RADIATION INDUCED GRAFT COPOLYMERIZATION OF ACRYLAMIDE ONTO POLY (3-HYDROXYBUTYRATE)

Maykel González Torres[1], Manuel Rapado Paneque[2], Mayte Paredes Zaldívar[2],
Sonia Altanés Valentín[2], Gisela Barrera González[2]

[1]Instituto de Ciencia y Tecnología de Materiales (IMRE), Universidad de La Habana, Cuba
[2]Centro de Aplicaciones Tecnológicas y Desarrollo Nuclear (CEADEN)
Calle 30 N° 502 e/ 5ta Ave. y 7ma, Playa, Ciudad de La Habana, Cuba
mikegcu@gmail.com, rapado@ceaden.edu.cu

Abstract

The graft copolymer poly (3-hydroxybutyrate)-g- polyacrylamide [P (HB-g-AAm)] was synthesized by radiation induced graft copolymerization of acrylamide onto poly (3-hydroxybutyrate). The study was conducted by the simultaneous irradiation method. The structure of [P (HB-g-AAm)] was identified by Fourier Transform Infrared (FTIR) spectroscopy. Thermal behavior of the graft copolymer was also studied by Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). According to the results, FTIR studies showed new signals (stretching-N-H) as an important evidence of grafting. The grafting degree, determined by ATG, was 10% and changes in thermodynamic parameter obtained from the DSC were detected. Such changes show a decrease in crystallinity and an increase in the glass transition temperature. These results demonstrate that the gamma radiation-induced graft copolymerization reaction of acrylamide onto PHB was successively achieved.

COPOLIMERIZACIÓN POR INJERTO RADIOINDUCIDO DE ACRILAMIDA EN EL POLI (3-HIDROXIBUTIRATO)

Resumen

En el trabajo se realizó la síntesis del copolímero por injerto poli (3-hidroxibutirato)-g- poliacrilamida [P (HB-g-AAm)] por copolimerización de injerto radioinducido del monómero acrilamida en el PHB. El estudio se llevó a cabo por el método de la irradiación simultánea. La estructura del copolímero se identificó por espectroscopía Infrarrojo por Transformada de Fourier (FTIR). Además, se realizó el estudio térmico del compuesto obtenido por análisis termogravimétrico (TGA) y calorimetría diferencial de barrido (DSC). De los resultados se encontraron señales (vibraciones de valencia -N-H) por FTIR que constituyen una importante evidencia de la reacción de injerto. El grado de injerto determinado por ATG fue de 10% y se detectaron cambios en los parámetros termodinámicos estudiados por DSC, que muestran una disminución de la cristalinidad y un aumento de la temperatura de transición vítrea. Los resultados demostraron la formación del copolímero por injerto inducido por radiaciones gamma.

Key words: acrylamide, graft polymers, irradiation procedures, fourier transform spectrometers, thermal gravimetric analysis, copolymers, radiation doses, gamma radiation

INTRODUCTION

Poly (3-hydroxybutyrate) (PHB) has received considerable attention in the last decade as biodegradable and biocompatible biomaterial. PHB is a thermoplastic material with physical properties similar to polypropylene (PP) [1]. Its various properties make it suitable for a variety of applications in the field of medicine [2]. However, the PHB homopolymer main drawbacks are its relatively hydrophobicity, brittleness and thermal instability. It is known that these problems can be solved by the incorporation of new molecules to the PHB backbone by graft copolymerization.

On the other hand, polyacrylamide has shown to be «biocompatible», although some controversy exists with respect to its blood biocompatibility [3, 4]. The covalent grafting of hydrophilic polymers onto hydrophobic substrates is widespread. Graft polymerization is a well-known method to modify the chemical properties of polymers for specific application [5-9].

Lee et al studied graft copolymerization of acrylamide onto poly (hydroxybutyrate-co-hydroxyvalerate) film to test the application of the grafted film on permselectivity [10].

Hydrophilic monomers, including methyl methacrylate (MMA), 2-hydroxyethyl methacrylate (HEMA) and acrylic acid (AAc) have been grafted onto PHB and its copolymers P (HB-co-HV) through radiation induced graft copolymerization [11-13]. Other monomer such as styrene (St) was grafted by using the simultaneous radiation and pre-irradiation techniques from a ^{60}Co g-ray source

[14]. In addition Hu et al reported the graft copolymerization of isoprene (Ip) obtained by directly irradiating the polymer immersed in isoprene solution [15].

In previous paper the radiation induced graft copolymerization of vinyl acetate onto PHB was performed [16, 17]. The study reported here is concerned with the radiation induced graft copolymerization of typical acrylamide onto PHB by the simultaneous irradiation method. Simultaneous irradiation is the simplest irradiation technique for preparation of graft copolymers. In this method a polymer backbone is irradiated in the presence of a monomer available in different forms: vapor, liquid or in bulk solution. The purpose of grafting AAm onto PHB is to improve its hydrophilic characteristics. The product obtained in this work has not been reported before by any authors. It was characterized by means of several techniques to verify the graft copolymer synthesis.

MATERIALS AND METHODS

Materials

Poly (3-hydroxybutyrate) (PHB) was available 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 GPC at room temperature with a PUMP 64 HPLC (KNAUER), equipped with a series of five columns PL-Gel and KNAUER differential refractometer. Tetrahydrofuran (THF) solvent was used at 1 mL/min flow rate, and it was also used injection volumes of 20 µL. Polystyrene standards with low polydispersity were used to generate a calibration curve. The results were: $\overline{M}n = 27000$, $\overline{M}w = 60000$; $\overline{M}z = 98000$; Polydispersity = 2.22.
Acrylamide was available from Merck (Ge) and was previously purified by recrystallization method.

Graft copolymer synthesis (P (HB-g-AAm))

The irradiation experiment was carried out in glass sealed vacuum ampoules at room temperature. PHB (200 mg) was immersed in AAm (1g) and 1 mL of the solvent (acetone). The mixture was subjected to ^{60}Co ã-ray at a dose rate of 1. 62 kGy/h and a dose of 10 kGy. The grafted PHB so obtained was extracted in a Soxhlet apparatus with ethanol and acetone for 72 h, to remove any acrylamide monomer and PAAm homopolymer obtained as collateral products. The copolymer P (HB-g-AAm) was dried under vacuum, at 40^{o} C, to constant weight.

The following equation to determine the degree of grafting (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 % by means of the mass increase.

Characterization

Thermal analysis

The study of the graft copolymer (P (HB-g-AAm)) obtained by radiation induced graft copolymerization was conducted by Thermal Gravimetric Analyses (TGA) in a Q500 TA Instruments, at a heating rate of 10^{o} C/min at nitrogen atmosphere. The samples weight was of 5-15 mg and the temperature range of 50- 600^{o} C at atmosphere.

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

FTIR studies

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

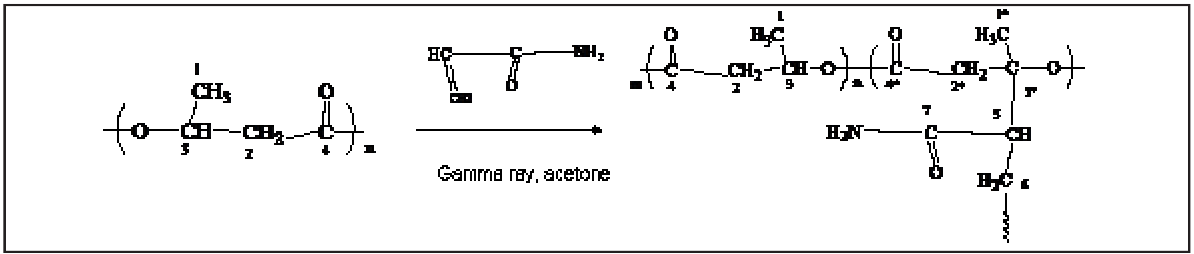

Figure 1. Radiation-induced graft copolymerization of acrylamide onto PHB: Structure of the graft copolymer P (HB-g-AAm).

RESULTS AND DISCUSSION

Figure 1 show the radiation induced graft copolymerization reaction of acrylamide onto PHB. The simultaneous irradiation technique with ^{60}Co gamma-ray was used. The dose rate was 1. 62 kGy/h and the dose was 10 kGy at room temperature. The selection of the source, dose rate and dose used are based on the results obtained in the radiation induced graft copolymerization of other monomers onto PHB synthesized by the authors. For instance the P (HB-g-VAc). These parameters have also been used in the syntheses of the graft copolymers found in the literature [11-15]. It is important to mention here that generally, higher irradiation doses lead to higher degrees of grafting. This is due to the enhancement of free radical formation. But the graft copolymer is always obtained at doses over 5 KGy. We have chosen 10 KGy because it was verified experimentally that this value is appropriate to be used.

The structure shown in the figure suggested that the graft occurs through the tertiary PHB carbon. This can be considered because of previous studies [18]. Sevilla et al reported that the tertiary radical formed by the exposition of PHB to gamma-radiation would be favored with respect to the rest possible radicals formed. In our previous studies, the P (HB-g-VAc) was reported [19]. Spectroscopic studies showed that quaternary substituted carbons were obtained. This result is in agreement with the propose structure given for P (HB-g-AAm). On the other hand, Grushevskaya et al reported that acetone is the more convenient solvent to be used in the radiation induced graft copolymerization of acrylamide onto PE. From this finding acetone was used as diluent in this work [20].

FTIR

FTIR studies were performed in order to confirm the syntheses of a graft copolymer. Evidence of grafting was obtained by using this technique. Figure 2 shows the transmittance mode FTIR spectra of pure PHB and P (HB-g-AAm). From the IR spectra, it was obvious that PHB showed the bands at 1185, 1228 and 1279 cm^{-1} characteristic of ν_a (C-O-C) and the band at 1382 cm^{-1} characteristic of δ_s (CH_3). In the ester carbonyl region, it can be considered the band of the C=O stretching (1729 cm^{-1}). All this mentioned signals are common for both materials. However in the graft copolymer, apart of the previous peaks, four additional peaks were present. Two peaks at 3300 cm^{-} (broad peak) and 3182 cm^{-} were for the NH_2 groups, corresponding to symmetrical and antisymmetrical stretching -N-H bonds. The peak position at 1676 cm- is probably caused by the amide carbonyl group and the 1608 cm^{-} peak represents the adsorption of δ (NH). The absorption frequency of carbonyl stretching vibrating of the amide group is well separated from that of the ester group. The new peaks observed are a strong evidence of grafting and clearly indicate the formation of a graft copolymer.

Differential Scanning Calorimetry (DSC) investigation

Thermal properties of the grafted PHB (figure 3) and the P (HB-g-AAm) were investigated by DSC with the purpose to demonstrate the graft copolymer formation by means of the differences observed among both materials. Figure 4 is the thermogram of graft copolymer. In the DSC thermogram of the first scan was observed the fist anomaly among both materials. The graft

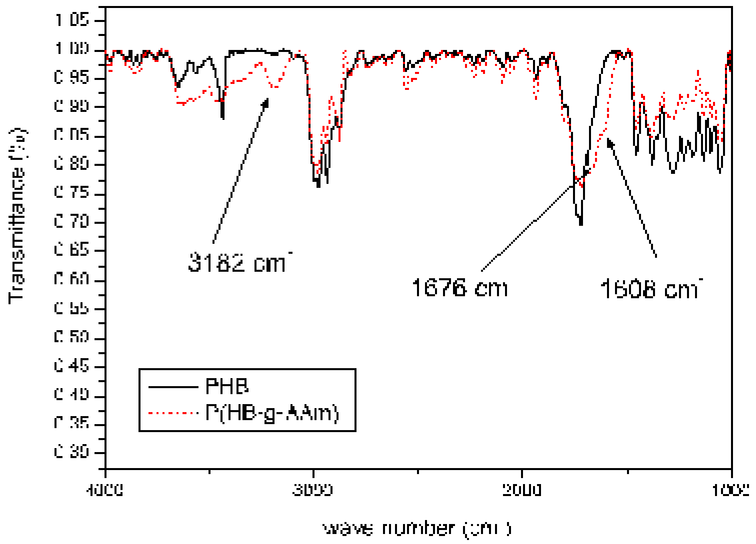

Figure 2. FTIR spectra of the PHB and the P (HB-g-AAm) obtained by radiation induced graft copolymerization.

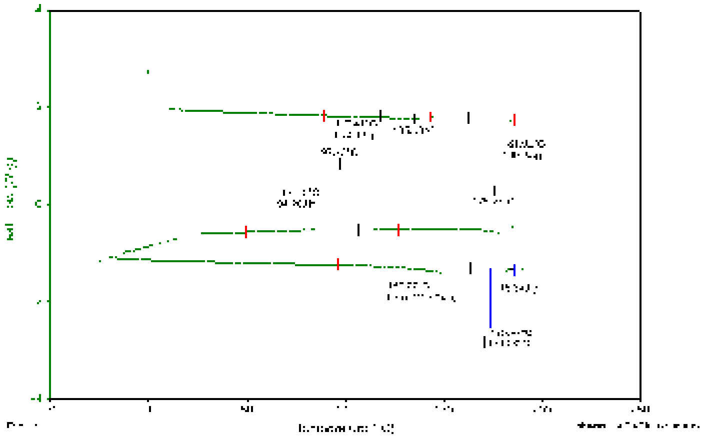

Figure 3. DSC curves of PHB.

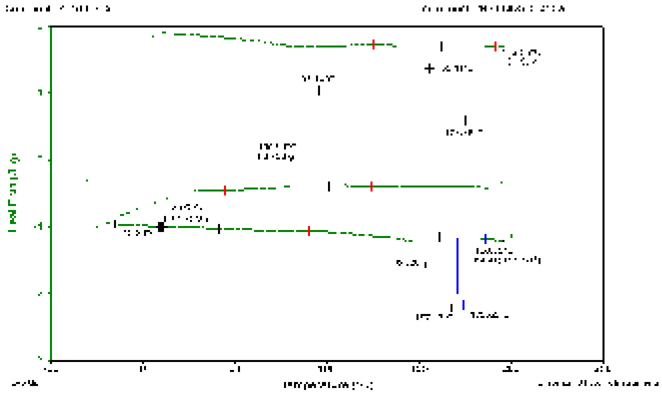

Figure 4. DSC curves of P (HB-g-AAm) obtained by radiation induced graft polymerization.

copolymer showed bimodal peaks at 175.11° C and 174.46° C with respect to PHB endothermic melting (175.23° C). In addition in the DSC of the second scan was observed that the crystallization temperature changed its value from 97.4° C (PHB) to 95.4° C (P (HB-g-AAm)) and the enthalpies of crystallization (ΔH_c) changed its value from 94.28 J/g (PHB) to 82.42 J/g (P (HB-g-AAm)). What is more, in the DSC thermogram of the third scan was also observed anomalies. The thermogram of the product showed bimodal peaks in the melting region. Surprisingly the melting point (T_m) of the graft copolymer was three degrees up and down the value of the T_m given for PHB. Consequently, the enthalpies of melting (ΔH_m) of the plain PHB and the graft copolymer differed in about 15 units (J/g). The decrease of the ΔH_m for the graft copolymer indicated that the cristallinity decreased after the introduction of AAm chains onto the PHB backbone by radiation induced graft copolymerization. It is of interest to mention here that the T_g of plain PHB changed from -2° C to 9.61° C in the graft copolymer, laying between those of the two homopolymers. This result is consistent with the fact that is natural that the introduction of AAm chains onto PHB increases the glass transition temperature.

Table lists the thermodynamic parameters obtained from the DSC thermogram of the experiment sample. It was summarized the melting point (T_m), the enthalpies of melting (ΔH_m), the enthalpies of melting $(\Delta H_m)_{corr}$ corrected by the weigh fraction of the polymer that conform the graft copolymer, calculated according to the following equation:

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

Table. Enthalpies of fusion (ΔHm), melting points (Tm) and glass transitions of PHB and P (HB-g-AAm) graft copolymers

No	Polymer	(W (%))	ΔH_c (J/g)	T_c(°C)	ΔH_m (J/g)	T_m(°C)	ΔHm $(J/g)_{corr}$	Tg (°C)
1	PHB	0	94.28	97.43	112	170.23	112	-2
2	P(HB-g-AAm)	10%	82.12	95.1	87.93	167.27 173.97	107.72	9.61

the crystallization temperature (T_c) and the enthalpies of crystallization (ΔH_c). From the results obtained by the DSC experiments a strong evidence of grafting is given.

Thermogravimetric analysis (TGA)

Figure 5 illustrates TGA thermogram of the graft copolymer P (HB-g-AAm). The TGA was conducted to show the difference in the thermal behavior of the obtained product with respect to the base polymer (PHB) and the grafting degree calculus. The TG curve of PHB grafted with AAm shows two steps in its smooth weight loss curve because the decomposition temperature of PHB and AAm are not the same. The first step represents the plain PHB material and the second step represents the grafted PAAm. In addition, the DTGA shows two rates of weight loss (dW/dt) peaks defining the temperature of each step. The first step at 395° C belongs to PHB characteristic temperature. The others step at 395° C correspond to PAAm decomposition. From figure 5 can be seen that the PHB composition in the graft copolymer can be calculated by dividing the weight loss of the first step to the total weight loss. This result indicates that the copolymer grafting degree (W (%)) is 10% (This percentage represent the quantities in mass of PAAm grafted onto PHB with respect to the total mass of the sample) (see table).

CONCLUSIONS

The radiation induced graft copolymerization reaction of AAm onto PHB has been studied by the simultaneous irradiation method. The results obtained can be summarized as follows:

1- In spite of the PHB inactive structure, AAm can be grafted onto PHB by directly irradiating PHB and AAm immersed in acetone solution, using a ^{60}Co γ-ray source.
2- The synthesized material was characterized by means of several techniques such as FTIR, ATG and DSC
3- FTIR studies showed new signals that strongly confirm the synthesis of P(HB-g-AAm), such as the peaks at 3300 cm^{-} and 3182 cm^{-} assigned for the NH_2 groups, corresponding to symmetrical and antisymmetrical stretching -N-H bonds. In addition, the absorption frequency of carbonyl stretching vibrating of the amide group is well separated from that of the ester group.
4- TGA results showed that graft degree (W (%)) in the graft copolymer is about 10% calculated by dividing the weight loss of the second step to the total weight loss of the sample.
5- From DSC results, the melting enthalpy (ΔH_m) slightly decreased. The decrease of the ΔHm for the graft copolymer indicated that the cristallinity decreased after the introduction of AAm chains

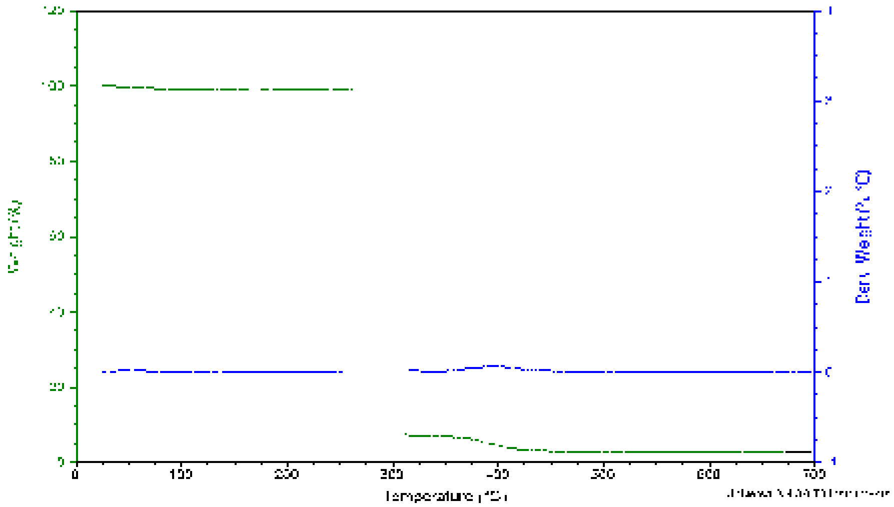

Figure 5. TGA thermogram of the graft copolymer P (HB-g-AAm).

onto the PHB backbone by radiation induced graft copolymerization. Some experiments displayed bimodal peaks during the DSC in the third scan, which could be caused by recrystallization processes. Consequently, the glass transition temperature increased its value as a result of the grafting.

6- These results demonstrate that the radiation induced graft copolymerization reaction of acrylamide onto PHB was successively achieved.

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