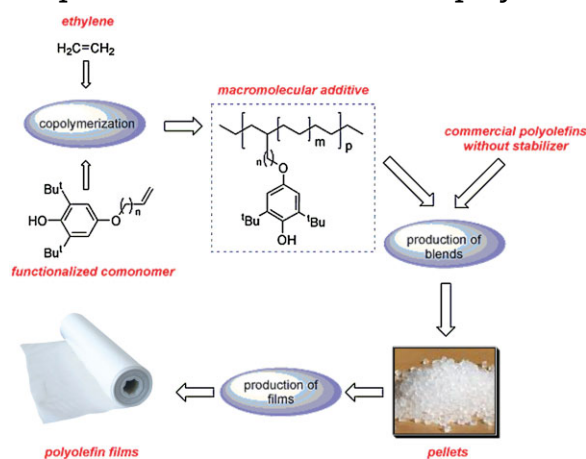


Design and Synthesis of Olefin Copolymers with Tunable Amounts of Comonomers Bearing Stabilizing Functionalities

Maria Carmela Sacchi,* Simona Losio, Paola Stagnaro, Stefano Menichetti, Caterina Viglianisi

The aim of this work is to search for innovative solutions to avoid physical migration of the stabilizers from plastic films. New families of macromolecular additives bearing tuned amounts of a selected functionality were explored, in particular, novel random copolymers of ethylene with 1-olefin co-units bearing an efficient antioxidant and/or anti-UV moiety covalently bonded to a mono- or disubstituted olefinic bond. Polyolefin blends containing the novel macromolecular additives showed higher degradation temperatures with respect to the neat matrix and its blends with 2,6-*t*-butyl-4-methoxyphenol (BHA). Aging tests showed that the novel antioxidants also constitute a protection against photo-oxidation.



1. Introduction

It is well known that polyolefins are prone to degradation at all stages of their life cycle, i.e., during processing, storage, and use. This degradation process is irreversible and ultimately leads to polymer discoloration and loss of physical properties. For this reason, polyolefin materials are usually stabilized by melt-blending with

antioxidant additives and UV stabilizers, known as free radical scavengers, to inhibit or retard degradation.^[1]

Figure 1a and b displays a few examples of the two main families of commercial stabilizers with antioxidant and anti-UV activity, respectively. As stabilizing functional unit, the antioxidants contain a hindered phenol, while the anti-UV stabilizers contain a hindered amine (i.e., hindered amine light stabilizers (HALS)). These commonly used stabilizers are relatively low molecular weight polar compounds, with structures very different from that of the non-polar polymeric matrices. This leads to several disadvantages such as: (i) poor compatibility of the stabilizers with the polyolefinic matrices, (ii) physical loss of the stabilizers by migration during both the processing and the storage, and, finally (iii) undesirable food contamination that might lead to changes of the organoleptic properties and even some risk of allergenic phenomena.

The present work addresses the problems due to migration, as well as to volatility and extractability of

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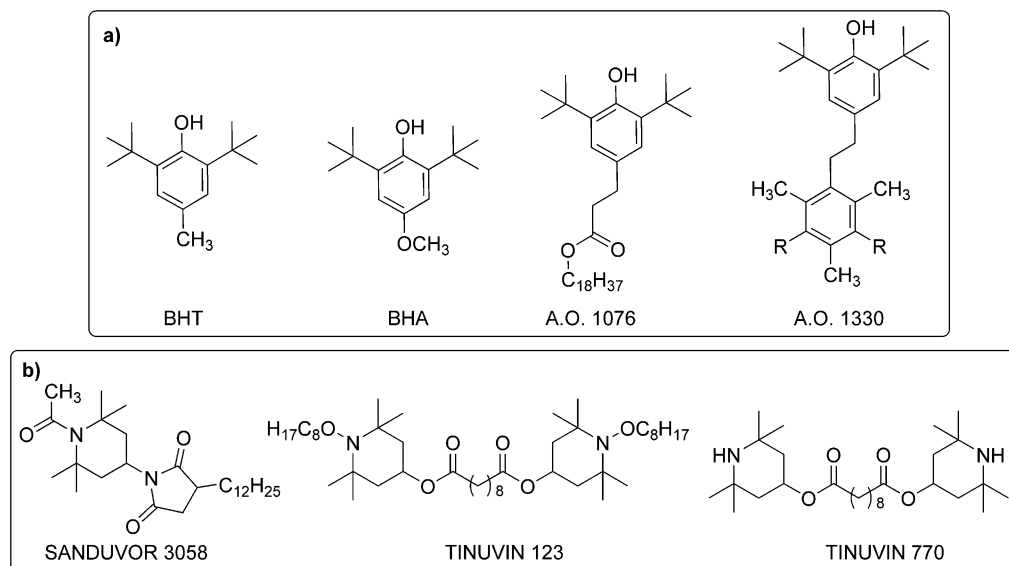
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■ Figure 1. (a) selected antioxidant stabilizers, (b) selected anti-UV stabilizers.

stabilizers by designing macromolecular stabilizers in which the stabilizing functional unit is covalently linked to a polymeric chain. Once synthesized, the polymeric additives are intended to be used as “masterbatches” for commercial polyolefins to prepare polymeric films characterized by stability to auto- and photo-oxidation comparable to that obtained with low molecular weight additives, but with reduced, if not eliminated, risk of migration of the stabilizer into the food in contact with the film. Moreover, due to their non-releasing nature, a single addition of these additives at the exit of the plant is expected to protect the polymeric material for all its life-time, from extrusion and compounding processes to its shelf-life as final product, thus avoiding the need of further addition of additives.

2. Experimental Section

2.1. Materials

All experiments and manipulations involving air-sensitive compounds were carried out under dry nitrogen atmosphere in glovebox or by using standard Schlenk line techniques. Methylaluminoxane (MAO; 10 wt% as toluene solution, Crompton) was used after removing all volatiles and drying the resulting powder at 50 °C for 3 h in vacuum (0.1 mmHg). Toluene was dried and distilled from sodium under nitrogen atmosphere. Triisobutylaluminum (TIBA; Witco, in solution of toluene) was used as received. Norbornene (**N**), purchased from Aldrich, was distilled on Na/K alloy and used as a stock solution in toluene. The metallocene complexes *rac*-ethylenebis(tetrahydroindenyl)-zirconium dichloride, [*rac*-(EBTHI)ZrCl₂] (EBTHI), *rac*-ethylenebis(indenyl)zirconium dichloride, [*rac*-Et(Ind)₂ZrCl₂] (EBI) (kindly

provided by Basell Poliolefine Italia) and *rac*-dimethylsilyl(*bis*(2-methylbenz[e]indenyl)zirconium dichloride, [*rac*-Me₂Si(2-Me-BenzInd)₂ZrCl₂] (MBI) (supplied by Targor) were used without further purification. Nitrogen and ethylene gases were dried and deoxygenated by passage over columns of CaCl₂, molecular sieves, and BTS catalysts.

The additive-free commercial LDPE (Lupolen LP 2420F), used as polymer matrix, was kindly supplied by Lyondellbasell Italia. 2,6-Di-*t*-butyl-4-methoxyphenol (butylhydroxy anisole, BHA) was purchased from Sigma–Aldrich.

2.2. Copolymerization

Typically, the copolymerization was performed in a round-bottom flask at the chosen temperature (30/35 °C) and ethylene gas pressure (0.3/0.5 atm). The total volume of toluene (50/100 mL) was introduced into the evacuated and N₂ purged flask. The synthesized comonomer was added with TIBA and the solution was stirred for 2 h under N₂ pressure. Afterward, the flask was filled with the MAO solution and the catalyst. The ethylene pressure was maintained with the correct proportion of N₂ and gas in the flask. The copolymerization was stopped through the addition of ethanol and HCl. The collected copolymer was dissolved in boiling toluene, precipitated in acidified ethanol, and washed several times with pure ethanol. Such a procedure ensures the absence of unreacted comonomer and residual alumina in the polymeric additive.

2.3. Blends and Films

Blends of the additive-free LDPE and selected synthesized copolymers were prepared in an internal batch mixer (Brabender Plasti-Corder) by melt-blending at 130 °C and 50 rpm for 15 min

under N_2 . In order to have a final content of 500 ppm of antioxidant moieties into the polyethylene matrix, for each blend a proper amount of copolymer was added, taking into account the composition of the specific copolymer. The value of 500 ppm was chosen being an amount of antioxidant typically used to stabilize polyolefinic materials. Neat LDPE and its mixture with 500 ppm of commercial BHA antioxidant were treated under identical processing conditions and used for reference purposes.

Films $120 \pm 15 \mu\text{m}$ thick were obtained from the blends by compression moulding at 130°C . Films ensure correct sampling for thermogravimetric analysis (TGA) experiments and successive characterization.

2.4. TGA Analysis

Thermo-oxidative stabilities were tested by TGA under O_2 atmosphere using a PerkinElmer TGA7 instrument. TGA measurements were carried out both in dynamic (heating rate $20^\circ\text{C} \cdot \text{min}^{-1}$) and isothermal conditions. In the dynamic mode, the explored temperature range was $50\text{--}700^\circ\text{C}$. Isothermal experiments were carried out by rapidly reaching 180°C under N_2 ; and, after 10 min of purge, switching to pure O_2 atmosphere to start the oxygen induction time (OIT) measurement (t_0 refers to the moment in which oxygen enters the instrument furnace). In order to guarantee the comparison and reproducibility of the OIT experimental results, all the isothermal measurements were carried out on film specimens with the same weight and the same surface area exposed to the oxygen action.

3. Results and Discussion

Since the early 1970s, a challenging approach was developed to solve the problems due to migration and extractability of stabilizers, based on the idea of copolymerizing the commonly used α -olefins (e.g., ethylene or propylene) with a comonomer bearing the polar stabilizing group.^[2] An important breakthrough in the field was reached when Wilén and co-workers^[3] succeeded in the copolymerization of ethylene and propylene with comonomers bearing either an antioxidant phenolic or a hindered amine moiety by using metallocene catalysts. Moving from their pioneering work, we tackled research on new polymeric non-releasing stabilizing additives, conducted through the following three actions:

- (i) synthesis of new comonomers bearing the antioxidant and anti-UV functional units (FUs) and an easily polymerizable olefinic double bond;
- (ii) controlled copolymerization of the synthesized comonomers bearing the stabilizing FUs with ethylene (E), to attain novel polymeric stabilizing additives;

- (iii) production of blends and films from the obtained polymeric additives and commercial polyolefins, and testing of their thermo- and photo-oxidative stability.

3.1. Synthesis of New Comonomers Bearing Stabilizing Functionalities

A selection of significant functionalized novel comonomers so far synthesized is presented in Figure 2. In particular, we have prepared three comonomers (**1–3**) bearing a phenol antioxidant moiety placed at different distances from the olefinic double bond ($n = 1, 4, 8$). Such comonomers are analogues of 2,6-*t*-butyl-4-methoxyphenol (BHA; see Figure 1a), one of the most effective commercial antioxidants. The relatively simple synthesis devised and used for all three comonomers is described in previous papers.^[4]

The functionalized norbornene comonomer **4** (2,6-di-*t*-butyl-phenol-norbornene), analogue of 2,6-*t*-butyl-4-methylphenol (BHT; see Figure 1a) was investigated because norbornene (N) is proved to be extremely effective in polymerization with metallocene based catalysts.^[5] Moreover, a norbornene comonomer could be quite interesting for the preparation of non-releasing additives specifically destined to protect commercial E/N copolymers, a package material particularly used for pharmaceuticals, with high added value and health impact. A route was designed to obtain the pure *exo*-isomer (*exo*-**4**),^[6] known to be more reactive than the *endo*-isomer in polymerization.^[7] However, we verified that *exo*-**4** was not stereostable on standing, since variable amounts of the *endo*-isomer were formed, due to a retro-Diels-Alder/Diels-Alder process. The synthetic route and the effect of the *exo/endo* ratio of the comonomer on the copolymerization are described in ref.^[6]

The possibility of synthesizing bifunctional comonomers, bearing both the antioxidant and the anti-UV FUs on the same molecular skeleton, was explored by preparing **5** (Figure 2). This option would open up new opportunities since, in principle, it would allow using half the molar amount of functionalized comonomers. In Scheme 1 the synthetic route to **5** is sketched. With the first four steps of the synthesis we prepared a potential anti-UV comonomer

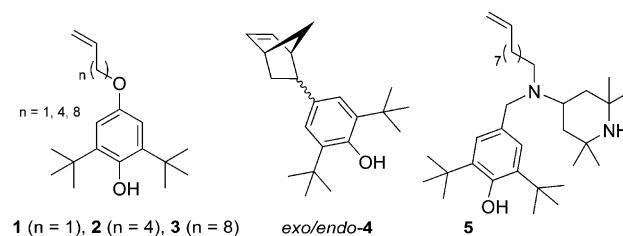
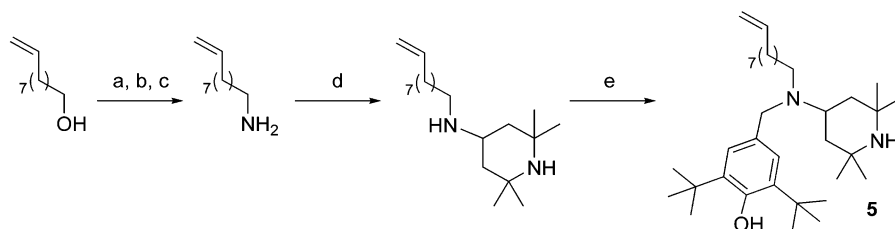


Figure 2. Synthesized functionalized comonomers **1–5**.



Scheme 1. Synthetic procedure of comonomer **5**. (a) Tosyl chloride, Py, 0 °C, 3 h, 88%; (b) Potassium phthalimide, DMF, 120 °C, 24 h, 86%; (c) Hydrazine, EtOH, 50 °C, 3 h, 90%; (d) (i) 2,2,6,6-Tetramethyl-4-piperidone, titanium(IV) isopropoxide, 3 h, (ii) NaBH₄, MeOH, rt, 24 h, 95%; (e) 3,5-Di-*t*-butyl-4-hydroxybenzaldehyde, NaBH(OAc)₃, DCE, rt, 2 h, 72%.

that was reacted with 3,5-di-*t*-butyl-4-hydroxybenzaldehyde to give the bifunctional comonomer **5** (Scheme 1).

3.2. Controlled Ethylene Copolymerization with Functionalized Comonomers

All five comonomers were copolymerized with ethylene (E) (Scheme 2). Three different metallocene catalysts *rac*-(EBTHI)ZrCl₂ (EBTHI), *rac*-Et(Ind)₂ZrCl₂ (EBI), and *rac*-Me₂Si(2-MeBenzInd)₂ZrCl₂ (MBI), have been used in combination with MAO cocatalyst, depending on the comonomer. Triisobutylaluminum (TIBA) was used for protecting the functional units to prevent the catalyst deactivation. By varying the E/comonomer molar ratio in the feed, it was possible the tuning of the functionalized comonomer content up to 5 mol%.^[4,6]

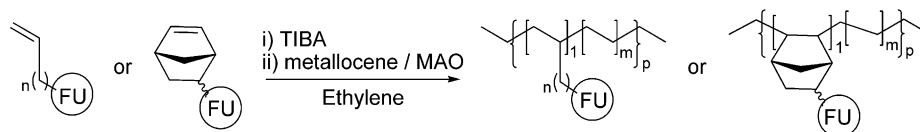
Here following, a selection of experiments will be presented in which the comonomer insertion was con-

trolled up to about 1 mol%, since comonomer concentrations higher than that were proved to result in poor miscibility with the polyolefinic matrix.^[8]

3.2.1. Copolymerization Ethylene/Comonomers 1–3

In Table 1, the polymerization data are shown along with the polymerization conditions. EBTHI catalyst was chosen mainly because its activity has been shown to be only partially affected by the ether oxygen of the functionalized comonomer.^[4] A polyethylene sample obtained under similar conditions was taken as a reference point.

All three comonomers were shown to be capable of copolymerizing with E. As expected, the comonomer with eight methylenes as spacer gave the best results in both polymerization activity and comonomer incorporation: indeed, the highest comonomer conversion (33.3%) was obtained at the highest E/comonomer ratio (2.61).



Scheme 2. Copolymerization procedure.

Table 1. Ethylene/1–3 copolymerization catalyzed by *rac*-(EBTHI)ZrCl₂/MAO catalytic system.

Comonomer	[E]/[com]	Bound com. ^{a)} [mol%]	Bound com. ^{a)} [wt%]	Conversion [%]	Activity ^{b)}	$\overline{M}_n^c)$ [10 ³]	$\overline{M}_w/\overline{M}_n^c)$
–	–	–	–	–	355 ^{d)}	15.5	2.1
1	1.75	1.0	8.6	10.1	407	21.0	2.8
2	1.75	0.5	5.7	5.2	371	26.0	2.8
3^{e)}	2.61	1.0	11.5	33.3	388	11.0	2.4

Polymerization conditions: solvent = toluene, total volume = 50 mL, [catalyst] = 5 μmol, t_{pol} = 30 min, [com]/[TIBA] = 1:2; [Al]/[Zr] = 1500 (mol/mol), T = 35 °C, P_{ethylene} = 0.3 atm;^{a)}determined by ¹³C NMR; ^{b)} $[(g_{\text{pol}}/\text{mmol}_{\text{cat}} \cdot \text{h})/P_E]$; ^{c)}determined by SEC; ^{d)}polymerization time = 15 min; ^{e)}[catalyst] = 6 μmol, polymerization time = 60 min.

3.2.2. Copolymerization Ethylene/Comonomer 4

Two comonomer **4** isomeric mixtures (*exo/endo* = 1.1/1 and 6/1) were used. EI catalyst was chosen because it is known to be able to incorporate norbornene (N) in controlled amount in E based copolymers.^[5] A E/N copolymer obtained under similar conditions was taken as reference. In Table 2, the polymerization data are shown.

In comparison to N, the highly demanding TIBA protected comonomer **4** showed the expected lower incorporation rate into the polymer chain. A sensible difference in incorporation was also observed between the 6/1 and 1.1/1 comonomer mixtures. The results reported in Table 2 showed that the *exo*-enriched comonomer mixture (6/1) is markedly more reactive than the 1.1/1 sample. As a consequence, with the former a higher comonomer conversion ($\approx 20\%$) could be obtained. Both copolymers resulted enriched in the more reactive *exo* form with respect to the starting comonomer, so confirming the general preferential insertion of the *exo* isomer in the growing chain.

3.2.3. Copolymerization Ethylene/Comonomer 5

Table 3 shows the polymerization data along with the copolymerization conditions of the bifunctional comonomer **5** with E. MBI catalyst was chosen since it was representative of a metallocene family expected to be the most suitable to incorporate bulky comonomers such as comonomer **5**.^[9] For reference purpose a polyethylene sample was prepared under similar conditions.

The bifunctional comonomer shows, as expected due to its bulkiness, a moderate incorporation capacity (with consequent low comonomer conversion). The problem is the low polymerization activity: apparently this comonomer acts as a partial catalyst poison. The synthesis of a differently structured bifunctional comonomer, in which the tri-substituted nitrogen is more effectively protected, is under investigation.

3.3. Production of Blends and Films from the Novel Polymeric Additives and Commercial Polyolefins and Tests of Thermo- and Photo-Oxidative Stability

A selection of results will be presented in the following, namely, those regarding the ethylene copolymer series containing comonomers **1**, **2**, and **3**.^[8]

3.3.1. Blends and Films

Blends of an additive-free commercial LDPE and the copolymers containing comonomers **1**, **2**, and **3** were prepared by melt-blending in a Brabender batch mixer (130 °C, 50 rpm, 15 min under N₂) in order to have a content of 500 ppm of antioxidant moieties, taking into account the specific copolymer composition. The value of 500 ppm is a typical amount of antioxidant added to stabilize polyolefinic materials. Neat LDPE matrix and its mixture with 500 ppm of commercial BHA antioxidant were treated under identical processing conditions and used for reference purposes. From the blends, 120 μm thick films were obtained by compression moulding at 130 °C.

Table 2. Ethylene/4 copolymerization catalyzed by *rac*-Et(Ind)₂ZrCl₂/MAO catalytic system.

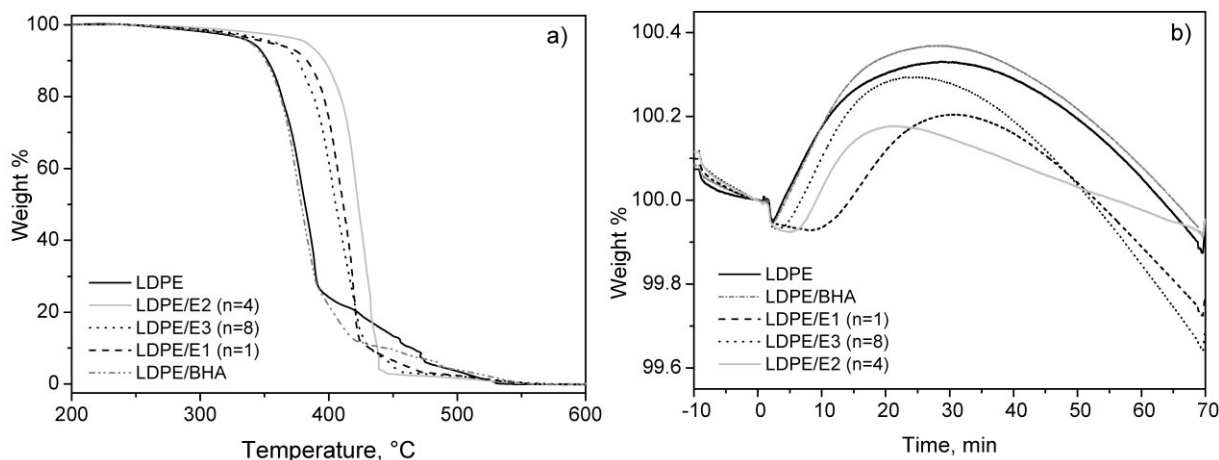
Comonomer (<i>exo/endo</i>)	[E]/[com]	Bound com ^{a)} [mol%] [<i>exo/endo</i>]	Bound com ^{a)} [wt%]	Conversion [%]	Activity ^{b)}	\overline{M}_n ^{c)} [10 ³]	$\overline{M}_w/\overline{M}_n$ ^{c)}
N	13.34	1.98	–	36.9	1642	322	2.2
4 ^{d)} (1.1/1)	6.67	0.43 (3/2)	4.4	7.0	1880	418	3.0
4 ^{e)} (6/1)	13.34	0.78 (9/1)	7.7	20.1	1560	n.d. ^{f)}	n.d. ^{f)}

Polymerization conditions: solvent = toluene, total volume = 100 mL, [catalyst] = 2 μmol , $t_{\text{pol}} = 15$ min, [com]/[TIBA] = 1:1.2, [MAO]/[Zr] = 3000 (mol/mol), $T = 30$ °C, $P_E = 0.5$ atm; ^{a)}Determined by ¹³C NMR; ^{b)} $[(g_{\text{pol}}/\text{mmol}_{\text{cat}} \cdot \text{h})/P]$; ^{c)}Determined by SEC; ^{d)}Three weeks aged; ^{e)}Freshly prepared; ^{f)}not determined.

Table 3. Ethylene/5 copolymerization catalyzed by *rac*-[Me₂Si(2-MeBenzInd)₂]ZrCl₂/MAO catalytic system.

Comonomer	[E]/[com]	Bound comonomer ^{a)} [mol%]	Bound comonomer ^{a)} [wt%]	Conversion [%]	Activity ^{b)}
–	–	–	–	–	1484
5 ^{c)}	6.67	0.18	3.2	0.6	21

Polymerization conditions: solvent = toluene, total volume = 100 mL, [catalyst] = 5 μmol , [com]/[TIBA] = 1:3, [MAO]/[Zr] = 2000 (mol/mol), $t_{\text{pol}} = 15$ min, $T = 30$ °C, $P_E = 0.5$ atm; ^{a)}Determined by ¹³C NMR; ^{b)} $[(g_{\text{pol}}/\text{mmol}_{\text{cat}} \cdot \text{h})/P_E]$; ^{c)} $t_{\text{pol}} = 120$ min.



■ Figure 3. TGA curves under O₂: (a) in dynamic mode (20 °C · min⁻¹), (b) in isothermal conditions (180 °C).

3.3.2. Thermo-oxidative Stability Studies

Dynamic TGA experiments carried out under O₂ atmosphere (temperature range 50–700 °C, heating rate 20 °C · min⁻¹) showed (Figure 3a) that for films containing the polymeric non-releasing antioxidants the degradation process takes place at temperatures higher of 40–50 °C compared to neat LDPE or its blend with BHA.

Tests of thermo-oxidative stability in isothermal conditions (180 °C under O₂) were carried out as well, in order to explore the behavior of the new antioxidants in conditions mimicking those normally applied in the industrial processing of polyethylene-based materials ($T = 180$ °C) or even worse (pure oxygen atmosphere). Figure 3b shows that, for both the neat LDPE and its blend with BHA, the oxygen uptake starts as soon as O₂ is introduced in the furnace (time = 0). Instead, the samples containing the polymeric additives exhibit quite higher induction times before the oxygen reacts with the polymer starting the degradation process. It is worth noticing that such induction times are comparable or even longer than the normal residence time of a polymer in an extruder during compounding or processing.

3.3.3. Aging tests

Tests were conducted on the same films by artificially aging them through exposure to a sun-like lamp radiation at 50 °C for 21 days in oxygen-rich atmosphere. In particular, the concentration of the carbonyl groups (carbonyl index) being formed upon photo-oxidation, was monitored by FTIR analysis. A slightly slower increase of the carbonyl index with time was observed for films with the polymeric additives with respect to those added with BHA.

Similar and further investigations are in progress for the other synthesized copolymers.

4. Conclusion

The overall results showed that: (i) all the new macromolecular polymeric stabilizers prepared so far exert a protection against thermo- and photo-oxidation when melt-blended to polyolefins, better or at least comparable to that offered by a conventional low molecular weight additive; and (ii) their non-releasing nature allows, on one hand, protection of the polymer matrices for all their life-cycle, from processing to storage and final use; and, on the other hand, the avoidance of all drawbacks related to contamination of foodstuff in food-packaging applications.

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