

Natural antioxidants: a new way to stabilize polyethylene

PhD Thesis

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Abbreviations

AO	<i>antioxidant</i>
BDE	<i>bond dissociation enthalpy</i>
DFT	<i>density functional theory</i>
DHM	<i>dihydromyricetin</i>
DPPH•	<i>diphenyl-picryl-hydrazyl radical</i>
DSC	<i>differential scanning calorimetry</i>
EPDM	<i>ethylene-propylene-diene monomer rubber</i>
FTIR	<i>Fourier-transform infrared spectroscopy</i>
HAT	<i>hydrogen atom transfer mechanism</i>
HDPE	<i>high-density polyethylene</i>
k	<i>constant of chemical reaction rate</i>
L*	<i>optical brightness parameter</i>
LCB	<i>long-chain branch</i>
LDPE	<i>low-density polyethylene</i>
LLDPE	<i>linear-low-density polyethylene</i>
MFR	<i>melt flow rate</i>
¹ O ₂	<i>singlet-state oxygen molecule</i>
O ₂ • ⁻	<i>superoxide radical</i>
OH•	<i>hydroxyl radical</i>
OIT	<i>oxidation induction time</i>
PCL	<i>poly-ε-caprolactone</i>
PE	<i>polyethylene</i>
PHB	<i>polyhydroxybutirate</i>
PLA	<i>polylactic-acid</i>
PP	<i>polypropylene</i>
Q	<i>quercetin</i>
R	<i>rutin</i>
R•	<i>alkyl centered radical</i>
RAF	<i>radical adduct formation mechanism</i>
RNS	<i>reactive nitrogen species</i>
RO•	<i>alkoxy centered radical</i>
ROO•	<i>peroxy centered radical</i>
ROOH	<i>hydroperoxide molecule</i>
ROOR	<i>peroxide molecule</i>
ROS	<i>reactive oxygen species</i>
Sb	<i>silybin</i>
SET	<i>single electron transfer mechanism</i>
Si, Sm	<i>silymarin</i>
SPLET	<i>sequenced proton loss-electron transfer mechanism</i>
STA	<i>simultaneous thermal analyzer (coupled DSC-TGA device)</i>
TGA	<i>thermogravimetric analysis</i>
YI	<i>yellowness index</i>

Chapter 1 Background

1.1 Introduction

Plastic production reached 335 million tons worldwide in 2016 representing a growth rate of 3.88 % compared to the previous year and it grows continuously even today. Plastic demand increased to 49.9 million tons in that year in Europe alone and this huge amount of material is applied mainly by the packaging (39.9 %) and the construction (19.7 %) industry. High and medium density polyethylene (HDPE, MDPE) represents 12.3 %, while low and linear low density polyethylene (LDPE, LLDPE) a considerable 17.5 % share of this market, indicating that polyethylene (PE) in general, is one of the plastics produced and applied in the largest amount in the world [1].

Temperatures and shear stresses are considerable in modern plastic processing technologies of high productivity. Chemical reactions take place during the processing of polymers, which change the structure of the polymer, modify its properties and usually decrease the lifetime of the product. The product must be often protected against various external effects during its application; temperature may vary in a wide range, UV radiation, moisture and other extractive media, etc. may consume stabilizers or initiate degradation. The additive package must be tailored accordingly to render the polymer the required lifetime.

Protection against chemical changes during processing and application is achieved by stabilization, the application of appropriate stabilizers. Practically all polyolefin products contain processing stabilizers, usually a primary, hindered phenolic antioxidant and a phosphorous or sulfur containing secondary stabilizer, while the stabilizers necessary for the application are determined by the conditions under which the product is used. More or less standard additive packages are used in industrial practice, the actual type of the applied stabilizer is usually determined by its efficiency and price.

In the last two decades, the scientific interest turned toward fresh and more interesting areas, the applications of biopolymers in healthcare, or the development of functional and intelligent materials, just to mention a few examples. However, the stabilization and degradation of polyolefins still holds unanswered questions and the Laboratory of Plastics and Rubber Technology of the Budapest University of Technology and Economics and the Institute of Materials and Environmental Chemistry of the Hungarian Academy of Sciences carried out extensive research in this area between 1992 and 2008. The Joint Laboratory, formed by the cooperation of the above mentioned institutes, worked in collaboration with the polymer producer Tisza Chemical Group Plc. (later MOL Petrochemicals Ltd.) and the additive producer Clariant and successfully developed additive packages, which are applied in the industry even today. The scientific impact of the collaboration is represented by the numerous BSc and MSc theses and publications, and two PhD theses. However, because of a reorganization and redefinition of targets, Clariant left the collaboration, which meant a turning point in the research in 2008.

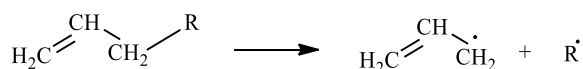
A decade ago the study of Brocca et al. [2] called the attention to the possible health and environmental hazard represented by traditional phenolic antioxidants. Accumulation of phenolic antioxidants like 2,6-ditertbutyl-hydroxy-toluol, or 2-tertbutyl-4-hydroxyanizole, generally applied as polymer and food stabilizers, is measureable in our close environment [3,4] and the potential health effects of their reaction products and metabolites are not understand satisfactory yet [5]. As a consequence, lately the attention turned towards the possible use of natural antioxidants as potential stabilizers for polymers including polyolefins. Nature produces a large number of natural antioxidants to regulate the widest variety of chemical processes. They can be found in the leaves, fruits and roots of plants, and are used as medicine for ages. Natural antioxidants play a key role in radical reactions taking place in the human body, which are more or less similar to reactions occurring during the processing of polyolefins. The beneficial effect of these compounds is well known, the risk of the formation of harmful byproducts is much smaller than in the case of synthetic phenolic antioxidants. In 2008, only a few articles were available, which considered this promising approach [6-10]. This new direction gave impetus to the research, which lead to a collaboration with Sabic, to numerous articles, the thesis of Dóra Tátraaljai, and even to this present work.

1.2 Degradation of polyethylene during processing

The exposure of polyolefins to elevated temperature, shear forces and traces of oxygen initiates thermo-mechanical or thermo-oxidative degradation depending on the availability of oxygen. The thermo-oxidation of polyolefins is an autocatalytic free radical chain reaction consisting of initiation, propagation and termination steps [11-13].

1.2.1 Initiation

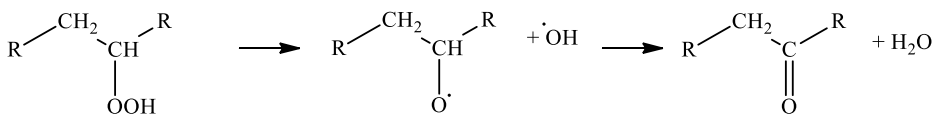
At elevated temperatures an alkyl radical forms in the initial step as a result of C-H or C-C bond cleavage, which rapidly reacts with oxygen during propagation. However, the origin of the alkyl radicals is still controversial [14]. Polyolefin chains always contain weak sites and at these points the activation energy of dissociation is lower than at a regular repeating unit. According to Holström and Sörvik [15-17], in the case of PE, initiation occurs at allylic carbon atoms by the cleavage of a C-C bond (see Scheme 1.1)



Scheme 1.1 Formation of a primary alkyl radical by the cleavage of an allylic C-C bond.

1.2.2 Propagation

The formed alkyl radicals rapidly react (10^7 - 10^9 mol⁻¹s⁻¹) with oxygen molecules forming peroxy radicals as the first step of the propagation process [18]. The activation energy of this reaction is negligible and thus this step of degradation is not influenced by temperature. Peroxy radicals abstract further hydrogen atoms from the polymer chain by the dissociation of C-H bonds, which has considerable activation energy [19], consequently this is the rate determining step of the chain reaction. The rate of hydrogen atom abstraction reaction decreases in the following order: hydrogen atom in allylic position > benzyl hydrogen > secondary hydrogen > primary hydrogen atom [14]. The formed hydroperoxides easily decompose to alkoxy-, hydroxyl- and peroxide radicals under the conditions of polyolefin processing. The rate of decomposition increases with temperature [14] and by the presence of transition metal traces [20]. These radicals abstract further hydrogen atoms from the polymer leading to the auto-acceleration of the degradation. Alcohols, ethers, water and additional alkyl radicals are among the reaction products. Alkoxy radicals participate in β -scission reactions too, which lead to the formation of aldehydes and ketones (see Scheme 1.2)



Scheme 1.2 β -scission reaction of a secondary alkoxy radical.

1.2.3 Termination

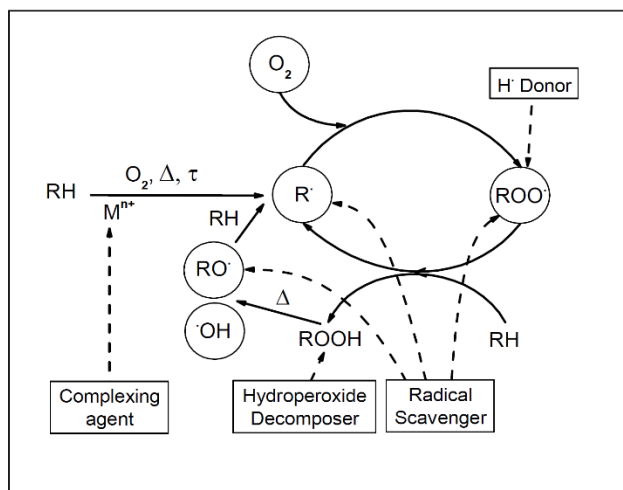
Recombination and disproportion are typical termination reactions of radical processes. The termination of primary and secondary radicals usually occurs by recombination [16], but the increase of temperature makes the reaction route of disproportion thermodynamically more favorable [21]. While fragmentation and β -scission reactions decrease the average molecular weight in the initial and propagation stages of degradation [15], disproportion takes place without changes in molecular weight and recombination leads to increased weight of the molecule [14].

The propagation of radical reactions is rarely straightforward, as there are chances to quite a few reaction pathways to occur and products to form. Therefore, the initial conditions have great impact on the outcome of the degradation process. In the case of thermo-oxidative degradation the average molecular weight of the polymer either decreases or increases [22, 23]. The concentration of oxygen is limited during the processing of polyolefins, which leads to much larger concentration of alkyl than peroxy radicals, consequently to larger number of termination reactions. Increased shear rates lead to fragmentation and additional alkyl radical formation, while traces of transition

metals catalyze the overall process. At large concentration of unsaturated groups, recombination reactions are predominant during processing [20, 24], while at small amount of unsaturations (Ziegler-Natta and metallocene catalyzed polyethylene) the number of reactions leading to extension or scission are comparable [12, 25]. Phillips type polyethylenes have a double bond at one end of each chain thus their dominating degradation reaction during processing is the formation of long chain branches [12]. The viscosity of the polymer increases as a result and its MFR decreases at the same time. The effect of temperature is complex too, as increasing temperature accelerates both the hydrogen atom abstraction and termination reactions, which leads to the formation of long chain branches (if there is a sufficient number of unsaturated groups available), however, chain scission becomes thermodynamically favored at higher temperature [12].

1.3 Processing stabilization of polyolefins

Thermo-oxidative degradation changes the molecular weight of the polymer, which cause premature failure of the product during its application or even during production. In order to prevent degradation, stabilizer packages are applied in small concentrations (usually up to 2 w/w%). The aim of stabilization is to hinder propagation reactions and transform the formed radicals into harmless species without further hydrogen abstraction from the polymer backbone. The scheme of effective stabilization is shown in Scheme 1.3 [14].



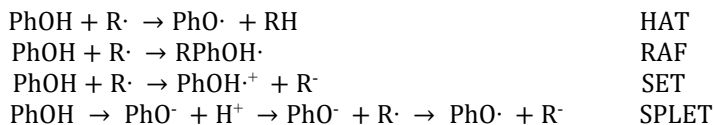
Scheme 1.3 Prevention of thermo-oxidative degradation.

Complexing agents are able to chelate metal ions, which originate from catalyzer traces or from the exposure of the product to metal parts, like wires or springs, during its application. The rate of the reaction of alkyl radicals with molecular oxygen is large; furthermore, alkoxy and hydroxyl radicals cannot be scavenged because of their high reactivity. The two steps of degradation in which stabilizers can intervene are the

hydrogen abstraction of peroxy radicals and the decomposition of the formed hydroperoxides to alkoxy and hydroxyl radicals. The antioxidants applied in industrial practice can be classified as primary and secondary stabilizers, based on this phenomenon.

1.3.1 Primary stabilizers

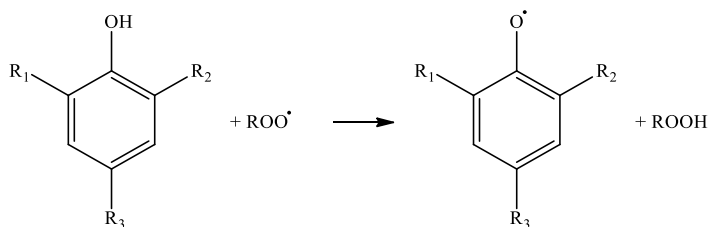
The main principle of the stabilization mechanism of primary stabilizers is that the activation energy of hydrogen abstraction from them is lower compared to hydrogen abstraction from the polymer backbone. The most important radical scavenging mechanisms are hydrogen atom transfer (HAT) [26, 27], radical adduct formation (RAF) [28], single electron transfer (SET) [29, 30], and sequential proton-loss electron transfer (SPLET) [31, 32] (see Scheme 1.4), but the latter two mechanisms rarely occur during polyolefin stabilization, because of the non-polar character of the polyolefin serving as the medium of these reactions.



Scheme 1.4 *The radical scavenging mechanisms of antioxidants.*

Primary stabilizers act as hydrogen donors, or chain braking donors, as peroxy radicals abstract hydrogen atoms from these species rather than from the polymer chain, which would lead to the formation of polymer bound hydroperoxides as a result. Typical primary antioxidants are hindered phenols, secondary aromatic amines, as well as diamine and hydroxylamine substances. Hindered phenols are the most widely applied hydrogen donors used for the stabilization of polymers [33, 34]. After hydrogen atom abstraction by a peroxy radical a phenoxy radical forms [35], which is stabilized by the delocalized electrons of the aromatic ring (see Scheme 1.5), while the steric hindrance of the substituents (e.g. methyl, or tertiary butyl groups) at the 2- and 6-positions should prevent further interactions [36]. The smaller is the steric hindrance generated by these substituents, the more efficient the stabilizer becomes, however, the chances for further reactions with the polymer backbone and the formation of hydrogen bonds among the phenolic hydroxyl groups increase too [37].

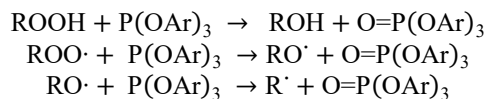
In a hydrocarbon matrix however, the decay of phenoxy radicals is thought to proceed according to first order kinetics with $k \sim 4 \cdot 10^4 \text{ s}^{-1}$ rate [36], which indicates that these radicals participate in further reactions despite the steric hindrance of the substituents. These reactions eventually lead to the formation of chromophoric groups and the discoloration of the product [38].



Scheme 1.5 *The key reaction of hindered phenolic hydrogen donors.*

1.3.2 Secondary stabilizers

The main task of secondary stabilizers is the decomposition of hydroperoxides generated by the peroxy radicals by hydrogen abstraction from the primary stabilizers. The hydroperoxides formed are labile molecules and their thermolysis takes place easily during processing. A proper secondary stabilizer compete efficiently with the thermolysis of hydroperoxides and transform them to thermodynamically stable non-radical molecules. Organic compounds of sulfur and trivalent phosphorus substances, i.e. phosphites and phosphonites are widely applied as hydroperoxide decomposers. Their key reactions are presented in Scheme 1.6.



Scheme 1.6 *Key reaction of hydroperoxide decomposers.*

Trivalent phosphorous substances reduce hydroperoxides to harmless alcohols, meanwhile they oxidize to the corresponding five-valent derivatives. However, hydroperoxide decomposers are able to react also with other peroxide species, like hydroxyl-, peroxy- and alkoxy radicals, that leads to the formation of ethers, water, alkoxy- and alkyl radicals, respectively [14]. The reactivity of trivalent phosphorus compounds depends on their chemical structure based on the electron-acceptor ability and steric effects of the substituents. The rate of reduction decreases according to the following order: phosphonites > alkyl-phosphites > aryl phosphites > hindered aryl-phosphites [39]. The results of earlier studies revealed that synergetic effects occurred, when trivalent phosphorus substances were blended with a primary stabilizer, which lead to the efficient scavenging of peroxy radicals [40]. The consumption of phosphorous secondary stabilizers blended with hindered phenolic antioxidants showed a significant decrease compared to the case when the stabilizer was applied alone [41, 42]. While one of the main roles of the primary stabilizer is to hinder the oxidation of the secondary stabilizer, the rheological properties of polyolefin melts depend on the efficiency of the latter [43].

1.4 Natural antioxidants

Living organisms are constantly exposed to oxidation. Endogenous byproducts (peroxides, transition metals) and exogenous exposure, like UV and other radiations with high energy and heat, lead to the formation of reactive oxygen- (ROS) and nitrogen species (RNS) [44], such as hydrogen peroxide (H_2O_2), superoxide (O_2^-), singlet oxygen ($^1\text{O}_2$), hydroxyl- (OH^\cdot), peroxy- (ROO^\cdot) and alkoxy (RO^\cdot) radicals [45]. More than hundred diseases are caused by or lead to oxidative stress [46-48]. Living organisms synthesize various substances with strong antioxidant effect in order to reduce the number of reactive oxygen species and other free radicals in the body [44, 49, 50]. The reaction mechanisms of these species are similar to those of polymer stabilizers [48]. The idea of applying natural antioxidants as stabilizers instead of synthetic compounds emerged first in the food industry to hinder the decay of food and beverages [50].

1.4.1 Classification, sources

Natural antioxidants (AO) can be divided into two main groups, namely enzymatic and non-enzymatic antioxidants [51]. Enzymatic antioxidants either catalyze directly the decomposition of reactive oxygen species to harmless compounds (catalase, superoxide dismutase enzymes) [52], or regenerate non-enzymatic antioxidants (glutathione reductase, glucose-6-phosphate dehydrogenase) [53]. Non-enzymatic antioxidants represent a wide group of substances, which can be classified in various ways. They can remove pro-oxidative transition metal contaminations, scavenge alkoxy-, or peroxy radicals, or quench singlet oxygen [54]. A classification based on chemical structure is shown in Table 1.1. In the following discussion we focus only on compounds that keep their activity at the processing temperature of polyolefins, as enzymatic antioxidants decompose under these parameters.

Table 1.1 *Classification of non-enzymatic natural antioxidants by their chemical structure.*

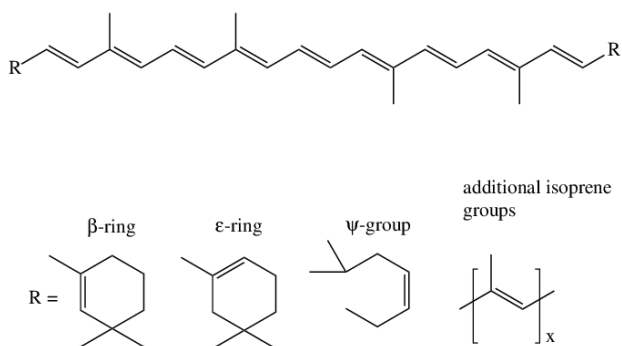
Type	Mechanism	Reacts with	Examples
Carotenoids	quenching, electron transfer, radical adduct formation	singlet oxygen, alkyl, alkoxy, peroxy radicals	carotenes, xanthophylls
Polyphenols	H-atom transfer, transition metal chelation	alkoxy, peroxy radicals, transition metals	flavonoids, curcuminoids, tocopherols, phenolic acids
Phenolic polymers	H-atom transfer, transition metal chelation	alkoxy, peroxy radicals, transition metals	lignin, tannin

The antioxidants presented in Table 1.1 can be found in seeds, leaves of plants, berries, peels of fruits and vegetables, since these species are constantly exposed to ultraviolet radiation, which demand a large concentration of available antioxidants [55]. The main sources of carotenoids are sweet potatoes [56], carrots [57], tomato [58], peppermint and spearmint [59]. Spinach, corn [60] and kale [61] are rich in xanthophylls. Flavonoids form the largest group of natural phenolic antioxidants with more than 6000 candidates [62]. They can be found in the skin of red grapes [63, 64] and red wine [64], in various citruses [65], onion [66] and honey [67] but leaves of stevia [68] and green tee contain them in considerable amounts too [69]. Various seeds and spices like mustard, ginger, fennel or pepper contain large amounts of phenolic acids [70], and curcuminoids can be found in turmeric [57]. Lignin is the major component of the cell wall of vascular plants [71], while tannins can be found in the seed and skin of grapes [72] and in some exotic fruits [73], but also in the leaves and barks of woods [74].

1.4.2 Application of natural antioxidants in polymer stabilization

Carotenoids

Carotenoids are natural pigments with two main subclasses: the carotenes and the xanthophylls. Carotenes are highly conjugated hydrocarbons with a specific end group, and their oxidized species form the xanthophyll subgroup. There are about 600 different type of carotenoids in nature [75]. The typical structure of carotenes is presented in Scheme 1.7. The most important representatives of this subgroup are lycopene, α -, β -, γ -, and δ -carotene, phytofluene, torulene, as well as shorter and longer terpenoids. Members of the xanthophyll subgroup of some significance are lutein, β -cryptoxanthin, as well as alcohols, esters and glycosides of carotenes.



Scheme 1.7 Typical structure of carotenes.

The antioxidant and preservative characteristics of carotenoids are thoroughly studied in food products, but only a few experiments have been carried out in polymer matrices. Cerruti [76] claimed that the extract of tomato skin and seed improves the processing stability of polypropylene (PP) because lycopene scavenges alkyl radicals

efficiently. The additive increased the activation energy of thermal decomposition of PP in nitrogen, but decreased it considerably in oxygen atmosphere. The efficiency of β -carotene was investigated also in a Phillips type polyethylene by Tátraaljai [77]. The stabilizer was used in combination with a phosphorous secondary antioxidant, PEPQ, and α -tocopherol. The latter prevents the oxidation of β -carotene [78, 79]. The additive package protected the polymer against oxidation; the number of carbonyl groups formed during processing decreased to zero when the amount of residual β -carotene was larger than 250 ppm. On the other hand, the additive lost its antioxidant activity and became a pro-oxidant at the large oxygen concentrations prevailing during the measurements of residual thermo-oxidative stability.

The effect of carotenoids is different at high and low oxygen pressure, since they can quench oxygen physically and chemically. Carotenoids are able to quench singlet oxygen molecules physically by energy transfer from the excited singlet oxygen to the carotenoid molecule. The latter returns to the ground state by dissipating its energy through rotation and vibration and thus it is able to quench another singlet oxygen molecule [80]. Chemical quenching or the direct addition of an oxygen molecule, on the other hand, competes with physical quenching [80] and leads to the decomposition of the carotenoid molecule by the formation of epoxy-carotenoids, apocarotenals and various other substances [81].

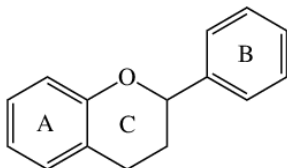
Natural polyphenols

The members of this group of compounds contain at least one phenolic hydroxyl group resulting in their antioxidant activity. Most literature sources agree that the main pathway of the radical scavenging effect of phenolic substances is hydrogen atom transfer (HAT) from the phenolic hydroxyl group to the reacting radical [82]. The energy barriers of the different mechanisms depend on the molecular structure of the reactants and on the properties of the surrounding medium. Hydrogen atom transfer has the smallest energy barrier in a non-polar medium, followed by radical adduct formation [83].

Among other factors, the activity of a phenolic antioxidant molecule depends on the number and position of its phenolic hydroxyl groups, the enthalpy of bond dissociation between the oxygen and the hydrogen atom (BDE), and on the solubility of the antioxidant in the medium of the reaction. Substituents around the phenolic hydroxyl groups affect the activation energy of hydrogen abstraction similarly to hindered phenolic stabilizers. Bond dissociation enthalpies of different phenols are collected in Table 1.2. The values were derived by computation [84] and they clearly show that the energy barrier required for hydrogen abstraction decreases considerably with increasing number of hydroxyl groups in the molecule if they are in the *ortho*-position, while the effect of additional hydroxyl groups is smaller, if they are located in the *para*- and *meta*-positions.

Quite a few subclasses of natural antioxidants belong to flavonoids, the largest group of natural polyphenols [55]. Their structure is derived from the basic structure of flavane (2-phenyl-benzo- γ -pyrane) (Scheme 1.8), which actually lacks any antioxidant activity. Further classification of the compound family is based on the number and

position of hydroxyl groups in the **A**, **B** or **C**, etc. rings, as well as on the degree of conjugation and oxidation of ring **C**. Subclasses of flavonoids are flavones, isoflavones, flavanols, flavonols, flavanones, anthocyanins and proanthocyanidins [85].

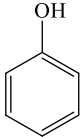
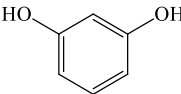
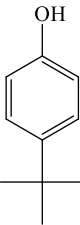
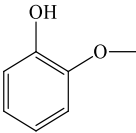
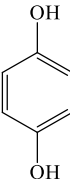
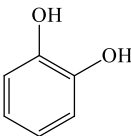
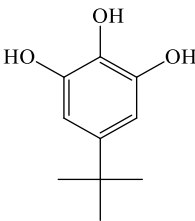


Scheme 1.8 Basic structure of flavonoids, the flavane backbone.

The efficiency of specific flavonoids as processing stabilizers was studied by various research groups [86]. Zaharescu [87] stabilized an ethylene-propylene-diene terpolymer (EPDM) efficiently against γ -radiation with naringenin, caffeic acid and selenium. Both antioxidants delayed the oxidation of the polymer even under irradiation with a sterilization dose. The oxidation induction time of EPDM samples increased significantly with increased amounts of antioxidants and the addition of selenium further improved their efficiency. Cerruti [76] claimed that the flavonoid content of red grape seeds resulted in more efficient thermo-oxidative stabilization of PP than that of tomato extract containing lycopene. The stabilizing effect of a wide range of flavonoids (chrysin, quercetin, hesperidin, naringin, silybin) and α -tocopherol were investigated against thermo-oxidative degradation and ultraviolet radiation in various polyolefins [88, 89]. The researchers found that the flavonol type natural antioxidants ensured the longest oxidation induction times and hindered the most efficiently the formation of carbonyl groups during ultra violet irradiation. Chen [90, 91] investigated the stabilizing efficiency of dihydromyricetin in polyethylene and polypropylene. The author applied the additive at 2000 ppm without any secondary antioxidant. The efficiency of dihydromyricetin was better than that of one of the usually applied synthetic antioxidant, Irganox 1010 in both matrices.

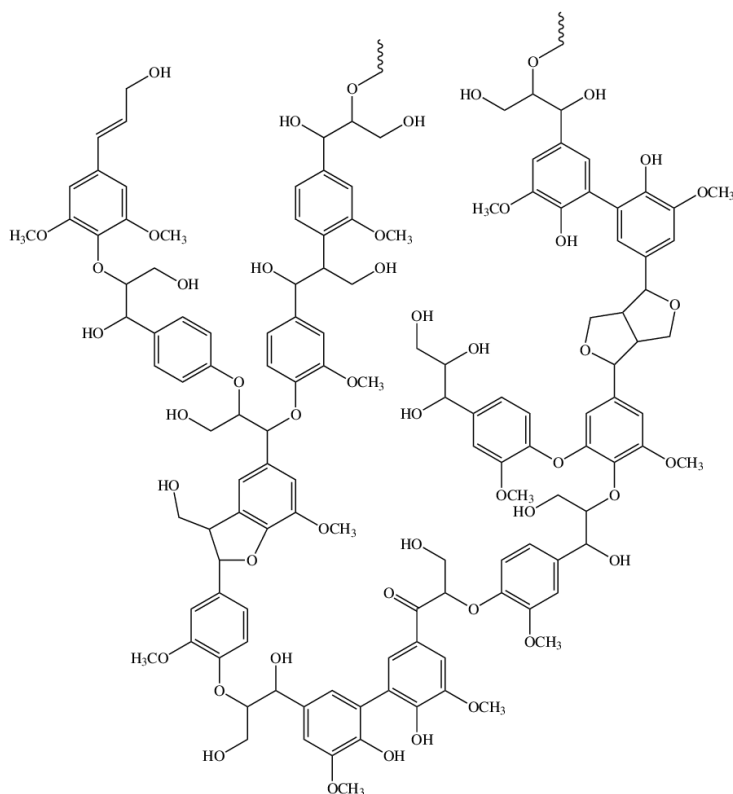
The efficiency of α -tocopherol as processing stabilizer was thoroughly investigated by Al-Malaika [6-10]. Vitamin E outperformed Irganox 1010 and Irganox 1076 in low density polyethylene [6]. The efficiency of vitamin E can be further increased by the synergistic interaction with phosphite type secondary stabilizers, like Ultrinox 626. The secondary stabilizer hinders the consumption of α -tocopherol and decreases the discoloration effect of the quinoidal byproducts of vitamin E [9].

Table 1.2 Bond dissociation enthalpies (BDE) of different phenolic compounds.

Compound	Structure	BDE (kJ/mol)
Phenol		344.2
Resorcinol		340.0
5-tert-butyl-phenol		337.0
Guaiacol		336.6
Hydroquinone		323.2
Catechol		307.3
5-tert-butyl-pyrogallol		278.8

Phenolic polymers

Lignin is a natural cross-linked polyphenol which is formed from monolignols through enzymatic dehydrogenative polymerization in plants [92]. The assumed chemical structure of softwood lignin [93] is shown in Scheme 1.9. The monolignols forming the repeat units of lignin are *para*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol, which can be connected with each other through various covalent bonds. The changing ratio and combination of these units result in various molecular structures [94] and determine the properties of lignin, which is a major component of the cell walls of grasses, soft- and hardwoods [95].



Scheme 1.9 *The assumed chemical structure of softwood lignin [93].*

Lignin is applied, or at least studied for possible applications in polymers. It can be used as a filler, as polyol for polyurethane and polyester synthesis, in phenol formaldehyde and phenol epoxy resins and it was blended with polyolefins, vinyl-polymers, but most successfully with various polyesters, just to mention a few areas [96, 97]. Because of the presence of the phenolic hydroxyl groups in its chemical structure, lignin also has metal ion chelating [98], radical scavenging and stabilizing effects in

polymers. Utilizing the radical scavenging capability of the phenolic OH groups of lignin, considerable number of attempts have been made to use it as stabilizer for the protection of the matrix polymer against oxidation. The antioxidant and stabilizing characteristics of lignin have been studied in several polymers, but mainly in PE [99-102], PP [99, 103-110], PLA [111, 112], PHB [113], PCL [114] and in natural rubber [115, 116].

Kosikova et al. [104, 105] examined the stabilizing efficiency of lignin in polypropylene and found that stabilization may change to initiation of degradation depending on the source and type of the additive. Later the authors [101] extended their work in order to specify the role of lignin in the degradation of PP and PE under different conditions. They found that lignin acted as processing stabilizer, but initiated degradation during long term heat stress or ultra violet irradiation, when it was applied at large concentrations (above 10 wt%). Based on image analysis, Pouteau et al. [117] came to the conclusion that small differences in the solubility parameter of the polymer used influences considerably the compatibility of lignin and the matrix material. Compatibility determines the stabilizing efficiency of lignin, since phase separation limits its protective effect [118]. The authors claimed that lignins with small molecular weight are more compatible both with apolar and polar polymer matrices. Levon et al. [100] found that the thermo-oxidative stability of PE improves considerably when it is blended with lignosulfonate. Most other studies also indicated almost invariably that lignin stabilizes polyolefins, unfortunately less attention was paid to the effect of lignin type on stabilization efficiency and to the comparison of its effect to existing stabilizer systems. Although the phenolic hydroxyl groups of lignin scavenge radicals and improve stability indeed, but because of their relatively small molar number, less efficiency is expected from industrial lignins than from traditional, small molecular weight stabilizers. Lignin does not stabilize the polymer sufficiently, if it is added at small concentrations to the polymer and it forms a separate phase, if the polymer contains it in larger amounts. Heterogeneity is a major obstacle before the use of lignin as stabilizer, it decreases stabilizing efficiency and deteriorates the mechanical properties of the polymer. Using small molecular weight lignin or modifying it chemically by alkylation, acetylation or grafting may improve the compatibility between lignin and the polymer matrix, but such modifications usually decrease the number of active phenolic hydroxyl groups [119].

Chapter 2 Scope

Classic stabilization packages proved to be very efficient and cost effective in the industry thus the development of new stabilizers has not been in the focus of attention lately. Nevertheless, the potential health hazard caused by the reaction products formed from synthetic phenolic antioxidants during processing and application represent a threat. The industry is not prepared with new solutions for the case if the fears about the harmful effect of phenolic antioxidants substantiated or if regulations change dramatically.

More than a few papers focus on the study of the efficiency of natural polyphenols as processing stabilizers and compare their activity to that of hindered phenols frequently applied in industrial practice (Irganox 1010, Irganox 1076, etc.). Some of the results indicate that they are efficient and have potentials as stabilizers. The mechanism of stabilization of these substances is similar to that of synthetic phenolic stabilizers. Their effect on human health is the concern of medical research, however, the risk of their use on human health is assumed small because of their traditional application as medicine. The effect of antioxidant concentration is often not investigated in the studies mentioned above, the authors compare the various compounds at a single, often quite large, 1000 or even 30000 ppm [120] antioxidant content. The aim of this thesis is to carry out a thorough comparison of natural polyphenols under the processing conditions of polyolefins and find relationship between their molecular structure and stabilizing efficiency.

The stabilizing efficiency of curcumin is investigated in **Chapter 4**, based on the promising results of an earlier study carried out in the Joint Laboratory [121]. Curcumin outperformed the generally applied synthetic phenolic stabilizer, Irganox 1010 in the cited study, which became the groundwork of following research. Encouraged by the results, we decided to analyze the mechanism of stabilization and the dependence of the stabilizing efficiency of the natural antioxidant on the concentration applied.

The flavonoid type natural antioxidant, quercetin was studied at the same time together with curcumin and showed similarities and also differences compared to it [122]. The wide variety of the flavonoid family, however, gave us the opportunity to understand the relationship between the chemical structure and the efficiency of these substances more accurately. On the other hand, only a few substances belong to the curcuminoids. Because of this reason, we decided to compare the stabilizing effect of different flavonoid type antioxidants to quercetin and study the influence of bond dissociation enthalpy on efficiency, the interactions between flavonoids and the secondary stabilizer and coloring effects through the examples of silymarin, rutin and dihydromyricetin, respectively, in **Chapter 5-7**.

Natural antioxidants are frequently obtained as mixtures, rather than pure substances from nature. We characterized the effect of the composition of a natural extract and compared it to its main, purified component silybin in **Chapter 8**. In the final chapter, in **Chapter 9**, we briefly summarize the results and collect the new findings of this Thesis.

Chapter 3 Materials and methods

3.1 Applied materials and their sources

The polymer applied in the experiments of the following Chapters was an additive-free, Tipelin FS 471 grade ethylene/1-hexene copolymer powder (melt flow rate: 0.3 g/10 min at 190 °C, 2.16 kg; nominal density: 0.947 g/cm³) polymerized by a Phillips type catalyst. The additive-free polymer powder was provided by the MOL Petrochemicals Ltd., Hungary. Different natural antioxidants were added to the polymer in various amounts, at 0-5-10-25-50-100-250-500 ppm (or up to 1000 ppm in the case of curcumin, see **Chapter 4**) concentrations, to study the effect of additive content on stability. Each compound contained also 1000 ppm (and 2000 ppm, see again, **Chapter 4**) Sandostab PEPQ phosphonite type secondary stabilizer. Source and important physical parameters of the applied additives are summarized in Table 3.1-3.2, while chemical structure of the additives are represented in the 1. Appendix.

Table 3.1 Structure and characteristics of the applied natural antioxidants.

Compound	M (Da)	T _m (°C)	Source
Curcumin (> 65%)	368	179	Sigma Aldrich
Quercetin (Q) (94%)	302	316	Sigma Aldrich
Silymarin (Silybin, 70%) (Si, Sm, Sb)	482	159	Department of Applied Chemistry, University of Debrecen; Sigma Aldrich
Rutin (R) (95%)	611	135	Department of Applied Chemistry, University of Debrecen; Sigma Aldrich
Dihydromyricetin (DHM) (98%)	320	243	Y&L Biotech Co., Ltd., China

Table 3.2 Structure and characteristics of the components of PEPQ.

Compound	M (Da)	T _m (°C)	Source
Diphosphonite (70%)	1035	85-95	Clariant
Monophosphonite (20%)	595		
Phosphite (10%)	647		

3.2 Sample preparation

The polymer and the additives were homogenized in a high speed mixer (Henschel FM/A10) at a rate of 500 rpm for 10 min. In the case of quercetin, the necessary amount of antioxidant had to be dissolved in 200 mL acetone prior to homogenization and the solution was added to the PE powder in the mixer. PEPQ was added in powder form to the polymer powder in all experiments. The resulting powder mixture was dried overnight to remove acetone. The other stabilizers were added to the polymer together with PEPQ directly, without acetone, and homogenized in the high speed mixer under the same conditions as described above. Dry blends were processed and pelletized by six consecutive extrusion steps at 50 rpm and barrel temperatures of 180, 220, 260 and 260 °C under normal laboratory conditions using a Rheomex S ¾" type single screw extruder attached to a Haake Rheocord EU 10V driving unit. Samples were taken after each extrusion step. For further studies films of about 100 µm thickness were compression molded at 190 °C and 5 min using a Fontijne SRA 100 machine.

3.3 Characterization

3.3.1 Characterization of the additives

The thermal behavior of the applied natural antioxidants and that of their mixtures with PEPQ was studied by differential scanning calorimetry (DSC). The measurements were carried out in nitrogen atmosphere with constant, 20 mL/min flow rate in open aluminum pans at a heating rate of 10 °C/min from 0 to 300°C, or 350 °C using a Perkin Elmer Diamond DSC-IC apparatus. The thermal stability of the natural antioxidants was checked by thermogravimetry using a Perkin Elmer STA-6000 apparatus. Samples were heated from 30 °C up to 260 °C at 20 °C/min rate and then held there for 15 min. The measurements were carried out in oxygen atmosphere with constant, 20 mL/min flow rate, in order to include the effects of available oxygen during processing. The possible interactions of the components were estimated also by molecular modeling using the density functional theory (DFT), (the details of the calculations are given in the respective sections, in **Chapter 6-7**), and by Fourier-transform infrared

spectroscopy (FTIR) using a Bruker Tensor 27 spectrophotometer. Infrared spectra of the powder samples were recorded between 4000 and 400 cm^{-1} wavenumbers at 2 cm^{-1} resolution and 16 scans, and then shifts in specific peaks were analyzed.

3.3.2 Characterization of polymer samples

The concentration of the unsaturated functional groups of polyethylene were determined by FTIR spectroscopy on the 100 μm thick compression molded films in transmission mode using the above mentioned Bruker Tensor 27 spectrophotometer. Five spectra were recorded on each sample using the technique mentioned above. The concentration of vinyl groups were calculated from the absorption at 908 cm^{-1} . FTIR spectroscopy was used also for the determination of residual PEPQ content based on the absorption of the P(III)-O-C group at 850 cm^{-1} . The melt flow rate (MFR) of the polymer was determined according to the ASTM D 1238-79 standard at 190 $^{\circ}\text{C}$ with 2.16 kg load using a Göttfert MPS-D MFR tester. Residual thermo-oxidative stability was characterized by the determination of the oxidation induction time (OIT) measured at 200 $^{\circ}\text{C}$ in oxygen atmosphere with constant, 20 mL/min flow rate in open aluminum pans using a Perkin Elmer DSC-7 apparatus. The color of the samples was characterized by the yellowness index (YI) and the optical L^* parameter determined with a Hunterlab Colourquest 45/0 apparatus at normal laboratory conditions.

Chapter 4 The use of curcumin as processing stabilizer in PE

4.1 Introduction

As we mentioned earlier, the stabilization of polyolefins with natural antioxidants got into the focus of attention recently because of the unknown effects of the reaction products of synthetic phenolic antioxidants on human health [2]. Health safety has vital importance in many application areas, like objects contacting food (e.g., packaging materials, water pipes), medical applications, toys, etc. The small molecular mass additives used in polyolefins for stabilization, coloring, or anti-blocking are generally polar compounds, therefore their solubility is small and so they may migrate onto the surface of the polymer during application [123]. Their dissolution into contacting substances cannot be avoided but any harmful effect must be prevented.

Curcumin, 1,7-bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione, is the principal curcuminoid of the *Curcuma longa* rhizomes (turmeric), and usually obtainable as a mixture with demethoxycurcumin and bisdemethoxycurcumin. The powdered root is used as spice, food colorant, and food preservative. The effects and reactions of curcumin have been the subject of investigation in the fields of biology, medicine, pharmacology, and in the food industry yielding a large number of publications for many years. The medical activity of curcumin has been known since ancient times. The beneficial influence can be attributed to its antioxidant activity which involves radical and hydroperoxide scavenging, as well as metal chelating ability [124-130]. The actual reaction site and the mechanism of free radical scavenging have not been clarified unambiguously yet. According to some authors the OH groups on the two phenyl rings participate in the reactions [127, 131, 132], others claim that the β -diketone moiety is responsible for the antioxidant action [133], while other publications [134-136] indicate that the strong antioxidant activity of curcumin originates mainly from the phenolic OH groups, but the central methylene group of the heptadione link plays also an important role.

The effect of curcumin on the processing and high temperature oxidative stability of polyethylene (PE) was studied first in our laboratory [121]. The efficiency of 1000 ppm curcumin was compared to that of the same amount of the commercial phenolic antioxidant Irganox 1010 without and in combination with 2000 ppm phosphonite secondary antioxidant (Sandostab PEPQ) during multiple extrusions. We concluded that curcumin is an efficient melt stabilizer of PE and similarly to the synthetic phenolic antioxidants its efficiency is enhanced by the addition of a phosphorous secondary antioxidant. The effects of curcumin and the synthetic phenolic antioxidant on the characteristics of polyethylene during multiple extrusions are compared in Table 4.1. The reaction with vinyl groups is not affected by the type of the phenolic antioxidant and the consumption rate of the phosphorous secondary antioxidant is reduced by both phenolic stabilizers. On the other hand, melt flow rate increases and the yellowness index decreases as a function of the number of extrusions in the presence of curcumin, while just the opposite occurs in the presence of the synthetic phenolic antioxidant. Curcumin protects the polymer against oxidation more efficiently than Irganox 1010. These results indicate

different stabilizing mechanisms for the two phenols. The goal of the present stage of the work was the determination of the effect of antioxidant concentration on the melt stabilizing efficiency of curcumin/phosphonite additive pair in polyethylene.

Table 4.1 *Effect of 1000 ppm phenolic antioxidant (Irganox 1010 and curcumin) combined with 2000 ppm phosphonite (Sandostab PEPQ) on the characteristics of polyethylene during multiple extrusions.*

Synthetic phenolic antioxidant	Curcumin
Similar number of reactions with vinyl groups	
Long chain branching	Reduced long chain branching
Oxidation of polymer chains	Restricted oxidation of polymer chains
Rate of phosphonite consumption is slower than without a phenol derivative	
Small discoloring effect; increase of YI with increasing processing steps	Strong discoloring effect; decrease of YI with increasing processing steps

4.2 Materials and methods

The properties of the applied materials and the characterization methods can be found in **Chapter 3**.

4.3 Effect of additive content

The concentration of the vinyl groups of the polymer powder decreases significantly (from 1.15 to 0.82-0.84 vinyl/1000 C) in the first extrusion step. Changing the concentration of curcumin from 0 to 1000 ppm and that of PEPQ from 1000 to 2000 ppm does not affect significantly the vinyl group concentration measured after the first extrusion. Considering that <1000 ppm PEPQ is consumed in the first extrusion step even in the absence of curcumin, this result confirms the essential role of the secondary antioxidant in the melt stabilization of polyethylene [41, 42]. However, vinyl group concentration decreases in a slightly lesser amount with increasing curcumin concentration (Fig. 4.1). In further extrusion steps the vinyl groups participate in more reactions leading to a gradual decrease in their concentration. Changing the concentration of PEPQ from 1000 ppm to 2000 ppm does not affect this process, while increasing curcumin concentration leads to a somewhat slower decrease in the number of vinyl groups with increasing number of extrusions. The polymer oxidizes in some extent during processing especially in the first extrusion step (Fig. 4.2). Curcumin protects polyethylene against oxidation, the concentration of carbonyl groups formed decreases with increasing concentration of the antioxidant.

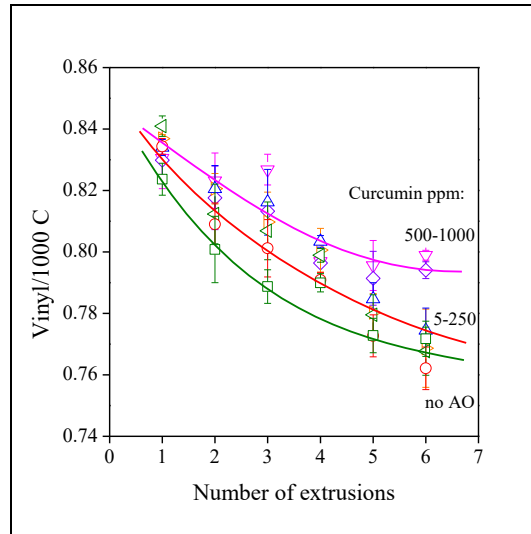


Fig. 4.1 Effect of additive concentration and processing history on the vinyl group content of polyethylene stabilized with 0 (\square), 5 (\circ), 25 (\triangleleft), 50 (\triangle), 100 (\triangleright), 500 (\diamond), and 1000 (∇) ppm curcumin in combination with 1000 ppm PEPQ.

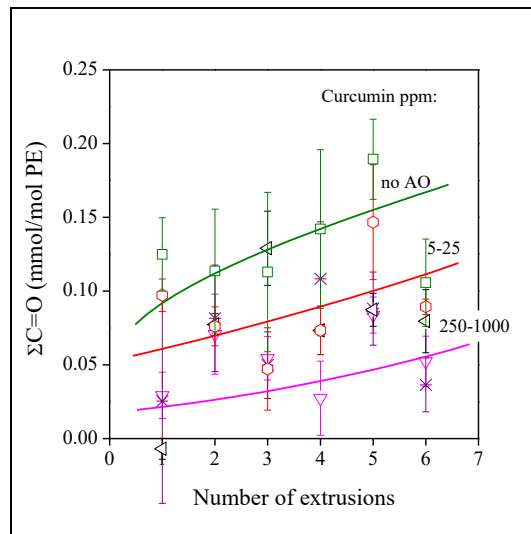


Fig. 4.2 Effect of additive concentration and processing history on the carbonyl group content of polyethylene stabilized with 0 (\square), 5 (\circ), 25 (\triangleleft), 250 ($*$), and 1000 (∇) ppm curcumin in combination with 2000 ppm PEPQ.

Curcumin slows down the consumption of phosphonite in each processing step. 5 ppm of curcumin is already effective in this process, and the increase in its concentration results in a continuous decrease in the consumption rate of PEPQ, as shown in Fig. 4.3.

The changes in the melt flow rate of polyethylene are influenced by the concentration of both types of antioxidants. In the presence of 1000 ppm PEPQ MFR decreases with increasing number of extrusions (Fig. 4.4). The decrease is the most significant in the absence of curcumin. This natural antioxidant contributes to the melt stabilizing efficiency of PEPQ already at the concentration of 5 ppm and the change in the melt flow rate as a function of the number of extrusions decreases with increasing curcumin concentration. At 1000 ppm curcumin content the melt flow rate increases slightly in the multiple processing operations. Processing history influences the melt flow rate less at 2000 ppm PEPQ concentration than at 1000 ppm (the maximum difference among the MFR values does not exceed 0.035 g/10 min). The melt flow rate does not change without curcumin, while it increases continuously with increasing number of extrusions at curcumin concentrations of ≥ 250 ppm. It is worth to note that the MFR values are larger at 250 than at 1000 ppm curcumin content. Comparison of MFR values with the melt flow rate of the PE powder (0.3 g/10 min) shows that the first extrusion step is crucial.

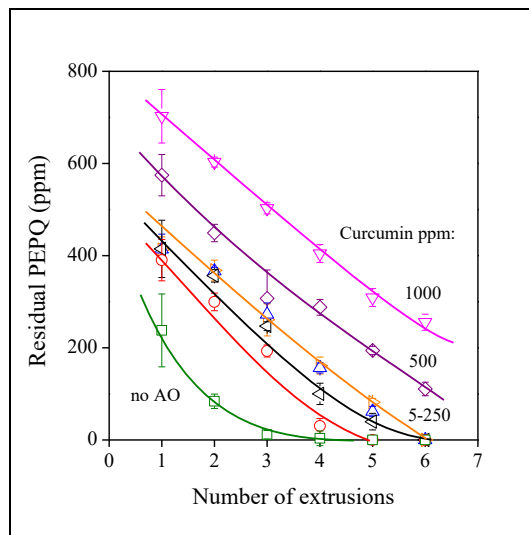


Fig. 4.3 Effect of additive concentration and processing history on the residual amount of phosphonite antioxidant in polyethylene stabilized with 0 (\square), 5 (\circ), 25 (\triangleleft), 50 (\triangle), 100 (\triangleright), 500 (\diamond), and 1000 (∇) ppm curcumin in combination with 1000 ppm PEPQ.

While it is often applied only for the determination of primary stabilizer concentration [137], the high temperature oxidative stability (OIT) is affected by both types of antioxidants (Fig. 4.5). The increase in the concentration of curcumin and PEPQ results in the increase of OIT. At large curcumin concentrations the high temperature oxidative stability decreases with decreasing residual concentration of the phosphonite, while at small concentrations curcumin does not contribute significantly to the effect of PEPQ (Fig. 4.6). Similar effects were reported when additive packages containing hindered phenols and PEPQ were applied for PE stabilization [12].

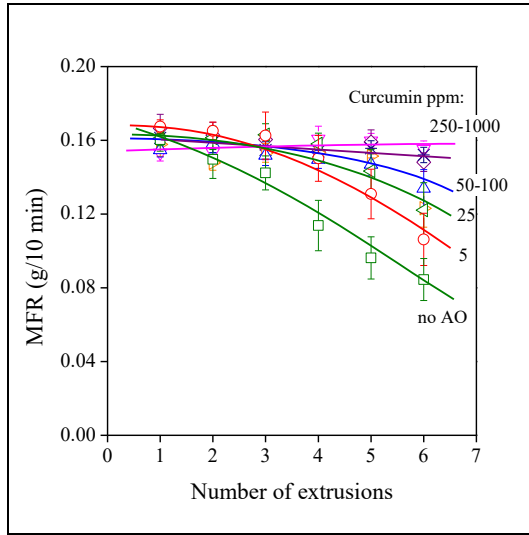


Fig. 4.4 Effect of processing history on the melt flow rate of polyethylene stabilized with 0 (\square), 5 (\circ), 25 (\triangleleft), 50 (\triangle), 100 (\triangleright), 250 ($*$), 500 (\diamond), and 1000 (∇) ppm curcumin in combination with 1000 ppm PEPQ.

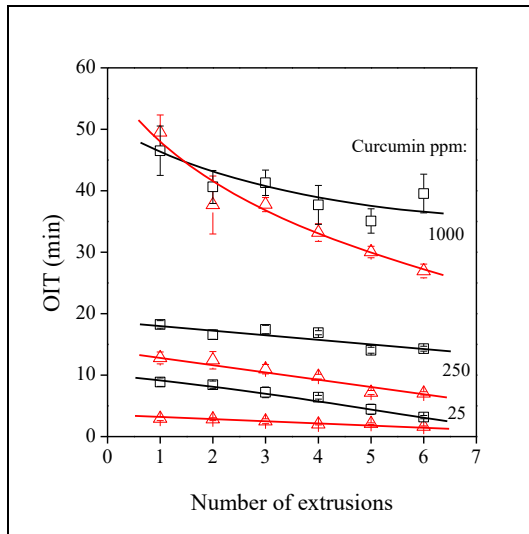


Fig. 4.5 Effect of additive concentration and processing history on the high temperature ($200\text{ }^{\circ}\text{C}$) oxidative stability of polyethylene stabilized with different amounts of curcumin in combination with 1000 (\triangle) and 2000 (\square) ppm PEPQ, respectively.

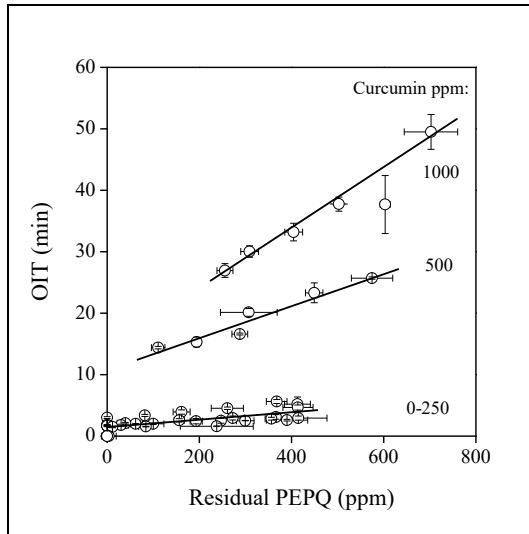


Fig. 4.6 Correlation between the residual amount of phosphonite antioxidant and the high temperature oxidative stability of polyethylene processed by multiple extrusions and stabilized with different amounts of curcumin in combination with 1000 ppm PEPQ.

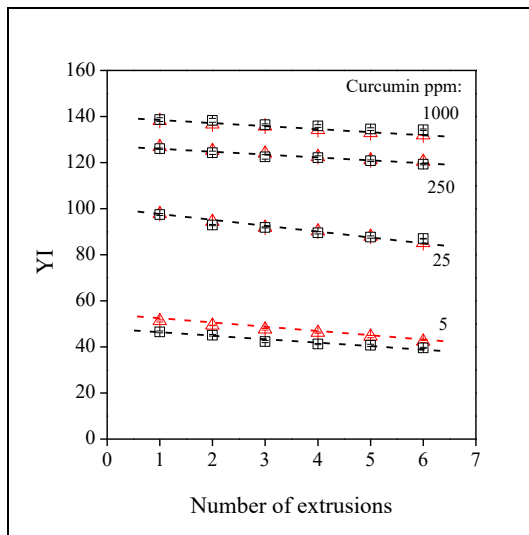


Fig. 4.7 Effect of additive concentration and processing history on the yellowness index of polyethylene stabilized with different amounts of curcumin in combination with 1000 (Δ) and 2000 (\square) ppm PEPQ, respectively.

Curcumin discolors PE strongly already at small concentrations (Fig. 4.7). The phosphonite does not influence discoloration, except at very small curcumin contents (5 ppm), at which an insignificant effect can be observed. Yellowness index decreases with increasing number of extrusions that indicates the participation of the unsaturated linear moiety of curcumin in chemical reactions during the processing of polyethylene.

4.4 Discussion

The reactions of vinyl groups are influenced by several factors. In the presence of a phosphonite antioxidant the concentration of vinyl groups decreases linearly with the residual amount of PEPQ (Fig. 4.8). After the complete loss of the secondary antioxidant vinyl concentration continues to decrease further. The reactions of the vinyl groups are not accompanied by a decrease in the melt flow rate of polyethylene until any phosphonite stabilizer is present. Although there are some small differences in MFR values, a significant decrease of the melt flow rate starts only after the complete loss of the phosphorous antioxidant (Fig. 4.9). The correlation between the concentration of vinyl groups and the melt flow rate (Fig. 4.10) provides some information on the melt stabilizing effect of curcumin after the complete loss of the phosphonite stabilizer (<0.79 vinyl/1000 C). The melt flow rate of polyethylene stabilized with the phosphonite antioxidant alone is affected by the reactions of the vinyl groups more than in the presence of curcumin. In the latter case the decrease in the vinyl concentration is accompanied by a smaller reduction of melt flow rate. This result can be attributed to the reactions alkyl radicals with curcumin.

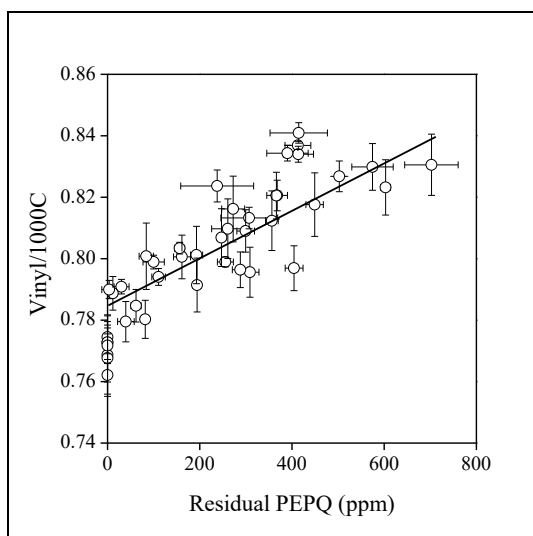


Fig. 4.8 Correlation between the residual amount of phosphonite antioxidant and the vinyl group concentration of polyethylene processed by multiple extrusions and stabilized with different amounts of curcumin in combination with 1000 ppm PEPQ.

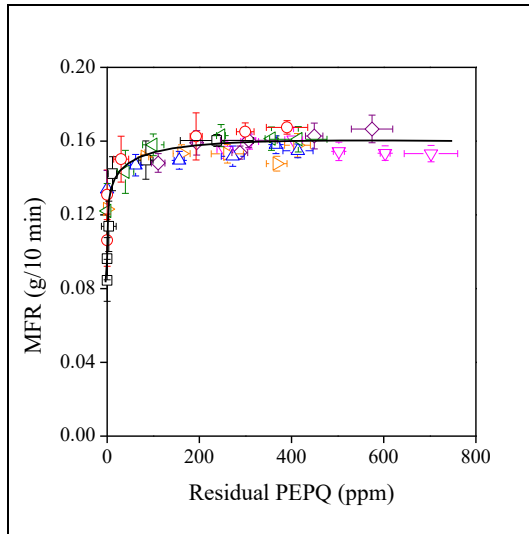


Fig. 4.9 Correlation between the residual concentration of PEPQ and the MFR of polyethylene, processed by multiple extrusions and stabilized with 0 (\square), 5 (\circ), 25 (\triangleleft), 50 (\triangle), 100 (\triangleright), 500 (\diamond), and 1000 (∇) ppm curcumin in combination with 1000 ppm PEPQ.

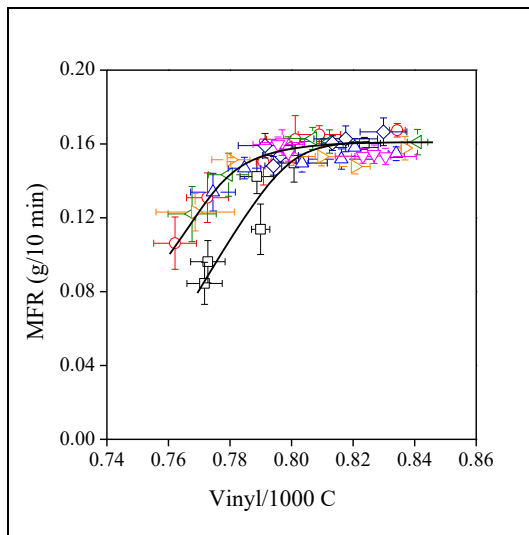
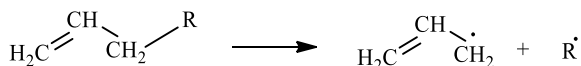


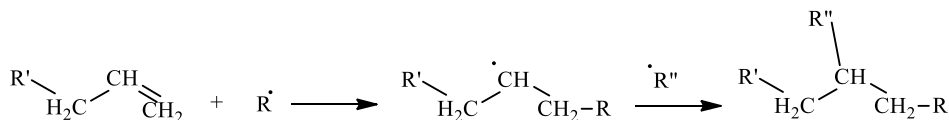
Fig. 4.10 Correlation between the vinyl group concentration and the MFR of polyethylene, processed by multiple extrusions and stabilized with 0 (\square), 5 (\circ), 25 (\triangleleft), 50 (\triangle), 100 (\triangleright), 500 (\diamond), and 1000 (∇) ppm curcumin in combination with 1000 ppm PEPQ.

As we described earlier, the decrease in vinyl group concentration can be attributed to two reactions: a) elimination and b) addition reactions (see **Chapter 1**). Although the formation of alkyl radicals during processing is still controversial [14], Holström and Sörvik claimed [15-17] that the thermal degradation of polyethylene starts with the scission of C–C bonds in allylic position to a double bond. The scission at the carbon atom next to a vinyl group results in the formation of an allyl and an alkyl radical without an essential change in the molecular mass of the polymer (Scheme 4.1).



Scheme 4.1 Formation of a primary alkyl radical by the cleavage of an allylic C-C bond (the same as Scheme 1.1).

The allyl radical can further react and/or leave the system by evaporation at the high temperatures of polyethylene processing resulting in a decrease of vinyl group concentration without any significant change in MFR. The addition of an alkyl radical to the vinyl group leads to the formation of a secondary radical [138, 139] which can react with a further alkyl radical resulting in long chain branching [14] (see Scheme 4.2) and an increase in the viscosity of the polymer.

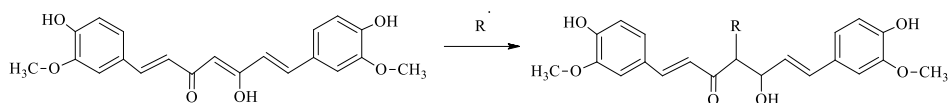


Scheme 4.2 Addition reaction of an alkyl radical with the unsaturation of PE leading to the formation of long chain branches.

The results presented above reveal that the dominating reaction of vinyl groups during processing is the one shown in Scheme 4.1 in the presence of the phosphonite secondary antioxidant. The alkyl radicals formed in the first degradation step react with the small amount of oxygen present during processing. The resultant hydroperoxide groups are decomposed by the phosphonite to stable products. After the oxidation of all phosphonite molecules the addition reaction (Scheme 4.2) becomes predominant resulting in the formation of long chain branches accompanied by a decrease in MFR.

The beneficial effect of curcumin on the melt stability of polyethylene is twofold. The reaction of curcumin with alkyl radicals hinders the oxidation of the polymer (Fig. 4.2) and the formation of long chain branches (Fig. 4.10). The observed increase in the melt flow rate of polyethylene with increasing number of extrusions at large antioxidant concentrations (Figs. 4.4) may be explained by the chain scission of polymer molecules at the α -position to vinylidene and vinylenic groups and/or β -scission of secondary radicals [15-17], and their subsequent addition to a double bond in the linear linkage of curcumin molecules. In the assumed addition reaction (see Scheme 4.3), the number of

conjugated double bonds of curcumin decreases resulting in a lighter color, which seems to be confirmed by Fig. 4.7. The reaction mechanism of curcumin at high temperatures is under further investigation by model experiments.



Scheme 4.3 Assumed addition reaction of alkyl radical to the double bond of curcumin.

The melt flow rate of polyethylene measured after the first extrusion shows some decrease as a function of curcumin concentration. Fig. 4.11 shows that MFR decreases with increasing concentration of the natural antioxidant. The effect is the most significant at small curcumin concentrations and Δ MFR does not exceed -0.02 g/10 min even at 1000 ppm. The small decrease in the stabilizing efficiency of the natural stabilizer can be attributed to the specific interaction of the two antioxidants. This phenomenon is typical for partially- and unhindered phenols. These antioxidants are efficient stabilizers already at small concentrations even when used alone, but their efficiency is often limited by the interactions of their functional groups [37, 140].

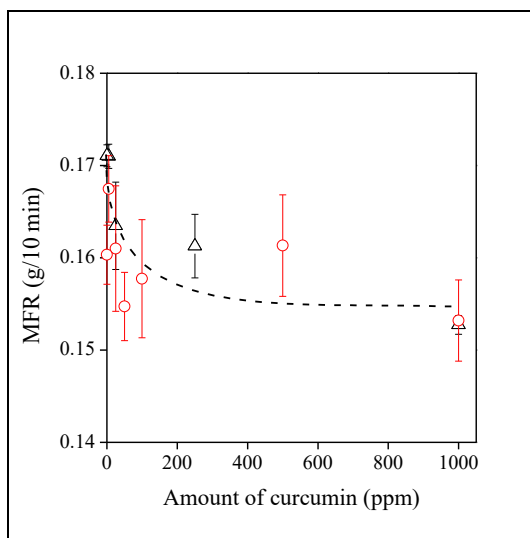


Fig. 4.11 Correlation between the amount of curcumin and the melt flow rate of polyethylene measured after the first extrusion. PEPQ contents: 1000 (○) and 2000 ppm (△).

4.5 Conclusions

The study of the stabilizing effect of curcumin in polyethylene under processing conditions revealed that this natural antioxidant enhances the stabilizing efficiency of phosphonite secondary antioxidants even at the concentration of 5 ppm; the consumption of the secondary antioxidant reduces gradually with increasing curcumin concentration. Curcumin hinders the oxidation of the polymer and the formation of long chain branches. The melt and the high temperature oxidative stabilizing efficiency are controlled by both types of antioxidants. Curcumin colors polyethylene even at low concentrations. The decrease the yellowness index with increasing number of extrusions, as well as the correlation between the concentration of vinyl groups and the melt flow rate of the polymer indicate that besides the reactions of the phenolic OH groups, the double bonds in the linear linkage between the two methoxyphenyl rings also take part in addition reactions with the alkyl macroradicals formed during processing. Model reactions are in progress to explore the exact reaction mechanism of curcumin. In order to more sensitively characterize the efficiency of further natural antioxidants, only 1000 ppm PEPQ will be applied in the following Chapters.

Chapter 5 The importance of bond dissociation enthalpy in stabilization

5.1 Introduction

In recent years, our group set out to explore the possible range of natural compounds to be used as stabilizer in PE. The antioxidant effect of curcumin [121] and quercetin [122] were studied in a Phillips type polyethylene in the presence of a phosphorous secondary stabilizer. Both of them proved to be very efficient, their stabilization efficiency exceed considerably that of the synthetic phenolic antioxidant used in the largest quantity in industrial practice [121, 122].

Quercetin, i.e. [2-(3,4-dihydroxyphenyl)-3,5,7-trihydroxy-4H-chromen-4-one] (Q), is a natural antioxidant found in fruits, vegetables, leafs and seeds in nature. The compound is a flavonol type flavonoid, which has proven antioxidant, antiviral and anti-inflammatory effects in the human body. It was already used for the stabilization of polyolefins [88, 89], and also as a component of active packaging materials [141-144]. Quercetin was added to polyethylene [88], polypropylene [89] and an ethylene vinyl alcohol copolymer and it proved to be an efficient stabilizer in all these cases. However, quercetin was applied at concentrations of 2000-3000 ppm [88, 89] or at even larger quantities in most studies, which left the questions of solubility and mechanism in general unanswered.

Another candidate among flavonoids is silymarin, a flavonolignan compound with the same basic structure as quercetin, and it is used in therapy for more than two thousand years [145]. Silymarin is a unique flavonoid complex that is derived from the milk thistle plant and it contains, among others, silybin, silydianin, and silychristin [146]. The name comes from the traditional use of the substance by nursing mothers to increase milk, but it is best known for its use as a liver protectant and decongestant [147]. Similarly to other flavonoids, silymarin has antioxidant and antiviral effects [148, 149], but it also increases glutathione levels and stimulates protein synthesis [150], thus the substance is a promising candidate for cancer therapy [151-155]. According to our knowledge, no attempt has been made to use silymarin as an antioxidant in polyethylene yet.

The goal of our work was to add another flavonoid type natural antioxidant, silymarin to the compounds studied up to now and explore the possibility of its use as antioxidant in PE and to understand structure-efficiency correlations of flavonoids more thoroughly. Just like in our previous works [121, 122], silymarin was used in combination with a phosphorous secondary stabilizer to comply with industrial practice. The effect of the new antioxidant was compared to that of quercetin used as reference compound. The attention was focused first of all onto melt stabilization, but the effect of the two substances on residual stability and color was also determined. An attempt was made to explain similarities and differences based on the number, position and bond dissociation enthalpies of the phenolic hydroxyl groups located on the two compounds compared.

5.2 Materials and methods

The applied materials are presented in **Chapter 3**. Silymarin was the courtesy of the Department of Applied Chemistry at the University of Debrecen [156]. Purple *Silybum marianum* seeds were collected in the region of Arad, Romania to produce it. 1200 grams of dried fruits were powdered, homogenized and defatted by hexane in a Soxhlet extractor for 6 h. The resulting powder was dried and then macerated with acetonitrile, the solid was removed by sieving, then the solvent was evaporated and the crude silymarin was washed with ice-cold dichloromethane. The yield was 40 g, which is 3.3 wt% of the initial quantity. The methods used for sample preparation and characterization are described in **Chapter 3**. In figures, silymarin is abbreviated as Si, while quercetin as Q in order to increase clarity and help understanding.

5.3 Results and discussion

5.3.1 Composition, properties

Silymarin is not a single well defined compound, but a combination of various substances. The material extracted from milk thistle consists of two main components, 70-80 % are flavonolignans and 20-30 % are fatty acids. The active component also contains several compounds, three main constituents and several minor ones, the latter being present in very small amounts. Silybin is the major component of the mixture being present at about 70 %. The composition of silymarin, the chemical structure of the components and their relative amounts are summarized in Table 5.1 [156].

The comparison of chemical structures reveals similarities, but also differences in the structure of the compounds and shows that they contain different number of phenolic hydroxyl groups at dissimilar positions. Obviously all are active compounds with stabilization activity, but their efficiency may differ considerably. At this stage, in further discussion we assign the structure of silybin to the term silymarin. Although the other compounds react more efficiently with the DPPH[•] radical [157], their amount is much smaller in the mixture and the effect of silybin dominates. One might question the use of such a mixture as industrial additive, but the material is natural, extracted routinely and is available on the market.



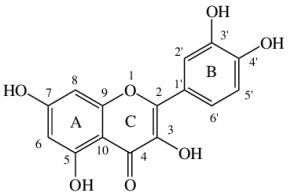
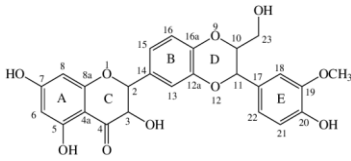
Table 5.1 Average composition of the natural flavonolignan, silymarin [156].

Component	Chemical structure	Amount (wt%)
Silybin		70
Isosilybin		18
Silydianin		10
Silychristin		1
Other		1

The most important characteristics of the two compounds, quercetin and silymarin, compared to each other are listed in Table 5.2. Quercetin which proved to be a very efficient melt stabilizer for PE had two drawbacks: its high melting temperature and strong yellow color. Silymarin is amorphous, the melting temperature of its main component, silybin is much smaller thus it melts during processing that must improve homogeneity. Unfortunately, the color of silymarin is also strong, but instead of yellow it is ochre. The chemical structure of the two compounds show some similarities and differences as well. The **A** and **C** rings are identical, but silymarin lacks the double bond between the **C2** and **C3** carbon atoms. On the other hand, the **B** ring is modified considerably. The number of active hydroxyls is also different as a result, while quercetin has four (actually the unsaturation in ring **C** increase conjugation as well as the activity of the hydroxyl group located at this ring [158]), but it is still not considered as a classic

phenolic hydroxyl group), silymarin has only three active hydroxyl groups. The difference in the number of reactive groups and also in the molecular weight of the two compounds must be taken into account during the evaluation of the efficiency of silymarin as stabilizer for PE.

Table 5.2 Comparison of the characteristics of the two antioxidants used in the study.

Characteristics	Quercetin	Silymarin
M (g/mol)	302.2	482.4
Melting point (°C)	316	amorphous (159°C for pure silybin)
Color		
Structure		
Structural differences	<ul style="list-style-type: none"> – double bond in ring C – 2 hydroxyls at ring B 	<ul style="list-style-type: none"> – single bond in ring C – 0 hydroxyl at ring B – 1 hydroxyl at ring E
No. of phenolic OH groups	4	3

5.3.2 Functional groups, reactivity

The reactivity and stabilization effect of phenolic antioxidants depend on their chemical structure, on the number of hydroxyl groups and their position. The four main mechanisms: SET, SPLET, RAF and HAT have been introduced earlier (see **Chapter 1**). Because of the chemical character of the matrix and the radicals formed, the dominating mechanism is hydrogen atom transfer in polyethylene, but other reactions may also take place during processing. The rate of hydrogen transfer depends on the dissociation enthalpy of the hydrogen atom of the phenolic hydroxyl group.

Dissociation enthalpies can be predicted by quantum chemical calculations and they are listed in Table 5.3 for the compounds compared here. We compare the BDE values of silybin, as the main component of silymarin with quercetin, and identify them

as the BDE values of silymarin in the followings. However the corresponding values of additional components of the silymarin mixture are presented in the table. Although the values were calculated by two different groups on different base sets, they offer some information about the expected reactivity of the two compounds. The **B4'** and **B3'** hydroxyls of quercetin have the smallest bond dissociation enthalpies thus they are expected to be the most active. These groups are absent in silymarin and even the hydroxyl group located in the **C3** position lost its activity, because of the lack of double bond between the positions **C2** and **C3**. The **E20** hydroxyl is expected to be the most active in silymarin, but the bond dissociation enthalpy of even this hydroxyl is rather large.

Table 5.3 Bond dissociation enthalpies of active hydroxyl groups of the flavonoid type natural antioxidants studied [157, 159].

Active OH	Bond dissociation enthalpy (kJ/mol)				
	Quercetin	Silybin	Isosilybin	Silydianin	Silychristin
A5	398.3	410.45	410.45	409.61	410.45
A7	361.9	399.99	399.99	399.99	399.57
C3	339.5	455.64	455.64	455.22	455.22
B3'	315.9	–	–	–	–
B4'	305.0	–	–	–	–
B15	–	–	–	–	352.71
D12	–	–	–	412.12	–
E19	–	–	–	–	352.29
E20	–	367.77	367.77	358.99	–

Based on bond dissociation enthalpies, the activity of silymarin must be much smaller in stabilization reactions than that of quercetin. However, we must consider also the fact that the reactivity of hydroxyl groups changes after the first reaction, which may modify stabilizing efficiency completely. Nevertheless, preliminary considerations predict smaller activity and less efficiency for silymarin than for quercetin.

5.3.3 Processing stabilization

The efficiency of the two antioxidants as melt stabilizers is characterized by the changes in the MFR of the polymer during multiple extrusions. MFR is plotted against the number of extrusions in Fig. 5.1 for compounds containing the two stabilizers in different amounts. We did not plot all the results in the figure, because the large number of points would make comparison very difficult, if not impossible. Moreover, the two stabilizers are not always compared at the same concentration, because of their very different efficiency. This latter statement is amply demonstrated by Fig. 5.1. 25 ppm quercetin has the same effect as 100 ppm silymarin and the comparison of the two compounds at the largest concentration added also shows that silymarin is inferior to

quercetin in melt stabilization as predicted by the comparison of bond dissociation enthalpies in Table 5.3.

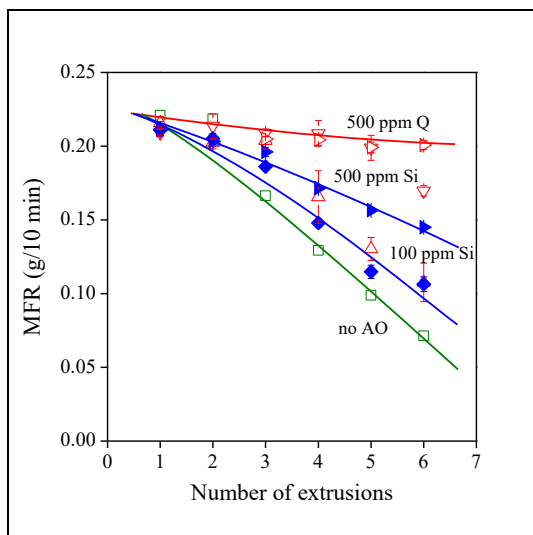


Fig. 5.1 Comparison of the melt stabilization efficiency of the natural antioxidants studied. Symbols: (\square) no antioxidant, (\blacklozenge) 100 ppm Si, (\blacktriangleright) 500 ppm Si, (\triangle) 25 ppm Q, (∇) 50 ppm Q, (\triangleright) 500 ppm Q.

However, because of the dissimilar molecular weight of the compounds and their different number of active OH groups, comparison on a weight basis is misleading. Accordingly, MFR is plotted against the amount of natural antioxidant used in mmol active OH/kg PE in Fig. 5.2 after the first and sixth extrusions in order to simplify the figure. The comparison shows that after the first extrusion, the effect of the two additives is very similar, but it differs considerably at longer processing history. Silymarin cannot protect the polymer against degradation after the sixth extrusion and the correlation indicates that even an increase in additive content would not result in better stability, in the prevention of the formation of long chain branches. The similarity after the first processing run needs further considerations and explanation.

The role of the secondary, phosphorous antioxidant in stabilization is crucial, especially in the first processing step. We showed in our earlier study [121] that the larger efficiency of curcumin resulted from the fact that it protected the phosphorous antioxidant better than Irganox 1010 during processing. Accordingly we may assume that the effect of silymarin on the reaction and consumption of the phosphorous antioxidant differs from that of quercetin. The residual amount of PEPQ is plotted against the number of extrusions in Fig. 5.3.

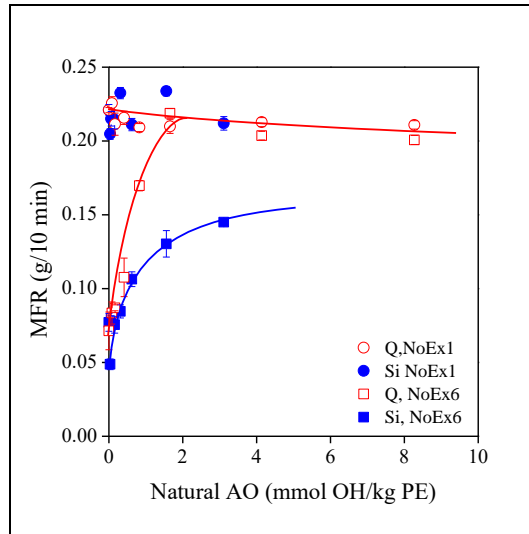


Fig. 5.2 Effect of the amount of natural antioxidant on the MFR of polyethylene at different processing histories. Symbols: (●) Si, NoEx1, (■) Si, NoEx6, (○) Q, NoEx1, (□) Q, NoEx6.

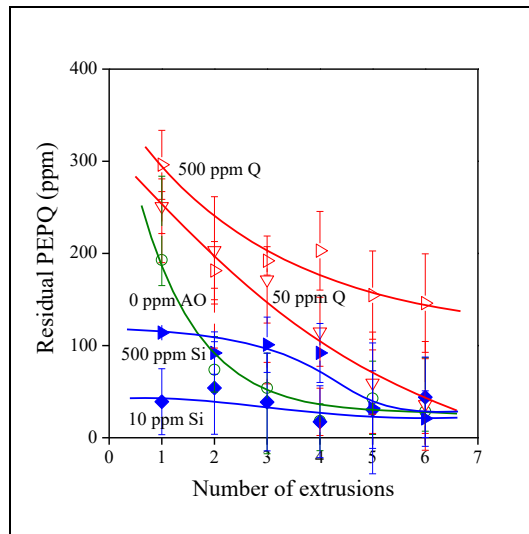


Fig. 5.3 Changes in the amount of residual phosphorous antioxidant with increasing number of extrusions. Symbols: (○) no antioxidant, (◆) 10 ppm Si, (►) 500 ppm Si, (▽) 50 ppm Q, (▷) 500 ppm Q.

The assumption presented above is completely justified. Quercetin protects the secondary stabilizer during processing and the amount of this latter is always larger when the combination of antioxidant/PEPQ is used than in the compound not containing the primary antioxidant. The situation is reversed in the presence of silymarin. Already 10 ppm of silymarin decreases the level of PEPQ below that measured in the compound containing only the phosphorous antioxidant and after the first extrusion the concentration is quite small even at 500 ppm silymarin content. We must emphasize here that the first extrusion is crucial, most of the chemical changes in the structure of the polymer take place at this stage, and the secondary stabilizer is the one that protects the polymer efficiently against such changes. Although at large silymarin content the consumption of PEPQ is slower than without it, PEPQ levels are still smaller than those achieved with the combination of PEPQ and 50 ppm quercetin. The interactions between the primary and secondary stabilizers are obviously different when quercetin or silymarin are used and these interactions seem to play an important role in the determination of the efficiency of the additive package.

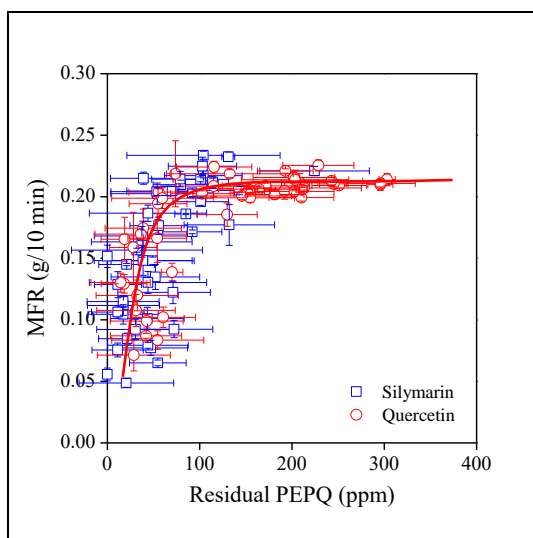


Fig. 5.4 Correlation between the melt viscosity (MFR) of the polymer and the residual amount of PEPQ in the compound. Symbols: (□) silymarin, (○) quercetin.

The crucial role of the primary antioxidant is clearly shown by Fig. 5.4 in which the melt flow rate of the polymer is plotted against its residual PEPQ content. The viscosity of the polymer remains constant until a certain level of PEPQ content is maintained, approximately at 75-100 ppm, but decreases drastically at smaller concentrations. The larger efficiency of quercetin is clearly shown by the fact that larger number of circles are located in the right hand side of the graph, while the opposite is valid for the left hand side, for smaller PEPQ contents. The interaction of the two compounds is certainly one of the main factors determining stabilizer efficiency and it needs further study.

5.3.4 Residual stability, color

Some products, like gas and water pipes, must possess sufficient residual stability in order to reach the necessary lifetime and this must be provided by the stabilizer package. As a consequence, primary stabilizers must be efficient and added in the necessary amounts. The residual stability characterized by the oxidation induction time is plotted against the number of extrusions in Fig. 5.5. All the data were plotted in the figure this time. According to the results 250 or 500 ppm quercetin are sufficient to achieve adequate residual stability, but all the rest of the compounds have OIT values smaller than 10 min, including the one containing 500 ppm silymarin. Obviously, this latter natural antioxidant cannot protect the polymer during long term use and cannot be applied in practice.

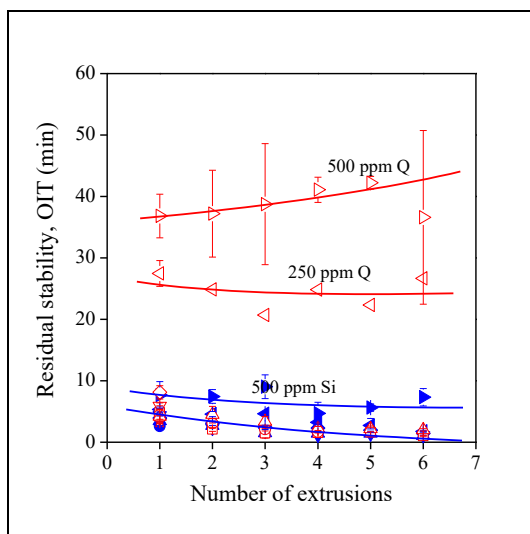


Fig. 5.5 Residual stability (OIT) of polyethylene containing various amounts of the natural antioxidants studied. Symbols: (\triangleright) 500 ppm Q, (\triangleleft) 250 ppm Q, (\blacktriangleright) 500 ppm Si, the rest of the series cannot be distinguished thus the corresponding symbols are not given here. See compositions in the experimental part in **Chapter 3**.

However, comparison is biased again by the dissimilar number of active hydroxyl groups and by the different molecular weight of the compounds studied. Residual stability is plotted against the concentration of the natural antioxidants expressed in mmol OH/kg PE in Fig. 5.6. Residual stability changes linearly with increasing amount of phenolic antioxidant as shown by several literature references [12, 137, 160], but the slope of the change differs considerably for the two compounds. Obviously, the active hydrogens in silymarin are less efficient than those in quercetin and the different efficiency is probably the consequence of dissimilar bond dissociation enthalpies. One

might wonder about the similar stabilities after the first and the sixth extrusion, but this effect was explained earlier with the limited solubility of these compounds in polyethylene and the dissolution of the stabilizer from the dispersed, heterogeneous stabilizer particles during subsequent extrusions [122]. Although the solubility of silymarin is somewhat larger on weight basis, around 45 ppm compared to the 20 ppm for quercetin, but it is practically the same in mmols. OIT results confirm the conclusions drawn from the study of MFR and show that the efficiency of silymarin is considerably smaller than that of quercetin.

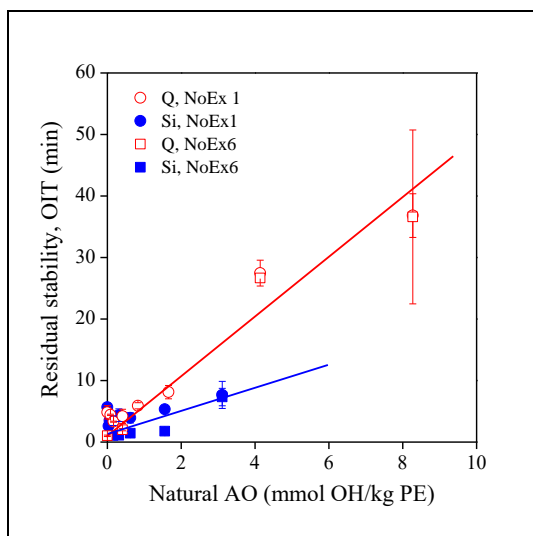


Fig. 5.6 Comparison of the effect of the two antioxidants on the residual stability of PE. The comparison is done on equal functional group content. Symbols: (●) Si, NoEx1, (■) Si, NoEx6, (○) Q, NoEx1, (◻) Q, NoEx6.

The strong color of most natural antioxidants might be regarded an obstacle before their application in certain areas. Quercetin was shown to discolor the polymer considerably. The yellowness index of the polymer is plotted against additive content in Fig. 5.7. The yellow color of the polymer containing quercetin is very strong and similar after the first and sixth extrusions. In fact a more thorough scrutiny reveals that color decreases with increasing number of extrusions which is quite unusual. The yellow color is caused by the stabilizer itself, its degradation products are less colored thus the color of polyethylene decreases with increasing number of extrusions because of the consumption of the additive. Table 5.2 showed that silymarin is other thus it also discolors the polymer. However, the color obtained is somewhat less intense than that with quercetin and it increases with increasing number of extrusion indicating that reaction products are more colored. In spite of the smaller intensity, the color of PE containing silymarin is still quite strong for applications in which colorless or white product is needed. Fortunately, many products are dark or even black in practical applications.

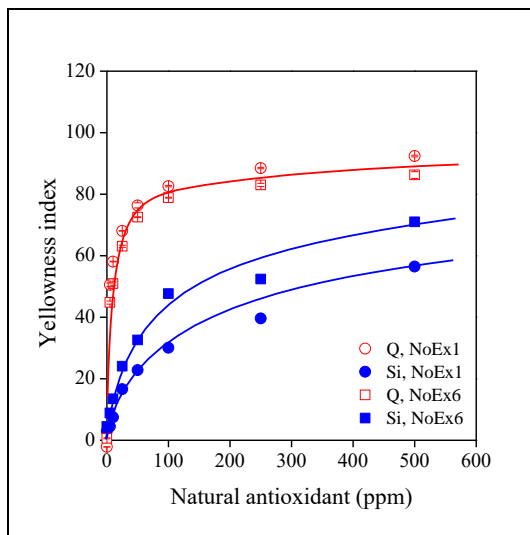


Fig. 5.7 Effect of the amount of natural antioxidants and the number of extrusions on the color of PE. Symbols: (●) Si, NoEx1, (■) Si, NoEx6, (○) Q, NoEx1, (□) Q, NoEx6.

5.4 Discussion

The results obtained clearly show that silymarin is a less efficient natural antioxidant than quercetin. The consumption of vinyl groups is much faster in the presence of silymarin than with quercetin (Fig. 5.8) indicating the formation of long chain branches. As a consequence MFR decreases faster and also the residual stability of the polymer containing silymarin is inferior. The comparison of the two compounds on the basis of equal number of active hydroxyl groups indicated that the smaller efficiency does not result from the smaller number of reactive groups, but probably from the larger bond dissociation enthalpies of the hydrogens on the phenolic OH groups. All these results indicate that silymarin is not a good candidate for practical use as stabilizer in polyethylene.

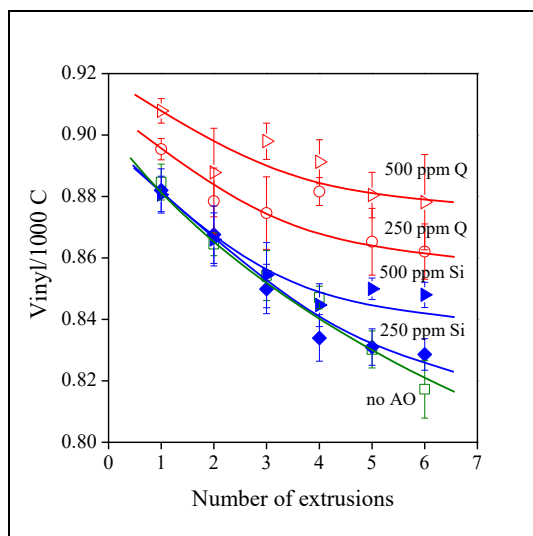


Fig. 5.8 Changes in the vinyl group content of polyethylene as a function of the processing history. Symbols: (□) no antioxidant, (◆) 250 ppm Si, (▲) 500 ppm Si, (○) 250 ppm Q, (▽) 500 ppm Q.

However, the measurement of residual PEPQ content also showed clear differences between the two natural antioxidants. Quercetin protected the phosphorous compound, its consumption became slower with increasing amounts of the flavonoid. On the other hand, the rate of PEPQ consumption accelerated in the presence of silymarin that might have also contributed to the smaller efficiency of this additive. The differences in PEPQ consumption cannot be explained with the dissimilar bond dissociation enthalpies of the hydrogens in the two compounds. We assume that the different rate of PEPQ consumption is the result of the interaction of the primary and secondary antioxidants, which probably differs in the two cases. We proved the existence of such interactions earlier by changes in the DSC traces of the combination of natural antioxidants and PEPQ [121, 122]. We carried out similar measurements for silymarin as well, and a few traces are presented in Fig. 5.9. According to the traces the small melting peak of PEPQ disappears already at 30 % silymarin content and the decomposition of this latter starts at higher temperature with increasing PEPQ content. Both changes indicate indeed that the two compounds interact with each other. However, we do not know anything about the nature of these interactions. The consumption of the secondary, phosphorous antioxidant must be related to these interactions, since it was slow in the presence of quercetin, while the consumption was very fast in the presence of silymarin, which accelerated it, and the melt stabilization efficiency of the two compounds changed accordingly. It is safe to assume that the two processes, i.e. PEPQ consumption and melt stabilization, are related and worth more attention, considerations and study in the future. The amorphous structure of silymarin makes the flavonolignan mixture vulnerable against thermo-oxidative decomposition too. Partial decomposition of silymarin during the processing can lead to the formation of further radicals, which react with both the remaining flavonolignans and PEPQ (see **Chapter 6**).

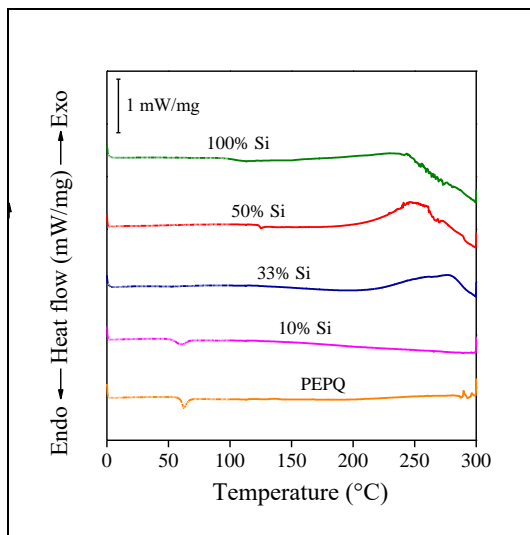


Fig. 5.9 DSC traces of silymarin, PEPQ and mixtures of the two recorded in the first heating run. Effect of interactions on melting (PEPQ) and decomposition (Si).

5.5 Conclusions

The comparison of two natural antioxidants, silymarin and quercetin used as reference showed that silymarin is a much less efficient stabilizer in polyethylene than quercetin. The consumption of vinyl groups is faster and melt flow rate as well as residual stability is smaller in its presence. Silymarin contains less active hydroxyls than quercetin, but comparison on equal molar basis also shows the inferiority of the compound. The difference can be partially explained by the larger bond dissociation enthalpies of the hydrogens in silymarin, but the flavonolignan mixture also accelerates the consumption of the phosphorous secondary stabilizer that must contribute to its inferior efficiency as well. DSC measurements indicate the interaction of the two compounds probably leading to the faster consumption of the phosphorous antioxidant and poor stabilization. Unlike quercetin and curcumin, the natural antioxidants studied earlier, silymarin is not a good candidate as stabilizer for practical applications.

Chapter 6 Interaction of additives in stabilizer packages

6.1 Introduction

The antioxidant effect of curcumin [121], quercetin [122] and silymarin (see **Chapter 5**) was studied in a Phillips type polyethylene in the presence of a phosphorous secondary stabilizer by our group. Two of them are very efficient, their stabilization efficiency exceed that of the synthetic phenolic antioxidant used in the largest quantity in industrial practice. The stabilizers protected the polymer against degradation during processing already at the concentration of 50 ppm and provided sufficient residual stability at 250 ppm. Silymarin was less efficient, because of its slightly different chemical structure (see **Chapter 5**). In this work we study the possible stabilization effect of rutin, another natural antioxidant which belongs to the family of flavonoid glycosides. The compound is the glycoside of quercetin formed with the rutinose disaccharide. It can be found in numerous fruits, citruses, apple, buckwheat and Japanese acacia. It obtained its name from the flower *Ruta graveolens* that contains it in large quantities similarly to other yellow flowers [161]. Rutin has several beneficial effects on the human body; it protects the heart and the arteries, as well as the neural system, since as an antioxidant it neutralizes free radicals [162]. Research is going on to use it as an antidepressant [163] as well as to treat Alzheimer disease [164] and stroke [165] with it.

Most of the flavonoid type natural antioxidants investigated in the previous projects proved to be very efficient processing stabilizers for PE, but they all had some drawbacks like high melting temperature, limited solubility in the polymer and strong color. Consequently, the primary goal of this work was to try another member of the flavonoid family, rutin, as antioxidant in PE. Similarly to previous works [121, 122], (**Chapters 4-5**), rutin was used in combination with a phosphorous secondary stabilizer to comply with industrial practice. The effect of the new antioxidant was compared to that of quercetin used as reference compound. Besides the effect of rutin on the processing stability of polyethylene, we paid more attention to mechanistic aspects and to the possible interaction of the primary and the secondary antioxidant, since previous results indicated that the two types of compounds, i.e. the flavonoids and the phosphonite, interact with each other and the developing interactions might affect their efficiency (see **Chapters 4-5**).

6.2 Materials and methods

The applied materials are listed in **Chapter 3**. Rutin, just like silymarin, was the courtesy of the Department of Applied Chemistry at the University of Debrecen. The applied sample preparation processes and characterization methods are also presented in **Chapter 3**, however additional details must be mentioned here. Neat blends of primary and secondary stabilizers were prepared by mixing the components in 2-propanol to study their interactions without a polymer matrix. The solvent was evaporated in a Büchi Rotavapor R-210 vacuum assisted rotary distillation apparatus in about 1 hour at 40 °C, then the mixtures were dried further overnight at 100 °C and 200 mbar in a vacuum oven. The possible interactions of the components were studied by FTIR and DSC

measurements, which were carried out on the blends, but also by molecular modeling using the density functional theory (DFT). Shifts of characteristic peaks of PEPQ were determined by FTIR spectroscopy using a Bruker Tensor 27 spectrophotometer. Potassium-bromide pellets were prepared containing the above mentioned blends of stabilizers and their spectra were recorded between 4000 and 400 cm^{-1} wavenumber range at 2 cm^{-1} resolution and 16 scans. The DSC measurements were carried out in nitrogen atmosphere with constant, 20 mL/min flow rate in open aluminum pans, with a heating rate of 10 $^{\circ}\text{C}/\text{min}$ from 0 to 350 $^{\circ}\text{C}$ using a Perkin Elmer Diamond DSC-IC apparatus.

The association energies of the complexes were determined by the density functional theory (DFT) using the Perdew-Burke-Ernzerhof (PBE) functional [166]. The DFT calculations were performed with the mRCC program suite [167]. D3 corrections for dispersion were also carried out using the DFT-D3 software [168, 169]. Complex geometries were optimized in the following steps. First, conformers with the lowest energies for PEPQ, quercetin, and rutin were identified using the Merck molecular force field (MMF94) [170] by the MarvinSketch (ChemAxon) program. These structures were then further optimized using the MOPAC2016 program suite by applying the modified neglect of diatomic differential overlap (NDDO) based semi-empirical quantum chemistry method PM6 [171] with D3H4 [172] corrections for hydrogen bonding and dispersion. The termination criterion for the geometry optimization was 0.042 $\text{kJ}/\text{mol}/\text{\AA}$ for the gradient norm. Starting geometries for the complexes were produced using the Maestro 11 program. The ligands were placed over and under the (2,4-di-tert-butylphenyl) groups at one side of the PEPQ molecule, and also over and under its biphenyl groups. In each of these four placements four starting geometries were produced which were rotated by 90 $^{\circ}$ with respect to each other, resulting in 16 initial geometries for both the quercetin and rutin complexes. These structures were then also optimized by PM6-D3H4. The DFT calculations were converged with the 6-31G* basis set, and first-order corrections to the energy were evaluated with the aug'-cc-pVDZ basis set. First, the association energies were calculated as the difference between the energy of the complex and the sum of the energies of the individual molecules. These energies were then corrected for basis set superposition error applying counterpoise correction [173]. Finally probabilities were rendered to each complex structures based on the Boltzmann distribution of their corrected association energies.

6.3 Results and discussion

The results are reported in several sections. First, the characteristics of the two antioxidants are compared and based on their structure an attempt is made to predict their performance. The stabilization efficiency of the two compounds is presented in the next section. Mechanistic aspects and additive interactions are considered in the following two sections, while unresolved issues as well as consequences for practice are discussed in the final section of this chapter. In figures, rutin is abbreviated as R, while quercetin as Q in order to increase clarity and help understanding.



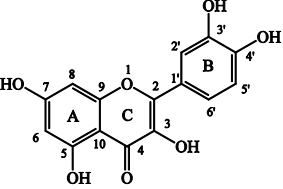
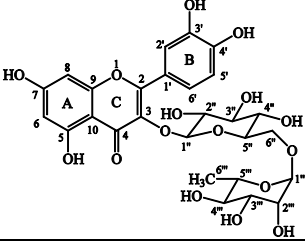
6.3.1 Antioxidant characteristics

Rutin is a flavonoid type antioxidant with very similar structure to quercetin. The latter is a very efficient antioxidant not only in nature, but also in polyethylene under processing conditions [122], thus we expected rutin to perform similarly well. Besides its strong stabilization effect quercetin has several drawbacks, like the high melting temperature resulting in difficulties during homogenization, its small solubility in the polymer and discoloration effect even at small concentrations [122].

The characteristics of the two natural antioxidants are compared to each other in Table 6.1. Their chemical structure is quite similar, the only difference is the two saccharide rings attached through the OH group in position **3** of ring **C**. The number of phenolic OH groups is the same and the double bond is present in ring **C** as well. Consequently, stabilizing efficiency should be approximately the same, although also the OH group in ring **C** was shown to take part in stabilization reactions [158, 159]. The effect of the attachment of the rutinose disaccharide is difficult to predict, it may change the bond dissociation enthalpy of the phenolic OH groups (later in **Chapter 6.3.3**) or can interact with them thus decreasing their efficiency.

If we consider the drawbacks of quercetin listed above, the melting temperature of rutin is much smaller than that of quercetin, which is a clear advantage. The lower melting point facilitated homogenization; rutin was added directly to the polymer powder without the use of a solvent-based procedure. The color of the two additives comes from the conjugation of the double bond in ring **C** mainly with the free electrons on the oxygen atoms of ring **C** and the aromatic π electrons in ring **A**. Accordingly, strong discoloration effect is expected also from rutin in spite of the fact that the color of the two antioxidants differ somewhat. Unfortunately, not much difference is expected in the solubility of the two compounds either, the large number of polar OH groups in the disaccharide moiety does not facilitate the dissolution of the rutin molecule in PE. Based on Table 6.1, similar efficiency, but small solubility and strong discoloration is expected when rutin is used as stabilizer in polyethylene.

Table 6.1 Comparison of the characteristics of the two antioxidants used in the study.

Characteristics	Quercetin	Rutin
M (g/mol)	302.2	610.5
Melting point (°C)	316	167
Color		
Structure		
Structural differences	- 1 hydroxyl at ring C	- no hydroxyl at ring C - 2 sugar rings attached
Phenolic OH groups	4	4

6.3.2 Stabilization efficiency

The vinyl group content of the polymer is plotted as a function of the number of processing steps in Fig. 6.1. Only a few, selected compositions are shown to avoid confusion and facilitate the viewing of the results. Vinyl content decreases with increasing processing history as expected and both stabilizers hinder the reactions resulting in long chain branching. Quite surprisingly, the vinyl group content of the polymer is smaller at 5 but especially at 10 ppm rutin content than that of the neat polymer containing only the secondary antioxidant. Vinyl content increases at all concentrations in the presence of quercetin compared to the sample containing only PEPQ. However, such differences are not observed at large additive contents; the concentration of vinyl groups is practically the same in the presence of both natural antioxidants. The negative effect of rutin at small additive contents needs further study and considerations.

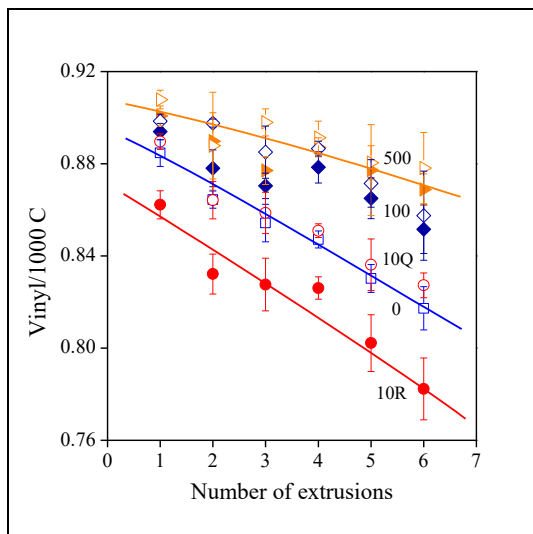


Fig. 6.1 Effect of the number of extrusion steps and additive concentration on the vinyl group content of PE. Symbols: (□) neat, (○, ●) 10 ppm, (◇, ◆) 100 ppm, (▷, ►) 500 ppm additive; empty: quercetin, full: rutin.

The influence of the additives was presented as a function of processing history in Fig. 6.1. However, the molecular weight of the two antioxidants differs considerably, thus the molar concentration of the active phenolic groups is also different. In order to check the effect of the two compounds at equal molar concentrations, the number of vinyl groups is plotted against antioxidant content in Fig. 6.2. Apart from small concentrations, the effect of the two natural antioxidants is very similar confirming the conclusions drawn above. At very small additive contents, rutin accelerates the consumption of the double bonds, but it protects the polymer against degradation similarly to quercetin at large concentrations.

Earlier studies have shown that the presence of the secondary antioxidants, the phosphonite in our case, is essential for the protection of the polymer. The residual amount of the phosphonite antioxidant is plotted against the number of extrusions in Fig. 6.3. At 10 ppm, rutin accelerates the consumption of the secondary antioxidant and it seems to be inferior even at 100 ppm than quercetin. On the other hand, the effect of the two natural antioxidants is very similar at the largest additive content, at 500 ppm. Apparently, rutin takes part in a reaction or reactions, which results in the consumption of PEPQ and the insufficient amount of secondary antioxidant leads to the faster consumption of vinyl groups. This latter usually indicates the formation of long chain branches and the increase of viscosity.

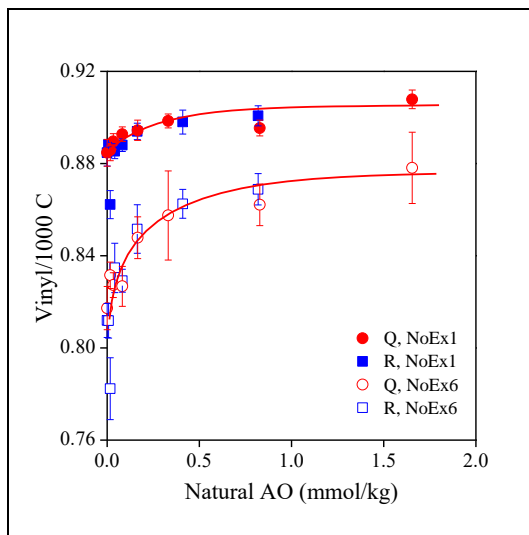


Fig. 6.2 Dependence of the number of vinyl groups of PE on the concentration of the natural antioxidant. Symbols: (●) *Q*, NoEx1, (■) *R*, NoEx1, (○) *Q*, NoEx6, (□) NoEx6.

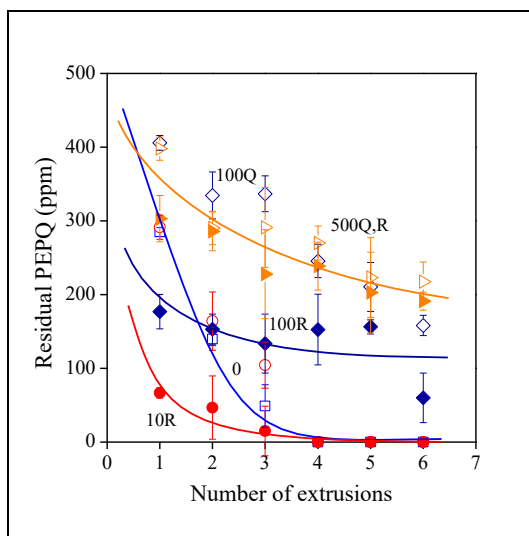


Fig. 6.3 Influence of processing history (NoEx) and additive content on the amount of residual secondary stabilizer (PEPQ) remaining in the polymer after extrusion. Symbols: (□) neat, (○, ●) 10 ppm, (◇, ◆) 100 ppm, (▷, ►) 500 ppm additive; empty: quercetin, full: rutin.

The MFR of the polymer is plotted against the number of extrusion steps in Fig. 6.4. The differences predicted above are clearly seen in the figure. Compared to the neat polymer, MFR decreases considerably at the rutin content of 10 ppm, while the presence of quercetin results in visible improvement in MFR already at this small concentration. The differences are obviously related to the consumption of the secondary antioxidant and the reaction of the vinyl groups as described above. On the other hand, the effect of the two additives is practically the same at large concentrations, above 100 ppm. In order to see the effect of additive content better and account for the dissimilar molecular weight of the two additives, MFR is plotted against additive content in molar concentrations in Fig. 6.5. Considerable improvement is seen in viscosity after the sixth extrusion with increasing antioxidant concentration, while a slight decrease in efficiency after the first processing step. This latter was explained with the interaction of the two kinds of antioxidants before [122]. However, the results clearly prove that apart from small concentrations, both natural antioxidants protect the polymer against degradation during processing equally efficiently.

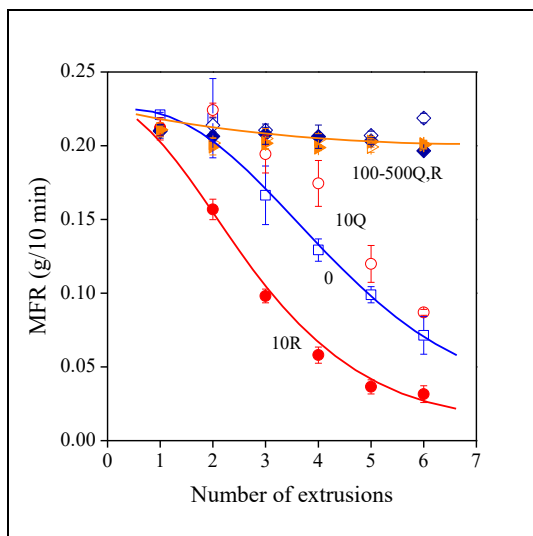


Fig. 6.4 Effect of the number of extrusions and the amount of natural antioxidant added on the viscosity (MFR) of PE. Symbols: (\square) neat, (\circ , \bullet) 10 ppm, (\diamond , \blacklozenge) 100 ppm, (\triangleright , \blacktriangleright) 500 ppm additive; empty: quercetin, full: rutin.

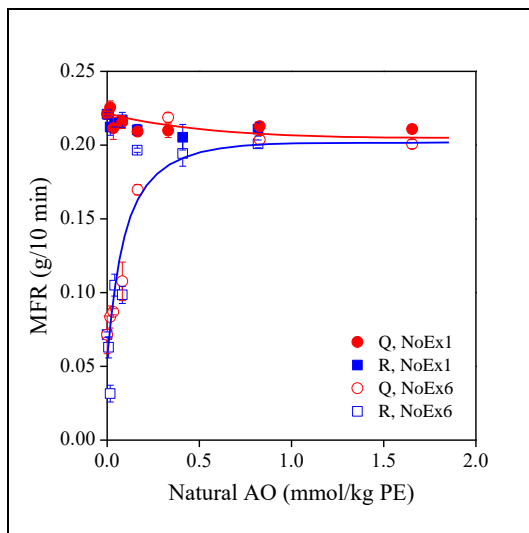


Fig. 6.5 Dependence of MFR on the concentration of natural antioxidant after the 1st and 6th extrusions. Symbols: (●) *Q*, NoEx1, (■) *R*, NoEx1, (○) *Q*, NoEx6, (□) NoEx6.

The residual stability of the polymer is very important in certain, long-term applications, e.g. for pipes. Residual stability, characterized by the oxygen induction time (OIT), is plotted against the amount of the natural antioxidants on a molar basis in Fig. 6.6. Although the standard deviation of OIT results is usually quite large, the tendency is clear, residual stability increases practically linearly with the increasing amount of the natural phenolic antioxidants in accordance with some previous results [137, 160]. Taking into account the uncertainty of the measurement, one cannot observe any difference in the efficiency of the two compounds. Considering all the results related to the stabilization effect of the two natural antioxidants studied, we must conclude that the replacement of the OH group in ring C with the disaccharide moiety does not influence the efficiency of the compound. On the other hand, some reaction or effect results in the deterioration of properties at small rutin contents, which needs further considerations.

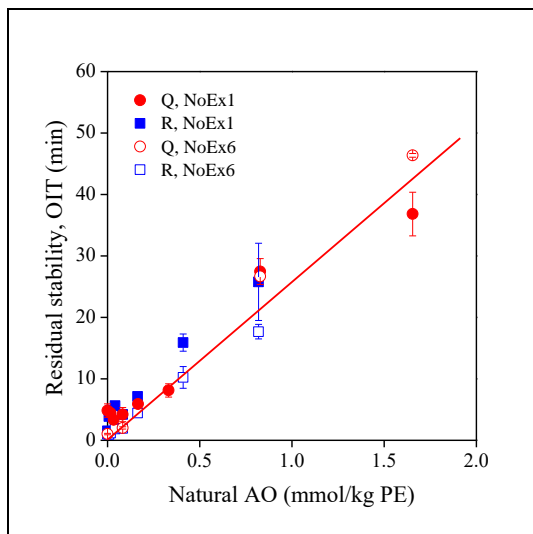


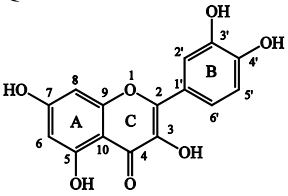
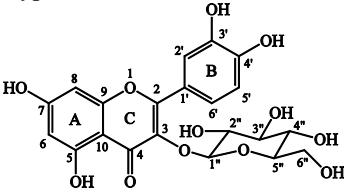
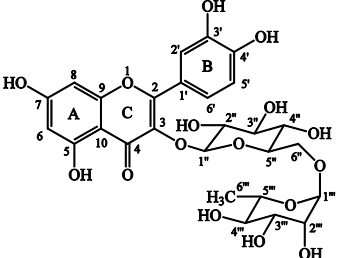
Fig. 6.6 Linear dependence of the residual stability of PE on the concentration of the natural antioxidant. Similar effect of quercetin and rutin. Symbols: (●) Q, NoEx1, (■) R, NoEx1, (○) Q, NoEx6, (□) R, NoEx6.

6.3.3 Mechanistic aspects

The four main mechanisms of stabilization reactions of phenolic antioxidants and the relationship between their efficiency and their characteristic bond dissociation enthalpy values were discussed earlier (see **Chapter 1**). The rate of hydrogen transfer depends on the dissociation enthalpy of the hydrogen atom from the phenolic hydroxyl groups and a relatively close correlation was found between the smallest bond dissociation enthalpies of the phenolic hydroxyl groups of selected natural antioxidants and the consumption of a secondary antioxidant (PEPQ) [174].

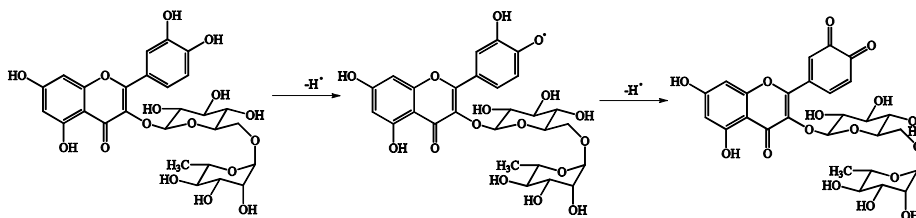
Bond dissociation enthalpies (BDE) can be determined by molecular modeling approaches. Cai et al. [175] calculated the bond dissociation enthalpies of the four phenolic hydroxyl groups of quercetin, hyperin containing one saccharide ring and rutin at the UB3LYP/6-311G level. The results are summarized in Table 6.2. According to the table, substitution at position **3** in ring **C** with increasing number of saccharide rings results in an increase of the BDE of all phenolic OH groups. The authors explained the increase with the increasing rotation of rings **A** and **B** relative to each other [175]. Similar results were obtained also by Renganathan et al. [176] showing the increase of BDE in rutin as the result of the substitution with the disaccharide ring. According to these calculations, the efficiency of rutin should be smaller than that of quercetin, but apart from small concentrations, this did not prove true. Obviously, in spite of the close correlation mentioned above [174], bond dissociation enthalpy is not the only factor determining the efficiency of the natural antioxidants studied.

Table 6.2 Effect of substitution on the reactivity of the active hydroxyl groups of natural antioxidants; comparison of quercetin, hyperin and rutin [175].

Structure	BDE (kJ/mol) of the hydroxyl group			
	B4'	B3'	A5	A7
Quercetin 	317.57	275.31	375.30	319.24
Hyperin 	318.82	282.84	378.65	323.84
Rutin 	339.32	308.78	396.64	345.64

According to the HAT mechanism, quercetin first loses a hydrogen atom during its stabilization reaction and then transforms into a quinoidal compound. Because of its hydroxyl group in ring C, quercetin can take a keto and an enol form [177, 178]. Only the keto form occurs in rutin, because of the lack of hydroxyl in ring C. The stabilization reaction of rutin is presented in Scheme 6.1. Reaction with the DPPH[•] radical showed that hydrogen abstraction occurs from the hydroxyls at the **B3'**, **B4'** and **C3** positions in quercetin, while at the **B3'** and **B4'** positions in rutin. The participation of the **C3** hydroxyl in stabilization is supported by the fact that the number of DPPH[•] radicals scavenged by a quercetin molecule in N,N-dimethylformamide solution is 2.35, compared to the value of 2.00 for rutin [179]. These results predict again smaller efficiency for rutin than for quercetin, which is not supported by the experimental results. Obviously, neither the smaller BDE values nor the lack of the OH group at the **C3** position determines efficiency, since the reaction of the **B3'** and **B4'** hydroxyl groups is the decisive factor in

stabilization. However, the calculations and the model experiments do not explain the smaller efficiency of rutin at small concentrations and the similar effect at large additive contents.



Scheme 6.1 Assumed HAT reaction mechanism of rutin.

6.3.4 Interactions

Some of the results obtained during the study of the stabilization efficiency of various natural antioxidants indicated that the primary and the secondary antioxidants interact with each other and that the interaction influences their efficiency [121, 122], (see **Chapters 4-5**). The consumption of the phosphonite secondary stabilizer was quite different in the presence of the various natural antioxidants, which determined the efficiency of the entire package. The existence of interactions could be deduced from other phenomena as well. The melting traces of quercetin, PEPQ and the mixture of the two recorded by DSC are presented in Fig. 6.7. Quercetin has a sharp melting peak at around 320 °C, which becomes diffuse and shifts to lower temperatures in its 75 mol% blend with PEPQ clearly indicating the interaction of the components. The effect is less clear in the case of rutin, because of its less regular structure. Interactions also might differ between rutin and PEPQ compared to quercetin and the secondary stabilizer. The composition dependence of melting temperatures is presented in Fig. 6.8, showing strong changes in the melting temperature of quercetin, but hardly any effect for rutin. One might conclude that interactions are stronger between quercetin and PEPQ than for the rutin-PEPQ pair.

Changes in melting temperatures indicate the development of interactions, but do not tell anything about their character. The two components, PEPQ and the natural antioxidant, may form hydrogen bonds or enter into aromatic, π electron interaction with each other. FTIR spectroscopy is an adequate tool to detect the formation of strong hydrogen bonds between two substances. A shift in the absorbance of the hydroxyl groups of the natural antioxidant or the change of the POC absorbance of PEPQ would be a clear indication of such interactions. The dependence of the wavenumber of this latter vibration on the composition of natural antioxidant/PEPQ blends is presented in Fig. 6.9. Similarly to melting temperatures, FTIR band shifts indicate stronger interactions between quercetin and PEPQ than between rutin and the secondary antioxidant.

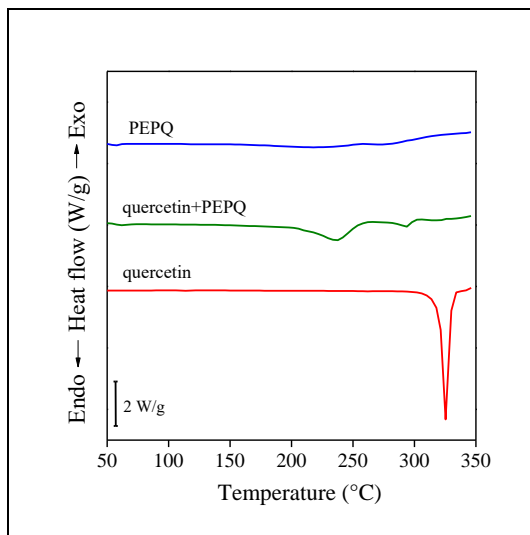


Fig. 6.7 DSC melting traces of PEPQ, quercetin and their mixture (75 mol% quercetin and 25 mol% PEPQ). Interaction of the additives.

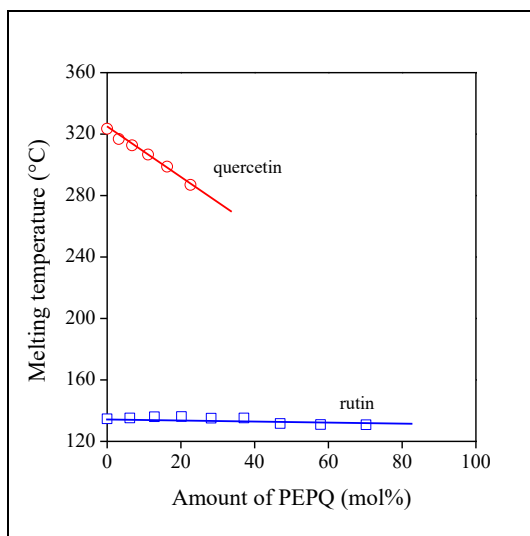


Fig. 6.8 Effect of composition on the melting temperature of the blend of PEPQ and the natural antioxidants. Symbols: (○) quercetin, (□) rutin.

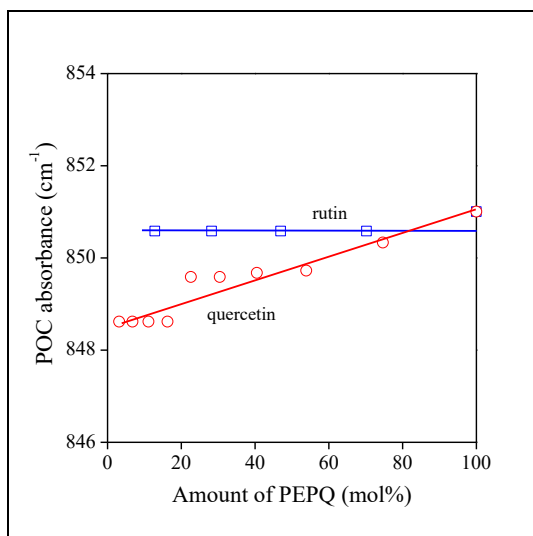


Fig. 6.9 Dependence of the position of the POC absorbance at around 850 cm^{-1} wavenumber on the composition of PEPQ/natural antioxidant blends. Symbols: (○) quercetin, (□) rutin.

The reliability of these observations was checked by molecular modeling. We also hoped that the calculations reveal further details about the character of these interactions and identify the participating groups. We described the calculation process earlier in this chapter.

The calculations predicted the development of strong interaction between quercetin and PEPQ. The complex presented in Fig. 6.10 forms with 96.5 % probability. Besides the formation of hydrogen bonds, also the overlapping of the aromatic rings of the two components contribute to interactions. Interesting and important to note that rings A and C participate in the interaction and not the hydroxyl groups taking part in the stabilization reactions. The formed complex explains the changes in the melting temperature of quercetin, the shift in the POC bond of PEPQ as well as the large efficiency of the stabilizer. The development of interactions between rutin and PEPQ leads to a complex structure (Fig. 6.11), the formation of which has the probability of 99.5 %. Only aromatic interactions form between the two molecules and some intramolecular hydrogen bonds within rutin. At larger rutin concentrations, sufficient amount of the natural antioxidant is present to protect the polymer against degradation. Since the interactions do not involve the hydroxyl groups located in ring B, neither the POC group in PEPQ, they do not affect the efficiency of the natural antioxidants and the characteristic absorption wavelength of PEPQ remains the same. Results of the modelling are in agreement with the outcome of FTIR and DSC measurements: PEPQ can only participate as hydrogen acceptor in hydrogen bonding interactions.

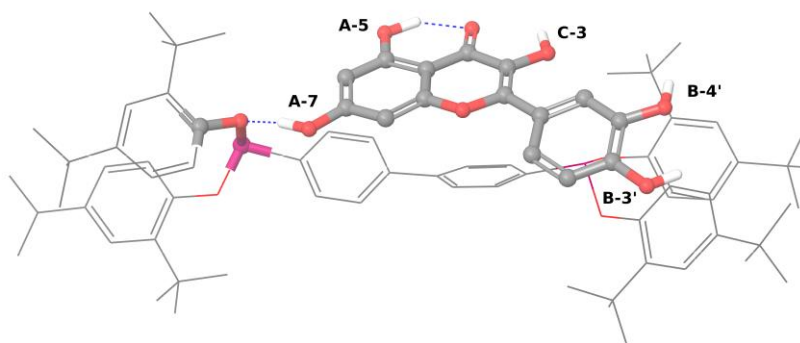


Fig. 6.10 The most probable configuration of the complex formed through the interaction of quercetin and PEPQ. Thin lines: PEPQ, thick lines: quercetin and one of the POC groups of PEPQ.

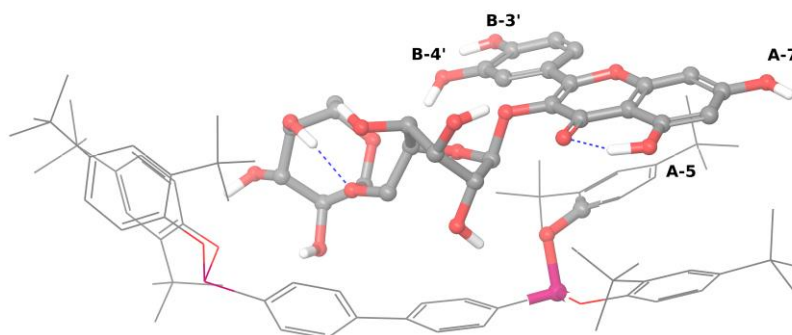


Fig. 6.11 Complex formed in the interaction of rutin and PEPQ; the formation of intramolecular hydrogen bonds. Thin lines: PEPQ, thick lines: rutin and one of the POC groups of PEPQ.

6.4 Discussion

The main degradation route of the Phillips polyethylene used in this study is the reaction of its chain end double bonds to form long chain branches [12, 180]. As Fig. 6.12 shows, very close correlation exists between the number of vinyl groups and the MFR of the polymer. Viscosity starts to increase below a certain concentration of the vinyl groups, thus the prevention of their reactions is crucial for stabilization. Long chain branches form through the addition of C centered radicals onto the vinyl group and phenolic antioxidants are assumed to react more efficiently with oxygen-centered radicals. On the other hand, phosphite and phosphonite secondary antioxidants are supposed mainly to decompose hydroperoxides and not to react with alkyl radicals. Nevertheless, clear correlation exists between the amount of residual PEPQ and the vinyl group content of the polymer (Fig. 6.13). Obviously, the secondary antioxidant or the combination of the two stabilizers prevents the formation of long chain branches. The interaction of the two additives, which leaves intact the most important hydroxyl groups in ring B, may also contribute to this effect. Based on the results presented in Figs. 6.12 and 6.13, the efficiency of the two natural antioxidants seems to be very similar at least at large additive contents.

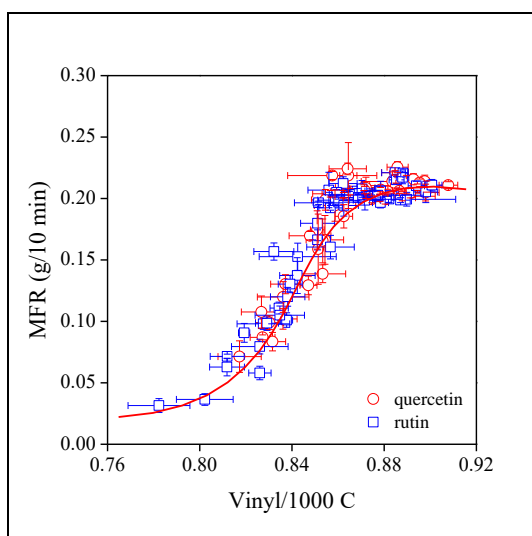


Fig. 6.12 Correlation between the vinyl content of the polymer and its melt flow rate; effect of the type of the natural antioxidant. Symbols: (○) quercetin, (□) rutin.

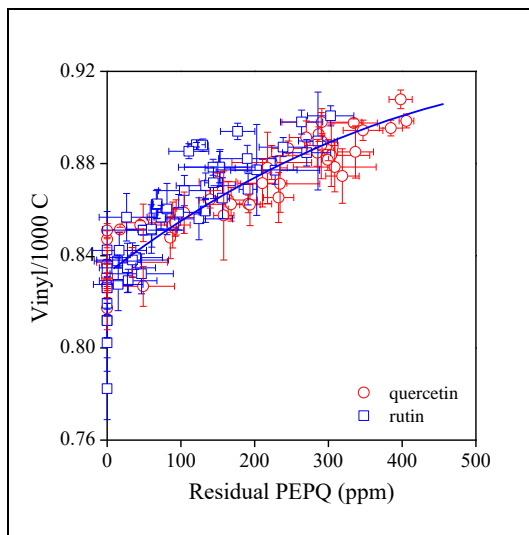


Fig. 6.13 *Dependence of the vinyl concentration of PE on the residual amount of the secondary antioxidant (PEPQ); similar effect of the natural antioxidants studied.*
Symbols: (○) quercetin, (□) rutin.

One question remained open in this study, the deteriorating effect of rutin at small concentrations. One plausible explanation might be the partial degradation of the natural antioxidant. Saccharides are sensitive to temperature and the high temperature of processing, 260 °C in this case, might result in the degradation of the disaccharide substitution in rutin. Degradation may involve the entire molecule, or only the saccharide moiety, but the degradation products may also interfere with the stabilization reactions. TGA measurements were carried out in order to check this hypothesis. The sample was heated up to 260 °C with a rate of 20 °C/min and then held there until the end of the run (15 min). The results presented in Fig. 6.14 clearly show the inferior stability of rutin compared to quercetin. The figure shows that silymarin undergo similar decomposition under the measurement conditions, which stabilizer also performed poor efficiency at low concentrations (see **Chapter 5**). Consequently, although rutin is as efficient as quercetin at large concentration, its deteriorating effect at small additive contents and limited thermal stability does not make it a good candidate as processing stabilizer for polymers. Nevertheless, the relationship between inferior thermal stability and deteriorating effect at small antioxidant contents needs further study and proof.

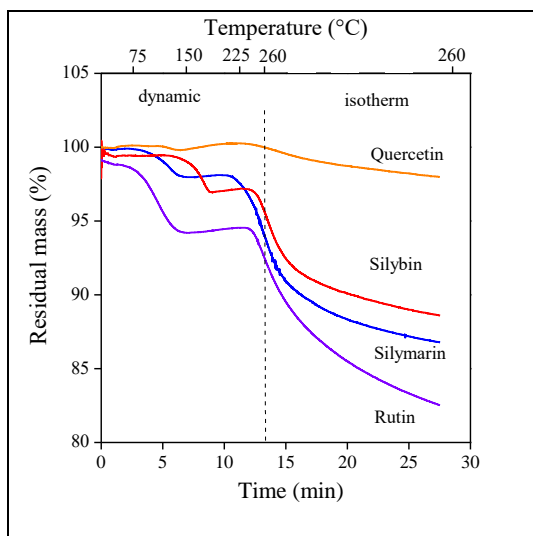


Fig. 6.14 Thermal stability of quercetin, silybin, silymarin and rutin in TGA measurements simulating processing conditions. Heating rate in the dynamic stage: 20 °C/min; temperature in the isotherm stage: 260 °C.

6.5 Conclusions

The study of the effect and efficiency of rutin, a flavonoid type natural antioxidant, in the melt stabilization of polyethylene showed that rutin is as efficient melt stabilizer as quercetin, the compound used as reference. On the other hand, rutin has a deteriorating effect on the stability of the polymer at small concentrations probably because it partially decomposes at the high temperature of degradation testing and maybe also during processing. The comparison of bond dissociation enthalpies showed that the substitution of the hydroxyl group in ring C of quercetin by saccharide moieties increases their value, but the small increase does not influence the efficiency of the stabilizer much. This result indicates that bond dissociation enthalpies play a role in stabilization, but other factors also influence efficiency. FTIR and DSC measurements indicated the interaction of the natural antioxidants and the phosphonite secondary stabilizer and the development of interactions was confirmed also by molecular modeling. Hydrogen bonds and aromatic, π electron interactions develop between the two types of components, mainly between the hydroxyl groups in ring A, as well as with rings A and C thus they do not influence the stabilization efficiency of the antioxidants. Effects of the interactions are difficult to predict as other factors: steric effects, changing of electron structures, decomposition, reactions of decomposition byproducts and the competition of these effects also play important roles in the determining of stabilizing efficiency of the additive package. The natural antioxidants quercetin [122] and curcumin [121], (see **Chapter 4**) are very efficient melt stabilizers, but silymarin (see **Chapter 5**) and rutin are less advantageous.

Chapter 7 *The use of dihydromyricetin as primary stabilizer*

7.1 Introduction

Stabilizing efficiency of quercetin (Q) was described earlier [88, 89, 122], but also in the previous Chapters (see **Chapters 5-6**). There were indications that quercetin interacted with the phosphonite secondary stabilizer used and that the mechanism of stabilization might differ from that of hindered phenolic stabilizers routinely used in practice (see **Chapter 6**). However, besides the advantages of quercetin, its very high melting temperature, limited solubility in polyethylene and strong yellow color are definite drawbacks for this compound.

Although the other two flavonoids, silymarin and rutin also had weaker or stronger stabilizing efficiency, they had drawbacks as well. We hoped to overcome these disadvantages by the use of another flavonoid type natural antioxidant dihydromyricetin (2R,3R)-3,5,7-trihydroxy-2-(3,4,5-trihydroxyphenyl)-2,3-dihydrochromen-4-one (DHM) in the next scope of the research. The compound is very similar to quercetin, but it is colorless and has a lower melting temperature. Chen et al. added DHM to polyethylene [90] and polypropylene [91] at 2000 ppm and without any secondary antioxidant. According to the authors the additive is more efficient than the commercial stabilizers used as reference. They explained the large efficiency with the position and the large number of hydroxyl groups in the molecule, but did not offer any information about melt stability, color, the effect of concentration or stabilization mechanism. As a consequence, the goal of study was to explore the possibility of using DHM as stabilizer in polyethylene. As earlier, the effect of the compound was compared to that of quercetin. Stabilization was studied as a function of composition at much smaller amounts than that used by Chen et al. [90, 91].

7.2 Materials and methods

The properties of the applied materials and sample preparation methods were described in **Chapter 3**. The list of characterization methods described in **Chapter 3** were complemented by molecular modelling in this Chapter. The UV-VIS spectra of the reaction products of quercetin and dihydromyricetin were predicted by time dependent density functional theory (TDDFT) calculations at PBE0/6-311++G** level [181, 182]. Geometries were optimized for these calculations in three steps. First conformations with the lowest energies were identified by molecular mechanics using the Merck molecular force field (MMF94) [170] from 2D structures drawn by using the MarvinSketch (ChemAxon) program, then the selected conformers were optimized by DFT calculations at the PBE0/6-311++G** level with Gaussian09 [183]. The obtained geometries were optimized again after manually orienting hydrogen atoms towards possible intramolecular hydrogen bonds resulting in lower energies. Finally, vibrational frequencies of the resulting conformers were calculated by the same DFT method ensuring their correspondence to local minima.



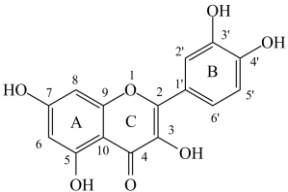
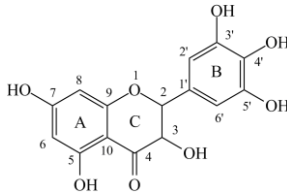
7.3 Results

7.3.1 Antioxidant characteristics

We selected DHM as a potential natural antioxidant because its chemical structure is similar to that of quercetin, but it also differs in several aspects. Both are flavonol type flavonoid compounds with the same basic structure. The most important characteristics of the two antioxidants are listed in Table 7.1. The lower melting point can be a clear advantage for DHM, since one can hope that, contrary to quercetin, the stabilizer melts during processing that may lead to its more homogeneous distribution in the polymer. The difference in the color of the two compounds is obvious for the first sight. The strong discoloration of the polymer in the presence of quercetin was regarded as a disadvantage in the study dealing with quercetin [122]. We hoped that DHM being a white powder would not have the same effect and we can produce compounds without a strong color.

The difference in color is a direct consequence of the chemical structure of the two compounds also shown in Table 7.1. The strong yellow color of quercetin comes from the conjugation of the double bond in ring **C** with the delocalized π electrons of ring **B**. This double bond is missing from DHM. The additional phenolic -OH group in ring **B** of DHM is a further difference which might be beneficial for the use of this antioxidant as stabilizer in PE (see **Chapter 5**). The larger number of phenolic hydroxyl groups would be expected to result in larger efficiency [90, 91] further emphasized by the smaller dissociation enthalpy of the H atom of the pyrogallol structure compared to that of the pyrocatechol moiety [184, 185] (see Table 1.2 in **Chapter 1**). All these differences in the chemical structure and physical properties promised improved homogeneity, better efficiency and a colorless product, which strongly supported the selection of dihydromyricetin as a potential stabilizer for PE.

Table 7.1 Characteristics of the two natural antioxidants used in the experiments.

Characteristic	Quercetin	Dihydromyricetin
M (g/mol)	302.24	320.25
Melting point (°C)	316	243
Color		
Structure		
Structural differences	<ul style="list-style-type: none"> – double bond in ring C – 2 hydroxyls at ring B 	<ul style="list-style-type: none"> – single bond in ring C – 3 hydroxyls at ring B
No. of phenolic – OH groups	4	5

7.3.2 Processing stabilization

As we discussed earlier, the reactions of vinyl groups in PE with alkyl radicals results in the formation of long chain branches (LCB), increasing viscosity and leading to processing problems. As a consequence, changes in the vinyl group content of the polymer is a sensitive indicator of processing stability and they are closely related to the variation, usually increase, of viscosity.

The MFR of polymer containing either DHM or Q in different amounts is plotted against the number of extrusions in Fig. 7.1. At zero antioxidant content MFR decreases quite rapidly with increasing number of extrusions. The increase in viscosity is usually associated with the formation of long chain branches [20, 180], but cross-linking may also occur eventually. Both antioxidants efficiently hinder these reactions already at very small concentrations. The correlation is shown only for selected antioxidant contents in order to avoid over cramming and confusion in the figure. Already 25 ppm stabilizer is

effective and 50 ppm protects the polymer quite efficiently. Above 100 ppm additive content MFR practically does not change. According to the results, DHM seems to be more efficient than quercetin, since the viscosity of the polymer remains constant already at only 50 ppm additive content. Apparently either the larger number of phenolic hydroxyl groups or the smaller dissociation enthalpy of the phenolic hydrogens renders this compound more effective than quercetin.

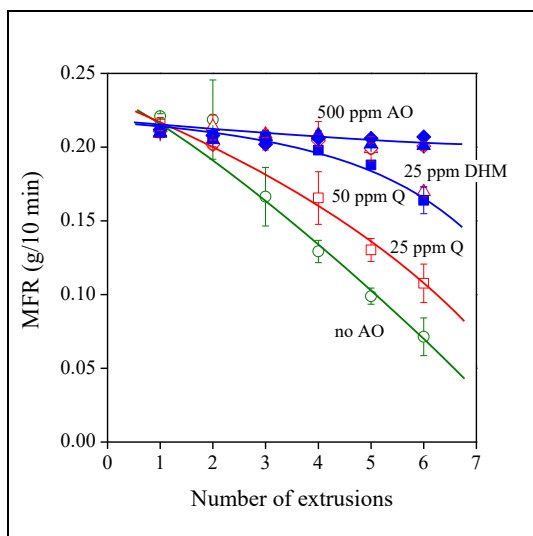


Fig. 7.1 Effect of additive content and the number of extrusions on the melt stability (MFR) of a Phillips polyethylene. Symbols: (○) no primary antioxidant, (□) 25, (△) 50, (◇) 500 ppm quercetin, (■) 25, (▲) 50, (◆) 500 ppm DHM.

Melt flow rate is plotted against the amount of stabilizer added to the polymer (Fig. 7.2) to show the effect of additive content. Since the molecular weight of the two compounds is different (see Table 7.1), stabilizer content is expressed in mmols. MFR values measured after the 1st and 6th extrusions are plotted to avoid confusion. The effect of the two additives is very similar in the first extrusion, but their dissimilar efficiency is clearly shown after the 6th extrusion at least at small additive contents. Both natural antioxidants protect the polymer very efficiently against degradation at large antioxidant concentrations. It is interesting to note that at very small stabilizer contents MFR decreases, i.e. viscosity increases, after the first extrusion of the polymer that could indicate the formation of long chain branches. This effect is quite surprising considering the considerable efficiency of these stabilizers. However, the phenomenon is the same for both stabilizers and we explained it earlier with the interaction of the primary and the secondary antioxidant (PEPQ) used in this study (see **Chapter 6**).

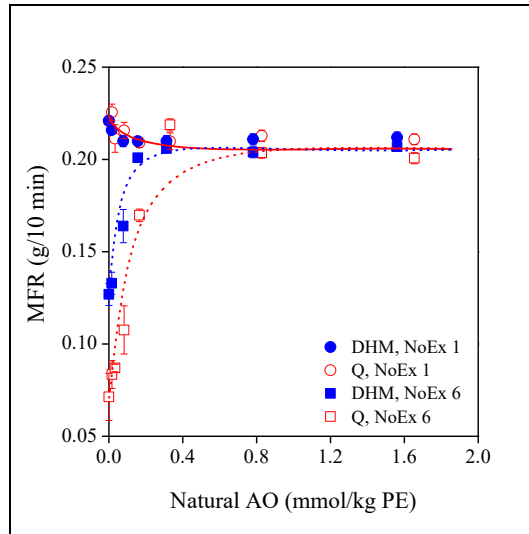


Fig. 7.2 Dependence of the MFR of polyethylene on stabilizer content at different number of extrusions. Symbols: (○) Q, 1st extrusion, (●) DHM, 1st extrusion, (□) Q, 6th extrusion, (■) DHM, 6th extrusion.

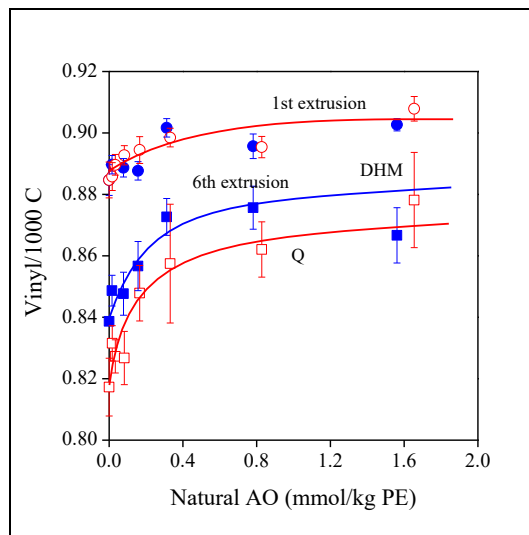


Fig. 7.3 Changes in the vinyl group content of polyethylene as a function of antioxidant content and processing history. Symbols: (○) Q, 1st extrusion, (●) DHM, 1st extrusion, (□) Q, 6th extrusion, (■) DHM, 6th extrusion.

Changes in viscosity and processability are attributed to the formation of LCBs going through the chain-end vinyl groups of the polymer [20, 180]. The effect of additive content and processing history (No. of extrusions) on the vinyl group content of the polymer is presented in Fig. 7.3. The number of vinyl groups increase with increasing additive concentration indicating that less vinyl groups enter into chain extension reactions during processing. The effect of the two additives is similar in the first extrusion, but DHM is more efficient than quercetin at larger number of extrusions. The correlations presented in Fig. 7.3 clearly prove that changes in MFR are caused by the reactions of the vinyl groups indeed. Several studies proved that the role of the secondary stabilizer is essential in the protection of the polymer against degradation especially in the first processing step [41].

The amount of residual secondary stabilizer is plotted against the number of extrusions in Fig. 7.4 at two additive contents. All the differences observed earlier in Figs. 7.1-7.3 can be detected also here. PEPQ content decreases drastically with increasing number of extrusions at small antioxidant content, while much slower at 500 ppm stabilizer concentration. The larger efficiency of DHM can be clearly seen in the figure. Obviously all the processes taking place during the extrusion of polyethylene are related to each other. The natural antioxidant and the phosphorous secondary stabilizer prevents the reaction of the vinyl groups in a synergistic action, while the natural antioxidant protects PEPQ and decreases its rate of consumption. We may conclude that both natural antioxidants used in this study are efficient processing stabilizers and that the effect of DHM surpasses that of quercetin in melt stabilization.

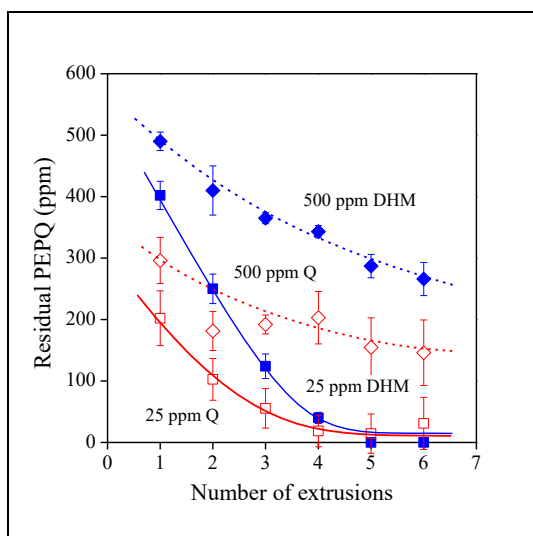


Fig. 7.4 Effect of the number of extrusions and antioxidant content on the residual amount of PEPQ in polyethylene processed in multiple extrusions. Symbols: (□) 25, (◇) 500 ppm Q; (■) 25, (◆) 500 ppm DHM.

7.3.3 Residual stability

Processing stability is important for most products, but long term stability can be also crucial in certain applications like in gas or water pipes. Moreover, residual stability may offer further information about the mechanism of stabilization and the effect of the chemical structure of the stabilizer on efficiency. The residual stability of PE is plotted against the amount of stabilizer used in Fig. 7.5. Concentration is expressed in mmol antioxidant/kg PE units, which disregards the different number of phenolic -OH groups in the molecule. The correlation is linear and the effect of the two antioxidants is similar. The linearity is not very surprising, since several authors have proved that OIT is linearly proportional to the amount of phenolic antioxidant [12, 137, 160], as we saw already also in previous Chapters. Obviously the slope of the straight line depends on the structure of the stabilizer and on the additive package, i.e. on the type and amount of secondary stabilizer and other components used [12]. However, only limited information is available on the effect of these latter factors on residual stability.

The unique correlation is much more surprising. Based on the larger number of phenolic hydroxyls in DHM, as well as on the results presented in the previous section, one would expect larger stability in polymers containing this additive [90, 91]. According to these results not all phenolic -OH groups react during the measurement of OIT and the stabilization effect does not depend on the number of functional groups, but only on the amount of stabilizer present. This result raises the question of reaction mechanism and the activity of the reaction products formed in the first stabilization reaction.

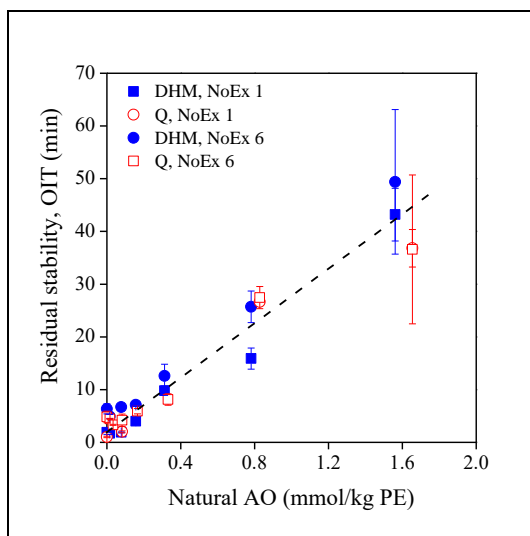


Fig. 7.5 Unique correlation between the amount of the natural antioxidant used and the residual stability (OIT) of polyethylene. Symbols: (○) Q, 1st extrusion, (●) DHM, 1st extrusion, (□) Q, 6th extrusion, (■) DHM, 6th extrusion.

7.3.4 Solubility

The solubility of stabilizers is important for their effect. Larger solubility results in better homogeneity and efficiency [186]. Quercetin was shown to have very limited solubility in PE indicated by the composition dependence of color and by the fact that quercetin crystals were observed in the polymer at larger additive contents [122]. The yellowness index of the polymer is plotted against antioxidant concentration in Fig. 7.6. The measurement was done after the first extrusion step. The discoloration effect of quercetin is very strong, yellowness index reaches more than 90 at large additive content. Rather surprisingly DHM originally being a white powder also discolors the polymer quite strongly, yellowness indices in the range of 50 were measured. Apparently, the reaction products of the stabilizer are not colorless, they discolor the polymer significantly.

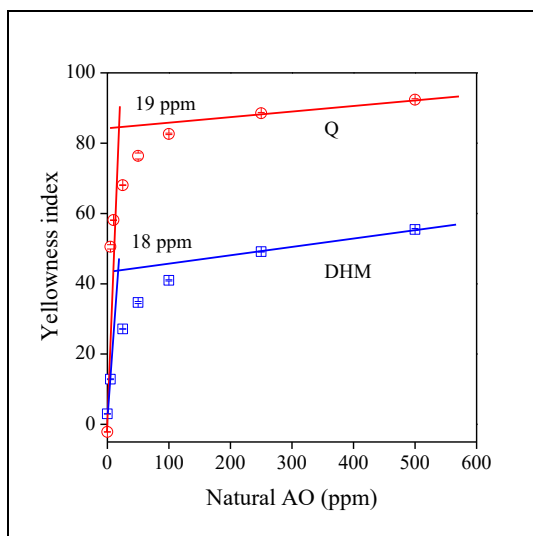


Fig. 7.6 Determination of the solubility of the natural antioxidants studied from the concentration dependence of color after the 1st extrusion step. Symbols: (○) Q, (□) DHM.

The composition dependence of color was used earlier for the determination of the solubility of quercetin in polyethylene [122]. The same approach was used in this study and the result is shown in Fig. 7.6. The basic idea behind the determination of solubility is that dissolved stabilizer molecules have a much stronger effect on color than the additive being present as a separate phase, in the form of crystals. This concept is definitely valid for quercetin, but more difficult to accept for DHM, since discoloration seems to be caused by the reaction products of the additive. Comparison is further complicated by the small number of points in the steeply increasing leg of the correlation and the different levels of color caused by the two additives. Nevertheless, we can state that the correlations as well as the solubility levels are similar, the latter being very small, in the range of 15-20 ppm. This similarity is not surprising since the molecular structure

of the two additives is similar. Fortunately, this limited solubility does not influence the efficiency of the two compounds in stabilization.

7.3.5 Color

The color of the product is very important in some applications, while much less of an issue in others. In black products the possible discoloration effect of the additive does not matter, but colorless compounds are often much more advantageous. The yellowness index of polyethylene is plotted against the number of extrusions in Fig. 7.7 for compounds containing the two additives in selected amounts. The very strong coloring effect of quercetin is seen already at 5 ppm additive content and discoloration is extremely intense at 500 ppm. As mentioned above, DHM colors the polymer less. Interestingly the measured values slightly decrease during consecutive processing steps in the case of quercetin, and increase for dihydromyricetin. The consumption of the dissolved yellow stabilizer results in the decrease in the first case, while the formation of colored reaction products leads to the deepening of color in the second. However, yellowness index does not reflect the hue of the color well, especially if it differs from yellow.

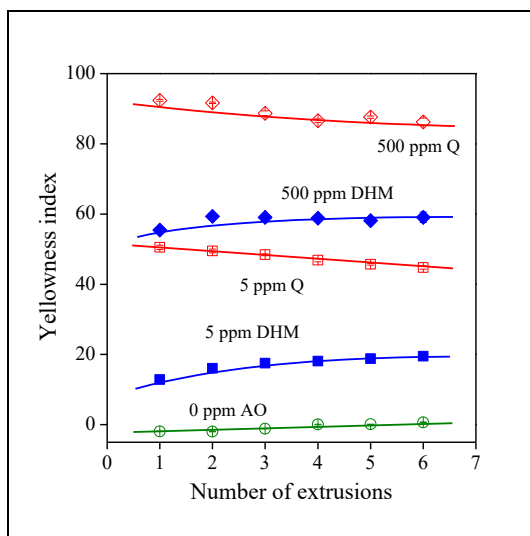


Fig. 7.7 Effect of additive content and processing history (No. of extrusions) on the yellowness index of polyethylene. Symbols: (○) no primary antioxidant, (□) 5, (◇) 500 ppm Q; (■) 5, (◆) 500 ppm DHM.

The Optical L* parameter gives an idea about the deviation from white; the larger the value is, the closer is the color to white. The L* parameter decreases slightly with increasing quercetin content and does not change much with increasing number of extrusions; it takes values between 76 and 63. On the other hand, the L* parameter decreases both with additive content and the number of extrusions for DHM and changes between 76 and 37 in the studied range. These relationships are demonstrated much better by Figs. 7.8a and b than by the optical L* parameter. In Fig. 7.8a the effect of additive content on color is shown after the first extrusion, while the influence of processing history can be seen in Fig. 7.8b at 500 ppm additive content. It is clear from the figure that quercetin colors the polymer to yellowish red, while DHM from light ochre to dark brown. Obviously, we could not solve the problem of discoloration by the selection of the new natural antioxidant, dihydromyricetin.

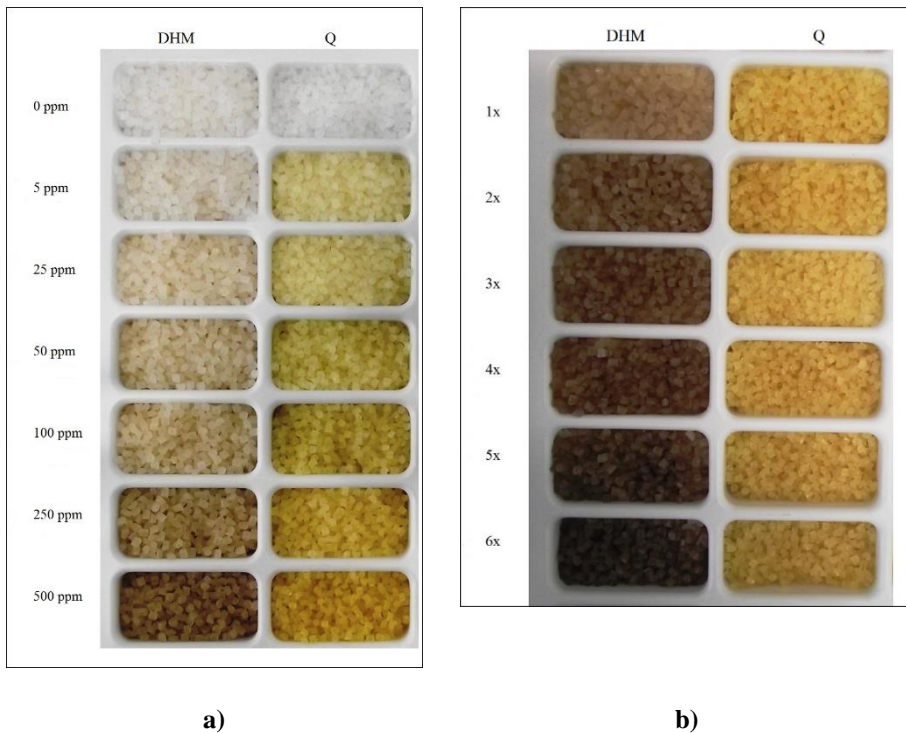


Fig. 7.8 *Changing color of polyethylene in the presence of the two natural antioxidants studied; a) effect of additive content, 1st extrusion, b) effect of the number of extrusions, 500 ppm.*

7.4 Discussion

The result presented above prove that both natural antioxidants are efficient melt stabilizers for polyethylene. However, some of the results, like the similar effect on residual stability, or the discoloration of the polymer in the presence of DHM were somewhat unexpected. The reactivity and stabilization effect of phenolic antioxidants depend on their chemical structure, on the number of hydroxyl groups and their position. As we discussed earlier, four mechanisms have been proposed in the literature for the stabilization reactions of phenolic antioxidants (see **Chapter 1**): single electron transfer (SET) [29, 30], sequential proton loss electron transfer (SPLET) [31, 32], radical adduct formation (RAF) [28] and hydrogen atom transfer (HAT) [26, 27]. In polyethylene the last one is the most probable and accepted mechanism of stabilization. The rate of hydrogen transfer depends on the dissociation enthalpy of the hydrogen atom from the phenolic hydroxyl groups and this is smaller for the hydrogens located at the OH groups in the ring **B** of DHM than in quercetin [184, 185], (see Table 1.2 in **Chapter 1**). According to the OIT results shown in Fig. 7.5, DHM is not more efficient than quercetin in spite of the larger number of -OH groups in the molecule. This indicates that after the first reaction, in spite of the reactivity of the products formed, both molecules become much less active than the original compound. This explains the similarity of their effect, but not the differences in efficiency in protecting the polymer during processing.

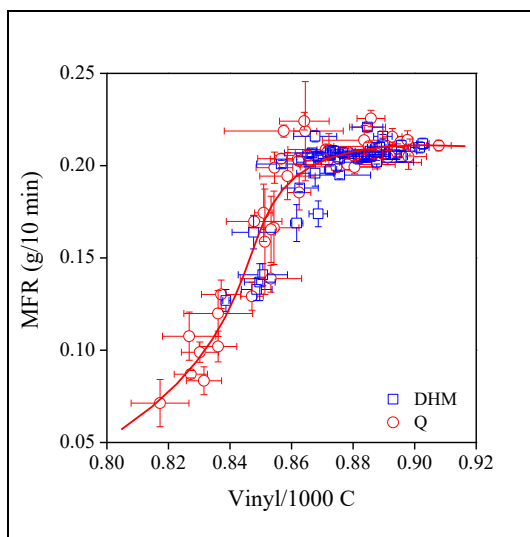


Fig. 7.9 Correlation between the vinyl content of polyethylene and its melt flow rate. Symbols: (○) Q, (□) DHM.

As discussed earlier long chain branches form during processing through the reaction of the vinyl groups located at one end of the polyethylene chains. The combined,

synergetic effect of the primary and secondary antioxidant hinders this reaction, but the interaction of the two stabilizers decreases also their rate of consumption. The correlation between the vinyl content of the polymer and MFR is presented in Fig 7.9. It is clear that viscosity is constant above a certain vinyl content and increases drastically below that (approximately at 0.87 vinyl/1000 C). The larger efficiency of DHM is shown by the fact that the points (squares) for the polymer containing this additive are located on the upper right part of the correlation, while many of those belonging to quercetin (circles) appear in the lower left range. The crucial role of the phosphorous antioxidant is demonstrated well by the fact that below a certain PEPQ content (approximately 100 ppm) MFR starts to decrease drastically to very small values. The interaction of the two types of stabilizers (primary, secondary) is important and different for the two natural antioxidants leading to the larger efficiency of DHM. The exact nature of this interaction and the mechanism of stabilization need further study. For some considerations and possible explanations, see **Chapter 6**.

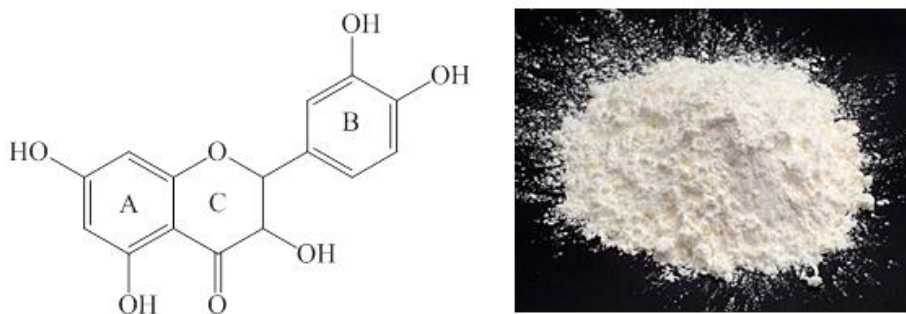
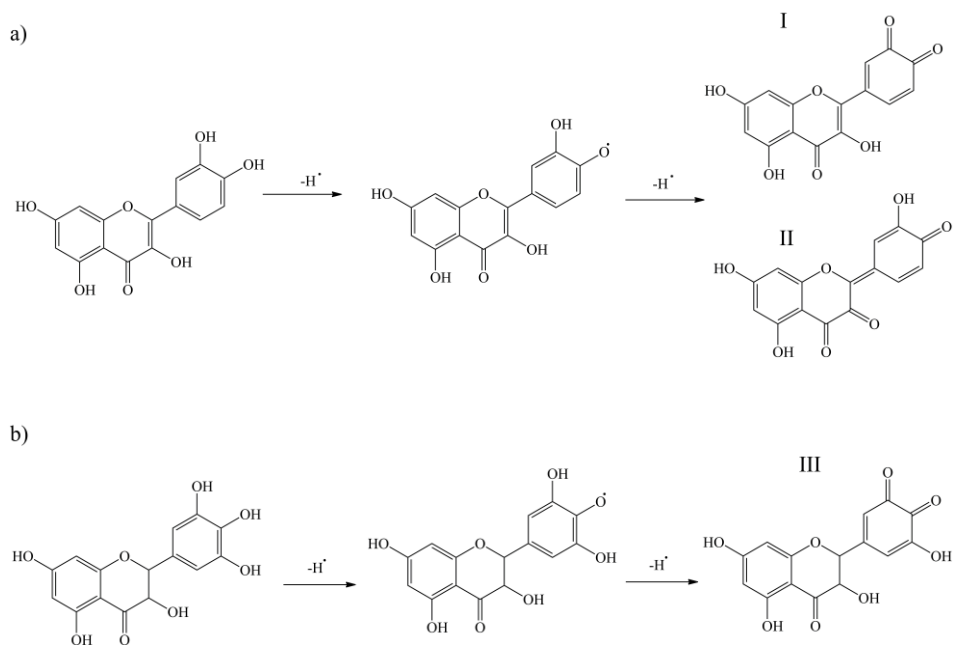


Fig. 7.10 Chemical structure and appearance of dihydroquercetin (taxifolin) having no double bond in its ring C.

The disappointing color change also requires explanation. The strong yellow color of quercetin results from the conjugation of the double bond in ring C with the electrons in ring B. Dihydroquercetin (or taxifolin) is a white powder similarly to DHM (Fig. 7.10). As a consequence, the brownish color must form during the processing of the polymer containing the antioxidants. Various quinoidal compounds may form as a result of stabilization reactions which depend on the molecular structure of the antioxidant. Assuming that hydrogen transfer occurs from ring B, the reaction of quercetin results in two compounds, while that of DHM in one. The reaction leading to these compounds and their structures are presented in Scheme 7.1. Obviously all three products are conjugated systems absorbing light in the visible range.



Scheme 7.1 Formation of quinoidal compounds in stabilization reactions; a) quercetin, b) dihydromyricetin.

An attempt was made to estimate the color of these compounds by molecular modeling. The spectra resulting from the calculations are shown in Fig. 7.11 for two compounds, compound I formed from quercetin and compound III derived from DHM. Absorption bands appear at 240, 314, 364, 394 and 509 nm in the spectrum of the first, but we are interested only in the visible region. At 394 and 509 nm the violet and green components of visible light are absorbed leading to a mixture of red and yellow colors. The absorption of compound II also results in yellow-orange colors confirmed by Figs. 7.8a and b. Similarly, compound III absorbs at 378, 452, 511 and 537 nm corresponding to lilac, blue, and green colors. Brown is a mixed color resulting from the absorption of the blue components of light, thus it is highly probable that this absorption leads to the ochre-brownish color of the polymer processed in the presence of dihydromyricetin (see Fig. 7.8). However, in spite of this discoloration the natural antioxidants studied in this work are efficient stabilizers of PE and can be used for certain products.

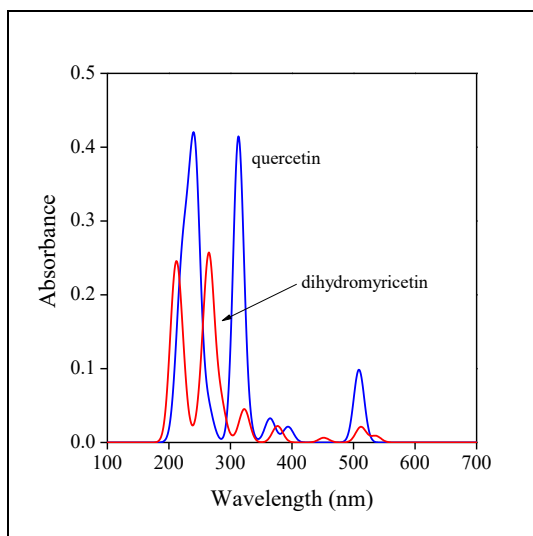


Fig. 7.11 Predicted UV-VIS spectra of the quinoidal compounds forming from the natural antioxidants during stabilization; a) quercetin I, b) dihydromyricetin III.

7.5 Conclusions

Experiments carried out to determine the stabilization activity of two flavonoid type natural antioxidants in polyethylene proved that both stabilize PE very efficiently. At small concentrations dihydromyricetin proved to be more efficient melt stabilizer than quercetin, less vinyl groups were consumed during processing, less long chain branches formed and thus MFR was larger in its presents than with the same amount of quercetin. DHM protected the secondary antioxidant better than quercetin, less PEPQ was consumed in its presence during processing. In spite of its better efficiency in melt stabilization, polymers containing DHM had the same residual stability as those prepared with quercetin. Accordingly, the larger efficiency does not result from the larger number of active phenolic hydroxyls in this molecule, but from their position, and from interaction with the phosphorous secondary stabilizer that is stronger or at least different for DHM than for quercetin. Although DHM is a white powder, it gave the polymer brownish color which became stronger with increasing number of extrusions and additive content. In spite of this slight disadvantage both natural antioxidants can be efficiently used for the stabilization of polymers in applications in which color is of secondary importance.

Chapter 8 Efficiency of a natural extract and its main component

8.1 Introduction

Plants produce and use a large number of antioxidants very efficiently. These can have diverse structures, functions and efficiency. Quite a few of them have been tried as stabilizers also in polymers with different successes. Natural oils [174], carotene [76, 77, 187, 188], curcumin[121], Vitamin E [6-10], lignin [100, 102, 103, 106, 108] and many other compounds were shown to have smaller or larger stabilizing activity in a range of polymers, but mostly in polyolefins. Recently, the interest in natural antioxidants has increased considerably and a number of papers have been published on them [174]. Although natural antioxidants are very efficient, they have several drawbacks as well, their melting temperature can be very high, higher than the processing temperature of PE, their solubility is small and they discolor the polymer.

In **Chapter 5** we dealt with the characterization of the stabilizing efficiency of silymarin, a member of the flavonoid family. It is a natural extract with a standard composition and it is widely used in human therapy, mainly for the treatment of ailments related to alcoholism. Its main component is silybin, which is used for the treatment of cancer [189, 190]. Silymarin is a mixture of flavonolignans and other compounds (see Table 5.1 in **Chapter 5**), which raised some questions about the benefits of using the pure compound instead of the extract. The application of stabilizer mixtures is not a rare phenomenon in the field of stabilization: a very good example is Sandostab PEPQ, the secondary stabilizer applied in the previous Chapters, which is the mixture of three compounds (see Table 3.3 in **Chapter 3**). Many other examples can be found from fatty acids, through natural waxes and oils, to many other products [191]. We must also call the attention here to the fact that the pure compound is about ten times more expensive than the extract. This counts very heavily in an industrial application.

Accordingly, the goal of this project was to compare the pure compound obtained from Sigma Aldrich to the natural extract. We used the same techniques as before (see **Chapters 3, 5**) and determined the effect of the two products on the degradation and stabilization of PE. We were interested mainly in their efficiency, but also wanted to explain differences, if there were any.

8.2. Materials and methods

The applied materials are presented in **Chapter 3**. Silybin was purchased from Sigma-Aldrich with 95 % purity. Silymarin was the courtesy of the Department of Applied Chemistry at the University of Debrecen, its extraction process was described in **Chapter 5** [156]. The methods of samples preparation and characterization are described in **Chapter 3**. In figures, silybin is abbreviated as Sb, while silymarin as Sm in order to increase clarity and help understanding.

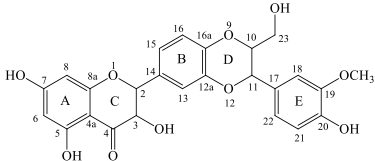
8.3. Results and discussion

8.3.1 Composition, properties

As mentioned above, silymarin is an extract with a standard composition. It is extracted from milk thistle and it contains 70-80 % flavonolignans and 20-30 % fatty acids. The active component also contains several compounds, three main components and several minor ones, the latter being present in very small amounts. The main component of the active part is silybin; it constitutes about 70 % of the flavonolignans. The composition of the active part and the structure as well as the amount of the components are listed in Table 5.1. Besides silybin, the other three components are isosilybin, silydianin and silychristin and their total amount is about 29 % of the active component. The basic structure of the active compounds is similar, but considerable differences can be seen in the moiety attached to the basic flavonoid structure. On the other hand, the number of phenolic OH groups of the four compounds is very similar and even their chemical environment does not differ considerably. Accordingly, one would expect similar effect and efficiency in stabilization, i.e. the efficiency of the extract and the pure compound, silybin, should be the same.

The characteristics of the two products are compared to each other in Table 8.1. As mentioned above, the main features of the chemical structure of the four active components are very similar. Unlike in the case of several of the flavonoids, there is no double bond in ring **C**. The double bond and the attached OH group was shown to contribute to stabilization [159]. No phenolic hydroxyl group is located in ring **B** and the most active OH group, which is assumed to take part in stabilization reactions, is located in ring **E**. As expected, all characteristics of the two products are close, their molecular weight, color and even the number of active phenolic OH groups are similar. The hydroxyl group located in the **D12** position in silydianin was taken into account in the calculation of the number of active phenolic groups of silymarin. Although one would expect the same effect and efficiency from the two products, the extract can be obtained at tenth of the price of the pure compound.

Table 8.1 *The most important characteristics of silymarin, the natural extract, and its main component, silybin.*

Characteristics	Silymarin	Silybin
M (g/mol)	482.4	482.4
Melting point (°C)	amorphous	159
Color	ochre	ochre
Structure	see Table 5.1	
Structural differences	see Table 5.1	<ul style="list-style-type: none"> - single bond between C2 and C3 - no hydroxyl at ring B - 1 hydroxyl at ring E
Phenolic OH groups	3.11	3

8.3.2 Effect and efficiency

Reaction of chain-end vinyl groups of Phillips type polyethylene leads to long chain branching and the increase of viscosity during processing [20, 192]. Accordingly, changes in the vinyl group content of the polymer offers information about the efficiency of a stabilizer. The number of vinyl groups per 1000 carbon atoms is plotted against the number of extrusion steps in Fig. 8.1. Results are presented only for selected compounds to facilitate viewing and to avoid confusion. Vinyl group content decreases quite considerably even at large additive contents indicating that the stabilization efficiency of neither of the products is exceptionally good. Vinyl group content decreases as the result of its reaction with radicals, mostly alkyl centered radicals due to the oxygen poor environment of extrusion. Efficient stabilizers hinder this reaction, thus vinyl group content does not change or decreases only slightly during multiple extrusions in such cases [41]. Other flavonoid compounds proved to be much more efficient in the stabilization of PE than silymarin and silybin (see **Chapters 4, 7**). Rather surprisingly, differences can be observed in the efficiency of the two products, which contradicts expectations. Vinyl group content decreases drastically at 5 ppm silymarin content, while silybin seems to have a better stabilization efficiency at this composition. At larger concentrations, on the other hand, silymarin seems to be more efficient. A plausible explanation cannot be given for the phenomenon at the moment, further data and considerations are needed even for a tentative explanation.

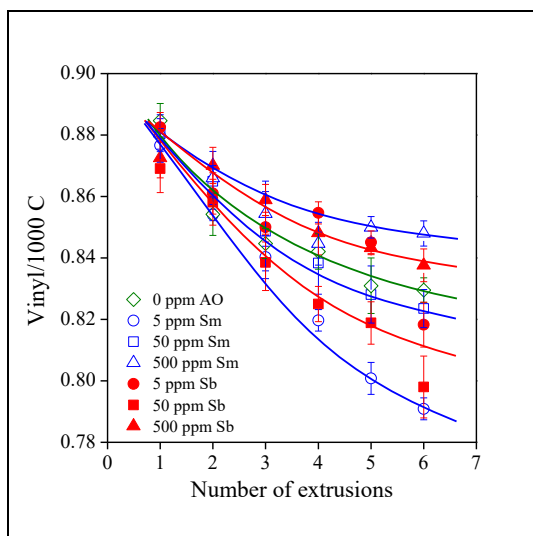


Fig. 8.1 Effect of additive content and the number of extrusions on the number of vinyl groups in Phillips polyethylene. Symbols: (◇) neat, (○) 5 ppm Sm, (□) 50 ppm Sm, (△) 500 ppm Sm, (●) 5 ppm Sb, (■) 50 ppm Sb, (▲) 500 ppm Sb; empty symbols: silymarin, full symbols: silybin.

The residual amount the phosphonite secondary stabilizer is plotted against the number of extrusions in Fig. 8.2. Phosphorus secondary antioxidants were shown to be essential in processing stabilization [41, 42], since they protect the polymer from degradation especially during the first extrusion. The compounds contained 1000 ppm PEPQ before processing, of which very little was preserved in the polymer after extrusion. The results presented are even more surprising than those shown in Fig. 8.1. Silybin is clearly much more efficient in protecting the secondary stabilizer than silymarin; the amount of PEPQ left intact after extrusion is very small in the latter case indeed. Unlike for vinyl group content, silybin is more efficient even at larger concentrations that is a further contradiction needing explanation.

The pivotal point of melt stabilization is maintaining viscosity at the same level during multiple extrusions. The MFR of PE containing various amounts of the two stabilizers is shown in Fig. 8.3 as a function of processing history. MFR decreases even at larger additive contents showing again the limited efficiency of the flavonoids used in this study for the stabilization of PE. The same differences can be seen in the effect of the two stabilizers, as in the case of the vinyl groups, i.e. silybin is better at small concentrations, while silymarin is more efficient at large additive contents. The similarity calls the attention to the close relationship between vinyl group content and viscosity, on the one hand, and to the effect of some factor or factors resulting in the phenomenon. In Fig. 8.4, MFR is plotted against the amount of natural antioxidant added to the polymer. The phenomenon mentioned above is clearly shown by the figure. Silymarin is more efficient at large additive contents than silybin after both the 1st and the 6th extrusion.

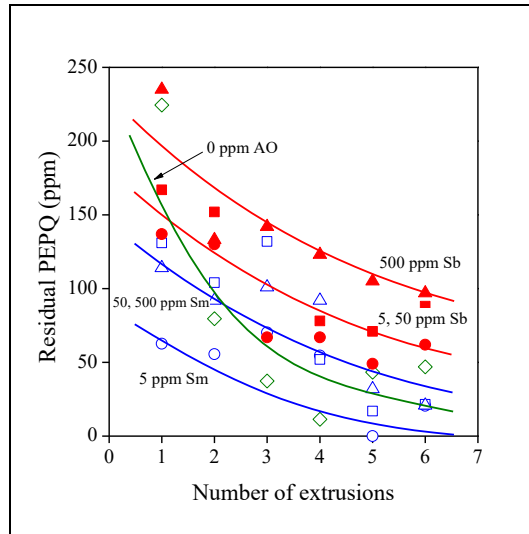


Fig. 8.2 Residual PEPQ content of the polymer plotted against the number of extrusion steps at various additive contents. Symbols: (\diamond) neat, (\circ) 5 ppm Sm, (\square) 50 ppm Sm, (\triangle) 500 ppm Sm, (\bullet) 5 ppm Sb, (\blacksquare) 50 ppm Sb, (\blacktriangle) 500 ppm Sb; empty symbols: silymarin, full symbols: silybin.

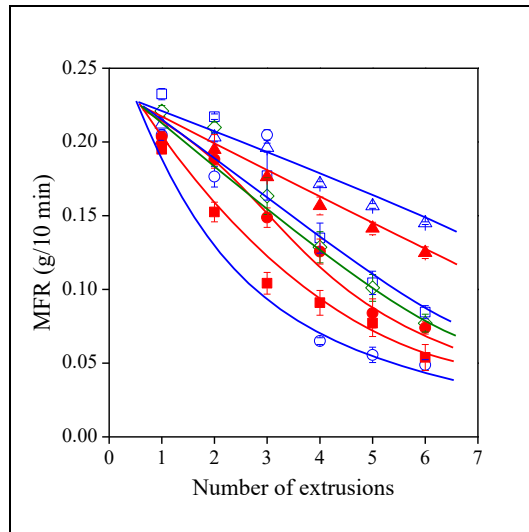


Fig. 8.3 Dependence of the viscosity (MFR) of the polymer on additive content and processing history. Effect of long chain branching. Symbols: (\diamond) neat, (\circ) 5 ppm Sm, (\square) 50 ppm Sm, (\triangle) 500 ppm Sm, (\bullet) 5 ppm Sb, (\blacksquare) 50 ppm Sb, (\blacktriangle) 500 ppm Sb; empty symbols: silymarin, full symbols: silybin.

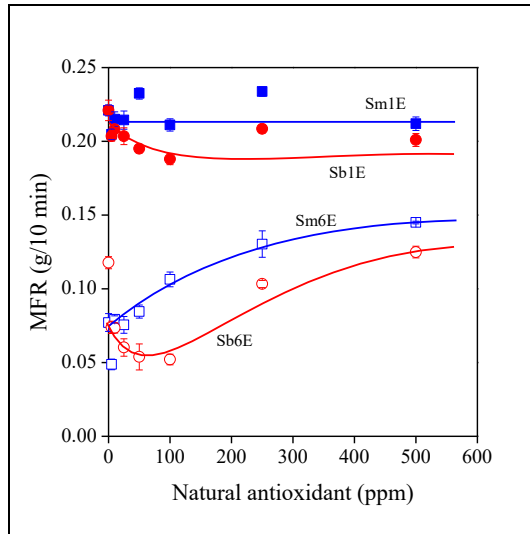


Fig. 8.4 MFR of polyethylene plotted as a function of the amount of natural antioxidant added to the polymer. Symbols: (○, ●) silybin, (□, ■) silymarin; full: 1st extrusion, empty: 6th extrusion.

Residual stability is determined mainly by the amount of the active phenolic antioxidant, but the concentration of the secondary antioxidant and the composition of the additive package also play a role [193]. The dependence of residual stability characterized by the oxygen induction time on the number of processing steps is presented in Fig. 8.5. Residual stability is very small, less than 10 min, and the standard deviation of the measurement is large. Often at least 20 minute residual stability is required in many long term applications. OIT decreases with increasing number of extrusions as expected. The general tendency can be observed again, silybin is more efficient at small additive contents, while silymarin is better at large concentrations, which proves the consistency of the measurements and the effect of an unknown factor influencing efficiency.

OIT is plotted against additive content in Fig. 8.6. The scatter of the points is considerable because of the small stability and the large standard deviation of the measurement. Nevertheless, the usual linear correlation is obtained after both the 1st and the 6th extrusions. The slope of the straight lines differs considerably. Both the small values and the different slope indicate the limited efficiency of these flavonoid type antioxidants in the stabilization of PE. In the case of very efficient flavonoids, the same slope was obtained for the 1st and the 6th extrusions that was explained with the large efficiency, as well as the small solubility and continuous resupply of dissolved active stabilizer in subsequent extrusions [122]. Although it is difficult to draw farfetched conclusions about the relative efficiency of the two products, silymarin seems to offer better stability than silybin at concentrations offering some performance.

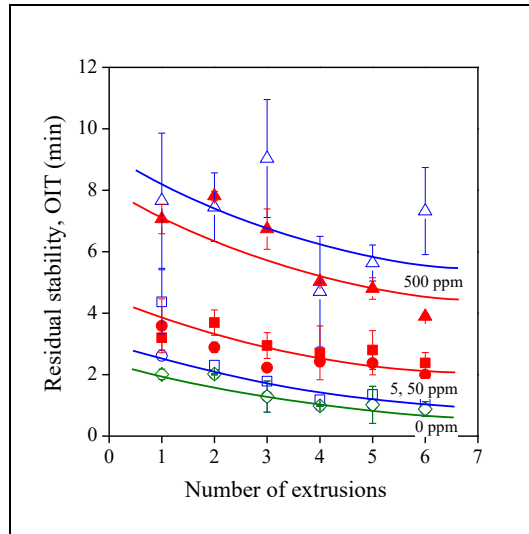


Fig. 8.5 Effect of the number of extrusions and additive content on the residual stability of PE. Symbols: (\diamond) neat, (\circ) 5 ppm Sm, (\square) 50 ppm Sm, (\triangle) 500 ppm Sm, (\bullet) 5 ppm Sb, (\blacksquare) 50 ppm Sb, (\blacktriangle) 500 ppm Sb; empty symbols: silymarin, full symbols: silybin.

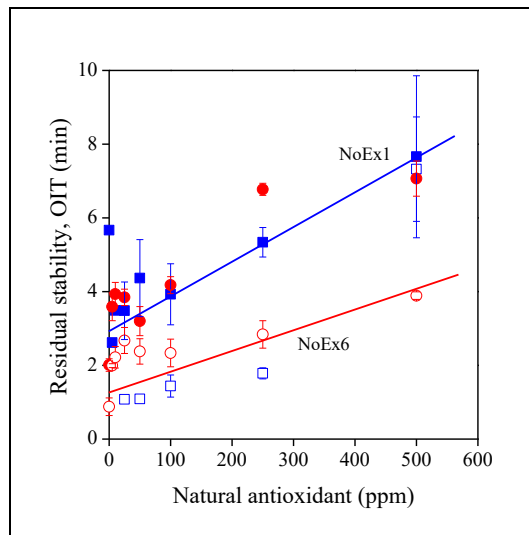


Fig. 8.6 Influence of the amount of natural antioxidant on the residual stability of polyethylene. Symbols: (\circ , \bullet) silybin, (\square , \blacksquare) silymarin; full: 1st extrusion, empty: 6th extrusion.

8.4 Discussion

The consideration of all results presented above in the previous section indicates that contrary to our expectations, at large concentrations silymarin is a more efficient stabilizer for PE than the pure compound, silybin, and some factor or factors decrease the efficiency of silymarin at small additive contents. This phenomenon merits further considerations. The difference of efficiency is difficult to explain and the interpretation of the results is made even more complicated by the fact that silybin protects the secondary antioxidant better than silymarin at all concentrations. The main role of processing stabilizers is to prevent the reaction of the vinyl groups and the formation of long chain branches. The close relationship between vinyl group content and viscosity was shown before [20, 192]. Fig. 8.7 confirms the close correlation again, but also corroborates our conclusion about the larger efficiency of silymarin over silybin. Most of the points obtained on compounds containing silymarin are located above the line drawn to guide the eye, while those for silybin are situated below it.

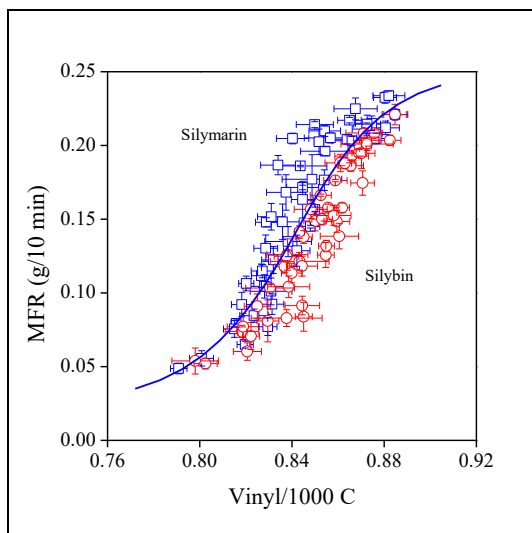


Fig. 8.7 General correlation between the vinyl group content of polyethylene and its viscosity (MFR). Differences in the efficiency of the two products. Symbols: (○) silybin, (□) silymarin.

A tentative explanation for the larger efficiency of silymarin might be offered by the slight differences in the chemical environment of the phenolic OH groups of the flavonoids leading to different bond dissociation enthalpies (BDE). These enthalpies are listed in Table 8.2 for all the studied compounds. Phenolic hydroxyl groups located at the positions **E19** and **E20** have the smallest BDE values, thus they are supposed to react first with radicals and determine stabilization. Although the **E20** hydroxyl group of the main components, silybin and isosilybin, have the same bond dissociation enthalpies, silydianin and silychristin have OH groups with smaller BDE values. The consequence on stabilization is definitely not proportional to composition, the OH groups with smaller

BDE will clearly react first, and thus in spite of their smaller amount the presence of the two minor components may lead to the larger efficiency of the extract.

Table 8.2 Bond dissociation enthalpies of the phenolic hydroxyl groups of the main components of silymarin [157].

Phenolic OH at	BDE value of OH groups in compound (kJ/mol)			
	Silybin	Isosilybin	Silydianin	Silychristin
A5	410.45	410.45	409.61	410.45
A7	399.99	399.99	399.99	399.57
C3	455.64	455.64	455.22	455.22
B15	–	–	–	352.71
D12	–	–	412.12	–
E19	–	–	–	352.29
E20	367.77	367.77	358.99	–

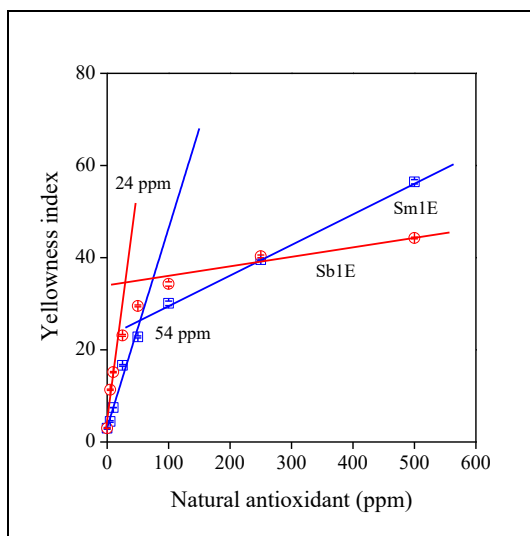


Fig. 8.8 Determination of the solubility of the natural extract and its main component in polyethylene. 1st extrusion. Larger solubility of silymarin. Symbols: (○) silybin, (□) silymarin.

Another factor, which merits some consideration, is the solubility of the two products in polyethylene. The solubility of these polar compounds is extremely small in the polymer and it is very difficult to determine. We estimated solubility earlier from the change in the color of the polymer with increasing additive content (see **Chapter 7**). Dissolved flavonoids discolor the polymer very strongly, but above solubility the additive

forms a separate phase, the coloring effect of which is weaker, proportional to the size of the dispersed particles. The color of PE is plotted against its antioxidant content in Fig. 8.8. The use of the approach described above allows the estimation of solubility, which is larger for silymarin than silybin. Larger solubility means more dissolved molecules and larger probability to scavenge radicals causing degradation. The larger solubility of the active components of silymarin might result from the presence of the accompanying material contained by the extract.

Bond dissociation enthalpies and solubility might explain the larger efficiency of the natural extract, but not its inefficiency at small concentrations. The available results do not offer any ground for a plausible explanation for the phenomenon. Thermal decomposition could lead to this phenomenon during the processing. Silymarin had somewhat poorer self-stability than silybin, but the difference was slight. More than one study also indicated that the primary stabilizer, the flavonoid, and PEPQ interact with each other, [122, 174] (see **Chapter 6**). This interaction influences efficiency, thus it is possible that the most active component forms stronger bonds with PEPQ than silybin thus decreasing the efficiency of the extract at small concentrations. Information about the interaction of the two components was obtained earlier from DSC and FTIR measurements [174]. Based on those results, homogeneous blends were prepared from the two flavonoids and PEPQ. The traces recorded during the heating of the pure components and the blends are presented in Figs. 8.9a and b. The figures show that silymarin is amorphous and PEPQ improves its stability, decomposition temperature increases with increasing PEPQ content (Fig. 8.9a). The degradation of the stabilizer itself could lead to a decrease in its stabilizing efficiency. On the other hand, silybin is crystalline, which partly might explain its smaller solubility from the practical point of view. Moreover, its combination with PEPQ results in decreased decomposition temperatures (Fig. 8.9b). The lack of crystallinity for silymarin and the earlier disappearance of the melting peak of PEPQ from the DSC trace in its blends with silymarin than with silybin indicates the formation of stronger interactions in the former case. This interaction may contribute and explain the apparently smaller residual PEPQ content of the blends after extrusion, as well as the larger efficiency of silymarin. Both the role of thermal stability and interactions must be studied more in detail in the future in order to verify the explanation offered here.

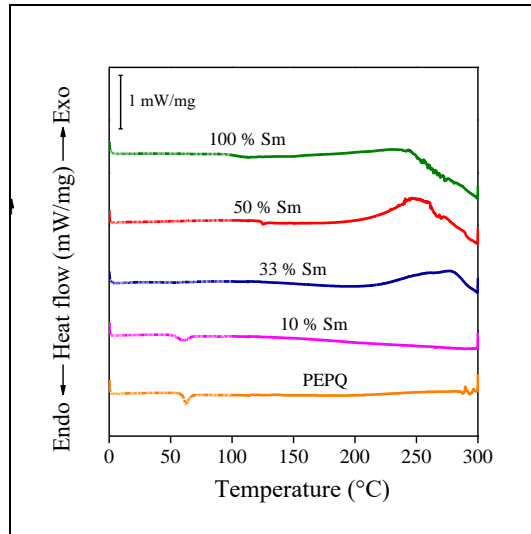


Fig. 8.9a DSC traces recorded on silymarin/PEPQ blends with different compositions during heating. Flavonoid content increases from bottom to top (same as Fig. 5.9).

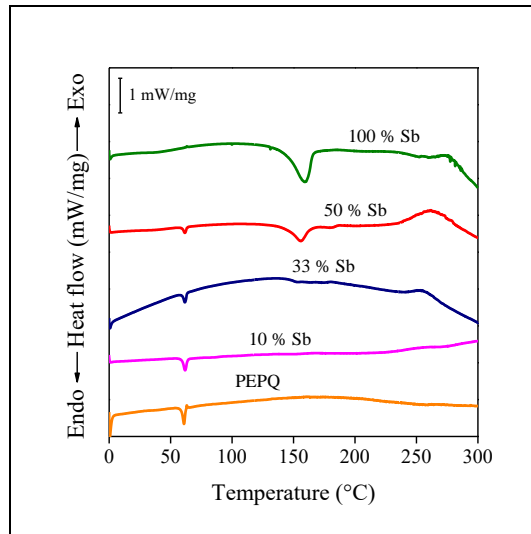


Fig. 8.9b DSC traces recorded on silybin/PEPQ blends with different compositions during heating. Flavonoid content increases from bottom to top.

8.5 Conclusions

The comparison of the stabilizing efficiency of a natural extract of flavonolignans to its main component showed that the extract is more efficient than the pure compound at large concentrations. The vinyl group content and MFR of the polymer is preserved more in the presence of the extract than with the pure compound, silybin. The residual stability of the polymer containing silymarin is slightly better at the same additive content than that prepared with silybin. Larger efficiency was explained by the smaller bond dissociation enthalpies of the most active phenolic hydroxyl groups of some of the components of the extract. The larger solubility of silymarin probably resulting from its amorphous character and the presence of the accompanying components of the extract may also contribute to its better efficiency. At small concentrations silymarin proved to be inferior to silybin, which was explained by the interaction of the components. Silybin protected the secondary stabilizer more efficiently than silymarin, but this effect did not manifest itself in better stabilization efficiency. The use of the extract is more advantageous because it is more efficient and significantly cheaper than its pure main component. On the other hand, the stabilizing efficiency of silymarin and the related compounds is inferior to other flavonoids like quercetin or dihydromyricetin.

Chapter 9 Summary

Polymers generally and polyolefins particularly must be protected against degradation during their processing and use. Stabilization is done routinely in industry with more or less standard additive packages containing a primary antioxidant and a secondary stabilizer, usually a phosphorous compound. In spite of the long tradition in stabilization, problems occur frequently, which must be solved either by the adjustment of the composition of the additive package to the actual conditions of processing or use, or simply by optimization. Because of the routine use of conventional stabilizer packages, hardly any new products appeared on the market in the last few decades and no new concept at all. Nevertheless, a few years ago, some questions were raised about the possible detrimental environmental and health effect of some of the metabolites of phenolic antioxidants and the questions have not been answered even today. Another factor, which may influence the use of any chemical including stabilizers, is the increasing environment awareness of the industry and the public. The demand for raw materials from natural resources increases continuously and increasing amounts of these materials are used in everyday practice now. Our group has a long tradition in the study of the degradation and stabilization of polyolefins and the research as well as the cooperation with industrial enterprises resulted in the accumulation of considerable knowledge and experience. The factors mentioned above led us to the idea of using natural compounds as stabilizers for polymers. Nature produces and uses a large number of natural antioxidants rather successfully, and some of these compounds are applied already extensively in the food industry. The idea was converted into practice and the results of the first experiments indicated that natural antioxidants are efficient melt stabilizers of polyethylene indeed. This thesis reports our further progress in this direction as well as the most important results that were achieved during the work. Although we summarized the most important results at the end of each chapter, we briefly repeat them here to give a concise overview. We compile our most important new findings in a few thesis points at the end of this chapter.

An earlier study showed that curcumin is an efficient processing stabilizer of polyethylene under processing conditions. Further and more detailed investigations showed that this natural antioxidant enhances the stabilizing efficiency of phosphonite secondary antioxidants even at the concentration of 5 ppm. The consumption of the secondary antioxidant reduces gradually with increasing curcumin content. Curcumin hinders the oxidation of the polymer and the formation of long chain branches. Not only the primary antioxidant, but also its combination with the secondary stabilizer determines the melt and the residual stability of the polymer. Curcumin colors polyethylene even at small amounts; yellowness index decreases with increasing number of extrusions. Both the change in color and the correlation between the concentration of vinyl groups and the melt flow index of the polymer indicate that the double bonds in the linear linkage between the two methoxyphenyl rings also take part in addition reactions with the alkyl macroradicals formed during processing.

In another study two natural antioxidants, silymarin and quercetin were compared to each other and the results showed that silymarin is a much less efficient stabilizer in polyethylene than quercetin. The consumption of vinyl groups is faster and melt flow rate as well as residual stability is smaller in its presence. Silymarin contains a fewer number of active hydroxyl groups than quercetin, but comparison on equal molar basis also shows the inferiority of the compound. The difference can be partially explained by the larger bond dissociation enthalpies of the hydrogens in silymarin, but silymarin also accelerates the consumption of the phosphorous secondary stabilizer that must contribute to its inferior efficiency as well. DSC measurements indicate the interaction of the two compounds probably leading to the faster consumption of the phosphorous antioxidant and poor stabilization. Unlike quercetin, silymarin is not a good candidate as stabilizer for practical applications.

The study of the effect and efficiency of rutin, another flavonoid type natural antioxidant, for the melt stabilization of polyethylene showed that rutin is as efficient melt stabilizer as quercetin, the compound used as reference. However, rutin has a deteriorating effect on the stability of the polymer at small concentrations and partially decomposes at the high temperature of degradation testing and probably also during processing. The comparison of bond dissociation enthalpies showed that the substitution of the hydroxyl group in ring **C** of quercetin by saccharide moieties increases their value, but the small increase does not influence the efficiency of the stabilizer much. This result indicates that bond dissociation enthalpies play a role in stabilization, but other factors also influence efficiency. FTIR and DSC measurements indicated the interaction of the natural antioxidant and the phosphonite secondary stabilizer and the development of interactions was confirmed also by molecular modeling. Hydrogen bonds and aromatic, π electron interactions develop between the two components, mainly between the hydroxyl groups in ring **A**, as well as with rings **A** and **B** thus they do not influence directly the stabilization efficiency of the antioxidants.

Experiments carried out to determine the stabilization activity of another flavonoid type natural antioxidant, dihydromyricetin, in polyethylene proved that it stabilizes PE very efficiently. At small concentrations dihydromyricetin proved more efficient melt stabilizer than quercetin, less vinyl groups were consumed during processing, less long chain branches formed and thus MFR was larger in its present than with the same amount of quercetin. DHM protected the secondary antioxidant better than quercetin; less PEPQ was consumed in its presence during processing. In spite of its better efficiency in melt stabilization, polymers containing DHM had the same residual stability as those prepared with quercetin. Accordingly, the larger efficiency does not result from the larger number of active phenolic hydroxyls in this molecule, but from their location, and from interaction with the phosphorous secondary stabilizer that is stronger or at least different for DHM than for quercetin. Although DHM is a white powder, it gave the polymer brownish color, which became stronger with increasing number of extrusions and additive content.

The comparison of the stabilizing efficiency of a natural extract of flavonolignans, silymarin, to its main component, silybin, showed that the extract is more efficient than the pure compound at large concentrations. The vinyl group content and MFR of the polymer is preserved more in the presence of the extract than with the pure compound. The residual stability of the polymer containing silymarin is slightly better at the same additive content than that prepared with silybin. Larger efficiency was explained by the smaller bond dissociation enthalpies of the most active phenolic hydroxyl groups of some of the components of the extract. The larger solubility of silymarin probably resulting from its amorphous character and the presence of the accompanying components of the extract may also contribute to its better efficiency. At small concentrations, silymarin proved inferior to silybin, which was explained by the interaction of the components. Silybin protected the secondary stabilizer more efficiently than silymarin, but this effect did not manifest itself in better stabilization efficiency. The use of the extract is more advantageous because it is more efficient and significantly cheaper than its pure main component.

The most important conclusions of this Thesis can be summarized briefly in the following main points:

1. We proved that the secondary stabilizer plays an important role in the determination of high temperature oxidative stability of polyethylene if applied in combination with non-hindered phenolic antioxidants too (**Chapter 4**).
2. We pointed out that curcumin is also an efficient stabilizer of PE and that not only its phenolic -OH groups, but the double bonds in the linear linkage between the two methoxyphenyl rings also take part in stabilization reactions. The double bonds react with alkyl radicals thus preventing the formation of long chain branches (**Chapter 4**).
3. Through the analysis of the chemical structure of the natural antioxidants, we pointed out that the bond dissociation enthalpy of their phenolic hydroxyl groups play an important role in their efficiency as stabilizers under the processing conditions of polyolefins. However, other factors may also influence stabilization (**Chapters 5-8**).
4. We established that rutin, another flavonoid type antioxidant, is also an efficient stabilizer, but its efficiency is decreased at small concentrations because of the partial decomposition of the saccharide moieties (**Chapter 6**).
5. Using various measurements and model calculations, we proved that natural antioxidants and the secondary stabilizer used in the additive package can interact with each other. The interaction may leave the stabilizing efficiency of the natural antioxidant intact, but occasionally it can have a negative effect on efficiency (**Chapters 5-7**).

6. In another series of experiments carried out with dihydromyricetin as natural antioxidant, we pointed out that one result of additive interactions can be the efficient protection of the secondary antioxidant. Dihydromyricetin protects the secondary antioxidant better than other natural antioxidants examined by us and less phosphonite secondary stabilizer is consumed in its presence during processing than with the others (**Chapter 7**).
7. We proved the first time that a natural extract of flavonolignans could be more efficient stabilizer than its main purified component. The better effect is the result of the multicomponent nature of the extract containing more efficient components and its improved solubility resulting from the presence of the accompanying natural compounds other than flavonolignans (**Chapter 8**).

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Appendix 1: Chemical structure of applied materials

Table A1 Structure and characteristics of the applied natural antioxidants.

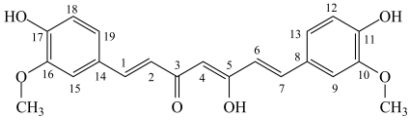
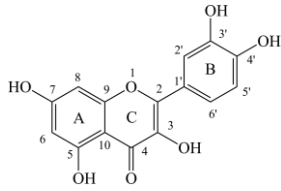
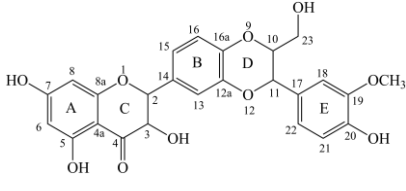
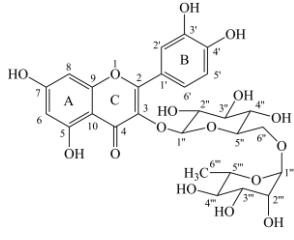
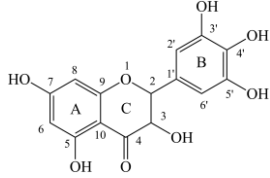
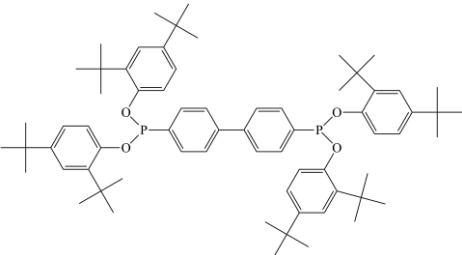
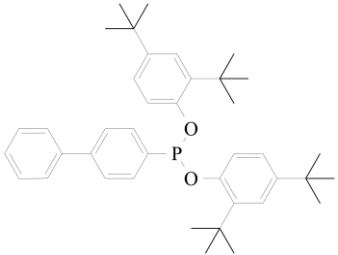
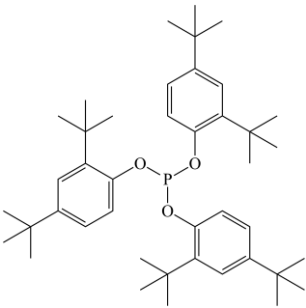
Compound	Structure
Curcumin (> 65%)	 <p>The structure of Curcumin is a polyphenolic compound consisting of two 4-methoxyphenyl rings connected by a heptadiene chain. The rings are numbered 1 through 19, and the methoxy groups are labeled CH₃. The central chain contains a ketone group at position 4 and a hydroxyl group at position 5.</p>
Quercetin (94%)	 <p>The structure of Quercetin is a flavonoid with a chromone core. It features a 3,5,7-trihydroxyflavone skeleton. The A ring is numbered 5-8, the C ring is numbered 1-4, and the B ring is numbered 1'-6'. Hydroxyl groups are present at positions 3, 5, 7, and 3'.</p>
Silymarin (Silybin, 70%)	 <p>The structure of Silymarin (Silybin) is a complex polyphenolic compound. It consists of a silybinin core with a methoxy group at position 18 and a hydroxyl group at position 23. The rings are labeled A, B, C, D, and E, and numbered 1 through 23. Hydroxyl groups are present at positions 3, 5, 7, and 23.</p>
Rutin (95%)	 <p>The structure of Rutin is a flavonoid glycoside. It consists of a quercetin core with a rhamnosyl sugar attached at position 3. The quercetin core is numbered 1-6, and the B ring is numbered 1'-6'. The rhamnosyl sugar is numbered 1''-6'' and has a methyl group at position 6''.</p>
Dihydromyricetin (98%)	 <p>The structure of Dihydromyricetin is a flavonoid with a chromone core. It features a 3,5,7-trihydroxyflavone skeleton. The A ring is numbered 5-8, the C ring is numbered 1-4, and the B ring is numbered 1'-6'. Hydroxyl groups are present at positions 3, 5, 7, and 3'.</p>

Table A2 Structure and characteristics of the components of PEPQ.

Compound	Structure
Diphosphonite (70%)	 <p>The structure shows a central biphenyl core. Each phenyl ring of the biphenyl is connected via an oxygen atom to a phosphorus atom. Each phosphorus atom is also bonded to two additional oxygen atoms, each of which is further bonded to a 2,4,6-trimethylphenyl group.</p>
Monophosphonite (20%)	 <p>The structure features a central phosphorus atom bonded to two oxygen atoms. One oxygen atom is part of a diphenyl ether group (two phenyl rings connected by an oxygen atom). The other oxygen atom is bonded to a 2,4,6-trimethylphenyl group. The phosphorus atom also has a double bond to an oxygen atom.</p>
Phosphite (10%)	 <p>The structure shows a central phosphorus atom bonded to three oxygen atoms. Each oxygen atom is connected to a 2,4,6-trimethylphenyl group.</p>

Appendix 2: List of relevant publications

1. Tátraaljai, D., Kirschweng, B., Kovács, J., Földes, E., Pukánszky, B.: *Processing Stabilization of PE with a Natural Antioxidant, Curcumin*, European Polymer Journal, **49**:1196-1203, 2013, IF: 3,477.
2. Kirschweng, B., Tátraaljai, D., Földes, E., Pukánszky, B.: *Efficiency of curcumin, a natural antioxidant, in the processing stabilization of PE: Concentration effects*, Polymer Degradation and Stability, **118**:17-23, 2015, IF: 3,120.
3. Kirschweng, B., Bencze, K., Sárközi, M., Hégyely, B., Samu, Gy., Hári, J., Tátraaljai, D., Földes, E., Kállay, M., Pukánszky, B.: *Melt stabilization of polyethylene with dihydromyricetin, a natural antioxidant*, Polymer Degradation and Stability, **133**:192-200, 2016, IF: 3,120.
4. Kirschweng, B., Bencze, K., Sárközi, M., Hári, J., Tátraaljai, D., Földes, E., Pukánszky, B.: *Phillips típusú polietilén feldolgozási stabilizálása a dihidromyricetin természetes antioxidáns felhasználásával*, Polimerek, **3(5)**:151-155, 2017.
5. Kirschweng, B., Vörös, B., Tátraaljai, D., Földes, E., Pukánszky, B.: *Natural antioxidants as melt stabilizers for PE: comparison of silymarin and quercetin*, European Polymer Journal, **90**:456-466, 2017, IF: 3,477.
6. Kirschweng, B., Tátraaljai, D., Földes, E., Pukánszky, B.: *Natural antioxidants as stabilizers for polymers*, Polymer Degradation and Stability, **145**:25-40, 2017, IF: 3,386.
7. Kirschweng, B., Tilinger, MD., Hégyely, B., Samu, Gy., Tátraaljai, D., Földes, E., Pukánszky, B.: *Melt stabilization of PE with natural antioxidants: Comparison of rutin and quercetin*, European Polymer Journal, **103**:228-237, 2018, IF: 3,531.
8. Kirschweng, B., Vörös, B., Arroussi, M., Tátraaljai, D., Pukánszky, B.: *Melt stabilization of polyethylene with natural antioxidants: comparison of a natural extract and its main component, in preparation*

Appendix 3: List of other publications

1. Tuboly, V., Kirschweng, B., Horváth, Zs., Imre, B., Pukánszky, B.: Biopolimerek az orvostudományban - Lebontható vázanyagok, Műanyag és Gumi, **51(7)**:275-279, 2014.
2. Kirschweng, B., Polyák, P., Pukánszky, B, Vörös, Gy.: *A poli(3-hidroxi-butirát) hidrolitikus degradációja*, Polimerek, **1(5)**:136-140, 2015.
3. Kirschweng, B., Nagy, O., Imre, B., Pukánszky, B.: *PLA-zselatin keverék szálak előállítása elektromos szálhúzással, szövettenyésztés céljára*, Műanyag és Gumiipari Évkönyv, **7**:86-93, 2016.