POLYMER DEGRADATION AND STABILITY

AVAILABLE ONLINE 11 JULY 2017

https://doi.org/10.1016/j.polymdegradstab.2017.07.012

http://www.sciencedirect.com/science/article/pii/s0141391017302021

NATURAL ANTIOXIDANTS AS STABILIZERS FOR POLYMERS

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ABSTRACT

The additive packages routinely used today usually consist of a phenolic antioxidant and a phosphorus or sulfur containing secondary stabilizer. Several years ago some questions were raised about the health and environmental hazard of these additives and industry has not offered an alternatively solution yet. Nature produces a large number of antioxidants, which play a key role in radical reactions taking place in the human body. The substances containing these antioxidants are used in natural medicine for ages and they are applied in increasing quantities also in the food industry. The application of natural antioxidants for the protection of polymers is in its infancy, the information available is limited and often contradictory. This review paper summarizes published results, analyzes them and points out the advantages and drawbacks of the approach. Although a wide variety of compounds have been added to polymers to improve their stability, the most promising candidates are the carotenoids, the flavonoids, other natural phenols and phenolic polymers including lignin. Available results indicate that flavonoids are much more efficient stabilizers than the hindered phenols used in industrial practice. On the other hand, most of the natural antioxidants discolor the polymer and their solubility is limited. Nevertheless, natural antioxidants can be efficiently used in specific applications, but further research is needed to explore all their advantages and include them into additive packages used in practice.

KEYWORDS: natural antioxidants, polyolefins, processing stabilization, carotenoids, flavonoids, lignin, bond dissociation enthalpy, color, solubility

1. INTRODUCTION

Polymers used in industrial practice contain additive packages tailored for the application practically always, and stabilizers usually are one of the most important constituents of these packages. A variety of stabilizers, and usually a combination of them, must be applied for the proper stabilization of polyethylene (PE) exposed to different conditions, because of the various possible effects leading to its degradation. Elevated temperature, shear forces and the amount of oxygen present are the main factors determining degradation during processing [1]. The exposure to these factors initiates thermo-mechanical or thermo-oxidative degradation depending on the availability of oxygen. Thermo-oxidation of polyolefins is an autocatalytic free radical chain reaction consisting of initiation, propagation and termination steps [2]. Alkyl, alkoxy, peroxy and hydroxyl radicals take part in these processes.

Stabilizer packages protecting polyolefins usually contain a hindered phenolic primary antioxidant and a phosphorous or sulfuric type hydroperoxide decomposer (secondary stabilizer), which significantly improve the thermo-oxidative stability of the polymer melt [3]. The most important radical scavenging mechanisms are hydrogen atom transfer (HAT) [4,5], radical adduct formation (RAF) [6], single electron transfer (SET) [7], and sequential proton-loss electron transfer (SPLET) [8,9], but the latter two mechanisms occur rarely in polyolefin stabilization, because of the non-polar character of the polyolefin serving as the medium of these reactions.

The decomposition of hydroperoxides to hydroxyl- and alkoxy radicals increases the concentration of reactive species in the polymer and thus also the rate of degradation. Secondary stabilizers reduce hydroperoxides to harmless alcohols, thus the application of phosphorous and sulfuric secondary stabilizers is mandatory during the processing of the polymer. While one of the main roles of the primary stabilizer is to hinder the oxidation of

the secondary stabilizer, the rheological properties of the polyolefin melt depends on the efficiency of the latter [10].

Several years ago the study of Brocca et al. [11] called the attention to the possible health and environmental hazard represented by traditional phenolic antioxidants and the plastic and additive industries do not have alternative solutions yet for the case, if the danger proves true. 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 during their use than in the case of synthetic phenolic antioxidants. The application of natural antioxidants for the protection of polymers is in its infancy, the only compound used routinely in practice is α-tocopherol [12]. The substance hinder the degradation reactions of polyethylene efficiently and in spite of its high price, it is used for the stabilization of medical devices made from ultra-high molecular weight polyethylene (UHMWPE) [13].

Natural antioxidants are frequently used in food products, but further research must be done to apply them routinely in polyolefins or more generally in plastic products during their processing and application. Because of the uncertainties related to synthetic phenolic antioxidants [11] more and more papers are published on the use of natural antioxidants as stabilizers. At the moment the available information is limited and the results are often contradictory, thus the goal of this paper is to summarize and analyze results and check the advantages as well as drawbacks of the approach. Because of our experience, we focus

mainly, but not exclusively, on the processing stabilization of polyethylene, and report the most important results obtained up to now in this field without even attempting to be comprehensive.

2. NATURAL ANTIOXIDANTS

Living organisms are constantly exposed to oxidation. Endogenous byproducts (peroxides, transition metals) and exogenous exposure, like UV and other radiations with higher energy and heat, lead to the formation of reactive oxygen- and nitrogen species [14], such as hydrogen peroxide (H_2O_2), superoxide ($O_2^{-\bullet}$), singlet oxygen ($^1O_2$) hydroxyl ($OH^\bullet$), peroxy ($ROO^\bullet$) and alkoxy ($RO^\bullet$) radicals [15]. More than hundred diseases are caused by or lead to oxidative stress [16-18]. Living organisms synthetize various substances with strong antioxidant effect in order to reduce the amount of reactive oxygen species and other free radicals [14,19,20]. The reaction mechanisms of these species are similar to those of polymer stabilizers [18]. 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 [20].

2.1. Classification, source

Natural antioxidants (AO) can be divided into two main groups, namely enzymatic and non-enzymatic antioxidants [21]. Enzymatic antioxidants either catalyze directly the decomposition of reactive oxygen species to harmless compounds (catalase, superoxide dismutase enzymes) [22] or regenerate non-enzymatic antioxidants (glutathione reductase, glucose-6-phosphate dehydrogenase) [23]. Since these substances are catalysts, they are not consumed in their reactions. 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 [24]. A classification based on the mechanism of action is shown in **Table 1**. In the following discussion we focus only on compounds that keep their activity at the processing temperature of polyolefins.

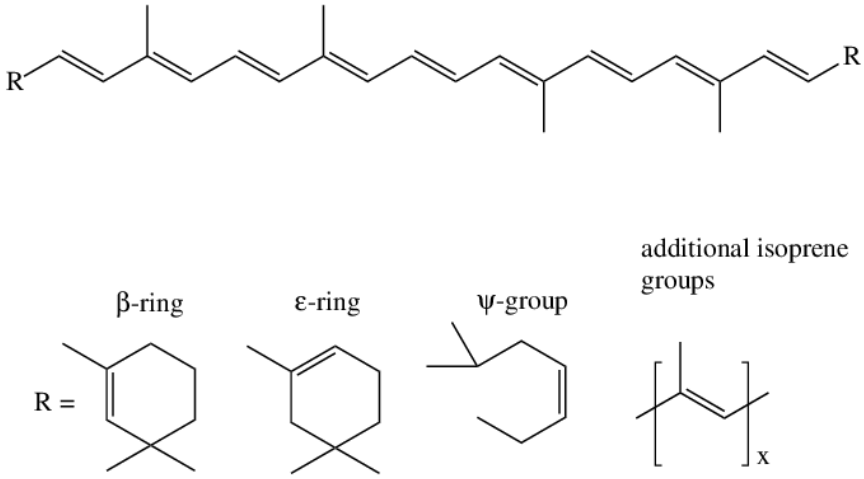
Table 1 Classification of non-enzymatic natural antioxidants by their mechanism

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** 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 high level of antioxidants [25]. The main sources of carotenoids are sweet potato [26], carrots [27], tomato [28], peppermint and spearmint [29]. Spinach, corn [30] and kale [31] are rich in xanthophylls. Flavonoids form the largest group of natural phenolic antioxidants with more than 6000 representatives [32]. They can be found in the skin of red grapes [33,34] and in red wine [34], in various citruses [35], onion [36] and honey [37], but leaves of stevia [38] and green tee contain them in considerable amounts too [39]. Various seeds and spices like mustard, ginger, fennel and pepper contain large amounts of phenolic acids [40], and curcuminoids can be found in turmeric [27]. Lignin is the major component of the cell wall of vascular plants [41], while tannins can be found in the seed and skin of grapes [42] and in other exotic fruits [43], but also in the leaves and barks of woods [44].

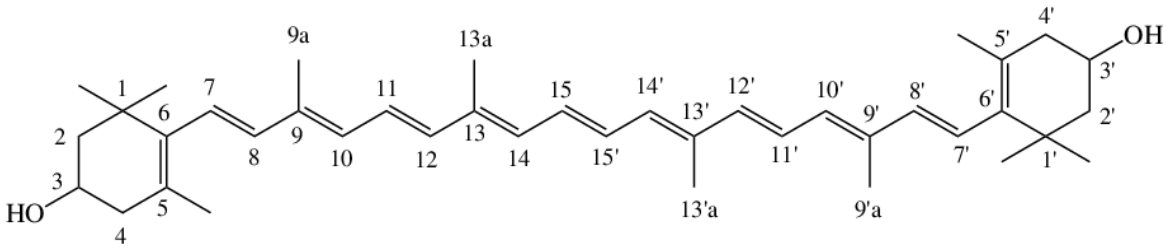
2.2. Carotenoids

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 xanthophylls subgroup. There are about 600 different type of carotenoids in nature [45]. The typical structure of carotenes is presented in **Scheme 1**.



Scheme 1 Typical structure of carotenes.

The most important representatives of this subgroup are lycopene, α-, β-, γ-, and δ-carotene, phytofluene, torulene, as well as shorter and longer terpenoids. The chemical structure of the xanthophyll zeaxanthin is shown in **Scheme 2**. Members of this subgroup of some significance are lutein, β-cryptoxanthin, as well as alcohols, esters and glycosides of carotenes.



Scheme 2 The structure of the xanthophyll zeaxanthin.

Biological activity. Carotenoids form an important part of the human diet. About 50 dietary carotenoids, including β-carotene possess provitamin A activity [46], since in the intestinal mucosa they can be metabolized to vitamin A, usually in the form of different retinyl esters [47]. Serious deficiency of vitamin A can lead to oculus diseases or even premature death [48]. Carotenoids become pro-oxidants in certain cases [49] and even increase the risk of lung cancer for smokers [49,50]. Their inhibitory effect in lipid oxidation makes carotenoids promising substances against cardiovascular and ocular diseases [51].

Application as food additive. Lipid oxidation leads to unsavory odor, color, taste and altered texture of food products, which can be hindered by the proper application of antioxidants [52]. Carotenes are usually applied as natural yellow, orange or red colorants in various foods like cakes, sauces, marinades, spice blends, beverages and dairy products [53]. Carotenes are rarely applied alone because of their sensitivity towards oxygen and ultraviolet radiation leading to undesired color loss [54].

Application in polymers. 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 [55] 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 authors claimed that lycopene is a promising processing stabilizer at small oxygen concentrations. Abdel-Razik [56] studied the stabilizing efficiency of β-carotene in an ABS copolymer. The stabilizer decreased the number of carbonyl and hydroxyl functional groups formed compared to non-stabilized samples. The effect was explained with the

reaction of carotenoid biradicals with molecular oxygen, which hindered the formation of peroxy and alkoxy radicals in the propagating step of the thermo-oxidation of acrylonitrile butadiene styrene (ABS). López-Rubio et al. [57] studied the effect of β-carotene on the thermal and mechanical properties as well as UV stability of various biopolymers including poly(lactic-acid) (PLA), poly(ε-caprolactone) (PCL) and poly(hydroxybutyrate-co-valerate) (PHBV). They found that the additive plasticizes biopolymers, especially poly(ε-caprolactone), and increases their UV stability. The studied samples maintained their mechanical properties at the original level even after irradiation with ultraviolet light. The processing stabilization efficiency of β-carotene was investigated also in a Phillips type polyethylene [58]. The stabilizer was used in combination with a phosphorous secondary antioxidant, PEPQ (Sandostab PEPQ, a mixture of diphosphonite, monophosphonite and phosphite compounds) and α-tocopherol, which protects β-carotene against oxidation [59,60]. Such synergistic effects are exploited also in applications in the food industry [61]. The additive protected the polymer from oxidation; the number of carbonyl groups formed during processing decreased to zero, when the amount of residual β-carotene was larger than 250 ppm (**Fig. 1**).

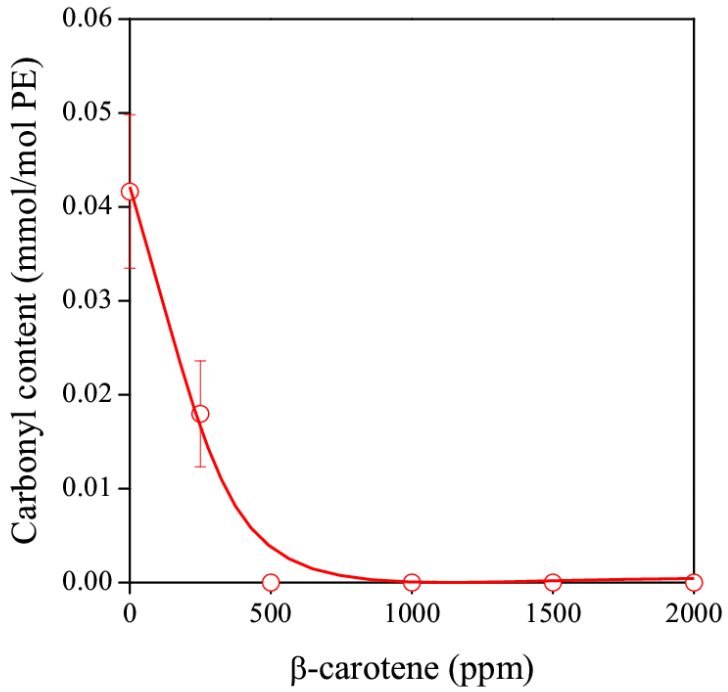


Fig. 1 Effect of β-carotene content on the concentration of carbonyl groups formed during processing of Phillips PE. Conditions: 500 ppm Vitamin E and 2000 ppm PEPQ, 1st extrusion [58].

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. OIT decreased with increasing concentration of β-carotene remaining in the polymer after extrusion (**Fig. 2**). β-carotene acts as a sensitizer at elevated temperatures and large oxygen concentrations, because the autoxidation of the substance becomes the thermodynamically favored reaction [62]. However, oxygen concentration must be below this critical value during polyolefin processing, since the formation of oxidized species was not noticed in the presence of β-carotene.

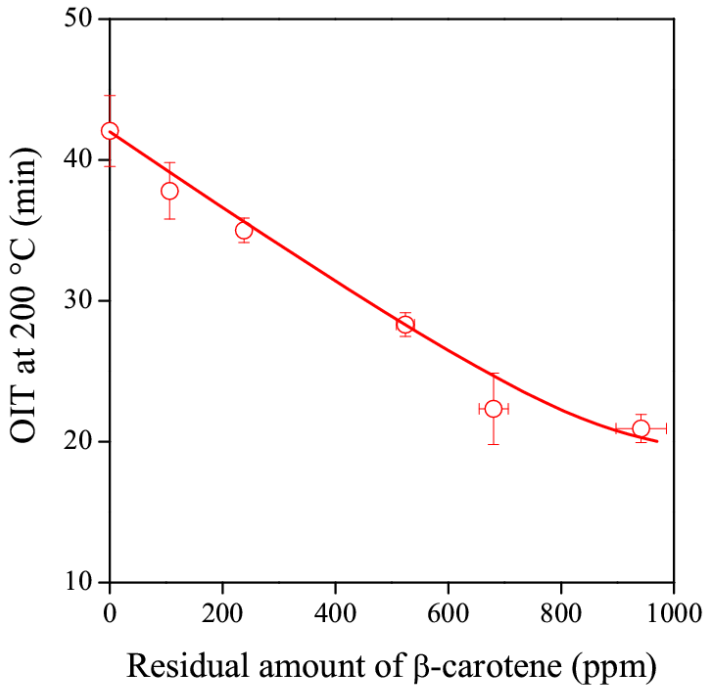


Fig. 2 Oxidation induction time (OIT) of Phillips PE plotted against the amount of unreacted β-carotene. Conditions are the same as in **Fig. 1** [58].

The additive severely discolored polyethylene, but the strong color disappeared during storage, if the samples were exposed to oxygen and ultraviolet radiation or sunlight (**Fig. 3**). The loss of color results from reactions with peroxides and from quenching singlet oxygen chemically, and both types of reaction lead to the irreversible oxidation of carotenes.

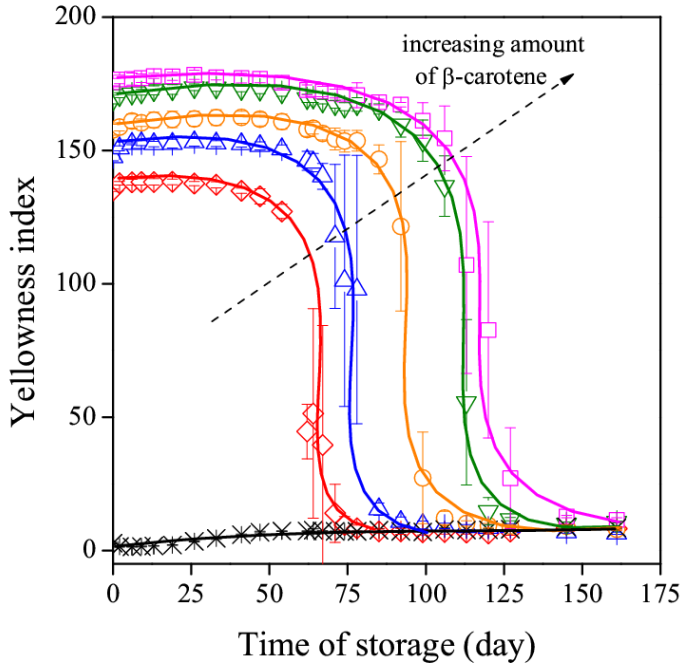


Fig. 3 Bleaching of 1 mm thick polyethylene plates containing β-carotene. The samples were exposed to sunlight at ambient temperature. Conditions are the same as in **Fig. 1**. Symbols: (X) 0, (◇) 250, (△) 500, (○) 1000, (▽) 1500, (□) 2000 ppm β-carotene [58].

Mechanism. 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, as the energy barrier between their ground and excited states is rather small [63] and decreases with increasing number of double bonds [45]. The result of the energy transfer is an oxygen in the ground ($^3O_2$) and a carotenoid molecule in the triplet state ($^3CAR^*$). The latter returns to the ground state (^1CAR) by dissipating its energy through rotation and vibration (Δ), and thus it is able to quench another singlet oxygen molecule (**Scheme 3**) [64].

$$^{1}O_2^{*} + {}^{1}CAR \rightarrow {}^{3}O_2 + {}^{3}CAR^{*} \rightarrow {}^{1}CAR + \Delta$$

Scheme 3 The mechanism of singlet oxygen quenching of carotenoids.

Chemical quenching or the direct addition of an oxygen molecule compete with physical quenching [64] and lead to the decomposition of the carotenoid molecule by the formation of epoxycarotenoids, apocarotenals and various other substances [65].

Carotenoids can react with alkyl, alkoxy and peroxy radicals too [55,66]. For a long time carotenoids were thought to scavenge radicals only by the single electron transfer (SET) mechanism [67]. Carotenoids can act as electron donors, but also as electron acceptors, depending on the polarity of the solvent and the relative values of the electron affinity (EA) and ionization energy (IE) of the reacting radical and the carotenoid [68]. Martinez and coworkers [69] created a complete electron donor-acceptor map, in which the reacting antioxidant and its radical partners can be positioned and matched showing whether the radical stabilizes by electron donation or abstraction. Computational calculations analyzing the possible mechanisms of antioxidant activity clarified that the dominating pathway of the radical scavenging reactions of carotenoids actually depends on the chemical structure of the compound. Besides electron transfer both hydrogen atom abstraction (HAT) and the formation of radical adducts (RAF) are important [70,71]. The most favored sites of hydrogen abstraction are the allylic **C4** and **C4'** carbon atoms in the terminating β-rings of the carotenoid molecule (see **Scheme 2**) [72]. Although hydrogen atom transfer is more favored thermodynamically than radical adduct formation, the former is less important than the latter, which is favored kinetically [67].

Carotenoids efficiently hinder the oxidation of polyolefins and scavenge alkyl- and alkoxy radicals at small oxygen concentrations. However, the efficiency of the additive

has limitations, since the formation or diffusion of singlet oxygen is rather uncommon during the processing of polyolefins [73]. Carotenoids react slower with peroxy radicals compared to alkyl- and alkoxy radicals, adducts formed in these reactions are rather instable and their decomposition leads to oxidized carotene products and additional alkoxy radicals [66]. Carotenes completely lose their efficiency as stabilizers at elevated oxygen concentrations and become pro-oxidants.

2.3. Vegetable oils

While the addition of oil extracts from vegetables and fruits to diet have beneficial effects on the human health, the application of sunflower oil, pumpkin seed oil, flax oil or milk thistle seed oil as processing stabilizer leads to deteriorated properties compared to the neat polyolefin. Oils from different seeds are usually produced by cold pressing and they contain high levels of transient metals. Such contaminations initiate and accelerate the degradation of polyolefins under processing conditions.

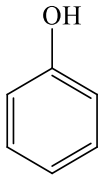
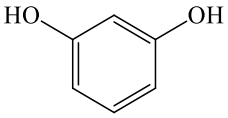
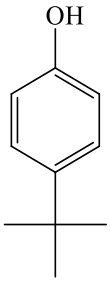
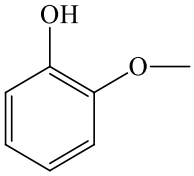
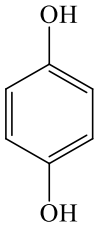
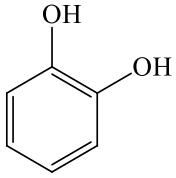
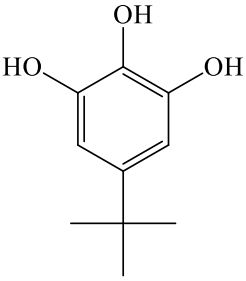
2.4. Natural polyphenols

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 from the phenolic hydroxyl group to the reacting radical [74]. 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, followed by radical adduct formation [75].

Among others, the activity of a phenolic antioxidant molecule depends on the number and position of its phenolic hydroxyl groups, the enthalpy of bond dissociation

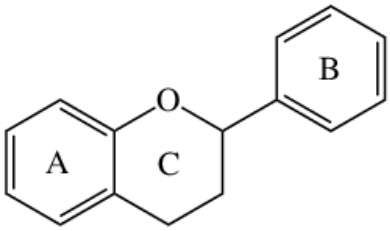
between the oxygen and the hydrogen atom (BDE), and on the solubility of the antioxidant in the medium of the reaction. Substituents around the phenolic hydroxyl groups affect the activation enthalpy of hydrogen abstraction. Bond dissociation enthalpies of different phenols are collected in **Table 2**. The values were derived from computational calculations [76] 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 *orto*-position, while the effect of additional hydroxyl groups is smaller, if they are located in the *para*- and *meta*-positions.

Table 2 Bond dissociation enthalpies (BDE) of different phenolic compounds [76]

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

2.4.1. Flavonoids and other polyphenol compounds

Quite a few subclasses of natural antioxidants belong to the flavonoid group [25]. Their structure is derived from the basic structure of flavane (2-phenyl-benzo-γ-pyrane) (**Scheme 4**), 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** ring, as well as on the degree of conjugation and oxidation of the latter. Subclasses of flavonoids are flavones, isoflavones, flavanols, flavonols, flavanones, anthocyanins and proanthocyanidins [77].



Scheme 4 Basic structure of flavonoids, the flavane backbone.

Biological activity. The structure-activity correlations of flavonoids have been discussed in other reviews [78-80] and are out of the scope of this paper, thus only the most important aspects are mentioned here. Similarly to carotenoids, flavonoids are able to stabilize reactive oxygen species and thus prevent oxidative stress [81]. However, they are not singlet oxygen quenchers and the mechanism of stabilization is based on hydrogen atom transfer or singlet electron transfer, depending on the structure of the compound and the radical [82]. They also form stable complexes with metal ions thus preventing their contribution to reactions generating free radicals [83]. A limiting factor of medical applications is the poor bioavailability of flavonoids [84,85]. Curcuminoids form a much thinner family of natural antioxidants containing only a few members, i.e. curcumin and its derivatives [86]. Similarly to flavonoids, the absorption of curcumin is very limited in

the body [87]. Tocopherols and tocotrienols consist of four closely related compounds each collectively called vitamin E, differing only in the position and number of methyl substituents at the aromatic ring. Dietary intake recommendations include only α-tocopherol, which is the most efficient antioxidant among tocopherols and tocotrienols under physiological conditions [88]. α-tocopherol efficiently reacts with peroxy radicals by hydrogen atom donation from its phenolic hydroxyl group resulting in a more stable tocophenoxyl radical, which undergoes further reactions [89]. The phytyl moiety with the length of six carbon atoms ensures the solubility of the substance in phospholipid biomembranes [90].

Application as food additive. As we discussed above, natural phenolic antioxidants inhibit the peroxidation of lipids, which is a major concern in the food industry [52]. Different types of flavonoids [91], tocopherols and tocotrienols [92] are applied as stabilizers in food, while curcumin is a natural colorant with additional stabilizing effect [93]. Natural antioxidants can be applied in the food itself, or in the packaging material wrapped around the product [94-96].

Application in polymers. The efficiency of specific flavonoids as processing stabilizers was studied by various research groups [97]. Zaharescu et al. [98] stabilized an ethylene-propylene-diene terpolymer (EPDM) efficiently against γ-radiation with naringenin and caffeic acid combined with 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. The authors [99] stabilized UHMWPE against γ-radiation also with rosemary extract and pointed out that 5000 ppm of the extract ensures the long term stability of the product. Cerruti [55] claimed that the flavonoid content of red grape seeds resulted in a more efficient thermo-

oxidative stabilization of polypropylene than that of tomato extract containing lycopene. Ambrogi et al. [100] studied the efficiency of extracts from French maritime pine, grape seeds and tomato seed and skin on the short- and long-term stability of PP. They found that the grape extract provides long-term, while the pine extract only short-term stability for the polymer samples. The tomato extract became inactive in oxidation induction time measurements, because of its autoxidation. The effect and efficiency of quercetin, α-tocopherol and their cyclodextrin complexes were studied by Koontz [101] in metallocene and Ziegler-Natta type polyethylene. The additives increased the oxidation induction times of both polymers, however, the efficiency of the quercetin complex decreased compared to the free quercetin molecule. Samper et al. [102] examined the stabilizing effect of a wide range of flavonoids (chrysin, quercetin, hesperidin, naringin, silibin) against thermo-oxidative degradation and ultraviolet radiation in polypropylene. They found that the flavonol type natural antioxidant ensured the longest oxidation induction times and hindered the most efficiently the formation of carbonyl groups during ultra violet irradiation. Chen [103,104] investigated the stabilizing efficiency of dihydromyricetin in polyethylene and polypropylene. The author applied the additive in 2000 ppm without any secondary antioxidant. The efficiency of dihydromyricetin was better than that of Irganox 1010 in both matrices.

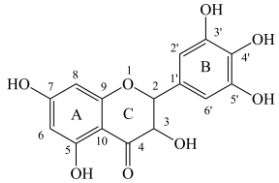
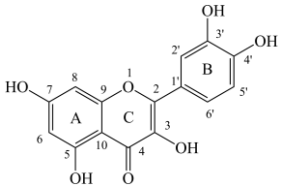
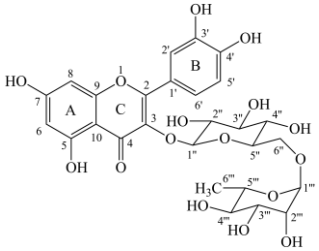
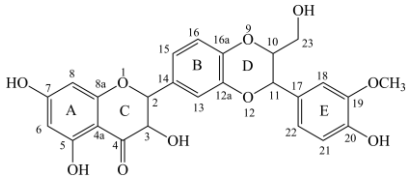
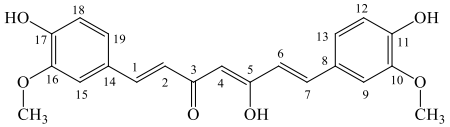
The efficiency of α-tocopherol as processing stabilizer was thoroughly investigated by Al-Malaika [12,105-108]. Vitamin E outperformed the usually applied synthetic antioxidants Irganox 1010 {pentaerythritol tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl]propionate)} and Irganox 1076 [octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate] in low density polyethylene [12]. The natural additive efficiently hindered the decrease of the melt flow rate of polyethylene during multiple extrusions even at low additive concentrations. The reaction of α-tocopherol with a peroxy

radical leads to the formation of tocopheroxyl radical, which isomerizes to the corresponding benzyl radical. This radical participates in various reactions resulting in the formation of dihydroxydimers, spirodimers, trimer aldehydes and quinoidal products [107,108]. Most of the byproducts have additional stabilizing effect in the polymer [105] that has been confirmed also in polypropylene [106]. The efficiency of vitamin E can be further increased by the synergistic interaction of phosphite type secondary stabilizers, like Ultranox 626 [bis(2,4-di-tert-butylphenyl) pentaerythritol diphosphite)]. The secondary stabilizer hinders the consumption of α-tocopherol and decreases the discoloration effect of the quinoidal byproducts of vitamin E [106].

More than a few papers focus on the study of the efficiency of specific natural antioxidants as processing stabilizers and compare their activity to that of hindered phenols frequently used in industrial practice (Irganox 1010, Irganox 1076, etc.). The effect of antioxidant concentration is rarely investigated in these studies, the authors compare the various compounds at a single, often quite large, 1000 or even 30000 ppm [109] antioxidant content. Natural antioxidants are compared to each other usually only in food and health science studies.

The structure and characteristics of a few natural antioxidants are presented in **Table 3** without any attempt of being comprehensive. Besides their structure also the number of active phenolic hydroxyl groups and their smallest hydrogen bond dissociation enthalpy (BDE) are also listed in the table, the latter was calculated by time-dependent functional density theory methods by various authors [76,110-113]. The solubility of the compounds in polyethylene was estimated from changes in the color of the polymer as a function of antioxidant content.

Table 3 Structure and characteristics of various polyphenols

Compound	Structure	No of OH groups	BDE (kJ/mol)	T_m (°C)	Solubility (ppm)
Dihydromyricetin		5	282.0	243	18
Quercetin		4	305.0	316	19
Rutin		4	336.2	135	24
Silymarin		3	367.8	167	54
Curcumin		2	329.9	179	28

In a series of recent studies, Phillips type polyethylene samples containing various amounts of the antioxidants listed in **Table 3** and PEPQ secondary stabilizer were produced by multiple extrusions [114-117]. Their efficiency as processing stabilizer was determined and it was shown to depend on their chemical structure, dispersion and interaction with the secondary antioxidant. In **Fig. 4** the vinyl group content of the polymer is plotted against the amount of the natural antioxidant after six consecutive extrusion steps. The five polyphenols hinder the reactions of the vinyl groups during processing with different efficiency. All reached their maximum effect already around 100 ppm additive content, but the ultimate concentration of vinyl groups differ considerably, thus the structure and characteristics of the natural antioxidant play a role in the determination of efficiency.

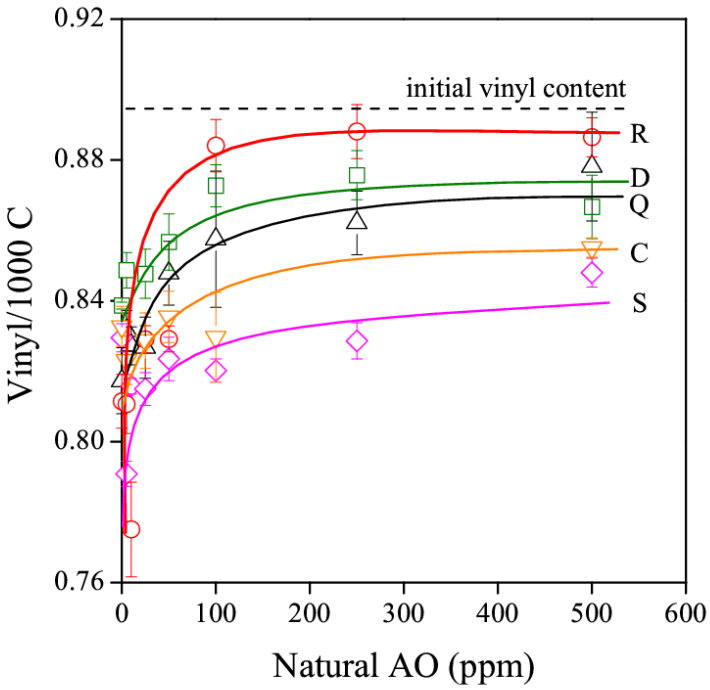


Fig. 4 Vinyl group content of polyethylene plotted against the amount of natural antioxidants added. Conditions: 1000 ppm PEPQ, 6th extrusion. Symbols: (○) curcumin, C; (□) dihydromyricetin, D; (△) quercetin, Q; (▽) rutin, R; (◇) silymarin, S.

Decreasing number of unsaturations indicates the formation of long chain branches during processing, which leads to increased viscosity and decreased melt flow rate of the polyolefin melt (**Fig. 5**), which is a typical phenomenon for Phillips type PE [2]. Differences in melt flow rate values can be distinguished only at small antioxidant contents, below 2 mmol OH/kg PE, since the reactions of vinyl groups lead to the formation of long chain branches only after the consumption of the applied secondary antioxidant [118]. This statement is strongly corroborated by **Fig. 6** showing the amount of residual PEPQ as a function of the natural antioxidant added. The natural antioxidant

protects the phosphonite secondary antioxidant during extrusion thus more PEPQ is available to react with the forming hydroperoxides. The results presented in **Fig. 6** show that the consumption of PEPQ decreases with decreasing energy barrier of hydrogen abstraction (**Table 3**).

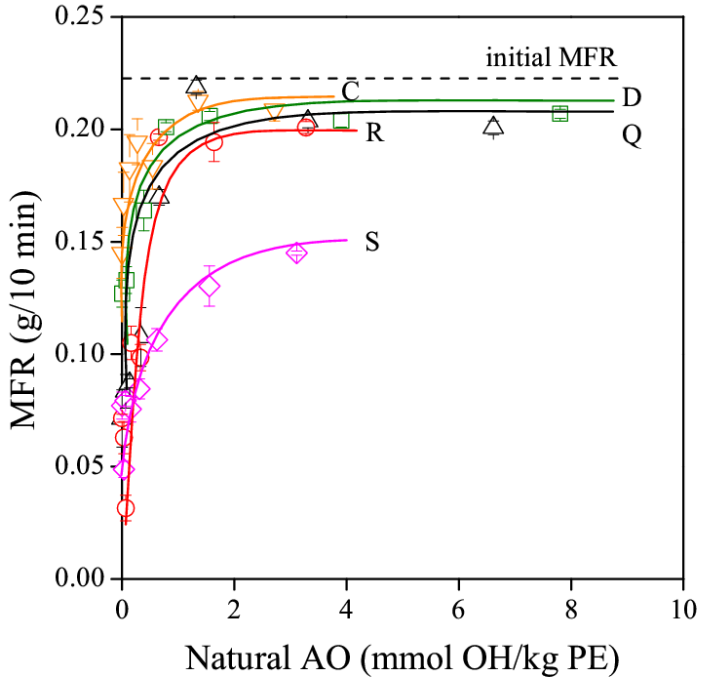


Fig. 5 Effect of the amount of natural antioxidant on the melt flow rate of PE. Conditions: 1000 ppm PEPQ, 6th extrusion. Symbols are the same as in **Fig. 4**.

The correlation between BDE and PEPQ consumption might explain the differences in the efficiency of flavonoid type antioxidants, but is not valid for curcumin from which hydrogen atom abstraction is more difficult. On the other hand, one may assume that the different behavior of curcumin is caused by the fact that it participates in a variety of radical scavenging reactions other than hydrogen atom donation from the phenolic moiety.

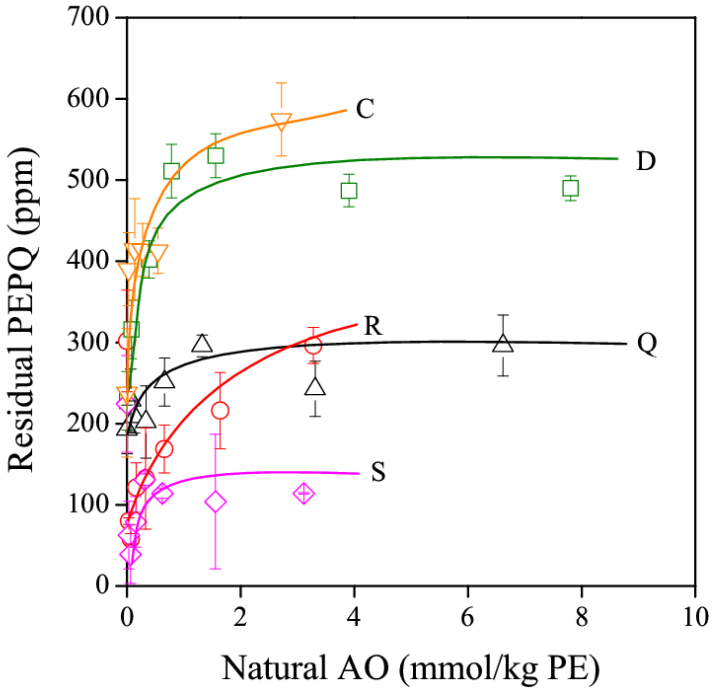


Fig. 6 Dependence of the residual amount of PEPQ secondary antioxidant in Phillips PE, on the amount of natural antioxidant added. Conditions: 1000 ppm PEPQ, 1st extrusion. Symbols are the same as in **Fig. 4**.

Residual thermo-oxidative stability measurements (OIT) offer information about the amount and activity of primary antioxidants remaining in the polymer after processing [119]. The oxidation induction times (OIT) of samples containing the antioxidants discussed above is presented in **Fig. 7** as a function of antioxidant content. The concentration of the natural antioxidants was normalized by the number of phenolic hydroxyl groups in the molecule. Besides functionality, also the reactivity of the phenolic groups and the interaction of the primary and secondary stabilizers seem to influence the efficiency of the additive package.

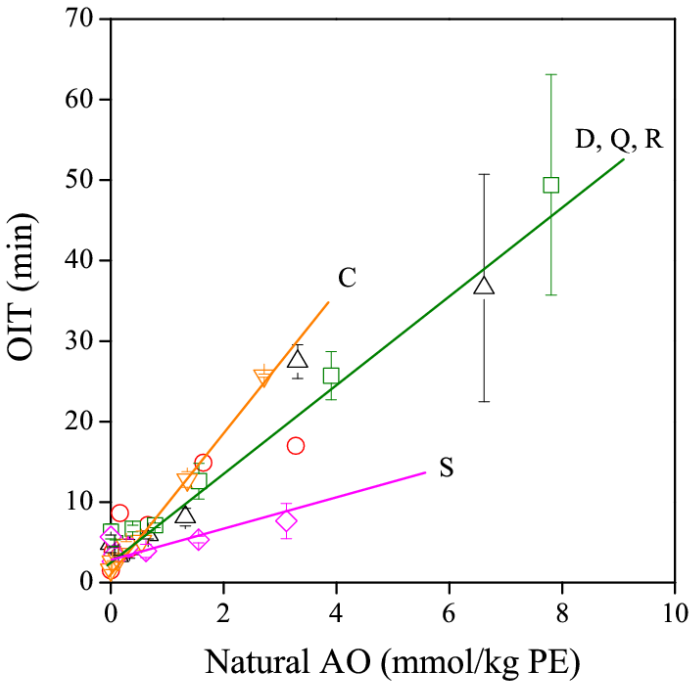


Fig. 7 Oxidation induction times of PE samples containing different type and amount of natural antioxidants. Conditions and symbols are the same as in **Fig. 4**.

All the natural antioxidants studied seriously discolor polyethylene. Changes in the yellowness index of PE samples are plotted as a function of additive content in **Fig. 8** after the first extrusion. Yellowness index increases linearly with stabilizer concentration up to the solubility limit of the additive in the PE matrix. The results indicate that the stabilization efficiency of the various natural antioxidants depends on kinetic and thermodynamic factors. The physical state of the additive during processing and its solubility in the matrix polymer are just as important aspects as the energy barrier of hydrogen atom transfer and the interaction of the primary and secondary stabilizers. In subsequent paragraphs we discuss the effect of the most important factors somewhat more

in detail.

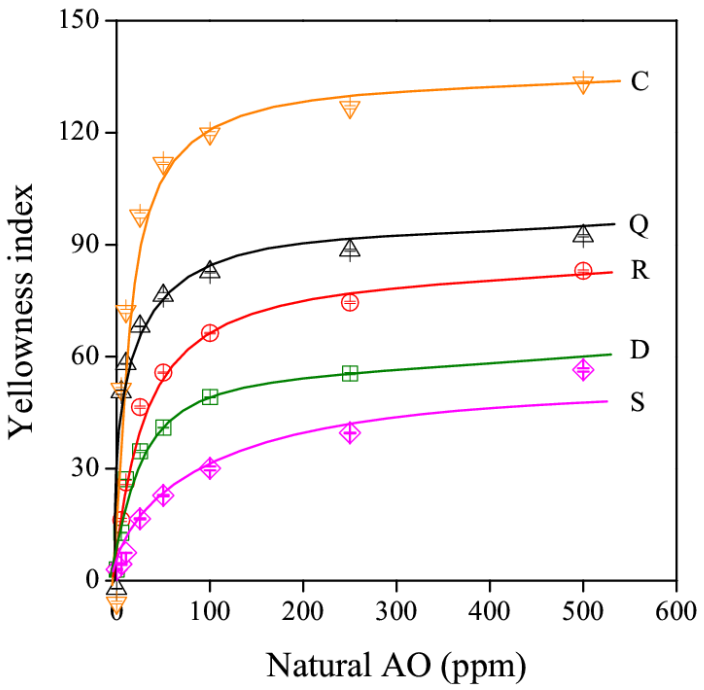


Fig. 8 Yellowness index of PE samples plotted against the amount of natural antioxidant added. Conditions: 1000 ppm PEPQ, 1st extrusion. Symbols: are the same as in **Fig. 4**.

Chemical structure. Dihydromyricetin, quercetin, rutin and silymarin are flavonoid type compounds, differences in their efficiency are related to the dissimilar number and location of the available phenolic hydroxyl groups, to the different degree of delocalization and dissimilar substitution. Predictions based on computational calculations [120] and actual measurements with 2,2-diphenyl-1-picrylhydrazyl (DPPH•) radicals [78] showed that the various phenolic hydroxyl groups of flavonoids are not equally active sites for hydrogen abstraction, the reaction primarily proceeds through the phenolic hydroxyl groups located at the aromatic B ring [78]. These results are in agreement with the bond

dissociation enthalpies listed in **Table 2** for different phenols, which show that hydroxyl substitution in the *orto*-position results in significantly smaller BDE values than substitution in the *para*- or *meta*-positions. As Lucarini [121] pointed out and Jean-Mary Aubry and coworkers [122] confirmed with numerous calculations, the substitution of electron donating groups onto phenols decreases their BDE, as these groups increase the stability of the forming phenoxy radical. Substitution with an additional hydroxyl group is even more efficient, since besides resonance stabilization, it stabilizes the phenoxy radical through intramolecular hydrogen bonding, if it is in the *orto*-position. A hydroxyl group in the *para*-position increases the stability of the phenoxy radical only by electron donation, while hydroxyl groups in the *meta*-position are electron withdrawing substituents with negligible impact on the stability of phenoxy radicals [76]. These relationships explain partially the results presented above. In the case of silymarin, less efficient phenolic hydroxyl groups are available in rings **A** and **E** (resorcinol and phenyl moieties respectively) resulting in poor stabilization. Easier hydrogen atom abstraction from the pyrogallol moiety increases the radical scavenging ability of dihydromyricetin, which protected PEPQ much better and hindered its consumption. The substitution of the hydrogen atom of the hydroxyl group at ring **C** of quercetin to large saccharide groups slightly increased the bond dissociation enthalpies of all phenolic hydroxyls leading to the decreased activity of rutin [123]. These considerations are strongly supported by **Fig. 9** showing the amount of PEPQ remaining in the polymer after the first extrusion as a function of the lowest dissociation enthalpies of the studied antioxidants.

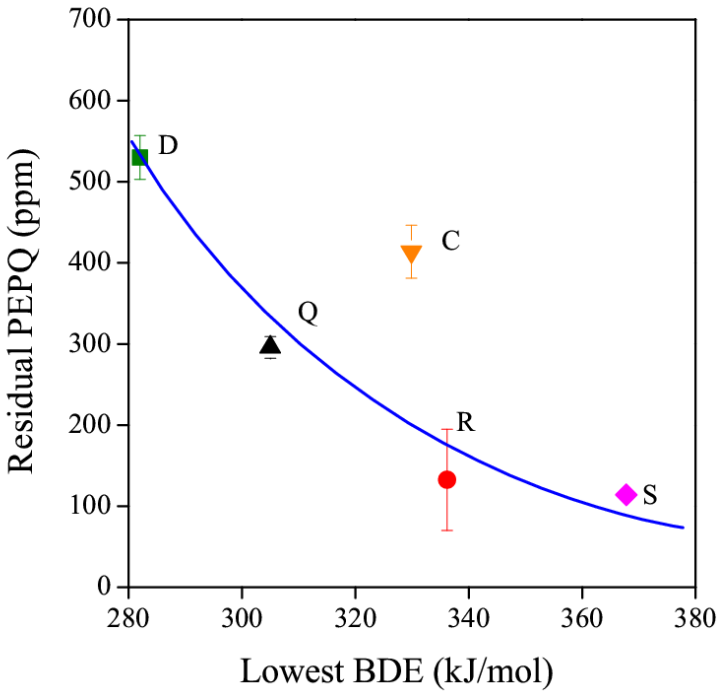


Fig. 9 The amount of PEPQ remaining in Phillips PE after the first extrusion step in samples containing different natural antioxidants. Conditions: antioxidant 0.3 mmol/kg PE, 1000 ppm PEPQ, 1st extrusion. Symbols are the same as in **Fig. 4**.

The conjugated hydrocarbon chain of curcumin, similarly to carotenoids, can scavenge radicals also according to the radical adduct formation (RAF) mechanism. As Galano [75] showed, the activation enthalpy of this mechanism is only slightly larger than that of hydrogen atom transfer and the actual value depends also on the type and structure of the reacting radical. Based on HPLC-MS results alkyl- and alkoxy radicals were assumed to react with the conjugated double bonds of curcumin, but the results are the subject of further study. Presumably the secondary reaction pathway of adduct formation becomes more important for phenoxy radicals, which might lead to the increased OIT

values of the samples containing curcumin (**Fig. 7**).

The extent of discoloration is related to the degree of delocalization; the double bond in ring **C** of flavonoids extends delocalization to the entire molecule. The saturation of this bond leads to weaker color as in the case of dihydromyricetin and silymarin. The resonance stability of the forming phenoxy radicals also decreases with decreasing degree of delocalization. This phenomenon affects negatively the activity of these antioxidants [110,120], which is somewhat compensated by the hydroxyl groups located in the *orto*-position in the pyrogallol moiety of dihydromyricetin.

Interaction with the secondary antioxidant. The studied natural antioxidants act like primary stabilizers, the oxidation of PEPQ is hindered in their presence. However, differences in their chemical structure and in the reaction of hydrogen atom donation do not explain fully their dissimilar efficiency. PEPQ influences the thermal characteristics of the natural antioxidants by modifying their melting temperatures and thermal stability. A plausible explanation for the phenomenon is the interaction of the primary and the secondary stabilizer.

The phenolic hydroxyl groups of primary stabilizers are hydrogen donor sites, while the non-bonding electron pairs of the oxygen atoms in PEPQ makes them hydrogen acceptors. The shifting wavelength of the -P-O-C vibration in the FTIR spectra of antioxidant/PEPQ mixtures indicates smaller bonding energy for the –P-O-C group (**Fig. 10**), which can be explained by intermolecular hydrogen bonding between the primary and the secondary antioxidant.

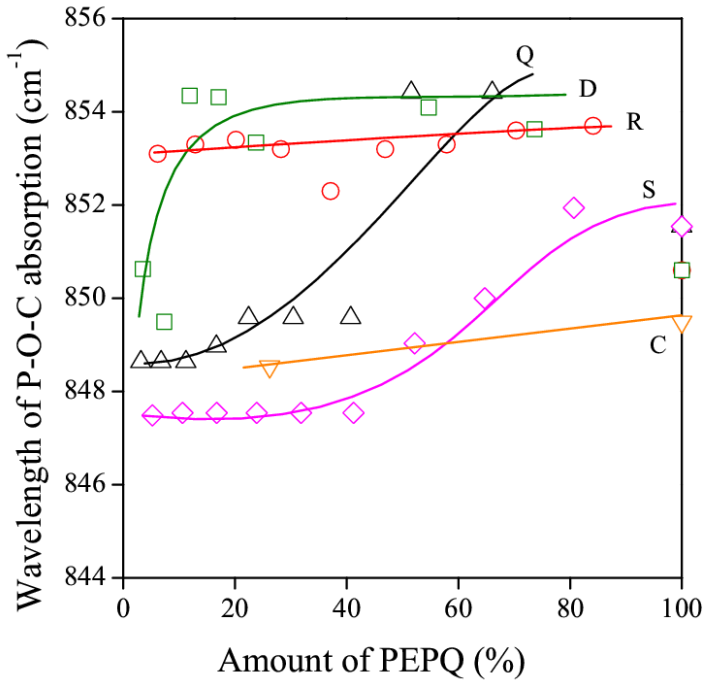


Fig. 10 Effect of component interactions on the shift of the -P-O-C absorbance of PEPQ in antioxidant/PEPQ powder mixtures without any polymer or processing. Conditions: KBr pastille. Symbols are the same as in **Fig. 4**.

Solubility. Several authors studied the stabilization effect of natural antioxidants, but added them to the polymer in relatively large amounts in 2000 ppm or even more. Occasionally they claimed that these stabilizers are dispersed completely homogenously in polyolefins [103]. However, solubility values estimated from the changing color of PE compounds (**Table 3**) and practical experience showed that the stabilizers precipitate from the polymer and relatively large crystals appear already around 50 ppm additive content. Quercetin could be homogenized with the PE powder only after solving it in acetone, but at larger concentrations quercetin crystals appeared in plates compression molded from the polymer even in this case (**see Fig. 11**). The limited solubility of polar, small molecular

weight stabilizers affects homogeneity and efficiency negatively and eventually leads to their migration from the polymer matrix. The application of α-tocopherol as primary stabilizer in UHMWPE clearly shows the importance of both low BDE (289.1 kJ/mol [76]) and sufficient solubility in the polymer matrix, which is enhanced by the saturated hydrocarbon chain. Considerable effort is put into the chemical modification, even polymerization of phenolic antioxidants in order to increase their solubility in and slow down their migration from the matrix [124], but such a modification increases price and chances for potential health issues.

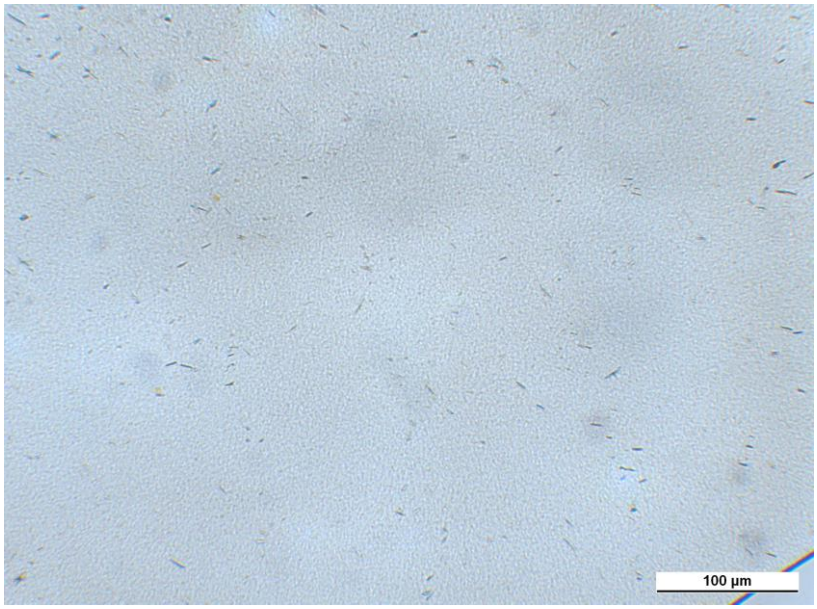
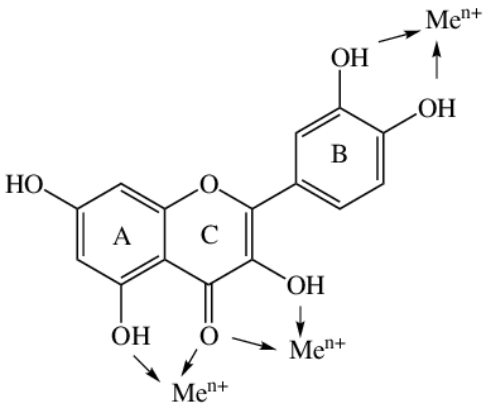


Fig. 11 Optical micrograph recorded on a polyethylene film of 100 µm thickness containing 1000 ppm quercetin [115].

Formation of chelate complexes. Natural polyphenols are able to form complex structures with transition metal ions by the non-bonding electron pairs of their hydroxyl and carboxyl groups (**Scheme 5**). Chelation is an important characteristics of these compounds, since transition metal contaminations induce the degradation of polyolefins easily under the conditions of polymer processing, but even more during application.

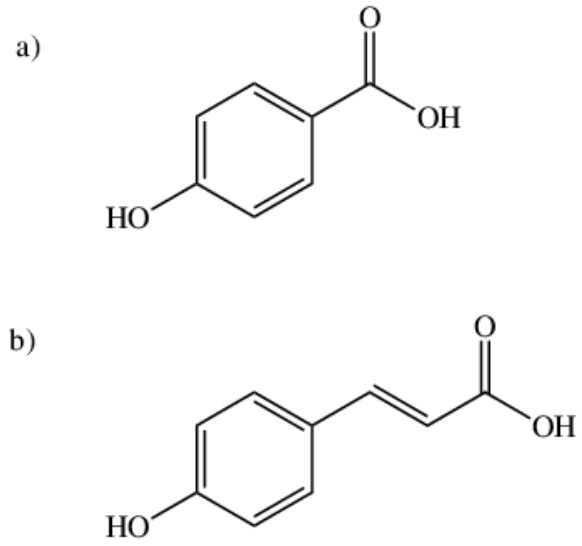
Flavonoids, tocopherols and curcuminoids are chelators of Fe^{3+}, Al^{3+}, Cu^{2+}, Cr^{3+}, and Pb^{2+} metal ions [125].



Scheme 5 Possible sites of quercetin for the formation of transition metal complexes.

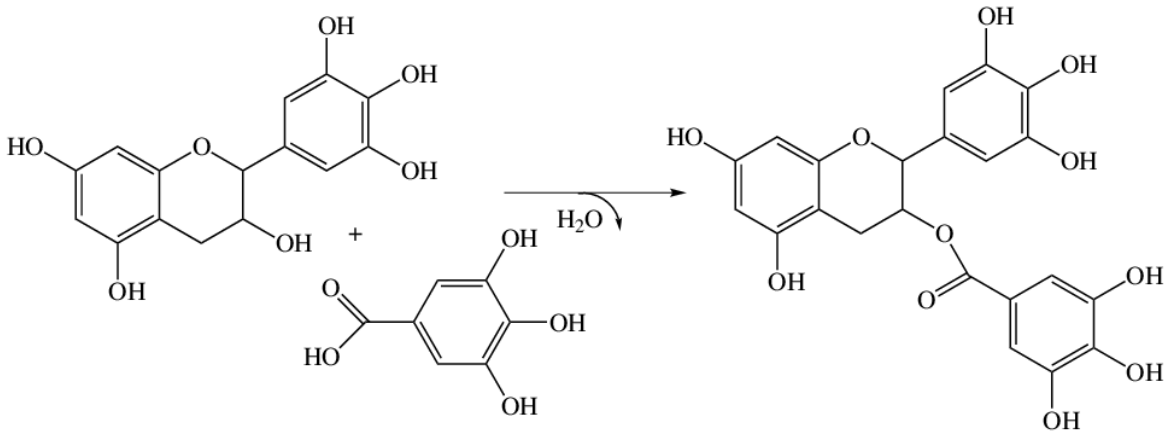
2.4.2. Phenolic acids

In contrast to flavonoids, phenolic acids are not members of a well-defined family of substances. Based on their precursors they can be divided into two subgroups: hydroxybenzoic acids and hydroxycinnamic acids (**Scheme 6a and b**, respectively). The radical scavenging mechanism of phenolic acids relies basically also on hydrogen atom donation from the phenolic hydroxyl group, but efficiency depends on the actual chemical structure of the compound. Gallic acid acts as prooxidant in the presence of transition metals, while chlorogenic acid present in eggplant is among the most efficient radical scavengers [18,126-128]. Carnosic acid (a hydroxybenzoic acid) is an important stabilizer of oils, animal fats and various meat products [129], while ferulic acid (a hydroxycinnamic acid) is usually applied in gels and edible film products [130]. Rodrigues [109] increased the length of induction period and decreased the rate constant of thermo-oxidation of *cis*-1,4-polyisoprene with cashew nut shell liquid, a natural antioxidant mixture rich in anacardic acid, cardol and cardanol.



Scheme 6 Chemical structures of hydroxybenzoic acid (a) and hydroxycinnamic acid (b).

Most phenolic acids have limited thermo-oxidative stability [131] and negligible solubility in non-polar polymer matrices, which result in poor processing stabilization efficiency. Their largest advantage is the reactivity of the carboxyl group, which can be used in acylation reactions leading to esters with increased number of phenolic hydroxyl groups and increased antioxidant activity, solubility and thermal stability [132]. The enzymatic synthesis of epigallocatechin-3-gallate is shown in **Scheme 7** as an example. The reaction usually occurs in young tea leaves [133,134] through the esterification of epigallokatechin with gallic acid. Compared to their precursors, gallates formed from epicatechin or epigallocatechin possess increased stabilizing efficiency by the DPPH• radical scavenging capacity (DRSC) assay. On the other hand, these compounds performed worse in the oxygen radical absorbance capacity (ORAC) assay [133].



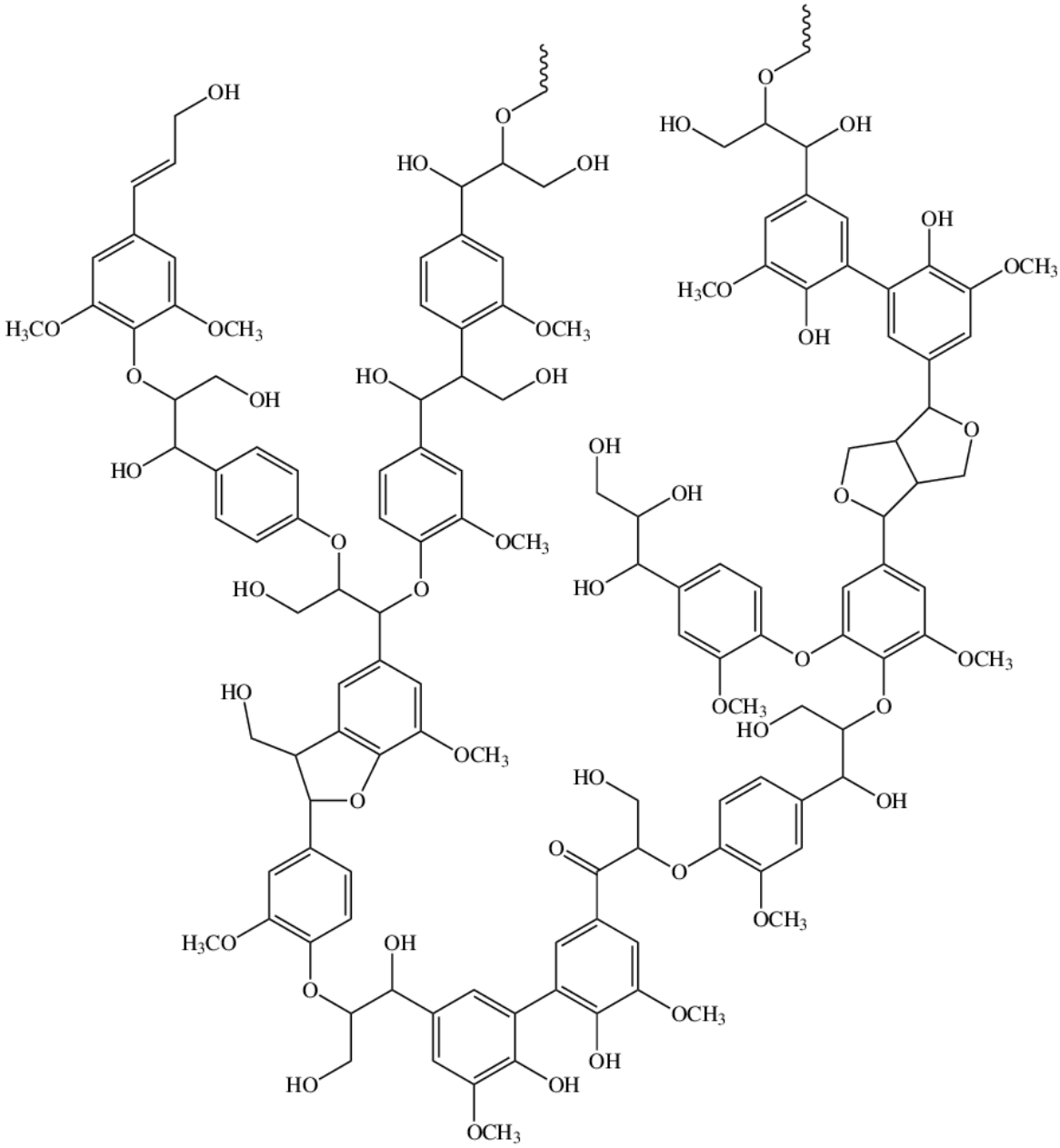
Scheme 7 The formation of epigallokatechin-3-gallate.

Cui [135] successfully polymerized pyrogallic acid using horseradish peroxidase as catalyst. Poly(pyrogallic acid) outperformed Irganox 1010, BHT and BHA in the scavenge of DPPH• and in the oxidation induction times of polypropylene samples. Esterification is another way to increase the stability and solubility of phenolic acids. Methyl-, butyl-, octyl- and stearyl esters of rosmarinic acid showed improved thermal stability compared to the nascent phenolic acid, while octyl- and stearyl esters efficiently stabilized low density polyethylene (LDPE), linear low density polyethylene (LLDPE) and PP [132]. The studied derivatives outperformed Irganox 1010 and 1076 at 1000 ppm antioxidant content, but the effect of additive concentration and solubility have not been investigated and reported yet.

2.4.3 Phenolic polymers – lignin, tannin

The assumed chemical structure of softwood lignin [136] and a condensed tannin are shown in **Schemes 8 and 9**, respectively. Lignin is a natural cross-linked polyphenol, which is formed from monolignols through enzymatic dehydrogenative polymerization in plants [137]. The monolignols forming the repeat units of lignin are *para*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol, which may be connected with each other

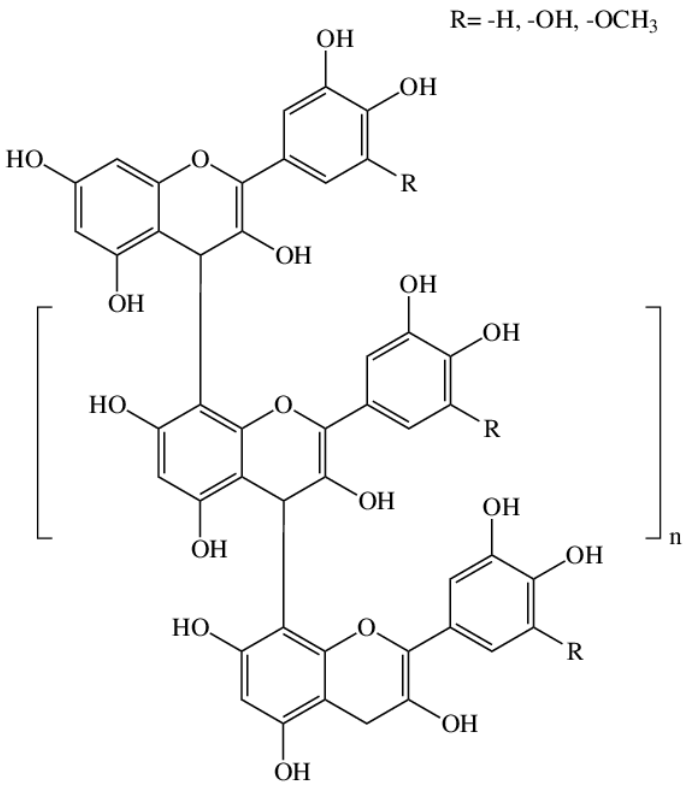
through various covalent bonds. Changing ratio and combination of these units result in various molecular structures [138] and determine the properties of lignin, which is a major component in the cell walls of grasses, soft- and hardwoods [139].



Scheme 8 The assumed chemical structure of lignin [136].

Tannins can be divided into two subgroups, into hydrolysable and condensed tannins [140]. Hydrolysable tannins are esters of gallic acid, ellagic acid or other phenolic

acids and a polyol, like D-glucose, fructose or xylose, which release the corresponding phenolic acid in the reaction with an acid [141]. Their molecular weight ranges from 500 to 5000 Da [142]. The repeat units of condensed tannins, or proanthocyanidins, are different flavonoid derivatives with the flavan-3-ol monomer structure. Proantocyanidins are enzymatically synthetized flavonoid polymers and their molecular weight can be as large as 30000 Da [140]. Hydrolysable tannins usually can be found in leaves, in galls and in the bark of woods, similarly to condensed tannins, but the skin, seed or stems of grapes and various wines are also typical sources of the latter [141].



Scheme 9 The chemical structure of condensed tannins.

Biological activity. The application of lignin in medicine is limited because of its varying chemical structure and complicated characterization. Only a few papers deal with its beneficial biological influence, Ito et al. [143,144] for example proved that lignin protects neurons against oxidative damage. Hydrolysable tannins exhibit numerous

biological activities like antioxidant, anti-inflammatory and antibacterial effect [140,145].

Application as food additive. Lignin is rarely applied as a food additive directly. Hydrolysable tannins are natural components of various foodstuffs and they are included in the list of food flavorings of the European Union and usually applied as food additives for animal fodder [146]. Both lignin and tannins are more likely applied as additives in food packaging materials because of their antioxidant and antimicrobial activities [147-149].

Application in polymers. Lignin is applied, or at least studied in possible applications in polymers. It can be used as 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 [150,151]. Because of the presence of phenolic hydroxyl groups in its polyphenol structure, lignin has metal ion chelating [152], radical scavenging and stabilizing effect 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 polymers against oxidation. Most of the attempts proved the antioxidant effect of lignin. The antioxidant and stabilizing characteristics of lignin have been studied in several polymers, but mainly in PE [153-156], PP [153,157-164], PLA [165,166], poly(3-hydroxybutyrate) (PHB) [167], PCL [168] and in natural rubber [169,170].

Kosikova et al. [158,159] examined the stabilizing efficiency of lignin in polypropylene and found that the source and type of the additive may change its effect from stabilization to the initiation of degradation. Later the authors [155] 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%). Pucciariello et al. [153] showed that steam-explosion lignin protects LDPE, HDPE, linear low density polyethylene and atactic polystyrene against UV radiation. The lignin used in their experiments increased the modulus and decreased the tensile strength of the samples. Lignin particles formed a separate phase in the polymer matrix used and adhesion was quite poor between the components. Based on image analysis, Pouteau et al. [171] 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, since phase separation limits the protective effect of lignin [172]. The authors claimed that lignins with small molecular weight are more compatible both with apolar and polar matrices. Levon et al. [154] found that the thermo-oxidative stability of PE improves considerably when it is blended with a 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. Gregorová et al. [162] proved that lignin increases the thermo-oxidative stability of both neat and recycled polypropylene. The authors found synergistic interaction between lignin and the synthetic phenolic stabilizer Irganox 1010.

Sadeghifar and Argyropoulos [156] studied the role of the phenolic hydroxyl groups of lignin in its stabilizing effect. They modified the phenolic hydroxyl groups by selective methylation and found that the modification decreased the antioxidant activity of lignin. They checked the stabilizing effect of neat and methylated lignin in polyethylene blends. The blends contained the two lignin samples in varying amounts from 1 to 25 wt%. Blends containing the methylated lignin had smaller oxygen induction temperature compared to those prepared with the non-methylated sample.

Lignin efficiently hinders the formation of long chain branches as shown by the results presented in **Fig 12**. Its efficiency is close to that of curcumin, if the sufficient amount of secondary stabilizer is present.

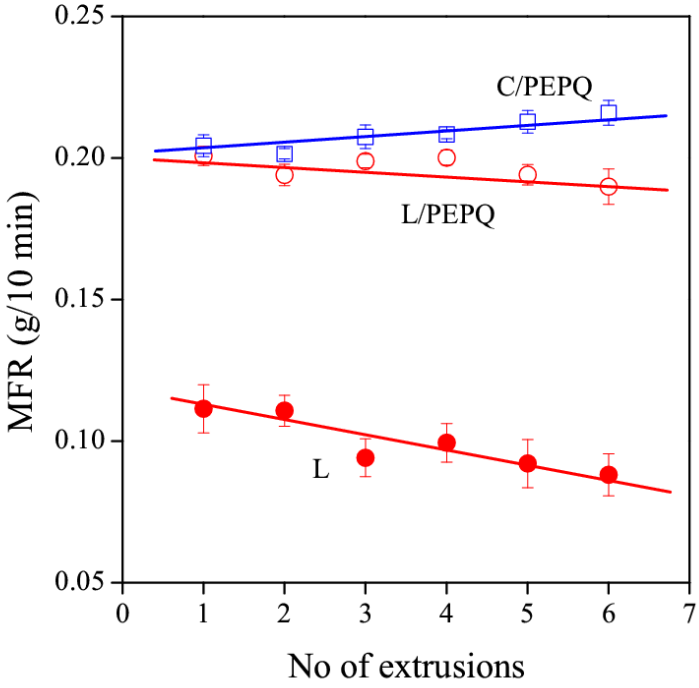


Fig. 12 Effect of the number of extrusions on the melt flow rate of polyethylene samples during consecutive extrusions at 1000 ppm natural antioxidant content. Symbols: (□) curcumin (C)/PEPQ; (○) lignin (L)/PEPQ; (●) lignin (L). PEPQ content was 2000 ppm.

Although the phenolic hydroxyl groups of lignin scavenge radicals and improve stability indeed, because of the relatively small molar number of their phenolic OH groups 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 smaller 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 of 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 phenolic hydroxyl groups [173].

Similarly to lignin, condensed and hydrolysable tannins can be used as polyols for polyurethane synthesis [174,175]. The application of condensed tannins as processing stabilizers is hindered by the same problems as in the case of lignin. The polar material forms a heterogeneous phase in the polymer and phase separation increases with increasing tannin content [124]. Attempts are made to improve the miscibility of these compounds with polymers by esterification with anhydrides. The application of various pine bark tannin esters increased resistance against photo-degradation caused by ultraviolet radiation in PLA [176], while photo- and thermo-oxidative degradation was hindered in PP and Bionell (poly-butylene-succinate-adipate) [177]. The efficiency of the additives increased with the length of the esters, which beneficially modified the solubility of the substance in the polymers [178]. Unfortunately, this approach increases cost, reduces the concentration of functional groups with antioxidant activity, and its success is often questionable [179]. Another way to overcome the difficulties of using polar polymeric antioxidants is the addition of amphiphilic copolymers to reduce interfacial energy between the additives and the polymer matrix and thus improve their dispersion. The miscibility of lignin-phthalate with LDPE was improved by the application of maleic anhydride grafted polyethylene as compatibilizer [180]. Ethylene-vinyl-alcohol (EVOH), maleic anhydride grafted polyethylene (MAPE) and ethylene acrylic ester maleic anhydride terpolymer (AEMAPE) compatibilizers decreased the average size of dispersed

mimosa and pine bark tannin particles in LLDPE, which led to the increased thermo-oxidative stability of the samples [124]. Both lignin and condensed tannins are cheap and easily accessible raw materials with stabilizing activity, which most likely will be exploited in the future, but further research is needed to overcome their drawbacks.

4. CONCLUSIONS

The analysis of the results published in the literature on the application of natural antioxidants as processing stabilizers for polyethylene indicate that some of them protect the polymer very efficiently during processing. Carotenoids are antioxidants at small concentrations, but pro-oxidants when their amount is large. They strongly discolor to the polymer, but fade when they are exposed to light. Flavonoids are the most efficient processing stabilizers, they protect the polymer against thermo-oxidative degradation already at 100 ppm. Their efficiency is considerably larger than that of the commercial hindered phenolic antioxidants used in industrial practice. They stabilize the polymer by hydrogen donation and their efficiency is related to the smallest bond dissociation enthalpy of their phenolic hydroxyl groups. Polymeric polyphenols, including lignin and tannin, also have some antioxidant effect, but because of the small molar value of phenolic hydroxyl groups their efficiency is smaller than that the flavonoids or even the commercial stabilizers used today. Natural antioxidants interact with each other and with the secondary stabilizer added simultaneously. Interaction changes melting temperature and bond dissociation energies and thus the efficiency of the stabilizer. Interactions may lead to synergy shown by the beneficial combination of Vitamin E and carotene. Most of the natural antioxidants discolor the polymer and their solubility in apolar matrices is small resulting in decreased efficiency. Because of their extreme efficiency, natural antioxidants can be used in certain applications, but further research must be carried out to utilize their

advantages in their full extent.

5. ACKNOWLEDGEMENTS

The National Research Fund of Hungary (OTKA K 120039) is greatly appreciated for the financial support of the research related to natural antioxidants and lignin.

6. REFERENCES

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