

The Effect of Gamma Radiation on Mechanical Properties of Biodegradable Polymers poly(3-hydroxybutyrate) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate)

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Brazilian poly(3-hydroxybutyrate), P(3-HB), and its copolymer, poly(3-hydroxybutyrate-co-3-hydroxyvalerate), P(3-HB-co-3-HV) were irradiated with gamma radiation (⁶⁰Co) at room temperature and in the presence of oxygen. The viscosity-average molar mass (M_v) was analyzed by viscometry using an Ostwald-type capillary viscometer. Both polymers showed a decrease in molar mass with the increase in dose, reflecting that random main chain scissions occurred. The value G (scissions/100 eV of energy transferred to the system) and the parameter α (scissions per original molecule) were also determined. Mechanical properties decrease with the increase in dose, revealing that P(3-HB) underwent significant changes, especially at doses higher than 50 kGy. Tensile at break and impact resistance properties were the most affected by radiation, while the elastic modulus remained virtually unaltered up to 100 kGy dose.

Keywords: gamma irradiation, PHB, PHB-co-HV, mechanical properties

1. Introduction

Poly(3-hydroxybutyrate) (P(3-HB)) and its copolymer, poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (P(3-HB-co-3-HV)), are biodegradable thermoplastic polymers generally referred to as Poly(hydroxyalcanoates) (PHA's). These polymers are synthesized by microorganisms cultivated in the presence of excess carbon sources such as glucose, sucrose and fructose, and in the restricted presence of other nutrients, such as nitrogen^{1,2}. Due to their characteristics, P(3-HB) and P(3-HB-co-3-HV) can be largely used in applications that range from domestic utensils³ and packaging^{4,6} to material for medical devices⁷⁻¹⁰, given their good mechanical, thermal and biocompatibility characteristics.

P(3-HB) is a linear and stereoregular aliphatic polyester (Figure 1), synthesized and accumulated for energy storage by a number of bacteria in the form of intracellular grains^{1,11}. The biotechnological processes for the fermentative production of P(3-HB) and P(3-HB-co-3-HV) by strains of the bacterium *Wautersia eutropha* were established in the 1970's and resulted in materials for manufacturing of various products¹².

Although P(3-HB) presents good ductility after molding, ageing process frequently provokes embrittlement, probably caused by progressive crystallization upon

ambient temperature storage¹³. Many approaches have been presented to solve rigidity problem in P(3-HB). Among them, copolymerization of 3-hydroxybutyrate with a variety of monomers, such as 3-hydroxyvalerate (3-HV), to give P(3-HB-co-3-HV), and 3-hydroxyhexanoate (3-HHx), to yield P(3-HB-co-3-HHx), allowed these copolymers to present improved mechanical properties when compared to P(3-HB) homopolymer, hence, becoming commercially attractive enough to enter in large-scale production¹⁴.

Some of P(3-HB) characteristics give this polymer a wide variety of applications. Its viscosity-average molar mass (M_w) varies from 10^4 to 10^6 g.mol⁻¹, with polydispersity index around 2. The glass transition temperature (T_g) is ~ 4 °C, while the melting temperature (T_m) is ~ 175 °C. The densities of crystalline and amorphous P(3-HB) are 1.26 and 1.18 g.cm⁻³, respectively. Mechanical properties, like Young's modulus (3.5 GPa) and tensile at break (43 MPa), present values which are close to those found for isotactic polypropylene (iPP)¹¹.

One of the most promising PHA's applications is medical devices. FDA approval of poly(4-hydroxybutyrate) (P(4-HB)) for surgical sutures¹⁵ and meshes¹⁶ in 2007 might pave the way for more specialized uses¹⁷. In this context, assessing the influence of sterilization methods in the properties of P(3-HB) and other PHA's is of extreme

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importance. At the present, radiosterilization is the technique of choice for many polymer medical devices¹⁸⁻²¹, especially when processing closed packaged products or materials prone to absorb/adsorb chemical sterilants. However, irradiated polymers may undergo physicochemical changes such as embrittlement, discoloration, odor generation, stiffening, softening, and alterations in chemical resistance or melting temperature. These changes result, primarily, due to main chain scission and cross-linking of macromolecules generated by interactions with gamma rays²².

Radiolysis mechanism for some polyesters, including P(3-HB) and P(3-HB-co-3-HV)^{23,24}, poly(lactide-co-glycolide) (PLGA)^{25,26} and polyethylene adipate (PEA)²⁷ were investigated by electron paramagnetic resonance (EPR) at low temperature. Many similarities were found in the nature of radicals formed during irradiation process. EPR data collected under oxygen-free atmosphere suggest massive occurrence of main chain scissions and minor contribution of side-chain elimination. A tentative cationic mechanism for P(3-HB) and P(3-HB-co-3-HV) is shown in Figure 2. The primary event is the abstraction of an electron by Compton Effect²⁸, with the generation of a radical cation II²⁵. Proton elimination and electrons rearrangements lead to *alpha*-ester radical III^{25,27}. Main chain scission might occur through *beta* homolysis of III to give a stable vinyl end group in IV and a radical carboxyl in V, which undergoes elimination of a neutral

CO₂ molecule, to yield a macromolecular fragment bearing a methylene radical end group (VI). Additional experimental supporting data to this mechanism relies on the observation of volatile products released during irradiation process, with the prevalence of CO and CO₂, but only small amounts of methane, ethane and propane²³.

Table 1 shows the effects of gamma radiation on the mechanical properties of P(3-HB-co-3-HV). A quite significant reduction is noted in tensile strength and elongation at break, showing that the radiation is making the material even more brittle. On the other hand, elastic modulus does not. According to Luo and Netravali²⁹, the most significant scissions occur in the amorphous fraction. As a result, properties related to break and deformation are more affected than the elastic modulus, because the modulus of elasticity is more affected by modifications in

Table 1. Effects of gamma radiation on mechanical properties of P(3-HB-co-3-HV)²⁹.

Dose (kGy)	Tensile at break (MPa)	Modulus of elasticity (GPa)	Elongation at break (%)
0	31.69 ± 0.43	1.90 ± 0.05	3.52 ± 0.43
100	24.24 ± 1.24	1.91 ± 0.08	1.75 ± 0.20
250	12.57 ± 1.07	1.87 ± 0.05	0.73 ± 0.08

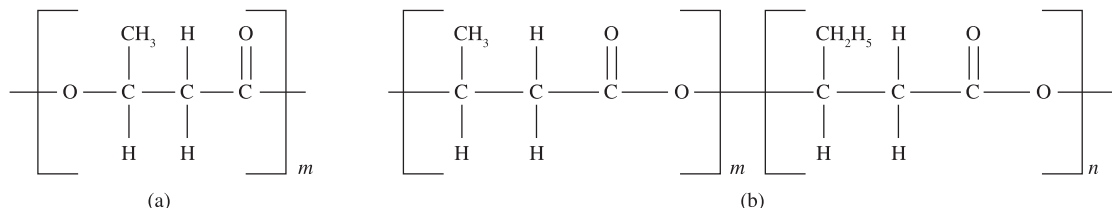


Figure 1. Chemical structures of a) poly(3-hydroxybutyrate); b) poly(3-hydroxybutyrate-co-3-hydroxyvalerate).

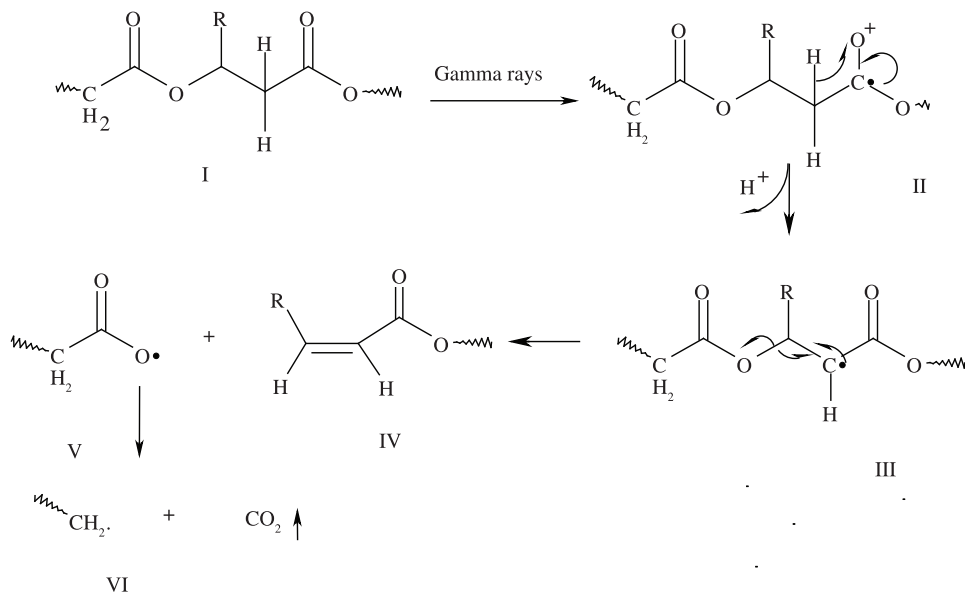


Figure 2. Radiolysis mechanism of Poly(hydroxyalcanoates). R = -CH₃, CH₂CH₃.

the crystalline rather than in the amorphous region. More recently, Hermida et al.³⁰ reported the effects of gamma irradiation on the mechanical properties of P(3-HB) and P(3-HB-co-3-HV) (12% of 3-HV) films in doses up to 80 kGy. No major alterations were found in tensile modulus and tensile at break in doses up to 20 kGy. Nevertheless, when irradiated up to 80 kGy, both polymers underwent reduction of 41% in tensile strength.

Mechanical properties correlate with the crystallization conditions, i.e., after quenching from the melt, small-grain spherulites are formed, but when cooled slowly spherulites with large cracks are formed. El-Hadi et al.³¹ studied the influence of the morphology and glass temperature on mechanical properties (elongation, stress, impact strength). According to these authors, P(3-HB) is a hard and brittle polymer, its elongation at break is less than 10%, its modulus and fracture stress are 1.7 GPa and 35 MPa, respectively. P(3-HB-co-3-HV) is also brittle, its elongation at break is less than 15%, its modulus and fracture stress are 1.2 GPa and 25 MPa.

In the present work, the P(3-HB) and its copolymer P(HB-co-3-HV) were irradiated and evaluated as to the radiolytic degradation by main chain scissions reflected in molar mass reduction. Furthermore, the consequences of radiolysis on the mechanical properties are discussed. While most reports in literature investigated film samples, our work focused on test specimens results, bring the knowledge of gamma-irradiation effects on P(3-HB) and its copolymer P(3-HB-co-3-HV) a step forward in terms of performance estimations aiming future practical applications.

2. Experimental

2.1. Material

In the present work the effects of gamma radiation on samples of P(3-HB) and P(3-HB-co-3-HV) containing 6.3 mol% of 3-HV, produced by the bacterium *Wautersia eutropha*, were analyzed. The samples were kindly provided by PHB Industrial S.A., owner of the brand Biocycle®.

Powder samples used as received and after reprecipitation from chloroform with hexane as non-solvent. Alternatively, samples were washed with hydrochloric acid (HCl) 0.1 mol.L⁻¹, then water, and vacuum dried under a 150 W infrared light for over a week. These procedures aimed the elimination of processing additives, along with other possible impurities present, such as oligomers or bacterial cell wall residues.

The films were prepared from powder samples dissolved in chloroform by casting polymer solutions (0.8 g of P(3-HB) 1.8 g of P(3-HB-co-3-HV) to 20 mL of chloroform) onto Petri dishes followed by slow evaporation of the solvent at room temperature. Free-standing films, presenting approximately 90 μm in thickness, were obtained.

The test specimen samples (dimensions 150 × 20 × 3 mm), were produced from Lot 81, according to ISO R 179 by injection process using an injection machine, brand PIC, model PIC 62. These test specimens were assayed as supplied by the manufactures, with their original additive formulation.

2.2. Viscosity-average molar mass

The viscosity of the samples was calculated from the relative viscosity (η_{rel}) using chloroform as solvent, in an Ostwald-type capillary viscometer, No. 50, immersed in a water bath at 30 ± 0.5 °C.

The relative viscosity was then obtained from the relation $\eta_{rel} \approx t/t_0$, for a regime of dilute solution where the densities of the solution and of the solvent are about the same.

Here, t and t_0 are, respectively, the solution and solvent flow times, necessary for the liquid to pass through the two viscometer menisci marks.

The relative viscosity was determined as an average of at least eight flow time measurements for each solution. To calculate the average only the measurements with precision of 1% were considered.

After obtaining the relative viscosity, the specific viscosity ($\eta_{esp} = \eta_{rel} - 1$) and the reduced viscosity ($\eta_{red} = \eta_{esp}/C$), C being the concentration of the solution, were calculated. The intrinsic viscosity was determined by the reduced viscosity extrapolation curve ($[\eta] = \lim_{c \rightarrow 0} \eta_{red}$) plotted by the concentration function.

The intrinsic viscosity, $[\eta]$, is a function of the molar mass of the polymer in solution, the polymer-solvent system, and the temperature.

Huggins proposed a relation between reduced viscosity, η_{red} , and concentration, c , for dilute polymeric solutions, or solutions with densities very close to the density of the solvent³². These conditions are satisfied in $1 < \eta_{rel} < 2$.

$$\eta_{red} = [\eta] + K_H [\eta]^2 c \quad (1)$$

where K_H is a proportionality constant with value close to 0.4 for a large variety of polymer-solvent systems.

Equation 1 represents a straight line on the plot of η_{red} versus c , and $[\eta]$ can be obtained by extrapolation to zero concentration.

The choice of the two concentration levels is based on Huggins conditions, where the lower limit of relative viscosity is higher and close to 1, while the upper limit is lower and close to 2.

Viscosity tests were carried out with sample sets 1 and 2, under powder or film forms. In this case, doses ranged from 5 to 300 kGy. Viscometric studies were also carried out in solutions prepared from samples molded as test specimens.

With the values for intrinsic viscosities, the viscosity-average molar mass (M_v) is easily obtained by means of the Mark-Houwink relation³³:

$$[\eta] = K(M_v)^a \quad (2)$$

where the constants K and a , calculated by Akita et al.³⁴ for the chloroform-P(3-HB) system at 30 °C are $K = 1.18 \times 10^{-4} \text{ dL.g}^{-1}$ and $a = 0.78$.

The degradation degree G , which represents the number of scissions in the main chain for each 100 eV of absorbed energy, is obtained by means of the Equation 3³⁵:

$$10^6/M_v = 10^6/M_{v_0} + 0.0548GD \quad (3)$$

where D is the absorbed dose of irradiation in kGy and G the degree of degradation (number of scissions/100 eV of absorbed energy).

This parameter is obtained from the slope of the curve $10^6/M_v \times D$ (kGy), in the interval where the inverse of the molar mass is linear in relation to the dose. This condition represents the dose interval where the scissions occur at random in the main chain.

2.3. Irradiation

The samples were irradiated at the Institute of Energy and Nuclear Research - IPEN-CNEN/SP with doses that varied from 5 to 300 kGy. A Gammacell-type ^{60}Co source was used at dose rates of 4.3 kGy/h for the irradiation of P(3-HB) test specimens and 3.6 kGy/h for the irradiation of polymer films. In both cases the irradiation occurred at 25 °C. For comparison, as-received P(3-HB) samples were also irradiated, in powder form, at 3.6 kGy/h dose rate and 25 °C.

2.4. Mechanical tests

The tensile tests were performed according to ASTM D-882 Standards in a universal testing machine EMIC, DL line, maximum force of 500 N, under the following conditions: temperature 25 °C, claw speed 50 mm/min and distance between claws 110 mm. The tests were done with non-irradiated test specimens and test specimens irradiated at 5, 15, 25, 35, 50, 100 and 200 kGy doses.

The impact-strength tests were performed according to ASTM D-256 in an Izod impact tester (Hammer 2J), with a hammer impact speed of 3.46 m/s and an approximate notch depth of 2.54 mm, in $60 \times 10 \times 3$ mm P(3-HB) test specimens irradiated 5, 15, 25, 35, 50 and 100 kGy doses.

3. Results and Discussion

Table 2 shows the values for M_{v0} for as-received and reprecipitated samples. The small difference in molar mass between the two samples may be related to the elimination of small structures that might interfere in the flow properties the solution.

For viscometric analyses carried out with as-received samples of P(3-HB) and P(3-HB-co-3-HV) in powder form, the M_{v0} values were 3.63×10^5 g/mol and 1.06×10^5 g/mol, respectively.

Figure 3 shows the reciprocal of the molar mass of films prepared with reprecipitated or as-received P(3-HB), from non-irradiated material or irradiated at 5, 15 or 25 kGy. A lower G value of 5.4 scissions/100 eV found in the reprecipitated P(3-HB) suggest that the degradation of this sample after irradiation is less severe when compared to as-received P(3-HB) films (G value = 7.0 scissions/100 eV). Hence, this simple purification step helped in preventing extensive radiation damage in the homopolymer matrix. Similarly, alterations in reciprocal of the molar mass for films prepared from as-received or reprecipitated P(3-HB-co-3-HV) (Figure 4), in the interval of 0-25 kGy evidenced a lower susceptibility of this copolymer to radiation after reprecipitation procedure, when G value decreases to 7.4 scissions/100 eV, while reaching 10.6 scissions/100 eV in the as-received material. In addition, a direct comparison between G values for P(3-HB-co-3-HV) and P(3-HB) suggests that the copolymer is intrinsically less resistant to radiation than the homopolymer.

As-received P(3-HB) samples in powder form were also irradiated and showed an 85% reduction in their initial molar mass at the dose of 25 kGy. In comparison, at the same dose, films casted from reprecipitated or as-received P(3-HB) showed 38% and 25% molar mass reduction, respectively. Polymer films are less susceptible to the effects of radiation when compared to the powder material, possible because the dissolution process allows impurities to be dislodged from bulk and deposited in the surface of the film during the casting process, thus triggering less degrading effects to the matrix when exposed to radiation. Alternatively, powder samples are more susceptible to photo oxidation events than film samples because of the larger contact surface of the former.

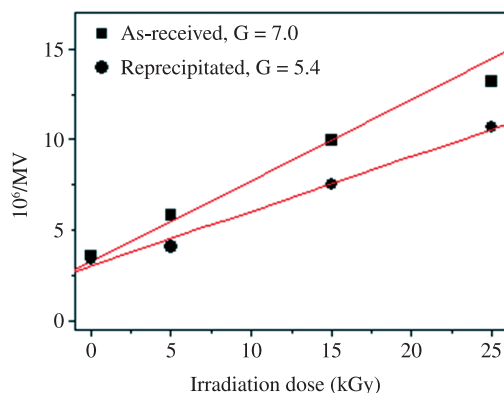


Figure 3. Reciprocal of the viscosity-average molar mass (M_v) as a function of the dose absorbed by the P(3-HB) films prepared from as-received or reprecipitated material.

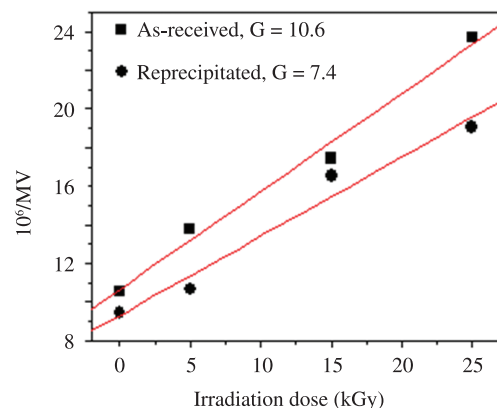


Figure 4. $10^6/M_v$ and G value (scissions/100eV) for P(3-HB-co-3-HV) irradiated films from as-received or reprecipitated samples.

Table 2. Molar mass (M_{v0}) of P(3-HB) and P(3-HB-co-3-HV) films.

Sample	$M_{v0}(10^5 \text{ g/mol}^{-1})$ (Reprecipitated film)	$M_{v0}(10^5 \text{ g/mol}^{-1})$ (non-treated)
P(3-HB)	2.92	2.79
P(3-HB-co-3-HV)	1.05	0.98

Viscometric studies carried out with P(3-HB) test specimens revealed M_{v0} equals to $2.0 \times 10^5 \text{ kg}\cdot\text{mol}^{-1}$. Based on the reciprocal of M_v , the value G (scissions per 100 eV) was obtained. The results for low (0-25 kGy) and high doses (35-200 kGy) are shown in Figure 5. Test specimens underwent less molecular degradation than powder samples. This fact evidences the importance of initial molar mass and samples shape when assessing gamma-irradiation effects. As a consequence of their higher degradation resistance, the percentage reduction of molar mass is less pronounced for test specimens. As can be observed in Figure 6, at 5 kGy dose, molar mass reduction was about 40%. At 25 kGy, molar mass suffered a reduction of 80%, and reached above 95% of reduction at 100 kGy. Table 3 summarizes the degradation parameters of P(3-HB) and P(3-HB-co-3-HV) at the sterilization dose. The degree of degradation G (scissions/100 eV) obtained from the interval of 0-25 kGy is higher for powder than for film samples.

The small differences between films prepared from as-received or reprecipitated materials show that, at the purity stage supplied by the industry, P(3-HB) and P(3-HB-co-3-HV) may appear less resistant to radiation than they really are. An alternative purification step was performed in our work, in order to verify the viability of an affordable, less harsh, readily scaled-up purification method, suitable to industrial post- production procedures. We used diluted HCl aqueous solutions to simple wash ups in samples at the powder form. The value G for P(3-HB) films from samples treated with diluted HCl showed to be very close to that obtained for films prepared with reprecipitated P(3-HB), indicating the efficiency of this acid in removing impurities responsible for radiolysis. In the other hand, using diluted NH_4OH solutions did not result in any improvements. This findings suggest than a simple, straightforward washing procedure is able to improve P(3-HB) performance when submitted to gamma irradiation, and yields approximately the same results obtained with reprecipitation with hexane from chloroform, a much less environmentally-friendly procedure. This washing procedure is easily scaled-up and may be introduced as a previous purification procedure for industrial production of radiosterilization-grade P(3-HB).

Gas Chromatography-Mass Spectrometry (GC-MS) analysis performed in methanol extracts of P(3-HB) revealed a considerable amount of fatty acids, such as lauric (39.6%), butyric (26.5%) and oleic acid (20.4%), in addition,

around 5% of phthalate esters were present, probably used as plastifiers³⁶. Fatty acids might be formed during the biosynthesis process. Their composition and proportion are dependent of many factors, such as aeration rates during fermentation. Oxygen limitation frequently leads to higher contents of organic acids and other metabolites

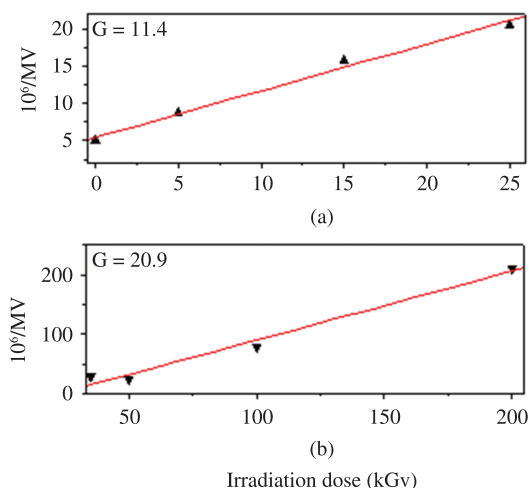


Figure 5. Reciprocal of the molar mass (M_v) as a function of the irradiation dose to P(3-HB) test specimens. a) 0–25 kGy; b) 35–200 kGy.

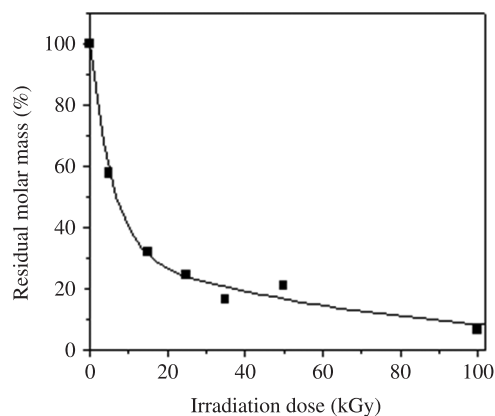


Figure 6. Residual molar mass of P(3-HB) test specimens.

Table 3. Summary of the degradation parameters for irradiated P(3-HB) and P(3-HB-co-3-HV).

Samples	Form	Treatment	G (0-25 kGy)	α (25 kGy)	Reduction of molar mass (%) (25 kGy)
PHB	Powder	-	12.9	6.6	86.8
	Film	-	7.0	2.64	72.8
	Film	Reprecipitated	5.4	2.12	67.9
	Film	HCl	5.9	2.27	65.2
	Specimen	-	11.4	3.10	76.7
P(3-HB-co-3-HV)	Powder	-	13.8	5.05	67.2
	Film	-	10.6	1.25	55.5
	Film	Reprecipitated	7.4	1.01	50.4

and deprives biopolymer formation³⁷. These by-products might be responsible for increased molecular damage observed in non-treated irradiated samples. Nevertheless, it is difficult to predict how such complex mixture behaves under irradiation. In addition, each biopolymer batch may have a different set of contaminants. Thus, performing pre-washings are recommendable or even essential in case of radiation-grade products manufacturing.

Table 4 summarizes some results gathered from literature on radiolytic degradation of P(3-HB) and P(3-HB-co-3-HV), caused by gamma irradiation, along with some results obtained in the present work. It must be pointed out that the samples are of different origins so, their characteristics will be different, as well.

P(3-HB) suffers scissions in its main chain with consequent changes in its mechanical properties. Considering this fact, the analyzed properties were: tensile at break, which assesses how much load is applied to the polymer at the moment of break; elongation at break, which assesses the stretchability of the polymer; modulus of elasticity, which is related to material stiffness; and impact resistance.

The mechanical behavior of non-irradiated and irradiated P(3-HB) test specimens at different doses was analyzed. The results show that the material becomes more fragile and brittle with the increase in irradiation dose. The degradation suffered due to the chain scissions under the radiation effect reflects mainly in the decrease of tensile at break and impact resistance, while the elastic modulus is the least affected by the irradiation process.

Figure 7 shows the behavior of the tensile at break as a function of the irradiation dose in P(3-HB) test specimens. At the dose of 25 kGy, the loss in tensile strength suffered by the sample was 20%. On the other hand, at higher doses, as 100 and 200 kGy, the loss in this property was 40 and 75%, respectively.

The behavior of the elongation at break as a function of the irradiation dose is shown in Figure 8. The change in this property is less pronounced than that observed for the tensile strength. At 25 kGy dose, the loss in elongation at break due to radiation was 10%, while at higher ones, as 100 and 200 kGy, the losses were 25 and 40%, respectively.

In Figure 9, the behavior of the property of elastic modulus for P(3-HB) can be observed with the dose. This property did not present any significant change up to the dose of 100 kGy, with 50% loss detected after a 200 kGy dose. This property is related to material stiffness, which means that it reflects the resistance of this material to elastic deformation. For crystalline polymers, it is common to notice milder gamma radiation effect on elastic modulus. Luo and Netravali²⁹ stated that the property of elastic

modulus is more intimately related to the crystalline content of the polymer, which is less affected by radiation than the amorphous content. This may explain why the elastic modulus is altered only at doses higher than 100 kGy as the radiation is not able to destroy the crystalline portions, responsible for the stiffness of the material.

The property of impact resistance Izod was significantly affected by gamma radiation. In Figure 10 it can be observed that, at the 25 kGy dose, the loss in this property was 25%, while at the dose of 100 kGy this loss was about 87%. It was not possible to perform these studies with samples irradiated at a dose of 200 kGy.

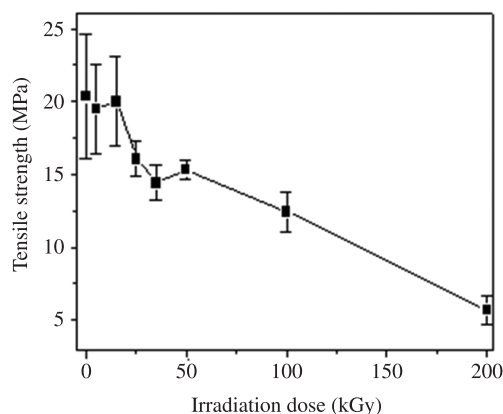


Figure 7. Tensile at break as a function of irradiation dose in P(3-HB) test specimens.

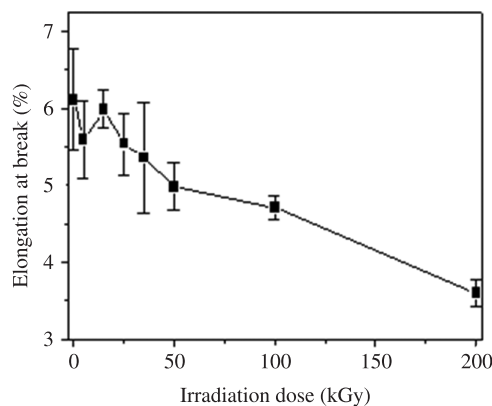


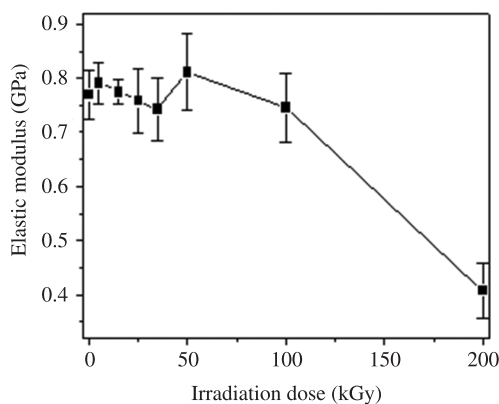
Figure 8. Elongation at break as a function of irradiation dose for P(3-HB) test specimens.

Table 4. Values G (scissions/100 eV) obtained for P(3-HB) and P(3-HB-co-3-HV) irradiated in air.

Reference	PHB Form	P(3-HB-co-3-HV) Form	Dose Interval (kGy)	G value PHB	G value P(3-HB-co-3-HV)
[29]	-	Film	0-250	-	0.9
[38]	Powder	-	0-200	5.9	-
[38]	Film	-	0-200	6.0	-
Present work	Film	Film	0-25	5.4	7.4
Present work	Powder	Powder	0-50	15.7	12.9

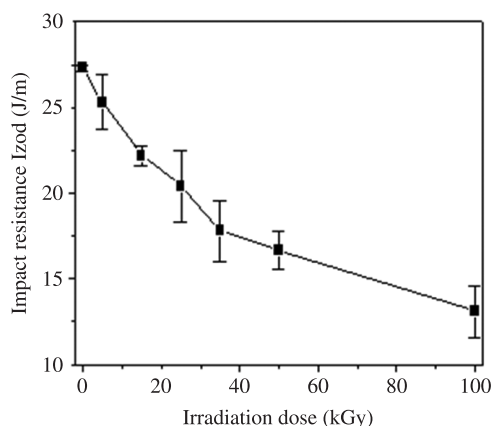
Table 5. Results of mechanical studies in P(3-HB) test specimens.

Dose (kGy)	Tensile at break (MPa)	Elongation at break (%)	Modulus of elasticity (GPa)	Impact resistance izod (J/m ⁻¹)
0	20.35 ± 4.294	6.11 ± 0.65	0.76 ± 0.04	27.3 ± 0.21
5	19.49 ± 3.051	5.59 ± 0.56	0.79 ± 0.03	25.3 ± 1.60
15	20.00 ± 3.074	5.98 ± 0.24	0.77 ± 0.02	22.2 ± 0.63
25	16.06 ± 1.223	5.53 ± 0.39	0.75 ± 0.06	20.4 ± 2.12
35	14.42 ± 1.172	5.35 ± 0.71	0.74 ± 0.05	17.8 ± 1.83
50	15.31 ± 0.689	4.98 ± 0.31	0.81 ± 0.07	16.7 ± 1.16
100	12.42 ± 1.416	4.70 ± 0.14	0.74 ± 0.06	13.1 ± 1.57
200	5.68 ± 1.01	3.60 ± 0.18	0.40 ± 0.05	-

**Figure 9.** Elastic modulus as a function of irradiation dose for P(3-HB) test specimens.

Gamma radiation causes scissions first and predominantly in molecules of the amorphous region³⁸. The property of tensile at break is more closely related to damages in the amorphous region of the material³⁹. However, scissions in the linked molecules are the ones that cause the highest losses in mechanical properties to a crystalline polymer⁴⁰.

The properties of tensile at break and impact resistance Izod in P(3-HB) test specimens were the most affected by radiation at sterilization dose (25 kGy), as is shown in Table 5, while elongation at break and modulus of elasticity suffered negligible decreasing. Nevertheless, general mechanical performance of P(3-HB) samples worsens at irradiation doses higher than 100 kGy.

**Figure 10.** Impact Resistance Izod with irradiation dose for P(3-HB) test specimens.

4. Conclusions

Radiostability of P(3-HB) and P(3-HB-co-3-HV) was showed to be improved by simple purification procedures, as either reprecipitation of the samples with hexane from chloroform solutions or washing with diluted HCl promoted reduction in the degree of radiolytic degradation.

The mechanical studies showed that P(3-HB) properties decrease, especially at doses higher than 50 kGy. The properties of tensile at break and impact resistance were the most affected by radiation, while the property of elastic modulus remained virtually unaltered up to the dose of 100 kGy, due the presence of crystalline regions in the polymer matrix, which confer stiffness to the matrix and are less affected by irradiation than amorphous regions.

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