Use of Isothermal and Nonisothermal Chemiluminescence Measurements for Comparison of Stabilizing Efficiency of Hydroxytyrosol (3,4-Dihydroxy-phenylethanol), α-Tocopherol and Irganox®1076 in Polypropylene

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ABSTRACT: Hydroxytyrosol (3,4-dihydroxyphenylethanol) is a phenolic compound obtained during olive processing in oil manufacturing. It plays a role in enhancing the oxidative stability of olive oil with positive effects on human health. The raising interest towards the use of natural antioxidants as stabilizers in polymer formulations makes hydroxytyrosol a potential candidate to substitute synthetic antioxidants in polyolefin formulations. In this study, hydroxytyrosol was compared in antioxidant efficiency with two other compounds, one of them obtained from natural resources (α-tocopherol) and a synthetic commercial phenolic antioxidant (Irganox®1076). Chemiluminescence was used to as a tool to assess the increase in the polypropylene stability to thermo-oxidative degradation. A significant increase in the value of oxygen induction time with the initial concentration of natural antioxidants tested under isothermal conditions at 140, 150 and 160°C was observed. A comparison at the same concentration level (0.1 wt %) between the three antioxidants showed an order of stabilizing efficiency as: α-tocopherol > Irganox®1076 > hydroxytyrosol, but all them showed clearly their stabilization performance in polypropylene. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 3393–3399, 2011

Key words: natural antioxidants; hydroxytyrosol; α-tocopherol; luminescence; polypropylene

INTRODUCTION

The olive oil production is an important agro-industrial activity in the Mediterranean area, where around 95% of the world's olive oil is produced.[1] The use of current technologies for the olive oil extraction generates a semisolid waste that could be harmful to the environment. This residue is usually eliminated in incinerators, as fuel with high calorific value. However, greater environmental and economical benefits could result from the conversion of these by-products to chemicals with higher added value.[2] Some studies showed that large quantities of phenolic compounds, in particular 3,4-dihydroxy-phenylethanol, also called hydroxytyrosol (HT), can be obtained by means of steam water from olive cake and olive stones during processing, and consequently it could be a possible by-product from olive oil mill waste water.[2–4] HT stands out as a high added value compound, due to its properties to prevent oxidation by scavenging hydroperoxides joined to beneficial effects with regards to both human nutrition and oil stability. In addition HT has a positive effect on human health.[4]

The interest in the use of natural antioxidants as stabilizers in polymer formulations in the food-packaging area is continuously increasing by their good performance in limiting oxidation processes in the material and/or food as well as the good acceptance by consumers of the use of natural additives in material formulations. Some natural antioxidants, such as α-tocopherol (α-Toco), have been already used in polymer formulations with good results in polyolefins stabilization during processing.[5,6] Strandberg et al.[7] reported the efficiency of α-Toco compared with commercial synthetic antioxidants in the melt stabilization of polypropylene (PP). It is advisable to ascertain if other natural phenolic compounds, such as HT, could play a similar role in enhancing the thermo-oxidative resistance of polyolefins and, if it does, to which extent. It is of interest that the stabilizing efficiencies of natural antioxidants in commercial polymers are usually lower than those for their synthetic analogues. The question may be put forward

$$RO_2^\bullet + RO_2^\bullet \longrightarrow ketone^* + O_2^* + ROH$$
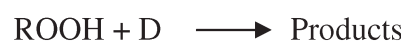
Scheme 1

why Nature prefers the former—does there exist the unknown mechanism of stabilization in Nature which differs significantly from that commonly accepted for synthetic stabilizers? The comparison studies of respective groups of stabilizers in accelerated tests are, therefore, necessary to give proper insight to that question. In this study, the chemiluminescence (CL) method, widely used to monitor *in situ* degradation phenomena in polymers,[7–9] was used as the testing tool. CL measures the light emission from excited states formed during a chemical reaction and became popular for testing of PP stability in the last years.[10,11] There was some discussion on the exact mechanistic nature of CL emission reactions,[12,13] but most importantly, thermal degradation reactions of hydrocarbon-based polymers are accompanied by the emission of visible photons,[14] with their intensity related to the progress of the degradation process.[8–15] One of the main advantages of CL measurements is the determination of oxidation induction time and other oxidation parameters at temperatures below the polymer melting, as well as in the case of those reactions with time-dependent degradation rates.

Typical oxidation curves of polymers during isothermal CL tests show the induction time whose duration is dependent on the efficiency and the concentration of antioxidant within the polymer matrix. During the induction period the chemiluminescence intensity is typically low. The CL-time curves show further a sudden increase to the maximum intensity and after the majority of the material was degraded the light emission clearly decreases.[16] Any change in the chemiluminescence induction time (CL-OIT) is the reflection of the acceleration or inhibition of the reaction rate during the thermo-oxidative degradation process.

It has been reported that chemiluminescence is supposed to increase during the self-recombination of secondary peroxyl radicals according to the Russell's mechanism (Scheme 1).[17]

Antioxidants in polymer formulations (InH, D) either scavenge peroxyl radicals yielding harmless products according to Scheme 2 or decompose hydroperoxides into nonradical products (Scheme 3). Both reactions lead to a substantial reduction in the degradation rate and consequently in the CL intensity. This process is observed until the antioxidant is completely consumed leading to the beginning of thermo-oxidative degradation reactions and to the

$$RO_2^\bullet + InH \longrightarrow Products$$

Scheme 2

$$ROOH + D \longrightarrow Products$$
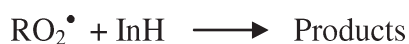
Scheme 3

typical auto-accelerating chemiluminescence-time curves, where the CL intensity is very low when antioxidants are present and increases when they are gradually consumed by the reaction with peroxyl radicals or in hydroperoxides decomposition.

The aim of this study is the evaluation of the effect of HT in the thermo-oxidative stabilization of PP with comparison with two well-known antioxidants, one of them from natural origin (α-Toco) and the second a phenolic compound commercially available (Irganox®1076).

EXPERIMENTAL

Materials and sample preparation

Pure commercial polypropylene without any additive (ISPLEN® PP 040 G1E, Repsol YPF, Spain) was used. Hydroxytyrosol with purity 90% solved in ethanol (30% v/v) was kindly supplied by Instituto de la Grasa-CSIC, Sevilla (Spain). Testing samples were prepared by mixing PP with HT in three different concentrations (0.01 wt %, 0.1 wt %, and 0.5 wt %). For comparison purposes, samples of PP stabilized with α-tocopherol 92% (Irganox E201, Ciba Speciality INC, Switzerland) were also prepared in the same concentration levels. In addition, PP samples mixed with octadecyl 3-(3,5-di-*tert*-butyl-hydroxyphenyl)-propionate (Irganox®1076, Ciba Speciality Inc, Switzerland) at 0.1 wt % as well as pure PP without any antioxidant were also prepared as control samples. Figure 1 shows the chemical structures of all the antioxidants used in this study. Since α-Toco is normally too viscous to be correctly incorporated to PP during processing it was dissolved in absolute ethanol before the addition to the polymer to improve the mixing process. Before their incorporation to the extruder, mixtures were previously blended by introducing all components in an orbital mixer during 30 min at 25 rpm rotation speed. Samples stabilized with natural antioxidants were further treated in a vacuum-ventilated oven at 40°C to evaporate the excess of solvent. Then, each mixture was processed in a twin-screw extruder at 30 rpm and 185°C using these conditions for all segments. Extruded materials were further pelletized and 100 μm films were prepared by hot-pressing of polymer pellets in two consecutive steps on Fontune Holland high-pressure equipment at 170°C and 20 MPa for 10 min.

Chemiluminescence tests

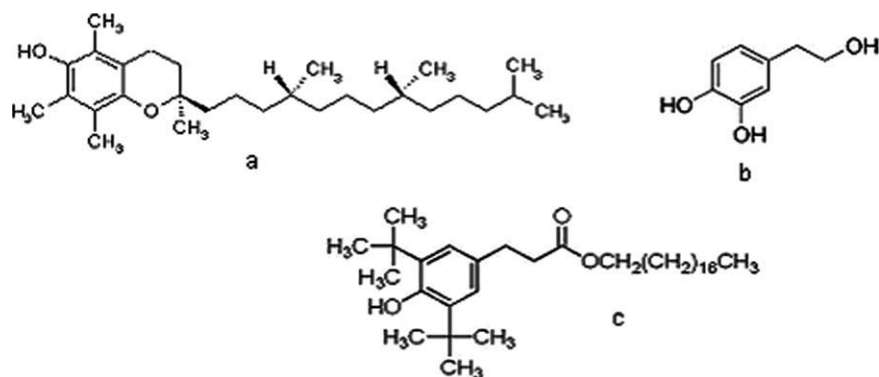CL experiments were performed on a photon-counting instrument Lumipol-2 manufactured by the

Figure 1 Molecular structures of (a) α-tocopherol; (b) hydroxytyrosol; c) Irganox®1076.

Polymer Institute of Slovak Academy of Sciences [Bratislava, Slovakia (www.lumipol.com)]. Measurements were performed in pure oxygen flow (3 L h^{-1}) introduced directly over the sample surface. Circular samples (9 mm diameter) obtained from PP films were placed into aluminum pans and tests were run until completion of the thermo-oxidative degradation process. The instrument background was two to four counts s^{-1} at 40°C. Isothermal measurements were performed at 140, 150, and 160°C, for stabilized samples; while for the nonstabilized PP several isothermal temperatures were tested in the range 80–160°C. Induction time for each test was calculated as the intersection between the tangent of the signal in the inflection point and the time axes. In addition, some dynamic CL tests were performed from 40 to 180°C at 2.5°C min^{-1} heating rate to assess the temperature range for all materials tested in this study.

RESULTS AND DISCUSSION

Isothermal tests

As a first approach, PP without any antioxidant was studied by CL at different isothermal temperatures. Figure 2 shows the CL patterns at temperatures between 80 and 160°C. As expected, the increase in testing temperatures shortened the induction time related to the advanced stages of oxidation and increased the maximum chemiluminescence intensity. Figure 2(a) shows in more detail the increase in induction time at lower temperatures (from 80 to 110°C) and the decrease on CL intensity following the same behavior than those curves obtained for higher temperatures.

A comparison between the antioxidant performance of HT with those of α-Toco and Irganox®1076 at the same concentration level (0.1 wt %) is shown in Table I. For such study the chemiluminescence oxidation induction time was determined at three temperatures: 140, 150, and 160°C.

It was observed (Table I) that induction time for α-Toco was significantly higher when compared

with those obtained for materials stabilized with the other two antioxidants, i.e., HT and Irganox®1076. We should note that the stabilization performance of HT in PP was not as high as for the other two antioxidants. Results showed that α-Toco is a very effective stabilizer to PP thermo-oxidative degradation, even at very low concentrations (0.01 wt %), with clearly better performance than HT and Irganox®1076 at the same concentration level. This high stabilizing efficiency of α-Toco was also observed by other authors.[18] They attributed the high antioxidant activity of this additive to both, the parent molecule and its oxidation products, which were found to include dimers and trimers as well as tocoquinones and aldehydes.[6] These oxidation products are themselves very good processing antioxidants for PP as it was demonstrated elsewhere.[7] The oxidation products of Irganox®1076 may also improve the antioxidant efficiency of this compound but to a lower extent. The chemical decomposition of the propionate group in Irganox®1076 yields several oxidation products, including quinone methides
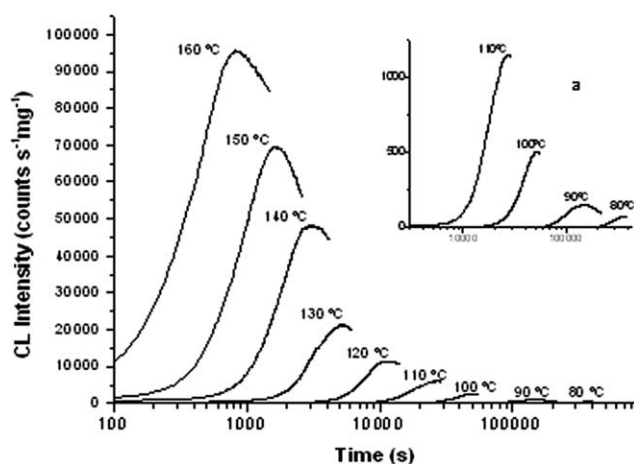

Figure 2 Logarithmic coordinates of CL intensity—time runs from the temperature interval 80–160°C. (a) Zoom of logarithmic coordinates of CL intensity—time runs from the temperature interval 80–110°C.

TABLE I
Oxidation Induction Times for Stabilized Samples of Polypropylene at the Same Antioxidant Concentration (0.1 wt %)

	Induction time (min)			Maximum CL intensity (counts s^{-1} mg^{-1}) $\times$ 10^{-4}		
Sample	140°C	150°C	160°C	140°C	150°C	160°C
Non stabilized PP	13.7	5.2	1.3	3.3	8.8	13.8
PP + Irganox®1076 (0.1 wt %) (1.9 10^{-3} mol kg^{-1})	633	79.8	32.4	1.8	6.4	12.7
PP + α-Toco (0.1 wt %) (2.3 10^{-3} mol kg^{-1})	1177	433	185	1.3	5.8	17.0
PP + HT (0.1 wt. %) (6.5 10^{-3} mol kg^{-1})	59.1	22.2	10.1	1.8	6.7	14.0

and dimers,[5,19] which are able to scavenge carbon-centered free radicals, and their further aromatization can subsequently regenerate the phenolic function.[20,21] As these products result by chemical depletion of the antioxidant, they should be present in the oxidation propagation stage, and should result in a reduction of the oxidation rate as compared to the nonstabilized polymer.

With regards to HT, it was reported that this compound plays an important role in polymer protection to thermo-oxidative degradation as hydrogen peroxide scavenger.[22] The formation of dimers and quinones during HT auto-oxidation was also reported.[22,23]

The effect of the initial concentration of both natural additives in the antioxidant activity was studied at 150°C. Figure 3 shows curves for CL intensity versus time at 150°C for PP stabilized with α-Toco at different concentrations. As expected, higher amounts of antioxidant resulted in higher induction times. The same behavior was observed for HT-stabilized PP (Fig. 4). In this case a significant increase in the induction time was observed for 0.5 wt % of the additive when compared with the other two concentrations tested in this study. Therefore, it seems that HT in polymer formulations in amounts higher than 0.1 wt % could give a real inhibition of oxida-

tion reactions in PP and consequently that the threshold of the antioxidant activity of HT is higher than in the case of using α-Toco.

The fact that an overdose of HT would be necessary to obtain a similar stabilization effect does not appear to be an obstacle for its application. The absolutely natural origin of HT used in this study and its availability and/or low price would be a clear advantage when compared with other synthetic commercial antioxidants. However, it should be taken into account that the molecule of HT is hydrophilic and low compatibility with polyolefins could be expectable, especially at high concentrations. Some data concerning the long term stability of the PP/HT mixtures should be useful to evaluate the applicability limitations. In addition, higher amounts of HT and its release from the polymer could be useful to think in the development of an active packaging system, where the antioxidant migrates from the polymer to foodstuff in contact with it, protecting it against oxidation. Further studies will be carried out to assess HT performance at longer times.

It was shown that isothermal CL runs can be fitted by Equation 1 as it was indicated by Matisová-Rychlá et al.[18]

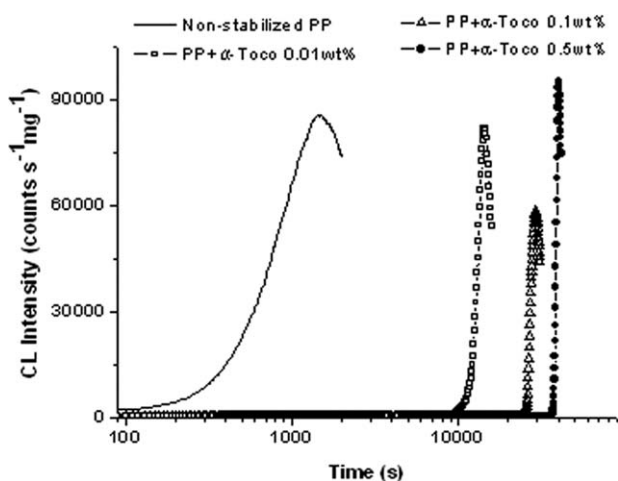$$I = \frac{A \exp(-k_1 t)}{[1 + Y \exp(-k_2 t)]^2} \tag{1}$$

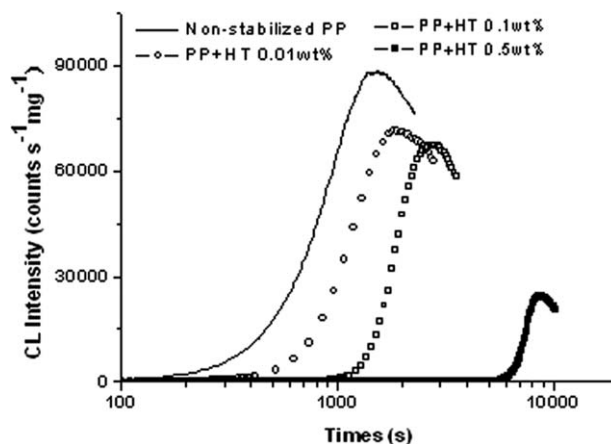**Figure 3** CL intensity versus time curve for PP stabilized with α-Toco at 150°C.

Figure 4 CL intensity versus time curve for PP stabilized with HT at 150°C.

TABLE II
Parameters Calculated with Eq. (1) for the Thermal
Oxidation of Pure Polypropylene

T (°C)	A ($\times 10^{-4}$)	k_1, s^{-1} $\times 10^4$	Y	k_2, s^{-1} $\times 10^3$
80	2.1	0.05	283	0.02
90	1.9	0.07	77	0.05
100	10	0.3	74	0.12
110	6.6	0.1	31	0.24
120	24	0.9	41	0.53
130	0.53	0.7	20	1.2
140	1.1	1.7	14	1.9
150	1.5	2.9	8.5	3.2
160	2.0	3.6	4.6	6.3

Figure 5 Chemiluminescence-time curves at 120, 110, and 100°C. Lines correspond to theoretical fit by Eq. (1). Dots correspond to experimental results.

where Y is positive in the case of CL plots with sigmoidal shape and negative in the case of CL curves showing a monotonous decay. Authors reported that the main advantage of using this equation would be its direct relation with the oxidation process and consequently it could give an idea of the rate constants for decomposition of isolated and associated hydroperoxides after the antioxidant consumption. Thus in Eq. (1), the value of k_1 corresponds to the rate constant of isolated hydroperoxides decomposition, while k_2 corresponds to the rate constant for associated hydroperoxides decomposition.[18] All parameters calculated by fitting experimental data with Eq. (1) for pure PP at different temperatures are shown in Table II.

Figure 5 shows the curves for CL intensity versus time for PP at low temperatures (100, 110, and 120°C). The theoretical fitting obtained by using parameters A, Y, k_1, and k_2 calculated by nonlinear regression analysis is represented by a line, while dots represent experimental values. An excellent fitting between experimental results and the theoretical model was observed giving an indication of the validity of the model proposed by the application of Eq. (1).

The oxidation induction time could be also determined by calculation of Y in Eq. (1), since it represents the ratio between the maximum hydroperoxides concentration, $[POOH]_\infty$ and their initial concentration $[POOH]_0$ [Eq. (2)].
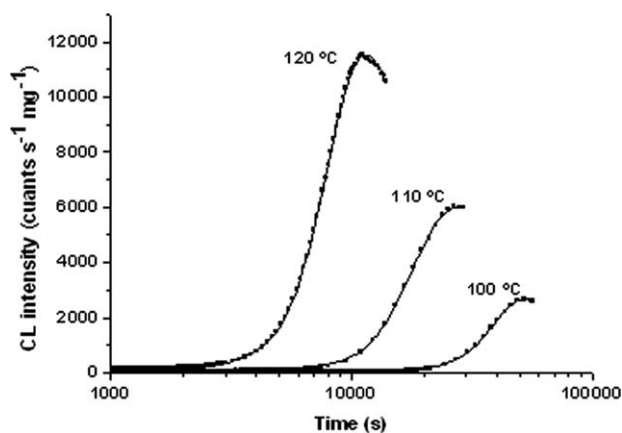
$$Y = \left\{ \frac{[POOH]_\infty}{[POOH]_0} \right\} - 1 \qquad (2)$$

It should be considered that $[POOH]_\infty$ is related with the maximum CL intensity. Moreover, the initial concentration of hydroperoxides $[POOH]_0$ should be considered as an indirect measurement of the polymer structural quality, including all those defects in the polymer caused by incorrect processing, reactions of catalyst residuals and any other parallel reactions during polymerization and/or processing. These defects are points where degradation reactions could start by the conversion of such irregular structures to hydroperoxides. Therefore, if the concentration of these structural defects is high, the value of Y should be low. This concept of polymer quality obtained for the nonstabilized material, introduced through the term Y, is also applicable to stabilized formulations.

Table II shows a general tendency for the decrease in Y value when the temperature increases, corresponding to the presence of higher concentration of defects in the polymer structure. The expectable increase in the rate constants of hydroperoxides decomposition with temperature were also observed,

TABLE III
Parameters Calculated by Eq. (1) for Stabilized and Neat PP at 150°C

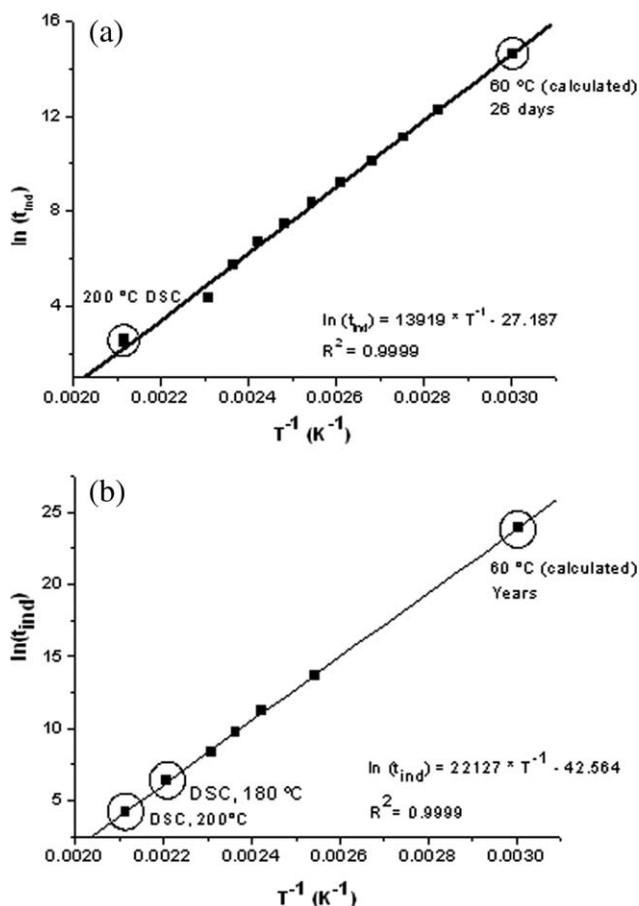| Sample	I_{max} (counts s^{-1} mg^{-1}) $\times 10^{-4}$	A	k_1, s^{-1} ($\times 10^4$)	Y	k_2, s^{-1} ($\times 10^3$)
Non-stabilized PP	8.8	1.5×10^4	2.9	8.5	3.2
PP+α-Toco 0.01 wt %	8.1	8.3×10^9	7.4	8.6×10^6	1.2
PP+α-Toco 0.1 wt %	5.8	2.6×10^8	2.8	5.9×10^{12}	1.1
PP+α-Toco 0.5 wt %	9.5	8.5×10^{11}	3.7	9.8×10^{11}	0.7
PP+HT 0.01 wt %	7.1	1.1×10^5	2.0	29	3.6
PP+HT 0.1 wt %	6.7	1.7×10^5	3.0	174	3.0
PP+HT 0.5 wt %	2.4	7.8×10^6	2.7	977	0.9
PP+Irganox®1076 0.1 wt %	6.4	2.1×10^5	2.8	6.1×10^{12}	1.1

Figure 6 Life-time prediction at 60°C. (a) Nonstabilized PP, (b) PP stabilized with α-Toco 0.01 wt %.

since the reaction rate is obviously enhanced at higher temperatures.

Parameters calculated through the application of Eq. (1) to PP stabilized with all the antioxidants used in this work are shown in Table III. It can be observed that the presence of antioxidants increased significantly the Y value depending directly to their concentration, indicating once again that the addition of such compounds during PP processing reduced the concentration of structural defects in the polymer and consequently limited the initiation of oxidation processes. As it was previously indicated, k_2 values were proportional to the rate constant of hydroperoxides decomposition during the advanced oxidation stages (associated hydroperoxides). In this case, those samples stabilized with α-Toco showed the lowest value for k_2, indicating the best antioxidant performance. It was finally observed that all parameters calculated for stabilized formulations (i.e., lower Y and higher values for k_1 and k_2) were consequent with the fact that these formulations represented stabilization for PP for all additives and concentrations.

Life-time prediction of PP stabilized with α-Tocopherol

Life-time predictions are useful for stabilized polymers since they would be an indication of their potential use in adequate conditions. In this case these predictions were performed by plotting the induction time calculated by CL tests versus the reciprocal of the absolute temperature. In Figure 6(a) results for nonstabilized PP are plotted and an additional point at 200°C was also determined by using DSC in pure oxygen as previously reported.[24,25] This comparison would be useful to relate data obtained by CL and DSC at high oxidation temperatures. As can be seen, a straight line extending to temperatures above the PP melting point (165°C) indicates that results for oxygen induction time calculated from DSC runs might be used as a fast-screening method for PP degradation studies at high temperatures, even considering the inherent loss of sensitivity already reported for such method.[26] This
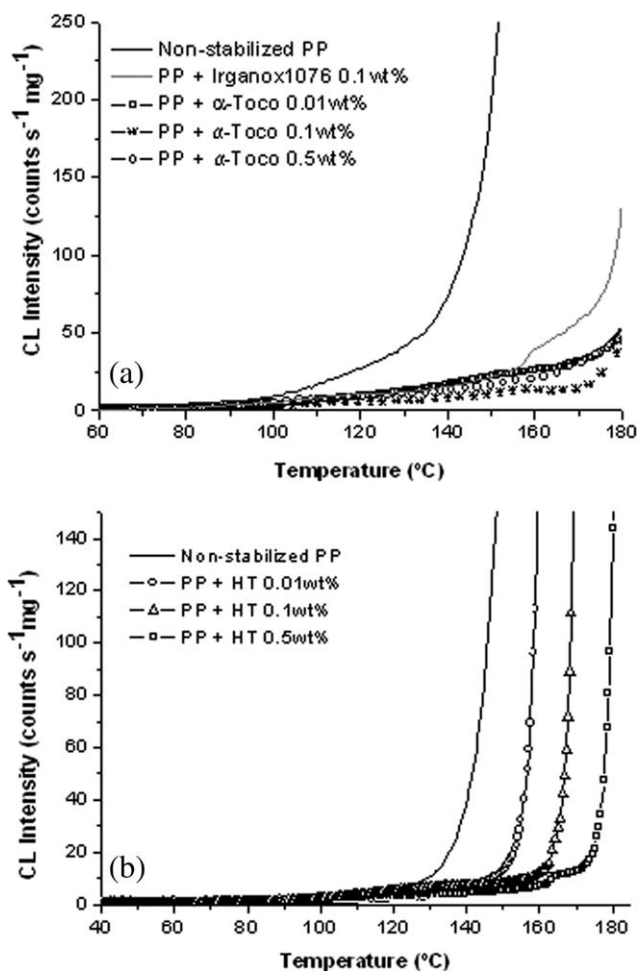

Figure 7 Dynamic CL runs. (a) Neat PP, PP stabilized with: α-tocopherol 0.01 wt %, 0.1 wt %, and 0.5 wt % and Irganox®1076 0.1 wt % samples. (b) Neat PP, PP stabilized with HT 0.01 wt %, HT 0.1 wt %, and HT 0.5 wt % samples.

correlation was also used to predict the induction time for pure PP at 60°C giving 26 days as life-time for such material in this temperature conditions.

The same test was performed for materials with α-Toco at very low concentrations from 200°C (DSC results) to 120°C [Fig. 6(b)]. A similar prediction at 60°C was carried out and the increase in resistance to thermo-oxidation by the addition of α-Toco was evident, since life-time at 60°C was extended to some years.

Nonisothermal tests

Figure 7 shows the dynamic CL tests for all materials. They are useful since they could help to assess those temperatures where the antioxidant performance of each additive could be maximum and their optimum concentrations, as well as the higher temperature limit for processing and use without any risk of oxidation. It was observed that the oxidation of neat PP proceeded at a higher rate than in the case of any stabilized material. Nonisothermal curves for PP stabilized with α-Toco are shown in Figure 7(a) and it could be observed that all of them were shifted to higher temperatures with the increasing antioxidant content. A similar behavior was observed in samples stabilized with HT [Fig. 7(b)]. It should be noted that the highest concentration of HT (i.e., 0.5 wt %) leads to a shift in the CL intensity to temperatures similar to those obtained with α-Toco at the same concentration level. This result confirms that high concentrations of HT could be adequate to reach good antioxidant performance for PP stabilization. In addition, both α-Toco and HT showed to be better antioxidants for PP than the synthetic counterpart (Irganox®1076), since their temperatures for the beginning of the oxidation process were higher in both cases.

CONCLUSIONS

Chemiluminescence measurements have shown that HT could be used for PP stabilization in thermo-oxidative conditions, but considering that high concentrations would be necessary to reach a good antioxidant performance when compared with Irganox®1076 and α-Toco. Although HT showed poor performance as PP stabilizer at concentrations lower than 0.1 wt %, it showed a clear increase in CL oxidation induction time with respect to the non-stabilized material at higher concentrations. On the other hand, low concentrations of α-Toco (0.01 wt %) were enough to stabilize PP, since life-time predic-

tion at 60°C was for some years for the stabilized material while it was 26 days for the pure PP.

References

1. Available at: http://www.internationaloliveoil.org/downloads/importations1_ang.PDF, accessed 07/12/2009.
2. Fernández-Bolaños, J.; Rodríguez, G.; Gómez, E.; Guillen, R.; Jiménez, A.; Heredia, A.; Rodríguez, R. J Agric Food Chem 2004, 52, 5849.
3. Castro, A.; Brenes, M. Processing Process Biochem 2001, 36, 797.
4. Fernández-Bolaños, J.; Rodríguez, G.; Rodríguez, R. J Agric Food Chem 2002, 50, 6804.
5. Al-Malaika, S.; Goodwin, C.; Issenhuth, S.; Burdick, D. Polym Degrad Stabil 1999, 64, 145.
6. Al-Malaika, S.; Issenhuth, S.; Burdick, D. Polym Degrad Stabil 2001, 73, 491.
7. Standberg, C.; Albertsson, A.-C. J Appl Polym Sci 2005, 98, 2427.
8. Celina, M.; George, G. A. Polym Degrad Stabil 1993, 40, 323.
9. Ashby, G. E. J Polym Sci 1961, 50, 99.
10. Catalina, F.; Peinado, C.; Allen, N. S.; Corrales, T. J Polym Sci: Part A: Polym Chem 2002, 40, 3312.
11. Zaharescu, T.; Jipa, S.; Henderson, D.; Kappel, W.; Maris, D. A.; Maris, M. Rad Phys Chem 2010, 79, 375.
12. Billingham, N. C.; Bott, D. C.; Manke, A. S. In Developments in Polymer Degradation-3; Grassie, N., Ed.; Applied Science: London 1981, p 63.
13. Jacobson, K.; Eriksson, P.; Reitberger, T.; Stenberg, B. J Adv Polym Sci 2004, 169, 151.
14. Ruiz-Gutierrez, D. V.; Juan, M. E.; Cert, A.; Planas, J. M. Anal Chem 2000, 72, 4458.
15. Blakey, I.; George, G. A.; Billingham, N. C. Macromolecules 2001, 34, 9130.
16. Celina, M.; George, G. A.; Billingham, N. C. Polym Degrad Stabil 1993, 42, 335.
17. Dinou, V.; Gorghiu, L. M.; Jipa, S.; Zaharescu, T.; Setnescu, R.; Dumitrescu, C. Polym Degrad Stabil 2004, 85, 615.
18. Matisová-Rychlá, L.; Rychly, J.; Tiemblo, P.; Gomez-Elvira, J. M. Macromol Symp 2004, 214, 261.
19. Al-Malaika, S.; Issenhuth, S. Polymer 2001, 42, 2915.
20. Pospisil, J.; Nespurek, S.; Zweifel, H. Polym Degrad Stabil 1996, 54, 15.
21. Pospisil, J.; Nespurek, S.; Zweifel, H. Polym Degrad Stabil 1996, 54, 7.
22. De Lucia, M.; Panzella, L.; Pezzella, A.; Napolitano, A.; D'Ischia, A. M. Tetrahedron 2006, 62, 1273.
23. Vogna, D.; Pezzella, A.; Panzalla, L.; Napolitano, A.; D'Ischia, M. Tetrahedron Lett 2003, 44, 8289.
24. Peltzer, M.; Jiménez, A. D. J Therm Anal Cal 2009, 96, 243.
25. Peltzer, M.; Navarro, R.; López, J.; Jiménez, A. Polym Degrad Stabil 2010, 95, 1636.
26. Pospisil, J.; Horák, Z.; Pilar, J.; Billingham, N. C.; Zweifel, H.; Nespurek, S. Polym Degrad Stabil 2003, 82, 145.