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1 **Enhancing the thermal stability of polypropylene by blending with low amounts of**  
2 **natural antioxidants**

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13  
14 **Abstract**

15 Natural antioxidant were added in very low amount to protect polypropylene  
16 (PP) matrix against thermo-oxidative degradation during processing. Thus, PP was  
17 melt-blended with caffeic, chlorogenic, trans-ferrulic and p-coumaric acids, and also  
18 with flavone and 3-hydroxyflavone at 0.1%wt with respect of PP matrix. Neat PP and  
19 PP blended with three traditional antioxidants were prepared for comparison. A  
20 complete structural, thermal and mechanical characterization was conducted. Ferrulic  
21 acid and particularly caffeic acid increased the thermal stability, showing also the  
22 highest activation energy. The structural changes of PP based films due to the polymer  
23 thermal degradation at high temperature (i.e.: 400 °C) followed by FTIR reveals that  
24 antioxidants effectively delayed the thermal degradation process. The wettability and  
25 the mechanical performance was also studied to get information regarding the industrial

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26 application of such films. While caffeic acid provided a more flexible material, ferrulic  
27 acid provided higher water resistant. Finally, AFM-QNM showed that PP with caffeic  
28 acid showed the highest miscibility.

30 **Keywords:** Polypropylene; natural antioxidant; thermal stability.

## 32 **1. Introduction**

33         Despite the increasing attention for biodegradable polymers, especially in short  
34 term application, polyolefins are still the most common polymers used in the industrial  
35 sector.<sup>[1]</sup> Among others polyolefins, polypropylene (PP) is the most widely used  
36 thermoplastic for packaging purposes whose demand has increased during the last  
37 decades mainly due its easy of processing, low density, low cost and good chemical  
38 stability. The PP demand by plastics converters in Europe reach almost 10 millon tones  
39 the last year to produce several products for several industrial applications i.e.: food  
40 packaging, sweet and snack wrappers, hinged caps, microwave containers, pipes,  
41 automotive parts, bank notes, among others.<sup>[2]</sup> Thus, PP is widely used for the  
42 production of short term applications, which generates a huge amount of plastic waste  
43 ever years which can be recovered in the form of energy or material. Fortunately, more  
44 than 70% of plastic waste are retrieved using industrial recycling (31% of plastic waste)  
45 and by energy recovery (41,6%), closing the loop of circular economy.<sup>[2, 3]</sup> That means  
46 that around 8,5 millon tones of plastics are recycled every year.<sup>[2]</sup> However, polyolefins  
47 are susceptible to suffer degradation during recycling and also during typical industrial  
48 melt-processing approaches such as injection moulding, extrusion and film forming. In  
49 fact, the thermo-oxidative degradation provokes an undesired brittle material.<sup>[4, 5]</sup> In  
50 fact, with increasing times of reprocessing the molecular weight and melt viscosity of

1 51 PP decrease leading to a reduction on the mechanical performance.<sup>[6]</sup> The degradation  
2 52 in PP is an irreversible process in which, among several possible mechanisms, oxidation  
3 53 is usually dominant.<sup>[7]</sup> The thermal degradation of polyolefins, including PP, and other  
4 54 polymeric matrices during thermal processing is frequently avoided by adding  
5 55 antioxidants.<sup>[8-10]</sup> However, most frequently antioxidants used at industrial level are  
6 56 petroleum-based and non-convenient for several applications as the case of toy, baby  
7 57 care, medicine or food packaging industries. Moreover, antioxidants are not only added  
8 58 to inhibit PP oxidation reaction during melt processes at elevated temperatures, but also  
9 59 to protect the polymer matrix in outdoor applications under UV exposure.<sup>[11]</sup> This is  
10 60 why, there is a worldwide trend to replace synthetic additives, including antioxidants,  
11 61 for non-toxic additives coming from renewable resources due to the phenomenon of  
12 62 migration which transfers part of the additives to the product which it is in contact with  
13 63 and, that, can lead to toxicity problems.<sup>[12, 13]</sup> In this sense, one currently strategy is the  
14 64 use of natural antioxidant (NA) to protect polyolefins from the thermo-oxidative  
15 65 degradation during processing.<sup>[11, 14]</sup> Thus, the use of NA as polymers additives has  
16 66 become an interesting strategy to protect the polymeric matrix during processing from  
17 67 thermo-oxidative degradation and from UV radiation during the material service, at the  
18 68 same time as the environmental impact is reduced due to their renewable nature.

19 69 The melt stability of polyolefins has been widely studied by testing the typical  
20 70 thermal processing conditions controlling the melting atmosphere under limited oxygen.  
21 71 <sup>[8, 15]</sup> Several traditional synthetic antioxidants have been used as useful additives to  
22 72 protect the polymeric matrix during processing in really small amounts (i.e.: between  
23 73 0.1 wt% and 0.3 wt%).<sup>[16-18]</sup> Most of the natural occurring antioxidants are polyphenolic  
24 74 compounds derived from flavonoids, which are gaining considerable interest in the  
25 75 plastic processing industry to replace the traditional synthetic antioxidants used for

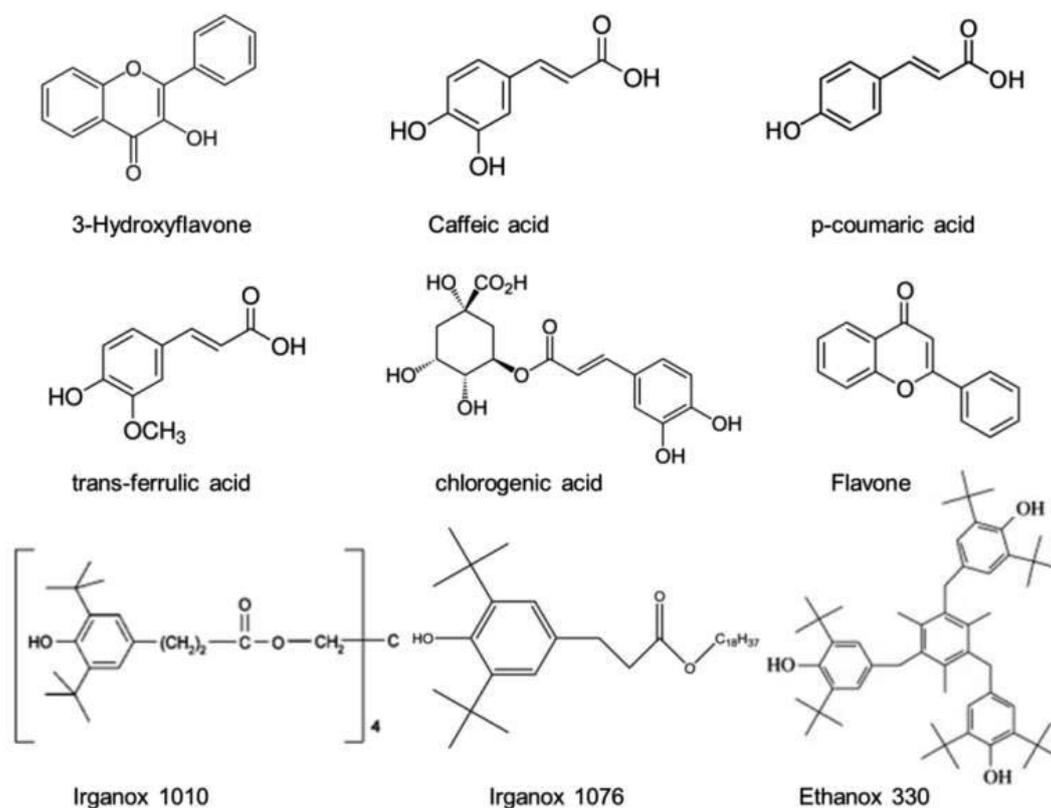
76 more environmental ones.<sup>[8, 9, 13, 14, 19]</sup> For instance, Samper et. al, processed PP with  
77 several NA and they demonstrated that flavonoids such silibinin and quercetin provide  
78 better stabilizing effect to PP matrix than flavanone glycosides (i.e.: hesperidin and  
79 naringin), providing similar stabilization effect that those provided by conventional  
80 petroleum derived antioxidants,<sup>[14]</sup> typically used at industrial level, such as ethanox and  
81 Irganox. In fact, the polyphenols chemical structure characterized by several phenol  
82 rings and hydroxyl groups is able to act as natural stabilizers against the polymer  
83 degradation.<sup>[20]</sup> In this study, natural antioxidants were used in low amount as  
84 antioxidant additives for the stabilization of PP: caffeic acid, p-coumaric acyd, trans-  
85 ferrulic acid, chlorogenic acid, flavanone and also with 3-hydroxyflavone since it  
86 represents the backbone of all flavonols. Thus, PP based blends were prepared by  
87 adding each antioxidant at 0.1%wt and processed by means of melt extrusion approach  
88 in order to simulate the industrial processing conditions. The optical properties of the  
89 obtained films were evaluated by means of UV-vis and colourimetric measurements.  
90 Their thermo-oxidative behavior was analyzed by Melt Flow Index (MFI), Differential  
91 Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA). Since kinetic  
92 analysis represents a useful tool for monitoring the thermal decomposition kinetics of  
93 polymers, apparent activation energy ( $E_a$ ) was also calculated.<sup>[21-23]</sup> Moreover, to  
94 evaluate the concrete possibility to scale up these PP based materials blended with low  
95 amounts of NA, the developed formulations were exposed at high temperature (i.e.:  
96 400°C) to induce the polymeric matrix thermal degradation and the structural changes  
97 were followed by FTIR analysis. Meanwhile, the influence of the low amounts of NA  
98 on the mechanical performance of PP based blends was evaluated by nanoindentation  
99 technique as well as by Atomic Force Microscopy (AFM). For comparative purposes,  
100 neat PP as well as PP stabilized with three commercial widely used synthetic

101 antioxidants at industrial level: Ethanox-330, Irganox-1010 and Irganox-1076 were also  
102 studied to get information about the possibility to replace these traditional antioxidants  
103 used in the industrial sector for the natural antioxidants proposed here.

## 105 2. Experimental

### 106 2.1. Materials

107 The polypropylene (PP) used in this study was supplied in the form of powder without  
108 additives by Propilco Company (Colombia). The synthetic antioxidants (98% purity)  
109 were provided by Ciba (Colombia), while natural antioxidants (98% purity) were  
110 provided by Sigma Aldrich (Mostoles, Spain), with the exception of chlorogenic acid  
111 (98% purity) which was provided by Acros Organics (Madrid, Spain). The chemical  
112 structures of natural and synthetic additives used in this study are shown in **Fig. 1**.



**Fig. 1.** Molecular structure of the antioxidant additives used in the study.

## 116 **2.2. Sample preparation**

117 PP-antioxidant blend samples were premixed by adding 0.1%wt of each  
118 antioxidant additive to PP powder using a Prodex Henschel 115JSS standard mixer at  
119 800 rpm for 7 minutes at room temperature. Subsequently, samples were blended by  
120 melt-extrusion by means of a Welex-200 24.1 extruder being the operating temperatures  
121 measured inside the extruder paths 190 °C, 195 °C, 200 °C, 210 °C and 220 °C. The  
122 blends were further processed into films (300 mm diameter films of ~100 µm in  
123 thickness) by compression moulding in a hot press CARVER 3895. A neat PP film was  
124 also prepared under the same processing conditions for comparative purposes.

## 126 **2.3. Characterization techniques**

### 127 **2.3.1. Optical and Colorimetric parameters**

128 The visual appearance of films was qualitative evaluated by taken photographs.  
129 The transmittance of the films was measured in the 700-250 nm region of the spectra in  
130 a UV-VIS spectrometer of StellarNet Inc. (Florida, US) model Black-comet-SR. The  
131 colourimetric changes provoked by the addition of antioxidants into PP matrix were  
132 studied by measuring the colour coordinates in the CIELab colour space L (lightness),  
133 a\* (red-green) and b\* (yellow-blue) by means KONICA CM-3600d, HunterLab, (USA).  
134 The instrument was previously calibrated using a white and black standard tiles.  
135 Measurements were conducted in quintuplicate on random positions.

### 137 **2.3.2. Melt Flow Index**

138 The melt flow index (MFI) was determined using a Plastometer instrument  
139 (Tinius Olsen model MP600) following the guidelines of ISO standard,<sup>[24]</sup> at 230 °C  
140 under 2.16 kg load.

### 142 **2.3.3. Thermal Analysis**

#### 143 **2.3.3.1. Differential Scanning Calorimetry**

144 Perkin Elmer DSC 4000 Differential Scanning Calorimeter (DSC) was used to  
145 determine the oxidation induction time (OIT) following a previously described  
146 method.<sup>[25]</sup> The study was conducted with samples' weight in the range of 5 to 10 mg.  
147 Firstly, the DSC was programmed under isothermal mode at 60 °C for 5 minutes.  
148 Subsequently, it was heated from 60 to 200 °C at a rate of 20 °C min<sup>-1</sup> under a nitrogen  
149 atmosphere at a flux rate of 50 ml min<sup>-1</sup> and then, the temperature was held for 15 min  
150 at 200°C. Finally, the inner gas was changed to oxidation conditions (air atmosphere) at  
151 a flux rate of 50 ml/min, keeping the temperature at 200 °C during 30 min.

#### 153 **2.3.3.2 Thermogravimetric Analysis**

154 Thermogravimetric Analysis (TGA) were conducted using a Perkin Elmer  
155 thermobalance TGA 7. The sample weights were in the range between 18 and 22 mg.  
156 Experiments were performed by heating the samples from 30° to 700 °C at a constant  
157 rate of 10 °C min<sup>-1</sup>, under nitrogen atmosphere at a flow rate of 50 ml/min. The onset  
158 degradation temperature was calculated as the temperature at 5% wt. loss (T<sub>5%</sub>) from the  
159 TGA curve, while the maximum degradation temperature was calculated from the DTG  
160 curve.

161 The determination of the kinetic parameters to estimate the lifetime and the  
162 degree of degradation of the prepared thermoplastics were obtained using the Coats-  
163 Redfern<sup>[26]</sup> and the Horowitz-Metzger<sup>[27]</sup> methods. The Coats-Redfern method was used  
164 for the determination of the pre-exponential factor (A) and the apparent activation

165 energy ( $E_a$ , kJ mol<sup>-1</sup>) by means of the general equation of the reaction kinetics (Equation  
166 1):

167

$$\ln \frac{\alpha}{T^2} = \ln \left( \frac{A R}{\beta E_a} \right) \left[ 1 - \left( \frac{2 R T}{E_a} \right) \right] - \frac{E_a}{R T} \quad \text{Eq. 1}$$

169

170 where,  $A$  is a pre-exponential term,  $T$  is temperature,  $\beta$  the heating rate and  $\alpha$  is given by  
171 the relation  $\alpha = (W_0 - W_t)/(W_0 - W_f)$  where,  $W_0$  is the initial weight of the sample,  $W_t$   
172 corresponds to the residual weight of the sample at the measured temperature and  $W_f$  the  
173 final weight of the sample. However, Coats-Redfern method tend to produce highly  
174 uncertain values of  $E_a$  and  $A$ , since it uses single  $\alpha - T$  data for the determination of the  
175 kinetic parameters.<sup>[28]</sup> Thus, the activation energy of all formulations was also  
176 calculated by the Horowitz-Metzger model, which s showed in Equation 2:

177

$$\ln \left[ \ln \left( \frac{1}{1-\alpha} \right) \right] = \frac{E_a \theta}{R T_s^2} \quad \text{Eq. 2}$$

179

180 where:  $\theta$  is the difference between temperatures,  $T_s$  is the actual temperature,  $E_a$  the  
181 apparent activation energy (kJ mol<sup>-1</sup>),  $R$  the gas constant (8.3143 J K<sup>-1</sup> mol<sup>-1</sup>) and  $\alpha$  is  
182 the extent of reaction.

183

#### 184 **2.3.4. Infrared Spectroscopy Analysis (FT-IR)**

185 Fourier transform infrared spectroscopy (FT-IR) was used to follow the  
186 structural changes of the polymeric matrix due to induced thermal degradation after the  
187 exposition to high temperature of 400 °C. FT-IR analysis was performed using an  
188 infrared spectrometer Nicolet 6700 (Thermo Scientific). Each measurement was  
189 performed between 4000 and 600 cm<sup>-1</sup> with a resolution of 2 cm<sup>-1</sup> in the reflection

190 mode. PP molecular degradation was estimated by carbonyl index (CI), which was  
191 calculated by the following equation:

192

$$CI = \frac{A_C}{A_R} \quad \text{Eq. 3}$$

194

195 where  $A_C$  is the area of the carbonyl absorption band (1850–1650  $\text{cm}^{-1}$ ) and  $A_R$  is the  
196 area of the band at  $841\text{cm}^{-1}$ , corresponding to C-C in neat PP sample.<sup>[7]</sup>

197

### 198 **2.3.5. Water contact angle**

199 The water contact angles of PP based films were determined by an Easydrop  
200 model FM140 (Krüss GmbH), standard contact angle measurement system. The  
201 obtained water contact angles were measured by placing a drop onto each sample that is  
202 illuminated from one side while a camera at the opposite side records an image of the  
203 drop. The captured image is analyzed by DSA1 software that permits time-proven tools  
204 for analyzing the drop image to calculate the water contact angle for each analyzed  
205 sample.

206

### 207 **2.3.6. Mechanical properties**

#### 208 **2.3.6.1. Nanoindentation**

209 In order to study the influence of the additives in the resultant mechanical  
210 features of the melt-extruded films, a G-200 nanoindenter of Agilent Nanotech (Santa  
211 Clara, California) was used to obtain the elastic modulus (E) and hardness (H) of the  
212 additive samples. The area function of the Berkovich tip was previously calibrated using  
213 a pyrex block as a reference material, resulting in a tip radii of 10 nm. A matrix of 25  
214 indentations at 1000 nm depth was performed on each sample. The indentation strain

215 rate was  $0.05 \text{ l s}^{-1}$  and depth correction of the surface contact was calculated by the  
216 Loubet method.<sup>[29, 30]</sup>

217

### 218 **2.3.3.2. Atomic Force Microscopy**

219 Furthermore, the very superficially elastic modulus of the surface of several samples  
220 was analyzed by atomic force microscope (Veeco Nanoscope) working at peak-force  
221 mode. By forcing the tip at a maximum constant 5 nm depth the force curves were  
222 recorded and subsequently fitted by the DMT model,<sup>[31, 32]</sup> it obtaining elastic maps of  
223 the analyzed square  $10 \times 10 \text{ }\mu\text{m}$  areas.

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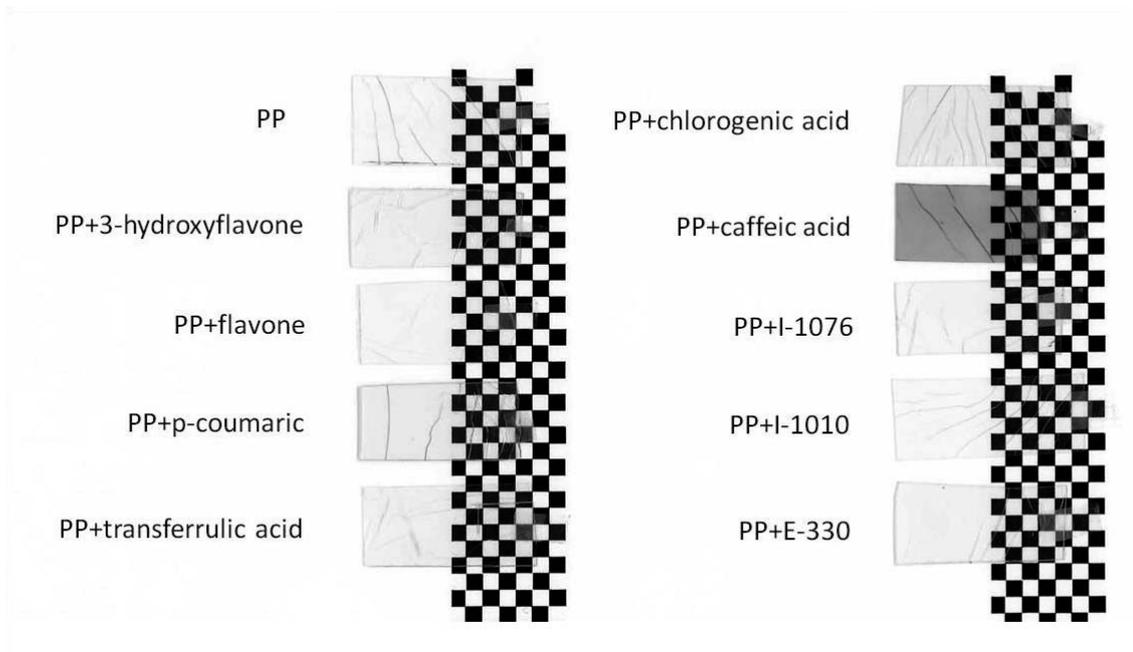
## 225 **3. Results**

226

### 227 **3.1. Optical and Colorimetric results**

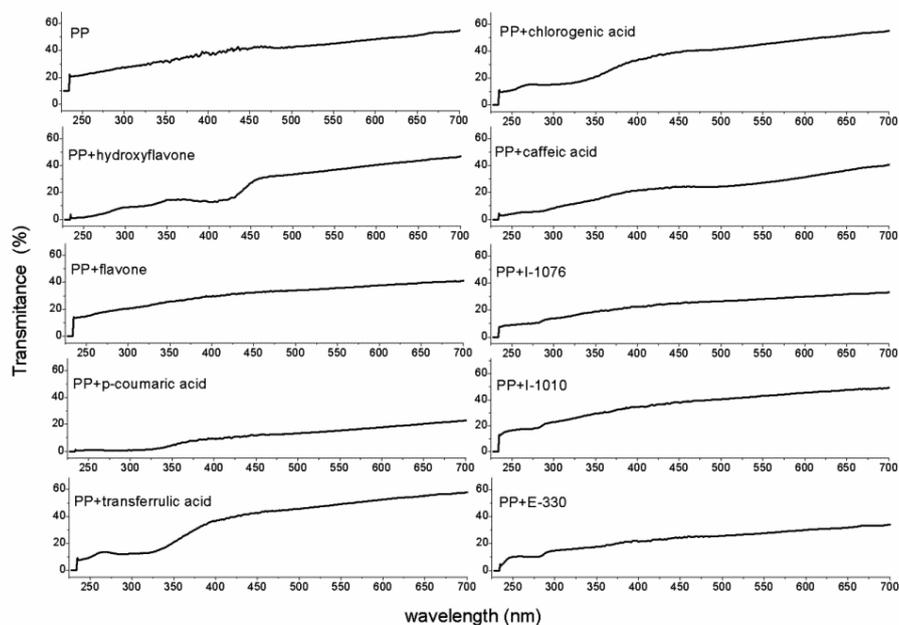
228 **Fig. 2** shows the visual appearance of the obtained films where is possible to  
229 observe that some antioxidant agents provided somewhat colour to the polymeric PP  
230 matrix. Nevertheless, all PP films allowed seeing through the film. The transparency is  
231 interesting since it is required in several applications, such as the case of food packaging  
232 in which it represents one of the most important requirements for consumer acceptance.

233 [33, 34]



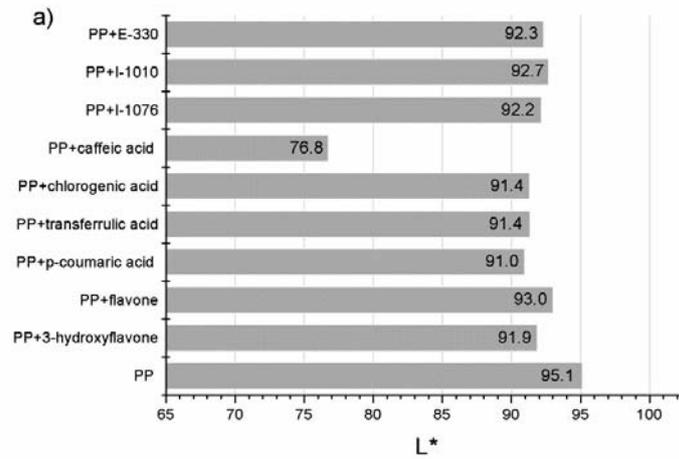
**Fig. 2.** Visual appearance of PP based films.

These findings were corroborated by means of UV-vis measurements (**Fig. 3**). As expected, all PP based blends showed high transmission in the visible region of the spectra (400–700 nm). Recently, Nanni et al. (2019) have developed PP based materials blended with wine seeds derived additives that absorb in the whole UV and visible region. The main drawbacks were changes of color and opacity in PP matrix.<sup>[20]</sup> In our work, some antioxidants, mainly caffeic and chlorogenic acids, p-coumaric, as well as 3-hydroxyflavone although showed PP colour changes they also provide a positive blocking effect on the UV-B region (280–315 nm) of the spectra, the most energetic component of natural UV light.<sup>[35]</sup> In this sense, it is known that the UV-B light causes the most photochemical degradation of plastics and, thus, the reduction on the UV-B transmission results advantageous for the industrial application of these films to prevent undesired photo-oxidation reactions for instance in packed food or in crops in agricultural applications.<sup>[36]</sup>

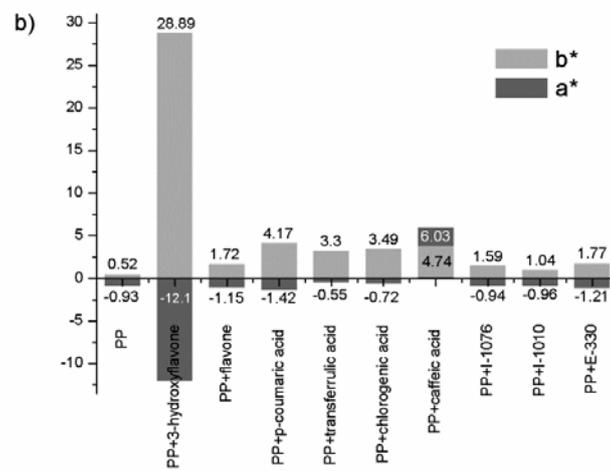


**Fig. 3.** UV-VIS spectra of all PP-antioxidant based films

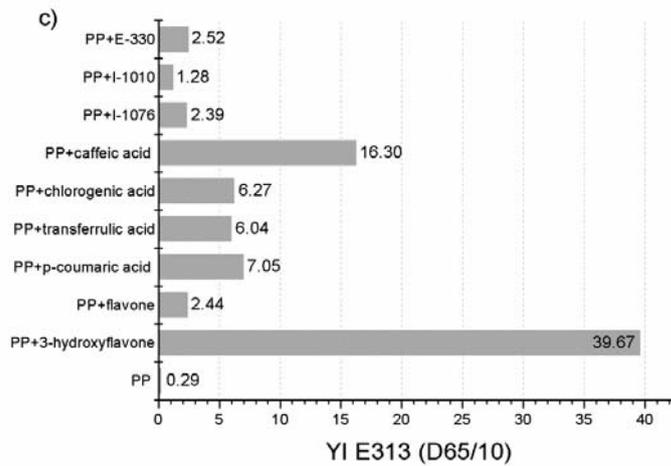
Colour properties of PP films were also measured (**Fig. 4**). As expected neat PP film showed the highest lightness value (**Fig. 4-a**), while films added with caffeic acid showed the lowest one in good agreement with the visual appearance and transparency tendency. In general, films showed small negative values of  $a^*$  coordinate similarly to neat PP suggesting a small trend towards green (**Fig. 4-b**). However, hydroxyflavone showed significant increase of  $a^*$  coordinate with a trend towards green accompanied with a significant tendency towards yellow, revealed by the increase of the  $b^*$  coordinate (**Fig. 4-b**) and yellowness index (**Fig. 4-c**), as it was observed in the visual appearance of the films. On the other side, caffeic acid was the only antioxidant that produced a significant trend towards red (positive  $a^*$  values, **Fig. 4-b**) accompanied with a significant tendency towards yellow (positive  $b^*$  values **Fig. 4-b** and YI values of 16.3 **Fig. 4-c**).



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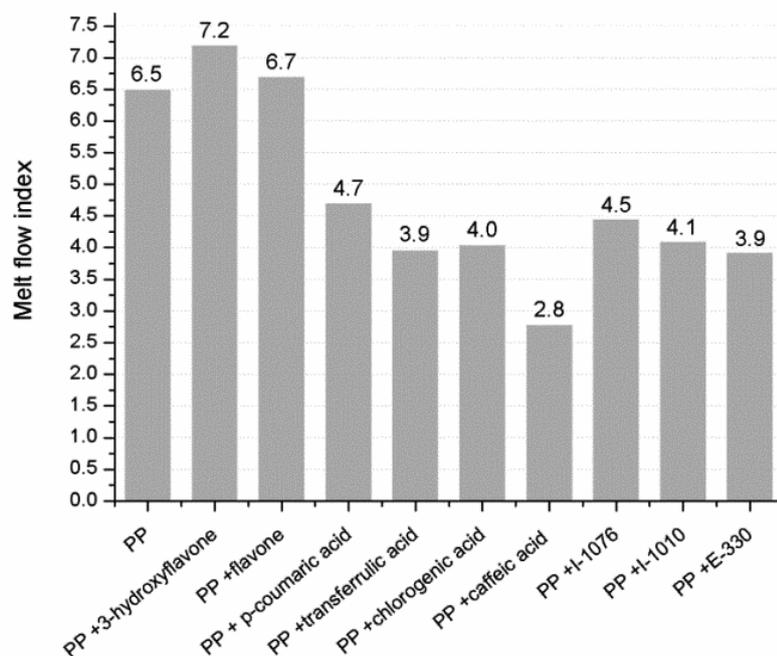
**Fig. 4.** Colourimetric parameters of PP based films from the CIELab space: **a)**

269

Lightness (*L*) values, **b)** *a*\* and *b*\* coordinates and **c)** yellowness index (YI).

### 270 3.2. Thermal properties

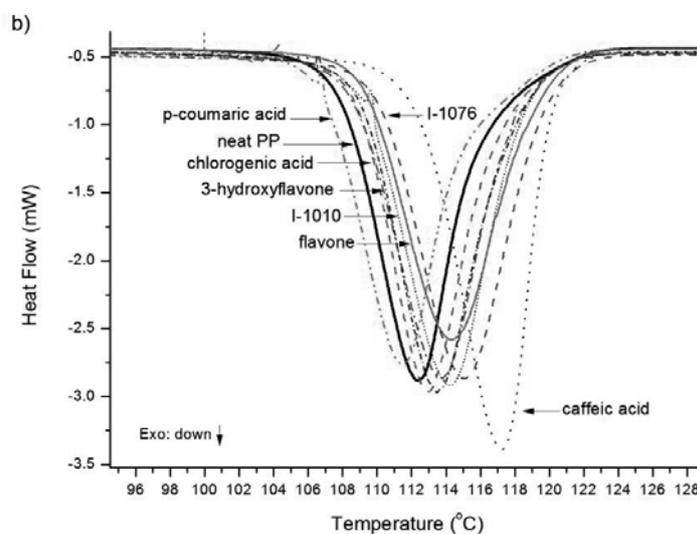
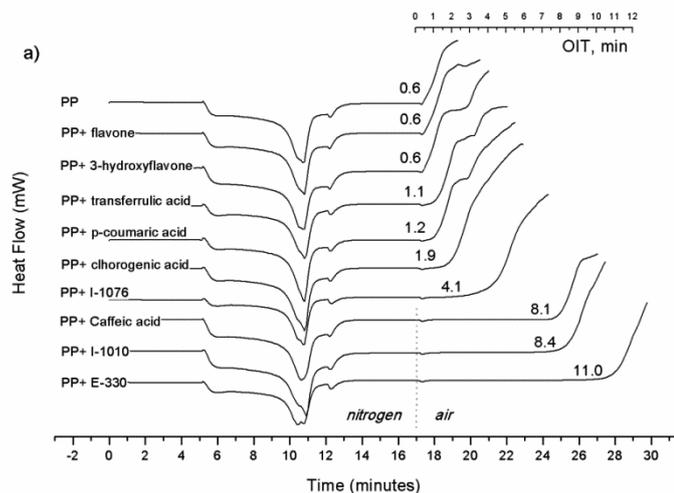
1 271 The evaluation of thermal properties is very important not only from a  
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4 272 processing point of view, but also because of the changes on thermal properties can also  
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6 273 affect the recycling performance of polymers after their useful life.<sup>[1, 5]</sup> One important  
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8 274 effect is the possible alteration of the melt flow index (MFI) of the polymeric  
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11 275 formulations, since this property is very important for melt processing.<sup>[1]</sup> The result of  
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13 276 MFI are shown in **Fig. 5** and it could be observed that in general the MFI decreases with  
14  
15 277 the addition of antioxidant showing their positive effect on the stabilization of PP  
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18 278 matrix, with the exception of flavonones that mainly maintain the MFI or even  
19  
20 279 increased it. The non-stabilized polypropylene shows a melt flow index of 6.5, with not  
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22  
23 280 any protection. PP blended with typical antioxidants used at industrial level (Ethanox  
24  
25 281 330, Irganox 1010 and Irganox 1076) have MFI values ranging from 3.92 to 4.45,  
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27  
28 282 which are close to those values achieved by trans-ferrulic acid and chlorogenic acid  
29  
30 283 whose range is between 3.96 to 4.04, showing the potential of those antioxidants to  
31  
32  
33 284 replace the typical used at industrial level. PP with p-coumaric acid has a similar MFI  
34  
35 285 than that of PP containing Irganox 1076, but higher than the Ethanox 330 and Irganox  
36  
37 286 1010. Meanwhile, caffeic acid, whose MFI was 2.78, was the antioxidant with the  
38  
39  
40 287 higher potential to reduce the PP MFI.



**Fig. 5.** values of melt flow index (MFI) for each tested sample

In order to get information about the ability of the NA to protect PP from thermo-oxidative process, isothermal DSC test were conducted at the processing temperature of 200 °C (**Fig. 6-a** and **6-b**). The isothermal DSC curves evidence that degradation is delayed by typical commercial additives, but also by most of natural antioxidants. In fact, the longer the OIT, the more stable the PP based blend. Furthermore, the induced oxidation time is notably different for each composition. The calculated oxidation times for each PP based film are shown on **Fig. 6-a**. Results, evidence that the OIT value of neat PP was 0.6 min. Similar values were found for PP samples with 3-hydroxyflavone and flavone additives (0.6 min), indicating that flavonones are not able to protect PP matrix against thermal degradation. This unexpected results can be related with the fact that flavonones mainly interact with polymeric matrices by hydrogen bonding interactions between hydroxyl groups and carbonyl groups of the polymeric matrices,<sup>[16]</sup> which are not present in PP. In this sense, López de Dicastillo et al. blended maleic anhydride modified poly(propylene) (MAPP)

305 with flavonoids and found the formation of intermolecular hydrogen bonds due to the  
306 maleic anhydride modification on polypropylene which allowed hydrogen bonding  
307 interactions between hydroxyl groups of catechin and carbonyl groups of MAPP.<sup>[37]</sup>  
308 Slightly higher OIT values were found when the PP was blended with p-coumaric,  
309 trans-ferrulic and chlorogenic acids, resulting in 1.1 min, 1.2 min and 1.9 min,  
310 respectively. The higher antioxidant protection provided by these antioxidants could be  
311 related with their longer aliphatic chains which allowed higher molecular mobility and  
312 thus facilitating their interaction with PP polymeric matrix. Nevertheless, the great  
313 difference was notably marked when the commercial and NA caffeic acid were added.  
314 Cerruti et al. stabilized PP with natural antioxidants extracted from tomato, white and  
315 red grapes wastes, while they also studied PP stabilized with Irganox 1010 as synthetic  
316 antioxidant for comparison. However, the synthetic antioxidant imparted far better  
317 stabilization to PP at 180 °C. In the present work, among the NA tested caffeic acid  
318 revealed the highest OIT value (8.1 min) achieving better results than commercial I-  
319 1076 antioxidant (4.1 min) and close to the I-1010 (8.4 min.). Caffeic acid presents a  
320 very similar molecular structure with p-coumaric and trans-ferrulic acid, but it has one  
321 more hydroxyl group (**Fig. 1**), and this is why it provides higher antioxidant protection  
322 during thermal processing. In fact, polyphenols are able to work as radical scavengers  
323 antioxidant for PP (R•), or alkoxy (RO•) or peroxy (ROO•) free radical by hydrogen  
324 donation and resonance stabilization, to form a PP (RH), alcohol (ROH) or  
325 hydroperoxide (ROOH) product, interrupting the degradative radical reaction of the  
326 polymer chains.<sup>[20]</sup> But it should be mentioned that, all the obtained OIT values for PP-  
327 NA blends were significant lower than those of PP + E330 (11.0 min).

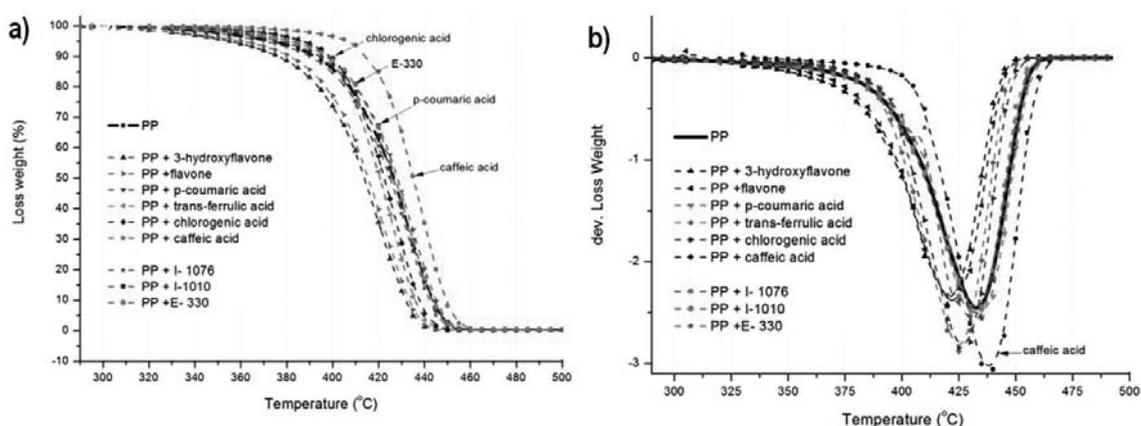


**Fig. 6. a)** Isothermal DSC curves at 200°C of the PP based films, and heat flow against temperature **b)** dynamic DSC first heating scan of PP based films.

The mechanism involved in the PP protection against thermo-oxidative degradation provided by antioxidant agents depends on the configuration and the total number of hydroxyl groups. As it was already commented the caffeic acid structure shows more active -OH groups in the phenolic rings than other tested NA. Further the conjugation of the double C=C bonds and the carboxylic groups are also involved, on the substituent groups. Free radical scavenging capacity is primarily attributed to the high reactivity of hydroxyl substituents that participate in the reactions.<sup>[38]</sup>

340 The influence of antioxidants on the melting temperature of PP (**Fig. 6-b**) was  
 341 also studied. No significant changes on the melting temperature of PP were observed  
 342 whit the exception of caffeic acid which was the only antioxidant with the ability to  
 343 significant increase the melting temperature of PP, confirming its ability to stabilize PP  
 344 matrix. Moreover, it should be highlighted that the melting process of PP-caffeic acid  
 345 blend takes place over a narrow temperature range, which ends at the same temperature  
 346 of all blends studied here, including typical synthetic ones used in the industrial sector  
 347 (I-1076, I-1010 and E330). Thus, the stabilization effect provided by caffeic acid does  
 348 not requires an increase of the processing temperature which is extremely important for  
 349 the industrial sector.

350 The thermogravimetric analysis was performed under nitrogen atmosphere. **Fig.**  
 351 **7-a** and **Fig. 7-b** show the TGA thermograms and the corresponding DTG curves, while  
 352 **Table 1** summarizes the TGA thermal parameters obtained from those curves.



353  
 354 **Fig. 7** a) TGA and b) DTG curves of the PP based films

355  
 356 **Table 1.** Onset degradation temperatures ( $T_{5\%}$ ) and the maximum degradation  
 357 temperatures ( $T_{max}$ ) of PP based films.

Sample	$T_{5\%}$	$T_{max}$	% lost at 350°C	% lost at 400°C
--------	-----------	-----------	-----------------	-----------------

PP	373	460	2.5	14.0
PP + 3-hydroxyflavone	355	450	1.6	11.2
PP + flavone	361	450	2.0	13.0
PP + p-coumaric	382	460	2.7	15.4
PP + transferrulic	388	450	0.2	3.4
PP + Chlorogenic	386	454	0.9	11.9
PP + caffeic acid	406	465	1.7	11.0
PP + I-1076	370	460	1.1	10.6
PP + I-1010	377	460	4.3	26.3
PP + E330	382	460	3.6	22.9

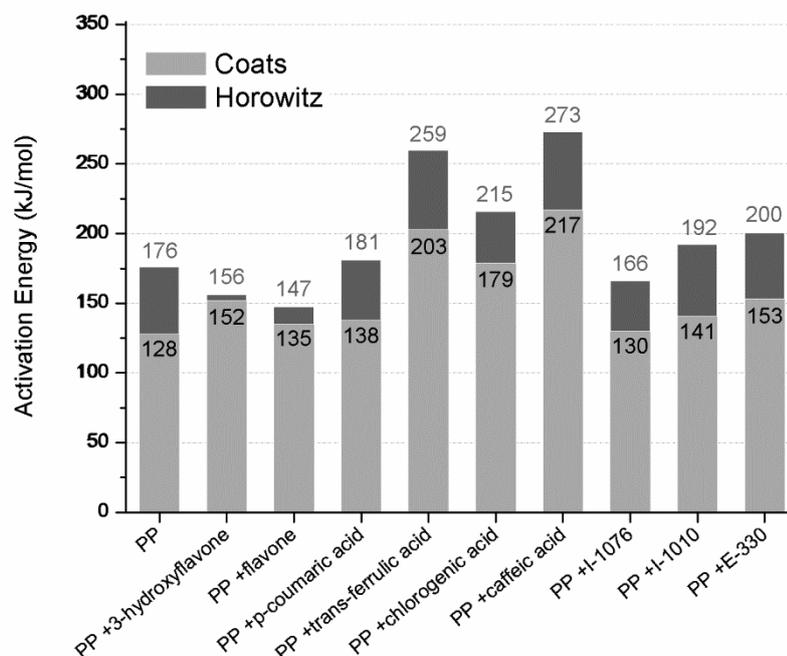
358

359 While flavonones shifted the onset degradation temperature of PP to lower  
360 values, chlorogenic, transferrulic and caffeic acids significant shifted the onset  
361 degradation temperature to higher values. In fact, caffeic acid was able to increase  
362 around 30 °C the onset degradation temperature of PP, confirming ones again its good  
363 ability to stabilize PP matrix. Flavonones, were not able to act with the free radicals  
364 formed during thermo-oxidation, and thus they were not able to block further polymer  
365 degradation, as it was observed in MFI and OIT results. Then, two temperature ranges  
366 were taken into consideration for further TGA study, from 250 to 350 °C and from 250  
367 to 400 °C (**Table 1**). The PP loaded with caffeic acid resulted in a less weight loss,  
368 indicating a minor degradation effect than the studied antioxidants derived from  
369 petrochemical source. The transferrulic, chlorogenic and p-coumaric acids also  
370 demonstrated less weight loss in the 250-350 °C temperature range, but their behavior  
371 drop above the 350 °C, in agreement with OIT results. Nevertheless, while caffeic acid  
372 gives the greater antioxidant protection, the 3-hydroxyflavone and flavanone showed

373 the worst results, achieving a 26% of weight loss in the 250-400°C range versus the  
374 14% of the non-stabilized PP. These results evidence again that flavonones were not  
375 able to act as natural stabilizer agents for PP matrix.

376 The study of the kinetic parameters by TGA for the estimation of the polymer  
377 stabilization is common in literature and it has been widely used for different polymeric  
378 materials and experimental conditions.<sup>[23, 27, 39-41]</sup> Among all kinetic parameters  
379 calculated from the Arrhenius equation, apparent activation energy ( $E_a$ ) is the most  
380 indicative one for comparison among materials in terms of their thermal stability. In this  
381 case the Horowitz and Coats method have been used because they provide simple  
382 approaches to obtain information about the thermal and thermo-oxidative degradation of  
383 non-stabilized and stabilized-PP.<sup>[39, 40]</sup>  $E_a$  of each film was calculated by using the  
384 Equation 1 and 2, and the results are summarized in **Fig. 8**. Although slight differences  
385 on the  $E_a$  results were observed depending on the model used, the tendency among  
386 values was maintained. These results, corroborate that PP added with caffeic,  
387 chlorogenic and trans-ferrulic acids were those that showed the highest values of  
388 activation energy, indeed exceeded the values of the others studied phenolic  
389 antioxidants. These findings clearly prove the protective effect of caffeic acid,  
390 chlorogenic acid and trans-ferrulic acids on PP matrix against thermal degradation.  
391 Meanwhile, PP added with p-coumaric acid, flavanone and 3-hydroxyflavone show  
392 lower  $E_a$  values than typical industrial synthetic antioxidants (I-1076, I-1010 and E330)

393

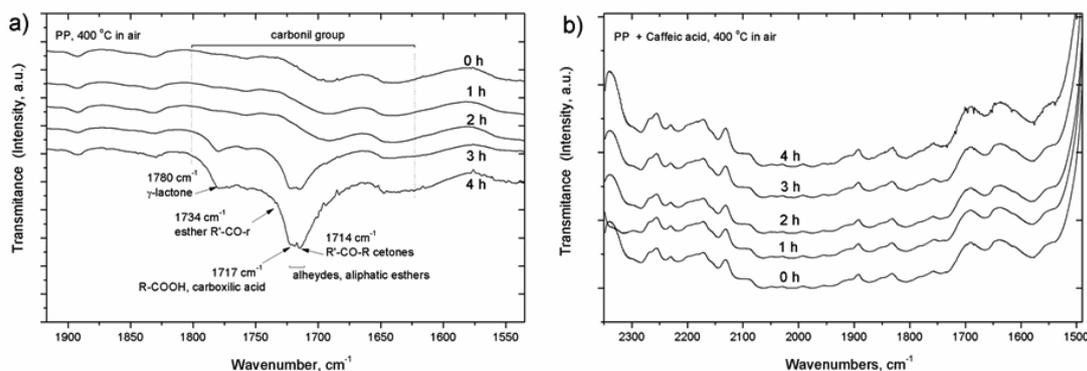


**Fig. 8.**  $E_a$  values of PP based films calculated by Coats and Horowitz models.

### 3.3. FT-IR characterization

PP is known for generating numerous low molecular oxidized compounds under oxidizing conditions.<sup>[42]</sup> Thus, in order to study the structural changes of PP based film samples produced by thermal degradation, the films were exposed at 400 °C in the presence of oxygen to induce thermal degradation of the polymeric matrix, since it is a considerable higher temperature than that used for PP processing. During PP degradation either by the action of UV-radiation nor by the action of oxygen, the main product is the formation of the tertiary hydroperoxide.<sup>[6, 20, 43]</sup> Then, the oxidation of the various products which are formed continues up to the production of carboxylic acids, esters, peresters, lactones and other oxidized species.<sup>[20, 43]</sup> Therefore, the degree of oxidation is characterized by an increase of carbonyl band accompanied with a decrease of average molecular weights.<sup>[42]</sup> Thus, the structural changes of PP based films after 1, 2, 3, and 4 h of exposition at 400 °C in air atmosphere were followed by FT-IR. **Fig. 9** displays the obtained FT-IR spectra at different heated lapsed times of the neat PP in the

411 region that corresponds to the carbonyl band (1800-1650  $\text{cm}^{-1}$ ). The non-stabilized PP  
 412 samples revealed a broad carbonyl band after 3 h at 400°C (**Fig. 9-a**) evidencing the  
 413 thermal degradation of PP at this lapsed time. The PP thermal degradation produce  
 414 secondary products characterized by cetones ( $\text{R}'\text{-CO-R}$ ) visualized as a band centered at  
 415 1714  $\text{cm}^{-1}$  and a band corresponding to carboxylic acid ( $\text{R-COOH}$ ) at 1717 $\text{cm}^{-1}$ .  
 416 Furthermore, at higher times at 400 °C it could be observed the appearance of a band at  
 417 1734  $\text{cm}^{-1}$  corresponding to esters ( $\text{R}'\text{-CO-O-R}$ ) and/or aldehydes ( $\text{R-CO-H}$ ) groups.  
 418 Thus, the molecular degradation of PP caused by the thermal degradation produced by  
 419 the exposition at high temperature under oxidative conditions was estimated from the  
 420 carbonyl index (CI).<sup>[7]</sup> The obtained CI for all PP based composition is summarized in  
 421 **Table 2**. The carbonyl index (CI) is useful tool for the indirect determination of the  
 422 embrittlement time in polymers, which has been considered as the time to achieve a  
 423 carbonyl index of 0.06.<sup>[44]</sup>



424  
 425 **Fig. 9.** FT-IR spectrum **a)** of non-stabilized PP and **b)** stabilized PP with caffeic acid  
 426 exposed during 0, 1, 2, 3 and 4 hour at 400 °C and air conditions.

428 Meanwhile, **Fig. 9-b** shows the infrared spectrum of the PP stabilized with  
 429 0.1wt% caffeic acid as an example. For this sample the carbonyl band was constant at  
 430 the same experimental conditions of neat PP, corroborating the good antioxidant

431 protection provided by caffeic acid at 0.1%wt to PP polymeric matrix. In fact,  
432 PP+caffeic acid did not suffer thermal degradation until 4 h showing even better  
433 effectiveness than synthetic antioxidants I-1076, I-1010 and E330. While neat PP is  
434 notable thermo-degraded at 3 hours, the stabilized PP based samples with antioxidants  
435 practically maintain the structural stability. In this sense, it is known that antioxidants  
436 are added to protect the polymer matrices from thermo-oxidative degradation since they  
437 are able to act with the free radicals formed during thermo-oxidation blocking further  
438 polymer degradation.<sup>[14, 16]</sup> Although, flavone was not able to increase the thermal  
439 stability of PP matrix during processing (as it was observed by MFI, DSC and TGA  
440 analysis), PP+flavone film also showed good maintenance of the structure as revealed  
441 the CI. The antioxidant capacity of flavone was not able to protect the PP matrix from  
442 thermal degradation at the first stage, but when the degradation at higher temperatures is  
443 accelerated it seems that it is able to rather protect the decomposition reaction of PP.  
444 However, in order to know which is the optimum flavone amount to protect PP matrix,  
445 more formulations should be investigated. Finally, 3-hydroxyflavone showed a high  
446 value of CI after 4 hour of expositions at high temperature, although notably lower than  
447 neat PP and with somewhat retardant effect. The results showed here for flavonones is  
448 in good accordance with the slightly higher  $E_a$  observed for these films than that of neat  
449 PP film.

452 **Table 2.** Evolution of the carbonyl peak of the PP based film formulations after 0, 1, 2,  
 453 3 and 4h of exposition at 400 °C in the presence of oxygen.

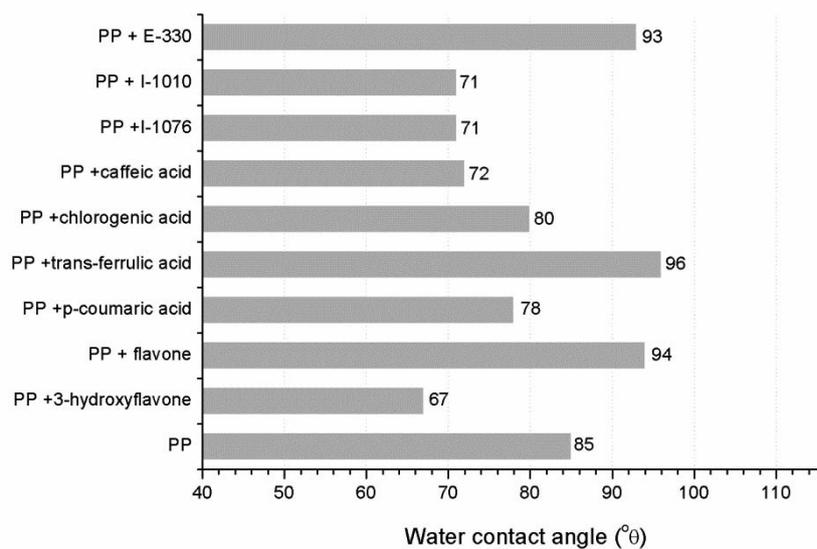
Carbonyl band area					
Sample	0 hour	1 hour	2 hours	3 hours	4 hours
Polypropylene (PP)	-	0.7	0.9	38.2	49.5
PP +3-hydroxyflavone	-	1.3	1.4	1.4	6.4
PP +flavone	-	-	0.1	0.2	0.3
PP +p-coumaric acid	-	-	0.1	0.2	0.3
PP +trans-ferrulic acid	-	0.4	0.5	0.5	0.6
PP +chlorogenic acid	-	-	0.1	0.1	0.1
PP +caffeic acid	-	-	-	-	0.3
PP +I-1076	-	0.4	0.4	0.4	0.4
PP +I-1010	-	-	-	0.2	0.6
PP +E-330	-	-	0.1	0.1	0.1

454

### 455 3.4. Water contact angle

456 Although the surface wettability is not a mass transfer phenomenon, it is  
 457 relevant in materials intended for several applications such as medicine and food  
 458 packaging as well as for agricultural mulch films, since it determines the material's  
 459 surface hydrophobicity/hydrophilicity.<sup>[45]</sup> Thus, water contact angle measurements were  
 460 conducted to study the surface hydrophobicity/hydrophilicity of PP films (**Fig. 10**). PP  
 461 is a well known hydrophobic material <sup>[46]</sup>. In the present work, surface hydrophobicity  
 462 of PP was in general reduced with the addition of antioxidants, particularly with 3-  
 463 hydroxiflavone, but still showing higher water contact angle values than 65°, that

464 implies a hydrophobic surface.<sup>[47]</sup> This is unexpected result since hydroxylflavones  
465 present low solubility in water. Nevertheless, the wetting performance of polymeric  
466 materials is not only governed by the chemical composition, but also by the topography  
467 of the surface.<sup>[45]</sup> In fact, the increased surface water affinity can be related with the  
468 thermal degradation of PP matrix during processing,<sup>[48]</sup> which leads to shorter polymer  
469 chains that can change the topographical surface of the film. An increase of the PP  
470 surface hydrophobicity was observed with the incorporation of ethanox-330, flavone as  
471 well as trans-ferrulic acid, in good agreement with the low solubility in water showed  
472 by these antioxidants.

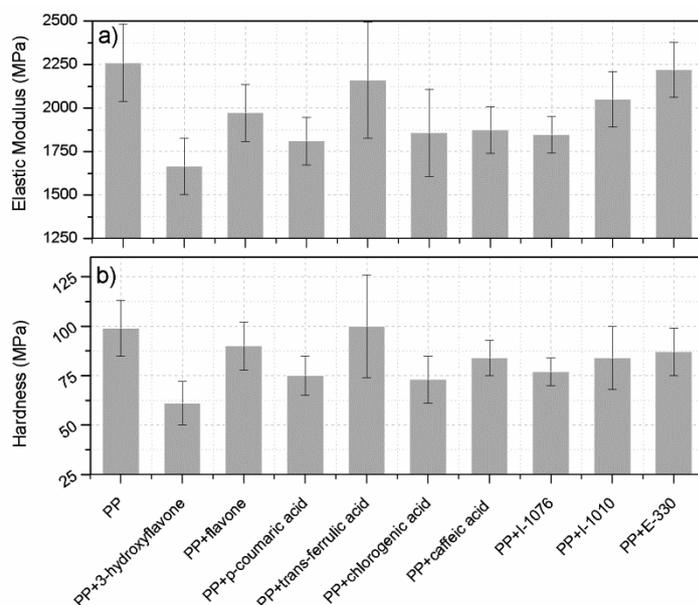


474  
475 **Fig. 10.** Water contact angle of PP based films.

### 477 **3.5. Mechanical characterization**

478 The mechanical performance of PP stabilized with antioxidants can vary due to  
479 the antioxidants presence. Thus, in order to evaluate the mechanical changes of the  
480 obtained materials the hardness and elastic modulus of the prepared formulations were  
481 obtained by nanoindentation. The **Fig. 11-a** shows the obtained E and H for each

482 analyzed formulation. Although the concentration of the antioxidant is very low  
1 483 (0.1%wt) the resultant mechanical properties are visible different since the  
2  
3 484 incorporation of antioxidant decreased the E and H values producing a plasticizing  
4  
5 485 effect. The highest elastic modulus was obtained for the neat PP (E = 2.26 GPa) close to  
6  
7  
8 486 the value obtained on PP additivated with 0.1%wt E-330 (E = 2.22 GPa) and  
9  
10 487 transferrulic acid (E = 2.16 GPa). However, the antioxidant additivation dimisished this  
11  
12 488 value, it achieving the lowest moduli on PP added with 3-hydroxyflavone (E =1.67  
13  
14 489 GPa), probably due to the previously mentioned thermal degradation ocured in this film  
15  
16 490 that lead to the formation of shorter PP chains wich can also produce somewhat  
17  
18 491 plasticization effect. Caffeic acid (E =1.87 GPa) and p-coumaric acid (E =1.81 GPa)  
19  
20 492 also showed considerable lower values than neat PP, but similar to that observed for  
21  
22 493 traditionally used I-1076 (E = 1.85 GPa). The measurement of the indentation hardness  
23  
24 494 showed a similar tendency than that of the elastic modulus, showing in general a  
25  
26 495 diminution of the mechanical performace. The oberved dispersion in the H and E  
27  
28 496 values of some samples (i.e.: PP+transferrulic acid) can suggest an heterogoneous  
29  
30 497 distribution of the antioxidant additives into the PP matrix. The possible lack in  
31  
32 498 miscilibity between PP and the antioxidant additivies used here was subsequently  
33  
34 499 analyzed by AFM.  
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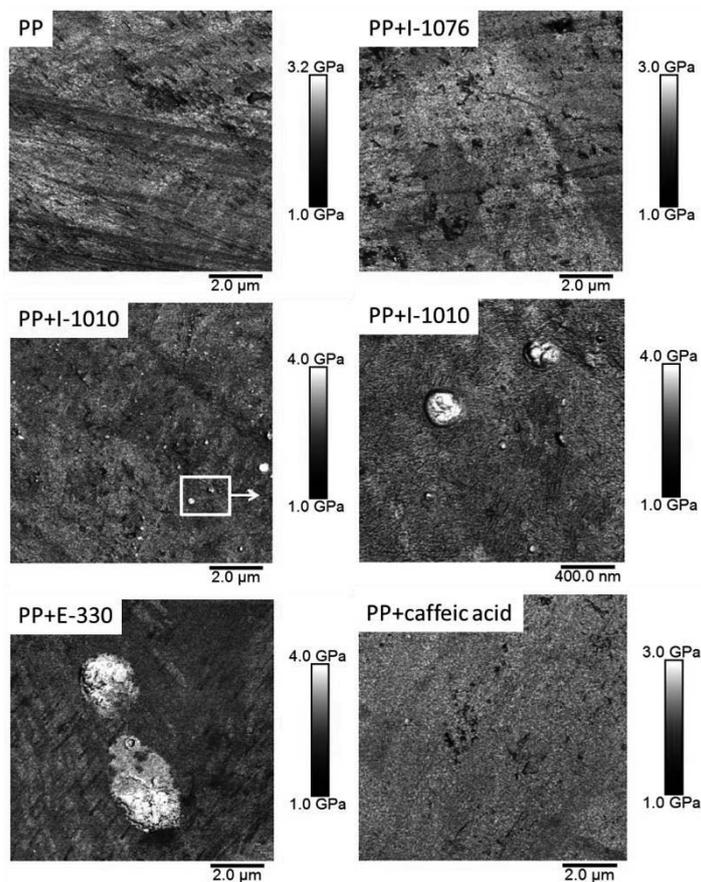


**Fig. 11.** Hardness and elastic modulus of the PP based films analyzed by nanoindentation.

The nanomechanical results indicate that the antioxidant additives studied here, in low concentration, act reducing the mechanical resistance of the PP polymeric matrix producing somewhat plasticizing effect. Some of them, as the caffeic acid and the 3-hydroxyflavone evidenced the greatest effect, but all the experimented formulations reveal this effect.

The elastic modulus was also analyzed by a Quantitative Nanomechanical Method using an AFM-QNM. This technique allows to perform a map of elastic modulus on the surface of samples by indenting very small volumes of material at very low depths 2~5 nm.<sup>[31]</sup> In this study, we propose and explore the possibility to use this technique to reveal a possible lack of miscibility between the PP matrix and the additives by studying the homogeneity of the properties reached. Due to the long time required to analyze enough sizes on these type of samples by this technique, the AFM-QNM was analyzed only in the formulation containing caffeic acid since it was the NA

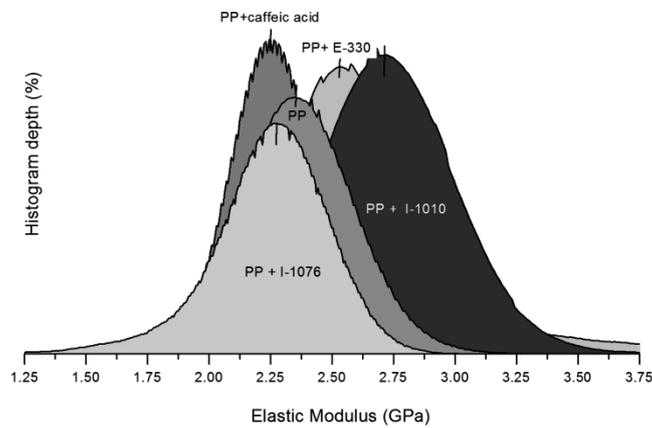
518 that gives better protection to PP matrix against thermal oxidation and it was compared  
519 with PP stabilized with commercial antioxidants (PP+E-3300, PP+I-1010 and PP+I-  
520 1076). The **Fig. 12** shows the elastic modulus maps of the analyzed samples.



522  
523 **Fig. 12.** Elastic Modulus maps acquired by AFM-QNM on PP based films that give  
524 better protection against thermal oxidation

525  
526 As it was expected neat PP resolved a map with homogeneous characteristics.  
527 Meanwhile, the maps of PP added with commercial antioxidants (I-1076, I-1010 y E-  
528 330) showed small particles. In the case of PP+I-1010 and PP+E-330 films those  
529 particles can be ascribed to the presence of small amount of antioxidant particles that  
530 were not totally miscible with PP matrix (brilliant regions in AFM images of PP+I-1010  
531 and PP+E-330, **Fig. 12**). Less rigid points can be observed in PP+I-1076 sample. In PP+

532 I-1010 and E-330 those points present higher elastic modulus. Therefore, PP+caffeic  
533 acid sample shows a map with homogeneous characteristics, suggesting that a higher  
534 miscibility is achieved in this sample.



536  
537 **Fig. 13.** Elastic modulus distribution extracted from **Fig. 12**

538  
539 The distribution of the elastic modulus values extracted from each represented  
540 AFM map is shown in **Fig. 13**. The nanometric scale of elastic modulus values shows  
541 that neat PP elastic modulus values are centered at 2.2 GPa, it agreeing with previously  
542 reported values for this material by instrumented indentation test.<sup>[49]</sup> However, in those  
543 samples where rigid immiscible particles have been revealed (PP+I-1010 and PP+E-330)  
544 the elastic modulus values were shifted to higher values due to the presence of those  
545 particles, 2.6 and 2.8 GPa, respectively. On the other side the elastic modulus of  
546 PP+caffeic acid sample was shifted to lower values. It should be mentioned that the  
547 reinforcing effect produced by immiscible particles could not be observed by  
548 nanoindentation technique in which the volume of the analyzed sample is higher and,  
549 thus, the rigid particle effect is masked by the less rigid matrix. Thus, it can be  
550 concluded that some additives such as caffeic acid present better miscibility with PP  
551 matrix than other commercial antioxidant additives at the concentration used here.

552 Moreover, it seems that AFM technique in AFM-QNM mode is an useful method to  
553 study the miscibility between polymeric matrices and antioxidant additives.

554

#### 555 **4. Conclusion**

556 Several natural antioxidants (NA) have been proposed and tested as antioxidant  
557 additives for PP protection from thermal degradation during processing at very low  
558 loadings (0.1%wt). The obtained PP based films were mainly transparent, while the  
559 addition of some NA such as caffeic acid produced somewhat amber tonality, but still  
560 showing transparency. Moreover, antioxidants showed somewhat blocking effect on the  
561 UV-B region wich result very interesting for outdoor applications. The PP based films  
562 were full characterized in terms of their thermal performance and it was observed that  
563 natural antioxidants were able to reduce the MFI of PP, with the exception of  
564 flavonones which were not able to protect PP from thermal degradation during  
565 processing. The addition of natural antioxidants did not change the thermal degradation  
566 behavior of PP, but greatly enhanced the thermo-oxidative stability. Caffeic acid  
567 showed the greater thermal stabilization effect as revealed DSC results. Furthermore,  
568 the positive effect of caffeic acid on the protection of PP matrix from the thermo-  
569 oxidative degradation processes shows that it offers greater protection than the typical  
570 used commercial I-1076. TGA results confirmed the effectiveness of caffeic acid as the  
571 best PP stabilizer, shifting the onset degradation temperature of PP 30°C to higher  
572 values. The improvement of the  $T_{5\%}$  values was followed by transferrulic acid,  
573 chlorogenic acid and p-coumaric (between 10 and 15°C), showing even higher values  
574 than that provided by traditional petroleum derived antioxidants (i.e.: I-1010 and E330,  
575 between 5 and 10°C). Caffeic acid and transferrulic acid showed the highest activation  
576 energy. Transferrulic showed the highest water resistant with the highest contact angle

577 values, comparable with that observed in PP+E330. Meanwhile, the rest of antioxidants  
578 reduced the WCA of PP film. The FTIR analysis reveals a strong absorption of the  
579 carbonyl band in neat PP due to the induced thermal degradation at 400 °C. The addition  
580 of antioxidants into the PP matrix effectively reduced its intensity, while in PP+caffeic  
581 acid the carbonyl band does not appear until 4 h at 400°C. Regarding the mechanical  
582 performance it was observed that trans ferrulic acid mainly maintain the E and H values,  
583 while caffeic acid and p-coumaric acid mainly reduced both values due to somewhat  
584 plasticizing effect. Moreover, AFM-QNM results showed that caffeic acid leads to  
585 samples with higher miscibility than those observed for commercial antioxidants  
586 typically used. It can be concluded that, among all the studied NA, caffeic acid can be  
587 successfully used to replace traditional synthetic antioxidants for PP protection during  
588 processing and service. Thus, PP blended with 0.1 wt% of caffeic acid result interesting  
589 for a wide variety of industrial applications such as packaging and outdoor applications.

590

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597

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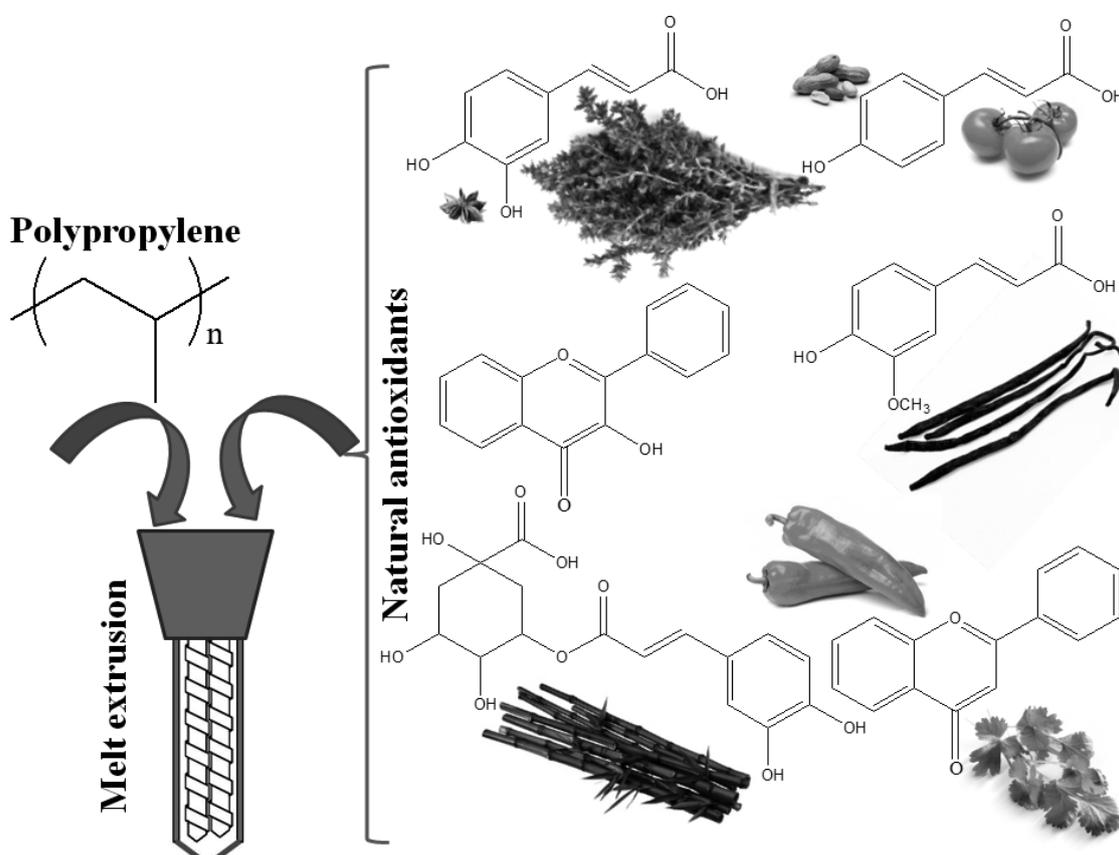
692 **Table of contents**

693 In order to replace traditional petroleum derived antioxidant additives frequently used in  
694 the plastic industry, six natural antioxidant were blended with polypropylene matrix to  
695 protect it against thermo-oxidative degradation during processing. Among all the  
696 antioxidant tested, caffeic acid was the most miscible antioxidant with PP matrix and  
697 provided the major thermal protection.

698

699 **Graphical Abstract**

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