

Stabilization of PE with the natural antioxidant *t*-resveratrol: Interaction of the primary and the secondary antioxidant

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ARTICLE INFO

Keywords:

Natural antioxidant
t-resveratrol
Viscosity
Processing stabilization
Residual stability
Color
Component interactions

ABSTRACT

The study focuses on the possibility of using resveratrol, a stilbenoid-type natural antioxidant, as a stabilizer in polyethylene. The experiments were carried out in two stages. First, the efficiency of the natural antioxidant was compared to that of a commercial product, and then polymer properties were determined as a function of additive content. Stabilization efficiency was determined by multiple extrusion experiments. Resveratrol proved a very efficient stabilizer, more efficient than the commercial hindered phenolic antioxidant. Resveratrol provides excellent processing stability and the residual stability of PE containing it is exceptional. Because of its large efficiency, 400–500 ppm additive is sufficient to achieve adequate stability for practice. Resveratrol interacts with the secondary phosphorous stabilizer used in the study, and the effect is antagonistic; resveratrol performs better alone than in combination with PEPQ. Accordingly, this unusual effect must be taken into account during formulation and the construction of the actual additive package. Resveratrol is used in other industries, thus it is available in large quantities and relatively cheap. Besides its advantages, the natural antioxidant has some drawbacks, like its high melting temperature, limited solubility in polyethylene, and strong color of its reaction products. Nevertheless, resveratrol has great potential as a stabilizer in certain products.

1. Introduction

Although plastics are severely criticized for being responsible for pollution and their negative environmental impact, plastic production and use do not abate and reached almost 460 Mt in 2019 [1]. In spite of the fact that the European Union has imposed severe restrictions on single-use plastic products [2], these materials play an important role in our lives and must be handled properly. Plastics are subjected to shear, heat, and oxygen during their transformation into products and also their use leading to the deterioration of their properties [3]. Accordingly, plastics must be protected against such changes, i.e. degradation, by stabilization [4]. The legal measures mentioned above increase the importance of stabilization further; multiple reprocessing and recycling of plastics is impossible without the severe deterioration of the material [5]. Stabilization is a mature technology now, and stabilizer packages usually contain a synthetic phenolic antioxidant and a secondary stabilizer, mostly a phosphorous or sulfur-containing compound [6].

However, traditional stabilizers raised some health and environmental concerns some time ago [7,8], and simultaneously the interest in raw materials from natural resources increases continuously. Accordingly, more and more information is available on the use of natural compounds as stabilizers also in plastics [9–16].

Polyolefins degrade by oxidation through radical chain reactions [3, 5,17]. These can be hindered by antioxidants produced by nature in very large numbers. A wide variety of compounds possess antioxidant effects, including lignans, phenolic acids, flavonoids, and stilbenes [18]. Many attempts have been made to use various forms of lignin as a stabilizer in polymers, and reports usually claim large efficiency [19–23], but the small specific phenolic hydroxyl group content and the complete immiscibility of lignin with polymers make its application as stabilizer impractical [24]. Flavonoids, on the other hand, proved very efficient stabilizers in polyolefins, but also in other polymers [25]. Quercetin [26], dihydromyricetin [27], and rutin [28] were all shown as efficient stabilizers, even better than Irganox 1010, the synthetic phenolic

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<https://doi.org/10.1016/j.polymdegradstab.2024.111046>

Received 30 July 2024; Received in revised form 11 September 2024; Accepted 18 October 2024

Available online 19 October 2024

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Table 1

Characteristics of the stabilizers used in the study.

Abbreviation	Commercial name (Producer)	Chemical structure	Molecular mass (g mol ⁻¹)
PEPQ	Sandostab PEPQ (Clariant)	diphosphonite >70 %	1035
		mono-phosphonite ~20 %	595
		phosphite <10 %	647
I1010	Irganox 1010 (BASF)	~100 %	1178
res	<i>t</i> -resveratrol	~100 %	228

antioxidant used currently in the largest quantity in the industry. Besides neat compounds, natural extracts containing considerable amounts of various antioxidants also proved efficient processing stabilizers, although the residual stability of the polymer containing them remained small [29,30]. Some of the natural antioxidants mentioned, as well as the extracts, have several drawbacks; thus, the search for new and efficient natural compounds continues.

Trans-resveratrol, *trans*-3,5,4'-trihydroxy stilbene, is a very efficient antioxidant. It has two isomers, but *trans*-resveratrol has considerable biological effects. It is a radical scavenger studied also as an anti-tumor agent in health care, and it proved to be efficient in all stages of carcinogenesis [31]. Moreover, it might influence cell apoptosis, and proliferation and may have anti-inflammatory effect as well [32–35]. It is used as an additive in packaging films [36], and as an antioxidant in various food products or as supplementary nutrition [37]. It was applied as a reference antioxidant in different polymeric systems and found to be an effective stabilizer [38]. We also used *trans*-resveratrol as a kind of reference material in one of our previous studies [30], and the results

encouraged us to continue research with this natural antioxidant at a greater depth.

As mentioned above, industrial additive packages usually contain a phenolic antioxidant and a secondary stabilizer. The role of the first is to scavenge radicals, while that of the second is to decompose hydroperoxides [39]. The two antioxidants protect each other and often have synergistic effects. Synergism is assumed practically always but never investigated. However, occasionally negative interaction of the components of a plastic product may also occur, like the interaction of the calcium stearate acid scavenger with sorbitol clarifiers or the adsorption of stabilizers on the surface of pigments [40]. The combination of a phosphorous secondary stabilizer with various natural antioxidants was beneficial in most cases, but occasionally, the effect was small [24]. An antagonistic effect has never been observed but cannot be excluded.

Red grapes, especially their skin and seed, contain a relatively large amount of resveratrol [41]. Hungary produces a considerable amount of such grapes every year [42]. Considering the positive antioxidant effect of resveratrol reported in the literature [33] and experienced earlier

[30], it seems obvious that its stabilizing efficiency should be investigated in more depth. First, a comparative study was carried out to check its stabilizing efficiency relative to Irganox 1010 (I1010), the commercial hindered phenolic antioxidant currently used in one of the largest quantities, and then the effect of resveratrol on polymer properties was studied as a function of additive content. Changes in the chemical structure of the polymer, processing, and residual stability, as well as color, were determined by routine techniques in multiple extrusion experiments. All additive packages contained a phosphonite secondary stabilizer as well. The first results indicated the negative interaction of resveratrol and the phosphonite; thus, the phenomenon was investigated in more detail and reported in one of the sections of the paper. General conclusions and relevance for practice are mentioned in the last section.

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/cm³) polymerized with a Phillips catalyst. The additive-free polymer powder was provided by the MOL Group Ltd. (Tiszaújváros, Hungary). The Irganox 1010 hindered phenolic antioxidant (I1010, BASF, Ludwigshafen, Germany) was used as reference, and apart from the neat polymer, all packages also contained a phosphonite-type secondary antioxidant, Sandostab PEPQ (PEPQ, Clariant, Basel, Switzerland). The *trans*-resveratrol (99 %) was purchased from CurEase (McEwen, Tennessee, USA). Acetonitrile, 2-propanol and formic acid used for analysis were purchased from VWR International (Leuven, Belgium) as LC-MS grades. Ultrapure water was prepared in-house by using an ELGA Veolia PURELAB Chorus water purification system (High Wycombe, UK). The chemical structure, composition, and molecular weight of the stabilizers used in the study are listed in Table 1.

2.2. Characterization

The possible crystalline structure of resveratrol was studied by differential scanning calorimetry (DSC). The equipment used was a Perkin Elmer DSC 7 (Norwalk, CT, USA) apparatus. The measurements were performed on 3–5 mg samples, which were heated from 30 to 300 °C at 10 °C/min heating rate in oxygen and nitrogen. X-ray diffraction (XRD) was also applied for the verification of the crystalline structure of *trans*-resveratrol, using a Philips X'Pert apparatus with CuK α radiation at 40 kV and 35 mA anode excitation. XRD traces were recorded between 5 and 50° 2 θ angles. The inherent stability of the stabilizers and that of their mixture was investigated by thermogravimetric analysis (TGA). A Perkin Elmer TGA 6 (Norwalk, CT, USA) apparatus was used for the measurements. Samples of 3–5 mg weight were heated from 30 to 700 °C at 10 °C/min heating rate in nitrogen and oxygen, and an isothermal investigation was also carried out in oxygen atmosphere. The sample was heated up from 30 to 260 °C at 50 °C/min heating rate and held there for 10 min.

The volatile and condensed compounds from the isothermal TGA measurement (oxygen atmosphere) were collected from the cover of the cell. The composition of the condensed material was investigated with a Shimadzu NexeraX2 system (Kyoto, Japan) consisting of two LC-30AD pumps, a DGU-20A5R degassing unit, a CTO-20AC column oven, a SIL-30AC autosampler, a SPD-30A diode array detector with a CBM-20A communication bus module coupled to a Shimadzu LCMS-8060 triple quadrupole tandem mass spectrometer (Kyoto, Japan). 1 μ L of the sample (dissolved in 2-propanol) was injected into the chromatograph equipped with an ACE Ultracore C18 column (2.1 $\times$ 75 mm, 2.5 μ m, Avantor) thermostated at 30 °C. Gradient elution was applied with mobile phases A: 0.1 % formic acid/water and B: 0.1 % formic acid/

acetonitrile at a flow rate of 0.5 mL/min. The initial eluent composition was kept at 10 % of eluent B. Then, a linear gradient from the post-injection time of 1 min was started at 10 % of eluent B reaching 100 % in 7 min. The composition was kept constant for 7 min and then the column was reequilibrated back to the initial eluent. The total runtime was 16 min. The wavelength range of the photodiode array detector was set between 190 and 700 nm. The mass spectrometric parameter settings were as follows: Q1 scan detection mode, atmospheric pressure chemical ionization (APCI) both in the negative and positive mode, interface temperature: 350 °C, desolvation line temperature: 200 °C, interface voltage: 4 kV/–3 kV, nebulizing gas flow: 3 L/min, drying gas flow: L/min.

2.3. Sample preparation

The additives were mixed with the PE powder in a Henschel FM/A10 high-speed mixer (Thyssen, Kassel, Germany) at the rate of 1000 rpm for 10 min. *Trans*-resveratrol was added to the powder in the form of ethanol (96 %) solution to provide uniform distribution. The ethanol was removed by storage at ambient temperature. 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 3/4" (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 μ m thickness were prepared by compression molding for further studies at 190 °C and 5 min (3 min preheating and 2 min compression time) using a Fontijne SRA 100 (Vlaardingen, The Netherlands) machine.

Trans-resveratrol was added to the polymer at 1000 ppm in combination with 1000 ppm Sandostab PEPQ (PEPQ, Clariant, Basel, Switzerland) secondary stabilizer in the comparative study. The effect of 1000 ppm PEPQ alone was also determined for comparison. The polymer was stabilized also by 1000 ppm Irganox 1010 (I1010, BASF, Nienburg/Weser, Germany) in combination with 1000 ppm PEPQ for comparative purposes. The neat polyethylene powder was also investigated as reference. Resveratrol content changed between 0 and 1000 ppm in 8 steps to determine the effect of additive concentration on stability. All packages contained 1000 ppm PEPQ as well.

2.4. Measurements

The concentration of the unsaturated functional groups of polyethylene was determined by Fourier-transform infrared spectroscopy (FTIR) on the 100 μ m 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} wavelengths 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}, while *trans*-vinylene concentration was determined from the absorption band at 965 cm^{–1}. The calculation of the above-mentioned concentrations is described in detail in our earlier publication [29]. 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 7 (Norwalk, CT, USA) apparatus. The measurements were done in open aluminum pans in an oxygen atmosphere at a constant 20 mL/min flow rate and 190 °C in triplicates. 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 discussed in several sections. The characteristics of

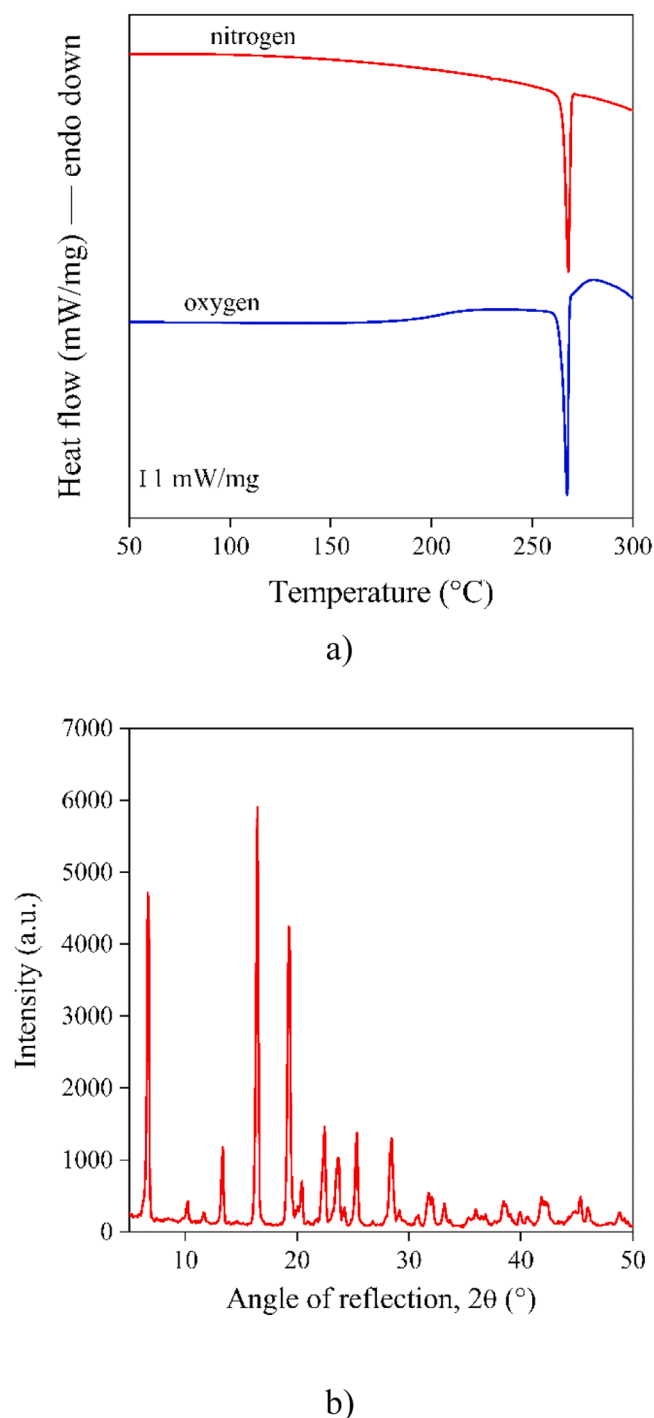


Fig. 1. DSC (a) and XRD (b) traces showing the crystallinity of *t*-resveratrol used as a natural antioxidant in the study.

resveratrol are considered first from the point of view of potential stabilizing effect. The efficiency of the antioxidant is compared to that of I1010 next, followed by the presentation of the influence of antioxidant content on polymer properties. The interaction of the primary and secondary stabilizers is discussed next followed by the presentation of general correlations and the discussion of possible practical relevance.

3.1. Resveratrol characteristics

Many requirements exist for a compound to function as an efficient stabilizer. It must have the proper chemical structure with the necessary

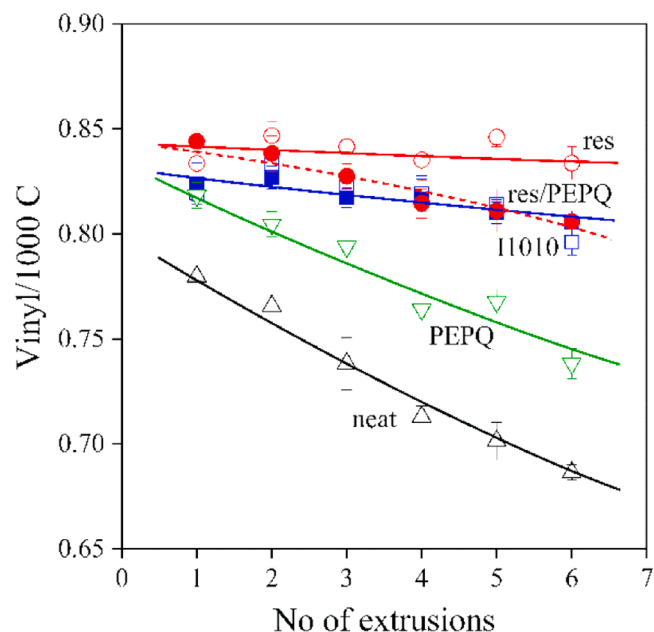


Fig. 2. Vinyl group content of polyethylene containing various additive packages plotted against the number of extrusions. Symbols: (Δ) neat PE, (∇) PEPQ, ($\square$, $\blacksquare$) I1010, ($\circ$, $\bullet$) resveratrol; empty symbol: without PEPQ, full symbol: with PEPQ.

functional groups to trap radicals, but its physical-chemical characteristics should also be within certain limits. Most natural antioxidants are quite polar, small molecular weight compounds, which usually form regular crystals with a high melting point [26]. The same applies to resveratrol, the compound studied here. According to DSC measurements, its melting point is around 270 °C (see Fig. 1a), which is higher than the usual processing temperature of polyethylene. Regular structure and large crystallinity are further corroborated by Fig. 1b, presenting the XRD trace recorded on the resveratrol powder. The amorphous halo is minimal, and the characteristic reflections of the crystals are very sharp confirming the regularity of the structure. The regular crystalline structure and the high melting temperature make homogenization difficult and probably decrease the efficiency of the compound as a stabilizer.

Solubility is another important aspect of stabilizer efficiency. High melting temperature hinders homogenization and dissolution, while the strong polarity of the compound, further limits the solubility of natural antioxidants in polymers; their solubility is usually around 15–30 ppm in PE [24]. The solubility of natural extracts is somewhat better, but still very small [43,44]. A further aspect to consider is the self-stability of the compound in question. Several of the natural antioxidants are found in the form of glycosides in nature [45], a form that has limited thermal stability. Small self-stability has been shown to decrease the efficiency of a natural antioxidant and to limit the possibility of its practical use [28]. Similarly, the double bond in the structure of curcumin makes the compound sensitive to light and limits its application in spite that it is a very efficient thermal stabilizer [46]. At the beginning of the study, we hoped that resveratrol would meet the requirements of a good primary antioxidant, and preliminary results encouraged us to continue the research in this direction.

3.2. Comparison to an industrial product

The primary antioxidant currently used in the largest amount in industrial practice is Irganox 1010. For a new stabilizer to have a chance for industrial application, it must compete with I1010 in both efficiency and price. Resveratrol is used in the food industry, and as a nutrition

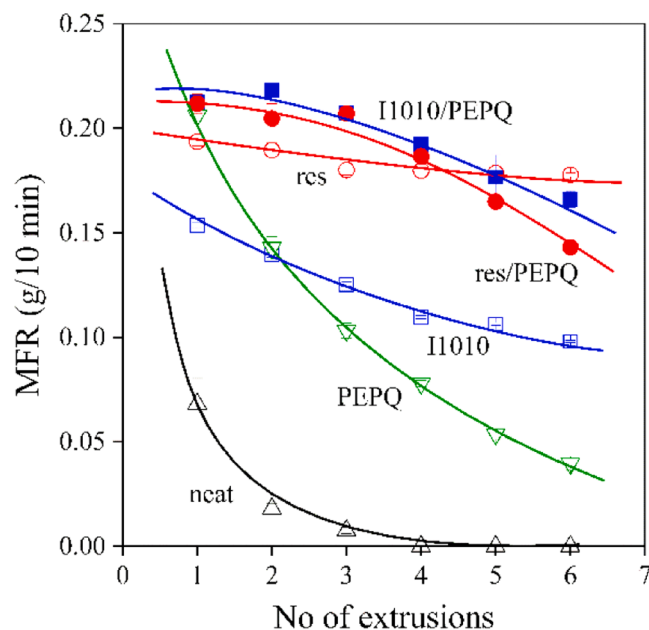


Fig. 3. Changes in the viscosity (MFR) of polyethylene with increasing processing history (number of extrusions). Symbols are the same as in Fig. 2.

supplement; thus, it is available in large quantities. The primary degradation of the polyethylene used in this study is the reaction of the vinyl groups located at one end of each chain. The reaction leads to long chain branching and the increase of molecular weight and viscosity. The efficiency of an antioxidant can be followed by the determination of the number of vinyl groups in the polymer and its change during multiple extrusions. The vinyl group content of PE is plotted against processing history in Fig. 2 for several packages. Empty symbols indicate the additive alone, while full symbols are the combination of the primary antioxidant and the phosphonite secondary stabilizer (PEPQ). The vinyl group content of the neat polymer and the one containing only PEPQ is plotted as reference. The vinyl group content of the neat polymer decreases drastically, and PEPQ cannot protect the polymer sufficiently against degradation either. Both I1010 and resveratrol are very efficient, vinyl group content remains practically constant during the multiple extrusion experiment. In fact, resveratrol alone is significantly more efficient than the commercial stabilizer. What is quite surprising is that the combination of resveratrol and PEPQ performs relatively poorly. Although the initial values are similar for neat resveratrol and the package with PEPQ, the performance of the latter drops relatively rapidly and vinyl content decreases below that of I1010. The secondary antioxidant boosted the performance of the natural antioxidant practically in all previous studies. The effect needs further consideration and study.

Changes in the melt flow rate of PE reflect very sensitively the efficiency of a stabilizer or a stabilizer package. MFR is plotted against the number of extrusions in Fig. 3 for the same compounds as in the previous figure. The performance of the neat polymer and the one containing only PEPQ corresponds to the expectation. I1010 alone does not perform very well, but its combination with PEPQ is quite efficient. Resveratrol is a good processing stabilizer; however, the same phenomenon is observed here as in the case of the vinyl group content of the polymer, i.e. the combination of resveratrol and PEPQ performs well at small number of extrusions but becomes poorer than that of the neat compound at longer processing history. We can establish, though, that resveratrol is a quite good processing stabilizer for polyethylene.

The residual stability of the polymer is important for long-term applications. The oxidation induction time of the packages studied is presented in Fig. 4 as a function of the number of extrusions. The neat

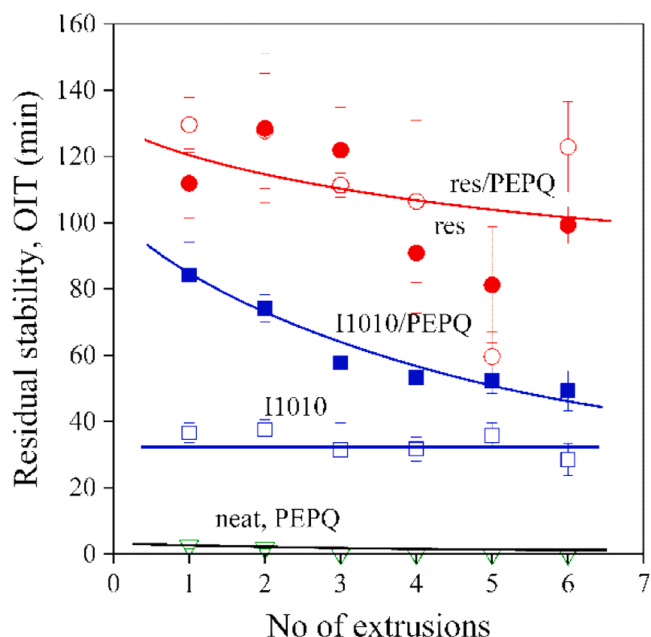


Fig. 4. Effect of the additive package and the number of processing steps on the residual stability (OIT) of PE. Symbols are the same as in Fig. 2.

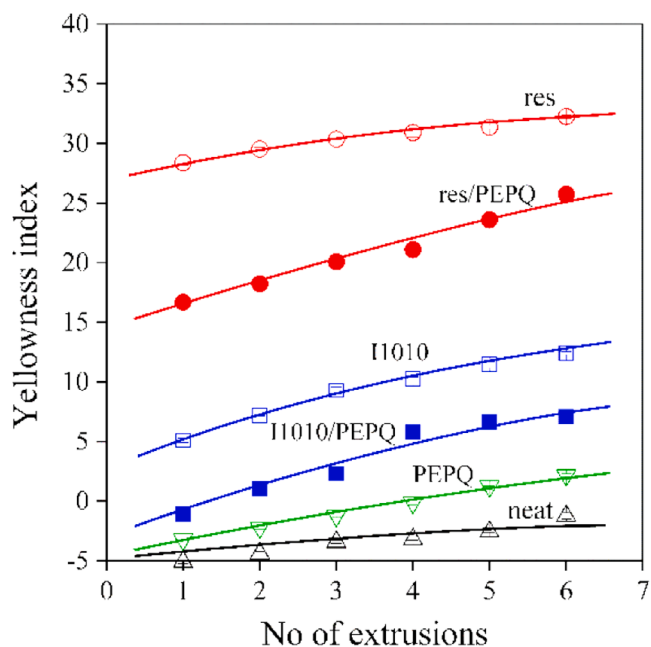


Fig. 5. Dependence of the color of PE on the stabilizer package used and the number of extrusions. Symbols are the same as in Fig. 2.

polymer and the one containing only PEPQ do not have any residual stability at all, as expected. The performance of I1010 is acceptable, and it is further improved by the presence of the phosphonite secondary antioxidant. Resveratrol, on the other, is far more efficient than the commercial stabilizer both with and without PEPQ. The scatter of the points is quite large in the latter case, probably because of the assumed poor solubility and limited homogeneity of the natural compound. Because of the large standard deviation of the measurement, the effect observed earlier, i.e. the negative effect of the secondary stabilizer cannot be identified here.

The major disadvantage of natural antioxidants is that they usually discolor the polymer quite strongly. The yellowness index of PE is

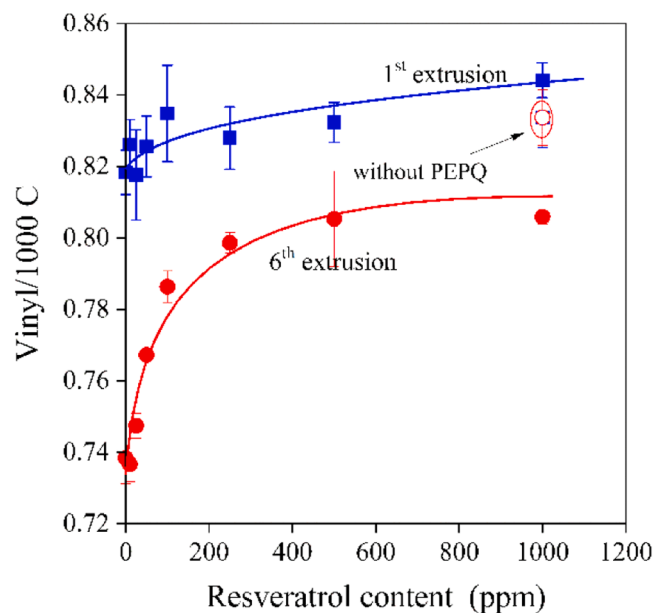


Fig. 6. Effect of resveratrol content on the number of vinyl groups of PE after the first (■) and sixth (●) extrusions. Empty symbols belong to compounds prepared without PEPQ.

plotted against the number of extrusions in Fig. 5. The neat polymer has the slightest color while the one containing resveratrol alone is the strongest. In all probability, a quinoidal structure forms from the compound during stabilization, which colors the polymer [47,48]. The presence of the double bond in the middle of the molecule results in extensive conjugation and strong color. Interestingly, PEPQ hinders discoloration considerably, i.e. it improves the performance of resveratrol and does not deteriorate it as in the case of the rest of the properties. These effects indicate the strong interaction of the primary and secondary antioxidants, which needs further attention, as mentioned above. Nevertheless, the presented results clearly prove that resveratrol is a very efficient stabilizer for PE; its efficiency exceeds that of I1010 considerably, especially in the case of residual stability.

3.3. Concentration dependence

The comparison of the efficiency of resveratrol as a stabilizer with that of a commercial additive showed that it could compete successfully with the latter. The experiments were done at 1000 ppm additive content in the comparative study. Since the stabilizer is very efficient, a small amount might also achieve the desired effect; thus, experiments were carried out as a function of resveratrol content as well. Only the most important characteristics are discussed here in order to save space. The vinyl group content of PE is plotted against additive content in Fig. 6. Vinyl content increases with increasing amount of resveratrol as expected, since the stabilizer protects the polymer and hinders its reaction with radicals. At small additive content, the stabilizer is consumed rapidly and the reaction mentioned above takes place. At larger resveratrol content, a sufficient number of stabilizer molecules are present to prevent all reactions. The effect reaches saturation at around 500 ppm resveratrol content. The effect of the number of extrusions can also be seen in the figure; a longer processing history leads to more reactions and a smaller number of vinyl groups. The series was done with PEPQ, but points for the compounds not containing the secondary stabilizer are also plotted in the figure. As mentioned in the previous section, the presence of PEPQ is disadvantageous at longer processing history.

The dependence of MFR is plotted against composition in Fig. 7. Resveratrol is very efficient even in small amounts; the viscosity of the

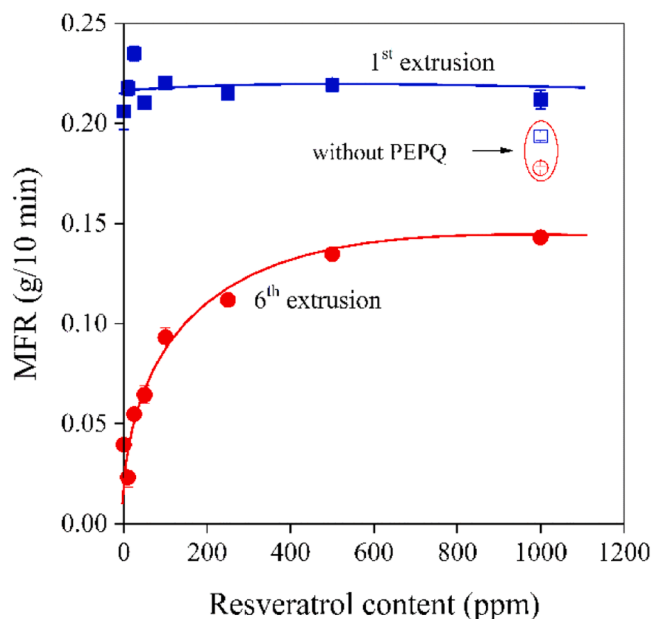


Fig. 7. Dependence of the MFR of PE on the amount of resveratrol added. Symbols are the same as in Fig. 6.

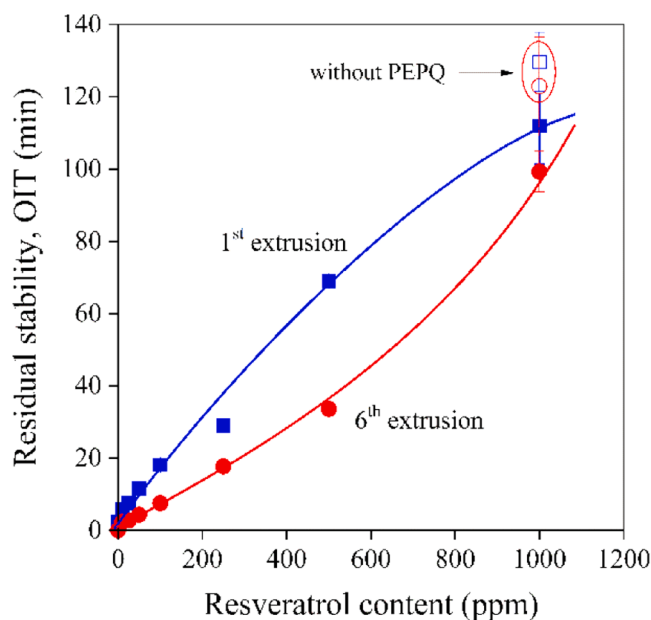
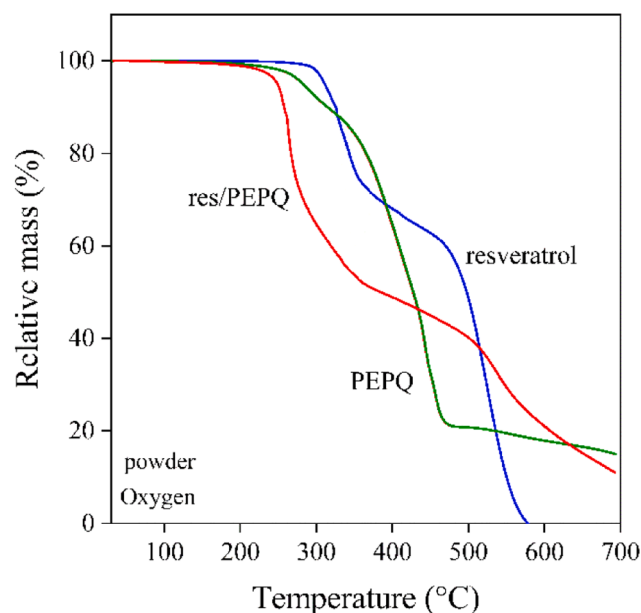


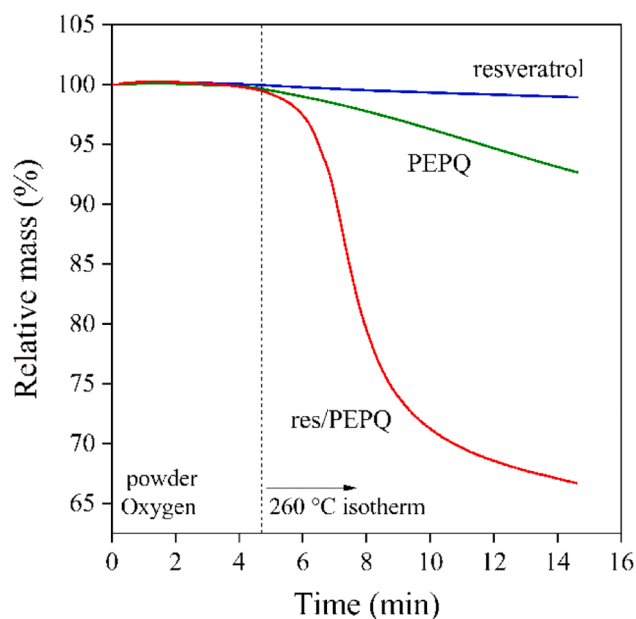
Fig. 8. Residual stability of PE plotted against its resveratrol content. Symbols are the same as in Fig. 6.

polymer does not change practically at all with increasing number of extrusions. 500 ppm resveratrol is sufficient to maintain processing stability even if we assume severe processing loads or multiple recycling steps. That is a clear advantage compared to commercially hindered phenolic antioxidants, which are often used at 1000 ppm or more. The possible interaction of resveratrol and PEPQ is reflected also by the changes in MFR. As shown earlier, the natural antioxidant studied is especially efficient in preserving residual stability. OIT increases more or less linearly with increasing resveratrol content (Fig. 8). Although multiple processing has its effect, 500 ppm additive ensures sufficient residual stability for practical applications.

The results of the experiments carried out as a function of resveratrol content confirmed those obtained in the comparative study. This natural



a)



b)

Fig. 9. Decomposition of resveratrol, PEPQ and their 50:50 wt% mixture; TGA traces recorded (a) at 10 °C/min heating rate, b) isothermally at 260 °C.

antioxidant is obviously very efficient, better than the commercial stabilizer used for comparison. Composition dependence indicates that less stabilizer is enough for an efficient package used in industrial practice and the optimum package can be developed using the results generated in this study. All results indicate unambiguously that the two antioxidants strongly interact with each other during processing, and the interaction is not beneficial, in fact, outright antagonistic, a phenomenon needing further considerations.

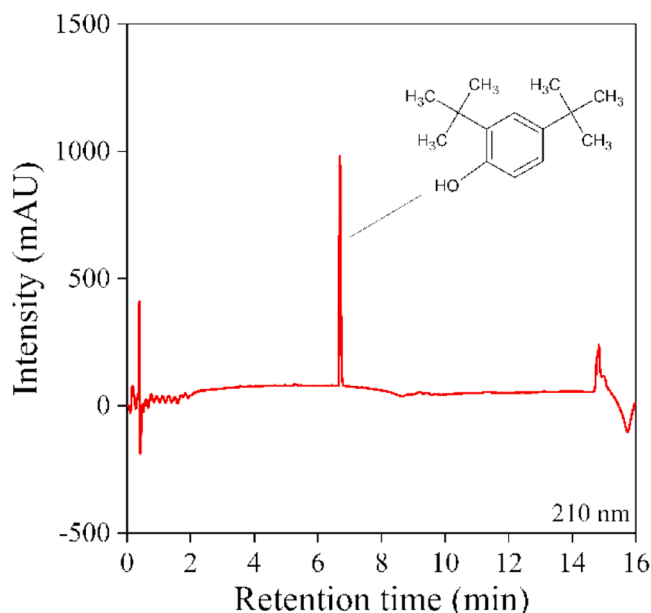


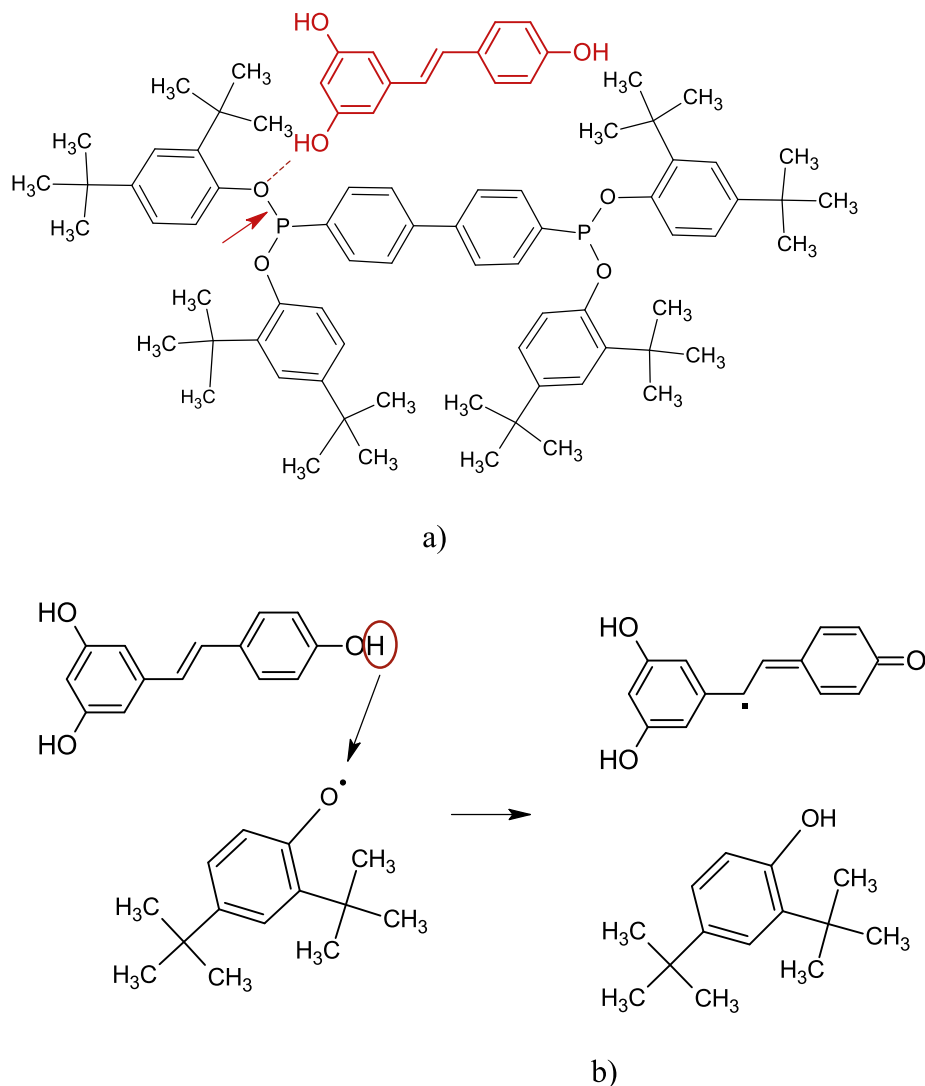
Fig. 10. HPLC chromatogram of the compound recovered from the cover of the TGA cell after heating the resveratrol/PEPQ mixture up to 260 °C.

3.4. Interactions

As a first step in the investigation of possible interactions, the fine powders of the two additives were mixed and studied by TGA analysis. The thermograms recorded on the two components and their mixture are presented in Fig. 9a. The samples were heated from 30 to 700 °C at a heating rate of 10 °C/min. According to the results, resveratrol is stable up to about 300 °C and the neat PEPQ is more stable as well than the mixture. This latter starts to decompose at a lower temperature and decomposition proceeds much faster than in the case of the two individual components. In a further experiment, the same materials were heated fast up to 260 °C, the temperature of multiple extrusions, and then held there for 10 min to model the effect of processing at this high temperature (Fig. 9b). Resveratrol is very stable under the conditions used, and PEPQ decomposes relatively slowly. The mixture of the two compounds, on the other hand, decomposes extremely fast; more than 30 % weight loss was recorded in the time span of the experiment. These results unambiguously support our assumption that the two stabilizers interact with each other, and one accelerates the decomposition of the other.

The white powder corresponding to 30 % weight loss recovered from the cell cover of the TGA apparatus was analyzed by LC-MS/MS in the next step. The chromatogram recorded is presented in Fig. 10, and it shows that a well-defined, uniform material is eliminated from the mixture of the two stabilizers during heating. Its molecular weight is 206 g mol⁻¹, which might correspond to the structure shown in the inset of the figure. A possible explanation for the elimination of this compound is presented in Scheme 1a, showing that resveratrol initiates the cleavage of the P-O bond in PEPQ, resulting in a radical. This radical may abstract a hydrogen atom from resveratrol, having a relatively small bond dissociation energy in the way shown in Scheme 1b. The reaction leads to a quinoidal compound, which discolors the polymer. In all probability, the formed radicals take part in further reactions explaining the fact that discoloration is smaller in the presence of PEPQ than without it. The interaction of the two compounds and the abstraction of the active hydrogen from resveratrol explains also the fact, that resveratrol is more efficient alone than in combination with PEPQ.

The reaction presented in Scheme 1b involves the double bond of resveratrol, which may take part in other reactions as well. The involvement of the *t*-vinylene group in various reactions is confirmed by



Scheme 1. Interactions and reactions leading to the possible antagonistic effect of resveratrol and PEPQ.

the change of its concentration during multiple extrusions (Fig. 11). The much larger concentration of this functional group in PE that contains resveratrol shows that it is located on the stabilizer and not on the polymer. Moreover, the number decreases with increasing number of extrusions, while it increases in all other cases. The decrease is somewhat larger in the presence of PEPQ further corroborating the scheme presented in Scheme 1b. Although the tentative explanation presented above needs further confirmation, it explains plausibly the unusual phenomenon observed, the antagonistic interaction of resveratrol and PEPQ.

4. Discussion

The Irganox 1010 commercial stabilizer is a hindered phenol, the molecules of which do not interact with each other in the melt. The natural antioxidant, resveratrol, used in the study is a stilbenoid compound with three active hydroxyl groups which are not hindered, and such natural antioxidants often lose their efficiency at small additive contents [26] because of self-interactions. In this study, we did not observe such interactions, and the compound proved a very efficient stabilizer for polyethylene, better than the reference compound. On the other hand, because of its strong polarity, its solubility in the polymer is small, leading to heterogeneity showing in the large standard deviation of the OIT measurements.

The most active of the hydroxyls is at the 4'-position. According to Cao et al. [49] it has a bond dissociation energy (BDE) of 352 kJ/mol, which is not the smallest among the natural antioxidants studied up to now [24]; nevertheless, the compound is a very efficient stabilizer, equaling or besting quercetin with a much smaller BDE. Obviously, the double bond located between the two aromatic rings also plays an active role in stabilization proved by our results as well. Since resveratrol is used in the food industry, it is available in large quantities; it might be used successfully for the stabilization of polymers. Its major drawback is its discoloring effect, which might not be tolerated in certain products.

The main degradation step of the Phillips polyethylene used in this study is the reaction of the chain-end vinyl groups with radicals forming during processing and use. The role of the primary antioxidant is to prevent this reaction, leading to chain branching, increased molecular weight, and decreased MFR. The relationship between the reaction of the vinyl groups and viscosity is demonstrated well in Fig. 12, showing the correlation between the two quantities. The close correlation implies that the same radical reactions take place in the presence of resveratrol as in the case of other primary antioxidants including I1010. Interestingly, two correlations can be identified in the plot, one belonging to PE containing the neat stabilizers, resveratrol and I1010, and another, which contains the combination of resveratrol and PEPQ, the phosphorous secondary stabilizer used. The two correlations emphasize the unusual, antagonistic interaction of the two stabilizers, which has not

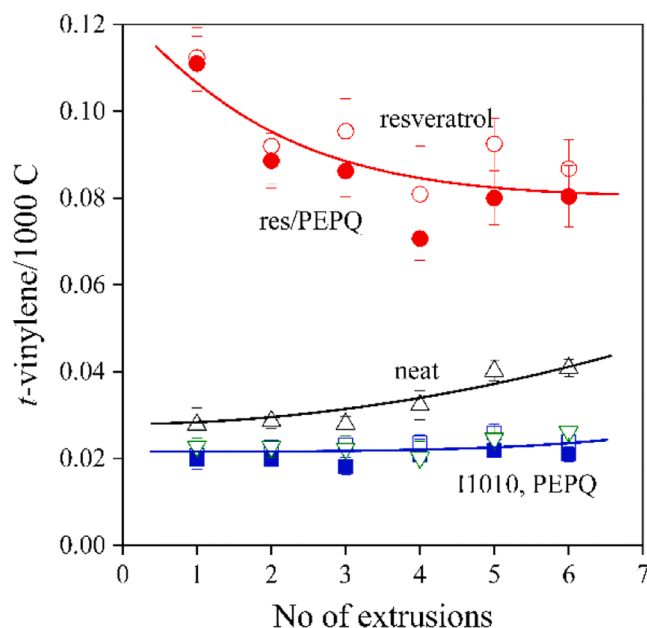


Fig. 11. Consumption of t-vinylene groups during the multiple extrusion of PE stabilized with resveratrol. Symbols are the same as in Fig. 2.

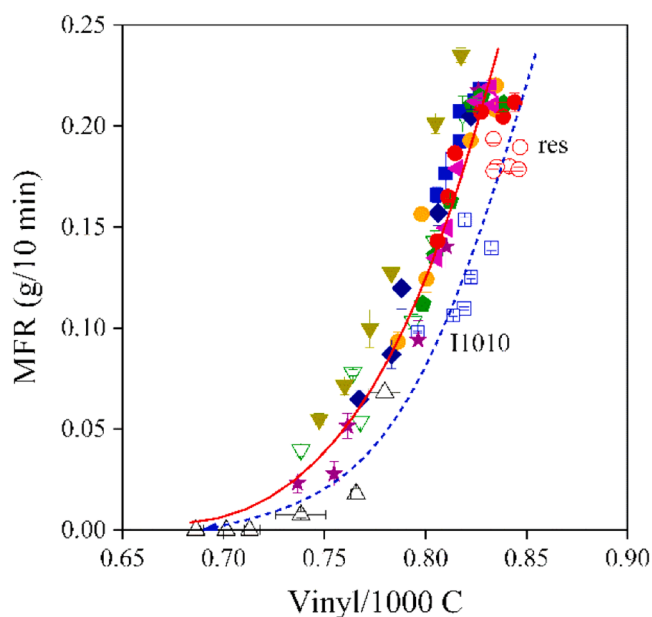


Fig. 12. Correlation between the viscosity (MFR) and vinyl content of PE containing various additive packages. Empty symbols belong to compounds prepared without PEPQ.

been observed in other combinations of natural antioxidants and PEPQ. This negative interaction must be considered during the formulation of the additive package.

5. Conclusions

The study on the possibility of using resveratrol, a stilbenoid-type natural antioxidant, as a stabilizer in polyethylene showed that the compound is a very efficient stabilizer, more efficient than the commercial hindered phenolic antioxidant used in the largest quantity in practice. The antioxidant provides excellent processing stability and the residual stability of PE containing it is exceptional. Because of its large

efficiency, 400–500 ppm additive is sufficient to achieve adequate stability for practice. The results indicate that resveratrol interacts with the secondary phosphorous stabilizer used in the study, and the effect is antagonistic; resveratrol performs better alone than in combination with PEPQ. The reason for the negative effect is the strong electron-attracting activity of resveratrol, resulting in the decomposition of the secondary antioxidant by the cleavage of a P–O bond. Accordingly, this unusual effect must be taken into account during formulation, the creation of the actual additive package. The stabilizer is used in other industries, thus it is available in large quantities and relatively cheap. Besides its advantages, the natural antioxidant have some drawbacks, like its high melting temperature, limited solubility in polyethylene and the strong color of its reaction products. Nevertheless, resveratrol has great potentials as a stabilizer in certain products.

CRedit authorship contribution statement

Kata Takács: Visualization, Investigation. **Miklós Ákos Németh:** Visualization, Investigation. **Tibor Renkecz:** Methodology, Investigation. **Dóra Tátraaljai:** Writing – original draft, Visualization, Supervision, Resources, Methodology, Investigation. **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 National Research Development and Innovation Office and the Hungarian Academy of Sciences Kata Takacs reports that financial support was provided by National Research Development and Innovation Fund. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors are grateful to Bálint Imre for the FTIR measurements, to Nóra Hegyesi for the XRD measurement, and to Péter Huszthy for the development of the explanation related to the chemistry of stabilizer interactions. The National Research, Development, and Innovation Fund of Hungary (OTKA PD 138507) is greatly acknowledged for the financial support of the research. Dóra Tátraaljai was awarded a fellowship by the Hungarian Academy of Sciences to support researchers raising children (236/2024/KP). The project is supported by the Doctoral Excellence Fellowship Programme (DCEP) funded by the National Research Development and Innovation Fund of the Ministry of Culture and Innovation and the Budapest University of Technology and Economics, under a grant agreement with the National Research, Development and Innovation Office.

Data availability

Data will be made available on request.

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