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Effect of PPG-PEG-PPG on the Tocopherol-Controlled Release from Films Intended for Food-Packaging Applications

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Supporting Information

ABSTRACT: The feasibility of novel controlled release systems for the delivery of active substances from films intended for food packaging was investigated. Because polyolefins are used highly for food-packaging applications, the reported high retention degree of antioxidants has limited their use for active packaging. Thus, in this study, PP films modified with different chain extenders have been developed to favor and control the release rates of the low molecular weight antioxidant tocopherol. The use of different chain extenders as polymer modifiers (PE-PEG M_w, 575; and PPG-PEG-PPG M_w, 2000) has caused significant changes in tocopherol-specific release properties. High-performance liquid chromatography coupled to PDA-FL and PDA-MS was used to test tocopherol and chain extender migration, respectively. The release of tocopherol from the prepared films with two chain extenders into two food simulants was studied. Different temperatures and storage times were also tested. Varying the structural features of the films with the incorporation of different levels of PPG-PEG-PPG, the release of tocopherol (food-packaging additive) into different ethanolic simulants could be clearly controlled. The effect of the temperature and storage time on the release of the antioxidant has been outstanding as their values increased. The migration of the chain extender, also tested, was well below the limits set by European legislation.

KEYWORDS: *PPG-PEG-PPG, tocopherol, controlled release*

1. INTRODUCTION

Traditionally, food packaging provides protection against contamination by external agents such as water, light, or odorants; however, increasing demands for greater safety and quality have led to the development of new concepts in food packaging.[1] Active and intelligent packagings are intended to prevent or retard any deterioration quality of packaged foods by including the concept of the controlled release of active compounds to foodstuffs. Thus, they show a great potential to improve storage stability without adding an excess of additives to food,[1−3] which could also cause neutralization or rapid diffusion into the bulk of food.[4]

Polymeric materials react with oxygen, producing chemical aging or degradation of the polymer, which may be associated with irreversible changes in their chemical structure such as reduction in molecular weight, increased melt flow index, and worsened physical and mechanical properties.[5,6] Therefore, the use of stabilizers against mechanical and thermo-oxidative phenomena is a key factor to preserve polymer physical and mechanical properties over time.[7,8]

Synthetic antioxidants, such as butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), or Irganox 1076, have been used extensively.[9,10] Their low molecular weight also makes them suitable for migration from the package into foodstuffs. Nevertheless, there has been an emerging concern regarding their possible toxicity and carcinogenic potential.[9−12]

In short, antioxidants are widely used in plastic formulations both to protect the film from degradation and to improve the oxidation stability of food lipids.[13,14] They can prolong the food shelf life since they can be released in a controlled manner from the antioxidant active packaging into the food.[2]

An increasing interest in the application of natural antioxidants such as tocopherol, carnosic acid, oregano, savory, and essential oils, carvacrol or hydroxytyrosol,[15] has been developed recently. Besides being effective antioxidants for reducing oxidation in foods, tocopherols are also excellent stabilizers for polymer processing since they have proved to be very stable under processing conditions and very soluble in polyolefins.[16,17] Therefore, tocopherols could serve dual functions when added to packaging: as a stabilizer for polymer processing and as an antioxidant in controlled release to reduce oxidation.[3] They are also nontoxic compounds with a positive public perception classified as substances generally recognized as safe (GRAS) for intended use in food.[18]

Low-density polyethylene (LDPE) and, especially, polypropylene (PP) are two of the most commonly used polymers in packaging applications involving contact with food.[19] The use of antioxidants is especially essential to preserve PP due to its numerous tertiary carbons, which are very sensitive to oxidation and radical degradation.[7,20] However, a high retention degree of tocopherols in both LDPE and PP in contact with foodstuffs and food-simulating liquids has been reported, being practically total in the latter.[19,21,22] Thus, the use of tocopherols as additives for active PP packaging materials may be limited. In

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Table 1. Composition of the Different Tocopherol-Based Antioxidants Tested

Tocobiol-PV		Nutrabiol-T50 PV		Nutrabiol-T90	
Tocobiol	65.0%	Tocopherols	50.3%	Tocopherols	90.2%
tocopherols	18.6%	α-tocopherol	12.5%	α-tocopherol	15.5%
sterols	9.7%	γ- and β-tocopherol	59.6%	γ- and β-tocopherol	63.3%
squalene	4.3%	δ-tocopherol	27.9%	δ-tocopherol	21.1%
monoglycerides	19.8%	vegetable oil	9.7%	vegetable oil	9.8%
rest: vegetable oil		excipient: silica gel	40.0%		
excipient: silica gel	35.0%				

Table 2. Composition of the Prepared Film Samples and OIT Values for Stabilized and Nonstabilized PP at 200 °C

		commercial antioxidants (%)		tocopherol-based additives (%)			extensors (%)		
sample code	matrix (PP)	I168	I1010	Nutrabiol T90	Tocobiol PV	Nutrabiol T50 PV	PE-PEG	PPG-PEG-PPG	OIT values (min^{-1})
M1	X								4.20
M2	X	0.2							4.50
M3	X		0.4						24.00
M4	X	0.2		5					133.9
M5	X	0.2	0.4						56.01
M6	X	0.2	0.4	5					188.1
M7	X			5					140.4
M8	X			1					53.43
M9	X			0.5					29.85
M10	X				5				28.14
M11	X				1				25.06
M12	X				0.5				15.17
M13	X					5			92.14
M14	X					1			36.63
M15	X					0.5			39.81
M16	X	0.2		1					51.54
M17	X	0.2		1			1		50.82
M18	X	0.2		1			2		51.20
M19	X	0.2		1			5		45.54
M20	X	0.2		1				1	47.00
M21	X	0.2		1				2	41.01
M22	X	0.2		1				5	32.89

that sense, β-cyclodextrin complexation with antioxidants recently has been used as a strategy to try to control antioxidant delivery mainly from LLDPE.[17,23]

Physical, chemical, mechanical, aesthetic, and processing polymer properties can be enhanced or modified by the incorporation of additives. Chain extenders have been blended into polymer matrixes to modify polymeric chain extension, which leads to enhanced physicochemical polymer properties such as stability, degradability, or permeability.[24−26] In this sense, for example, polyethylene glycol has been used recently and widely as a chain extender to improve biocompatibility and degradation rates of polyesters, thus modifying their properties.[27] All of those applications have been reported for polymers such as poly(lactic acid), poly(lactic-*co*-glycolic acid), or polyurethane with certain polar characteristics since the chemical bond between the polymeric matrix and the chain extender should be implemented by the presence of groups able to interact with the hydroxyl groups of the latter. However, little or no applicability in the food-packaging field has been reported for them.

Therefore, in this work, two block copolymers of polyethylene glycol (M_w, 575) and PP glycol (M_w, 2000) were tested as chain extender additives for the preparation of porous PP films via an extrusion process. The effects of type and amount of chain extender used in the film's formulation on the release of the antioxidant tocopherol from the polymer were studied. The influence of the type and amount of tocopherol as well as the type of foodstuffs or food simulant in contact, temperature, and time conditions were also discussed. Some physical properties of the blend films were also studied.

2. EXPERIMENTAL SECTION

2.1. Materials. PP ISPLEN^R PP 070 G2M was provided by Repsol YPF. Nutrabiol T90, Tocobiol PV, and Nutrabiol T50 PV were supplied by BTSA (Madrid, Spain). Irgafos 168 [Tris(2,4-di-*tert*-butylphenyl)phosphate; I168], Irganox 1010 [pentaerythritol tetrakis-(3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate, I1010], polyethy-

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lene-*block*-poly(ethylene glycol) (PE-PEG), and poly(propylene glycol)-*block*-poly(ethylene glycol)-*block*-poly(propylene glycol) (PPG-PEG-PPG) were supplied by Sigma-Aldrich (Steinheim, Germany).

Methanol and ethanol (EtOH) high-performance liquid chromatography (HPLC) gradient for instrumental analysis were supplied by Merck (Darmstadt, Germany). Formic acid (98−100% puriss p.a.) was from Sigma-Aldrich. Water was purified using a Milli-Q Ultrapure water-purification system (Millipore, Bedford, MA). Table 1 shows the composition of the different antioxidants tested (information provided by the company).

2.2. Polymer Samples Manufacture. The monolayer compounding packaging was prepared, and subsequently, extrusion of PP, commercial antioxidants I168 and I1010, tocopherol-based additives Nutrabiol T90, Tocobiol PV, and Nutrabiol T50 PV, and/or PE-PEG and PPG-PEG-PPG chain extenders at different composition ratios was performed (Table 2).

Extrusion was carried out using a miniextruder equipped with twin conical corotating screws and a capacity of 7 cm^3 (Minilab Haake Rheomex CTW5, Thermo Scientific). A screw rotation rate of 40 rpm, temperature of 180 °C, and 1 min of residence time were used.

2.3. Release Studies. Release tests were performed by total immersion of rectangular strip film pieces (80 mm × 0.4 mm × 0.17 mm) in 9 mL of food simulant contained in a glass-stoppered tube with PTFE closures. The migration test parameters were based on the European Commission Regulation No. 10/2011.[28] Two food simulants A (10% EtOH) and D_1 (50% EtOH) were selected; the release tests were conducted at 4 and 40 °C. Samples of all of the treatments were taken at 1, 2, 5, and 10 days of storage. Test materials were also run simultaneously to check for interferences.

After the contact period, the film samples were removed, and the simulants were leveled up to 10 mL. An aliquot was filtered through an Acrodisc^R PTFE CR 13 mm, 0.2 μm filters (Waters, Milford, MA) and analyzed by HPLC. As the polymer test pieces were less than 0.5 mm thick,[29] the surface area of only one side of the film was taken into account to determine the migration value.

Measurements of the stability of the antioxidants were made in the two selected simulants under selected exposure conditions, by storing a solution of the additive in the simulant in parallel with the migrations tests. Analyses were carried out using the same procedure as for the samples.

The release process is normally described by the kinetics of the diffusion of the antioxidant in the film and is expressed by the diffusion coefficient (D). D is usually estimated using the Fickian diffusion model.[30] When the release of antioxidant reached equilibrium, eq 1 is used as the rigorous model for describing the migration controlled by Fickian diffusion in a packaging film:

$$\frac{M_t}{M_{F,\infty}} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} \exp\left[\frac{-D(2n+1)^2\pi^2 t}{{L_P}^2}\right] \quad (1)$$

where M_t is the mass of the migrant in the food at a particular time t (s), $M_{F,\infty}$ is the mass of the migrant in the food at equilibrium, L_P (cm) is the film thickness, D ($cm^2\ s^{-1}$) is the diffusion coefficient, and t (s) is time.

Nevertheless, when release is slow and equilibrium is not reached at the end of the experiment, eq 2 can be used when M_t/M_P is <0.6:

$$\frac{M_t}{M_P} = \frac{4}{L_P}\left(\frac{Dt}{\pi}\right)^{0.5} \quad (2)$$

M_P is the initial loading of antioxidants in the film. D is estimated from the slope of the plot of M_t/M_P versus $t^{0.5}$.

2.4. Methods. *2.4.1. Dynamical Rheological Properties.* The influence of PE-PEG and PPG-PEG-PPG on the dynamic rheological properties of the films was studied using the miniextruder. Measurements of viscosity and shear stress versus share rate were carried out for film samples containing I168 (0.2%), Nutrabiol T90 (1%), and PE-PEG or PPG-PEG-PPG (5%). Test materials without polyethylene glycol copolymers were also tested. Measurements were carried out at 180 °C in the frequency region from 5 to 200 rpm.

2.4.2. Differential Scanning Calorimetry. Film samples of the extruded polymers (Table 2) were taken out for oxidation induction time (OIT) measurements. The OIT was measured on a Perkin−Elmer series 7 DSC isothermally at 200 °C under an inert atmosphere, which was subsequently switched to an oxygen atmosphere. Analyses were carried out according to EN 728:1997.[31] The obtained results are means of two measurements.

2.4.3. Chromatographic Methods Conditions. 2.4.3.1. HPLC−Photodiode Array Detection (PDA)−Fluorescence Detection (FL). A Waters 2695 (Waters) HPLC system with a gradient pump and automatic injector was used for the HPLC analysis. The chromatographic experiments were carried out using a stainless steel column 150 mm × 3.0 mm packed with SunFire C_{18}, 3.5 μm particle size (Waters), kept at 35 °C. Detection was carried out using a model 996 UV PDA and a model 2475 FL (Waters). PDA detection was performed in the range between 200 and 500 nm. Two hundred ninety-five nanometers was selected as quantification wavelength. $\lambda_{excitation}$, 295 nm, and $\lambda_{emission}$, 325 nm, were selected for fluorescence quantification. The output signals were monitored and integrated using a personal computer operated under the Empower software (Waters). A two-solvent gradient elution was performed, with a flow rate of 0.5 mL min^{-1} and injection volume of 20 μL. The mobile phase was composed of water (A) and methanol (B). Used was the following gradient elution profile: mobile phase composition started at 30% B and was maintained for 0.5 min. Then, it was linearly increased to 90% B in 2 min, maintained for 1 min, and linearly increased to 100% B in 0.5 min. Finally, it was maintained for 10.5 min and brought back to the initial conditions.

Each compound was identified by the comparison between its retention time employing spectroscopic and fluorescence detection with corresponding peaks in the standard solution and its UV spectrum. The quantification of the analytes was carried out using a calibration plot of an external standard.

2.4.3.2. HPLC−Mass Spectrometry (MS). An Agilent 1200 Series Rapid Resolution LC system (Agilent Technologies, Waldbronn, Germany) equipped with an online degasser, a binary pump delivery system, a high-performance SL autosampler, a thermostatted column department, and online coupled to a mass spectrometer was used for analysis. Samples were filtered through a 0.2 μm Acrodisc^R PTFE CR (Waters) and injected in Zorbax SB-C18 (50 mm × 2.1 mm, 1.8 μm) column (Agilent Technologies). A mobile phase system consisting of a mixture of water−0.1% formic acid (A) and methanol (B) under the following gradient system was used. The mobile phase initially set at 30% B was linearly increased to 100% B in 3 min and maintained for 13 min. It was then brought back to initial conditions. The mass spectrometer was an Agilent 6410 Triple Quad LC/MS (Agilent Technologies). The column effluent was directly introduced into the triple quadrupole mass detector operated in a positive ionization mode. Ions were formed using electrospray ionization (ESI). Used were the following ESI source parameters: the temperature of the drying gas (N_2) was set to 350 °C and flowed at 10 mL min^{-1}. The nebulizing pressure (N_2) was maintained at 35 psi. The capillary voltage was set at 4 kV. Integration and data elaboration were performed using Agilent MassHunter Workstation software, version B03.00 (Agilent-Technology, Santa Clara, CA). The full mass scan range was m/z 50−1000 (1 s/scan), and the target ions generated by PE-PPG and PPG-PEG-PPG were as follows: $(M + H)^+$: m/z 637, 652, 681, and 695. Selective ion monitoring (SIM) was used to quantify the target ions. Mass spectral data and retention times were used for peak identification. Quantification of extender was based on an external standard calibration method.

2.4.4. Spectroscopic Characterization of the Chain Extender. PPG-PEG-PPG chain extender stability was tested through its chemical structure by means of Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance (NMR). FTIR was performed in the transmission mode with an OPUS/IR PS 15 spectrometer (Bruker, Germany). The spectra were the results of 32 coadded interferograms at 2 cm^{-1} resolution between 400 and 4000

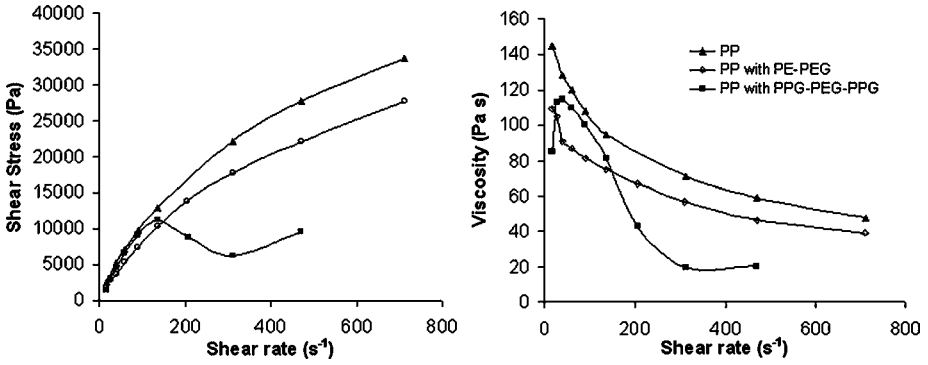

Figure 1. Rheological curves of PP films containing two types of chain extenders: PE-PEG and PPG-PEG-PPG.

cm^{-1}, using a cell specially designed for liquids. ^1H NMR spectra were measured at room temperature by a Bruker AVANCE 500 (Bruker) spectrometer. Samples dissolved in *D*-chloroform ($CDCl_3$) at a concentration of 1×10^{-4} M were tested to determinate the chemical structure.

3. RESULTS AND DISCUSSION

Several commercial antioxidants formulated with tocopherol are comercially available. Among them, Nutrabiol T90, Tocobiol PV, and Nutrabiol T50 PV were assayed as tocopherol based additives in this paper (Table 1). The thermal stability of these commercial tocopherol-based antioxidants under processing temperature significantly differed from that of naturally occurring tocopherols. According to Barbosa-Pereira et al.,[32] dynamic experiments conducted under oxidant atmosphere in a thermo balance has indicated that the degradation process of those antioxidants did not begin until roughly 250 °C, well above the PP processing temperature (180 °C).

The most appropriate tocopherol-based additive was first selected through OIT values. Aimed at controlled release, migration of tocopherol from processed films into food simulants was then measured. To the desired film application, the factors influencing the migration process were tested considering the film application.

3.1. Assessing Chain Extender Influence on Processability. To predict the behavior during material handling when chain extenders are used in films formulations, dynamic rheological properties of the films were studied. The rheological curves of PP films containing two types of chain extenders, PE-PEG and PPG-PEG-PPG, are shown in Figure 1 and compared with PP without chain extender. As the shear was increased, the viscosity decreased. Until roughly 136 s^{-1}, all of the materials showed a similar decrease in viscosity; nevertheless, over it, PP with PPG-PEG-PPG showed a greater decrease in viscosity, which may prevent its processing and comparison with the other formulations under the same conditions. Thus, 136 s^{-1} (roughly 40 rpm) was selected as the most adequate processing condition.

3.2. Selection of the Most Suitable Additive. As the OIT is a relative measure of the degree or level of stabilization of the material tested, the longer the OIT, the more stable is the material. To assess the oxidation stability of the samples with different proportions of Nutrabiol T90, Tocobiol PV, and Nutrabiol T50 PV, OITs of pure and doped PP were measured by means of DSC. They were also compared with samples doped with synthetic antioxidants, Irganox 1010, and Irgafos 168. The influence of the chain extenders (PE-PEG and PPG-PEG-PPG) on the oxidation stability of the samples was also tested. The obtained results for OIT at 200 °C are compiled in Table 2. Tocopherol-based additives showed very good performance as stabilizers of PP, as higher values for OIT than those for the control samples were achieved.

As it was expected, there were no important differences in OIT values between the nondoped PP and the Irgafos 168-doped PP (M2) samples (4.20 vs 4.50, respectively). It is because Irgafos 168 acts as a decomposer of hydroperoxides, and OIT only measures stabilization if the compounds act as a hydrogen atom donor.[33] Doping PP with a mixture of Irgafos 168 and Irganox 1010 led to a higher stabilization. From Table 2, it is evident that Nutrabiol T90, Tocobiol PV, and Nutrabiol T50 PV increased PP oxidative stability to almost the same extent of Irganox 1010, even though different amounts of Irganox 1010 and tocopherol-based additives were used (0.4 vs 0.5−5%, respectively). OIT values for the stabilized PP increased with the concentration for all of the tocopherol-based additives, in agreement with the fact that in polymer matrices containing fairly uniform antioxidant dispersions, the OIT increases approximately linearly with increasing antioxidant concentration.[34] The addition of 0.5% antioxidant did show stabilization, as OIT was prolonged for more than 20 min. It is a clear indication of the good stabilization obtained with the addition of low amounts of antioxidant to PP. Furthermore, at the same concentration level, the maximum onset time was measured for Nutrabiol T90, confirming that in the range tested, the highest content of tocopherol led to the highest PP stabilization (Nutrabiol T90 > Nutrabiol T50 PV > Tocobiol PV).

3.3. Release of Tocopherol from Film into Food Simulant. The use of tocopherols as additives for active PP packing materials has been limited by their practically total lack of migration into foodstuffs and food-simulating liquids.[19] To achieve a useful migration level of tocopherol, the possibility of including PE-PEG and PPG-PEG-PPG in the PP formulation was tested. The preparation of porous PP films with chain extender additives was via extrusion process. OITs of those pure PP and doped with different proportions of PE-PEG and PPG-PEG-PPG showed an almost negligible influence of the chain extender onto the oxidation stability of the sample, even though a very slight decrease of OIT is observed by increasing the amount of chain extender in the polymeric formulation.

The effects of film composition as well as thermal and temporal conditions on the antioxidant levels released from the film were tested. One percent of Nutrabiol T90 was selected as the most appropriate concentration for the release studies since

some tocopherol exudation from PP doped with 5% of Nutrabiol T90 was observed.

3.3.1. Effect of Chain Extender on the Release of Tocopherol. To determine the effect of the incorporation of chain extender on the release of tocopherol from the film, two block copolymers of polyethylene glycol and PP glycol of different molecular weights, PE-PEG (M_w, 575) and PPG-PEG-PPG (M_w, 2000), at three levels of concentration (1, 2, and 5%) were tested as chain extender additives for the preparation of porous PP films (formulations M17−M22, Table 2). They were brought into contact with 50% EtOH (simulant D_1). The release tests were conducted at 40 °C. Samples were taken at 1, 2, 5, and 10 days of storage and analyzed by means of HPLC-PDA-FL. Test materials (M16, Table 2) were also run simultaneously to check for interferences. Figure 2 shows the

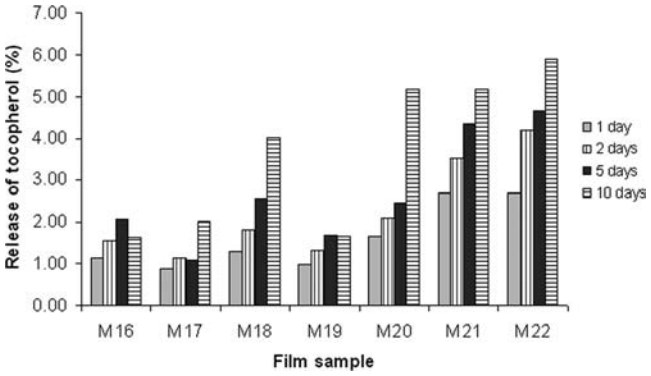

Figure 2. Influence of chain extender on release of tocopherol from films M16 to M22 in contact with simulant D1 at 40 °C, 1−10 days.

migration of Nutrabiol T90 as δ-tocopherol because this showed to be the most stable isomeric form of tocopherol (coefficient of variation <1% for δ-tocopherol vs CV > 10 and 60% for γ- and α-tocopherol, respectively, under the same studied conditions). The use of PE-PEG as a chain extender has barely changed the ability of the polymer to release tocopherol into the food simulant D_1 in comparison with the blank samples. Nevertheless, PPG-PEG-PPG showed a significant effect with regard to the antioxidant migration into the food simulant D_1. The maximum levels of tocopherol released from films containing PPG-PEG-PPG were between 2- and 3.6-fold higher than the corresponding films containing PE-PEG. Moreover, Figure 2 shows the gradual increase of antioxidant released from the film as the amount of chain extender is increased (just about 2-fold). It could show a slight increase in film porosity when PPG-PEG-PPG is used as a chain extender.[35] Diffusion coefficients (Table 3), estimated by eq 2 (section 2.3), also showed that the release of tocopherol was

Table 3. Estimation of Diffusion Coefficient (D, $cm^2\ s^{-1}$) for the Release of Tocopherol from the Studied Films to Simulants A and D_1 at 4 and 40 °C[a]

	simulant A		simulant D_1	
sample	4 °C	40 °C	4 °C	40 °C
M16	not estimated	4.9×10^{-18}	7.8×10^{-17}	2.9×10^{-13}
M20	1.6×10^{-18}	5.5×10^{-16}	7.2×10^{-15}	1.9×10^{-11}
M21	1.3×10^{-17}	2.4×10^{-18}	9.6×10^{-15}	2.4×10^{-12}
M22	5.2×10^{-15}	2.1×10^{-15}	1.4×10^{-13}	3.1×10^{-12}

[a] D estimated by eq 2, section 2.3.

accelerated by the presence of the chain extender. In the absence of PPG-PEG-PPG, a D ($cm^2\ s^{-1}$) value of 2.9×10^{-13} at 40 °C and into simulant D_1 was estimated. When the chain extender is incorporated, D values ranging from 2.4×10^{-12} to 2.0×10^{-11} $cm^2\ s^{-1}$ were calculated. Hence, adding PPG-PEG-PPG increased tocopherol diffusivity between 1 and 2 orders of magnitude. Moreover, as compared to reported literature diffusion coefficients for the release of tocopherol from PP films,[30] the data from the present work also showed how the incorporation of PPG-PEG-PPG has significantly improved the release of tocopherol from that material (D of at least 5 orders of magnitude higher than that reported in the literature).

3.3.2. Effect of Contact Time and Temperature on the Release of Tocopherol. Both time and temperature during the contact period showed a significant effect with regard to the antioxidant migration of tocopherol from PP + PPG-PEG-PPG systems into food simulant.

Regarding time, release levels of tocopherol were studied over the following range: 1−10 days. Samples analyzed by means of HPLC-PDA-FL showed that increasing amounts of tocopherol were released from the films into food simulant over time (Figure 2). At the end of the storage period, the maximum had not been reached yet. Therefore, the release was expected to continue. A controlled release of antioxidant with time was then proved.

Release tests of tocopherol from PP were also done for two different temperatures: 4 °C aimed to packaging materials for refrigerated food and 40 °C to simulate room temperature conditions. The results obtained using PPG-PEG-PPG as a chain extender and D_1 as a food simulant are reported in Figure 3. From these results, significant differences were found by

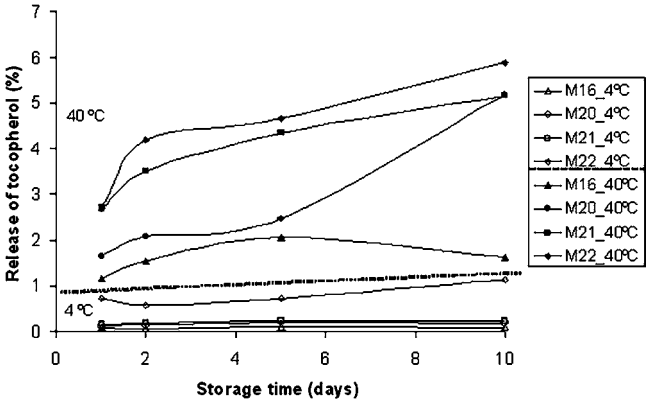

Figure 3. Influence of temperature (4 and 40 °C) on the release of tocopherol from films with PPG-PEG-PPG in contact with simulant D_1 from 1 to 10 days.

effect of temperature when the release of tocopherol from the films at 4 and 40 °C was compared. An increase in the amount of released tocopherol can be observed when the temperature increases, which can be related to an increase in the vibration and motion of polymer chains as the temperature increases, favoring the migrant movement through the amorphous zones of the polymer.[36] In the same way, estimated diffusion coefficients also increase as the temperature does, showing D values ($cm^2\ s^{-1}$) between 1 and 4 orders of magnitude higher at 40 °C than at 4 °C (Table 3).

3.3.3. Effect of Food Simulant on the Release of Tocopherol. Specific release tests designed to determine the dependence of tocopherol released with the food simulants

were performed. At this stage, the tests were carried out at two different temperatures (4 and 40 °C), from 1 to 10 days. Two food simulants were selected to cover a wide range of food products: simulant A (10% EtOH) and simulant D_1 (50% EtOH). Figure 4 shows the percentage of tocopherol migrated from the different studied samples into simulants A and D1.

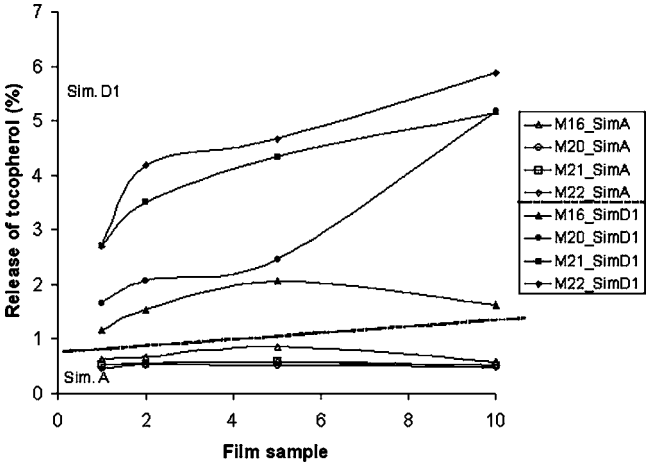

Figure 4. Influence of simulant A (10% EtOH) and D_1 (50% EtOH) on the release of tocopherol from films at 40 °C from 1 to 10 days.

As expected, simulant A was the simulant presenting the lowest levels of migrant. The nonsignificant differences found in the migration of tocopherol from the films could be clearly attributed to the polarity difference, which does not favor the mass transfer of the antioxidant into the food simulant, which results in the very low water solubility of tocopherol. However, the migration increased with the percentage of EtOH in the simulant (Figure 4) because the higher percentage of EtOH in the solution decreases its polarity, favoring the mass transfer of the migrant from the film into the food simulant.[27]

Estimated diffusion coefficients of tocopherol from the studied films into the different simulants (Table 3) also reinforce that statement, showing D values ($cm^2\ s^{-1}$) even 4 orders of magnitude higher as the percentage of EtOH in the simulant is increased. The different migration values obtained indicated that the migration of tocopherol from the polymer also depends on the type of food simulant in contact with the plastic film and the solubility of the migrant into the food simulant tested.

3.4. Migration of Chain Extender from Film into Food Simulant. The introduction of chain extenders into film formulations may be accompanied by the occurrence of their own release from the film into the food or food simulant contained. Because that could have a potential influence on the packed foods properties, their migration was also controlled. However, according to European Regulations,[20] polymeric substances with a molecular mass of at least 1000 Da comply with the requirements of the regulation.

To determine the migration of the chain extender from the film, release tests under the most favorable conditions intended for migration and aimed at the biggest consumer protection were selected: 40 °C, into simulant D_1, from 1 to 10 days. Samples with 1, 2, and 5% of PPG-PEG-PPG were analyzed by means of HPLC-PDA-MS as described in section 2.4.3.

The migration of the chain extender from films was dependent on the storage time and the amount of chain extender in the film formulation. Figure 5 shows the percentage of PPG-PEG-PPG migrated from the manufactured films into

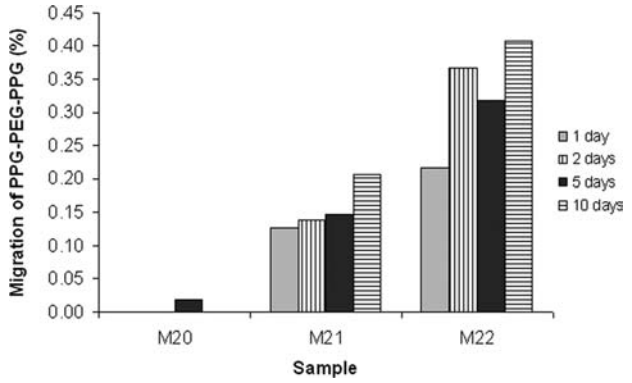

Figure 5. Migration of chain extender PPG-PEG-PPG from film to simulant D_1 at 40 °C from 1 to 10 days.

the food simulant under the tested conditions. The data show that there is essentially no migration from the film when a low amount (1%) of PPG-PEG-PPG was introduced into the film formulation (sample 20). Higher amounts (>2%) of PPG-PEG-PPG have meant slight release of PPG-PEG-PPG from the film.

The effect of the time on the migration behavior can be explained as increased time resulted in higher percentages of PPG-PEG-PPG. This effect is more remarkable, though, the higher is the percentage of extender in the film.

PPG-PEG-PPG as a chain extender is not on the Union list of authorized monomers, other starting substances, and macromolecules;[20] moreover, as having a molecular mass higher than 1000 Da and being capable of forming the main structural component of the plastic material, it complies with the requirements of the regulation. Because no specific migration limit (SML) or other restrictions are provided for it, a generic specific migration limit of 60 mg kg^{1-} shall apply. Migration of PPG-PEG-PPG from all of the studied films resulted in migration levels quite lower than SMLs allowed by legislation. Values ranging from 1 to 25 mg kg^{-1} depending on the type of sample, simulant, and release conditions considered were obtained, which represents 50−98% less than legislation.

3.5. PPG-PEG-PPG Stability Characterization: FTIR and NMR. PPG-PEG-PPG chain extender stability was tested through its chemical structure by means of FTIR and NMR. Pure PPG-PEG-PPG and blended into PP matrix were tested. Spectral FTIR and NMR data are illustrated in the figures in the Supporting Information.

FTIR spectra showed a characteristic hydroxyl stretching band at 3480 cm^{-1}. Moreover, the band at 1095 cm^{-1} can be assigned to the CH, CO, and CC stretch vibrations.

A strong proton signal at δ 3.65 ppm assigned to $-OCH_2CH_2-$ repeating unit in PEG segments and proton signals at δ 3.45, 3.40, and 1.20 ppm associated with $-O(CH_3)CHCH_2-$ a repeating unit of PPG were observed by NMR.

Regardless of intensity considerations, the presence of such bands into PP + PPG-PEG-PPG extruded samples supported PPG-PEG-PPG no degradation through the extrusion process. Thus, this study clearly showed the good potential of PPG-PEG-PPG as a PP modifier to control the release of tocopherol. Changing the composition of the film by using the chain extender, the desired release rates of tocopherol were obtained.

The percentage of PPG-PEG-PPG and tocopherol into the film composition, as well as storage time and temperature, were key factors to control the release process. The higher the tocopherol and chain extender concentrations in the films are, the higher the amount of antioxidant is that migrated from the film into the food simulant. Increasing the PPG-PEG-PPG content from 0 to 5% has resulted in an increase of tocopherol released from 50 to 75%, depending on the contact time. The storage time and temperature also had a great effect on migration. An increase in the storage temperature from 4 to 40 °C and in time from 1 to 10 days resulted in a significant increase in the migration (from 70 to 95 and from 20 to 55%, respectively, as temperature and time were increased). It could be related to an increase in vibration and motion of polymer chains as the temperature increases, favoring the migrant movement through the amorphous zones of the polymer.

No significant differences in migration from the films were found toward the simulant A (10% EtOH). Nevertheless, increasing the percentage of EtOH in the simulant D_1 (50% EtOH), higher migration levels were found. An 80−90% increase of tocopherol was released depending on the film sample considered.

Although PPG-PEG-PPG was introduced as a new component into the polymer composition, its migration from the polymer into the food simulant has resulted to be well below the limits set by European legislation. Thus, the PP-modified films for controlled release of tocopherol have shown good potential to ensure the availability of the antioxidant to protect the film and the packed product in conditions of storage and commercialization using a material based on PP from which the absence of released properties has been previously reported.

■ ASSOCIATED CONTENT

Supporting Information

Figures of FTIR spectra and ^{1}H NMR spectrum. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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■ ABBREVIATIONS USED

BHT, butylated hydroxytoluene; BHA, butylated hydroxyanisole; ESI, electrospray ionization; EtOH, ethanol; FL, fluorescence detection; FTIR, Fourier transform infrared spectroscopy; GRAS, generally recognized as safe; HPLC, high-performance liquid chromatography; I1010, pentaerythritol tetrakis(3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate; I168, Tris(2,4-di-*tert*-butylphenyl)phosphate; LDPE, low-density polyethylene; MS, mass spectrometry; OIT, oxidation induction time; PDA, photodiode array detector; PE-PEG, polyethylene-*block*-poly(ethylene glycol); PP, polypropylene; PPG-PEG-PPG, poly(propylene glycol)-*block*-poly(ethylene glycol)-*block*-poly(propylene glycol); NMR, nuclear magnetic resonance; SIM, selective ion monitoring

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