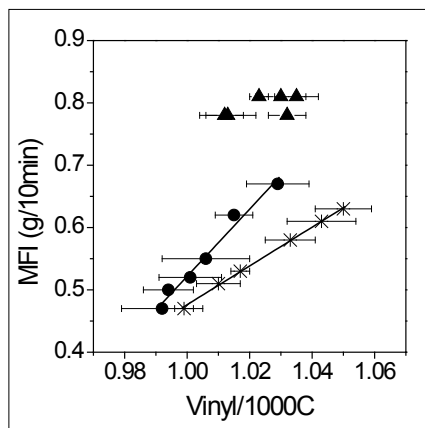


Figure 5.11 Correlation between the vinyl content and the melt flow index of polyethylene stabilised with various phosphorous compounds (● phosphonite, * phosphite, ▲ phosphine).

Close correlation exists between MFI and the vinyl concentration of the polymer, but the same decrease in MFI is accompanied by larger changes in the vinyl content in the presence of the phosphite than with the phosphonite (Figure 5.11). Although aryl phosphites are expected to act also as primary antioxidants [71], the performance of the phosphite was the poorest among the

three phosphorous compounds studied in the present work. The linear correlation between the concentration of the P(III) and P(V) compounds (Figure 5.1) indicates that the substitution reaction (2.44b) does not play a significant role in the stabilisation reactions of the phosphite in the processing of polyethylene.

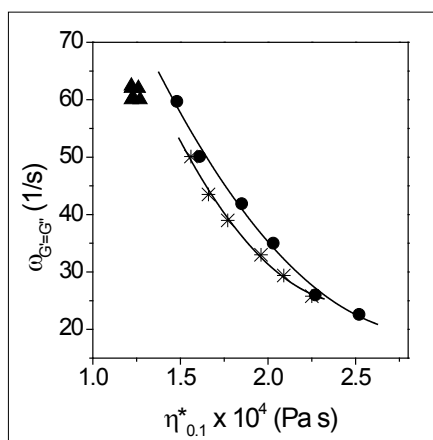


Figure 5.12 Correlation between the low frequency complex viscosity and the crossover frequency of polyethylene stabilised with different phosphorous compounds (● phosphonite, * phosphite, ▲ phosphine).

ity, crossover frequency, and Ostwald – de Waele power law index is similar to that observed for MFI, comparison of the different rheological parameters reveals further deviations. Figure 5.12 shows that the complex viscosity measured at low frequency ($\eta^*_{0.1}$) and the crossover frequency ($\omega_{G'=G''}$) do not follow the same correlation pattern. In the presence of the phosphine the viscosity of the polymer is the lowest and $\omega_{G'=G''}$ the highest, and neither of these parameters change noticeably upon the effect of multiple extrusions. In the case of the two other antioxidants $\omega_{G'=G''}$ decreases with increasing $\eta^*_{0.1}$ but lower crossover frequencies belong to the same complex viscosities in the presence of the phosphonite than with the phosphite, which may originate from different number of LCB and/or molecular mass distributions. All these comparisons prove that under the processing conditions (high temperature, shear and low oxygen content) the chemical structure of the phosphorous additives strongly affects the direction and rate of chemical reactions.

Color retention is the best in the presence of phosphonite. This performance was observed earlier and it was assumed that the phosphonite or its reaction products interacts with the phenolic antioxidant or its derivatives [112], since the discoloration of the polymer is caused mainly by the latter. The phosphite proved to be the least effective color stabilizer. Considering the possibility of interactions between the additives and/or

According to the literature, the rheological properties of the polymer are related to the formation of long chain branches (LCB) in polyethylene [e.g. 150-155]. Vega *et al.* [156] claim that branch position and architecture along the main polymer chain are the main factors controlling rheology. According to some other sources [150,155,157] the crossover frequency of storage (G') and loss (G'') moduli of PE is determined by its molecular mass distribution and by the number of LCB. An increase in these parameters decreases the crossover frequency, as well as the corresponding modulus. The rheological properties of PE stabilized with the three phosphorous stabilizers were compared in order to analyze the formation of LCB during multiple extrusions. Although the variation in the effect of the three additives on the low frequency viscos-

their reaction products, we can assume that steric effects also influence the color stabilizing efficiency of phosphorous antioxidants.

5.5 Conclusions

The processing stabilizing efficiency of an aryl phosphite, an aryl phosphonite and an alkyl-aryl phosphine antioxidant was compared in Tipelin FB 472 grade Phillips type polyethylene in the presence of the same phenolic antioxidant. The polymer containing 700 ppm hindered phenol and 700 ppm phosphorous additives was processed by six consecutive extrusions and samples were taken after each processing step. A FT-IR spectroscopic method was developed for quantitative analysis of the non-reacted P(III) molecules in PE. Functional group content (methyl, unsaturated, oxygen containing), rheological properties, color, and residual thermo-oxidative stability of the polymer were determined and compared with the amount of the P(III) compound remained in the polymer after processing.

The results proved that the stabilizing efficiency of phosphorous secondary antioxidants studied depends on their chemical structure, as well as on the type and concentration of reactive groups and macroradicals formed from the polymer. Under the processing conditions, where chemical reactions are initiated by heat, shear and low concentration of oxygen, the direction and rate of reactions are strongly affected by the chemical structure of the phosphorous compound. The alkyl-aryl phosphine investigated has the best melt stabilizing efficiency by preventing the recombination of macroradicals. On the other hand, in oxygen atmosphere, where the formation of oxygen-containing groups dominates, the three different phosphorous antioxidants showed similar efficiency yielding OIT values which depend only on the concentration of the efficient P(III) molecule and are independent from its type. The phosphonite studied protects the most effectively the polymer from discoloration, which may be explained by the interaction of the additives and/or their transformation products.

Chapter 6

The role of phenolic and phosphorous antioxidants in the melt stabilization of polyethylene

6.1. Introduction

The results of the studies described in the previous chapter showed that the processing stabilizing efficiency of phenol/phosphorous antioxidant packages depends significantly on the chemical structure of the phosphorous molecule and also on the characteristics of the polymer in question. In the present work the role of the individual components of phenolic/phosphorous antioxidant combinations was studied in the processing stabilization of polyethylene. The Tipelin FA 381 grade Phillips type polyethylene was processed by multiple degradative extrusions in the absence and the presence of a phenolic antioxidant. Three different phosphorous stabilizers were used alone as single additives, as well as in combinations with the phenol. The properties of the polymer and the films produced from it were characterized by different methods. The effect of the chemical structure of the antioxidant on the characteristics of the polymer was analyzed in detail.

6.2. Effect of single antioxidants

The additives were added to the polymer alone as single stabilizers in an amount of 700 ppm. The additive-free polyethylene was also investigated for comparison. The multiple extrusions of the polymer result in essential changes in its chemical structure. The results indicate that the chemical reactions occurring in the first extrusion, which are affected significantly by the antioxidants, play a determining role in the further reactions of the polymer during subsequent processing steps. Although the entire amount of 700 ppm of the phosphorous compounds is consumed already in the first extrusion revealed by the FT-IR spectra, the characteristics of the polymer stabilized with various antioxidants change differently in further extrusions. This is demonstrated well by Figure 6.1 where the methyl group content is plotted as a function of the number of extrusions. Apart from the polymer stabilized with the phosphite, the number of the methyl groups goes through a maximum as a function of the number of extrusions. In the presence of the phosphite the methyl content decreases in the first extrusion and remains essentially the same in the further processes. The number of other functional groups changes differently during multiple processing. The number of vinyl groups decreases as a function of the number of extrusions and the most significant change occurs in the first processing step (Figure 6.2), similarly to the results presented in

Chapter 5. After the first extrusion, the vinyl group content of the samples containing the various additives does not differ significantly from each other, but the differences among them increases with increasing number of extrusions. After the sixth extrusion, the largest vinyl group content is measured in the samples processed with the phosphonite and the phosphine, while the smallest one in the polymer stabilized with the phosphite.

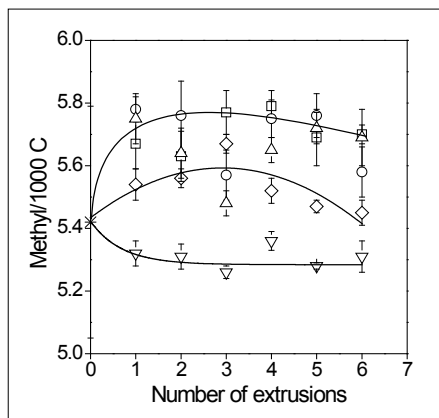


Figure 6.1 Changes in the methyl group content of polyethylene as a function of the number of extrusions. Samples: nascent polymer powder (*); processed without any antioxidant (□), with 700 ppm phenolic antioxidant (◇), 700 ppm phosphite (▽), 700 ppm phosphonite (○), 700 ppm phosphine (Δ).

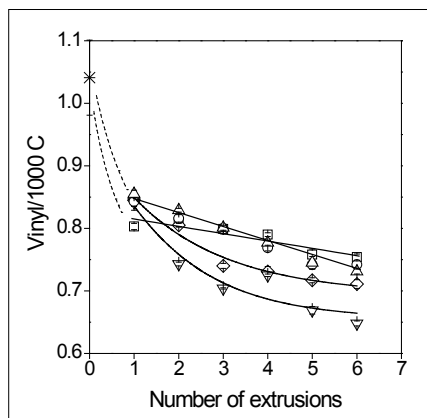


Figure 6.2 Changes in the vinyl group content of polyethylene as a function of the number of extrusions. Samples: nascent polymer powder (*); processed without any antioxidant (□), with 700 ppm phenolic antioxidant (◇), 700 ppm phosphite (▽), 700 ppm phosphonite (○), 700 ppm phosphine (Δ).

The polymer oxidizes during processing. The largest number of carbonyl groups forms in the first extrusion, especially in the additive-free polymer (Figure 6.3). In further processing steps the number of carbonyl groups increases only moderately. It is remarkable that carbonyl groups are not detected in the polymer stabilized with the phosphonite after the first extrusion, their concentration increases almost linearly with the number of processing steps from the second extrusion, and reaches the smallest value among the investigated samples even after the sixth extrusion. The carbonyl content of the polymer stabilized with the phenolic antioxidant is larger than in the case of single phosphorous antioxidants, but the carbonyl groups of the antioxidant itself may bias the results of the measurements. The comparison of the effect of the three phosphorous stabilizers shows that the largest carbonyl content is measured in the polymer processed with the phosphine.

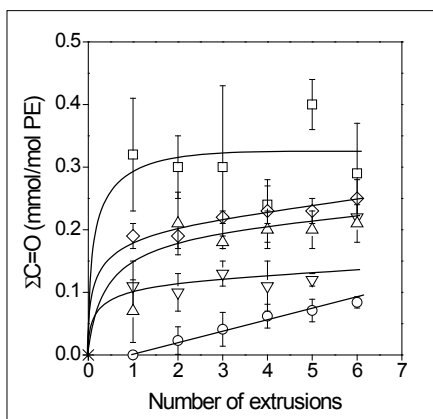


Figure 6.3 Changes in the carbonyl group concentration of polyethylene as a function of the number of extrusions. Symbols are the same as in Figure 6.1.

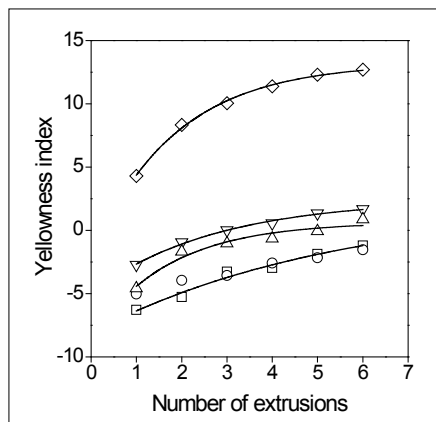


Figure 6.4 Changes in the yellowness index of polyethylene as a function of the number of extrusions. Symbols are the same as in Figure 6.1.

The discoloration of the polymer is characterized by the yellowness index (YI) and the results are presented in Figure 6.4. As expected, the additive-free polymer discolors only slightly and gradually with increasing number of processing steps, and the sample stabilized with the phenolic antioxidant has the strongest color. Figure 6.4 reveals that the reaction products of the phosphonite do not discolor the polymer, while those of the two other phosphorous antioxidants increase YI significantly, especially the derivatives of the phosphite.

The MFI of the polymer decreases continuously with increasing number of extrusions both in the absence and in the presence of antioxidants, as shown in Figure 6.5. The MFI of the additive-free polymer drops from 0.44 g/10 min to 0.15 g/10 min after the first extrusion, then the change slows down with the increase in the number of extrusions. 700 ppm of the phenolic antioxidant does not protect the polymer from degradative chemical reactions in the first extrusion; MFI decreases by a value of 0.23 g/10 min. In the further processing steps the change slows down. The phosphorous antioxidants stabilize the polymer melt more efficiently in the first extrusion than the hindered phenol. The phosphite is the least effective melt stabilizer among them. The phosphine shows the best performance not only in the first, but also in the second extrusion. However, in further processing steps, the MFI of the sample stabilized with the phosphine decreases drastically with processing history indicating that the reaction products of this additive catalyze recombination reactions under the conditions of the melt flow index measurement. Similar conclusions can be drawn from the creep compliance measurements about the melt stabilizing efficiency of the various antioxidants as from the changes in the MFI values.

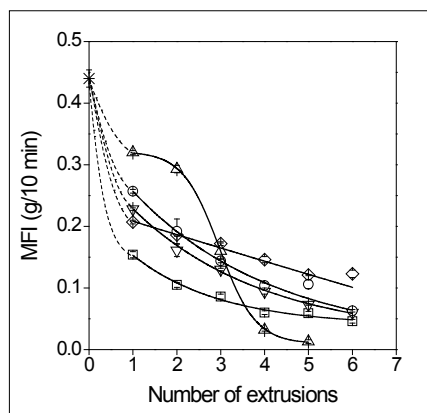


Figure 6.5 Changes in the melt flow index of polyethylene plotted as a function of the number of extrusions. Symbols correspond to those in Figure 6.1.

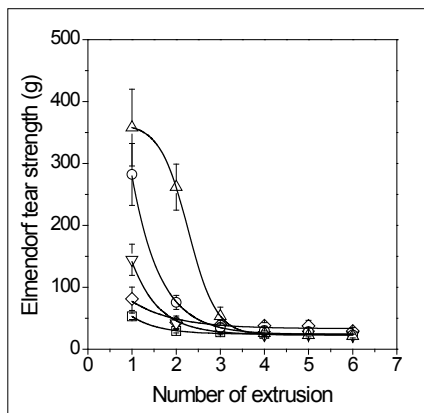


Figure 6.6 Changes in the Elmendorf tear strength measured perpendicularly to the direction of flow as a function of the number of extrusions. Symbols are the same as in Figure 6.1.

The strength of the films blown from the pellets also decreases with increasing number of extrusions and depends on the type of antioxidant used for stabilization. The Elmendorf tear strength measured in perpendicular direction to the flow (Figure 6.6) is very low already after the first extrusion when the polymer is processed without any antioxidant. The phenolic antioxidant improves the strength of the film insignificantly, while the presence of the phosphorous antioxidants is much more beneficial. The phosphonite and especially the phosphine preserve film strength more significantly than the phosphite. After the second extrusion, the strength of the film stabilized with the phosphine is only slightly smaller than its original strength. The perpendicular Elmendorf tear strength drops to the low value of the other films only after the third extrusion. Since the Elmendorf tear strength measured in perpendicular direction is extremely sensitive to long chain branching [36,158], these results indicate that the phosphorous antioxidants hinder considerably all reactions leading to the increase of molecular mass (revealed by the decrease in MFI) including the formation of long chain branches.

The results of these experiments clearly prove that the chemical reactions occurring in the first extrusion of polyethylene determine the properties of the polymer going through several processing operations (pelletizing, shaping, reprocessing). Phosphorous stabilizers can hinder recombination reactions leading to the increase of molecular mass and long chain branching, while the phenolic antioxidant is completely inefficient in this respect.

6.3. Combined effect of phenolic and phosphorous antioxidants

The contribution of the phenolic antioxidant to the performance of phosphorous compounds is discussed in this part. The effect of the combination of 700 ppm hindered phenol and 700 ppm phosphorous antioxidant on the properties of polymer and on the consumption of stabilizer is compared to that of the corresponding phosphorous stabilizer used alone in 700 ppm.

In the presence of the phenolic antioxidant the consumption of phosphorous stabilizers decreases during the processing of the polymer, as shown by Figure 6.7. The phenolic antioxidant reduces considerably the consumption rate of the phosphine. Only 100 ppm of phosphine oxidizes in the first extrusion when it is combined with the hindered phenol and 155 ppm of the stabilizer remains unchanged even after the sixth extrusion. The other two phosphorous stabilizers oxidize much faster. The phosphonite is consumed the most rapidly.

The change in the methyl group content of the polymer is basically not affected by the addition of the phenolic antioxidant to the phosphonite and the phosphine. The methyl group content of the polymer increases in the presence of the combination of the hindered phenol and the phosphite similarly to that of the sample stabilized with 700 ppm single phenolic antioxidant. The vinyl group content also changes the most significantly in the sample stabilized with the phosphite. As shown in Figure 6.8, in which the effect of single phosphorous antioxidants and two-component antioxidant compositions are compared to each other, the vinyl content of the polymer increases considerably after each processing step when hindered phenol is added to the phosphite. This result indicates that the phenol modifies the stabilization reactions of the phosphite, while does not affect those of the phosphonite and the phosphine shown by the same change in vinyl group content in the first extrusion both in the presence and absence of the phenol. The hindered phenol has a positive effect in further extrusion steps, especially in the presence of the phosphine. The vinyl group concentration of polyethylene stabilized with the phenol/phosphine antioxidant combination does not decrease significantly during multiple extrusions. On the other hand, the presence of the hindered phenol affects only slightly the vinyl content in the sample containing the phosphonite. These results indicate that the vinyl group content of the polymer must correlate with the residual amount of phosphorous

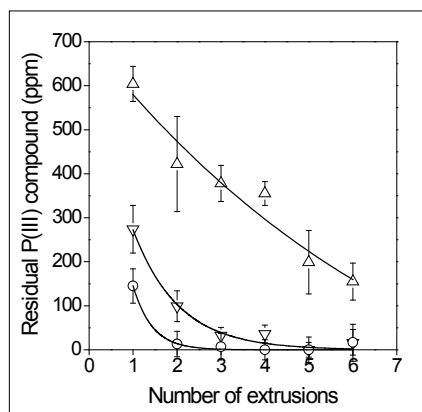


Figure 6.7 Consumption of phosphorous antioxidants in polyethylene stabilised with 700 ppm hindered phenol and 700 ppm phosphorous antioxidant plotted as a function of the number of extrusions. Phosphorous stabilisers: phosphite (∇), phosphonite ($\circ$), phosphine (Δ).

stabilizer. Figure 6.9 confirms this assumption by revealing that the considerable decrease in vinyl content results from the loss of the secondary antioxidant. Note that vinyl content is larger in the polymer stabilized with the phosphite than in the presence of the phosphine at the same residual amount of phosphorous antioxidant.

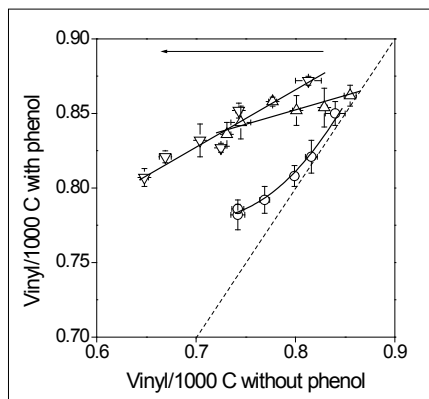


Figure 6.8 Effect of addition of phenolic antioxidant to the phosphorous stabiliser on the vinyl group concentrations of polyethylene processed by six consecutive extrusions. Symbols are the same as in Figure 6.7. The arrow indicates increasing number of extrusions.

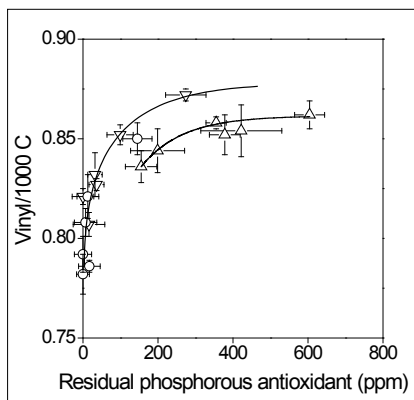


Figure 6.9 Correlation between the residual amount of phosphorous antioxidant and the vinyl group content of polyethylene stabilised with phenol/phosphorous antioxidant combinations and processed by six consecutive extrusions. Symbols are the same as in Figure 6.7.

The results presented above indicate that the main role of the phenolic antioxidant is reducing the consumption rate of phosphorous stabilizers in the multiple processing operations. The hindered phenol used does not modify significantly the melt stabilization reactions of the phosphonite and the phosphine, but it affects those of the phosphite, besides reducing its consumption rate. This conclusion is confirmed by the changes in the rheological properties of the polymer and in the mechanical strength of the films. The correlation between the MFI of the polymer stabilized with single phosphorous antioxidants and two-component antioxidant combinations is shown in Figure 6.10 for demonstration. The MFI of the polymer measured after the first extrusion is determined primarily by the type of the phosphorous antioxidant and does not depend significantly on the presence or the absence of the phenolic antioxidant. The MFI of the polymer stabilized with phenol/phosphine combinations does not change in further extrusion steps, while it decreases in the presence of the phosphonite and the phosphite, but in a smaller extent than without the hindered phenol. The Elmendorf tear strength of the films measured in perpendicular direction to the flow (Figure 6.11) changes in a similar way with two exceptions: 1) The strength of the polymer stabilized with the phosphonite and the phosphine does not differ significantly after the first extrusion; 2) The Elmendorf tear strength of the polymer stabilized with the phosphite is larger in the

presence of the phenolic antioxidant than without it, and it is much smaller than might be expected on the basis of the MFI.

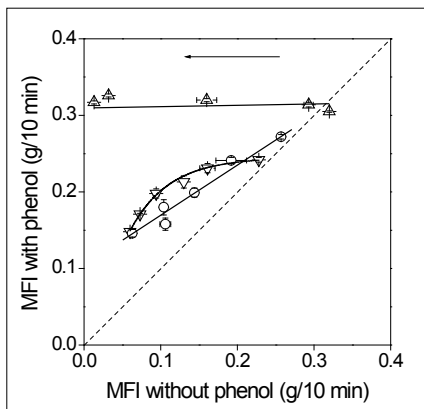


Figure 6.10 Effect of additive combinations on the melt flow index of polyethylene processed by six consecutive extrusions. Symbols are the same as in Figure 6.7. The arrow indicates increasing number of extrusions.

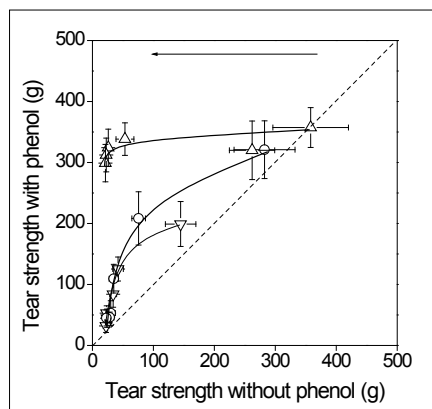


Figure 6.11 Effect of additive combinations on the Elmendorf tear strength measured in perpendicular direction processed by six consecutive extrusions. Symbols are the same as in Figure 6.7. The arrow indicates increasing number of extrusions.

As expected, the addition of the phenolic antioxidant to the phosphorous stabilizers increases the discoloration of the polymer (not shown). The effect depends both on the chemical composition of the phosphorous antioxidant and the number of extrusions. With increasing number of processing steps the yellowness index increases more in the polymer stabilized with two-component stabilizer packages than without the phenolic antioxidant. The least change in color is observed in the phosphine-containing polymer. The yellowness index of the polymer stabilized with the phenol/phosphite combination is stronger after each processing step than in the case of the phenolic antioxidant used alone. This means that the phosphite does not reduce the discoloring effect of the phenolic antioxidant, but contributes to color development.

It is an accepted fact that primarily the phenolic antioxidant determines the thermo-oxidative stability of polyethylene. Accordingly, the residual stability increases considerably when the phosphorous antioxidants are combined with the hindered phenol. However, the effect of the phosphorous compounds cannot be neglected either, as they can enhance the efficiency of the hindered phenol. Figure 6.12 shows the OIT values of the polymer stabilized with two-component antioxidant systems as a function of the number of extrusions. Obviously, the combination of the hindered phenol and the phosphine has a strong synergetic effect on the residual thermo-oxidative stability of the polymer.

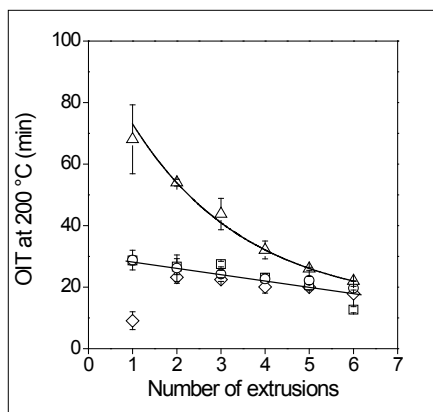


Figure 6.12 Changes in the residual thermo-oxidative stability of polyethylene as a function of the number of extrusions. Stabilisers: 700 ppm phenolic antioxidant (◇), two-component antioxidant compositions of 700 ppm phenolic antioxidant with 700 ppm phosphite (▽), phosphonite (○) and phosphine (Δ).

The results obtained on antioxidant combinations unambiguously prove that phosphorous antioxidants play a major role in the melt stabilization of polyethylene. Their efficiency depends primarily on their chemical structure. The consumption of phosphorous stabilizers during processing is decreased in the presence of the phenolic antioxidant. The hindered phenol used does not change the stabilization mechanism of the phosphonite and the phosphine, but it modifies the reactions of the phosphite. The phosphonite and the phosphine decrease the discoloring effect of the phenolic antioxidant, but the phosphite increases it. The phosphine is not only an excellent melt stabilizer, but it also enhances the thermo-oxidative stabilizing efficiency of the phenolic antioxidant.

6.4. Discussion

As it was described in detail in the previous chapters, during the processing of polyethylene many different chemical reactions take place simultaneously. Alkyl radicals form as an effect of heat and shear, which react rapidly with oxygen present in small concentrations and yield reactive peroxy and oxy radicals. The reactions are affected strongly by the amount of oxygen, the processing conditions and the additives present. The polymer powder contains more oxygen than the pellets resulting in fast oxidation of polyethylene in the first extrusion step (Figure 6.3), which is followed by a much slower increase in carbonyl content during further processing. The comparison of the effect of the different phosphorous stabilizers used alone in polyethylene proves that the chemical reactions occurring during the first extrusion of the polymer powder determines the changes in chain structure in further processing steps. Although the phosphorous antioxidants are consumed completely in the first extrusion step, significant differences can be observed in the properties of the polymer extruded several times.

The unsaturated groups of the polymer, especially the vinyl groups, considerably influence the direction and the extent of the chemical reactions of polyethylene. Chain scission and extension processes compete during processing. The reactions of the vinyl groups with alkyl radicals result in the formation of long chain branches [33,36,158]. The number of vinyl groups may decrease also by isomerization reactions of the double bond, which lead to the formation of *trans*-vinylene groups [3,5-7,29]. The chemical reactions of polyethylene do not only consume, but also produce vinyl groups. The

scission of hydroperoxides, alkyl and peroxy macroradicals, as well as the disproportionation of alkyl radicals can lead to an increase in the concentration of vinyl groups [3,5-7,135].

The reactions of the vinyl groups leading to the extension of the polymer chains and the formation of long chain branches predominate during the processing of Phillips type polyethylenes [3,5-7]. This is confirmed by the correlation between the vinyl group content and the rheological characteristics of the polymer. With decreasing vinyl content the melt flow index and the viscous compliance decrease, while the creep (low shear) viscosity increases, though the relationships are affected also by the chemical structure of the antioxidants used. Figure 6.13 shows the correlation between the vinyl group content and the creep viscosity (η_0) of the polymer as an example. The creep viscosity of the polymer stabilized with the phosphonite and the phosphine either as a single antioxidant or in combination with the hindered phenol changes similarly and depends only on the number of vinyl groups. This correlation confirms again that the phenolic antioxidant does not modify the stabilization mechanism of the phosphonite and the phosphine. The behavior of the phosphite is different. At the same vinyl content the viscosity of the polymer processed with the phosphite alone is smaller than that of the polymer stabilized with the other two phosphorous antioxidants; the addition of phenolic antioxidant to the phosphite changes the correlation between the vinyl content and η_0 . The polymer stabilized with the phenol/phosphite combination has larger viscosity at the same vinyl content than those containing the phosphonite or the phosphine.

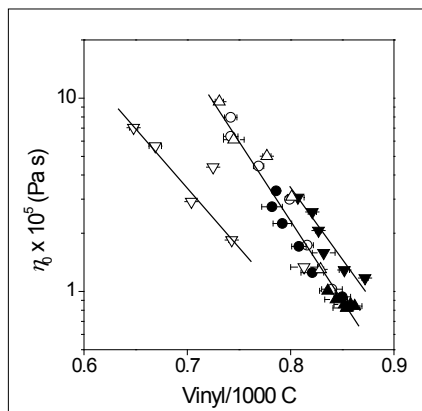


Figure 6.13 Correlation between the vinyl group content and the creep viscosity of polyethylene processed without any antioxidant ($\square$); with 700 ppm phenolic antioxidant ($\diamond$); 700 ppm phosphorous antioxidant: phosphite (∇), phosphonite ($\circ$), phosphine (Δ); combinations of 700 ppm phenolic antioxidant with 700 ppm phosphite ($\blacktriangledown$), phosphonite ($\bullet$), phosphine ($\blacktriangle$).

The inferior melt stabilizing efficiency of the phosphite is shown also by the correlation between the vinyl group content of the polymer and the Elmendorf tear strength of the film measured in the perpendicular direction, as shown in Figure 6.14. The strength, which is sensitive to long chain branching [36,158], is large when vinyl group content is large and decrease steeply with decreasing number of vinyl groups down to a value, at which no further change occurs. Above 0.8 vinyl/1000 C, the perpendicular tear strength of the films stabilized with the phosphonite and the phosphine are much larger than those processed with the phosphite. Changes in the perpendicular tear strength of the films with processing history and composition confirm that the phenolic antioxidant

itself cannot hinder the reactions of vinyl groups leading to long chain branching, while the phosphonite or the phosphine are themselves effective melt stabilizers. The reduction in film strength results from the consumption of these antioxidants.

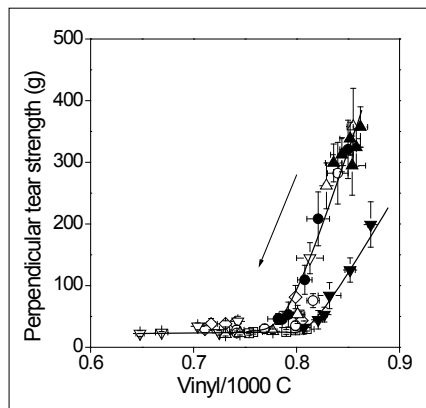


Figure 6.14 Correlation between the vinyl group content of polyethylene and the Elmendorf tear strength of films measured in the perpendicular direction. Symbols are the same as in Figure 6.13. The arrow indicates increasing number of extrusions.

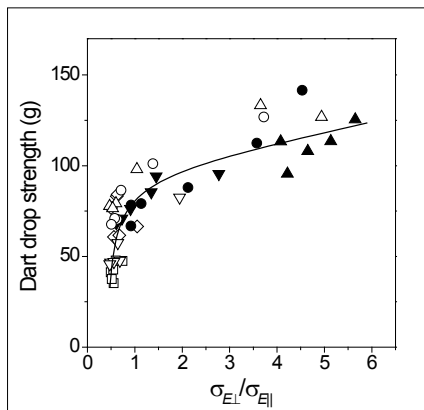


Figure 6.15 Correlation between the ratio of the perpendicular and parallel Elmendorf tear strength values and the Dart drop strength of films. Symbols are the same as in Figure 6.13.

The Dart drop strength of the films is also controlled by the chemical structure of the polymer but is less sensitive to long chain branching than the perpendicular Elmendorf tear strength. The correlation shown in Figure 6.15 reveals that the Dart drop strength decreases moderately with decreasing ratio of the Elmendorf tear strengths measured in perpendicular and parallel directions ($\sigma_{E\perp}/\sigma_{E\parallel}$) down to the value of 1. The Dart drop strength starts to decrease steeply when the Elmendorf tear strength measured in parallel direction to the flow equals to or exceeds that measured in perpendicular direction ($\sigma_{E\perp}/\sigma_{E\parallel} \leq 1$).

The discoloration of the polymer is also related directly to the reactions of the vinyl groups and is affected by the antioxidants used for stabilization. Yellowness index increases linearly with the decrease in vinyl group content. The phosphonite and the phosphine reduce considerably the inherent discoloring effect of the phenolic antioxidant at high vinyl contents, while the phosphite enhances it. It was shown earlier [112] that in a two-component antioxidant system the high color stabilizing efficiency of the phosphonite is caused mainly by specific interactions developing among the reaction products of the two antioxidants. The discoloring effect of the phosphite is attributed to compounds forming in side-reactions [87], which are claimed to improve the thermo-oxidative stability of the polymer [83,87], but in fact this claim is not proved by the results of our OIT measurements (see Figure 6.12).

All these results prove that the direction and rate of the reactions of vinyl groups during processing control the properties of polyethylene. The decrease in the concentration of vinyl groups is accompanied by significant changes in the structure and characteristics of the polymer including the strength of films produced from it. The polymer discolors gradually, its viscosity increases, and the strength of the film decreases with decreasing number of vinyl groups. Antioxidants affect these reactions strongly.

6.5. Conclusions

Phosphorous stabilizers determine the rheological properties of polyethylene and the strength of films produced from it even when they are used alone without a phenolic antioxidant. The properties of the polymer processed by multiple extrusions are affected significantly by the reactions taking place in the first extrusion even after the total consumption of the phosphorous stabilizer. In two-component antioxidant packages, the main role of the phenolic antioxidant is to decrease the oxidation rate of the phosphorous compound. The hindered phenol does not change the stabilization mechanism of the phosphonite and the phosphine, but changes the reactions of the phosphite. Phosphorous antioxidants prevent better the reactions of vinyl groups leading to the increase of molecular mass than the phenolic antioxidant. The efficiency of the phosphorous stabilizer depends on its chemical structure. The changes in the characteristics of the polymer during processing are directly related to the decrease in the number of vinyl groups. The most efficient melt stabilizer is the phosphine and the least efficient one is the phosphite. If we accept that the Elmendorf tear strength measured in perpendicular direction depends mostly on long chain branching, we can conclude that less branches form in the presence of the phosphine and the phosphonite than with the phosphite. The phenolic antioxidant prevents the long chain branching of the polymer during processing only in a very small extent. The discoloration of the polymer caused mainly by quinoidal derivatives of the phenolic antioxidant is reduced by the phosphonite and the phosphine, but it is enhanced by the phosphite. Although the reaction derivatives of the phosphite might be expected to increase the thermo-oxidative stability of the polymer, the results of this study do not prove that. The combination of the phenolic antioxidant and the phosphine studied results in a synergistic improvement of the thermo-oxidative stability of the polymer.

Chapter 7

Correlation between additive consumption during polyethylene processing and polymer properties

7.1. Introduction

To explore the melt stabilizing mechanism of different antioxidants the effect of stabilizer consumption during the processing of polyethylene on the properties of the polymer was studied in the present work. The Tipelin FA 381 grade Phillips type polyethylene was stabilized with antioxidant packages consisting of different amounts of phosphorous stabilizers combined with 700 ppm hindered phenol. The amounts of the phosphorous stabilizers (Table 7.1) were selected on the basis of the results described in Chapters 5 and 6.

Table 7.1
Antioxidant compositions investigated

Sample No.	Additive amount (ppm)			
	Hindered phenol	Phosphite	Phosphonite	Phosphine
S1	-	-	-	-
S2	700	-	-	-
S3	-	700	-	-
S4	700	350	-	-
S5	700	700	-	-
S6	700	1050	-	-
S7	700	1400	-	-
S8	700	1750	-	-
S9	-	-	700	-
S10	700	-	700	-
S11	700	-	1050	-
S12	700	-	1400	-
S13	700	-	1750	-
S14	700	-	2100	-
S15	-	-	-	700
S16	700	-	-	100
S17	700	-	-	200
S18	700	-	-	350
S19	700	-	-	700
S20	700	-	-	1050

The polymer was processed by multiple extrusions; sample was taken and film was blown from the pellets after each extrusion step. The consumption of the phosphorous and the phenolic antioxidants was compared to the various characteristics of the polymer and their effect in the stabilization process was analyzed.

7.2. Consumption of the phosphorous stabilizer

The effect of the consumption of the phosphorous antioxidants used in combinations with the hindered phenol on the characteristics of the polymer is presented in this section. Their residual concentration measured in the polymer after each extrusion step is listed in Table 7.2. The table shows that the rate of consumption of phosphorous stabilizers depends on their chemical structure and initial concentration, as well as on the number of extrusions. The phosphonite is consumed the most rapidly, while the smallest amount reacts from the phosphine that agrees with the observations described in the previous chapters. The consumption of the phosphite and the phosphonite increases with their initial concentration in the first extrusion, while from the phosphine only about 100 ppm is oxidized independently from the amount mixed to the polymer. The phosphite and phosphonite are consumed completely in six consecutive extrusions in the concentration ranges investigated, while only a maximum amount of about 550 ppm reacts from the phosphine.

The chemical characteristics and the molecular mass of the nascent polymer powder change significantly in the first processing step. Polydispersity increases, carbonyl groups form and the concentration of vinyl groups drops from 1.04 to 0.85-0.9 vinyl/1000 C depending on the antioxidant system. In further extrusions the number of carbonyl groups increases only slightly and that of the vinyl groups decreases (Fig. 7.1) only moderately until the concentration of phosphorous antioxidants is not reduced to a critical value of about 100-200 ppm. The difference in the behavior of the polymer during the first and the subsequent extrusions can be attributed to smaller amount of oxygen adsorbed by the pellets compared to the polymer powder having larger surface and porous structure [43]. Below the critical concentration of the phosphorous antioxidant the vinyl group concentration decreases significantly with increasing number of extrusions.

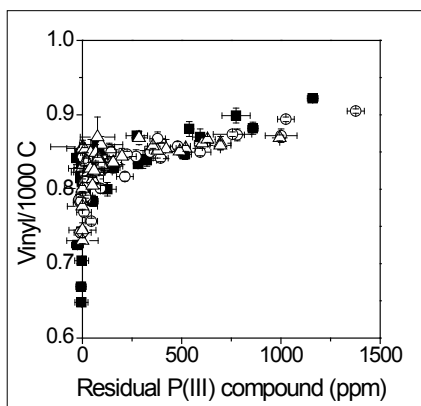


Figure 7.1 Correlation between the residual amount of phosphorous antioxidant and the vinyl group content of polyethylene stabilized with combinations of 700 ppm hindered phenol and various amounts of phosphite (■), phosphonite (○) and phosphine (△), processed by multiple extrusions at 260 °C.

Table 7.2

Residual amount of phosphorous stabilizers in the FS 381 grade Phillips type polyethylene processed by six consecutive extrusions at 260 °C in the presence of 700 ppm phenolic antioxidant

Phosphorous antioxidant added (ppm)	Residual amount of phosphorous antioxidants in polyethylene (ppm)																	
	Phosphite after extrusion No.						Phosphonite after extrusion No.						Phosphine after extrusion No.					
	1	2	3	4	5	6	1	2	3	4	5	6	1	2	3	4	5	6
100													0	0	0	0	0	0
200													94	96	106	98	53	51
350	70	30	0	0	0	0							285	67	76	79	40	59
700	270	99	32	36	0	0	140	0	0	0	0	0	604	422	378	355	199	155
1050	538	325	157	47	0	0	360	78	0	0	0	0	994	696	695	630	520	490
1400	774	593	305	143	52	0	630	270	117	32	0	0						
1750	1160	859	517	280	128	52	875	401	225	99	0	0						
2100							1190	593	394	214	91	45						

The performance of the polymer stabilized with the phosphite deviates somewhat from that processed with the phosphonite and the phosphine. The number of vinyl groups is slightly larger at high residual concentrations and decreases more intensely with the consumption of the phosphite than in the case of the other two stabilizers.

The rheological characteristics of the polymer are affected by both the type and the concentration of the phosphorous antioxidants. The creep viscosity (η_0) is plotted as a function of the residual concentration of the phosphorous stabilizers in Fig. 7.2. The η_0 values of the polymer stabilized with the phosphonite and the phosphine are similar and do not depend on their residual concentration above ~ 200 ppm; they start to increase only below that value. The viscosity of the polymer stabilized with the phosphite is larger and increases continuously with the consumption of the additive. Similarly, MFI, the HLMI/MFI ratio and the viscous component of creep compliance (J_v) are independent of the residual concentration of the phosphonite and phosphine above ~ 200 ppm, but change continuously with decreasing phosphite content: MFI and J_v decrease, while the HLMI/MFI ratio increases.

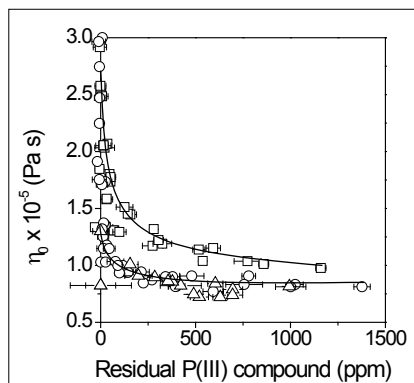


Figure 7.2 Correlation between the residual amount of phosphorous antioxidant and the creep viscosity of polyethylene stabilized with combinations of 700 ppm hindered phenol and various amounts of phosphite ($\square$), phosphonite ($\circ$) and phosphine (Δ), processed by multiple extrusions at 260 °C.

These results prove that the rheological properties of the polymer are controlled by the amount of phosphorous antioxidant in the first place, but depend also on its chemical structure. The melt stabilizing efficiency of the phosphonite and the phosphine are similar. The difference is in their consumption rate (Table 7.2). The phosphite hinders the recombination reactions of macroradicals less efficiently even at high residual concentrations.

The correlation between the residual concentration of phosphorous antioxidants and the Elmendorf tear strength of the films measured in perpendicular direction to the flow (Fig. 7.3) indicates that the phosphonite and the phosphine hinder efficiently the formation of long chain branches above the critical residual concentration of about 200 ppm. The phosphite is less efficient in this respect: the Elmendorf strength decreases linearly with its consumption. The dart drop strength is also larger (not shown) when the polymer is stabilized with the phosphonite or the phosphine than in the presence of the phosphite, although the difference is smaller than in the case of the Elmendorf tear strength.

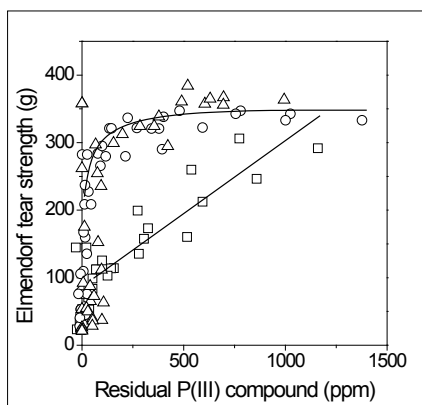


Figure 7.3 Correlation between the residual amount of phosphorous antioxidant and the Elmendorf tear strength measured in the perpendicular direction to the flow of polyethylene films stabilized with combinations of 700 ppm hindered phenol and various amounts of phosphite (□), phosphonite (○) and phosphine (Δ) processed by multiple extrusions at 260 °C and film blowing at 195 °C.

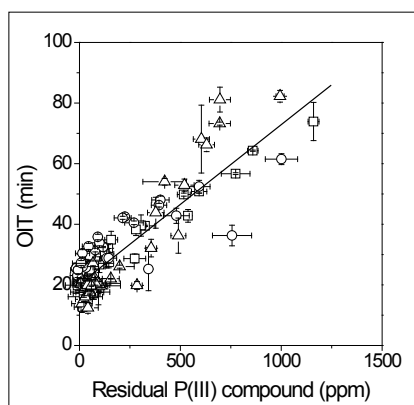


Figure 7.4 Correlation between the residual amount of phosphorous antioxidants and the thermo-oxidative stability of polyethylene stabilized with combinations of 700 ppm hindered phenol and various amounts of phosphite (□), phosphonite (○) and phosphine (Δ) processed by multiple extrusions at 260 °C. OIT was measured at 200 °C in oxygen.

These results confirm the conclusions drawn in Chapter 6 that the phosphonite and the phosphine inhibit efficiently the chemical reactions leading to the formation and recombination of alkyl radicals during the processing of polyethylene. Significant changes in polymer characteristics start below a critical value of the residual concentration of these phosphorous stabilizers. The phosphite is a less effective melt stabilizer than the two other compounds, as it can reduce but cannot hinder the formation and recombination reactions of macro-radicals. Both the rheological characteristics of the polymer and the strength of the films stabilized with phenol/phosphite compositions are inferior to the polymer stabilized with the two other additive combinations.

The oxidation induction time (OIT) of the polymer stabilized with phenolic/phosphorous antioxidant combinations measured at 200 °C under oxygen is plotted as a function of the residual amount of the phosphorous antioxidants in Fig. 7.4. The correlation reveals that the concentration of the residual phosphorous compounds determines the thermo-oxidative stability of the polymer in the presence of a given phenolic antioxidant under these conditions. The efficiency depends only on the amount of the phosphorous stabilizer and it is independent of its chemical composition. This confirms that the efficiency of antioxidant systems cannot be deduced from OIT values [160], which are often used to rate different antioxidant packages.

The relationship between the amount of oxidized phosphorous antioxidant and the yellowness index of the polymer demonstrates well that both types of antioxidants affect the color stability of polyethylene (Fig. 7.5). The discoloring effect of the phenolic antioxidant is reduced by the phosphonite and the phosphine, while the investigated phosphite enhances it. The latter effect can be attributed to the reaction of the phosphite with alkoxy radicals according to reaction (2.44b) yielding a hindered phenolic radical which undergoes a number of subsequent reactions including the formation of pro-oxidant peroxydienes, as well as ortho-quinone [86]. The actual value of yellowness index at a given extrusion step and type of phosphorous stabilizer is, however, not influenced by the amount of phosphorous molecules participating in the reactions. This reveals that even if the secondary antioxidant can modify (diminish or enhance) the discoloring effect of the phenolic antioxidant, the reactions of the hindered phenol determine the changes in the color of polyethylene during processing at a given antioxidant combination.

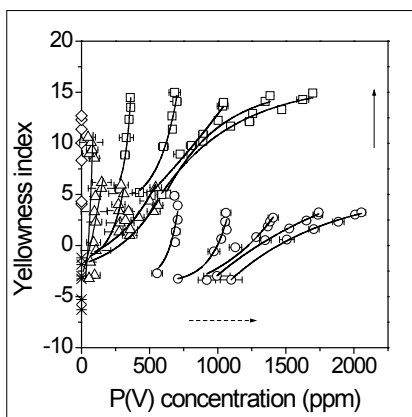


Figure 7.5 Effect of the amount of reacted phosphorous antioxidant on the yellowness index of polyethylene processed by multiple extrusions at 260 °C without any antioxidant (*), with 700 ppm hindered phenol (◇) and its combinations with phosphite (□), phosphonite (○) and phosphine (Δ). increasing number → of extrusions, increasing initial concentration of phosphorous antioxidants.

We can conclude from the results presented above that the antioxidants affect the various characteristics of polyethylene differently. The chain structure of the polymer and the related characteristics (rheology, film strength) are protected efficiently by the phosphonite and the phosphine during melt processing. The effect of these two phosphorous stabilizers is similar and only their consumption rate differs. The phenolic antioxidant and the phosphite are less efficient melt stabilizers than the two other phosphorous compounds. Their combinations cannot hinder the recombination reactions of alkyl radicals. The high temperature thermo-oxidative stability determined by OIT measurement of the polymer processed with the combinations of the same phenolic and different phosphorous antioxidants is a linear function of the residual concentration of the phosphorous compound and does not depend on the chemical structure of the latter. Although the phosphorous stabilizers affect the color of the polymer considerably, the amount of hindered phenol participating in chemical reactions determines primarily the degree of discoloration during processing of polyethylene at a given phenolic/phosphorous antioxidant combination.

7.3. Consumption of the phenolic antioxidant

Not only the phosphorous stabilizers oxidize slower in the two-component antioxidant packages, but also the phenolic antioxidant takes part in a smaller number of reactions compared to the case when it is used alone. Fig. 7.6 shows the relationship between the amounts of phosphorous and phenolic antioxidants reacted in the first extrusion step. With increasing amount of reacted phosphite and phosphonite the consumption of the hindered phenol decreases monotonously in a similar way. The attention must be called here to the fact that more phosphonite and less phenolic antioxidant molecules react at the same initial concentrations than in the case of phenol/phosphite combinations. The correlation is completely different for the phenol/phosphine system. The amount of the reacted phenolic antioxidant is reduced drastically already at low level of phosphine consumption.

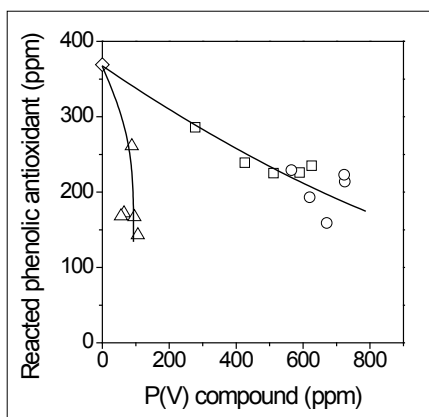


Figure 7.6 Correlation between the amount of phosphorous and phenolic antioxidants reacted in the first extrusion of polyethylene stabilized with 700 ppm hindered phenol ($\diamond$) and its combinations with various amounts of phosphite ($\square$), phosphonite ($\circ$) and phosphine (Δ). Extrusion temperature: 260 °C.

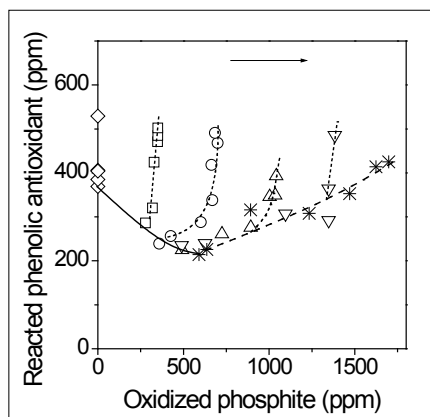


Figure 7.7 Correlation between the consumption of the phosphite and the hindered phenol in polyethylene processed by multiple extrusions at 260 °C with 700 ppm phenolic antioxidant ($\diamond$) and its combinations with 350 ($\square$), 700 ($\circ$), 1050 (Δ), 1400 (∇) and 1750 ($*$) ppm phosphite. Concentrations measured after the first extrusion are connected with solid line. The arrow indicates increasing number of extrusions.

The relationship between the concentration of the reacted phosphite and that of the phenolic antioxidant is shown in Fig. 7.7. Although the consumption of the phenolic antioxidant decreases when the phosphite is added as co-stabilizer, the change depends both on the initial concentration of the phosphite and on the number of extrusions. The concentration of the reacted phenolic antioxidant decreases with increasing amount of oxidized phosphite in the first processing of the polymer powder (solid line in the fig-

ure). In further extrusions the consumption of the phenol increases gradually up to the point where the whole amount of the phosphite added is oxidized completely (dashed line in the figure). After that the consumption rate of the phenolic antioxidant accelerates (dotted lines in the figure). This result reveals that more and more phenol molecules participate in the chemical reactions during the multiple extrusions of polyethylene even at high phosphite concentrations. As shown in Chapter 6, the phenolic antioxidant itself does not prevent long chain branching and the increase in polymer viscosity (decrease in MFI) during processing. Therefore the gradual decay in the properties of polyethylene stabilized with phenol/phosphite combinations may originate from the stabilization reactions of the phenolic antioxidant. The relationships between the consumption of the phenolic antioxidant and the characteristics of the polymer support this assumption.

The concentration of vinyl groups (Fig. 7.8), melt flow index (Fig. 7.9) and viscous compliance decrease linearly, while creep viscosity increases exponentially with increasing amount of the phenolic antioxidant reacted in the processing operations. The gradual decrease in the Elmendorf tear strength measured in perpendicular direction to the flow and the dart drop strength during multiple extrusions even at high phosphite concentration can be explained also by the increase in the number of reactions of the phenolic antioxidant. The perpendicular Elmendorf tear strength decreases fast (Fig. 7.10) and the dart drop strength decreases linearly with increasing concentration of the reacted phenol. All these results confirm that the participation of the phenolic antioxidant in the stabilisation reactions is significant when the phosphite is used as secondary antioxidant.

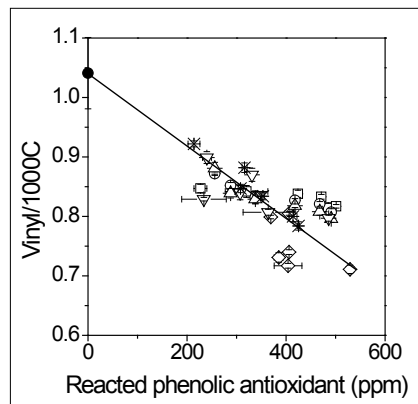


Figure 7.8 Correlation between the amount of reacted phenolic antioxidant and the vinyl group concentration of polyethylene (● nascent powder) processed by multiple extrusions at 260 °C with 700 ppm phenolic antioxidant and its combinations with the phosphite. Symbols are the same as in Fig. 7.7.

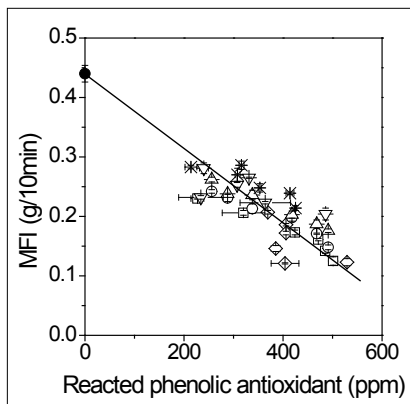


Figure 7.9 Correlation between the amount of reacted phenolic antioxidant and the melt flow index of polyethylene (● nascent powder) processed by multiple extrusions at 260 °C with 700 ppm phenolic antioxidant and its combinations with the phosphite. Symbols are the same as in Fig. 7.7.

7.4. Discussion

The results presented above show that the vinyl group content and the rheological characteristics of polyethylene are unchanged or change only moderately until the residual concentration of the phosphorous stabilizer exceeds a critical value of about 100–200 ppm. Below that concentration the polymer deteriorates fast. This result proves that phosphorous antioxidants play a main role in protecting the polymer from degradative chemical reactions during processing. Studying the inhibition of AIBN-initiated oxidation of hydrocarbons by hindered aryl phosphites Schwetlick et al. [88] also observed the existence of a critical antioxidant concentration and attributed it to the oxidation of the phosphite by hydroperoxides formed in the reactions. Gugumus [161] proposed to call the experimentally observed critical antioxidant concentration a “characteristic inhibitor concentration” at which the reaction mechanism of initiation changes. In our case, where two types of antioxidants are present in the polymer, the mechanism of inhibition reactions changes at the critical concentration of the phosphorous stabilizer. The phosphorous stabilizer dominates in the inhibition reactions above the critical concentration, while the phenol determines stabilization below it. The phenol remains the only inhibitor after the complete consumption of the phosphorous stabilizer.

The reactions of the polymer during processing in the presence of antioxidants are shown in Scheme 7.1. The single phosphorous antioxidant (P_{III}) reacts with the peroxy radical formed from the polymer as an effect of heat and shear in the presence of oxygen and yields an oxy radical and a stable compound (reaction 2.46). The reaction of the oxy radical with another phosphorous molecule leads to the formation of an alkyl radical (reaction 2.44c). At high oxygen level (OIT measurement) further peroxy radicals are formed and the phosphorous antioxidant is consumed rapidly. At low oxygen concentration (under processing conditions) the reactivity of the phosphorous antioxidant, which is a function of its chemical structure, affects the direction of the reactions of oxy radicals. More reactive antioxidants can hinder more efficiently the recombination reactions of oxy radicals with alkyl radicals (reaction 2.34) than less reactive ones.

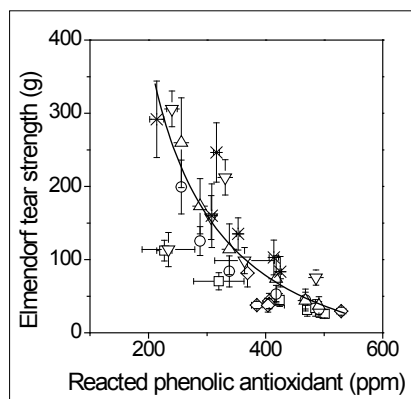
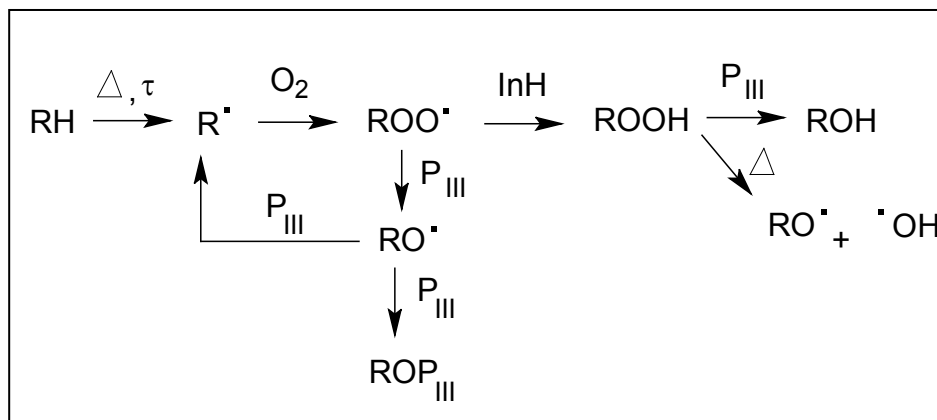


Figure 7.10 Correlation between the amount of reacted phenolic antioxidant and the Elmendorf tear strength measured in the perpendicular direction to the flow of polyethylene processed by multiple extrusions at 260 °C and film blowing at 195 °C in the presence of 700 ppm phenolic antioxidant and its combinations with the phosphite. Symbols are the same as in Fig. 7.7.



Scheme 7.1 Reactions of alkyl radicals formed from polyethylene as an effect of heat (Δ) and shear (τ) under thermo-oxidative conditions in the presence of phenolic (InH) and phosphorous (P_{III}) antioxidants.

When a single phenolic antioxidant (InH) is added to the polymer hydroperoxides form by the transfer of a hydrogen atom from the phenolic molecule to the peroxy radical. As an effect of heat, the hydroperoxide group decomposes to oxy and hydroxyl radicals, which react with further phenol molecules or abstract hydrogen from the polymer chains leading to recombination reactions (reactions 2.32-2.34). Since the phenolic antioxidant is consumed gradually and long chain branches form on the polymer chains (indicated by the decrease in the perpendicular Elmendorf tear strength [36,156]) at the same time, we can conclude that both types of reactions take place during the multiple extrusions of polyethylene.

In the case of phenolic/phosphorous antioxidant combinations the reactions of the polymer is reduced and stable compounds are formed from the macroradicals until enough hydrogen donor phenolic antioxidant molecules and an active phosphorous compound are present in the system. In oxygen rich environment hydroperoxide groups form continuously and the main function of the phosphorous antioxidants is to decompose them. OIT measurements reveal that the investigated antioxidants are equally efficient in this respect. In oxygen poor environment the thermal decomposition of hydroperoxide groups, the dehydration of alcohols and the reactions of alkyl radicals play also an important role. The reactivity of the antioxidants towards the radicals formed under these conditions defines the direction of reactions. The results of the experiments indicate that the studied phosphonite and phosphine are more reactive than the phenolic antioxidant; they can hinder efficiently the recombination reactions of macroradicals above their critical concentration. The reactivity of the investigated phosphite is smaller, therefore both the phenol and the phosphite participate in inhibition reactions even at high phosphite levels and neither of them can hinder completely the recombination of macroradicals. Consequently the observed changes in the characteristics of the polymer are related to the consumption of both types of stabilizers.

7.5. Conclusions

The synergetic effect of phenol/phosphorous antioxidant combinations compared to single antioxidants can be partly attributed to the reduced rate of consumption of each type of stabilizer during the processing of polyethylene. The phosphorous antioxidant inhibits the degradation reactions of the polymer. Its efficiency is affected strongly by the amount of oxygen present. The efficiency of the three investigated phosphorous stabilizers is similar at high temperature in oxygen rich environment (OIT measurement) due to their ability to decompose hydroperoxide groups. Under processing conditions (oxygen poor environment) both the level of oxygen and the chemical activity of the phosphorous stabilizer affect the mechanism of the reactions. The most significant antioxidant consumption and changes in polymer properties occur in the first extrusion of the polymer powder. This can be attributed to the larger amount of oxygen adsorbed by the powder particles compared to pellets, as they have pores and larger surface.

The melt stabilizing efficiency of the phosphonite and phosphine is larger than that of the phosphite studied. The former inhibit the recombination reactions of macro-radicals with similar efficiency, but the rate of consumption of the phosphonite is large, while significantly smaller amounts are oxidized from the phosphine. Neither the investigated phenolic antioxidant, nor its combination with the phosphite can hinder the formation of long chain branches, which results in a gradual decrease of the strength of films blown from polymers produced in subsequent extrusion steps even at high concentrations of the antioxidants.

Discoloration of polyethylene is determined by both types of antioxidants. Although the phosphorous stabilizers contribute strongly to color stability by decreasing or increasing it, the reactions of the phenolic antioxidant determine the degree of discoloration at a given antioxidant pair.

Chapter 8

Study of the high temperature reactions of a hindered aryl phosphite secondary antioxidant

8.1. Introduction

Although the chemical reactions of phosphites and phosphonites are assumed to be similar in the literature [71,74,89], studies on the stabilization of polyolefins presented in the previous chapters revealed that not only the efficiency but also the reaction mechanism of various phosphorous stabilizers are strongly influenced by their chemical structure. Detailed analysis showed that the phosphonite and the phosphine studied hinder effectively the recombination of macroradicals. Their efficiency is similar, but the phosphonite is consumed fast, while the phosphine oxidizes slowly. The phosphite is the least efficient melt stabilizer among the three phosphorous derivatives studied. Its reaction mechanism depends on the presence or absence of a phenolic antioxidant and differs from that of the two other stabilizers. DTBPP cannot prevent the long chain branching of polyethylene during processing even in high concentrations. The aim of the present work was to explore the reaction mechanism of DTBPP by running high temperature experiments. The reactions of the phosphorous antioxidant with molecular oxygen, hydroperoxide and oxy radicals were studied at ≥ 200 °C according to Table 3.5. The experiments were carried out in melt (without using any solvent) because 1) the question is the direct reactions of the phosphite with reactive groups and radicals formed during the thermo-oxidative degradation of polyethylene, 2) the thermo-oxidative degradation of polyolefins is a heterogeneous local process [162-166], and 3) the effect and reactions of solvents can be excluded. The composition of the solid reaction products was analyzed by several techniques. Note: besides the main product gaseous substances were also formed in each reaction carried out at high temperatures as revealed by the materials condensed in the cooler.

8.2. Reactions under thermal and thermo-oxidative conditions

DTBPP has a relatively high fusion temperature (T_m) at 181-187 °C, as shown by the DSC traces of the antioxidant measured in nitrogen and oxygen flow (Fig. 8.1). The antioxidant starts to loose mass at around 200 °C (Fig. 8.2), which is not accompanied by any detectable heat effect in inert atmosphere (Fig. 8.1). The rate of mass loss is accelerated by oxygen, and oxidation reactions result in an exothermic heat flow (Fig. 8.1) without any mass gain (Fig. 8.2). Simultaneous mass loss can be observed instead indicating that some thermal decomposition products of DTBPP oxidize and not the antioxidant itself. The rate of mass loss is further accelerated when the volatile products

of the thermo-oxidative reactions are not removed by gas flow (Fig. 8.2), which reveals their reactive nature.

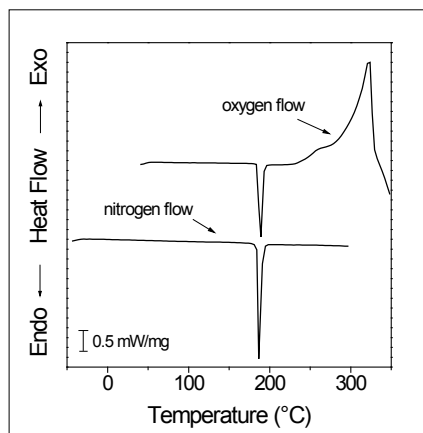


Figure 8.1 DSC traces of DTBPP measured under nitrogen and oxygen at a heating rate of 10 °C/min.

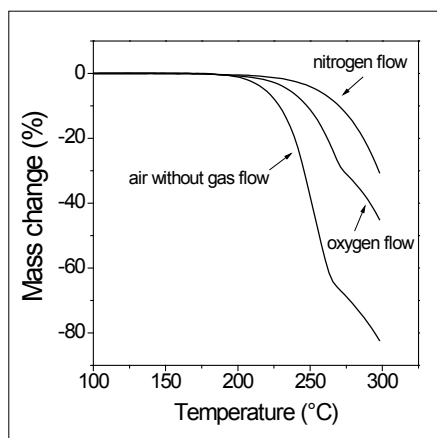


Figure 8.2 Mass change of DTBPP measured by TGA at a heating rate of 3.5 °C/min.

HPLC-MS analysis of DTBPP reveals that besides the active stabilizer the additive contains also some DTBPPO and two other components with molecular masses of 590 and 513 g/mol in small amounts. The MS/MS spectrum of the component with a molecular mass of 590 ($m/z=591$) g/mol is shown in Fig. 8.3 [structure (I)]. The structure of the second component was not identified. It can be a side product formed during the production of DTBPP, which seems to be confirmed by its presence also in DTBPPO used as reference material.

Heat treatment of DTBPP at 200 °C under nitrogen and oxygen resulted in crystalline solid products, while that carried out 240 °C yielded mixtures of crystalline and amorphous materials. The analysis of the solid products confirms the results of the thermal analyses: DTBPP decomposes thermally under these conditions without any remarkable oxidation. The FT-IR spectra of DTBPP taken before and after heat treatment under argon and oxygen are similar (Fig. 8.4). The peak of DTBPPO in the HPLC chromatogram of the reaction mixtures (Fig. 8.5) is very small (it cannot be even seen in the figure) because its amount is less than 1 w/w % (Table 8.1) independently of atmosphere or reaction temperature. More than 20 w/w % of the solid reaction mixtures is formed in side reactions. The amount of these products increases slightly with increasing temperature. Note: the amount of residual DTBPP in the solid material measured after heat treatment under oxygen is somewhat higher than in argon atmosphere, which can be attributed to the formation of more volatile products in the first case.

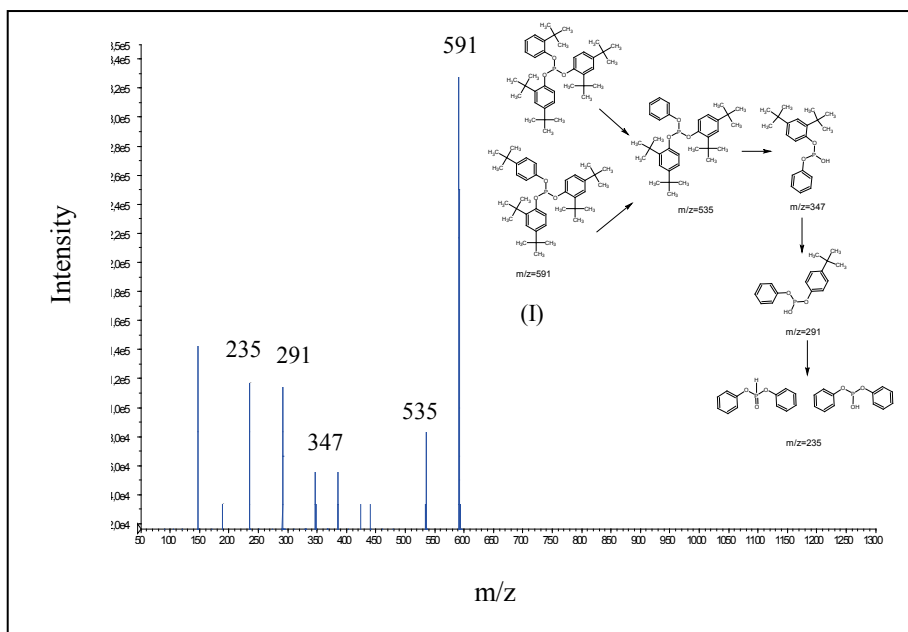


Figure 8.3 A typical tandem mass (MS/MS) of a reaction product (structure (I)) of DTBPP formed at 200 and 240 °C in argon and oxygen atmosphere.

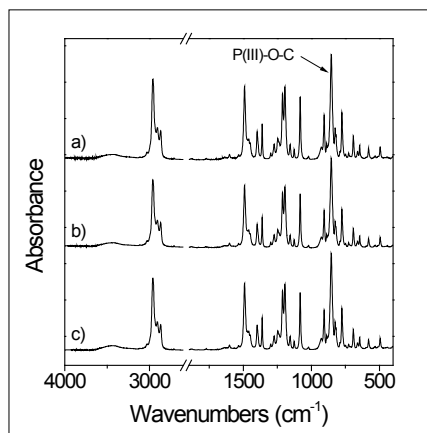


Figure 8.4 FT-IR spectra of DTBPP taken before (a) and after heat treatment in argon (b) and oxygen (c) atmosphere at 200 °C for 1 min.

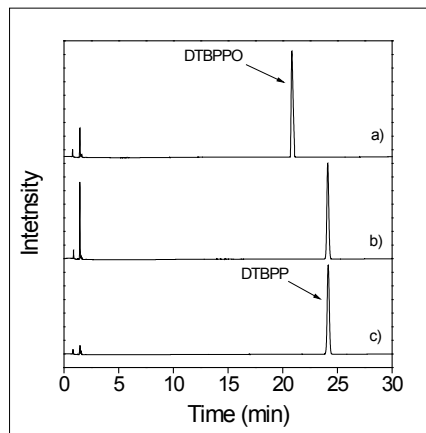


Figure 8.5 HPLC chromatograms of DTBPPO (a), DTBPP treated in oxygen atmosphere at 240 °C for 1 min (b) and DTBPP (c).

Table 8.1

Composition of the reaction products of DTBPP formed under different conditions as determined by HPLC

Reagent	Gas	Temperature (°C)	Amount (w/w %)		
			DTBPP	DTBPPO	Side products
-	Ar	200	77.3	0.6	22.1
-	Ar	240	74.1	0.7	25.2
-	O ₂	200	79.3	0.5	20.2
-	O ₂	240	75.7	0.5	23.8
AIBN	Ar	200	61.6	1.0	37.4
AIBN	O ₂	200	77.9	0.9	21.1
DCP	O ₂	200	25.9	4.9	69.2
CHP	Ar	200	0.4	63.8	35.8

According to the HPLC-MS analysis the main component of the solid side products has a molecular mass of 590 g/mol. The MS/MS spectrum of this compound (structure (I)) is shown in Fig. 8.3 from which we can deduce that first a tertiary butyl group splits off from the stabilizer at ≥ 200 °C both in inert and in oxidative environment.

8.3. Reaction with carbon centered radicals

The two heating methods applied for reacting DTBPP with carbon centered radicals (heating the reaction mixture gradually and immersing the reaction flask into the heated oil bath, respectively) yielded identical reaction products, which crystallized in the course of cooling from 200 °C to ambient temperature. Although the FT-IR spectra do not reveal any significant change after the reaction of DTBPP with carbon centered radicals, the HPLC and HPLC-MS analyses show that a large number of fragmentation and recombination reactions take place. Only about 62 w/w % of DTBPP remained intact as revealed by the HPLC analysis of the solid reaction mixture (Table 8.1). More than 37 w/w % of side products formed and 1 w/w % DTBPPO can also be identified, although the reaction was carried out in oxygen-free environment. The m/z values of the side products determined by HPLC-MS are given in Table 8.2. The tentative molecular structures assigned to the various m/z values on the basis of MS/MS analysis are summarized in Table 8.3. Thermal fragmentation of DTBPP at ≥ 200 °C is well demonstrated by structure (II), which is formed by breaking of a P-O bond and splitting off a tertiary butyl group. The occurrence of hydrolysis is revealed by structure (III). The presence of structure (IV) indicates that both P-O and C-O bonds break in this high temperature reaction. Free oxygen can be released, which may be the source of oxidation of DTBPP. A smaller amount of DTBPPO could have been formed also in this case, if the phosphite had been oxidized by some traces of oxygen molecules remained adsorbed on the surface of solid reagents after purging with argon prior to the reaction (see previous section).

Table 8.2

m/z values of the solid products formed in the high temperature reactions of DTBPP carried out at 200 °C and determined by HPLC-MS

m/z	Reaction with			
	C-centered radicals	peroxy radicals	oxy radicals	hydroperoxides
387	X			
408			X	
457			X	X
459	X		X	
471			X	
473			X	X
517				
526	X	X		
542		X		
558	X			
575			X	X
647	X	X	X	X
661				X
663	X	X	X	X

The reaction of DTBPP with the carbon centered radicals is demonstrated by the formation of structure (V). The mechanism of the reaction is not known. It might go through the formation of a common four-coordinate phosphorus-centered radical intermediate [102], or could be the result of thermal decomposition of DTBPP. The former mechanism seems to be more plausible, as thermal decomposition of DTBPP in the absence of any radical resulted only in the loss of tertiary butyl groups.

8.4. Reaction with peroxy radicals

Because of the reactivity of peroxy radicals formed from AIBN in oxygen atmosphere at high temperature only a small ratio of AIBN to DTBPP was used in the experiment. AIBN melted at 120 °C but the reaction started only above 190 °C following the melting of DTBPP. Yellowish crystalline material was obtained at the end of the reaction, the FT-IR spectrum of which reveals that some part of the phosphite molecules oxidized to five-valent phosphorus compound (Fig. 8.6). According to the HPLC analysis (Table 8.1) the residual amounts of non-reacted DTBPP and DTBPPO in the reaction mixture are similar to those measured after the heat treatment in argon or in pure oxygen at the same temperature. However, the composition of the side products (Table 8.2) differs significantly from that determined after heat treatment. The main components correspond to structures (V) and (VI) in Table 8.3. Compound (V) was detected also in the reaction mixture of DTBPP with carbon centered radicals and its formation was assumed to be the result of the decomposition of a four-coordinate phosphorus-centered radical intermediate. The appearance of the P(V)-O-C absorption band in the

FT-IR spectrum can be attributed to structure (VI). The formation of this latter molecule proves that reactive radicals accelerate the oxidation of the phosphorus atom.

Table 8.3

Molecular structures identified as side products of the reaction of DTBPP with carbon centered and peroxy radicals formed from AIBN at 200 °C

Structure	m/z	Chemical structure
II	387	
III	459	
IV	559	
V	526	
VI	542	

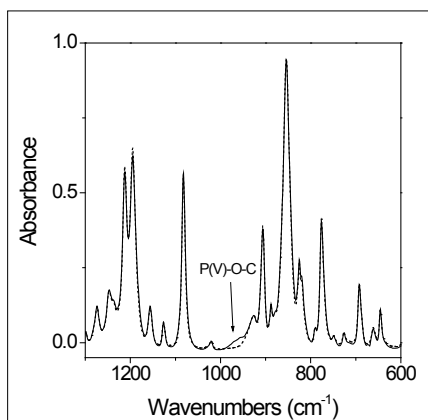


Figure 8.6 FT-IR spectra of DTBPP taken before (---) and after) (—) reaction with 0.08 mol AIBN/mol DTBPP under oxygen at 200 °C for 1 min.

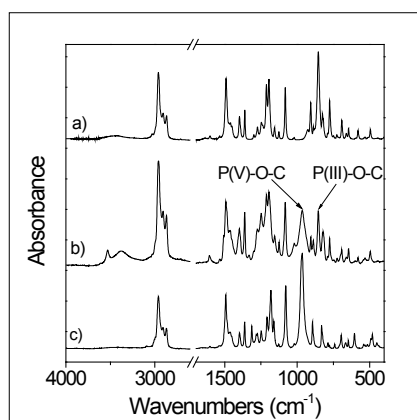


Figure 8.7 FT-IR spectra of DTBPP (a), the product of the reaction of DTBPP with DCP at 200 °C under oxygen (b), and DTBPPO (c).

8.5. Reaction with oxy radicals

A greasy yellow mixture was obtained after the reaction of DTBPP with cumyl oxy radicals at 200 °C. DTBPP oxidized partially revealed by the presence of both the P(III)-O-C (at 850 cm⁻¹) and P(V)-O-C (at 866 cm⁻¹) absorption bands in the FT-IR spectrum (Fig. 8.7). Broadening of the P(V)-O-C band compared to the reference DTBPPO indicates that different oxidation products are present in the reaction mixture. The HPLC chromatogram of the product (Fig. 8.8b) shows also that several compounds formed in the reaction. According to the quantitative analysis (Table 8.1) 26 w/w % of DTBPP did not react, the amount of DTBPPO does not exceed 5 w/w %, while the majority (69 w/w%) of DTBPP participated in different reactions. The m/z values of the products are summarized in Table 8.2, while the chemical structures assigned to them are given in Table 8.4.

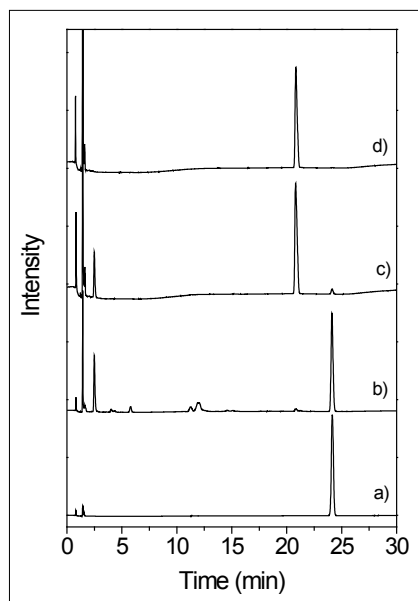


Figure 8.8 HPLC chromatograms of DTBPP (a), the products of the reaction of DTBPP with DCP under oxygen (b) and CHP under argon (c) at 200 °C, and DTBPPO (d).

Table 8.4

Molecular structures identified as side products of the reaction of DTBPP with oxy radicals formed from DCP in oxygen at 200 °C

Structure	m/z	Chemical structure
VIIa	457	
VIIb		
VIII	471	
IX	473	
Xa	575	
Xb		

The results reveal that hydrolysis (product (III) in Table 8.3), decomposition and recombination reactions of DTBPP (products (VIIa), (VIII) and (Xa)) and DTBPPO (products (VIIb), (IX) and (Xb)) take place simultaneously at high temperature in the presence of reactive oxy radicals. The structure of the product with an m/z value of 408 was not identified. The various side products indicate that the fragmentation occurs both at the P-O and C-O bonds.

The O-H absorption bands in the region of 3600 and 3200 cm^{-1} of the FT-IR spectrum (Fig. 8.7) indicate the presence of molecules with C-OH groups in the reaction mixture. They can be assigned to di-*tert*-butyl-phenol formed according to reaction (2.45) and/or to some derivatives of cumene (e.g., cumene alcohol), all of them with a molecular mass less than 300 g/mol, which is the lower limit of the HPLC/MS method applied.

8.6. Reaction with hydroperoxide

As expected, DTBPP reacts readily with hydroperoxide. Fig. 8.9 shows the FT-IR spectra of DTBPP before and after the reaction with CHP at 200 °C. As seen from Fig. 8.9b, the hydroperoxide starts to oxidize DTBPP already at ambient temperature. After the reaction at 200 °C a dark yellow amorphous solid product was obtained in which the entire amount of DTBPP was in oxidized form (Fig. 8.9c). The HPLC chromatogram (Fig. 8.8c) indicates that more than one oxidation products are present in the mixture. The amount of DTBPPO is only about 64 w/w % (Table 8.1), which proves that side reactions play also an important role under this condition.

The m/z values of the reaction products determined by HPLC-MS are given in Table 8.2 and some of the chemical structures assigned to them are presented in Tables 8.4 and 8.5 revealing that they formed in decomposition and recombination reactions also in this case. As the vibration band of the P(III)-O-C group is missing from the FT-IR spectrum of the reaction mixture, the product with $m/z = 457$ can correspond to structure (VIIb). For the same reason structure (Xb) can be assigned to $m/z = 575$, while structure (IX) to $m/z = 473$. In the HPLC chromatogram of the reaction mixture (Fig. 8.8c) a small peak can be observed at the retention time corresponding to non-reacted DTBPP. The MS/MS spectrum of the product with $m/z = 647$ reveals

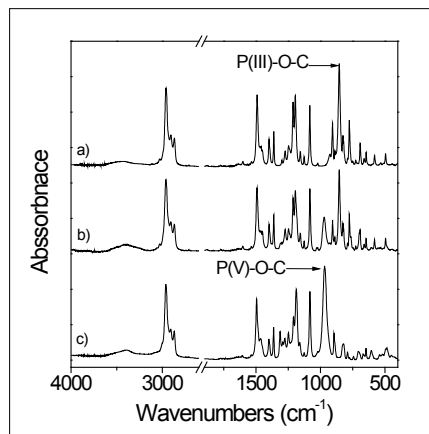


Figure 8.9 FT-IR spectra of DTBPP (a), the mixture of DTBPP with CHP before (b) and after reaction at 200 °C under argon (c).

that this molecule has a structure different from that of DTBPP. Considering the mechanism of thermal decomposition of CHP [167] and taking into account the result of MS/MS analysis, structure (XI) is proposed as a possible derivative. Similarly, structure (XII) can be assigned to the molecule with $m/z = 661$.

Table 8.5

Molecular structures identified as side products of the reaction of DTBPP with CHP at 200 °C

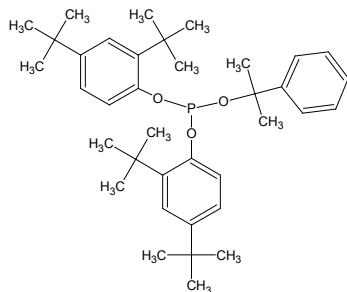
Structure	m/z	Chemical structure
XI	647	
XII	661	

In the FT-IR spectrum of the reaction mixture (Figs. 8.9b and 8.9c) a broad band can be observed at $3700\text{--}3200\text{ cm}^{-1}$. It originates most probably from cumene alcohol formed in the reaction of CHP with DTBPP and/or from some derivative(s) of cumene.

8.7. Discussion

All the results of the model experiments presented above reveal that thermal decomposition of DTBPP plays a very important role in the reactions taking place above its melting temperature. DTBPP is thermally unstable at $\geq 200\text{ }^{\circ}\text{C}$, tertiary butyl groups split off first. This hindered aromatic phosphite does not react directly with molecular oxygen even at high temperatures. The exothermal reactions measured by DSC under oxygen can be attributed to the oxidation of the tertiary butyl radicals, which is an auto-catalytic process. The results of the thermogravimetric analysis, as well as the model experiments indicate that all kind of radicals (carbon or oxygen centered) accelerate the decomposition of DTBPP.

DTBPP does not hydrolyze easily; only one hydrolysis product (structure (III)) was identified in a small amount after the reaction carried out under various conditions. The role of the thermal stability of the reagents is demonstrated well by the reactions of DTBPP with DCP at 200 °C in oxygen atmosphere (oxy radicals). According to the literature sources [71,82,83], the sterically hindered aryl phosphite takes part in a substitution reaction (reaction 2.45) yielding a product with $m/z = 577$ (structure (XIII)). This molecule is not present among the reaction products. Various molecules are formed instead as a result of decomposition and recombination reactions.



(XIII)

The results of these experiments are important also from the practical point of view. Under the processing conditions of polyolefins the investigated phosphite does not participate only in stabilization reactions, but it undergoes also thermal fragmentation, which does not reduce but increases the number of reactive radicals in the system. Although not confirmed, but the fragmentation products of DTBPP might also contribute to the stabilization by recombining with the polymeric radicals and cutting off the propagation chain.

8.8. Conclusions

In this study the reactions of the sterically hindered phosphite, DTBPP, used as processing stabilizer for polyolefins in practice, was investigated by modeling the conditions of polyethylene processing. The thermal and thermo-oxidative stability of the additive was determined, and its reactions with molecular oxygen, hydroperoxide (cumene hydroperoxide), as well as with carbon centered (cyanoisopropyl), peroxy (cyanoisopropyl peroxy) and oxy (cumene oxy) radicals were investigated at 200 °C. DTBPP is instable above its high melting temperature; it starts to decompose at around 200 °C. The rate of decomposition increases with temperature and it is accelerated by molecular oxygen and even more by radicals. Various products were identified in all reaction products, which formed in decomposition and recombination reactions. Consequently, besides chemical structure and effectiveness, the heat-stability of phosphorous stabilizers has to be taken also into account in their application, as it plays also an important role in the processing stabilization of polyolefins.

Chapter 9

Summary

Although polyethylene belongs to the commodity plastics, many questions concerning its stability have not been cleared, yet. Some aspects of degradation and stabilization of Phillips type polyethylene was studied in our work presented in the thesis. We investigated the hydrolytic stability of nascent polyethylene, the effect of different antioxidants on the processing stability of the polymer, and the reaction mechanism of phosphorous antioxidants under the processing conditions of polyethylene.

In the first part the thermo-oxidative stability of nascent polyethylene was studied at elevated temperature under hydrolytic conditions. The polyethylene was processed without any antioxidant then stored in distilled water at 80 °C in closed glass container for 1 year. Samples were withdrawn at regular intervals and characterized by standard techniques. The results revealed that the dominating chemical reaction is the oxidation of the polymer and the amount of oxygen present determines the direction of reactions during storage. All the reactions taking place are related to each other. The increase in oxygen content leads to the scission of polymer chains resulting in an increase of the concentration of methyl groups and formation of carbonyl groups. The oxidation proceeds mainly through unsaturated groups, especially through vinyl groups. The changes in the polymer properties are determined by the modification of chain structure. Any variation in the conditions of storage is reflected in the properties of the polymer.

In the further part of the work the efficiency and reaction mechanism of phosphorous antioxidants used alone and in combination with a phenolic antioxidant were studied. A hindered aryl phosphite, a mixture of hindered aryl di- and mono-phosphonites, and an aryl-alkyl phosphine were investigated by multiple extrusions in polyethylene. First an infrared spectroscopic method was developed to determine the amount of reacted and residual phosphorous antioxidant in the polymer. The method is based on the absorption intensity of the P(III)-O-C group in the case of phosphite and phosphonite, and that of the P(III)-C and P(V)=O bands for the phosphine. The advantage of the method is that the concentration of the additives can be determined directly in the polymer film without using extraction.

The processing experiments confirmed the conclusion of the earlier studies run at the Joint Laboratory: the chemical structure of the polymer undergoes the most significant change during the first processing operation either in the absence or in the presence of antioxidants then it is modified less in the further extrusions. This can be attributed to the larger amount of oxygen adsorbed by the powder particles compared to pellets, as they have pores and larger surfaces. The importance of the changes in the first processing of the polymer powder is confirmed also by the results of the experiments carried out with single phosphorous antioxidants. They showed that the properties of the polymer processed by multiple extrusions are affected basically by the reactions taking

place in the first extrusion even after the total consumption of the phosphorous stabilizer.

The phosphorous stabilizers determine the rheological properties of polyethylene and the strength of films produced from it either they are used alone or in combination with a phenolic antioxidant. In the case of two-component antioxidant packages the main role of the phenolic antioxidant is to decrease the oxidation rate of the phosphorous compound. The stabilizing efficiency of phosphorous antioxidants depends on their chemical structure and the concentration of oxygen. It is similar at high temperatures in oxygen rich environment (OIT measurement), as all the three investigated phosphorous compounds are efficient hydroperoxide decomposers. In oxygen poor environment (under processing conditions of polyethylene) both the level of oxygen and the chemical activity of the phosphorous antioxidant affect the mechanism of reactions. The most efficient melt stabilizer is the phosphine among the three investigated phosphorous compounds and the least efficient one is the phosphite.

The changes in the rheological properties of the polymer and the strength of film processed from that is related directly to the changes in the number of vinyl groups. The viscosity of the polymer increases and the strength of the film decreases with decreasing number of vinyl groups. The phosphine and phosphonite inhibit the chemical reactions of the polymer and the recombination reactions of macroradicals with similar efficiency above a critical residual concentration of about 100-200 ppm. The reaction mechanism is not affected by the phenolic antioxidant. Below the critical concentration the mechanism of inhibition changes and the properties of the polymer start to deteriorate fast. The significant difference between these two phosphorous stabilizers is that the phosphine is efficient already in small concentrations and its consumption rate is much slower than that of the phosphonite, when it is used in combination with a phenolic antioxidant. The reaction mechanism of the phosphite differs somewhat from that of the two other phosphorous compounds and depends also on the absence or presence of a phenolic antioxidant. The phosphite does not hinder the recombination reactions and long chain branching of polyethylene. Consequently the film strength decreases gradually with increasing number of extrusions even at high concentrations of the phosphite. Although the reaction products of the investigated hindered aryl phosphite might be expected to increase the thermo-oxidative stability of polyethylene on the basis of literature sources, the results of the processing experiments do not confirm that.

Discoloration of polyethylene is determined by both the phenolic and the phosphorous antioxidants. The color stabilizing efficiency of the phosphorous antioxidants depends on their chemical structure. The phosphonite protects the most efficiently the polymer from discoloration, which may be explained by the interaction of the additive and/or its reaction products with the discoloring derivatives of the phenolic antioxidant. Contrary to that the reaction products of the investigated phosphite have coloring effect and increase that of the phenolic antioxidant. Although the phosphorous compounds contribute strongly to the color stability, the reactions of the phenolic antioxidant determine the degree of discoloration in the subsequent processing operations of polyethylene at a given antioxidant pair.

High temperature model experiments were carried out to explore the inferior behavior of the phosphite in the melt stabilization of polyethylene compared to that of the phosphine and phosphonite. We investigated the thermal stability of the phosphite, its reactions with molecular oxygen, hydroperoxide group, as well as with carbon centered, peroxy and oxy radicals at ≥ 200 °C without using any solvent. The results revealed that the phosphite is not stable thermally at the temperatures of polyethylene processing. It starts to decompose at around 200 °C. The rate of decomposition increases with temperature and is accelerated by molecular oxygen and radicals. Decomposition and recombination processes take place besides the known reactions and various side products form. The substitution reactions measured in solvents at moderate temperatures and described in the literature sources for the reaction of sterically hindered phosphites with oxy radicals is not proved by the high temperature experiments carried out with exclusion of any solvent. These results draw the attention to the risk of predicting the reactions of additives in polymers under the processing conditions from the results of model experiments run in solutions at much lower temperatures.

The most important conclusions of this thesis can be summarized in the following points:

1. Based on the results of long term soaking experiments we proved that all reactions taking place in neat polyethylene under these conditions are related to each other. In spite of the enormous number of reactions proposed in the literature we proved that only a few dominating one determine changes in the chain structure of the polymer. Close correlation exists between this latter and the properties of the polymer.
2. We developed spectroscopic procedures for the quantitative determination of the consumption of phosphorous secondary stabilizers during the processing of PE.
3. We proved that in spite of numerous references claiming the same stabilization mechanism for all phosphorous antioxidants, under the conditions of PE processing the effect, efficiency and mechanism of phosphite, phosphonite and phosphine stabilizers depend on their structure and differ significantly from each other.
4. We showed the first time that phenolic antioxidants do not hinder the degradation of PE in its first processing operation, but phosphorous stabilizers do. The efficiency of these latter depends on their chemical structure.
5. We found that the efficiency of phenolic antioxidant/phosphorous stabilizer package used extensively in practice depends strongly on the structure of the phosphorous compound. The phenol does not change the reaction mechanism of phosphonite and phosphine stabilizers, but interacts with phosphites. The efficiency of this latter combination is the smallest of the three.
6. We proved that a critical concentration of the phosphorous stabilizer determines the stability of polyethylene and not that of the phenolic antioxidant, as proposed in the literature. Below the critical level the mechanism of stabilization changes and the reactions of the phenolic antioxidant determine property changes. However, this antioxidant cannot protect the polymer as efficiently as phosphorous stabilizer or phenol/phosphor combinations.

7. Through the analysis of the results of well defined model experiments we showed that the relatively limited efficiency of the phosphite secondary stabilizer studied results from its instability at the processing temperature of polyethylene. The compound does not react directly with oxygen, but undergoes fragmentation that is accelerated by oxygen and radicals. The phosphite reacts readily with hydroperoxides that is its main stabilization reaction and mechanism.

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Abbreviations

ε	elongation-at-break
ε_y	tensile yield strain
η_0	creep viscosity
$\eta^*_{0.1}$	complex viscosity measured at 0.1 min ⁻¹ frequency
λ	mean retardation time
ρ	density
σ	tensile strength
σ_{EL}	Elmendorf tear strengths measured in perpendicular direction
$\sigma_{E \parallel}$	Elmendorf tear strengths measured in parallel direction
σ_y	tensile yield stress
τ	shear
$\omega_{G'}=G''$	crossover frequency
A_{inv}	intensity of the investigated absorption band
A_{ref}	intensity of the reference absorption band
AIBN	azobisisobutyronitrile
APCI	atmospheric pressure chemical ionization
BHT	butyl hydroxy toluene
C	concentration
CHP	cumene hydroperoxide
DCP	dicumyl peroxide
DRIFT	diffuse reflectance Fourier transform infrared (spectroscopy)
DSC	differential scanning calorimetry
DTBPP	tris(2,4-di-tert-butylphenyl)phosphite
DTBPPO	tris(2,4-di-tert-butylphenyl)phosphate
FT-IR	Fourier transform infrared (spectroscopy)
G'	storage modulus
G''	loss modulus
GPC	gel permeation chromatography
HAS	hindered amine stabilizer
HALS	hindered amine light stabilizer
HD	hydroperoxide decomposer
HDPE	high density polyethylene
HLMI	high load melt index
HPLC	high performance liquid chromatography
HPLC-MS	high performance liquid chromatography coupled with a mass spectrometer
ID	inside diameter
InH	phenolic antioxidant
IR	infrared (spectroscopy)
J_0	instantaneous creep compliance
J_e	elastic creep compliance
J_m	viscoelastic creep compliance
J_{max}	maximum creep compliances

J_t	creep compliance at time t
J_v	viscous creep compliance
K	absorption coefficient
LC	liquid chromatography
LCB	long chain branch
LDPE	low density polyethylene
M^{n+}	metal ion
M_c	critical molar mass
M_n	number average molecular mass
M_w	mass average molecular mass
M_z	Z average molecular mass
MFI	melt flow index
mPE	metallocene polyethylene
MS/MS	tandem mass spectrometry
m/z	mass-to-charge ratio
NOR'	hydroxylamine ether
NMR	nuclear magnetic resonance (spectroscopy)
O10	Hostanox O10
OIT	oxidation induction time
PE	polyethylene
R, R', R'', R''', R_1	alkyl group
$R^\bullet$	alkyl radical
$RO^\bullet$	oxy radical
$ROO^\bullet$	peroxy radical
ROOH	hydroperoxide
t	time
T_{CO}	absorption intensity of carbonyl group
TGA	thermogravimetric analysis
TVK	Tiszai Vegyi Kombinát (Tisza Chemical Work)
WI	whiteness index
XPS	X-ray photoelectron spectroscopy
YI	yellowness index

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List of publications

Papers

1. I. Kriston, E. Földes, P. Staniek, B. Pukánszky: Dominating Reactions in the Degradation of HDPE during Long Term Ageing in Water, *Polym. Degrad. Stab.*, **93**, 1715-1722 (2008).
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