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ARTICLE

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The chances of thermooxidation stabilization of poly (3-hydroxybutyrate) during processing–A critical evaluation

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Abstract

The performance of a series of thermooxidation stabilizers was investigated in poly(3-hydroxybutyrate) (PHB) during processing by multiple extrusion at 190°C. The issue was to find out if PHB may be processing stabilized or not. Phenols of different steric hindrance, phosphites, amine oxide, hydroxylamine, lactone, hindered amine and carbodiimide were tested as potential stabilizers and their efficiencies compared with non-stabilized polymer as a reference. Multiple extrusion data was evaluated using the processing degradation index (PDI) formerly designed for polypropylene. Changes in molecular weight were monitored as well. The results have shown that none of the stabilizing structures, currently successfully used in other polymers, have the ability to protect PHB. This indirectly implies that no radical chain scission takes place during PHB processing, i.e. no thermooxidation takes place. Moreover, nearly all of the tested structures act as prodegradants in PHB, some of them very strong. The strongest ones contain P or N atoms with asymmetrical free electron pairs in their molecules that evidently accelerate the main degradation mechanism of PHB—thermally induced cis-elimination.

KEYWORDS

biopolymers and renewable polymers, degradation, extrusion, polyesters, stabilization

1 | INTRODUCTION

Poly(3-hydroxybutyrate) (PHB) first described in the twenties of the past century has been known as a bio-sourced polymer with a great future, proposed as a potential substitute of some petrochemical based polymers, Figure 1. In numerous papers its properties were compared to those of polypropylene, but PHB high tendency to crystallization resulting in consequent brittleness still made its comparison problematic and its practical use limited. A lot of attention was paid to improving its properties, especially to elimination of high crystallinity resulting in very low strain at break making its application problematic.[1–3]

Investigating mechanical properties, many scientific papers reported PHB processed under laboratory conditions. In these papers tensile test specimens were cut from the films prepared by solution casting from chloroform.[4–6] This approach did not provide full information on polymer behavior, since it skipped the step of extrusion which is inevitable in processing on industrial scale. Thus, the papers reporting processing using single- or twin-screw extrusions or kneading techniques were found to be much closer to reality.[7–9]

During extrusion, polymers commonly undergo degradation due to high temperatures and thermo-mechanical stress, both under the limited access to oxygen. In the case of PHB the processing temperature

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window is limited by its melting point 175–180°C and the upper threshold 200–220 °C above which the volatiles start to be released. In the course of processing, hydrolysis leading to the formation of acidic and alcoholic functionalities and random scission by cis-elimination leading to the crotonic acid derivatives may take place, Figure 2. Both occur statistically within the polymer chain and decrease its molecular weight.[10–12]

While hydrolysis at high temperatures, typical for esters, may be prevented by drying, decomposition by cis-elimination is purely temperature dependent and needs no other reactant. Beside the main ester functionalities, PHB polymer backbone is composed of hydrocarbon parts that may be affected by heat and mechanical stress during processing and subsequently oxidized. The problem of PHB stability concerns especially its extrusion. Relatively narrow processing window 180–190°C and sensitivity to processing by extrusion induce a question if there is a way how to protect PHB during processing and make it more resistant to higher temperatures, higher screw rotation speed and longer residence time in the barrel. At this point published literature data is inconsistent, some papers report the use of thermooxidation stabilization by phenols, some by phenol-phosphite blends, some use only phosphite and many other do not use thermooxidation protection at all.[6,12–16] Some information on stabilization appeared already in the 80s; however, it was not supported by accessible experimental results.[12] Also our laboratory results were not unambiguous so that we decided to generate enough experimental data in order to elucidate this problem. A series of polymer stabilizers (antioxidants) was investigated with respect to their possible use in PHB during processing in order to answer the question if PHB can be efficiently stabilized or not. Presently, protective agents such as chain extenders are used as well. Their effect on PHB matrix is more provable and they are sometimes presented as “stabilizers” but their mechanism of action is different.[17,18] They do not retard thermooxidation itself, but they heal the consequences of thermal or hydrolytic decomposition. They react with free carboxylic and hydroxyl functionalities, forming new cross-links in polymer and increasing the viscosity of polymer melt. The action of chain extenders was not the area of our interest but one of them tested in this work was used as a reference.

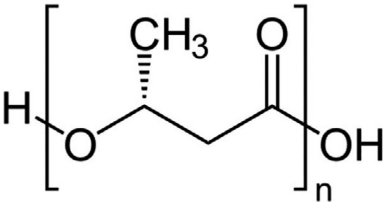

FIGURE 1 Poly(3-hydroxybutyrate) structure (PHB)

2 | MATERIALS

Poly(3-hydroxybutyrate) Biomer PHB—a custom compound with 0.5% boronitride (BN) and 5% tributyl citrate (TBC) provided by Biomer (dr. Haenggi). The following compounds were used as stabilizers: Butylated hydroxytoluene (BHT, Sigma–Aldrich); 1,3,5-Tris(4-t-butyl-3-hydroxy-2,6-dimethylbenzyl)isocyanurate (Cyanox 1790, Cytec); Pentaerythrityl tetrakis[3-(3,5-di-tert-Bu-4-hydroxyphenyl)propionate] (Irganox1010; BASF); Tris (2,4-di-t-Bu-phenyl)phosphite (Irgafos 168, BASF); Irganox B225 blend (BASF); Bis(2,4-di-t-butylphenyl)pentaerythrityl diphosphite (Ultranox 626, Addivant); Bis(hydrogenated rape-oil alkyl)methyl amine, N-oxides (Genox EP, Chemtura); distearyl hydroxylamine (Irgastab FS042, BASF); 5,7-di-t-butyl-3-(3,4-di-methylphenyl)-3H-benzofuran-2-one (HP136, Ciba); N,N′-bis (2,2,6,6-tetramethyl-4-piperidyl)-N,N′-diformyl hexamethylenediamine (Uvinul 4050H, BASF); D,L-α-tocoferol (Ronotec 201, Roche); Natural curcuma (food grade); Polymeric carbodiimide (Stabilizer 9000, Raschig).

Native PHB granulate received from the supplier was surface treated with 0.2% TBC, then blended with 0.5% stabilizer and compounded.

3 | METHODS AND MEASUREMENT

Extrusion experiments involving both compounding and multiple extrusion were carried out using a laboratory

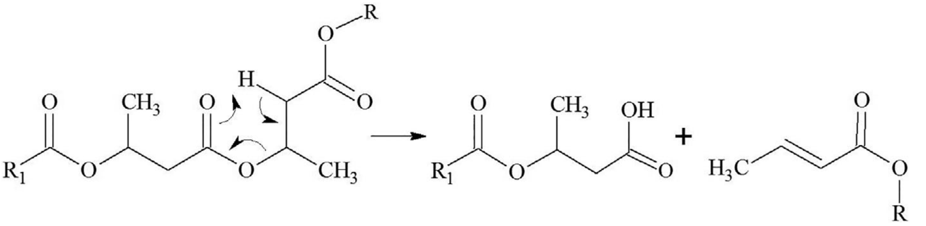

FIGURE 2 Poly(3-hydroxybutyrate) (PHB) thermal decomposition by cis-elimination[11]

HAAKE single-screw extruder, D = 19 mm, L/D = 30 at temperatures 190, 190, 185 and 180°C (hopper to die)/ 60 rpm; nozzle diameter 3 mm. Polymer melt was water quenched at 60°C and pelletized. Before each extrusion polymeric material was dried at 60°C for 2 h. Multiple extrusion was realized by 5-fold extruder pass, after each one polymer melt-volume rate (MVR) was measured on Dynisco LMI5000 melt-indexer at 190°C/2.16 kg (EN ISO 1133). Compounding step was denoted as zero extrusion, multiple extrusions 1 to 5. Thermogravimetric analysis (TGA) was carried out on TGA Q500 at 50–400°C temperature range, using samples 10–13 mg under the atmosphere of nitrogen (60 ml/min). Average molecular weights were determined by means of SEC method using Agilent Technologies 1100 Series. Instrument is equipped with isocratic pump, fraction collector, refractive index detector and autosampler. PLgel 10 μm mixed B column thermostated to 30°C with chloroform as the eluent at a flow rate 1 ml/min. Calibration using 12 standards 1.6–1100 kDa.

4 | RESULTS AND DISCUSSION

The tested series of stabilizing structures was designed in order to cover the most important stabilization mechanisms widely utilized in industry as well as the mechanisms marginal but existing and capable of potential interference with radical thermooxidation scission of hydrocarbons.

The class of sterically hindered phenols is represented by the fully hindered low molecular BHT (AO-1), fully hindered high-molecular Irganox 1010 (AO-2), partly hindered high-molecular Cyanox AO 1790 (AO-3) and low-hindered, low-molecular weight vitamin E and curcuma (AO-11 and 12). All these structures act as "chain breaking antioxidants" and interfere with radical oxidative scission of hydrocarbons by eliminating alkylperoxyl radicals. Consequently they form relatively stable fenoxyl radicals, the stability of which is dependent on the degree of 2,6- sterical hindrance of active phenolic moiety.[19–21]

Organic phosphites applied as secondary stabilizers are represented by non-hydrolysable Irgafos 168 (AO-4), its synergistic 1:1 blend with phenol Irganox B225 (AO-5) and partially hydrolyzed Ultranox 626 (AO-6). Phosphites are often described as hydroperoxide decomposers, but their reaction mechanism is more complex and beside hydroperoxides they also react with alkoxyl and alkylperoxyl radicals.[19,20,22] Phenol-phosphite synergistic blends such as AO-5 are widely used in industry. The efficiency of phosphites also depends on their hydrolyzability, which in some cases positively contributes to the overall stabilization performance. In this respect partially hydrolyzed AO-6 is a typical example.[23]

The structures such as aminoxide, hydroxylamine and lactone (AO-7 to 9) belong to those known but marginally used. They possess the ability to react with C-centered radicals formed during processing and prevent their oxidation.[19] Their overall efficiencies and price/performance ratios, however, are not much advantageous, as well as their administrative (patent) and hygienic limitations. This all makes their practical use limited. Nevertheless, the reactions of their structures are highly specific so that they had to be involved in this series as well.

AO-10 is a representative of hindered amine light stabilizers (HALS) class. Despite not being processing stabilizer, it was also enrolled in the series due to its complex mechanism. HALS are known by the ability to react with C-centered, alkoxyl and alkylperoxyl radicals, as well as the ability to non-radically decompose hydroperoxides and neutralize acidic species in polymer.[19,20,24] Beside protection from the effects of light, HALS are very efficient thermooxidation stabilizers. This is the main reason of involving AO-10 in this screening series.

The last one—carbodiimide Stabilizer 9000 (Ch-X) has nothing to do with polymer thermooxidative protection. Despite it is often presented as "stabilizer," it reacts with hydrolytic scission intermediates, forms crosslinks, and partially improves the properties of polymer matrix. Its use in the series was only illustrative and it served as another reference for the stabilizers tested.[17]

Investigation of stabilization efficiencies was carried out by multiple extrusion. This approach has been frequently used for polyolefins, where the basic cylinder temperatures 240°C for HDPE and 260°C for PP are usually used in order to cause the maximum thermo-mechanical deterioration of the material tested. In the case of PHB, this method had not been applied yet, so that the optimum processing conditions providing applicable data had to be set at first. Definition of optimum processing temperature was carried out with the basic PHB matrix additivated with 0.5% BN and 5% TBC, no other additives were used.

As shown in Figure 3 processing temperature 180°C appeared to be low, the changes in MVR were minimum and occurred relatively late. On the other hand, processing at 200°C increased MVR so far that it was unmeasurable after 5th extrusion. These extremes delimited 190°C as the optimum temperature providing reasonable degree of deterioration and well measurable MVR.

In order to provide an evidence that degradation changes due to extrusion are not caused by the thermal

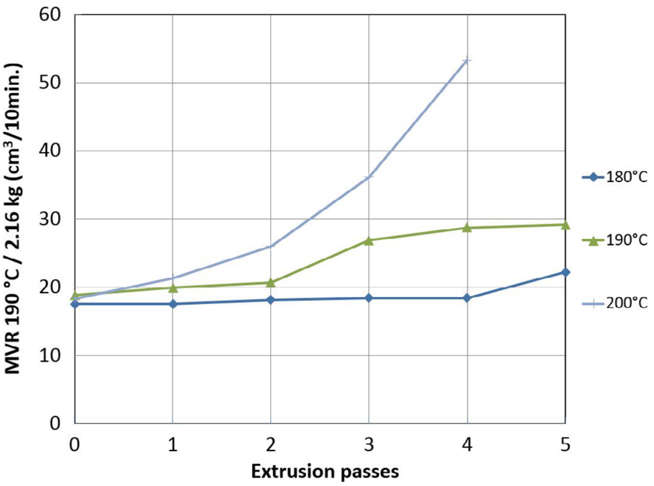

FIGURE 3 Poly(3-hydroxybutyrate) (PHB) - multiple extrusion at 60 rpm carried out at 180, 190 and 200°C [Color figure can be viewed at wileyonlinelibrary.com]

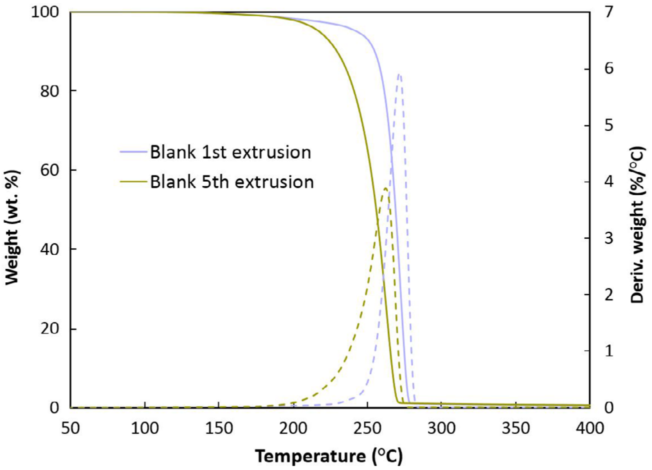

FIGURE 4 Thermogravimetric analysis (TGA) of blank under N_2 atmosphere determined after first and fifth extrusion at 180–190°C [Color figure can be viewed at wileyonlinelibrary.com]

decomposition of PHB itself, TGA analysis of Blank after 1st and 5th extrusion was carried out, Figure 4, Table 1. It can be seen that the purely thermal stability of Blank is sufficient and at 180–190°C temperature range used for extrusions remains practically unchanged even after five extrusions. Deterioration due to fifth extrusion decreases the onset of thermal decomposition down to 200°C that is still at least 10°C above the maximum processing temperature applied in extruder. Moreover, even the minimum mass loss (1 to 1.4%) observed at processing temperatures may be more accounted for the partial loss of TBC added as plasticizer, originally present in PHB at 5% concentration.

Polymer behavior during processing was evaluated by means of multiple extrusion at 190°C/60 rpm with PHB formulated such as shown in Table 2.

TABLE 1 TGA - temperatures indicating 1% and 5% mass loss

	Temperature (°C)	
	1% loss	**5% loss**
Blank–first extrusion	180.8	243.3
Blank–fifth extrusion	180.1	217.8

Abbreviation: TGA, thermogravimetric analysis.

TABLE 2 PHB sample coding and formulations (base: 0.5% boronitride, 5.2% tributylcitrate)

Sample	Formulation	Stabilizer type
Blank	Base	None
AO-1	Base +0.5% BHT	Low-molecular phenol, 2,6-di-tBu substituted
AO-2	Base +0.5% Irganox 1010	High-molecular phenol, 2,6-di-t-Bu substituted
AO-3	Base +0.5% Cyanox AO 1790	High-molecular phenol, 2-methyl-6-t-Bu substituted
AO-4	Base +0.5% Irgafos 168	Phosphite, non-hydrolyzable
AO-5	Base +0.5% Irganox B225	Phenol-phosphite synergy blend (1:1)
AO-6	Base +0.5% Ultranox 626	Phosphite, partially hydrolysed *(30–34% free DTBP)*
AO-7	Base +0.5% Genox EP	Amine oxide
AO-8	Base +0.5% Irgastab FS042	Hydroxylamine
AO-9	Base +0.5% Irganox HP136	Lactone, benzofuranone
AO-10	Base +0.5% Uvinul 4050H	HALS, low the -molecular
AO-11	Base +0.5% Ronotec 201	Vitamin E, 2,6-dimethyl substituted phenol
AO-12	Base +0.5% natural curcuma	Low-molecular phenol, 2-methoxy substituted
Ch-X	Base +0.5% Stabilizer 9000	Carbodiimide chain extender

Abbreviation: PHB, poly(3-hydroxybutyrate).

The results attained were rather surprising and stabilizers could be divided into two groups according to the performance. In the first group depicted in Figure 5 it is evident that performance of stabilizers practically does not differ up to 3rd extrusion and exhibits processing stability comparable with that of unstabilized polymer. During 4th and 5th extrusions, the phenols, phosphites and their combinations, despite being very efficient in other

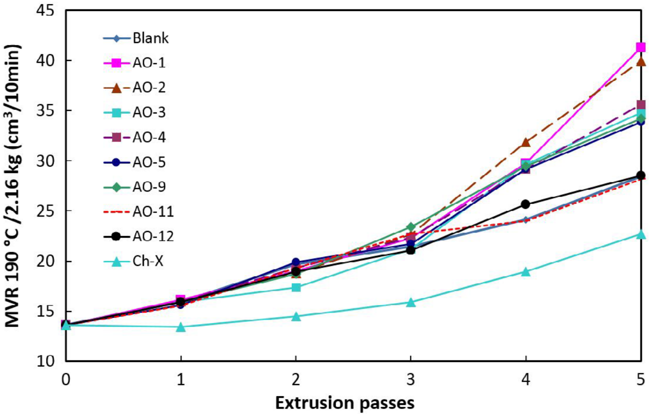

FIGURE 5 Poly(3-hydroxybutyrate) (PHB) + base + 0.5% stabilizer - multiple extrusion at 190°C/60 rpm [Color figure can be viewed at wileyonlinelibrary.com]

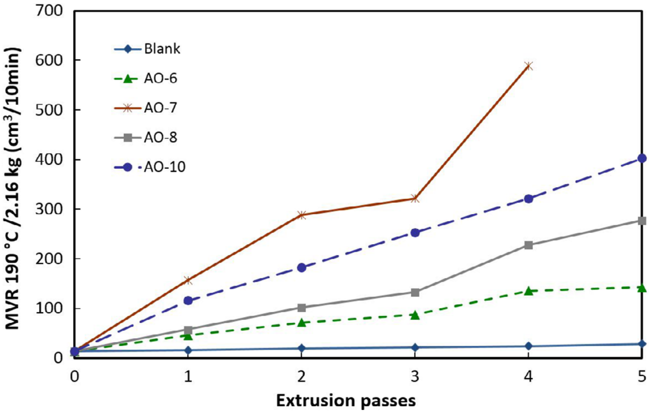

FIGURE 6 Poly(3-hydroxybutyrate) (PHB) + base + 0.5% stabilizer - multiple extrusion at 190°C/60 rpm [Color figure can be viewed at wileyonlinelibrary.com]

polymers, act prodegradatively and visibly decrease the processing stability of polymer. Natural antioxidants such as curcuma and vitamin E (AO-11, AO-12) behave completely neutrally and do not affect processing stability of polymer during the whole test.

A visibly different (and relatively the best) performance is exhibited by carbodiimide chain extender (Ch-X). Much less increased MVR compared to the non-stabilized reference polymer is a result of Ch-X reaction mechanism, forming bonds among polymer chains, changing morphology and consequently increasing the viscosity of polymer melt. Being not the issue of this work, however, the use of Ch-X only illustrates how different its effect in PHB can be.

The performance of the second group of stabilizers was found completely different, Figure 6. Compared to the reference Blank, they all exhibit extremely intensive increase in MVR starting even within the 1st extrusion, with AO-7 the fifth extrusion was not possible at all. Except AO-10 which is not a processing stabilizer, all the remaining ones performing more or less efficiently in other polymers act as very strong prodegradants in PHB. In order to quantify the extent of deterioration due to multiple extrusion, processing degradation index (PDI) was calculated according to Equation (1). PDI is a useful tool describing the processing deterioration of polymer by one single parameter.[25] The higher it is, the higher degree of degradation polymer exhibits.

$$\mathrm{PDI} = \frac{(\mathrm{MFI}_0 + \mathrm{MFI}_1 + \ldots + \mathrm{MFI}_n) - (n+1)\mathrm{MFI}_0}{(n+1)\mathrm{MFI}_0}100 = \frac{(\mathrm{MFI}_1 + \ldots + \mathrm{MFI}_n) - n\mathrm{MFI}_0}{(n+1)\mathrm{MFI}_0}100 \tag{1}$$

where MFI is the melt flow index (rate) and 0 to n is the number of extrusion.

The use of PDI was originally designed for polypropylene (PP), the processing degradation of which goes exclusively through the chain scission mechanism. In such a case, changes due to processing are reliably reflected by MFI, which is increased with increasing chain scission. All under the condition that no other interfering reactions such as cross-linking take place. Despite polypropylene and PHB differ in chemistry of their degradation, the chain scission as a prevailing mechanism is their common feature. In PHB the possible re-esterification reactions leading to the certain portion of chain extension take place only at the beginning of heating where terminal hydroxyl groups initially present in polymer are consumed. With consequent chain scission due to cis-elimination no new terminal hydroxyl groups are released. Possible release of hydroxyl groups due to hydrolysis is prevented by the patient drying of pellets before each extrusion. These facts show that the portion of possible cross-links related to the main polymer chain scission is negligible in PHB and the calculation of PDI originally proposed for PP may be applied directly without any changes. Not having exact data on PHB melt density, MVR were used instead of MFI, Figure 7.

PDI allowing the direct comparison of processing stability indicates that the common phenols, phosphites and their blends in the first group decrease processing stability 1.2 to 1.5 times, while in the second group 10 up to 37 times. No effect can be seen with AO-11 and 12, the relatively positive effect of Ch-X cannot be used for consideration due to its different mechanism of action.

During multiple extrusion most of the MVR values were found between 13 and 320 dg/min. Within the measured series some typical MVRs roughly covering this interval were selected and molecular weights of these samples were determined. Their plot against MVR is

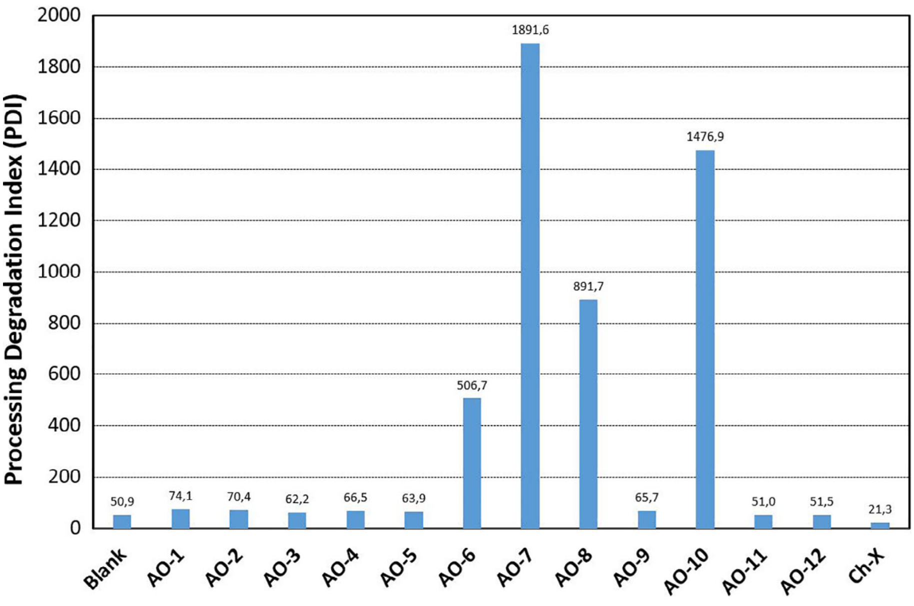

FIGURE 7 Processing degradation index (PDI) calculated for particular stabilizers based on multiple extrusion data [Color figure can be viewed at wileyonlinelibrary.com]

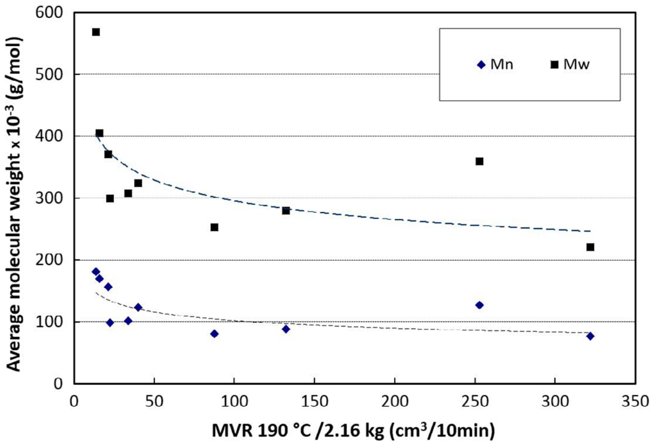

FIGURE 8 Molecular weights versus melt volume rate (MVR) [Color figure can be viewed at wileyonlinelibrary.com]

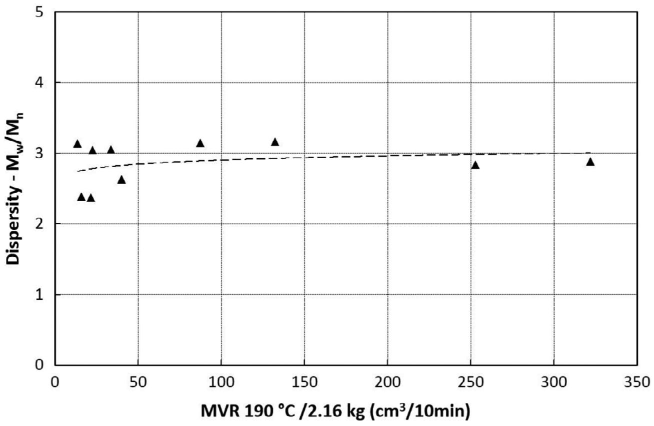

FIGURE 9 Dispersity M_w/M_n versus melt volume rate (MVR)

shown in Figure 8, dispersities given by M_w/M_n ratio in Figure 9.

The highest molecular weights are reflected in the lowest MVR values. The most intensive drop in molecular weights is connected with the primary increase of MVR at the initial extrusion steps, while with a higher extent of degradation indicated by higher MVR values, molecular weights decrease only moderately. Concerning the dispersities, some slight increase may again be connected with the beginning of processing but further on their dependence on MVR is very flat and exhibiting only minimum changes. Broken lines in Figures 8 and 9 only depict the trends. This indicates that the effect of mechanical stress preferably attacking the longest chains in PP and usually leading to the narrowing of M_w/M_n ratio [26,27] is much less important at processing of PHB. The main degradation mechanism – cis-elimination is mostly temperature dependent, takes place statistically along all polymer chains regardless of their lengths and prevails. This results in keeping the M_w/M_n ratio more or less constant.

Color development due to extrusions is shown in Figure 10. One can observe that the color of PHB itself is brownish and the addition of stabilizers does not change it so far. The exceptions are AO-6 and AO-12. In case of AO-6 the formation of discolored species can be accounted for the reaction between phosphitic species of hydrolyzed stabilizer and PHB, while the yellow color of AO-11 is the inherent property of its active component - curcuma. Considering the effect of multiple extrusion, the discoloration is not any dramatic as well. The changes are mostly very moderate and even the pronounced prodegradation effect exhibited by stabilizers AO-7,8,10 does not result in adequate worsening of color.

FIGURE 10 Color development due to multiple extrusion at 190°C/60 rpm (* = fourth extrusion) [Color figure can be viewed at wileyonlinelibrary.com]

The results of this work show that none of the thermooxidation stabilizer systems improved the stability of PHB during processing. The absence of their stabilization efficiency indirectly indicates that throughout extrusion at 180–190°C no hydrocarbon part of PHB is oxidized and no radical scission takes place. In such a case the typical protective actions of antioxidants such as chain breaking mechanism or hydroperoxide decomposition are of no use. The revealed completely adverse effect making them to act as prodegradants stem from their chemical structures. The highest prodegradation effect was observed with structures containing P and N atoms with asymmetrical free electron pairs that may act as nucleophilic catalysts of cis-elimination. A similar effect on PHB thermal decomposition at processing temperatures between 180 and 220°C has already been reported for glycerol, while its triacetyl derivative exhibited no effect.[28] Relatively low prodegradation effect of AO-4, AO-5 also containing phosphite functionality may be caused by the presence of bulky aromatic substituents limiting the steric accessibility of P free electron pair.

5 | CONCLUSIONS

This work answered the question if PHB could be stabilized by the currently known antioxidants or not. A specially selected series of stabilizers involving the structures most used as well as those used marginally was tested as protective agents for PHB processing. It was confirmed that common primary and secondary antioxidants, as well as multifunctional HALS, are ineffective in PHB and the potential of their mechanism of action cannot be utilized. This also indirectly confirmed the fact that no radical scission takes place in PHB during extrusion at temperatures 180–190°C. Beside this, the presence of common antioxidants in PHB matrix has shown a completely adverse effect that increased the rate of thermal decomposition where practically no oxygen was involved. The prodegradation effect of the structures containing phosphorus and nitrogen atoms with asymmetric free electron pairs was even dramatic. Finally, it can be concluded that none of the commonly used stabilizer structures exhibits the ability to protect PHB during processing and its presence in the matrix is not only useless but in some cases may be even harmful. In such a case only the use of chain extenders makes sense, despite they do not have a real ability to protect polymer but only ”rectify the damage” caused by preceding degradation.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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