MELT STABILIZATION OF PE WITH NATURAL ANTIOXIDANTS: COMPARISON OF RUTIN AND QUERCETIN

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ABSTRACT

The stabilization effect of a flavonoid type natural antioxidant, rutin, was compared to that of quercetin in polyethylene. Additive concentrations changed between 0 and 500 ppm in several steps and also 1000 ppm Sandostab PEPQ phosphorus secondary stabilizer was added to each compound. Stabilization efficiency was determined by changes in vinyl group content, melt flow rate, oxygen induction time, color and the consumption of the secondary antioxidant during multiple extrusions. The results showed that rutin is as efficient melt stabilizer as quercetin used as reference. On the other hand, rutin has a deteriorating effect on the stability of the polymer at small concentrations and partially decomposes during processing. The comparison of bond dissociation enthalpies indicated that the substitution of the hydroxyl group in the C ring of quercetin by saccharide moieties increases their value, but the small increase does not influence the efficiency of the stabilizer. FTIR and DSC measurements indicated the interaction of the natural antioxidant and the phosphonite secondary stabilizer, and the development of interactions was confirmed by molecular modeling. Mainly hydrogen bonds and aromatic, π electron interactions develop between the hydroxyl groups in ring A and the POC group of the phosphonite, as well as between the aromatic rings of PEPQ and the flavonoids, but they do not influence the stabilization efficiency of the antioxidants.

KEYWORDS: polyethylene, processing stabilization, long chain branching, natural antioxidants, rutin

1. INTRODUCTION

Plastics are exposed to heat, shear and oxygen during their processing and to various effects during their application that may result in degradation [1]. In order to prevent

changes in their chemical structure and properties, they contain heat and/or light stabilizers practically always. Polyethylene is routinely protected against degradation during processing with the combination of a synthetic phenolic antioxidant and a secondary, processing stabilizer, usually a phosphorous compound. This simple stabilization package proved to be very efficient and cost effective thus very few new stabilizers appeared on the market in the last few decades. However, for various reasons, the interest turned towards natural antioxidants recently. The general concern of the politicians and the public about sustainable economy is one of the driving forces, while doubts about the possible environmental and health hazard [2] of the degradation products of phenolic antioxidants used routinely also may play a role in this increased interest. Consequently, the number of publications about the possible use of natural antioxidants for the stabilization of polymers increases continuously.

A considerable number of natural compounds proved to be beneficial for the human health because of their antioxidant, anti-inflammatory, antiviral or other effects and many of them are being used for therapy for a very long time. Natural antioxidants are used in increasing quantities also in food products [3,4]. Attempts have been made to apply various natural compounds for the stabilization of polymers, and specifically polyolefins as well. Vitamin E is a very efficient stabilizer [5-8] and it is presently used as antioxidant in ultrahigh molecular weight polyethylene implants [9-11]. Because of its polyaromatic structure and the number of phenolic hydroxyl groups in it, lignin has a stabilization effect in polymers, which was proved both in polyethylene and polypropylene [12-14]. Several attempts were reported in the literature to use flavonoids for the stabilization of polyolefins. Quercetin, a natural antioxidant, was explored as possible stabilizer both in food [15] and in polymers [16,17] and most of the results obtained confirmed its efficiency indeed. Dihydromyricetin, another flavonoid was also studied as stabilizer in both PE and PP and

proved more efficient than the commercial stabilizers used as reference [18,19].

Among other groups, we also carried out experiments to explore the effect and efficiency of several natural compounds as stabilizer in PE. The antioxidant effect of curcumin [20,21], quercetin [22], dihydromyricetin [23] and silymarin [24] was studied in a Phillips type polyethylene in the presence of a phosphorous secondary stabilizer. Three 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 [24]. In this work we study the possible stabilization effect of rutin, [2-(3,4-dihydroxyphenyl)-5,7-dihydroxy-3-{[(2*S*,3*R*,4*S*, 5*S*,6*R*)-3,4,5-trihydroxy-6-({[(2*R*,3*R*,4*R*,5*R*,6*S*)-3,4,5-tri-hydroxy-6-methyloxan-2-yl]oxy}methyl)oxan-2-yl]oxy}-4*H*-chromen-4-one], a 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 [25]. 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 [26]. Research is going on to use it as an antidepressant [27] or to treat Alzheimer disease [28] and stroke [29] 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 [20-24], 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.

2. EXPERIMENTAL

2.1. Materials

The polymer used in the experiments was the Tipelin FS 471 grade ethylene/1-hexene copolymer (melt flow rate: 0.3 g/10 min at 190 °C, 2.16 kg; nominal density: 0.947 g/cm^3) polymerized with a Phillips catalyst (PE). The number average molecular weight of the polymer is 15.4 kg/mol, its polydispersity 7.6 and it contains 1.81 comonomer/1000 C. The additive free polymer powder was provided by MOL Group Ltd., Hungary. Both stabilizers, i.e. rutin and quercetin, were purchased from Sigma-Aldrich with 95 and 94 % purity, respectively. The antioxidants were added to the polymer in various amounts, in 5, 10, 25, 50, 100, 250 and 500 ppm, to study the effect of additive content on stability. Each compound contained also 1000 ppm Sandostab PEPQ (PEPQ, Clariant) phosphonite secondary stabilizer.

2.2. 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. The necessary amount of quercetin was dissolved in 200 mL acetone and the solution was added to the PE powder in the mixer. The resulting

powder was dried overnight to remove acetone. Rutin was added to the polymer together with PEPQ directly and homogenized in the high-speed mixer under the same conditions as described above. The dry blend was processed and pelletized in six consecutive extrusion steps at 50 min^{-1} 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. Blends of the two stabilizers, i.e. the natural antioxidant and PEPQ, were prepared by mixing the components in various amounts in 2-propanol to study their interactions. 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, 200 mbar in a vacuum oven.

2.3. Characterization

The melt flow rate (MFR) of the polymer was determined according to the ASTM D 1238-79 standard at 190 °C with 2.16 kg load using a Göttfert MPS-D MFR tester. Residual thermo-oxidative stability was characterized by the oxidation induction time (OIT) measured at 200 °C in oxygen atmosphere with constant, 20 mL/min flow rate in open aluminum pans using a Perkin Elmer DSC-7 apparatus. 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 a Tensor 27 (Bruker) spectro-photometer. Five spectra were recorded on each sample between 4000 and 400 cm^{-1} wavelengths at 2 cm^{-1} resolution and 16 scans. 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 groups at

850 cm^{-1}. The color of the samples was described by the yellowness index (YI) and the optical L* parameter determined with a Hunterlab Colourquest 45/0 apparatus. The thermal behavior of rutin, that of its blends with PEPQ, and component interactions were 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 350 °C using a Perkin Elmer Diamond DSC-IC apparatus. The thermal stability of the two 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. 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 section (**section 3.4**). In figures, rutin is abbreviated as R, while quercetin as Q in order to increase clarity and help understanding.

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 the paper.

3.1. Antioxidant characteristics

Rutin is a flavonoid type antioxidant with very similar structure to quercetin. The
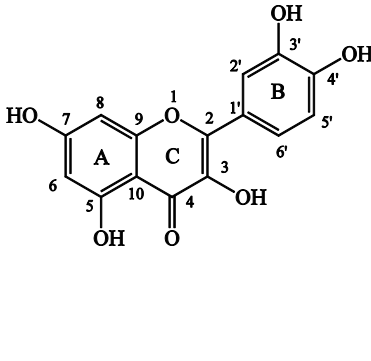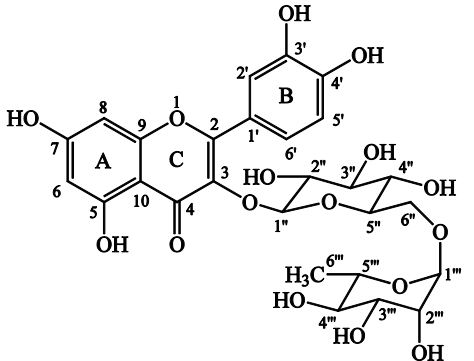
latter is a very efficient antioxidant not only in nature, but also in polyethylene under processing conditions [22], thus we expected rutin to perform similarly well. Besides its strong stabilization effect quercetin has several drawbacks, like the high melting temperature resulting in difficulties during homogenization, its small solubility in the polymer and discoloration effect even at small concentrations [22].

The characteristics of the two natural antioxidants are compared to each other in **Table 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 [30,31]. The effect of the attachment of the rutinose disaccharide is difficult to predict, it may change the bond dissociation energy of the phenolic OH groups (see **Section 3.3**) or can interact with these latter 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 1**, similar efficiency, but small solubility and strong discoloration is expected when rutin is used as stabilizer in

polyethylene.

Table 1   Comparison of the characteristics of the two antioxidants used in the study

Characteristics	Quercetin	Rutin
M_n (g/mol)	302.2	610.5
Melting point (°C)	316	167
Color		
Structure		
Structural differences	− hydroxyl in C ring	− no hydroxyl in C ring − two sugar rings attached
Phenolic OH groups	4	4

3.2. Stabilization efficiency

Phillips type polyethylenes have a double bond at one end of each chain thus its dominating degradation reaction during processing is the formation of long chain branches [32]. The viscosity of the polymer increases as a result and its MFR decreases at the same time. The vinyl group content of the polymer is plotted as a function of the number of processing steps in **Fig. 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 reference compound. 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.
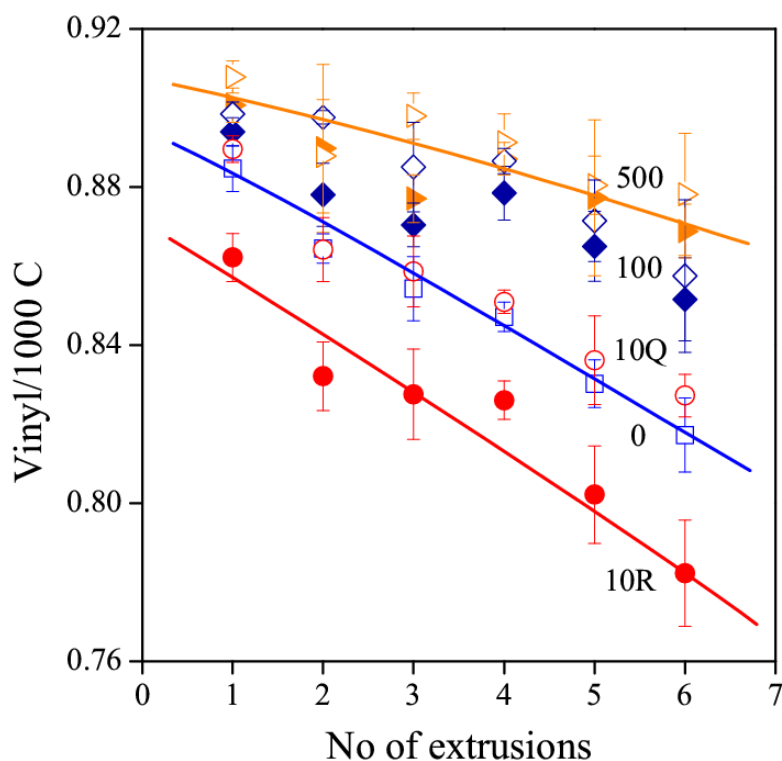

Fig. 1   Effect of the number of extrusion steps and additive concentration on the vinyl group content of PE. Symbols: (□) neat, (○,●) 10 ppm, (◇,◆) 100 ppm, (▷,▶) 500 ppm additive; empty: quercetin, full: rutin.

The influence of the additives was presented as a function of processing history in **Fig. 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. 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.
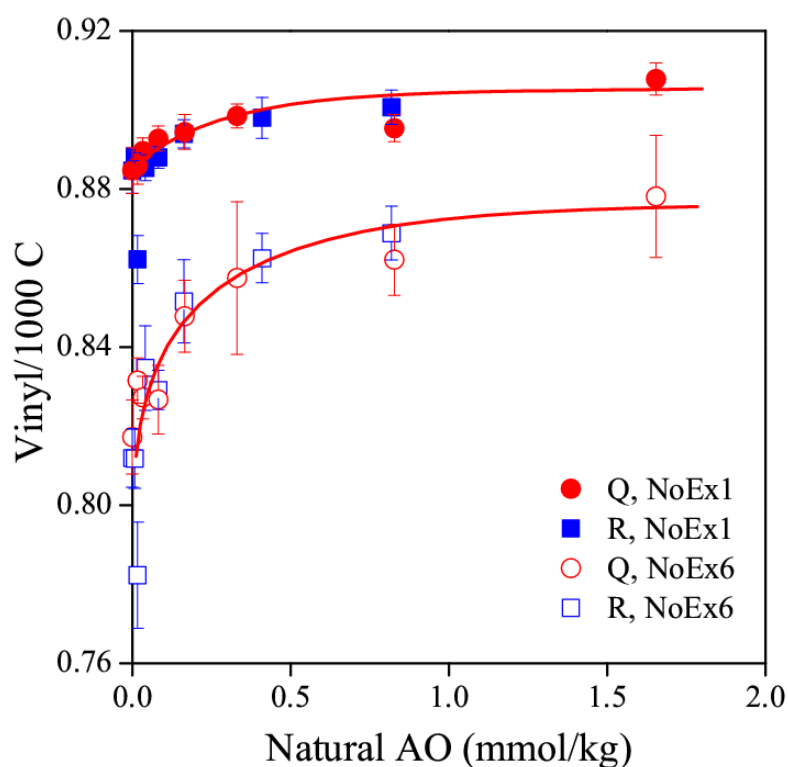

Fig. 2   Dependence of the number of vinyl groups of PE on the concentration of the natural antioxidant. Symbols: (●) Q, NoEx1, (■) R, NoEx1, (○) Q, NoEx6, (□) NoEx6.

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. 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.
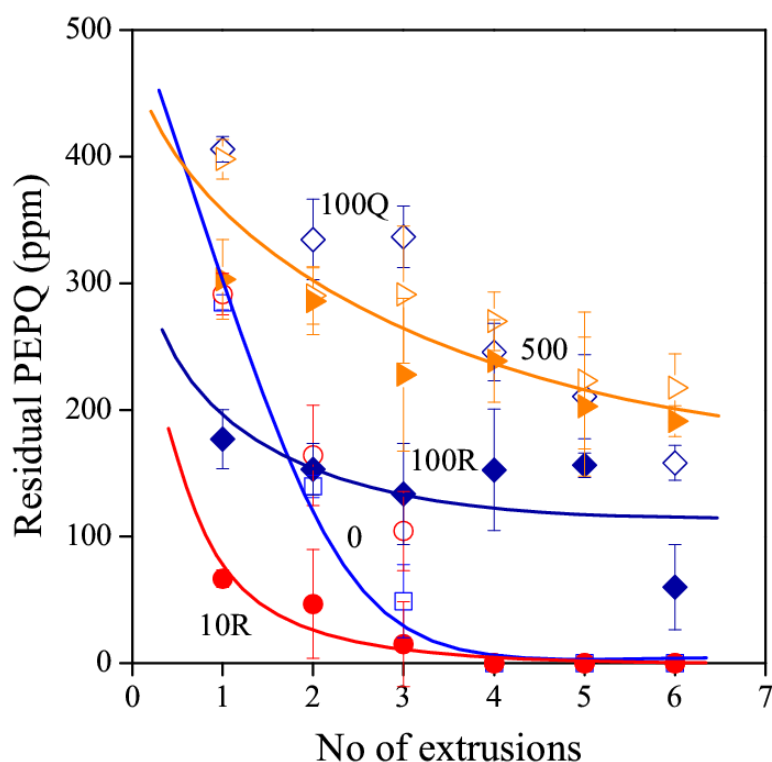

Fig. 3   Influence of processing history (NoEx) and additive content on the amount of residual secondary stabilizer (PEPQ) remaining in the polymer after extrusion.
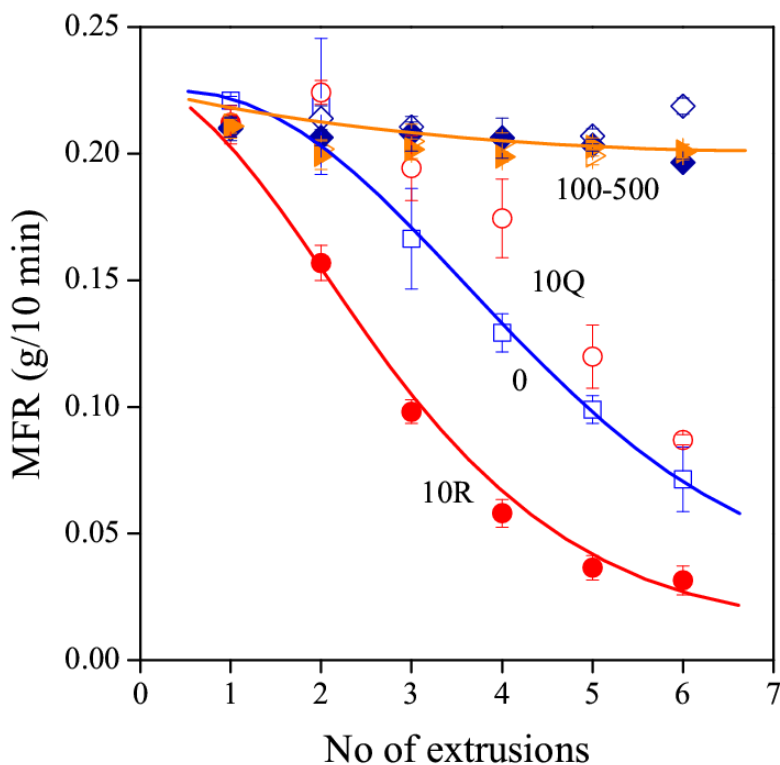
Fig. 4   Effect of the number of extrusions and the amount of natural antioxidant added on the viscosity (MFR) of PE. Symbols: (□) neat, (○,●) 10 ppm, (◇,◆) 100 ppm, (▷,▶) 500 ppm additive; empty: quercetin, full: rutin.

The MFR of the polymer is plotted against the number of extrusion steps in **Fig. 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

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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. 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 [22,24]. However, the results clearly prove that apart from small concentrations, both natural antioxidants protect the polymer against degradation during processing equally efficiently.
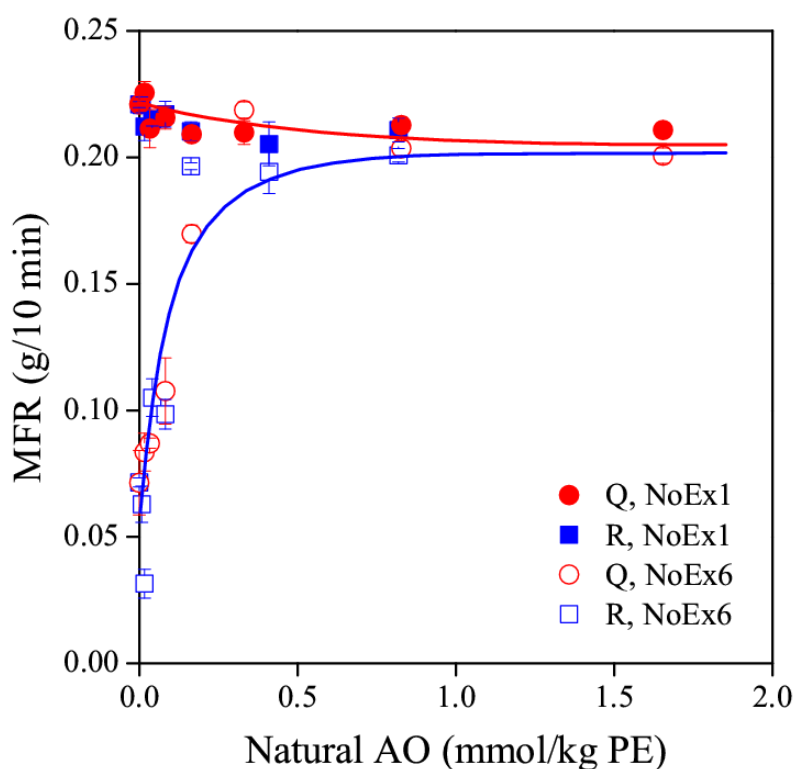

Fig. 5   Dependence of MFR on the concentration of natural antioxidant after the 1st and 6th extrusions. Symbols: (●) Q, NoEx1, (■) R, NoEx1, (○) Q, NoEx6, (□) NoEx6.
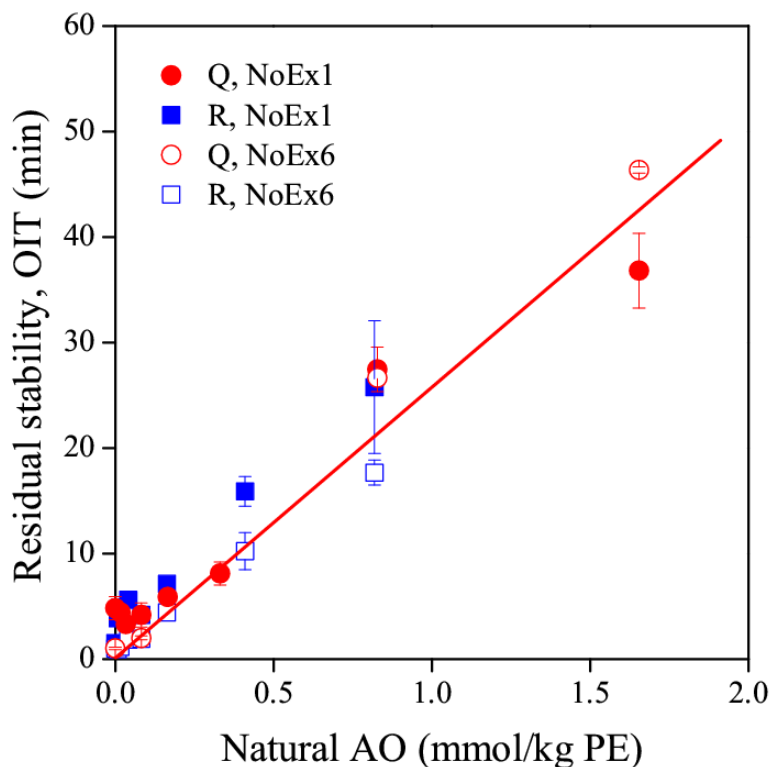
Fig. 6 Linear dependence of the residual stability of PE on the concentration of the natural antioxidant. Similarity of quercetin and rutin. Symbols: (●) Q, NoEx1, (■) R, NoEx1, (○) Q, NoEx6, (□) NoEx6.

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**. 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 [33-34]. 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.
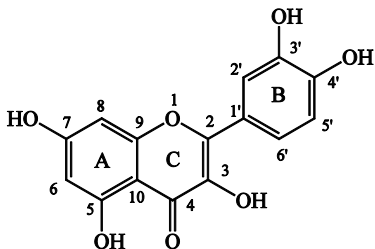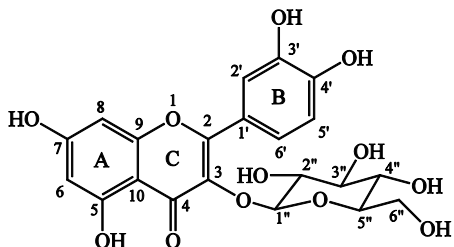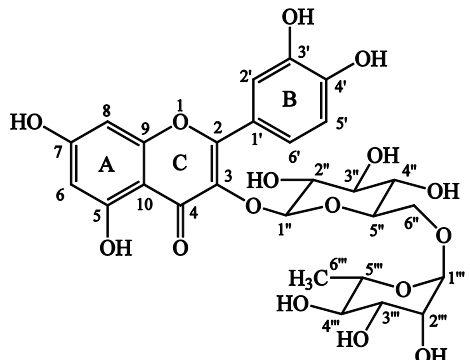
3.3. Mechanistic aspects

Four mechanisms have been proposed in the literature for the stabilization reactions of phenolic antioxidants: single electron transfer (SET) [35-36], sequential proton loss electron transfer (SPLET) [37-38], radical adduct formation (RAF) [39] and hydrogen atom transfer (HAT) [40-41]. In polyethylene the last one is the most probable and accepted mechanism of stabilization [42-43]. 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) [44].

Bond dissociation enthalpies (BDE) can be determined by molecular modeling approaches. Cai et al. [45] 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 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 [45]. Similar results were obtained also by Renganathan et al. [46] 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 [44], bond dissociation enthalpy is not the only factor determining the efficiency of the natural antioxidants studied.

Table 2   Effect of substitution on the reactivity of the active hydroxyl groups of natural antioxidants; comparison of quercetin, hyperin and rutin [45]

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 during its stabilization reaction quercetin first loses a hydrogen atom and then transforms into a quinoidal compound. Because of its hydroxyl group in ring C, quercetin can take a keto and an enol form [47-48]. 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 1**. Reaction with the DPPH$^\bullet$ 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$^\bullet$ radicals scavenged by a quercetin molecule in N,N-dimethylformamide solution is 2.35, compared to the value of 2.00 for rutin [49]. 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.
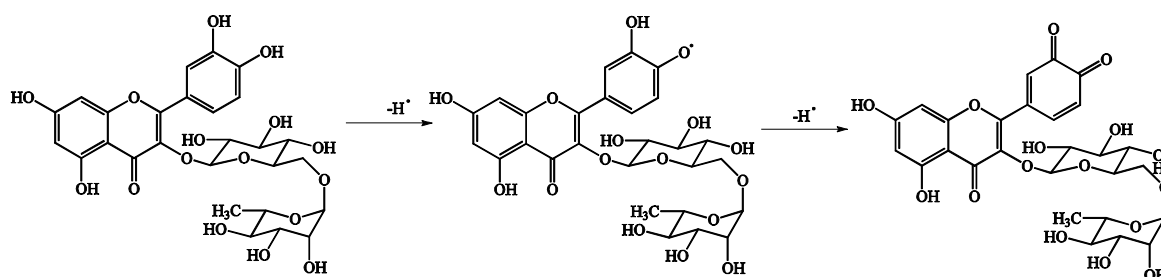
Scheme 1   Assumed HAT reaction mechanism of rutin.

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 [20,22]. 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. 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. The composition dependence of melting temperatures is presented in **Fig. 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.
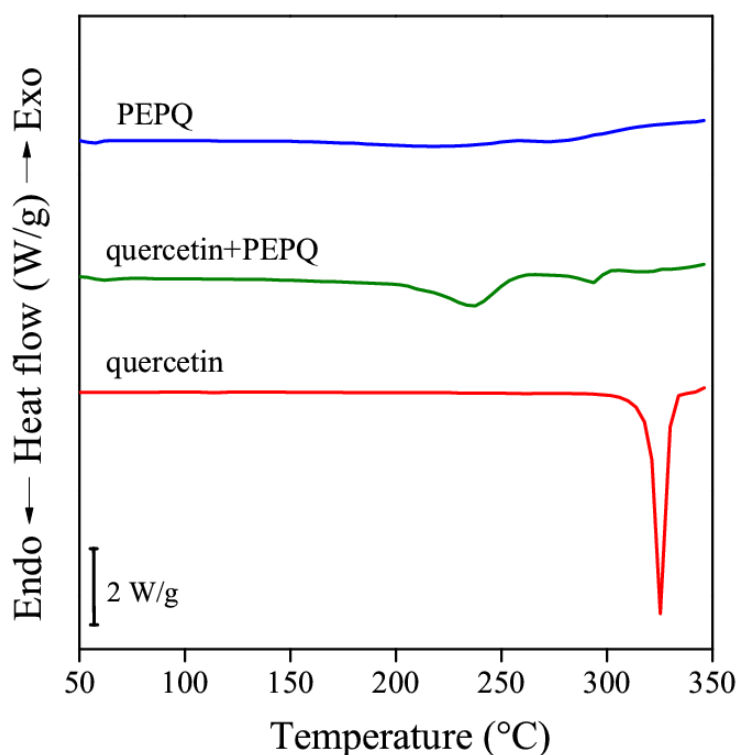

Fig. 7   DSC melting traces of PEPQ, quercetin and their mixture (75 mol% quercetin and 25 mol% PEPQ). Interaction of the additives.
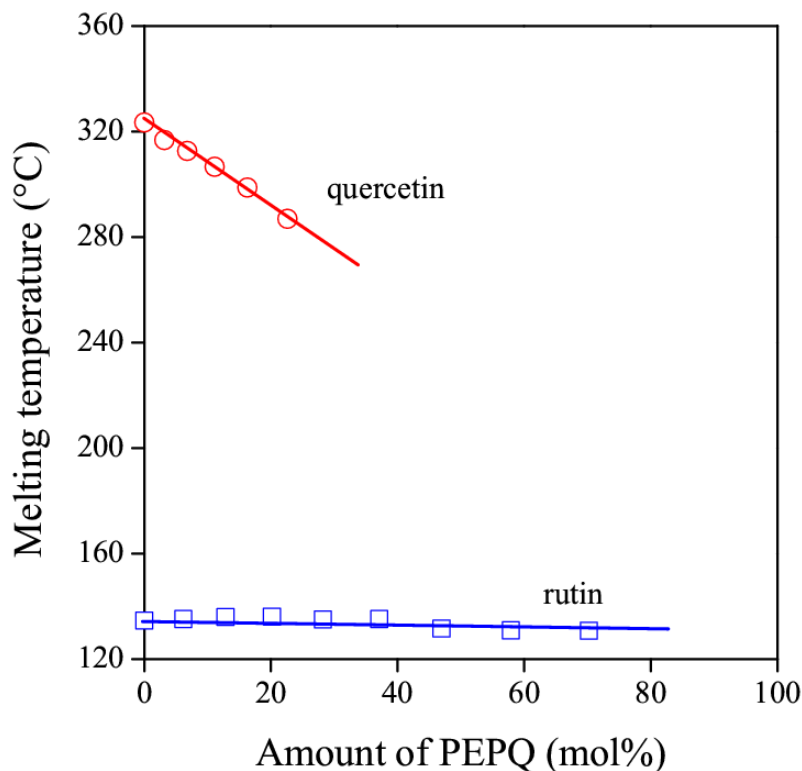
Fig. 8   Effect of composition on the melting temperature of the blend of PEPQ and natural antioxidants. Symbols: (○) quercetin, (□) rutin.

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 interactions. The dependence of the position of this latter vibration on the composition of natural antioxidant/PEPQ blends is presented in **Fig. 9**. Similarly, to melting temperatures, FTIR band shifts indicate stronger interactions between quercetin and PEPQ
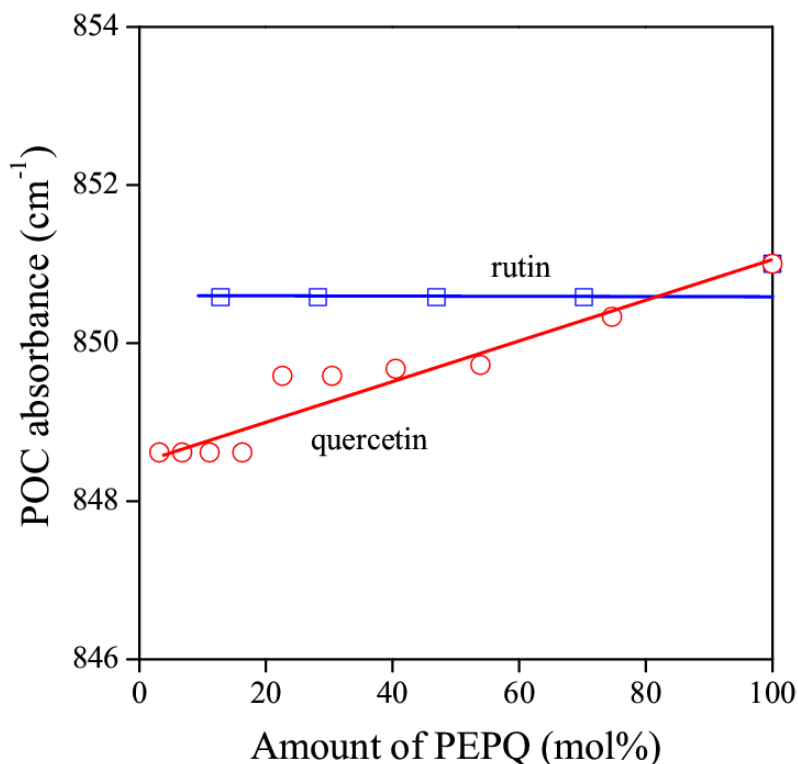
than between rutin and the secondary antioxidant.

Fig. 9   Dependence of the position of the POC absorbance at 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 identifies the participating groups. The association energies of the complexes were determined by the density functional theory (DFT) using the Perdew–Burke–Ernzerhof (PBE) functional [50]. The DFT calculations were performed with the MRCC program suite [51]. D3 corrections for dispersion were also carried out using the DFT-D3 software [52-53]. 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) [54] by the MarvinSketch (ChemAxon) program [55]. These structures were then further optimized using the MOPAC2016 program suite [56] by applying the modified neglect of diatomic differential overlap (NDDO) based semi-empirical quantum chemistry method PM6 [57] with D3H4 [58] corrections for hydrogen bonding and dispersion. The termination criterion for the geometry optimization was 0.042 kJ/mol/Å for the gradient norm. Starting geometries for the complexes were produced using the Maestro 11 program [59]. 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° 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 [60]. Finally probabilities were rendered to each complex structures based on the Boltzmann distribution of their corrected association energies.
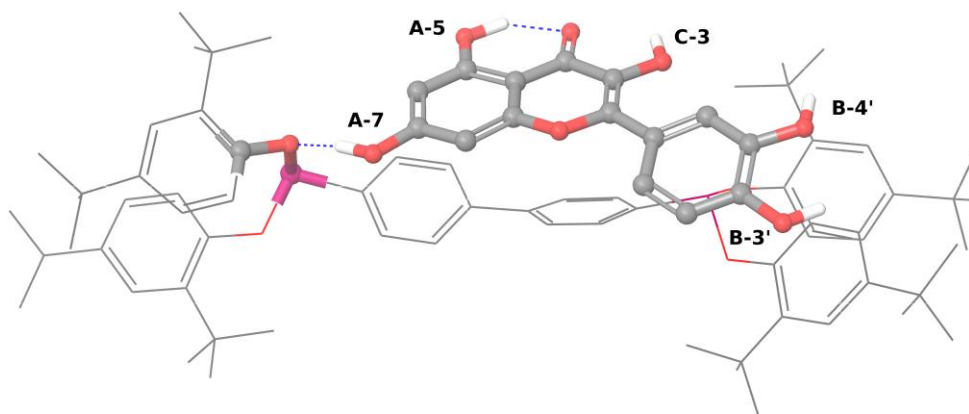
Fig. 10   The most probable configuration of the complex formed through the interaction of quercetin and PEPQ. Thin lines: PEPQ, thick lines: quercetin, and one of the POC groups of PEPQ.

The calculations predicted the development of strong interaction between quercetin and PEPQ. The complex presented in **Fig. 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. 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, they do not affect the efficiency of the natural antioxidants.
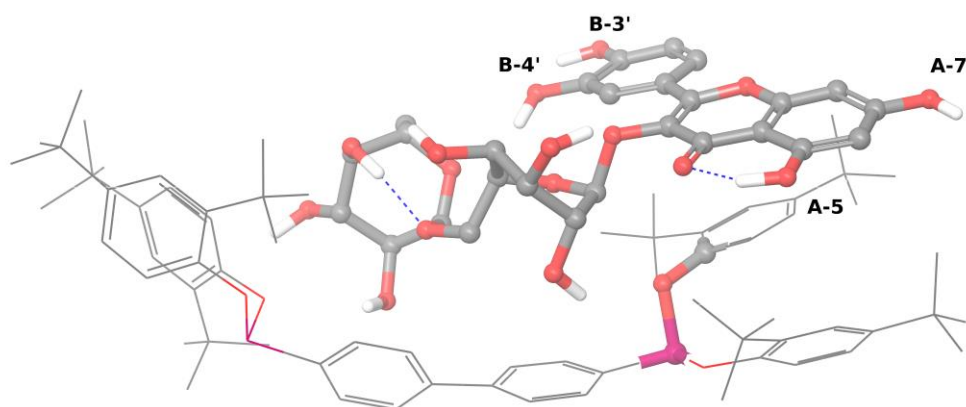

Fig. 11   Complex formed in the interaction of rutin and PEPQ; the formation of intramolecular hydrogen bonds. Thin lines: PEPQ, thick lines: rutin ,and one of the POC groups of PEPQ.

3.5. 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 [32,61]. As **Fig. 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. 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. 12** and **13**, the efficiency of the two natural antioxidants seems to be very similar at least at large additive contents.
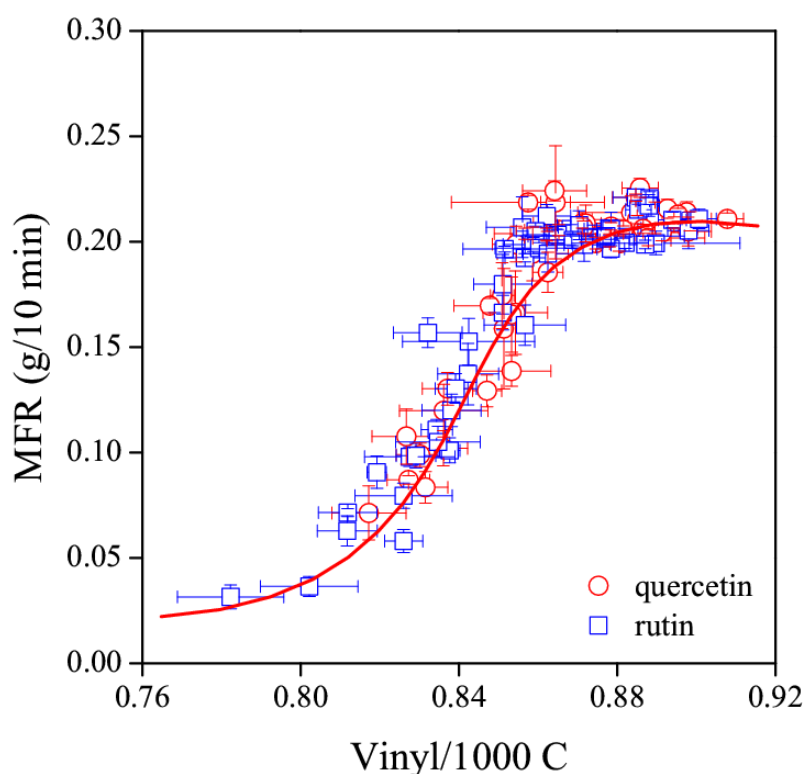

Fig. 12   Correlation between the vinyl content of the polymer and its melt flow rate; effect of the type of the natural antioxidant. Symbols: (○) quercetin, (□) rutin.
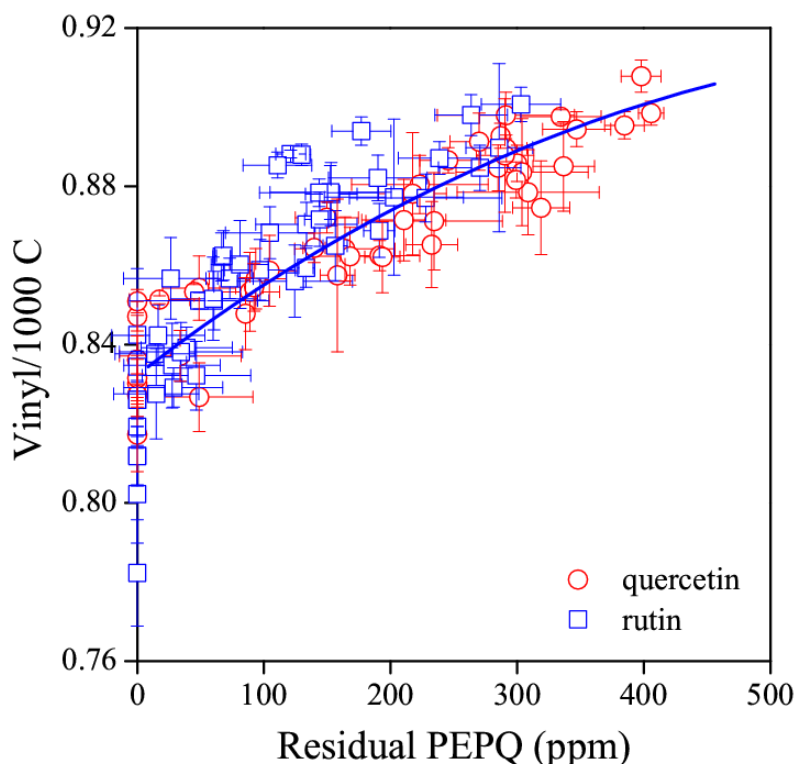
Fig. 13   Dependence of the vinyl concentration of PE on the residual amount of the secondary antioxidant (PEPQ); similar effect of the natural antioxidants studied. Symbols: (○) quercetin, (□) rutin.

One question remained open in this study, the deteriorating effect of rutin at small concentrations. One plausible explanation might be the partial degradation of rutin. 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. 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. 14** clearly

show the inferior stability of rutin. 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.

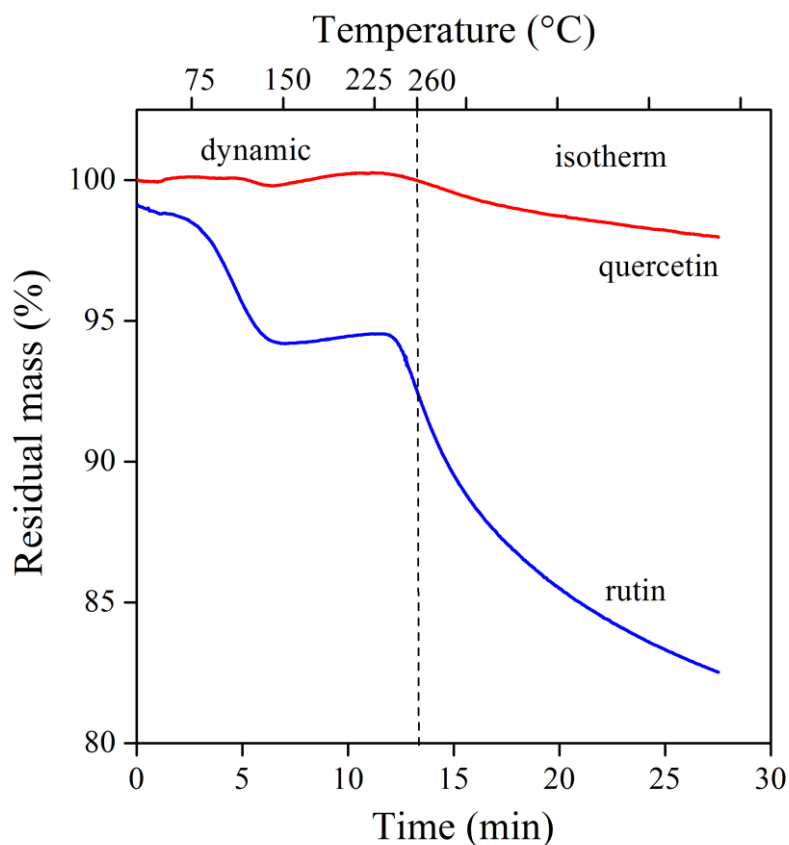Fig. 14   Thermal stability of the two natural antioxidants studied in TGA measurements simulating processing conditions. Heating rate in the dynamic stage: 20 °C/min; temperature in the isotherm stage: 260 °C.

4. 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. The natural antioxidants quercetin [22], dihydromyricetin [23] and curcumin [20-21] are very efficient melt stabilizers, but rutin and silymarin [24] are less advantageous.

5. ACKNOWLEDGEMENTS

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