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CONCENTRATION EFFECTS IN THE STABILIZATION OF PE WITH A NEW NATURAL-BASED PHOSPHINE ANTIOXIDANT: COMPARISON, REACTIONS, INTERACTIONS

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ABSTRACT

The effect and efficiency of the new, phosphine-type, natural-based secondary antioxidant developed recently were compared to those of two other phosphorus stabilizers available on the market. The stabilizers were added to the polymer in amounts changing from 0 to 1000 ppm in 7 steps. The primary, hindered phenolic antioxidant used was Irganox 1010. The efficiency of the stabilizer packages was studied in multiple extrusion experiments following changes in the chemical structure of the polymer, viscosity, color, and residual stability. Component interactions were studied by thermal analysis. The comparison of the various phosphorus stabilizers showed that the efficiency of the new stabilizer is comparable to that of the commercial products. The phosphine rendered the polymer excellent melt stability and very good color. The concentration dependence of properties indicated that about 500 ppm of the secondary antioxidant is sufficient to achieve adequate performance. The phosphine stabilizer interacts synergistically with the hindered phenol primary antioxidant, resulting in the excellent performance observed. The new stabilizer has numerous benefits (natural-based, good melt stabilization and color), and it can compete with phosphorus secondary antioxidants available on the market.

HIGHLIGHTS

- The efficiency of the new stabilizer is comparable to existing commercial products.
- The phosphine rendered the polymer excellent melt stability and very good color.
- 500 ppm of the new phosphine is sufficient to achieve adequate performance.
- The phosphine stabilizer interacts positively with the primary antioxidant.

KEYWORDS: natural-based phosphine, processing stabilization, residual stability, color, component interactions

1. INTRODUCTION

Polymers are organic materials that may degrade during the relatively high temperature of thermoplastic processing, but often also during their use, in the case of long-term applications[1]. The mechanism of degradation depends on the conditions of processing or application and on the chemical structure of the polymer[2,3]. Irrespective of the mechanism, the structure of the polymer changes as a result, leading to processing problems and/or the deterioration of properties[4]. Accordingly, polymers must be protected against degradation to preserve their inherent properties[5]. Stabilization is a routine task for commodity polymers, but systems are also developed for biopolymers[6]. The importance of stabilization increases even further with the advent of circular economy. Instead of the one-way use of plastics, they are recycled and used multiple times, but each processing step results in changes in their structure and properties, leading to inferior performance in the end[4]. Replenishing the consumed stabilizer is an absolute necessity to achieve a circular economy and the successful reprocessing and reuse of polymers[7].

Stabilizer systems used in commodity polymers are well established now[8]. Usually, they contain a hindered phenolic antioxidant and phosphorus or sulfur-containing secondary stabilizer[6]. The use of other ingredients depends mostly on the application and its conditions. Because of the efficiency of currently used industrial additive packages, only limited development occurred in stabilization, and very few new stabilizers have been introduced onto the market[5]. However, mainly because of the increasing environmental awareness of the public, but also due to political pressure, the interest in natural raw materials, including stabilizers, increases considerably[9]. Numerous compounds with antioxidant activity can be found in nature, in the various parts of plants[10]. Many of these are successfully used in the food industry, but several attempts are made to apply them also for the stabilization of pol-

ymers[11-18]. The successful use of various compounds like lignin[19], carotene[14,20-23], flavonoids[24], and flavonols[25], as well as various polyphenols, has been reported in the literature in recent years[26,27]. Besides the neat compounds, natural extracts could also be used for the stabilization of polyethylene (PE) or polypropylene (PP) quite efficiently[14]. The use of stabilizers from natural resources is even more important in biopolymers in order to produce materials not containing any synthetic components[9,28].

The currently used industrial additive packages are composed of synthetic materials[18]. However, as mentioned above, the general goal is to decrease the number of synthetic components in the package as much as possible[29,30]. Hindered phenolic antioxidants can be replaced relatively easily by various phenols or polyphenols produced by nature, but finding natural secondary antioxidants, phosphorus, or sulfurous compounds is much more difficult[31,32]. In an attempt to circumvent this difficulty, a novel phosphine type secondary stabilizer was synthesized successfully with large natural raw material content[33]. The relatively large molecular weight and the long aliphatic moiety decrease the danger of its migration from the matrix. The new compound reacts with oxygen during storage but the reaction is rather slow, and the efficiency of the stabilizer does not decrease within a reasonable time frame. The new stabilizer was tried as a secondary antioxidant in high density polyethylene (HDPE) and it proved to be an excellent secondary stabilizer with comparable efficiency to phosphite and phosphonite stabilizers currently used in industrial practice. The new stabilizer proved especially efficient in improving the processing stability of the polymer, but also in preserving its color[33]. The additive was used at 1000 ppm in all experiments, which clearly proved the feasibility of using it also in practice. However, both technical and financial aspects require the optimization of the additive package, the use of an optimal amount for the application of the polymer. However, it often occurs, especially in the case of natural antioxidants, that the amount of stabilizer used is selected randomly; very large amounts,

often 0.5 wt%[34], 1 wt%[16,35], 2 wt%[14,36,37], or even 10 wt%[38] stabilizer, are added to the polymer. The large amounts occasionally are not financially viable, but they can often deteriorate homogeneity and the properties of the polymer as well. The knowledge of the effect of additive concentration on efficiency is essential for the optimization of the composition of the additive package.

In accordance with the considerations presented above, the goal of the present study was the determination of the effect of phosphine concentration on the efficiency of the new additive in order to assist the optimization of the additive package. The primary antioxidant was the hindered phenolic stabilizer used in the largest quantity in industrial practice (Irganox 1010). The effect of the new phosphine stabilizer was compared to that of commercial phosphorus secondary stabilizers, which were also added to the polymer in various amounts. The stabilizers were added to polyethylene, and their effect was studied in multiple extrusion experiments. Changes in polymer properties were followed by the characterization of the structure of the polymer as well as the measurement of viscosity, color, and residual stability. Besides concentration effects, the possible interaction of the components was also studied, since very little is known about the stabilization mechanism of the new antioxidant. Correlations as well as possible consequences for practice are also mentioned briefly 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 a primary antioxidant was Irganox 1010 (I1010, BASF, Ludwigshafen, Germany), while the industrial secondary antioxidants were a phosphite (Irgafos 168, BASF, Ludwigshafen, Germany) and a phosphonite, Sandostab PEPQ (PEPQ, Clariant, Basel, Switzerland). The experimental phosphine secondary antioxidant (Ph) was synthesized in our laboratories according to the method described earlier[33]. The additive packages contained 1000 ppm I1010 and various amounts of the secondary antioxidant. The amount of I1010 varied from 0 to 1000 ppm in seven steps, i.e., the compounds contained 0, 50, 100, 250, 500, 750, and 1000 ppm of the phosphorous stabilizers.

2.2. Sample preparation

The polymer and the additives were mixed in a Henschel FM/A10 high-speed mixer (Thyssen, Kassel, Germany) at the rate of 1000 rpm for 10 min. The dry mixture was processed and pelletized in six consecutive extrusion steps at 50 rpm with 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 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 groups of polyethylene was determined by Fourier-transform infrared spectroscopy (FTIR) on 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}. The calculation of the above-mentioned concentration is described in our earlier publication in detail[39]. 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 MPSD (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 an oxygen atmosphere at a constant 20 mL/min flow rate, and 200 °C in triplicate. OIT was determined at 200 °C instead of 190 °C because of the very long times obtained at the lower temperature. The interaction of the additives was studied also by thermogravimetric analysis using a Perkin Elmer STA 6000 (Norwalk, CT, USA). The two additives in question were mixed in equal amounts and then placed into the STA pans. The samples were heated up to 260 °C at the rate of 50 °C/min in oxygen atmosphere and then kept at that temperature for 10 min. Differential scanning calorimetry was also carried out to follow transitions and interactions. The measurements were done on 5-15 mg samples, which were heated from 30 to 350 °C at a heating rate of 10 °C/min in the Perkin Elmer STA 6000 TGA-DSC apparatus, in oxygen atmosphere. The color of the samples was determined on granules using a Hunterlab ColorQuest 45/0 (Reston, VA, USA) apparatus. Color was characterized by the yellowness index (YI).

3. RESULTS AND DISCUSSION

The results are presented in several sections. The effect of the number of extrusions, i.e., processing history, on properties is presented in the first section, which also allows the comparison of the efficiency of the three different phosphorus stabilizers at various concentrations. The concentration dependence of properties is shown in the next section for the new phosphine-based antioxidant, followed by the discussion of possible reactions and interactions. Correlations and consequences for practice are mentioned in the last section of the paper.

3.1. Multiple processing, comparison

The main route of degradation of the Phillips-type polyethylene used in the study is the reaction of the chain-end vinyl groups with alkyl radicals formed during processing [40-43]. This reaction results in long chain branching, the increase of viscosity, and the decrease of MFR. The consumption of vinyl groups is usually an indication of the number of reactions and the expected changes in the rheological properties of the polymer. The vinyl group content of the polymer is plotted against the number of extrusion steps in **Fig. 1** for polymers processed in the presence of the three phosphorus secondary antioxidants. All the compounds contained 1000 ppm I1010 phenolic antioxidant as well. The amount of the secondary stabilizer changed between 0 and 1000 ppm in 7 steps. This resulted in a large amount of data and very crowded plots. Consequently, we do not go into the detailed analysis of concentration effects here, but focus on general tendencies and the relative effect of the three stabilizers. The comparison of the results clearly shows that the presence of the three additives affects differently the vinyl group content of the polymer. The smallest values were measured for the phosphonite stabilizer (PEPQ), indicating the largest number of reactions

and forecasting the largest decrease in MFR. This result clearly contradicts previous experience proving that PEPQ is a very efficient secondary antioxidant. The largest vinyl group content is determined for the PE containing the phosphite (I168) stabilizer, which again is a slight contradiction. The concentration of the vinyl groups is in between in polymers prepared with the new phosphine type (Ph) stabilizer. Another observation worth noting is that the effect of concentration on vinyl group content is also contradictory. The number of vinyl groups should increase with increasing stabilizer content, as in the case of the phosphite (I168) stabilizer (**Fig. 1c**), but no such tendency is observed for the other two stabilizers (**Figs. 1a** and **b**). These observations clearly require further considerations.

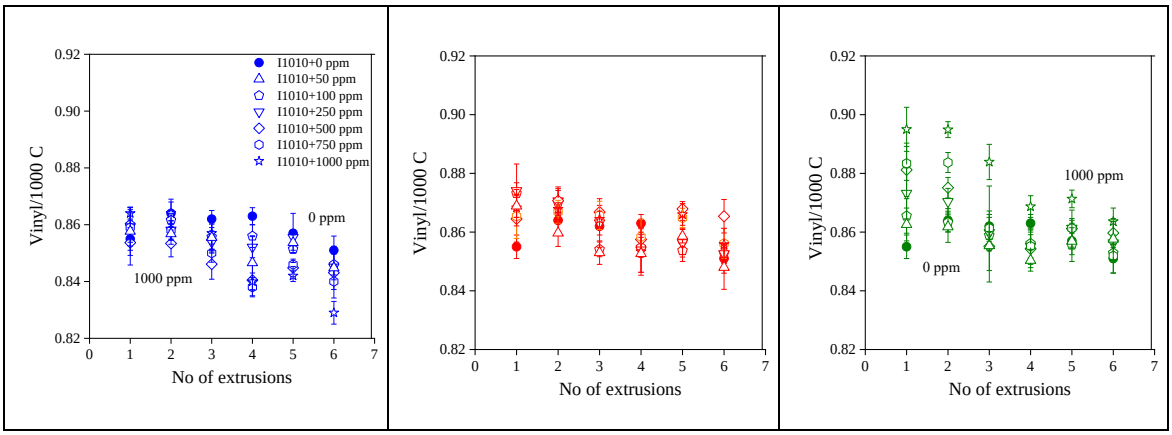

Fig. 1 Effect of the amount of the secondary antioxidant and the number of extrusions on the vinyl group content of polyethylene; a) phosphonite (PEPQ), b) phosphine (Ph), c) phosphite (I168), additive content changes from 0 to 1000 ppm in 7 steps. Symbols are the same in **Figs. 1-4** as shown in **Fig. 1a**.

The dependence of MFR on the number of extrusions (**Fig. 2**) raises further questions. The most efficient in preventing any change in viscosity is the new phosphine-type

stabilizer, especially at large concentrations. The effects of the other two stabilizers are similar to each other (**Figs. 2a** and **c**). The effect of concentration is also interesting; the packages containing the largest amount of additive are the most efficient in this case, as expected. Obviously, the general conclusion drawn earlier about the close correlation of vinyl group content and rheological properties is not valid here, indicating that the reactions taking place during processing are not limited to the addition of radicals to the vinyl groups, but other reactions must be considered as well.

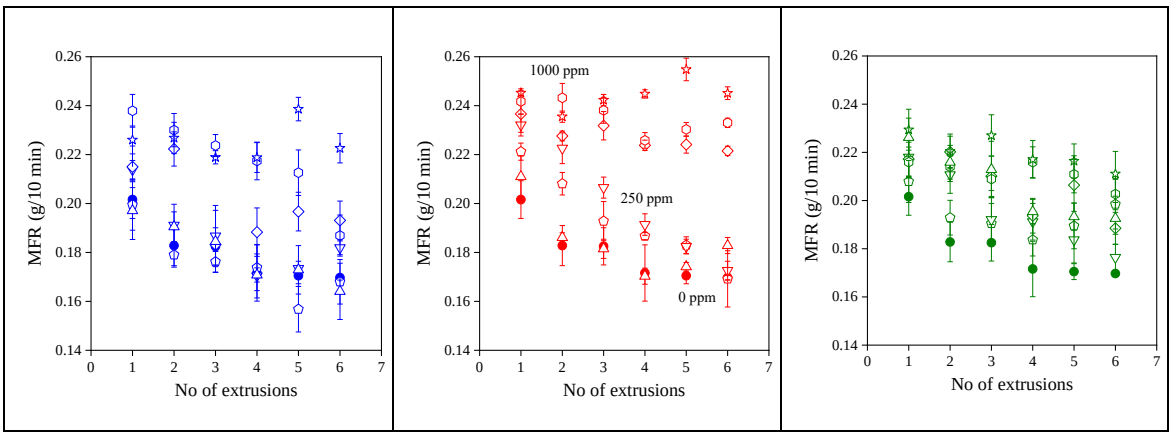

Fig. 2 Dependence of the melt flow rate (MFR) of PE on the type of the phosphorous secondary antioxidant, its concentration and processing history (No. of extrusions); a) phosphonite (PEPQ), b) phosphine (Ph), c) phosphite (I168).

The residual stability of a polymer is very important in long-term applications, e.g., for pipes and automotive parts. Residual stability is routinely characterized by the measurement of the oxidation induction time (OIT) determined by differential scanning calorimetry. The OIT of the polymers containing the three secondary stabilizers is compared to each other in **Fig. 3**. The two commercial stabilizers are quite efficient; they result in large residual stabilities exceeding by much the 20 min required by the corresponding standard for pipes (**Fig. 3a** and **c**). The stability of the polymer containing I168 is somewhat better than

that prepared with PEPQ, because I168 is more stable and does not interact very strongly with the phenol. The efficiency of the new natural phosphorus stabilizer is somewhat smaller at this temperature (**Fig. 3b**), which seems to contradict previous results[33]. However, those results clearly proved that the phosphine stabilizer also reacts with molecular oxygen; thus, it is consumed quite fast at higher temperatures in an oxygen-rich atmosphere. This large reactivity results in its efficiency as a processing stabilizer and probably also in improving the color of the processed polymer to such a large extent. Residual stability improves with increasing additive content for all three stabilizers, as expected.

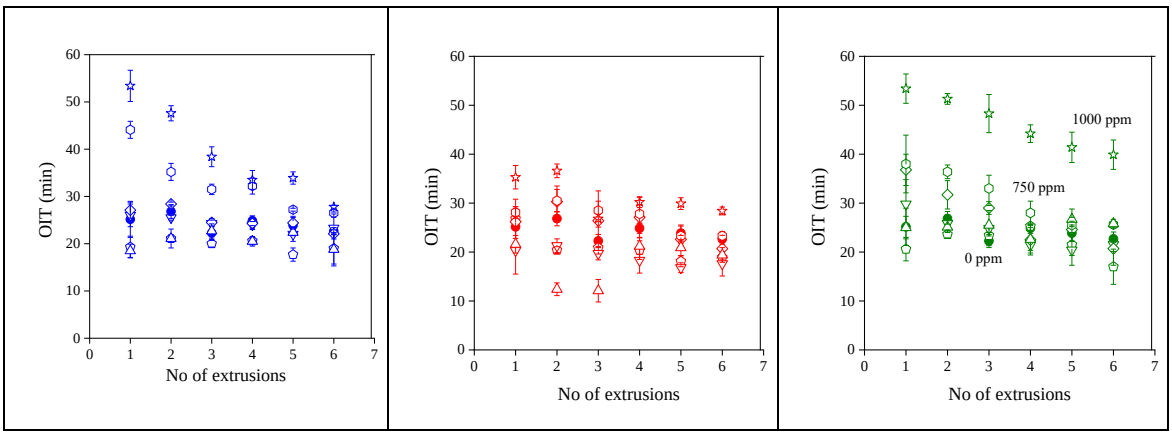

Fig. 3 Influence of the number of extrusion steps, additive concentration and the type of the phosphorous secondary antioxidant on the residual stability (OIT) of PE; a) phosphonite (PEPQ), b) phosphine (Ph), c) phosphite (I168).

The color of the compounds is another attribute, which might be important in certain applications, such as packaging. Phosphorus secondary antioxidants usually improve color and compensate for the yellowish, purplish color caused by the quinoid compounds formed in the reactions of the phenolic primary antioxidant[5,44]. The yellowness index of the polymer processed in the presence of the three additives is plotted against the number of extrusion steps at different additive contents in **Fig. 4**. The largest efficiency of the new phosphine

type additive is clear from the figure; the smallest yellowness index is achieved with it (**Fig. 4b**). The least efficient is the phosphite (I168, **Fig. 4c**), which agrees with previous results and general experience with this secondary stabilizer. I168 itself contributes to color development through reaction products forming in the stabilization reactions. Its main advantage is its price; it is one of the cheapest phosphorus antioxidants available on the market. The results presented in this section clearly confirm previous results showing that the novel phosphine-type natural secondary antioxidant is at least as efficient as its commercial counterparts, and its effect is even better in improving certain properties. It is also clear from the results that the 1000 ppm additive content used in the previous study is excessive; acceptable performance can be achieved at smaller concentrations as well. The results also called attention to some discrepancies needing further considerations.

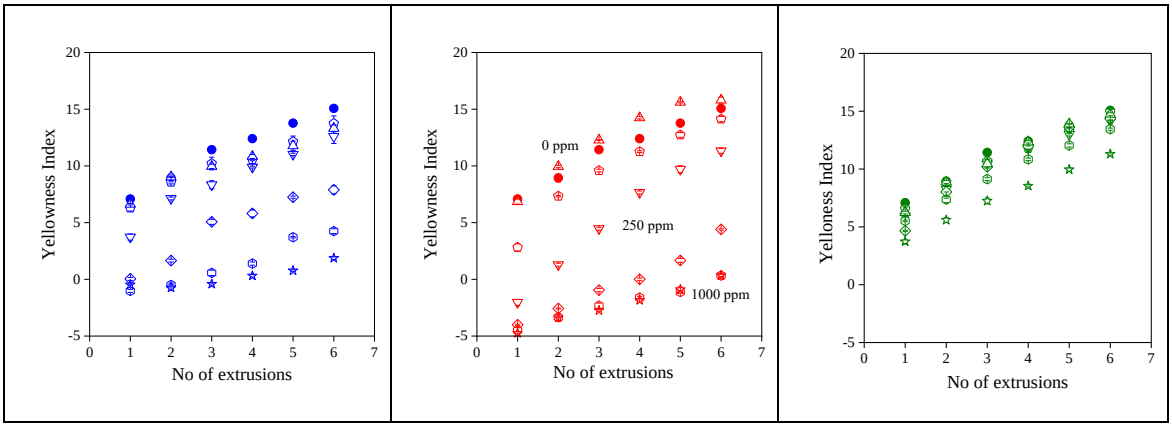

Fig. 4 Discoloration of polyethylene with increasing number of extrusions. Effect of the type of phosphorus antioxidant and its concentration; a) phosphonite (PEPQ), b) phosphine (Ph), c) phosphite (I168).

3.2. Concentration dependence

Concentration effects are analyzed mainly for the new phosphine stabilizer and only for the most important characteristics in order to save space. The effect of phosphine content

on the MFR of the polymer is presented in **Fig. 5** for extrusions 1 and 6. The viscosity of the polymer after intermediate extrusions is located between the two correlations drawn in the figure to guide the eye. The correlations correspond to the expectations; the presence of the novel, natural-based secondary stabilizer results in the improvement of rheological properties, and MFR increases gradually with increasing amount of the stabilizer. The correlation is not linear, and the further addition of the stabilizer above 500 ppm does not lead to significant improvement in MFR, at least in the first extrusion. It must be noted here that the difference in MFR between the 1st and 6th extrusions is quite small at the largest additive contents, which leads to two conclusions. The first is that the new additive is very efficient and contributes significantly to stabilization, to the protection of the polymer against degradation. The second conclusion is that the increase of additive content does not lead to proportional improvement in properties; thus, 5-600 ppm phosphine is sufficient to protect the polymer, at least at the 1000 ppm I1010 content used. Naturally, the package, including the amount of the primary antioxidant, must be optimized further, taking into account the conditions of processing and application. Nevertheless, we can state that several[14,36,37] or even 10 weight percent[38] additive content used occasionally are exaggerated and definitely not beneficial.

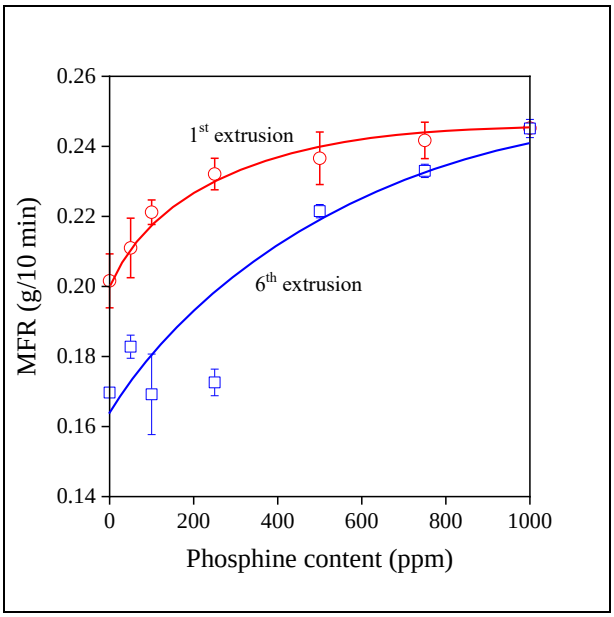

Fig. 5 Concentration dependence of the MFR of polyethylene processed with the new phosphine secondary antioxidant. The amount of the primary antioxidant, I1010, is 1000 ppm. Symbols: (○) 1st extrusion, (□) 6th extrusion.

The residual stability (OIT) of the polymer is plotted against phosphine content after the first and sixth extrusions in **Fig. 6**. Increasing the number of extrusions results in larger stabilizer consumptions as expected, but the difference is not very large and does not change with Ph concentration. However, residual stability increases with increasing phosphine content, indicating that the secondary stabilizer also contributes to stabilization and to the increase of residual stability. Reports have been published in the literature claiming that residual stability is determined primarily by the amount of the original, unreacted primary antioxidant remaining in the polymer after processing or use[45].

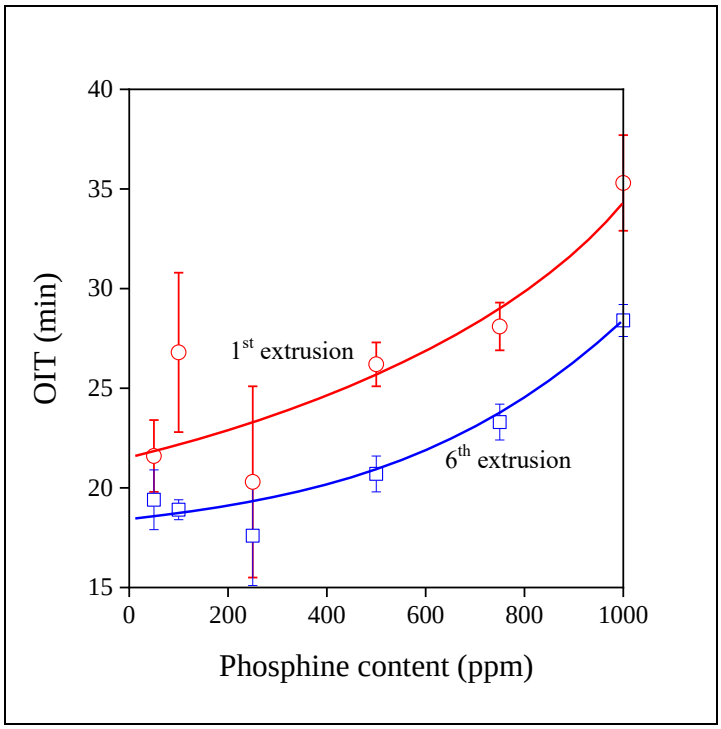

Fig. 6 Changes in the residual stability (OIT) of PE with increasing phosphine content. Symbols: (○) 1st extrusion, (□) 6th extrusion.

The effect of the new additive on the color of the polymer is one of its main assets and advantages. Yellowness index is plotted against the amount of phosphine stabilizer added to the polymer in **Fig. 7**. Color is compared for materials subjected to one and six extrusions, just as before. Very low yellowness indices are achieved after the first extrusion, and the color of the polymer is much better, even after the 6th extrusion, than for the compounds stabilized with Irgafos 168, the phosphite stabilizer (see Fig. 4). The color of the polymer containing only the primary antioxidant, I1010, is relatively strong because of the quinoid compounds forming during the stabilization reactions. The secondary stabilizer prevents the formation of oxygen centered radicals or decomposes hydroperoxides thus decreases the number of reactions leading to these compounds. The prevention is naturally more efficient with increasing amount of the phosphine in the polymer and color approaches

that of the neat polymer after the first extrusion since the formation of quinoid compounds is almost completely prevented. Just like the other properties, the concentration dependence of color indicates that 500-600 ppm phosphine is sufficient to achieve optimum effect. The very good color retention observed must be related to the positive interaction of the primary and secondary stabilizer; the use of the newly developed phosphine secondary antioxidant is clearly beneficial from many aspects, including environmental (natural-based) and technical (melt stability, color) considerations.

The corresponding figures (Figs. SI4-6) are collected in the Supplementary Information file for the other two phosphorous secondary stabilizers, i.e. I168 and PEPQ. Very similar correlations were obtained with differences in the actual level of the given property as shown in Figs. 1-4. PEPQ offered good color retention and somewhat poorer melt stabilization than the phosphine, while the polymer containing I168 had very good residual stability, but strong color.

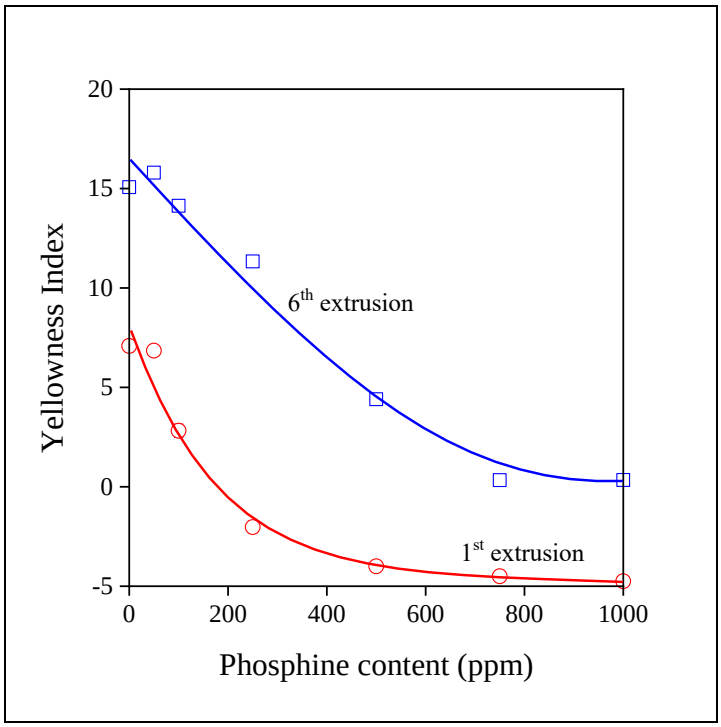

Fig. 7 Beneficial effect of the amount of the phosphine secondary antioxidant on the color of polyethylene. Symbols: (○) 1st extrusion, (□) 6th extrusion.

3.3. Interactions, reactions

Besides proving the value of the new phosphine stabilizer, the results presented above also call attention to some phenomena, which clearly need further considerations. The vinyl content of the polymer was small in the presence of the phosphonite (PEPQ) stabilizer, but its MFR was large; the stabilizer protected the polymer against degradation quite efficiently. The new phosphine stabilizer was very efficient in improving processing stability and color, but its residual stability was relatively small. All these observations indicate that contrary to some claims in the literature[46], the mechanism of the phosphorus secondary antioxidants differs from each other, on the one hand, and the phenolic and phosphorus antioxidants interact with each other in one way or the other, on the other hand.

In order to check the possibility of interactions, the stabilizers and their combination were studied by thermal analysis. DSC and TGA measurements were carried out on the

antioxidants and their 50:50 m/m% mixtures. DSC traces recorded on I1010, the new phosphine stabilizer (Ph) and the phosphite antioxidant (I168), as well as on their mixture with I1010 are presented in **Fig. 8**. The traces recorded on the phosphonite (PEPQ) and its combination with the phenolic antioxidant are omitted from the figure to avoid confusion, but they are very similar to those obtained for the phosphite stabilizer (see Supplementary Information, Figs. SI1 and 2). Only the melting of I168 and I1010 appears on the correspondint traces of the two additives; further transition cannot be seen on their traces at all. The melting of both components, I168 and I1010, appears on the trace of their mixture. The shift of the melting peak of the phosphite towards lower temperatures and a slight increase in heat flow at high temperatures indicate some kind of interaction of the two components, but these interactions and changes do not seem to be very strong.

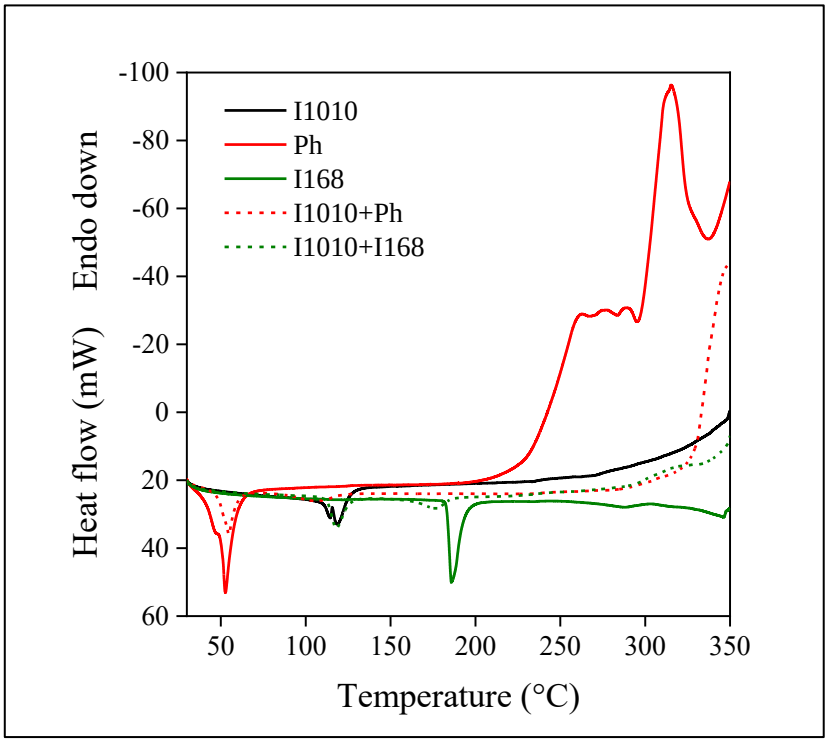

Fig. 8 DSC traces recorded on the phosphite (I168) and phosphine (Ph) secondary antioxidants and their 50:50 m/m% mixture with the primary stabilizer (I1010). Oxidation of the phosphine and the positive effect of I1010 on its stability.

Strong transitions and more drastic changes can be observed in the traces of the phosphine and its mixture with the phenolic antioxidant. We know that the phosphine stabilizer reacts with molecular oxygen, and these measurements were done in oxygen atmosphere. Oxidation starts at around 200 °C and proceeds quite fast. This reactivity with oxygen results in the relatively short OIT values measured for polymers stabilized with the new phosphine stabilizer. The reaction is largely suppressed by the presence of the phenolic antioxidant, and severe oxidation starts only above 300 °C. The two antioxidants obviously enter into a strong interaction, which is beneficial for both components.

Thermogravimetry (TGA) supplies further proof for the interaction of the two kinds of antioxidants (**Fig. 9**). The measurements were done in two steps. First, the components

were heated up to 260 °C and then kept there for 10 min. These measurements were also carried out in oxygen atmosphere. I1010 and the phosphite stabilizer are stable, the weight loss during the time span of the measurement is small, and the weight loss of the secondary antioxidant decreases further in the presence of the phenolic antioxidant. On the other hand, the phosphine stabilizer decomposes quite drastically; it loses almost 30 % of its weight during the measurement. The phenolic antioxidant protects the secondary stabilizer; the weight loss of the mixture is quite small. However, the phosphine protects the primary antioxidant as well shown by the decreased discoloration of the polymer in the case of this stabilizer combination. The positive interaction of the two stabilizers is a further benefit of using the new, natural-based phosphine stabilizer.

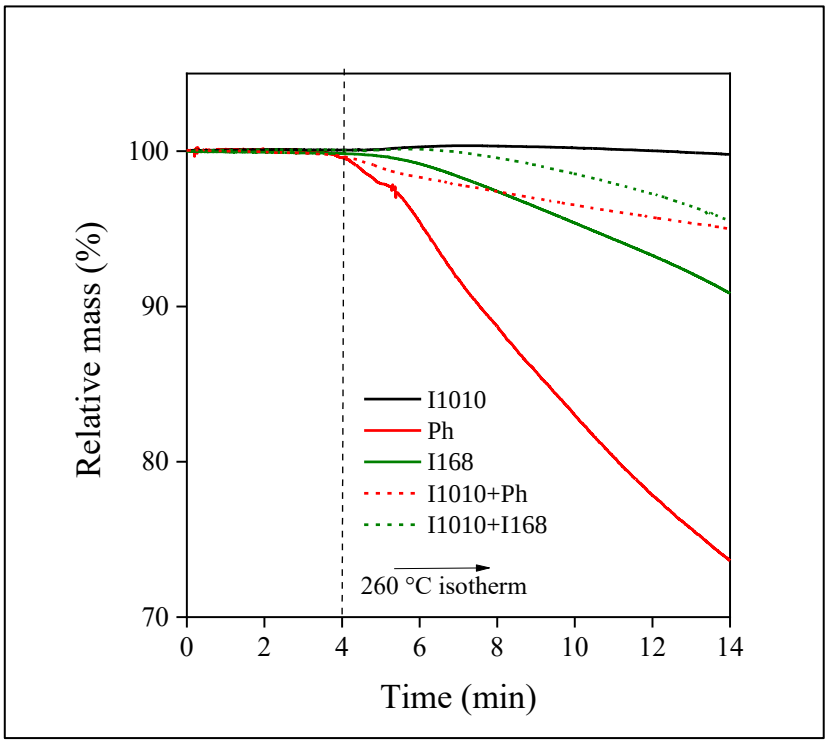

Fig. 9 Thermogravimetric (TGA) analysis of the decomposition of phosphorus secondary antioxidants (I168, Ph) and their 50:50 m/m% mixture with Irganox 1010. The combination of fast heating and isothermal treatment in oxygen atmosphere. Fast decomposition of Ph and its stabilization by I1010.

3.4. Correlations, discussion

The results obtained in this set of experiments revealed two slight contradictions or deviations from previous experience. The first is the contradiction between the excellent melt stabilization efficiency of the new phosphine stabilizer, as well as its positive effect on color, and the relatively small residual stability of the polymer containing it. All of these observations can be explained by the high reactivity of the phosphine and its reaction with molecular oxygen. The scavenging of the small amount of oxygen dissolved in the polymer melt[47] results in fewer radicals, fewer hydrogen abstractions from the chains, and less long-chain branching. It also leads to a smaller number of oxygen-centered radicals, which may react with the primary antioxidant, resulting in discoloration. On the other hand, this reaction with the oxygen results in the consumption of the antioxidant and thus shorter OIT values, especially at higher temperatures. **Fig. 6** clearly shows that the phosphine secondary antioxidant contributes to residual stability; thus, its consumption shortens the OIT measured in oxygen atmosphere at high temperature. However, this high temperature reactivity does not hinder the application of the stabilizer in practice. Previous experiment showed that the stabilizer reacts with oxygen also at room temperature but very slowly, consequently its storage stability is excellent and it does not lose its efficiency even in a longer time span[33].

The other apparent contradiction was the strong decrease of vinyl group content of the polymer in some cases, usually indicating strong long chain branching, which was not accompanied by a decrease of MFR and the deterioration of processability. MFR is plotted against the vinyl group content of the polymer in **Fig. 10**. This correlation was strong and unambiguous in many cases, before showing that the increase of vinyl group content led to increased MFR[48,49]. The large number of points scattered all over the plot indicates the complete lack of correlation, which is quite surprising. A closer scrutiny hints at the existence of a loose correlation only for polymers containing the phosphite stabilizer at most. The lack

of correlation in the other two cases indicates that the mechanism of stabilization is different for compounds containing only P(III)-O groups from those having P(III)-C groups in their structure. In the case of stabilizers containing P(III)-C group, the interaction of the primary, phenolic antioxidant and the secondary, phosphorus stabilizer was shown to lead to the fragmentation of the phosphorous containing compound, and the addition of the resulting radical to the chain-end vinyl groups of the polymer. This reaction results in a decrease in vinyl group content, but does not change MFR, thus it contributes to melt stabilization.

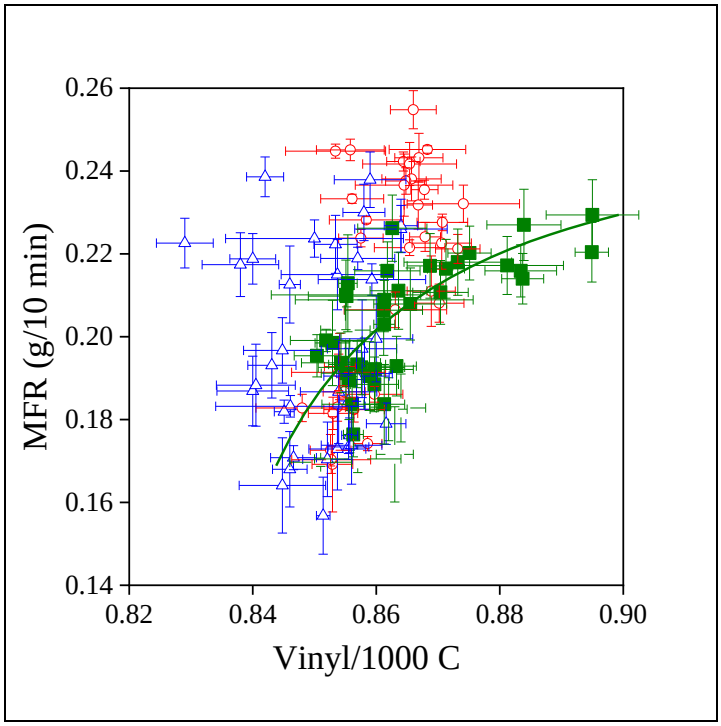

Fig. 10 MFR plotted against the vinyl group content of the Phillips polyethylene used in this study. Loose correlation for polymers containing the phosphite (I168; ■) stabilizer and the complete lack of any relationship for the other two secondary antioxidants (PEPQ; △, Ph;○).

4. CONCLUSIONS

The comparison of the new natural-based phosphine secondary antioxidant to other phosphorus stabilizers currently used in industry showed that the efficiency of the new stabilizer is comparable to that of the commercial products. The application of the phosphine rendered the polymer excellent melt stability and very good color. The determination of concentration dependence indicated that about 500 ppm of the secondary antioxidant is sufficient to achieve adequate performance at the 1000 ppm level of the primary antioxidant used. The additive package must be optimized further to adjust it to the intended application. The phosphine stabilizer interacts positively with the hindered phenol primary antioxidant, resulting in the excellent performance observed. The two stabilizers protect each other; the phenol increases the stability of the phosphine while Ph prevents the consumption of the phenol and discoloration. The relatively short residual stability measured at high temperature for polymers containing the phosphine is the result of its high reactivity and reaction with molecular oxygen, but it does not hinder its application, since at room temperature it reacts with oxygen very slowly thus its storage stability is excellent. The new stabilizer has numerous benefits including natural raw material content, good melt stabilization efficiency and color retention, and it can compete with phosphorus secondary antioxidants available on the market. Moreover, it can be combined with natural phenolic compounds as primary antioxidants and applied in biopolymers to create natural-based and biodegradable materials.

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