



CROSSLINKING OF RECYCLED POLYETHYLENE BY GAMMA AND ELECTRON BEAM IRRADIATION

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ABSTRACT

Recycling of polymeric materials is usually accompanied by degradation and deleterious properties. Irradiation crosslinking of recycling low density polyethylene by electron beam and gamma rays could be the solution to improve their properties. This paper presents a comparison on the effects of gamma and electron irradiation on virgin and recycled polyethylene. Their mechanical, thermal and chemical properties were analyzed. VPE samples shown higher crosslinking percentages than RPE samples in all range of doses studied, unirradiated RPE samples had higher values on their tensile properties than VPE. Percentage crystallinity was similar in all range of doses studied.

KEYWORDS

Crosslinking, Gamma rays, Electron beam, Polyethylene, Recycling polyethylene.

INTRODUCTION

Recycling of polymeric materials collected from household waste (bottles, packaging materials, etc.), is more than a necessity, it is our obligation towards an conscientious and clean society. Polyethylene PE is one of the most used polymer material and also one of the most non biodegradable waste products.

However, repeated recycling is accompanied by serious technical problems, such as molecular weight decrease due to degradation and poor mechanic properties. PET, HDPE and PVC (Zemlitskii, 1990) have received more attention because it is more economically viable to collect plastic beverage bottles and because the market for these polymers exist in far greater size. Recycling of LDPE has been less studied in spite of its higher consumer amount (Andrews 1992).

Recycled LDPE could easily be crosslinked by ionizing radiation, gamma ray sources or electron beam accelerators, and therefore used to produce polyethylene foam (Salamone 1996).

It is well known that the effect of radiation in polymers is degradation or the formation of intermolecular bonds (crosslinking). This latter effect leads to an increase in the average molecular mass and to an increase in their intrinsic viscosity. At a comparatively high absorbed dose, a fraction of the crosslinked polymer (gel) is insoluble in solvents.

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Crosslinking was first studied in detail for polyethylene (Charlesby 1960). PE undergoes considerable change as a result of radiation induced crosslinking. It become flexible and rubbery after large doses (many kGy to several MGy), with reduced solubility in organic solvents and with higher melting point.

Because of this effect, the properties of recycled PE could be enhanced by the effect of ionizing radiation.

The aim of this work is to study the effects of gamma and electron beam irradiation on recycled low density polyethylene (RPE) at different irradiation doses and their chemical, thermal and mechanic properties.

EXPERIMENTAL

Materials

Samples consisted of virgin low density polyethylene (VPE) pellets from PEMEX (Petróleos Mexicanos), with a molecular weight of 39000, density of 0.926 g/cm³ (determined by flotation method) and a crystallinity of 46 percentage (calculated by X-ray spectroscopy) and recycled low density polyethylene (RPE) from Reich Mexicana de Plásticos, with a molecular weight of 29000, density of 0.88 g/cm³, and crystallinity of 46 percentage.

Radiation Sources

The irradiation process was performed using two separate sources. For ⁶⁰Co gamma ray irradiation, a Gammabeam 651 PT with 49 000 Ci was used, with a dose rate of 5.1 kGy/h, and doses from 0 to 350 kGy. For electron irradiation, a Van de Graaff accelerator of 2 MeV (High Voltage Engineering Corporation) was used. The electron irradiation was carried out at 1.3 MeV, at a dose rate of 42 kGy/h, and doses from 0 to 350 kGy.

Sample Preparation

One Kg of VPE or RPE was extruded in a Rheomex 254, formed by the mixer Rheomex 600 and a Haake Rheocord System 90 under the following conditions: mixer temperature 180°C, extruder temperature 190°C, speed of 32 rpm and atmospheric pressure. Sheets of 10 cm wide and 1 cm thick were formed and cut according to ASTM D-1708, for the mechanical determinations. Strips of 1cm wide, 3 cm long and 1 cm thick were used in the gel determinations.

Characterization

The crystalline structure of the films was analyzed using a Philips X¹ Pert diffractometer with Cu K α radiation of 1.5406 Å wavelength. Crystalline percentage was calculated by profile, fitting the X-ray spectrum in the range 12 to 28 degrees. This procedure found three peaks in this range, a broad one assigned to the amorphous component, and two less-narrow peaks, arising from crystalline components. The percentage crystallinity was calculated according to the standard formula %C = $I_c / (I_c + I_a)$, where I_c was the integrated counts for the crystalline peaks, and I_a was the integrated counts for the amorphous peak. Attenuated total reflection (ATR) IR analysis of the surface of grafted films was carried out with a Perkin Elmer FTIR (model 1600) spectrophotometer. A TA Instruments (model 2910) operated at a heating rate of 10 C/min was used to study the thermal behavior (DSC) of the samples.

Tensile measurements were carried out by means of an Universal testing machine (Instron model 1125), according ASTM D-1708. A crosshead speed of 100 mm/min, was used in all measurements.

The gel fractions of the irradiated samples were determined by extraction in Xylene at 135°C during 30 h in a soxhlet system. From this data, the dose of incipient gel R_g , G_c and G_d (radiochemical yields of crosslinking and degradation) were deduced with the Charlesby-Pinner relation (Charlesby 1960).

$$S + \sqrt{S} = p/q + 2/quD$$

Where, S is the soluble fraction of the polymer, D is the radiation dose in Mrad, q is the proportion of units crosslinked, p is the ratio of main chain fractures to chain units, and u is the weight average of the initial degree of polymerization. G_c and G_d were estimated from the following equations. where G correspond to the number of crosslinks or scissions per 100 ev.

$$G_c = 0.48 \times 10^6 q/w \quad G_d = 0.96 \times 10^6 p/w$$

here w is the chain unit of molecular weight.

RESULTS AND DISCUSSION

Figure 1 shows the percentage of gel formed in VPE and RPE irradiated with electron beam accelerator and gamma rays as a function of radiation doses.

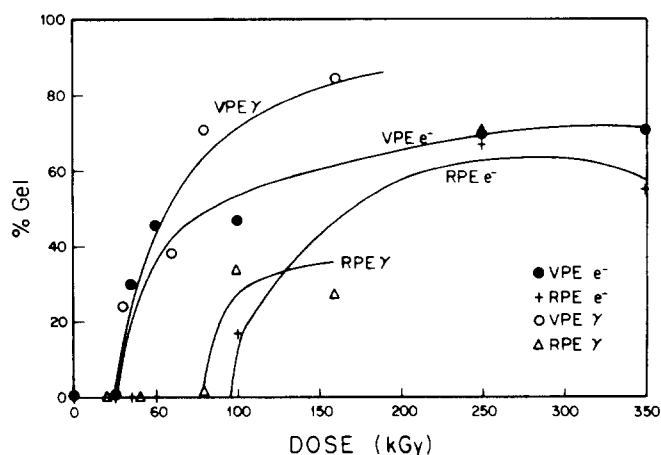


Fig.1. % Gel in irradiated samples

Electron beam irradiated PEV samples required lower doses than RPE to be crosslinked. The dose of incipient gel R_g found for VPE and RPE were .025 and .07 MGy respectively. Gamma irradiated RPE shows higher R_g (0.8 MGy) than electron beam irradiated RPE. Adem et al.(1995) found R_g and the ratio of scission and crosslinking yield (Δ) as 0.3 MGy and 0.46 in powder VPE samples irradiated by electron beam in presence of the foaming agent (azodicarbonamide). For gamma irradiated samples they found R_g and (Δ) as 0.018 MGy and 0.70 respectively. In this paper the increase on the R_g in RPE samples could be due to the effect of its lower molecular weight .

Thermal behavior

Results of DSC melting thermograms for VPE and RPE at different irradiation doses, with electron beam and gamma rays are shown in table 1. The melting point of electron beam irradiated VPE decrease with the increase in the radiation dose. A similar behavior is show for the RPE case.

This increase is less considerable in VPE and RPE gamma irradiated samples, as can be observed in table 1. Powder RPE samples have a melting point of 113.8 °C, but when it was extruded, some reaction occurred, due perhaps to some additives or to the different procedures required for recycling. This caused an increase in the melting point to 126.6°C (Figure 2).

Table 1. DSC melting point (°C) for RPE and VPE samples at different radiation doses

Dose kGy	Electron Beam		Gamma Rays	
	RPE	VPE	RPE	VPE
0	126.6	117.2	126.6	117.2
35	125.0	114.5	—	115.0
50	125.6	113.7	126.5	115.4
100	122.6	111.5	125.9	114.5
250	121.0	110.3	122.6	115.2
0	113.7*	112.5*		

* powder sample

Infrared Determinations

Figure 3 presents the FTIR-ATR spectra of RPE and VPE electron beam irradiated samples. CH stretching vibrations of the CH₂ groups, for both polymers irradiated at doses from 0 to 250 kGy are located at 2914 and 2486 cm⁻¹. Double bond stretching vibrations were found at 1649 cm⁻¹.

Typical bands of carbonyl at 1700 cm⁻¹ can be seen in RPE samples irradiated at 250 kGy and at 1740 cm⁻¹ in VPE irradiated samples at only 100 kGy.

We did not observed carbonyl bands in gamma irradiated VPE and RPE samples, irradiated at doses lower than 250 kGy, but double bond stretching vibrations were found in both polymers near 1646 cm⁻¹. The carbonyl formation in electron beam irradiated samples could be due to the residual amount of oxygen due to different vacuum system in gamma and electron beam irradiation. RPE and VPE unirradiated samples show similar spectra.

Mechanical Properties

The tensile mechanic properties of RPE and VPE gamma and electron beam irradiated, are given in figures 4 and 5. Figure 4 gives the percentage strain at break as a function of radiation

doses. VPE and RPE irradiated samples exhibit an apparent maximum at 25 kGy. The percentage of strain at break for RPE is higher than in case of VPE, but it is because the initial value of RPE without irradiation is higher than the initial value of VPE. The percentage of increase of them at 25 kGy are 52 percentage and 15 percentage for VPE and RPE respectively.

This maximum was not present in gamma irradiated samples. In this case, both polymers VPE and RPE decrease with increase in dose. Figure 5, shows Young's modulus values in MPa, as a function of doses in kGy. Electron beam irradiated RPE and VPE present similar behavior with a minimum value at 25 kGy. Gamma irradiated RPE and VPE samples also present similar behavior.

Unirradiated RPE samples present higher values on their mechanic properties of stress at break, stress at peak, Young's modulus, and strain at break than VPE. Both polymers are transparent (before testing at the Instron), but after these determinations RPE seems to be more crystalline (non transparent material), because of some molecular orientation on the strain process. VPE, on the other hand, continue to have the same transparent characteristics.

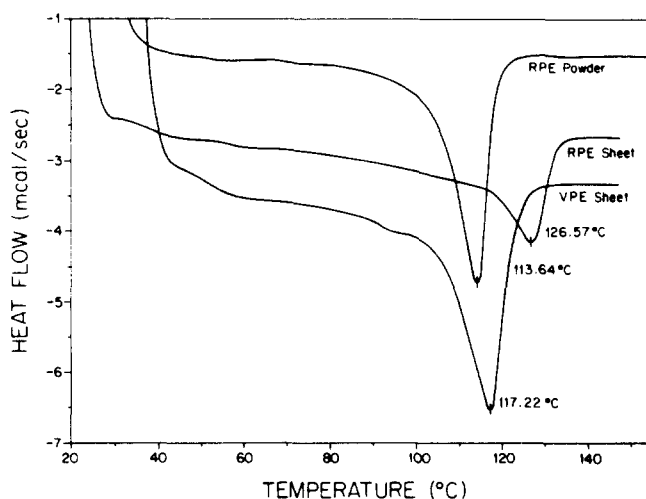


Fig.2. DSC Thermograms of unirradiated samples

X-ray diffractometry

The crystalline structure of the RPE and VPE determined by X-ray is similar in both polymers did not show considerable changes with irradiation in the range of doses studied. We consider that crosslinking was taking place in the amorphous regions of PE, and therefore, crystallites were not affected in the process.

CONCLUSIONS

RPE samples shown a considerable increase on its melting point after be extruded and higher initial values on the unirradiated samples in all mechanic properties studied, than VPE. More studies have to be done to explain these contradictory results.

RPE samples required higher doses than VPE to be crosslinked in spite of his high level of branching (low value of density) and because of his lower molecular weight found than VPE. The increase on mechanical properties in both polymers was less considerable in gamma irradiated samples than in electron beam irradiated ones.

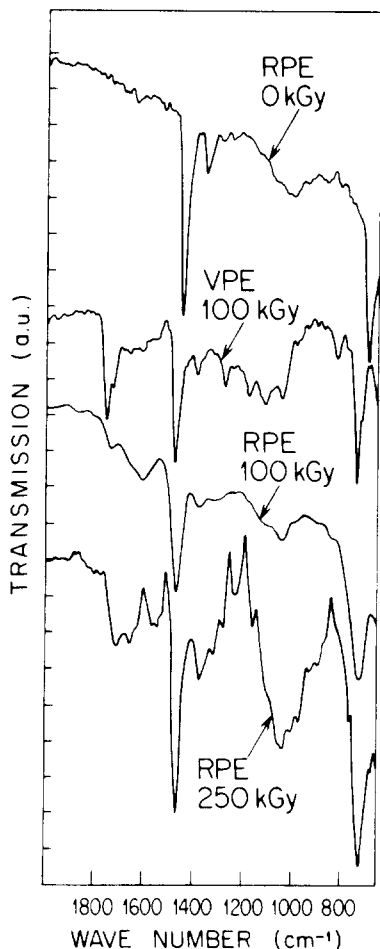


FIG. 3 FTIR SPECTRA OF ELECTRON BEAM IRRADIATED SAMPLES

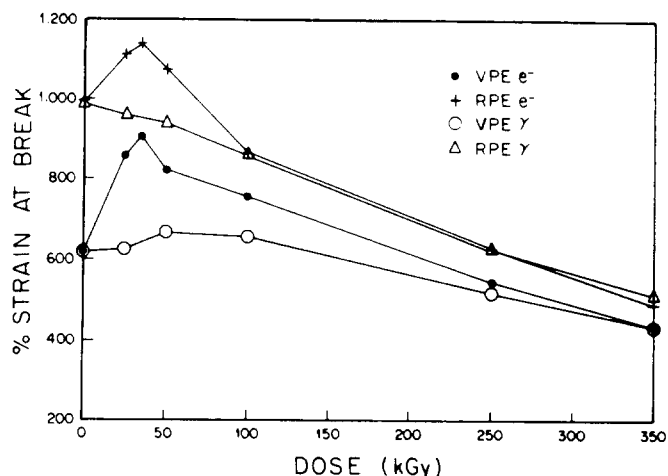


Fig.4. % Strain at break in irradiated samples

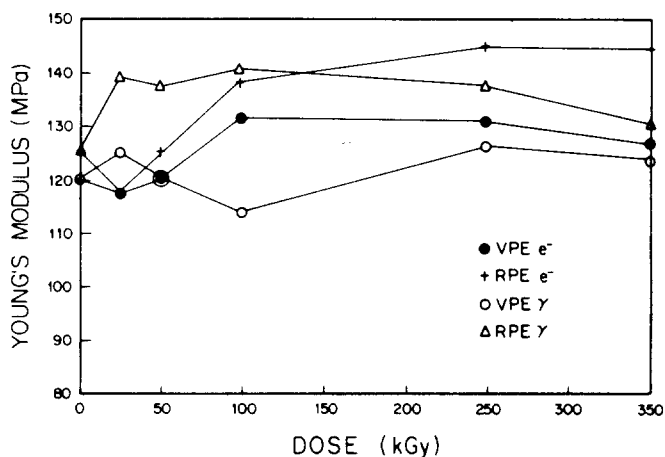


Fig.5. Young's modulus in irradiated samples

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