

γ -Radiation (0-150 KGy) Effects on Slow and Fast Cooled HDPE/LDPE Blends

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Summary

The influence of gamma radiation on the morphology, thermal, mechanical and rheological properties of blends of high density polyethylene/low density polyethylene (HDPE/LDPE) was investigated. Prior to irradiation blends of different thermal history were prepared by fast cooling and slow cooling from the melt. Results showed that there were not significant changes in the degree of crystallinity of the blends with radiation. Higher values of degree of crystallinity and melting peak temperature were obtained for the slowly cooled blends. A small increase in the Young modulus and the yield stress were observed by irradiating the blends, and the elongation at break was reduced about 70% when compared to non-irradiated blends. High degree of crosslinking is expected to occur due to the decrease in melt flow rate of the blends irradiated to 50 kGy, and no flow was detected at 150 kGy. Transmission electron microscopy observations failed to show important changes in morphology with radiation.

Introduction

Blends of high density polyethylene (HDPE) and low density polyethylene (LDPE) have a good balance between processing and mechanical properties, due to the excellent processability of LDPE and the good mechanical resistance of HDPE. Moreover, gamma radiation induced crosslinking in polyethylenes is also used to improve mechanical and thermal properties in final products. According to Suarez et al.¹, the degree of crystallinity of recycled HDPE/LDPE blends has a tendency to decrease with γ -irradiation dose. The degree of crystallinity of LDPE, as reported previously², also tends to show a small increase, and the endothermic peak temperature decreases as the dose increases, showing stabilization at doses above 100 kGy. At relatively low doses (100 kGy), changes in mechanical properties occur due to induced crosslinking¹⁻³. Nevertheless, important changes evidenced on differential scanning calorimetry thermograms usually occur at doses higher than

5000 kGy indicating a transition of the crystalline unit cell from orthorhombic to hexagonal⁴.

Suarez et al⁵ investigated blends of HDPE/LDPE irradiated under various doses. The study suggests that compatibility may be increased depending on the dose radiation.

Based on previous research carried out by other authors in neat polyethylene⁶⁻⁸, we have set as the aim of this work to investigate the effect gamma irradiation has on blends of HDPE/LDPE of different morphologies in presence of air. Chain scission and crosslinking taking place in the samples is followed by changes in crystallinity and gel content measurements, respectively. Changing the composition of the mixture results in materials of various degrees of crystallinity and it is expected the solubility of oxygen in polyethylene be a function of the amorphous fraction.

Materials and Methods

Two injection grade commercial polyethylenes, manufactured by Polinter, were employed, a high density polyethylene (HDPE) 2908A of density 0.9595 g/cm³ and a low density polyethylene (LDPE) MD-2002 of density 0.9233. HDPE/LDPE blends were prepared by extrusion at 200°C with a screw speed of 60 rpm. HDPE/LDPE blends contents were: 0/100, 10/90, 25/75, 50/50, 75/25, 100/0. Then, compression molded sheets of about 0.7-0.8 mm thick were obtained at 190 °C followed by cooling to room temperature. Two cooling methods were employed: a fast one by immersing the hot plates in a mixture of water and ice and a slow one using a circulating water system. All samples for testing were obtained from the molded sheets. Exposure to several doses of gamma rays (0, 50 and 150 kGy at 4.8 kGy/h rate) was carried out in air at room temperature.

Small specimens were used for tensile testing, employing a tensile testing machine (JJ Instruments), at a test speed of 50 mm/min. The approximate dimensions of the narrow area of the specimens were: 23 mm long, and 5 mm wide. Average values of Young modulus and mechanical properties at yield and break are reported.

For differential scanning calorimetry experiments (DSC), discs with a weight between 10 and 12 mg were subject to a heating process from 0°C to 160°C using a heating rate of 10°C/min. A Mettler Toledo calorimeter model DSC822e was employed for DSC experiments and these were carried out under nitrogen atmosphere. The values of the temperature of the endothermic melting peaks were obtained with a precision of 0.1°C and the degree of crystallinity was calculated using a heat of fusion for 100% percent crystalline sample as 289.3 J/g⁹.

The density of the blends at room temperature was determined employing samples of 0.1-0.2 g in weight, conformed by 5 or 6 discs of approximately 20 mg each. A Mohr weighing scale was used and ethanol was employed as the immersion medium of the samples, using a standard density glass sphere (0.9000 g/cm³). The melt flow index (MFI) of the blends was measured employing a plastometer (Ray-Ran) at 190°C, using a 2.16 kg weight, in accordance to ASTM D1238 test method. Twenty MFI measurements were directly reported by the plastometer in a range of 15 mm for the non-irradiated blends and 5 mm for the rest.

The morphology of samples was studied using a Transmission Electron Microscope Jeol JEM-1220, operated at 100 kV. The samples were stained with RuO₄¹⁰. Thin sections were obtained at room temperature using a Leica Ultracut UCT equipped with a diamond knife.

Results and Discussion

The usual melting behavior of LDPE, HDPE and their blends was found by DSC. Their thermal properties such as melting temperature peaks are shown in Table 1. It is interesting to observe that in the case of LDPE and 50% LDPE blend, non-irradiated and irradiated samples show contrasting behavior. In non-irradiated samples the melting temperature peak is located at higher temperatures for the quenched samples whereas for irradiated samples the melting temperature peak is higher or at about the same temperature. For the neat HDPE changes in melting temperature peak are much more pronounced for the irradiated samples. Higher temperature peaks for non-irradiated quenched branched polyethylene samples than those found for slow cooled samples, as shown in Table 1, have been reported in the past and explained on the basis of crystalline structure reorganization during heating¹¹. Therefore, the results presented in Table 1 indicate for this kind of samples, the changes in chemical structure that occur due to Gamma irradiation, such as the formation of enough crosslinks to prevent crystals from reorganization or to inhibit crystalline rearrangement during heating in the DSC. HDPE, being a higher crystalline material, however, exhibit a different behavior. As expected the melting temperature peak of the fast cooled HDPE sample is lower than for the slow cooled sample, crystals due to their higher perfection are less prone to rearrangement during heating. Irradiation has the effect of increasing the melting temperature for the slow cooled HDPE sample, whereas the fast cooled HDPE sample follows the trend exhibited by the branched samples. For HDPE with a large degree of crystallinity it would be expected that the heat resistance of large and perfect crystals surrounded by crosslinked amorphous layer is increased.

Upon HDPE content in the blend (0-100 %), the initial degree of crystallinity varied between 43 and 64 % for fast cooled samples whereas for the slow cooled blends varied between 44 and 71 %. Measurements of degree of crystallinity failed to show significant changes with irradiation (less than 10%). These results agree with those obtained previously which showed that changes in degree of crystallinity occurred at higher doses than the ones studied in this work⁴. It turned out to be more dependent on the type of cooling applied to the blends, larger values were found for slowly cooled samples.

Table 1. Melting temperature peaks (°C) of some of the HDPE/LDPE blends studied

HDPE/LDPE Blend	Dose (kGy)		
	0	50	150
0/100 S	112.1	110.5	111.0
0/100 R	113.3	110.3	111.6
50/50 S	109.7	109.3	110.0
	131.2	130.6	131.1
50/50 R	132.2	129.3	128.3
100/0 S	134.7	136.0	136.4
100/0 R	133.6	131.9	131.5

S = slowly cooled, R = rapidly cooled.

Figures 1 and 2 show the Young modulus for the slowly and rapidly cooled blends, respectively. The Young modulus showed an increase with radiation for both sets of rich HDPE content blends. That is not the case for the rich LDPE content blends.

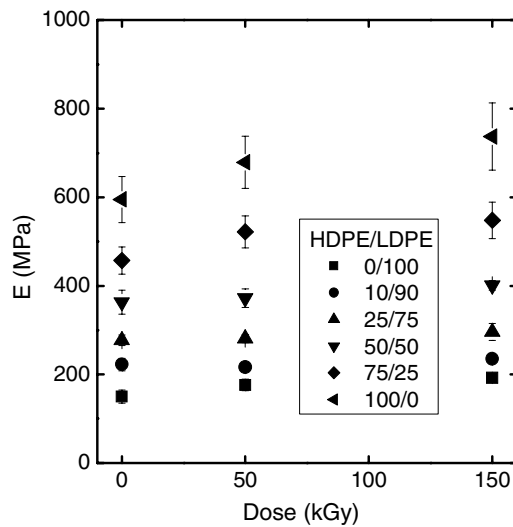


Figure 1. Variation of the Young modulus with radiation dose for the slowly cooled blends.

Slow cooled blends showed higher Young modulus than the fast cooled blends. Apparently, there are not differences between the tendencies observed for slowly cooled blends and the rapidly cooled ones; although the fast cooled neat HDPE showed a larger increase in Young Modulus than the slow cooled HDPE. The increase of this property with irradiation might be attributed to the radiation induced crosslinking, having a reinforcing effect of the non-crystalline phase³ and to the increase in crystallinity caused by chain scission.

The yield stress showed a similar behavior as the one shown by the Young modulus, such behavior is usually observed in polymers¹². Otherwise, the increase of the yield

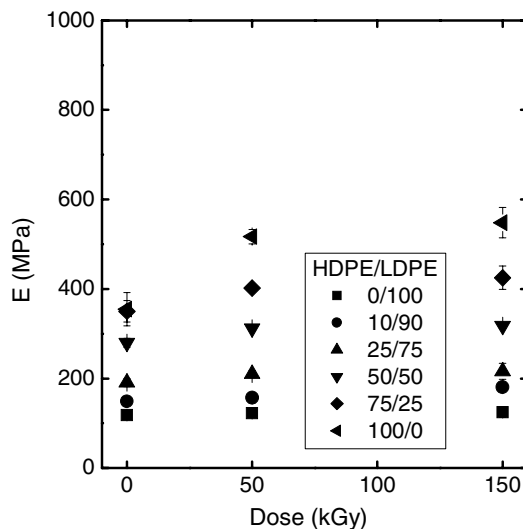


Figure 2. Variation of the Young modulus with radiation dose for the rapidly cooled blends.

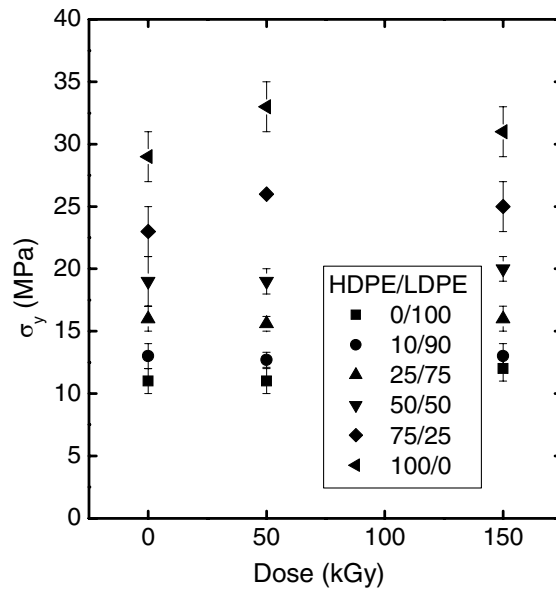


Figure 3. Variation of the yield stress with radiation dose for the slowly cooled blends.

stress for slowly and rapidly cooled samples seems to be smaller, compared to the one seen for the Young modulus, as it can be observed in figures 3 and 4, respectively. The strain at break did not have important changes in blends with high LDPE content; but there was a large decrease (74%) in the rapidly cooled HDPE as expected from the large increase in the Young Modulus observed in Figure 2. This behavior is generally caused by the ductile-fragile transition the material is subject to, induced by

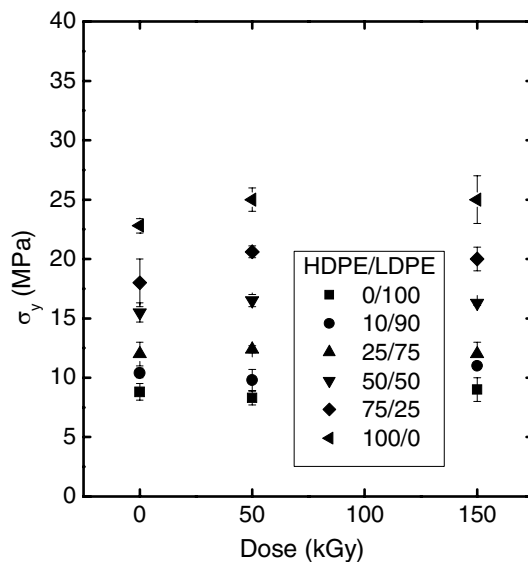


Figure 4. Variation of the yield stress with radiation dose for the rapidly cooled blends.

crosslinking¹. According to Teng et al¹³ quenched neat HDPE has a higher gel content than the slow cooled sample. This explains that the modulus of quenched HDPE experiences a larger increase with radiation than the slow cooled sample (46% and 14%, respectively), i.e. a greater formation of crosslinks is expected. The stress at break of all blends increased with radiation.

The values of MFI of the non-irradiated blends are shown in table 2. Taking into account that melting of the unirradiated samples erases the thermal history, it was meaningless to measure the MFI of the slowly or rapidly cooled blends. With radiation, this property decreased drastically for all blends, due to the radiation induced crosslinking¹⁴. At 50 kGy, the MFI values are shown in table 3. The blends irradiated at a dose of 150 kGy did not flow. The values reported at 50 kGy were much larger for the rapidly cooled blends. The lower values of MFI of slow cooled samples are due to the larger number of free radicals that are trapped in the crystallites^{7,15}. On melting the active radicals quickly react forming additional crosslinks¹⁶. In the other hand, fast cooled blends exhibit lower crystallinity and a larger amorphous fraction enhancing oxygen diffusion and chain scission processes. As a result fast cooled samples show higher values of MFI than slow cooled samples.

We expect that crosslinking occurs randomly between segments of all chains which it would explain that the values of MFI reported in Table 3 are nonlinear function of the content of HDPE. In addition, compatibility between HDPE and LDPE contributes to the above effect.

Table 2. MFI values of the HDPE/LDPE blends, with unirradiated

HDPE/LDPE Blend	MFI Value
0/100	16 ± 1
10/90	15 ± 0.8
25/75	12 ± 0.7
50/50	9.6 ± 0.8
75/25	8.8 ± 0.7
100/0	9 ± 0.4

Table 3. MFI values for both sets of HDPE/LDPE blends, irradiated at 50 kGy

HDPE/LDPE Blend	MFI values			
	Slow Cooled Blends		Fast Cooled Blends	
0/100	0.17	± 0.01	0.21	± 0.03
10/90	0.085	± 0.009	0.16	± 0.03
25/75	0.072	± 0.007	0.27	± 0.02
50/50	0.028	± 0.003	0.10	± 0.01
75/25	0.13	± 0.01	0.30	± 0.02
100/0	0.070	± 0.006	0.24	± 0.02

The density of the blends showed a slight increase with the radiation dose, no larger than 2% in variation, and, as expected due to differences in crystallinity, the slowly cooled blends showed higher values of density than the rapidly cooled ones, as shown

in figures 5a and 5b. The low variation in density with radiation agrees with the tendency obtained for the degree of crystallinity as measured by DSC.

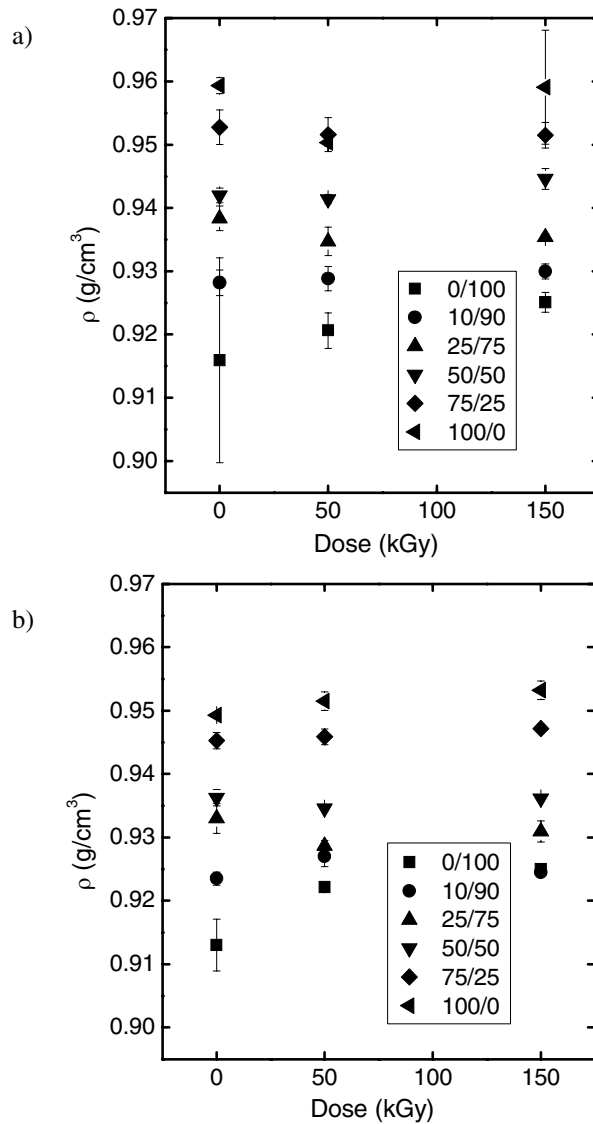


Figure 5. Variation of the density for the HDPE/LDPE blends with radiation dose: (a) slowly cooled blends (b) rapidly cooled blends.

The intimate degree of mixing at the lamellar detail observed in TEM micrographs (Figures 6 and 7) supports the existence of compatibility between both components in the blends.

Figure 6 shows the morphology of a 10/90 blend that was slowly cooled from the melt, for 0 and 150 kGy radiation doses, respectively. In both micrographs the

crystalline lamellar detail is observed. Long and short lamellae are observed. The long lamellae are associated to HDPE component in the blend whereas the short lamellae are due to the presence of LDPE in the blend. There are not clear differences in crystalline features of the slowly cooled blend with radiation at 150 kGy compared to the non-irradiated sample, which is a sign of what was observed in DSC results, showing that there were not important changes in the crystalline region. In addition to this, there were not important changes on the lamellar thickness (5-6 nm approximately for both non-irradiated and irradiated samples).

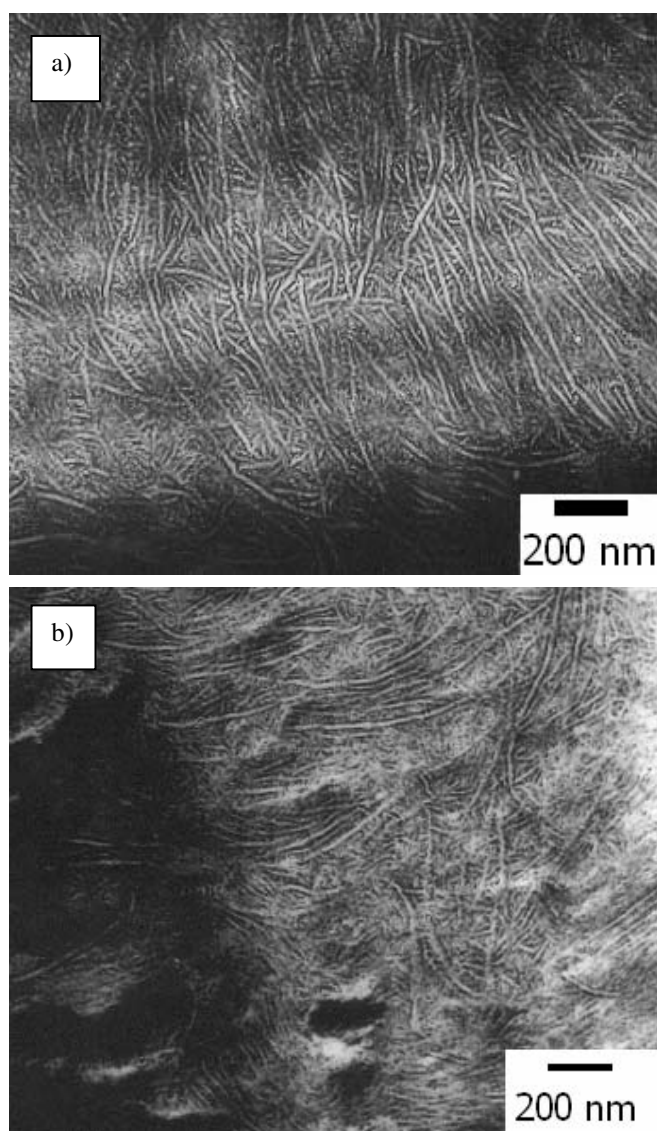


Figure 6. Electron micrograph of a slowly cooled 10/90 blend: (a) unirradiated, (b) irradiated at 150 kGy. Scale bar represents 200 nm.

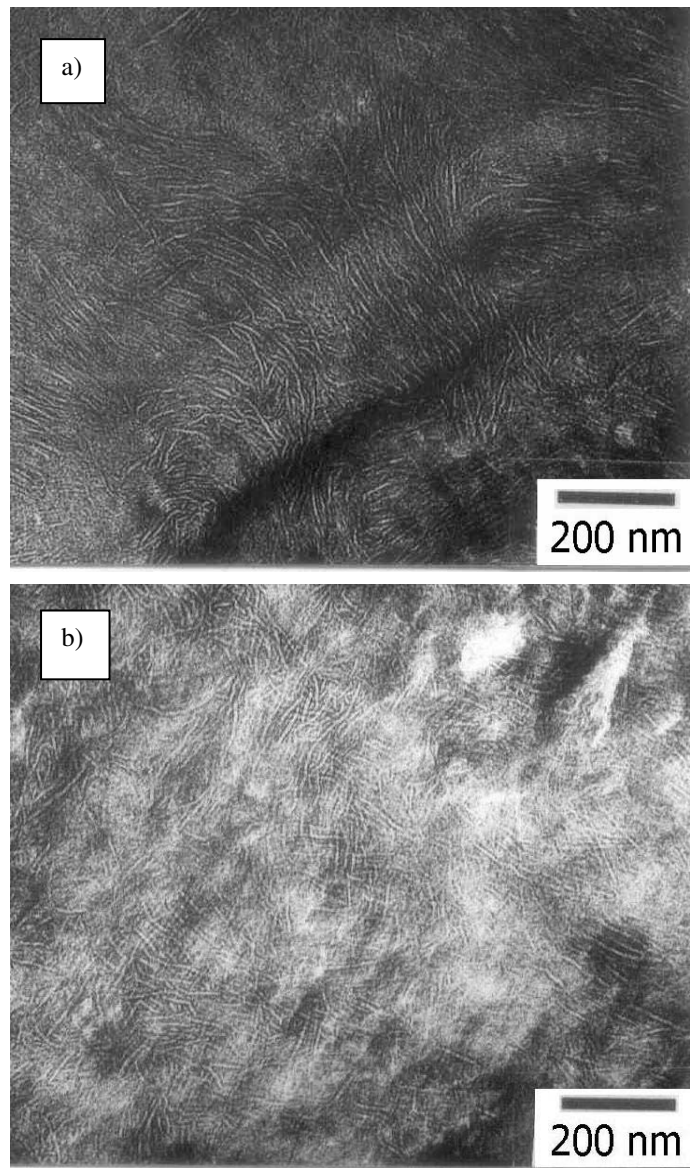


Figure 7. Electron micrograph of a rapidly cooled 10/90 blend: (a) unirradiated, (b) irradiated at 150 kGy. Scale bar represents 200 nm.

Figure 7 shows the morphology of a 10/90 blend that was fast cooled from the melt, for 0 and 150 kGy radiation doses (a, b respectively). In both micrographs the crystalline lamellar detail is observed.

As occurred in the slowly cooled blend, there were not important variations in their crystalline features. Crystals are about 4-5 nm thick in both cases and all are about the same length. In the case of the rapidly cooled blend, there appears to be some network-like arrangement in the irradiated blend, which is not seen in the non-irradiated sample.

This may be due to possible displacements of the crystalline lamellae between the amorphous, mobile zone, which experiments the formation of a radiation induced crosslinked network.

Conclusions

Drastic changes in rheological behavior between slow and fast cooled blends on irradiation were found. Radicals remained active while trapped in the crystalline layers. On melting radicals react forming new crosslinks. For the blends and neat LDPE irradiation prevent crystals from reorganization during heating in the DSC. Crystallinity, density and mechanical properties were not strongly affected by radiation; these properties were more dependent of the type of cooling. The modulus of quenched HDPE experienced a larger increase than the slow cooled sample, due to the heterogeneous nature of radiation effect in the amorphous and crystalline layers. A small increase in crystallinity was found for the rich LDPE content blends as a result of irradiation.

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References

- 1.- Suarez JCM, Mano EB, Pereira RA (2000) *Polym Degr Stab* 69:217
- 2.- Suarez JCM, Da Costa EE, Mano EB (2002) *Polym Deg Stab* 75:143
- 3.- Lyons BY, Weir FE (1972) The effect of Radiation on the Mechanical Properties of Polymers, in Dole M (ed.), vol II, Academic Press New York
- 4.- Vaughan AS, Ungar G, Bassett DC, Keller A (1985) *Polymer* 26:726
- 5.- Suarez JCM, Mano EB, Tavares MIB (2000) *J Appl Polym Sci* 78:899
- 6.- Jones RA, Groves DJ, Ward IM, Taylor DJR, Stepto RFT (1999) *NIMB* 151:213
- 7.- Dole M (1972) *The Radiation Chemistry of Macromolecules*, Academic Press, New York
- 8.- Shinde A, Salovey R (1985) *J Polym Sci, Polym Phys Ed* 23:1681
- 9.- Wunderlich B, Cormier CM (1967) *J Polym Sci* 5:987
- 10.- Montezinos D, Wells BG, Burns JL (1985) *J Polym Sci, Polym Lett* 23:421
- 11.- Peeters M, Goderis B, Vonk C, Reynaers H, Mathot M (1997) *J Polym Sci Part B Polym Phys* 35:2689
- 12.- Brown N (1986) *Yield Behavior of Plastics*, in Brostow W, Corneliusen RD (eds.) Hanser Publishers, Munich
- 13.- Teng H, Dong W, Shi Y, Jin X (2003) *J Appl Polym Sci* 88:536
- 14.- Harper BG (1959) *J App Polym Sci* 2:363
- 15.- Chapiro A (1962) *Radiation Chemistry of Polymeric Systems*, John Wiley & Sons, New York
- 16.- Albano C, Perera R, Silva P, Sánchez Y (2003) *Polym Bull* 51:135