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Characterization of irradiated PEs/PA6 blends

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Summary

In this work, changes caused by γ-radiation on binary blends of different PEs (high, low and linear low-density polyethylenes) with PA6 were studied. The structure and property changes in these samples induced by γ-irradiation were characterized by the ESR, DSC and FTIR techniques. These techniques provide relevant information concerning the reaction mechanisms of the structural modifications that take place during the irradiation of polymers. The experimental results suggest that allyl, alkyl and polyenyl radicals are generated in the materials by the irradiation process. The dynamics dominating the process kinetics seem to be crosslinking, chain scission and a coexistence of both, depending on the sample composition and the absorbed dose. The degradation of the materials produced a disruption in the ethylene sequences in polyethylenes thus decreasing their melting point. Bands attributed to carbonyl groups (C=O) were observed in FTIR spectra after the materials were irradiated.

Introduction

Polyamide (PA) is often blended with some polyolefins, such as polyethylene (PE) or polypropylene (PP), to overcome its disadvantages, such as brittleness, high moisture sorption and poor dimensional stability, though they are incompatible [1-3]. In fact, PA is a polar molecule, whereas PE and PP are not polar. Consequently, they do not present segmental chemical similarity. One possible solution to improve the compatibility of this system is the modification of the interface by adding co-reactive functional groups into the polyolefins' backbones which are able to interact with the terminal groups of the PA.
On the other hand, gamma radiation effects on polymers have been widely investigated [4-13]. They consist mainly in degradation and crosslinking phenomena, whose extension depends on many factors, such as the chemical structure and morphology of the polymer, the irradiation dose and rate, the environmental irradiation conditions, etc.

[14-16]. However, few studies are available in the literature concerning the radiation effects on polymer blends, despite the increasing interest towards these "new materials" which can be used to prepare tailor made plastics with selected properties by a suitable choice of the polymeric components. Yet, in the last years, the interest towards this subject has increased due to the variety of its applications.

Detailed studies on the possibility to have γ-compatibilized materials are needed because it could enlarge the variety of polymer blends. Ionizing radiation induces chemical reactions in polymers that result in changes in both molecular structure and macroscopic properties.

The energy transfer from the radiation to the polymer does not take place selectively relative to mixed components. The probability of the generation of free radicals depends on the strength of interatomic bonds. The lower the bond energy, the easier the bond scission will be. Radiochemical studies on crosslinking or degradation of polymer blends are important for designing new materials. The present work studies the changes caused by γ-radiation on binary blends of different PEs (high, low and linear low-density polyethylenes) with PA6. The structure and property changes induced by γ-irradiation on these samples were characterized by the ESR, DSC and FTIR techniques.

Experimental

A high-density polyethylene (HDPE, MFI of 0.10dg/min at 190°C, 2.16 kg), a low-density polyethylene (LDPE, MFI of 0.19dg/min at 190°C, 2.16 kg), a linear low-density polyethylene (LLDPE, MFI of 0.52dg/min at 190°C, 2.16 kg) and a polyamide 6 (PA6, MFI of 1.95dg/min at 230°C, 2.16Kg) were used in this study. Binary blends of each PE and the PA6 were made in a Werner&Pfleiderer corotating twin-screw extruder at 230 °C and 110 rpm. The composition of the blends was PE/PA6 80/20. Additionally, the homopolymers were extruded at the same conditions of blends preparation, with the purpose that all the used materials had the same thermal history. Samples of the extruded materials were cut into small cylinders or pellets (<3 mm of diameter for approximately 4 mm long). Films of all specimens (1.5-2mm of thickness) were compression molded at 235 °C for FTIR analysis. Both, films and pellets were irradiated with γ-rays from a ^{60}Cobalt source in air, at a dose rate of 4.8 kGy/h and at room temperature. Radiation doses were in the range of 0-1000 kGy.

The ESR spectra were obtained in the X band of an EMX BRUKER spectrometer, at room temperature. The total number of spins per gram of the samples was obtained using the 4-(2-iodoacetamide)-2,2,6,6-tetramethylpiperidinoxyl radical as standard of comparison. The experimental conditions (microwave power and the modulation field) were adjusted to avoid effects of saturation in the ESR spectra.

FTIR spectra were taken from the already irradiated films in a Nicolet Magna-IR 750 spectrometer, in the 4000-400 cm^{-1} interval, at a resolution of 4 cm^{-1} after 32 scans.

Differential scanning calorimetry (Mettler Toledo, DSC 821) was used to study the melting and crystallization behavior of samples weighing 10 mg. DSC was calibrated using indium with a melting temperature of 156.6°C, which resulted within ±1°C in accuracy. Samples were weighed with a precision within ± 0.02 mg. Three tests were carried out for each sample and the temperature difference was less than 1°C. Nitrogen was used as a dragging gas. To erase the previous thermal history, the samples were

heated up to 170°C and kept there for three minutes. Then, the first cooling and the second heating thermograms were recorded at a rate of 10 °C/min. Thermograms were recorded from samples cut out from the already mentioned films.

The Molau test was performed in the irradiated blends to ascertain whether a compatibilizing effect was present [17]. Samples of the blends were dissolved in concentrated formic acid (2% w/v solution) and allowed to rest for 8h at room temperature.

Results and Discussion

1.- Analysis of the ESR spectra.

Figure 1 shows the ESR spectra for the HDPE/PA6, LDPE/PA6 and LLDPE/PA6 blends irradiated at 930 kGy of total absorbed dose. Multiple peaks are observed in the figure due to the presence of different free radicals in the samples. The results can be interpreted as a superimposition of alkyl (- CH_2 -$\dot{C}H$-CH_2 -), allyl (- CH_2 - $\dot{C}H$-$CH=CH$-CH_2 -) and polyenyl (- CH_2 -$\dot{C}H$-(-$CH=CH$ -) n-CH_2 -) radicals [9,10,18]. The coupling hyperfine constants, as obtained from the spectra, are the same in all the blends and correspond to a_1 = 16.6 gauss for alkyl and a_2 = 11.7 gauss for allyl, which are in agreement with those values reported in the literature [10,19-21]. Furthermore, the same figure shows that all spectra are similar, displaying the same number of peaks, which is an indicative of the fact that the same type of radicals were generated, though they are better defined in the HDPE/PA6 blend and less resolved in the LDPE/PA6 one. The inset in figure 1 shows the spectrum for pure PA6. In this polymer, the predominant free radical is formed on the carbon atom α to the amide nitrogen. According to Zimmerman [22], the free radicals must be being produced at equal rates in both the crystalline and amorphous phases. The multiplet of the allyl and
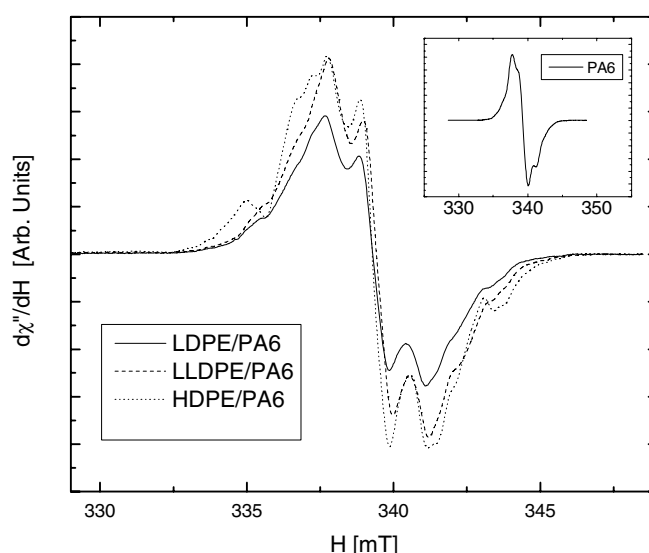

Figure 1: ESR spectra of HDPE/PA6, LDPE/PA6 and LLDPE/PA6 blends irradiated at 930 kGy.
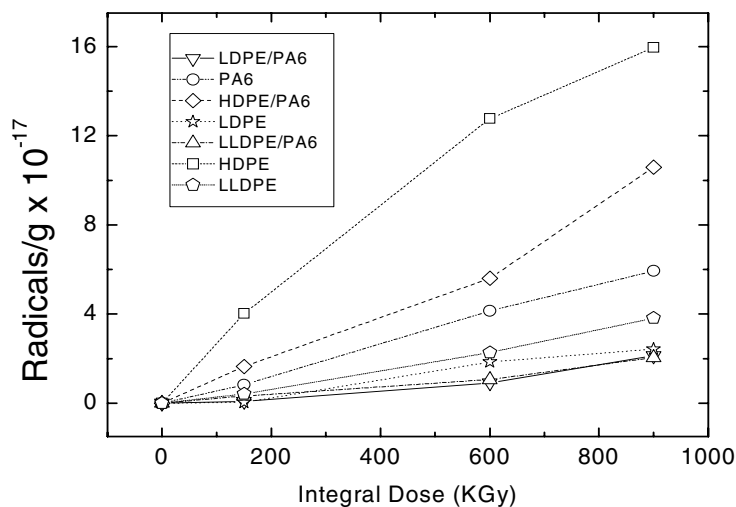
Figure 2: Free radical concentration as a function of the radiation dose of samples recently irradiated.

alkyl radicals is not observed due to their low concentration and a poor resolution in the figure. Once the radicals are formed, they quickly react with each other near their surroundings and are readily consumed owing to the low degree of crystallinity of the PA6 [18]. However, a strong signal is present around $g = 2.003$ corresponding to polyenyl radicals, which are very stable with time.

Figure 2 shows the dependence of the free radicals concentration on the absorbed dose in all the studied samples. An increase in the total free radicals concentration with the absorbed dose was obtained in all cases. In HDPE and LDPE the tendency of the curve unfolded a concavity facing downwards. This behavior can be interpreted in terms of the radical generation and recombination rates [18]. In these materials, the recombination rate is higher than the generation one. On the other hand, the behavior is slightly linear in PA6 and LLDPE. In these cases, the free radical generation and recombination dynamics are similar. Finally, the HDPE/PA6, LLDPE/PA6 and LDPE/PA6 blends showed a slight concavity facing upwards, which can be interpreted as a consequence of higher rates of free radical generation than those of their recombination.

Figure 3 displays the ageing effect on all samples after a month of being irradiated. A strong decay (of around one decade) is observed in the total free radical concentration of all the samples. HDPE unfolded a marked change in the curve concavity probably due to the fact that the recombination rates of the allyl and alkyl radicals are higher than that of the polyenyl recombination rate [18]. The high crystallinity degree of the HDPE is responsible of the higher free radical concentration in this material after 30 days of being irradiated, owing to the fact that free radicals remained trapped in the crystalline regions [21]. In the blends of PA6 and LDPE or LLDPE, a lower total free radical concentration is observed due to their higher reaction rates. It can be concluded that the total radical concentration decays more rapidly in blends than in the pure polymers, and this decay can be attributed to their easy recombination in the amorphous zones due to their high mobility in such zones.
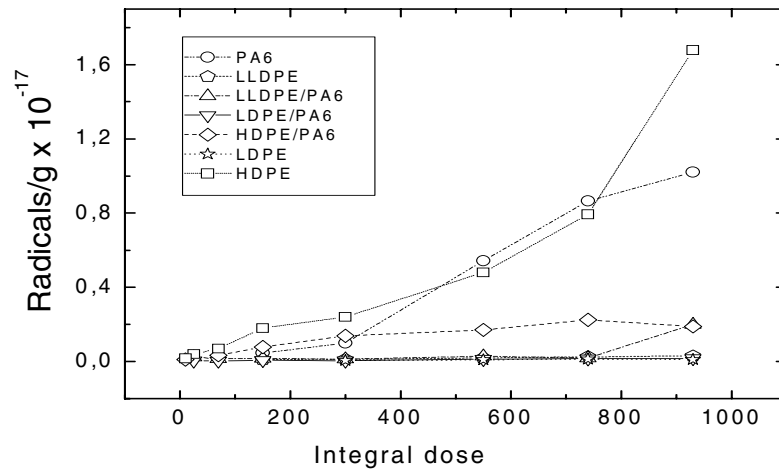
Figure 3: Free radical concentration as a function of the radiation dose of the irradiated samples kept in storage for a month.

2.- *Analysis of the DSC thermograms.*

The DSC technique employed was to examine the changes in the melting and crystallization transitions and in the melting enthalpy of the samples before and after γ irradiation. Figure 4 shows the DSC heating thermograms of the non-irradiated and irradiated blend of HDPE/PA6. A shifting of the endotherm towards lower temperatures is observed. This same behavior was also obtained from the thermograms of the LLDPE/PA6 and LDPE/PA6 blends.
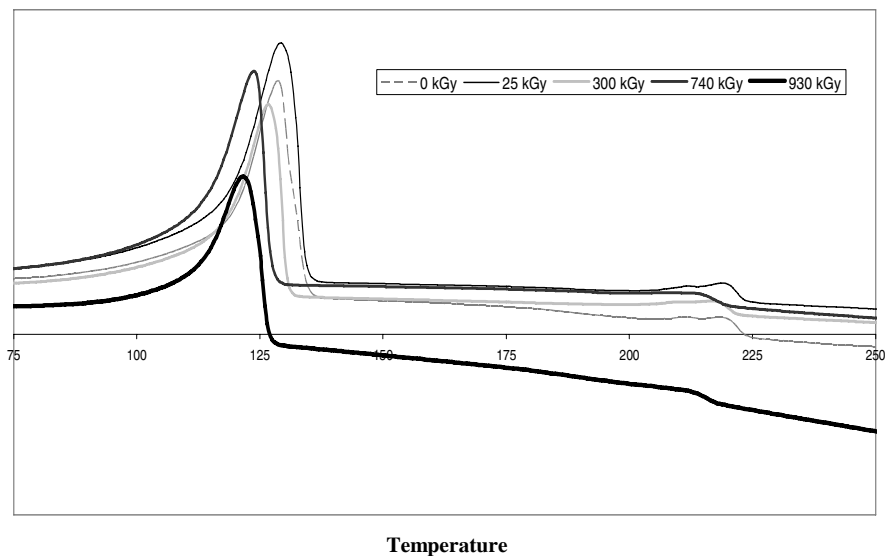

Temperature

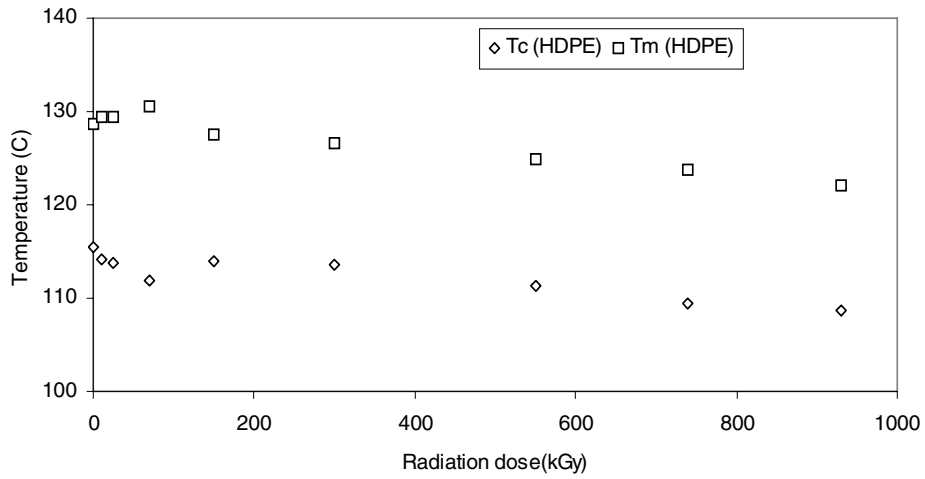Figure 4: DSC endotherms of irradiated HDPE/PA6 blends.

Figure 5: Thermal behavior (Tc and Tm) of HDPE in HDPE/PA6 blends as a function of the radiation dose.

From the recorded DSC thermograms, three main characteristic values such as the peak melting and crystallization temperatures and the melting enthalpy have been derived. In addition, the onset temperature, which is the temperature at which the sample starts to exhibit structural changes, can be taken into consideration and correlated to the irradiation dose.

The changes in the melting temperature (Tm) during heating and in the crystallization temperature (Tc) during cooling of the HDPE/PA6, LDPE/PA6 and LLDPE/PA6 blends were analyzed as a function of the absorbed dose. Figures 5 and 6 displays the Tc and Tm values of the HDPE and LLDPE in the blends with PA6, respectively.
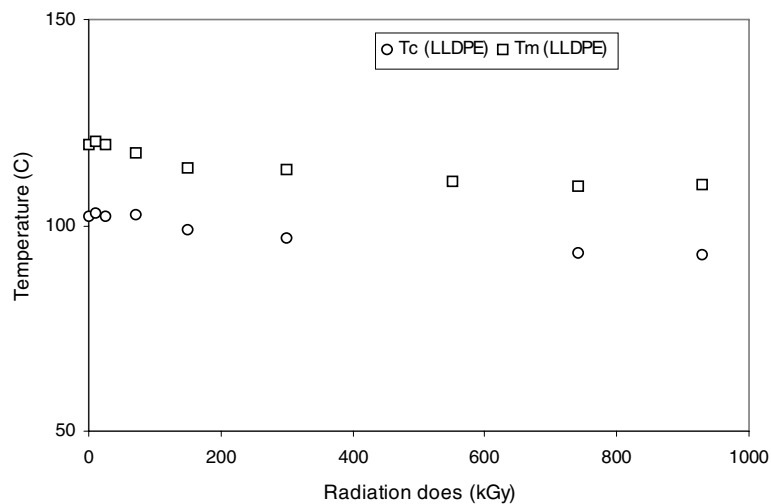

Figure 6: Thermal behavior (Tc and Tm) of the LLDPE in LLDPE/PA6 blends as a function of the radiation dose.
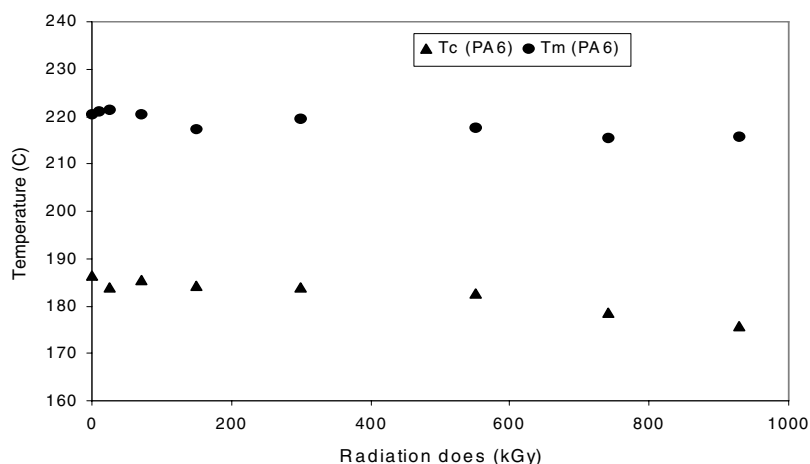
Figure 7: Thermal behavior of PA6 in LLDPE/PA6 blends as a function of the radiation dose.

Those figures unfold the fact that the melting and crystallization temperatures slightly decrease as the irradiation dose increases, showing a non linear behavior. A decrease in the melting point implies a smaller crystallite and/or a less perfect crystal formed after irradiation, because the melting point is an indication of the crystalline size and perfection. A possible explanation could be that branching and/or possibly cross-linking reactions take place after irradiation, causing a disruption in the ethylene sequences thus decreasing the melting point. The progressive decrease in the melting point was interpreted assuming a preferential destruction of the large crystallites by radiation. When the values of Tm and Tc of the PEs in the blends are compared with those of the same polymers individually (as reported by Albano et al [21]), no significant differences are found.

On the other hand, the decrease in Tm and Tc is more pronounced in PEs than in the PA6 present in each blend. Figure 7 displays the thermal behavior of the PA6 in LLDPE/PA6 blends. In those samples, the presence of large amounts of gel fractions in the PEs, already reported by Albano et al [21] in a previous work, hinders the crystallization kinetics, shifting the PA6's melting and crystallization temperatures towards lower values in the irradiated samples.

The melting enthalpy of pure LLDPE and of the LLDPE in its corresponding blend as a function of the absorbed dose is shown in figure 8. The values of the melting enthalpy of other PEs in their blends are reported in Table 1. As it can be seen, the values of the melting enthalpy slightly increase at low doses and then decrease as the absorbed doses increase further. Additionally, the values of ΔHm of the individual PEs are higher than those of the same PEs in the blends. This decrease in the ΔHm values of the polyethylenes in the blends can be attributed to different processes taking place simultaneously: 1) the PA6 could be acting as a diluent in the PEs matrices, thus hindering the crystallization process, 2) the long-chain branches and/or crosslinkings are excluded from the crystals, thereby increasing the defects in the crystallization process [23], 3) some compatibility between the two polymers, due to interactions in the blends at these radiation doses, which in turn decreases the crystallinity degree in the PEs in the different blends. This last possibility was discarded because no evidence of such interactions was obtained from the results of

the Molau test [17], which was performed in all the blends irradiated at every absorbed dose.
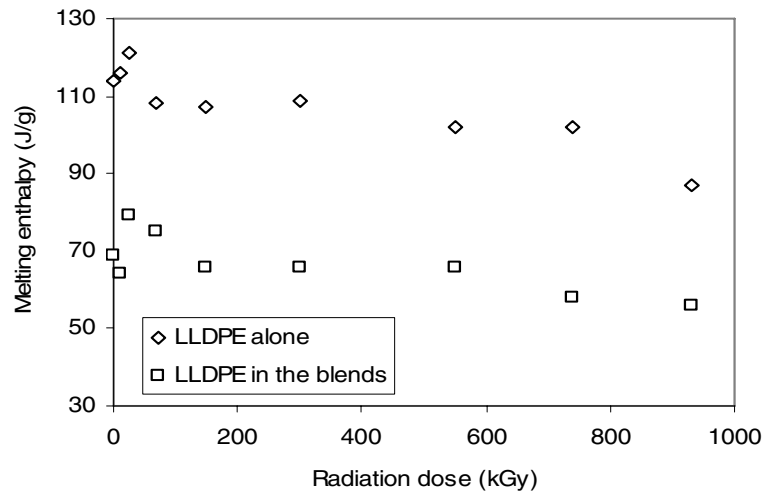

Figure 8: Melting enthalpy for pure LLDPE and LLDPE in the LLDPE/PA6 blends as a function of the radiation dose.

Table 1: Melting enthalpy for pure PEs (a) and PEs in blends (b) with PA6.

Di(kGy)	0	10	25	70	150	300	550	740	930
HDPEa	187	181	189	186	169	173	175	166	150
HDPEb	149	152	162	152	145	150	146	135	115
LDPEa	79	82	82	87	90	88	81	80	78
LDPEb	74	71	75	78	76	68	62	63	60

The critical absorbed dose from where some gel fractions begin to appear is higher than 100kGy [21]. Therefore, at lower doses, oxidative degradation prevails over crosslinking, and shorter chains, produced by such degradation, favors the crystallization process thus increasing the ΔHm value.

Figure 9 shows the Tm and Tc values of the PA6 in the LLDPE/PA6 blends. In this case, the same behavior is observed in both the PA6 forming the blends and the PA6 individually (Table 2). At low absorbed doses there is almost no change in its thermal behavior. Nonetheless, at doses higher than 500 kGy there is a slight decrease in the thermal parameters. The melting enthalpy of the PA6 is not reported owing to its low proportion in the blends and thus the uncertainty of such calculated values, which can be ascertained through the observation of the shape of its endotherm in figure 4. This fact can also be attributed to the dispersion of the PA6 in the polyethylene matrices, which makes its crystallization difficult. The likelihood of PEs being crosslinked further enhances these difficulties.

The behavior of polyethylenes towards radiation affects their crystallization in the blends. On the other hand, the physical results of irradiation onto PA6 include degradation and crosslinking. PA6 becomes crosslinked with high energy radiation
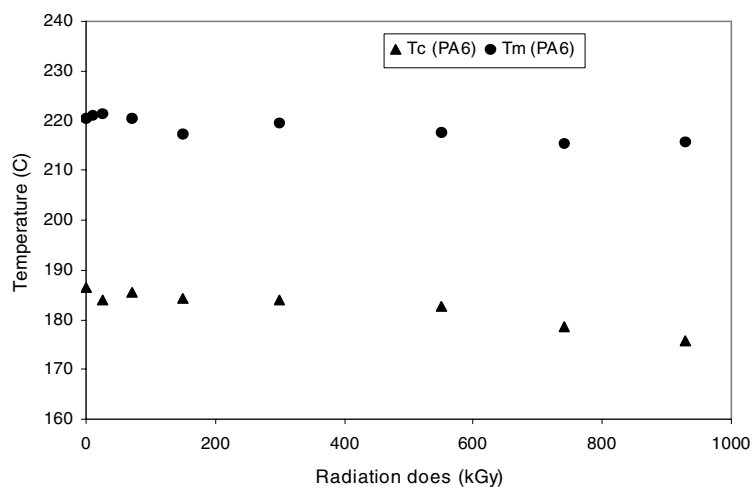
Figure 9: Melting and crystallization temperatures of PA6 in LLDPE/PA6 blends as a function of the radiation dose.

[25], which implies that its crystallinity is disrupted at high doses. According to Slovookhotova [26], the crosslinking in polyamides proceeds via hydrogen abstraction from the CH_2 group. The intermolecular hydrogen bonds are gradually destroyed while intramolecular hydrogen bonds appear leading to cyclic structures. Another probable cause of this behavior is that the molecular weight of the PA6 irradiated at high doses increases through chain branching according to the literature [15].

Table 2: Melting and crystallization temperatures of pure PA6 as a function of the radiation dose.

Di(kGy)	0	10	25	70	150	300	550	740	930
Tc (ºC)	183	184	184	184	183	184	182	179	182
Tm(ºC)	220	220	220	219	218	219	217	215	214

3.- Analysis of the FTIR spectra.

From the analysis of the FTIR spectra, similar behaviors are observed in the different PEs/PA6 blends. Figure 10 displays some spectra of pure HDPE and its blend with PA6, irradiated at an absorbed dose of 300 kGy.
In the 1600-1800 cm^{-1} interval, the increase of the band attributed to carbonyl groups (C=O) when the materials are irradiated can be observed. The degradation products containing the carbonyl group are mainly ketones (1718 cm^{-1}), carboxylic acids (1713 cm^{-1}) and esters (1741 cm^{-1}). When the HDPE and HDPE/PA6 spectra are compared, the fact that PA6 must be interfering in the degradative process of the HDPE could be taken into consideration, because the degradation bands are less pronounced in the blends. No conclusions other than a slight decrease in the band at 909 cm^{-1} with irradiation can be drawn from the analysis of the 900-1000 cm^{-1} interval.

Figure 11 shows the effect of the absorbed dose in the chemical structure of the HDPE/PA6 blend. In the 1600-1800 cm^{-1} interval, the increase of the band attributed to carbonyl groups (C=O) with the radiation dose could also be observed. Due to the simultaneous presence of different degradation products, the band ascribed to -C=O groups appears broader with the increase in the irradiation dose. In the same figure, the band at 965 cm^{-1}, attributed to the trans-vinylene groups (trans-RCH=CHR), seems to become broader with the irradiation dose at the expense of the decrease in that at 909 cm^{-1} (attributed to terminal vinyl groups), which implies the possibility that crosslinking and/or long chain branching could be taking place in HDPE.
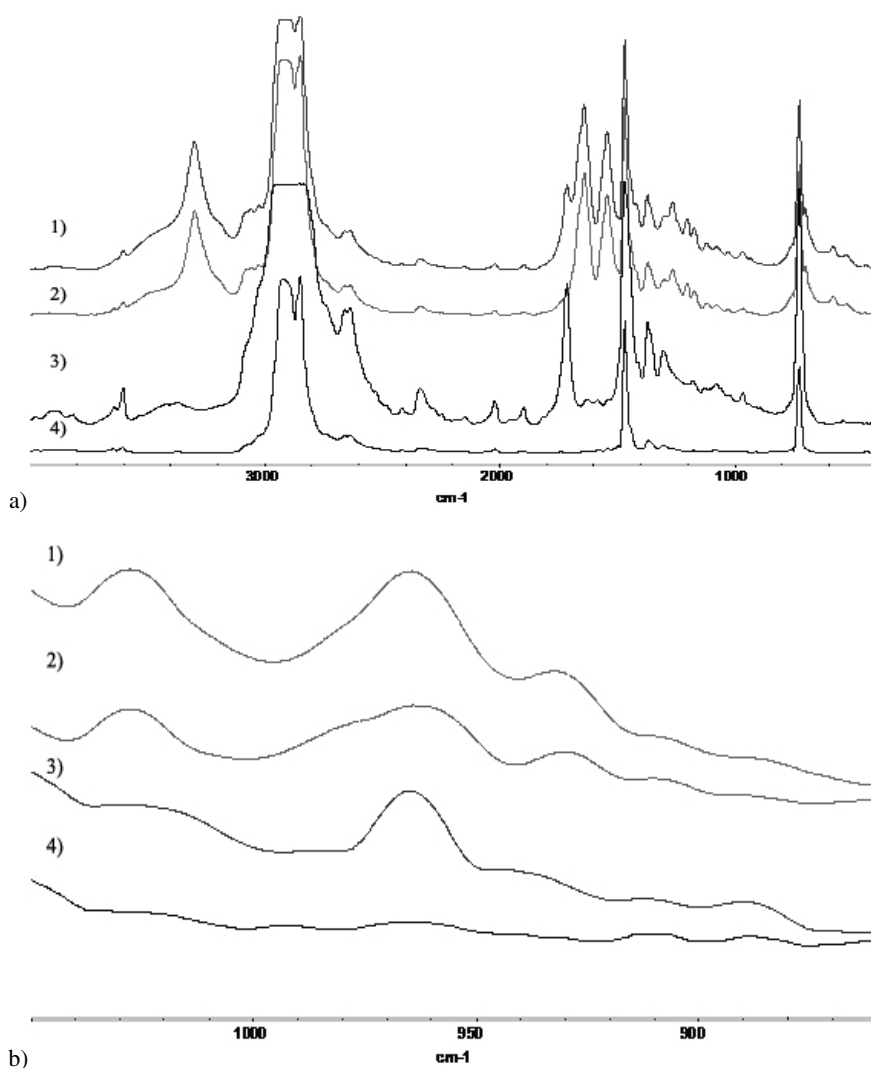

Figure 10: a) FTIR spectra of pure HDPE and its blends with PA6 irradiated at 300 kGy. 1) HDPE, non irradiated, 2) HDPE, irradiated at 300 kGy, 3) HDPE/PA6, non irradiated, 4) HDPE/PA6, irradiated at 300 kGy. b) Detail of the 900-1000 cm^{-1} interval.
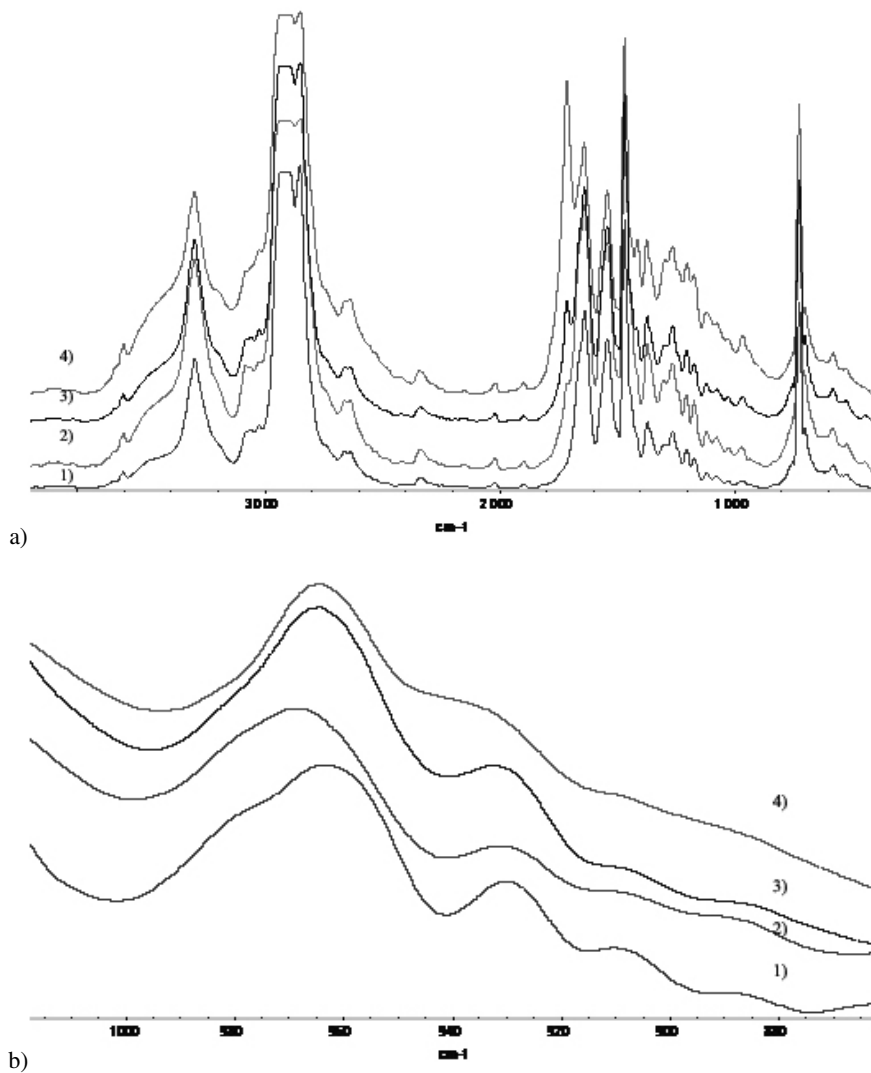
a)

b)

Figure 11: a) FTIR spectra of HDPE/PA6 blend irradiated at different absorbed doses. 1) HDPE/PA6, non irradiated, 2) HDPE/PA6, irradiated at 150 kGy, 3) HDPE/PA6, irradiated at 300 kGy, 4) HDPE/PA6, irradiated at 930 kGy. b) Detail of the 900-1000 cm^{-1} interval.

Conclusions

The experimental results suggest that allyl, alkyl and polyenyl radicals are generated in the materials after the irradiation process. The dynamics dominating the process kinetics seems to be crosslinking, chain scission and a coexistence of both, depending on the sample composition and the absorbed dose. The degradation of the materials produced a disruption in the ethylene sequences in polyethylenes thus decreasing their melting point. Bands attributed to carbonyl groups (C=O) after the materials were irradiated could be observed through FTIR analysis.

References

1. Valenza A, Spadaro G, Calderaro E, Acierno D (1993) Polym Deg Stab 33(13):845
2. Valenza A, Geuskens G, Spadaro G (1977) Eur Polym J 33(6):957
3. Spadaro G, Acierno D, Dispenza C, Calderaro E, Valenza A (1996) Radiat Phys Chem 48(2):207
4. Rizzo G, Spadaro D, Acierno D, Calderaro E (1983) Rad Phys Chem 21(4):349
5. Spadaro G, Rizzo G, Acierno D, Calderaro E (1984) Rad Phys Chem 23(4):445
6. Spadaro G, Valenza A, Calderaro E, Brucato V (1993) Thermodinamica Acta 227:75
7. Adem E, Burillo G, Avalo-Borja M, Carreón MaP (2005) Nuc Inst and Meth In Phys Res 236:295
8. Singh A, Silverman J (1992) Progress in Polymer processing Vol 3: Radiation Processing of Polymers, Hanser Publishers, Chapter 4
9. Ikada Y, Nakamura K, Ogata S, Makino K, Tajima K, Heñido N, Hayashi T, Fujita S, Fujisawa A, Masuda S, Ooonishi H (1999) J Polm Sci Part A Polym Chem 37:159
10. Jahan MS, McKinny KS (1999) Nuc Inst and Meth In Phys Res 151:207
11. Grecu VV, Chipara MD, Georgescu L, Chipara MI (1994) Romanian Reports in Phys 46:535
12. Chipara MD, Chipara MI (1992) Polym Deg Stab 37:67
13. Chipara MI, Ifrim A, Grecu VV, Toacsn MI, Popescuy-Pogrion N, Ionescu A, Chipara MD, Reyes J (1994) Polym Deg and Stab 43(2):165
14. Dole M (1972) The Radiation Chemistry of Macromolecules, Academic Press, New York
15. Charlesby A (1972) Radiation effects in Polymers, in AD Jenkins (Ed), Polymer Science, North-Holland, Amsterdan
16. Charlesby A (1991) The effects of ionizing radiation on polymers, in Clegg DW, Collyer AA (Ed), Elsevier, London , UK
17. Molau G. E. (1965) J. Polym. Sci. A3, 1267
18. Silva P, Albano C, Perera R, Gonzalez J, Ichazo M (2004) Nuc Inst and Meth In Phys Res 226: 320
19. Jahan MS, Wang C, Schwartz G, Davidson JA (1991) J Biomed Mater Res 23: 1005
20. Davidson JA, Schwartz G (1978) J Biomed Mater Res 21: 261
21. Albano C, Perera R, Silva P, Sanchez Y (2003) Polymer Bulletin 51:135
22. Zimmerman J (1960) J Polym Sci 46: 151
23. Flory P (1956) J Am Chem Soc 78:5222
24. Chapiro A (1962) Radiation Chemistry of Polymeric Systems, John Wiley & Sons, New York
25. Charlesby A (1953) Nature 171:167
26. Slovokhotova NA, Ilïcheva ZF, Valisiev LA, Kargin VA (1964) Polymer Science USSR 6(4): 671