

MELT STABILIZATION OF POLYETHYLENE WITH DIHYDROMYRICETIN, A
NATURAL ANTIOXIDANT

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ABSTRACT

Experiments have been carried out to compare the stabilization effect of two flavonoid type natural antioxidants, dihydromyricetin (DHM) and quercetin (Q) in polyethylene (PE). Additive concentrations changed between 0 and 500 ppm in several steps and 1000 ppm Sandostab PEPQ phosphorus containing secondary stabilizer was also added to each compound. Both antioxidants are very efficient stabilizers for PE, sufficient melt stability was achieved already at 50 ppm DHM content. At small concentrations dihydromyricetin proved to be more efficient melt stabilizer and it protected the secondary antioxidant better than quercetin. In spite of its better efficiency in melt stabilization, polymers containing DHM had the same residual stability as those prepared with quercetin. Accordingly, the larger efficiency does not result from the larger number of active phenolic hydroxyls in the molecule, but from interactions with the phosphorous secondary stabilizer that is stronger or at least different for DHM than quercetin. In spite that DHM is a white powder, it gave the polymer a brownish color which became deeper with increasing number of extrusions and additive content. Nevertheless, both natural antioxidants can be used efficiently for the stabilization of polymers in applications in which color is of secondary importance.

KEYWORDS: polyethylene, processing stabilization, long chain branching, natural antioxidants, dihydromyricetin, solubility, color

1. INTRODUCTION

Polyethylene (PE) is exposed to heat, shear, and oxygen during its processing and use. Adequate stabilization is essential to protect the polymer already during the manufacture of the final product and hinder degradation which usually results in the deterioration of properties. Synthetic antioxidants (AO) are used for stabilization in industrial practice, but

sometime ago questions emerged regarding the effect of their reaction products on human health [1]. Most of these questions have not been answered satisfactorily yet. As a consequence, more and more attempts are made to find new solutions including the use of natural antioxidants for the stabilization of food [2-4], but also of polymers [5-15]. These compounds usually can be found in vegetables and fruits, are often used as spices and are known to have beneficial effect on the human health.

Several compounds with different chemical structures have been studied as potential stabilizers in polymers and also in polyethylene. Vitamin E, i.e. α -tocopherol, is a natural phenolic compound which was shown to be a very efficient antioxidant [5-8] and it is used in practice for the stabilization of hip replacements prepared from ultra-high molecular weight polyethylene (UHMWPE). Attempts were made to use lignin, a natural polyphenol, as stabilizer and it proved to have some antioxidant effect indeed [9-11]. Recently, the stabilization of PE with another natural compound, curcumin, was studied in detail [16] and it was found that its melt stabilizing efficiency is superior to that of the synthetic antioxidant extensively used in industrial practice. The effect of the antioxidant was further enhanced by the addition of a phosphorus containing secondary stabilizer. The study has shown that besides its phenolic –OH groups, also the linear linkage between the two methoxyphenyl rings participates in stabilization reactions leading to a unique reaction route and increased efficiency.

Quercetin, i.e. [2-(3,4-dihydroxyphenyl)-3,5,7-trihydroxy-4*H*-chromen-4-one] (Q), is also a natural antioxidant found in fruits, vegetables, leafs and seeds in nature. The compound is a flavonol type flavonoid, which has proven antioxidant, antiviral and anti-inflammatory effect in the human body. It was already used for the stabilization of polyolefins [17,18], and also as a component of active packaging materials [19-22]. Quercetin was added to polyethylene [17], polypropylene [18] and an ethylene vinyl alcohol copolymer

and it proved to be an efficient stabilizer in all cases. However, quercetin was applied at concentrations of 2000-3000 ppm [17,18] or at even larger quantities in most studies, which raises the question of solubility, efficiency and price.

Although the studies cited above [17,18] proved that quercetin is a very efficient stabilizer in various polymers, several questions remained open. Quercetin is a polar compound with a melting temperature of around 320 °C, thus its solubility in the polymer is limited. Its efficient homogenization is questionable under the usual conditions of polyolefin processing, since the additive does not melt. The concentrations used in previous studies also seemed to be quite large [17,18]. In a recent study the melt stabilization effect of quercetin was investigated in a Phillips type polyethylene at much smaller concentrations, in the range of 5 to 1000 ppm [23]. It proved to be very efficient and prevented the formation of long chain branches already at a concentration as small as 50 ppm, while its dosage at 250 ppm provided the polymer sufficient residual stability. There were indications that quercetin interacted with the phosphonite secondary stabilizer used and that the mechanism of stabilization might differ from that of hindered phenolic stabilizers routinely used in practice. However, besides the advantages of quercetin, its very high melting temperature, limited solubility in polyethylene and strong yellow color are definite drawbacks for this compound.

The disadvantages mentioned in the previous paragraph might be overcome by the use of another flavonoid type natural antioxidant dihydromyricetin (2R,3R)-3,5,7-trihydroxy-2-(3,4,5-trihydroxyphenyl)-2,3-dihydrochromen-4-one) (DHM). The compound is very similar to quercetin, but it is colorless and has a lower melting temperature. According to our knowledge only two attempts were made to use DHM as a stabilizer in polymers and both were done by the same group [24,25]. Chen et al. added DHM to polyethylene [24] and polypropylene [25] at 2000 ppm and without any secondary antioxidant. According to the authors the additive is more efficient than the commercial stabilizers used as reference.

They explained the large efficiency with the position and the large number of hydroxyl groups in the molecule, but did not offer any information about melt stability, color, the effect of concentration or stabilization mechanism. As a consequence, the goal of this study was to explore the possibility of using DHM as stabilizer in polyethylene. The effect of the compound was compared to that of quercetin discussed above. Stabilization was studied as a function of composition at much smaller amounts than that used by Chen et al. [24,25]. Special attention was paid to processing stability, solubility and color in the study.

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/cm³) polymerized by a Phillips catalyst. The additive-free polymer powder was provided by Tisza Chemical Ltd. (TVK), Hungary. Quercetin (Sigma-Aldrich, 95%) and dihydromyricetin (Y&L Biotech Co., Ltd., China, 98%) were added to the polymer in various amounts, at 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. DHM 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 rpm and barrel temperatures of 180, 220, 260 and 260 °C under normal laboratory conditions using a Rheomex S ¾" type single screw extruder attached to a Haake Rheocord EU 10V driving unit. Samples were taken after each extrusion step. For further studies films of about 100 µm thickness were compression molded at 190 °C and 5 min using a Fontijne SRA 100 machine.

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. The residual thermo-oxidative stability of the polymer was characterized by the oxidation induction time (OIT) measured at 200 °C in oxygen atmosphere with constant, 20 ml/h flow rate in open aluminum pans using a Perkin Elmer DSC 2 apparatus. The functional groups (methyl, unsaturated and carbonyl) of polyethylene were determined by FTIR spectroscopy on the 100 µm thick compression molded films in transmission mode using a Tensor 27 (Bruker) spectrophotometer. Five parallel measurements were carried out on each sample between 4000 and 400 cm⁻¹ wavelengths at 2 cm⁻¹ resolution by 16 scans. Concentration of methyl, trans-vinylene and vinyl groups were calculated by absorptions at 1378 cm⁻¹, 965 cm⁻¹ and 908 cm⁻¹, respectively. Amount of carbonyl groups were measured by calculating the peak area between 1780 and 1680 cm⁻¹. FTIR spectroscopy was used also for the determination of residual PEPQ content based on the absorption of 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 measured on a Hunterlab Colourquest 45/0 apparatus. The UV-VIS spectra of reaction products of quercetin and dihydromyricetin were predicted by Time-Dependent Density Functional Theory (TDDFT) calculations at PBE0 [26]/6-311++G** [27] level. Geometries were optimized

for these calculations in three steps. First conformations with the lowest energies were identified by molecular mechanics using the Merck molecular force field (MMF94) [28] from 2D structures drawn by using the MarvinSketch (ChemAxon) program, then the selected conformers were optimized by DFT calculations at the PBE0/6-311++G** level with Gaussian09 [29]. The obtained geometries were optimized again after manually orienting hydrogens towards possible intramolecular hydrogen bonds resulting in lower energies. Finally, vibrational frequencies of the resulting conformers were calculated by the same DFT method ensuring their correspondence to local minima.

3. RESULTS AND DISCUSSION



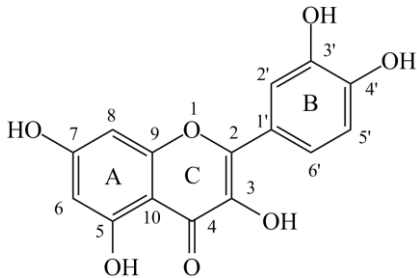
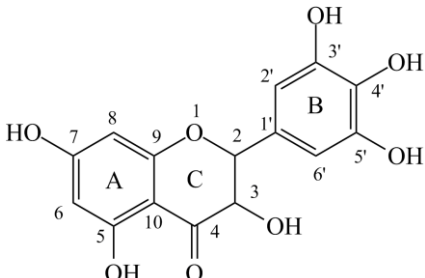
The results are presented in several sections. First the structure and physical characteristics of the two natural antioxidants are compared to each other and then their effect on processing stability, residual stability, solubility and color are presented in the respective sections. The possible reason for the differences observed and the mechanism of stabilization are discussed in the last section of the paper. Special attention is paid to color and practical consequences in this final section.

3.1. Antioxidant characteristics

We selected DHM as a potential natural antioxidant because it is similar in chemical structure to quercetin, but also differs in several aspects. Both are flavonol type flavonoid compounds with the same basic structure. The most important characteristics of the two antioxidants are listed in [Table 1](#). The lower melting point can be a clear advantage for DHM, since one can hope that, contrary to quercetin, the stabilizer melts during processing that may lead to its more homogeneous distribution in the polymer. The difference in the color of the two compounds is obvious for the first sight. The strong discoloration of the

polymer in the presence of quercetin was regarded as a disadvantage in the previous study [23]. We hoped that DHM being a white powder would not have the same effect and we can produce compounds without any strong color.

Table 1 Characteristics of the two natural antioxidants used in the experiments

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

The difference in color is a direct consequence of the chemical structure of the two compounds also shown in [Table 1](#). The strong yellow color of quercetin comes from the conjugation of the double bond in ring C with the delocalized π electrons of ring B. This double bond is missing from DHM. The additional phenolic –OH group in ring B of DHM is a further difference which might be beneficial for the use of this antioxidant as stabilizer

in PE. The larger number of phenolic hydroxyl groups would be expected to result in larger efficiency [24,25] further emphasized by the smaller dissociation enthalpy of the H atom of the pyrogallol structure compared to that of the pyrocatechol moiety [30,31]. All these differences in chemical structure and physical properties promised improved homogeneity, better efficiency and a colorless product, which clearly justified the selection of dihydromyricetin as a potential stabilizer for PE.

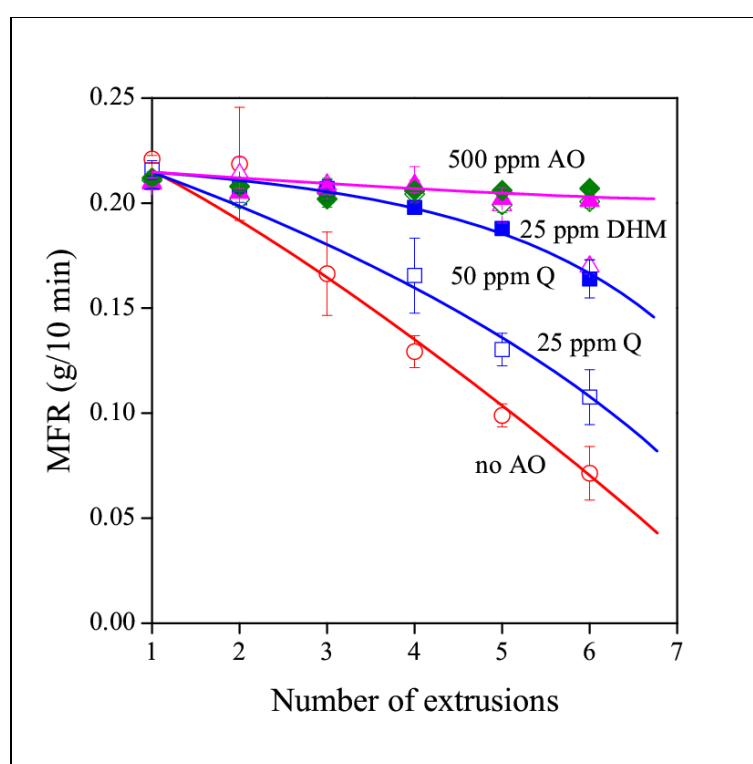


Fig. 1 Effect of additive content and the number of extrusions on the melt stability (MFR) of a Phillips polyethylene. Symbols: (○) no primary antioxidant, (□) 25, (△) 50, (◇) 500 ppm quercetin, (■) 25, (▲) 50, (◆) 500 ppm DHM.

3.2. Processing stabilization

The processing of polymers is accompanied by chemical reactions which change their structure. Most polymers, including polyolefins must be protected against these effects

to maintain their processing and application characteristics. This is especially valid for polyethylenes produced by the Phillips technology, since each molecule contains a vinyl group which reacts readily with oxygen, but also with alkyl radicals. This latter reaction results in the formation of long chain branches (LCB) increasing viscosity and leading to processing problems. As a consequence, changes in the vinyl group content of the polymer is a sensitive indicator of processing stability and they are closely related to the variation, usually increase, of viscosity. Most of these reactions take place in the first processing step and phosphorous secondary stabilizers, PEPQ in this case, protect the polymer very efficiently against such changes.

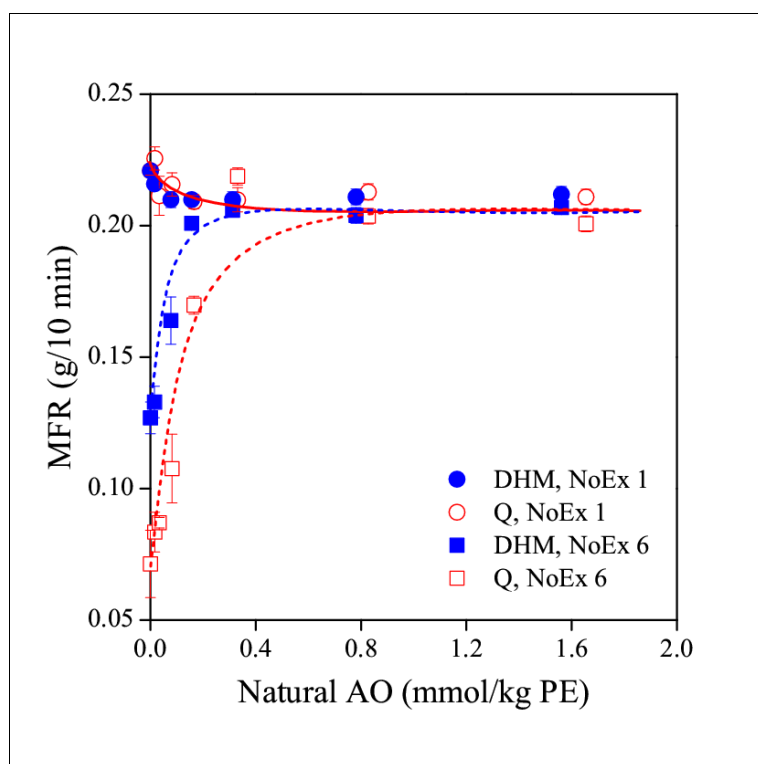


Fig. 2 Dependence of the MFR of polyethylene on stabilizer content at different number of extrusions. Symbols: (○) Q, 1st extrusion, (●) DHM, 1st extrusion, (□) Q, 6th extrusion, (■) 6th extrusion.

The MFR of polymers containing either DHM or Q in different amounts is plotted against the number of extrusions in [Fig. 1](#). At zero antioxidant content MFR decreases quite rapidly with increasing number of extrusions. The increase in viscosity is usually associated with the formation of long chain branches [32,33], but cross-linking may also occur eventually. Both antioxidants efficiently hinder these reactions already at very small concentrations. The correlation is shown only for selected antioxidant contents in order to avoid over cramming and confusion in the figure. Already 25 ppm stabilizer is effective and 50 ppm protects the polymer quite efficiently. Above 100 ppm additive content MFR practically does not change. According to the results, DHM seems to be more efficient than quercetin, since the viscosity of the polymer remains constant already at only 50 ppm additive content. Apparently either the larger number of phenolic hydroxyl groups or the smaller dissociation enthalpy of the phenolic hydrogens renders this compound more effective than quercetin.

Melt flow rate is plotted against the amount of stabilizer added to the polymer ([Fig. 2](#)) to show the effect of additive content. Since the molecular weight of the two compounds is different (see [Table 1](#)), stabilizer content is expressed in mmols. MFR values measured after the 1st and 6th extrusions are plotted to avoid confusion. The effect of the two additives is very similar in the first extrusion, but their dissimilar efficiency is clearly shown after the 6th extrusion at least at small additive contents. Both natural antioxidants protect the polymer very efficiently against degradation at large antioxidant concentrations. It is interesting to note that at very small stabilizer contents MFR decreases, i.e. viscosity increases, after the first extrusion of the polymer that could indicate the formation of long chain branches. This effect is quite surprising considering the considerable efficiency of these stabilizers. However, the phenomenon is the same for both stabilizers and we explained it earlier with the interaction of the primary and the secondary antioxidant (PEPQ) used in this study [23]. The interaction was confirmed by DSC measurements as well [23], but needs further attention

in the future.

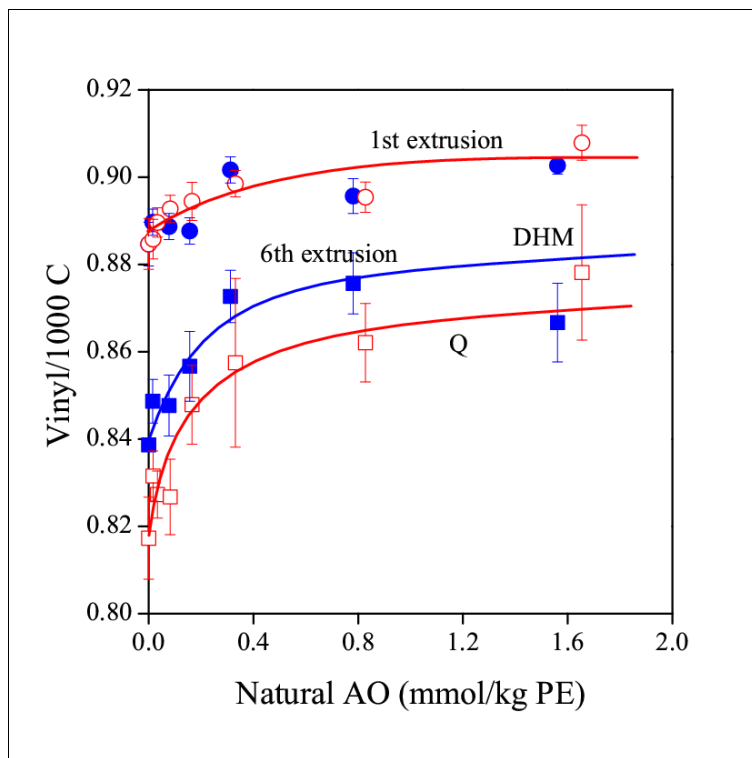


Fig. 3 Changes in the vinyl group content of polyethylene as a function of antioxidant content and processing history. Symbols are the same as in Fig. 2.

Changes in viscosity and processability are attributed to the formation of LCBs going through the chain-end vinyl groups of the polymer [32,33]. The effect of additive content and processing history (No. of extrusions) on the vinyl group content of the polymer is presented in Fig. 3. The number of vinyl groups increase with increasing additive concentration indicating that less vinyl groups enter into chain extension reactions during processing. The effect of the two additives is similar in the first extrusion, but DHM is more efficient than quercetin at larger number of extrusions. The correlations presented in Fig. 3 clearly prove that changes in MFR are caused by the reactions of the vinyl groups indeed. Several studies proved that the role of the secondary stabilizer is essential in the protection of the polymer

against degradation especially in the first processing step [34]. The amount of residual secondary stabilizer is plotted against the number of extrusions in Fig. 4 at two additive contents. All the differences observed earlier in Figs. 1-3 can be detected also here. PEPQ content decreases drastically with increasing number of extrusions at small antioxidant content, while much slower at 500 ppm stabilizer concentration. The larger efficiency of DHM can be clearly seen in the figure. Obviously all the processes taking place during the extrusion of polyethylene are related to each other. The natural antioxidant and the phosphorous secondary stabilizer prevents the reaction of the vinyl groups in a synergistic action, while the natural antioxidant protects PEPQ and decreases its rate of consumption. We may conclude that both natural antioxidants used in this study are efficient processing stabilizers and that the effect of DHM surpasses that of quercetin in melt stabilization.

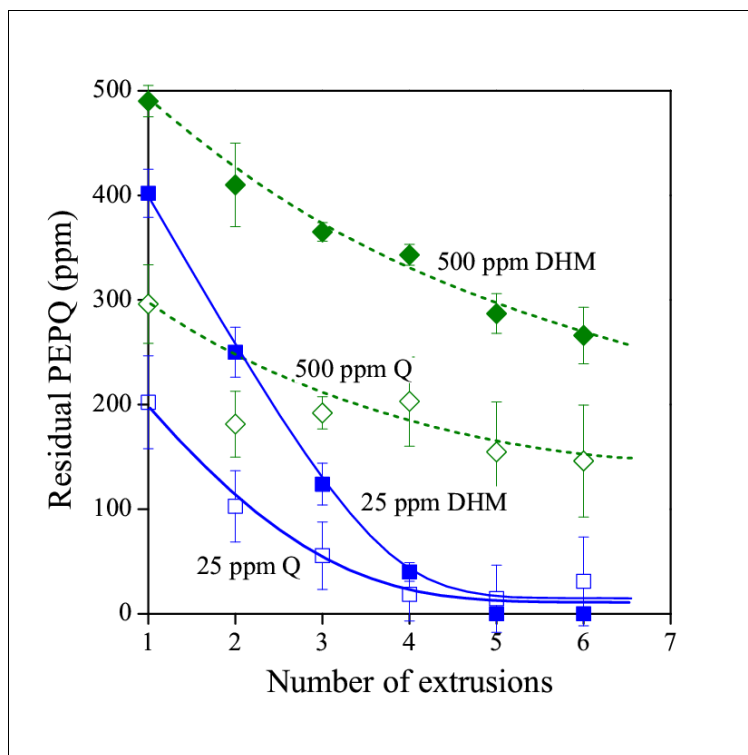


Fig. 4 Effect of the number of extrusions and antioxidant content on the residual amount of PEPQ in polyethylene processed in multiple extrusions. Symbols: (\square) 25, (\diamond)

500 ppm Q; (■) 25, (◆) 500 ppm DHM.

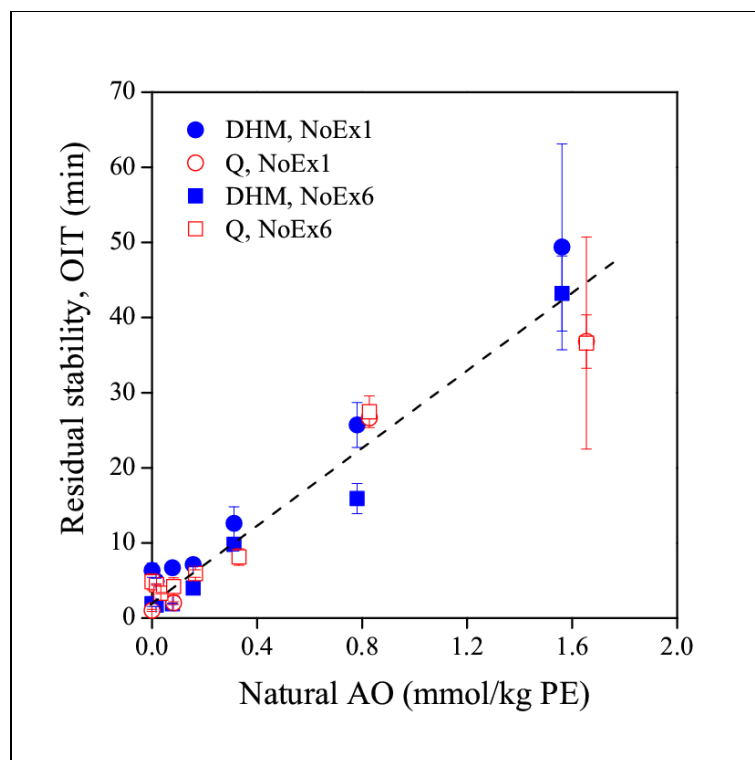


Fig. 5 Unique correlation between the amount of the natural antioxidant used and the residual stability (OIT) of polyethylene. Symbols are the same as in Fig. 2.

3.3. Residual stability

Processing stability is important for most products, but long term stability can be also crucial in certain applications like in gas or water pipes. Moreover, residual stability may offer further information about the mechanism of stabilization and the effect of the chemical structure of the stabilizer on efficiency. The residual stability of PE is plotted against the amount of stabilizer used in Fig. 5. Concentration is expressed in mmol antioxidant/kg PE units, which disregards the different number of phenolic –OH groups in the molecule. The correlation is linear and the effect of the two antioxidants is similar. The linearity is not very surprising, since several authors have proved that OIT is linearly proportional to the amount of phenolic antioxidant [35-37]. Obviously the slope of the straight

line depends on the structure of the stabilizer and on the additive package, i.e. on the type and amount of secondary stabilizer and other components used [35]. However, only limited information is available on the effect of these latter factors on residual stability.

The unique correlation is much more surprising. Based on the larger number of phenolic hydroxyls in DHM, as well as on the results presented in the previous section, one would expect larger stability in polymers containing this additive [24,25]. According to these results not all phenolic –OH groups react during the measurement of OIT and the stabilization effect does not depend on the number of functional groups, but only on the amount of stabilizer present. This result raises the question of reaction mechanism and the activity of the reaction products formed in the first stabilization reaction.

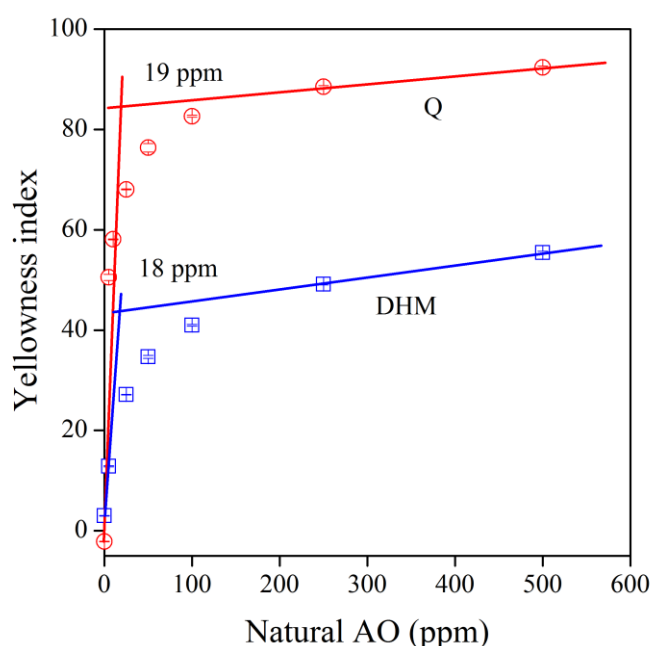


Fig. 6 Determination of the solubility of the natural antioxidants studied from the concentration dependence of color after the 1st extrusion. Symbols: (○) Q, (□) DHM.

3.4. Solubility

The solubility of stabilizers is important for their effect. Larger solubility results in better homogeneity and efficiency [38]. Quercetin was shown to have very limited solubility in PE indicated by the composition dependence of color and by the fact that quercetin crystals were observed in the polymer at larger additive contents [23]. The yellowness index of the polymer is plotted against antioxidant concentration in **Fig. 6**. The measurement was done after the first extrusion step. The discoloration effect of quercetin is very strong, yellowness index reaches more than 90 at large additive content. Rather surprisingly DHM originally being a white powder also discolors the polymer quite strongly, yellowness indices in the range of 50 were measured. Apparently, the reaction products of the stabilizer are not colorless, they discolor the polymer significantly.

The composition dependence of color was used earlier for the determination of the solubility of quercetin in polyethylene [23]. The same approach was used in this study and the result is shown in **Fig. 6**. The basic idea behind the determination of solubility is that dissolved stabilizer molecules have a much stronger effect on color than the additive being present as a separate phase, in the form of crystals. This concept is definitely valid for quercetin, but more difficult to accept for DHM, since discoloration seems to be caused by the reaction products of the additive. Comparison is further complicated by the small number of points in the steeply increasing leg of the correlation and the different levels of color caused by the two additives. Nevertheless, we can state that the correlations as well as the solubility levels are similar, the latter being very small, in the range of 15-20 ppm. This similarity is not surprising since the molecular structure of the two additives is similar. Fortunately, this limited solubility does not influence the efficiency of the two compounds in stabilization.

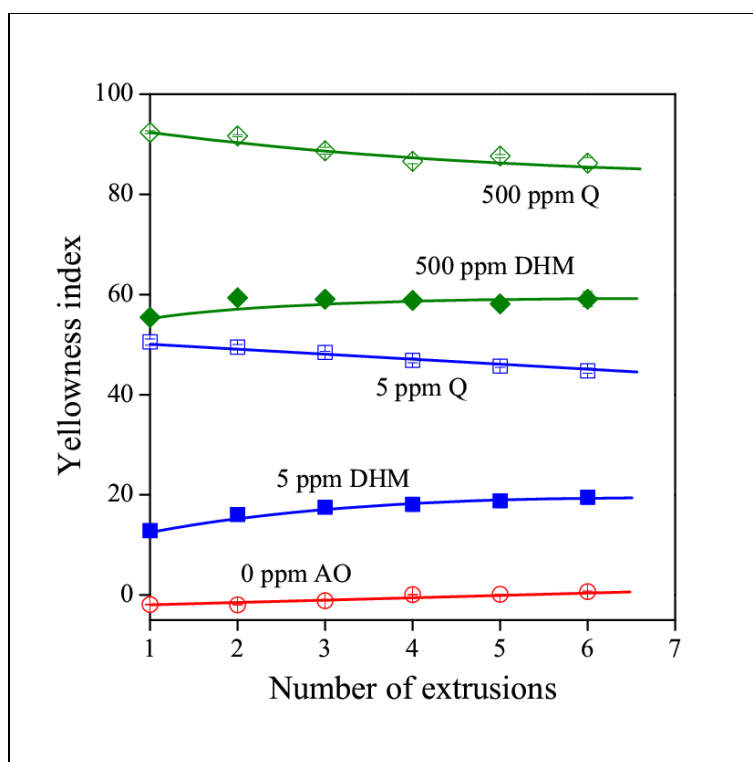


Fig. 7 Effect of additive content and processing history (No. of extrusions) on the yellowness index of polyethylene. Symbols: (○) no primary antioxidant, (□) 5, (◇) 500 ppm Q; (■) 5, (◆) 500 ppm DHM.

3.5. Color

The color of the product is very important in some applications, while much less of an issue in others. In black products the possible discoloration effect of the additive does not matter, but colorless compounds are often much more advantageous. The yellowness index of polyethylene is plotted against the number of extrusions in [Fig. 7](#) for compounds containing the two additives in selected amounts. The very strong coloring effect of quercetin is seen already at 5 ppm additive content and discoloration is extremely intense at 500 ppm. As mentioned above DHM colors the polymer less. Interestingly the measured values slightly decrease during consecutive processing steps in the case of quercetin, and increase

for dihydromyricetin. The consumption of the dissolved yellow stabilizer results in the decrease in the first case, while the formation of colored reaction products leads to the deepening of color in the second. However, yellowness index does not reflect the hue of the color well, especially if it differs from yellow. The Optical L^* parameter gives an idea about the deviation from white; the larger the value is, the closest is the color to white. The L^* parameter decreases slightly with increasing quercetin content and does not change much with increasing number of extrusions; it takes values between 76 and 63. On the other hand, the L^* parameter decreases both with additive content and the number of extrusions for DHM and changes between 76 and 37 in the studied range. These relationships are demonstrated much better by **Figs. 8a and b** than by the optical L^* parameter. In **Fig. 8a** the effect of additive content on color is shown after the first extrusion, while the influence of processing history can be seen in **Fig. 8b** at 500 ppm additive content. It is clear from the figure that quercetin colors the polymer to yellowish red, while DHM from light ochre to dark brown. Obviously, we could not solve the problem of discoloration by the selection of the new natural antioxidant, dihydromyricetin.

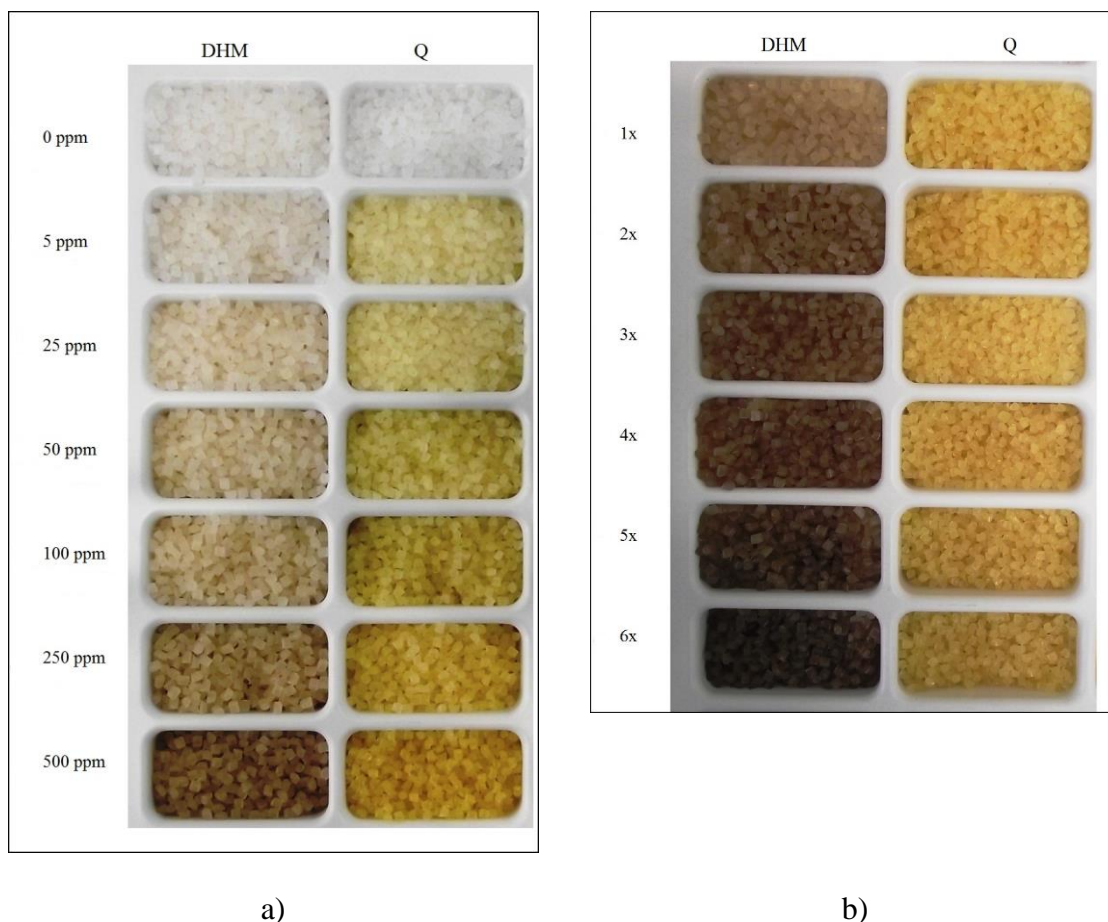


Fig. 8 Changing color of polyethylene in the presence of the two natural antioxidants studied; a) effect of additive content, 1st extrusion, b) effect of the number of extrusions, 500 ppm.

3.6. Discussion

The result presented above prove that both natural antioxidants are efficient melt stabilizers for polyethylene. However, some of the results, like the similar effect on residual stability, or the discoloration of the polymer in the presence of DHM were somewhat unexpected. The reactivity and stabilization effect of phenolic antioxidants depend on their chemical structure, on the number of hydroxyl groups and their position. Four mechanisms have been proposed in the literature for the stabilization reactions of phenolic antioxidants: single electron transfer (SET) [39-40], sequential proton loss electron transfer (SPLET) [41-

42], radical adduct formation (RAF) [43] and hydrogen atom transfer (HAT) [44-45]. In polyethylene the last one is the most probable and accepted mechanism of stabilization. The rate of hydrogen transfer depends on the dissociation enthalpy of the hydrogen atom from the phenolic hydroxyl and this is smaller for the hydrogens located on the OH groups in the B ring of DHM than in quercetin [30-31]. According to the OIT results shown in Fig. 5 DHM is not more efficient than quercetin in spite of the larger number of –OH groups in the molecule. This indicates that after the first reaction, in spite of the reactivity of the products formed, both molecules become much less active than the original compound. This explains the similarity of their effect, but not the differences in efficiency in protecting the polymer during processing.

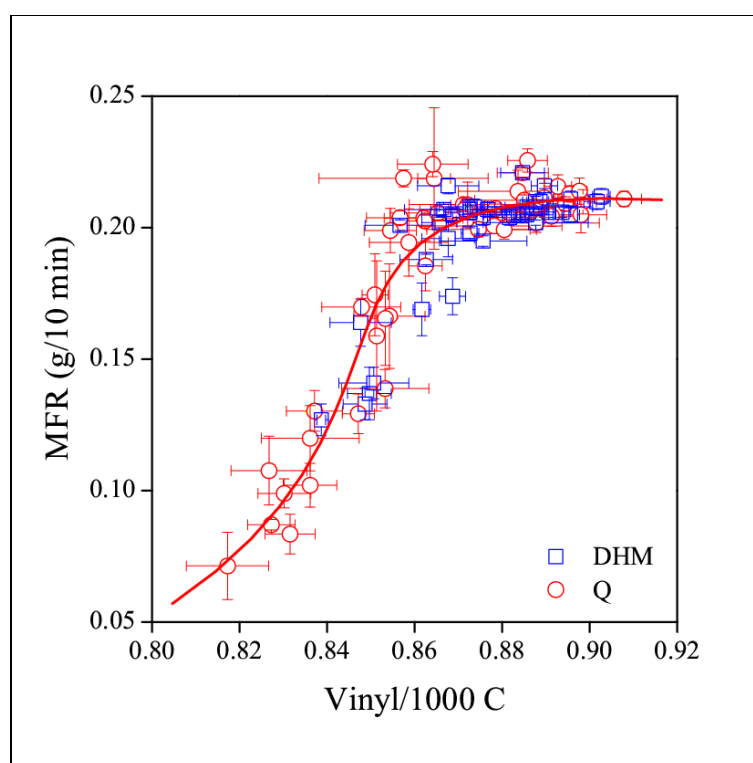


Fig. 9 Correlation between the vinyl content of polyethylene and its melt flow rate. Symbols: (○) Q, (□) DHM.

As discussed earlier long chain branches form during processing through the reaction of the vinyl groups located at one end of the polyethylene chains. The combined, synergistic effect of the primary and secondary antioxidant hinders this reaction, but the interaction of the two stabilizers decreases also their consumption rate. The correlation between the vinyl content of the polymer and MFR is presented in Fig 9. It is clear that viscosity is constant above a certain vinyl content and increases drastically below that (approximately 0.86 vinyl/1000 C). The larger efficiency of DHM is shown by the fact that the points (squares) for the polymer containing this additive are located on the upper right part of the correlation, while many of those belonging to quercetin (circles) appear in the lower left range. The crucial role of the phosphorous antioxidant is demonstrated well by the fact that below a certain PEPQ content (approximately 100 ppm) MFR starts to decrease drastically to very small values. The interaction of the two types of stabilizers (primary, secondary) is important and different for the two natural antioxidants leading to the larger efficiency of DHM. The exact nature of this interaction and the mechanism of stabilization need further study and considerations.

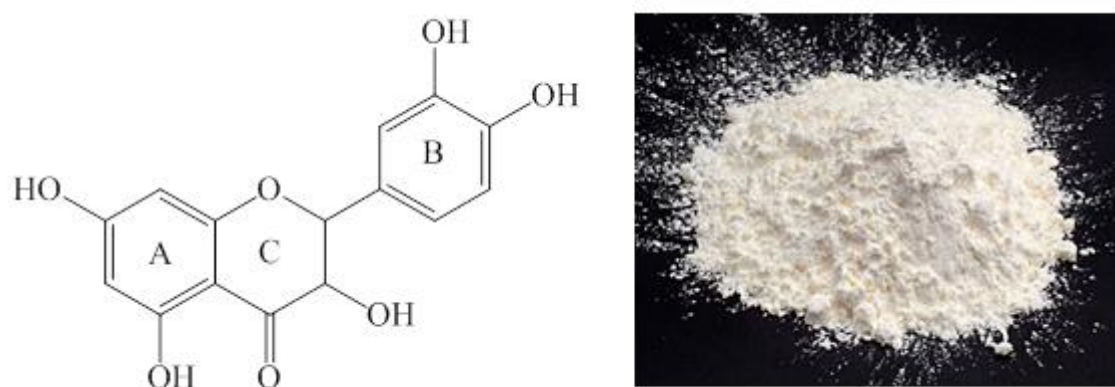


Fig. 10 Chemical structure and appearance of dihydroquercetin (taxifolin) having no double bond in its ring C.

The disappointing color change also requires explanation. The strong yellow color of quercetin results from the conjugation of the double bond in the C with the electrons in the B ring. Dihydroquercetin (or taxifolin) is a white powder similarly to DHM (Fig. 10). As a consequence, the brownish color must form during the processing of the polymer containing the antioxidants. Various quinoidal compounds may form as a result of stabilization reactions which depend on the molecular structure of the antioxidant. Assuming that hydrogen transfer occurs from the B ring, the reaction of quercetin results in two compounds, while that of DHM in one. The reaction leading to these compounds and their structures are presented in Fig. 11. Obviously all three are conjugated systems absorbing light in the visible range.

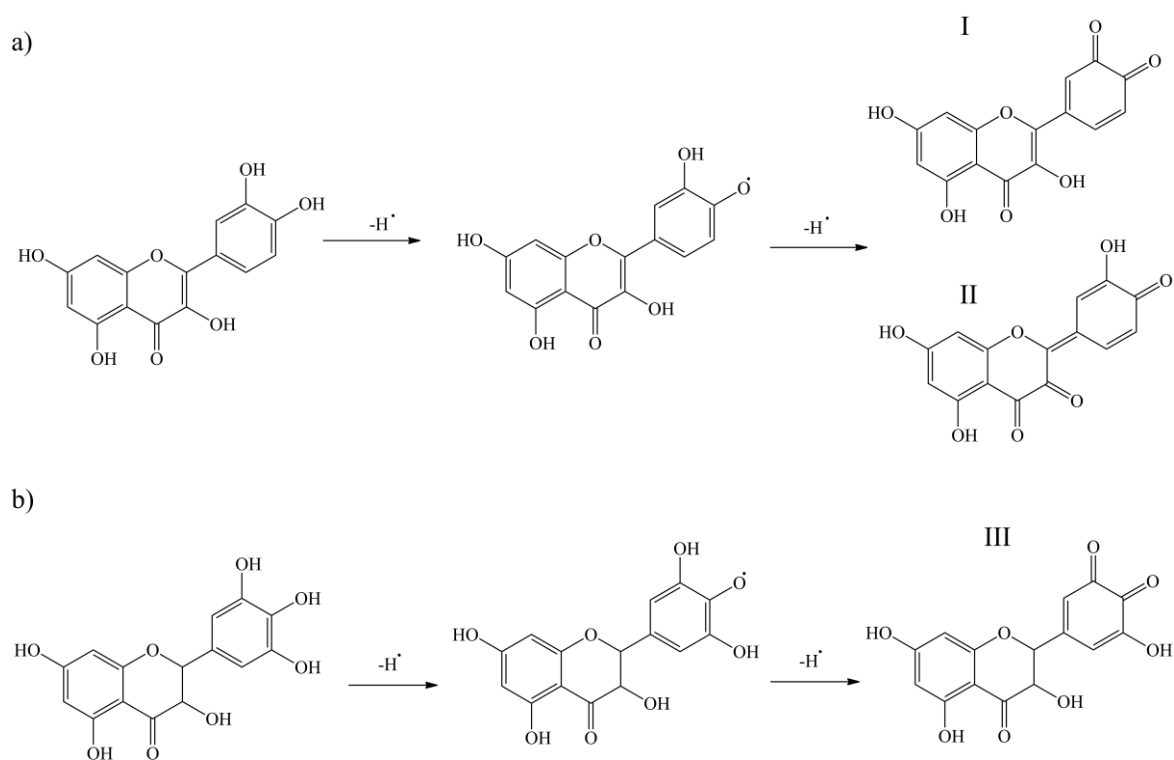


Fig. 11 Formation of quinoidal compounds in stabilization reactions; a) quercetin, b) dihydromyricetin.

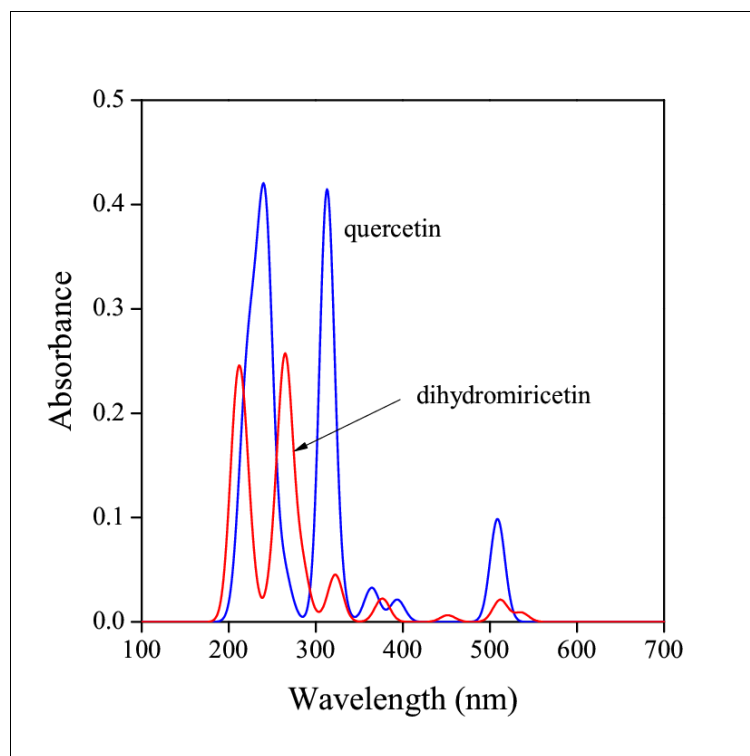


Fig. 12 Predicted UV-VIS spectra of the quinoidal compounds forming from the natural antioxidants during stabilization; a) quercetin I, b) dihydromyricetin III.

An attempt was made to estimate the color of these compounds by molecular modeling. The spectra resulting from the calculations are shown in [Fig. 12](#) for two compounds, compound I formed from quercetin and compound III derived from DHM. Absorption bands appear at 240, 314, 364, 394 and 509 nm in the spectrum of the first, but we are interested only in the visible region. At 394 and 509 nm the violet and green components of visible light are absorbed leading to a mixture of red and yellow colors. The absorption of compound II also results in yellow-orange colors confirmed by [Figs. 8a and b](#). Similarly, compound III absorbs at 378, 452, 511 and 537 nm corresponding to lilac, blue, and green colors. Brown is a mixed color resulting from the absorption of the blue components of light, thus it is highly probable that this absorption leads to the ochre-brownish color of the polymer

processed in the presence of dihydromyricetin (see [Fig. 8](#)). However, in spite of this discoloration the natural antioxidants studied in this work are efficient stabilizers of PE and can be used for certain products.

4. CONCLUSIONS

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

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