Radiation-Induced Graft Copolymerization of Vinyl Acetate onto Poly(3-hydroxybutyrate): Synthesis and Characterization

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Abstract: Radiation-induced graft copolymerization of vinyl acetate (VAc) onto poly(3-hydroxybutyrate) (PHB) was performed to improve the polymer hydrophilicity. The grafting reaction was carried out by the simultaneous irradiation technique with ^{60}Co γ-ray. The grafting degree (W), composition (C), and grafting index (γ_g) were determined using different techniques. Characterization of the grafted PHB was also carried out by structural and thermal

techniques. All the experimental results indicated that the PHB-graft-PVAc was synthesized with a graft degree of 39 PVAc percent. The swelling behavior was also studied. The results showed a water uptake increase tendency.

INTRODUCTION

The polyhydroxyalkanoates (PHA) are alternative polymeric materials.[1–4] These polymers are obtained from biomass. Among their advantages are the fact that they originate from renewable sources and constitute biodegradable and biocompatible materials. The first member of this polymeric family is poly(3-hydroxybutyrate) (PHB). It is a semicrystalline thermoplastic with mechanical properties similar to those of polypropylene (PP).[5] Presently it is still far from being a possible substitute for PP because of its high price, however, it is a material with great prospects in a sustainable development and its application is directed to very timely uses.

In addition, PHB is useful for medical applications, such as matrices for drug delivery, biomaterials, and tissue engineering.[6–10] In all these cases, the hydrophilic characteristics of the polymer are important.[6] In this sense, it must be mentioned that PHB is a moderately hydrophobic polymer.[11] It has been found that it is possible to change this property by graft polymerization: grafting hydrophilic polymers onto the hydrophobic substrate.

Radiation is useful to prepare and modify different materials for medical use, and ionizing radiation processing offers unique advantages.[6] Through these processes, materials of high purity can be obtained. Radiation does not require any catalyst or initiator and it can prepare polymeric materials at low temperature from high energy of radiation. In addition, the doses used do not generally affect the polymer substrate properties significantly. The variation of the radiation dose and the grafting solution composition and temperature permit the control of the extent and depth of the grafting, graft-substrate interpenetration, and surface composition. However, it is not possible to control the length of the grafted polymer because of the complexity of the reaction.

Several authors studied radiation-induced graft polymerization onto PHB.[11–15] Mitomo and coworkers[12–14] obtained the graft polymerization of methyl methacrylate (MMA), 2-hydroxyethyl methacrylate (HEMA), and styrene (St) onto PHB and its copolymers P (HB-co-HV). These investigations were carried out by using the simultaneous radiation and pre-irradiation techniques from a ^{60}Co γ-ray source.

   In addition, Jiang and Hu[15] investigated the graft copolymerization of isoprene (Ip) onto PHB by using a ^{60}Co γ-ray source with the purpose of toughening it. The PHB-graft-PIp was obtained by directly irradiating the polymer immersed in isoprene solution.

   On the other hand, Grøndal et al.[16] have also studied polymeric grafting of acrylic acid (AAc) onto P (HB-co-HV) using gamma irradiation. The experimental results showed that the modified substrates are suitable for biomolecular attachment.

   Recently, Wada and coworkers[17,18] reported the radiation-induced graft copolymerization of AAc and VAc onto PHB, the graft copolymer thermal remolding of the first, and studies of the enzymatic degradability of the new materials.

   One solution to improve PHB hydrophilic characteristics is by grafting VAc. In this study, the radiation-induced graft copolymerization of VAc onto PHB was achieved, notwithstanding that graft copolymerization onto PHB is rather difficult to obtain due to its high crystallinity and nonactive chemical structure. In the investigation reported in this article, an attempt was made to apply the simultaneous irradiation method. The resulting graft copolymers are considered as intermediate materials. We have chosen vinyl acetate as monomer, since PVAc is a more hydrophilic polymer than PHB and it is susceptible to subsequent modification.[18]

   In this work, the graft polymerization of vinyl acetate onto PHB by immersing it as a film or powder in vinyl acetate ethanol solution or PHB powder in bulk has been carried out using a ^{60}Co γ-ray source.

MATERIALS AND METHODS

Materials

Poly(3-hydroxybutyrate) (PHB) was obtained from the Institute of Research and Technology, Biotechnology Section (Brazil). It was purified by precipitation in ethanol from chloroform solutions. The molecular weights were determined by gel permeation chromatography (GPC) at room temperature with a Knauer 64 HPLC pump, equipped with a series of five PL-gel columns and Knauer differential refractometer. Tetrahydrofuran (THF) was used as eluent at 1 mL/min flow rate, and the injection volume of the samples dissolved in THF was 20 μL. Polystyrene standards with low polydispersity were used to construct a calibration curve. The results for PHB were: $\overline{M}n = 27,000$, Mw = 60,000 g/mol; $\overline{M}z = 98,000$ g/mol; polydispersity = 2.22.

Vinyl acetate (VAc) was obtained from Merck AG (Ge) and was previously distilled.

Other chemical substances were used without purification.

Graft Copolymer Synthesis (PHB-graft-PVAc)

The irradiation experiments were carried out in an oxygen-free system at room temperature. PHB film/vinyl acetate ethanol solution (PHB (1 g)/VAc (300 g)) and PHB powder/vinyl acetate (PHB (1 g)/VAc (6 g)) were used. The samples were exposed to ^{60}Co γ-ray, with a dose rate about 1, 57 kGy/h. The grafted PHB so obtained was extracted in a Soxhlet apparatus with ethanol for 72 h and with acetone for 24 h to remove any vinyl acetate monomer and PVAc homopolymer obtained as collateral products. The copolymer PHB-graft-PVAc was dried under vacuum, at 40°C, to constant weight.

The following equation to determine the grafting degree (W (%)) in the graft copolymerization reactions is often used:

$$(W(\%)) = (m_g - m_i)/m_i \times 100$$

where m_i (g) is the initial weight of the original base backbone polymer and m_g (g) is the graft copolymer weight after grafting. This variable is an alternative to elucidate the graft degree by means of the mass increase.

In this study, two different parameters were introduced to measure the graft degree. One is the composition (C (%)), calculated by using the equation:

$$(C(\%)) = (m_c/m_t) \times 100$$

where m_C (g) is the mass of the analyzed component (for instance, the mass of PVAc grafted onto PHB) and m_t (g) is the total mass of the sample (m (PHB) + m (grafted PVAc)). From the grafting point of view, the only difference between (W (%)) and (C (%)) is the way that they are utilized to calculate the graft degree. These parameters represent a measurement of the components' mass distribution in the polymeric material.

The grafting index (γ_g (%)) parameter was also introduced in this work, which is determined by the following equation:

$$(\gamma_g \ (\%)) = (n_{Ci}/n_{Ct}) \times 100$$

where n_{Ci} is the number of grafted carbons (quaternary substitute carbons) and n_{Ct} is the total number of tertiary carbons in the PHB backbone.

Carswell-Pomerantz et al.[19] reported that the PHB tertiary carbons were the most favored grafting sites. The study was conducted to investigate the stability of the radical formed when the polymer

was exposed to gamma radiation by means of electron spin reson-ance.[19] This allows the characterization (γ_g (%)) by nuclear magnetic resonance (NMR) spectroscopy. The above expression depends only on the graft copolymer structure. It has been expressed as grafted carbons percentage.

Hereafter the term graft degree will be used to generalize all kinds of measurements when using the parameters grafting degree (W (%)), composition (C (%)), or grafting index (γ_g (%)).

CHARACTERIZATION

Thermal Analysis

Thermogravimetry (TGA) of the samples was carried out in a Mettler TA 4000, at a heating rate of 20°C/min. The samples weighed 5–15 mg and the temperature range was 50°–600°C at atmosphere.

Nuclear Magnetic Resonance (^{1}H-NMR and ^{13}C-NMR)

The NMR spectra were taken with a Bruker Ac 250 F at the frequencies of 250 MHz (^{1}H) and 62.9 MHz (^{13}C). The nature of each carbon atom was established with the aid of the distortionless enhancement by polarization transfer (DEPT) spectral issue technique. For quantitative evaluation ^{13}C-NMR spectrum was obtained by the inverse gated decoupling tech-nique with D_1 (relaxation delay) = 10 s. The polymer sample was dissolved in $CDCl_3$ and tetramethylsilane (TMS) was used as internal reference.

Crystallinity Study

The crystallinity was studied by traditional X-ray diffraction (XRD) technique and by Fourier transform-infrared (FT-IR) spectroscopy.

The XRD diagrams were obtained by wide-angle X-ray (WAXS) powder method. An Enraf Nonius X-ray generator, with a Ni filter to provide Cu Kα radiation ($\lambda = 0.1542$ nm), was used. Every scan was recorded in the range of $2\theta = 6$–$60°$ at a scan speed of $0.1°/3$ s. Crystal-linity percentages were calculated by measuring the amorphous and total area in the diffractogram. All the diffractograms were normalized[19]:

$$Xc = [(\text{total area}) - (\text{amorphous area})]/(\text{total area})$$

All samples were kept 15 days at room temperature to develop full crystallization.[20,21]

IR spectra of the samples were recorded with Jasco FT/IR- 460 Plus (Jasco Instrument Corp., Japan) equipment. Milligrams of the sample were used in solid form. The 64 scans were carried out at $2 \, cm^{-1}$ of resolution, scan rate of 2 mm/s, and a gain of 4.

Furthermore, the changes in the degree of crystallinity were observed by FT-IR spectroscopy. The inverse of the relative intensity of the band at $1185 \, cm^{-1}$ was analyzed,[21] which displays the largest difference in intensity between the crystalline and amorphous states. The crystallinity index (CI) was defined as the ratio of the intensities of the bands at $1382 \, cm^{-1}$ δ_s (CH3), which are insensitive to the degree of crystallinity, to the sensitive band at $1185 \, cm^{-1}$. This CI is not an absolute measure of the crystallinity degree, but it is useful as a comparison criterion. Another possible criterion is the crystallinity criterion (CC), discussed later.

Swelling Measurements

The water sorption capacity of the polymers was measured for polymeric films by immersing in water at 25°C for several days. Graft copolymer films of known weights were previously cleaned and dried and then immersed in deionized water at room temperature. After the excess of water was removed by filtration, the weight of the swollen samples was measured at various time intervals. The procedure was repeated until there was no further weight increase. The swelling percentage, S, was then calculated by:

$$S = [(m - m_o)/m_o] \times 100$$

where m_o and m represent the weights of the dry and wet grafted films respectively. PHB and PVAc films were also investigated for comparison.

RESULTS AND DISCUSSION

Table I shows different experimental conditions of the radiation induced graft copolymerization reaction. The A experiment was conducted under critical conditions: dose 23 kGy, PHB film/VAc ethanol solution (30% of VAc), PHB/VAc (g/g) = 1/300, and pressure: $1.33 \times 10^{-3} \, N/m^2$ (Table I). A graft copolymer ($W_{TGA} = 10\%$ and $C_{TGA} = 9\%$) was obtained. The homopolymerization of vinyl acetate was very important in this experiment. This result can be explained by a mass effect. Hence, the other experiments (B, C, D in Table I) were performed under less extreme conditions.

In all cases, the same dose rate (1, 57 kGy/h) was used.

Table I. Grafting conditions of the radiation-induced graft copolymerization reaction

	A experiment	B experiment	C experiment	D experiment
Dosis (kGy)	23	10	10	10
(PHB/PVAc) (g/g)	1/300	1/6	1/6	1/6
Pressure (Torr)	10^{-3}	10^{-3}	10^{-6}	10^{-6}
$\overline{M}_w$ (g/mol)	60000	60000	60000	27000
Samples	PHB film/VAc, ethanol solution (30% of VAc)	PHB powder/VAc	PHB powder/VAc	PHB powder/VAc

M_w = weight average molar mass.

The grafting degree (W (%)) and the composition (C (%)) were determined using gravimetric (G) and TGA experiments, in excess of PHB homopolymer that it is not separated, as in other works.[11,15] In the investigation reported in this article, the ^{13}C-NMR technique was used similarly. The grafting degree (W (%)) and the composition (C (%)) were determined by ^{13}C-NMR spectra from the carbonyl signals of PVAc and PHB respectively.

Table II lists the results of B and C experiments. No important differences in the results were found. Hence, the reduction of the pressure from 1.33×10^{-3} to $1.33 \times 10^{-6}\,\mathrm{N/m^2}$ in the mentioned experiments was unimportant.

In addition, all results are in good agreement with the grafting degree and the composition of graft copolymer obtained by different techniques. It is important to mention that the ^{13}C-NMR spectroscopy results are similar to those obtained by means of the other applied techniques.

Table II. Experimental results of grafting reaction

Exp.	W (%)				C (%)			
	G	TGA	NMR	$\overline{W}$	G	TGA	NMR	$\overline{C}$
B	44	42	34	40	30	30	26	29
C	39	36	38	38	33	34	36	34

W and $\overline{C}$ are average values of the graft degree and the composition respectively. Exp = experiment, G = gravimetry, TGA = thermogravimetric analyses, NMR = nuclear magnetic resonance, W (%) = values of the graft degree determined by means of different techniques, C (%) = values of the composition determined by means of different techniques.

It can be estimated that the quaternary substituted carbons can be better determined by using NMR spectroscopy if a smaller molecular weight PHB is used. Hence, the D experiment was carried out using a degraded PHB (Mn = 9,000 g/mol; $\overline{M}w$ = 27,000 g/mol; polydispersity Mw/Mn = 3). It was obtained by thermal degradation of original PHB and was further characterized by IR and NMR spectroscopies. It is important to stress that no anomalies in the structure were detected. However, the results obtained in the D experiment (W (G) = 28, 7%; C (G) = 22, 3%; W (TGA) = 31, 7%; C (TGA) = 24% and the grafting index was less than 5%) were not those expected (degraded PHB molecules were expected to be more susceptible to graft reaction because of their shorter length and higher mobility).

The graft percentage decreased instead of the anticipated increase in value. Thereby, the crystallinity percentage (CP) of the degraded PHB (Mn = 9,000) was analyzed by XRD. The results showed that the CP was 63%, higher than the original PHB. From the results obtained, it can be concluded that the graft percentage in the D experiment is smaller due to the increase in the crystallinity degree.

Reaction Yield

It is a well-known fact that despite being the most efficient process, in principal, radiation-induced graft copolymerization has a serious limitation arising from the high level of homopolymer formation. However, a number of conditions can be adopted to overcome this problem and improve the grafting efficiency.[22]

The two main polymerization reactions have been studied in the system: the copolymerization reaction, leading to the graft copolymer formation (PHB-graft-PVAc) [a] and the homopolymerization reaction (PVAc) [b].

Considering the possible reactions, the copolymerization reaction yield (Rc) and the homopolymerization reaction yield (Rh) were calculated by mass balance.

Table III shows the results. Rc is calculated by the PVAc mass in the graft copolymer divided by the initial mass of VAc. Rh is calculated by the PVAc mass (homopolymer that was extracted by means of the Sohxlet) divided by the initial mass of VAc. The homopolymerization yields are higher than the copolymerization yields in all cases, above 85%. This finding suggests the optimization of the copolymerization reaction by keeping the formation of radicals in the polymer backbone at higher rates than that in the monomer units. These conditions include the addition of polymerization inhibitors such as Fe (II) salts, the use of solvents, the selection of low dose rates to avoid rapid termination of graft growing chains, and the appropriate monomer concentration.

Table III.   Polymerization reaction yields

	mi_{VAc} (g)[a]	$m_{PHB-g-PVAc}$ (g)[b]	m_{PVAc} (g)[c] (copolymer)	Rc (%)	Rh (%)
B	1.395	0.3900	0.1282	9.1	90.8
C	1.395	0.4324	0.1706	12.2	87.7
D	1.395	0.3284	0.0733	5.2	94.7

[a]Initial mass of vinyl acetate used in the experiment.
[b]Mass of the graft copolymer after Soxhlet extraction.
[c]Mass of PVAc grafted to PHB in the graft copolymer.

Thermal Analyses

Figure 1 illustrates TGA thermogram of the graft copolymer in B experiments. The TG curve of PHB grafted with PVAc shows three steps in its smooth weight-loss curve. This is so because the decomposition temperatures of PHB and PVAc are not the same. Therefore, the homopolymer has two steps in its characteristic weight-loss curve. In addition, the DTGA shows three rates of weight loss (dW/dt) peaks defining the temperature of each step. The first step at 290°C belongs to PHB's characteristic temperature. The other steps, at 339°C and 440°C, correspond to PVAc decomposition. It can be seen from Figure 1 that the PHB composition in the graft copolymer can be calculated by dividing the weight loss of the first step by the total weight loss. This result indicates that the copolymer grafting degree (W_{ATG}) is 42%. Table II summarizes the results of all experiments.
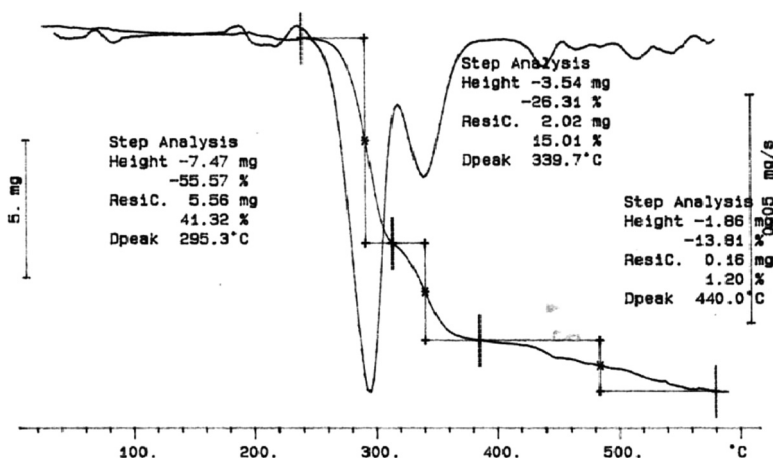
Figure 1.   TGA thermogram of the graft copolymer in B experiments.

Nuclear Magnetic Resonance (^{1}H-NMR and ^{13}C-NMR)

Figure 2 shows the ^{1}H-NMR (a) and ^{13}C-NMR (b) spectra of the PHB-graft-PVAc copolymer. Figure 3 shows the proposed structure of molecular fragment. The signals of the carbon and hydrogen atoms of PHB and PVAc that compose the graft copolymer can be clearly seen. The ^{1}H-NMR spectrum shows a doublet with center at 1.25 ppm, which is assigned to protons of methylic groups (numbered 1 in Figure 3), and a signal at 2.00 ppm, which was assigned to methylic groups (number 2
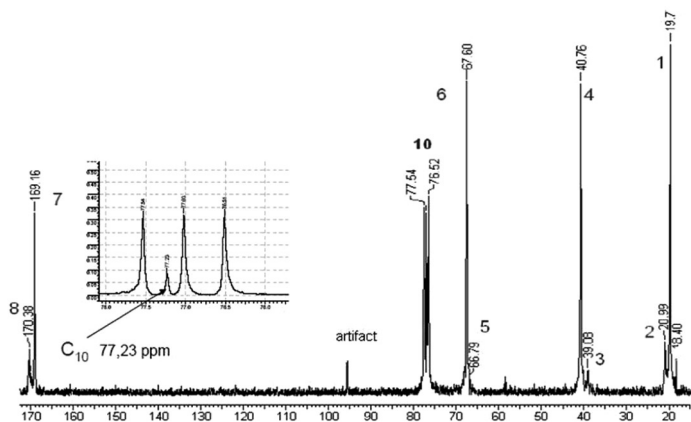
(a)
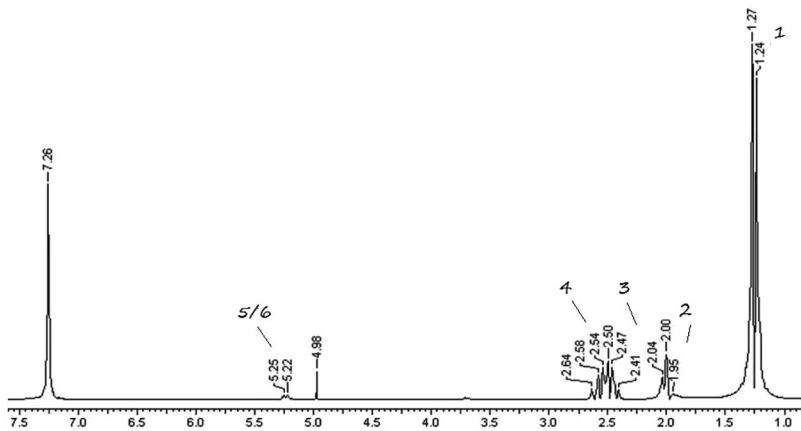
(b)

Figure 2. Spectra of PBH-graft-PVAc: a) ^{13}C-NMR spectrum. b) ^{1}H-NMR spectrum.

Figure 3. Structure and assignment of the graft copolymers PHB-graft-PVAc.

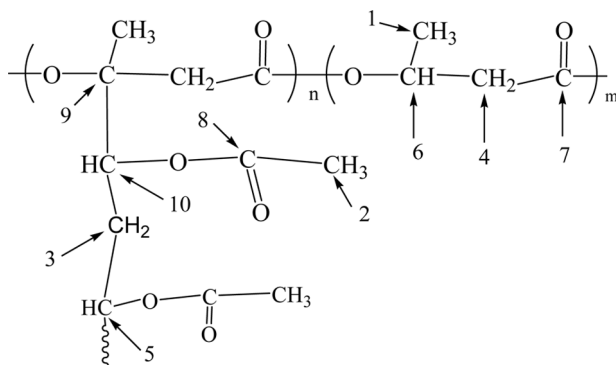in Figure 3). The multiplet with center at 2.50 ppm includes the protons of the methylenic groups (numbers 3 and 4 in Figure 3). At the spectral range of 5.20–5.40 ppm are the signals of the protons (numbers 5 and 6 in Figure 3) in accordance with the proposed structure. The assignment of the signals of the ^{13}C-NMR, Figure 2(b), was supported by the DEPT-135° technique. The signal at 19.7 ppm (CH$_3$) corresponds to methylic groups (numbers 1 and 2 in Figure 3). In addition, the signal at 40.7 ppm (CH$_2$) corresponds to methylenic groups (number 4 in Figure 3), and the signal at 67.6 ppm (CH) corresponds to methynic groups (number 6 in Figure 3).

In the enlarged spectral region of the ^{13}C-NMR spectrum, the signal at 77.2 ppm (CH) is assigned to ^{13}C atom of methynic groups (number 10 in Figure 3). The relative abundance of these groups is low in the polymer in accordance with the intensity of the signal at 77.2 ppm.

After the graft copolymerization reaction, new chemical bonds are formed. These bonds are related to the formation of a quaternary substituted carbon (C9 in Figure 2). As well as previous authors[15] who have studied radiation-induced graft copolymerization of monomers onto PHB by some structural techniques, we do not find direct evidence to confirm the formation of quaternary substituted carbon C9 by ^{13}C NMR spectroscopy.

However, after the product was subjected to Sohxlet treatments with ethanol and acetone for extensive periods of time, the solubility in chloroform indicated that there is a mixture of a graft copolymer and PHB.

The results demonstrate that graft copolymerization of VAc onto PHB was achieved.

Therefore, it was assumed it was possible to quantify C9 by measuring C10, which is quantitatively equivalent. This last signal appears inside

the chloroform signals at 77, 2 ppm in the ^{13}C-NMR spectra. The suppression of NOE spectrum was necessary to quantify C10 (Figures 2 and 3). This allowed reporting the grafting index (γ_g (%)) by determining the grafted sites with respect to the total possible sites that can be grafted.

The grafting index was found to be 25% in the B experiment. This indicates that 25% of tertiary carbons in the PHB backbone were grafted. However, it is the smallest possible value because PHB homopolymers not grafted were not separated, which then affects the result of calculations.

The graft copolymer structure indicates that the graft is formed by the coupling reaction of PHB radical (formed by γ radiation) and active center (free radical) of VAc.

Therefore, the length of the PVAc grafted chains per molecule in the radiation-induced graft copolymerization reaction of VAc onto PHB using the parameter (γ_g (%)) was estimated. The substrate used in the determination was $\overline{M}n = 27,000$ g/mol (original PHB). The structural unit mass was 86 g/mol and Xn = 314, corresponding to 314 units per PHB molecule. It has to be stressed that each monomer unit contains one tertiary carbon. The grafted sites per PHB macromolecule ((γ_g (%)), $\overline{X}n = 79$) were calculated and the total grafted sites were 79(2.39 × 10^{18} amorphous PHB molecules) = 189 × 10^{18}. Table IV lists some results obtained in this calculation.

It was necessary to consider that the reaction was carried out in amorphous phase. Subsequently, it was also necessary to consider the crystallinity percentage of the original and grafted PHB. Finally, the distribution of VAc molecule per total grafted sites was calculated (4.76 units). These results show that an average of 5 VAc molecules per grafting was achieved. It can be concluded that the length of PVAc grafted chains is very short and it was possible to graft only PVAc oligomers.

Thereby, the grafted short chain could be attributed to the fact that the oligomer chains' mobility decreases with the increase of molecular weight. This is probably due to the graft reaction, which is a diffusion-controlled process.

Table IV. Estimated calculus of the grafting length chain

Samples	$\overline{M}n$ (g mol^{-1})^a	Mass (g)	Moles	Molecules^b
Amorphous PHB	27000	0.1073	3.97 × 10^{-6}	2.39 × 10^{18}
Vac	86	0.1282	1.49 × 10^{-3}	8.97 × 10^{20}

^{a}Number average molecular weight.
^{b}Moles × Na (Na = 6.02 × 10^{23} molecule per mol).

Crystallinity Studies

It is obvious that the increase of PVAc graft degree in PHB-graft-PVAc leads to a decrease in material crystallinity. Nevertheless, it is important to note that the determination of the crystallinity degree is very useful for the evaluation of the novel graft polymer as a replacement material for commodity plastics. It is also useful to carry out a study of the enzymatic degradability, as well as other physical property changes in PHB substrate.

Figure 4 shows FT-IR spectra of PHB and the PHB-g-PVAc obtained in the B experiments. The bands at 1185, 1228, and 1279 cm^{-1} are characteristic of ν_a (C-O-C). These bands are crystalline-sensitive. The first band is better resolved than the others. The band at 1382 cm^{-1} is is characteristic of δ_s (CH$_3$). It is insensitive to the PHB crystallinity. Crystallinity index (CI) was defined as the ratio of the intensities of the bands at 1382 cm^{-1} to the sensitive band at 1185 cm^{-1}.[21] Table V shows these results. The PHB crystallinity index is higher than that of the graft copolymer.

In addition, in the ester carbonyl region (Figure 5), the bands of the C = O stretching (1722 and 1740 cm^{-1}) appear. On one hand, the band at 1722 cm^{-1} is characteristic of the crystalline state and on the other hand, the band at 1740 cm^{-1} is characteristic of the amorphous state.[21]
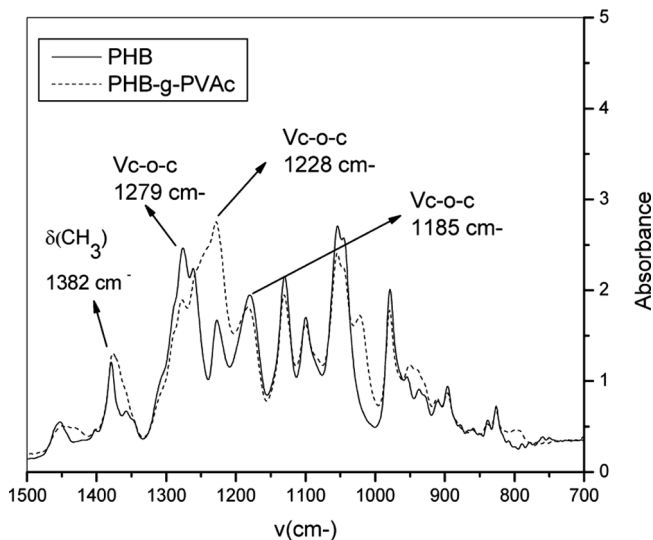

Figure 4. FT-IR spectrum of the PHB-graft-PVAc obtained in B experiment in $\bar{\nu}$ region, corresponding to $\bar{\nu}$ (C−O−C).

Table V. Crystallinity study of the PHB and the PHB-graft-PVAc samples

Samples	CP (%)[a]	CI (%)[b]	CC (%)[c]
PHB	59	62	2.52
PHB-g-PVAc	43	59	2.12

[a]Crystallinity percentage.
[b]Crystallinity index.
[c]Crystallinity criterion.

The amorphous band is broader than the corresponding one for the crystalline state, thus reflecting an increase in conformational freedom. Consequently, the crystallinity criterion (CC)[21] was defined as the ratio between the absorbance value at $1722\,cm^{-1}$ and that at $1740\,cm^{-1}$. This definition corresponds also to a relative measurement of the crystallinity degree. Table V shows the results, which are in agreement with CI, but in this case, CC is more sensitive than CI. This is because the PVAc FT-IR spectrum has ν_a (C-O-C) bands more intensive than the (C=O) band. The CC better illustrates the decrease of the crystallinity percentages in the graft copolymer.

XRD is the most important technique in the crystallinity studies, because it can provide an absolute criterion calculated from the areas under the diffractograms. The diffractograms used to determine
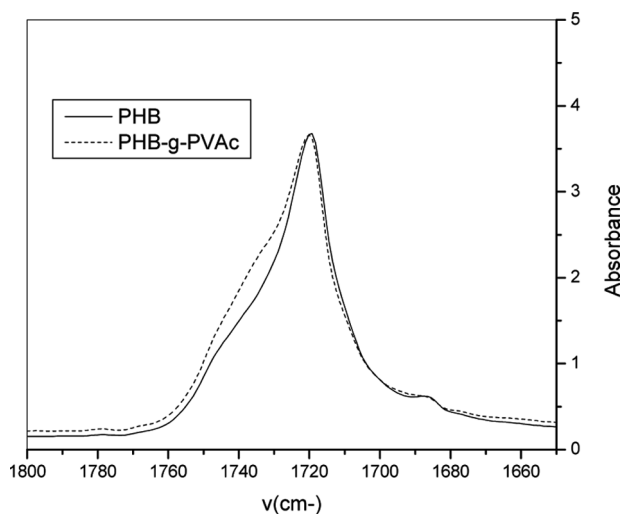

Figure 5. FT-IR spectrum of the PHB-graft-PVAc obtained in B experiment in $\bar{\nu}$ region, corresponding to $\bar{\nu}$ (C=O).
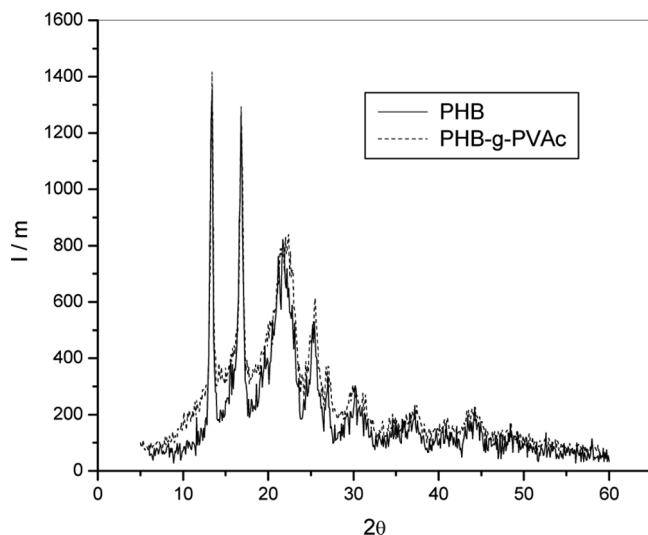
Figure 6. X-ray diffractograms of the PHB and PHB-graft-PVAc in B experiment.

the crystallinity percentages (CP) of the PHB and the PHB-graft-PVAc obtained in the B experiments are shown in Figure 6. From this illustration, it can be concluded that both are semicrystalline materials. All the diffractograms were normalized.[21]

Unit cell parameters of PHB were already calculated by Škrbić and Divjaković[22] on the basis of the positions (2θ) of well-separated diffraction maxima, using the quadratic form for the rhombic cell. Figure 6 shows that there was no significant change of the crystal lattice of PHB and PHB-graft-PVAc.

Table V lists the results of the crystallinity study. The fact that the extent of the crystallinity percentage decrease was not very significant can clearly be seen. On the other hand, there is a clear decrease in the CP from 59 to 43%.

The conclusion is that all the methods used in the crystallinity study agree in the fact that the introduction of PVAc graft chains onto the PHB polymeric substrate leads to a less crystalline material, which is due to the PVAc increase in the amorphous phase of the graft copolymer.

Swelling Behavior

Table VI shows the swelling percentage (S) for PVAc, PHB, and PHB-graft-PVAc in the B experiments. The highest of these values are obtained

Table VI. Swelling experimental results

Samples	S (%)[a]	V_o (water mg/h)[b]
PVAc	8.28	0.36
PHB	3.3	1.22
PHB-g-PVAc	4.3	2.17

[a]Swelling percentage.
[b]Initial rates of the swelling process.

after 24 h for PHB and the copolymer samples and after 40 h for the PVAc sample. In each case, after these times the swelling percentage does not change.

It can be seen that the swelling of PHB-graft-PVAc is very poor, but there is a clear water uptake increase tendency. It is important to note that PVAc does not significantly absorb water. These results are in agreement with the swelling studies of radiation-induced graft copoly-merization of PVAc chains onto low density polyethylene films (LDPE-graft-PVAc) by mutual irradiation technique[23] and with PVAc grafting onto poly(vinyl chloride) (PVC).[24]

Table VI shows the initial rates of the swelling process (water mass that the polymer absorbs at the beginning of the swelling process per hour). These values were calculated by linear regression of the data of water mass that was absorbed by the materials versus time at the begin-ning of the swelling. Thus the slopes of these lines correspond to the initial rates of the swelling process. Also it is in agreement with the fact that graft copolymer increases the PHB hydrophilic characteristic.

These results suggest that the hydrolysis of the PVAc graft chains in the graft copolymer is necessary in order to observe a significant increase of the hydrophilic properties by means of swelling experiments. Basically, an intermediate graft copolymer was already synthesized.

CONCLUSIONS

The grafting of VAc onto PHB has been studied by radiation-induced graft polymerization. The results obtained can be summarized as follows:

1. In spite of the PHB inactive structure, VAc can be grafted onto PHB by directly irradiating PHB, immersed in vinyl acetate or vinyl acetate ethanol solution, using a ^{60}Co γ-ray source.
2. Under all experimental conditions, graft copolymers were obtained as reaction product but better results were obtained in the B and C experiments.

3. The synthesized material was characterized by means of several techniques. NMR spectroscopy has elucidated the copolymer structure. This investigation revealed that oligomers of PVAc are grafted onto PHB. Thermal studies helped to corroborate the graft degree and composition compared with the other used techniques. Moreover, FT-IR and XRD confirmed the decrease of the graft copolymer crystallinity degree.

4. Swelling behavior of PVAc, PHB, and PHB-graft-PVAc was also studied. The results revealed a water uptake increase tendency from the graft copolymer with respect to PHB. However, further hydrolysis is necessary to observe significant swelling.

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