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DETERMINATION OF OXIDATION PARAMETERS BY DSC FOR POLYPROPYLENE STABILIZED WITH HYDROXYTYROSOL (3,4-DIHYDROXY-PHENYLETHANOL)

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Oxidation thermal parameters on samples of polypropylene (PP) stabilized with hydroxytyrosol were determined. For comparison purposes, α-tocopherol and a synthetic phenolic commercial antioxidant (Irganox 1076), were also analyzed. Oxidation induction time (OIt) and oxidation induction temperature (OIT) were determined by differential scanning calorimetry (DSC). The addition of hydroxytyrosol 0.1 mass% to PP was enough to obtain efficient stabilization during processing. Certain decrease in stabilizing properties of natural antioxidants was observed for compression moulded materials at high temperatures. However, these samples were still efficiently stabilized in comparison to the pure material. Hydroxytyrosol showed good performance as polypropylene antioxidant and it might be considered as promising alternative to the use of phenolic synthetic compounds.

Keywords: *DSC, hydroxytyrosol, oxidation induction temperature (OIT), oxidation induction time (OIt), polypropylene, α-tocopherol*

Introduction

A growing tendency for the use of natural additives in polymers has been observed during the last years. Many herbs and spices, normally used to flavour dishes, are excellent sources of phenolic compounds that were reported to show good antioxidant activity in polymers [1–10]. Some examples of those compounds and their use in polymers are carvacrol (obtained from oregano) [1, 2], carnosic acid [3–5] or rosemarinic acid (from rosemary) [4]. Nevertheless, the most popular natural antioxidant used in polymers is α-tocopherol. Many authors have claimed the good stabilization properties of this antioxidant [3, 5–11] as well as its ability to protect polymers from air oxidation.

On the other hand, the use of subproducts or derivatives obtained from agricultural resources is considered a good alternative for preparation of natural polymer additives. For example, the olive fruits contain a wide variety of bioactive components [12–14]. Among them, hydroxytyrosol (3,4-dihydroxy-phenylethanol) stands out as a compound of potentially high added value due to its excellent antioxidant abilities [15] as well as beneficial properties (with regard to both nutrition and oil stability). Hydroxytyrosol was found to play a role in enhancing the oxidative stability of olive oil [16] and also to have a positive effect on human health by inhibition of lipid oxidation and peroxide formation [17, 18]. These findings, joined to the increasing consumer interest in natural additives, lead us to study the stabilization efficiency of hydroxytyrosol and a comparison with a well-known natural antioxidant (α-tocopherol) in polyolefins.

The relatively high temperatures required for thermoplastics processing are a major cause of degradation in many of the most important operations, such as extrusion injection and compression moulding. In addition, the presence of oxygen, even at small concentrations, is another major factor for promoting degradation during processing. Polyolefins are particularly susceptible to oxidative degradation during processing [18] by the only presence of carbon-carbon chain bonds in the case of polyethylene (PE), polypropylene (PP) and copolymers.

A simple method to compare the efficiency of several antioxidants and/or stabilising systems is by determination of the oxidation induction time (OIt) and oxidation induction temperature (OIT) of the material after processing. Especially for polyolefins, OIt and/or OIT tests are well established for quality control purposes as a quick screening method to check the activity of the stabilization systems [19–21].

The experiment could be conducted in two different modes: dynamic and static [22]. In dynamic mode, the test sample is heated at a constant heating rate under air or pure oxygen gas flow. The OIT is determined by the onset of the oxidation process that is characterized by an exothermic peak in the heat flow–temperature plot. In the static mode, the sample is heated under inert gas which is switched to oxygen or air once the desired test temperature was reached. Then, the time to reach the onset of an exothermic

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oxidation peak determines the OIt. Under OIt standard conditions, the initial breakdown of antioxidant protection is accompanied by a release of energy causing an upward deflection of the curve above the baseline. The time without any oxidation is commonly referred to as the induction time. This induction time can be either a measurement of the amount of antioxidant present in the polymer or the effectiveness of any particular antioxidant in the formulation [23–25].

The aim of the present work is the efficiency of the antioxidant performance of hydroxytyrosol and the comparison with α-tocopherol and Irganox 1076 when added to polypropylene in different amounts with a standard PP formulation. This behavior will be evaluated by measuring OIt at different temperatures and OIT at 10°C min^{-1} in air atmosphere.

Experimental

Materials

Samples preparation

A commercial powder polypropylene (ISPLEN® PP 040 G1E, Repsol YPF, Spain) with no antioxidant in its composition was used for the preparation of samples. Each of them consisted of 2 kg (approximately) of PP mixed with different antioxidants: (i) hydroxytyrosol (85.7 mass%) 0.01 mass% and 0.1 mass% (ii) (±)α-tocopherol 92 mass% (Irganox E201 Ciba Specialty Inc.) in the same concentration levels and (iii) octadecile 3-(3,5-di-ter-butyl-hydroxy-phenyl)-propionate (Irganox 1076, Ciba Specialty Inc.) 0.1 mass% in mass. In addition, a control sample (pure PP) was prepared. Natural antioxidants were dissolved in ethanol (Merck KgaA, Germany) before their addition to the polymer to get a more homogeneous distribution of the additives into the polymer structure.

Polymer and additives were mixed in a turbo mixer at 750 rpm during 5 min at room temperature. Then, each mixture was extruded on 25 mm single-screw extruder (L/D: 25, Collin) with five temperature zones. These temperatures were set at 140/170/190/210/200°C [26–29]. After the extrusion process, samples were pelletized.

Sheet preparation

Pellets obtained from the extrusion processing were compression moulded in order to obtain 307 cm^2 sheets. Compression moulding conditions were: 10 min at 190°C without pressure; 8 min at 190°C under 3.2 bar, with further increase to 4.8 bar at the same temperature for 2 min. Cooling was carried out under pressure (1.6 bar) until 40°C at 12°C min^{-1}.

DSC tests – OIt and OIT

Tests were performed in a TA Instruments Q100 calorimeter (New Castle, DE, USA). Samples weighing approximately 5 mg were enclosed in an aluminum pan (40 μL). OIt tests for samples stabilized with hydroxytyrosol (0.01 and 0.1 mass%) were performed by heating the sample at the maximum heating rate given by the instrument (55°C min^{-1}) in an inert atmosphere (N_2, 50 mL min^{-1}) up to temperatures between 180 and 240°C. Comparison of hydroxytyrosol with the other antioxidants was carried out by evaluation of oxidation induction parameters at temperatures between 210 and 240°C. These temperatures were selected to ensure the finalization of the reaction in a reasonable time. It was also stated that sensitivity of these methods for polyolefins is not good at temperatures below 180°C [21]. Therefore, with the selected temperatures sensitivity problems were avoided. After reaching the selected isotherms, test atmosphere was switched to air (50 mL min^{-1}) and the isothermal heat evolution was observed up to the detection of the

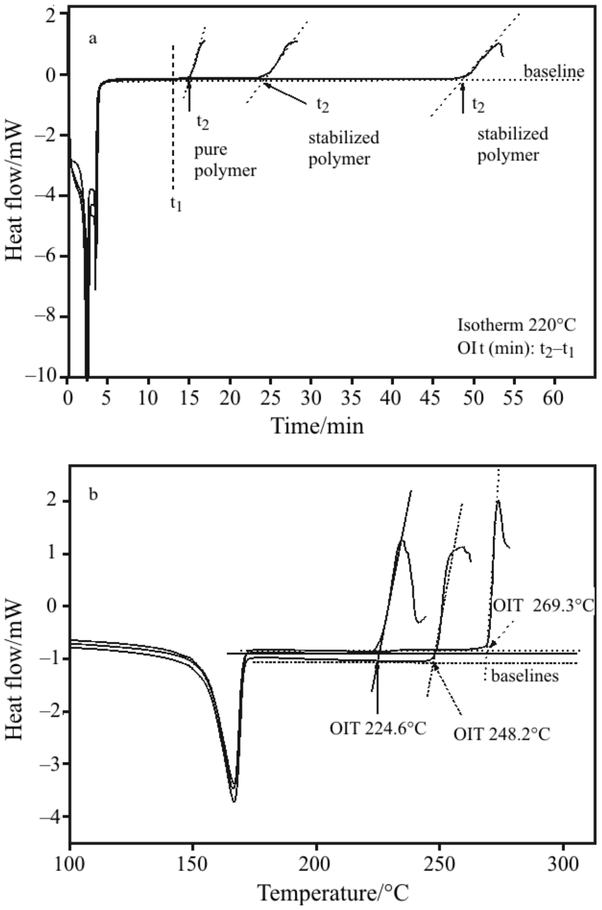

Fig. 1 Determination of a – OIt at 220°C and b – OIT for a non-stabilized polymer and two stabilized polymers

exothermic peak indicating the oxidation reaction (Fig. 1a) [30]. The OIt value could be determined as the difference between t_2 and t_1 where t_1 is the time after stabilization of the baseline and t_2 the time for the onset corresponding to the beginning of the exothermal peak [25].

In order to determine the OIT, samples were heated at 10°C min^{-1} in oxygen atmosphere (50 mL min^{-1}) from 30°C to the appearance of the exothermic peak (Fig. 1b). OIT was calculated as the temperature for the intersection between the baseline and the slope of the exothermic peak in each case.

Results and discussion

Oxidation induction temperature

Table 1 shows results of OIT for all samples. Stabilized samples showed higher values for the oxidation temperature than the control sample. This was expectable in general, and results showed that even the addition of very small amounts of hydroxytyrosol (0.01 mass%) resulted in some increase in OIT. This effect was much more significant for α-tocopherol at the same concentration level meaning that the stabilization given by α-tocopherol was highly noticeable at low concentrations. Nevertheless, both natural antioxidants showed similar OIT results at concentrations usual in commercial formulations (0.1 mass%). This is a good feature for hydroxytyrosol as a PP stabilizer similar in performance to α-tocopherol. It is also significant that the increase in OIT for the same antioxidant concentration was higher for both natural antioxidants than for the synthetic one (Irganox 1076). This could mean that lower amounts of additive should be enough to reach a particular protection level.

Table 1 OIT$_{emp}$ values (°C) of stabilized and non-stabilized PP

Sample	OIT/°C
Pure PP	219.5±7.2
PP+α-tocopherol 0.01 mass%	249.8±3.2
PP+α-tocopherol 0.1 mass%	262.1±0.2
PP+hydroxytyrosol 0.01 mass%	228.1±5.7
PP+hydroxytyrosol 0.1 mass%	267.0±0.6
PP+Irganox 1076 0.1 mass%	226.3±19.4

Stabilization of PP samples

Table 2 shows all results for OIt at different temperatures (210–240°C). Hydroxytyrosol 0.1 mass% showed very good performance as stabilizer at 210°C, as higher values for OIt than those for α-tocopherol and Irganox 1076 formulations were observed. At lower concentration, hydroxytyrosol did not show any significant stabilization for PP, since there were no important differences in OIt values with the control sample. All concentrations of α-tocopherol showed similar stabilization performance at 210°C, and consequently concentrations as low as 0.01 mass% seem to be enough to effectively stabilize the polymer, as the oxidation time increased around 88 min when compared to the material without any antioxidant. Therefore, it could be concluded that while α-tocopherol is excellent as PP stabilizer at low concentrations, hydroxytyrosol showed better performance at concentrations around 0.1 mass%.

OIt values at 220°C for the stabilized PP increased with the concentration for both natural antioxidants, as it was expected. Low concentrations of hydroxytyrosol (0.01 mass%) did not show any stabilization, since no significant differences in OIt with respect to the pure polymer were observed. Nevertheless, the addition of 0.01 mass% of α-tocopherol did show stabilization, as OIt was prolonged for more than 10 min. This is a clear indication of the good stabilization obtained with the addition of low amounts of α-tocopherol to polyolefins [31]. Moreover, relatively low amounts of hydroxytyrosol could be used to stabilize polypropylene, since concentrations of 0.1 mass% are enough to get a good stabilization (increase in more than 10 min with respect to the pure polymer). The stabilization properties of samples with Irganox 1076 0.1 mass% are not as good as those observed for hydroxytyrosol at the same concentration.

Higher temperatures (230 and 240°C) could be too high for polypropylene OIT conditions, as temperatures

Table 2 OIt (min) values for stabilized and non-stabilized PP at 210, 220, 230 and 240°C

Sample	T_{iso}=210°C/min	T_{iso}=220°C/min	T_{iso}=230°C/min	T_{iso}=240°C/min
Pure PP	3.4±0.9	1.0±0.1	0.5±0.1	0.3±0.1
PP+α-tocopherol 0.01 mass%	90.8±9.3	17.6±10.1	4.7±2.9	1.2±1.0
PP+α-tocopherol 0.1 mass%	72.8±7.1	31.9±6.2	15.6±2.0	5.9±1.6
PP+hydroxytyrosol 0.01 mass%	3.4±0.8	1.6±0.4	0.7±0.1	0.4±0.1
PP+hydroxytyrosol 0.1 mass%	120.2±14.6	15.2±1.7	10.8±4.5	8.2±3.3
PP+Irganox 1076 0.1 mass%	13.5±1.4	4.0±0.1	1.2±0.4	0.5±0.2

for these tests are normally between 190 and 220°C, as reported by other authors [32], but they were also studied in order to know what could happen if the material suffers high temperatures during its service life. Hydroxytyrosol 0.1 mass% could be a good stabilizer for PP at high temperatures, as OIt is prolonged for 10 min at 230°C with respect to the control sample. α-Tocopherol 0.01 mass% prolonged the oxidation time for just 5 min, but 0.1 mass% of α-tocopherol increased OIt 14 min with respect to the pure material. This time should be enough to avoid a prolonged malfunction and the material should resist these conditions without any significant oxidation.

Schmid *et al.* [33, 34] stated that t_2 (Fig. 1a) should be increased to a time range above 20 min. Values lower than 15 min must be regarded critically and consequently these results at high temperatures should be considered carefully. OIt values at temperatures lower than 220°C could be more representative of the real thermo-oxidation process and were used for our comparison purposes.

As previously indicated, some studies at lower temperatures were also carried out. Isotherms at 180, 190 and 200°C were used (Fig. 2) in order to avoid a sensitivity loss [25]. From these results it could be concluded that while α-tocopherol 0.01 mass% was enough to obtain an efficient stabilization during extrusion at temperatures between 210 and 230°C, hydroxytyrosol 0.01 mass% can be considered an efficient antioxidant at lower temperatures (190°C). Hydroxytyrosol 0.1 mass% was also tested at 190°C but, as it was expected, the time of the test was too long to be practical (>200 min, as indicated in Fig. 2).

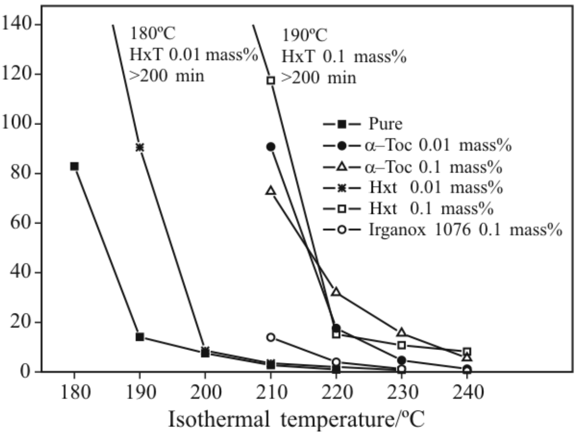

Fig. 2 OIt (min) values *vs*. temperature. α-Toc – α-tocopherol, Hxt – hydroxytyrosol

Stabilization during compression moulding

The effect of some common processing operations in the stabilization performance of natural antioxidants was also studied. Figure 3 shows OIt at 210°C for several materials processed by just extrusion (pellets) and extrusion plus compression moulding (CM). As expected, samples with just one process (pellet) showed higher values of OIt than CM samples. A similar behaviour was observed for OIT tests (Fig. 4). The slight degradation caused by high temperatures and pressures during compression moulding is responsible of a certain loss of stabilizing properties in natural antioxidants. However samples after compression moulding are still well stabilized in comparison to the pure material and this stabilization degree could be acceptable for many applications. In Fig. 5, samples stabilized with HxT 0.01 mass% and pure sample, compressed moulded and pellets were compared at 190°C. A similar behavior was observed meaning that concentrations as low as 0.01 mass% of

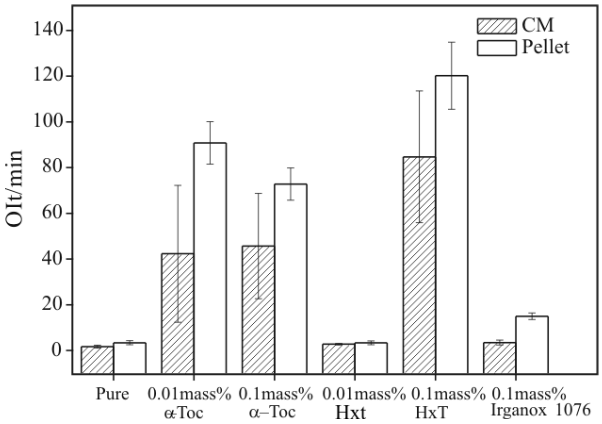

Fig. 3 Oxidation induction time: comparison between pellet samples (after extrusion) and compressed moulded samples (CM) in PP at 210°C. α-Toc – α-tocopherol; Hxt – hydroxytyrosol; Irg 1076 – Irganox 1076

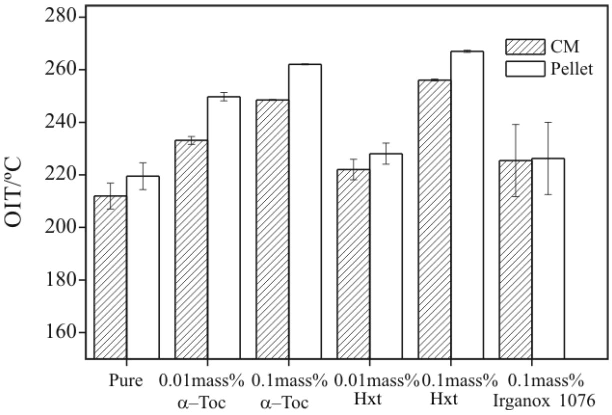

Fig. 4 Oxidation induction temperatures: comparison between pellet samples (after extrusion) and compressed moulded samples (CM) in PP. α-Toc – α-tocopherol; Hxt – hydroxytyrosol; Irg 1076 – Irganox 1076

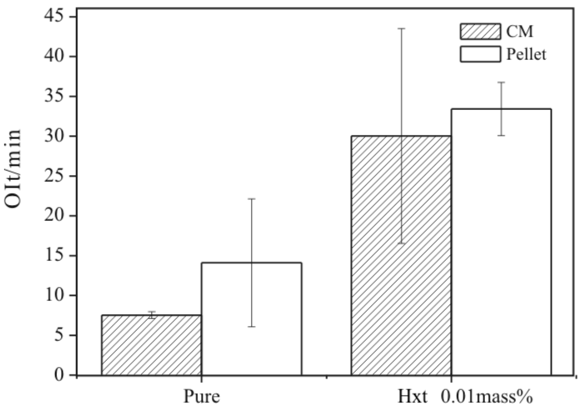

Fig. 5 Comparison between pellet samples (after extrusion) and compressed moulded samples (CM) in PP stabilized with hydroxytyrosol 0.01 mass% and pure PP at 190°C. Hxt – hydroxytyrosol

hydroxytyrosol were still adequate to avoid PP thermo-oxidative degradation.

Conclusions

OIt values were clearly increased for PP when natural antioxidants were added to their formulations. This behavior was observed in samples stabilized with both natural antioxidants (α-tocopherol and hydroxytyrosol), but the stabilization degree for each of them was different. Hydroxytyrosol should be considered as an efficient antioxidant since an important increment in t_2 was observed at 210°C. This latter temperature was the most adequate for this study, except for samples stabilized with 0.01 mass% of hydroxytyrosol. The use of hydroxytyrosol can be important from the economical point of view, as it gives added value to agricultural residues and because it could be potentially used in active food packaging systems, with controlled release of antioxidant to foodstuff.

As a final conclusion natural antioxidants showed good performance as polyolefins stabilizers and antioxidants and they can be considered as a promising alternative to the use of phenolic synthetic compounds to stabilize PP.

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