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Interaction and Release of Catechin from Anhydride Maleic-Grafted Polypropylene Films

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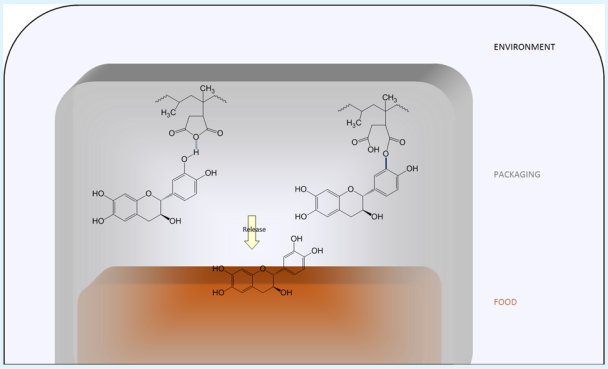
ABSTRACT: In this paper, investigations were carried out on catechin-loaded maleic anhydride (MAH)-modified polypropylenes (PP). Two maleic-modified polypropylenes (PPMAH) with different maleic concentrations have been blended with PP and catechin to obtain composites of improved catechin retention with the aim of studying the possible interactions between these grafted polymers with antioxidants, and a secondary interest in developing an active antioxidant packaging. Composite physicochemical properties were measured by thermal analysis (thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and oxidation induction time (OIT)) and infrared spectroscopy studies. Catechin release profiles into food simulants were obtained by HPLC-PDA-QqQ, following European legislation. Antiradical activity of composites was analyzed by the ABTS and DPPH method. The formation of intermolecular hydrogen bonds between catechin and functionalized PP has been confirmed by Fourier transform infrared (FTIR) studies. Besides, a small fraction of ester bonds, formed as a result of a chemical reaction between a fraction of the hydrolyzed anhydride and the catechin hydroxyl groups, is not discarded. OIT results also showed an increase in antioxidant effectiveness caused by the presence of catechin- and maleic-modified PPMAH in the blend formulations. Incorporation of MAH-grafted PP increased substantially the retention rate of catechin, being dependent on the MAH content of the grafted polypropylene. The described interactions between catechin and maleic groups, together with changes in PP morphology in comparison with reference PP explained lower antioxidant release. Besides formulation, antioxidant release was dependent on the type of food, the temperature, and the time.



KEYWORDS: *maleic anhydride grafted polypropylene, natural antioxidants, catechin, active antioxidant packaging, release, immobilization*

INTRODUCTION

New polymer formulations are emerging, as far as new applications are considered. Despite the increasing demand for biodegradable materials, polyolefins are still the most common polymers used for food packaging. Polyolefins, similar to most synthetic polymers, have a hydrophobic and chemically inert surface which, therefore, leads to low adsorption of dyes or inks, poor adhesion to coatings or other materials, the generation of static electricity, incompatibility with hydrophilic substances, and many other problems. Among the techniques employed to modify polymers, grafting of polyolefins with polar monomers have received special attention, because of their potential applications, by which a variety of desired graft chains can be introduced onto the polymer surface without changing the bulk properties.[1−3] There are a wide variety of these materials, such as polyolefins with grafted maleic anhydride (MAH), fumarate and maleate esters, methacrylate esters, or methacrylic acid. These polymers often serve as precursors of other polyolefin graft copolymers.

Maleic anhydride (MAH)-modified polyolefins are one of the most important class of functionalized polyolefins in commercial applications, because of their low cost, high activity, and good processability. Free radical-induced grafting of MAH onto polyolefin substrates has been carried out in the melt phase in various forms of extruders and batch mixers, in solution, and in the solid state. In all cases, controversy arises concerning the final structure of the functionalized polymer, with respect to the nature of the grafted units and the distribution of the graft sites.[4−7] Maleic anhydride grafting onto polypropylene (PPMAH) has been carried out basically with the objective of achieving compatibility between polar and nonpolar polymers.[7−9] In addition, nowadays it is a proved alternative as a compatibilizer between PP and fibers or more hydrophilic materials in order to obtain "biocomposites". The

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latter are composites containing at least one constituent which is derived from renewable resources, offering several advantages such as reducing the cost per unit volume, low density, high strength-to-weight ratio, and nonbrittle fracture. Furthermore, improvements in mechanical properties attributed to fiber/matrix interface enhancement interaction by the addition of PPMAH have been evident.[10,11] The compounds with anhydride groups are generally active, with a tendency to undergo a wide variety of organic reactions such as hydrolysis, esterification, amination, etc. Through these reactions, the graft-modified surface containing anhydride groups are promising to perform extensive post-functionalizations.[12]

Moreover, because of the limited stability of polyolefins to high temperatures and ultraviolet (UV) light, antioxidants are key ingredients in the formulation of polypropylene (PP) in order to protect the polymer during package manufacture and use. Most of the common antioxidants are phenolic compounds, secondary arylamines, organophosphates, and thioesters of synthetic origin that are approved by the national and international regulations for plastics in contact with food. Nevertheless, migration of these additives and their degradation products into food during storage may change the sensory properties of the product they contain or even lead to toxicity upon consumption. For these reasons, several research studies have focused on the development of alternative polymer formulas with natural antioxidants.[13,14]

In recent years, antioxidants have been incorporated on polymer formulations, not only to protect the polymer during package manufacture and use, but as an active substance to be released on food in order to extend its shelf life. It is the definition of antioxidant active packaging that absorbs radical oxidizing species by the incorporation of an antioxidant into the polymer, being a good choice for many products sensitive to oxidation.[14−16] As mentioned previously, several studies have shown improvements of mechanical properties attributed to enhancement interaction by the addition of PPMAH, but no evidence of interaction between antioxidant substances, incorporated for polymer protection, and functionalized grafted polymer have been studied. In this light, the existence of these interactions is considered interesting, because they can have consequences on the retention of the antioxidant by the polymer matrix.

The objective of this work is to study the interaction of catechin, reported as useful natural antioxidant for PP protection,[17] within anhydride maleic-modified polypropylenes (PPMAH). Catechin was also selected because it is a flavonoid with multiple biological effects, and it is nonvolatile, reducing the loss during packaging manufacturing that occurs with other compounds such as carvacrol or essential oils. For that, two different maleic anhydride modified polypropylenes (PPMAH) with different MAH concentrations have been blended with polypropylene (PP) and catechin (CAT). Resulting materials were physicochemically characterized, and antioxidant properties were analyzed in comparison with a simple catechin loaded PP as reference material. An important aspect of this study is the characterization of the physical and/or chemical interactions that might have occurred during melt blending between the hydroxyl groups of catechin and grafted PPMAH in order to analyze the influence of these interactions on polymer properties and release profiles in contact with aqueous and fatty food simulants. As well as projecting their future application as food packaging materials, since these systems could extent the shelf life of packaging and packed food products.

EXPERIMENTAL SECTION

Chemicals and Reagents. Polypropylene PP 070 G2M (PP) was provided by Repsol YPF (Madrid, Spain). Chemically modified polypropylenes (PP-MAH) Fusabond PMD511D and PMZ203D were purchased from DuPont (Barcelona, Spain). Both chemically modified polypropylenes have medium and high graft level, respectively. Specific graft levels of both commercial Fusabond-modified polypropylene were reported as confidential by DuPont. Liu and Konlopoulou[18] reported an estimated concentration of maleic anhydride in Fusabond PMD511D between 0.25% and 0.5%. No data were reported for PMZ203D.

Reagent-grade absolute ethanol, methanol, catechin dihydrate (CAT), epicatechin (EPI), 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS), and 2,2-diphenyl-1-picrylhydrazyl (DPPH) 95% free radical were purchased from Sigma (Madrid, Spain).

Materials Preparation. Different PP formulations containing catechin as antioxidant agent were obtained in a miniextruder equipped with twin conical co-rotating screws and a capacity of 7 cm^3 (MiniLab Haake Rheomex CTW5, Thermo Scientific). The following parameters were used: a screw rotation rate of 40 rpm, a temperature of 180 °C, and a residence time of 1 min.

Ternary mixtures of PP:PPMAH:CAT (4:2:1 w/w/w) were formulated with chemically modified polypropylenes DuPont Fusabond PMD511D and PMZ203D (called PPMAH511CAT and PPMAH203CAT, respectively). Binary blends of PP:CAT (6:1 w/w) were called PPCAT. For comparison, reference samples of PP and modified PPMAH without catechin (PPMAH511 and PPMAH203) were also extruded and submitted to the same characterization. The resulting films were ∼120−130 μm thick.

Fourier Transform Infrared Spectroscopy (FTIR). Fourier transform infrared spectroscopy (FTIR) was used to characterize the presence of specific chemical groups in the materials. For IR measurements, the extruded materials were compression-molded in a hot plate press (IQAP LAP S.L. Model PL15-Series 1381, Barcelona, Spain), in order to obtain very thin films (∼35−45 μm). FTIR was performed in the transmission mode using an OPUS/IR PS15 spectrometer (Bruker). The spectra were the results of 64 co-added interferograms at 2 cm^{-1} resolution between 4000 cm^{-1} to 500 cm^{-1}.

Thermal Characterization. Thermogravimetric analyses (TGA) were carried out using a thermal analyzer (Perkin−Elmer TGA 7). Samples (ca. 10 mg) were heated in 100-μL platinum sample pans from room temperature to 800 °C under a nitrogen atmosphere at 10 °C/min, to determine the degradation temperatures of the antioxidant-containing materials.

Differential scanning calorimetry (DSC) measurements (Perkin−Elmer, Series 7) were also performed, to analyze the effect of the interaction between the grafted PPMAH and catechin on the morphology and crystallinity of the PP matrix. Crystallinity was also evaluated and contrasted through FTIR data. Thermograms were obtained from −20 °C to 200 °C with a heating rate of 10 °C/min, cooled to −20 °C, and held at this temperature for 2 min, and a second heating process to 200 °C was conducted. The melting and crystallization temperatures (T_m and T_c, respectively) and the enthalpies of melting and crystallization (ΔH_m and ΔH_c, respectively) were calculated from the cooling and the second heating process.

Oxidation induction time (OIT) analyses were conducted to study changes of polymer stability and antioxidant effectiveness caused by the incorporation of PPMAH and catechin in the blend PP formulations. The sample temperature was stabilized for 2 min at 200 °C under an inert atmosphere, which was subsequently switched to an oxygen atmosphere to start the test. Analyses were carried out according to Standard EN 728.

All thermal analyses were done in triplicate.

Release Studies. A study of the release of the bioactive flavonoid catechin was carried out by determining the specific migration from the polymer into two food simulants specified in European regulations: simulant A (10% ethanol) and simulant D1 (50% ethanol), as aqueous and fatty food simulants, respectively.[19] Release tests were performed by total immersion of rectangular strips film

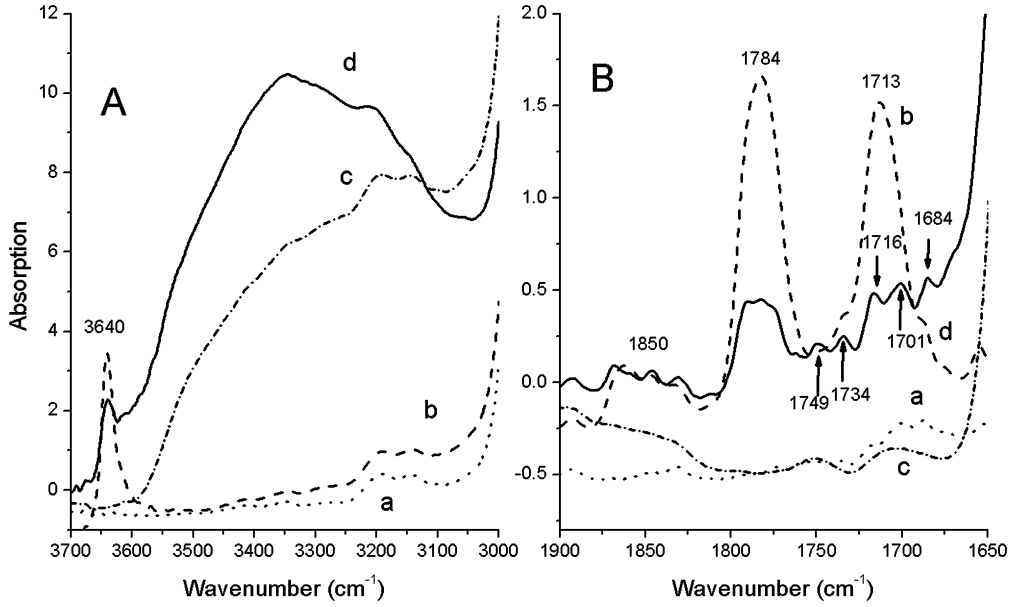

Figure 1. FTIR spectra of original PP (spectrum a), MAH-modified polymer (PPMAH203) (spectrum b), catechin-loaded PP (spectrum c), and catechin-loaded PPMAH203 (spectrum d) in (A) the hydroxyl vibration region and (B) the carbonyl vibration region.

pieces (8 mm × 0.4 mm × 0.13 mm) in 10 mL of food simulant contained in glass-stoppered tubes with PTFE closures at 40 °C. Milli-Q water was deoxygenated by bubbling nitrogen, and a final nitrogen flush was done before closing the cells to reduce the oxygen percentage in the cell headspace. Samples were taken after 1, 5, 10, and 20 days of storage. Test materials were also run simultaneously to check for interferences and all samples were performed in triplicate. Legislation just order migration tests at 40 °C, but measurements at 25 °C on day 20 were also performed to observe a possible positive antioxidant release for future active packaging application at room temperature. After the contact period, an aliquot of each simulant was filtered through an Acrodisc PTFE CR 13-mm, 0.2-μm filter (Waters, Milford, MA, USA) and analyzed by HPLC-PDA-QqQ, to calculate the released catechin concentration. Release data was expressed as the percentage of catechin released into the food simulants after the contact period: amount of catechin released per kilogram of film with reference to the initial amount of catechin loaded per kilogram of film formulation.

HPLC-QqQ MS Conditions. An Agilent 1200 Series Rapid Resolution LC system (Agilent Technologies, Waldbronn, Germany) equipped with an online degasser, binary pump delivery system, high-performance SL autosampler, thermostatic column department and is coupled online to a mass spectrometer detector (MS), which was used for analysis. Samples were injected in Zorbax SB-C18 (50 × 2.1 mm, 1.8 μm) column (Agilent Technologies) thermostatted at 35 °C. Binary gradient elution was performed, with flow rate of 0.3 mL min^{-1} and injection volume of 3 μL. Mobile phases were composed by water−1% formic acid (A) and methanol (B). The following gradient elution profile was used: mobile phase composition started at 25% of B, was linearly increased to 40% B in 3 min, followed by a linear increase to 60% B in 0.5 min finally reaching 100% B in other 0.5 min. The column effluent was directly introduced into the triple quadrupole mass detector Agilent 6410 Triple Quad LC/MS (Agilent Technologies) operated in the positive ionization mode. Ions were formed using electrospray ionization (ESI) with temperature of the drying gas (N_2) set at 350 °C and flowed at 10 mL min^{-1}. The nebullizing pressure (N_2) was maintained at 35 psi. Capillary voltage was set at 5.5 kV. Selective ion monitoring (SIM) was used to quantify the target ions. Mass spectral data and retention time were used for peak identification. Quantification of catechins was based on an external standard calibration method. Integration and data elaboration were performed using Agilent MassHunter Workstation software, version B03.00 (Agilent Technologies).

Antiradical Activity of Materials. Antioxidant activities of catechin-loaded materials were measured by two different antioxidant assays—DPPH and ABTS methods—that measure the antioxidant effectiveness by monitoring the inhibition of their corresponding radicals. The DPPH and ABTS assays are based on the bleaching rate of the free radicals 2,2-diphenyl-1-picrylhydrazyl (DPPH$^\bullet$), and the radical cation 2,2′-azinobis(3-ethylbenzothiazoline-6-sulfonate) (ABTS$^{\bullet+}$), monitored spectroscopically at 517 and 734 nm, respectively. Both radicals, DPPH$^\bullet$ and ABTS$^{\bullet+}$, are neutralized either by direct reduction via electron transfers or by radical quenching via H atom transfer.[20] These assays were selected, not only because of their simplicity, but also to study the radical scavenging behavior of the developed materials in different environments, because DPPH$^\bullet$ is dissolved in ethanol and ABTS$^{\bullet+}$ in water.

Approximately 30 mg of each material was immersed in 10 mL of DPPH$^\bullet$ and ABTS$^{\bullet+}$ radical solutions, and their absorbance was kinetically monitored. Both radical solutions were obtained as follows: (i) DPPH radical scavenging activity was based on the method of Okada and Okada with slight modifications[21] (2 mM ethanolic solution of radical DPPH$^\bullet$ was diluted to an absorbance value of one at 517 nm); (ii) ABTS radical cations were produced by reacting 7 mM ABTS in water with 2.45 mM potassium persulfate ($K_2S_2O_8$) and then stored in darkness at room temperature for 16 h. The ABTS radical solution was diluted to give an absorbance value of 1 at 734 nm. All experiments were performed in triplicate.

In both assays, the antioxidant activity is obtained as the percentage inhibition values (I (%)), calculated using this equation:

$$I\ (\%) = \left(\frac{\mathrm{Abs}_{\mathrm{control}} - \mathrm{Abs}_{\mathrm{sample}}}{\mathrm{Abs}_{\mathrm{control}}}\right) \times 100$$

To standardize the results, scavenging activities of the DPPH$^\bullet$ and ABTS$^{\bullet+}$ radicals were expressed as catechin concentration, using a calibrated curve of catechin concentration versus inhibition value (I (%)) of each radical.

Parameters Estimation of Kinetics of Antioxidant Activities. The diffusivity (D) and partition coefficient (K) were estimated based on the experimental results from the antioxidant activities, measured as the percentage inhibition of radicals DPPH$^\bullet$ and ABTS$^{\bullet+}$ over time. Because antioxidant activity is based on the antioxidant release to the solvent where radicals are dissolved, through the calibrated curve of catechin concentration versus I (%), results were understood as catechin release. Hence, the extent of the antioxidant activities can be

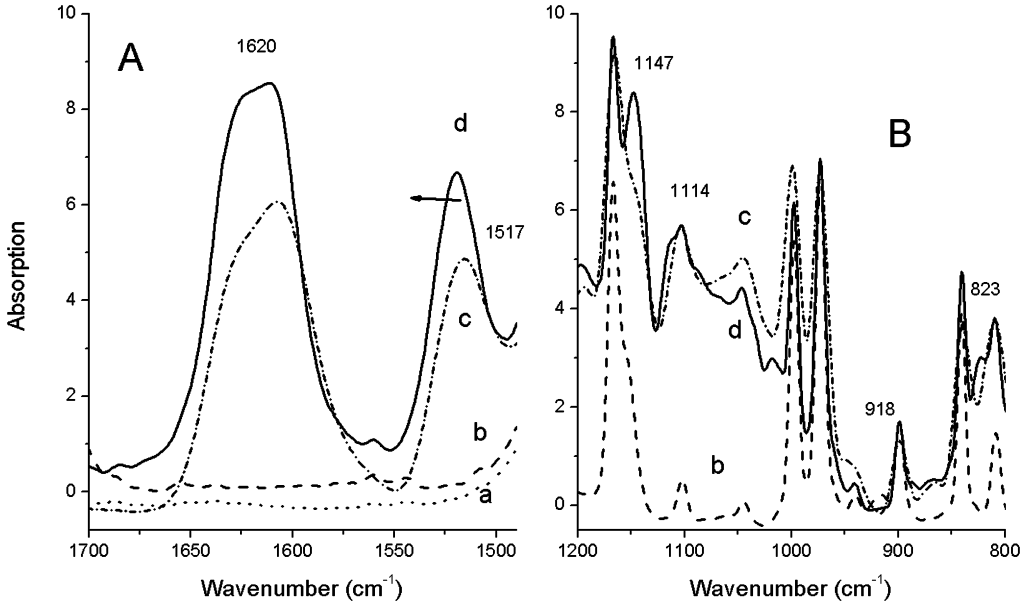

Figure 2. FTIR spectra of original PP (spectrum a), MAH-modified polymer (PPMAH203) (spectrum b), catechin-loaded PP (spectrum c), and catechin-loaded PPMAH203 (spectrum d) in (A) the C=C aromatic ring stretching vibration region and (B) the region between 1200 cm^{-1} and 800 cm^{-1}.

characterized by the partition coefficient, K, which is defined as the ratio of the amount of catechin in the polymeric phase, relative to the concentration of released catechin.

The kinetics of the antioxidant activities, translated to catechin released, were also monitored. Several works have demonstrated that the release kinetics of the compounds followed the same profile as antioxidant activity.[16,22] To characterize the kinetics of the mass transport process within the film, it is necessary to solve Fick's law considering the boundary conditions of the experiments. In this work, the presence of a partition equilibrium and a limited volume of solvent were considered. Also, the diffusion coefficient (D) for the transport of that antioxidant in the film is considered independent of time and position. By integration of Fick's law with these assumptions, the ratio of the mass of catechin release into the solvent at time t and at equilibrium can be expressed through eq 1:

$$\frac{m(t)}{m_S^f} = 1 - \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n^2} \exp\left(\frac{-4Dq_n^2 t}{l^2}\right) \quad (1)$$

where $m(t)$ is the mass of the migrant in the food at a particular time t (s), M_s^f the mass of migrant in the food at equilibrium, l, the film thickness (cm), D the diffusion coefficient ($cm^2\ s^{-1}$), and t the time (s). The parameter α represents the ratio between the mass of compound in the liquid and that in the polymer at equilibrium ($\alpha = V_S/(KV_P)$, where V_S and V_P are the solution and polymer volumes, respectively), l is the thickness and q_n represents the positive solutions of eq 2:[23]

$$\mathrm{tg}(q_n) = -\alpha q_n \quad (2)$$

RESULTS AND DISCUSSION

Molecular Interaction Study. Information on the nature of the molecular interactions between catechin and maleic groups within the modified functionalized PP matrix was monitored using infrared spectroscopy. FTIR spectra for PP, MAH-modified polymer (PPMAH203), catechin-loaded PP, and catechin-loaded PPMAH203 are shown in Figures 1 and 2. MAH-modified polymer PPMAH203 was selected because of its higher content of maleic anhydride. The FTIR spectrum of PPMAH203 (Figure 1B) exhibits a double absorption band at 1861−1844 cm^{-1}, which is assigned to the asymmetric stretching of the anhydride carbonyl groups, along with a strong broad band centered at 1784 cm^{-1} (the second derivative spectrum reveals that this band is composed of two bands at 1792 and 1779 cm^{-1}), corresponding to the symmetric stretching of the carbonyl groups, with the 1792 cm^{-1} peak being an absorbance characteristic of carbonyl from cyclic anhydrides with five-membered rings.[24,25] The band involving the stretching vibration of the C−O−C group appears at 918 cm^{-1} in cyclic five-membered ring acid anhydrides. An extra strong absorption band centered at 1713 cm^{-1} corresponds to the carbonyl stretching ($\nu_{C=O}$) of the acid form, indicating that a high proportion of maleic anhydride incorporated into PPMAH203 has been hydrolyzed during the sample processing. The well-defined band at 3640 cm^{-1} (OH stretching of the acid form) corroborates the high level of anhydride hydrolysis (Figure 1A).

For catechin-loaded PP, the FTIR spectrum shows the characteristic catechin bands. Catechin has five hydroxyl groups in one molecule, and the most relevant feature of its FTIR spectrum is the broad band centered at 3200 cm^{-1}, attributed to the summation of several contributions corresponding to hydroxyl groups in different situations (intramolecular and intermolecular self-association, non-hydrogen-bonded groups) (Figure 1A).[26] Other bands are the C=C aromatic ring stretching vibrations (1620 and 1517 cm^{-1}), the C−O stretching of the oxygen in the ring (1281 cm^{-1}), the alcohols C−O stretching vibrations (1140, 1108 cm^{-1}), and the aromatic =C−H out-of-plane deformation vibration (814 cm^{-1}) (see Figures 2A and 2B).[27]

Some differences in the catechin structure as well as in the MAH bands can be observed in the sample that was blended with PPMAH203. The most significant change lies in the hydroxyl vibration region (3600−3000 cm^{-1}). When catechin is blended with PPMAH203, the maximum of the band is shifted toward higher wavenumbers (3345 cm^{-1}) and the band increased in terms of energy absorption. These observations suggest that catechin OH groups are associated with the

Table 1. Information of Developed Materials Obtained from Thermal Analysis and FTIR Data

	Cooling Process		Second Heating Process		FTIR Data
sample	T_c (°C)	$\Delta H_{c,correg}$ (J/g)	T_m (°C)	$\Delta H_{m,correg}$ (J/g)	$A_{998/973}$
PP	111.8 ± 2.5	101.4 ± 3.3	166.3 ± 0.3	79.2 ± 1.0	0.82 ± 0.02
PPMAH511	114.7 ± 3.1	107.6 ± 4.9	164.9 ± 0.3	83.2 ± 1.1	0.85 ± 0.03
PPMAH203	114.4 ± 2.9	98.3 ± 2.1	164.3 ± 0.4	78.5 ± 2.0	0.84 ± 0.02
PPCAT	115.6 ± 2.1	101.0 ± 1.7	165.1 ± 0.6	81.5 ± 1.9	0.91 ± 0.05
PPMAH511CAT	114.9 ± 3.5	103.2 ± 0.4	164.5 ± 0.4	79.6 ± 2.8	0.91 ± 0.02
PPMAH203CAT	119.4 ± 2.6	96.3 ± 3.1	163.8 ± 0.4	79.5 ± 1.7	0.89 ± 0.01

carbonyl groups of MAH moieties by hydrogen bonds. The difference between the wavenumber of self-associated hydrogen bond and that of intermolecular hydrogen bonded one could be due to the balance between the number of broken catechin−OH···HO−catechin self-associations and the number of formed catechin−OH···O═C−maleic bonds. The fact that the new band lies in the higher wavenumber region indicates that the strength of catechin−maleic acid hydrogen bonds is weaker than that of the catechin−O···HO−catechin ones.[28] Furthermore, there is a significant decrease in the peak intensity at 3640 cm^{-1} corresponding to the OH stretching of the non-hydrogen-bonded maleic acid (Figure 1A).

More to the point, as catechin exhibits no absorption in the 1800−1650 cm^{-1} region, any changes observed in the FTIR spectrum in this region should be attributed to those in the chemical environment of maleic anhydride/acid carbonyls such as the formation of covalent bonds (ester bonds) and/or hydrogen bonds. For catechin-loaded PPMAH203, a significant reduction on the intensity of the formerly described anhydride and maleic acid bands is clear, as a result of the PP and catechin dilution effect.

Nevertheless, the appearance of new bands due to the interaction with catechin can be detected, namely, 1749, 1734, 1716, and 1701 (as a result of the splitting of the former peak at 1713 cm^{-1}) and 1684 cm^{-1} (Figure 1B). The bands at 1749 and 1734 cm^{-1} could be ascribed to non-hydrogen-bonded and hydrogen-bonded ester bands, respectively, and the bands 1701 and 1684 cm^{-1} could be assigned to hydrogen-bonded carbonyls of the acid form. Apparently, these bands suggest two types of interactions between catechin and maleic moieties. First, a stable ester bond may have been formed as a result of the chemical reaction between a fraction of the hydrolyzed anhydride and catechin OH groups. Second, hydrogen bonds are formed between the different kind of carbonyl groups present in the polymer mixture (anhydride and acid carbonyls) and the various catechin OH groups. Nevertheless, as the intensities of these bands are very small, near the signal-to-noise ratio, one must be cautious, especially when asserting the presence of ester bands.

Additional changes in the catechin absorption bands lay in the regions of C═C aromatic ring stretching vibrations at ∼1600 cm^{-1} and C−O stretching of alcohol groups (1150−1070 cm^{-1}) (Figures 2A and 2B). Concerning the region of 1680−1490 cm^{-1}, the narrowing and up-shifting of the two bands assigned to the C═C aromatic ring stretching vibrations (1620 and 1517 cm^{-1}) is detected. Similar changes have been observed in catechin polymer blends upon forming hydrogen bonds between the ester carbonyl group in the polymer (PCL) and the hydroxyl groups in catechin.[29] Significant modifications in the C−O stretching region are the intensity increase of the bands at 1147 and 1114 cm^{-1}. An increase in absorption is also observed at 823 cm^{-1}, corresponding to the aromatic =C−H out-of-plane deformation vibration. Concerning maleic anhydride, the band at 918 cm^{-1}, alloted to the stretching vibration of the C−O−C group, can no longer be detected in the catechin−PPMAH203 blends. Changes in catechin bands have been perceived in both catechin-loaded PPMAH203 and PPMAH511 in comparison with the catechin−PP blend, although intensity changes are greater for the catechin−PPMAH203 blends. Conversely, possible modifications in carbonyl anhydride and acid bands have not been clearly observed in the latter mixtures.

From another point of view, the degree of crystallinity of the PP fraction estimated from the isotacticity ratio or band ratio $A_{998/973}$ increases in all catechin−PP blends in comparison with both original and functionalized PPs, as a result of the induction effect of the catechin crystallites on the crystal nucleation of iPP (Table 1).[30,22] This behavior has been observed in previous works.[31,32] In conclusion, the formation of intermolecular hydrogen bonds between catechin and functionalized PP has been confirmed by FTIR analysis in both catechin-loaded PPMAH203 and PPMAH511. Accordingly, the possible molecular interaction between catechin and maleic anhydride-grafted polypropylene is graphically proposed in Figure 3.

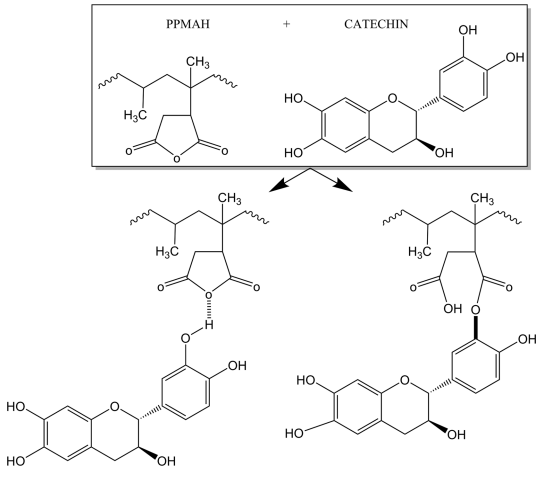

Figure 3. Proposed molecular interaction between catechin and maleic anhydride-grafted polypropylene.

Besides, the formation of a small fraction of ester groups as a result of a chemical reaction between a fraction of the hydrolyzed anhydride and catechin OH groups is not discarded, especially in the former blends. Anyway, not only the content but the strength of intermolecular hydrogen bonding between catechin and PPMAH may be lower than expected due to the high crystallinity of i-PP (isotactic polypropylene). Nevertheless, the described interactions, together with changes in the morphology of the polymer matrix, explain the reduction of

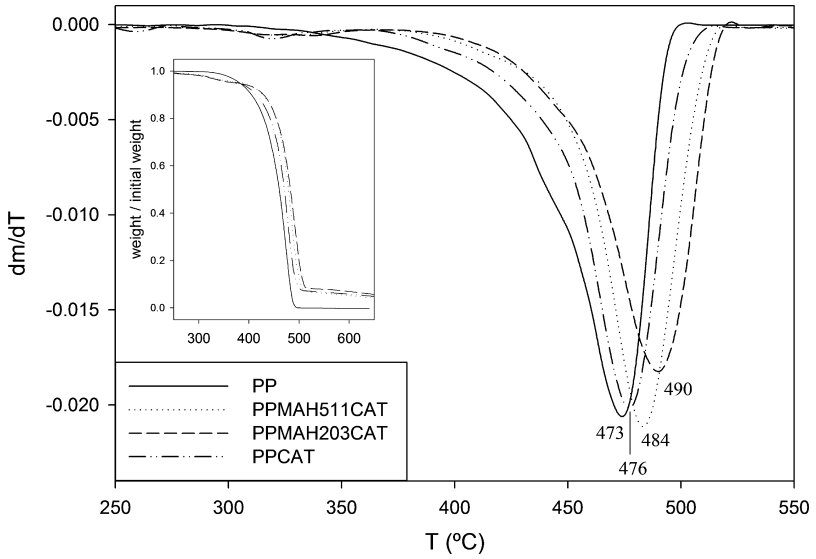

Figure 4. Weight loss and derivative of the weight loss of developed materials.

"free" available catechin molecules, as shown in the following sections.

Thermal Characterization. The results of TGA analysis revealed that catechin incorporation slightly improved thermal stability of polypropylene whereas when added with maleic anhydride modification significantly increased degradation temperatures. In the derivative weight loss curves of catechin-loaded PP (Figure 4), the maximum degradation rate always shifted to higher temperatures, with respect to neat PP (T_{max} = 473 °C) and the largest increased being observed for the sample with the highest maleic anhydride content. In previous works, it was already described how the incorporation of catechins and green tea extract (natural extract composed basically by catechins) increased the thermal stability of EVOH copolymers considerably, possibly because of the better affinity, which is due to the hydrophilicity of EVOH copolymer.[16,31,32] PPMAH, normally used as compatibilizer between PP and polar compounds, probably enhanced interaction between catechin and PP matrix, improving thermal stability and increasing maximum degradation temperatures. Furthermore, the presence of maleic modified polymer did not induce additional degradation process, and values of degradation temperatures for reference materials without catechin were pretty similar to PP (471 and 473 °C for PPMAH511 and PPMAH203, respectively).

DSC analysis is usually used to provide some evidence of miscibility of polymer blends according to physical phenomena, such as glass transition, melting, and crystallization. Table 1 summarizes the significant thermal properties. Differences were not extremely relevant, even though some small details are presented. First of all, T_c values are increased by both the presence of MAH-grafted PP and catechin. The highest shift is observed for the composite including the "highest" maleic content and catechin, PPMAH203CAT, together with a decrease in ΔH_c. These results are in accordance with other studies related to the use of PPMAH as a compatibilizer, which higher T_c of the compatibilized systems may result from the enhanced interaction between the two phases.[7] Besides, during the second heating process, the melting points and enthalpies of ternary blends PPMAH511CAT and PPMAH203CAT, slightly shifted to lower temperatures, which is probably due to the fact that functionalized groups interrupted crystallization of the polymer chain.

Normally, the reduction in melt and crystallization capacities and melting points of blends is attributed to the strong intermolecular interaction between catechin and MAH-grafted PP and the presence of catechin disturbs the crystallization of the polymer. Higher T_c values also indicated that polymer chain movements are more restricted, probably due to hydrogen-bonding interactions between catechin hydroxyls and MAH groups. Nevertheless, no clear increase in crystallinity is evidenced in catechin-loaded PP in relation with reference samples, as occurred in previous works dealing with antioxidant-incorporated polymers.[22,31] These results are not consistent with FTIR data obtained. This inconsistency may arise from the fact that DSC data were calculated from the cooling and the second heating process, which may have changed crystallization conditions, with respect to compression molding.

OIT results (4.20 ± 0.05 min for PP, 8.18 ± 0.02 min for PPMAH511, 7.15 ± 0.27 min for PPMAH203, 39.73 ± 3.08 min for PPMAH511CAT, 33.25 ± 1.17 min for PPMAH203-CAT, and 35.16 ± 1.50 min for PPCAT) showed that the incorporation of catechin increased the OIT values for all materials considerably. The presence of maleic anhydride groups in the blend leads to greater protection of the materials, since higher OIT values were observed, compared to neat PP. It may be an indication of catechin that has been retained on polymer matrix being available to serve as protection.[33] The thermal stability of PP doped with synthetic antioxidants was previously measured and the PPMAH203 and PPMAH511 films doped with catechin showed longest OIT values than that PP doped with synthetic antioxidants, which confirmed that these compounds provided polypropylene with highest stabilization against thermal-oxidation.[34] Moreover, standard deviations of OIT values showed that there are more variations when modified polypropylenes doped with catechin are considered. The clarification of these values is a complex subject, because they are reliant on the appearance of degradation species, according to Thörnblom et al.[35]

Catechin Release. The migration profiles of the three studied films, expressed as the percentage of catechin released

into the food simulant per unit of time, are compared in Figure 5. The initial added amount of catechin was considered to

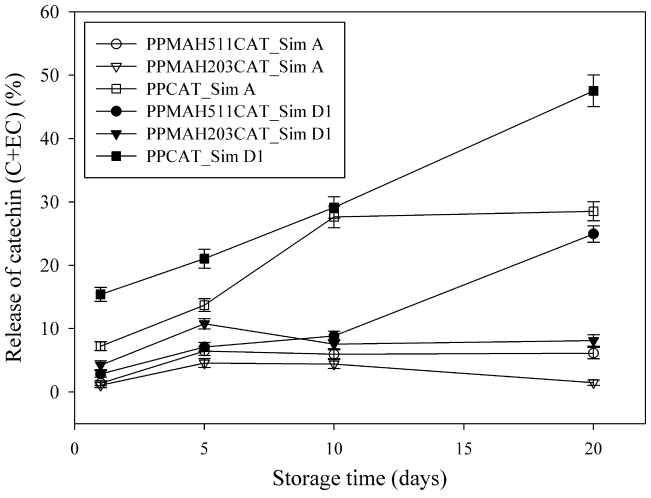

Figure 5. Migration of catechin from PP-grafted films (PPMAH511-CAT, PPMAH203CAT), compared to pure PP film (PPCAT) at 40 °C during an analysis period of 20 days.

calculate the percentage of catechin and epicatechin released. Although quantification of catechin retained into the films was attempted by means of extraction with both decahydronaphthalene and microwave extraction with different solvents, very low recoveries values were obtained (<50%). Therefore, quantification data were not considered to be appropriate. It is in concordance with the 2007 work of Croptom,[36] who reported that direct determination of such additives in polymers and their extraction with solvents are not always possible, because of possible spectral interferences from other additives, low relatively molecular weight mass matrix oligomers, or the extraction solvents, among others.

Moreover, released catechin data are expressed as the sum of catechin and epicatechin, because epimerization was observed when films were exposed to mild and high temperatures.[37]

Large differences in the rate and amount of migration were observed; these differences were dependent on the type of PP used, grafted films versus nongrafted films, and on the type of food simulant. When nongrafted PP films are exposed to 40 °C, catechin concentration in simulant increased gradually according to its release from the film. After 20 days of storage, the antioxidant concentration in simulant D1 (50% ethanol) reached 50% of the nominal content, but only 30% in simulant A (10% ethanol). These data mean that half of the incorporated catechin has been released after a short storage time in food simulant D1. Conversely, the use of grafted PP has notably changed the ability of the polymer to release catechin into the food simulant over time: the amount of catechin released decreased with increasing the degree of grafted PP. In fact, compared to the migration from PP films, the amount of catechin released from both MAH-grafted PP films decreased between 2-fold and 5-fold into Simulant D1, and between 2-fold to 20-fold into Simulant A, depending on the contact time.

There was also a large difference in the migration of catechin between the two food Simulants A and D1. As expected from catechin solubility parameters, the release of catechin into aqueous food simulant (Simulant A) was significantly lower than the release into fatty food simulant (Simulant D1). At room temperature, catechins are slightly soluble in water (2.26 g L^{-1}) but highly soluble in ethanol (50 g L^{-1}).[38]

On the other hand, time and temperature also showed a significant effect with regard to the release of catechin from materials into food simulants. In Figure 5, the time dependence is clear: the higher the contact times, the broader the difference between grafted and nongrafted samples. Regarding the effect of temperature, the antioxidant concentration released into both simulants was significantly smaller at 25 °C than at 40 °C (see Figure 6). This result can be related to an increase in

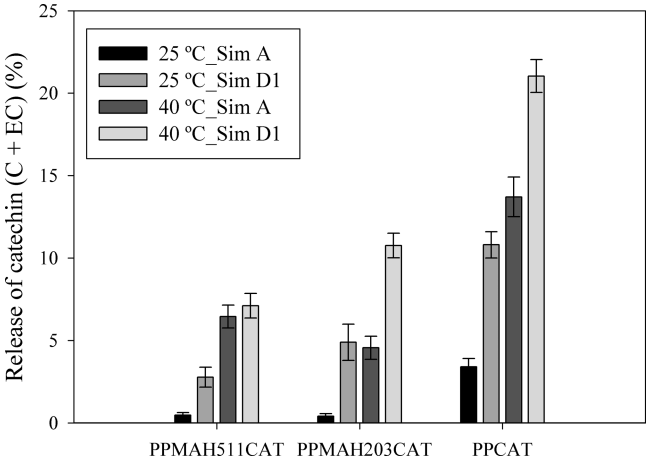

Figure 6. Catechin released (expressed as sum of epimers catechin and epicatechin) after 20 days of storage.

vibration and motion of polymers chains as temperature increased, favoring the migrant movement through amorphous zones of the polymer.[39]

Antioxidant Activities of the Materials. The extent of the antioxidant activity can be characterized by the partition coefficient, *K*, which is defined as the ratio of the amount of catechin in the polymeric phase, relative to the concentration of released catechin. The *K* values, which are displayed in Figure 7, show the influence of both the type of solvent where the radicals are immersed and the morphology of the evaluated systems. As Figure 7 shows, PPMAH blends presented higher values of *K*; the immobilization of catechin through the interaction between maleic anhydride groups in the PPMAH polymers inhibited its release, decreasing the antioxidant activity. Differences in the value of *K* were also noticeable between methods, because of the limited solubility of catechin in water. Antioxidant activity was higher for the DPPH assay ($K < 100$), because of the higher solubility of catechin in ethanol.

The kinetics of the antioxidant activity as $ABTS^{\bullet+}$ and $DPPH^{\bullet}$ scavengers followed similar profiles for the different materials. From a kinetics point of view, the antioxidant activity is dependent on the release of catechin into the radical-containing solution, which is further dependent on the diffusion of the migrant through the polymer matrix and the extent of the process. The diffusion coefficient (*D*), as defined in Fick's laws, is commonly used to characterize the kinetics of transport in polymeric matrices and reports about material morphologies.[31,40]

The *D* values that best fit the experimental results for both antioxidant assays in all evaluated systems are plotted in Figure 7. *D* values were calculated using the equation that yielded the best fit to experimental data. For the ABTS assay, there was good agreement between the theoretical values and the

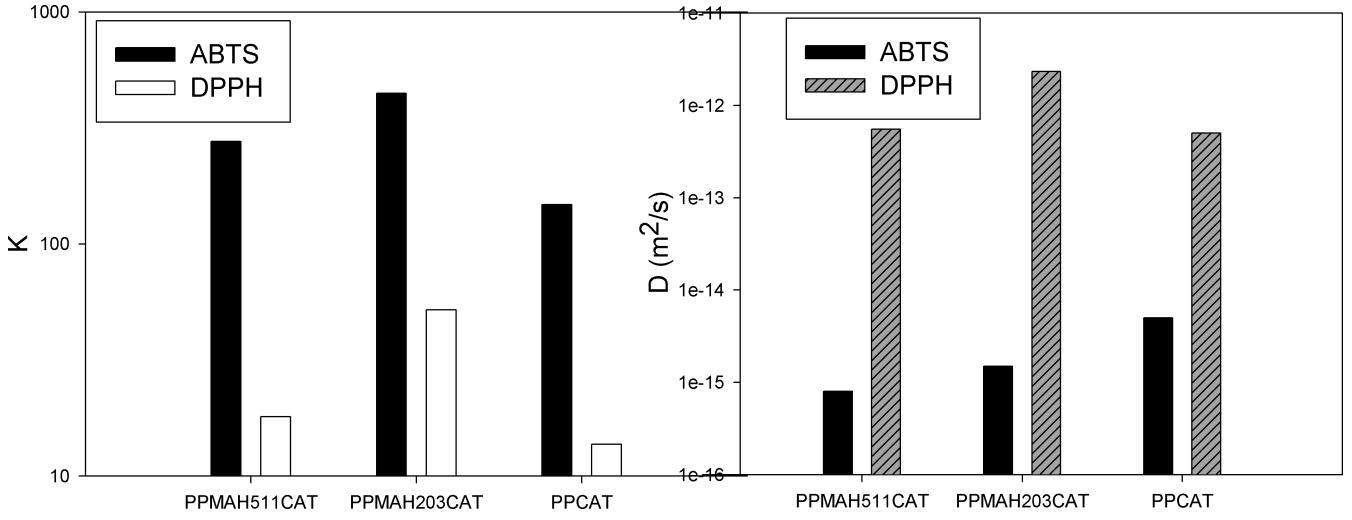

Figure 7. Partition and diffusion coefficients of catechin (K and D, respectively) of developed materials for ABTS and DPPH assays.

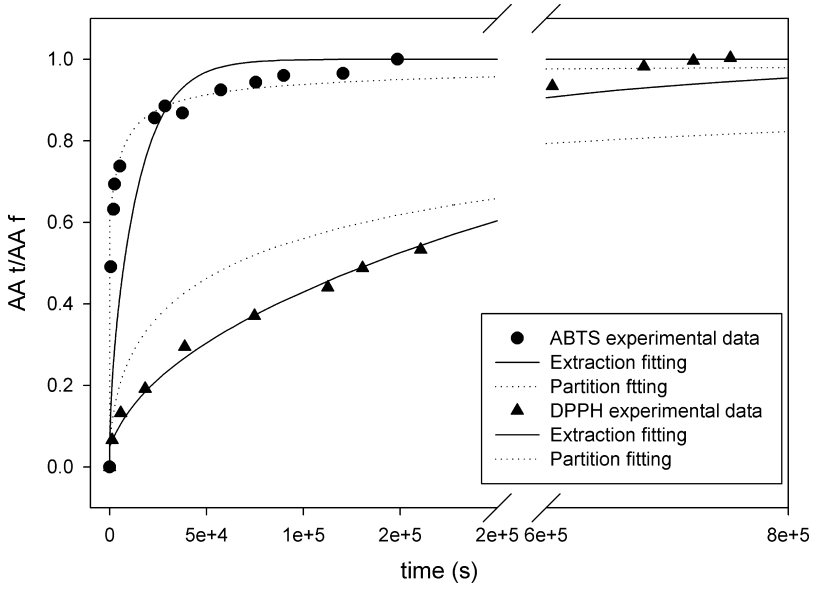

Figure 8. Antioxidant activity of catechin from PPMAH511CAT material as ABTS and DPPH radical scavengers: symbols represent experimental data, and lines are values predicted using eq 1, in the case of partition model for ABTS data assay, and eq 3, in the case of extraction model for DPPH method, both calculated with the K and D values indicated in Figure 7.

experimental antioxidant activities applying eq 1. Conversely, eq 1 did not describe the experimental results obtained from the DPPH assay. The model applicable to the antioxidant activities in an extraction process clearly fit better. Equation 3 is the Fickian solution to this case, in which diffusion is the only variable controlling the process:

$$\frac{m(t)}{m_S^f} = \left[1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left(\frac{-D(2n+1)^2\pi^2 t}{l^2}\right)\right] \quad (3)$$

It is obvious from Figure 8 that the extraction model described the catechin release from the designed materials to the DPPH solution better than the partition model. Similar behavior was described in 2012 by Iñiguez-Franco et al., who reported on diffusion studies of catechin and epicatechin from PLLA.[41] When materials were exposed to 95% ethanol, the systems were considered with an infinite simulant volume, because the release of the antioxidants was almost complete, and eq 3 provided a better fit to obtain D. These findings indicated that, in DPPH tests, a large proportion of catechin added to the polymer formulation was extracted during the test; by contrast, the molecules remaining in the polymer were not available for transport. That is to say, they have been immobilized within the polymer matrix. The remaining catechin fraction could only be released during a extraction process in a mixture of dichloromethane and methanol, and even so, not completely. Figure 8 shows the curves obtained using the K and D values determined from Figure 7.

Other active films using different antioxidants have been studied in previous papers. The levels of antioxidant added to these films are lower than catechin levels used in the present study. Therefore, antioxidant activities also are minor.[42]

CONCLUSIONS

An improvement on thermal stability and a reduction of catechin release levels is shown by films with maleic anhydride

(MAH)-modified polypropylene (PP). This behavior has been related to interactions between catechins and MAH groups.

Therefore, considering real food packaging applications, catechin loaded MAH-grafted PP materials have been proven to be effective systems for controlled release of the antioxidant during longer periods of time, with catechin also being available in the film formulation to protect it from aging (or its own degradation). Besides, with this system, a great release of the active compound during the first days is avoided, with the remaining additive in the polymer being intended for greater protection of both the polymer and the food.

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Notes

The authors declare no competing financial interest.

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