

# An Approach to Assess the Synergistic Effect of Natural Antioxidants on the Performance of the Polypropylene Stabilizing Systems

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Received 4 October 2011; accepted 20 January 2012

DOI 10.1002/app.36863

Published online in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** A study on the efficiency of natural antioxidants from agri-food industry wastes as long-term antioxidants for polypropylene (PP) is reported. Special attention is paid to the usage of vegetal wastes as a source of natural antioxidants such as alternatives to synthetic long-term antioxidants. The potential of the lignin-derived fractions generated during autohydrolysis processing of lignocellulosic agricultural, forestal, and food wastes was assessed. The measurements of oxidation induction time were used for obtaining information on long-term antioxidant effec-

tiveness, showing the protective effect of natural extracts. The protective effect was improved in combinations of natural extracts with 0.1% and 0.2% of Irgafos 168 (short-term antioxidant) besides a synergistic effect was exhibited when 0.4% of Irgafos 168 is added. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

**Key words:** oxidation induction time; antioxidant effectiveness; synergistic effect; polypropylene; vegetal wastes

## INTRODUCTION

Polypropylene (PP) is one of the most widely used commodity polymers. During the processing and application periods, polymeric materials suffer degradation caused by light, heat, oxygen, humidity, shearing forces, and so on. Degradation results in the deterioration of chemical, physical, and mechanical properties of polymeric materials and, therefore, reduced service life. Although its degradation is similar to that of polyethylene, the presence of the methyl groups of side chains results in intramolecular hydrogen transfer being more preferable in its degradation.

Protection from the combined degradative effects of oxygen, temperature, and light is usually

achieved by the addition of antioxidants. Commercial polyalkenes need the addition of suitable amounts of agents able to prevent the polymer degradation both during processing [phosphorous (phosphate, phosphonite, and phosphine), secondary antioxidants, “short-term antioxidants”] and during lifetime (hindered phenols, primary antioxidants, “long-term antioxidants”), and to get best performances in their specific end-use applications. Combinations of both are usually used in PP as stabilizing systems. When hindered phenols are used in combination with phosphites or phosphonites, the melt flow behavior during processing and the thermo-oxidative stability of the polymer improve significantly.<sup>1–11</sup>

Extensive researches have been conducted to use some natural antioxidants such as phenolic compounds as alternatives to synthetic antioxidants.<sup>12–14</sup> Special attention has been paid to the usage of vegetal wastes (e.g., coming from agricultural, forestry, or industrial activities) as raw materials for these purposes, due to their low cost and to the possibility of addressing some environmental problems.<sup>15</sup>

Until now, antioxidant activity of natural extracts was assessed almost solely based on free radical scavenging activity tests. The chemical components

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Contract grant sponsor: Spanish Ministry of Education and Science; contract grant number: AGL2003-03596-FEDER (European Union).

Contract grant sponsor: Xunta Galicia; contract grant number: PGIDT06 TAM38301PR.

Contract grant sponsor: MEC; contract grant number: PTA-2003-02-00194.

of these extracts are tannins and polyphenolic compounds,<sup>15</sup> which represent the major family of natural antioxidants and are chemical analog of synthetic long-term stabilizers widely used in plastic industry as well. The radical scavenging potential of lignin is acknowledged.<sup>16,17</sup>

The use of natural antioxidants to eliminate a not desired stabilizing effect of synthetic antioxidants after expiry of the service life of PP articles has been reported.<sup>18</sup> Accordingly, natural antioxidants could affect the degradation of PP matrix.

Hydrothermal processing of lignocellulosic materials is an environmentally friendly process suited to fractionate vegetal biomass into the major constituents, which can be valorized for chemicals, food ingredients, and additives and fuels.<sup>19</sup> The fraction of lignin solubilized during autohydrolysis reduces the purity of xylooligosaccharides and inhibits microbial action during bioconversion processes into chemicals and fuels. The selective separation and valorization of this fraction could contribute to the technoeconomical feasibility of biorefinery processes. In this article, extracts obtained from the hydrolyzates of various lignocellulosic materials, containing benzoic and cinnamic acids,<sup>20,21</sup> were tested as potential long-term antioxidants for PP, to partially substitute synthetic stabilizers. The measurement of oxidation induction time (OIT) by differential scanning calorimetry (DSC) was used for obtaining information on polymer stability and antioxidant effectiveness.

## MATERIALS AND METHODS

### Chemical and materials

PP granules and natural extracts were used. The commercial antioxidants Irganox 1010 (IN) and Irgafos 168 (IF) were kindly donated by Ciba-Geigy, Switzerland.

Barley (*Hordeum vulgare*) husks (BH) were collected in a local malting factory (San Martín, San Cibrao das Viñas, Ourense, Spain), corn (*Zea mays*) cobs (CC) were collected from a local farm, and eucalypt (*Eucalyptus globulus*) wood (EW; chips were obtained from a local pulp mill (ENCE, Pontevedra). Almond (*Prunus amygdalus*) shells (AS) were kindly provided by Borges S.A. (Tárrega, Lleida, Spain) and chestnut (*Castanea sativa*) burs (CB) were collected in Ribeira Sacra (Ourense, Spain). Grape (*Vitis vinifera*) pomace (GP), the stream leaving the spirit distillation stage from white grapes in wineries, was kindly supplied by Cooperativa Vitivinícola do Ribeiro (Ourense, Spain).

Samples of these materials were air-dried at room temperature, milled and sieved to pass a 1 mm

screen (particle size smaller than 1 mm), and stored in a single lot, to avoid differences in composition, in the darkness at room temperature in sealed plastic bags. Bags containing GP were kept at  $-80^{\circ}\text{C}$  until use.

### Preparation of crude extracts

Samples of the various raw materials were treated with water in a batch reactor with temperature control (Parr Instr. Co., Moline, IL) under nonisothermal conditions to reach maximal temperatures in the range  $200\text{--}240^{\circ}\text{C}$ , using a liquid : solid ratio of 8 : 1 g : g (oven-dry solid basis). The autohydrolysis liquors were recovered by filtration and extracted twice with ethyl acetate using a hydrolyzate : ethyl acetate volume ration of 1 : 3 (v : v) during 20 min. The organic phase was separated by decantation and vacuum-evaporated to remove solvent. This concentrate was dissolved in ethanol/water (1 : 4, v : v), subjected to successive stages of vacuum evaporation, washed with the same ethanol/water solution used previously, neutralized, and freeze dried, yielding purified extracts denoted CC, EW, AS, CB, and GP.<sup>20,21</sup> The relative concentration of phenolics in the freeze-dried extract was measured in terms of gram gallic acid equivalents/100 g extract (oven-dry solid basis).<sup>19–22</sup>

### Polymer processing

PP and several stabilizing systems were melt mixed using a miniextruder equipped with twin conical co-rotating screws and a capacity of  $7\text{ cm}^3$  [Minilab Haake Rheomex CTW5 (Thermo Scientific)]. A screw rotation rate of 60 rpm, a temperature of  $180^{\circ}\text{C}$ , and a residence time of 2 min were used.

Processing stability was tested by extrusion at different times on both the neat polymer and stabilized samples. Samples of the extruded polymer were taken out at different times for evaluating their OIT which is the time when the onset of thermal oxidation occurs in the melt.

To evaluate the performance of natural extracts as antioxidants for PP, several samples were prepared: directly stabilized with the natural extracts and with a mixture of natural extracts and IF. Comparison with a nonstabilized sample and a sample additivated with the mixture of the synthetic antioxidants, IN and IF, was also carried out.

### Methods

#### Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed using a Perkin–Elmer TGA-7 microbalance coupled to a 1022 Perkin–Elmer microprocessor. The

microbalance was calibrated making use of the Curie points of perkalloy and nickel. Dynamic experiments were conducted under oxygen atmosphere. The heating rate was  $10^{\circ}\text{C min}^{-1}$ . The temperature of the experiments ranged from room temperature to  $700^{\circ}\text{C}$ . The sample weight was 5–10 mg.

#### Thermal stability

The thermo-oxidative stability of a polymeric formulation was assessed by DSC test measuring its OIT (each sample had weighed ca. 15.0 mg). A Perkin-Elmer series 7 DSC isothermally was used to OIT measurements. The sample temperature was stabilized for 2 min at  $200^{\circ}\text{C}$  under inert atmosphere, which was subsequently switched to oxygen atmosphere to start the test. Analyses were carried out according to EN 728. The OIT was measured as the onset point at which the DSC thermogram suffers a sudden drop respect to the instrument baseline.

#### Calculation of synergy

Synergy between additives was calculated by comparing the OIT values:

$$\% \text{synergism} = 100$$

$$\frac{[\text{OIT}(a+b) - \text{OIT}(c)] - [(\text{OIT}a - \text{OIT}c) + (\text{OIT}b - \text{OIT}c)]}{[(\text{OIT}a - \text{OIT}c) + (\text{OIT}b - \text{OIT}c)}$$

where OIT is oxidation induction time,  $a$  is extract or IN,  $b$  is IF, and  $c$  is PP.

Besides, the optimum base stabilization is studied.<sup>23</sup>

## RESULTS AND DISCUSSION

### Thermogravimetric analysis

When added as stabilizers to polymers, significant amounts of the extracts could be lost during mixing into the melted polymer. TGA is often used to determine thermal stability. Thermogravimetric curves for all extracts taken into consideration in this study are shown in Figure 1. From those curves, their degradation temperatures were calculated as the temperature leading to a mass loss of the sample of 5% respect to the initial mass. The degradation temperatures for BH, CC, EW, AS, CB, and GP were 177.1, 174.1, 162.2, 163.4, 180.1, and 154.1, respectively.

According to these curves and the melting temperature of the PP,  $180^{\circ}\text{C}$  was chosen as the lowest temperature necessary to prepare the samples in the extruder without or with minimum degradation of the extracts.

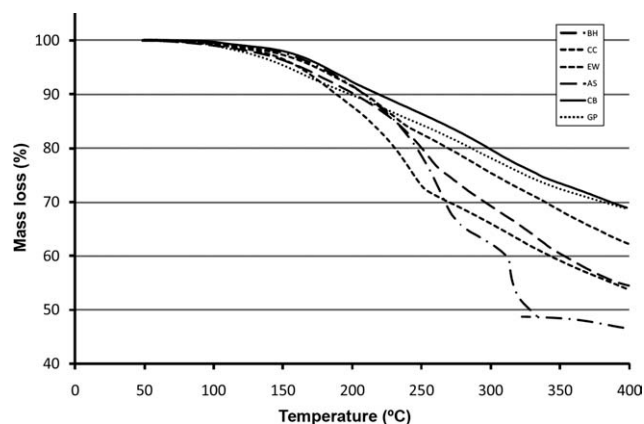


Figure 1 Thermogravimetric curves for crude extracts.

### Synergistic effect between additives against thermal-oxidation degradation of polypropylene

Numerous degradation reactions take place during the extrusion of PP due to temperature and shear rate. OIT is one of the most commonly used indicators of polymer stability both in academic and industrial environment,<sup>24</sup> being the preferred test used by the industry to assess the oxidative stability of polyolefins. As the OIT is a relative measure of the degree or level of thermal stabilization of the material at temperature tested, the longer the OIT, the more thermally stable is the material at that temperature.

Usually, the OIT measurements was realized at processing temperature to secure that the polymer extrusion will not produce thermal degradation in the materials and subsequently, changes in their macroscopical properties.

The combination of IN and IF was chosen to be the most used stabilization system in commercial contact food PP films.<sup>25</sup> As it is expected, these antioxidants show a synergistic reduction in the rate of development of oxidation, with significant increase in OIT value. Traditionally, chain-breaking donating phenolic antioxidants of the Irganox<sup>®</sup> family in combination with peroxide decomposers of the Irgafos<sup>®</sup> type have provided satisfactory antioxidant protection for polyolefins during processing and service life. In commercial antioxidant formulations containing IN and IF, the former compound acts as a hydrogen atom donor, whereas the latter serves as a decomposer of hydroperoxides.

Natural antioxidants from lignocellulosic materials have well-documented capacity to act as hydrogen atom donor and long-term antioxidants. Lignin from wood pulping can act as thermo-oxidative stabilizer of PP composites<sup>26,27</sup> and natural or synthetic polymers<sup>28,29</sup> with the advantage of the absence of health hazards and to the environmental benefits derived from its biodegradable nature. Therefore, the protective effect of the stabilization system, form by crude

**TABLE I**  
Synergistic Effect between Natural and Synthetic Antioxidants against Thermal-Oxidation Degradation of Polypropylene

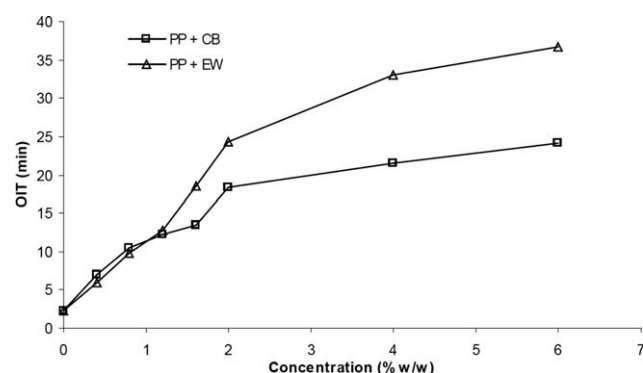
Extract concentration (g extract/100 g PP)	Phenolic concentration (g GAE/100 g PP)	OIT (min)		% Synergy
		Without Irgafos 168 (0.2%)	With Irgafos 168 (0.2%)	
PP	PP	2.25	1.86	
PP + IN (0.4 %)	PP + IN (0.4 %)	22.59	53.96	148.21
PP + BH (0.4 %)	PP + BH (0.128 %)	6.12	8.80	54.95
PP + CC (0.4 %)	PP + CC (0.128 %)	6.32	7.83	28.21
PP + EW (0.4 %)	PP + EW (0.209 %)	5.99	7.08	20.83
PP + AS (0.4 %)	PP + AS (0.144 %)	6.13	8.92	57.12
PP + CB (0.4 %)	PP + CB (0.172 %)	6.92	7.57	9.09
PP + GP (0.4 %)	PP + GP (0.152 %)	6.58	8.76	39.99

extracts of phenolic nature and IF (long- and short-term antioxidants), was checked.

The longest OIT obtained for natural extracts confirmed that these extracts provided PP with stabilization against thermal-oxidation degradation (Table I). Nevertheless, the studied natural extracts added in equal levels of commercial long-term antioxidants (0.4%) showed a protection effectiveness lower than synthetic additives. The maximum synergistic effect with short-term antioxidant (0.2% IF) was achieved by almond shells extracts (57%). The greater effect observed for the PP + IN (0.4%) sample may be attributed to the high efficiency of IN and the highest antioxidant : PP ratio in the sample, which was 1.9–3.1 times higher than in PP + natural extracts samples.

#### Effect of the concentration of natural extracts on the OIT

The effect of the natural extract levels in polymer performance was studied. Samples with the lowest synergy values, regardless their high levels in phenolic compounds, were chosen: CB and EW extracts. As judged by OIT values (Fig. 2), addition of 0.4–6% (w/w) of natural extracts to PP causes a notable protection against oxidation of the material. A rapid



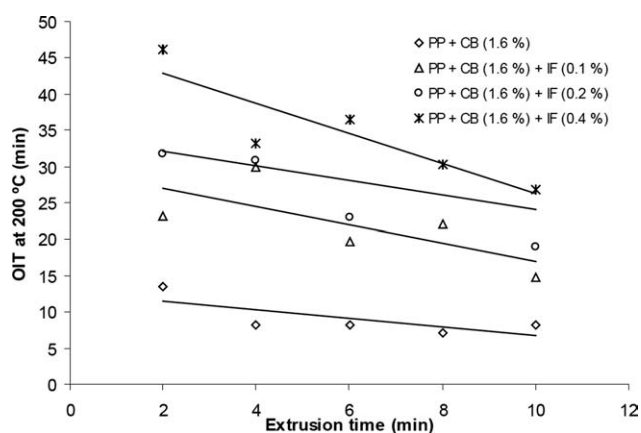
**Figure 2** Effect of the concentration of the chestnut burs (CB) and eucalypt wood (EW) extracts on the OIT.

increase of OIT values was observed for natural extract levels between 0% and 2%. Minor shifts were observed for natural extract levels upper than 2%.

#### Long-term thermal stability

To evaluate the long-term oxidation, the OIT values of the samples were measured after several extrusion residence times. Samples of PP stabilized with combinations of the natural extract with the best thermal stability 1.6% CB extract (Fig. 1, Table I), and different amounts of IF (0.1, 0.2, and 0.4%) were processed by five consecutive residence times (2–10 min). A sample of the extruded polymer after 2 min was taken out for OIT measurements. The remaining polymer sample was re-extruded under the same conditions up to four times (4, 6, 8, and 10 min) with polymer sampling for further analysis.

Figure 3 shows the OIT values of the polymer stabilized with two-component antioxidant systems as a function of the extrusion time. As judged by OIT measurements, the sample with CB extract at 1.6% was thermally stable. Obviously, the combination of the natural extract (hindered phenol) and the



**Figure 3** Changes in the residual stability of PP containing mixtures of chestnut burs (CB) extract (1.6%) and Irgafos 168 (IF) (0, 0.1, 0.2, and 0.4%) as measured by DSC.

TABLE II

Details of PP Formulations Together with Corresponding Values of (i) the OIT at 0.4% (w/w) CB ( $\tau_1$ ), 0.8% (w/w) CB ( $\tau_2$ ), and 1.6% (w/w) CB ( $\tau_3$ ), (ii) the Antioxidant Efficiency Parameter,  $\tau_o$ , (iii) the Antioxidant Effectiveness Parameter,  $k_1$ , and (iv) Linear Least-Squares Regression,  $r^2$ , Analyses Performed on OIT Data Obtained at Different Loadings of CB Extract

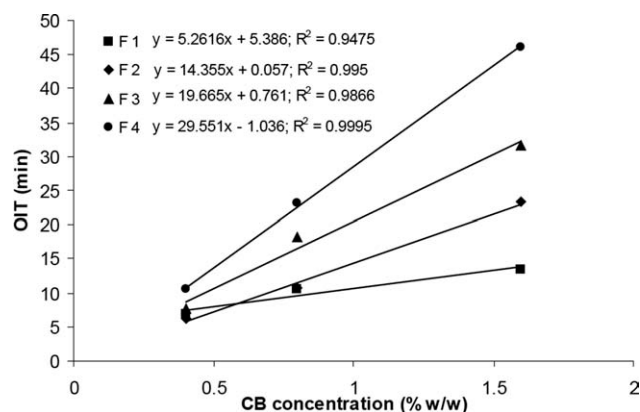
Formulation	Irgafos 168 concentration (%)	$\tau_1$ (min)	$\tau_2$ (min)	$\tau_3$ (min)	$\tau_o$ (min)	$k_1$ (min/% w/w CB)	$r^2$
F1	0	6.919	10.454	13.519	5.387	5.262	0.948
F2	0.1	6.268	10.838	23.26	0.057	14.355	0.995
F3	0.2	7.568	18.081	31.695	0.761	19.665	0.987
F4	0.4	10.488	23.05	46.098	-1.036	29.551	0.995

synthetic antioxidant IF (phosphite) has a strong synergetic effect on the residual thermo-oxidative stability of the PP. To achieve similar values of OIT, an IF amount twice as much is necessary if the residence time is modified from 2 to 10 min. The additive-additive interactions that occur in the systems investigated are complex, and there is an obvious need for further systematic experiments to be performed before a more definitive explanation.

#### Polymer formulations: Identification of the optimum base stabilization

A novel method involving stability parameter mapping and stability vector analysis was used for assessing the effect of the combination of natural and synthetic antioxidants on polymer performance.<sup>23</sup>

Four formulations containing IF, F1–F4 (0, 0.1, 0.2, and 0.4%) were prepared using three levels of CB extract, 0.4, 0.8, and 1.6% w/w, making a total of 12 formulations. Details are listed on Table II. Figure 4 shows plots of the OIT versus the level of concentration of CB extract for the studied formulations. The data suggest that there is a linear relationship between the OIT and the level of CB extract. At suf-



**Figure 4** Plots of OIT (min) versus the level of CB extract (% w/w) for formulations F1–F4. The values of  $\tau_o$  and  $k_1$  are indicative of the efficiency of the base stabilization and the effectiveness of CB within the formulation, respectively.

ficiently low levels of CB, the relationship between OIT and the level can be represented by the simple linear equation:

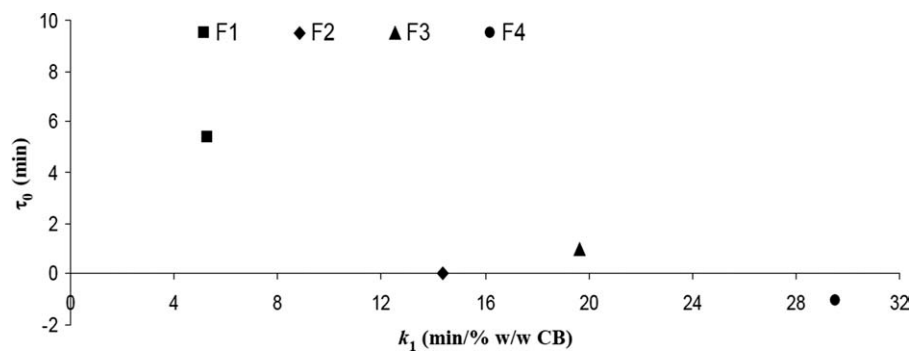
$$\text{OIT} = k_1 \times [\text{CB}] + \tau_o$$

where  $k_1$  is a constant, [CB] is the level of CB, and  $\tau_o$  is the OIT in the absence of CB.

Clearly, the value of  $\tau_o$  is indicative of the efficiency of the base stabilization, and the gradient  $k_1$  is indicative of the effectiveness of CB extract within the given formulation. In particular, for a given increment in the level of CB, the corresponding increase in OIT will be greater, as the value of  $k_1$  becomes greater. The highest IF contents (0.4%) led to  $k_1$  values that show higher rises of effectiveness of CB extract for the same rises of CB extract amount than samples with short percentage of IF.

The linear regression data listed in Table II can be used to determine the optimum levels of IF and CB extract within the sample sets that were studied. To easily identify any such formulation, the linear regression data in Table II were displayed in the form of a “map” where the constants  $k_1$  and  $\tau_o$  are plotted as the abscissa and ordinate, respectively (Fig. 5). It is clear that formulation set F4 contains the optimum base stabilization because its  $k_1$  parameter lies furthest from the origin.

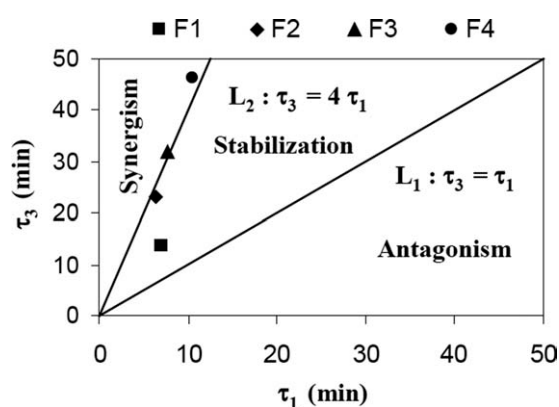
Figure 6 is a plot of  $\tau_3$  (OIT at 1.6% w/w CB extract) versus  $\tau_1$  (OIT at 0.4% w/w CB extract) for the formulations F1–F4. This plot illustrates the potential usefulness of the stability parameter mapping technique in resolving the relative stabilities of the formulations by giving a clear graphical representation of the order of these stabilities. F1 has the lowest stability of the formulations considered, which contain CB extract alone as the base stabilizer. The formulation that exhibits the greatest stability is F4. Synergetic effect was also found in formulation F3. The line L2 that represents cases where a “directly additive” effect is observed upon the incorporation of CB in the formulation has been drawn in Figure 6 for comparison. This line has a gradient of 4 which is the numerical value of the ratio  $[\text{CB}]_3/[\text{CB}]_1$  used in the series of CB-containing



**Figure 5** Plots of  $\tau_0$  (min) versus  $k_1$  (min/% w/w CB) parameters, which constitute a “map” enabling the optimum formulation.

formulations. Systems whose coordinates lie in the region between L1 and L2 are systems where the incorporation of CB results in stabilization of the polymer. Systems that lie in the region between L2 and the  $\tau_3$  axis are ones where the incorporation of CB at the higher level of [CB]<sub>3</sub> produces a greater than additive effect on stability and so this region is the one in which the coordinates of synergistic systems will be located. Using similar reasoning, the region between L1 and the  $\tau_1$  axis is the region in which the coordinates of antagonistic systems will be located.<sup>23</sup>

When different amounts of IF (0, 0.1, 0.2, and 0.4) are added to PP with 1.6% of CB extracts, a stabilization effect is observed for the 3 first formulations. A synergism effect is exhibited by the fourth formulation (higher  $\Delta\tau$ ). Consequently, the formulation F4 (1.6% CB extract, 0.4% IF) achieves equal OIT values with the lowest amount of stabilization system. A linearity relation is shown by  $\tau_3 - \tau_1$  versus  $k_1$  for the formulations F1–F4 ( $R^2 = 0.9993$ ). This linearity confirms that  $\tau_3 - \tau_1$  can be taken as a direct indicator of additive effectiveness within the formulation.



**Figure 6** Plots of  $\tau_3$  (min) versus  $\tau_1$  (min) for the formulations F1–F4 that contain CB extract, where  $\tau_3$  is the OIT at 1.6% (w/w) CB extract and  $\tau_1$  is the OIT at 0.4% (w/w) CB extract, respectively. The line L2 has gradient  $m = 4$  where  $m = [\text{CB}]_3/[\text{CB}]_1$ .

## CONCLUSIONS

Extracts from a residual phenolic stream generated during the hydrothermal fractionation of vegetal biomass, containing lignin depolymerization compounds, could be regarded as extracts from natural origin and structure. The possibility of using six phenolic extracts (BH, CC, EW, AS, CB, and GP as long-term antioxidants in PP was tested. The longest OIT obtained confirmed that these extracts (0–2%) have provided PP with stabilization against thermal-oxidation degradation. The protective effect was improved in combinations of natural extracts with IF (short-term antioxidant). A synergistic effect was exhibited by all studied extracts. A procedure to set the optimum levels of natural and synthetic antioxidant with better performance is shown. This procedure is also applied to achieve the best combination of mixtures of CB extracts and IF (F4 : 1.6 CB extract, 0.4 IF).

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