

POLYPROPYLENE-POLYETHYLENE BLENDS MODIFIED BY GAMMA RADIATION

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ABSTRACT

One way to obtain a better mechanical property of polypropylene and polyethylene is to increasing the number of polymer chains cross-linked by gamma radiation. After irradiation a network is formed as a result of various chemical reactions and the radicals formed are concentrated in the amorphous phase. With the objective to improve the mechanical properties of PP, blends with PE were prepared and irradiated in doses up to 500 kGy, in atmospheric ambient. The molecular characterization of the blends was made by infrared spectroscopy and the data showed an increase in rigidity and a unique behaviour in Izod impact resistance

1. INTRODUCTION

Polypropylene (PP) is extensively used in many fields because of its excellent properties, such as an outstanding chemical and moisture resistance, low density, easy processability and relatively low cost. However, its application as an engineering thermoplastic is limited because of the poor impact toughness, especially at low temperature. Therefore, various methods have been developed to overcome this shortcoming. One of the most used methods is blending PP with other alpha olefins, such as polyethylene.

The physical, optical and mechanical properties of polymer blends are affected to various degrees by the phase morphology. Mechanical properties such as tensile strength, tensile elongation and impact strength for a particular polymer blend vary with the morphology and to a lesser extent with the crystallinity. The morphology [1-4], mechanical properties [5-8] and crystallization behavior [9-11] of PE/PP blends were reported by several researchers. Gohil [12] has found a synergism in mechanical properties through epitaxial growth in PE/PP blends. Spardaro and Rizzo [13] have observed that mixing parameters have significant effects on the mechanical properties and suggested that it is very important to find optimum

mixing procedures for each kind of blends. Lee [14] found that mechanical properties of PE/PP blends are closely related to the morphology.

The aim of this work is to compare the effect of gamma rays on the mechanical properties of polypropylene and polyethylene blends. Methods to access the extent of radiation-induced changes in polymeric materials include mechanical testing (impact resistance, yield stress, elongation at yield, stress at break and elongation at break) and chemical determination, i.e. infrared spectroscopy.

2. MATERIALS AND METHODS

2.1 Materials

The materials used in this investigation were polypropylene (PP) produced by Quattor Petroquímica S.A., MFI 1.5 g/10min, density 0.905 g/cm³, namely RP; high density polyethylene (HDPE), MFI 7.0 g/10min, density 0.960 g/cm³ and linear low density polyethylene (LLDPE), MFI 2.8 g/10 min, density 0.918 g/cm³ both also produced by Quattor Petroquímica S.A.

2.2 Preparation of PP-PE blends

LLDPE and PP (20%/80%), namely RP20LBD, and HDPE and PP (20%/80%), namely RP20AD were mixed in melt condition by using a double screw extruder Reifenhäuser (26mm, L/D 44).

2.3 Specimen Preparation

The injection molding of standard samples (RP) and blends (RP20LBD and RP20AD) for the tensile-strength measurements and impact resistance have been performed on a Battenfeld TM750/210. All rounder 210°C, computer assisted injection molding machine, at conditions according to the ASTM D638 standard.

2.4 Gamma irradiation

All the samples were subjected to gamma irradiation in air at room temperature and in ambient humidity. The absorbed doses were 25, 50, 100, 200 and 500 kGy at irradiation dose rate 1.1 kGy/h.

2.5 Mechanical Measurements

Tensile tests were performed in accordance with ASTM D638 standard test method using dumb-bell shaped test pieces at a cross-head speed of 50 mm/min using an Instron Universal Testing Machine (Model 1026). The notched Izod impact test was carried out in accordance with ASTM D 256 standard using an impact tester (Tinius Olsen) at +10°C. All the mechanical tests were performed at room temperature (23 ±1°C) and controlled humidity in 60%.

2.6 Infrared Spectroscopy: Fourier transform infrared (FTIR)

The Nicolet/Nexus spectrometer was used to characterize the chemical changes caused by gamma radiation in the polymer films. The compression-molded films were 0.09 mm thick. Spectra were obtained at 4 cm⁻¹ resolution and averages of at least 16 scan in the standard wave number range 400 – 4000 cm⁻¹. The variation in the absorbance in the region of 1600 to 1800 cm⁻¹, corresponding to carbonyl region with irradiation dose was measured [15]. Our interest was mainly focused on the changes in carbonyl compound to follow gamma induced oxidation. The concentration of carbonyl group in the films was measured in reference to absorption at 1720 cm⁻¹ described by Gupta [16].

3. RESULTS AND DISCUSSION

Mechanical properties: The stress–strain behavior of the injection-molded PP dumbbell specimens has been analyzed to describe their mechanical behavior. The influence of the low-dose irradiation (25-100 kGy) on the mechanical properties of the pure PP and the blends are presented in Figs 1 to 3. For all three samples, up to dose of 100kGy, they exhibit a stress–strain behavior typical of ductile and semi crystalline polymers which show at a low strain, a nearly linear rise in stress characterizing the major pure elastic deformation behavior. At the yield point, where a deviation from linearity in the stress–strain curve is observed at a strain at about 15%, the polymer chains start to slip, and usually necking occurs. As the strain level increases, strain hardening appears until the samples finally break. Above 100 kGy, all the samples exhibit behavior typical of brittle polymers, without yielding.

The variation of yield stress, elongation at yield and stress at break for RP, RP20LBD and RP20AD are shown in Figs. 1-3. The yield stress increased with irradiation dose, but because of their greater degree of crystallinity the RP samples had higher yield stresses, followed by RP20AD and RP20LBD.

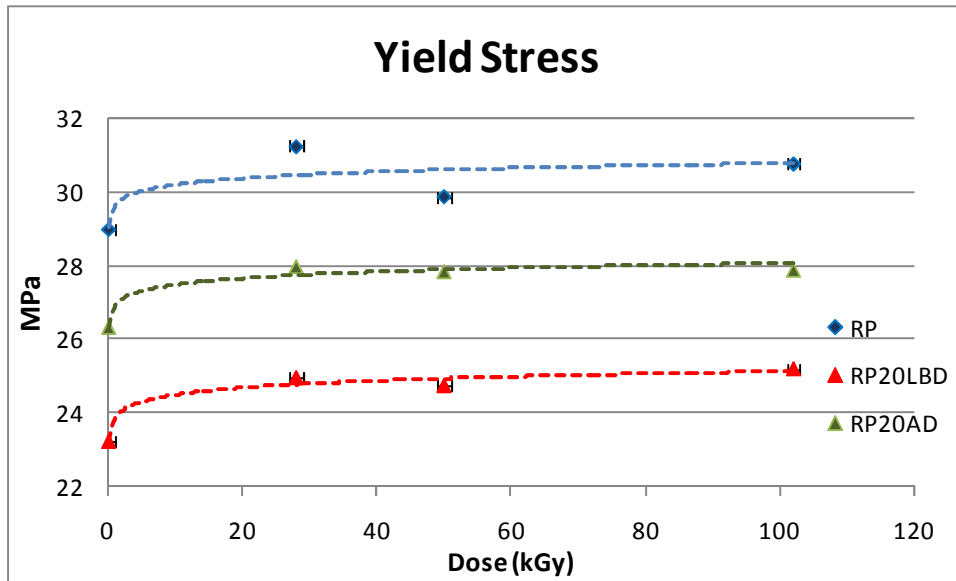


Figure 1. Yield stress.

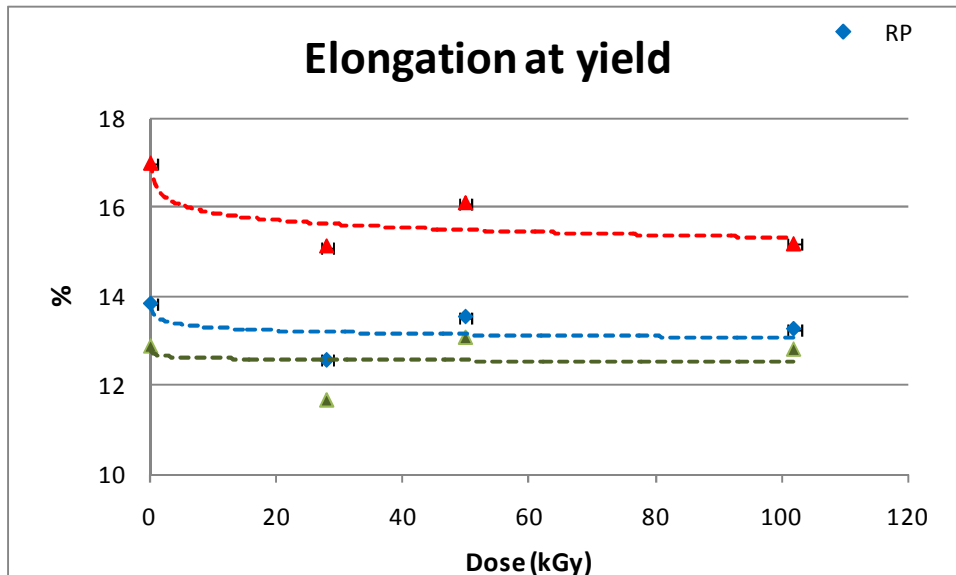


Figure 2. Elongation at yield.

The yield in a partially crystalline polymer is associated with interlamellar deformation and slip, such as in a homopolymer that the yield stress increases with crystallinity [17]. The increase of crystallinity for all samples is believed to be linked to degradation. The generation of new crystalline domains in gamma degraded samples is known as chemi-crystallization [18], explained by the oxidation and cleavage of tie-molecules or entangled chains in the amorphous regions of the polymer, growing up new crystalline domains at the lamellar surfaces or within the amorphous regions [18,19].

From the literature [20] it is known that the ductile-to-brittle transition usually appears when the molecular weight is twice the entanglement molecular weight. This theory is explained by the fact that the entanglements between lamellae are responsible for carrying a large amount of the stress during the tensile test, so the absence of entanglements strongly affects the fracture behavior. The stress at break, Fig. 3, show that the RP sample degenerate the

entanglements molecules more severe than RP20LBD and RP20AD samples, which even present a higher stress at 500 kGy dose. This behavior is in accordance with elongation at break.

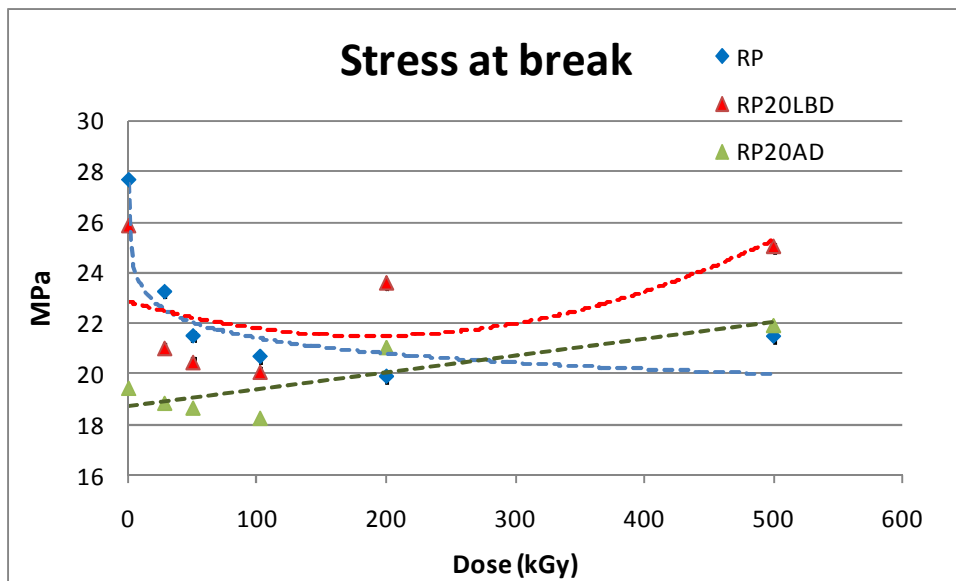


Figure 3. Stress at break.

In Fig 4 shows that the absorbed doses at 25kGy have practically negligible effect on the reduction of the elongation at break. The RP sample shows a different behavior with absorbed doses where the decrease of the elongation at break is more rapid than in the case of RP20LBD and RP20AD samples. The explanation for this effect is that the gamma ray induced oxidative degradation due to chain scission of polymer backbone [21], where the elongation at break of RP sample significantly decreases with dose. RP sample degrades whereas RP20LBD and RP20AD blends appear to crosslink in a small portion [22, 23].

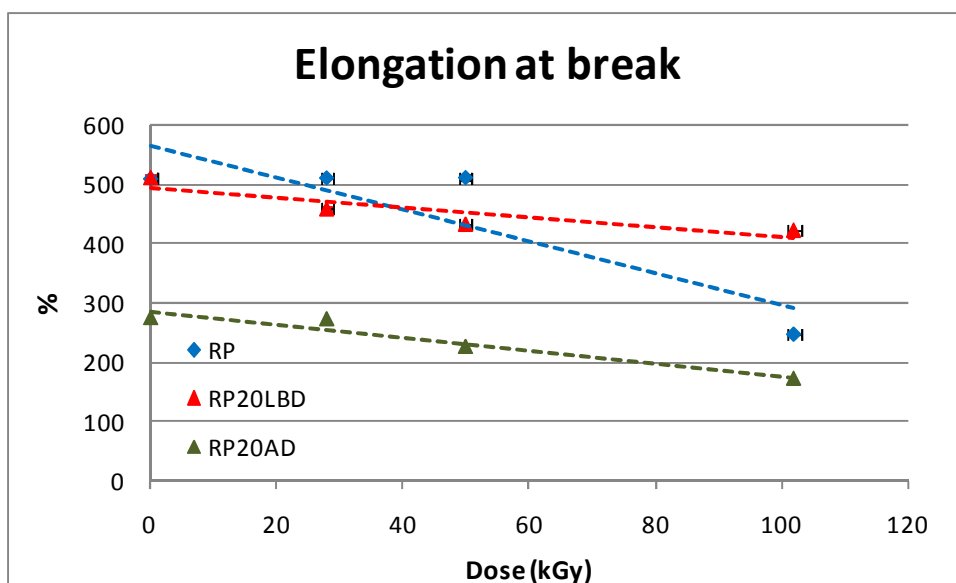


Figure 4. Elongation at break.

Impact Properties of PP and blends: Fig. 5 shows the effect of radiation dose on notched Izod impact strength of PP and blends at +10°C temperature. The impact toughness is often the deciding factor in material selection because impact test measures the ability of a polymer to withstand the load imposed upon being struck by an object at high velocity. Thus it is a measurement of the energy required to propagate a crack across the specimen. Therefore, the impact properties of these blends are especially important and the addition of LLDPE increases the impact strength of polypropylene to about 800 J/m, while HDPE reduced the impact strength to about 100 J/m. The decrease of the impact strength as a function of radiation dose for RP20LBD is less rapid than in the case of RP and RP20AD samples, mainly up to doses of 100 kGy. This behavior suggests that the blend of LLDPE with PP can preserve the impact resistance more efficiently than HDPE blend.

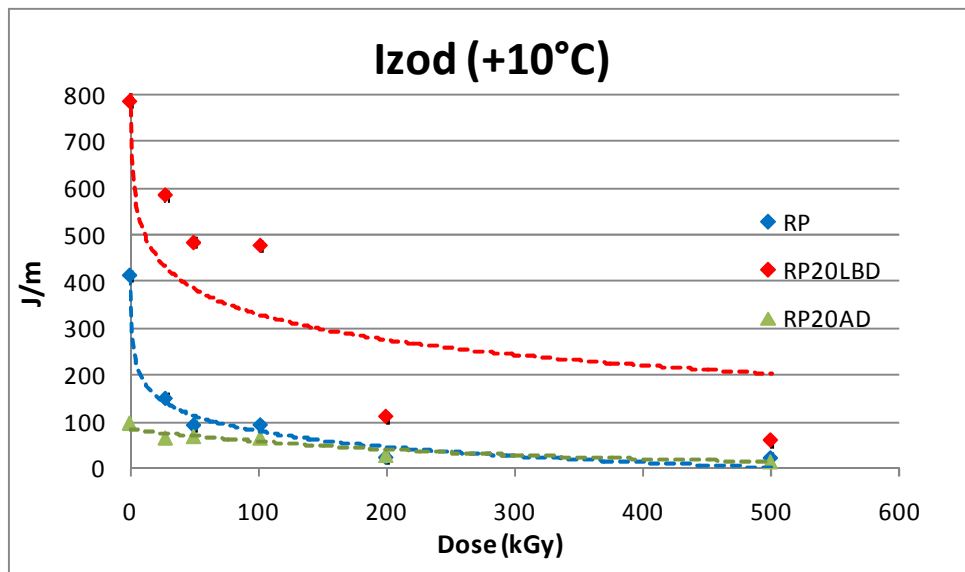


Figure 5. Impact resistance.

IR spectroscopic analysis: IR spectroscopy is a straightforward tool for monitoring the oxidative degradation by following evolution at carbonyl regions. Fig. 6 shows the carbonyl group evolution upon gamma irradiation at different doses (0 to 500 kGy). It was observed that the RP20AD sample shows higher rate of carbonyl group evolution.

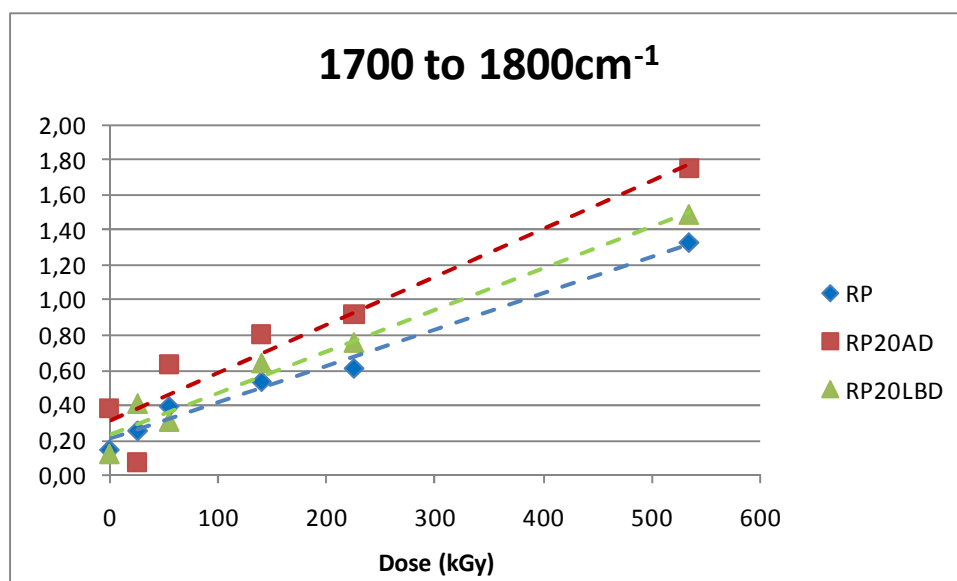


Figure 6. Carbonyl region.

3. CONCLUSIONS

The increase in the gamma radiation dose causes a decrease in elongation at break for all samples but it was more severe for RP which undergoes substantial degradation. The addition of PE in the blend can change this behavior because it has occurred a cross-linking after irradiation, mainly in RP20LBD sample.

The reduction in impact resistance after gamma irradiation is less severe when LLDPE is present in the blend, confirming the tensile analysis.

The increase in the radiation dose also influences the carbonyl compounds generation for all samples, showing almost the same performance for PP and for the blends.

Thus, it can be concluded that the stability of polypropylene against gamma irradiation can also be improved by blends of different PE which causes the PP protection via a specific mechanism of crosslinking.

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REFERENCES

1. M. Kojima, H. Satake, *J. Polym. Sci. Polym. Phys.*, **22**, pp. 285 (1984).
2. M. Levij, F. H. J. Maurer, *Polym. Eng. Sci.*, **28**, pp. 670 (1988).

3. L. Wang, B. Haung, J. *Polym. Sci. Part B: Polym. Phys.*, **28**, pp. 937 (1990).
4. J. Li, R. A. Shanks, Y. Long, *J. Appl. Polym. Sci.*, **76**, pp. 1151 (2000).
5. P. Cheung, D. Suwanda, S. T. Balke, *Polym. Eng. Sci.*, **30**, pp. 1063 (1990).
6. G. A. Gallagher, R. Jakeways, I. M. Ward, *J. Appl. Polym. Sci.*, **43**, pp. 1399 (1991).
7. Y. K. Lee, Y. T. Jeong, K. C. Kim, H. M. Jeong, B. K. Kim, *Polym. Eng. Sci.*, **31**, pp. 944 (1991).
8. E. Vaccaro, T. D. Anthony, S. J. Huang, *J. Appl. Polym. Sci.*, **63**, pp. 275 (1997).
9. E. Martuscelli, M. Pracella, M. Avella, R. Greco, G. Gosta, *Die. Macromol. Chem.* **181**, pp. 957 (1980).
10. A. Galeski, M. Pracella, E. Martuscelli, *J. Polym. Sci. Polym. Phys.*, **22**, pp. 739 (1984).
11. Z. Bartczak, A. Galeski, *Polymer*, **27**, pp. 544 (1986).
12. R. M. Gohil, *J. Polym. Sc. Polym. Phys.*, **23**, pp. 1713 (1985).
13. G. Spadaro, G. Rizzo, *Eur. Polym. J.*, **25**, pp. 1189 (1989).
14. Y. K. Lee, Y. T. Jeong, K. C. Kim, H. M. Jeong, B. K. Kim, *Polym. Eng. Sci.*, **31**, pp. 944 (1991).
15. N. Nagai, T. Matsunobe, T. Imai, *Polym. Deg. Stab.*, **88**, pp. 224 (2005).
16. A. P. Gupta, U. K. Saroop, V. Gupta, *J. Appl. Polym. Sci.*, **106**, pp. 917-925 (2007).
17. R. Popli, L. Mandelkern, *J. Polym. Sci., Polym. Phys.* **25**, pp. 441 (1987).
18. M. S. Rabello, J. R. White, *Polymer*, **38**, pp. 6379 (1997).
19. J. F. Rabek, *Polymer Photo Degradation – Mechanism and Experimental Methods*; Chapman and Hall; London, (1995).
20. P. J. Barham, In *Materials Science and Technology: A Comprehensive Treatment*; Cahn, R. W.; Haasen, P.; Kramer, E. J., Eds.; VCH: Weinheim, **12** (1993).
21. M. Hagiwara, T. Kagiya. In: H. H. G. Jellinek, editor. *Degradation and stabilization of polymers*, **1**. Amsterdam: Elsevier; (1983).
22. M. Dole, *The Radiation Chemistry of Macromolecules*. Academic Press, London, (1972).
23. T. S. Dunn, J. L. Williams, *J. Indust. Irrad. Tech.* **1**, pp. 33 (1983).