Tensile Behavior of Irradiated Recycled Polyolefin Plastics

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ABSTRACT: Solid wastes represent a potential source for raw materials in the world. In Brazil, municipal solid waste (MSW; 2–%) is expected to grow at a rate per year higher than the worldwide rate (1%). On the other hand, the consumption of polymer blends increases at a rate more than twice that of all plastics. Therefore, the recycling of polymeric blends has gained increasing attention in the world due to economic and environmental considerations. A two-step process, developed at the Institute (IMA/UFRJ), allows one to recover plastic residues and permits the production of materials with controllable composition and homogeneous characteristics. The compression behavior of polyblends, composed of typical polymers that appear in domestic wastes—low and high polyethylenes—can be improved by gamma irradiation. In the present work, the tensile behavior of recycled 75/25 blends of low-density polyethylene (LDPE) and high-density polyethylene (HDPE), after exposure to gamma rays in the air, was investigated. Tensile testing, scanning electron microscopy, infrared and solid-state ^{13}C-nuclear magnetic resonance spectroscopy, as well as gel content were used to study the effect of gamma irradiation on the polymer blends. The tensile strength was found to increase with radiation dose while the elongation at break decreased. Our experimental results indicate that the gamma irradiation degradation process involves crosslinking at lower doses and chain scission at higher doses. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 899–909, 2000

Key words: recycling; PE blend; gamma radiation; tensile behavior; fracture

INTRODUCTION

In Brazil, the quantity of plastic materials in urban wastes, as compared to the world, is relatively low. However, its municipal solid waste (MSW, 2–3%) is expected to grow at a rate per year higher than the worldwide rate (1%).[1] On the other hand, the consumption of polymer blends increases at a rate more than twice that all of plastics.[2,3]

Several aspects of the reprocessing of waste plastics to obtain materials with good properties was discussed in the literature.[4–8] The institute (IMA/UFRJ) developed several materials with good properties using plastic residues found in municipal urban wastes.[9–12] One of those materials is a recycled 75/25 blend of low-density polyethylene (LDPE) and high-density polyethylene (HDPE) that shows good compatibility between its components, but does not have the necessary deformation strength requirements for some applications in housing items.

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Table I Gel Content of Recycled 75/25 LDPE/HDPE Blend Before and After Gamma Irradiation

Dose (kGy)	Gel Content (%)
0	0
100	92
500	66
2000	32

Polymer materials are sensitive to various types of high-energy radiation such as gamma rays, neutrons, and alpha particles. The potential commercial use of recycled materials increased our interest to investigate the effectiveness of high-energy radiation to improve the mechanical properties of such materials.[13,14] The controlled exposure of virgin PE products to gamma rays improved their tensile properties due to partial crosslinking was reported in the literature, but few data on the behavior of irradiated recycled polyolefins were found.[15]

The present work is part of a general investigation on recycled polyolefin blends that has been undertaken in our laboratories.[13–17] The results of the tensile evaluation and the relationship between the fracture behavior and the macromolecular modifications in a recycled 75/25 LDPE/HDPE blend, after exposure to various doses of ^{60}Co gamma radiation in the air, is reported now.

EXPERIMENTAL

The gel fraction was determined using a Soxhlet extractor, using xylene as a solvent. Samples were exposed to refluxing xylene close to its boiling point for at least 72 h, until the sample attained a constant weight. The extraction residue was taken as the gel content. A 75/25 LDPE/HDPE blend was prepared from postconsumer flexible plastic items (bags and other packaging film residues) found in the municipal solid plastic waste of the city of Rio de Janeiro, Brazil, as described elsewhere.[10,11]

Gamma irradiation was carried out directly on the tensile specimens in a ^{60}Co industrial equipment at room temperature in the air. The samples were exposed to 100-, 500-, and 2000-kGy doses at a 2.5-kGy/h dose rate. Tension testing, scanning electron microscopy (SEM), infrared (IR), and ^{13}C-nuclear magnetic resonance (^{13}C-NMR) spectroscopy as well as the gel content were used to investigate the behavior of the recycled PE blend, before and after irradiation.

A Model 4204 Instron universal testing machine with a crosshead speed of 10 mm/min was used for the tensile tests, according to ASTM D1708.[18] The specimens were machined from injection-molded plates parallel to the flow direction.

A JSM 5800LV JEOL scanning electron microscope was used to study the topography of the tensile fracture surfaces to determine the failure mechanisms. Before examination, the fracture surfaces were sputter-coated with a thin layer of gold in a vacuum chamber.

IR measurements were performed using a Perkin–Elmer Model 1720 spectrometer in the 4000–400 cm^{-1} region, using the multiple internal reflectance (MIR) technique and a TGS detector. One hundred scans were signal-averaged.

The ^{13}C-NMR solid-state spectra were obtained on a Varian Inova 300 spectrometer operating at 75.4 MHz at ambient probe temperature. The ^{13}C determinations were carried out in the cross-polarization mode with magic-angle spinning (CP/MAS), magic-angle spinning (MAS), and cross-polarization with magic-angle spinning and dipolar decoupling (CP/MAS/DD).

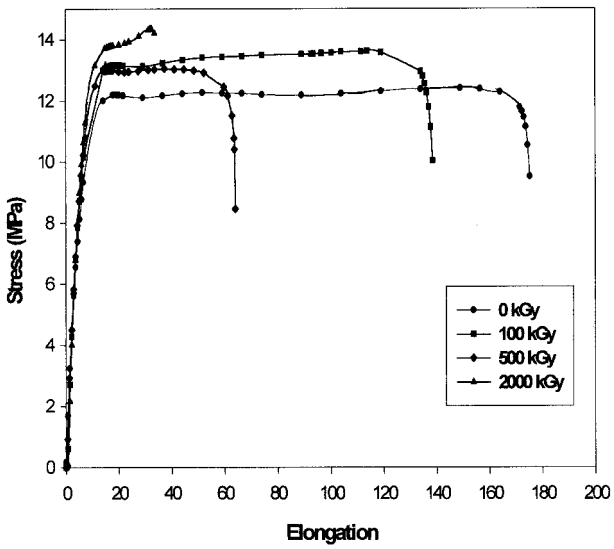


Figure 1 Stress–strain curves of recycled 75/25 LDPE/HDPE blend before and after gamma irradiation.

Table II Tensile Properties of Recycled 75/25 LDPE/HDPE Blend Before and After Gamma Irradiation

Dose (kGy)	Maximum Stress (MPa)	Elongation at Break (%)
0	12.4	176
100	13.3	163
500	13.2	67
2000	14.4	33

RESULTS AND DISCUSSION

Degree of Crosslinking

Table I presents the gel contents of the nonirradiated and irradiated samples, obtained by xylene extraction. By gamma irradiation, the gel content shows a rapid increase up to 92% for a 100-kGy dose, followed by a continuous decrease as the dose was increased to 2000 kGy. This seems to indicate that there is a limiting effect in the crosslinking of the recycled blend: Crosslinking occurs for lower doses of gamma radiation and molecular chain scission at higher doses, resulting in a decrease of the crosslinking.

Tension Test

Figure 1 presents typical stress–strain curves, showing clearly that the irradiation changes the tensile behavior. The nonirradiated and 100-kGy irradiated blends exhibited significant ductility, while higher doses caused brittle behavior. The yield strength of the irradiated PE blends is very close to the nonirradiated yield value. Table II presents the results of tension tests as maximum stress and elongation at break. As expected, there is a general increase in the maximum stress with a corresponding decrease in the elongation at break. The nonirradiated material has a maximum stress of 12.4 MPa and 176% for the elongation at break, showing high plasticity and constriction in the fracture zone. The elongation at break is significantly lower in the irradiated materials.

The results of the tension test are plotted against the gel content as a function of the radiation dose in Figure 2. The curves suggest that two simultaneous and conflicting effects occur:

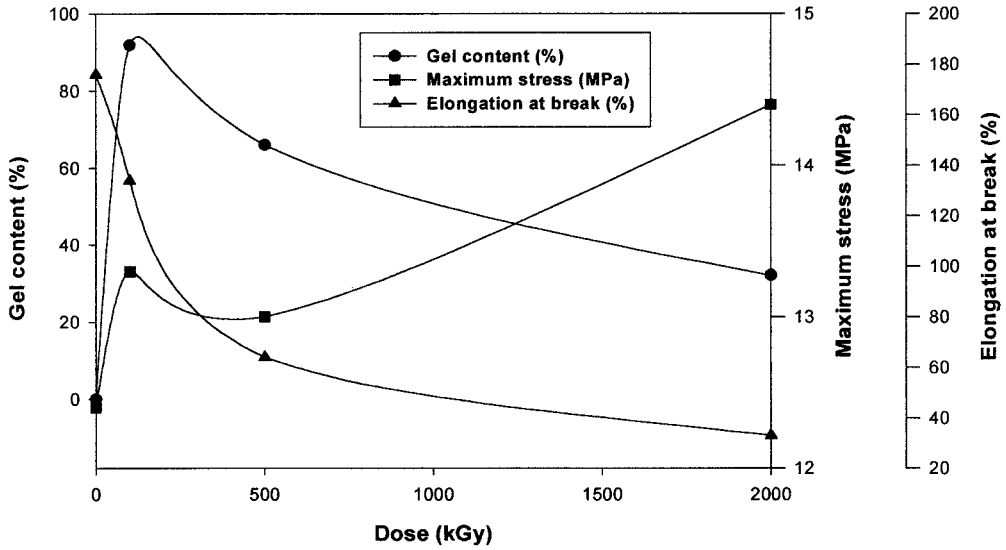


Figure 2 Gel content and tensile properties of recycled 75/25 LDPE/HDPE blend before and after gamma irradiation.

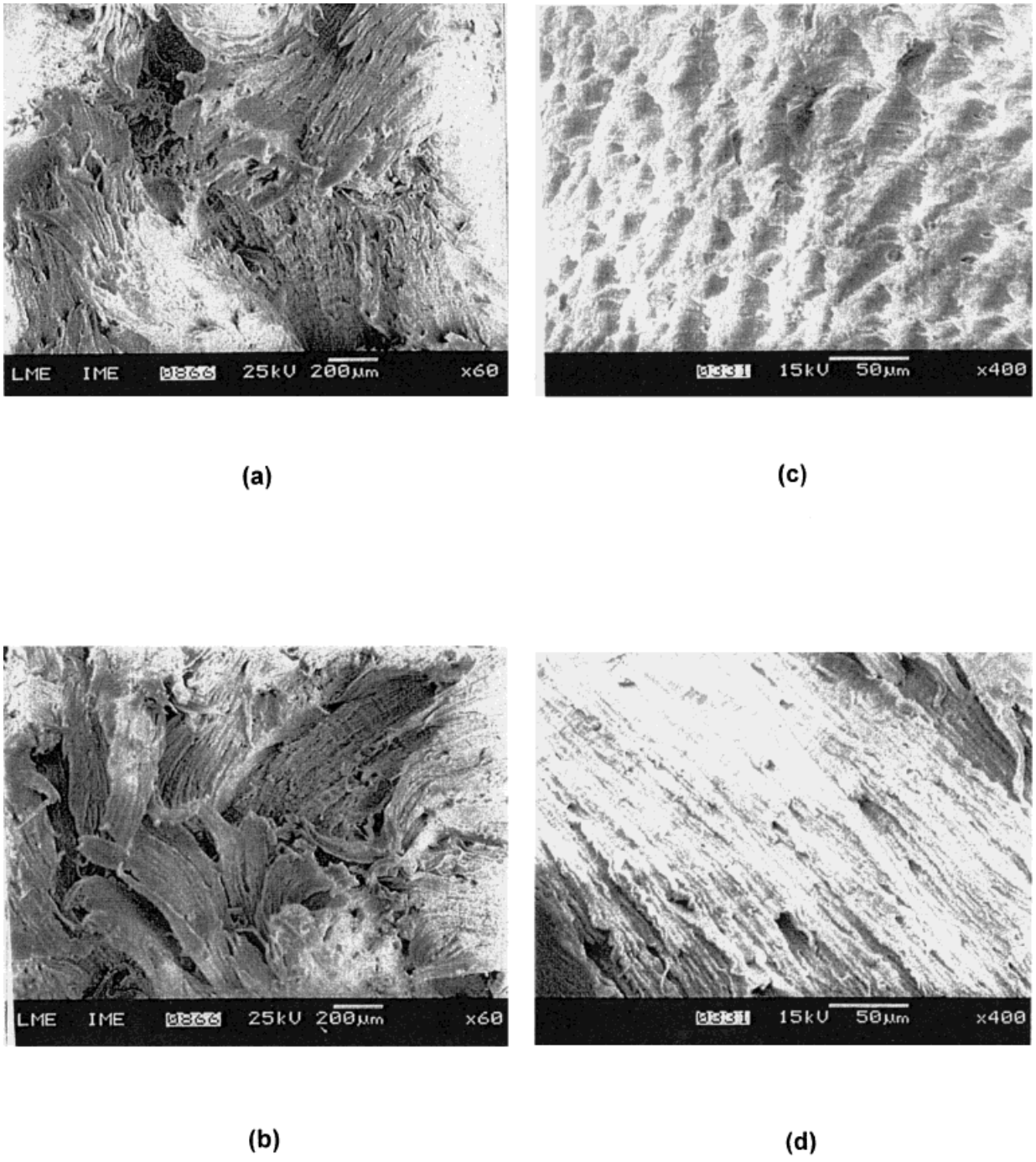


Figure 3 SEM micrographs of tensile fracture surfaces of recycled 75/25 LDPE/HDPE blend: (a) nonirradiated; (b) irradiated with 100 kGy; (c) detail of (a); (d) detail of (b).

chain crosslinking and chain scission, so that there is a partial compensation as the gamma irradiation proceeds. The intensity of the crosslinking effect is gradually less effective; the polymer molecule degrades due to chain scission as the radiation dose increases. The gel content values indicate a maximum of crosslinking at a 100-kGy dose.

Figure 1 and Table II show that the recycled PE blend presents a gradual ductile–brittle transition

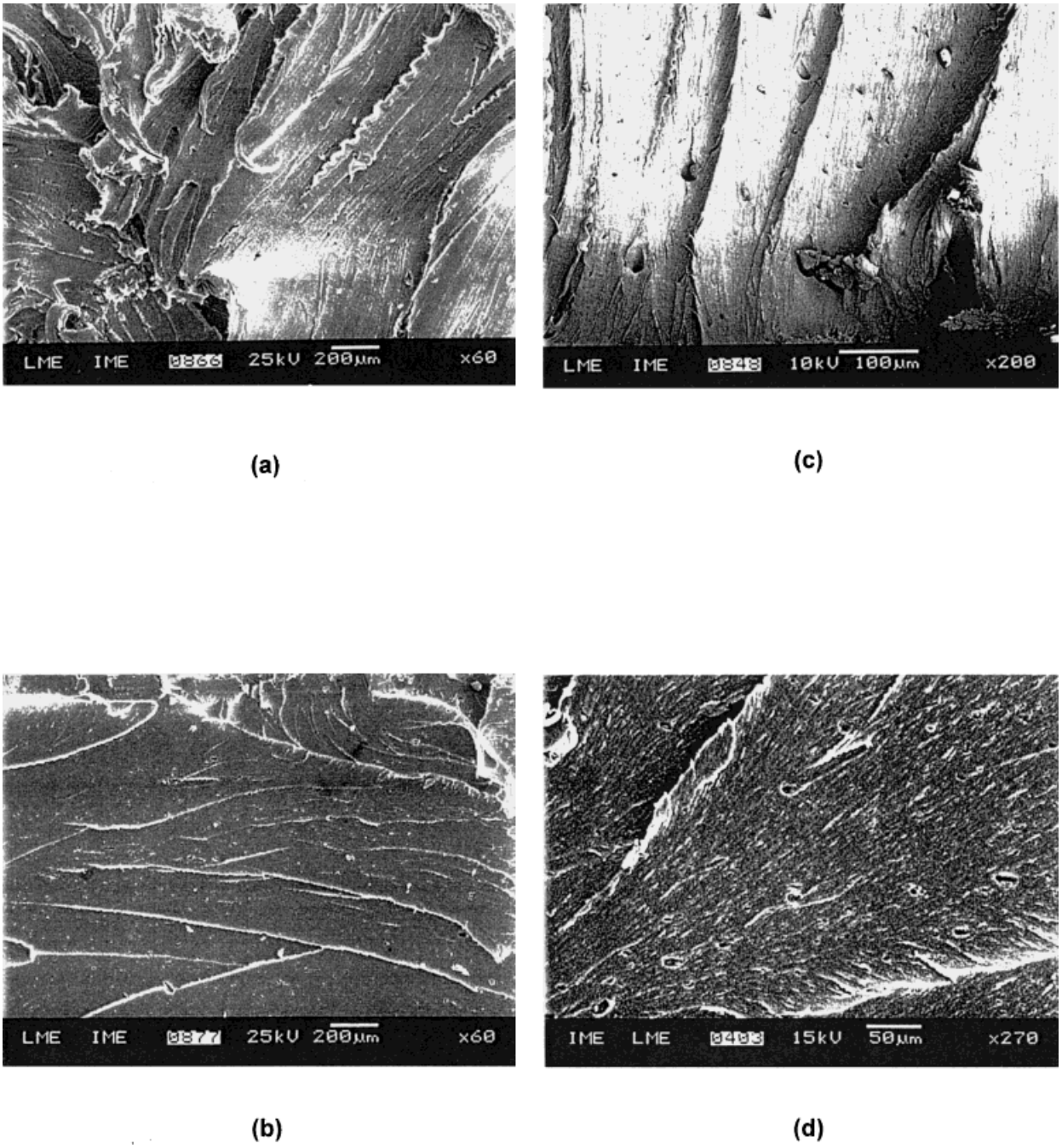


Figure 4 SEM micrographs of tensile fracture surfaces of recycled 75/25 LDPE/HDPE blend: (a) irradiated with 500 kGy; (b) irradiated with 2000 kGy; (c) detail of (a); (d) detail of (b).

as the gamma radiation dose reaches values higher than 100 kGy. This transition is characterized by the reduction on the elongation at break (176% in the nonirradiated blend to 33% for the 2000-kGy irradiated material). It occurs when the material is irradiated at lower doses, close to 500 kGy. This value coincides with the *half-value-dose*, which is the dose that reduces a significant mechanical property to 50% of its initial value, characterizing the radiation resistance of the material.[19]

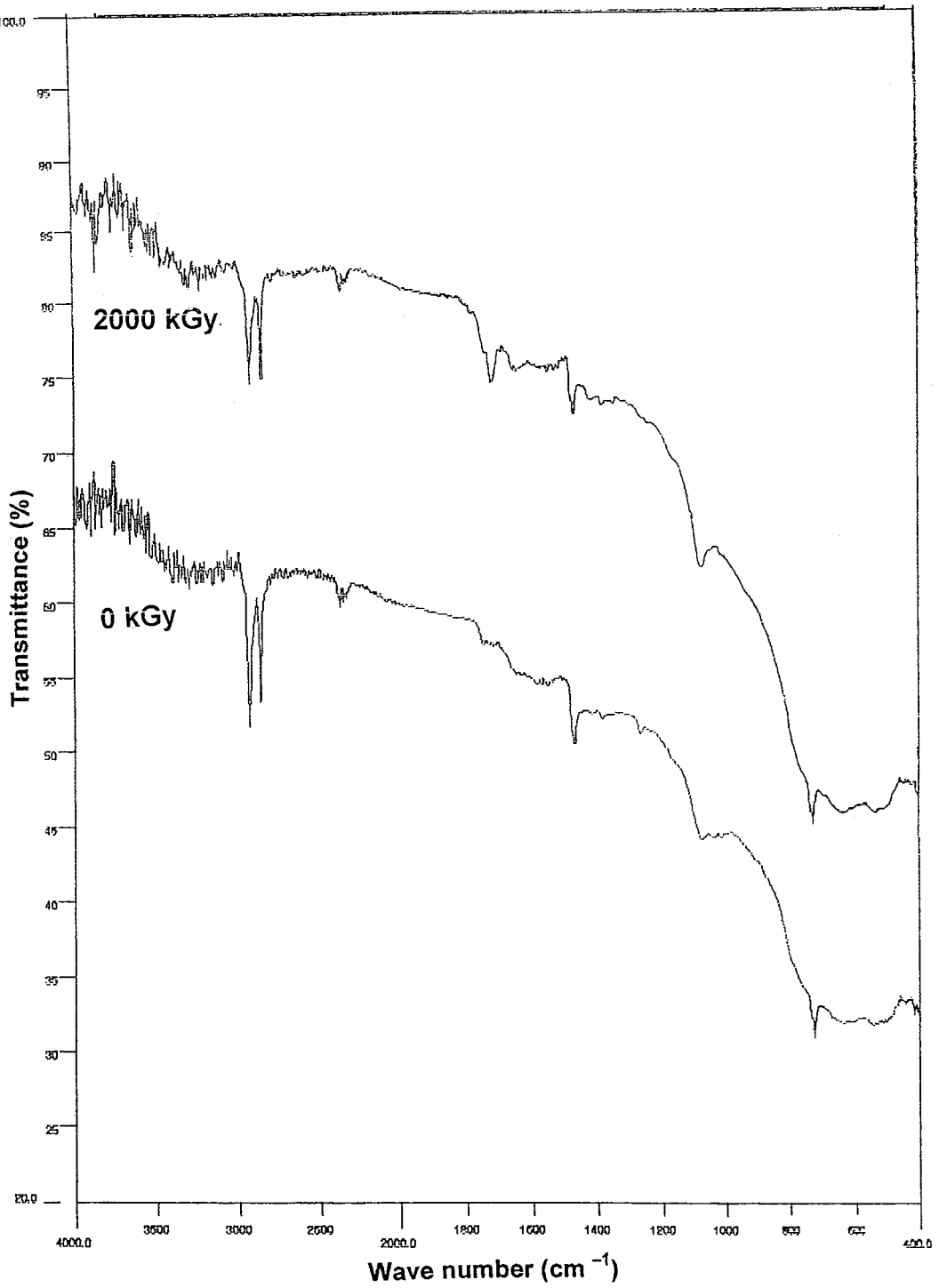


Figure 5 MIR spectra of recycled 75/25 LDPE/HDPE blend: (bottom) nonirradiated (0 kGy) spectrum; (top) 2000 kGy irradiated spectrum.

Due to irradiation of the scission chains, the polymer blend's molecular weight was reduced,[13] with the consequent decrease in the brittle strength. This occurred, because below a certain molecular weight, the material does not strain-harden sufficiently by stretching and cold-draw-

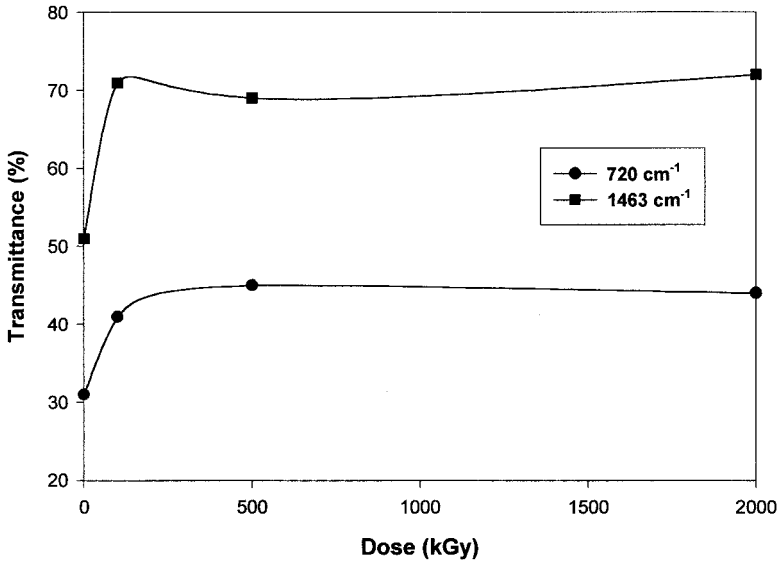


Figure 6 IR transmittance on typical bands of recycled 75/25 LDPE/HDPE blend before and after gamma irradiation.

ing is impossible.[20] So, upon tension testing at a low strain rate, the material reaches its fracture critical stress before yielding, changing its fracture mechanism from ductile to brittle.

According to the ASTM D 3826 standard,[21] a polyolefin material [PE and polypropylene (PP)] presents a brittle point when 75% of the specimens under investigation show 5% or less tensile elongation at break. Then, although the recycled 75/25 PE blend shows a ductile–brittle transition, the 2000-kGy irradiated material shows a 33% elongation at break, so it is not brittle and is still adequate for some engineering applications.

SEM

Scanning electron photomicrographs of the tension fracture surfaces are presented in Figures 3 and 4. The flatness of the fracture surfaces increases with the radiation dose, indicating greater degradation and the occurrence of a ductile–brittle transition in the tensile fracture.

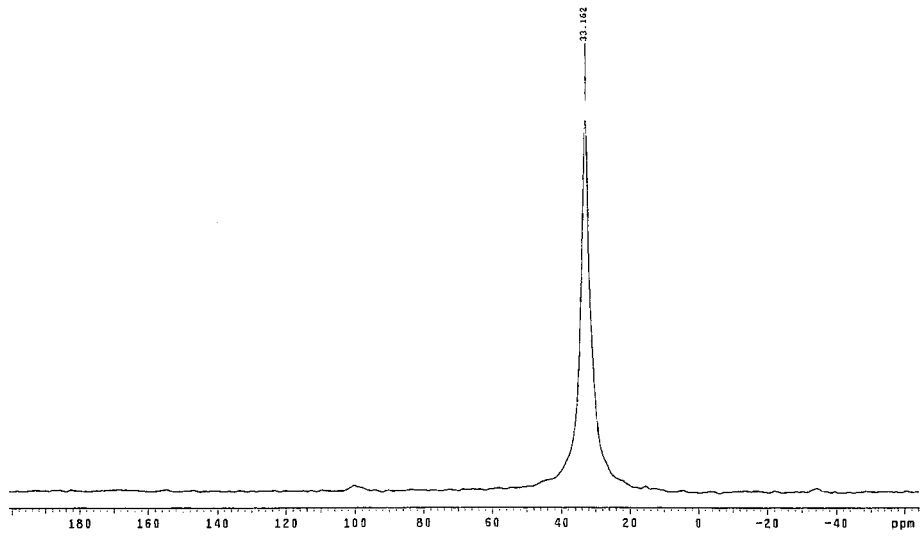
SEM examination of the specimens nonirradiated and irradiated with 100 kGy [Fig. 3(a,b)] shows that all the fracture surfaces are clearly fibrous with highly stretched regions, characterizing a ductile fracture mechanism with a large macroscopic plastic strain. These observations are in agreement with the high values found for the elongation at break. However, there is a marked difference in the fibrillar appearance—the specimens irradiated with 100 kGy have coarser fibrils, showing that the gamma irradiation influenced the deformation mechanism. This variation has been attributed to an increase in the mechanical strength of the material due to radiation crosslinking.[22,23] Higher magnification SEM micrographs of the fracture surfaces [Fig. 3(c,d)] showed general yielding, with dimples and tearing, indicating that the material failed by a void coalescence, ductile mechanism.

The 500-kGy PE blend presents a mixed mode of fracture, being more brittle, with smooth areas associated to localized plastic strain regions [Fig. 4(a,c)]. There are also corrugations that run perpendicular to the drawn direction and are presumably a result of the retraction of the material fibers after stretching.[24]

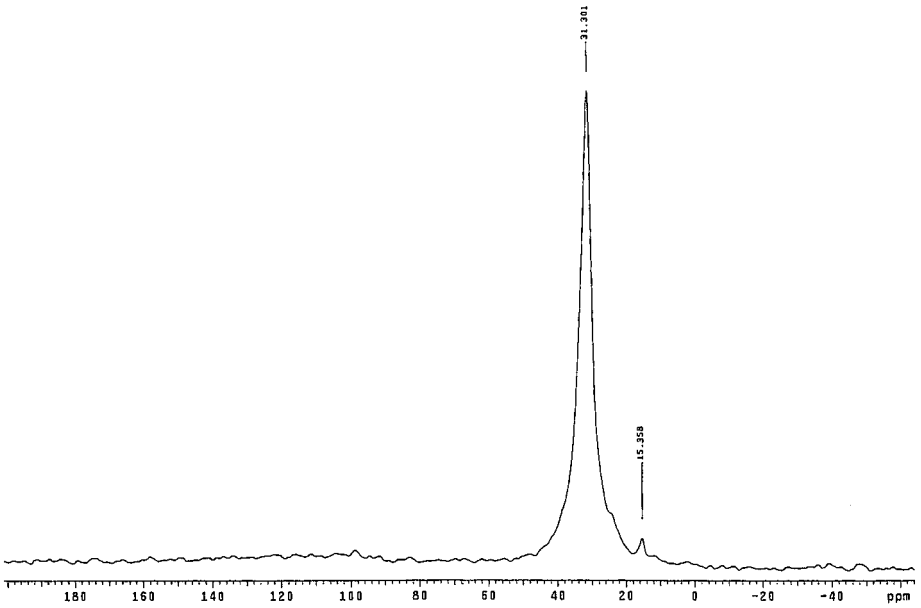
The specimens irradiated with 2000 kGy showed characteristics related to a typical brittle fracture mechanism—a flat surface with quasi-cleavage facets, tear ridges, and river patterns [Fig. 4(b,d)]. The presence of flat regions limited by rivers suggests that an interlamellar-type fracture has occurred.[25] The SEM analyses are in agreement with the tension test results.

Infrared Spectroscopy

MIR spectra of recycled PE blends were used for the interpretation of structural changes in the material after irradiation. Modifications in the



(a)



(b)

Figure 7 Solid-state ^{13}C-NMR spectra of nonirradiated recycled 75/25 LDPE/HDPE blend: (a) CP/MAS spectrum; (b) MAS spectrum.

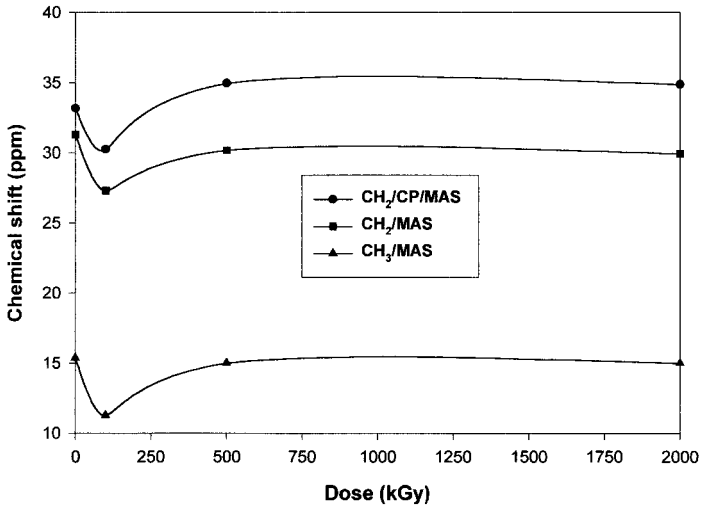


Figure 8 Methylene and methyl group chemical-shift displacements of recycled 75/25 LDPE/HDPE blend before and after gamma irradiation.

intensity of the characteristic bands of PE were detected (Fig. 5). Figure 6 shows IR transmittance for typical bands of the PE chains at 720 and 1463 cm^{-1}. The high increase in the transmittance of the methylene group after irradiation with 100 kGy confirms that the larger modifications occur at the initial, lower doses.

For 500- and 2000-kGy doses, a new absorption band at 1720 cm^{-1} was found; it may be imputed to carbonyl groups originated from the main-chain scission due to oxidative degradation.[26,27] For doses over 100 kGy, the chain scission starts to prevail and the crosslinking decreases. These results are coherent with the gel content and tension tests data.

NMR Spectroscopy

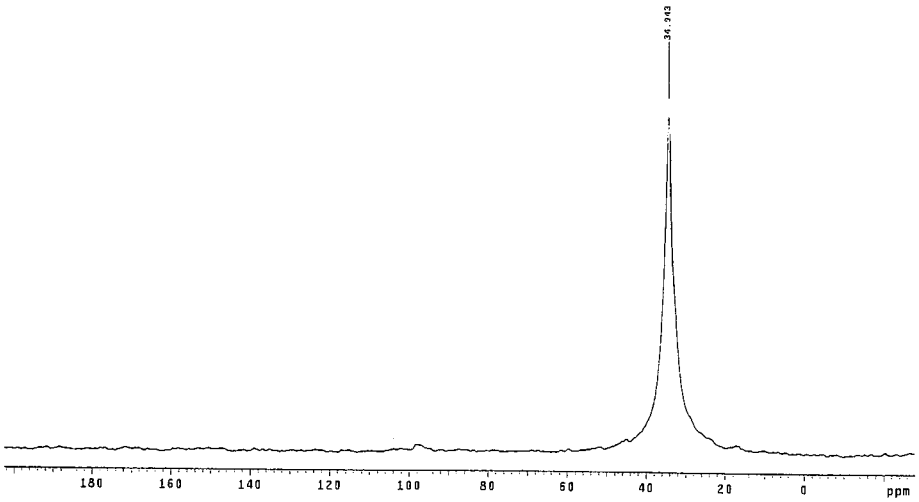
The ^{13}C-CP/MAS spectra present only the methylene group signal. The methylene and methyl groups signals are shown in the ^{13}C-MAS spectra. Figure 7 shows typical spectra: (a) a methylene group for the CP/MAS mode, and (b) methylene plus methyl groups for the MAS mode. The gamma irradiation modifies the chemical shifts. The displacement of the peaks position as a function of radiation dose is shown in Figure 8.

The signal detected in the CP/MAS spectra is split into two peaks in the CP/MAS/DD spectra. One peak is related to the methylene groups and the other may be derived from the CH group or else the CH_2 group of the amorphous region, as seen in Figure 9.

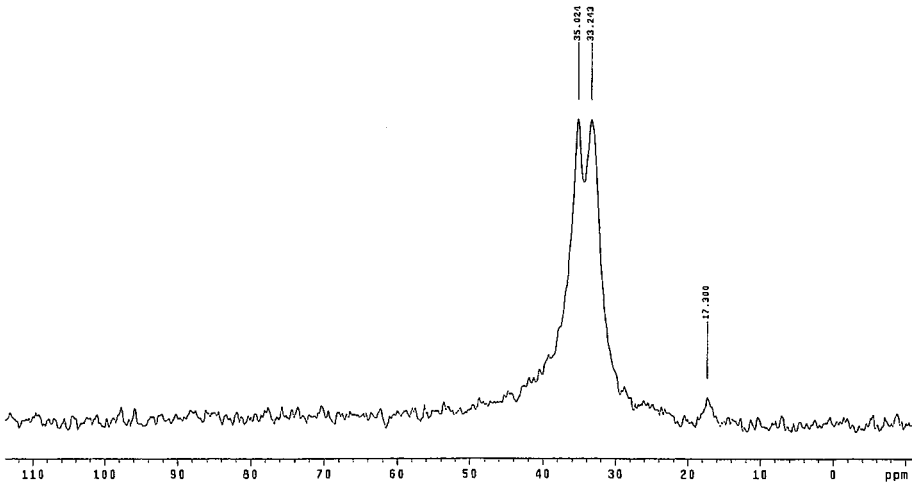
The lower chemical shift observed after 100-kGy irradiation and the eventual appearing of the CH signal indicate the existence of new structures at the end of the polymeric chains. This is evidence of the occurrence of radiation crosslinking. On the other hand, for 500- and 2000-kGy doses, the chemical shifts occur at higher frequencies, showing the existence of domains with more rigid interactions.[28] This can be imputed to scission chains that resulted from irradiation. As long as the chains are broken, the resultant shorter chains are able to pack together more easily, leading to a higher-order material, that is, a more rigid polymer. These experimental data are in agreement to the previous results and discussions.

CONCLUSIONS

The exposition of a recycled 75/25 LDPE/HDPE blend to ^{60}Co gamma radiation up to a 2000-kGy dose causes crosslinking and chain scission and modifies significantly its tensile behavior. An increase in the radiation dose caused a ductile–brittle transition characterized by a general decrease in the elongation at break. At same time, there is an increase in the maximum stress. The recycled polyolefin materials do not degrade completely under gamma irradiation; the polymer mechanical properties reach a plateau within a useful technological range. This recycled material



(a)



(b)

Figure 9 Solid-state ^{13}C-NMR spectra of recycled 75/25 LDPE/HDPE blend gamma irradiated with 500 kGy: (a) CP/MAS spectrum; (b) CP/MAS/DD spectrum.

may be suitable for a long-term application even under gamma-ray exposition.

SEM studies of the fracture tensile surfaces reflect clearly the effects of the exposure to gamma radiation. The fracture mechanism changes from a ductile mode by void coalescence to a shear failure brittle mechanism as the radiation dose increases.

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