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EFFICIENT MELT STABILIZATION OF POLYETHYLENE WITH QUERCETIN, A FLAVONOID TYPE NATURAL ANTIOXIDANT

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ABSTRACT

The potential use of quercetin, a flavonoid type natural antioxidant, as a stabilizer in polyethylene was explored in this work. Its efficiency was compared to that of Irganox 1010, a hindered phenolic antioxidant used routinely in industrial practice, both in the presence and the absence of a phosphorous secondary stabilizer. The study was carried out with a Phillips type polyethylene and the efficiency of the additive packages was checked by various methods on samples produced by multiple extrusions. Quercetin content changed from 0 to 1000 ppm in 10 steps. The results showed that quercetin is a very efficient antioxidant. It prevents the formation of long chain branches already at a concentration as small as 50 ppm and its dosage at 250 ppm renders the polymer sufficient long term residual stability. The efficiency of quercetin is considerably better than that of Irganox 1010, the hindered phenolic antioxidant used as reference stabilizer. The difference in efficiency might be explained with the dissimilar number of active –OH groups on the two molecules, but the stabilization mechanism of quercetin may be also different from that of I1010. Quercetin interacts with the phosphonite secondary stabilizer used, which improves dispersion and increases efficiency. Besides its advantages, quercetin has also some drawbacks (very high melting temperature, poor solubility in polyethylene and strong yellow color), which must be overcome before the substance can be used in practice.

KEYWORDS: polyethylene, processing stabilization, natural antioxidant, quercetin, solubility, long chain branching

1. INTRODUCTION

Polyethylene (PE) is a commodity polymer applied in large quantities in many areas of life. The polymer is exposed to heat, shear, and oxygen during its processing, both during granulation and the production of the final product. Adequate stabilization is essential to protect the polymer and hinder degradation resulting in the deterioration of properties. Synthetic antioxidants are used for stabilization in industrial practice, but about a decade ago questions emerged regarding the effect of the reaction products of phenolic antioxidants on human health [1]. Most of these questions have not been answered yet. As a consequence, more and more attention is paid to the potential use of natural antioxidants for the stabilization of food, but also of polymers [2-10]. These compounds usually can be found in vegetables and fruits, are often used as spices and have known beneficial effect on human health.

Several compounds with different chemical structures may be considered as natural stabilizers in polymers and specifically in polyethylene. Vitamin E, i.e. α-tocopherol is a natural phenol and its effect as an antioxidant was studied in detail, among others, by Al-Malaika et al. [2-5] and it was shown to be a very efficient stabilizer. Similarly, lignin also proved to have some antioxidant effect [6], while natural oils and β-carotene are expected to scavenge alkyl radicals by their unsaturated groups. Using some of these materials as stabilizers was more or less successful, while some of the compounds proved to be inefficient or impractical. In a recent study, the antioxidant effect of another natural compound curcumin was investigated in detail [11]. The results revealed that the melt stabilizing efficiency of curcumin is superior to that of the synthetic antioxidant used as comparison and is further enhanced by the addition of a phosphorous containing secondary antioxidant. Besides the phenolic –OH groups of curcumin, also the linear linkage between the two methoxyphenyl rings of the compound participates in stabilization reactions leading to a unique reaction route and increased efficiency.

Another natural antioxidant, which might potentially be used for the stabilization of polyolefins is quercetin, i.e. [2-(3,4-dihydroxyphenyl)-3,5,7-trihydroxy-4*H*-chromen-4-one], 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. Some research groups have attempted already to use quercetin as an antioxidant in polyolefins [12, 13], while others tried to apply it as a component of active packaging material [14-17]. In the latter case mostly the migration and dissolution of the antioxidant was studied in various solvents modeling food. Koontz et al. [12], for example, homogenized quercetin and its complex with cyclodextrin with PE in a twin-screw extruder and investigated homogeneity as well as stability. The authors did not find any aggregates in the polymer, stability increased considerably, while oxygen permeation decreased simultaneously. Samper et al. [13] studied the thermo- and photooxidative stabilization of polypropylene (PP) with different flavonoids and found that flavonol type compounds, like quercetin, are the most efficient antioxidants. Lopez de Dicastillo and co-workers [15] stabilized successfully an ethylene vinyl alcohol copolymer with quercetin.

Although the studies cited above prove that quercetin is a very efficient stabilizer of various polymers, several questions remain open. Quercetin is a polar compound with a melting temperature of around 320 °C, thus its solubility in the polymer must be limited. Its efficient homogenization is also questionable under the usual conditions of polyolefin processing, since the additive does not melt. In most studies quercetin was added at concentrations of 2-3000 ppm [12, 13] or in even larger quantities, which raises again the question of solubility, but also price, since the compound is rather expensive. As a consequence, the goal of our work was to study the stabilization effect of quercetin in a wide concentration range not investigated before. We wanted to compare the effect of this compound to a frequently used commercial antioxidant in an additive package routinely used in industrial practice in order to determine the possibility as well as the benefits and drawbacks of using this natural antioxidant in polymer stabilization.

2. EXPERIMENTAL

2.1. Materials

The polymer used in the experiments was the Tipelin FS 471 grade ethylene/1-hexene copolymer (melt flow rate of the powder: 0.3 g/10 min at 190 °C, 2.16 kg; nominal density: 0.947 g/cm^3) polymerized by a Phillips catalyst. The additive-free polymer powder was provided by Tisza Chemical Ltd. (TVK), Hungary. For comparative measurements the polymer was stabilized with 1000 ppm quercetin (Sigma-Aldrich) and with a mixture of 1000 ppm quercetin and 2000 ppm Sandostab PEPQ (PEPQ, Clariant), or with Irganox 1010 (I1010, BASF Switzerland) alone and in combination with PEPQ as reference. Quercetin was added in various amounts, in 5, 10, 15, 20, 50, 100, 250, 500 and 1000 ppm to study the effect of additive content on stability. The compounds contained also 2000 ppm PEPQ phosphonite secondary stabilizer. A sample without any additive and one containing only 2000 ppm PEPQ were also prepared for comparison.

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 powder was dried overnight to remove acetone and then pelletized by six consecutive extrusions at 50 rpm and barrel temperatures of 180, 220, 260 and 260 °C 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 were compression molded at 190 °C and 5 min using a Fontijne SRA 100 machine.

2.3. Methods

The MFR of the polymer was determined according to the ASTM D 1238-79 standard at 190 °C with 2.16 kg load in a Göttfert MPS-D MFR tester. The thermo-oxidative stability of the polymer was characterized by the oxidation induction time (OIT) measured at 200 °C in oxygen atmosphere using a Perkin Elmer DSC 2 apparatus. The thermal characteristics of the components and also those of their blends as well as component interactions were studied using a Mettler TA 4000 Thermal Analyzer. Differential scanning calorimetric (DSC) measurements were carried out in a DSC 30 cell under nitrogen (50 mL/min) at a rate of 10 ^{o}C/min from -50 to 300 °C in a cooling and two heating cycles. The functional groups (unsaturated and carbonyl) of polyethylene were determined by FTIR spectroscopy using a Tensor 27 (Bruker) spectrophotometer. Five parallel measurements were carried out on each sample. The color of the samples was described by the yellowness index (YI) measured on a Hunterlab Colourquest 45/0 apparatus. The dispersion of the additive and homogeneity were checked by light microscopy using a Zeiss Axioscop equipped with a Leica DMC 320 digital camera. Micrographs were recorded with the Leica IM 50 software on samples compressed between glass plates.

3. RESULTS AND DISCUSSION

The results are presented in several sections. First those of the preliminary experiments are reported which were designed to compare traditional antioxidants with the natural one. The effect of additive content on efficiency is shown next, followed by the estimation of the solubility of quercetin in PE. The mechanism of stabilization and impact on practice are discussed in the last section of the paper.

3.1. Preliminary experiments, comparison

Before launching a larger project we wanted to check, if quercetin stabilizes polyethylene at all, and in the case of a positive answer we intended to determine its efficiency compared to an industrial antioxidant used routinely. Although all previous reports indicated considerable stabilization effect, they did not answer the second question, efficiency. Four compounds were prepared for this comparative purpose, PE containing the two antioxidants, quercetin and I1010 at 1000 ppm and their combination with 2000 ppm PEPQ phosphonite processing stabilizer. The melt flow rate of the polymer processed in the presence of the four additive combinations is presented as a function of the number of extrusions in Fig. 1. Considerable differences are shown in stabilization efficiency when the antioxidants are used alone, without the processing stabilizer. The MFR decreases in the presence of I1010 with increasing number of processing steps, while it increases when quercetin is used as antioxidant. This latter behavior is quite strange and needs explanation. We know that Phillips type polyethylenes contain a chain-end double bond on each molecule, which reacts during processing forming long chain branches. Increasing MFR indicates fewer branches with increasing number of extrusions. Possible explanations might be the dissimilar stabilization mechanism of quercetin compared to traditional hindered phenol stabilizers. Hindered phenols are known to react mainly with oxygen centered radicals. Increasing MFR indicates the lack or at least the decrease of the number of reactions leading to long chain branching, i.e. reaction also with alkyl radicals. The mechanism of stabilization and this tentative explanation naturally needs further study and proof. Large efficiency and resupply of reacted stabilizer in subsequent processing steps due to its limited solubility might also contribute to the increase in MFR observed. The solubility of most antioxidants is rather small in polyolefins. Irganox 1010, for example, dissolves in amounts less than those used in industrial practice [18]. Quercetin being more polar than I1010 is expected to dissolve in PE in even lesser amounts. As a consequence, the stabilizer is dispersed as a separate phase in the form of droplets, particles or crystals in the polymer. Dissolved stabilizer molecules react during processing thus preventing long chain branching, oxidation or other degradation processes. Reacted molecules are replaced or resupplied from dispersed stabilizers particles in each subsequent step of multiple extrusions, i.e. molecules dissolve from the separate phase into the polymer matrix. This resupply process appears as increased stability, i.e. larger MFR and OIT (see later). However, an increase in MFR can occur only, if alkyl radicals are absent either because their formation is prevented or because they react with the stabilizer. In the presence of the secondary stabilizer the efficiency of the two stabilizers is practically the same.

The large efficiency of the natural antioxidant is reflected even better in the residual stability of the polymer. The OIT is plotted against the number of extrusions for the four compounds in Fig. 2. The stability of PE containing quercetin exceeds several times that of the compounds stabilized with I1010. The effect is especially strong when quercetin is combined with PEPQ, the phosphorous secondary stabilizer. One may speculate about the large difference in efficiency which tentatively might be explained with the dissimilar functionality of the two compounds. However, a simple comparison based on molar number of functional groups does not make much sense, since we do not know almost anything about the mechanism of stabilization, and the five functional groups must have different roles and functions. Literature references indicate indeed that one quercetin molecule can react only with two radicals and not with five [19]. Increasing stability with increasing number of processing steps also merits some attention since it implies that these systems become more stable with increased processing. This is indeed very unusual and requires an explanation as one would normally expect a decrease in the stability of the system with increased processing due to the reduction in the unspent stabilizer concentration, formation of hydroperoxide species, etc. However, increasing stability was observed before [20], which could be explained with the poor solubility of the stabilizer and the resupply of consumed molecules as well as with improving homogeneity with each subsequent processing step. The effect must be even more pronounced in the case of quercetin, which is more polar than I1010, the stabilizer used before. Nevertheless, the preliminary study led to the conclusions that quercetin is a very efficient antioxidant in polyethylene and it is worth to study its effect and efficiency further.

3.2. Stabilizer content

As mentioned in the introductory part, the stabilizing effect of quercetin was always studied at quite large additive contents at around and above 2000 ppm [12,13]. Figs. 1 and 2 indicate that quercetin is more efficient than I1010 already at 1000 ppm, thus it seemed to be obvious to carry out further investigations in a range between 0 and 1000 ppm quercetin content. Several groups showed that degradation is accompanied mainly by the formation of long chain branches and a decrease of MFR in Phillips polyethylene [21-23]. The related reactions go through the chain-end vinyl group of the polymer, thus changes in vinyl content indicate sensitively both the modification of the chemical structure of the polymer and the efficiency of the stabilizer package used. The vinyl group content of our polyethylene is plotted against the number of extrusions at selected quercetin contents in Fig. 3. All packages contained 2000 ppm PEPQ as well. The number of vinyl groups decreases quite rapidly with increasing processing history at small additive concentrations, but the slope of the decrease becomes smaller as the quercetin content increases. The dependence of vinyl content on the number of processing steps is quite small above

100 ppm antioxidant content. Obviously quercetin hinders very efficiently the reactions of the vinyl groups and prevents the formation of long chain branches.

The effect is clearly visible in Fig. 4 presenting the effect of processing history on viscosity at various quercetin contents. The correlations are very similar to those shown in Fig. 3 for vinyl groups. The MFR decreases with an increasing number of extrusions at small concentrations and practically does not change at large quercetin contents. The MFR is more or less constant already at and above 50 ppm quercetin content showing the extreme efficiency of this natural antioxidant as a stabilizer in PE. The OIT proportional to the residual stability of the polymer is plotted against the number of processing steps in Fig. 5. The increase in stability with increasing number of extrusions is unusual and can be explained by a dissimilar stabilization mechanism, but especially by the limited solubility of the additive, the resupply of active molecules and improved homogeneity during subsequent processing steps, as discussed above. Although OIT also improves with increasing quercetin concentration, the composition dependence of this property is slightly different from that of the other two shown in previous figures; OIT increases more or less linearly with increasing additive content and at least 250 ppm is needed to achieve practically acceptable levels of stability. We must keep in mind, though, that different products require different levels of stabilization. One way packaging must be protected only during processing and 50 ppm quercetin is sufficient, while pipes must usually have an OIT of at least 20 min, thus 200-250 ppm is needed in this case. However, the composition dependence of all properties indicates unambiguously that already much smaller amounts of quercetin stabilize PE efficiently than those reported before [12, 13].

The color of the polymer is plotted against the number of processing steps at various quercetin contents in Fig. 6. The main drawback of this additive is shown clearly by the figure. Quercetin is inherently yellow and colors also products prepared with it; discoloration is quite strong at large quercetin contents. It is interesting to note that with increasing number of extrusions the yellowness of the samples decreases at small additive contents, it is more or less constant at 500 and increases at 1000 ppm. Although the effect is slight, it appears to be consistent and must have some reason. We may assume that the reaction of the antioxidant yields colorless products and the depletion of the stabilizer results in the decrease of yellowness at small quercetin contents. Obviously, the resupply of active, dissolved molecules from dispersed particles cannot keep up with their consumption in stabilization reactions at small quercetin concentrations. On the other hand, increasing color at large additive contents indicates that homogeneity improves with each processing step; either the particles become smaller or more molecules are dissolved due to the changing chemical structure (increasing number of functional groups, reaction products) of the PE compound. The dependence of color on processing history is in complete agreement with the change of OIT and MFR and indicates the strong effect of solubility in stabilization.

3.3. Solubility, homogeneity

Besides color the major problem of the application of quercetin as stabilizer is its high melting temperature and polarity, which results in limited solubility in apolar polymers. Although Koontz et al. [12] claimed complete homogeneity at 2000 ppm, one has slight doubts. Experimental results and the blooming of the additive indicate that the solubility of Irganox 1010 is around or less than 1000 ppm in polyethylene [18], thus complete homogeneity or even solubility of quercetin at larger concentrations would be quite surprising. The MFR of the polymer is plotted against quercetin content in Fig. 7 for samples taken after the first and sixth extrusions. After the first extrusion the MFR of PE containing only 5 ppm quercetin is considerably larger than that of the material prepared with

PEPQ alone. The MFR reaches a maximum between 15 and 20 ppm quercetin content then decreases slightly to a value which does not change appreciably above 50 ppm. After six extrusions the MFR of the polymer does not show the small maximum, but the steep increase and leveling off can be observed as a function of quercetin content. Differences at small quercetin contents and the composition dependence of MFR indicate that branching reactions control viscosity at small quercetin concentrations, while solubility plays an important role at larger additive contents.

Yellowness index measured after the first extrusion is plotted in Fig. 8 in the same way. Similarly to MFR, or even more so, the slope of color change differs drastically at small and large additive contents. It seems to be obvious that the dissolved yellow molecules of quercetin discolor the polymer much more than dispersed crystals, thus the change in slope must be related to the solubility of the additive in PE. The solubility value indicated by the arrow in Fig. 8 is around 15 ppm. A further proof for the very limited solubility of quercetin in PE is supplied by Fig. 9 showing the optical micrograph of a PE film containing 1000 ppm quercetin. The needle like crystals of the additive are clearly visible in the photo. Their presence is not so obvious at smaller concentrations, most probably because of the limited resolution of optical microscopy. The consequence of limited solubility is demonstrated well by Fig. 10 presenting the dependence of residual stability on quercetin content after the 1st and 6th extrusions. The OIT is considerably larger after the 6th processing step because of the resupply of reacted quercetin and the better homogeneity of the additive with increasing processing history. Continuously increasing OIT seems to contradict the composition dependence of MFR and color and also the effect of limited solubility. We must consider here, however, the different conditions of processing and OIT measurement. Only dissolved molecules are effective during processing by reacting with the limited amount of oxygen and/or radicals generated by it. On the other hand, during the OIT measurement oxygen concentration is large with constant resupply, thus stabilization reactions must proceed also on the surface of dispersed particles by scavenging all kinds of radicals and preventing extensive oxidation. In fact the increase of homogeneity with increasing number of processing steps may result in the finer dispersion of smaller particles, larger surface and better stability explaining the increase of OIT in Figs. 2 and 5. These results confirm our assumption that the solubility of quercetin is very limited in PE and it must be considered during the application of this compound as a stabilizer.

3.4. Discussion

The results presented in previous sections unambiguously verify the strong antioxidant effect of quercetin. Its positive effect has been known for the human body for some time and indicated also for polymers, but its efficiency at very small concentrations has not been demonstrated before. The comparison of the effect of Irganox 1010, a traditional phenolic antioxidant, and that of quercetin clearly shows the superiority of the latter. The larger efficiency might be explained by the larger molar functionality of quercetin, but the reactivity of its five hydroxyl groups is not the same, not all of them participate in stabilization reactions. Previous results showed that ring B (see Fig. 11) is responsible for the antioxidant effect of quercetin, especially if it contains the catechol moiety [24]. High efficiency probably results from the electron donating effect of the –OH group located in position 3 in ring C [25, 26]. According to the latest results, unlike most flavonoids, one quercetin molecule can react with two radicals, which may partly explain its efficiency [19].

Polyphenols, like quercetin, may react with radicals according to four mechanisms: hydrogen transfer from the antioxidant to the radical (HAT) [27, 28], electron transfer-proton transfer (ET-PT) [25], sequential proton loss-electron transfer (SPLET) [29, 30] and adduct formation [31]. In apolar solvents, and probably also in polyethylene, HAT is expected to be the dominating mechanism, but the electron affinity of the radical also influences the actual mechanism. Both carbon and oxygen centered radicals are present in polyethylene during its processing. The scavenging of the first prevents the formation of long chain branches, and viscosity can even decrease during processing, like in the presence of curcumin, another natural antioxidant [11]. At least a few long chain branches always form if the stabilizer preferably reacts with oxygen centered radicals. In such cases close correlation is expected between the vinyl group content of Phillips polyethylene and its MFR. The two quantities are plotted against each other in Fig. 12. The concentration of vinyl groups decreases gradually during multiple extrusions in an extent depending on the amount of quercetin used for stabilization (Fig. 3). The MFR changes as well and relatively close correlation can be found between the two characteristics independently of the number of extrusions indeed, which confirms the role of long chain branching in the determination of MFR. On the other hand, the existence of the two correlations indicates differences in stabilization mechanism and/or efficiency. All the points for compounds containing the natural antioxidant fall onto a different correlation as those for the neat polymer, for the compounds containing only PEPQ, and those obtained on PE stabilized with I1010 with or without the secondary antioxidant. The difference appears already at 5 ppm quercetin content. The dissimilar efficiency of the two additives, i.e. quercetin and I1010, respectively, may be explained with the known threshold concentration of hindered phenol stabilizers, which does not exist for the non-hindered phenols [32] like quercetin. The larger reactivity of the natural antioxidant may allow reactions with some of the C-centered radicals as well. However, further, more detailed study of the stabilization mechanism of quercetin is needed to explain the reason for the existence of the two correlations in Fig. 12.

The increased efficiency of quercetin in the presence of PEPQ also needs explanation. The small solubility of the antioxidant in PE and its high melting temperature indicates strong interaction among quercetin molecules. The PEPQ may interact with quercetin in one way or other, helping homogenization and increasing reactivity. Some indication of the existence of such an interaction is offered by Fig. 13, in which the melting traces of the two additives, i.e. quercetin and PEPQ, is compared to that of their mixture containing the same amount of each component. The very sharp melting peak of quercetin appearing at around 320 °C becomes diffuse and shifts to a much lower temperature, to about 235 °C. The interaction might influence solubility, but the composition dependence of color contradicts this, since it indicated a solubility limit of only 15 ppm (Fig. 8). Obviously further study is needed to explain satisfactorily the stabilization mechanism of quercetin in PE and its interaction with the phosphonite secondary antioxidant. Nevertheless, we may conclude that the natural antioxidant studied in this work is a very efficient stabilizer also in polyethylene and merits further consideration and study.

4. CONCLUSIONS

The study of the melt stabilization effect of quercetin, a flavonoid type natural antioxidant, showed that it is a very efficient stabilizer in polyethylene. Quercetin prevents the formation of long chain branches already at a concentration as small as 50 ppm and its dosage at 250 ppm renders the polymer sufficient residual stability. The efficiency of quercetin is considerably larger than that of Irganox 1010, the hindered phenolic antioxidant used as reference stabilizer. The difference in efficiency might be explained with the dissimilar number of active –OH groups on the two antioxidant molecules, but the stabilization mechanism of quercetin might be also different from that of I1010. Quercetin interacts with the phosphonite secondary stabilizer used, which presumably improves dispersion and thereby increases efficiency. The mechanism of stabilization and interactions need further study in the future. Besides its advantages, quercetin has also some drawbacks, it has a very high melting temperature, its solubility in polyethylene is very small and it gives a strong yellow color to the product. These disadvantages might be overcome by the use of colorless derivatives and the use of a solid support to help dosage.

5. ACKNOWLEDGEMENTS

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CAPTIONS

Fig. 1	Comparison of the effect of 1000 ppm quercetin and 1000 ppm Irganox 1010 on the melt flow rate of Phillips polyethylene. Symbols: (⬟) quercetin, (■) I1010, (⬠) quercetin with 2000 ppm PEPQ, (□) I1010 with 2000 ppm PEPQ.
Fig. 2	Effect of the natural antioxidant and I1010 on the residual stability of polyethylene in the presence and absence of PEPQ. Symbols are the same as in Fig. 1.
Fig. 3	Changes in the vinyl group content of polyethylene as a function of quercetin content and processing history. Symbols: (○)5, (◇)20, (▷)100, (⬡)250, (☆)500, (⬠)1000 ppm quercetin with 2000 ppm PEPQ.
Fig. 4	Effect of the number of extrusions and quercetin concentration on the melt flow rate of PE. Symbols: (✳)0, (○)5, (△)10, (▽)15, (◇)20, (◁)50, (▷)100, (⬡)250, (☆)500, (⬠)1000 ppm quercetin and 2000 ppm PEPQ.
Fig. 5	Changes in the residual stability of polyethylene as a function of quercetin content and processing history. Symbols are the same as in Fig. 4.
Fig. 6	Dependence of the color of PE on quercetin content. Effect of the number of extrusions. Symbols are the same as in Fig. 3.
Fig. 7	Changes in the melt flow rate of polyethylene with quercetin content after the 1th and 6th extrusions. Symbols: (□) one, (○) six extrusions.
Fig. 8	Effect of the amount of quercetin on the color of PE after the first extrusion. Determination of solubility.
Fig. 9	Optical micrograph of a polyethylene film containing 1000 ppm quercetin. Needle crystals of the additive.
Fig. 10	Effect of quercetin content and processing history on the residual stability

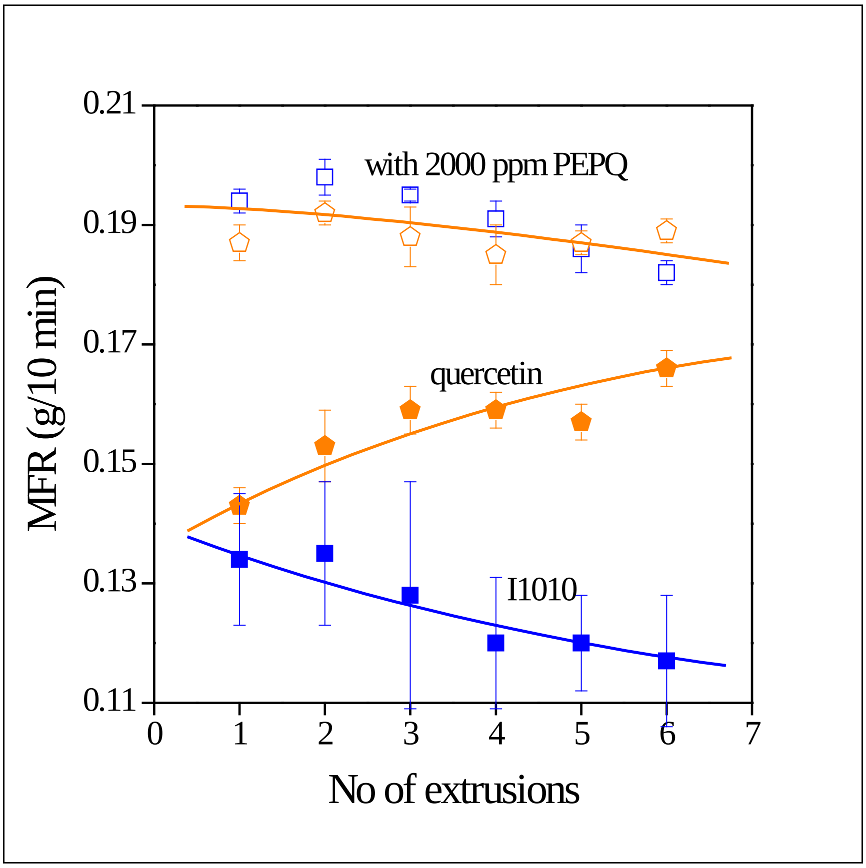
of polyethylene stabilized with quercetin. Symbols: (□) one, (○) six extrusions.

Fig. 11 Molecular structure of quercetin.

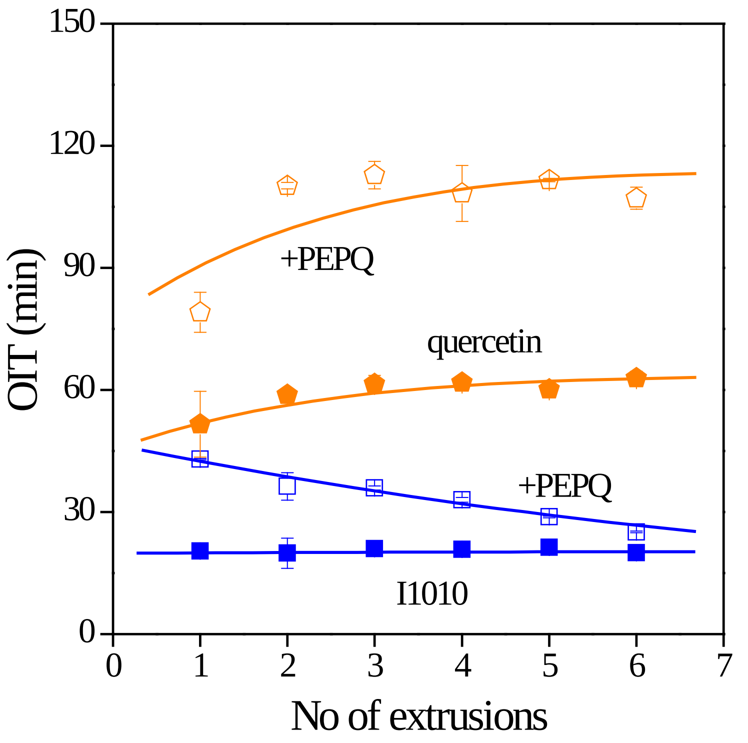
Fig. 12 Correlation between the vinyl group content of the polymer and its melt flow rate. Different effects and mechanisms independently of the number of extrusions. Symbols: (◕)Neat, (■)1000 ppm I1010, (□)1000 ppm I1010 and 2000 ppm PEPQ, (⬟)1000 ppm quercetin, (✳)0, (○)5, (△)10, (▽)15, (◇)20, (◁)50, (▷)100, (⬡)250, (☆)500, (⬠)1000 ppm quercetin and 2000 ppm PEPQ; each symbol is related to results generated in six consecutive extrusion steps, i.e. the effect of processing can be followed by moving from left to right along the points.

Fig. 13 DSC melting traces of quercetin, the phosphonite secondary stabilizer, and their mixture containing equal amounts of the two additives. Heating rate: 10 °C/min.

Tátraaljai, Fig. 1



Tátraaljai, Fig. 2



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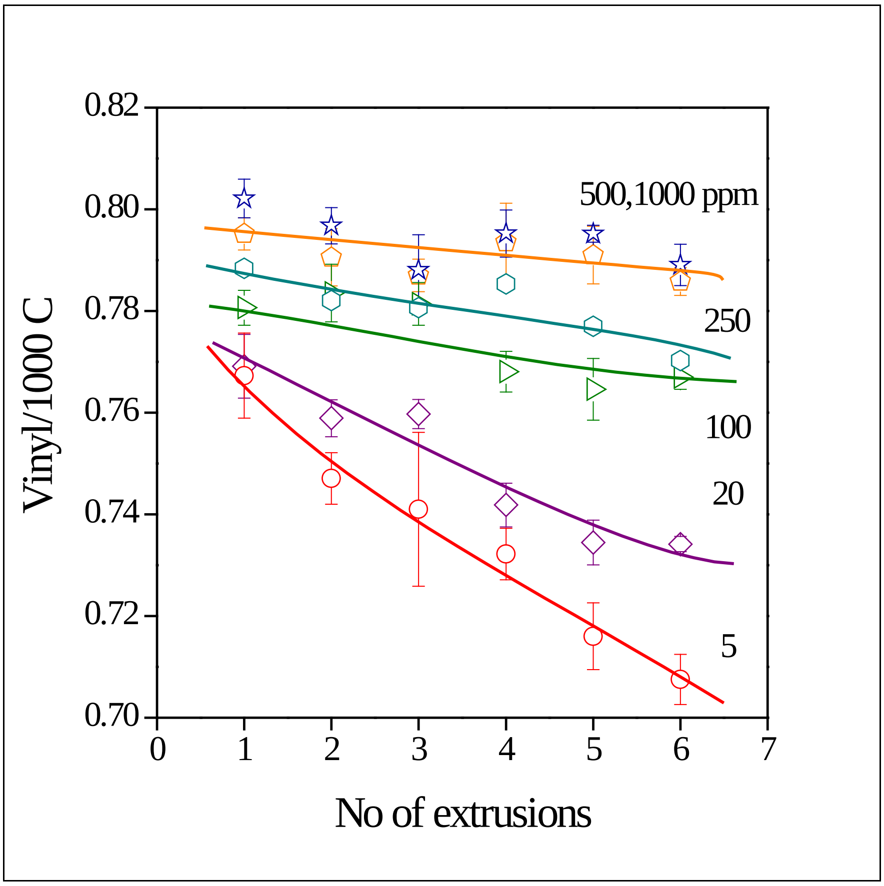

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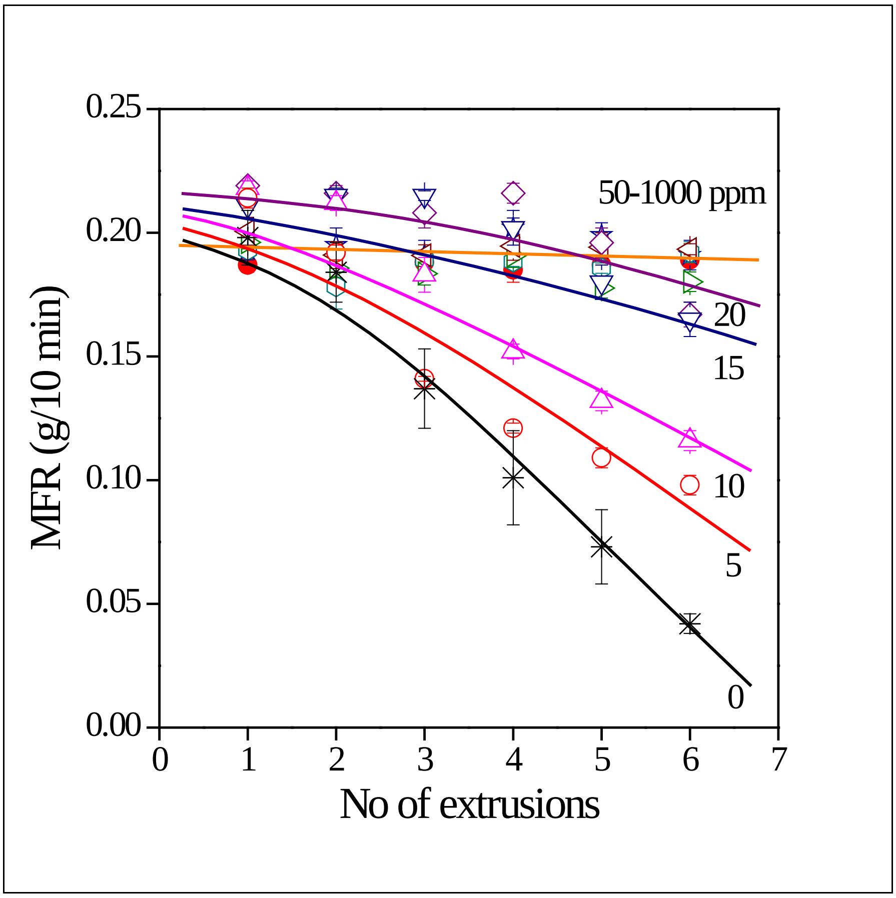
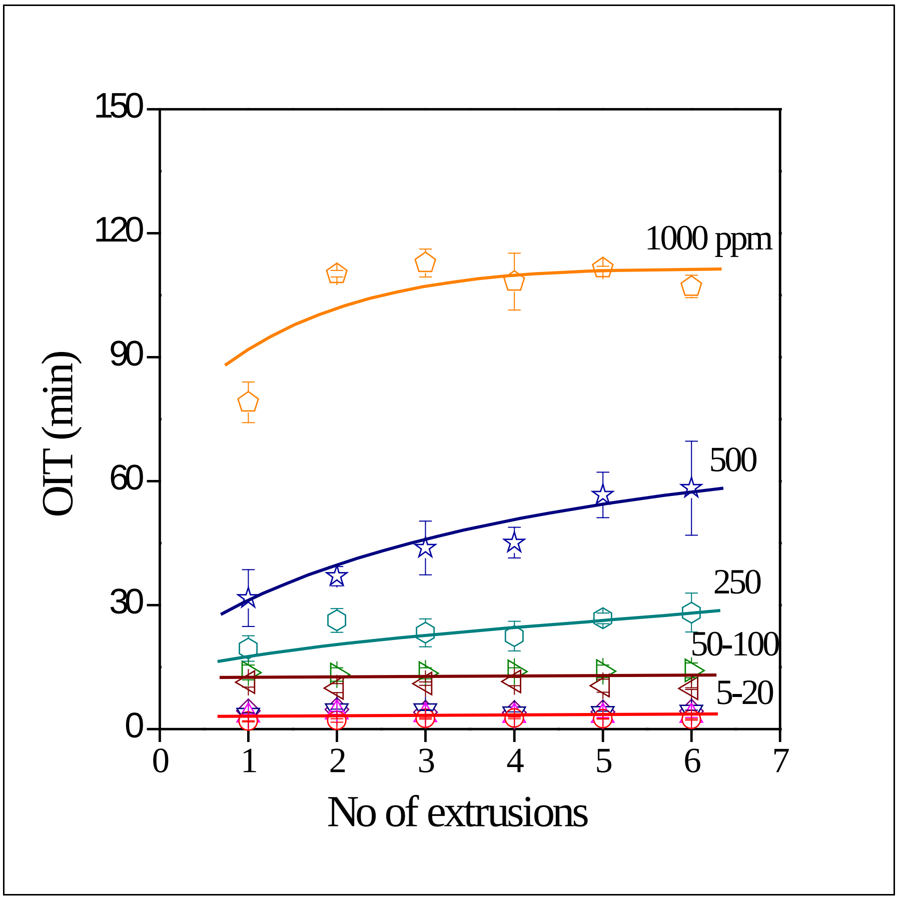
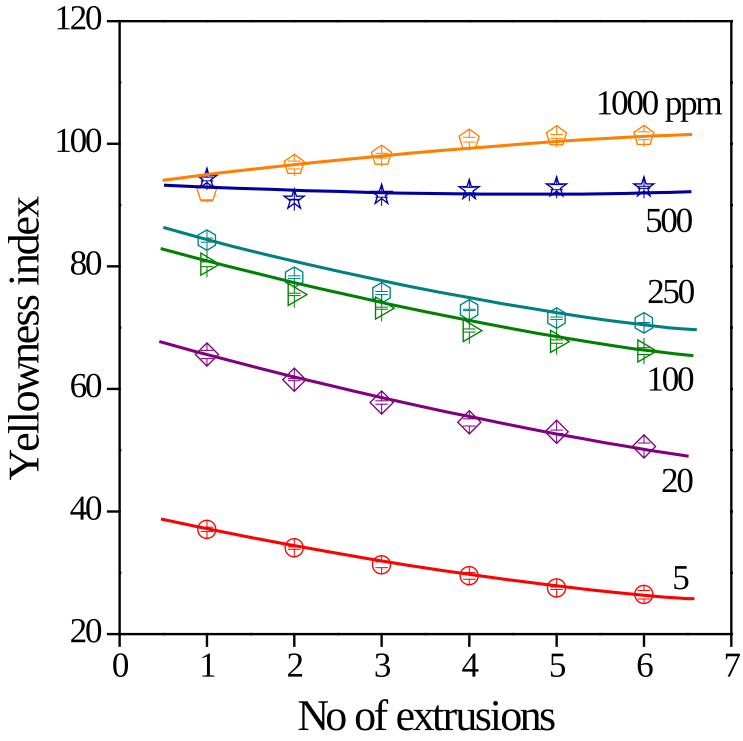


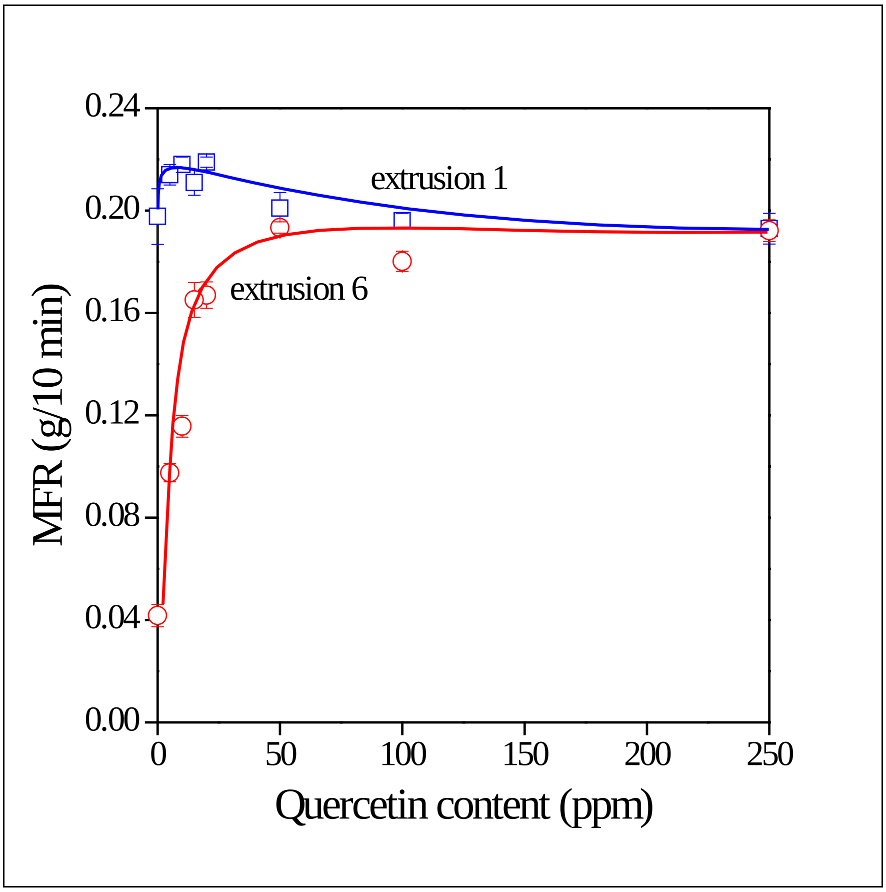
Tátraaljai, Fig. 5



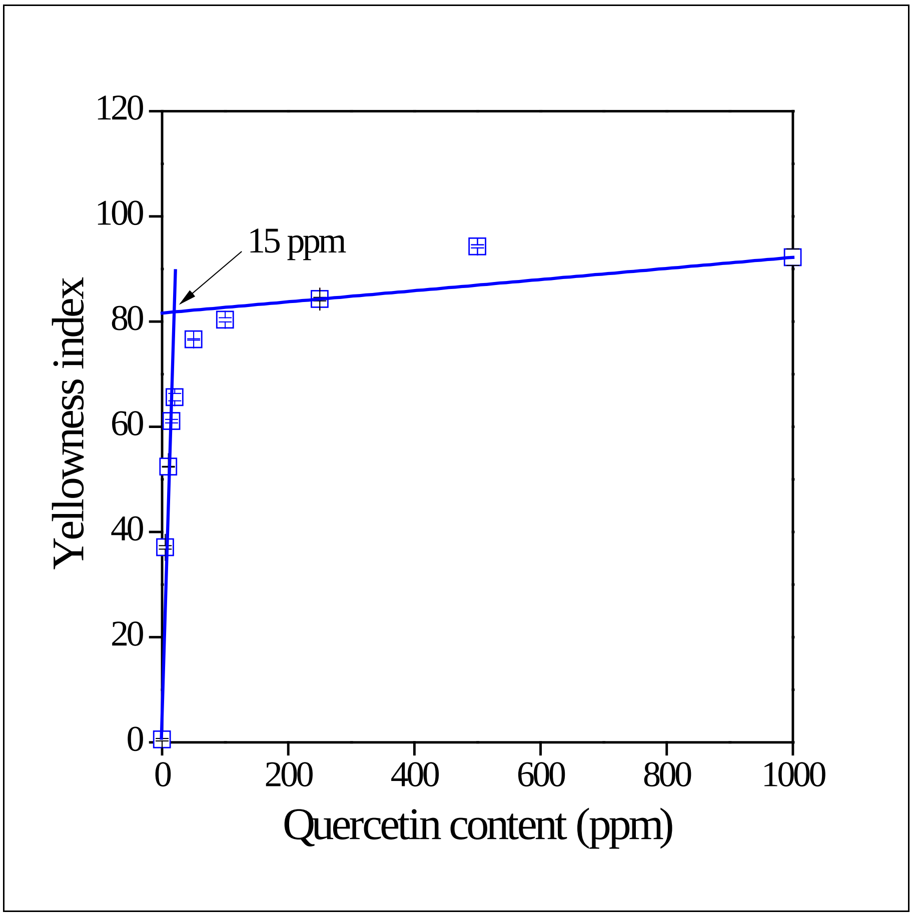
Tátraaljai, Fig. 6



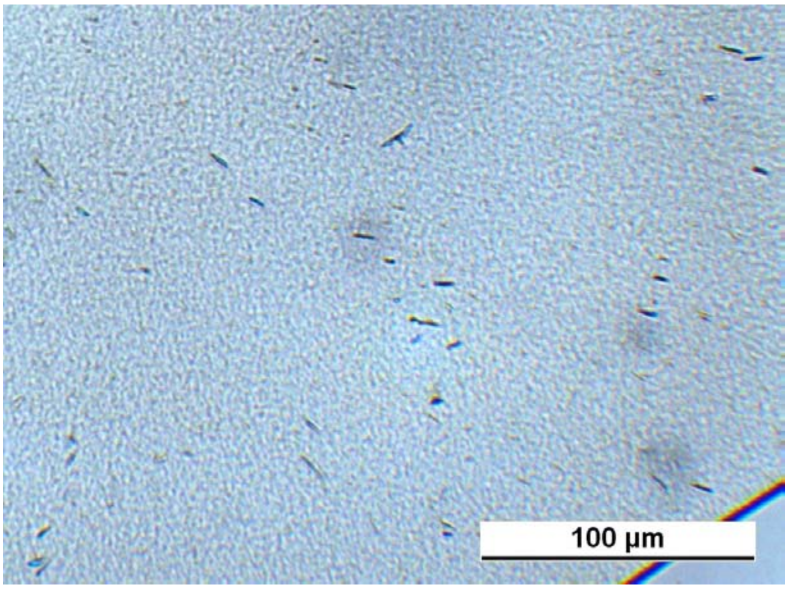
Tátraaljai, Fig. 7



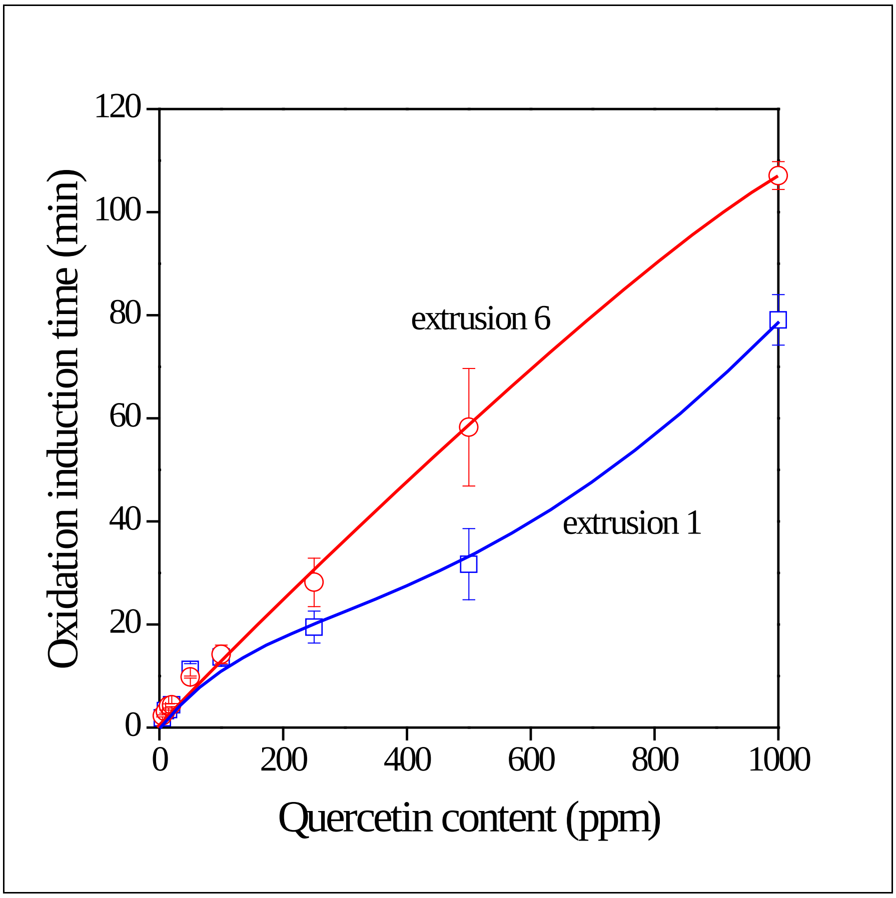
Tátraaljai, Fig. 8



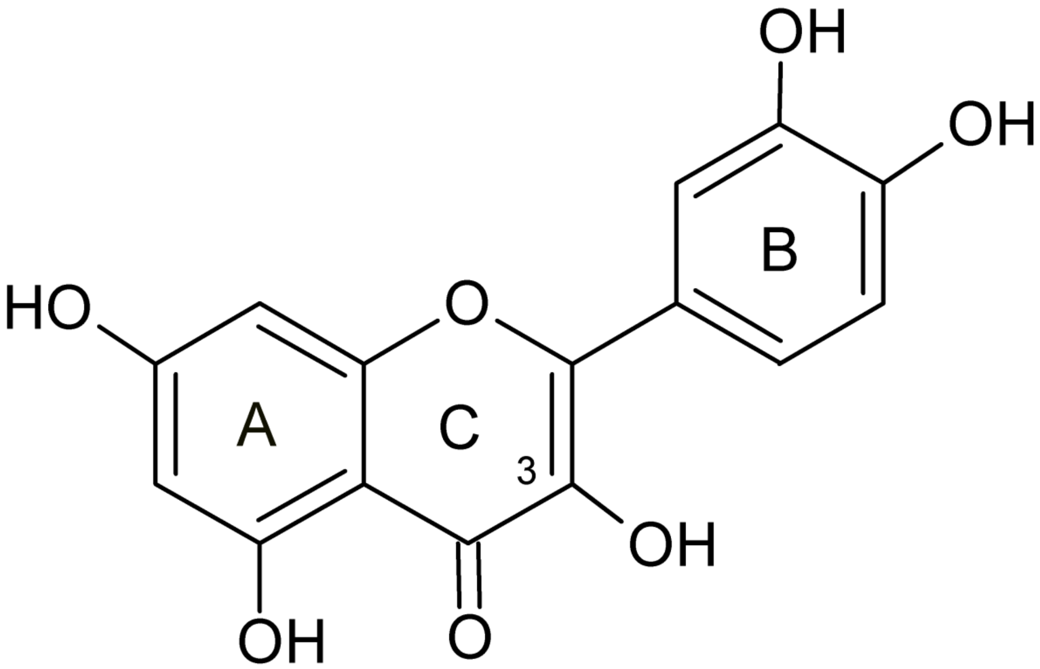
Tátraaljai, Fig. 9



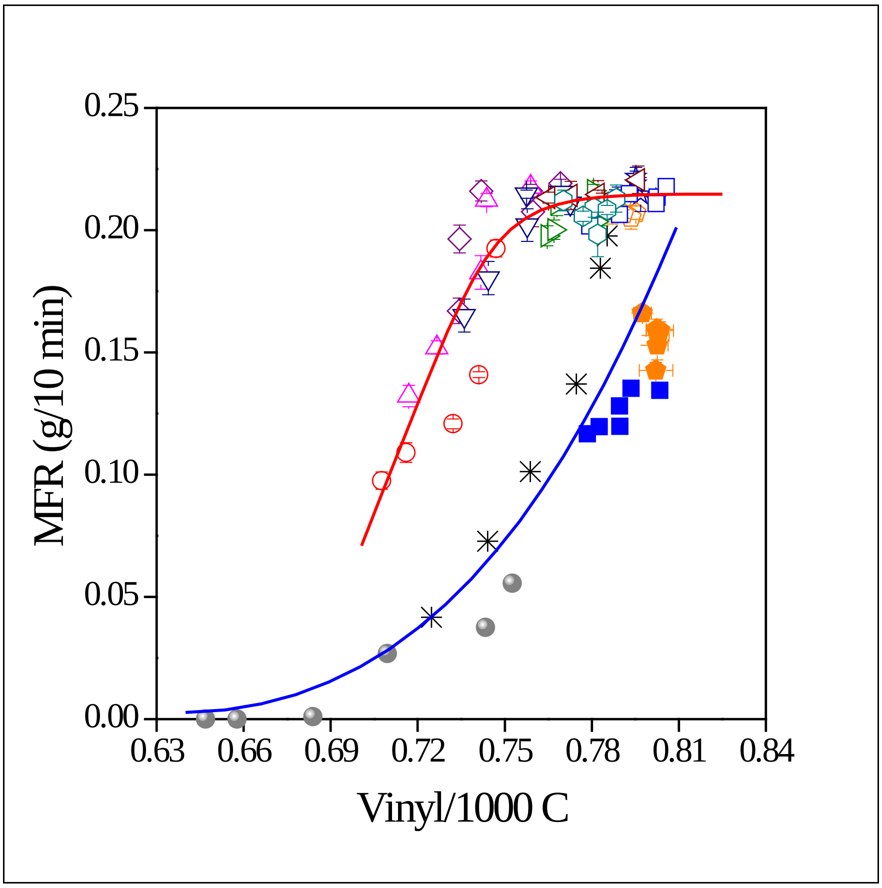
Tátraaljai, Fig. 10



Tátraaljai, Fig. 11



Tátraaljai, Fig. 12



Tátraaljai, Fig. 13