Synthesis and evaluation of a novel natural-based phosphine antioxidant for the thermal stabilization of polyethylene

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Abstract
A new phosphine-type potential secondary stabilizer was synthesized successfully with large natural raw material content. The stabilizer is a waxy white powder with a relatively low melting temperature. Both the thermal and the storage stability of the stabilizer are sufficient for practical use. The new stabilizer was introduced into a Phillips-type high-density polyethylene, and its stabilizing efficiency was determined by multiple extrusions. Commercial phosphate and phosphonite stabilizers were used as references. The additive packages contained a primary antioxidant and a phosphorus compound, both added at 1000 ppm. The chemical structure of the polymer, viscosity, color, and residual stability were determined after each extrusion. The comparison of the stabilizing efficiency of the three secondary antioxidants showed that the phosphine stabilizer is at least as efficient as the phosphorous secondary stabilizers available in the market. The new stabilizer proved to be the most efficient in melt stabilization and in preventing discoloration; the residual stability of the polymer was similar in the presence of all three secondary antioxidants. This feasibility study proved that the new compound could be used as a potential stabilizer in practice.

Keywords Processing stabilization · Phosphorous secondary antioxidant · Natural raw material content · Melt viscosity · Color · Residual stability

Introduction
Polyolefin polymers, such as polyethylene (PE) and polypropylene, are the commodity polymers used in the largest quantity among all polymers in every area of life. These polymers are converted into products at high temperatures; thus, they must be protected against heat, shear and oxygen in order to prevent their degradation. Adequate stabilization is also necessary for products with extended lifetime, like pipes or car parts. The stabilization of polyolefins is a mature technology; usually, a hindered phenolic primary antioxidant is added to the polymer in combination with a secondary stabilizer. Because of the efficiency of this combination and the maturity of the technology, very limited development has been done in the field of stabilization; thus, new antioxidants have rarely appeared on the market. However, some environmental and health issues were raised some time ago about the reaction products of phenolic antioxidants, especially in water pipes [1]. This information and strengthening public demand to use raw materials from renewable resources have increased the interest in natural antioxidants and generally in additives derived from natural resources.

Numerous antioxidants can be found in nature produced by different living organisms, including plants. Compounds with antioxidant activity have widely differing structures, functions, and efficiencies. Besides their antioxidant activity, they often have anti-inflammatory and anticarcinogenic effects [2–4]. Quite a few of these natural antioxidants are used in the food industry, but some of them have also been tried as stabilizers in polymers with different successes.
Carotene [5–7], curcumin [8], Vitamin E [9–11], lignin [12–14] and many other compounds have been shown to have smaller or larger stabilizing activity in a range of polymers, but mostly in polyethylene. Recently, several papers have been published on the use of natural antioxidants as stabilizers in polymers [15]. According to these articles, flavonoids seem to be the most efficient natural stabilizers, at least in polyethylene. Quercetin [16], dihydromyricetin [17], and rutin [18] provided sufficient melt stability for PE already at 50 ppm, and residual oxidative stability at 250 ppm additive content. Not only the pure compounds but also natural extracts have considerable stabilization efficiency; thus, sooner or later they will find their way into industrial practice [19–24].

Although quite a few primary antioxidants based on natural resources have been tried as a stabilizer in polymers, practically no attempt has been made to find a secondary antioxidant of similar origin for obvious reasons. The primary role of secondary or chain-breaking antioxidants is to decompose hydroperoxides and thus disrupt radical chain reactions [25–27]. Phosphorous or sulfur-containing compounds are used for the purpose, and they cannot be obtained from natural resources. Sulfur compounds are mainly used in high-temperature applications, especially in the automotive industry, where long-term stabilization is needed at elevated temperatures [27, 28]. In other areas, phosphorous secondary stabilizers are used more frequently, most often phosphites and sometimes phosphonites. They are assumed to act according to the same mechanism, i.e., decomposition of hydroperoxides accompanied by the oxidation of the additive to the corresponding pentavalent phosphorous compound [27, 29]. Some time ago, a phosphine compound was developed and tried as a secondary stabilizer and proved to be more efficient than the traditionally used phosphites and phosphonites [30]. Unfortunately, this specific phosphine compound failed to reach the market. However, a comparative study showed its efficiency and also proved that the three phosphorous antioxidants, i.e., phosphites, phosphonites and phosphines, act according to different mechanisms [30], in spite of the general assumption about their reaction mechanism described above [31].

The phosphine mentioned above was a small molecular weight synthetic compound with no natural raw material content [32]. Considering the general tendency to use materials from natural resources and the excellent efficiency of phosphines in reacting with oxidizing agents, including molecular oxygen, we decided to design and synthesize a secondary antioxidant, which contains the phosphine moiety and is based on natural resources. The goal of this study was to determine the efficiency, if any, of the novel compound as a secondary antioxidant and compare its effect to existing products used in industrial practice, i.e., to a phosphite and a phosphonite stabilizer. Additive characteristics most important for practice were determined together with the storage stability of the product. Stabilization efficiency was investigated in a high-density polyethylene; the effect of the three compounds on the structure of the polymer, melt stability, color, and residual stability was compared at a single additive content, at 1000 ppm. The consequences of the results for practice are also discussed briefly in the final section of this paper.

**Experimental**

**Materials**

The chemicals for the synthesis of the novel phosphine type stabilizer, i.e., stearic acid (reagent grade 95%), chlorodiphenylphosphine (99%), 1-bromooctadecane (97%), diethyl ether (anhydrous, 99.7%), and magnesium turnings (for Grignard reactions, 99.5%) were obtained from Sigma-Aldrich (Merck). N-hexane (96%) and dichloromethane (stabilized with amylene; 99.8%) were used for purification on silica gel 60 (0.063–0.2 mm) purchased from Molar Chemicals Ltd. The polymer used in the experiments was the Tipelin FS 471 grade ethylene/1-hexene copolymer (melt flow rate: 0.3 g/10 min at 190 °C, 2.16 kg; nominal density: 0.947 g/cm³) polymerized with a Phillips catalyst. The additive-free polymer powder was provided by the MOL Group, Hungary. The primary phenolic antioxidant used in the study was Irganox 1010 (I1010, BASF Switzerland) applied in the largest quantity in industrial practice. The stabilizer was used alone and in combination with the phosphorous secondary antioxidants. A phosphite, Irgafos 168 (I168, BASF, Switzerland) and a phosphonite, Sandostab PEPQ, (PEPQ, Clariant, Switzerland) were used as reference stabilizers. The chemical formulas of the commercial stabilizers used are shown in Scheme 1 and that of the phosphine synthesized by us (NatPhos) in Scheme 2. The characteristics of the latter are discussed in Sect. “Stabilizer characteristics” Stabilizer characteristics. All additives were added to the polymer at 1000 ppm.

**Synthesis of the stabilizer**

Octadecyldiphenylphosphine (NatPhos) was prepared by a modified procedure reported by Stuebe et al. [33]. Magnesium turnings (1.29 g, 53.07 mmol) were placed into a three-necked, round-bottomed flask equipped with a narrow capillary argon gas inlet, a reflux condenser with a gas flow measuring outlet filled with silicon oil at its top, and a dropping funnel. The flask was heated with a heat gun while a low flow of argon was passed through the flask to remove oxygen and moisture. Deoxygenated, dry diethyl ether was used in all procedures. After the flask was cooled down to
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...stirring. Following the addition, the reaction mixture was stirred at room temperature for 10 min then refluxed for two hours. After the reaction was complete (TLC monitoring), the mixture was cooled to 0 °C using an ice-water bath, and then, deoxygenated aqueous ammonium chloride solution (105 mL) was added to it. The phases were shaken well under argon and separated. The aqueous phase was shaken with diethyl ether (180 mL). The combined organic phase was dried with anhydrous magnesium sulfate, and the solvent was evaporated under reduced argon atmosphere. The solid raw material was purified by column chromatography on silica gel under argon using first hexane then dichloromethane/hexane 1:10 (v/v) mixture as eluents to give pure octadecyldiphenylphosphine (NatPhos, 15.06 g, 69%) as a white solid. Mp 55–56 °C. Reported mp 49–50 °C [34]. Rf: 0.35 (silica gel TLC, 1:10 (v/v) dichloromethane: hexane). IR (KBr) ν max 3070, 3054, 3030, 3016, 3002, 2955, 2918, 2849, 1585, 1571, 1472, 1454, 1433, 1419, 1375, 1328, 1306, 1265, 1099, 1025, 914, 906, 855, 801, 732, 715, 692, 506, 487, 464, 431, 422, 401 cm⁻¹. 1H NMR (300 MHz, CDCl₃) δ 0.78 (t, J = 6 Hz, 3H), 1.38–1.51 (m, 32H), 2.09 (t, J = 6 Hz, 2H), 7.29–7.38 (m, 10H). 31P NMR (121.5 MHz, CDCl₃) δ – 16.01. Reported 31P NMR (CDCl₃) δ – 16.2 [35].

Sample preparation

The additives were mixed with the PE powder and then homogenized in a Thyssen Henschel FM/A10 high-speed mixer (Kassel, Germany) at 1000 rpm for 10 min. The dry blend was processed and pelletized in six consecutive extrusion steps. The extrusion was done at 50 rpm and the barrel temperatures of 180, 220, 260 and 260 °C using a Haake Rheomex S ¾” (Saddle Brook, NJ, USA) type single screw extruder attached to a Haake Rheocord EU 10 V (Saddle Brook, NJ, USA) driving unit. Samples were taken after each extrusion step. For further studies, films of about 100 µm thickness were compression molded at 190 °C and 5 min using a Fontijne SRA 100 (Vlaardingen, The Netherlands) machine.

Characterization

The melting characteristics and crystallinity of the phosphine (NatPhos) were studied by differential scanning calorimetry (DSC) using a Perkin Elmer DSC 7 (Norwalk, CT, USA) apparatus. 3–5 mg of samples were heated from 30 to 300 °C at 10 °C min⁻¹ heating rate in nitrogen atmosphere. The thermal stability and decomposition of the phosphine were determined by thermogravimetric analysis (TGA) using a Perkin Elmer TGA 6 (Norwalk, CT, USA) apparatus. 3–5 mg of samples were heated from 30 to 700 °C at 10 °C min⁻¹ heating rate in nitrogen and oxygen atmosphere. Digital optical microscopy (DOM) was applied to study the
appearance of the new phosphine stabilizer. Micrographs were recorded using a Keyence VHX 5000 microscope (Osaka, Japan) at 400× magnification. The mass change of 1 g pure phosphine antioxidant during storage in daylight and dark under ambient conditions was measured for one year using an analytical balance.

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). The measurements were done in oxygen atmosphere at a constant 20 mL, flow rate and 190 °C in triplicates. Opened aluminum pans and the same Perkin Elmer DSC 7 (Norwalk, CT, USA) apparatus mentioned above were used in accordance with the ISO 11357–6:2018 standard. 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 Bruker Tensor 27 (Leipzig, Germany) spectrophotometer. Five parallel measurements were carried out on each sample between 4000 and 400 cm⁻¹ wavenumbers 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 details of the determination of the concentration of the vinyl group were described in our earlier publication [22]. The chemical structure of the novel phosphine additive was studied by FTIR spectroscopy using the same Tensor 27 apparatus in the Attenuated Total Reflectance (ATR) mode before and after one year of aging. 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.

Results and discussion

The results obtained in the study are discussed in several sections. The characteristics of the phosphine synthesized by us are presented first, followed by the characterization of its inherent stability. The stabilization efficiency of the potential secondary antioxidant is compared to that of the commercial phosphorous stabilizers in the subsequent section, followed by a discussion of the results and their practical consequences.

Stabilizer characteristics

The newly synthesized stabilizer, octadecyldiphenylphosphine (NatPhos), is a white solid material produced as fine waxy powder (Fig. 1). Its chemical structure is presented in Scheme 2. The molecular weight of the compound is 438.7 g mol⁻¹, and its natural raw material content is 57.8% (the ratio of the mass of the saturated fatty acid with an 18-carbon chain from stearic acid to the total mass of the compound) that is a considerable advantage compared to commercial secondary antioxidants.

The melting temperature ($T_m$) of the compound is an important characteristic of all additives used in a polymer. The additive should melt at the temperature of processing to help its distribution, but also its dissolution in the polymer. One of the disadvantages of some natural antioxidants is their high melting temperature, which complicates their handling and hinders their dissolution. For example, the melting point of quercetin is 316 °C and its solubility in HDPE is 15 ppm [16]. Bergbreiter and Chandran [34] reported 49–50 °C for the melting point of octadecyldiphenylphosphine. The melting temperature of the synthesized product was determined by differential scanning calorimetry. The trace recorded during the heating of the sample is presented in Fig. 2. The peak temperature of melting is 56.0 °C, but the melting peak shows a shoulder indicating the presence of two crystal modifications or imperfect crystals. The melting point is somewhat lower than the value reported in the literature [34]. The reason could originate in the different crystallization conditions or the higher purity of the product synthesized by us. The appearance of the stabilizer and its melting temperature indicate that the long aliphatic chains crystallize, the $T_m$ of NatPhos is very close to that of stearic acid (69.3 °C) also indicated in Fig. 2. Accordingly, the powder can be handled easily, and it definitely melts during processing; thus, one expects its homogeneous distribution in the polymer, while its chemical structure, the presence of the long aliphatic chain, is expected to assure sufficient solubility.
Stability of the additive

The inherent stability of an additive is an important issue that can influence its efficiency considerably [36]. The additive must be stable during the processing of the polymer but also during storage and use. The efficiency of rutin, a flavonoid type natural antioxidant, proved to be smaller than that of quercetin because of the thermal degradation of its glucoside moiety [18]. Phosphines are very reactive compounds, which were shown to react even with molecular oxygen; thus, their storage stability might be insufficient for practical applications [32].

The thermal stability of the additive was studied by thermogravimetry. Traces recorded in nitrogen and oxygen atmosphere are presented in Fig. 3. Considerable mass loss starts only above 300 °C; thus, the stabilizer has sufficient heat stability. Interestingly, the phosphine antioxidant loses more mass in nitrogen atmosphere than in oxygen. Obviously, mainly the aliphatic moiety of the compound decomposes in nitrogen atmosphere. At the same time, reactions with molecular oxygen may take place in oxygen atmosphere, thus leading to a smaller decrease in mass at the same temperature. The results clearly prove that the newly synthesized compound is sufficiently stable to be used as a processing stabilizer in polyethylene.

The storage stability of NatPhos was determined by following the change of its mass during storage under dark and in normal light. The experiment was carried out for a year, and possible chemical changes in the structure of the compound were followed by FTIR spectroscopy. The mass of the sample decreased when it was stored in dark, enclosed in a cabinet, while it increased during storage in daylight. The first change can be explained by the decomposition of the sample through the cleavage of some bonds, while the increase by the reaction with oxygen initiated by irradiation with light. The behavior of the compound during storage is in complete accordance with the results obtained by thermogravimetric analysis (see Fig. 3).

In order to obtain further information about the chemical reactions taking place during the storage of the additive under the two conditions, the powder was analyzed by FTIR spectroscopy. The spectra recorded on the original, neat the sample decreased when it was stored in dark, enclosed in a cabinet, while it increased during storage in daylight. The first change can be explained by the decomposition of the sample through the cleavage of some bonds, while the increase by the reaction with oxygen initiated by irradiation with light. The behavior of the compound during storage is in complete accordance with the results obtained by thermogravimetric analysis (see Fig. 3).

In order to obtain further information about the chemical reactions taking place during the storage of the additive under the two conditions, the powder was analyzed by FTIR spectroscopy. The spectra recorded on the original, neat
sample and on those stored for one year under different conditions are presented in Fig. 5. According to the spectra, the structure of the material changes during storage under both conditions. The structural changes occurring are related to the phosphorous moiety of the stabilizer; new peaks appear at 1261, 1183, and around 800 cm⁻¹ wavenumbers indicating the oxidation of the phosphine structure. The main difference between the spectra recorded on samples stored in dark and in light is the appearance of a relatively strong absorbance at 1183 cm⁻¹ wavenumber in the spectrum of the sample irradiated by daylight. The appearance of the vibration confirms the reaction with molecular oxygen and the formation of phosphine oxides during storage according to the reaction presented in Scheme 3. The oxidation of phosphines and their reaction with peroxides were shown to proceed through phosphorene intermediates [37–41]. The formation of these compounds and their transformation by different routes under dissimilar conditions might lead to the differences observed in Fig. 5. Although the new additive takes part in reactions during storage and its structure changes somewhat, these changes are not significant (see Fig. 4); thus, we might hope that it retains sufficient activity to stabilize polyethylene during processing and use.

Stabilization efficiency

Various reactions take place during the processing of polyethylene. The dominating reaction determining the processing characteristics of Phillips-type polyethylenes is the reaction of the vinyl groups which, under the oxygen-poor conditions of melt processing, lead to long-chain branching and the increase in viscosity [42–45]. The decrease in the number of vinyl groups during multiple extrusion is usually closely related to changes in the MFR of the polymer. The effect of the type of the phosphorous secondary stabilizer and processing history on the vinyl group content of the polymer is presented in Fig. 6. Vinyl content decreases in all cases with an increasing number of extrusions, but not drastically. The combination of the primary phenolic antioxidant and the phosphorous stabilizer results in quite efficient additive package, at least at the additive content used. The comparison of the effect of the three secondary stabilizers indicates that the most efficient in retaining vinyl content is the phosphite, while the poorest is the phosphonite. The effect of the newly synthesized phosphine stabilizer is somewhere in between but closer to the phenolic antioxidant, used as a single additive, and to the phosphonite. If we assume that long chain branching is the main reaction determining the properties of the polymer, the most efficient stabilizer must be the phosphite, and it should offer the most significant protection to the polymer during processing. We must call the attention to the fact here, though, that the largest change in the chemical structure of the polymer occurs during the first extrusion [46]. The vinyl group content of the nascent polymer powder obtained from the polymerization plant is

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**Scheme 3** Proposed reaction of the new phosphine with molecular oxygen

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**Fig. 5** FTIR spectra recorded on the neat, nascent phosphine after production (a) and after storage in dark (b) and in light (c). The range was selected to show the characteristic vibrations of the phosphorous and the largest changes in structure during storage.

**Fig. 6** Effect of processing history on the vinyl group content of the polymer for the four additive packages studied. Symbols: (O) phosphine, (Δ) phosphonite, (▽) phosphite, (◻) I1010.
1.271 vinyl/1000 C, which decreases to around 0.9 in the first extrusion. The largest change in vinyl content in the six consecutive extrusions is around 0.03 vinyl/1000 C, i.e., the changes in the first extrusion determine the structure and properties of the polymer.

The melt flow rate of the polymer reflects very sensitively all changes in the molecular structure of the polymer during processing. MFR is plotted against the number of extrusions in Fig. 7 for the four compounds prepared and studied in this work. All stabilizer packages offer adequate melt stabilization to the polymer; MFR changes only slightly during multiple extrusions. The beneficial effect of using a secondary stabilizer is clear from the figure. The smallest absolute values and the largest decrease in MFR during multiple processing are observed for the compound stabilized only with the primary stabilizer, I1010, alone. The effect of the reactions during the first extrusion of the polymer is also demonstrated by the figure (the MFR of the neat PE powder is 0.3 g min$^{-1}$). Different initial values are obtained with the different additive packages indicating that the chemical structure of the polymer changed to different extents in the first extrusion in their present. The most efficient package seems to be the combination of the newly synthesized phosphate and I1010; the largest MFR value and the smallest change in MFR were obtained with this package. The comparison of the effect of the three phosphorous secondary antioxidants on MFR and vinyl content indicates that besides the chain extension reaction of the vinyl group, other reactions also take place during processing; the different types of phosphorus secondary stabilizers play different roles in them.

Color is an important attribute of a polymer product in numerous applications. Phenolic antioxidants are known to discolor the polymer to smaller or larger extent due to the formation of quinoidal compounds and secondary antioxidants further modify discoloration. Yellowness index values measured on the compounds after multiple extrusions are plotted against processing history in Fig. 8. Color is not extremely strong, but considerable differences can be seen among polymers containing the different additive packages. The strongest discoloration is observed when the primary hindered phenolic antioxidant is used alone. The color of the polymer containing the package with the phosphite stabilizer has a similarly strong yellow tint. The most beneficial are the two packages containing the phosphonite and especially the new phosphine secondary stabilizer. As mentioned above, discoloration is caused by quinoidal compounds forming in the reaction of the phenolic antioxidant and similar reactions take place in the case of the-phosphite as well. The reactions are absent in the presence of the other two secondary stabilizers. Moreover, they modify the action of the primary stabilizer as well, thus hindering the formation of quinoidal compounds and discoloration.

Depending on their application, some products, like pipes, automotive parts, or geotextiles, must possess sufficient residual stability. This property of the polymer is usually characterized by the oxygen induction time (OIT) and claimed to depend mostly on the amount of the unreacted phenolic antioxidant remaining in the polymer after processing. The OIT of the compounds studied is plotted against the number of extrusions in Fig. 9. The hypothesis that primarily the amount of the phenolic antioxidant determines residual stability is not confirmed by the results. The
polymer prepared with I1010 has significantly smaller OIT than the other compounds containing also the phosphorous secondary stabilizers. These latter ones were shown to protect the primary antioxidant during processing, and the interaction of the two additives results in the beneficial outcome of increasing stability [27]. The effect of the three secondary stabilizers is quite similar, although the phosphate seems to perform somewhat better than the other two phosphorus compounds. The slower consumption of the phosphate can explain the better performance compared to the other two stabilizers, which take part in more reactions in the first, but also during subsequent extrusions. Nevertheless, the phosphonite and especially the phosphine are more favorable in other aspects, like melt stabilization and color, than the phosphate.

**Correlations, discussion**

The goal of this project was to explore the efficiency of the newly synthesized phosphate compound and check the feasibility of its application as a stabilizer in polyethylene, but possibly also in other polymers. As mentioned earlier, the main degradation reaction of Phillips-type polyethylenes is the addition of alkyl radicals to their terminal vinyl group, which occurs mainly under the oxygen-poor conditions of melt processing. Accordingly, often a very close correlation can be found between the vinyl content and the viscosity of polyethylene, especially if the same additive combination is used but in different amounts. In order to check this relationship, the MFR and the vinyl group content of our polyethylene were plotted against each other in Fig. 10. Apart from a few deviating points a correlation was obtained between the two quantities indeed, however, not a single one; a separate relationship can be seen for the three phosphorous stabilizers and the compound containing only I1010 alone. The separate correlations confirm our previous conclusion that the reactions of the vinyl groups are important and influence polymer properties, but other reactions also take place which have at least as large impact on properties as vinyl reactions.

Although the largest number of vinyl groups remain intact in the presence of the phosphate stabilizer, the smallest viscosity (largest MFR) is measured in the presence of the phosphonite and phosphine antioxidants. Moreover, the relatively poor performance of I1010 alone calls the attention to the necessity of using a secondary stabilizer. All results indicate that the reactions in the first extrusion step are at least as important, or maybe even more important, than those occurring in further processing steps. The phosphonite and the phosphine seem to take part in these reactions more efficiently than the phosphate and prevent structural changes which lead to the deterioration of polymer properties, primarily to the change of viscosity.

An additional issue that must be considered here is the functionality of the phosphorus additives, the molarity of the antioxidant added to the polymer. As Schemes 1 and 2 show, the three phosphorous antioxidants contain different number of the P(III) functionality and their molecular weight is also different. However, they were added to the polymer in the same amount, at 1000 ppm. The calculation of molar amounts shows that because of its smaller molecular weight, the phosphite contains 4.64 mmol/g P(III) moiety, the phosphonite 1.93, while the phosphine 2.28 mmol/g. Considering this fact and the effect of the three phosphorus antioxidants, we can conclude that the phosphonite and especially the
phosphine are much more efficient stabilizers than the phosphite. Their use is more beneficial especially because they interfere with reactions taking place in the first processing step, which deteriorates polymer properties.

Conclusions

A novel phosphine type potential secondary stabilizer was synthesized successfully with large natural raw material content. The relatively large molecular weight and the long aliphatic moiety decrease the danger of its migration from the matrix; thus, it might be used also in products in contact with food. The stabilizer was produced as a waxy white powder with a relatively low melting temperature. Both the thermal and the storage stability of the stabilizer were sufficient for practical use. Although it reacts with oxygen during storage, the reaction is rather slow, and the efficiency of the stabilizer does not decrease within a reasonable time frame. Comparing the stabilizing efficiency of the new additive to existing secondary antioxidants shows that it is at least as efficient as the products available on the market. The new stabilizer proved to be the most efficient in melt stabilization and in preventing discoloration, while the residual stability of the polymer is similar in the presence of all three secondary antioxidants. The feasibility study presented here proved that the new compound could be used as a potential stabilizer in practice but further work must be done to determine its effect at various additive contents and to find the optimum package offering maximum benefits in efficiency, cost and environmental impact.

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References

1. Brocca D, Arvin E, Mosbæk H. Identification of organic compounds migrating from polyethylene pipelines into drinking water. Water Res. 2002;36(15):3675–80. https://doi.org/10.1016/S0043-1354(02)00084-2.
2. Xu D-P, Li Y, Meng X, Zhou T, Zhou Y, Zheng J, et al. Natural antioxidants in foods and medicinal plants: extraction, assessment and resources. Int J Mol Sci. 2017;18(1):96. https://doi.org/10.3390/ijms18010096.
3. Moreno-Jimenez MR, Trujillo-Esquível F, Gallegos-Corona MA, Reynoso-Camacho R, González-Laredo RF, Gallegos-Infante JA, et al. Antioxidant, anti-inflammatory and anticarcinogenic activities of edible red oak (Quercus spp.) infusions in rat colon carcinogenesis induced by 1,2-dimethylhydrazine. Food Chem Toxicol. 2015;80:144–53. https://doi.org/10.1016/j.fct.2015.03.0119.
4. Reguengo LM, do Nascimento RD, da Fonesca Machado AP, Marostica MR. Signaling pathways and the potential anticarcinogenic effect of native Brazilian fruits on breast cancer. Food Res Int. 2022;155:111117. https://doi.org/10.1016/j.foodres.2022.111117.
5. Abdel-Razik EA. Aspects of degradation and stability of ABS copolymers. I. Effect of β-carotene as antioxidant. J Polym Sci Part A Polym Chem. 1989;27(1):343–55. https://doi.org/10.1002/pola.1989.080270129.
6. López-Rubio A, Lagaron JM. Improvement of UV stability and mechanical properties of biopolymesters through the addition of β-carotene. Polym Degrad Stab. 2010;95(11):2162–8. https://doi.org/10.1016/j.polymdegradstab.2010.03.002.
7. Tátraaljai D, Major L, Földes E, Pukánszky B. Study of the effect of natural antioxidants in polyethylene: performance of β-carotene. Polym Degrad Stab. 2014;102:33–40. https://doi.org/10.1016/j.polymdegradstab.2014.02.012.
8. Tátraaljai D, Kirschweng B, Kovács J, Földes E, Pukánszky B. Processing stabilisation of PE with a natural antioxidant, curcumin. Eur Polym J. 2013;49(6):1196–203. https://doi.org/10.1016/j.eurpolymj.2013.02.018.
9. Laermers S, Zambetti P. Alpha-tocopherol (vitamin E)—The natural antioxidant for polylefins. J Plast Film Sheeting. 1992;8(3):228–48.
10. Al-Malaika S, Ashley H, Issenhuth S. The antioxidant role of α-tocopherol in polymers. I. The nature of transformation products of α-tocopherol formed during melt processing of LDPE. J Polym Sci Part A Polym Chem. 1994;32(16):3099–113.
11. Koontz JL, Marcy JE, O’Keefe SF, Duncan SE, Long TE, Moffitt RD. Polymer processing and characterization of LDLPE films loaded with α-tocopherol, quercetin, and their cyclodextrin inclusion complexes. J Appl Polym Sci. 2010;117(4):2299–309.
12. Levon K, Huhtala J, Malm B, Lindberg J. Improvement of the thermal stabilization of polyethylene with lignosulphonate. Polymer. 1987;28(5):745–50.
13. Alexy P, Košiková B, Podstránská G. The effect of blending lignin with polyethylene and polypropylene on physical properties. Polymer. 2000;41(13):4001–8.
14. Sadeghifar H, Argyropoulos DS. Correlations of the antioxidant properties of softwood kraft lignin fractions with the thermal stability of its blends with polyethylene. ACS Sustain Chem Eng. 2015;3(2):349–56.
15. Kirschweng B, Tátraaljai D, Földes E, Pukánszky B. Natural antioxidants as stabilizers for polymers. Polym Degrad Stab.
16. Tátraaljai D, Földes E, Pukánszky B. Efficient melt stabilization of polyethylene with quercetin, a flavonoid type natural antioxidant. Polym Degrad Stab. 2014;102:41–8.

17. Kirschweng B, Bencze K, Sárközi M, Hégely B, Samu G, Hári J, et al. Melt stabilization of polyethylene with dihydromyricetin, a natural antioxidant. Polym Degrad Stab. 2016;133:192–200.

18. Kirschweng B, Tilinger DM, Hégely B, Samu G, Tátraaljai D, Földes E, et al. Melt stabilization of PE with natural antioxidants: comparison of rutin and quercetin. Eur Polym J. 2018;103:228–37.

19. Cerruti P, Malinconico M, Rychly J, Matisova-Rychla L, Carfagna C. Effect of natural antioxidants on the stability of polypropylene films. Polym Degrad Stab. 2009;94(11):2095–100.

20. Ambrogi V, Cerruti P, Carfagna C, Malinconico M, Marturano V, Perrotti M, et al. Natural antioxidants for polypropylene stabilization. Polym Degrad Stab. 2011;96(12):2152–8.

21. Tátraaljai D, Tang Y, Pregi E, Vági E, Horváth V, Pukánszky B. Stabilization of PE with pomegranate extract: contradictions and possible mechanisms. Antioxidants. 2022;11(2):418.

22. Tátraaljai D, Tang Y, Pregi E, Vági E, Pukánszky B. Pomegranate extract for the processing stabilization of polyethylene. J Vinyl Addit Technol. 2021. https://doi.org/10.1002/vnl.21874.

23. Rojas-Lema S, Torres-Giner S, Quiles-Carrillo L, Gomez-Caturla J, Garcia-Garcia D, Balart R. On the use of phenolic compounds present in citrus fruits and grapes as natural antioxidants for thermo-compressed bio-based high-density polyethylene films. Antioxidants. 2021;10(1):14.

24. Scott G. Mechanisms of polymer stabilization. In: Chemical transformations of polymers. Elsevier; 1972. p. 267–89.

25. Allen NS, Edge M. Fundamentals of polymer degradation and stabilization. New York: Springer Science & Business Media; 1992.

26. Zweifel H. Stabilization of polymeric materials. New York: Springer Science & Business Media; 2012.

27. Allen NS, Jones AP, Liaw CM, Edge M, Keck-Antoine K, Yeo J-H. High-temperature stabilization of polypropylene using hindered phenol–thioester stabilizer combinations. Part 2: optimization and efficacy via encapsulation with silicate fillers. J Vinyl Addit Technol. 2021;27(2):389–409. https://doi.org/10.1002/vnl.21814.

28. Allen NS, Edge M. Perspectives on additives for polymers. 1. Aspects of stabilization. J Vinyl Addit Technol. 2021;27(1):5–27. https://doi.org/10.1002/vnl.21807.

29. Földes E, Maloschik E, Kriston I, Staniek P, Pukánszky B. Efficiency and mechanism of phosphorous antioxidants in Phillips type polyethylene. Polym Degrad Stab. 2006;91(3):479–87. https://doi.org/10.1016/j.polymdegradstab.2005.03.024.

30. Schwetlick K, Habicher WD. Organophosphorus antioxidants action mechanisms and new trends. Die Angew Makromol Chem Appl Macromol Chem Phys. 1995;232(1):239–46.

31. Pénzes G, Domján A, Tátraaljai D, Staniek P, Földes E, Pukánszky B. High temperature reactions of an aryl–alkyl phosphine, an exceptionally efficient melt stabiliser for polyethylene. Polym Degrad Stab. 2010;95(9):1627–35. https://doi.org/10.1016/j.polymdegradstab.2010.05.031.

32. Stuebe C, Lesuer WM, Norman GR. The Preparation and reactions of diphenylphosphinous chloride. J Am Chem Soc. 1955;77(13):3526–9. https://doi.org/10.1021/ja01618a030.

33. Bagbreyer DE, Chandran R. Polyethylene-bound rhodium(I) hydrogenation catalysts. J Am Chem Soc. 1987;109(1):174–9. https://doi.org/10.1021/ja00235a027.

34. Davies JA, Mierzwiaz JK, Syed R. Synthesis, characterization, and coordination chemistry of long chain n-alkyldiphenylphosphine ligands. J Coord Chem. 1988;17(1):25–43.

35. Taghvaei M, Jafari SM. Application and stability of natural antioxidants in edible oils in order to substitute synthetic additives. J Food Sci Technol. 2015;52(3):1272–82. https://doi.org/10.1007/s11391-013-1080-1.

36. Cerruti P, Malinconico M, Ryhly J, Matisova-Rychla L, Carfagna C. Effect of natural antioxidants on the stability of polypropylene. Polym Degrad Stab. 2009;94(11):2095–100.

37. Ambrogi V, Cerruti P, Carfagna C, Malinconico M, Marturano V, Perrotti M, et al. Natural antioxidants for polypropylene stabilization. Polym Degrad Stab. 2011;96(12):2152–8.

38. Tátraaljai D, Tang Y, Pregi E, Vági E, Horváth V, Pukánszky B. Stabilization of PE with pomegranate extract: contradictions and possible mechanisms. Antioxidants. 2022;11(2):418.

39. Tátraaljai D, Tang Y, Pregi E, Vági E, Pukánszky B. Pomegranate extract for the processing stabilization of polyethylene. J Vinyl Addit Technol. 2021. https://doi.org/10.1002/vnl.21874.

40. Nanni A, Messori M. A comparative study of different winemaking by-products derived additives on oxidation stability, mechanical and thermal proprieties of polypropylene. Polym Degrad Stab. 2018;149:9–18. https://doi.org/10.1016/j.polymdegradstab.2018.01.012.

41. Rojas-Lema S, Torres-Giner S, Quiles-Carrillo L, Gomez-Caturla J, Garcia-Garcia D, Balart R. On the use of phenolic compounds present in citrus fruits and grapes as natural antioxidants for thermo-compressed bio-based high-density polyethylene films. Antioxidants. 2021;10(1):14.

42. Scott G. Mechanisms of polymer stabilization. In: Chemical transformations of polymers. Elsevier; 1972. p. 267–89.

43. Allen NS, Edge M. Fundamentals of polymer degradation and stabilization. New York: Springer Science & Business Media; 1992.

44. Zweifel H. Stabilization of polymeric materials. New York: Springer Science & Business Media; 2012.

45. Allen NS, Jones AP, Liaw CM, Edge M, Keck-Antoine K, Yeo J-H. High-temperature stabilization of polypropylene using hindered phenol–thioester stabilizer combinations. Part 2: optimization and efficacy via encapsulation with silicate fillers. J Vinyl Addit Technol. 2021;27(2):389–409. https://doi.org/10.1002/vnl.21814.

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