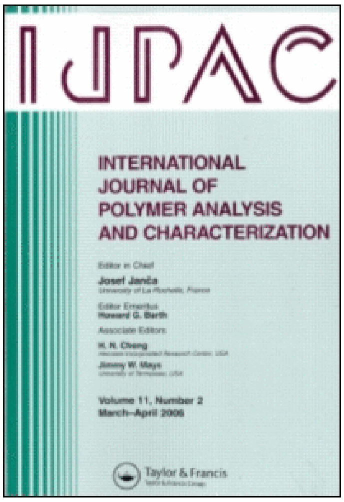

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Effect of Solvents on Gamma Radiation–Induced Graft Copolymerization of Vinyl Acetate onto Poly(3-hydroxybutyrate)

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Abstract: The effect of different solvents on the radiation-induced graft copolymerization of vinyl acetate onto poly(3-hydroxybutyrate) was studied. Structures of copolymers were determined with the techniques of thermogravimetric analysis and differential scanning calorimetry. From the thermal analysis results, it was found that the more favorable solvent to be used in the graft reaction is hexane. However, a much higher grafting degree can be achieved in bulk.

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The thermodynamic parameter obtained varied, showing that the enthalpy of melting and crystallization temperature of graft copolymers decreased with increasing grafting degree, which implies changes in the crystallization behavior and decrease in the material cristallinity. Further hydrolysis of the higher grafting degree graft copolymer was also studied.

Keywords: Copolymers; Gamma radiation; Graft copolymer; Graft polymer; Irradiation procedures; Poly (3-hydroxybutyrate); Radiation doses; Radiation-induced; Solvents; Thermogravimetric analysis; Vinyl acetate; Vinyl alcohol.

INTRODUCTION

Radiation-induced graft copolymerization is commonly used in the preparation of well-established graft copolymers nowadays. Several authors have utilized this technique to prepare polymeric materials based on biodegradable backbone polymers and different kinds of monomers.[1] The simultaneous irradiation technique is widely used because of its advantages. Among these biodegradable substrates are the polyhydroxyalkanoates (PHAs), which comprise a large family of bacterial storage polyesters.[2] The properties of these materials are useful in the field of medicine. Poly(3-hydroxybutyrate) (PHB) is the first member of this polymeric family. It is very well known because of its biocompatibility and biodegradability. This is the reason why many authors have used this material to prepare novel graft copolymers by radiation-induced graft copolymerization reactions. Materials such as P(HB-graft-methyl methacrylate),[3] P(HB-graft-isoprene),[4] P(HB-graft-2-hydroxy ethyl methacrylate),[3] P(HB-graft- styrene),[5] P(HB-graft-acrylic acid),[6,7] and P(HB-graft-acrylamide)[8] were reported. In previous works, the synthesis and characterization of the (HB-graft-vinyl acetate) were studied.[9–11] The effect of solvents on the radiation graft copolymerization reactions have also been subjected to a study.[12] This is of particular interest because the solvents are one of the obvious factors affecting not only the grafting degree but also the location of grafting. The diluents are basically used in radiation-induced graft copolymerization processes to bring about swelling of the base polymer and hence to enhance the monomer accessibility to grafting sites. Hence, the correct choice of the solvent in graft reaction is essential because it enhances the diffusion of the monomer into the polymer and increases the interactions with internal actives sites.[13,14]

It is well known that PHB graft sites are the tertiary carbons. Sevilla et al.[15] first reported that the tertiary carbon radical is the most favored and stable from the results obtained in model compounds. Carswell-Pomerantz et al.[16] also studied the electron spin resonance of the radiation chemistry of PHB, and this provided a basis to understand the PHB graft reaction with monomers. In this article, the results obtained from the study of the use of different solvents in the radiation-induced graft copolymerization of vinyl acetate onto poly(3-hydroxybutyrate) are presented. The investigation describes the thermal analyses of the products by means of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) techniques. Further hydrolysis and physical chemical characterization of the hydrolyzed grafting copolymer were also investigated.

MATERIALS AND METHODS

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 Pump 64 HPLC (Knauer), equipped with a series of five PLgel 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: $\overline{Mn} = 27000\,\mathrm{g/mol}$, $\overline{Mw} = 60000\,\mathrm{g/mol}$, $\overline{Mz} = 98000\,\mathrm{g/mol}$, and polydispersity = 2.22.

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

Graft Copolymer Synthesis P(HB-graft-VAc)

The irradiation experiments were carried out in glass sealed vacuum ampoules at room temperature. PHB (200 mg) was immersed in vinyl acetate (0.5 mL) and 1 mL of the solvent $m(\mathrm{PHB})/m(\mathrm{VAc}) = 2.32$. The mixture was subjected to ^{60}Co γ-rays at a dose rate of 1.62 kGy/h and a dose of 10 kGy. Different solvents such as ethyl acetate, *n*-butanol, diethyl ether, hexane, and acetone were used. For comparison, bulk reaction was also conducted. The grafted PHB so obtained was extracted in a Soxhlet apparatus with acetone for 72 h to remove any vinyl-acetate monomer and PVAc homopolymer obtained as collateral products. The copolymer P(HB-graft-VAc) was dried under vacuum, at 40°C to constant weight.

The following equatiosn 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 percentage by means of the mass increase.

Characterization

Thermal Analysis

The study of different solvents' effect on the grafting degree by thermogravimetric analysis (TGA) was conducted in a Q500 TA Instruments, at a heating rate of 10°C/min in nitrogen. The samples' weight was 5–15 mg and the temperature range was 50°–600°C in air.

Thermal properties were also investigated using differential scanning calorimetry (DSC), on a TA Instrument 2920 under nitrogen atmosphere. In the DSC experiments, first, at the heating rate of 10°C/min, the sample was heated from −30° to 180°C (first heating scan), and kept for few minutes at 180°C. After eliminating the thermal history, the sample was cooled to −30°C (−10°/min), and finally the sample was heated from −30° to 180°C at the heating rate of 10°C/min (second heating scan). The enthalpy and the transition temperatures were determined from exothermic and endothermic peaks in the second run.

Nuclear Magnetic Resonance (^{13}C NMR)

The NMR spectra were determined in a JEOL 300+ at the frequency of 62.9 MHz (^{13}C). The polymer sample was dissolved in $CDCl_3$ and tetramethylsilane (TMS) was used as internal reference.

Hydrolysis of P(HB-graft-VAc)

For the graft copolymer P(HB-graft-VAc) powder (F experiment), the saponification reaction carried out in a methanol solution (0, 05 M of NaOH) at 25°C for 8 h.

RESULTS AND DISCUSSION

The graft polymerization media play an important role in the radiation-induced graft reaction. One of the obvious factors affecting grafting is the solvent. It is thought that the correct choice of solvents is one of the essential elements determining the success of radiation-induced grafting reactions. However, this also depends on the base polymer and its relationship with the monomer and the solvents used.[13]

In order to enhance grafting degree (*W* (%)), solvents of low chain transfer constant and different polarities were selected for the radiation-induced graft polymerization (ethyl acetate, n-butanol, diethyl ether, hexane, and acetone). For comparison, bulk reaction was also carried out.

The radiation-induced graft polymerization of vinyl acetate onto PHB is very complex to be studied because of the variety of variables that affects graft reaction. Figure 1 shows the general scheme of the graft and the further saponification reactions. The mechanism of grafting is suggested from experimental results. We have found in previous studies a strong evidence that supports the location of the graft reaction on the tertiary carbons of PHB backbone as consequence of the more stable radicals formed by gamma exposure to radiation.[16] Consequently, it is possible to synthesize a family of novel materials based on PHB polymer. The polymeric materials should have the same properties of biocompatibility and biodegradability but be more hydrophilic and thus have great prospects in the field of medicine. It is important to state that although the product was subjected to Soxhlet treatments with ethanol and acetone for extensive periods of time, the solubility in chloroform indicated that in all cases there is a mixture of a graft copolymer and PHB.[10]

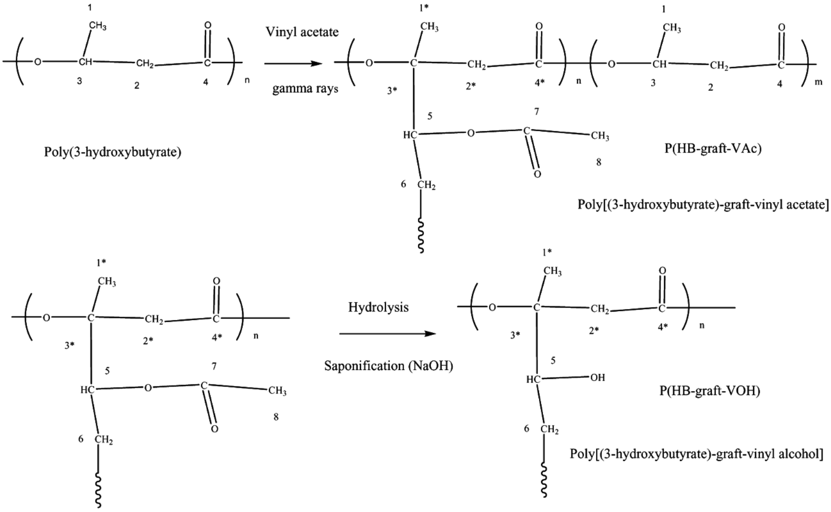

Figure 1. Radiation-induced graft copolymerization of vinyl acetate onto poly (3-hydroxybutyrate) and further saponification reactions.

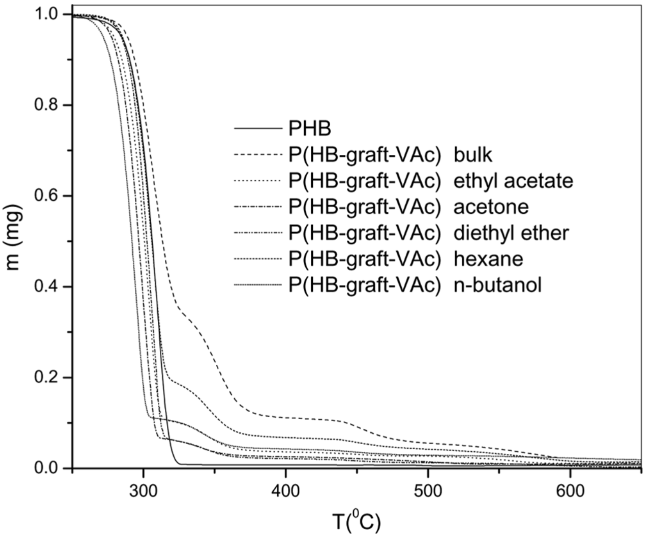

Figure 2. TGA of the P(HB-graft-VAc) in different solvents.

Thermal Analyses

Figure 2 illustrates TGA thermogram of the graft copolymers obtained under the same experimental conditions (PHB (200 mg) immersed in vinyl acetate (0.5 mL) and 1 mL of the solvent) (A, B, C, D, and E). For comparison, the thermogram of the graft copolymer obtained in bulk reaction is also shown (F experiment). In all cases the thermal behavior was similar. The TG curve of PHB grafted with PVAc shows three steps in its smooth weight-loss curve. This is because of the difference between PHB and grafted PVAc decomposition temperatures. Therefore, the grafted PVAc has two steps in its characteristic weight-loss curve. In addition, DTGA shows three rates of weight loss (dW/dt) peaks defining the temperature of each step. The first step was at about 290°C and belongs to PHB characteristic temperature. The second and third steps at about 339°C and 440°C correspond to the grafted PVAc decomposition (not shown in Figure 2). From Figure 2 it can be seen 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. From the thermal analysis results it was found that the more favorable condition to be used in the graft reaction is the bulk reaction (W (%) = 69.7%). Grafting degrees obtained for all experiments are listed in Table I. The results obtained when using solvents are the following: (1) the more favorable solvent to be used in the graft reaction is the hexane (W (%) = 26.2%), and (2) grafting degree is similar when using ethyl acetate

Table I. Thermodynamic parameters obtained from the DSC thermograms of P(HB-graft-VAc) graft copolymers in different solvents

No.	Polymer	W_{TGA} (%)	ΔH_c (J/g)	T_c (°C)	ΔH_m (J/g)	T_m (°C)	$\Delta H_{m\,\text{corr}}$ (J/g)
	PHB	0	92.4	97.43	103.8	170.23	103.8
A	P(HB-graft-VAc) acetone	6.54	79.0	85.65	96.9	174.32 166.28	103.27
B	P(HB-graft-VAc) diethyl ether	7.7	74.9	83.01	96.5	173.84 164.79	103.25
C	P(HB-graft-VAc) *n*-butanol	13.12	70.4	82.30	91.2	173.11 163.67	103.13
D	P(HB-graft-VAc) ethyl acetate	13.21	61.7	80.62	80.4	173.42 163.5	91.066
E	P(HB-graft-VAc) hexane	26.27	51.3	71.38	82.2	170.54	103.78
F	P(HB-graft-VAc) bulk	69.75	51.8	73.34	66.5	168.47	112.86
G	P(HB-graft-VOH)	42.85	16 12	66.02 58.43	31.9	162.91	45.52

(W (%) $= 13.2\%$) and n-butanol (W (%) $= 13.1\%$) and was fairly low in diethyl ether (W (%) $= 7.7\%$) and acetone (W (%) $= 6.5\%$).

Considering the results obtained in the study of the radiation-induced graft copolymerization reaction, bulk reaction was selected for further studies to verify the graft reaction. In addition, based on previous work,[10] ^{13}C-NMR was used to observe the evidence of grafting. According to the ^{13}C-NMR spectra of (P(HB-graft-VAc)) (Figure 3) we can find the signal at 77, 23 ppm as strong grafting evidence. It is important to state that all graft copolymers obtained in this study showed this signal that strongly demonstrates the formation of the polymer material. However, further hydrolysis of the copolymer obtained in bulk and the physicochemical characterization of the hydrolyzed polymer were also performed.

Differential Scanning Calorimetry Investigation

Typical DSC heating curves of PHB and the graft copolymers obtained in different solvents are shown in Figure 4. It was observed that the T_m values slightly changed. On the other hand, they remained almost unchanged as well as the peak area with the introduction of VAc. However, graft copolymer showed in some cases a doublet melting peak composed of the main peak and another small one at lower temperature.

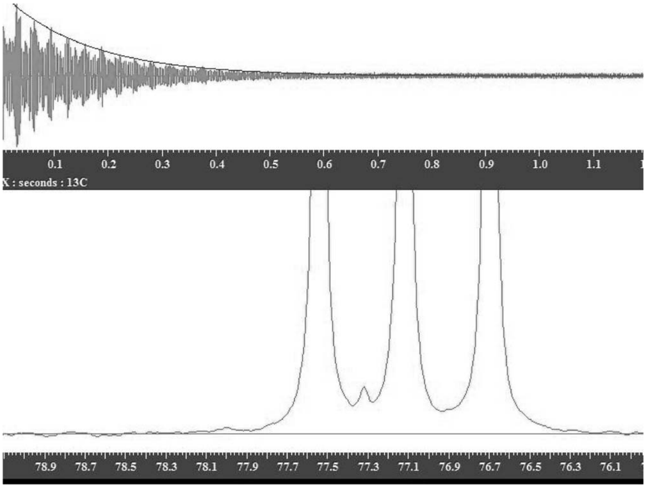

Figure 3. ^{13}C NMR spectra of the grafting copolymer P(HB-graft-VAc) (F experiment).

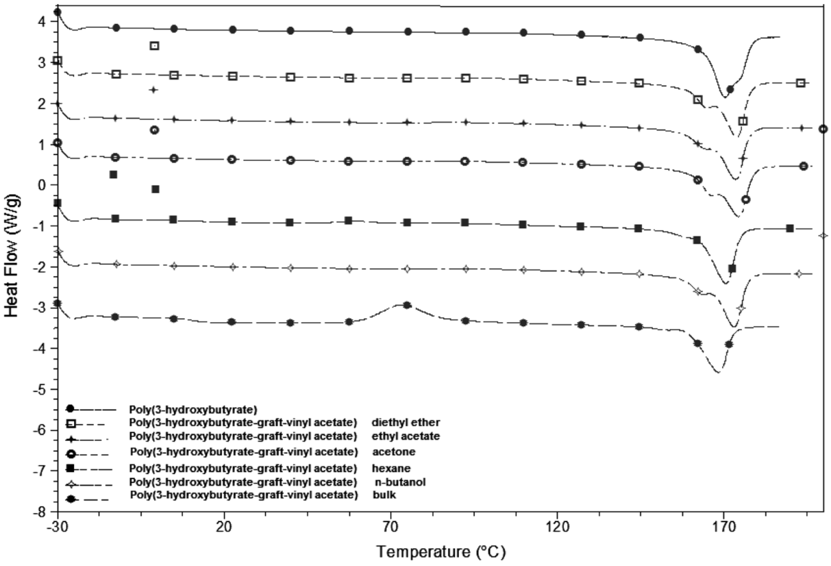

Figure 4. DSC curves of the second run of poly(3-hydroxybutyrate) and poly(3-hydroxybutyrate-graft-vinyl acetate) obtained by radiation-induced graft copolymerization in different solvents and bulk.

This phenomenon is called recrystallization and implies that graft occurs not only in amorphous regions but also proceeded heterogeneously in crystalline regions.[17]

The lower temperature peak should be attributed to the melting of the crystals formed during the cooling process, and the higher one should be attributed to crystals recrystallized during the heating process.[18]

The crystallization temperature (T_c) decreases with the increase of vinyl acetate grafting, which implies change in the crystallization behavior of PHB after irradiation and grafting with VAc.

Since the T_g of PVAc is 25°C and for PHB it is -1°C, it is natural that the T_g of the graft polymers increases with the introduction of PVAc. For instance, in the F experiment the T_g increased its value from -1°C (PHB) to 10°C (P(HB-graft-VAc)). In most of the cases the T_g was not clearly observed. This is probably due to the use of DSC, which is not the appropriate technique for this determination.

Table I lists the thermodynamic parameters obtained from the DSC thermograms of the samples of the experiments (A, B, C, D, E, F, and G). It summarizes the melting point (T_m), the crystallization temperature (T_c), and the enthalpies of crystallization (ΔH_c), the enthalpies of melting (ΔH_m), and the enthalpies of melting corrected by the weight fraction of the polymer that confirms the graft copolymer, calculated according to the following equation:

$$(\Delta H_m)_{\text{corr}} = (\Delta H_m)(1 + W\ (\%))$$

The ΔH_m of graft copolymers decreased its value with increasing grafting degree. However, this decrease is probably due to the relative decrease of PHB content in the grafted polymer. Therefore, the ΔH_m was corrected. From the results, it was observed that in some cases (diethyl ether, acetone, *n*-butanol, and hexane) the $(\Delta H_m)_{\text{corr}}$ remained almost unchanged and in other cases (ethyl acetate and bulk) it showed significant changes. It can be deduced that in the first cases, the grafting is barely introduced to crystalline regions, while in the second case the grafting proceeded uniformly also in crystalline regions after affecting the amorphous regions.

On the other hand, Table I shows that the crystallization enthalpy (ΔH_c) decreases with increase in grafting degree. This also implies that after grafting VAc onto PHB, the crystallinity of the base PHB polymer declines.

The higher grafting degree was obtained in the absence of solvent. Figure 5 shows the thermogram of the graft copolymer obtained in the F experiment (bulk). In the DSC thermogram of the first scan no anomalies were observed. However, in the DSC thermogram of the second scan, a strange behavior appeared because no cold crystallization peaks were

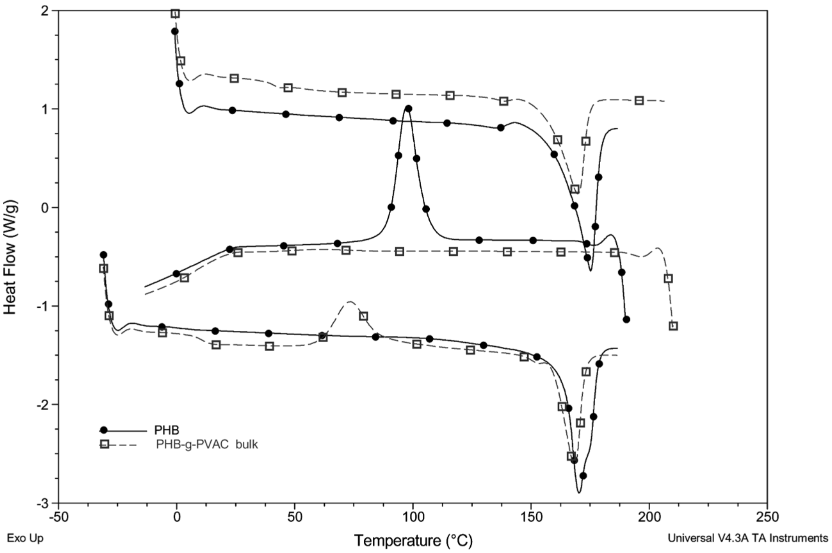

Figure 5. DSC curves of PHB and P(HB-graft-VAc) (F experiment).

observed for P(HB-graft-VAc). The exact reason for this phenomenon is not clear at this stage. It may be due to structural changes in the crystallization process provoked by the graft reaction. The more interesting result was in the DSC thermogram of the third scan when, surprisingly, both endothermic and exothermic crystallization peaks were observed. It is of interest to mention here that this phenomenon was observed only in the E experiment. It is known that the crystallization ability of PHB becomes weak due to the introduction of vinyl acetate, which can hinder the crystallization of PHB. Consequently, the increase in grafting degree (69.7%) leads to an increase of the amount of imperfect crystals, resulting in dramatic changes in the crystallization behavior.

FT-IR

Fourier transform-infrared (FT-IR) studies were performed in order to confirm the syntheses of a graft copolymer (P(HB-graft-VOH)). The evidence of grafting was obtained by using this technique. Figure 6 shows the transmittance mode FT-IR spectra of pure PHB and P(HB-graft-VOH). From the IR spectra, it was obvious that PHB showed bands at 1185, 1228, and 1279 cm^{-1} characteristic of ν_a(C–O–C) and a band at 1382 cm^{-1} characteristic of $\delta_s(CH_3)$. In the ester carbonyl region the band of C=O stretching (1729 cm^{-1}) can be considered. All these

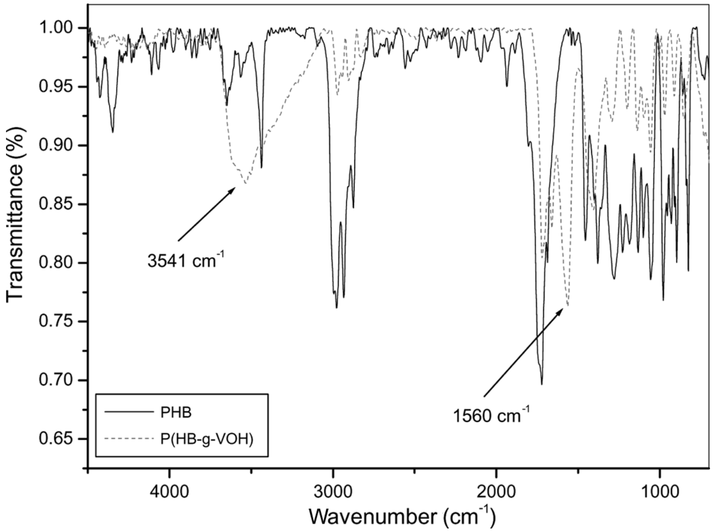

Figure 6. FT-IR spectra of the PHB and the P(HB-graft-VOH) obtained by saponification of the grafting copolymers P(HB-graft-VAc).

mentioned signals are common for both materials. However, in the graft copolymer, two additional peaks were present. The peak at $3541\,\mathrm{cm}^{-}$ (broad peak) corresponds to *ν*(OH) bonds. The difference between the PHB *ν*(OH) present in the terminals of PHB backbone and the broader graft copolymer *ν*(OH) related with the hydrolyzed polymer can be seen. The peak position at $1560\,\mathrm{cm}^{-1}$ is probably caused by the alcohol group and could represent the absorption by *δ*(OH). The absorption frequency of alcohol bond vibration is well separated from that of the carbonyl group. The new peaks observed are strong evidence of grafting and clearly indicate the formation of the novel graft copolymer.

Differential Scanning Calorimeter (DSC) Investigation (P(HB-graft-VOH))

Thermal analyses of the graft copolymer P(HB-graft-VAc) obtained in different solvents and the graft copolymer P(HB-graft-VAc) in bulk before and after saponification P(HB-graft-VOH) were carried out.

Thermal properties of P(HB-graft-VAc) and the saponified polymer were investigated by DSC. Table I shows the thermodynamic parameters obtained from the DSC thermogram, and Figure 7 shows the thermogram of the graft copolymer (P(HB-graft-VOH)). The first difference between both materials was observed in the DSC thermogram of the first

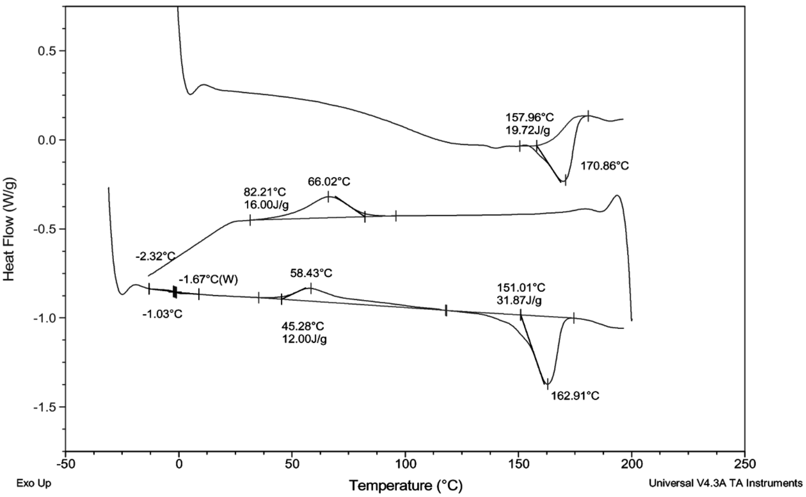

Figure 7. DSC curves of P(HB-graft-VOH) obtained by saponification of the grafting copolymers P(HB-graft-VAc) (F experiment).

scan. The saponified copolymer showed lower T_m (162°C) with respect to P(HB-graft-VAc) (168.47°C). This decrease reflects the introduction of vinyl alcohol groups not only in amorphous regions but also in crystalline regions of the PHB. In addition, in the DSC of the second scan it was observed that the crystallization temperature changed its value from 73.34°C P(HB-graft-VAc) to 66.2°C (P(HB-graft-VOH)) and the enthalpy of crystallization (ΔH_c) changed its value from 51.77 J/g (P(HB-graft-VAc)) to 16 J/g (P(HB-graft-VOH)). Moreover, in the DSC thermogram of the third scan anomalies were observed by means of another endothermic peak (crystallization temperature 58.43°C), which implies changes in the crystallization behavior. On the other hand, the enthalpy of melting (ΔH_m) of the P(HB-graft-VAc) was (66.49 J/g) and the saponified graft copolymer (31.87 J/g) differed in about 34 units (J/g). The decrease of the ΔH_m implies a decrease in the degree of crystallinity. Additionally, we observed an additional peak at 151°C (103.8 J/g), which is probably a consequence of the saponification of the grafted vinyl acetate groups. It was concluded that the decrease in T_m, ΔH_c, ΔH_m, and T_c as well as the formation of this last additional peak strongly supports the appearance of the P(HB-graft-VOH) graft copolymer.

Analysis of Grafting Degree in P(HB-graft-VOH)

The grafting degree for P(HB-graft-VOH) decreased with respect to P(HB-graft-VAc). This can be due to the calculation based on the mass balance. The saponification reaction implies a decrease in molecular weight. This result suggests that the grafting degree (W (%)) is mass dependent. The grafting degree should be invariable because the hydrolysis works only in the vinyl acetate grafted chains and it does not create new graft sites.

CONCLUSIONS

The graft copolymerization of vinyl acetate onto PHB in different solvents, further hydrolysis, and the physicochemical characterization of the obtained materials were investigated using the gamma ray of ^{60}Co by the simultaneous irradiation method. The effects of the solvents in the syntheses have been discussed in the light of grafting degree. The thermal behavior was studied with DSC and TGA. The results showed that the more favorable solvent to be used in the graft reaction is hexane (W (%) =26.27%). Grafting degree is similar when using ethyl acetate and *n*-butanol (13.21% and 13.12%), and it was fairly low in diethyl ether and acetone (W (%) = 7.7% and 6.54%). However, a much higher grafting degree can be achieved in bulk (W (%) = 69.75%).

The radiation-induced graft copolymerization is a diffusion-controlled process. We have found that PHB scarcely swells in solvents (except in chloroform, but this is not a desirable solvent due to the termination with chloride radicals Cl· by recombination reaction with polymer radicals). Therefore, surface grafting is most likely to take place due to the slowdown in monomer diffusion. The concentration of the absorbed monomer and the viscosity are low. We used PHB polymer powder in order to permit accessibility to internal grafting sites. We have found that vinyl acetate monomer swelling in PHB is about 10%, and the swelling of PHB in the used solvents is very poor. This fact probably explains the results obtained (bulk grafting is highly favored). The decrease in grafting degree when using solvents can be attributed to the suppression of monomer diffusion by the increase in the viscosity due to the homopolymerization. On the other hand, the use of vinyl acetate increases the polymer swelling and enhances the diffusion of the monomer to the internal layers of the substrate and also increases the interaction between the internal active sites and the monomer radicals formed by gamma irradiation. From the thermal analysis it was found that the melting temperature and the peak area remained almost unchanged with the introduction of VAc. Graft copolymer showed, in some cases, a doublet melting peak due to recrystallization processes, which implies that graft not only occurs in amorphous regions but also progresses heterogeneously in crystalline regions. The crystallization temperature and the melting enthalpy (T_c, ΔH_m) decrease with the increase of vinyl acetate grafting, which implies change in the crystallization behavior of PHB after irradiation and grafting with VAc. On the other hand, the crystallization enthalpy ΔH_c decreases with increase in grafting degree. This also implies that after grafting VAc onto PHB, the crystallinity of the base PHB polymer declines. Some interesting phenomena were observed in the thermal analyses of the bulk reaction. It was concluded that the introduction of vinyl acetate can strongly hinder the crystallization of PHB. Because of the saponification, the P(HB-graft-VAc) acetate groups were converted into vinyl alcohol group to obtain P(HB-g-VOH). The FT-IR and DSC results of the saponified graft copolymer showed strong evidence of the graft copolymers syntheses. The possibility of using these grafted polymers in practical applications is very promising.

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