

Gamma Irradiation Effects on Mechanical and Thermal Properties and Biodegradation of Poly(3-hydroxybutyrate) Based Films

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Summary: Their biodegradable properties make polyhydroxyalkanoates (PHAs) ideal candidates for innovative applications. Many studies have been primarily oriented to poly(3-hydroxybutyrate) (PHB) and poly(3-hydroxybutyrate-co-3-valerate) (PHBV) and afterwards to blends of PHAs with synthetic biodegradable polymers, such as poly(ϵ -caprolactone) (PCL). Medical and pharmaceutical devices require sterilization and γ irradiation could provide a proper alternative since it assures storage stability and microbiological safety. This contribution presents the effect of γ irradiation on the mechanical and thermal properties and on the biodegradation of PHB, PHBV and a commercial PHB/PCL blend. Samples, prepared by compression moulding, were irradiated in air at a constant dose rate of 10 kGy/h, from 10 to 179 kGy. Polymer chain scission was assessed by changes in the molecular weight, thermal properties and tensile behaviour. The correlation between absorbed dose and changes in the mechanical properties and biodegradation is discussed in detail. The optimum dose to guarantee microbiological sterilization without damage of the structure or meaningful loss of the mechanical properties is also reported.

Keywords: biodegradable; biopolymers; irradiation damage; mechanical properties; poly(hydroxyalkanoate) (PHA)

Introduction

The search for biodegradable substitutes of petrochemical thermoplastics has been a crucial driving force to increase the interest in biopolymer-based materials. Regarding

this search polyhydroxyalkanoates (PHAs) constitute a primary choice because they are bacterial polyesters obtained from renewable resources and degrade in normal environment, either by hydrolytic or enzymatic action.^[1] Over one hundred PHA compositions have been reported in the literature. The first PHA discovered was poly(3-hydroxybutyrate) (PHB), characterized by a high crystallinity; another well-known biosynthesized copolymer is poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), less crystalline because of the two-carbon-radical of each HV monomer.^[2]

Due to their biodegradability through nontoxic intermediates and easy processability, PHB and PHBV are considered as ideal candidates not only to replace non-biodegradable polymeric materials^[3–6] but also to develop bioabsorbable drug controlled release devices, medical applications

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and scaffolds for tissue engineering [7–9]. Also the blend of PHB with poly(ϵ -caprolactone) (PCL) is suitable for many of these applications, since both PHB and PCL are aliphatic polyesters hydrolysable in the human body; furthermore, mechanical properties and degradation of the PHB/PCL blends can be tailored by changing the composition.^[10]

Medical and pharmaceutical devices as well as food packaging requires sterilization to guarantee microbiological safety. Gamma irradiation is an alternative sterilization method since it provides increased storage stability and microbiological safety. Though γ -irradiation required lengthy validation procedures before approval for marketing, this situation was eased by the mid-1970s, partly at least due to growing concern over the probable carcinogenicity of ethylene oxide (the main alternative “cold” sterilization process available for heat sensitive plastics). Nowadays, the industrial scale ^{60}Co γ -irradiators operating through the world, dedicated 90% of their capacity to medical devices and food irradiation.^[11–14]

Irradiation of polymers generally produces simultaneous scission and cross-linking of the polymeric chains.^[15,16] The latest causes the formation of a macroscopic network, which reduces gas permeability and improves mechanical properties.^[17,18] The former, on the other hand, which occurs preferentially in the amorphous regions, reduces crystallinity, deteriorates mechanical properties but increases the biodegradation rate.

Radical species resulting from γ -irradiation of PHB and PHBV, obtained by radiolysis at 77 and 303 K, are detailed elsewhere.^[19] Mitomo et al.^[20,21] studied the effects of γ -irradiation in air and vacuum on the thermal and enzymatic degradations of PHB and PHB-20 and 40 mol % HV. They observed that the glass transition and the melting temperatures of PHB and PHBV irradiated in air or in vacuum presented virtually the same behaviour: both decreased almost linearly with increasing irradiation dose. Furthermore, they determined that chain scission occurred within amor-

phous regions below 100 kGy and continued further to crystalline regions at higher doses; on the other hand, cross-linking was observed only under irradiation in vacuum. Due to the cross-links, on increasing the dose the biodegradation rate increases slower in vacuum than in air.

Miyazaki et al.^[22] measured the γ -irradiation effect on PHB casting films with different molecular weights and correlated the molecular weight of PHB with the elongation at break. More recently, Oliveira et al.^[23] studied the effect of γ -rays on the molecular weight, the thermal properties and the X-ray diffraction patterns of PHB and PHB-6.3HV. They found a decrease in the molecular weight and an increase in the degree of crystallinity, associated to chain scissions and chemocrystallization, respectively.

In summary the previous work on PHB and PHBV demonstrate that γ -irradiation in air reduces the melting point and the average molecular weight but increases the biodegradation rate because of the scission of chains mainly in the amorphous region. However, a correlation of the irradiation dose to the loss in mechanical properties, the acceleration in biodegradation kinetics and the microstructural changes of copolymers and blends based on PHB has not been presented yet. Therefore, the aim of this contribution is to show the effect of γ -irradiation on the structure, mechanical properties and biodegradation of PHB, PHBV and a commercial PHB/PCL blend. On achieving this goal, the optimum dose to guarantee microbiological sterilization and biodegradation without meaningful mechanical loss will be determined for the three biopolymers.

Experimental Part

Material

Bacterial PHB (sold under the trade name Biocycle[®]1000), PHBV with 12 wt % of HV, and a commercial blend of PHB with PCL (sold as Biocycle[®]1400-2) were purchased from PHB Industrial SA, Brazil.^[24]

PHBV is a white powder with a viscosity average molecular weight $\overline{M}_v = 165$ kg/mol.^[25] PHB is a yellowish white powder, with a high degree of purity of over 99.5% and a weight-average molecular weight of approximately $\overline{M}_v = 600$ kg/mol. The PHB/PCL blend was purchased as brown yellowish pellets. All materials were used as received. The crystalline degrees of PHB, PHBV and PHB/PCL, determined by X-ray diffraction, were (55 ± 5) %, (45 ± 5) % and (30 ± 5) %, respectively.

Samples

Powder of PHB was placed between two stainless steel plates separated by a metallic ring 200 μm thick, and melted using a hydraulic hot press under compressive cycles of 5 MPa. After being held at 463 K for 10 min and quenched at 269 K, sheets around 100 mm in diameter and 200 μm thick were obtained. Samples for the mechanical, thermal and biodegradation tests were cut from these sheets. The same procedure was followed to get the PHBV and PHB/PCL specimens.

Irradiation Conditions

All samples were irradiated using the semi-industrial ^{60}Co irradiator at the Ezeiza Atomic Centre (Buenos Aires, Argentina). All samples were irradiated at a constant dose rate of 10 kGy/h in air at room temperature up to 10, 20, 40, 80 and approximately 180 kGy.

Mechanical Properties

Samples were cut according to the ASTM D1708 standard.^[26] The tensile tests were performed in an Instron Testing Machine, Model 1122 at a deformation rate of $9 \times 10^{-4} \text{ s}^{-1}$ at 30 °C. At least three samples were tested for each irradiation dose level and for not irradiated samples (control). From each test the tensile modulus, tensile strength, and percent of elongation at break were determined.

Thermal Properties

Thermal analysis of the irradiated biopolymers was carried out on samples of

approximate 10 mg weight using a DSC 822 from Mettler, Toledo, under inert N_2 atmosphere at 50 ml/min. The equipment was calibrated with high-purity standards.

To avoid thermal degradation of PHB, PHBV and PHB/PCL the following temperature program was considered: annealing at -14°C for 2 minutes, heating from -14°C to 200°C (1st heating), cooling from 200°C to -14°C (cooling), annealing at -14°C for 2 minutes and heating from -14°C to 200°C (2nd heating). In all cases the heating/cooling rate was $10^\circ\text{C}/\text{min}$.

Attenuated Total Reflectance-Fourier Transform Infrared Analysis (ATR-FTIR)

Fourier Transform-Infrared spectra were acquired using a Nicolet 5700, Thermo FTIR spectrometer equipped with a DTGS KBr detector. Samples were mounted on an ATR accessory equipped with ZnSe crystal prior to scanning. The spectra were obtained with an accumulation of 100 scans and with a resolution of 2 cm^{-1} .

Biodegradation

The mineral salt medium (MSM) contains, in g/L distilled water: K_2HPO_4 , 1; $\text{CaCl}_2 \cdot 2 \text{ H}_2\text{O}$, 0.01; $\text{FeSO}_4 \cdot 7 \text{ H}_2\text{O}$, 0.01; $\text{MgSO}_4 \cdot 7 \text{ H}_2\text{O}$, 0.4; $(\text{NH}_4)_2\text{SO}_4$, 0.1; pH was adjusted to 7. The microorganism was locally isolated from composting medium and maintained at $(28 \pm 1)^\circ\text{C}$ on *Actinomyces* agar slants containing, in g/l distilled water: yeast extract, 0.2; starch, 1; agar, 1.5, pH adjusted to 7.4.

For the polymer degradation experiment 150-ml Erlenmeyer flasks were used, each with 50 ml of the MSM, which were inoculated with a 2% v/v suspension of *Streptomyces* sp. Each flask contained one piece of surface sterilized (70% v/v ethanol) polymer. The reaction solution was agitated in a rotary shaker at 100 rpm and kept at $(30 \pm 1)^\circ\text{C}$. Control experiments were carried out without the inoculation of the MSM.

After 15 days a set of samples was removed from the solution, washed with distilled water under the ultrasonic action and dried at 40°C to constant weight. At

least three samples were tested for each irradiation and non-irradiation condition. This procedure was repeated after 30 and 45 days of the first immersion using inoculated solution. The weight loss of the polymer was determined gravimetrically and biodegradation was measured in terms of the relative weight loss, $100 \times \Delta w / w_0$, where w_0 and Δw are the initial weight and weight loss of the sample, respectively.

Results

Mechanical Behaviour

Figure 1 shows how the γ -irradiation affects the tensile curve of PHB, PHB/PCL and PHBV. Regarding the tensile response,^[28] characterized by a short linear dependence of the load-deformation followed by fracture, PHB and PHBV can be classified as extremely brittle, while PHB/PCL should also be considered brittle because the elongation at break is lower than 10% even for unirradiated samples.

Since PHB and PHBV samples irradiated up to 150 and 179 kGy, respectively, became extremely brittle they could not be mechanically tested; however, samples of PHB/PCL irradiated up to 179 kGy exhibited the same mechanical response as the ones irradiated up to 80 kGy. Figure 2 compares the tensile response of the three materials prior to irradiation and after having received a dose of 80 kGy.

The relevant mechanical features of the stress-strain curve are: the tensile modulus, E , the tensile strength, T.S., and the elongation at break, ε_b . The first one relates to the recoverable contribution, that is, to the elastic energy both in the crystalline and amorphous regions, while T.S. and ε_b characterize the plastic response by the toughness and the ductility of the material, respectively. Figure 3 shows the effect of the absorbed γ -irradiation dose on these mechanical properties for the three materials.

Regarding the tensile modulus, based on the data shown in Figure 3, the modulus does not change with the irradiation dose, within the standard deviation of the

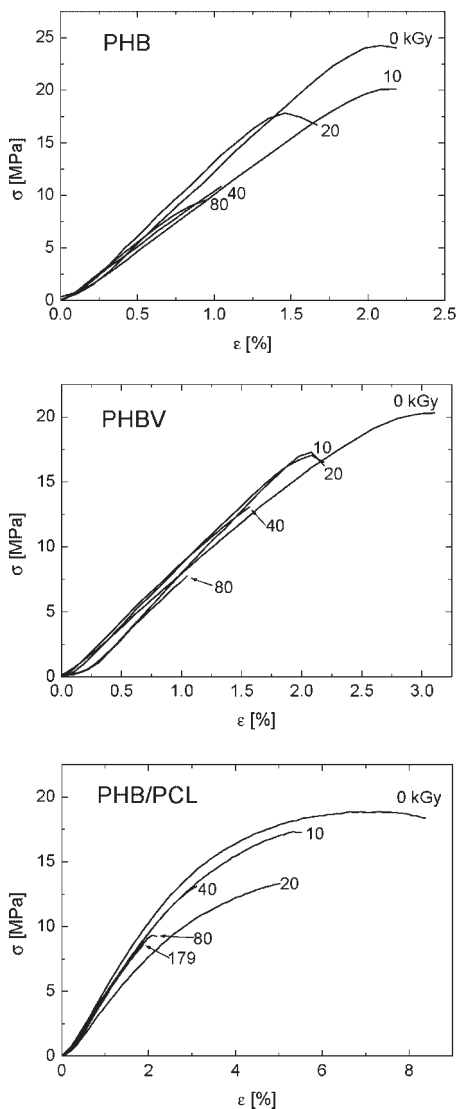


Figure 1. Tensile curves for samples of PHB, PHBV and PHB/PCL irradiated up to the indicated doses.

measured data. The relationship $E_{PHB} > E_{PHBV} > E_{PHB/PCL}$ summarizes the comparison of the elastic behaviour of the three materials.

Nevertheless, the tensile strength and the elongation at break strongly depend on the irradiation dose; both decrease as the irradiation dose increases, as depicted in Figure 3. When irradiated up to 80 kGy,

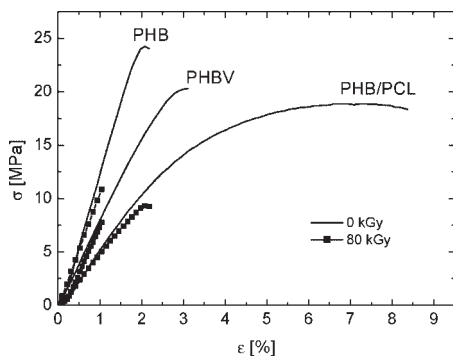


Figure 2. Mechanical response of PHB, PHBV and PHB/PCL unirradiated and after an absorbed dose of 80 kGy.

PHB and PHBV exhibited a reduction of 41% in the tensile strength while it was of 44% for PHB/PCL.

One important parameter to evaluate the irradiation damage is the relative radiation stability in air in this case at 10 kGy/h, defined as the dose required for reducing the tensile elongation to 50% of the elongation at break of the control. This value is around 80 kGy for PHB and 40 kGy for PHBV and PHB/PCL.

Figure 4 illustrates the proper fit to the experimental data given by the equation

$$\varepsilon_b = \varepsilon_{b\infty} + (\varepsilon_{bo} - \varepsilon_{b\infty})e^{-D/D_o} \quad (1)$$

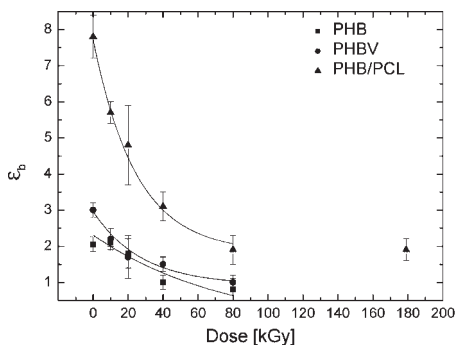


Figure 4. Decrease of the elongation at break with the irradiation dose, properly fitted by eq. (1).

where ε_{bo} is the elongation at break for the unirradiated sample and $\varepsilon_{b\infty}$, the asymptotic value reached at high irradiation doses; D_o is a characteristic constant of the irradiation damage. The values of the fitting parameters are indicated in Table 1.

Infrared Spectroscopy

Figure 5 shows the ATR-FTIR spectra for PHB, PHBV and PHB/PCL, for the control, and samples irradiated up to 80 kGy. Under the present experimental conditions the irradiation doses do not induce noteworthy changes in the absorption bands of the spectra. This result agrees with the

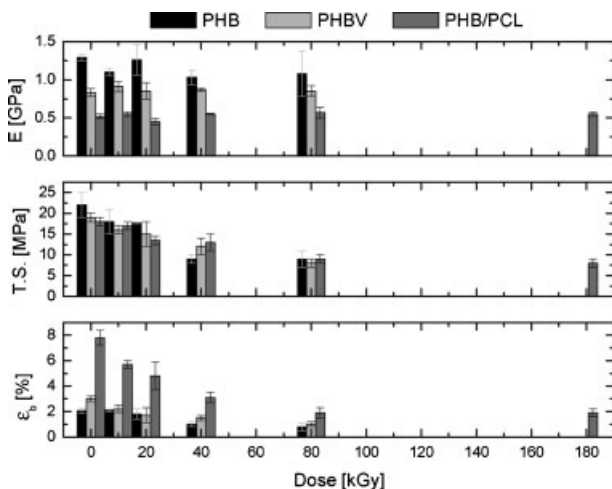


Figure 3. Dependence of the tensile modulus, tensile strength and elongation at break on the irradiation dose.

Table 1.

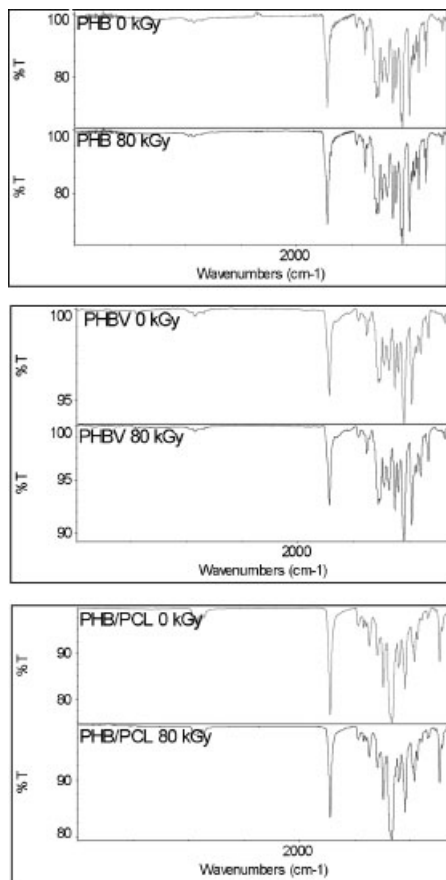
Elongation at break for the unirradiated sample, ϵ_{bo} , asymptotic value reached at high irradiation doses, $\epsilon_{b\infty}$, and characteristic constant of the irradiation damage, D_o , determined from the experimental data by using eq (1).

	PHB	PHBV	PHB/PCL
ϵ_{bo}	2.4	2.9	7.7
$\epsilon_{b\infty}$	0	0.9	1.8
D_o [kGy]	80	28	25

FTIR spectra of irradiated semi-crystalline petrochemical polymers.^[13]

Thermal Behaviour

The thermal response of PHB, PHBV and PHB/PCL irradiated at various doses was

**Figure 5.**

ATR-FTIR spectra of PHB, PHBV and PHB/PCL previous to irradiation (above) and after a dose of 80 kGy (below). No meaningful changes were observed.

analyzed on melting in order to determine irradiation damage in the crystalline structure, followed by cooling to observe changes in the crystallization temperature and enthalpy and finished by second melting to get insight on the crystallization mechanisms of irradiated chains, as illustrated in Figure 6 shows.

In both heatings PHB shows an endothermic melting peak centred at T_m that shifts to lower temperatures while the enthalpy of fusion ΔH_m slightly decreases as the dose increases (Table 2). Regarding the crystalline fraction, calculated as $\Delta H_m / \Delta H^*$ where $\Delta H^* = 146$ J/g is the enthalpy of fusion of PHB crystals,^[27] crystallinity reduces from 60 to 55%. This means that the irradiation promotes imperfections in the crystalline structure. Regarding the exothermal peak observed on cooling, due to the crystallization of the macromolecules, its maximum, T_c , shifts to lower temperatures while the crystallization enthalpy, ΔH_c , slightly decreases as the dose increases. This feature is due to the chain scission that enhances the mobility of the macromolecules; this increasing driving force promotes crystallization at a lower temperature.

During the second heating there is a secondary melting at $T_{m2} < T_m$, already observed by Oliveira et al.^[23] Multiple melting behaviours are usually due to melting of crystals with different lamellar thickness. Both T_m and T_{m2} decreases with the increase in the dose since the chain scissions arising after the irradiation give the macromolecules greater mobility, which induces the appearance of a disordered phase at lower temperatures.

The effect of irradiation on the thermal behaviour of PHBV is similar to that for PHB except for two new features appearing during the second heating. One corresponds to the glass transition temperature, T_g , which is independent of the irradiation dose. This transition can be detected in PHBV because of its higher amorphous fraction (ca. 50%). The other feature is the appearance of an exothermic peak around 50 °C, due to the crystallization of chain

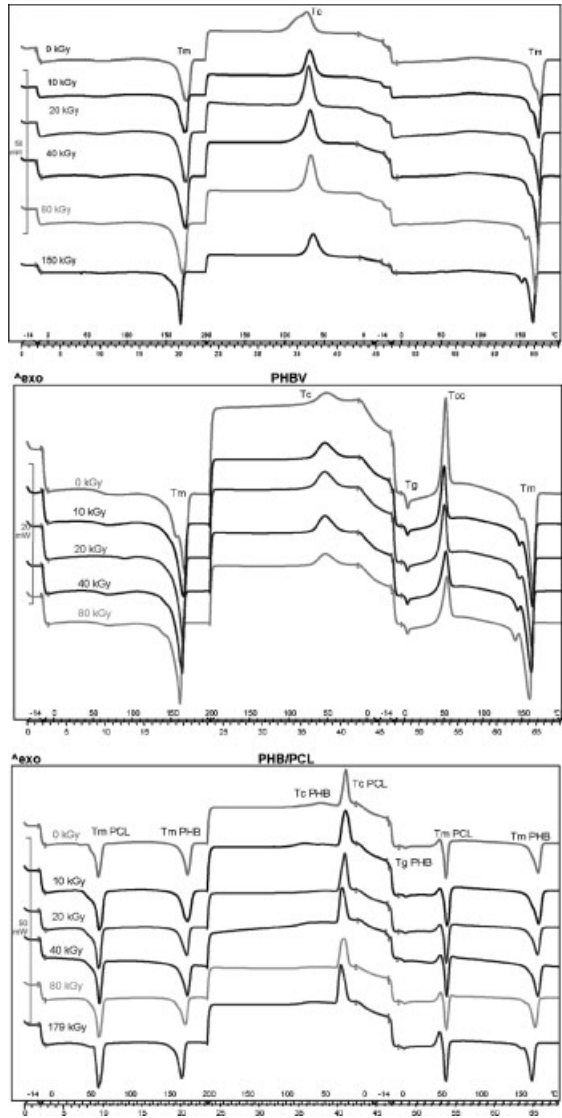


Figure 6. DSC curves (heating, cooling and 2nd heating) for PHB, PHBV and PHB/PCL at the various doses.

Table 2. Melting points (T_m), secondary melting points (T_{m2}), crystallization temperatures (T_c) and enthalpies of fusion (ΔH_m) and of crystallization (ΔH_c) of PHB.

PHB	1 st heating		Cooling		2 nd heating	
	T_m [°C]	ΔH_m [J/g]	T_c [°C]	ΔH_c [J/g]	T_{m2} [°C]	T_m [°C]
0	173.7 ± 0.2	87 ± 3	71.7 ± 1.3	73.0 ± 3.6	164 ± 1	172 ± 2
10	172.2 ± 0.2	86 ± 4	68.5 ± 0.3	67.2 ± 0.2	162.6 ± 0.1	172.7 ± 0.4
20	173.4 ± 0.3	86.0 ± 0.5	69.8 ± 0.7	69.4 ± 1.5	162 ± 1	173.6 ± 0.6
40	172.9 ± 0.5	86 ± 2	69.1 ± 0.7	70 ± 2	160.2 ± 0.2	171.2 ± 0.1
80	169.6 ± 0.1	82 ± 2	67.8 ± 0.4	69.0 ± 2.3	156.3 ± 0.3	168.2 ± 0.2
150	167.7 ± 0.6	80 ± 7	65.0 ± 0.4	58.0 ± 2.5	151.5 ± 0.1	165.4 ± 0.3

Table 3.

Melting points (T_m), secondary melting points (T_{m2}), glass transition temperatures (T_g), crystallization and cold crystallization temperatures (T_c , T_{cc}) and enthalpies of fusion (ΔH_m) and of crystallizations (ΔH_c , ΔH_{cc}) of PHBV.

PHBV	1 st heating		Cooling		2 nd heating				
Dose [kGy]	T _m [°C]	ΔH _m [J/g]	T _c [°C]	ΔH _c [J/g]	T _g [°C]	T _{cc} [°C]	ΔH _{cc} [J/g]	T _{m2} [°C]	T _m [°C]
0	166.4 ± 0.6	69 ± 1	52.1 ± 0.3	11 ± 1	1.7 ± 0.1	52.1 ± 0.8	38 ± 1	147.3 ± 0.1	163.5 ± 0.3
10	167 ± 1	62 ± 3	53.6 ± 0.6	18 ± 4	1.8 ± 0.1	50.0 ± 0.2	31 ± 5	145.6 ± 0.4	162.2 ± 0.2
20	164.0 ± 0.4	65 ± 2	53.3 ± 0.1	19 ± 1	2.0 ± 0.1	50.3 ± 0.3	28.1 ± 0.7	144.9 ± 0.1	161.6 ± 0.1
40	163.0 ± 0.3	68 ± 1	53.8 ± 0.3	21 ± 3	1.8 ± 0.1	52.3 ± 0.4	23 ± 3	143.8 ± 0.2	160.8 ± 0.1
80	160.5 ± 0.3	68 ± 1	53.0 ± 0.2	20.2 ± 0.4	1.8 ± 0.1	54.3 ± 0.1	28.8 ± 0.2	141.0 ± 0.1	159.2 ± 0.1

segments that could not crystallize while cooling. This behaviour, denoted as cold crystallization, is characterized by the temperature of the peak, T_{cc} , and the enthalpy ΔH_{cc} . T_{cc} slightly decreases as the dose reaches 20 kGy and then increases, while ΔH_{cc} reduces as the dose increases (Table 3).

Unlike the slight reduction in ΔH_m for PHB, for PHBV ΔH_m is independent of the absorbed dose; this feature indicates that the γ -radiation mostly damages the amorphous region.

DSC curves of PHB/PCL show the melting peak of PHB at T_m PHB and the one of PCL at T_m PCL < T_m PHB. During the second heating this endothermic peak appears overlapped with the PHB crystallization peak. Regarding the data of Table 2 and 4, the presence of PCL does not modify the thermal behaviour of PHB as a function of the irradiation dose. Glass transition temperature of PHB decreases slightly with the doses since the mobility of the macromolecules increases with the decrease of the molecular weight produced by the γ -irradiation.^[18]

Biodegradation

Figure 7 shows the evolution of the relative weight loss of PHB, PHBV and PHB/PCL irradiated at different doses. For the three materials, the degradation rate increases with the irradiation dose, however, the kinetics of the degradation process has different characteristics for each biopolymer. For irradiated PHB samples the degradation rate reduces dramatically after 14 days, except at the higher irradiation dose (160 kGy) where there is a weight loss of 45% after 21 days of degradation. In the case of PHBV, the degradation rate increases slowly as the dose increases, reaching a weight loss of 70% after 21 days of degradation for the higher dose. Regarding the biodegradation of PHB/PCL, unirradiated samples and those irradiated up to 10 and 20 kGy did not degrade after 21 days of cultivation, thus the experiment was extended up to 42 days. After this period unirradiated samples had lost only 2% of their original weight, while those irradiated up to 160 kGy had lost 18% of their weight. This means that the irradiation damages the morphology, par-

Table 4.

Melting points (T_m), crystallization temperatures (T_c), glass transition temperatures (T_g) and enthalpies of fusion (per g of the blend) of PHB and PCL.

PHB/PCL	1 st heating				Cooling	2 nd heating			
	Dose [kGy]	T_m PCL [°C]	ΔH_m PCL [J/g]	T_m PHB [°C]	ΔH_m PHB [J/g]	T_c PCL [°C]	T_g [°C]	T_m PCL [°C]	T_m PHB [°C]
0		59 ± 1	33 ± 5	173.9 ± 0.7	40 ± 2	25.8 ± 0.7	2.5 ± 0.1	55.9 ± 0.4	173.6 ± 0.5
10		60 ± 2	38 ± 10	173.3 ± 0.1	42 ± 0.5	24.3 ± 0.5	2.7 ± 0.1	56.5 ± 0.9	173.1 ± 0.6
20		61 ± 2	46 ± 6	172.7 ± 0.2	36.6 ± 0.1	25.4 ± 0.1	2.2 ± 0.1	56.1 ± 0.1	172.5 ± 0.3
40		61 ± 1	42 ± 8	173.2 ± 0.1	36 ± 5	28 ± 2	2.0 ± 0.3	56.4 ± 0.3	172.1 ± 0.9
80		60 ± 2	43 ± 8	170.9 ± 0.6	38.1 ± 0.2	26.5 ± 0.1	1.5 ± 0.1	56.4 ± 0.1	169.4 ± 0.1
150		56 ± 1	36 ± 4	166.0 ± 0.1	39 ± 2	29.5 ± 1	0.2 ± 0.1	55 ± 1	165.0 ± 0.1

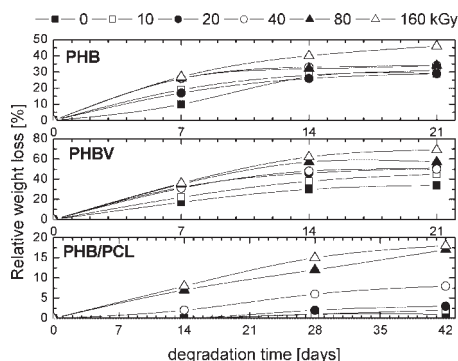


Figure 7. Biodegradation kinetics of PHB, PHBV and PHB/PCL at various doses.

ticularly in the amorphous regions where biodegradation proceeds.

Figure 8 illustrates the effect of the absorbed dose on the biodegradation process, after 21 days of degradation for PHB and PHBV and after 42 days for PHB/PCL.

After 21 days the relative weight loss of PHB films irradiated up to 160 kGy reached up to 46%, while films that received a smaller dose (10 to 80 kGy) lost 30% of its relative weight, independently of the irradiation damage. Nevertheless, the biodegradation of PHBV films increases as the absorbed dose does and for all doses the weight loss was higher than for PHB. The maximum weight loss, found in PHBV irradiated up to 160 kGy, was 69% after 21

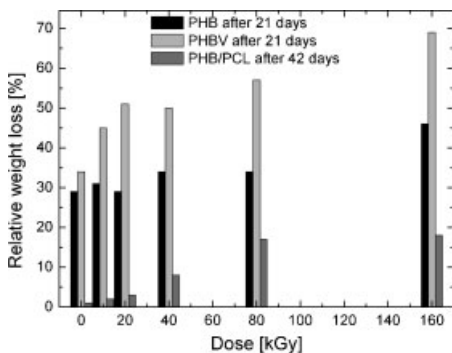


Figure 8. Relative weight loss of irradiated PHB and PHBV after 21 days and PHB/PCL after 42 days in mineral medium with *Streptomyces* sp.

days of degradation in mineral medium with *Streptomyces* sp.

Biodegradation of PHB/PCL was scarce except for absorbed doses above 40 kGy, even when the degradation time was extended up to 42 days. Thus, the presence of PCL highly inhibits the degradation action of the isolated bacterium *Streptomyces* sp. PCL is well biodegraded by fungi but not by bacteria.

The relative weight loss of PHB irradiated up to 40 kGy (34%) is the same as that of unirradiated PHBV films. If *Streptomyces* sp. has the same degradation behaviour then, the molecular morphology of both samples should be the same. This means that an absorbed dose of 40 kGy produces so many chain scissions that the average molecular weight of PHB samples reduces to that of the unirradiated PHBV.

Discussion

According to the thermal analysis of the irradiated samples, PHB—with the highest crystalline degree—exhibits a slight reduction of the enthalpy of fusion as the dose increases. Nevertheless, for irradiated samples of PHBV or PHB/PCL which have an important amorphous phase, ΔH_m remains constant and T_g reduces as the dose increases. The lower the T_g the greater the ability for chain segments in adjacent chains to move relative to each other. Hence, γ -irradiation damages mainly the amorphous phase by chain scission or, if the crystalline phase is dominant, it introduces defects in the ordered lamellae.

The same conclusion is reached if we consider the mechanical response of the irradiated samples. The elastic deformation can be almost entirely accounted for by reversible interlamellar slip, which involves shear of the lamellae parallel to each other with the amorphous phase undergoing shear.^[28] Bédoui et al. demonstrated that the elastic behaviour of semicrystalline materials which amorphous phase is in the rubbery state, does not depend on the spherulite structure but on the crystallite

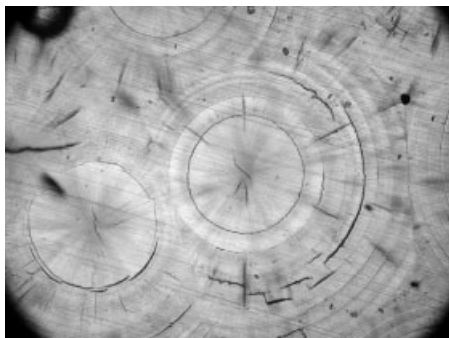


Figure 9.

Micrograph of an etched sample of unirradiated PHBV: circumferential and radial cracks determine the brittle behaviour of this material.

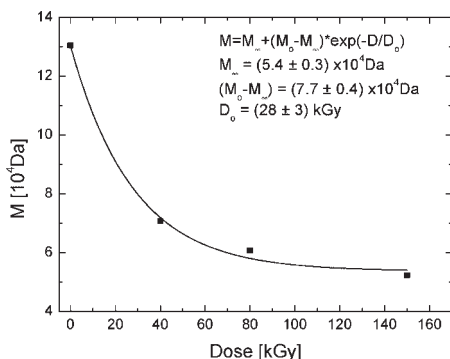


Figure 10.

The molecular weight of PHBV decreases exponentially with the dose, with the same characteristic parameter D_o as for the decrease in the elongation at break.

shape ratios.^[29] Thus, the slight decrease of the elastic modulus with the absorbed dose agrees with the scarce changes in the crystalline phase determined by the thermal analysis.

The brittle behaviour of the semi-crystalline polymers above T_g is due to the formation of crazes or shear bands in the mobile amorphous regions followed by the propagation of cracks within the spherulites or at the spherulitic boundaries.^[31] These cracks, which may be either radial or circumferential, were observed in PHB^[30] and copolymers,^[31] for example Figure 9 shows cracks in an etched sample of PHBV observed by polarized optical microscopy.^[31] Thus, the plastic deformation of these brittle semi-crystalline polymers is mainly due to the movement of chain segments in the amorphous fraction. Therefore, the meaningful reduction in the tensile strength and the elongation at break is due to the chain scissions in the amorphous phase produced by γ irradiation. This chain scission is evident, of course, if the molecular weight is measured by HPLC, as illustrated in Figure 10 for PHBV as an example. However we intend to demonstrate that the elongation at break is also a suitable property to evaluate the irradiation damage. In fact, a simple comparison of Figure 4 and 10 reveals that ε_b depends linearly on the average mole-

cular weight of the sample. This conclusion agrees with a previous work by Renstad et al.,^[32] who measured the elongation at break for PHB and PHBV samples with different molecular weights.

Therefore, on considering that linear relationship, eq. (1) can be rewritten in terms of the average molecular weight, M , as

$$M = M_{\infty} + (M_o - M_{\infty}) e^{-D/D_o} \quad (2)$$

where M_o and M_{∞} are the average molecular weight of the macromolecules of the unirradiated sample and of a sample after a long irradiation dose, respectively. If the irradiation effects are measured at low doses, then $M_{\infty} \ll M$ and eq. (2) reduces to

$$M^{-1} = M_o^{-1} e^{-D/D_o} \quad (3)$$

Particularly for low doses ($D \ll D_o$) the effect of the irradiation damage on the molecular weight might be calculated as

$$\frac{1}{M} = \frac{1}{M_o} + \frac{1}{M_o D_o} D \quad (4)$$

Eq. (4) agrees with the empirical results obtained recently from viscosity data of PHB and PHBV irradiated up to 50 kGy,^[23] regarding that

$$\frac{1}{M_o D_o} = 1.04 \times 10^{-7} (1 - \chi) G, \quad (5)$$

where χ is the degree of crystallinity and G is the radiolytic yield of chain scission, evaluated by the number of scissions per 100 eV.^[15] On replacing the molecular weight and the degree of crystallinity of the unirradiated samples in eq. (5) we get $G_{\text{PHB}} = 0.5$ and $G_{\text{PHBV}} = 3.8$. Unfortunately the radiolytic yield of chain scission could not be calculated for PHB/PCL because of technical difficulties with the column (PLgel 10 microns - 300×7.5 mm - MIXED-B) of our HPLC (Shimadzu Chromatopac C-R6A).

Conclusions

There is a similar effect of the γ -irradiation on the mechanical properties of PHB, PHBV and PHB/PCL. The major consequences are a decrease in both the tensile strength and the percentage of elongation at break while the tensile modulus remains almost constant as the dose increases.

Regular doses for food irradiation are lower than 10 kGy and for packaging sterilization the doses are lower than 25 kGy. Therefore, from the results presented in this work we claimed that there is no dramatic reduction of the mechanical properties of PHB, PHBV nor PHB/PCL within this range of γ -irradiation dose. Thermal properties, as well as, ATR-FTIR spectra of the biodegradable polyhydroxyalkanoates investigated did not show significant changes at the absorbed doses employed in this study. Furthermore, the influence of the irradiation dose on the biodegradation remarks that chain scission in the amorphous region promotes the degradation of PHBV and in a less extent that of PHB. The degradation of PHB/PCL is rather small because PCL are more suitable for degradation by fungi and this study considered only degradation by bacteria.

The linear relationship between the molecular weight and the elongation at break of irradiated PHB and PHBV enables to consider the elongation at break

as a suitable parameter to evaluate the irradiation damage. In fact, it has been shown that from the dependence of the elongation at break with the irradiation dose the radiolytic yield of chain scission can be calculated.

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