

CHARACTERISTICS OF RECYCLED AND ELECTRON BEAM IRRADIATED HIGH DENSITY POLYETHYLENE SAMPLES

Jessica R. Cardoso, Leandro Gabriel, Áurea B. C. Geraldo and Eduardo Moura

Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP)

Av. Professor Lineu Prestes 2242

05508-000 São Paulo, SP

jrcardoso@ipen.br; lgabriell@gmail.com; ageraldo@ipen.br

ABSTRACT

Polymers modification by irradiation is a well-known process that allows degradation and cross-linking in concurrent events; this last is expected when an increase of mechanical properties is required. Actually, the interest of recycling and reuse of polymeric material is linked to the increase of plastics ending up in waste streams. Therefore, these both irradiation and recycling process may be conducted to allow a new use to this material that would be discarded by an improvement of its mechanical properties. In this work, the High Density Polyethylene (HDPE) matrix has been recycled five times from original substrate. The electron beam irradiation process was applied from 50 kGy to 200 kGy in both original and recycled samples; in this way, mechanical properties and thermal characteristics were evaluated. The results of applied process and material characterization are discussed.

1. INTRODUCTION

High Density Polyethylene (HDPE) is a commodity material with a wide range of uses in the industry. What make this polymeric material so interesting to the market are its unique properties such as good conformability, high resistance to heat and chemicals, and a relative low cost. Another characteristic for this material is its good reprocessability, which is the ability of being recycled many times.

Recycling polymers is a technique that offers great solutions to the problem with plastic waste in the environment. In our country we have already many cooperatives that work with the recycling process of a large variety of materials such as paper, metals and plastics. One type of recycling that is constantly increasing is “primary recycling” which is the reuse of waste materials directly from the production site in the industry. Our polymeric samples are also from primary recycling. Among this polymeric waste, packaging dominates the waste generated from plastics, covering 62.2% of the total. Polyolefins account for more than 50% of the packaging production. Plastic recovery starts with the separate collection of post-consumer waste [1].

The interaction between radiation and polymeric materials is also studied when we come with the recycled materials. Irradiation process has two effects main in polymers, one is degradation and the other is the formation of “cross-links” between the polymer chains. There are also several reactions of exposed polymer materials including cross-linking, degradation and grafting [2]. Cross-linking is the most desirable reaction in order to enhance physical

properties such as chemical resistance, mechanical behavior and thermal stability. In our study, we conduct the irradiation of recycled HDPE samples in order to improve its properties. Polyethylenes belong among one of the most radiation cross-linked materials. They cross-link without need of any cross-linking additive and they can be easily tailored to suit specific application [3,4].

Mechanical tests are conducted to measure the resistance of the material when put onto different kinds of effort and, also, it simulates the behavior of the material in different work conditions. In a recycled material it is important that its resistance is maintained after being reused and that is why we measure the mechanical properties of our polymeric samples before and after it is recycled.

Recycled polymers may lose its original properties due to the process in the machine and the exposition to heat again in the melting process. In this case, the irradiation of these materials may help to guarantee its former mechanical resistance and durability. In this case, it is known that the irradiation of the polymeric material, by means of the ionizing radiation, mainly the high-energy electron radiation generated in accelerators, is a way to enhance the mechanical strength of the material [5].

There is a high concentration of information from previous works on irradiation of recycled polyolefins. Navratil, J., et al. [6] studied the reuse of recycled irradiated polyethylene using its powder as filler in a polymeric matrix of Low Density Polyethylene. The final product showed an increase of elasticity modulus and hardness, but less viscosity. Satapathy, S., and Nando, B. G., [7] studied the effects of electron beam irradiation on composites of waste polyethylene with glass fiber. It was shown that the former properties of polyethylene, its mechanical and thermal resistance were the same as before processing. Posterior tests showed the possibility of a commercial use of the composite.

2. EXPERIMENTAL METHODS

High Density Polyethylene (HDPE) was irradiated with a JOB 188 Dynamitron® Electron Beam Accelerator with 1.5 MeV energy, after being recycled one, two, and three times. Each stage of recycling was availed on mechanical and FT-IR infrared analysis.

The mechanical tests were performed in an Instron 5755 testing machine and the tests followed the strain-stress ASTM D678 standard. Infrared analysis was conducted in a Perkin Elmer machine, model Spectrum GX. HDPE samples have a density of 0,955 g/m³, melt flow index (MFI) of 6,0 (190 C\21, 6 kg) and were supplied from Braskem S.A. The testing specimens were prepared in a twin screw extruder machine SANDRETTO series SB UNO 430|110 (kindly provided by FATEC-LESTE).

3. RESULTS AND DISCUSSION

The behavior of stress at break in function of absorbed dose is shown in Fig.1. Pristine HDPE samples shows an increase of stress at break when absorbe dose increase. This is a well known behavior.

In the first reprocessing HDPE case, non-irradiated samples shows lower stress at break value than pristine sample; it suggests this reprocessing stage promotes chain scission. Irradiation in this samples promotes a decrease of this parameter in lower doses, but in higher doses the stress at break values increase and they are greater than pristine samples in the same condition. It suggests an improvement of reprocessed material by irradiation process.

Samples from second reprocessing present lower stress at break than pristine and first reprocessing samples, but irradiation at 50 kGy promote an increase of this parameter in values higher than pristine samples; at 150 kGy, all analyzed reprocessed samples have stress at break value higher than pristine samples and it suggests reprocessed HDPE samples may have mechanical properties improved by irradiation process.

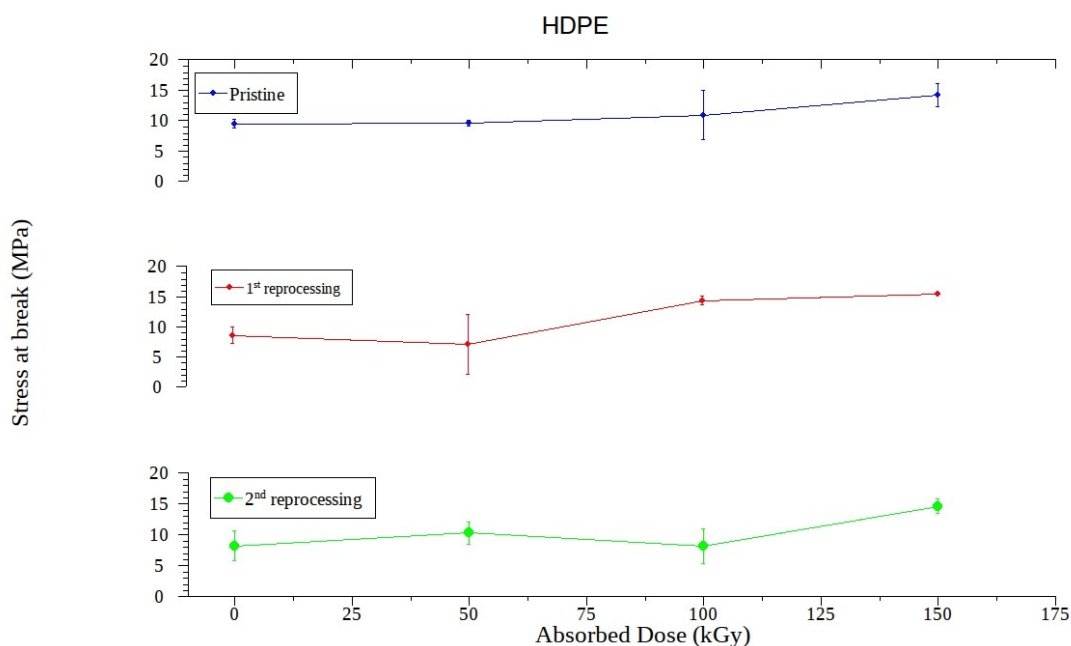


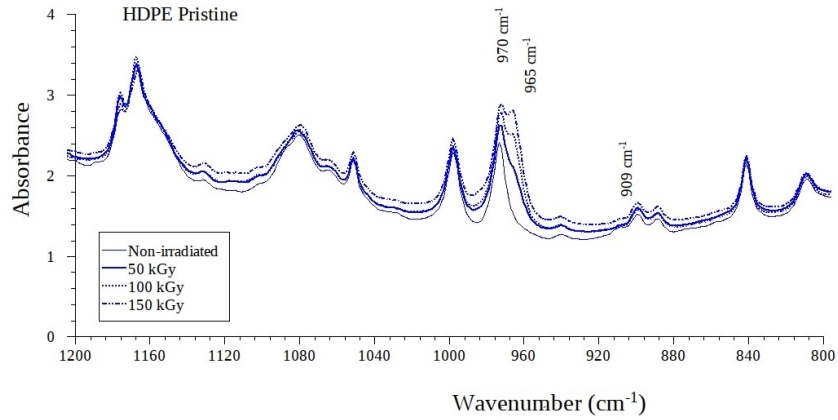
Figure 1. Stress at break in function of absorbed dose.

The infrared analysis of these samples reveal interesting results. In the first region analyzed, at 1200 cm^{-1} to 800 cm^{-1} , the band at 971 cm^{-1} is related to the bending of bond $=\text{C}-\text{CH}$ terminal in pristine samples (Fig. 1 a), but this band present deformation, enlargement and in some cases initial separation to 965 cm^{-1} region.

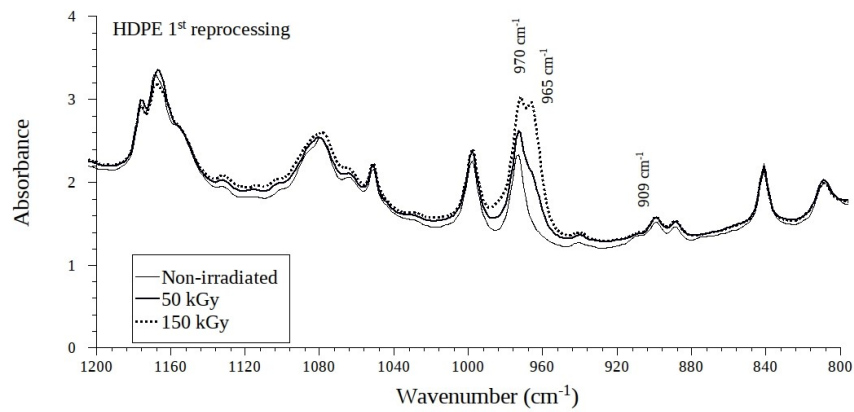
This occurs in all irradiated pristine samples; in the first HDPE reprocessing, non-irradiated samples have the same behavior of non-irradiated pristine, but irradiation changes the band behavior; finally in the second HDPE reprocessing band changes is observed in non-irradiated e irradiated samples. These results suggests chain scission in both irradiation process and second reprocessing.

The band at 909 cm^{-1} is related to out of plane bending bond $\text{C}-\text{CH}_2$ in the group $\text{RCH}=\text{CH}_2$ terminal [8]. This band exists in non-irradiated pristine and first reprocessed samples, however the irradiation process conducts to its disappearing and it suggests new bond formation and possible chain cross-link; second reprocessing irradiated and non-

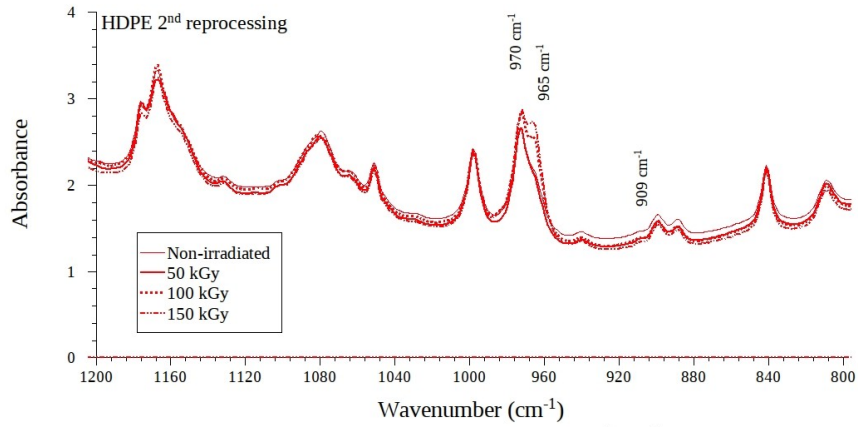
irradiated samples do not show this band, suggesting both irradiation and reprocessing allow chain cross-link.



a)

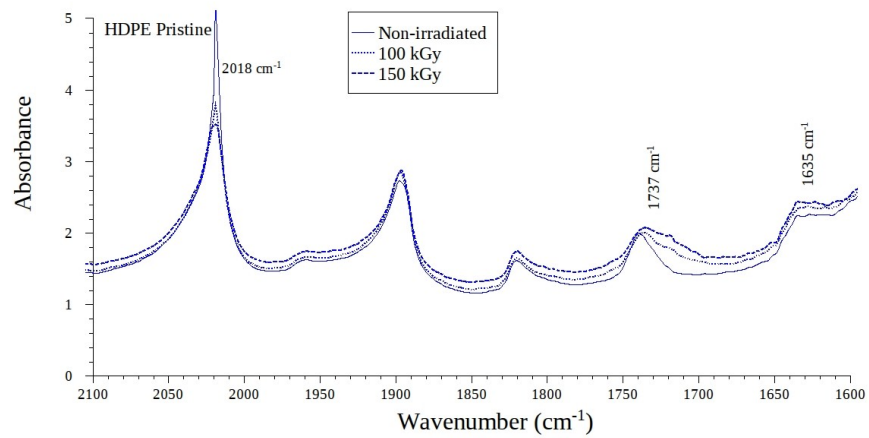


b)

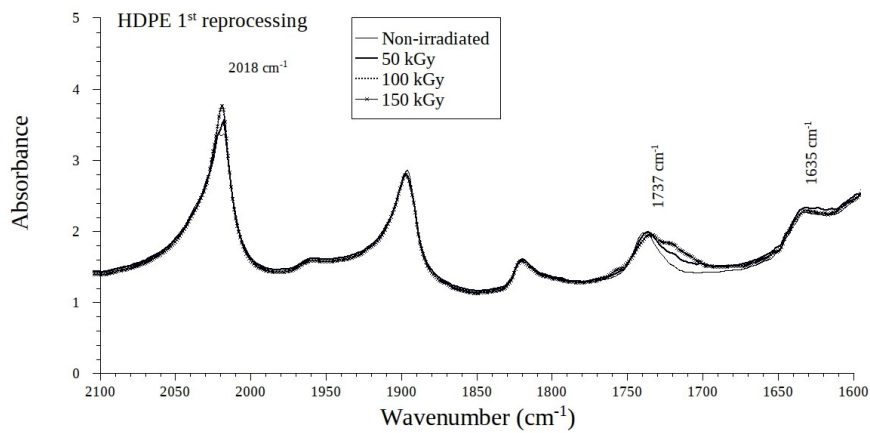


c)

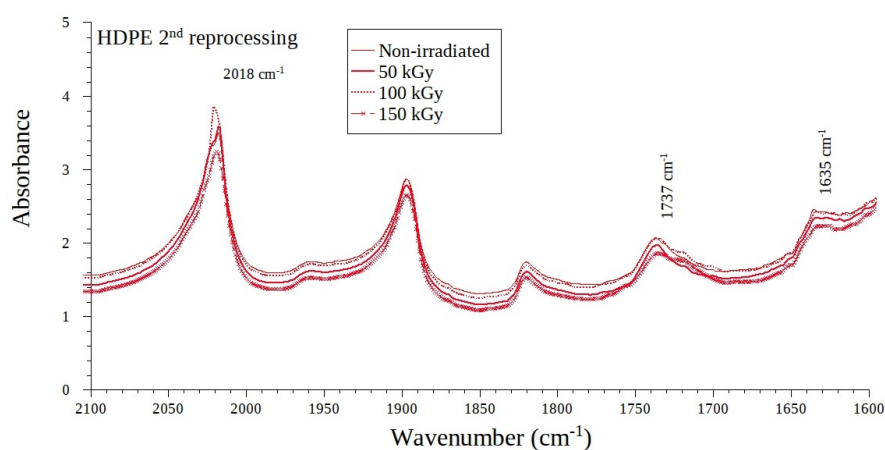
Figure 2. FTIR spectra of HDPE samples – Region of 1200 cm⁻¹ to 800 cm⁻¹. a) pristine, b) 1st reprocessing and c) 2nd reprocessing.



a)



b)



c)

Figure 3. FTIR spectra of HDPE samples – Region of 2100 cm⁻¹ to 1600 cm⁻¹. a) pristine, b) 1st reprocessing and c) 2nd reprocessing.

Fig. 3 shows the region from 2100 cm⁻¹ to 1600 cm⁻¹. In 2018 cm⁻¹ non-irradiated pristine sample shows the highest amplitude of all samples. This infrared band is related hydrocarbon backbone and it is intact in pristine samples, but in irradiated pristine samples the amplitude decrease with dose increase and it suggests the degradation of HDPE backbone. In non-irradiated reprocessed samples, the amplitude of this band is always lower than pristine sample, but irradiation process allow the increase on its amplitude and it suggests new bonds formation to recover the hydrocarbon backbone.

The bands 1735 cm⁻¹ region are related to C=O stretching at R-CO-OC-R group that enlarge in all irradiated samples, suggesting chain scission, in non-irradiated pristine and first reprocessing samples, this band is intact.

Finally, bands in 1635 cm⁻¹ is related to terminal bond vibration at R-CH=CH-R [8], that is intact in non-irradiated pristine samples but is enlarged at all irradiated samples and reprocessed samples. It suggests chain scission in these samples.

4. CONCLUSIONS

Reprocessing HDPE allow chain scission and consequent decrease of mechanical properties. Irradiation process allow improvement in mechanical properties in detriment of degradation process; chain scission and backbone degradation are expected but cross-link is a present phenomenon an it depends of absorbed dose. In each case there is an ideal absorbed dose to improve physical and chemical characteristics of HDPE.

Reprocessing became an interesting process for recycling HDPE with aims of electron beam irradiation process.

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