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ORIGINAL PAPER

Characterization of blends of PP with vitamins “C” and “E” exposed to gamma radiation at sterilization dose

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Abstract In this study, the influence of two vitamins (C and E) on the properties of isotactic polypropylene (PP) exposed to gamma radiation at the minimal sterilization dose of 25 kGy was evaluated. To do so, PP was blended in solution with the vitamins at varying concentrations. These formulations were irradiated with gamma rays at a dose of 25 kGy from a ^{60}Co source and then characterized using different techniques such as FTIR, GPC, DSC, TGA, and tensile testing. The incorporation of the different vitamins, either individually or combined, did not avoid the formation of carbonyl groups in the PP after irradiation. Moreover, the average molecular weight of the polypropylene decreased significantly, even in those samples where the additives were present. Tensile tests unfolded an increased stiffness in those samples with individual additives, whereas a decrease was detected in those systems with a combination of them. A decrease in both tensile strength and elongation at break was displayed by the compounds when compared to irradiated PP. An increase in the crystallization temperature was detected when Vitamins C and E were incorporated into the PP, which demonstrated a nucleating effect of these

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compounds. The highest nucleating effect was found for concentrations of 0.3% of Vitamin E and 0.5% of Vitamin C. For these formulations, more homogeneous melting endotherms and narrower crystallization exotherms were obtained. An increase in the nucleating density in PP was observed as well, when a combination of Vitamins E/C (0.5/0.5%) was employed.

Keywords Polypropylene · Vitamin C · Vitamin E · Gamma radiation · Sterilization dose

Introduction

Polypropylene (PP) is an easily processing polymer widely used in the manufacturing of syringes, security lenses, surgical clothing, etc. due to its high chemical resistance, high melting temperature, and low cost. Medical instruments employed in the diagnosis or treatment of a patient, especially those that can penetrate the protective barrier of the skin, must be completely exempt of germs. Thus, several physical and chemical methods of sterilization such as autoclave, ethylene-oxide treatment, etc., have to be used. Among them, gamma irradiation is one of the most effectives [1].

Sterilization with gamma rays is a safe alternative to effectively reduce the microbe charge without harmful effects to human beings. However, when polymers are subjected to ionizing radiations, some structural changes are produced such as crosslinking and main-chain scissions, which bring about modifications in their properties. During radiation, the surrounding atmosphere (air) has an influence in the degradative process, because oxidation of the polymer is promoted. Free radicals formed during the irradiation process react with oxygen to form peroxide radicals, which are capable of subtracting hydrogen atoms from the main chain and decomposing, generating more peroxide radicals. This mechanism operates especially at low dose rates [1–5].

Vitamin E or α-tocopherol is a monophenolic natural antioxidant, whose chemical oxidation leads to the formation of the dimer, trimer, tocoquinone and aldehydes, which are more stable products [6, 7]. Vitamin E acts as a primary antioxidant in polyolefins, demonstrating an excellent behavior at low concentrations (150 ppm). Its mechanism of action is displayed in Fig. 1, which is similar to that of hindered phenols. Phenolic antioxidants act as radical scavengers, where the key reaction is the transfer of a hydrogen atom from the phenoxyl group of the

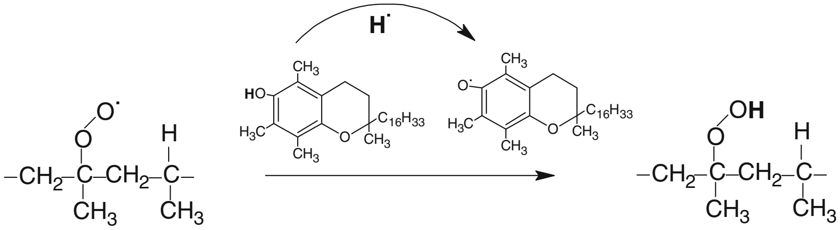

Fig. 1 Mechanism of action of Vitamin E

stabilizer to a peroxy radical in polypropylene, resulting in the formation of a hydroperoxide. The acceleration of the autoxidation through intramolecular H abstraction is effectively prevented [8].

Ascorbic acid or Vitamin C is a very common substance in nature, whose chemical structure is shown in Fig. 2 [6]. Vitamin C is an antioxidant which acts as a reducing agent, owing to its adjacent hydroxyl groups, that can lose a hydrogen and form a semideshydroascorbate radical and oxidise to deshydroascorbic acid. Thus, it is possible to use it to decrease the oxidative degradation of polymers. It acts as secondary antioxidant, decomposing the peroxides into non-radical products [6]. Its mechanism of action is displayed in Fig. 2, which is similar to that proposed by Othmer [9].

In living tissues, Packer at el. [10] reported that Vitamins E and C quickly react with the free radicals present. Reinton and Rogstad [11] studied the antioxidant activity of tocopherol and ascorbic acid onto linoleic acid, when oxidation is catalyzed by lipoxygenases.

On the other hand, Al-Malaika [7] studied the effects of α-tocopherol as thermal stabilizer when added to polypropylene. Additionally, she observed that Vitamin E does not degrade under severe conditions (up to 275 °C). The stability of iPP in the presence of Vitamin E has demonstrated that this substance can be as effective as some commercial antioxidants such as Irganox 1010® by Ciba, when added at concentrations as low as 150 ppm. At higher concentrations, it induces yellowing as a consequence of the formation of the dimer, trimer, tocoquinone, and aldehydes.

Mallégol et al. [12, 13] have reported the use of α-tocopherol as antioxidant in high-density polyethylene and have compared its performance with other known and commonly used stabilizers. Muller et al. [14] also studied the effects of Vitamin E as antioxidant in polyolefins such as PP, low-density polyethylene, high-density polyethylene, and linear low-density polyethylene, when they are extruded in presence of air. They concluded that when Vitamin E is used in a binary system with phenols and phosphites, no discoloring is produced.

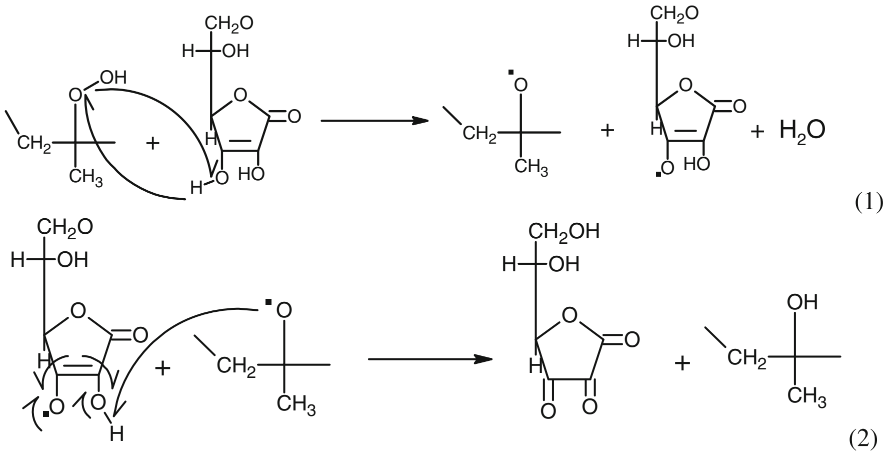

Fig. 2 Mechanism of action of Vitamin C

Based on the previous studies, the influence of adding natural substances such as Vitamins C and E to PP in its resistance to Gamma radiation at a sterilization dose of 25 kGy at room temperature in air at an average dose rate of 1.04 kGy/h was studied. The characterization techniques used were FTIR, DSC, GPC, TGA, and tensile testing.

Experimental

A commercial isotactic Polypropylene (PP J700, MFI: 11 dg/min) supplied by PROPILVEN C.A. of Venezuela was used as received. Two natural substances, known as Vitamins (Vit) E and C from Aldrich and Fisher Scientific, respectively, were employed. Samples of PP with the vitamins were prepared in solution. PP was dissolved in decalin at 165 °C under a nitrogen atmosphere, and then the vitamins were added, keeping a constant temperature and stirring during 3 min. Following the blending, the product was precipitated using ethanol. The resultant solid product was washed with ethanol twice and finally with hexane. The samples were then dried in a vacuum oven for 24 h.

The films and tensile specimens were molded at 190 °C, 6,000–15,000 psi, during 4.5 min. The thicknesses of the samples were 0.08 (films) and 1 (tensile specimens) mm, respectively. The samples were then irradiated at 25 kGy of integral dose with gamma rays from a ^{60}Co source at room temperature in air, at an average dose rate of 1.04 kGy/h. The ^{60}Co source was a MDS Nordiun (IR-216) with a Harwell-Red Perspex dosimeter (range 5–50 kGy, type 4034) located in the Venezuelan Institute for Scientific Research (IVIC).

FTIR spectra were collected from non-irradiated and irradiated films and the carbonyl Index values (I_c) were determined from the peak heights ratio of the carbonyl band from ketones (1,705–1,725 cm^{-1}) and that at 1,165 cm^{-1}, characteristic of the C–CH_3 bond stretching in PP. Differential Scanning Calorimetry (Mettler Toledo Star System, DSC 821) was used to study the melting and crystallization behavior of samples weighing approximately 9 mg. The DSC equipment was calibrated using indium with a melting temperature of 156.6 °C. Nitrogen was used as dragging gas (50 mL/min). Thermograms were recorded from samples cut out from untested tensile specimens. Samples were heated up to 200 °C at a rate of 10 °C/min and this first heating scan was recorded. The polymer was kept at that temperature for 5 min, to erase its previous thermal history. Then, the first cooling and second heating (second scan) thermograms were recorded at a rate of 10 °C/min. Thus, two melting peak temperatures are reported: one corresponding to the first heating scan (T_{m1}), and the other one to the second heating scan (T_{m2}). Likewise, two crystallinity degrees (X_1 and X_2) were determined, following standard procedure, calculating the ratio between the values ΔHm determined as the area under the endotherm peak, and the theoretical ΔH corresponding to the same polymer with a crystallinity degree of 100%. This last value is reported in the literature as 207 J/g [15]. The crystallization peak temperature from the first cooling scan is also reported (T_c).

The molecular weights and molecular weight distributions of the samples before and after irradiation were determined through Gel Permeation Chromatography

(GPC) using a Waters Alliance 2000 equipment with a differential refractive index detector. Three columns of Waters Styragel HT6E, HT5, and HT3 of cross-linked styrene-divinylbenzene copolymer particles in a range of 10^3–10^7 g/mol were employed. The calibration curve was obtained from polystyrene standards of narrow molecular weight distributions. M_w, M_n, M_z, M_{z+1} and the polydispersity values were recorded.

The thermal stability of the samples was analyzed using a Mettler Toledo Star System thermogravimetric analyzer (TGA). The thermograms were recorded at a heating rate of 10 °C/min in nitrogen atmosphere and in a temperature range from 20 to 650 °C. The average weight of the samples was 10 mg. The thermograms were analyzed using the kinetic model proposed by Chen et al. [16] to determine the activation energy (E_a).

The tensile properties of the specimens were tested in an Instron 4204 machine at a cross speed of 1 mm/min. The parameters analyzed were the Young's modulus (E), elongation at break (ε_B), and tensile strength (σ_B).

All samples were analyzed before and immediately after irradiation to minimize possible post-irradiation oxidation and post-irradiation storage effects.

Results and discussion

Table 1 shows the carbonyl index values (I_c) and thermal properties of irradiated and non-irradiated PP, with and without vitamins. As it can be seen, the I_c values

Table 1 Values of carbonyl index and thermal properties of neat non-irradiated PP, neat irradiated PP and irradiated PP with Vitamins E, C, and E/C

Radiation	Vitamin %	$I_c \pm 0.01$	T_{m1} °C ± 1	X_1 (%)	T_{m2} °C ± 1	X_2 (%)	T_c °C ± 1	E_a kJ/mol
Non-irrad. PP	0.0	0.02	168	45	165	53	115	332
Irrad. PP	0.0	0.06	165	49	156	56	114	273
Vitamin E	0.1	0.06	162	49	157	58	117	299
	0.3	0.08	163	49	157	58	119	314
	0.5	0.06	163	53	156	55	118	302
	0.8	0.08	162	54	155	52	115	291
Vitamin C	0.1	0.07	163	56	156	56	117	292
	0.3	0.06	163	53	157	58	120	309
	0.5	0.07	163	47	159	58	120	320
	0.8	0.08	160	47	159	49	117	285
Vitamins E/C	0.1/0.1	0.07	164	49	156	51	116	302
	0.3/0.3	0.08	162	45	155	50	116	318
	0.5/0.5	0.06	163	52	158	55	122	327
	0.8/0.8	0.11	161	59	155	54	118	287
	0.3/0.6	0.08	162	46	156	54	117	312
	0.7/1.0	0.07	162	50	157	52	118	305

increase with radiation. This fact is attributed mainly to the decomposition of hydroperoxides produced during irradiation, which brings about the formation of alcoxy radicals ($RO^{\bullet}$) that give way to chain scissions through the production of carbonyl groups [3, 17, 18].

GPC results indicate that a significant decrease in the average molecular weight of PP results as a consequence of the chain scission mechanism of degradation produced by irradiation. The polydispersity index increases, indicating a more heterogeneous population of molecular sizes in the polymeric material (Table 2).

Table 1 also shows that T_{m2} values are lower than those of T_{m1}, and that X_2 values are higher than those of X_1. These results are attributed to the fact that when samples are first heated up and melted during the DSC analysis, the free radicals still present in the material and trapped in the crystalline zones react quickly, bringing about chain scissions during the analysis, and consequently, a decreased average molecular weight. The decreased molecular weight produces thinner crystals, which melt at lower temperatures during the second scan, and also increases the crystallinity degree, due to an increased mobility of the chains that reorder forming more crystals. These results are in agreement with those reported by Kostoski and Stojanovic [19] and Busfield and O'Donnel [20]. These authors attributed the increased crystallinity degree to a molecular reorganization induced by chain scissions, and the decrease in melting peak temperatures to the decreased sizes and perfection of crystals.

Figure 3 displays the melting endotherms of irradiated and non-irradiated neat PP. As it can be seen, two peaks are present in the irradiated sample. On the contrary, only one endotherm is seen in the non-irradiated material. The presence of

Table 2 Values of average molecular weights and polydispersity index (PD) of neat non-irradiated and irradiated PP, and irradiated PP with Vitamins E, C and E/C

Radiation	Vitamin %	M_n (g/mol)	M_w (g/mol)	PD
Non irrad. PP	0.0	57,028	203,473	3.57
Irrad. PP	0.0	3,725	30,359	8.15
Vitamin E	0.1	6,687	47,979	7.17
	0.3	9,268	55,605	5.99
	0.5	8,398	50,706	6.04
	0.8	7,538	39,398	5.23
Vitamin C	0.1	16,585	52,654	3.17
	0.3	18,019	56,990	3.16
	0.5	28,198	83,773	2.97
	0.8	18,270	43,842	2.40
Vitamins E/C	0.1/0.1	6,380	93,550	6.83
	0.3/0.3	7,005	42,026	6.00
	0.5/0.5	6,823	43,019	6.30
	0.8/0.8	6,244	38,706	6.20
	0.3/0.6	7,705	53,558	6.95
	0.7/1.0	5,127	38,279	7.46

the two peaks is attributed to chain scissions occurring during irradiation. The melting peak located at a higher temperature is associated to populations with higher molecular weights and thicker crystals and that located at a lower temperature is associated to populations with lower molecular weights and thinner crystals. These results are in agreement with those of Yoshii et al. [21].

On the other hand, a decrease in the activation energy results when polypropylene is subjected to irradiation (Table 1). This behavior is attributed mainly to chain scissions, which give way to crystals of different sizes and degrees of perfection, as well as to the fact that irradiation produces defects in the polymer structure which decrease its thermal stability [22].

Table 3 displays the tensile properties of PP at both irradiated and non-irradiated conditions. The Young's modulus value is higher in the irradiated sample, due to molecular reorganization and increased crystallinity [23]. On the contrary, the tensile strength and elongation at break (σ_B and ε_B, respectively) decrease with irradiation, which is attributed to a decreased molecular weight [24]. From the results here presented, a significant degradative effect of the irradiation process onto PP is inferred, which produced chain scission reactions thus affecting the molecular weight, thermal behavior, and tensile properties.

In the irradiated compounds of PP, no significant changes either in the carbonyl index values or in the average molecular weights were ascertained when the vitamins were added. In other words, the addition of vitamins at the different concentrations did not delay the degradative process of PP. Nonetheless, the crystallization temperature (Table 1) increases when Vitamin E or Vitamin C are added to PP. Thus, these vitamins exert a nucleating effect in PP. This result is more important at a concentration of 0.3% of either one, as indicated by an increased crystallinity degree [25]. On the other hand, the activation energy (Table 1) slightly increases with the addition of both vitamins in irradiated samples, probably due to a

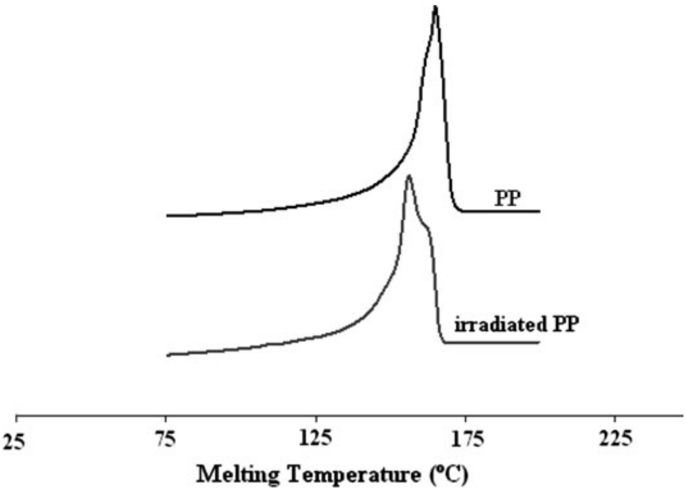

Fig. 3 Melting thermograms of pure PP

Table 3 Values of mechanical properties of neat non-irradiated PP, and neat irradiated PP, and PP with Vitamins E, C, and E/C

Radiation	Vitamin %	*E* (MPa)	σ_B (MPa)	ε_B (%)
Non irrad. PP	0.0	756 ± 10	20.7 ± 1.5	4.69 ± 0.3
Irrad. PP	0.0	1,023 ± 12	9.7 ± 0.1	1.75 ± 0.03
Vitamin E	0.1	768 ± 9	6.4 ± 1.0	0.72 ± 0.05
	0.3	1,096 ± 10	7.6 ± 0.2	1.02 ± 0.01
	0.5	1,224 ± 17	8.6 ± 0.2	0.08 ± 0.02
	0.8	692 ± 8	7.1 ± 0.7	1.07 ± 0.16
Vitamin C	0.1	805 ± 7	7.2 ± 0.2	0.84 ± 0.02
	0.3	1,277 ± 12	8.8 ± 0.1	1.02 ± 0.02
	0.5	1,093 ± 12	8.1 ± 0.3	1.03 ± 0.02
	0.8	923 ± 6	7.3 ± 0.2	0.96 ± 0.07
Vitamins E/C	0.1/0.1	556 ± 27	10.1 ± 2.2	1.84 ± 0.22
	0.3/0.3	561 ± 9	4.81 ± 1.16	0.82 ± 0.17
	0.5/0.5	578 ± 35	10.17 ± 0.8	1.49 ± 0.13
	0.8/0.8	559 ± 34	7.25 ± 1.88	1.21 ± 0.38
	0.3/0.6	632 ± 34	11.59 ± 1.8	1.79 ± 0.25
	0.7/1.0	559 ± 4	4.49 ± 0.1	0.72 ± 0.05

higher number of crystals formed which improves the thermal stability of the polymer.

Two important aspects are analyzed in the crystallization exotherms of irradiated PP, either with Vitamin E or C (Figs. 4, 5): the peak temperatures and peak widths.

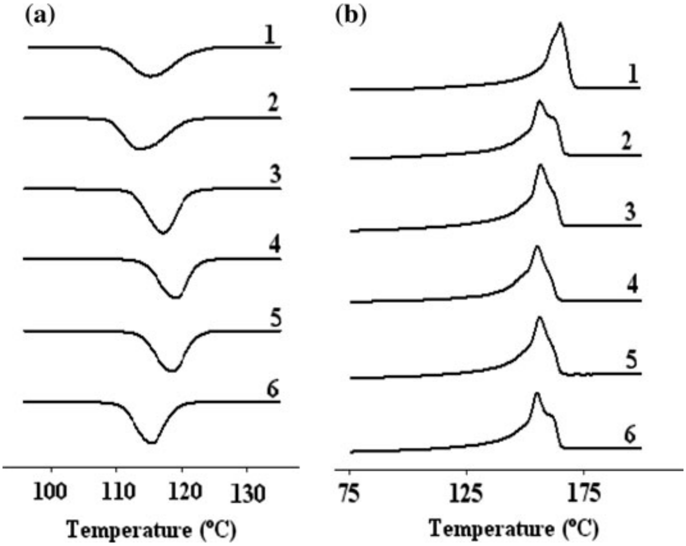

Fig. 4 Crystallization (**a**) and melting thermograms (**b**) of: (1) non-irradiated neat PP; Irradiated: (2) neat PP; (3) PP-0.1 Vit E; (4) PP-0.3 Vit E; (5) PP-0.5 Vit E; (6) PP-0.8 Vit E

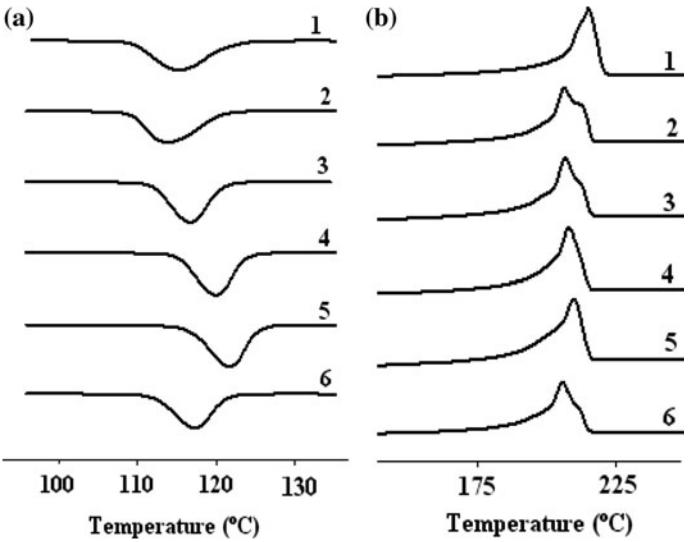

Fig. 5 Crystallization (**a**) and melting thermograms (**b**) of: (1) non-irradiated neat PP; Irradiated: (2) neat PP; (3) PP-0.1 Vit C; (4) PP-0.3 Vit C; (5) PP-0.5 Vit C; (6) PP-0.8 Vit C

As the different concentrations of vitamins are added up to 0.5%, the peak temperature increases, indicating the nucleating effect already mentioned. Similarly, a decrease in the peak width was obtained in those same compounds when compared to neat PP, as a sign of more homogeneous crystal populations [26].

The melting thermograms of irradiated PP, with or without vitamins are also displayed in the same Figs. 4 and 5. When pure PP is irradiated, a second melting peak appears at a lower temperature. Non-irradiated PP displays only one peak at a higher temperature and a small shoulder at a lower temperature. As the different concentrations of the vitamins are increased (up to 0.5%) only one peak is obtained. As the nucleating effect is increased (at 0.3%), a more uniform endotherm is obtained. At a concentration of 0.8% of both vitamins, the second melting peak again appears, indicating that heterogeneous populations of crystal sizes are present once again.

Tensile results from Table 3 show that in general there seems to be a slight increase in the Young's modulus when the vitamins are incorporated into PP at 0.3 and 0.5%, when compared to that of neat irradiated PP. This increase could be related to a higher crystallinity degree due to the nucleating effect of those vitamins. On the contrary, both tensile strength and the elongation at break seem to decrease when vitamins were incorporated into the formulation and it was irradiated. This behavior could be attributed to a decrease in the molecular length of the polymeric chains as a consequence of oxidative degradation. According to Kadir et al. [27], the incorporation of a nucleating agent into PP decreases its stability against radiation, because of a decreased size of the spherulites.

Different combinations of both vitamins added simultaneously (C and E) were also studied and their effect analyzed. Packer et al. [10] observed a synergistic effect

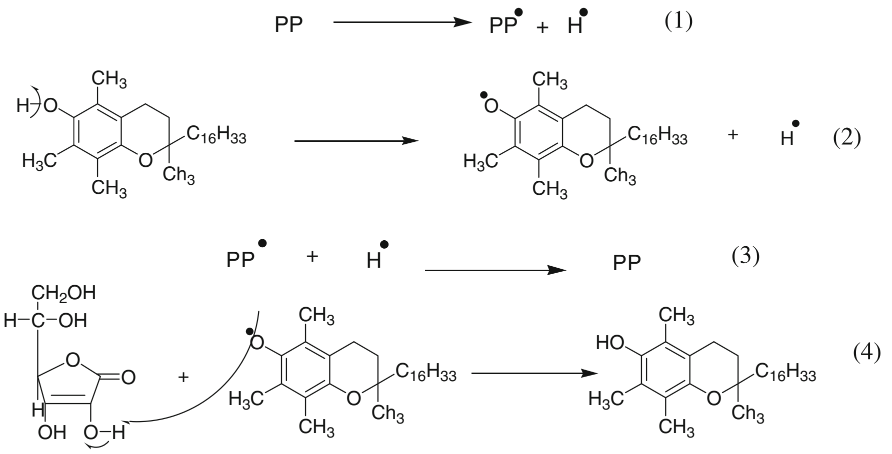

Fig. 6 Synergy mechanism of regeneration of vitamin E by vitamin C

between both vitamins, due to the fact that Vitamin C is effective regenerating tocopherol, introducing the freed hydrogen and thus reducing the tocoperoxyl radicals [6]. Figure 6 unfolds the synergistic mechanism when Vitamins C and E are used in combination as stabilizers. The reaction mechanism is initiated by the interaction of gamma radiation with the PP matrix, producing two radical species: $PP^\bullet$ and $H^\bullet$ (1). Additionally, the presence of vitamin E in the polymer matrix allows the production of the radical species of vitamin E, which is stabilized by the phenolic ring, plus a radical proton ($H^\bullet$) (2). This radical proton reacts neutralizing the $PP^\bullet$ radicals (3), thus stabilizing the matrix. Finally, the presence of vitamin C allows stabilizing the vitamin E radicals formed according to reaction (4), regenerating the vitamin molecule that initiates a new cycle of successive reactions.

Tables 1 and 2 display the results of the different parameters of PP determined in this study when Vitamins C and E are used in combination at different proportions. The results clearly indicate that no synergistic effect was produced in the different characteristics analyzed, contrary to what was expected. The behavior of the compounds was similar to those where vitamins were used separately.

When the thermal parameters are analyzed, it is clear that the crystallization temperature at a concentration of 0.5/0.5% of Vitamins C/E increases when compared to that of pure irradiated PP. This shows a probable nucleating effect which facilitates the crystal formation, giving way to a slightly increased thermal stability of PP.

When the crystallization exotherms of irradiated PP with a combination of Vitamins E and C are analyzed (Fig. 7), a significant increase in the peak temperature is clear. This fact is attributed to the nucleating effect of both additives, which produces a more homogeneous crystalline phase. Likewise, the melting endotherms of 0.5/0.5% and 0.7/1% of Vitamins E/C unfold that a second melting peak is absent.

Regarding the mechanical properties of the same compounds, Table 2 shows that their moduli are lower than that of pure non-irradiated polypropylene. A higher value

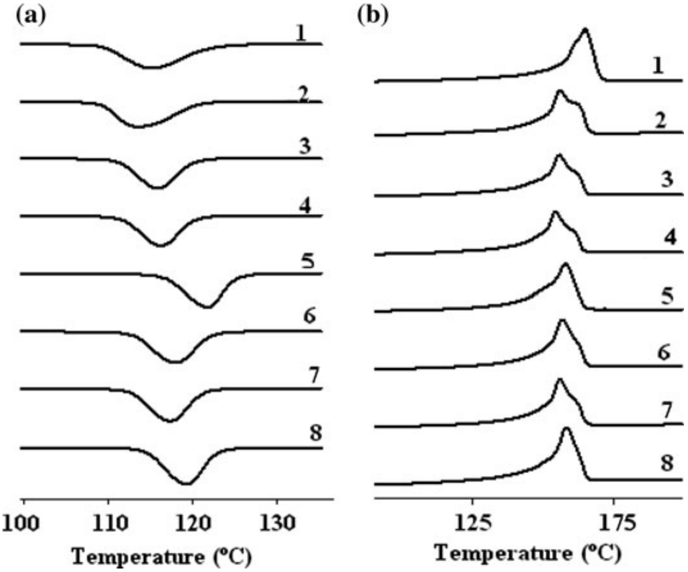

Fig. 7 Crystallization (**a**) and melting thermograms (**b**) of: (1) non-irradiated pure PP; Irradiated: (2) pure PP; (3) PP-0.1/0.1 Vits E/C; (4) PP-0.3/0.3 Vits E/C; (5) PP-0.5/0.5 Vits E/C; (6) PP-0.8/0.8 Vits E/C; (7) PP-0.3/0.6 Vits E/C; (8) PP-0.7/1.0 Vits E/C

of modulus was expected in PP with vitamins E/C, due to the also expected synergistic stabilizing effect. The tensile strength and elongation at break results display some dispersion, due to embrittlement of the samples because of the irradiation.

Conclusions

Vitamins C and E added either individually or combined in samples of polypropylene displayed a nucleating effect, detected by the increase in the crystallization temperature of PP. Reduced injection-molding and/or cooling cycles could result as a consequence of this fact. On the other hand, M_n, M_w, and tensile properties values of PP showed a significant decrease when samples were irradiated at the dose of 25 kGy. Hence, the irradiation of these materials produced polymer degradation, even though added vitamins were expected to behave as antioxidants. The results clearly indicate that no synergistic effect was produced in the different characteristics analyzed when Vitamins C and E are used in combination at different proportions, contrary to what was expected. The behavior of the compounds was similar to those where vitamins were used separately.

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