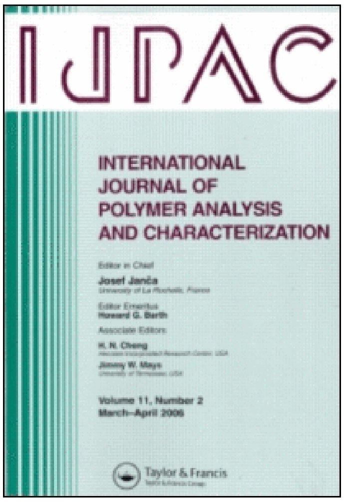

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Radiation-Induced Graft Copolymerization of Metacrylic Acid and Butyl Methacrylate onto Poly(3-hydroxybutyrate)

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Abstract: Poly(3-hydroxybutyrate) (PHB) is a biocompatible and biodegradable thermoplastic polyester obtained microbiologically. Its main drawbacks are its thermal instability, brittleness, and moderate hydrophobicity, which limit its applications. The present study involves the chemical modification of PHB by means of the synthesis and characterization of graft copolymers with two selected monomers. Typical monomers, methacrylic acid (MA) and butyl methacrylate (BuM), were graft polymerized onto PHB by radiation-induced graft copolymerization reaction to improve PHB's hydrophilicity. The effect

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of different solvents on the radiation-induced graft copolymerization of the monomers onto poly(3-hydroxybutyrate) was investigated. Structures of the graft copolymers obtained were determined by Fourier transform-infrared spectroscopy, thermogravimetric analysis, and differential scanning calorimetry. Examination of the infrared spectra of the polymeric materials showed that there are no significant changes in their spectra apart from slight changes in the intensities of absorption bands. The results are consistent with the successful grafting of MA and BuM monomer onto PHB. Double melting peaks for grafted PHB were observed, which was probably caused by recrystallization of the graft copolymer. For grafted PHB, the introduction of MA and BuM groups hinders its crystallization, causing a decrease in the degree of crystallinity. The swelling behavior was also studied. The results showed that water uptake significantly increased. Hence, such a grafting process improved the hydrophilic character of PHB. The possibility of using these grafted polymers in practical biomedical applications is promising.

Keywords: Butyl methacrylate; Copolymers; Gamma radiation; Graft copolymer; Graft polymer; Methacrylic acid; Poly(3-hydroxybutyrate); Radiation induced

INTRODUCTION

Poly(3-hydroxybutyrate) (PHB) is a homopolymer of 3-hydroxybutyric acid. It is a well known as a biocompatible and biodegradable thermoplastic polyester with physical properties similar to those of polypropylene.[1,2] Despite the high potential of this material, its brittleness, thermal instability, and moderate hydrophobicity have limited its application.[3] Chemical modification of PHB should lead to overcoming this limitation with the synthesis of an interesting and novel type of polymeric material to be used in the field of medicine.[4] There is a growing interest in the use of graft polymerization synthesis as an alternative for the manufacturing of advanced polymeric materials. Of the possible chemical modifications, radiation-induced graft polymerization of polar monomers onto PHB has now gained much more acceptance because of its advantages such as the high purity of materials that can be obtained.[5] Mitomo et al. have conducted extensive studies on the radiation-induced graft polymerization of methyl methacrylate (MMA),[6] 2-hydroxyethyl methacrylate (HEMA),[7] and styrene onto PHB and its copolymers P(HB-co-HV). Some syntheses of PHB-graft-isoprene,[8] PHB-graft-acrylic acid by the use of radiation-induced graft polymerization reaction using ^{60}Co gamma source were described in the literature.[9] Recent findings have shown that the surface grafting of acrylic acid onto PHB is suitable for biomolecular attachment.[10] The enzymatic degradability of PHB modified by radiation-induced graft polymerization of VAc and AAc has also been reviewed recently.[11] We have investigated the radiation-induced graft copolymerization of vinyl acetate, vinyl alcohol, and acrylamide onto poly(3-hydroxybutyrate).[12–14]

Gamma radiation graft copolymerization of MA and MBu monomers presents great potential for the synthesis of polymeric materials with desirable properties. Methacrylic acid has been graft polymerized onto polypropylene (PP)[15,16] by irradiation techniques. Some other investigations on the grafting of MA onto polyethylene were attempted by Guthrie.[17] MBu was also found to be attractive in radiation-induced grafting. Gamma radiation has also been used to graft butyl methacrylate onto cellulose.[18] However, to our knowledge the graft copolymerization of MA or BuM onto PHB has not yet been reported.

The most recent research in radiation-induced graft copolymerization involves two main methods: (1) simultaneous (direct or mutual) irradiation and (2) pre-irradiation (post-irradiation). Simultaneous irradiation is the simplest irradiation technique for the preparation of graft copolymers. In this method, a polymer backbone is irradiated in the presence of a monomer.[5]

The studies reported here are concerned with the synthesis and physicochemical characterization of the products obtained by simultaneous irradiation-induced graft copolymerization of metacrylic acid and butyl methacrylate onto poly(3-hydroxybutyrate).

The present investigation also describes the effect of some solvents in the graft reaction and the analyses of the reaction products by TGA, DSC, and FT-IR. We have chosen these monomers to improve PHB properties such as the thermal stability and hydrophilic characteristics since poly(metacrylic acid) and poly(butyl methacrylate) are more hydrophilic than PHB.

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

Methacrylic acid and butyl mathacrylate monomers were from Merck AG (Germany) and were distilled prior to use.

Graft Copolymer Synthesis

The irradiation experiments were carried out in glass sealed vacuum ampoules at 25°C. PHB (200 mg) was immersed in methacrylic acid or butyl methacrylate (0.5 mL) and 1 mL of the solvent: $m(\mathrm{PHB})/m(\mathrm{monomer}) = 2, 32$. The mixture was subjected to $^{60}\mathrm{Co}$ γ-rays at a dose rate of 1.62 kGy/h and a dose of 10 kGy. Different solvents such as ethanol, chloroform, and acetone were used. For comparison, a bulk reaction was also carried out. The grafted PHB so obtained was extracted in a Soxhlet apparatus with acetone for 72 h to remove any monomer and homopolymer obtained as collateral products. The polymeric material obtained in each case was dried under vacuum, at 40°C, to constant weight.

The following equation to determine the grafting degree (W (%)) in the graft copolymerization reactions was 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. The grafting degree determination was conducted by thermogravimetric analysis (TGA). However, it is important to mention here that gravimetric and thermogravimetric grafting degree determinations were in agreement in all cases. Hence, hereafter we discuss W (%) calculated by TGA.

Characterization

FT-IR Studies

Fourier transform-infrared (FT-IR) transmittance spectra (520 scans, 4 cm^{-1} resolution, wave number range 400–4000 cm^{-1}) were recorded using a Bruker Vertex 70 FT-IR Spectrometer. All spectra were baseline corrected. The sample was prepared in KBr pellets. The study was performed with the diffuse reflectance accessory EasiDiff.

Thermal Analysis

The study of different solvents' effects on the grafting degree by TGA was conducted with a TA Instruments Q500 apparatus, at a heating rate of 10°C/min at nitrogen atmosphere. The samples weighed 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 Instruments 2920 apparatus under nitrogen atmosphere. In the DSC experiments, the sample was heated from −30° to 180°C (first heating scan) at the heating rate of 10°C/min and then kept for few minutes at 180°C. After eliminating the thermal history, the sample was first cooled to −30°C (−10°C/min) and finally 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 the exothermic and endothermic peaks in the second run.

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 they were immersed in deionized water at room temperature. Thereafter, the excess of water was removed with a filter paper and the weight of the swollen samples was measured at various time intervals. The procedure was repeated until constant weight was reached. The swelling percent (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.

RESULTS AND DISCUSSION

Our previous work has concluded that it is possible to synthesize grafting copolymers by radiation-induced graft copolymerization reactions of polar monomers onto the poly(3-hydroxybutyrate) backbone polymer.[12–14] We have used the simultaneous irradiation method because of its advantages.[19] Our interest was focused on the synthesis and development of the techniques of radiation-induced grafting of polar materials onto polyhydroxyalkanoates. The products can be used in medicine and biotechnology for applications such as support materials in enzyme and protein immobilization, drug release, and bone tissue engineering. Recently, the graft of polar materials onto PHB has been found to be an efficient method, and many conventional radical graft copolymerization products have been reported.[19] However, not much has been done in physicochemical characterization of the polymeric products to confirm the chemical modification. For instance, it is speculated that the grafting site may be the methine carbon of PHB (numbered 3 in Figure 1), given that the methine protons on the PHB methine chains are the most active acidic protons. Chen and coworkers[20] concluded that they are easily abstracted from the backbones to generate radicals initiating the graft polymerization. Radiation chemistry researchers such as Sevilla and colleagues[21] have studied the radiation chemistry of model compounds such as butyric acid and isobutyric acid. In all cases, the tertiary (methine) carbon radical was found to be the abstracted radical. Carswell-Pomerantz et al.'s[22] radiation chemistry investigations were focused specifically on PHB and concluded that several radical formations are possible. However, the tertiary carbon radical seems to be more stable when PHB is exposed to gamma radiation. We have demonstrated experimentally that the graft site where vinyl acetate monomer initiates the reaction is the tertiary carbon forming a quaternary substituted carbon (numbered 3* in Figure 1). According to our studies, it is also possible to obtain other graft collateral products because of the complexity of the radiation graft reaction. However ^{13}C nuclear magnetic resonance (NMR) results suggest that most of the grafting occurs on methine radical carbon. Unfortunately, in this work we could not find evidence of that because the reaction products were insoluble in all solvents used for ^{13}C-NMR.

Figure 1 shows a scheme for the radiation-induced graft copolymerization reaction of methacrylic acid and butyl methacrylate onto PHB proposed on the basis of the experimental results. Obviously, more explicit experimental evidence is needed to prove and complete

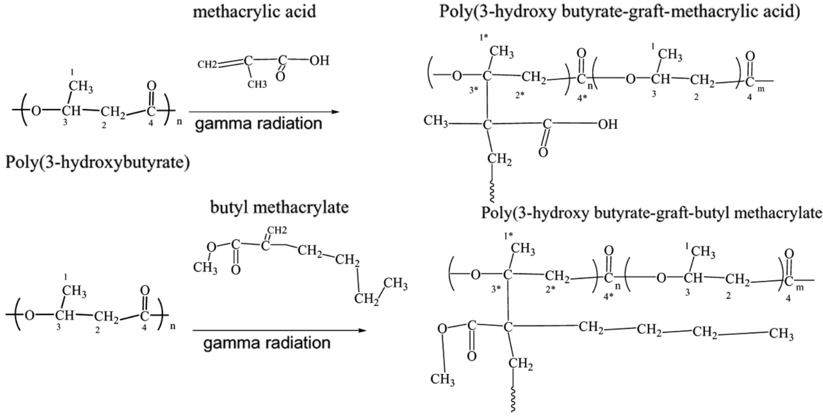

Figure 1. Scheme of radiation-induced graft copolymerization reactions of methacrylic acid and butyl methacrylate onto poly(3-hydroxybutyrate).

the mechanism. On the basis of general radiation-induced graft copolymerization, it could be supposed that in spite of PHB chemical inactivity, the selected monomer can react to some extent after the abstraction of the proton of the tertiary carbon of PHB backbone and further radical formation. Some solvents (acetone, ethanol, and chloroform) of low chain transfer constants and different polarities were selected in the radiation-induced graft polymerization in order to enhance grafting degree (W (%)) of the selected monomers onto PHB. Bulk reaction was also carried out for comparison.

Thermal Analysis

The grafting degree in PHB grafted with MA and BuM was estimated by TGA measurements. The TGA results provided evidence of the formation of grafting copolymer based on PHB backbone and the selected monomers. In general, the TG curve of grafted PHB shows two steps in smooth weight loss curves. These results indicated that the decomposition temperatures of PHB and grafted monomer are different. The composition in the graft copolymer can be determined by calculating the ratio of the weight loss of the first step to the total weight loss. Figure 2 shows the TGA curves of PHB and grafting copolymer P(HB-graft-MA) obtained in different solvents. The thermal analysis

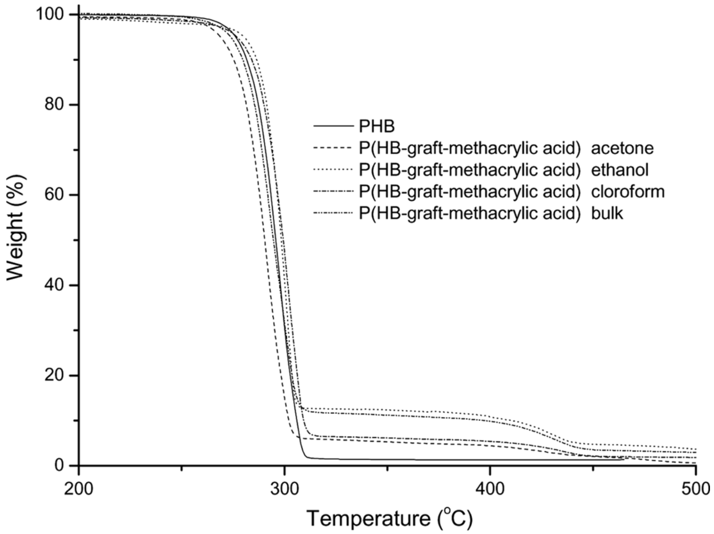

Figure 2. TGA thermograms of grafting copolymers (P(HB-graft-methacrylic acid)) in different solvents.

results showed that grafting degree was similar in chloroform (5.48%) and acetone (5.16%) for the reaction of MA onto PHB. A higher grafting degree can be achieved by using ethanol (10.9%) or bulk (9.69%). In all cases, the residual mass is less than 0.07 mg, which represents 1–1.5% of the initial mass. In addition, Figure 3 shows the TGA curves of PHB and grafting copolymer P(HB-graft-BuM) obtained in different solvents. Grafting degree was relatively low in bulk (6%), while a much higher grafting degree can be obtained for MBu onto PHB when using ethanol (32.21%) and acetone (22.5%) as solvents. In addition, MBu monomer could not be grafted onto PHB in chloroform solvent. It was concluded that ethanol is the more favorable solvent for the compared conditions used in the radiation-induced graft copolymerization reactions of MA or BuM onto PHB.

Differential Scanning Calorimetry

Figure 4 shows the DSC melting of pure PHB and the graft copolymer (P(HB-graft-MA)) synthesized in the same experimental conditions but in different solvents. From the thermograms of the second run, it was observed that the modified material showed in all cases a double melting peak. This phenomenon has been also observed in other grafted PHB polymers by Chen and coworkers; the appearance of two melting peaks

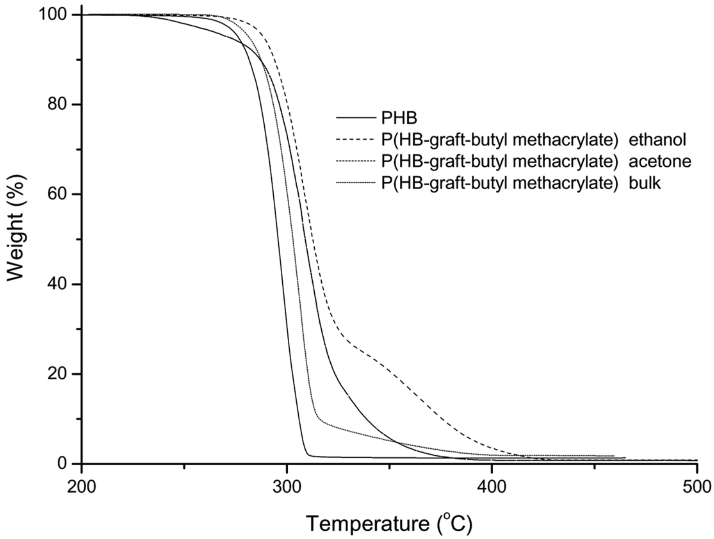

Figure 3. Thermograms of grafting copolymers P(HB-graft-butyl methacrylate) in different solvents.

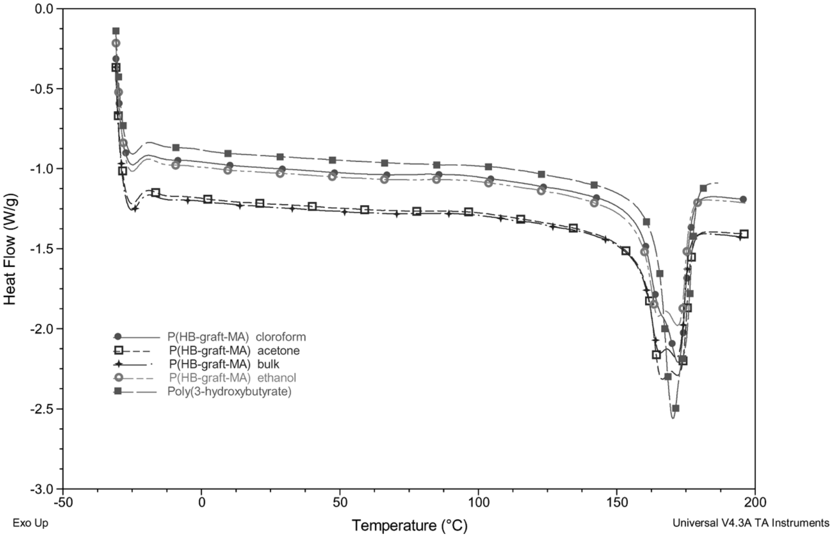

Figure 4. DSC curves (second scan) of PHB and grafting copolymers P(HB-graft-MA) in different solvents.

is attributed to recrystallization processes and implies that graft occurs not only in amorphous regions but also in crystalline regions.[20] Hence, the higher temperature peaks are attributed to crystals recrystallized during the heating process and the other peaks are probably the consequence of the melting of the crystals formed during the cooling process. It is clear that these results provide strong evidence of the disturbing of PHB crystallinity after grafting.

Table I lists the thermodynamic parameters obtained from the DSC thermograms of the samples of experiments A, B, C, D, and E, namely 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:

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

It can be seen that ΔH_m and $(\Delta H_m)_{\mathrm{corr}}$ of graft copolymers decreased with increasing grafting degree. It was concluded that the observed decrease is not due to the relative decrease of PHB content in the grafted polymer, but it is probably a consequence of a uniform grafting in crystalline regions of PHB after affecting the amorphous regions.

However, T_m as well as T_c decreased in all cases with respect to the PHB but there is no significant difference with the grafting degree

Table I. Thermodynamic parameters obtained from the DSC thermogram of PHB and the grafting copolymers P(HB-graft-MA)

Sample	Polymer	W (%)	ΔH_c (J/g)	T_c (°C)	ΔH_m (J/g)	T_m (°C)	ΔH_m $(\text{J/g})_{\text{corr}}$	T_g (°C)
A	PHB	0	92.45	97.43	103.8	170.23	103.8	1
B	P(HB-g-MA) acetone	5.16	71.50	82.81	52.29 41.98	167.90 172.47	54.98 44.14	9.5
C	P(HB-g-MA) chloroform	5.48	70.89	78.76	47.39 49.21	166.30 172.13	49.98 51.90	5.4
D	P(HB-g-MA) bulk	9.69	63.37	82.65	31.68 53.27	165.84 171.48	34.72 58.38	8
E	P(HB-g-MA) ethanol	10.9	65.92	83.67	32.16 55.72	165 171.97	35.67 61.80	7.5

variation. Hence, it can be concluded that the grafting degree results are rather low and are similar for the present experimental results. Consequently, the melting point and the crystallization temperature exhibit a certain variation too.

Moreover, the glass transition temperature (T_g) showed the following behavior. The T_g value increased its value in all cases with respect to PHB, but there is not a straighforward relation with W (%). This may be due to the structural changes occurring in the PHB molecule, which cannot be completely explained on the basis of the DSC results.

Typical DSC heating curves of PHB and the graft copolymers obtained from the radiation-induced graft reaction of BuM onto PHB in different solvents (A, F, G, and H) are shown in Figure 5. By analogy with the results obtained for the grafting of MA onto PHB, it may be argued that the P(HB-graft-BuM) material also exhibited in all cases a doublet melting peak, which implies the above discussed changes in the crystallization behavior. This result suggests that the crystallization ability of PHB becomes weak due to the introduction of butyl methacrylate, which can also hinder its crystallization as did methacrylic acid.

DSC analysis data of PHB and the mentioned grafting copolymers (P(HB-graft-BuM)) concerning complete thermal investigation are given in Table II. It was found that all the thermodynamic parameters (ΔH_m, $(\Delta H_m)_{\text{corr}}$, T_c, and T_m) of graft copolymers decreased their value with increasing grafting degree with respect to PHB. It is surprising to observe that the higher grafting degree sample showed a tendency to increase its value in all cases. However, the exact reason for these phenomena is not clear at this stage; this may be due to structural changes, but more

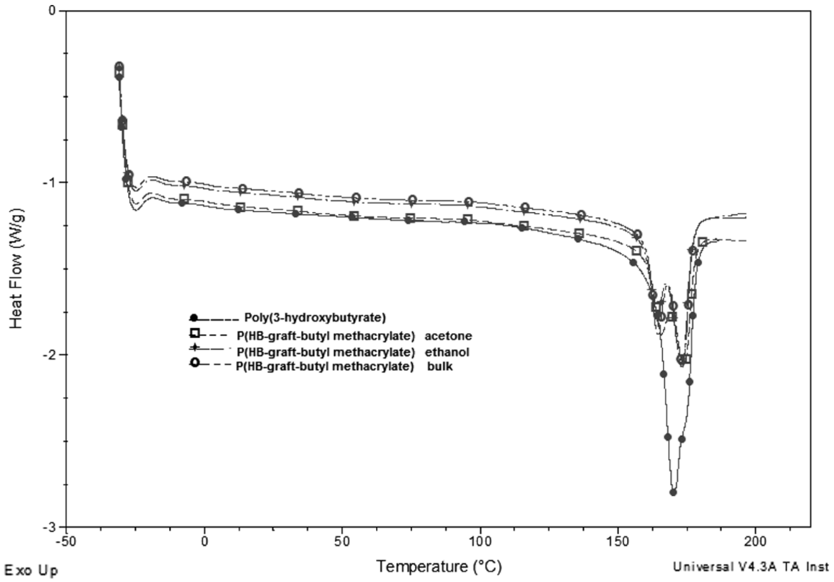

Figure 5. DSC curves (second scan) of PHB and grafting copolymers P(HB-graft-BuM) in different solvents.

experimental evidence is needed to explain it. Unfortunately, as discussed before, the insolubility in organic solvents made NMR studies of these solvents impossible.

On the other hand, it is clearly seen that T_g increases with increasing grafting degree. This observation implies that probably a stronger and more intensive interaction of the BuM with the PHB occurred than with the MA. Thus, visual inspection of the grafting degree clearly shows

Table II. Thermodynamic parameters obtained from the DSC thermogram of PHB and the grafting copolymers P(HB-graft-BuM)

Sample	Polymer	W (%)	ΔH_c (J/g)	T_c (°C)	ΔH_m (J/g)	T_m (°C)	ΔH_m $(\mathrm{J/g})_{\mathrm{corr}}$	T_g (°C)
A	PHB	0	92.45	97.43	103.8	170.23	103.8	1
F	P(HB-g-BuM)	6	54.34	87.18	37.40	164.31	39.64	4.5
	bulk				32.95	173.52	34.93	
G	P(HB-g-BuM)	22.5	46.71	82.21	30.08	165.83	36.848	4.9
	acetone				34.38	174.04	42.11	
H	P(HB-g-BuM)	32.21	50.98	83.13	35.70	163.86	47.19	5.7
	ethanol				40.18	173.00	53.12	

that the extent in grafting degree is greater than that of MA, where the grafting degree relatively scarcely changed.

It needs to be pointed out that the results obtained in the DSC investigations are consistent with a successful grafting of MA and BuM onto PHB.

Fourier Transform-Infrared Studies

Spectroscopic infrared techniques were used to verify BuM and MA grafting to the PHB polymer backbone. FT-IR transmittance spectra of the grafted PHB in different solvents are shown in Figure 6 (P(HB-graft-BuM)) and Figure 7 (P(HB-graft-MA)). Since the spectra were recorded in transmittance mode, peaks in the 1000–1400 cm^{-1} region are saturated (region not shown in the figures).

The ungrafted PHB shows 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, it was observed the band of the C=O stretching (1729 cm^{-1}) can be seen. All these mentioned signals are common for all studied polymeric materials. Unfortunately, the spectra of the grafted polymers did not reveal any significant difference in the bands' position, because the monomers used for grafting have the same functional groups as PHB. This fact explains

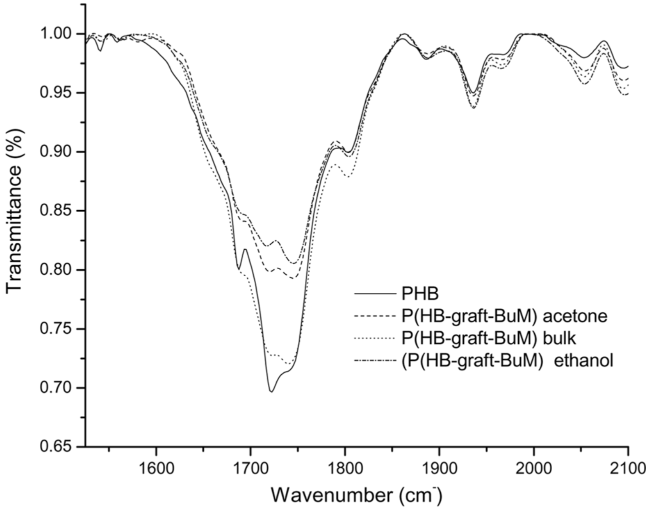

Figure 6. FT-IR transmittance spectra of PHB and grafting copolymers P(HB-g-butyl methacrylate) obtained in different solvents.

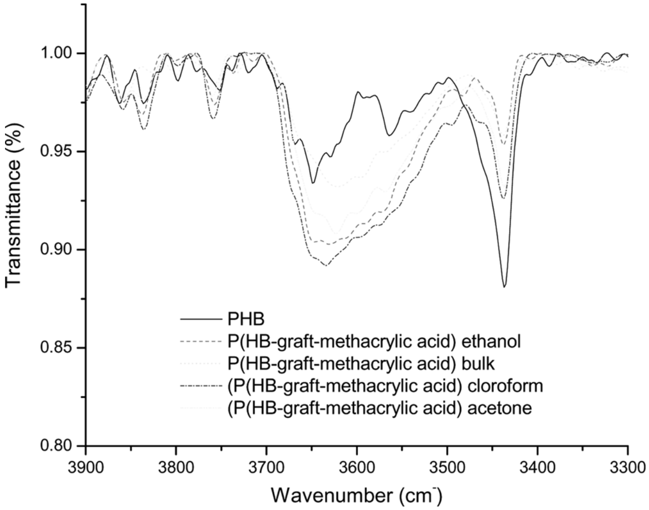

Figure 7. FT-IR transmittance spectra of PHB and grafting copolymers P(HB-graft-metacrylic acid) obtained in different solvents.

why other bands are not observed. However, some other differences were found to verify the grafting. The FT-IR transmittance spectra of PHB and grafting copolymers P(HB-graft-butyl methacrylate) obtained in different solvents are shown in Figure 6. These spectra exhibit the following spectral features: (a) the differences in the intensities of the carbonyl bands (1724, 1740 cm^{-1}), and (b) the band intensity decreases with increasing grafting degree. This result is consistent with the variation of the degree of crystallinity as a consequence of grafting. Calculus of the crystallinity criterion (CC) was conducted in order to determine the relative variation in the degree of crystallinity. The band at 1722 cm^{-1} is characteristic of the crystalline state, and the band at 1740 cm^{-1} is characteristic of the amorphous state. The CC (%) is defined as the ratio between the absorbance value at 1722 cm^{-1} and that at 1740 cm^{-1}. It is important to mention that this last definition represents a relative measure of the crystallinity degree. Table III shows these results. It can clearly be seen that the CC (%) of P(HB-graft-BuM) decreases with increasing grafting degree.

On the other hand, Figure 7 shows the infrared spectra in the 3300–3900 cm^{-1} region of PHB and grafting copolymer (P(HB-graft-MA)) obtained in different solvents. In the MA grafted sample, the broad band is assigned to OH stretching characteristic of carboxylic acid and the OH terminal groups of the PHB backbone. The spectrum also shows a variation in the intensities of the band centered at 3430 cm^{-1},

Table III. Crystallinity study of the PHB and the graft copolymer samples obtained by radiation-induced graft polymerization

		P(HB-graft-methacrylic acid)				P(HB-graft-butyl methacrylate)		
	PHB	Acetone	Chloroform	Bulk	Ethanol	Bulk	Acetone	Ethanol
W (%)	0	5.16	5.48	9.69	10.9	6	22.5	32.2
CC (%)	1.028	1.004	0.991	1.025	1.012	0.9926	0.9920	0.9858

thus verifying the successful grafting of MA onto PHB. The most striking feature observed in these spectra is the appearance of increasing intensity and broader band centered at approximately 3630 cm^{-1}. The degree of crystallinity was also determined for this material. The CC (%) for grafted PHB decreased in all cases. However, there is no clear relationship with respect to the grafting degree. This is probably due to the fact that grafting degree is rather low and similar for the studied graft copolymers (Table III).

Swelling Behavior

Table IV lists the swelling percentage (S (%)) data for P(HB-graft-methacrylic acid) and P(HB-graft-butyl methacrylate). These values are the highest obtained after 30 min by graft copolymer samples. In each case, the swelling percentages are invariant. Table IV also shows the initial rates of the swelling process (water mass (mg) that the polymer takes in at the beginning of the swelling process per hour). These values were calculated by linear regression of the data of water mass that was taken by the materials versus time at the beginning. The slopes of these lines are the initial rates of the swelling process. Figure 8

Table IV. Swelling experimental results

Samples	S (%)	V_o (water mg/h)
PHB	3.3	1.22
P(HB-g-BuM)	208	67.30
P(HB-g-MA)	118	26.36

S (%): swelling percentage; V_o (water mg/h): initial rates of the swelling process.

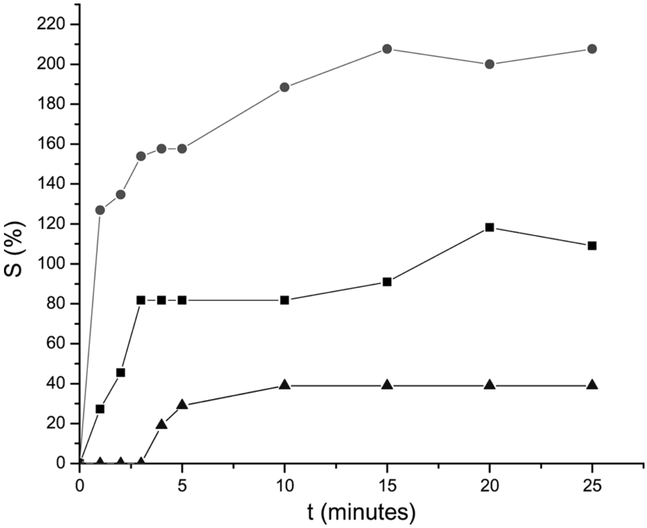

Figure 8. Swelling percentage vs. time for (-▲-) PHB, (-■-) P(HB-graft-methacrylic acid), and (-●-) P(HB-graft-butyl methacrylate).

shows the swelling percentage (S) versus time for PHB, P(HB-graft-methacrylic acid), and P(HB-graft-butyl methacrylate) from the experiments conducted in ethanol solvent. It can be seen clearly that the graft copolymers improved their hydrophilicity. These results are consistent with the increase of PHB hydrophilic characteristic.

CONCLUSIONS

Methacrylic acid and butyl methacrylate have been successfully grafted onto poly(3-hydroxybutyrate) by radiation-induced graft copolymerization in spite of PHB's chemically inactive structure. The grafting degree was quantified by using thermogravimetric analysis. TGA results showed that the more favorable solvent for graft reaction in both cases is ethanol, which presented the higher grafting degree. The extent of the grafting varied from 5% to 32%. Physicochemical characterization of the grafting copolymer was conducted by using DSC and FT-IR techniques. It was found that the thermodynamic parameters varied, showing that the introduction of MA and BuM groups hinders PHB crystallization, causing a decrease in the degree of crystallinity. In addition, the synthesis was verified by spectroscopic infrared analysis. Finally, the swelling behavior was also studied, showing an increase in the PHB hydrophilic characteristics of the polymeric materials.

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