Ildikó Kriston

Some aspects of the degradation and stabilization of Phillips type polyethylene

Ph.D. Thesis

Supervisor:
Enikő Földes

Laboratory of Plastics and Rubber Technology
Budapest University of Technology and Economics

Department of Applied Polymer Chemistry and Physics
Institute of Materials and Environmental Chemistry
Chemical Research Center
Hungarian Academy of Sciences

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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 components of electric and electronic devices are produced from or at least contain plastics. Polyethylene (PE) 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. Several factors led to the success and widespread use of polyethylene. It is cheap and its low density, flexibility, aesthetic appearance and other properties make it ideal as packaging material. It can be processed easily, 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 PE is a simple polymer with an apparently well defined structure, its molecular structure often contains irregularities. 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\textsuperscript{1}. 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. 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.

The stabilization mechanism of phenolic antioxidants is widely discussed in the literature\textsuperscript{1,2,3}. 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\textsuperscript{1}. The stabilizing action is attributed to three basic mechanisms: decomposition of hydroperoxides, reactions with peroxo and alkoxy radicals\textsuperscript{4}. 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\textsuperscript{5}. Phosphines yield esters in a higher portion than phosphites due to the predominance of displacement reactions. The mechanisms of the reactions with hydroperoxide and peroxo 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\(^6\). Phosphines had not been investigated as polyolefin stabilizers previous to the research conducted in our laboratories in cooperation with Clariant and Tisza Chemical Work. The aim of the larger project run at the Joint Laboratory of the Laboratory of Plastics and Rubber Technology at the Budapest University of Technology and Economics and the Department of Applied Polymer Chemistry and Physics at the Institute of Materials and Environmental Chemistry, CRC, HAS was 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, their role in melt stabilization was determined, and correlation was established between their consumption during processing and the properties of the polymer. In addition, high temperature reactions of a phosphite stabilizer with reactive species accelerating the degradation of polyethylene during processing (hydroperoxide, carbon-centered, peroxy and oxy radicals) were investigated by model reactions. 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.

The work in this thesis formed an important part of this larger project. One of its five thematic chapters focuses on the effect of water on the degradation of polyethylene, while the rest on the study of phosphorous antioxidants. Although the thesis was completed the project continues also in the future.

2. Materials and methods

The experiments were carried out with ethylene/1-hexene copolymers of the Tisza Chemical Work (TVK), Hungary, polymerized by Phillips catalyst. Irganox 1010 (Ciba) was used as phenolic antioxidant. Three commercial phosphorous secondary antioxidants supplied by Clariant were studied: a hindered aromatic phosphite (Hostanox PAR 24), a hindered aromatic phosphonite (Sandostab P-EPQ; consisting of di- and mono-phosphonites) and an aromatic-aliphatic phosphine (Pepfine).

The additive-free and the stabilized polymers were pelletized by six consecutive extrusions at 260 °C. Samples were taken after each extrusion step. Plates of 1 mm and films of 100-200 µm thickness were compression molded at 190 °C for characterizing the polymer. Blown films were prepared at 175, 195, 195, 195, 195 °C barrel temperatures, 40 rpm screw speed and 1:4 blow ratio.

The chemical structure of the polymer, the consumption of phosphorous antioxidants during the processing of polyethylene and the products of the phosphite stabilizer formed in model reactions were analyzed by Fourier Transform Infrared (FT-IR) spectroscopy. High performance liquid chromatography (HPLC) was applied for the analysis of the residual amount of hindered phenol after the processing of the polymer. The rheological properties of the polymer were characterized by different methods: MFI was measured at 190 °C with 2.16 kg load; dynamic viscosity measurements were carried out at 210 °C in the range of 0.1–600 s⁻¹; and creep compliance was determined at 190 °C, 500 Pa mean stress and 300 s creep/600 s recovery phase times. The molecular mass and mass distribution of the polymer was determined by GPC at 160 °C in 1,2,4-trichlorobenzene. The crystalline structure of the polymer was characterized by thermal analysis. The color of the samples was measured and the yellowness (YI) and whiteness (WI) indices were calculated as characteris-
tic parameters. The residual stability of the stabilized samples was determined by measuring the oxidation induction time (OIT) in oxygen at 200 °C. The tensile properties of the polymer were measured on dumb-bell specimens, while the mechanical strength of films was characterized by the Elmendorf tear strength measured in parallel and perpendicular directions to the flow, as well as by the dart drop strength. The thermal stability of the investigated phosphite [tris(2,4-di-tert-butylphenyl)phosphite; DTBPP] and its reaction with molecular oxygen were studied at 200 and 240 °C under argon and oxygen, respectively. The reactions of DTBPP with carbon-centered, peroxyl and oxy radicals, as well as with hydroperoxide were studied at 200 °C. The reaction products were analyzed by FT-IR spectroscopy, HPLC, and HPLC coupled with a mass spectrometer (HPLC-MS).

3. Results

In the first part of the research 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. The results proved unambiguously that most chemical reactions are related to each other and only one or two reactions dominate all changes in structure and properties, though several reactions are proposed in the literature. Carbonyl groups play an important role in the processes taking place during the soaking of the polymer. The chemical changes determine all properties including molecular mass, crystalline structure, rheological and mechanical properties.

The efficiency and the reaction mechanism of three phosphorous antioxidants (phosphite, phosphonite and phosphine) were studied under the processing conditions of polyethylene by multiple extrusions without and in
the presence of a phenolic antioxidant. We developed FT-IR spectroscopic procedures to determine the amount of the non-reacted and oxidized phosphorus molecules in polyethylene without using extraction.

We compared the processing stabilizing efficiency of additive packages containing 700 ppm of phosphorous stabilizer and 700 ppm phenolic antioxidant. The results revealed that the chemical structure of the phosphorous antioxidant influences significantly the melt stabilizing efficiency of the additive package during the processing of polyethylene, though the reaction mechanism of various phosphorous stabilizers is considered similar in the literature. The alkyl-aryl phosphine investigated has the best melt stabilizing efficiency by preventing the recombination of macroradicals. It is well reflected in the changes of the rheological properties in the course of multiple extrusions (Fig. 1). On the other hand, in oxygen atmosphere, where the formation of oxygen-containing groups dominates, the three different phosphorous antioxidants have 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 efficiently the polymer from discoloration, which may be explained by the interaction of the additives and/or their transformation products.

We investigated the role of phenolic and phosphorous antioxidants in

![Figure 1](image_url)  
Figure 1 Changes in the melt flow index of polyethylene stabilized with 700 ppm phenolic and 700 ppm phosphorous stabilisers (● phosphonite, * phosphite, ▲ phosphine) as a function of multiple extrusions.
the melt stabilization of polyethylene by studying the characteristics of polyethylene processed by multiple extrusions in the absence of any additive, with a phenolic and one of three different phosphorous antioxidants, respectively, used as a single stabilizer, as well as with phenolic/phosphorous antioxidant packages. The results proved that the chemical reactions occurring in the first extrusion play a determining role in the further reactions of the polymer during subsequent processing steps, even after the total consumption of the phosphorous stabilizer. Comparing the effect of single stabilizers we found that the phenolic antioxidant does not protect the polymer from degradative chemical reactions in the first extrusion, while the phosphorous antioxidants have stabilizing efficiency in an extent depending on their chemical structure (Fig. 2). The phosphite is the least efficient melt stabilizer among them. The phosphine shows the best performance not only in the first, but also in the second extrusion. However, the stabilizing effect of single antioxidants disappears fast in subsequent processing operations, as 700 ppm of phosphorous antioxidants is consumed already in the first extrusion. In two-component antioxidant packages, the main role of the phenolic antioxidant is to decrease the oxidation rate of the phosphorous compound. The hindered

![Figure 2 Changes in the Elmendorf tear strength measured perpendicularly to the direction of flow as a function of the number of extrusions. Samples: polymer processed without any antioxidant (□), with 700 ppm phenolic antioxidant (◇), 700 ppm phosphite (▽), 700 ppm phosphonite (○), 700 ppm phosphine (△).](image-url)
phenol does not alter the stabilization mechanism of the phosphonite and the phosphine, but modifies the reactions of the phosphite. The changes in the characteristics of the polymer during processing are directly related to the decrease in the number of vinyl groups. In the presence of the phosphine and the phosphonite less long chain branches form than with the phosphite. The phenolic antioxidant prevents the long chain branching of the polymer only in a very small extent. Although on the basis of literature sources we might expect that the reaction derivatives of the phosphite increase the thermo-oxidative stability of the polymer, the results of our study do not prove that.

To explore the melt stabilizing mechanism of the antioxidants we compared the additive consumption to the changes in the characteristics of polyethylene during processing. The polymer was stabilized with antioxidant packages consisting of different amounts of phosphorous stabilizers combined with 700 ppm hindered phenol and processed by multiple extrusions. Samples were taken and films were blown from the pellets after each extrusion step. The experiments revealed that 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 rheological characteristics of the polymer and the strength of films processed from that are controlled by the type and the amount of phosphorous stabilizer. The melt stabilizing efficiency of the phosphonite and the phosphine is similar. They differ in their consumption rate: the phosphonite is consumed fast, while significantly smaller amounts are oxidized from the phosphine. These phosphorous compounds hinder efficiently the formation of long chain branching of polyethylene above a critical residual concentration of about 200 ppm (Fig. 3). Below the critical residual concentration the characteristics of the polymer start to change significantly, as the mechanism of inhibition reaction changes; the reactions of the phenolic antioxi-
dant (which hardly prevents the recombination of macro-radicals) determine stabilization. The phosphite hinders the formation of long chain branches less effectively than the two other phosphorous antioxidants. This results in a gradual decrease of film strength even at high residual concentrations of the phosphite (Fig. 3). The discoloration of polyethylene is determined by both types of antioxidants. Although the phosphorous stabilizers contribute strongly to the color stability of polyethylene by decreasing or increasing it, the reactions of the phenolic antioxidant determine the degree of discoloration at a given antioxidant pair.

Model reactions were carried out in order to explore the reason of differences in the stabilization mechanism of the phosphite in the absence and the presence of a phenolic antioxidant, and in comparison to that of the phosphonite and phosphine. The reactions of the phosphite with molecular oxygen, hydroperoxide and oxy radicals were studied at ≥200 °C. 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\textsuperscript{7,8}, and 3) the effect and reactions of solvents can be excluded. The composition of the solid reaction products was analyzed by several techniques. The results of the experiments revealed that the investigated phosphite is thermally instable above its high melting temperature; it starts to decompose at around 200 °C. Besides the known reactions of hindered aryl phosphites, thermal decomposition and recombination reactions take also place at $\geq200$ °C. The phosphite does not react with molecular oxygen, but its decomposition is accelerated by oxygen and especially by radicals. Accordingly, the heat-stability of phosphorous stabilizers has to be taken also into account in their application, as it is one of the factors which influence the processing stabilization of polyolefins.

4. **New scientific results**

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 ones determine changes in the chain structure of the polymer. Close correlation exists between this latter and the properties of the polymer. [1]

2. We developed infrared spectroscopic procedures for the quantitative determination of the consumption of phosphorous secondary stabilizers during the processing of polyethylene. [2,3]


3. We proved that in spite of numerous references claiming the same stabilization mechanism for all phosphorous antioxidants, under the conditions of polyethylene processing, the effect, efficiency and mechanism of phosphate, phosphonite and phosphine stabilizers depend on their structure and differ significantly from each other. [2-4]

4. We showed the first time that phenolic antioxidants do not hinder the degradation of polyethylene in its first processing operation, but phosphorous stabilizers do. The efficiency of these latter depends on their chemical structure. [3]

5. We found that the reaction mechanism of phenolic antioxidant/phosphorous stabilizer packages 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. [3, 4]

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. [4]

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. Besides the reaction with hydroperoxides, the compound undergoes fragmentation that is accelerated by oxygen and radicals, and participates in various recombination reactions. [5]

5. Application of the new scientific results in practice

The research was carried out in cooperation with Clariant, an additive producer, and Tisza Chemical Work, producing polyolefin polymers. Therefore the new scientific results are important not only from the theoretical point of view, but they can be and are used directly in the development of new polyolefin products for specific purposes.
6. Publications

6.1. The thesis is based on the following papers


6.2. Conference presentations


12. Kriston, I., Szijjártó, G., Pénzes, G., Szabó, P., Földes, E., Pukánszky, B.: Foszfit típusú sekunder antioxidánsok stabilizálási mechanizmusának ta-
nulmányozása, Fiatal Analitikusok Előadóülése, MKE Analitikai Sza-
kosztálya, Budapest, November 20, 2007. (lecture)

13. Kriston, I., Pénzes, G., Szijjártó, G., Szabó, P., Földes, E., Pukánszky, B.: Modellkísérletek a foszfit szekunder antioxidáns reakcióinak meg-
határozására, Oláh György Doktori Iskola konferenciája, Budapest, Feb-
ruary 8, 2008. (poster)


15. Kriston, I., Pénzes, G., Szijjártó, G., Szabó, P., Földes, E., Pukánszky, B.: Comparison of the reaction of phosphite, phosphonite and phosphine po-
lymer stabilizers by model experiments, Meeting of the International Ad-
visory Board of CRC, Budapest, May 22, 2008. (lecture)


HPLC-MS and FT-IR, MoDeSt 2008, Liège, Belgium, September 7-11, 2008. (poster)

18. Kriston, I., Pénzes, G., Szabó, P., Földes, E., Pukánszky, B.: Foszforan-
tioxidánsok stabilizálási mechanizmusának tanulmányozása, MTA Kutatói
Fórum, Budapest, October 30, 2008. (lecture)

HPLC-MS and FT-IR, Oláh György Doktori Iskola konferenciája, Budap-
est, February 8, 2009. (poster)

20. Tátraaljai, D., Vámos, M., Kriston, I., Kovács, J., Staniek, P., Földes, E., Pukánszky, B.: Effect of additive combinations on the processing and hy-
drolytic stability of polyethylene pipes, 28th Meeting of Polymer Degra-
dation Discussion Group, Sestri Levante, Italy, September 6-10, 2009. (lecture)

21. Tátraaljai, D., Vámos, M., Kriston, I., Kovács, J., Staniek, P., Földes, E., Pukánszky, B.: Analysis of the efficiency of additive packages in the sta-
bility of polyethylene pipes, 4\textsuperscript{th} European Weathering Symposium, Budapest, Hungary, September 16-18, 2009. (poster)