Gamma Irradiation at low doses (0-50kGy) and ageing effects on PS/PP (80/20) blends with 7.5 wt% SBS. An EPR study.

Irradiación gamma a bajas dosis (0-50 kGy) y efectos de envejecimiento en las mezclas PS/PP (80/20) con 7.5wt% de SBS. Un estudio mediante RPE.

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Abstract.

In this study PS/PP(80/20) blends at 7,5wt% Styrene-Butadiene-Styrene (SBS), styrolux and stereon respectively, with antioxidant, Recyclostab-811, at 0.1 wt%, γ-irradiated, from a ^{60}Co source, after five years of storage in air at 10, 25 and 50 kGy integral doses of gamma irradiation and a dose rate of 4.8 kGy/h, in air at room temperature, (RT, 24ºC) are investigated by electron paramagnetic resonance (EPR) spectroscopy. The dependence of the line intensity, Ipp and resonance line shape, K on the integral doses, is analyzed. The nature of the free radicals is discussed. The Ipp and K parameters suggest exchange interactions. The RPE analysis shows that the blends under investigation induced a higher formation of free radicals than in the fresh samples γ-irradiated, analyzed in a previous work. Monomolecular processes, investigated in the production of free radicals, occur for both blends studied.

Keywords: Polymers blends, gamma irradiation, EPR, free radicals, SBS.

Resumen.

En el presente estudio mezclas de PS/PP(80/20) con 7,5wt%, Estireno-Butadieno-estireno (EBE), styrolux y stereon respectivamente, con 0.1wt% de antioxidante, Recyclostab-811, son investigadas mediante espectroscopia de resonancia paramagnética electrónica (RPE), luego de ser irradiadas con rayos gamma, provenientes de una fuente de ^{60}Co, irradiadas en aire después de 5 años de almacenamiento en aire; a dosis de irradiación de 10 , 25 y 50 kGy,

a 4.8 kGy/h, a temperatura ambiente (RT, 24ºC). Se analiza la dependencia de la intensidad de la línea de resonancia y la forma de la línea de resonancia versus la dosis integral es analizada. Adicionalmente se discute la naturaleza de los radicales libres. Los parámetros Ipp y K sugieren la existencia de interacciones de intercambio. El análisis de RPE muestra una mayor formación de radicales libres, en las muestras irradiadas con rayos gamma, almacenadas en aire durante 5 años en relación a las muestras sin almacenamiento, irradiadas con rayos gamma, analizadas en trabajos previos. Procesos monomoleculares, investigados en la producción de radicales libres, ocurren para ambas mezclas estudiadas.

Palabras claves: Mezclas de polímeros, irradiación gamma, RPE, radicales libres, EBE.

1) Introduction

By electronic paramagnetic resonance (EPR) we have investigated the effects of γ-irradiation in air, at integral doses (10, 25 and 50 kGy) after five years of storage in air, at room temperature (RT, 24ºC) on PS/PP (80/20)blends with Recyclostab-811, antioxidant at 0.1 wt%, and with styrene-butadiene- styrene, SBS (styrolux and stereon) at 7.5wt%.

2) Experimental part.

The compatibilizer used were Styrolux a commercial triblock copolymer based on SBS, 48% styrene and Stereon a commercial triblock copolymer based on SBS, 43% styrene. Recyclostab 811 Ciba-Geigy, commercial antioxidant at 0.1 wt%. The blends were prepared in a ratio equal to 80/20 wt % PS/PP. A styrene-butadiene-styrene copolymer, SBS, 7.5 wt% with respect to the blends, was used as modifier agent in the blends. The blends were prepared in a W&P intermeshing co-rotating twin-screw extruder. The samples were irradiated in air with γ rays at integral doses of 10, 25, 50 kGy, a 4.8 kGy/h in air, at RT=24ºC, after five years of storage in air storage with a $^{60}C_o$ source supplied by Venezuelan Institute for Scientific Research (IVIC). EPR measurements were carry out using the Varian E-line-X ESR spectrometer adjusted the microwave power level, so to avoid effects of saturation in the EPR

spectra. Strong Pitch was used as a field marker. Each experimental point represents five EPR spectra.

3) Results and discussion.

The EPR spectra for PS/PP(80/20) blends with compatibilizer SBS styrolux (48% styrene) and compatibilizer SBS stereon (43% Styrene), storage 5 years in air and after irradiated at 10, 25, 50 kGy, are shown in the figure 1a and figure 1b respectively. The *"g"* and *"a"* EPR parameters obtained for both blends can be attributed to the presence of peroxide radicals (table 1) (Reyes et.al, 2003).These radicals could rapidly react to carbonyl groups in the presence of oxygen. Accordingly, the presence of SBS results in the formation of peroxide radicals due to the butadiene part of the compatibilizer (Reyes et.al, 2003).

The dependence of resonance intensity line Ipp, on integral doses of gamma-irradiation, for blends under investigation, is shown in Fig.2a and Fig. 2b respectively. In both figures is observed a linear increase of Ipp values on the irradiation doses. This mean that monomolecular processes, in the production of free radicals, occur for both blends. However the increase of Ipp values for the blend with styrolux is slower than Ipp values of the blend with stereon. The behavior observe suggesting that SBS, styrolux delayer the production of free radicals in this case, due to the presence of higher amount of rings aromatics of the styrene present in SBS styrolux, 48% styrene in comparison with SBS stereon, 43% styrene. This is confirmed by (Valenza et.al, 1999),who reports that the presence of aromatic groups increases the resistance to irradiation and stabilizes the activated species formed by irradiation.The ESR analysis led to the conclusion that the γ-irradiation after of 5 years of storage in air on the blends investigated, induced a higher (about 31% and 42%, for blend with styrolux and stereon respectively, fig 2a and 2b) formation of free radicals than in the fresh samples with 7.5wt% SBS, γ-irradiated analyzed in a prior work. (Reyes et.al, 2003)

Table 2 presents the values of the resonance line asymmetry factor *"K"*, at integral γ-irradiation doses between 10 kGy and 50 kGy. The *K* was estimate using the tangent method. For both blends under investigation, the trend of the asymmetry factor (*K*) (Table 2), a 0 kGy, is Gaussian pure ($K \approx 2.22$) while a doses higher than 0 kGy a transition from a pure Gaussian towards a Lorentzian line shape is noted, due to the enhancement of exchange interactions and the presence of groups of radicals (Ursu, 1967). On the other hand, in the fresh samples, γ-irradiated (Reyes et.al, 2003) the Hpp and K parameters suggest the predominance of the dipolar interactions among free radicals and the presence of isolated free radicals**.**

4) Conclusions.

The radicals observed in the blends investigated are the same, peroxide, and probably carbonyls. For both blends studied, the Ipp and K parameters, suggest presence of groups of free radicals and exchange interactions among these free radicals. On contrary in previous work on fresh samples of PS/PP (80/20) with 7.5% SBS, γ-irradiated, the Hpp and K parameters suggest the predominance of the dipolar interactions among free radicals and the presence of isolated groups of radicals. In addition the EPR analysis shows that both, the effect of γ-irradiation and the storage in air for 5 years in the blends investigated induced a higher formation of free radicals than in the fresh samples with 7.5% SBS, γ-irradiated and that the most production of free radicals occur in the blend, with stereon. For both blends monomolecular processes occur in the production of free radicals.

5) References.

[1] Reyes J, Albano C, Claro M, Moronta D (2003), Electron spin resonance studies on PS, PP and PS/PP blends under gamma irradiation, *Rad. Phys. and Chem.* ***67*** *453-457.*

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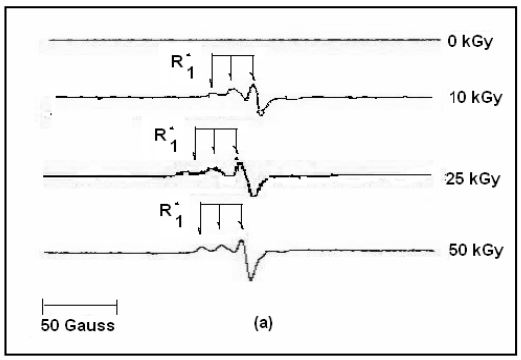
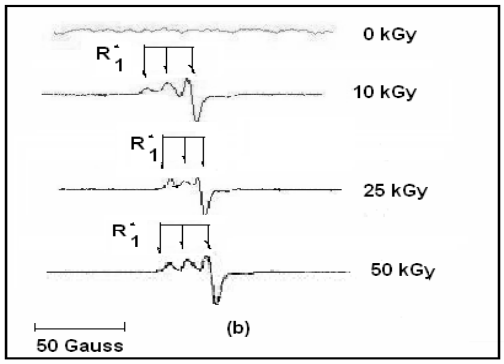
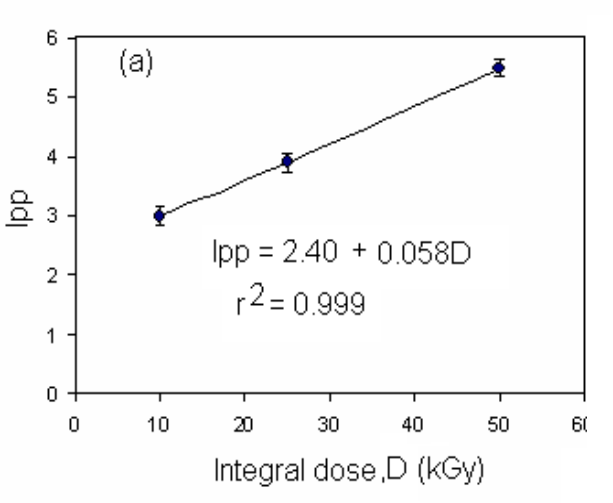
Figure 1a and 1b (As indicated in the caption)





R_1•= peroxide.

Figure 2a and 2b. (As indicated in the caption)



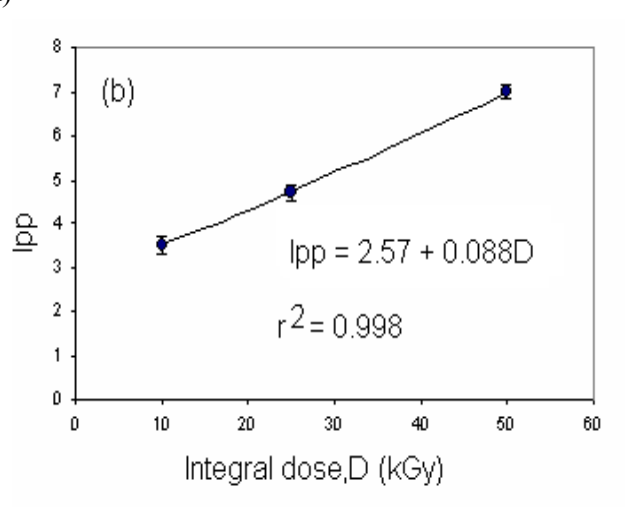


Table I.

Sample	Radiation Doses in kGy			
	0	10	25	50
PS/PP 80/20 with 0.1 wt % recyclostab 811 and with 7.5 wt % of SBS Styrolux	-	g= 2.020 (R_1·) g= 2.021 (R_1·) a_1=24x10^{-4}T g= 2.014 (R1·) a_2=23x10^{-4}T	g= 2.023 (R_1·) g= 2.036 (R_1·) a_1=19x10^{-4}T g= 2.012 (R_1·) a_2=17x10^{-4}T	g= 2.020(R_1·) g= 2.021(R_1·) a_1=22x10^{-4}T g= 2.014 (R_1·) a_2=21x10^{-4}T
PS/PP 80/20 with 0.1 wt % recyclostab 811 and with 7.5 wt % of SBS Stereon	-	g= 2.022 (R_1·) g= 2.023 (R_1·) a_1=23x10^{-4}T g= 2.012 (R_1·) a_2=22x10^{-4}T	g= 2.024 (R_1·) g= 2.021 (R_1·) a_1=22x10^{-4}T g= 2.014(R_1·) a_2=21x10^{-4}T	g= 2.026(R_1·) g= 2.021(R_1·) a_1=23x10^{-4}T g= 2.012 (R_1·) a_2=22x10^{-4}T

Table II.

Sample	Radiation Doses in kGy			
	0	10	25	50
PS/PP with 7.5 wt% Styrolux	2.22	3.20	3.70	3.75
PS/PP with 7.5 wt% Stereon	2.22	3.20	3.35	3.80

CAPTIONS

Figure 1. ESR spectra for PS/PP with 0.1wt% antioxidant and with 7.5 wt% SBS Styrolux blend **(a)**, PS/PP with 0.1wt% antioxidant and with 7.5 wt% SBS Stereon blend **(b)**, irradiated with γ-rays in air from 10 to 50 kGy after 5 years of storage in air at RT= 24ºC.

Figure 2. The dependence of resonance line intensity, Ipp, for, PS/PP with 0.1wt%**,** antioxidant and with 7.5 wt% SBS Styrolux blend **(a),** PS/PP with 0.1wt% antioxidant and with 7.5 wt% SBS Stereon blend **(b),** irradiated with γ-rays in air from 10 to 50 kGy after 5 years of storage in air at RT= 24ºC.

Table I .Gyromagnetic factor (g±0.001), hyperfine structure (a ± 1) and type of free radicals of the ESR spectra, for, the blend under investigation. R_1·= peroxide.

Table II. Resonance line asymmetry factor, *K*, on the integral dose for samples under study.