2011 International Nuclear Atlantic Conference - INAC 2011
Belo Horizonte,MG, Brazil, October 24-28, 2011
ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR - ABEN
ISBN: **978-85-99141-04-5**

GAMMA RADIATION EFFECT ON MOLECULAR STRUCTURE OF PP/PE BLENDS

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ABSTRACT

The effect of the incorporating 20% of polyethylene with 80% of polypropylene was investigated. The main objective was to study the mechanical behavior of these blends when submitted to different doses of radiation between 25 and 500kGy, in the presence of oxygen and also facing the influence of time. Sample tests were obtained by injection molding using pure polypropylene and two different kinds of polyethylene in each blend: linear low density polyethylene and high density polyethylene. In the mechanical tests it was evaluated the tension resistance and deformations. Analyses of differential scanning calorimetry, infrared spectroscopy and nuclear magnetic resonance were used to help in the understanding the generation of reactive species in the polymers. The behavior of stiffness for all of the samples was very similar, indicating an increase of the crystalline domain that was also verified by thermal analyses and by an increase in the yield stress during the stress-strain test. In the stress of rupture visualizes itself the crosslinking effect of the molecular chains mainly at highest doses of radiation, 200 and 500kGy. This result was also verified by nuclear magnetic resonance analysis which indicated a reduction in the molecular mobility of the linear low density polyethylene blends. Those results showed that both blends presented a better behavior facing the ionizing radiations than the pure polymer, having practical application in the polymers transformation industry.

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 [1,2,3,4], mechanical properties [5,6,7,8] and crystallization behavior [9,10,11] 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 efects 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/cm^3, namely RP; high density polyethylene (HDPE), MFI 7.0 g/10min, density 0.960 g/cm^3 and linear low density polyethylene (LLDPE), MFI 2.8 g/10 min, density 0.918 g/cm^3 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 Reifenhauser (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 500kGy 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 mechanical tests were performed at room temperature (23 ±1°C) and controlled umidity 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 0.09mm thick. Spectra were obtained at $4cm^{-1}$ resolution and averages of at least 16 scan in the standard wave number range 400 – $4000cm^{-1}$. The variation in the absorbance in the region of 1600 to $1800cm^{-1}$, 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 $1720cm^{-1}$ described by Gupta [16].

2.7 Nuclear magnetic resonance (RMN)

The samples were dissolved in 1,1,2,2 tetrachloro ethane PA approximately 20% w/v. The quantitative spectra were obtained ^{13}C NMR spectrometer Varian Mercury VX 300 MHz (7.4Tesla) at 95°C, operating in the following experimental conditions: ^{13}C core frequency of 75.4 MHz, 18.7 kHz spectral window, time acquisition of 1.7s, 90° pulse () and interval between pulses of 10s. The number of transients ranged from 500 to 1024. The ^{13}C chemical shifts were referenced to deuterated 1,1,2,2 tetrachloro ethane at 73.8ppm. All spectra were processed using exponential line broadening of 1Hz. The ^{13}C signals were determined according to the literature (Carman, 1971 and Carman, 1977).

2.8 Differential scanning calorimetry (DSC)

The measured using this technique of calorimetry were performed on a TA Instruments equipment, model 2920 DSC using sample mass between 3 and 8 mg. The behaviors of melting and crystallization curves of the polymer are strongly dependent on scan speed and adopted the thermal history of the sample. In this study set to scan at 10 ° C / min for fusion.

In order to ensure a thermal history analysis, post irradiation, constant for each sample, they were heated from room temperature to 210°C for the melting thermogram. The calibration of the equipment was performed with Indium metal, to check the temperature (Tm = 156.6 °C) and energy involved ($\Delta H_{fusão}$ = 28,45 J/g) The melting point of the samples was taken as the temperature of the melting peak.

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 (25-100kGy) 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 100kGy, 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.

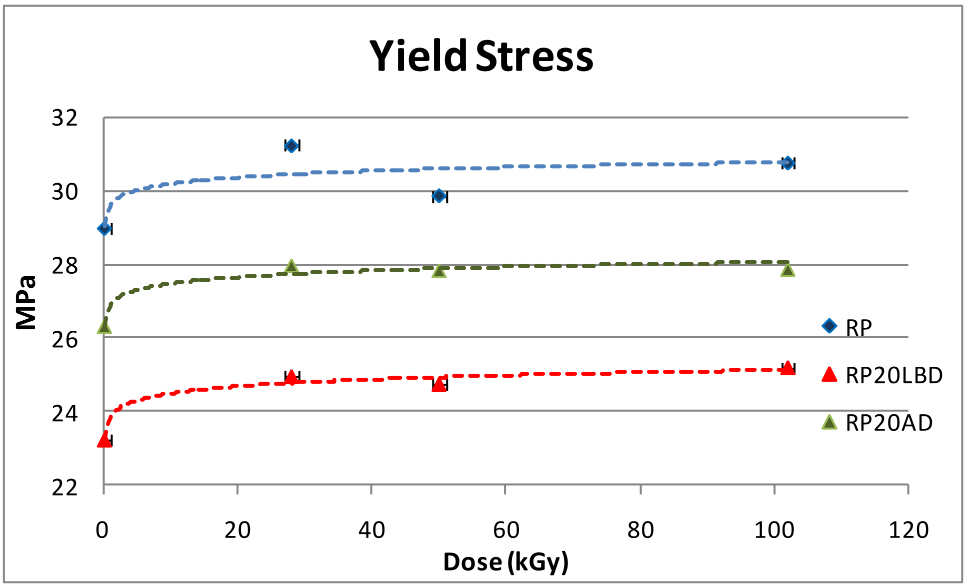

Figure 1.Yield Stress.

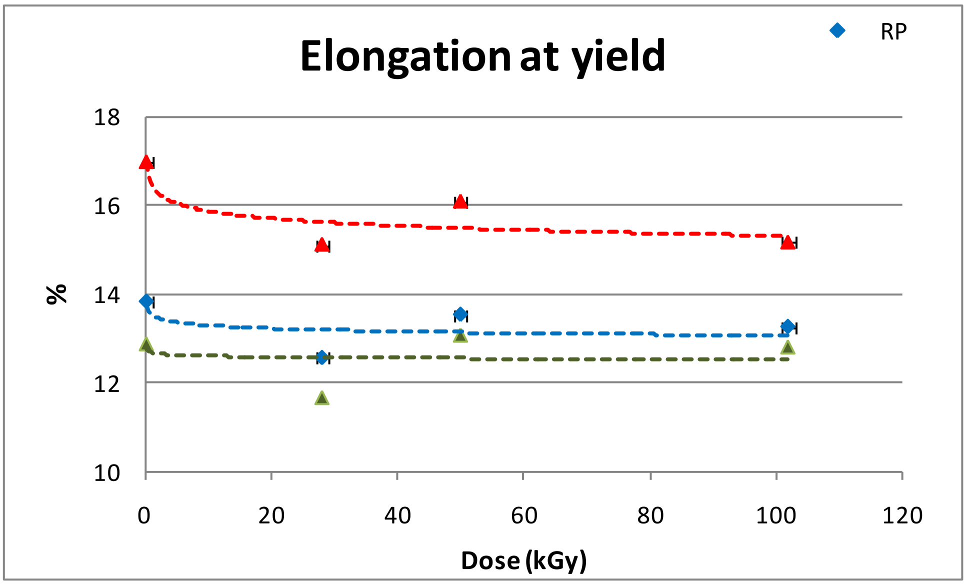

Figure 2. Elongation at Yield.

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 500kGy dose. This behavior is in accordance with elongation at break.

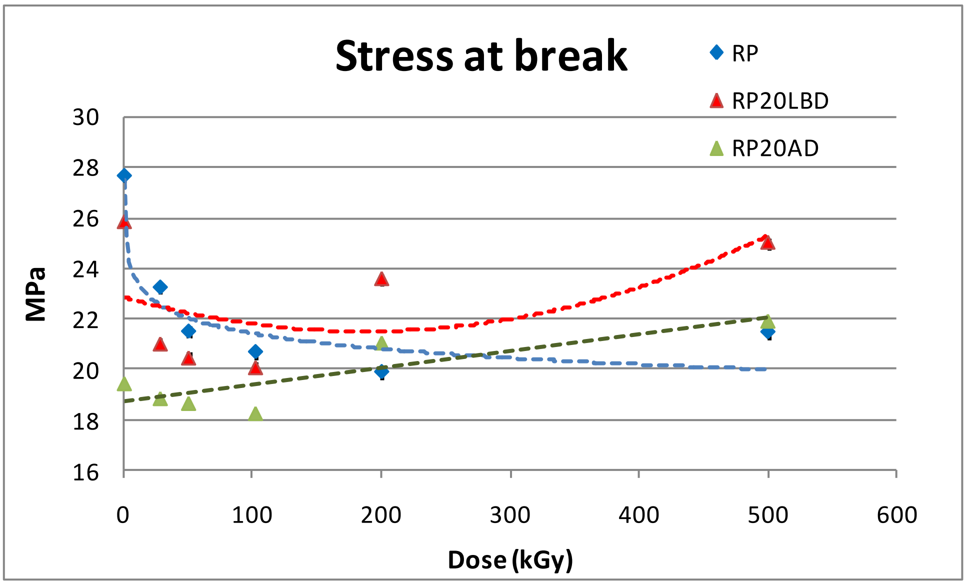

Figure 3. Stress at Brake.

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].

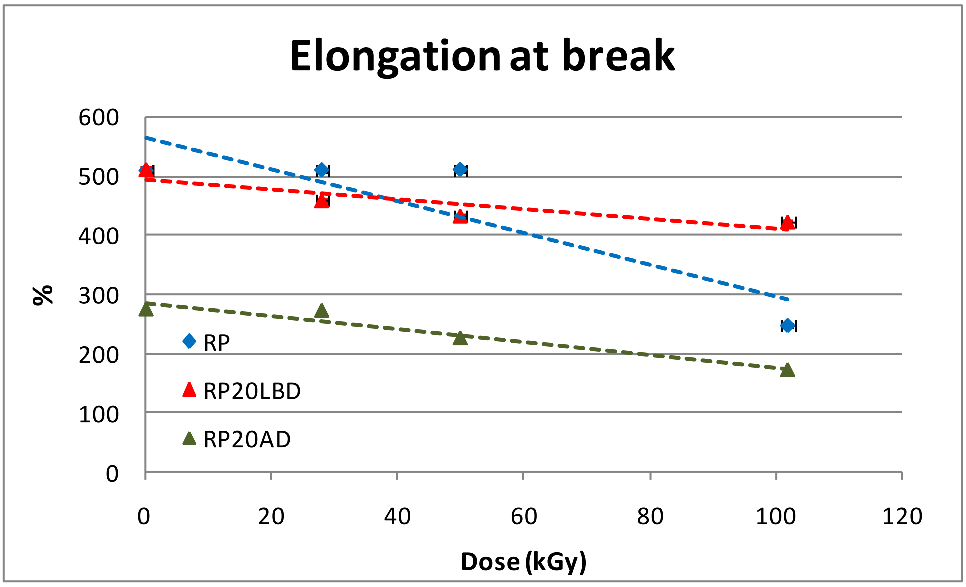

Figure 4. Elongation at break.

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

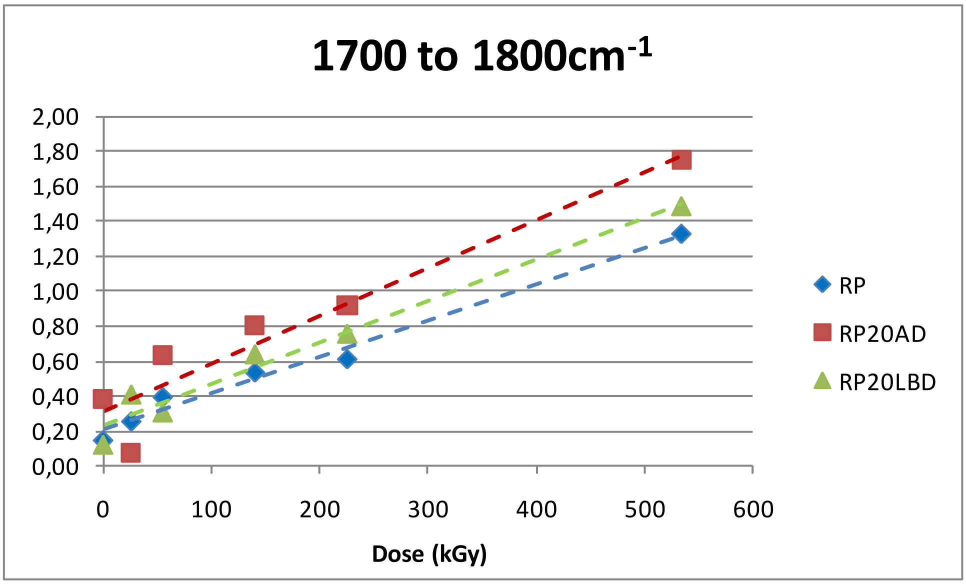

Figure 6. Carbonyl region.

Nuclear magnetic resonance: It is presented in spectra 4 and 5, the NMR spectra of samples before irradiated. Compared with the sample of pure PP, the blends and RP20LBD RP20AD have obviously NMR signals characteristic of PP and PE.

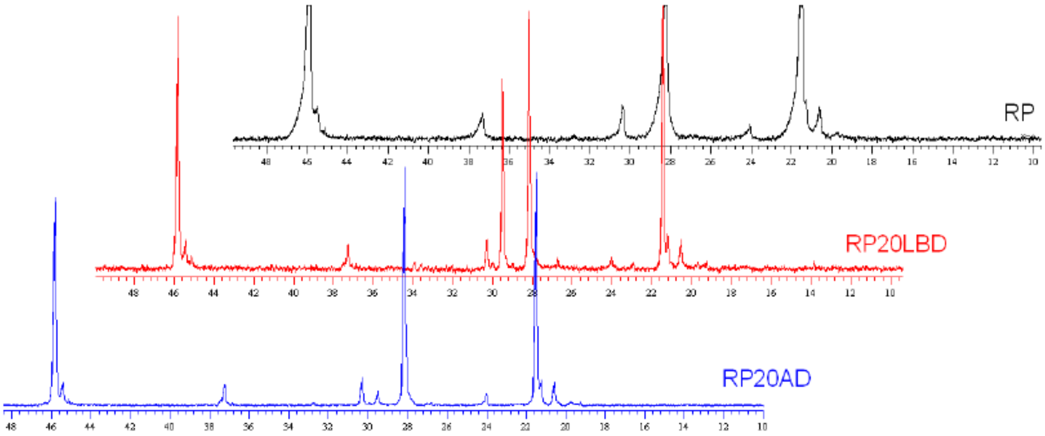

Figure 7. ^{13}C NMR spectrum of the samples not irradiated

Although the spectrum of pure PP has lower resolution than the others, it appears that the samples are subtle differences.

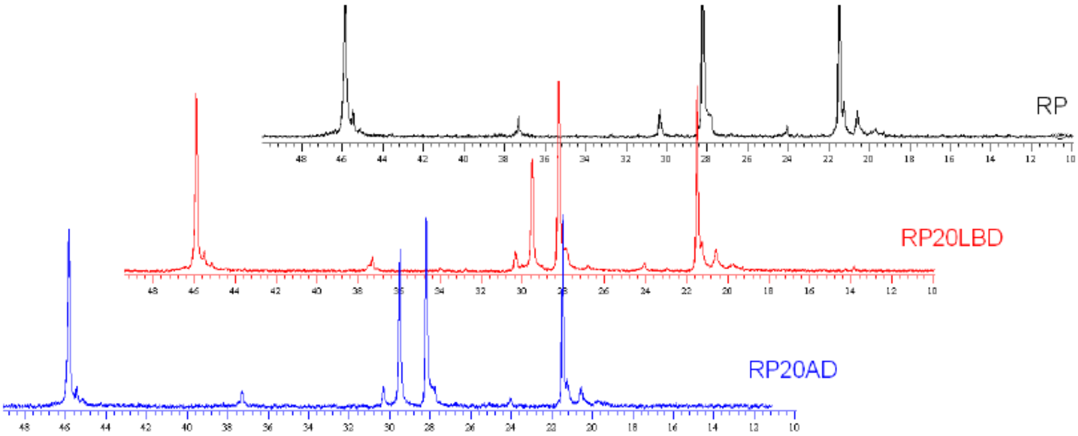

Figure 8. ^{13}C NMR spectrum of the samples irradiated at 500kGy

Comparing the spectra of higher radiation dose in the samples (Figure 8), the spectra of non-irradiated samples (Figure 7), there is not obvious differences.

Heat of fusion: The Table 1 shows the values of heat of fusion observed in the first fusion of the samples.

Table 1 - Heat of Fusion

DOSE (kGy)	*Heat Fusion (J/g)*		
	RP	RP20LBD	RP20AD
0	63,07	69,92	96,77
28	64,98	65,96	97,77
50	74,16	73,77	100,20
102	78,15	72,99	110,10
200	91,90	88,08	106,60
500	82,80	73,00	103,30

At the dose 500kGy, the value appears very distant to others, probably due to the high frequency of occurrence of chain scission and therefore decrease in molecular weight of polymer, which causes a reduction in melting temperature.

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 substancial 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.

The molecular mobility obtained by the ^{13}C NMR analysis indicated that the sample RP20LBD showed greater stiffness than the others, before increasing the dose of radiation, probably due to increased formation of branches.

Due to irradiation, all samples presented a decrease in melting temperature caused by the scission of molecular chains due to increased radiation dose. The components of the blends, PP and PE, have very similar behavior with respect to the reduction of Tm.

Irradiation affects more the pure crystalline phase of PP than PE, because the reduction in Tm of each component is different, with the slope being more pronounced for the PP.

ACKNOWLEDGMENTS

The authors are grateful to the Quattor Petroquímica S.A. for supplying the polymer of this study. One of the authors (F.C.R.) is grateful to Fundo Mackenzie de Pesquisa for the award of a scholarship.

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