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Efficient additive package with large natural material content for the stabilization of PE

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ABSTRACT

An additive package with large natural material content was prepared and its stabilization efficiency was compared to that of an industrial stabilizer combination. A new phosphine-type secondary antioxidant was synthesized to increase the bio-based content of the package. The stabilization effect of the packages was studied in multiple extrusion experiments followed by the measurement of chemical structure, rheology, residual stability, and color. The interaction of the components was studied by thermogravimetry and FTIR spectroscopy. The comparison of the additive packages showed that the bio-based package offers many advantages compared to the currently used industrial package; better stabilization efficiency is achieved at smaller additive content. The natural antioxidant used, quercetin, interacts with the secondary stabilizers. Quercetin initiates the decomposition of a phosphonite stabilizer containing P(III)O bonds, but it increases the inherent stability of the newly synthesized phosphine antioxidant. The interactions result in changes in the reactions of the vinyl groups of the polymer. Besides long chain branching, other competitive reactions take place, which consume vinyl groups but do not increase viscosity. The new stabilizer package offers excellent melt stability and exceptional residual stability for the Phillips polyethylene used in this study. The main drawback of the package is the limited solubility of quercetin and the strong color of the processed material.

1. Introduction

One of the advantages of plastics is that they can be converted into products with high productivity at relatively low temperatures, at least compared to metals or glass. Nevertheless, they are organic materials and degrade easily even at the moderate temperatures of plastic processing, at 200–300 °C, and many products must be protected against degradation also during their use [1–4]. Accordingly, most polymers contain stabilizers, which protect them during processing and conserve properties during use [1]. Stabilization has become increasingly important with the advent of the circular economy [5–8]; multiple processing of plastic waste is impossible without replenishing the original additive content of the polymer [9–13]. The considerations presented here are equally valid for polyolefins, which must be protected against heat, shear and oxygen during processing and multiple effects during their use [14,15].

The stabilization of polyolefins, in fact that of most polymers, is a mature technology now. Polyethylene (PE) or polypropylene (PP) products usually contain a hindered phenolic antioxidant as the primary stabilizer and a phosphorous or sulfur-containing compound as a secondary stabilizer [1]. Such additive packages have been optimized a long time ago and basic stabilization has not changed for a long time. However, recently the interest in natural, bio-based products has increased considerably in all areas of life, including stabilization [16–19]. Additionally, some time ago concerns were expressed about the possible harmful effect of the hindered phenolic antioxidants widely used in products in contact with water or food [20,21]. In the last decade, the number of studies on the use of natural antioxidants as stabilizers has increased considerably. Nature produces and uses numerous compounds, which have strong antioxidant effects [22] including lignin [23,24] , flavonoids or flavonols [25–27], curcumin [28], and a considerable number of other polyphenolic compounds [24].

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Although lignin has some antioxidant effect [29–31], it is not very efficient, because of the relatively small number of active phenolic hydroxyl groups in a unit mass [32]. On the other hand, flavonoids and flavonols proved to be very efficient stabilizers not only in nature but also for polymers [19,33–36]; their stabilizer efficiency often exceeds that of the currently used phenolic antioxidants [19]. Accordingly, potentially they can replace the traditional stabilizers any time in the future.

Natural compounds containing phosphor or sulfur, which could be used as secondary antioxidants, are rare or nonexistent. Accordingly, the phosphite and phosphonite compounds currently used in large quantities [37–39] cannot be replaced easily by natural materials, and thus, increasing the efficiency and natural material content of such stabilizers is a major challenge. A new phosphine secondary antioxidant was developed some time ago [40], which proved to be a more efficient secondary antioxidant than the routinely used phosphite and phosphonite compounds. Unfortunately, it did not pass the necessary biological tests and it was not approved for food contact applications. Recently, another phosphine stabilizer was synthesized, a considerable part of which was derived from natural resources [41]. The effect and efficiency of the stabilizer were compared to those of currently used secondary antioxidants and proved more efficient than those. However, the primary antioxidant was a traditional hindered phenol in the experiments, thus, only a small part of the additive package was replaced by bio-based material [41].

Natural antioxidants are very advantageous in many aspects. Besides originating from natural resources, they do not have adverse health effects and they are extremely efficient. Unfortunately, natural antioxidants have several drawbacks as well. They are crystalline materials usually with high melting temperatures, their solubility in polymers, especially in polyolefins, is very small and they discolor the polymer practically always [19]. Moreover, the antagonistic interaction of a natural antioxidant, resveratrol, and a traditional phosphonite secondary antioxidant has been observed in a recent study [42]. Accordingly, the application of natural or natural-based compounds for the stabilization of polymers is not straightforward; thorough experiments must be carried out to check their effect and efficiency as well as their possible interactions with other compounds in the additive package. The efficiency of an additive combination containing a natural antioxidant and the newly developed bio-based secondary antioxidant has never been tested in the past thus needs some attention.

Taking into account the considerations presented above, the goal of this study was to prepare an additive package from an efficient natural antioxidant, quercetin, and the newly developed phosphine-type secondary antioxidant, and study its effect and efficiency in multiple extrusion experiments. The efficiency of the package was compared to that of a traditional additive combination containing a hindered phenolic primary antioxidant and a phosphonite secondary stabilizer. The combination of the natural antioxidant and the traditional phosphonite stabilizer, as well as the neat natural antioxidant were used as references. The effect of the amount of the bio-based phosphine type stabilizer in the additive package was studied in a separate series of experiments. Stabilizing efficiency was characterized by the measurements of the vinyl content of the polymer, melt flow rate, residual stability, and color. The possible interaction of the components of the various packages was studied by differential scanning calorimetry, thermogravimetry, and infrared spectroscopy. Besides reporting primary results, correlations and possible consequences for practice are also discussed in the final section of the paper.

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 and 2.16 kg; nominal density: 0.947 g/cm^3) polymerized with a Phillips catalyst. The additive-free polymer powder was provided by the MOL Group Ltd. (Tiszaújváros, Hungary). The commercial hindered phenolic antioxidant used as reference was Irganox 1010 (I, BASF, Ludwigshafen, Germany), while the industrial secondary antioxidant was a phosphonite-type additive, Hostanox PEPQ (PQ, Clariant, Basel, Switzerland). The natural antioxidant selected for the experiments was quercetin (Q) purchased from Sigma Aldrich (≥95 %, Sigma-Aldrich, St. Louis, MO, US). The experimental phosphine secondary antioxidant (Ph) was synthesized in our laboratories according to the method described earlier [41]. The industrial additive package contained 1000 ppm I and 1000 ppm PQ. Since quercetin proved to be extremely efficient in our former study [33], and the OIT values measured were unpractically long in its presence at 1000 ppm additive content, thus we decided to use it at 500 ppm in this study to bring the measured values of the stabilized polymers to a comparable level. The amount of the secondary, phosphorous antioxidant was always 1000 ppm in the comparative study, while its amount changed between 0 and 1000 in six steps in the experiments aimed at the determination of the effect of concentration on stabilizing efficiency. The chemical structures of the additives are shown in Table 1.

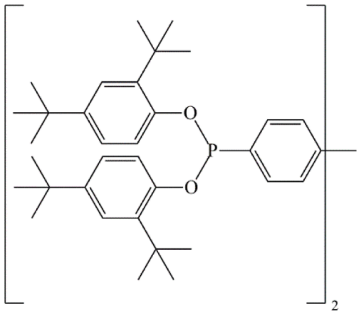
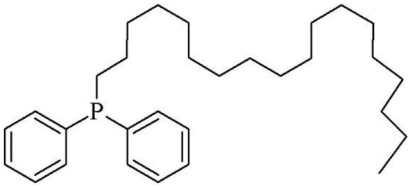
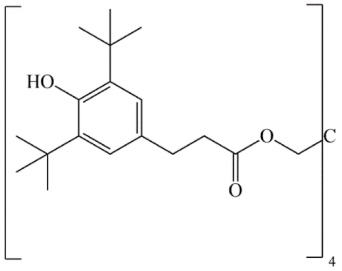
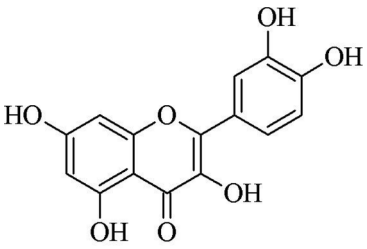
2.2. Sample preparation

The additives were added to the PE powder in the form of ethanol (96 %) solution to provide uniform distribution. The polymer and the additives were mixed in a Henschel FM/A10 high-speed mixer (Thyssen Henschel, Kassel, Germany) at the rate of 1000 rpm for 10 min. The ethanol was evaporated overnight. The dry mixture was processed and pelletized in six consecutive extrusion steps at 50 rpm and the barrel temperatures of 180, 220, 260 and 260 °C using a Rheomex S ¾" (Haake, Saddle Brook, NJ, USA) type single screw extruder attached to a Haake Rheocord EU 10 V (Haake, Saddle Brook, NJ, USA) driving unit. Samples were taken after each step. Films of about 100 μm thickness were prepared by compression molding at 190 °C and 5 min (3 min preheating and 2 min compression time) using a Fontijne SRA 100 (Vlaardingen, The Netherlands) machine for some of the measurements.

2.3. Characterization, measurements

The concentration of the unsaturated functional group content of polyethylene was determined by Fourier-transform infrared spectroscopy (FTIR) on the 100 μm thick compression molded films in transmission mode using a Tensor 27 (Bruker Optik GmbH, Leipzig, Germany) spectrophotometer. Five parallel measurements were carried out on each sample between 4000 and 400 cm^{-1} at 2 cm^{-1} resolution and 16 scans. The concentration of vinyl groups was calculated from the intensity of the absorption peak appearing 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 calculation of the above-mentioned concentrations is described in our earlier publication in detail [43]. FTIR spectroscopy was used to study the possible interactions of the additives as well. The pure additives were dry mixed in a mortar then the mixture was heated up to the melting point of the secondary antioxidant in a round-bottomed flask. An oil bath heated to 80 °C was applied for the melting process. The Attenuated Total Reflectance (ATR) technique was applied to determine the characteristic bands of the additives and their mixture. The Bruker Tensor 27 apparatus mentioned above was used for the measurement. The melt flow rate (MFR) of the polymer was determined according to the ASTM D 1238–79 standard at 190 °C and 2.16 kg load using a Göttfert MPS-D (Buchen, Germany) MFR tester. The measurements were repeated five times in each case. Residual thermo-oxidative stability was characterized by the oxidation induction time (OIT) using a Perkin Elmer DSC 8500 (Norwalk, CT, USA) apparatus. The measurements were done in open aluminum pans in oxygen atmosphere at a constant 20 mL/min

Table 1
Chemical structure and some characteristics of the additives used in the study.

Abbreviation	Commercial name (*Producer*)		Chemical structure	Molecular mass (g/mol)
PQ	Sandostab PEPQ (*Clariant*)	diphosphonite >70 %		1035
Ph	Natural-based phosphine [41]	~100 %		439
I	Irganox 1010 (*BASF*)	~100 %		1178
Q	Quercetin *(Sigma-Aldrich)*	~95 %		302

flow rate and 210 °C in triplicates. The interaction of the additives was studied also by thermogravimetric analysis. The two additives in question were mixed in equal amounts and then placed into the TGA pans. The samples were heated up to 260 °C at the rate of 50 °C/min and then kept at that temperature for 10 min. A Hunterlab ColorQuest 45/0 (Reston, VA, USA) apparatus was used for the determination of the yellowness index (YI), of the polymer samples in triplicates.

3. Results and discussion

The results are presented in several sections. First, the package consisting of the natural-based components is compared to the one representing industrial practice. The effect of the concentration of the newly developed phosphine secondary antioxidant on the efficiency of the stabilizer package is discussed next, followed by the analysis of the interactions between various additive pairs. Correlations, or the lack of them, are presented in the final section of the paper together with the discussion of consequences for practice.

3.1. Additive combinations, comparison

The main degradation reaction of the Phillips-type polyethylene used in this study is the addition of radicals onto the vinyl group located at one end of the chains, leading to long chain branching. The reaction results in the decrease of the vinyl group content of the polymer, the increase of molecular weight, and thus the decrease of the melt flow rate of the polymer. Changes in the vinyl group content of the polymer during multiple extrusions are presented in Fig. 1.

The number of vinyl groups decreases rather steeply with increasing number of extrusions for the industrial package (I/PQ), indicating the occurrence of a considerable number of branching reactions. In the presence of the natural antioxidant, quercetin, and for the combination of the newly developed phosphine and quercetin (Q/Ph) the change in vinyl content is much less pronounced indicating a smaller number of reactions of the vinyl groups. It is worth noting, however, that after the first extrusion, the vinyl group content of the polymer is much smaller for the three polymers prepared with quercetin than for the I/PQ combination. It has been shown earlier that a considerable number of reactions take place during the first extrusion of the polymer, most of which are different from those occurring in subsequent extrusion steps [43]. The large decrease in vinyl content in the first processing step forecasts a considerable number of long-chain branches and a large decrease in MFR.

The dependence of melt flow rate on processing history is presented

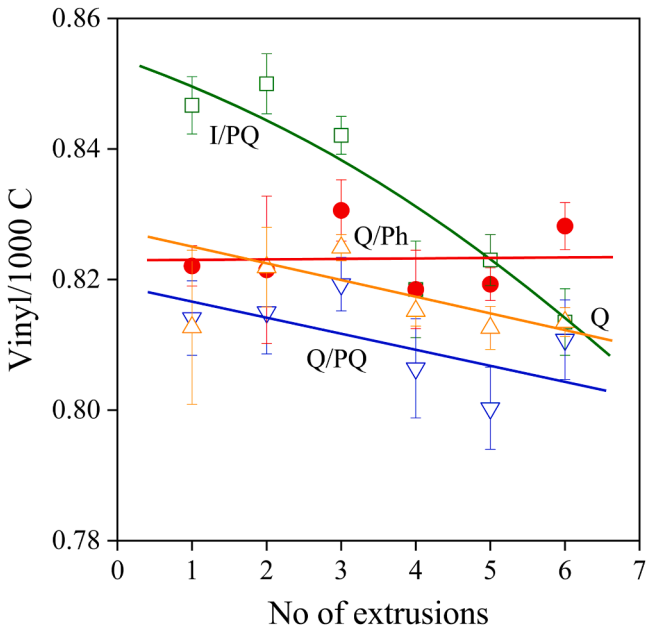


Fig. 1. Dependence of the vinyl group content of Phillips polyethylene on the number of extrusions. Symbols: (●) quercetin/phosphine (Q/Ph), (□) Irganox 1010/Hostanox PEPQ (I/PQ), (▼) quercetin/Hostanox PEPQ (Q/PQ), (△) quercetin (Q).

in Fig. 2. All three additive combinations, as well as quercetin alone, are very efficient in protecting the polymer during processing; MFR practically does not change with an increasing number of extrusion steps. Both phosphorus secondary antioxidants boost the efficiency of the package and contribute significantly to processing stability. In accordance with its smaller vinyl group content, the MFR of the polymer containing only quercetin is smaller than that of the other three polyethylene compounds, as predicted above. However, closer scrutiny reveals that in spite of the expectations, the MFR of the other two polymers containing quercetin is large, in fact, larger than for the industrial package. The largest MFR values were measured for the combination of quercetin and phosphine stabilizer (Q/Ph) showing the considerable efficiency of this package. This obviously contradicts earlier observations, which showed a close correlation between the vinyl content of the polymer and MFR [43,44], and thus, the phenomenon needs further consideration.

The residual stability of the polymer is important in certain, long-term applications. The OIT, the time indicating the start of the oxidation process and the complete consumption of the stabilizers, of the PE compounds is plotted against the number of processing steps in Fig. 3. The commercial additive package renders the polymer adequate stability corresponding to industrial standards even at the very high temperature of 210 °C used in the test. The stability of the other three materials, including the one containing only the natural antioxidant, is larger. The natural-based additive package seems to be especially advantageous in attaining 60–80 min residual stability. We must call attention here to the fact that these packages contained only 500 ppm quercetin compared to the 1000 ppm Irganox 1010 in the industrial package. It is also worth noting that the stability of the polymer does not decrease but increases or exhibits a maximum as a function of processing history. The increase and the maximum must be the result of the limited solubility of the natural antioxidant in polyethylene and the increase of homogeneity with an increasing number of extrusion steps [45].

A definite drawback of natural antioxidants is that they usually discolor the polymer quite strongly. Even when the antioxidant itself is colorless or has a slight whitish color, its reaction products forming during processing give the polymer a strong brown color [44]. The reason for the strong color is the conjugated electron system being present inherently in the antioxidant molecule or developing during the stabilization process. The yellowness index of the four polyethylene compounds compared is plotted against the number of extrusion steps in Fig. 4. As predicted, all three compounds containing quercetin have a very strong color, especially if we compare it to the yellowness index of the polymer prepared with the Irganox 1010/Hostanox PEPQ additive combination. Although the strong color hinders the use of the natural additive package in certain applications, many colored or black products are applied in practice, including, for example, gas pipes.

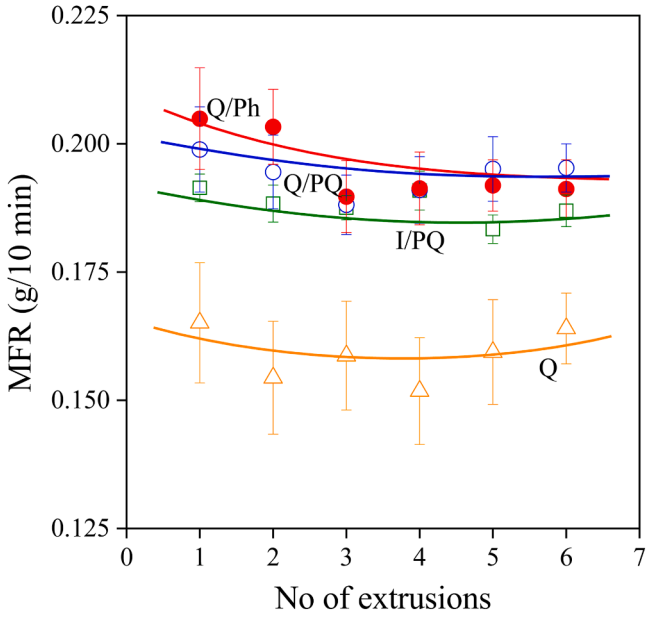


Fig. 2. Effect of processing history and the stabilizer package on the melt flow rate of PE. Symbols: (●) Q/Ph, (□) I/PQ, (▼) Q/PQ, (△) Q.

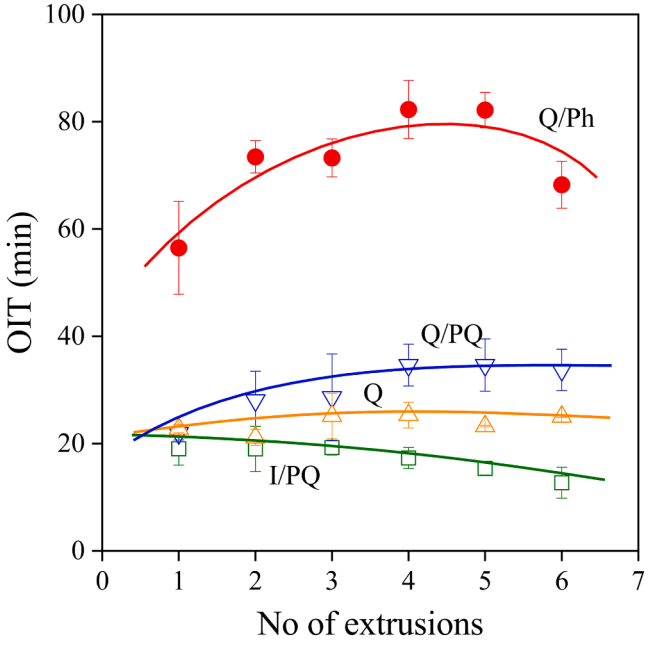


Fig. 3. Residual stability (OIT) plotted against the number of extrusion steps for polyethylenes containing various stabilizer packages. Symbols: (●) Q/Ph, (□) I/PQ, (▼) Q/PQ, (△) Q.

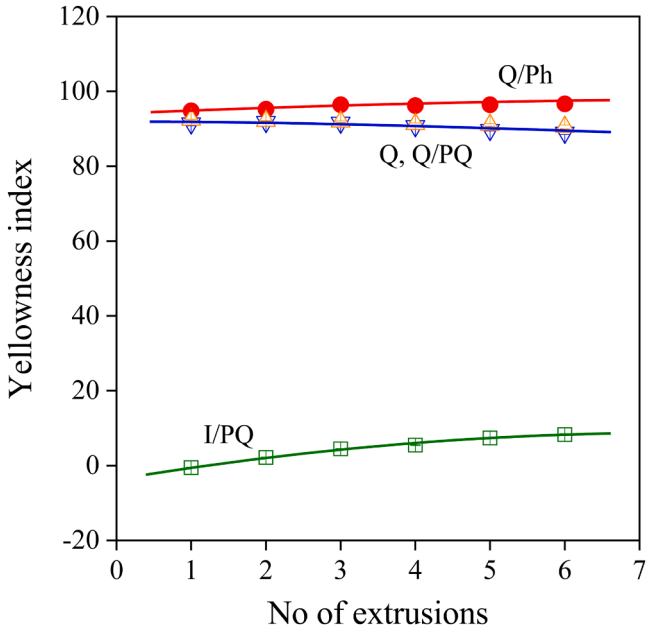


Fig. 4. Strong discoloration effect of the natural antioxidant (Q) during the multiple processing of PE. Symbols: (●) Q/Ph, (□) I/PQ, (▾) Q/PQ, (△) Q.

3.2. Concentration effects

The practical application of any stabilizer requires the optimization of its amount in the additive package. Since the bio-based phosphorus antioxidant was newly synthesized, we do not have any idea about the effect of its concentration in the package or the necessary amount for efficient stabilization. We refrain from the presentation of all available results here in order to save space, and show only the most important ones. The effect of phosphine content on the MFR of the PE prepared with the Q/Ph combination is presented in Fig. 5. MFR increases with an increasing amount of the secondary stabilizer, but only slightly since quercetin is a very efficient stabilizer in itself, as shown earlier. Because of the efficiency of the package, the difference in the MFR of the polymer processed once or six times is quite small. According to the results, 4–500 ppm phosphine is sufficient to achieve adequate processing stability with the Q/Ph combination. This means a smaller amount of additive, which is a considerable advantage compared to the industrial package. We may also conclude that the new phosphine stabilizer is more efficient than the currently used phosphite or phosphonite secondary stabilizers. The results also indicate that the combination of the two natural-based stabilizers is extremely efficient, they might even show a synergistic effect.

Quercetin proved to be very efficient in increasing the residual stability of the polymer, especially in the presence of the bio-based phosphine stabilizer. The effect of phosphine concentration on OIT is presented in Fig. 6. Stability is plotted after the first and sixth extrusions. Stability increases strongly with increasing phosphine concentration indicating that the phosphorous compound also contributes to stabilization, to residual stability. Occasionally it is claimed in the literature that residual stability depends only on the amount of the active phenolic antioxidant [1] but according to the results this is not the case for the combination of the two natural antioxidants used hinting again to synergy. OIT values are similar after the first and the sixth extrusions; they do not decrease during consecutive extrusions, probably because of the considerable efficiency of the package.

3.3. Mechanism, interactions

The results obtained on the bio-based additive package and presented above show some deviation from the general behavior observed in the case of traditional, industrial additive packages. The small vinyl content of the polymer after the first extrusion for polymers containing quercetin not accompanied by small MFR is unusual as well as the strong effect of the phosphine stabilizer on OIT. These results indicate different stabilization mechanisms or the interaction of the components. This latter is further confirmed by the changes in the residual PEPQ content of the polymer. This latter quantity is plotted in Fig. 7 as a function of the number of extrusions for two packages, the one containing Irganox 1010 and PEPQ and the other containing quercetin and PEPQ. The residual P (III) content of PEPQ decreases gradually in the first case but assumes a very small value already after the first extrusion in the second. The antagonistic interaction of a non-hindered natural polyphenol,

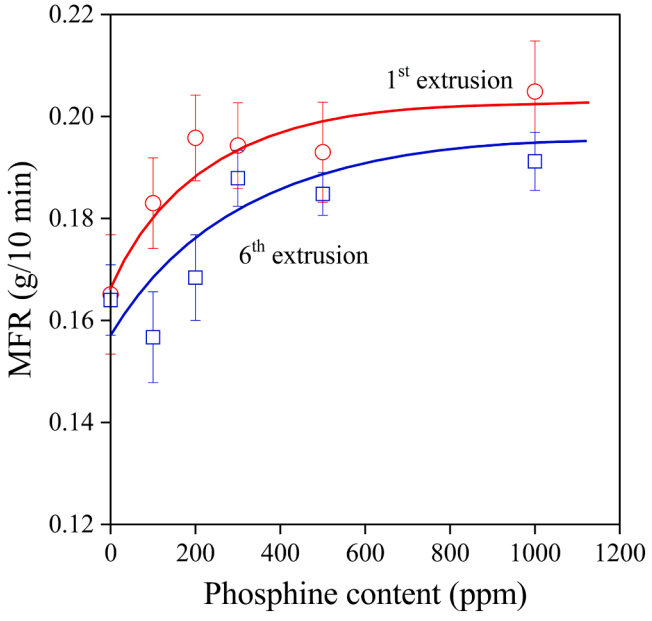


Fig. 5. Effect of the amount of the phosphine secondary stabilizer in the package on the melt flow rate of PE. Symbols: (○) 1st extrusion, (□) 6th extrusion.

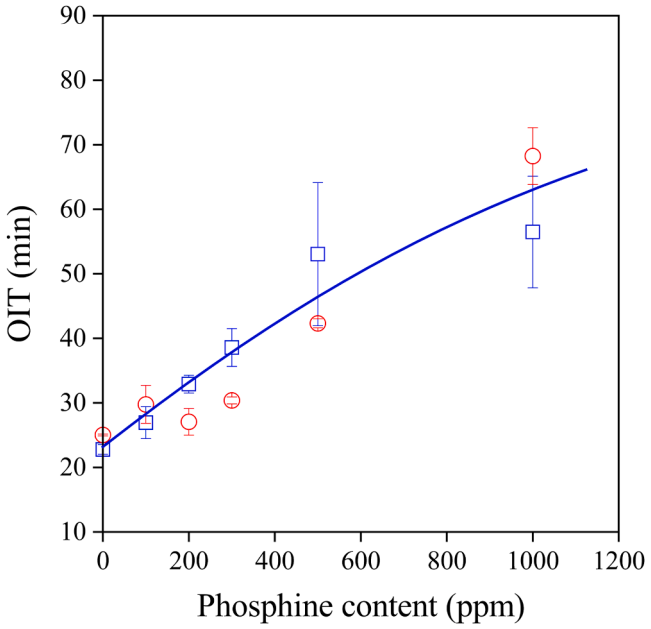


Fig. 6. Residual stability of PE plotted as a function of the phosphine content of the package. Symbols: (○) 1st extrusion, (□) 6th extrusion.

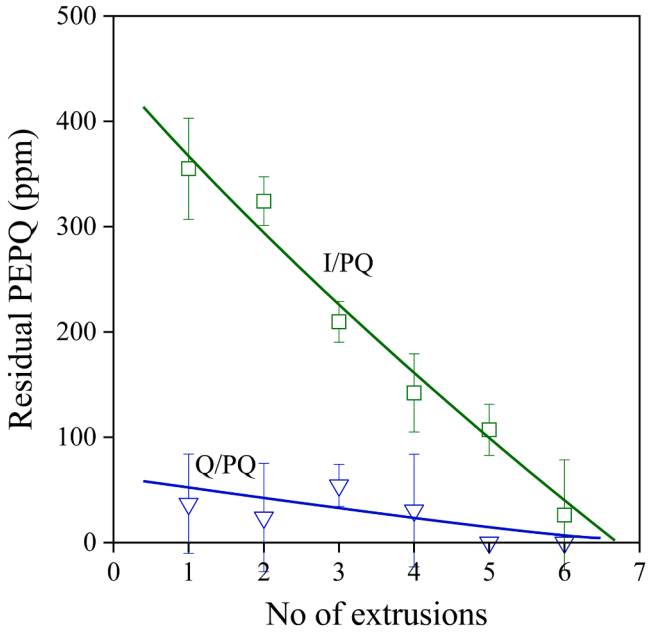


Fig. 7. Dependence of the residual P(III) content of polyethylene on the number of extrusions and on the chemical structure of the primary antioxidant. Symbols: (□) I/PQ, (▼) Q/PQ.

resveratrol, with PEPQ was shown earlier [42], and this may also occur here, in the case of quercetin. Resveratrol was shown to initiate the decomposition of the phosphonite (PEPQ). Similarly, in the present case the radical forming during decomposition may react with the vinyl groups of the polyethylene chains. This sequence of reactions may explain the loss of PEPQ, the small vinyl content, and the unexpectedly large MFR. Naturally, this tentative explanation needs further study and proof.

Thermal analysis further corroborated the interaction of the two stabilizers, quercetin, and PEPQ. The results of TGA measurements are presented in Fig. 8. Samples were heated rapidly up to 260 °C and held there for 10 min to check the stability of the components and that of the mixture of stabilizers. The primary antioxidants, I1010 and quercetin, are quite stable and the stability of PEPQ is only slightly smaller. More interesting is the behavior of the two mixtures. While the I/PQ combination is quite stable and its stability is located between that of its two components, the Q/PQ blend degrades very fast, and approximately 40 % of the material is lost in 10 min. In view of the results presented in Fig. 7, quercetin obviously initiates the decomposition of the phosphonite stabilizer leading to the loss of its activity. Similarly to the case of resveratrol, also quercetin enters into antagonistic interaction with PEPQ.

Contrary to the case presented above, the interaction of the natural antioxidant with the newly synthesized phosphine stabilizer results in a synergistic effect, in the improvement of the stability of the phosphine. TGA traces of the two components and the Q/Ph combination are presented in Fig. 9. The experiments were carried out in the same way as above. The inherent stability of the phosphine is relatively small, >80 % of the material decomposes in 10 min. The presence of quercetin, on the other hand, improves the stability of the secondary antioxidant considerably; only a few percent is lost during the same length of time because of the positive interaction of the two additives. The interaction of the two components is further corroborated by FTIR spectroscopy. As Fig. 10 shows, the characteristic vibrations of both components related to the absorption of mono- and trisubstituted aromatic rings [46] shift upon their blending (see the wavenumber range 750–650 cm^{-1}). The synergistic interaction of the two stabilizers results in the large efficiency in melt stabilization and in the exceptional residual stability of PE containing this package.

3.4. Discussion, correlations

The results presented in the previous sections indicate that the primary and secondary stabilizers interact with each other. The interactions can be synergistic or antagonistic, depending on the structure of the components. The unhindered phenolic structure of the natural antioxidant, quercetin, induces the decomposition of the phosphonite stabilizer while it enters into a strong positive interaction with the phosphine not containing P(III)O groups. These interactions result in

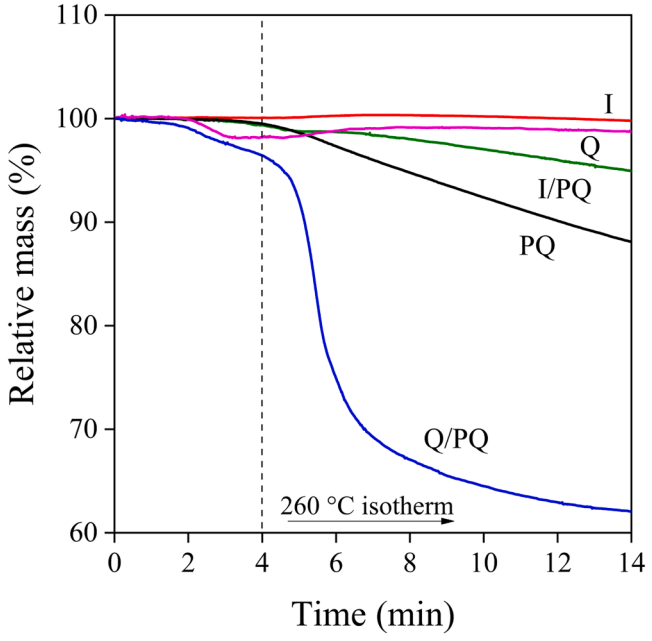


Fig. 8. Thermal stability of some of the stabilizers and their mixture. The TGA measurements were carried out in oxygen atmosphere. Negative influence of quercetin on phosphonite (PQ) stability.

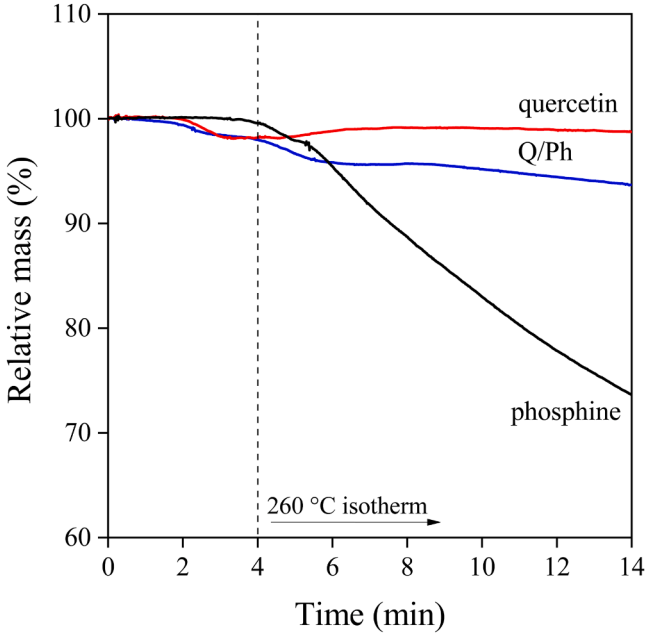


Fig. 9. Decomposition of quercetin, phosphine, and their combination during the TGA measurement carried out in oxygen atmosphere. The positive effect of quercetin on phosphine (Ph) decomposition.

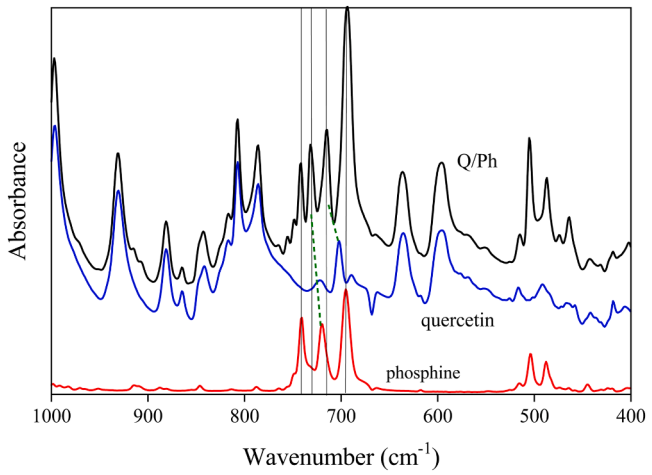
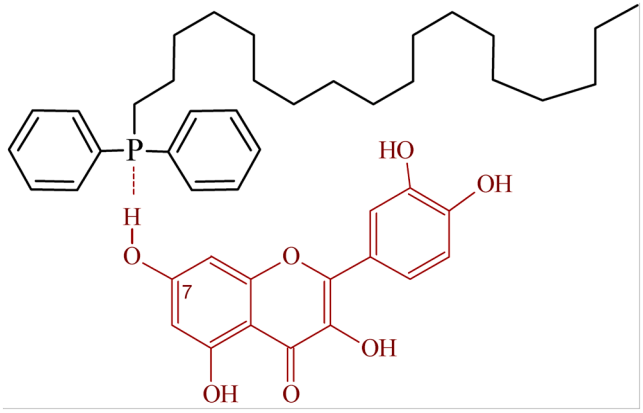


Fig. 10. Shift in the characteristic absorption bands of the primary (Q) and secondary (Ph) stabilizers due to their interaction.

different reactions and possibly dissimilar mechanism of stabilization. The possible way of interaction is the formation of a H-bond as shown in Scheme 1. The phosphorus atom in diaryl-alkyl-phosphines has a lone pair of electrons, making it a good hydrogen bond acceptor. It is especially true in the present case when the attaching groups at the phosphorus atom are electron-donating ones. The hydroxyl group (O-H) in phenols is a hydrogen donor, i.e. it gives a hydrogen atom to form a hydrogen bond. In quercetin, the most acidic OH group is located at position 7, (indicated in Scheme 1), thus it forms the most probably the H-bond [47,48] resulting in the increased stability of the phosphine and the reduction of its decomposition rate during the isotherm stage of the DSC experiment (Fig. 9). The interaction also has a positive effect for stabilization at the high temperatures of processing. It may reduce the reaction rate of molecular oxygen and the phosphine antioxidant, delaying its consumption during the OIT measurement thus improving residual stability (Fig. 6).

The unusual behavior of the quercetin/phosphine combination is further supported by Fig. 11, showing the correlation between the vinyl group content of the polymer and its melt flow rate. Earlier, this correlation was shown to be unambiguous and very close [43,44]. No correlation can be found between the two quantities in this case. The lack of correlation may have several reasons. One is definitely the narrow range of both variables; usually, the characteristics of the neat polymer and the one containing only the secondary antioxidant are also plotted, extending the range of the two quantities considerably. However, the narrow range alone does not explain the lack of correlation, the



Scheme 1. Possible hydrogen-bond interaction between the natural-based phosphine and quercetin.

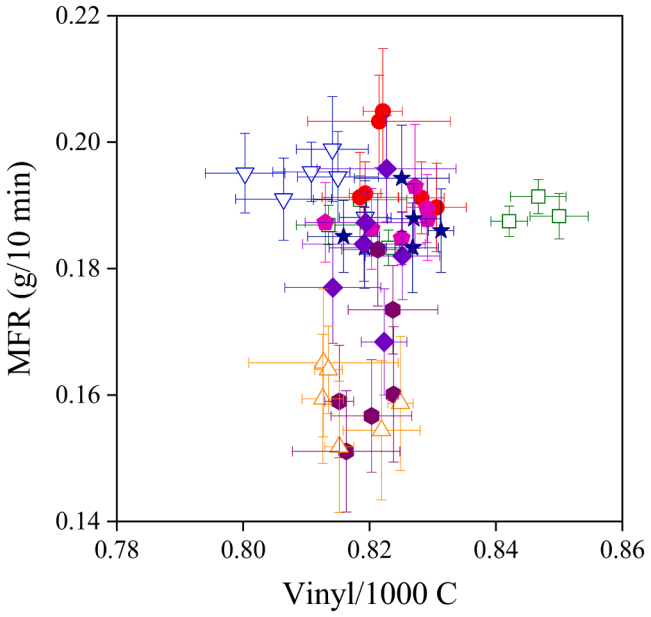


Fig. 11. Lack of correlation between the vinyl group content of polyethylene and its melt flow rate. Symbols: (□) I/PQ, (▼) Q/PQ, (△) Q, (●); Ph content: 100 ppm, (◆) 200 ppm, (⬟) 300 ppm, (★) 500 ppm, (⬤) 1000 ppm.

interactions and the additional reactions of the vinyl groups also contribute. Nevertheless, Fig. 11 allows the drawing of two conclusions. The presence of the phosphorous antioxidant positively influences the melt stability of the polymer irrespective of its type or chemical structure. We can also establish that at least 300 ppm phosphine is necessary to exert its beneficial effect, but above this concentration, the improvement is not very significant.

The comparison of the effect of the additive package with high bio-based material content proved that the use of such an additive combination has several benefits. Besides the environmental advantages, the combination allows the use of fewer amount of additives compared to the currently used industrial packages because of its extreme efficiency. The natural additive package offers very good melt stability and exceptional residual stability. The positive interaction of the components is a further advantage. The main drawbacks of natural antioxidants are their limited solubility and their negative effect on color. The effect and efficiency of the additive package can be further optimized and the mechanism of stabilization should be analyzed more in detail. The tentative explanations offered above must be confirmed in the future in order to utilize the advantages of the stabilizer combination fully.

4. Conclusions

The comparison of the additive package based on a natural antioxidant and a new phosphine-type secondary antioxidant containing some natural material content showed that the bio-based package offers many advantages compared to currently used industrial ones. The new package is more efficient than its commercial counterpart is; better stabilization efficiency is achieved at smaller additive content. The natural antioxidant used, quercetin, interacts with the secondary stabilizer. The interaction can be positive or negative; quercetin initiates the decomposition of the phosphonite stabilizer containing P(III)O bonds, while increase the inherent stability of the phosphine. The interactions result in additional reactions of the vinyl groups of the polymer; besides long chain branching, competitive reactions take place, which consume vinyl groups but do not increase viscosity. The new stabilizer package offers excellent melt stability and exceptional residual stability for the Phillips polyethylene used in this study. The main drawback of the package is the

limited solubility of quercetin in polyethylene and the strong color of the processed material. In spite of the drawbacks, the natural-based additive combination has strong potential for practical use.

CRediT authorship contribution statement

Medárd Koncz: Visualization, Investigation. **Dóra Plachi:** Visualization, Investigation. **Kata Takács:** Investigation. **Péter Huszthy:** Investigation. **Dóra Tátraaljai:** Writing – original draft, Supervision, Resources, Methodology, Conceptualization. **Béla Pukánszky:** Writing – review & editing, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Dóra Tátraaljai reports that financial support was provided by the Hungarian Academy of Sciences. Medárd Koncz reports that financial support was provided by the National Research Development and Innovation Fund of the Ministry of Culture and Innovation, Hungary. Kata Takács reports that financial support was provided by the National Research Development and Innovation Fund of the Ministry of Culture and Innovation, Hungary. The other authors, declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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