ELECTRONIC SPIN RESONANCE STUDIES OF GAMMA-IRRADIATED PS/PP (80/20) BLENDS WITH 2.5WT% SBS, AFTER FIVE YEARS OF STORAGE IN AIR

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SUMMARY

This study is a continuation of previous ones aimed at improving the stability of polystyrene/polypropylene (PS/PP 80/20) blends aged for 0, 4 and 5 years in non-controlled open air storage after γ-irradiation with different amounts of compatibilizer (block styrene-butadiene-styrene (SBS), styrolux with 48wt% of styrene and stereon with 43wt% of styrene). γ-irradiation from a ^{60}Co source at a dose rate of 4.8kGy·h^{-1} and at integral doses of 10, 25 and 50kGy, in air at room temperature (~298°K) after 5 years-aging in non-controlled open air storage, to evaluate the oxidative degradation resistance of (PS/PP (0/20) blends, with and without compatibilizer SBS, styrolux and stereon at 2.5wt%. Electron spin resonance showed that peroxide radicals prevail as a consequence of γ-irradiation and that there is an enhancement of exchange interactions and the presence of groups of free radicals. The blend with SBS, 2.5wt% stereon has a higher concentration of free radicals than the blend with 2.5wt% styrolux. For both blends the dependence of free radical concentration, Ipp, and resonance line width, Hpp, on the γ-irradiation dose are represented by first order kinetics (monomolecular process). In addition, a higher formation of free radicals is observed in comparison with non aged samples of PS/PP (80/20), 7.5wt% SBS, styrolux, γ-irradiated previously analyzed. Color centers are not observed on the studied blends.

Introduction

Compatibilizers are additives used to improve the interactions between components of polymer blends. They are added primarily to blends of commercial interest such as polyolefyns and polystyrene. However, there are few studies on the effects of gamma irradiation on polystyrene/polypropylene (PS/PP) blends (Albano *et al*., 2003; Reyes *et al*., 2003).

Additionally, the use of nuclear radiation is an alternative physical process to modify the structure of homopolymers, copolymers and blends, and they allow to improve the interactions of the additives with the polymers in order to increase their uses, both in scientific and industrial applications (Reyes *et al*., 2003).

The role of oxygen in aging and degradation studies is crucial for materials exposed to low dose rates for long periods or for storage of nuclear wastes. The radiation induces free radical formation, whose further evolution can cause scission and chain branching. Usually all these phenomena co-exist, the prevalence of one or another depending upon many factors that can affect the concentration of the

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ESTUDIOS CON RESONANCIA ELECTRÓNICA DE SPÍN DE LAS MEZCLAS PS/PP (80/20) CON 2,5 % EN PESO DE SBS, BAJO IRRADIACIÓN GAMMA TRAS 5 AÑOS DE ALMACENAMIENTO EN AIRE

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RESUMEN

Este trabajo es continuación de estudios previos con miras a mejorar la estabilidad de las mezclas utilizadas, aplicando irradiación-γ después de 0, 4 y 5 años de envejecimiento de mezclas de poliestireno/polipropileno (PS/PP 80/20) almacenadas en ambiente no controlado al aire, con diferentes cantidades de compatibilizantes (bloques de estireno-butadieno-estireno (EBE), styrolux con 48% estireno, y stereon con 43% estireno). Se irradió con una fuente de ^{60}Co a una tasa de dosis de 4,8kGy·h^{-1} y dosis integrales de 10, 25 y 50kGy, en presencia de oxígeno a temperatura ambiente (~298°K), tras 5 años de almacenamiento en un ambiente no controlado abierto al aire, para evaluar la resistencia a la degradación oxidativa de las mezclas de PS/PP (80/20) con y sin compatibilizante EBE a 2,5% en peso. Mediante resonancia electrónica de spín se mostró que los radicales peróxidos prevalecen como consecuencia de la irradiación-γ, y existe un aumento en las reacciones de intercambio y presencia de grupos de radicales libres aislados. La mezcla con EBE 2,5% stereon presenta una concentración de radicales libres más elevada que aquella con 2,5% en peso de EBE styrolux. Para ambas mezclas la dependencia de la concentración de radicales libres, Ipp, y el ancho de la línea de resonancia, Hpp, con la dosis integral de irradiación, corresponden a una cinética de primer orden (proceso monomolecular). Adicionalmente, hay mayor formación de radicales libres en las muestras estudiadas, en comparación con muestras no envejecidas de PS/PP (80/20), 7,5% en peso de EBE styrolux, irradiadas en trabajos previos. No se observaron centros de color en las mezclas estudiadas.

ESTUDO COM RESSONANCIA MAGNTICA ELETRONICA MISTURAS PP/PS (80/20) PARA 2,5% EM PESO DE SBS, COM IRRADIACAO-GAMMA APOS 5 ANOS DE ARMAZENAMENTO EM AR

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RESUMO

O presente trabalho é a continuação de anteriores objectivos visando melhorar a estabilidade de misturas usadas, irradiação-γ aplicada após de 0,4 e 5 anos de anvelhecimento de misturas com poliestireno/polipropileno (PS/PP 80/20) armazenadas em ambiente com ar descontrolada, com diferentes quantidades de compatibilizantes(bloques de estireno-butadieno-estireno (EBE), styrolux com 48% estireno e stereon com 43% estireno). Irradiados com uma fonte 60Co e taxa de dose de 4,8KGy·h^{-1} e dose integral de 10, 25 e 50KGy, na presença de oxigênio à temperatura ambiente (~298°K), após 5 anos de armazenamento em ambiente não controlado aberta para o ar, para avaliar a resistência à degradação oxidativa de misturas PS/PP(80/20) com e sem compatibilizante EBE para 2,5% em peso. Ressonância de spin eletrônico mostrou que os radicais de peróxido prevalem como resultado da irradiação-γ, e há uma reação de troca maior ea presença de grupos radicais livres isolados. A mistura com 2,5% Stereon EBE tem uma concentração de radicais livres superior à de 2,5% em peso de Styrolux EBE. Para ambas as misturas, a dependência concentração de radicais livres, IPP, ea largura da linha de ressonância, HPP, com a dose integral de irradiação, o que corresponde a uma ordem cinética primeiro (processo monomolecular). Além disso, há aumento da formação de radicais livres nas amostras estudadas, em comparação com as amostras não envelhecidas do PS / PP (80/20), 7,5% em peso de EBE Styrolux, irradiado em trabalhos anteriores. Não houve centros de cor nas misturas.

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reactive species and, consequently, the kinetics of the reactions involved.

Electron spin resonance (ESR) spectroscopy is a valuable tool in the identification of free radicals and the study of the degradation processes in polymers (Rånby and Rabek, 1977). In the present study ESR is used to analyze the effect of gamma irradiation from a ^{60}Co source at integral irradiation doses of 10, 25 and 50kGy and at a dose rate of 4.8kGy·h^{-1} in air at room temperature (~298°K) in the presence of air after five years in non-controlled open air storage on polystyrene/polypropylene (PS/PP 80/20) blends with styrene-butadiene-styrene (SBS) at 2.5wt%.

Experimental

The compatibilizers used in the present study were Styrolux, a commercial triblock copolymer based on styrene-butadiene-styrene (SBS, 48% styrene) supplied by BASF, and Stereon is a commercial triblock copolymer based on styrene-butadiene-styrene (SBS, 43% styrene) supplied by Shell. Recyclostab 811 Ciba-Geigy (0.1wt %), was added to the polymer as an additive to inhibit or delay the decomposition process. The blends were prepared in a ratio of 80/20wt% polystyrene/polypropylene (PS/PP). A styrene-butadiene-styrene copolymer (SBS), 2.5wt% with respect to the blend was used, and were prepared in a W&P intermeshing co-rotating twin-screw extruder. The samples (thickness 1mm) were irradiated with γ rays at low integral doses of 10, 25 and 50kGy, and a dose rate of 4.8kGy·h^{-1} in air, at room temperature (~298ºK) with a ^{60}Co source supplied by the Venezuelan Institute for Scientific Research (IVIC), after five years under non-controlled open air atmosphere. Electron spin resonance (ESR) measurements were carried out using the Varian E-line-X ESR spectrometer, adjusting the modulation frequency and microwave power level so as to avoid saturation effects in the ESR spectra. Strong pitch was used as a field marker. Each experimental point represents five ESR spectra.

Results and Discussion

Figure 1a shows the ESR spectra for PS/PP (80/20) blended with 0.1wt% antioxidant and 2.5wt% styrolux.

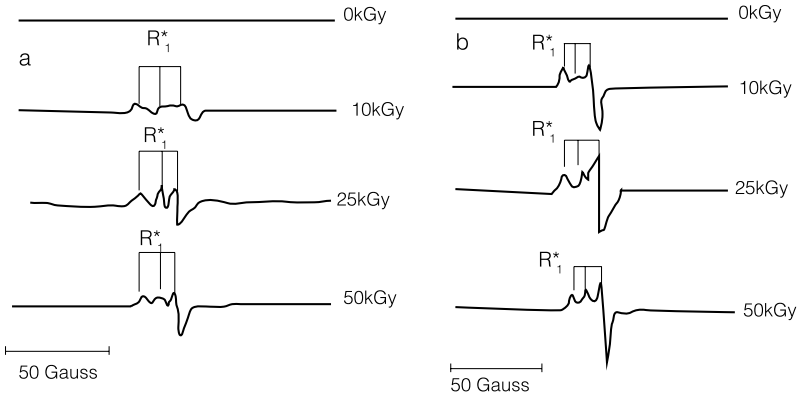

Figure 1. ESR spectra for a: PS/PP (80/20) 0.1wt% of antioxidant with 2.5wt%, SBS-styrolux, and b: PS/PP(80/20) 0.1wt% of antioxidant with 2.5wt% SBS-stereon. Both were irradiated with γ rays in air, after five years of storage in air at room temperature. R_1: peroxide.

No signal is observed in the case of the non-irradiated blend, while at 10, 25 and 50kGy of integral irradiation there are asymmetric triplets. The ESR spectrum at 10kGy dose shows an incompletely resolved and slightly asymmetric hyperfine structure located around g= 2.014 ±0.001 and g=2.021 ±0.001, and hyperfine parameters $a_1= 18\times10^{-4}$T and $a_2= 19\times10^{-4}$T, respectively (Table I) ascribed to peroxide radical (Rånby and Rabek, 1977; Reyes *et al*., 2003), which could be rapidly transformed into carbonyl groups in the presence of air (Reyes *et al*., 2003) At 25 and 50kGy the ESR spectra parameters 'g' and 'a' reflect the presence of peroxide radicals (Rånby and Rabek, 1977). The radical peroxides in presence of oxygen probable are converted into carbonyl groups (Rånby and Rabek, 1977, Reyes *et al*., 2003).

The ESR spectra for PS/PP (80/20) blended with 0.1wt% antioxidant and 2.5wt% SBS stereon (Figure 1b) show an asymmetric resonance line at 10, 25 and 50kGy, with ESR paramaters 'g' and 'a' (Table I) that can be attributed to peroxide radicals (Rånby and Rabek, 1977). These radicals in the presence of oxygen could be converted into carbonyl groups. (Reyes *et al*., 2003). At 0kGy no ESR signal is observed.

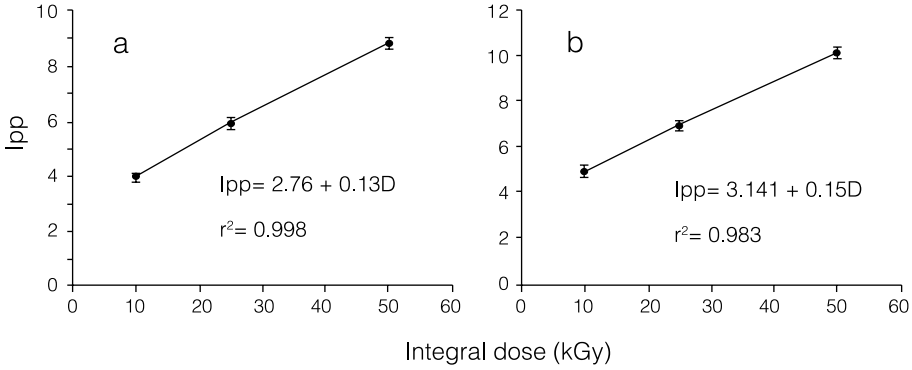

Figure 2. Dependence of the resonance line intensity, Ipp, on γ-irradiation dose (kGy), after storage in air at room temperature for five years, for a: PS/PP (80/20) 0.1wt% antioxidant with 2.5wt % SBS-styrolux, and b: PS/PP(80/20), 0.1wt% antioxidant with 2.5wt % SBS-stereon.

The presence of SBS in both blends under study results in the formation of peroxide radicals due to the butadiene parts of the compatibilizer (Reyes *et al*., 2003). The peroxide radicals could oxidize into carbonyls groups, as a consequence of the thinness of the samples (1mm), which favors the diffusion of oxygen on its surfaces.

The dependence of the resonance intensity line, Ipp, on integral doses of γ-irradiation, for samples irradiated between 0 and 50kGy for both blends, PS/PP (80/20) with styrolux and PS/PP (80/20) with stereon, are represented in Figures 2a and b, respectively. Both figures exhibit a linear increase of Ipp with an integral irradiation dose. This means that the dependence of free radicals concentration (Ipp values) on the γ-irradiation doses is represented by a first order kinetics (monomolecular process) for both blends. However, the increase in Ipp values for the blend with 2.5wt%, SBS, styrolux (48wt% styrene) is slower than the values for the blend with 2.5wt%, SBS stereon (43wt% styrene), and in this case the free radical concentration in the blend with 2.5wt% styrolux is 16% higher than in the blend with 2.5wt% stereon. The behavior in the blends suggests that styrolux is a better compatibilizer than stereon, due to fact that the amount of benzene rings of styrene present in the blend with styrolux (48wt% styrene) retards the production of free radicals, more than in the blend with stereon (43wt% styrene); this behavior is explained by the fact that the presence of aromatic groups increases the resistance to irradiation and stabilizes the activated species formed by irradiation (Valenza *et al*., 1999). Furthermore the appearance of centers of color was not observed either in the non-irradiated blends (0kGy) nor in the blends irradiated from 10 to 50kGy.

When the free radicals concentration of the PS/PP (80/20) blends under study is compared to a previous work (Reyes *et al*., 2003) on PS/PP (80/20) blends with

TABLE I
GYROMAGNETIC FACTOR (g ±0.001), HYPERFINE STRUCTURE (a ±1) AND TYPE OF FREE RADICALS OF THE ESR SPECTRA FOR THE SAMPLES UNDER STUDY

Sample	Radiation doses (kGy)			
	0	10	25	50
PS/PP (80/20) with 0.1wt% recyclostab 811 and with 2.5wt% of SBS styrolux	-	g= 2.014 (R_1) g= 2.021 (R_1) $a_1= 18x10^{-4}$ T g= 2.014 (R_1) $a_2= 19x10^{-4}$ T	g= 2.013 (R_1) g= 2.026 (R_1) $a_1= 20x10^{-4}$ T g= 2.014 (R_1) $a_2= 17x10^{-4}$ T	g= 2.022 (R_1) g= 2.019 (R_1) $a_1= 23x10^{-4}$ T g= 2.014 (R_1) $a_2= 22x10^{-4}$ T
PS/PP (80/20) with 0.1wt% recyclostab 811 and with 2.5wt% of SBS styrolux	-	g= 2.024 (R_1) g= 2.019 (R_1) $a_1= 71x10^{-4}$ T g= 2.014 (R_1) $a_2= 18x10^{-4}$ T	g= 2.026 (R_1) g= 2.022 (R_1) $a_1= 20x10^{-4}$ T g= 2.014 (R_1) $a_2= 21x10^{-4}$ T	g= 2.027 (R_1) g= 2.023 (R_1) $a_1= 22x10^{-4}$T g= 2.015 (R_1) $a_2= 21x10^{-4}$ T

R_1: peroxide.

7.5wt% SBB, increases of 50% for the blend with styrolux and 57% for the blend with stereon, respectively, are observed (Davidson *et al*., 2008). This result allows to infer that the higher styrene concentration of the SBS in the PS/PP (80/20) blend 7.5wt% SBS, styrolux un-aging and irradiated with γ-rays, increases the stability of both blends (PS/PP 80/20, 0.1wt% recyclostab 811, with styrolux, 48wt% styrene and PS/PP (80/20), 0.1wt% recyclostab 811, with stereon, 43wt% styrene), under γ-irradiation, since PS is one of the most stable polymers because of the high dosage of irradiation needed to produce significant changes in its structure (Albano *et al*., 2003). On the other hand, the behavior observed in the PS/PP (80/20) blend with 2.5wt% SBS, styrolux and stereon, in comparison with the PS/PP (80/20) blend not aging with SBS styrolux, could be indicative of the possible occurrence of degradation processes in these samples. In this case the effect of γ-irradiation, the storage for five years before irradiation in a non controlled open air atmosphere (oxygen and light), and the presence of peroxide radicals, could lead to degradation due to the peroxide free radicals left by the effects of γ-irradiation on the surface of the samples, could recombine to form ketones (carbonyl groups) and alcohols, or may abstract hydrogen atoms to form hydroperoxides (Yeom *et al*., 1998). This behavior is supported for the increase observed in the position average of the g-factor (Table I), which is indicative of the formation of carbonyl groups, since the g factor of carbon radicals increases when oxygen is attached to the radical center, similar to $-CH_2-C(=O)-CH\cdot-$ because of the higher polarity around the carbon radicals (Ikada *et al*., 2005).

TABLE II
RESONANCE LINE ASYMMETRY FACTOR (K) ON THE INTEGRAL IRRADIATION DOSES (KGY), FOR THE SAMPLES UNDER STUDY

Samples/Doses (kGy)	0	10	25	50
PS/PP (80/20) with 0.1wt% recyclostab 811 and with 2.5wt% of SBS styrolux	2.22	3.65	3.83	4.25
PS/PP (80/20) with 0.1wt% recyclostab 811 and with 2.5wt% of SBS styrolux	2.22	3.66	3.85	4.26

Table II presents the values of the resonance line asymmetry factor 'K', at integral γ-irradiation doses between 10 and 50kGy for PS/PP (80/20) blends with 0.1wt% Recylostab-811 and with 2.5wt% SBS styrolux and stereon, respectively. The K value was estimated using the tangent method (Rånby and Rabek, 1977, Reyes *et al*., 2003).

For both blends PS/PP (80/20) with 0.1wt% Recylostab-811 and with 2.5 SBS, styrolux and stereon, respectively, the trend of the asymmetry factor K (Table II), a 0kGy, is Gaussian pure (K ~2.22; Rånby and Rabek, 1977). This means that in the presence of isolated free radicals at doses >0kGy, a transition from a pure Gaussian towards a Lorentzian (K= 4) line shape is noted, due to the enhancement of exchange interactions and the presence of radical groups (Reyes *et al*., 2003). This result is supported by the behavior observed both in the resonance line intensity and the resonance width line (Figures 2a, b, and 3a, b, respectively). The Ipp values increase with the γ-irradiation dose, while the resonance width line, Hpp, decreases with irradiation, which confirms the predominance of exchange interactions (Reyes *et al*., 2003) and the presence of groups of free radicals (Ursu, 1967). Similar results were reported by Davidson *et al*. (2006) on PS/PP (80/20) blends with 30wt% SBS styrolux, γ-irradiated at 10, 25 and 50kGy in open air. On the contrary, Reyes *et al*. (2003) reported a prevalence of dipolar interaction for γ-irradiated PS/PP (80/20) blends, non-aging with 7.5wt% SBS styrolux. In addition the dependence of Hpp on integral irradiation shows a linear decrease that supports the occurrence of monomolecular process in the blends under study.

Conclusions

The ESR analysis shows that the free radicals are the same (peroxides and probably carbonyls) for both blends irradiated with gamma rays after five years of storage in non controlled air environment at room temperature. For the blends with SBS after five years of air storage and after gamma irradiation, the resonance line parameters (Ipp, K, Hpp) suggest the enhancement of exchange interaction among free radicals, due to the presence of groups of radicals. Similar results were reported by Davidson *et al*. (2006). On the other hand, Reyes *et al*. (2003) reported prevalence of dipolar interactions on PS/PP (80/20) blends non-aging with 7.5wt% SBS, styrolux. In addition, the dependence of Hpp on integral irradiation is a decreasing linear dependence, which supports that in the blends under study monomolecular processes take place. Also, the resonance line intensity (Ipp) analysis shows a linear increase in the production of free radicals, meaning that monomolecular process occurs in both blends. Despite the greater amount of styrene in the PS/PP (80/20) blend with styrolux (48wt% styrene), the increase in the production of free radicals is slower than in the PS/PP blend with stereon (43wt% styrene). In addition, an increase of about 50% and 57% is observed for the blends under study (2.5wt% SBS styrolux and 2.5wt% SBS stereon), in the free concentration radicals (Ipp values) as effects of γ-irradiation, in comparison with the PS/PP (80/20) blends non-aging with 7.5wt% SBS styrolux. Addition-

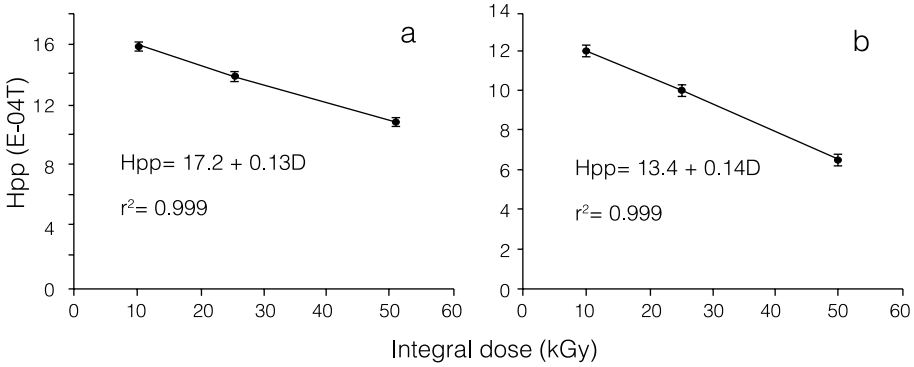

Figure 3. Dependence of resonance line width, Hpp, on γ-irradiation dose (kGy) after five years of storage in air at room temperature previous γ-irradiation for a: PS/PP(80/20), 0.1wt% antioxidant with 2.5wt % SBS-styrolux, and b: PS/PP(80/20), 0.1wt% antioxidant with 2.5wt% SBS-stereon.

ally, the PS/PP (80/20), 2.5wt% SBS styrolux (48wt% of styrene) blend showed a higher stability to the gamma irradiation after five years than the blend with 2.5wt% stereon (43wt% of styrene). Finally, for both blends no presence of color centers is observed after five years of storage in air at room temperature of 24ºC, neither in non-irradiated blends (0kGy) nor in the blends irradiated from 10 to 50kGy.

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