

## The Potential of Flavonoids as Natural Antioxidants and UV Light Stabilizers for Polypropylene

M. D. Samper,<sup>1</sup> E. Fages,<sup>2</sup> O. Fenollar,<sup>1</sup> T. Boronat,<sup>1</sup> R. Balart<sup>1</sup>

<sup>1</sup>Instituto de Tecnología de Materiales (ITM), Universitat Politècnica de València (UPV), Alcoy 03801, Alicante, Spain

<sup>2</sup>Textile Research Institute (AITE), Alcoy 03801, Alicante, Spain

Correspondence to: M. D. Samper (E-mail: masammad@upvnet.upv.es)

**ABSTRACT:** This article presents a study on the stabilization of polypropylene against thermo-oxidation and UV radiation by using natural phenolic compounds derived from the structures of flavonoids: a flavone (chrysin), a flavanol (quercetin), two flavanone glycosides (hesperidin and naringin), and flavanoligand (silibinin). Thermal stabilization has been assessed in an oxidizing atmosphere by means of differential scanning calorimetry both in isothermal and in dynamic conditions. In addition, the effectiveness of these phenolic compounds as thermal stabilizers at high temperature has been quantified with the use of thermogravimetric analysis. Stabilization against UV radiation has been estimated by studying the morphology changes of the exposed surfaces by scanning electron microscope (SEM); also, surface chemical changes have been followed by infrared spectroscopy. Global results show that flavonoid compounds of type flavonols (quercetin and silibinin) provide the best results in stabilizing both against oxidation and against the action of UV radiation. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 1707–1716, 2013

**KEYWORDS:** ageing; crystallization; degradation; properties and characterization; glass transition

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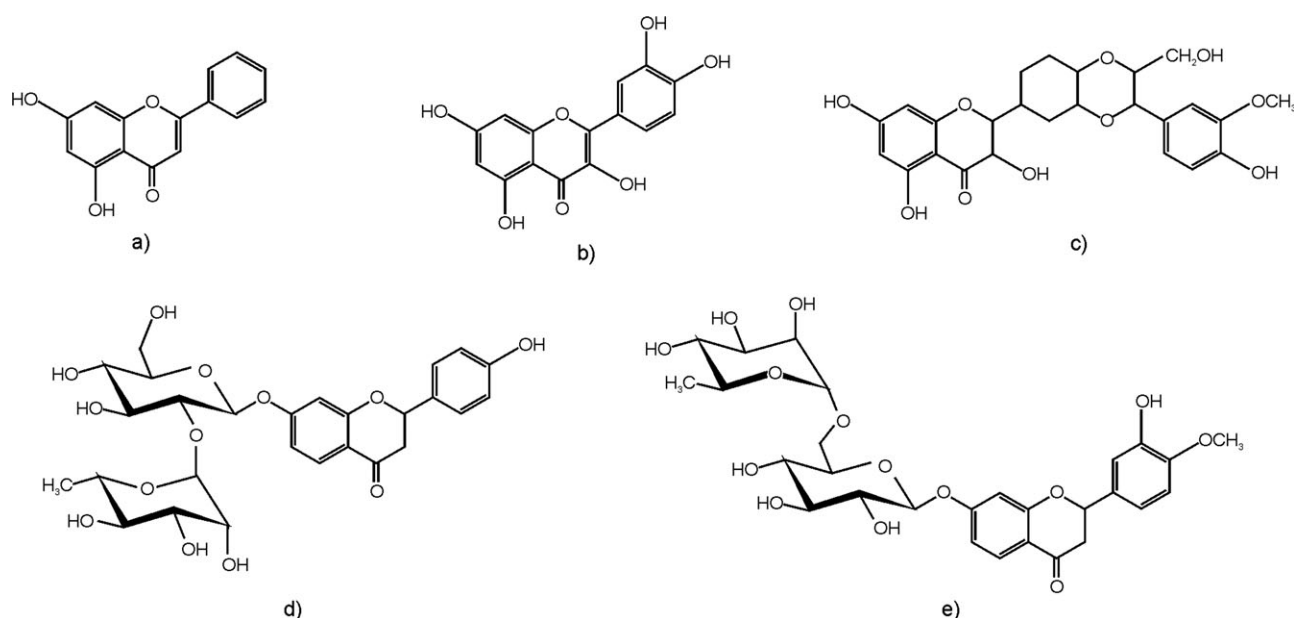
### INTRODUCTION

Polymers, in general and especially polyolefins, are highly sensitive to degradation processes when exposed to oxidant atmospheres and UV light. Hence, industrial formulations require the addition of antioxidants and light stabilizers to preserve their physical and mechanical properties for long periods. Polypropylene (PP) in particular may undergo degradation during processing at typical processing conditions (around 200°C) or because of its use in adverse conditions, that is in the presence of light, heat, or chemicals.

Antioxidants and UV stabilizers are used to inhibit the loss of physical properties and the subsequent increase in fragility. Because of environmental awareness and mainly to food safety considerations, the search for new additives in polymers has been stimulated in the last years.

The regulations of the European Union no. 10/2011 defines the use of additives in food packaging, because during the processing or storage of these materials, additives can migrate from the containers and packaging to the food, and for this reason many studies on the use of natural antioxidants to prevent the contact of food with synthetic antioxidants have been carried out in recent years; it is important to remark the excellent results obtained with  $\alpha$ -tocopherol at low concentrations (0.1–2%) for

the stabilization of polyolefins<sup>1–4</sup>; carnolic acid has also been used (0.125, 0.25, 0.50, and 0.75%) to delay the thermal oxidation of PP<sup>5</sup>; on the other hand, the use of small additions (1 wt %) of essential oils of oregano, savory, and cinnamon to alginate–polycaprolactone copolymer has given interesting stabilizing properties<sup>6</sup> as well as the use of essential oils of basil and thyme to provide higher stability to chitosan films has been reported.<sup>7</sup> Flavonoids represent a generic group of natural compounds with attracting potential in polymer stabilization owing to the presence of phenolic compounds in their structure. Their suitability for UV protection and antioxidation in plants is well known and this has led to the use of these compounds to prevent human aging. Phenolic compounds derived from flavonoids such as quercetin and catechin have been successfully used to delay oxidation on polyolefins<sup>1,8</sup> and ethylene-vinyl alcohol copolymers (EVOH).<sup>9</sup> Among the wide variety of flavonoids, flavonols and flavanols have been reported to be the most efficient antioxidant compounds. Quercetin is a flavonol found in red onion,<sup>10</sup> tea,<sup>8</sup> grapes,<sup>11</sup> and so on, and it has been successfully used as an antioxidant in low-density polyethylene,<sup>1</sup> increasing thermal stability with small additions of about 0.20 wt %. The potential of other flavonoids as antioxidant and/or UV stabilizers could be interesting to the polymer industry. For example, silibinin is a flavanoligand that can be obtained from



**Figure 1.** Chemical structures of the flavonoids used in this study, (a) chrysin, (b) quercetin, (c) silibinin A, (d) naringin, and (e) hesperidin.

the seeds of milk thistle<sup>12</sup>; chrysin is a flavone which is found in the *Passiflora caerulea*<sup>13</sup>; hesperidin is a flavanone glycoside found mainly in skin and in the white membrane of the citrus fruit<sup>14</sup>; and naringin is also a flavanone glycoside which is found in the grapefruit.<sup>15</sup> All these flavonoids could provide potential stabilization effects on polyolefins. Other phenolic compounds have been reported to provide attracting stabilizing effects on polyolefins. The use of 0.01 and 0.1 wt % of hydroxytyrosol to stabilize PP in processing has also been studied as typical processing conditions of PP (over 200°C) are enough to start oxidation and thus leading to yellowing and embrittlement.<sup>16</sup>

The use of natural antioxidants in polymers provides similar stabilizing properties to those of synthetic antioxidants (mainly phenolic types); in addition, they have low toxicity as many natural antioxidants are typical compounds used to protect human health. In this study, several flavonoids (quercetin, silibinin, chrysin, hesperidin, and naringin) were investigated as potential sources of antioxidants and UV light stabilizers for PP. Mixtures of PP with each one of the flavonoids were obtained by means of extrusion and their behavior under UV light radiation and thermo-oxidative behavior was analyzed. Differential scanning calorimetry (DSC) (both isothermal and dynamic) and thermogravimetric analysis (TGA) were used to characterize the antioxidant efficiency of each flavonoid. With regard to UV stabilizing effect, chemical changes were followed by infrared spectroscopy and surface changes (microcrack formation) were studied by scanning electron microscopy.

## EXPERIMENTAL

### Materials and Sample Preparation

The PP used in this study was a commercial grade Moplen HP648T of LyondellBasell (Basell Poliolefinas Ibérica, S.L., Barcelona, Spain) with a melt flow rate of 53 g/10 min (230°C/

2.16 kg) which is suitable for injection molding. Different flavonoids were used as stabilizer additives for PP: quercetin, silibinin, chrysin, hesperidin, and naringin and they all were supplied by Sigma-Aldrich (Sigma-Aldrich, Schnellendorf, Germany); the molecular structures of all of them are shown in Figure 1.

Initially samples were prepared with 0.5 wt % of the different types of flavonoids and subsequently, additional compositions with 0.25 and 0.75 wt % were prepared with flavonoids with best results in the initial characterization. We used small percentages of flavonoids according to the literature review.<sup>1,5,16</sup>

Sample preparation was carried out by mixing in a hot-extrusion process with a corotating twin-screw extruder supplied by Dupra (Dupra S.A., Castalla, Spain) at 190°C. Thermal characterization (DSC and TGA) was performed with the extruded pellet to evaluate the oxidative degradation. After that, sheets sizing 40 × 40 × 2 mm<sup>3</sup> were injection molded with a Babyplast 6/6 (Cronoplast SL, Abrera, Spain) at 190°C. We have selected this temperature profile because PP is characterized by a relatively narrow processing range between 180 and 200°C owing to its high sensitiveness to thermal degradation. Hence, the use of 190°C as processing temperature is enough to provide good processing conditions and does not produce thermal degradation during processing.

Finally, the aging treatment of materials was performed by using a high-pressure mercury lamp (1000 W and 350 nm wavelength), model UVASPOT 1000RF2 (Honle Spain SA, Barcelona, Spain). The exposure period was varied from 0 to 6 h.

### Thermal Characterization

The TGA was held in a thermobalance mod. TGA/E 851e by Mettler Toledo (Mettler-Toledo, Schwarzenbach, Switzerland). Samples with a total weight in the 5–10 mg range were placed into alumina crucibles and subjected to a temperature program used from 30 to 700°C at a heating rate of 10°C min<sup>-1</sup> in an

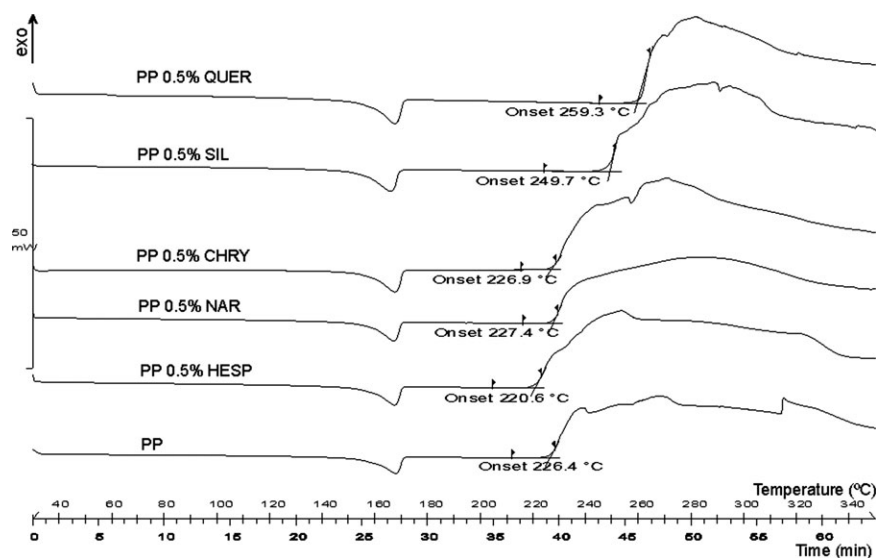


Figure 2. Dynamic DSC curves of PP formulations containing 0.5 wt % of different flavonoids.

oxygen atmosphere (flow rate, 50 mL min<sup>-1</sup>). The parameters analyzed were the  $T_{\text{onset}}$  and the inflection point of the material degradation. The  $T_{\text{onset}}$  was calculated as the intersection point between the tangents and the curve slope change, corresponding to the initial loss of mass. The inflection point is an interesting value to characterize a degradation process as it represents the temperature at which the maximum degradation rate occurs.

The calorimetric analysis was carried out using a DSC Mettler-Toledo cell 821 (Mettler-Toledo, Schwerzenbach, Switzerland). Samples with a total weight of about 5–10 mg were placed into aluminum crucibles. To evaluate the antioxidant efficiency of the different flavonoids on PP, two types of tests DSC were carried out. The first test was a dynamic program from 30 to 350°C at a heating rate of 5°C min<sup>-1</sup> in air atmosphere and the oxidative degradation was identified as the onset oxidation temperature (OOT). The second test was performed with a ramp from 30 to 210°C with a heating rate of 5°C min<sup>-1</sup> and after this isothermal conditions were maintained at this temperature (210°C) for 90 min, in air atmosphere. This test allowed obtaining the degradation onset by determining the oxidation induction time (OIT).

The degree of crystallinity of the samples was calculated using the following equation:

$$X_c(\% \text{ crystallinity}) = [\Delta H_f / w\Delta H_{f100}] \times 100 \quad (1)$$

where  $\Delta H_f$  is the latent heat of fusion of the sample,  $\Delta H_{f100}$  is the theoretical latent heat of fusion of a PP with 100% crystallinity (207.1 J/g),<sup>17</sup> and  $w$  is the weight fraction of PP in the sample.

DSC tests were also conducted to the UV-aged samples; the test was performed with a temperature ramp from 30 to 350°C at a heating rate of 5°C min<sup>-1</sup> in a nitrogen atmosphere (flow rate, 60 mL min<sup>-1</sup>) to avoid additional oxidations. In particular, changes in crystallinity were determined.

### Infrared Spectroscopy Analysis

Fourier transform infrared spectroscopy (FTIR) was performed on the aged samples using an infrared spectrometer Perkin-Elmer Spectrum BX (Perkin-Elmer Spain S.L., Madrid, Spain). 20 scans between 4000 and 600 cm<sup>-1</sup> were performed with a resolution of 2 cm<sup>-1</sup> in the reflection mode. PP molecular degradation was characterized by carbonyl index (CI),<sup>18</sup> which was calculated by eq. (2).

$$\text{Carbonyl index} = A_c/A_R \quad (2)$$

where  $A_c$  is the area of the carbonyl absorption band (1850–1650 cm<sup>-1</sup>) and  $A_R$  is the area of the reference band (2700–3000 cm<sup>-1</sup>). The reference band was not affected by UV irradiation.

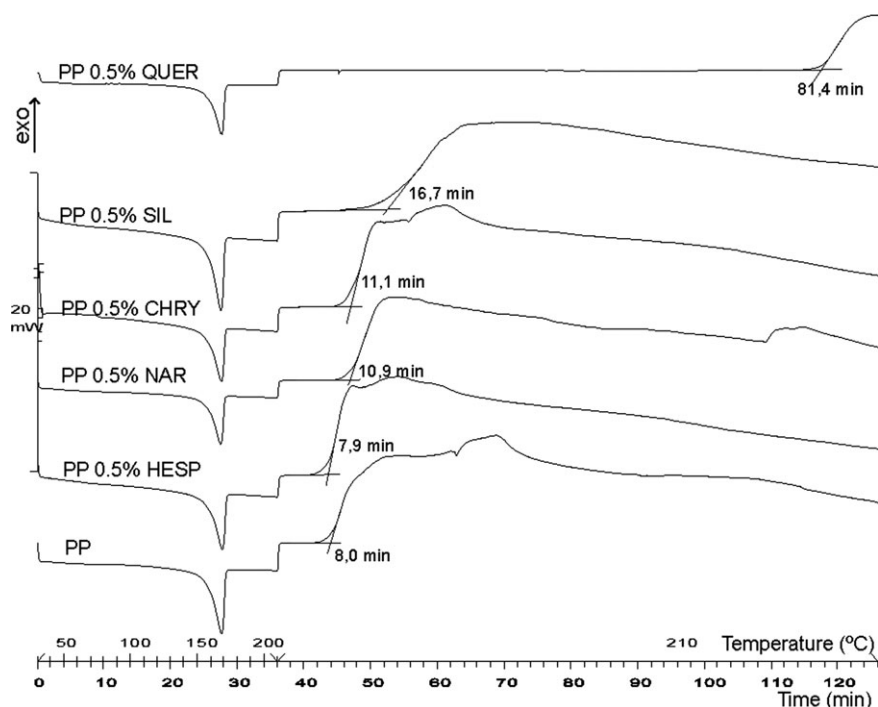
### Morphological Characterization

Surface characterization of the aged samples was performed using a scanning electron microscope (SEM), PhenomTM (FEI, Eindhoven, The Netherlands). Prior to sample observation, a sputtering process was carried out with a gold-palladium alloy with a Sputter Coater EMITECH mod. SC7620 (Quorum Technologies, East Sussex, United Kingdom).

## RESULTS AND DISCUSSION

### Characterization of the Oxidative Retardant Effect of Flavonoids

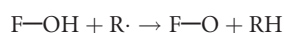
The oxidative retardant effect of flavonoids was evaluated using thermal analysis; Figure 2 shows the dynamic calorimetric curves of samples with a 0.5 wt % of different flavonoids. It can be seen that an endothermic melting peak of PP located about 170°C. Over this, we can see an exothermic process which is directly related to thermo-oxidative degradation. In the case of the nonstabilized PP, thermo-oxidation starts at 226.4°C, and the oxidative degradation of samples with 0.5 wt % of hesperidin, naringin, and chrysin occurs at a similar temperature. This indicates that these flavonoids have no significant oxidative



**Figure 3.** Isothermal (210°C) DSC curves of PP formulations containing 0.5 wt.% of different flavonoids.

retardant effect on PP at this concentration. On the other hand, sample containing 0.5 wt % silibinin delays the start of oxidative degradation about 25°C if compared to the nonstabilized PP so that degradation starts at around 251.1°C. With regard to the use of quercetin, it is important to remark its extraordinary stabilization effect; the OOT is remarkably increased up to the values of about 259.3°C, which represents a shift of 33°C. Therefore, silibinin and quercetin cause an oxidative retardant on PP as both they delay the onset of the thermal oxidation. This is a consequence of their chemical structure: a flavonol (quercetin) and a flavonoligand (silibinin) whose antioxidant properties in plants have been widely reported.<sup>1,8</sup>

The isothermal calorimetric curves are shown in Figure 3 and it can be clearly detected that the OIT for the nonstabilized PP is about 8 min. The addition of 0.5 wt % of the different flavonoids leads to an increase in the OIT values; so that, the OIT values for the stabilized formulations are 7.9, 10.9, 11.1, 16.7, and 81.4 min for hesperidin, naringin, chrysin, silibinin, and quercetin, respectively. Once again, these results indicate that only silibinin and quercetin, to a greater extent, promote a remarkable increase in the stability of PP against degradation. This effect may be owing to the structure of these flavonoids (quercetin and silibinin) with more active OH groups in phenolic rings than other flavonoids selected (Figure 1). Consistent with most polyphenolic antioxidants, both the configuration and the total number of hydroxyl groups substantially influence several mechanisms of antioxidant activity. Free radical scavenging capacity is primarily attributed to the high reactivities of hydroxyl substituents that participate in the following reaction<sup>19</sup>:



In addition, the difference in the OIT between these two compounds may be related to the size of the molecule as quercetin molecule is smaller than silibinin and therefore quercetin molecule is characterized by higher chain mobility. As we have described before, phenolic compounds work as free radical scavengers. Hence, when a free radical is formed as a consequence of thermo-oxidation, phenolic compounds move toward this unstable point to block further degradation and thus producing a stabilization effect. In the case of hesperidin, the stabilization effect is almost negligible at this concentration and the use of naringin and chrysin slightly improves stability.

As it was noted that silibinin and, to a greater extent, quercetin delay the oxidative degradation of PP, additional formulations containing 0.25 and 0.75 wt % were prepared to evaluate the effect of the flavonoid content. Table I summarizes the main

**Table I.** Results of DSC Dynamic Characterization ( $T_{Onset}$ ) and Isothermal ( $t_{Onset}$ ) of PP Formulations with Quercetin and Silibinin at Different Percentages (0.25, 0.5, and 0.75 wt %)

Sample	$T_{Onset}$ (°C) OOT	$t_{Onset}$ (min) OIT
PP	226.4	8.0
PP 0.25% QUER	263.8	77.1
PP 0.5% QUER	259.8	81.4
PP 0.75% QUER	264.8	94.3
PP 0.25% SIL	238.3	16.9
PP 0.5% SIL	249.7	16.7
PP 0.75% SIL	245.8	84.0

**Table II.** Thermal Degradation Data Obtained by TGA of PP Formulations with Quercetin and Silibinin at Different Percentages (0.25, 0.5, and 0.75 wt %)

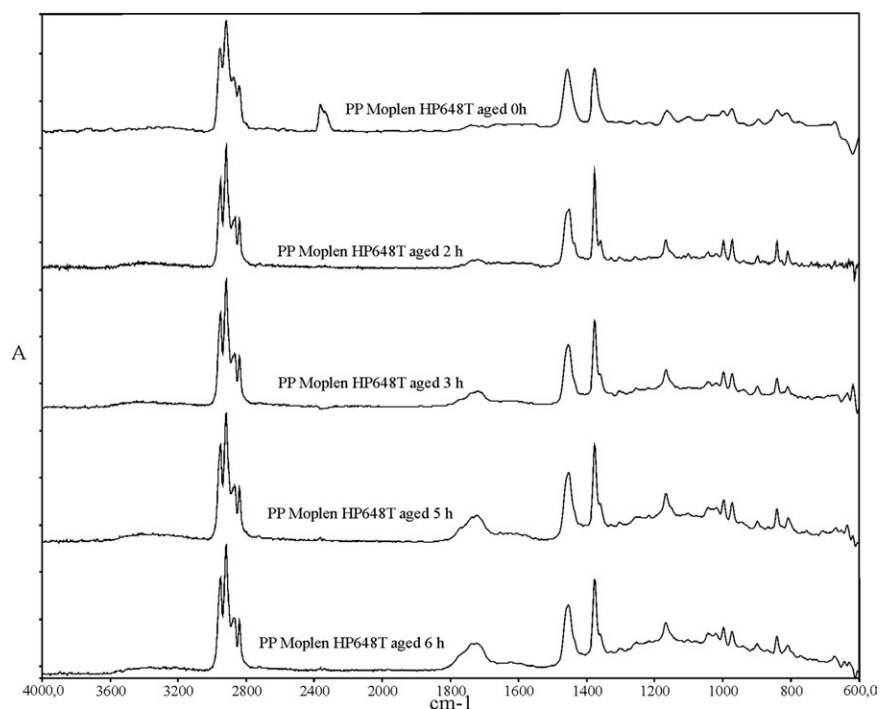
Sample	$T_{\text{Onset}}$ (°C)	Inflection point (°C)
PP	265.9	338.7
PP 0.25%QUER	301.1	391.5
PP 0.5% QUER	287.1	363.5
PP 0.75% QUER	298.0	380.6
PP 0.25% SIL	282.9	376.2
PP 0.5% SIL	289.0	367.7
PP 0.75% SIL	310.8	402.9
PP 0.5% NAR	276.8	341.4
PP 0.5% CHRY	278.9	357.1
PP 0.75% HESP	265.1	324.2

parameters obtained by isothermal and dynamic DSC characterization for PP stabilized with different amounts of silibinin and quercetin in the range of 0.25–0.75 wt %.

In the case of samples with quercetin, the OOT is similar for all compositions, with values around 260°C, but in isothermal conditions we observe a clear increasing tendency for oxidation onset temperatures as the quercetin content increases. With regard to silibinin, it is possible to detect some differences; the OOT in dynamic conditions changes in the range of 238–250°C, reaching the maximum for compositions with 0.5 wt %. With regard to OIT in isothermal conditions, the OIT value is similar for 0.25 and 0.50 wt %, whereas the stability is highly improved for compositions with 0.75 wt % as the OIT is increased up to the value of 84.0 min.

Table II summarizes the thermogravimetric results of samples with different flavonoids. This information is useful to know the thermal stability in aggressive conditions; as the thermal stability increases, the characteristic TGA is moved to higher temperatures. If we take the onset temperature as a comparative value, the nonstabilized PP is characterized by an onset temperature of 265.9°C. With regard to samples containing 0.5 wt % of silibinin and 0.5 wt % quercetin, the onset temperature is moved to higher values (289.0 and 287.1°C, respectively) which is in agreement with the previous results obtained by DSC. Although the use of 0.5 wt % of chrysin and naringin promotes a significant increase in thermal stability of PP (with degradation onset temperatures of about 278.9 and 276.8°C), their effectiveness is lower than the observed for quercetin and silibinin.

The results of TGA of PP stabilized with different percentages of quercetin and silibinin are also summarized in Table II. It can be observed that the samples containing 0.25 wt % of quercetin show a remarkable higher stability than nonstabilized PP and this thermal stability is not increased in a remarkable way for higher quercetin amounts. By contrast, the increase in the percentage of silibinin reduces degradation; both the degradation onset temperature and the inflection point show a clear increasing tendency. This is in agreement with the previous dynamic DSC results and thus indicating that the antioxidant efficiency of quercetin is less sensitive to the total content as in the case of silibinin. It is important to remark that the stabilizing efficiency of a particular phenolic compound is directly related to its structure (number of hydroxyl groups, chain mobility, etc.). Hence, each phenolic compound is characterized by an optimum amount which provides optimum stabilization effects. Addition of higher amounts (over the optimum point)



**Figure 4.** FTIR spectra of nonstabilized PP subjected to UV light exposure for 0, 2, 3, 5, and 6 h.

**Table III.** FTIR Results of the UV Light Aging<sup>a</sup>

Sample	Carbonyl index (t = 0 h)	Carbonyl index (t = 2 h)	Carbonyl index (t = 3 h)	Carbonyl index (t = 5 h)	Carbonyl index (t = 6 h)
PP	$8.6 \times 10^{-2}$	$12.9 \times 10^{-2}$	$22.7 \times 10^{-2}$	$26.8 \times 10^{-2}$	$28.8 \times 10^{-2}$
PP NAR	$7.1 \times 10^{-2}$	$8.5 \times 10^{-2}$	$19.8 \times 10^{-2}$	$24.3 \times 10^{-2}$	$28.7 \times 10^{-2}$
PP CHRY	$5.1 \times 10^{-2}$	$14.9 \times 10^{-2}$	$25.3 \times 10^{-2}$	$26.9 \times 10^{-2}$	$29.1 \times 10^{-2}$
PP HESP	$9.9 \times 10^{-2}$	$12.4 \times 10^{-2}$	$18.6 \times 10^{-2}$	$20.6 \times 10^{-2}$	$30.9 \times 10^{-2}$
PP QUER	$6.1 \times 10^{-2}$	$13.4 \times 10^{-2}$	$15.7 \times 10^{-2}$	$17.6 \times 10^{-2}$	$25.4 \times 10^{-2}$
PP SIL	$9.6 \times 10^{-2}$	$16.2 \times 10^{-2}$	$17.6 \times 10^{-2}$	$18.6 \times 10^{-2}$	$25.2 \times 10^{-2}$

<sup>a</sup>Evolution of the carbonyl peak for PP formulations with 0.5 wt % of different flavonoids subjected to UV light aging.

does not provide higher stabilization and even, a decrease in the stabilization effects can be detected as other degradation mechanisms can be activated.

### UV Light Stabilizing Effect of Flavonoids

PP is known to be sensitive to photo-degradation when exposed to sunlight or UV radiation in air, as well as at wavelengths of more than 300 nm. Aging was performed by sample exposure to UV light with PP formulations containing 0.5 wt % of the different flavonoids to evaluate the potential stabilizing effect against UV light of the natural phenolic compounds derived from flavonoids. UV aging was conducted for 6 h and samples were tested after 2, 3, 5, and 6 h.

The degradation in PP is an irreversible process in which, of its possible mechanisms, oxidation is usually dominant. The incorporation of one molecule of oxygen per hundred polymer chain repeat units can reduce the molecular weight by a factor of 2 or 3, and lead to a total embrittlement of the polymer.<sup>18</sup> FTIR can provide valuable information on the polymer degradation kinetics and mechanisms by identifying the oxidation products. The CI is used for the indirect determination of the embrittlement time in polymers. The carbonyl absorbance intensity ( $1850\text{--}1650\text{ cm}^{-1}$ ) is compensated for by the ratio of its value to the intensity of an internal reference peak ( $3000\text{--}2700$ ).

Chemical changes related to the accelerated aging by UV light were analyzed by means of FTIR spectroscopy. Figure 4 shows the FTIR absorbance spectra of the nonstabilized PP at different aging times. We can see a clear increase in the intensity of absorption in the range of  $1850\text{--}1650\text{ cm}^{-1}$ , which is characteristic of the carbonyl group; if we take into consideration that the

intensity of the carbonyl and hydroperoxide groups ( $3000\text{--}3600\text{ cm}^{-1}$ ) is commonly used to measure the amount of oxidation as described by other authors<sup>20,21</sup> it is possible to evaluate the effectiveness of the different flavonoids by following the evolution of the carbonyl peak as in our case the increase of the hydroperoxide group is very low and very difficult to assess.

The rest of the investigated samples show similar trends and main values are summarized in Table III using the carbonyl peak area of all the samples. It should be noted that the flavonoids have carbonyl groups in their structure. To calculate the increase in area caused by aging, we calculated the area of the carbonyl peak corresponding to the aging of each sample minus the carbonyl peak area of the material without aging.

Table III summarizes that once again samples with quercetin and silibinin aged for a total time of 6 h show the highest UV light stabilizing effect as the area of the carbonyl group is smaller than that of the nonstabilized PP. This indicates that these two flavonoids are suitable to stabilize PP against UV light; on the other hand, the other flavonoids have similar carbonyl group area to that of nonstabilized PP or a little higher.

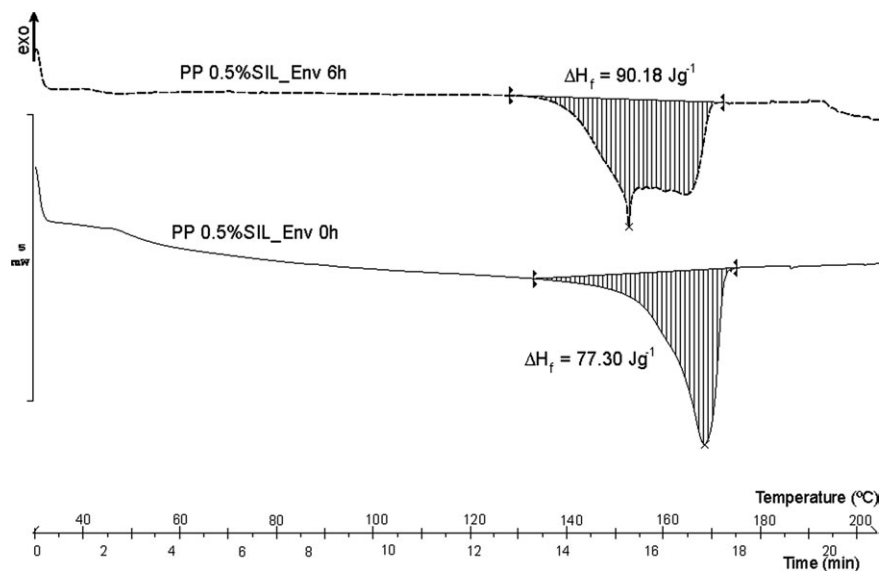
In addition to surface chemical characterization by FTIR, the effects of the UV light aging were also studied by DSC; Table IV summarizes that the crystallinity increases with the aging time in all samples.

The increase in crystallinity can be explained by a decrease in molecular size during aging, as the virgin material without aging has a high concentration of tangles that restrict chain crystallization during processing, and when exposed to UV radiation, chain scission occurs and subsequent oxidation. These reactions occur mainly in the amorphous region because of the

**Table IV.** DSC Results of the UV Light Aging<sup>a</sup>

Sample	$X_c$ (%) (t = 0 h)	$X_c$ (%) (t = 2 h)	$X_c$ (%) (t = 3 h)	$X_c$ (%) (t = 5 h)	$X_c$ (%) (t = 6 h)	$\Delta X_c$ (%)
PP	34.10	34.96	39.13	40.94	44.60	10.50
PP NAR	37.66	40.61	41.48	44.20	57.83	20.17
PP CHRY	35.47	40.38	40.87	42.12	50.40	14.93
PP HESP	34.95	35.15	41.16	41.74	50.13	15.17
PP QUER	43.66	43.77	44.57	45.60	45.81	2.14
PP SIL	39.29	42.54	43.05	44.78	45.84	6.55

<sup>a</sup>Evolution of the crystallinity for PP formulations with 0.5 wt % of different flavonoids subjected to UV light aging.

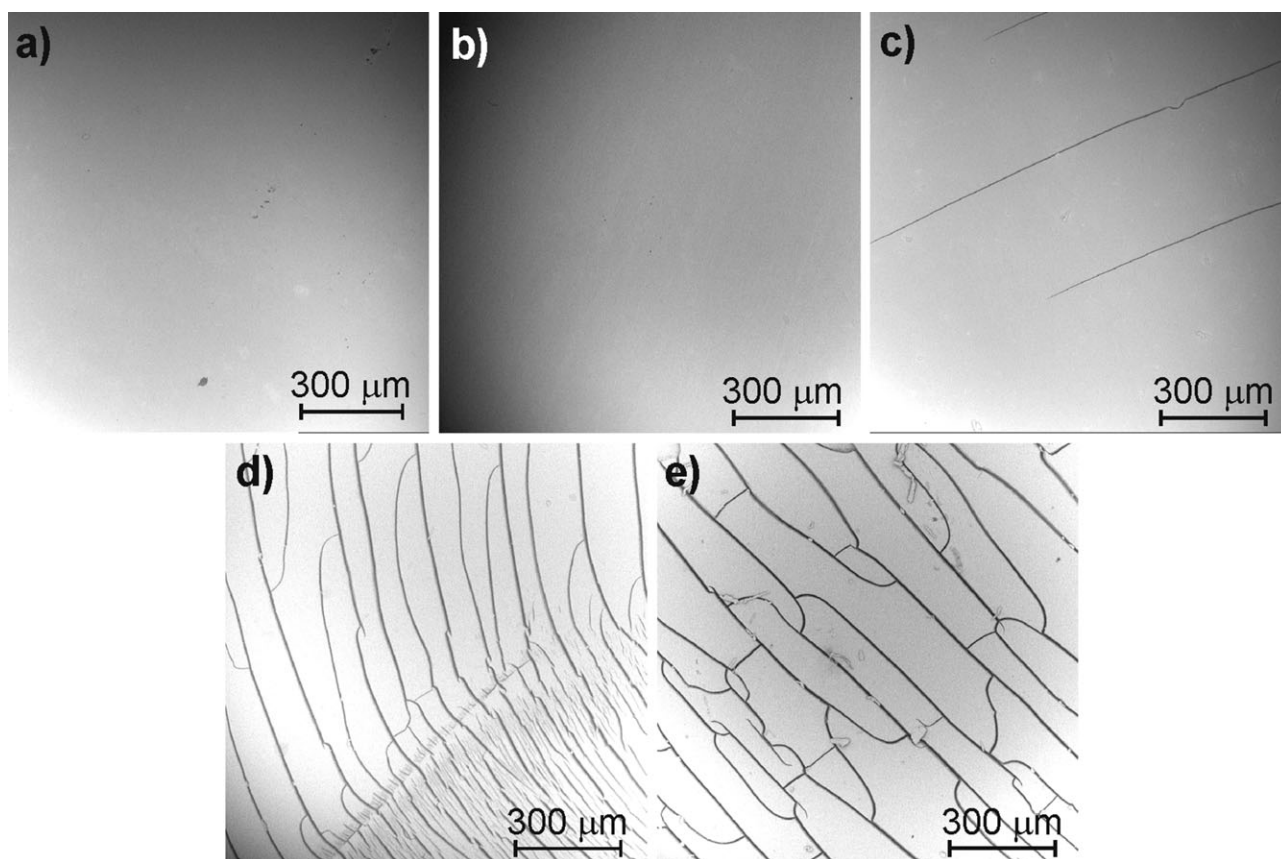


**Figure 5.** Dynamic DSC curves of the SIL 0.5% PP sample without exposure to UV light and 6 h of exposure to UV light.

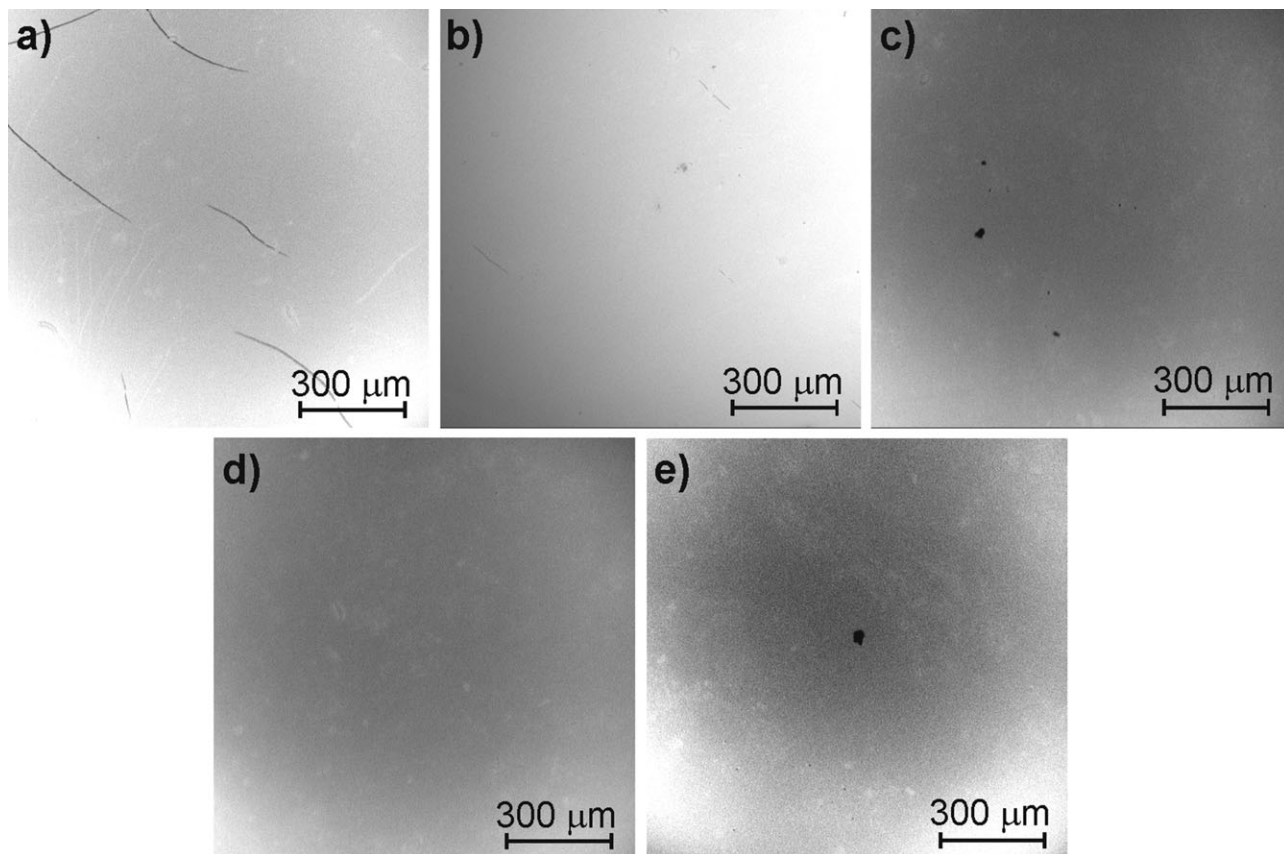
greater permeability of oxygen. These areas remain free and then reordered to increase the crystallinity of the samples.<sup>22</sup>

We can also observe that samples containing silibinin and quercetin subjected to UV light aging for 6 h show that the increment of crystallinity values is less than nonstabilized PP with an

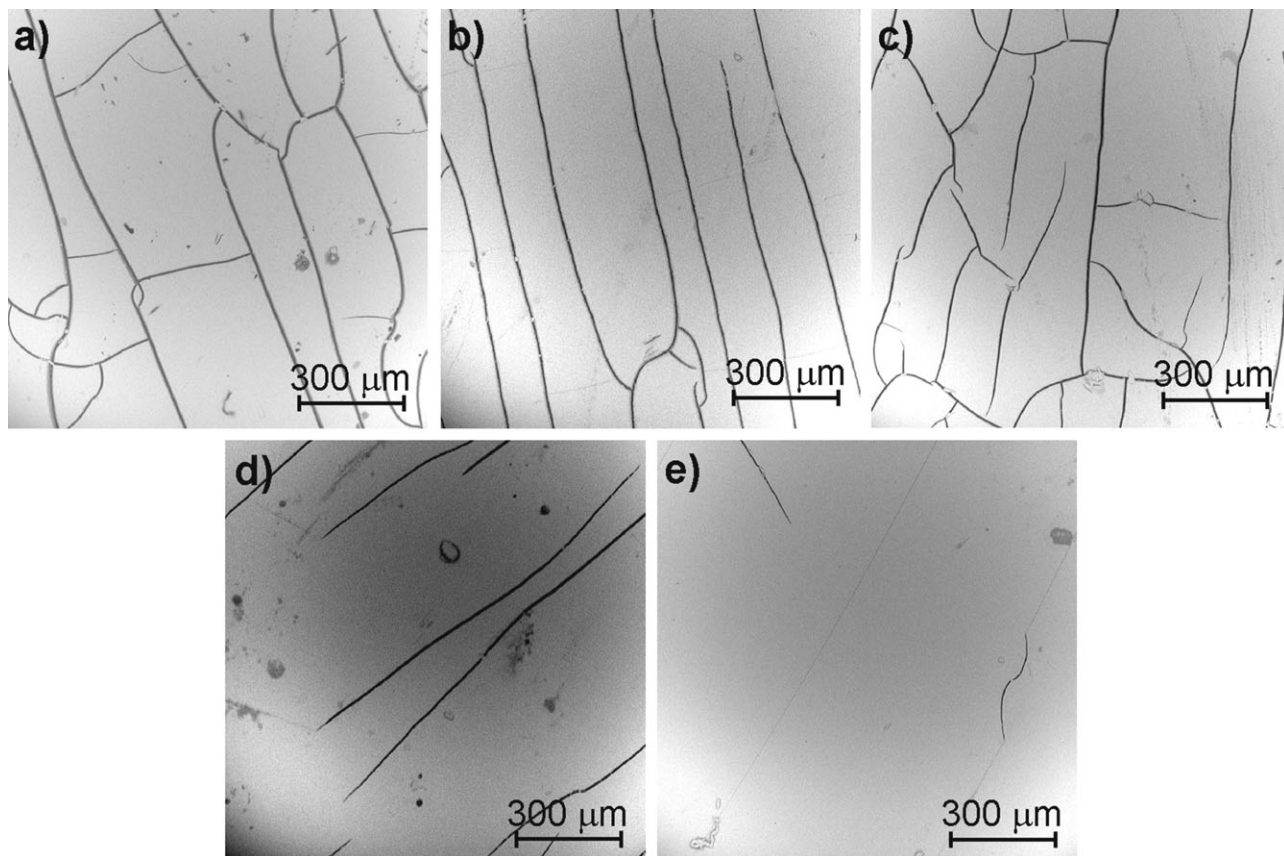
exposure time to UV light of 6 h; once again, this is a clear evidence that indicates that these two flavonoids can also stabilize PP against UV light, with greater intensity than the rest. Figure 5 shows DSC curves of the SIL 0.5% PP sample without exposure to UV light and 6 h of exposure to UV light. We can clearly see



**Figure 6.** SEM images of nonstabilized PP subjected to UV light aging process for different exposure times. (a) 0 h, (b) 2 h, (c) 3 h, (d) 5 h, and (e) 6 h.



**Figure 7.** SEM images of PP formulations with different flavonoids (0.5 wt %) subjected to UV light exposure for 3 h. (a) PP + naringin, (b) PP + chrysin, (c) PP + hesperidin, (d) PP + quercetin, and (e) PP + silibinin.



**Figure 8.** SEM images of PP formulations with different flavonoids (0.5 wt %) subjected to UV light exposure for 5 h. (a) PP + naringin, (b) PP + chrysin, (c) PP + hesperidin, (d) PP + quercetin, and (e) PP + silibinin.



that the latent heat of fusion is higher in the sample exposed to UV light which indicated higher crystallinity.

The morphological changes of the aged samples have also been studied by scanning electron microscopy (SEM). Figure 6 shows how the nonstabilized PP changes as the exposure time to UV light increases. Figure 6(a,b) that correspond to exposure times of 0 and 2 h, respectively, show a smooth surface without cracks, whereas in Figure 6(c) the first cracks appear owing to aging effects after 3 h of UV exposure. As the exposure time to UV light increases, it is clearly detectable the presence of more and higher in size as shown in Figure 6(d,e) corresponding to the samples with exposure times to UV light aging of 5 and 6 h, respectively. As we have described before, UV light promotes chain scission and subsequent oxidation and thus allowing rearrangement of polymer chains to increase crystallinity. This phenomenon is responsible for appearing internal stresses that lead to microcrack formation and thus causing a material embrittlement.<sup>23–25</sup>

Figure 7 shows SEM images of PP formulations containing 0.5 wt % of the different flavonoids as stabilizer additives, subjected to a UV light aging time of 3 h. It is possible to observe that the sample containing naringin [Figure 7(a)] and chrysin [Figure 7(b)] show some cracks owing to degradation. However, samples with hesperidin, quercetin, and silibinin show a clear smooth surface which is representative for slow or negligible UV light aging.

By contrast, samples exposed to UV light for a total period of 5 h present numerous cracks as shown in Figure 8 although in the case of samples with quercetin and silibinin, Figure 8(d,e), respectively, there are less cracks than with the rest of the materials, and thus indicating that quercetin and silibinin, additionally to the oxidative retardant effect, they can provide attracting stabilizing effects against UV light to PP to a greater extent than the rest.

## CONCLUSIONS

Flavonoids are well known for UV protection and antioxidation in plants owing to the presence of phenolic compounds in their structure and this has led to the use of these compounds to prevent human aging.

This study has allowed verifying and validating the usefulness of the flavonoids in the oxidation stabilization of PP which is highly sensitive to thermo-oxidative degradation. Addition of small amounts of flavonoids contributes to the development of more environmental friendly formulations for this type of polymers, and thus allowing full or partially replacement of petrochemical antioxidants. Furthermore, it has been shown that within the group of flavonoids, the subgroup of flavonols (silibinin and quercetin) provide the best-stabilizing results. These offer similar behavior to conventional petroleum-based phenolic antioxidants widely used in the stabilization of polyolefins.

Finally, it is important to remark that the composition ranges that provide good stabilizing effects are similar to those used in the industry with synthetic antioxidants offering very attractive possibilities for this set of natural compounds.

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