

ELECTRON BEAM IRRADIATION PROCESS APPLIED TO PRIMARY AND SECONDARY RECYCLED HIGH DENSITY POLYETHYLENE

Jéssica R. Cardoso, Eduardo de Moura and Áurea B.C. Geraldo

Instituto de Pesquisas Energéticas e Nucleares (IPEN/CNEN - SP)
Av. Professor Lineu Prestes 2242
05508-000 São Paulo, SP
ageraldo@ipen.br

ABSTRACT

Plastic bags, packaging and furniture items are examples of plastic utilities always present in life. However, the end-of-life of plastics impacts the environment because of this ubiquity and also often their high degradation time. Recycling processes are important in this scenario because they offer many solutions to this problem. Basically, four ways are known for plastic recycling: primary recycling, which consists in re-extrusion of clean plastic scraps from a production plant; secondary recycling, that uses end-of-life products that generally are reduced in size by extrusion to obtain a more desirable shape for reprocessing (pellets and powder); tertiary recover which is related to thermo-chemical methods to produce fuels and petrochemical feedstock; and quaternary route, that is related to energy recovery and it is done in appropriate reactors. In this work, high density polyethylene (HDPE) was recovered to simulate empirically the primary and secondary recycling ways using materials which ranged from pristine to 20-fold re-extruded materials. The final 20-fold recycled thermoplastic was irradiated in an electron beam accelerator under a dose rate of 22.4 kGy/s and absorbed doses of 50 kGy and 100 kGy. The characterization of HDPE in distinct levels of recovering was performed by infrared spectroscopy (FTIR) and thermogravimetric degradation. In the HDPE recycling, degradation and crosslinking are consecutive processes; degradation is very noticeable in the 20-fold recycled product. Despite this, the 20-fold recycled product presents crosslinking after irradiation process and the post-irradiation product presents similarities in spectroscopic and thermal degradation characteristics of pristine, irradiated HDPE. These results are discussed.

INTRODUCTION

The high production levels of plastic materials and the consequent high level of liabilities drives the recycling, reuse and reprocessing of these materials. In a recycling system, the production of new inputs from the re-use of pre-existing materials has advantages in terms of reducing virgin raw material production, which in turn has the effect of reducing the final cost of the product [1]. However, with the recycling and reprocessing of the plastic material some properties are lost compared to the original product, since it includes new steps of shear and melt.

High density polyethylene (HDPE) is classified as a commodity because it has a high industrial applicability due its high forming capability, thermal and chemical resistance and relative low cost. Its high demand implies high amounts of waste after its end-of-life, which makes recycling an interesting alternative.

On the other hand, radiation processing is also an alternative for increasing the mechanical resistance since it makes for higher durability of previously used materials [2]. Moreover, ionizing radiation has important uses for the modification of polymeric materials. Within this process, two concurrent and simultaneous effects are observed: degradation of polymers and

also the formation of crosslinks between molecules. The prevalence of one effect over another depends on empirical conditions [3].

In this work, HDPE was recycled by extrusion about twenty times, in order to empirically simulate a product which reaches its end of life and processed by ionizing irradiation to verify both temperature-induced degradation levels and shear conditions as well as the possibility of Improvement of this material after the irradiation process.

EXPERIMENTAL METHODOLOGY

For this work, virgin high density polyethylene (HD7255LSL Braskem), with a density of 0.954 g.cm^{-3} , was used.

The recycled material was obtained from the extrusion of pristine HDPE. Each extrusion cycle defined each reprocessing cycle: in the first extrusion cycle the first reprocessed batch of material was obtained; this material was then fed back to the extruder, making a retro-feed loop. Thus, the reprocessing was obtained from what is called industrial primary recycling.

2.1. Mechanical Processing

The reprocessing consisted of extruding the virgin HDPE in a double screw extruder of AX Plasticos, model AX DR16: 40 (Laboratory of Plastic Processes - CTR/IPEN/CNEN-SP).

The temperature profiles used in the machine zones (six zones and the head) are described in the Table 3. The feeder rotation was 9 rpm and the double thread was 60 rpm.

Table 1: Temperature zones for HDPE extrusion.

Zone	1	2	3	4	5	6	Head
Temperature (°C)	90	120	175	180	185	190	190

Subsequent steps consisted in using the product from the previous reprocessing, sequentially until the 19th reprocessing cycle. The twentieth and final reprocessing was done by injection molding test specimens of the reprocessed material.

In this work the extrusion process was used only as a way to obtain the primary reprocessing of the thermoplastic, without considering and adjusting rheological parameters of the original material at each stage of reprocessing.

At certain stages of reprocessing (5th, 10th, 15th and 19th), the samples were characterized by infrared spectrometry (FTIR) and thermogravimetry (TG).

2.2. Irradiation Processing

The extruded material was subjected to electron beam irradiation process. The absorbed doses were 50 kGy and 100 kGy at the dose rate of 22.4 kGy/s. The process was developed in a Dynamitron® electron accelerator, model JOB 188, with energy of 1.5 MeV and current of 2.81 mA (CTR-IPEN-CNEN/SP).

2.3 Characterization of Recycled HDPE

The recycled HDPE samples were characterized by Fourier Transform InfraRed (FTIR) and thermogravimetry as described below:

2.3.1 FTIR analysis

The technique was performed in transmission mode, from pressing of each sample plastic fragments, producing specimens thin enough to allow for the transmission of infrared radiation.

Transmittance FTIR spectra were obtained on a Perkin-Elmer Spectrum100 spectrometer in the medium infrared frequency range ($4,000\text{ cm}^{-1}$ to 400 cm^{-1}), with a resolution of 4 cm^{-1} and after 16 scans.

2.3.2 Thermogravimetry (TG)

Thermogravimetry was performed on a TA Instruments thermal analyzer, model Q600 STD (CTR/IPEN/CNEN-SP). In this equipment it is possible to obtain DSC data (specific heat/enthalpy) simultaneously during the thermodegradation scan.

The thermal degradation behavior was verified between room temperature (around $25\text{ }^{\circ}\text{C}$) and $800\text{ }^{\circ}\text{C}$ using platinum crucibles, applying a scan rate of $20\text{ }^{\circ}\text{C}/\text{min}$ and under the compressed air flow of $100\text{ ml}/\text{min}$. The analysis was performed thrice. Samples were not pretreated.

3. RESULTS AND DISCUSSION

3.1 FTIR Analysis

The pristine infrared spectrum (Fig. 1) shows three strong bands characteristic of this olefinic polymer [4]: at regions at 2970 cm^{-1} and 2850 cm^{-1} due to the vibration of the asymmetric and symmetrical axial deformation of the methylene group ($=\text{CH}_2$). The regions at 1477 cm^{-1} and 1430 cm^{-1} due to the symmetrical angular deformation in the plane of ($-\text{CH}_2-$) and in the region at 730 cm^{-1} and 710 cm^{-1} due to the vibration of asymmetrical angular deformation in the plane of ($-\text{CH}_2-$).

Weak vibrations are observed at 642 cm^{-1} due to out-of-plane angular vibration of the olefinic C-H bond; at 899 cm^{-1} due to the vibration of the vinyl group ($-\text{H}_2\text{C}=\text{CH}_2-$), vibrations are also observed in the region at 1350 cm^{-1} and at 1150 cm^{-1} due to the asymmetric angular deformation in the plane of the group ($-\text{CH}_2-$), More specifically a dumbbell at 1375 cm^{-1} and at 1351 cm^{-1} due to the vibration of deformation in the fan motion of that group, the bands in the region at 1639 cm^{-1} and at 1579 cm^{-1} are related to the vibration of the bond with termination $\text{R}-\text{CH}=\text{CHR}$ and derivatives of this grouping. Finally at 1735 cm^{-1} there is an axial strain vibration of the double bond $-\text{C}=\text{C}-$ [5].

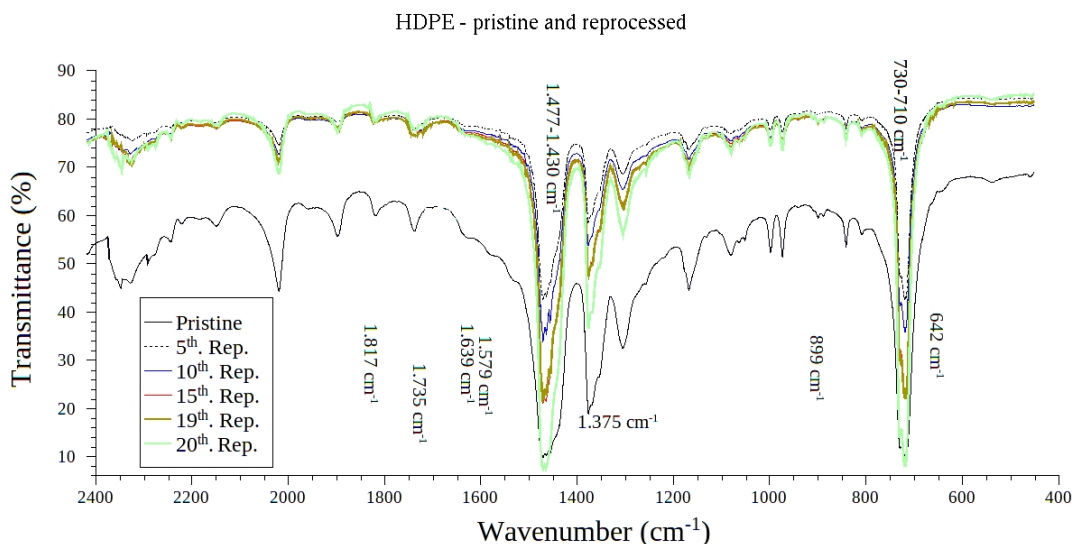


Figure 1: Infrared spectra of pristine and reprocessed HDPE samples.

Samples from distinct reprocessing levels (Fig.1) showed, besides the strong bands characteristic of the paraffin polymers, the disappearance of the band in the region at 642 cm⁻¹, at 1639 cm⁻¹ and at 1579 cm⁻¹ suggesting the formation of crosslinks under reprocessing conditions and also the appearance of a weak band in the region at 940 cm⁻¹, which is attributed to vibrations of the transvinylidene or vinyl ether group [6]; Its formation is attributed to the reactions of alkyl groups from the degradation process. In addition, a band at 1715 cm⁻¹, which is characteristic of the carbonyl group (>C=O), is observed, indicating oxidation of the material.

Therefore, the polymer reprocessing induces degradation as well as crosslinking which happen simultaneously from the first reprocessing cycles; This characteristic is due to the extrusion process, where the high temperature shear allows the occurrence of such competing processes.

When the virgin and recycled samples were submitted to irradiation (Fig. 2), similar behavior was observed in these two types of samples: the disappearance of the bands at 642 cm⁻¹, 1639 cm⁻¹ and at 1579 cm⁻¹ (pristine), Suggesting the occurrence of crosslinking and the appearance of a band at 1715 cm⁻¹ (pristine and reprocessed), characteristic of the carbonyl group (>C=O) and that appears as oxidation product, shows the degradation of these polymer samples.

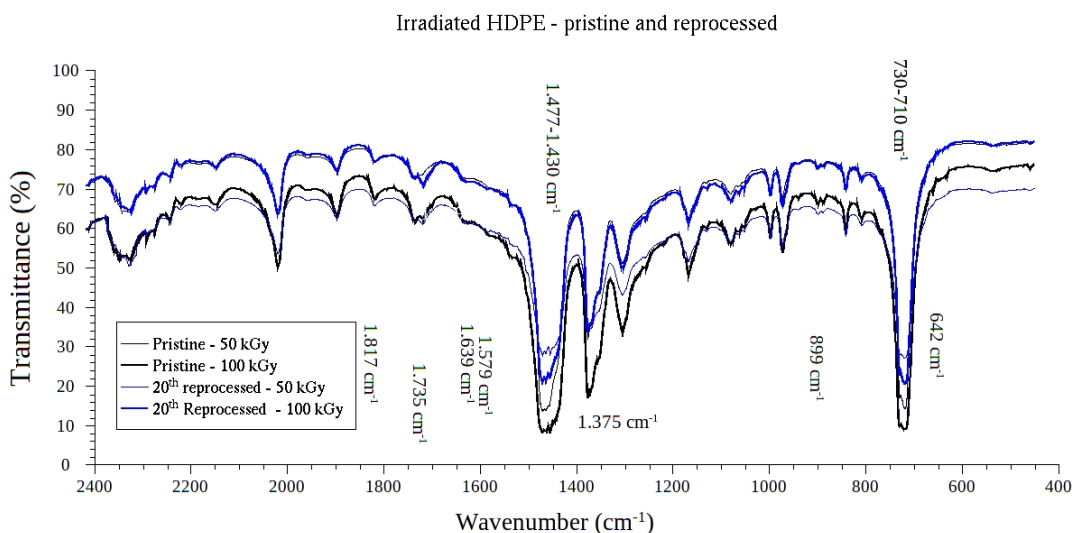


Figure 2: Infrared spectra of pristine and reprocessed HDPE samples by electron beam irradiation at 50 kGy and 100 kGy.

3.2 Thermogravimetry

The results are shown in Table 2 and Fig. 3 to Fig. 5. According to these results, the temperature of the first event (endothermic) occurs between the average values of 147 °C to 151 °C (peak in 144 °C) and with up to 3-5 % of mass loss; This event corresponds to the degradation of lighter substances. The main event occurs in the temperature range from 260 °C to 453 °C (peak in 423 °C), with an average mass loss of 88 % due to thermal degradation of the polymer matrix formed by the hydrocarbon skeleton.

These events are described in the literature, but two others were also observed: one in the range from 450 °C to 480 °C (peak in 479 °C) with an average mass loss of 8 %, which is not characteristic except for some contamination issue; and another in the range from 480 °C to 560 °C (peak in 539 °C - Table 1) which is possibly related to the degradation of the products from the oxidation of the material during the test, which was carried out under air flow [7].

After the 5th reprocessing, the material presents the same events as in the pristine sample, but the main event shows changes: the main degradation peak is enlarged with a tendency to occur another smaller event and the peak temperature is lower than the same peak in pristine sample.

In addition, the main event in this sample occurs in low mass loss (about 50 %) compared to the pristine sample. According to the literature [8], this behavior of thermal degradability is presented by high-density polyethylene after reprocessing, indicating degradation effects of the polymer matrix under these conditions.

The secondary event at 481 °C also occurs with 50 % of mass loss, suggesting the occurrence of chain scission induced by molecule oxidation, as evidenced by FTIR analysis.

From the 10th reprocessing cycle on, two maxima are observed in the main peak and the behavior of the materials is similar to that observed in the submitted to the 5th reprocessing. These results converge to those observed in the FTIR, where there are no abrupt differences

between reprocessing levels. Intense degradation occurs during reprocessing; however, the analysis carried out did not allow to evaluate the degree of degradability in each reprocessing cycle.

Epacher *et al* [9] achieved similar results studying the HDPE degradation submitted to multiple extrusion process. The results were reported by Melt Flow Index (MFI) and color test (yellowing index). Decreasing of sample MFI was also observed, which indicates crosslinking.

The irradiation process applied on pristine samples at 50 kGy dose shows, besides the endothermic event at 139 °C, that there are two events: the main one at 433 °C and the secondary one at 525 °C. The main event occurs at a temperature 10 °C above the temperature of the same event in the non-irradiated material and with a mass loss 5 % higher than that observed in the original sample, suggesting the occurrence of crosslinking. The last event has similarities to peak temperature and mass loss of the original sample.

Increasing the absorbed dose to 100 kGy, an increase of the main event temperature is observed, about 19 °C above the temperature of that same event in non-irradiated material that is related to the crosslinking events. Degradation process also occurs at the secondary event in this irradiated sample: about 90 °C above of the same event in original sample and with twice the mass loss. The last event occurs in percentage of degradation similar to that of the original material.

The twentieth reprocessed sample submitted to the irradiation process at doses of 50 kGy and 100 kGy presented qualitative and quantitative behavior similar to that observed in pristine irradiated sample, indicating that even reprocessed 20 times, the irradiation process allows for the occurrence of crosslinking. This result is according to FTIR analysis and the results presented by Cardoso and co-workers [10] which showed that 20-fold reprocessed and irradiated HDPE (100 kGy of absorbed dose) have increased mechanical resistance compared to pristine samples; in this case, impact resistance was 25 % higher when compared to pristine samples.

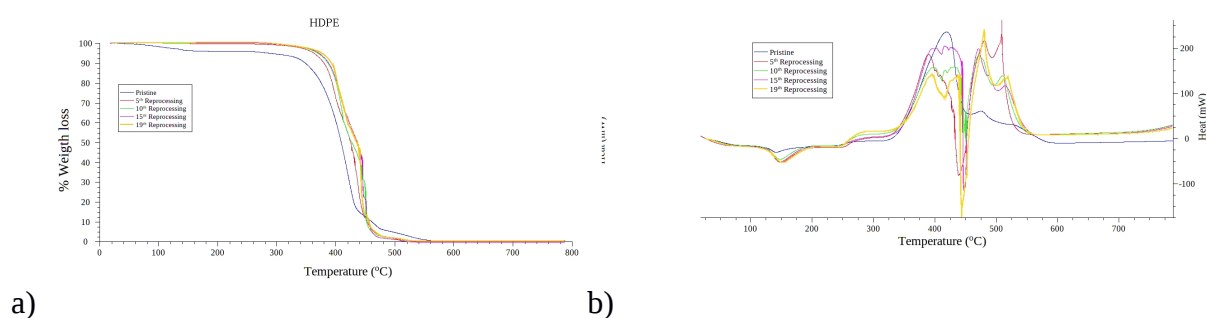


Figure 3: Thermogravimetry results: a) Weight loss and b) derivative scanning calorimetry (DSC) of HDPE samples (pristine, 5th, 10th, 15th, 19th reprocessing).

Table 2: Parameters from thermogravimetric curves of HDPE samples.

Sample	Peak Temperature (°C) Differential Calorimetry				Degradation rate (%) Thermogravimetry curves		
	Endothermic	Exothermic			Principal Event	Secondary Events	
		PE [†]	Secondary Events				
pristine	144 (4)	423 (5) [‡]	479 (4)	532 (4)	88 (8)	8 (2)	5 (1)
5 th . Rep.	150	390	481	508	50	50	N.R.
10 th . Rep.	147	400/434	471	510	46	36	3
15 th . Rep	147	401/426	472	515	56	42	2
19 th . Rep.	151	397/437	481	519	53	45	2
Pristine - 50 kGy	139 (4)	433 (0)	N.R.	525 (7)	93 (7)	N.R.	6 (2)
Pristine - 100 kGy	140 (0)	452 (2)	371 (3)	531 (1)	81 (1)	15 (1)	5 (1)
20 th . Rep. – 50 kGy	139 (1)	432 (2)	N.R.	529 (8)	92 (5)	N.R.	5 (1)
20 th . Rep. – 100 kGy	138 (1)	452 (1)	363 (7)	532 (2)	80 (1)	13 (0)	8 (0)

[†] PE: Principal event

N.R.: non-registered

[‡] Standard deviation: in brackets

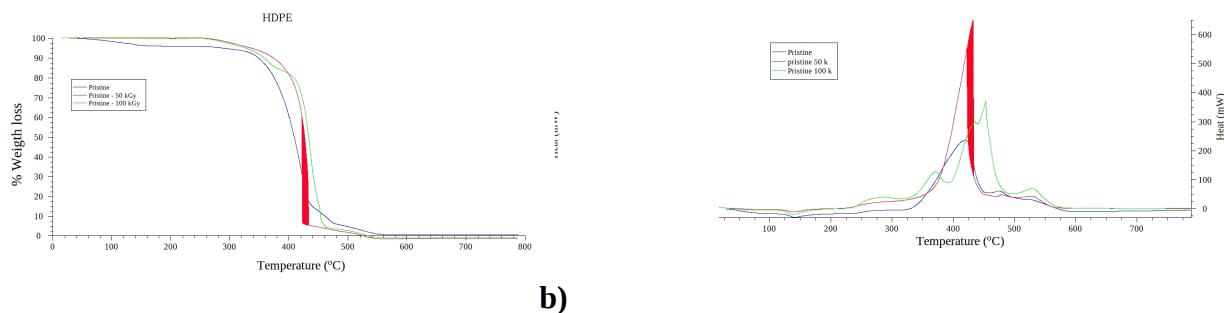


Figure 4: Results from thermogravimetry: a) Weight loss and b) derivative scanning calorimetry (DSC) of pristine HDPE samples (0 kGy, 50 kGy and 100 kGy).

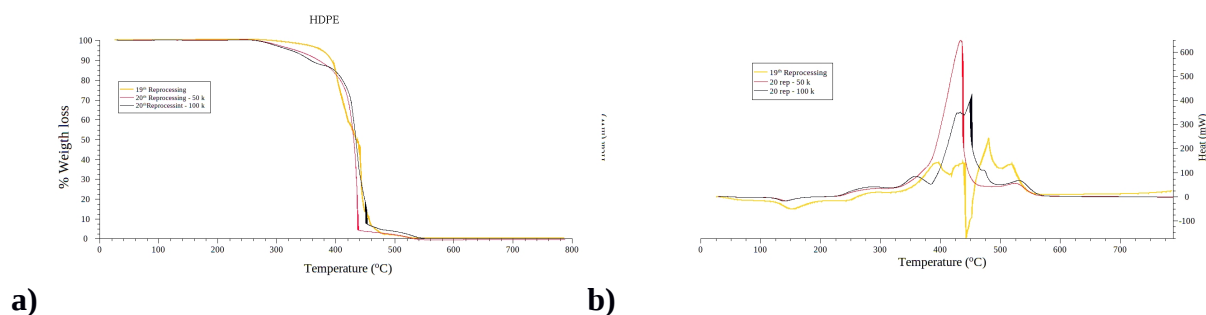


Figure 5: Thermogravimetry results: a) Weight loss and b) derivative scanning calorimetry (DSC) of 20th reprocessing HDPE samples (0 kGy, 50 kGy and 100 kGy).

4. CONCLUSIONS

HDPE reprocessing induces simultaneous degradation and crosslinking; even if degraded, the reprocessed polymer is still suitable for re-utilization due to the occurrence of crosslinking, principally if this material is submitted to ionizing irradiation processes. These results open a new interesting alternative for HDPE waste to be used in reprocessing plastics industry.

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REFERENCES

1. E. B. Mano, *Meio Ambiente, Poluição e Reciclagem*. 1st ed., Edgard Blücher, São Paulo, Brazil (2005).
2. T. Czvikovszky, “Expected and unexpected achievements and trends in radiation processing of polymers”, *Radiation Physics and Chemistry*, **67**, pp. 437 (2003).
3. A. Charlesby, “Effect of high energy radiation on long chain polymers”, *Nature*, **171**, pp.167 (1953).
4. R.M. Silverstein, G.C. Bessler, T.C. Morrill, *Identificação Espectrométrica de Compostos Orgânicos*, pp.65, 3rd. ed., Editor Guanabara, Rio de Janeiro, Brazil (1979).
5. R.M. Silverstein, G.C. Bessler, T.C. Morrill, *Identificação Espectrométrica de Compostos Orgânicos*, pp.75-76, 3rd. ed., Editor Guanabara, Rio de Janeiro, Brazil (1979).
6. L. Contat-rodrigo, A. Ribes-Greus, C.T. Imrie, “Characterization by Thermal Analysis of High Density Polyethylens/Polypropylene Blends with Enhanced Biodegradability”, *Journal of Applied Polymer Science*, **86**, pp.174-185 (2002).
7. J. Scheirs, S.W. Bigger, N.C. Billingham, “Effect of Chromium on the Oxidative Pyrolysis of Gas-phase High-density Polyethylene as Determined by Dynamic Thermogravimetry”, *Polymer Degradation and Stability*, **38**, pp. 139-145 (1992).
8. W. Camacho, & S. Karlsson, “Assessment of Thermal and Thermo-oxidative Stability of Multi-extruded Recycled PP, HDPE and a Blend Therof”, *Polymer Degradation and Stability*, **78**, pp. 385-391 (2002).
9. E. Epacher, J. Tolvéth, K. Stoll, B. Pukánszky, “Two-step degradation of high density polyethylene during multiple extrusion”, *Journal of Applied Polymers*, **74**, pp. 1596-1605 (1999).

10. J.R Cardoso, E. Moura, A.B.C. Geraldo, “Recycled HDPE/Vulcanized EPDM Mixtures Obtained by Irradiation Processes”, *International Conference on Applications of Radiation Science and Technology (ICARST2017)*, Vienna, Austria, 24 to 28 April (2017).